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1 **Multiple environmental tracers for a better understanding of water flux**
2 **in a wetland area (La Bassée, France)**

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9
10 **Abstract**

11
12 Understanding water exchange between groundwater and streams, or groundwater/surface-
13 water relationships, is of primary importance for solving conflicts related to water use and for
14 restoring water ecosystems. To this end, we tested a combination of classic geochemical
15 tools and isotopic tools on the Bassée study site, located in the alluvial plain of the River
16 Seine, to see whether they are relevant for tracing multiple and complex
17 groundwater/surface-water relationships. The Ca/Sr ratio associated with Sr isotopes shows
18 contrasted values and suggests that infiltration of surface water to groundwater increases
19 when approaching the Seine. Furthermore, stable isotopes of the water molecule indicate
20 that water from gravel-pit lakes may infiltrate into groundwater. Tritium and CFC tools
21 confirmed surface-water influence on the Alluvial and Chalk aquifers. This geochemical
22 approach, tested on the Bassée site, clearly demonstrates the need of using various
23 geochemical tools for describing groundwater/surface-water relationships, and can be
24 conclusively addressed to other case studies for helping decision makers in their
25 management of natural water resources.

26
27 **Keywords**

28 $\delta^{18}\text{O}$, $\delta^2\text{H}$, $^{87}\text{Sr}/^{86}\text{Sr}$, ^3H , CFC, SF_6 , wetland, groundwater, La Bassée, France

29
30
31 **1. INTRODUCTION**

32
33 In studies of hydrological systems over the past few years, new environmental tracers have
34 been successfully applied, such as strontium, boron and sulphate isotopes, as well as CFCs
35 and SF_6 (e.g. Vengosh et al., 2002; Négrel and Pauwels, 2004; Négrel and Petelet, 2005;
36 Gooddy et al., 2006). New-generation inductively-coupled plasma mass spectrometers (ICP-
37 MS) have allowed the development of much more precise isotopic measurements for various
38 elements and a wider use of these tools (e.g. Luais et al., 1997; Marechal et al., 1999; Halicz
39 et al., 1999; Rehkemper and Halliday, 1999; Galy et al., 2001; Rouxel et al., 2002; Beard et

40 al., 2003; Cardinal et al., 2003; Wombacher et al., 2003). This has provided larger means of
41 studying hydrological and environmental processes.

42 Recently, the combined use of various geochemical tracers has been successfully applied for
43 obtaining a better understanding of hydrological systems (Millot et al., 2007; Vengosh et al.,
44 2007; Bouchaou et al., 2009; Ma et al., 2010) as well as of the interaction between
45 groundwater and surface water (Oxtobee and Novakowski, 2002; Lamontagne et al., 2005;
46 Darling et al., 2010). In Millot et al. (2007), the combination of Li, B, Sr and Nd isotopic
47 systems highlights the complexity of studying geothermal reservoirs, as well as the fact that
48 using only one isotopic tool could lead to an incomplete interpretation of the origin of water.
49 For this reason, the use of a multi-tracer approach is relevant and should provide additional
50 information for the characterization of natural waters in relation to their source.

51 Langman and Ellis (2009), investigating the source of water, showed the usefulness of a
52 multi-isotope approach in a complex aquifer subject to natural and anthropogenic influences.
53 The use of traditional geochemical tracers commonly is insufficient for explaining the source
54 of water in deeper aquifers and the interactions between aquifers; in this case, additional
55 tools such as $\delta^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ permit a reinterpretation of the isotopic composition of water,
56 leading to a conclusive revision of the hydrological model.

57 The complementary information these tracers provide, generally confirms the initially
58 established conceptual hydrogeological model. But, in some cases all tracers provide the
59 same information, rendering the use of various tools to be less than cost effective.

60 Occasionally, the information obtained from various geochemical tracers appears to be
61 contradictory. Though, at first sight, his situation might be considered as a weakness of the
62 multi-tool geochemical approach, it commonly reveals the strength of the method.
63 Understanding a system can initially seem complicated, requiring reappraisal of the initial
64 hypothesis; the use of multiple methods then is the only way of by-passing pre-established
65 hydrogeological models and of proposing new models that consider the full complexity of
66 hydrological systems.

67 In the present study, we proposed to use various tracers for evaluating the interconnection
68 between aquifers and the possible relationships between surface water and groundwater in a
69 flooded plain. These include tracers of the water cycle ($\delta^2\text{H}$ and $\delta^{18}\text{O}$), of water-rock
70 interactions ($^{87}\text{Sr}/^{86}\text{Sr}$), of residence time and transfer mode (CFCs and SF_6), and of
71 anthropogenic impact (^3H).

72 La Bassée lies south-east of Paris in the alluvial plain of the River Seine. In this area,
73 hydrological flux between surface- and groundwaters is expected to be complex due to the
74 presence of several interconnected aquifers below wetlands, ponds, oxbow lakes, and rivers.
75 The Seine has been channelled since decades and natural flooding is quite reduced in the
76 area. The Bassée site is the last alluvial plain in the Paris Basin exploited for gravel (Baron

77 and Piketti, 2001). The intensive sand and gravel extraction throughout the alluvial plain
78 since 40 years has created large borrow-pits that, at the end of the exploitation period, are
79 filled by ground- and rain-water. The Bassée site is also the major wetland area of the Ile-de-
80 France region, labelled 'Natura 2000', and part of a Europe-wide network of sites tasked with
81 the preservation of our natural heritage. It is one of the 87 wetlands of major importance in
82 France and governmental action plans were established in order to protect the surface water
83 covering 20% of the plain ([http://natura2000.environnement.gouv.fr /sites/FR1112002.html](http://natura2000.environnement.gouv.fr/sites/FR1112002.html)).
84 The groundwater here is of great importance as a drinking-water supply and is considered as
85 a reservoir to be protected for the Paris metropolitan-area water supply (SDAGE,
86 Management Plan of Seine-Normandy basin). The study area covers 23 km² of the
87 downstream part of the alluvial plain. Previous hydrogeological studies (Mégnién, 1965;
88 Sogreah, 2004; Armines, 2005) using classical hydrogeological investigation methods
89 (water-level monitoring, geology, geophysics, geotechnics, and modelling) left uncertainties
90 on the magnitude of the relations between deep and alluvial aquifers, on the possible
91 hydraulic connections between deep aquifers and the river, and on the extent of the
92 relationships between the River Seine and shallow aquifers.
93 The scope of this study was to improve the hydrological understanding of the system through
94 the use of multiple geochemical tools, in order to arrive at a better protection of this floodplain
95 from qualitative and quantitative points of view. To this end, three different types of water
96 relationships had to be evaluated in the alluvial plain: Chalk and Alluvial groundwater
97 connections, groundwater (Chalk and Alluvial) and river water relationships, and the relation
98 between other surface waters (oxbow lakes, ponds, gravel pit lakes) and groundwater. The
99 alluvial plain in the past having been subject to periodic flooding by the Seine and today
100 being intensively exploited for sand and gravel extraction, the existing surface water is of
101 particular ecological and hydrological importance in the studied area.

102

103 **2. CHARACTERISTICS OF THE BASSÉE SITE**

104 The Bassée site, south-east of Paris, is of major importance for the drinking-water supply of
105 Paris and surroundings. The site lies in the large Seine floodplain, delimited upstream by
106 Bray-sur-Seine and to the west by the Montereau-Fault-Yonne at the junction between the
107 rivers Seine and Yonne (Fig. 1). In view of its numerous ponds, canals and river arms, the
108 Bassée plain was included in the "Natura 2000" program.

109 Sand and gravel exploitation and agriculture are the main economic activities in the area.
110 Three aquifers are interconnected: i) the Alluvial aquifer of the River Seine located within the
111 whole studied area, ii) the mainly unconfined Chalk aquifer below the alluvial one, and iii) the
112 Tertiary calcareous formations in the northern part of the area (Fig. 2). The Alluvial and Chalk
113 aquifers discharge into the Seine (Weng et al., 1999; Vernoux et al., 2004). Groundwater

114 within the Alluvial aquifer circulates following the Seine-flow direction, while groundwater flow
115 in the Chalk aquifer is south-east to north-west. This geometry induces most probably a
116 connection between the Chalk and Alluvial aquifers, with direct or indirect (by drainage) flow
117 of the Chalk aquifer into the Alluvial layers. The very low regional slope created various
118 meanders that have led to an important and heterogeneous Alluvial aquifer. The water-level
119 map (Mégnién, 1965) indicates hydraulic continuity between these two aquifers. The Chalk
120 aquifer is considered as a major component of Alluvial aquifer recharge.

121 In the northern part of the study area, the chalk formations are becoming less permeable and
122 the groundwater is sometimes in semi-oxic or anoxic conditions. The Tertiary aquifer is
123 located only in the northern part of the Seine floodplain and is a multilayer calcareous and
124 marly calcareous aquifer, which locally may recharge the alluvial layers. Thus, recharge of
125 the Alluvial aquifer occurs directly from precipitation, or through the other aquifers of the
126 studied site. Natural Seine channels and spaces left by sand and gravel pits form numerous
127 overflowing areas. During high-water periods, river water infiltration may be possible.

128 It is estimated that about 100 lakes were formed by sand and gravel extraction in the lowest
129 part of the Bassée plain. After closure of the gravel pits, the space left is filled with low-
130 permeability material such as clay and silt from recent alluvial deposits, and rapidly reaches
131 equilibrium with the Alluvial and Chalk groundwater. These gravel-pit lakes are believed to
132 have very low surface-groundwater exchanges (Schanen et al., 1998).

133 **3. MATERIAL AND METHODS**

134 **3.1 Sampling procedures**

135 Two sampling campaigns were carried out in June 2007 during the high water period and in
136 November 2007 during a low water period. Sampled were 7 locations in the Chalk (noted
137 Sc), and 12 locations in the alluvial aquifers (noted Sa), the Seine upstream at Bray-sur-
138 Seine and downstream just before the confluence of the Rivers Seine and Yonne. Sampling
139 was realised using 6" piezometers drilled in 2002. The complete technical description (total
140 depth, depth to groundwater, lithology, depth to screens,...) is available and allowed to
141 select only the piezometers exploiting a unic geological formation (Chalk or Alluvial). In
142 addition, two gravel-pit lakes at La Tombe and Bazoches-lès-Bray and a well located at La-
143 Chapelle-sur-Oreuse in the Chalk aquifer upstream from the Bassée alluvial plain were
144 sampled in November 2007 (Fig. 1). A complementary sampling campaign took place in
145 July 2008. Tritium analyses were carried out on water of all groundwater points sampled in
146 2007 and the Seine at Bray-sur-Seine.

147 The analyses of major chemical elements and stable water isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$), ^3H ,
148 $^{87}\text{Sr}/^{86}\text{Sr}$, were completed by the determination of apparent groundwater ages using CFCs

149 and SF₆.
150 The boreholes were sampled after pumping at least three purge volumes and stabilizing the
151 chemical groundwater parameters, such as pH and conductivity. Samples for cation and
152 ⁸⁷Sr/⁸⁶Sr determinations were kept in polyethylene bottles after acidification with nitric acid.
153 Raw water samples of 50 ml and 1 litre in HDPE bottles were used for δ²H, δ¹⁸O and ³H
154 analyses. Glass sampling bottles of 500 ml were used for CFC and SF₆ analyses (IAEA,
155 2006).

156 **3.2. Analytical methods**

157 Concentrations were measured on water samples by inductively coupled plasma-atomic
158 emission spectrometry (ICP-AES) for Ca²⁺, Na⁺, K⁺ and Mg²⁺, and by ion chromatography for
159 Cl⁻, NO₃⁻, SO₄²⁻ and PO₄²⁻ (uncertainty for both methods 5-10%). Anion analyses were done
160 by ion chromatography (model DX120, Dionex®), cations by Inductively Coupled Plasma
161 Atomic Emission Spectroscopy (ICP-AES; Ultima-2 model, Jobin Yvon®). The accuracy of
162 both techniques was around 5-10% depending upon the concentration.

163 Sr concentrations were measured by inductively coupled plasma mass spectrometry (ICP-
164 MS) (uncertainty 5%). Alkalinity was determined by HCl titration and Gran's method.
165 Strontium for isotopic analysis was separated using an ion-exchange column (Sr-Spec resin).
166 Procedural blank levels were lower than 0.5 ng. The ⁸⁷Sr/⁸⁶Sr ratio was measured using a
167 Finnigan MAT 262 multiple collector mass spectrometer. Sr isotopic ratios were normalized
168 to ⁸⁷Sr/⁸⁶Sr=0.1194. Average uncertainties on individual ⁸⁷Sr/⁸⁶Sr measurements were 8.10⁻⁶
169 (at 2σ level). International reference NIST-NBS987 measurements yielded ⁸⁷Sr/⁸⁶Sr=
170 0.710238±22 (2σ; N=18). Isotopic ratios of both O and H are given in per mil (‰) *versus*
171 VSMOW (Vienna Standard Mean Ocean Water) reference material in the usual δ-scale
172 defined as δ_{sample} ‰ = {(R_{sample}/R_{standard})-1}*1000, where R is the ²H/¹H and ¹⁸O/¹⁶O atomic
173 ratios. O and H isotopic composition of water was measured with a Finnigan MAT 252 mass
174 spectrometer with an uncertainty of ±0.1‰ and ±0.8‰ for δ¹⁸O and δ²H, respectively.

175 Samples for tritium activity measurements were collected in one litre polyethylene bottles.
176 Analyses were done by direct liquid scintillation counting. The detection limit was 10 TU
177 (Tritium Unit with 1 TU equal to 1 tritium atom in 10¹⁸ hydrogen atoms). All isotopic analyses
178 were carried out by the BRGM Geochemistry Laboratory.

179 Samples for CFC and SF₆ were collected in 500 mL glass bottles. To avoid any air
180 contamination, each bottle was kept in a water-filled metal box. A simplified sample collection
181 method described by IAEA (2006) was applied. The analyses were performed by gas
182 chromatography with an electron-capture detector after pre-concentration using the purge-
183 and-trap technique developed by Spurenstofflabor, Wachenheim (Germany). The detection
184 limit was close to 10⁻⁴ pmol, allowing the measurement of CFC concentrations down to

185 0.01 pmol L⁻¹ and SF₆ concentrations to 0.1 fmol L⁻¹. The reproducibility was about ±5% for
186 water samples.

187 **4. RESULTS**

188 **4.1 Chemical composition of groundwater**

189 Physico-chemical parameters (Table 1) indicate that groundwater conditions in the northern
190 part of the studied area, on the right bank of the Seine, are mainly semi-oxic. Eh is <200 mV
191 NHE (normal hydrogen electrode) for six wells in the Alluvial and Chalk aquifers. In addition,
192 the NO₃ concentration below the detection limit indicating possible denitrification for various
193 points compatible with semi-oxic conditions observed in part of the aquifer. Surface- and
194 groundwaters are of the Ca-HCO₃ type (Fig. 3). Water from one well, Sa26, is of the Ca-SO₄
195 type. Water in well Sc13 has very low SO₄ concentrations, representing the more anoxic
196 conditions and possible sulphate reduction.

197 Binary diagrams (Fig. 4a) confirm an excess of sulphate compared to chloride from rainfall
198 origin. All surface- and groundwaters fall above the theoretical dilution line for sea water.
199 Sulphate may originates from evaporates, but another possible source is gypsum for soil
200 improvement, or fertilizers. In Figure 4b some points are also clearly enriched in chloride
201 compared to sodium ions. As local rocks are evaporite free, potential chloride sources are
202 rainfall and Manmade ones. Around Paris, Cl concentrations in precipitation are close to
203 0.15 mol/L (Mégnyen, 1979). Considering an average enrichment factor (F) estimated by
204 $\text{Rainfall}_{(\text{mm yearly average})}/(\text{R-Evapotranspiration process}_{(\text{mm yearly average})})$ of 1.5, chloride
205 concentrations up to 0.23 mmol/L are from rainfall origin.

206 The anthropogenic impact on surface- and groundwater is important in the Bassée plain
207 where agriculture is the main economical activity, even if gravel extraction gains on cultivated
208 lands. On a NO₃ vs. Cl diagram (Fig. 5) both groundwater from shallow (Alluvial) and deep
209 (Chalk) aquifers present nitrate concentrations over 25 mg/L (0.4 mmol/L) and up to
210 83.1 mg/L (1.34 mmol/L; Sa21). Nitrate concentrations below the detection limit of 0.5 mg/L
211 and chloride contents over 0.23 mmol indicate possible denitrification processes for these
212 waters in wells Sa26, Sc09, Sc13, Sc16, SC22, ScH4, Sa16 and Sa38 (only for the
213 November campaign). In addition, the gravel-pit lakes have very low nitrate concentrations
214 (<0.5 and 2.8 mg/L or <0.01 and 0.05 mmol/L).

215 Intense pressure from agriculture is also reflected in groundwater by the presence of four
216 pesticides in 116 analysed samples, which were detected at concentrations above the
217 detection limits. These pesticides and degradation molecules are atrazine (max. 0.091 mg/L
218 in the Voulzie River), deethylatrazine (max. 0.3 mg/L in Sc09), glyphosate (max. 5.59 mg/L in
219 Sa37) and aminomethylphosphonic acid, AMPA (max. 2.52 mg/L in Sa21). Atrazine has not
220 been used in this area since 2003. Glyphosate has both agricultural and non agricultural
221 uses, which makes its origin difficult to identify.

222 Both x vs. y and Piper diagrams highlight a similar chemistry for both Alluvial and Chalk
223 groundwaters. In addition, the chemistry of the Seine and Voulzie is not very different from
224 that of groundwater.

225

226 **4.2 Strontium isotopes**

227 In the Bassée flood plain area, Ca vs. Sr shows a good correlation whereas the NO₃ vs. Sr
228 correlation is weak, indicating a dominant lithological origin for Sr (Figs. 6a and 6b). Sr and
229 the ⁸⁷Sr/⁸⁶Sr ratio may therefore be controlled only by water-rock interaction in the Bassée
230 flood plain, as anthropogenic input of Sr can be neglected.

231 The strontium-isotope range observed in this study agrees with values expected for Jurassic
232 carbonate rock (⁸⁷Sr/⁸⁶Sr = 0.7067 to 0.7078) and Cretaceous Chalk (⁸⁷Sr/⁸⁶Sr = 0.7072 to
233 0.7080) (Koepnick et al., 1985, 1990). Furthermore, values measured in this study for the
234 Chalk aquifer are compatible with those acquired by Négrel and Petelet-Giraud (2005) for
235 this aquifer in the Somme Basin, north of Paris. Nevertheless, values measured in this study
236 are globally higher than those documented in the previously cited article. This result implies
237 the contribution of other Sr sources in addition to carbonate dissolution. The hypothesis of a
238 strontium contribution from anthropogenic origin was rejected because of the low Sr
239 concentrations observed (<8 µmol/L) and the lack of significant correlation between Sr
240 concentrations and nitrate (Fig. 6b) or chloride concentrations (not shown here). On a
241 ⁸⁷Sr/⁸⁶Sr vs. 1/Sr (Fig. 7a) diagram, samples plot globally in a triangle. In this classic diagram,
242 such a distribution suggests that, at least, three sources of dissolved Sr must explain the
243 ground- and surface-water composition. One end-member should display low ⁸⁷Sr/⁸⁶Sr
244 values and high Sr concentrations (End-member 1). Another end-member is expected to
245 have high ⁸⁷Sr/⁸⁶Sr values and intermediate Sr concentrations (End-member 2). A third end-
246 member would display low ⁸⁷Sr/⁸⁶Sr values and low Sr concentrations (End-member 3). End-
247 member 1 displays a Sr concentration and Sr-isotope composition close to the composition
248 of the Sa26 sampling point (⁸⁷Sr/⁸⁶Sr = 0.70792 and 0.70796; 7.51 and 7.19 µmol/L) and
249 compatible with a Sr contribution from carbonate dissolution. End-member 2 is close to the
250 Sc22 and Sa37 sampling points, both of which display the highest ⁸⁷Sr/⁸⁶Sr and Ca/Sr ratios
251 measured in this study (Fig. 8). The Ca/Sr ratio was demonstrated elsewhere to be a good
252 tool for tracing contrasting lithological origins (Brenot et al., 2008). As there is no correlation
253 between ⁸⁷Sr/⁸⁶Sr (or for the Ca/Sr ratio) and the NO₃ concentration (index of anthropogenic
254 origin), End-member 2 most probably has a lithological origin. Nevertheless, the ⁸⁷Sr/⁸⁶Sr and
255 Ca/Sr ratios measured for the Sc22 and Sa37 sampling points (defining End-member 2) are
256 much higher than expected values for local carbonate rock (as discussed above). A similar
257 deviation towards a radiogenic composition (higher ⁸⁷Sr/⁸⁶Sr values) was earlier observed
258 locally in the Seine Basin (Roy et al., 1999; Brenot et al., 2008), and for the Chalk aquifer in

259 the Somme Basin (Négrel and Petelet-Giraud, 2005). In these cases, the authors suggested
260 that radiogenic Sr might derive in part by thin marly-clayey beds in carbonate rock through
261 ion exchange or desorption of Sr, or by dissolution of the potential dolomitic part of carbonate
262 rock with a more radiogenic isotopic signature. End-member 3 is close to the composition of
263 Seine water, water from gravel-pit lakes and the Sa48 and Sc13 sampling points.
264 Furthermore, the Sr-isotope composition of Seine water (Roy, 1996) falls between 0.70777
265 and 0.70793, close to the composition expected for End-member 3. Thus, End-member 3
266 could potentially reflect a contribution of dissolved elements in surface water. Water in the
267 Voulzie River has a different Sr isotopic signature compared to that of the Seine (Fig. 7) and
268 water from gravel-pit lakes, which could be explained by significant differences in water-rock
269 interaction. Indeed, the Voulzie River flows through Early Tertiary layers composed of clay
270 and organic matter, whereas the Seine above the Bassée floodplain mainly flows over
271 carbonate rock (Roy et al., 1999). The Chalk aquifer sampled upstream also has a quite
272 different Sr-isotope signature compared to the Chalk aquifer sampled in the Bassée
273 floodplain (Fig. 7).

274 On a $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Ca/Sr diagram (Fig. 7b), a positive correlation is seen between $^{87}\text{Sr}/^{86}\text{Sr}$
275 values and the Ca/Sr ratio for all sampling points. The lowest Sr-isotope composition and
276 Ca/Sr ratio in this study are in the Seine ($^{87}\text{Sr}/^{86}\text{Sr}=0.70793$ to 0.70778 ; Ca/Sr=424 to 964),
277 whereas the highest Sr-isotope compositions and Ca/Sr ratios occur in groundwater at the
278 Sc22 and Sa37 sampling points ($^{87}\text{Sr}/^{86}\text{Sr}=0.70832$ to 0.70858 ; Ca/Sr=1103 to 1253).
279 Based on only $^{87}\text{Sr}/^{86}\text{Sr}$ values, and 1/Sr and Ca/Sr ratios (Fig. 7), one cannot discriminate
280 the groundwaters of the Alluvial and Chalk aquifers sampled in the Bassée floodplain.

281 **4.3 Tritium and CFC data**

282 The trends of CFCs and SF₆ used as input functions in air correspond to those of the Mace
283 Head (Ireland) station from the ALE/GAGE/AGAGE program (available from
284 cdiac.esd.ornl.gov/ftp/ale_gage_Agage/; Prinn et al., 2000), the closest survey station to the
285 Bassée site. Apparent groundwater ages were evaluated by using Excel® programs for CFC
286 developed by the International Atomic Energy Agency (IAEA, 2006). The recharge date was
287 determined by comparing the calculated partial pressure of CFCs and SF₆ in solubility
288 equilibrium with the water sample, with historical CFC concentrations in local air. The
289 equilibrium concentration of CFCs in groundwater depends on the air pressure (i.e. altitude)
290 and temperature in the saturated zone. Recharge temperatures used are the temperature of
291 groundwater at high-water-stage sampling time. The mean altitude of recharge is close to
292 55 m, the average altitude of the alluvial plain. The uncertainty in recharge temperatures and
293 recharge elevations is respectively maximum 1°C and 50 meters.

294 CFC-11, CFC-12, CFC-113, and SF₆ were systematically measured for groundwater dating.
295 For five sampling points, Sa26, Sa38, Sa48, Sc16 and ScH4, semi-anoxic conditions most

296 probably caused a degradation of CFCs (Horneman et al., 2008), in which case SF₆ was
297 then used for dating the water, this element being less sensitive to microbial degradation.
298 All water samples could be dated at least once. Determination of apparent water ages using
299 CFC and SF₆ (Plummer and Busenberg, 2000) was done by applying a binary mixing model
300 considering old water before 1950 (CFC-free) and young water with an age between 1985
301 and Present. This model was given the best results in “age-dating” (example for CFC-11 and
302 CFC-113 given in Fig.8). Young-water mixing fractions ranged from 0.20 to 0.99. Results
303 from the two sampling campaigns are quite similar. The uncertainty in recharge temperature
304 estimation (about 1°C what is the annual variability of groundwater temperature) is leading to
305 an uncertainty in mixing ratio of a maximum of 5%. Anthropogenic contamination was
306 observed in few samples, mainly for CFC-12 and SF₆ possibly due to the proximity of large
307 urban areas (Oster et al., 1996; Santella et al., 2008).

308 The dissolved gases and age-dating interpretation show a significant differentiation between
309 the Chalk and Alluvial aquifers. Only two wells (<20%) located in the Alluvial aquifer (Sa5,
310 Sa20) have a percentage of young water below or equal to 50%, whereas five deep wells
311 (>71%) tapping the Chalk aquifer (Sc11, Sc16, Sc22, ScH3, ScH4) show a percentage of
312 young water below 50%. Surprisingly, wells Sc13 and Sc09 in the Chalk aquifer mainly
313 contain young water, and a direct influence of surface water on these points is expected.
314 Being far from the River Seine, the influence of ponds or gravel-pit lakes is supposed. The
315 Alluvial groundwater in 75% of the wells is represented by water with a present (1985-2007)
316 component below 80%. Therefore, the older and deeper groundwater component is
317 significant, confirming the initial conceptual hydrogeological model of the Chalk aquifer
318 discharging into the upper aquifer layers.

319 A few kilometres upstream from the Bassée floodplain, the nuclear power plant at Nogent-
320 sur-Seine regularly has released tritium into the Seine since its start-up in 1988-1989. Tritium
321 can thus be used as a radionuclide tracer (Sanchez-Cabeza and Pujol, 1999) of the
322 infiltration of the Seine to groundwater since then. In the Seine at Bray-sur-Seine, the tritium
323 concentration measured during the project is quite variable, from 21 TU in July 2008 up to
324 573 TU in April 2008, reflecting the variable release from the power plant (3.1 to
325 11.7 TBq/month for the period August 2006-August 2008, data provided by EDF, the
326 operator). By comparison, the tritium values for Orléans precipitation (closest station at about
327 120 km from the Bassée site) have on average below 6 TU since 1999 (IAEA/WMO, 2009).

328 Tritium values measured in groundwater are very high (>60 TU) for Sc13, Sa41, Sa48 and
329 Sa61, and high (>15 TU) for Sc09, indicating a more or less important influence of surface
330 water on the Chalk and Alluvial aquifers at these points.

331 **4.4. Stable isotopes**

332 The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope composition of groundwater is -47 to -25‰ and -7.1 to -2.4‰,
333 respectively (Table 1). In the $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ diagram (Fig. 9), most of the water falls on the
334 local meteorological line (LML) represented by Orléans station (IAEA/WMO, 2009) with no
335 significant difference between the Alluvial and Chalk aquifers and the River Seine. The
336 average annual composition of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of the Seine water measured from oct.74 to
337 sep.76 at Poses (upstream Paris, 200 km far from La Bassée; Conrad et al., 1978) is falling
338 very closed to the 1996-2010 weighted mean of precipitation collected at Orléans.

339 The most isotopically depleted groundwater is that sampled in the Chalk aquifer upstream
340 from the Bassée area, which thus can be considered as the Chalk aquifer without influence
341 by surface and/or alluvial water. Another groundwater sample taken in 2009 at 120 km west
342 of the Bassée area in the Chalk aquifer of Paris Basin, has a similar isotopic content as that
343 of the Chalk water sampled at La-Chapelle-sur-Oreuse. River water from the Seine or the
344 Voulzie shows more enriched values. All other samples may be considered to be a mix
345 between “pure” groundwater and surface (rainfall and/or river) water from different periods,
346 and therefore with different isotope contents. Variation of the Seine isotopic composition is
347 about 1 ‰ (Conrad et al., 1978).

348 Some points in the Alluvial (Sa26, Sa38) and Chalk (Sc13, Sc16) aquifers fall on a line with a
349 slope of 4.3 that may correspond to isotopic fractionation caused by evaporation
350 (evaporation lines have a slope between 3.5 and 6 as function of local atmospheric humidity ;
351 Gat, 1981). To test this hypothesis, we calculated the evaporation line with as starting point
352 the average weighted $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitation in Orléans for the period 1999-
353 2009, and which would explain the compositions of samples Sa26, Sa38 (Alluvial aquifer)
354 and Sc13, Sc16 (Chalk aquifer). The calculations show that the two gravel-pit lakes sampled
355 in November 2007 have a stable-isotope composition falling onto the same evaporation line
356 and display the most fractionated isotopic composition from all samples in the Bassée
357 floodplain; here, water renewal is limited and therefore evaporation is expected to be high.
358 Though to a smaller extent, river water is also evaporated and falls on the same evaporation
359 line. This clearly indicates that some sampling points in groundwater integrate evaporated
360 water that could be provided either by gravel-pit lakes or by river water.

361 **5. DISCUSSION**

362 **5.1. Groundwater-river relationships**

363 Existing models (Mégnyen, 1979; Armines, 2005), consider that the Chalk aquifer supplies
364 water to the Alluvial aquifer, which then discharges into the Seine. More specific studies
365 (Chabart et al., 1992) have shown that, locally and occasionally, the River Seine can
366 influence the Alluvial aquifer.

367 Based on only the major element concentrations, the geochemical composition of
368 groundwater and surface water cannot be discriminated. Other geochemical tools are thus
369 needed to reach a better understanding of the potential relationships between rivers and
370 groundwater.

371 Sr isotopes are known (Négrel and Petelet-Giraud, 2005) to be an interesting tool for
372 groundwater-surface water relationships. In the Bassée site the Sr ratio contrast observed
373 between groundwater and surface water confirms its potential use in this context.

374 The spatial distribution of sampling points in the Bassée floodplain allows the construction of
375 two north-south profiles perpendicular to the Seine. Along these profiles, the Ca/Sr ratio and
376 $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig. 10) show a significant decrease, with the lowest values close to the
377 Seine for the high- and the low-water-stage sampling campaigns. Knowing the Ca/Sr ratio
378 and $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Seine water, the concomitant decrease of these two geochemical
379 tracers suggests an increasing contribution of Seine water to the groundwater close to the
380 riverbanks. Furthermore, the Ca/Sr ratio (1139) and the Sr isotopic signature
381 ($^{87}\text{Sr}/^{86}\text{Sr}=0.70812$) of Chalk aquifer groundwater collected at “La Chapelle”, 10 km away to
382 the north (Fig. 1), are significantly higher than the signatures measured for groundwater
383 collected closed to the Seine (Sa48, Sa41, Sch3, Sa26, Sa21, Sa20 and Sc16). The Ca/Sr
384 ratio and Sr isotopic compositions thus clearly show a recharge of the aquifers by surface
385 water during the high- and low-water stages. Surface water contribution seems to be of the
386 same importance for both Alluvial and Chalk aquifers. River-water infiltration to groundwater
387 is possible close to the river banks, and around ponds and gravel-pit lakes.

388 The sampling points located upstream and far from the Seine (Sc22, Sa37, Sc09, Sa61 and
389 Sa65) have the highest Ca/Sr ratio (930 to 1134) and $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70817 to 0.70835)
390 compared to the Seine water composition. At the opposite, sampling points located
391 downstream of the Bassée alluvial plain and close to the Seine (Sc11, SCH3 and Sa02) have
392 a Ca/Sr (876 to 916) close to the ratio measured at the upstream Seine station (not all points
393 fall onto the N-S profiles and therefore cannot be seen in Figure 10).

394 Tritium-content data show that very high (>60 TU) values for Sc13, Sa41, Sa48 and Sa61
395 and high (>15) values for Sc09 indicate a direct influence of river water on the Chalk and
396 Alluvial aquifers at these points. For well Sc13, located far from the main stream but close to
397 a large flooded area, many of the ponds and gravel-pit lakes are most probably fed directly
398 by the River Seine and the canal parallele to the Seine. Tritium content then indicates the
399 input of river water into groundwater via a residence period in ponds and gravel-pit lakes. A
400 quantitative estimation is not possible as tritium input varies throughout the year.

401 **5.2 Relationship between groundwater and gravel-pit lakes**

402 Numerous gravel-pit lakes or natural ponds, swamps, oxbow lakes, and other backwaters
403 exist in the flood plain. Chemical data and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios do not show significant differences

404 between water from the aquifers and such surface waters. This was expected, as such
405 waters mostly consist of groundwater.

406 In these water bodies, water renewal is limited and evaporation is quite high. Evaporation of
407 water before infiltration was highlighted for some wells using the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope
408 composition.

409 Most of the lakes were created by gravel extraction, causing a change in the hydraulic
410 properties of the Alluvial aquifer. It is expected that these artificial holes also facilitate the
411 infiltration of surface water down to the deeper parts of the aquifers. The high permeability of
412 the walls suggests that water will mainly infiltrate horizontally into both the Chalk and Alluvial
413 aquifers.

414 Water sampled at Sc13 in the Chalk aquifer is the most intensively evaporated. Due to the
415 strong variability in H and O isotope signatures of the gravel-pit lakes (only two of them were
416 sampled), it is possible that fractionation is even stronger in other superficial water bodies.
417 The Sc13 water may result from a mixture of surface water with a more fractionated isotopic
418 signature (higher H and O isotopic signatures) than the two gravel-pit lakes sampled in this
419 study or the groundwater. The infiltration of surface water to the aquifer is also clearly shown
420 at sampling points Sa26, Sa38, Sc13 and Sc16 (Fig. 9).

421 Dissolved gases (CFC-11, CFC-12, CFC-113, SF_6) and age-dating interpretation give quite
422 heterogeneous results. Piezometers Sc13 and Sc09 in the Chalk aquifer mainly contain
423 young water, and a direct influence of surface water on these points is thus expected. Being
424 far from the Seine, the influence of ponds or gravel-pit lakes is most likely for these two wells.
425 However, the recharge functioning is quite complex for Sc09 located in the eastern part of
426 the study area, far from the Seine and any flooded area. No explanation could be found to
427 explain the geochemical parameters of groundwater at this point.

428 **5.3. Impact of the water dynamics on groundwater quality**

429 An understanding of the hydraulic connections in the Seine floodplain may help in
430 understanding groundwater contamination. Borrow pits were initiated in the area in the 1970s
431 and rapidly increase in number. This extraction activity does not seem to have a direct
432 qualitative impact on the groundwater. Agriculture today occupies 40% of the Bassée plain
433 as against 46% in 1976 (Fustec et al., 2001). The dominant crops are cereals (wheat, maize,
434 barley, rape, sunflower) and sugar beets, and diffuse pollution is expected at the study area.
435 Groundwater contamination can be quite high in the left bank of the Seine. Nitrate
436 concentrations measured in June and November 2007 were, for 9 wells of the 19 sampled,
437 over 17 mg/L and up to 83.1 mg/L (Sa21), confirming an anthropogenic impact. For 5 wells
438 (4 in the Chalk and 1 in the Alluvial aquifer), reducing conditions may have led to
439 denitrification. Existing data (www.eaufrance.adès.fr) underlines the importance of
440 contamination of the Alluvial aquifer. Actually, 40% of the wells in the Bassée Alluvial aquifer

441 in the past showed triazine contamination at least once. Pesticide (mainly atrazine and DEA)
442 and nitrate contamination have also been detected in wells tapping the Chalk aquifer. For the
443 Water Framework Directive, both groundwater bodies (FRHG006 Alluvial aquifer on the
444 Bassée site and FRHG209 Chalk aquifer) were classified as having a poor chemical status.
445 The percentage of young groundwater was compared to nitrate concentrations (Fig. 10). A
446 positive correlation was observed between the percentage of young water and nitrate
447 concentrations for water in aerobic conditions, circulating in the Alluvial and Chalk aquifers.
448 For most sampling points, the more important is the influence of the young groundwater, the
449 higher are the nitrate concentrations (Fig. 11), whereby the “youngest” groundwater dates
450 from 1985 up to 2007. In captive parts of the aquifer or around wetlands, the nitrate
451 concentrations are below the detection limit (0.5 mg/L), most probably due to denitrification
452 processes (in grey on Fig. 11). Seine water upstream and downstream from the study area
453 has an average nitrate concentration lower than groundwater (<0.5 mg/L to 35.4 mg/L).
454 For Sa61, Sa41, Sa48 relatively low nitrate concentrations compared to the apparent CFC
455 ages may be explained by surface water influence (Fig. 11). In fact, the very high tritium
456 content in groundwater from these three wells indicates a stronger influence of the Seine on
457 groundwater, an influence that was also felt in Sc13 and Sc09. At the latter two points, a low
458 redox potential suggests possible denitrification processes. In Sc09, the nitrate concentration
459 in November 2007 (74.2 mg/L) and the redox potential (311 mv NHE) are higher than during
460 the high water period (<0.5 mg/L and 345 mV NHE, respectively). As other chemical
461 elements have similar concentrations for the high and low water sampling campaigns,
462 denitrification is the most probable process for explaining major changes for only the NO₃
463 concentration.
464 The two sampled gravel-pit lakes have nitrate concentrations of 2.8 and <0.5 mg/L. Low
465 nitrate concentrations can be explained by dilution (from rainfall and/or rivers), adsorption by
466 plants and denitrification processes, as was earlier demonstrated in riparian wetlands
467 upstream from the present study area (Bendjoudi et al., 2002). Concentrations of other
468 chemical elements are similar or lower than in river water. Dilution by rainfall input is
469 probably the most important factor, as Redox conditions may not allow denitrification
470 processes and there are no or very few plants in the gravel-pit lakes. Previous work (Fuster
471 et al., 2001) showed that silt deposits at the bottom of the gravel-pit lakes greatly reduce
472 groundwater exchanges. Evaporation and recharge by precipitation therefore are dominating
473 factors of the hydraulic balance of these specific surface-water bodies. Infiltration of water
474 from gravel-pit lakes has a positive influence on groundwater quality. As for river water, the
475 infiltration of water from gravel pits reduces, at least locally, the nitrate concentration in wells
476 upstream from these artificial lakes.

477 **6. CONCLUSIONS**

478 From the geochemical tools the following conclusions may be drawn:

- 479 • No systematic chemical differentiation exists between the Chalk and Alluvial aquifer
480 waters. This confirms that the conceptual hydrogeological model is correct at a
481 regional scale, which considers that Chalk groundwater supplies water to the Alluvial
482 aquifer. However, at the local scale more complex hydraulic connections exist
483 between the different water bodies, as was highlighted by using isotope tools and
484 age-dating. Both the Chalk and the Alluvial aquifers may be influenced by surface
485 water.
- 486 • Age-dating highlighted the presence of young, i.e. less than 10 years old,
487 groundwater in the wells Sc09 and Sc13 tapping the Chalk aquifer.
- 488 • The influence of Seine water, direct or indirect through the alluvial deposits, was
489 shown using tritium and Sr isotope data for Sa41, Sa48 and Sa61.
- 490 • The impact on the aquifer of water stored in the gravel-pit lakes or other natural
491 shallow lakes, ponds or swamps, was highlighted by using stable-isotope tools. The
492 evaporation effect was clear on groundwater collected in wells Sc13, Sc16, Sa26 and
493 Sa38. For Sc13, both a surface-water influence by the Seine through alluvial deposits
494 and by infiltration from gravel-pit lakes is possible.
- 495 • $\delta^2\text{H}$ and $\delta^{18}\text{O}$, tracers of water-rock interaction processes ($^{87}\text{Sr}/^{86}\text{Sr}$, Ca/Sr) and of
496 water origin (^3H) differentiated the role of the River Seine, gravel-pit lakes (and most
497 probably other superficial water bodies) in local groundwater recharge. The
498 geochemical approach provided a spatial characterization of the origin of water and
499 dissolved elements from surface and groundwater bodies.
- 500 • The geochemical approach tested on this site clearly demonstrates the efficiency of
501 geochemical tools for describing the relationships between groundwater, river water
502 and lake water. In addition, it underlined the need of using multiple tools for
503 understanding a complex water system.
- 504 • The approach described in this paper can be usefully applied to other case studies,
505 and will help decision makers in the context of natural water management.

506

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510 **References**

511 ARMINES, 2005. Etude globale pour l'aménagement de la Bassée. Etude hydrogéologique
512 de faisabilité. Mine Paris.

- 513 Baron, P., Piketti, G., 2001. Plaine Alluvial de la Bassée. Inspection Générale de
514 l'Environnement, Affaire IGE/00/039.
- 515 Beard, B.L., Johnson, C.M., Skulan, J.L., Nealson, K.H., Cox, L., Sun, H., 2003. Application
516 of Fe isotopes to tracing the geochemical and biological cycling of Fe. *Chem. Geol.* 195(1-4),
517 87-117.
- 518 Bendjoudi, H., Weng, P., Guérin, R., Pastre, J.F., 2002. The riparian wetland of the middle
519 reach of the Seine River: Historical development, reconnaissance and present hydrologic
520 functioning, a case study. *J. Hydrol.* 263, 131-155.
- 521 Bouchaou, L., Michelot, J.L., Qurtobi, M., Zine, N., Gaye, C.B., Aggarwal P.K., Merah, H.,
522 Zerouali, A., Taleb, B., Vengosh, A., 2009. Origin and residence time of groundwater in the
523 Tadla basin (Morocco) using multiple isotopic and geochemical tools. *J. Hydrol.* 379, 323-
524 338.
- 525 Brenot, A., Baran, N., Petelet-Giraud, E. Négrel, P., 2008. Interaction between different water
526 bodies in a small catchment area in the Paris basin (France): Sr isotopic tracing of multiple
527 Sr sources. *Applied Geochemistry*, 23, 58-76.
- 528 Cardinal, D., Alleman, L.Y., de Jong, J., Ziegler, K., André, L. 2003. Isotopic composition of
529 silicon measured by multicollector plasma source mass spectrometry in dry plasma mode. *J.*
530 *Anal. Atom. Spectrom.* 18, 213-218.
- 531 Chabart, M., Lauverjat, J., Mariotti, A., Olive, P., 1992. Étude des caractéristiques
532 hydrochimiques et hydrodynamiques du champ captant de la Grande-Paroisse. Rapport
533 SAGEP-CRECEP-UPMC.
- 534 Conrad, G., Jouzel, J., Merlivat, L., Puyoo, S., 1979. La nappe de la craie en Haute-
535 Normandie (France) et ses relations avec les eaux superficielles. In: *Isotope Hydrology,*
536 *proceeding of an International Symposium on Isotope Hydrology held in Neuherberg in 1978,*
537 *STI/PUB/493, IAEA, Vienna.* pp. 265-287.
- 538 Darling, W.G., Goody, D.C., Riches, J., Wallis, I., 2010. Using environmental tracers to
539 assess the extent of river-groundwater interaction in a quarried area of the English Chalk.
540 *Appl. Geochem.* 25, 923-932.
- 541 Fustec E., Bendjoudi, H., Gaillard, S., Weng, P., Boyer, F., Boet, P., Shannen, O.,
542 Crogenec, S., Billen, G. 2001. Rapport de synthèse 1998-2001. Fonctionnement du
543 territoire 'Bassée'. UMR Sysiphe, UPMC.
- 544 Galy, A., Belshaw, N.S., Halicz, L., O'Nions R.K., 2001. High-precision measurement of
545 magnesium isotopes by multiple-collector inductively coupled plasma mass spectrometry.
546 *Int. J. Mass Spectrom.* 208, 89-98.
- 547 Gat, J., 1981. Isotopic fractionation. In: *Stable Isotope Hydrology - Deuterium and Oxygen-18*
548 *in the Water Cycle.* (Eds.J. Gat and R. Gonfiantini). Technical Report Series N. 210, IAEA,
549 Viena.
- 550 Goody, D.C., Darling, W.G., Abesser, C., Lapworth, D.J., 2006. Using chlorofluorocarbons
551 (CFCs) and sulphur hexafluoride (SF6) to characterise groundwater movement and
552 residence time in a lowland Chalk catchment. *J. Hydrol.* 330, 44-52.
- 553 Halicz, L., Galy, A., Belshaw, N.S., O'Nions, R.K., 1999. High-precision measurement of
554 calcium isotopes in carbonates and related materials by multiple-collector inductively coupled
555 plasma mass spectrometry (MC-ICP-MS). *J. Anal. Atom. Spectrom.* 14, 1835-1838.
- 556 Horneman, A., Stute, M., Schlosser, P., Smethie, W., Santella, N., Ho, D.T., Mailloux, B.,
557 Gorman, E., Zheng, Y, van Geen, A., 2008. Degradation rates of CFC-11, CFC-12 and CFC-
558 113 in anoxic shallow aquifers of Arahazar, Bangladesh. *J. Contam. Hydrol.* 97, 27-41.
- 559 IAEA, 2006. Use of Chlorofluorocarbons in Hydrology: A Guidebook. STI/PUB 1238, IAEA,
560 Vienna.

- 561 IAEA/WMO, 2009. Global Network of Isotopes in Precipitation. The GNIP Database.
562 Accessible at: <http://isohis.iaea.org>.
- 563 Koepnick R.B., Denison R.E., Burke W.H., Hetherington, E.A., Dahl, D.A., 1990.
564 Construction of the Triassic and Jurassic portion of the Phanerozoic curve of seawater
565 $^{87}\text{Sr}/^{86}\text{Sr}$. Chem. Geol. 80, 327-349.
- 566 Koepnick, R.B., Burke, W.H., Denison, R.E., Hetherington, E.A., Nelson, H.F., Otto, J.B.,
567 Waite, L.E., 1985. Construction of the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve for the Cenozoic and
568 Cretaceous: Supporting data. Chem. Geol. 58, 55-81.
- 569 Lamontagne, S., Leaney, F.W., Herczeg, A.L., 2005. Groundwater-surface water interactions
570 in a large semi-arid floodplain: implications for salinity management. Hydrol. Process. 19,
571 3063-3080.
- 572 Langman, J.B., Ellis, A.S., 2009. A multi-isotope (δD , $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{11}\text{B}$) approach for
573 identifying saltwater intrusion and resolving groundwater evolution along the Western
574 Caprock Escarpment of the Southern High Plains, New Mexico. Appl. Geochem. 25, 159-
575 174.
- 576 Luais, B., Telouk, P., Albarede, F., 1997. Precise and accurate neodymium isotopic
577 measurements by plasma-source mass spectrometry. Geochim. Cosmochim. Acta 61, 4847-
578 4854.
- 579 Ma, J.Z., Pan, F., Chen, L.H., Edmunds, M., Ding, Z., He, J., Zhou, K., Huang, T., 2010.
580 Isotopic and geochemical evidence of recharge sources and water quality in the Quaternary
581 aquifer beneath Jinchang city, NW China. Appl. Geochem. 25, 996-1007.
- 582 Marechal, C.N., Telouk, P., Albarede, F. 1999. Precise analysis of copper and zinc isotopic
583 compositions by plasma-source mass spectrometry. Chem. Geol. 156, 251-273.
- 584 Mégnién, C. 1965. Possibilités aquifères des alluvions du val de Seine entre Nogent-sur-
585 Seine et Montereau, incluant Carte géologique et géomorphologique de la Bassée, Rapport
586 BRGM DSGR 65A76.
- 587 Mégnién, C., 1979. Hydrogéologie du centre du bassin de paris. Mém. BRGM n°98.
- 588 Millot, R., Négrel, P., Petelet-Giraud, E., 2007. Multi-isotopic (Li, B, Sr, Nd) approach for
589 geothermal reservoir characterization in the Limagne Basin (Massif Central, France).
590 Appl. Geochem. 22, 2307-2325.
- 591 Négrel, P., Pauwels, H., 2004. Interaction between different groundwaters in Brittany
592 catchments (France): Characterizing multiple sources through strontium- and sulphur isotope
593 tracing. Water Air Soil Poll. 151, 261-285.
- 594 Négrel, P., Petelet-Giraud, E., 2005. Strontium isotopes as tracers of groundwater-induced
595 floods: the Somme case study (France). J. Hydrol. 305, 99-119.
- 596 Oster, H., Sonntag, C., Munnich, K.O., 1996. Groundwater age dating with
597 chlorofluorocarbons. Water Resour. Res. 32(10), 2989-3001.
- 598 Oxtobee, J.P.A., Novakowski, K., 2002. A field investigation of groundwater/surface water
599 interaction in a fractured bedrock environment. J. Hydrol. 269, 169-193.
- 600 Plummer, L.N., Busenberg, E., 2000. Chlorofluorocarbons: Tools for dating and tracing
601 young groundwater. In: P. Cook and A. Herczeg (Eds.), Environmental Tracers in Subsurface
602 Hydrology, Kluwer Academic Publishers, Boston. pp. 441-478.
- 603 Prinn, R.G., Weiss, R.F., Fraser, P.J., Simmonds, P.G., Cunnold, D.M., Alyea, F.N.,
604 O'Doherty, S., Salameh, P., Miller, B.R., Huang, J., Wang, R.H.J., Hartley, D.E., Harth, C.,
605 Steele L.P., Sturrock G., Midgley P.M., McCulloch, A., 2000. A history of chemically and
606 radiatively important gases in air deduced from ALE/GAGE/AGAGE. J. Geophys. Res. 105,
607 17751-17792.

608 Rehkamper, M., Halliday, A.N., 1999. The precise measurement of T1 isotopic compositions
609 by MC-ICPMS: Application to the analysis of geological materials and meteorites. *Geochim.*
610 *Cosmochim. Acta* 63, 935-944.

611 Rouxel, O., Ludden, J., Carignan, J., Marin, L., Fouquet, Y., 2002. Natural variations of Se
612 isotopic composition determined by hydride generation multiple collector inductively coupled
613 plasma mass spectrometry. *Geochim. Cosmochim. Acta*, 66, 3191-3199.

614 Roy, S., 1996. Utilisation des isotopes du Pb et du Sr comme traceurs des apports
615 anthropiques et naturels dans les précipitations et les rivières du Bassin de Paris. PhD
616 Thesis, Univ. Paris 7.

617 Roy, S., Gaillardet, J., Allègre, C.J., 1999. Geochemistry of dissolved and suspended loads
618 of the Seine River, France: anthropogenic impact, carbonate and silicate weathering.
619 *Geochim. Cosmochim. Acta* 63, 1277–1292.

620 Sanchez-Cabeza, J.A., Pujol, L., 1999. Study on the hydrodynamics of the Ebro River lower
621 course using tritium as a radiotracer. *Water Res.* 33, 2345-2356.

622 Santella, N., David, T.H., Schlosser, P., Stute, M., 2008. Widespread elevated atmospheric
623 SF6 mixing ratios in the Northeastern United States: Implications for groundwater dating.
624 *J.Hydrol.* 349, 139-146.

625 Schanen, O., Bendjoudi, H., Levassor, A., Fustec, E., 1998. Quantification des écoulements
626 Nappe-Gravières, en zone alluviale, par optimisation des paramètres du bilan hydrologique.
627 *C. R. Acad. Sci.* 326, 107-112.

628 Schultz, T.R., Randall, J.H., Wilson, L.G., Davis S.N., 1976. Tracing sewage effluent
629 recharge – Tucson, Arizona. *Groundwater.* 14, 463-470.

630 SOGREAH, 2004. Etude de compatibilité de l'aménagement de la Bassée avec les
631 ressources en eau. Juillet 2004.

632 Vengosh, A., Gill, J., Davisson, M.L., Huddon, G.B., 2002. A multi-isotope (B, Sr, O, H, and
633 C) and age dating (H-3-He-3 and C-14) study of groundwater from Salinas Valley, California:
634 Hydrochemistry, dynamics, and contamination processes. *Water Resour. Res.* 38, 1-17.

635 Vengosh, A., Hening, S., Ganor, J., Mayer, B., Weyhenmeyer, C.E., Bullen, T.D., Paytan, A.,
636 2007. New isotopic evidence for the origin of groundwater from the Nubian Sandstone
637 Aquifer in the Negev, Israel. *Appl. Geochem.* 22, 1052-1073.

638 Vernoux, J.F., Schomburgk, S., Hanot, F., Donsimoni, M., 2004. Projet d'aménagement du
639 site de la Bassée - analyse des travaux de reconnaissance réalisés en 2002-2003, rapport
640 BRGM/RP-52712-FR.

641 Weng, P., Coudrain-Ribstein, A., Kao, C., Bendjoudi, H., de Marsilly, G., 1999.
642 Demonstration of strong temporary vertical circulation between wetlands and alluvial and
643 regional aquifers. *CR. Acad.Sci.* 329, 257-263.

644 Wombacher, F., Rehkamper, M., 2003. Investigation of the mass discrimination of multiple
645 collector ICP-MS using neodymium isotopes and the generalised power law. *J. Anal. Atom.*
646 *Spectrom.* 18, 1371-1375.

647

648

649 **Figure and table captions**

650 Figure 1 - Map showing the studied area and location of sampling points

651 Figure 2 - N-S synthetic geological profile through the Bassée area

652 Figure 3 - Piper diagram for ground- and surface waters sampled in June and November
653 2007 in the Bassée floodplain and in one well upstream in the Chalk aquifer

654 Figure 4 - SO_4 vs. Cl and Na vs. Cl for surface and groundwater sampled in the Bassée plain
655 in June and November 2007 and groundwater sampled upstream (Chalk aquifer)

656 Figure 5 - NO_3 vs. Cl for surface and groundwater sampled at the Bassée plain in June and
657 November 2007 and groundwater sampled upstream (Chalk aquifer)

658 Figure 6 - Ca vs. Sr and NO_3 vs. Sr for surface and groundwater sampled at the Bassée plain
659 in June and November 2007 and groundwater sampled upstream (Chalk aquifer)

660 Figure 7 - $^{87}\text{Sr}/^{86}\text{Sr}$ vs. 1/Sr (molar) and $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Ca/Sr (molar) for surface and
661 groundwater sampled in the Bassée plain in June and November 2007
662 and in an upstream well

663 Figure 8 - CFC-11 vs. CFC-113 (in pptv) for groundwater collected in the La Bassée site in
664 June and November 2007 and piston flow, exponential and binaxy mixing of young water
665 (recharged in 1985 and 2005) with CFC-free water reference lines

666 Figure 9 - $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ for surface and groundwater collected in the Bassée site in June and
667 November 2007; local meteoric line and mean weighted values for precipitations at Orléans
668 (1996-2010), mean of Seine water at Poses (1974-1976) and calculated evaporation line

669 Figure 10 - $^{87}\text{Sr}/^{86}\text{Sr}$ vs. distance and Sr/Ca vs. distance for groundwater collected in June
670 and November 2007 along the two north-south profiles

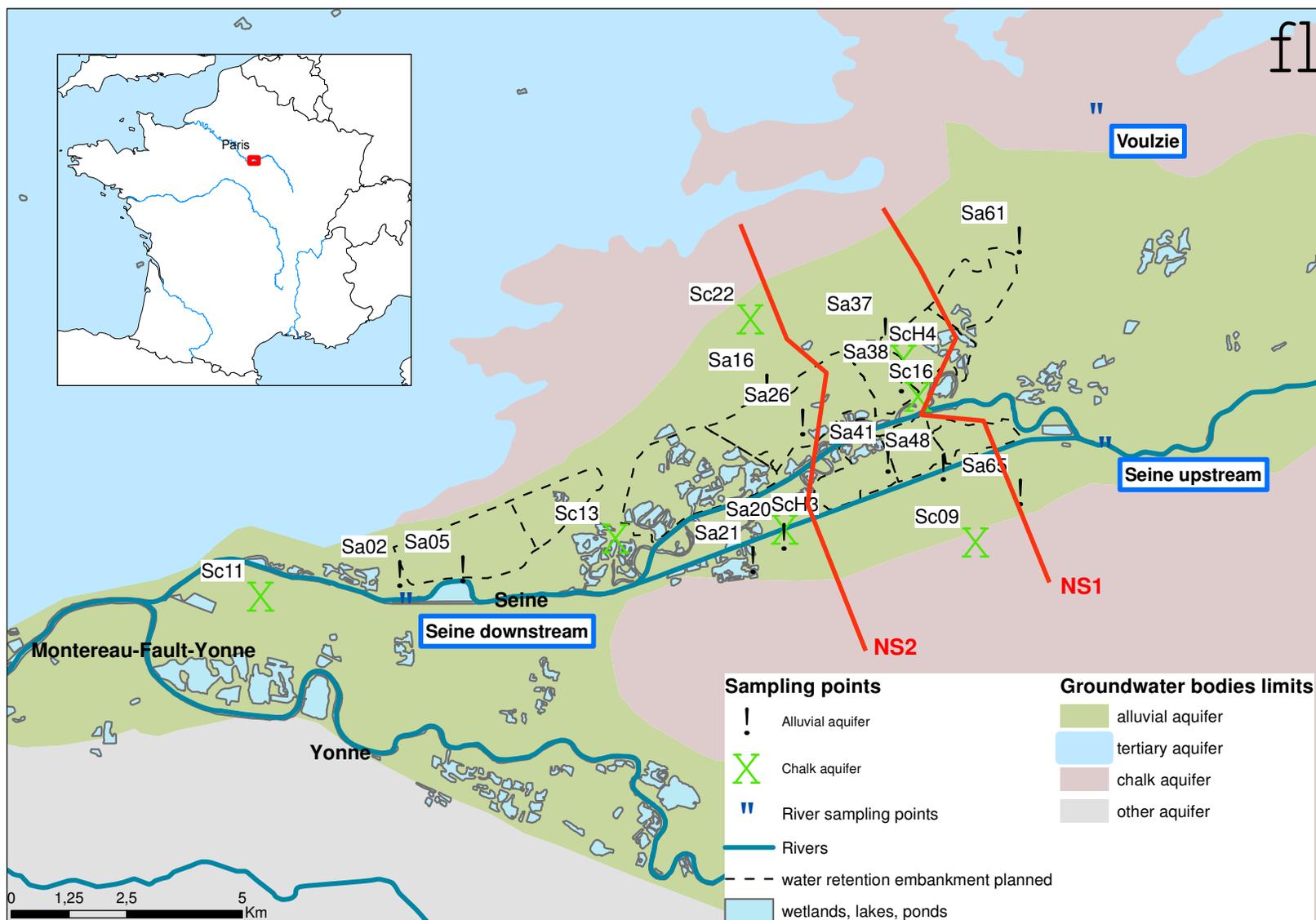
671 Figure 11 - NO_3 vs. % of young groundwater for groundwater sampled in June and
672 November 2007 in the Bassée alluvial plain

673

674 Table 1 - Analytical results for June and Novembre 2007 sampling campaign

N°	type	Date	Cond.	Eh(NHE)	Temp.	pH	Ca	Mg	Na	K	HCO ₃	Cl	NO ₃	SO ₄	Sr	Rb	⁸⁷ Sr/ ⁸⁶ Sr	δ ¹⁸ O	δ ² H	
			μS.cm ⁻¹	mV	°C	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	‰	‰
June-07 (high flow period)																				
Sa02	Alluvial aquifer	12/06/2007	734	383	11.9	7.1	3671	86	278	49	4607	775	969	723	4.01	0.01	0.708001	-6.4	-42.3	
Sa05	Alluvial aquifer	12/06/2007	643	359	12.3	7.1	3150	136	300	49	4869	541	658	353	3.89	0.00	0.708063	/	/	
Sa16	Alluvial aquifer	12/06/2007	725	250	12.8	7.1	3549	152	513	69	4902	868	161	931	3.40	0.01	0.708152	-6.4	-42.3	
Sa20	Alluvial aquifer	12/06/2007	579	311	12.0	7.2	2746	115	413	90	4721	515	458	214	3.38	0.02	0.707981	-6.7	-45.1	
Sa21	Alluvial aquifer	12/06/2007	578	350	12.5	7.4	2618	66	239	74	3508	617	1332	166	2.67	0.00	0.707940	-6.4	-42.5	
Sa26	Alluvial aquifer	13/06/2007	1135	173	11.7	7.0	6426	222	361	18	5639	606	<DL	3650	7.51	0.00	0.707925	-4.8	-35.7	
Sa37	Alluvial aquifer	13/06/2007	786	358	11.3	7.0	3469	169	983	128	5459	1270	540	510	3.06	0.01	0.708325	-6.6	-43.2	
Sa38	Alluvial aquifer	13/06/2007	668	154	12.0	7.0	3337	123	465	23	5459	676	94	524	3.29	0.00	0.708184	-4.8	-35.7	
Sa41	Alluvial aquifer	13/06/2007	541	351	13.2	7.2	2471	152	339	100	4164	361	276	257	3.34	0.02	0.708042	-6.6	-45.1	
Sa48	Alluvial aquifer	13/06/2007	533	302	15.9	7.3	2349	160	470	72	4066	637	95	323	3.03	0.01	0.707777	-6.5	-44.1	
Sa61	Alluvial aquifer	12/06/2007	860	287	12.1	6.9	4005	387	670	348	7213	901	202	712	3.77	0.00	0.708168	-6.8	-44.0	
Sa65	Alluvial aquifer	13/06/2007	763	375	17.3	7.1	3436	140	465	51	5049	989	989	339	3.56	0.00	0.708246	-6.4	-42.4	
Sc09	Chalk aquifer	13/06/2007	645	345	18.6	7.2	2885	128	474	0	4213	769	<DL	258	3.07	0.01	0.708168	-7	-46.9	
Sc11	Chalk aquifer	12/06/2007	525	386	12.3	7.2	2731	78	487	28	4557	538	432	232	3.09	0.00	0.708119	-6.9	-45.9	
Sc13	Chalk aquifer	12/06/2007	414	105	13.4	7.4	1788	111	313	38	3656	437	<DL	22	2.47	0.00	0.707807	-2.4	-25.2	
Sc16	Chalk aquifer	13/06/2007	682	175	11.5	7.0	3479	189	330	31	5705	462	<DL	715	3.81	0.01	0.708063	-6	-41.8	
Sc22	Chalk aquifer	12/06/2007	700	321	12.5	7.0	3519	103	452	15	5443	854	<DL	352	2.81	0.00	0.708582	-6.7	-44.5	
ScH3	Chalk aquifer	12/06/2007	500	282	14.7	7.3	2259	144	270	41	3787	352	626	163	2.82	0.00	0.707798	-6.8	-46.0	
ScH4	Chalk aquifer	13/06/2007	733	162	11.8	6.9	3451	193	643	33	5721	814	<DL	594	3.39	0.00	0.708156	-6.8	-45.1	
Seine Amont	River	13/06/2007	536	344	23.5	8.2	2334	165	591	66	3607	732	361	426	3.25	0.02	0.707728	-6.3	-43.6	
Voulzie	River	13/06/2007	661	364	18.7	8.2	2339	165	535	64	3689	718	368	425	2.24	0.00	0.708282	-6.6	-44.0	
Seine Aval	River	13/06/2007	538	391	23.1	8.2	3027	210	604	79	4836	941	600	363	3.14	0.00	0.707749	-6.2	-42.0	
October-07 (low flow period)																				
Sa02	Alluvial aquifer	06/11/2007	736	271	12.9	7.1	3641	74	243	49	4770	868	985	783	4.16	/	0.708019	-6.5	-41.3	
Sa05	Alluvial aquifer	06/11/2007	640	265	13.5	7.3	3137	115	257	51	5016	552	650	354	3.89	/	0.708108	-6.7	-42.8	
Sa16	Alluvial aquifer	06/11/2007	735	243	13.5	7.2	3456	160	296	28	5574	501	<DL	760	4.16	/	0.708242	-6.3	-41.5	
Sa20	Alluvial aquifer	06/11/2007	563	378	12.8	7.5	2626	95	343	90	4656	510	571	177	3.32	/	0.708002	-6.9	-45.7	
Sa21	Alluvial aquifer	06/11/2007	575	301	14.2	7.6	2656	58	200	64	3459	668	1340	166	2.72	/	0.707974	-6.4	-42.3	
Sa26	Alluvial aquifer	06/11/2007	1095	139	13.2	7.2	6095	189	335	18	5410	631	<DL	3373	7.19	/	0.707964	-4.7	-34.2	
Sa37	Alluvial aquifer	06/11/2007	818	302	13.5	7.4	3651	156	961	125	5705	1693	518	534	3.31	/	0.708349	-6.6	-42.5	
Sa38	Alluvial aquifer	07/11/2007	661	196	12.9	7.1	3257	119	430	28	5393	735	<DL	519	3.20	/	0.708231	-4.3	-34.3	
Sa41	Alluvial aquifer	07/11/2007	593	330	14.2	7.3	2698	148	330	113	4803	400	353	404	3.73	/	0.708066	-6.9	-45.6	
Sa48	Alluvial aquifer	07/11/2007	425	276	15.6	7.5	1900	119	287	51	3492	414	13	243	2.52	/	0.707802	-6.3	-43.0	
Sa61	Alluvial aquifer	06/11/2007	841	306	13.2	7.1	3868	296	587	315	6951	1090	192	575	3.55	/	0.708195	-6.8	-44.5	
Sa65	Alluvial aquifer	07/11/2007	678	325	12.8	7.4	3057	119	504	64	4459	1096	1129	177	3.28	/	0.708244	-6.6	-44.5	
Sc09	Chalk aquifer	07/11/2007	614	311	12.5	7.5	2890	107	422	0	4033	893	1197	212	3.11	/	0.708177	-7.0	-46.6	
Sc11	Chalk aquifer	06/11/2007	565	282	12.0	7.2	2678	70	387	31	4672	603	484	217	3.05	/	0.708127	-6.9	-46.2	
Sc13	Chalk aquifer	06/11/2007	418	88	14.9	7.6	1798	103	300	38	3885	462	<DL	21	2.49	/	0.707820	-2.4	-24.7	
Sc16	Chalk aquifer	06/11/2007	679	146	12.7	7.3	3579	148	413	51	5180	910	519	809	3.37	/	0.708015	-6.2	-41.5	
Sc22	Chalk aquifer	06/11/2007	645	283	12.2	7.3	3252	78	370	18	5410	701	340	259	2.81	/	0.708476	-6.9	-44.8	
ScH3	Chalk aquifer	07/11/2007	509	378	12.8	7.3	2292	128	239	41	3770	383	653	166	2.79	/	0.707837	-6.8	-45.5	
ScH4	Chalk aquifer	06/11/2007	740	149	12.2	7.3	3514	165	604	33	5836	966	<DL	687	3.08	/	0.708259	-6.9	-45.8	
Seine Upstream	River	07/11/2007	455	338	10.1	8.3	1980	144	322	54	3443	456	224	257	2.69	/	0.707783	-6.1	-42.4	
Voulzie	River	07/11/2007	674	329	8.7	8.0	2868	185	600	100	4721	1082	571	315	2.31	/	0.708247	-6.6	-43.9	
Seine Downstream	River	07/11/2007	443	341	10.5	8.4	1925	140	309	54	3295	451	219	250	2.61	/	0.707790	-6.1	-41.9	
Bassin Amont	Ponds	07/11/2007	287	320	9.1	8.0	1012	119	322	64	1754	459	45	190	2.39	/	0.707933	-4.9	-35.8	
Bassin Aval	Ponds	07/11/2007	346	348	10.2	8.2	1384	123	339	43	2787	558	<DL	63	2.32	/	0.707816	-3.7	-31.2	
AEP La Chapelle	Chalk aquifer	07/11/2007	522	387	12.0	7.3	2379	62	274	77	3820	454	811	97	2.09	/	0.708119	-7.1	-46.5	
Sampling of the Seine River at Bray/Seine on a monthly basis																				
Seine at Bray/Seine	River	13/06/2007	536	344	23.5	8.2	2334	165	591	66	3607	732	361	426	3.25	/	/	/	/	
Seine at Bray/Seine	River	03/08/2007	402		20.9	8.2	1910	144	300	43	3180	355	240	242	2.23	/	/	/	/	
Seine at Bray/Seine	River	21/09/2007	386	458	16.2	8.3	1796	144	322	46	3098	397	227	214	2.23	/	/	/	/	
Seine at Bray/Seine	River	06/11/2007	455	337	10.1	8.3	1980	144	322	54	3443	456	224	257	2.69	/	/	/	/	
Seine at Bray/Seine	River	04/01/2008	548	599	6.1	8.3	2673	152	326	54	4230	499	458	294	3.26	/	/	/	/	
Seine at Bray/Seine	River	15/02/2008	545	617	6.5	8.4	2676	148	330	49	4197	544	463	286	3.17	/	/	/	/	
Seine at Bray/Seine	River	25/03/2008	492	549	7.2	8.2	2377	136	235	49	4328	327	397	183	2.66	/	/	/	/	
Seine at Bray/Seine	River	30/04/2008	509	573	13.3	8.1	2387	132	239	38	4246	456	329	206	3.56	/	/	/	/	
Seine at Bray/Seine	River	27/05/2008	506		16.7	8.1	2444	144	378	51	3967	580	405	279	3.92	/	/	/	/	

Figure



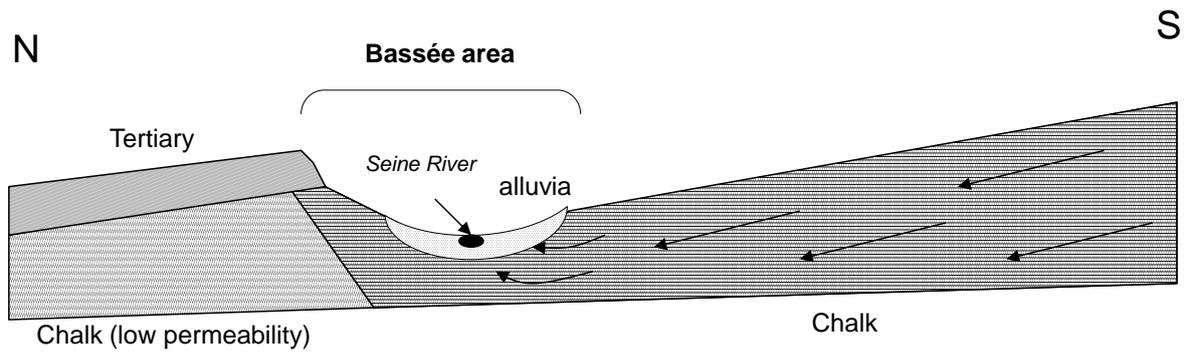


Figure 2 : Synthetic geological profile of the La Bassée area

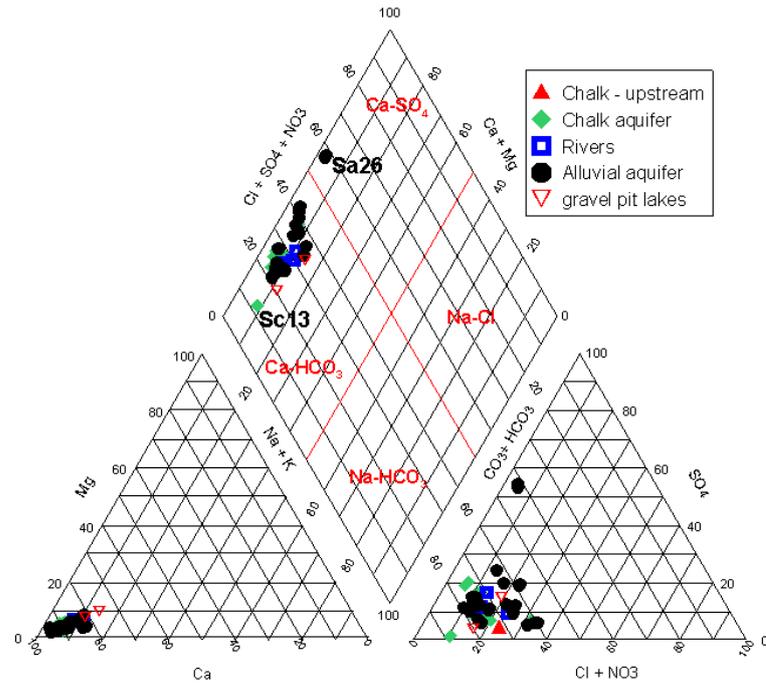


Figure 3 : Piper diagram for ground and surface water sampled in June and November 2007 in the La Bassée floodplain and one well groundwater upstream (chalk aquifer)

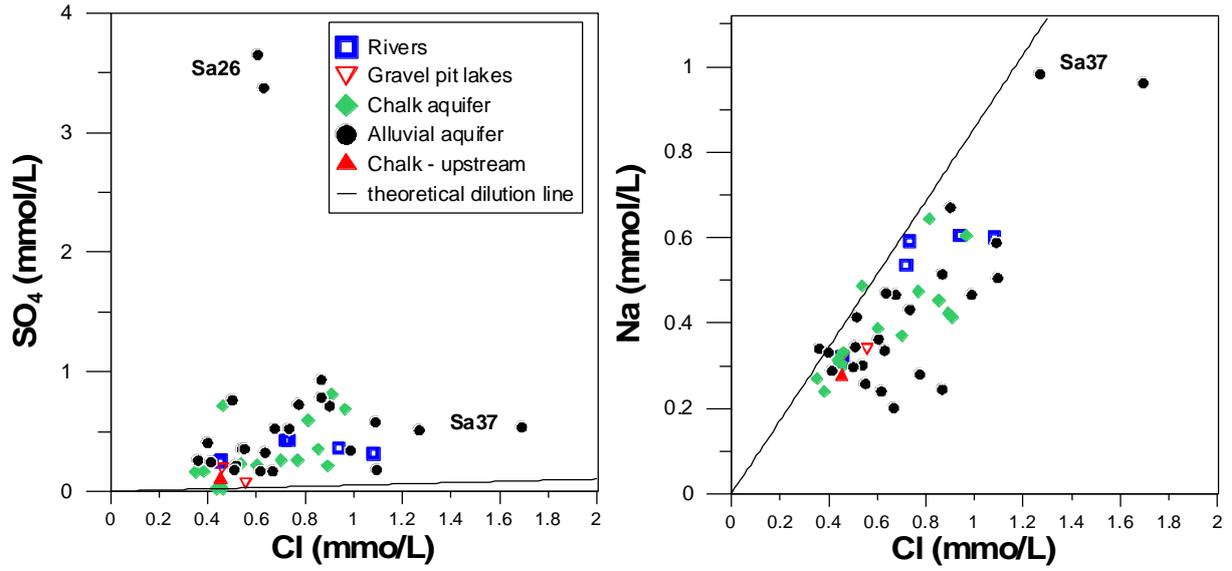


Figure 4 : SO₄ vs. Cl and Na vs. Cl for surface and groundwater sampled at the La Bassée plain in June and November 2007 and groundwater sampled upstream (Chalk aquifer)

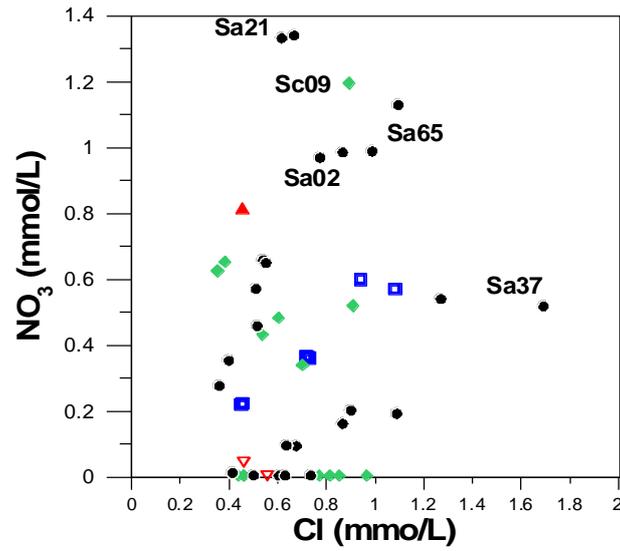


Figure 5 : NO₃ vs. Cl for surface and groundwater sampled at the La Bassée plain in June and November 2007 and groundwater sampled upstream (chalk Aquifer)

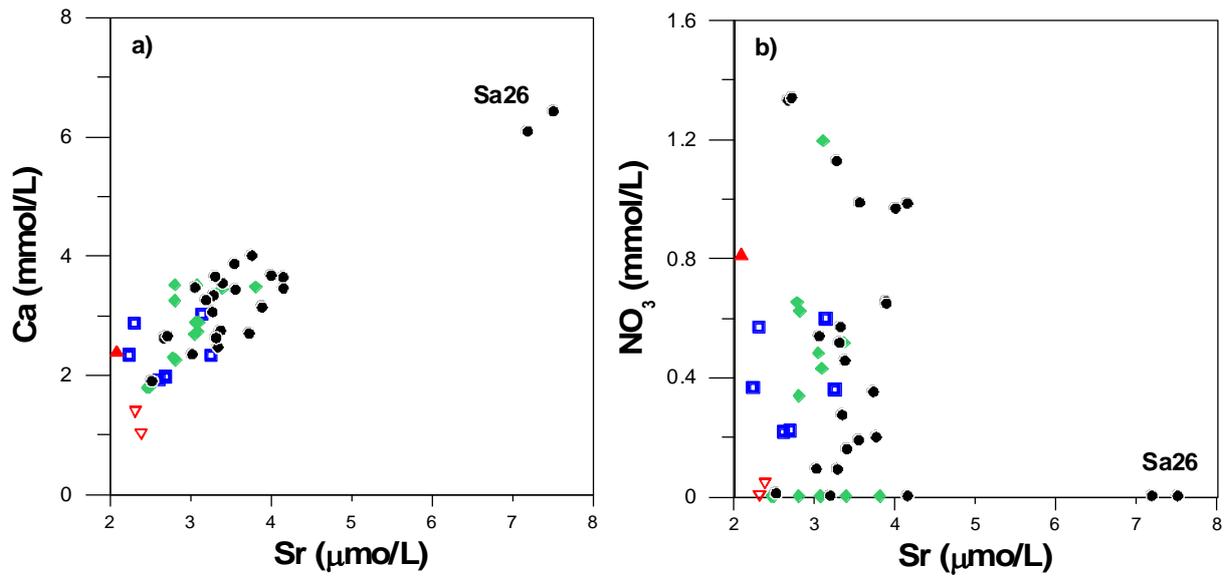


Figure 6 : Ca vs. Sr and NO₃ vs. Sr for surface and groundwater sampled at the La Bassée plain in June and November 2007 and groundwater sampled upstream (Chalk aquifer)

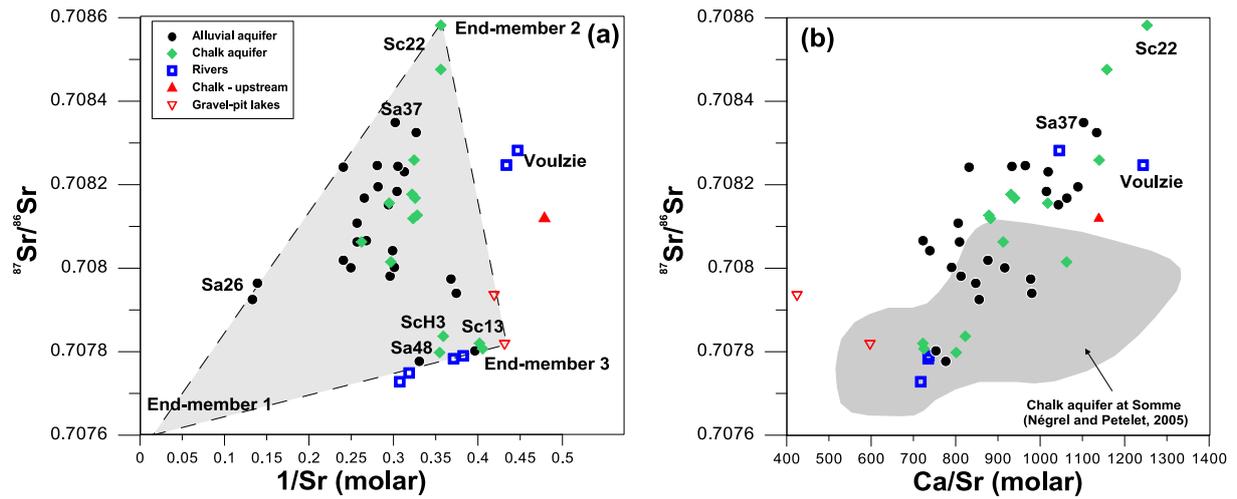


Figure 7 : $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/\text{Sr}$ (molar) and $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Ca/Sr (molar) for surface and groundwater sampled at La Bassée plain in June and Novembre 2007 and one upstream well

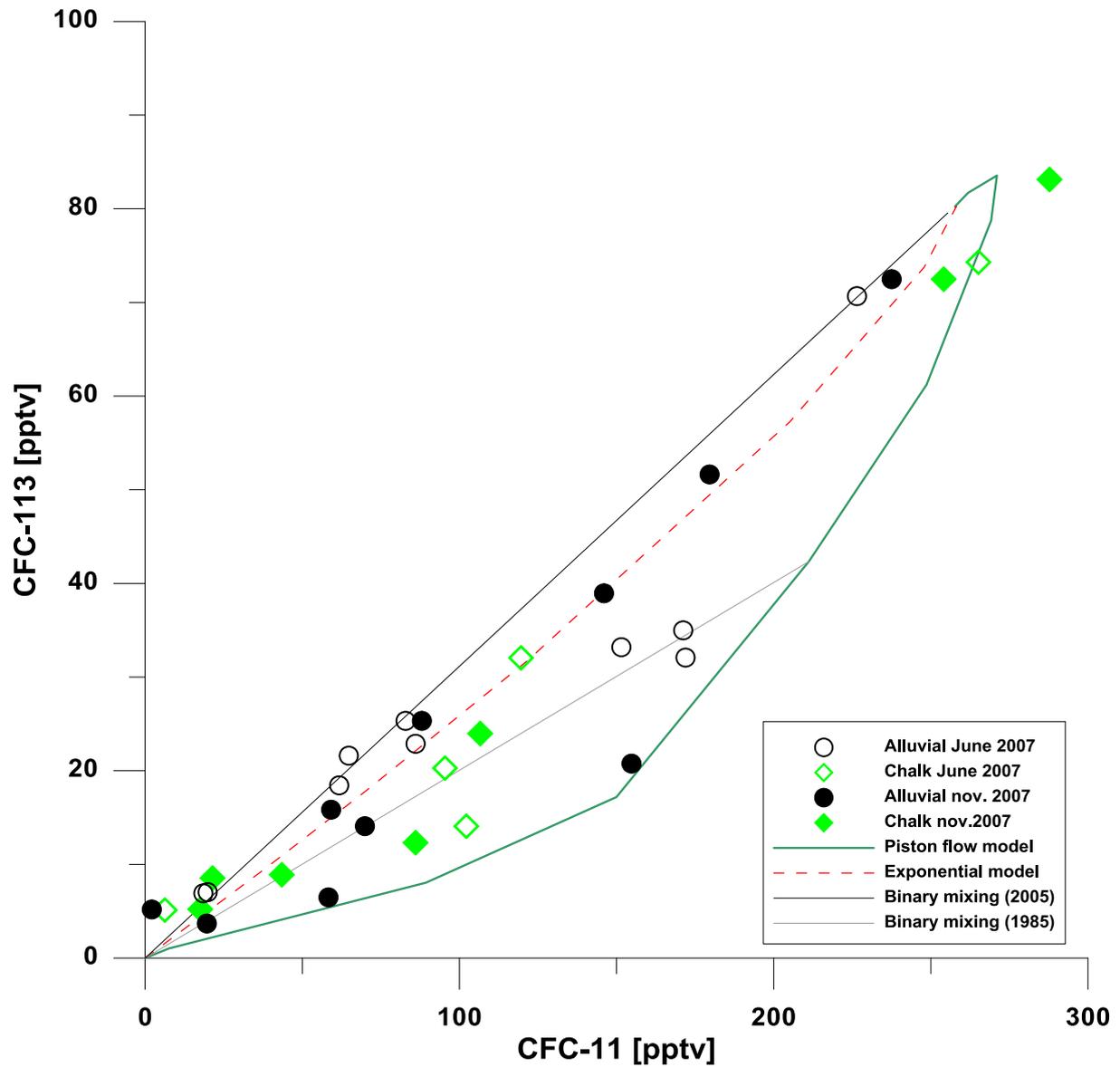


Figure 8 : CFC-11 vs. CFC-113 (in pptv) for groundwater collected in the La Bassée site in June and November 2007 and piston flow, exponential and binary mixing of young water (recharged in 1985 and 2005) with CFC-free water reference lines

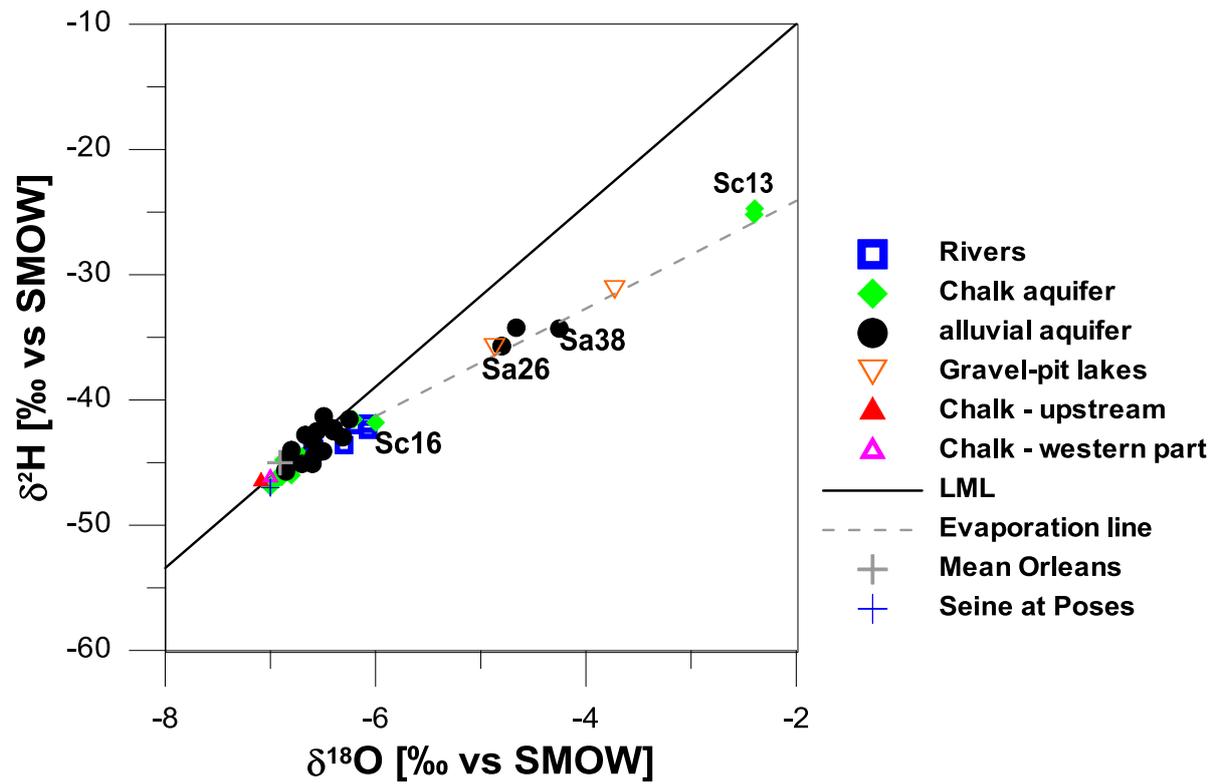


Figure 9 : $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ for surface and groundwater collected in the La Bassée site in June and November 2007; local meteoric line and mean weighted values for precipitations at Orléans (1996-2010), mean of Seine water at Poses (1974-1976) and calculated evaporation line

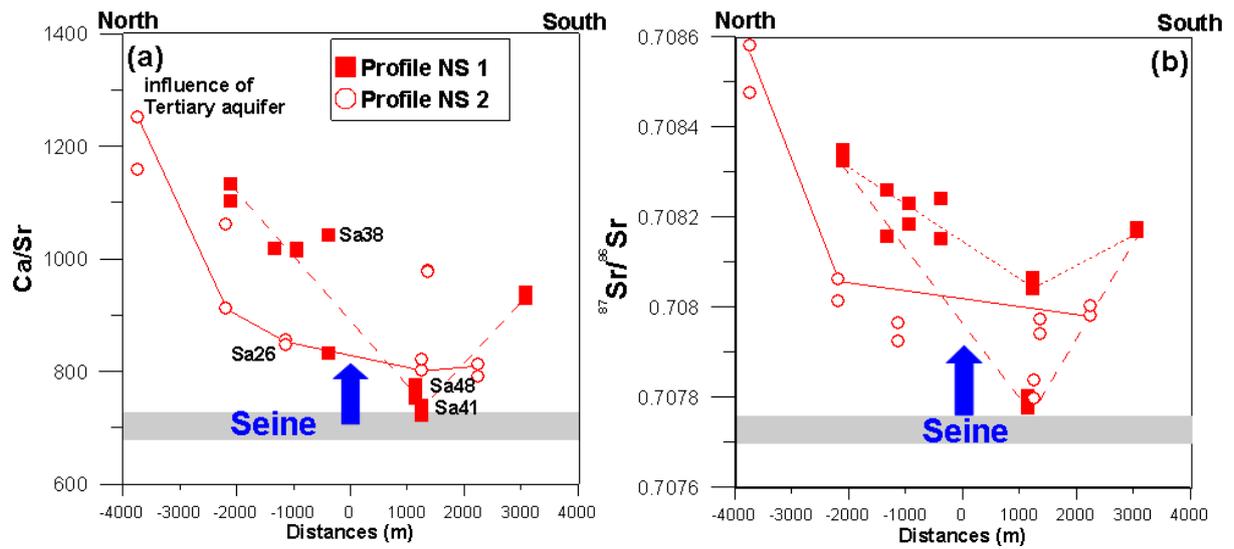


Figure 10: $^{87}\text{Sr}/^{86}\text{Sr}$ vs. distance and Sr/Ca vs. distance for the groundwater collected in June and November 2007 following the two North-South profiles

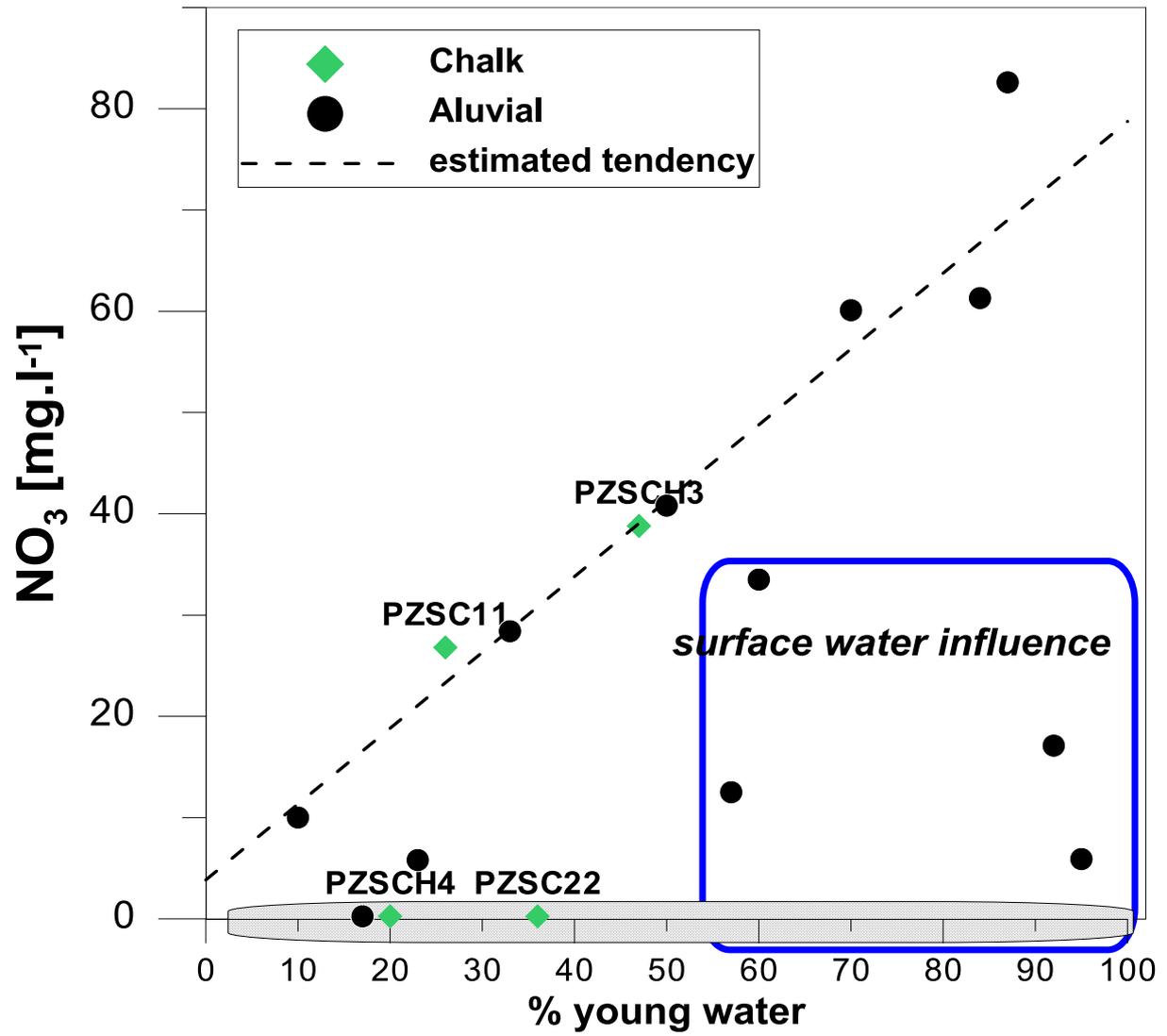


Figure 11: NO_3 vs. % of young groundwater for groundwater sampled in June and November 2007 in the La Bassée alluvial plain