A multi-isotope baseline (O, H, C, S, Sr, B, Li, U) to assess leakage processes in the deep aquifers of the Paris basin (France)

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A multi-isotope baseline (O, H, C, S, Sr, B, Li, U) to assess leakage processes in the deep aquifers of the Paris basin (France).

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Abstract

Groundwaters from the deep Dogger and Albian aquifers from the Paris Basin in France have been analysed for oxygen (H_2O and SO_4), hydrogen (H_2O), carbon, boron, lithium, sulphur (SO_4), strontium, and uranium isotopes. This study aims to establish a natural hydrogeochemical baseline against which any leak of saline fluids from deeper water masses could be evidenced in case of a hypothetic occurrence of non-conventional exploitation of the hydrocarbons that are present in the underlying Liassic shales. Waters from the Dogger and the Albian aquifers have respectively chloride-alkaline and calcium-bicarbonate geochemical facies, although some waters from the Albian aquifer tend to evolve towards the geochemical characteristics of the waters from the Dogger aquifer.

Stable isotopes of the water molecule indicate that waters from the Albian aquifer have a meteoritic origin, whereas saline waters of the Dogger aquifer are mainly influenced by primary and secondary brine inflow from the Triassic evaporitic deposits, and also by diffusive exchanges with the porewaters of the Liassic shales (Bensenouci et al., 2010). Carbon isotopes display $\delta^{13}C$ values that are much higher (> 0‰) in waters from the Dogger aquifer waters than those from the Albian (≤ - 9‰). Oxygen and sulfur isotopes of dissolved sulfates measured in the waters from the Dogger indicate that sulfur comes probably from the Triassic evaporites, whose signatures are overprinted by bacterial sulfate reduction. The water from the Pantin well near Paris displays isotopic characteristics that are comparable to the saline waters from the Dogger. On the other hand, dissolved sulfates of the other waters from the Albian indicate two different sources: sulfates derived from sulfides that have undergone abiotic oxidation processes, and atmospheric and/or crustal sources. Uranium activity ratios are very high in most groundwaters from the Albian, especially northwest of the Paris region where ratios as high as 20 have been measured. These activity ratios are in most cases higher than those of the saline waters from the Dogger, and suggest important water/rock interaction processes within the Albian aquifer in agreement with Li isotopes data. Boron and strontium isotopic data suggest

that some waters from the Albian record the geochemical influence of saline waters comparable to those of underlying aquifers of the Paris Basin, especially Northeast of Paris, in agreement with recent geophysical studies.

In the present work, we critically evaluate the information that can be derived from each of the tested isotope systematics in terms of leakage and mixing processes as might occur as the result of man-induced hydraulic shortcuts or changes in the pressure gradients between deep groundwater levels. Sulphur, oxygen, strontium and boron reveal the most sensitive indicators of mixing processes, whereas lithium and, in particular, uranium isotope ratios are strongly overprinted by water-rock interaction and redox processes.

1. Introduction

The intensification of concurrent uses of the deep subsoil in sedimentary basins creates new potential pathways for leakage of deep saline fluids into freshwater-bearing aquifers. Among those uses are the storage of gases, heat and wastes, the exploitation of geothermal energy but also the exploration and exploitation of conventional and unconventional hydrocarbons (Vernoux and Manceau, 2017). In the latter case, the use of hydraulic fracturing of impermeable hydrocarbon source rocks gives rise to the production of huges quantities of brines, mixed with variable proportions of residual additives (Kondash et al., 2017; Luek and Gonsior, 2017; Vengosh et al., 2017; Warner et al., 2014; Ziemkiewicz and He, 2015). These brackish to saline waters are derived from the dilution of residual sedimentary brines or, possibly, the dissolution of evaporitic minerals conserved in the pore space of shale formation by the injected fracking fluids. Flowback waters from hydraulic fracturing may thus mimic the composition of natural brines, in particular after a long period of pumping when the major part of injected fluids have been eliminated (Osselin et al., 2018; Osselin et al., 2019). It is thus of utmost importance for the evaluation of environmental impacts of such activities, to perform a stringent Environmental Baseline Assessment (EBA), covering both the gas baseline (Bell et al., 2017; Botner et al., 2018; Dai et al., 2016; Gal et al., 2018; Humez et al., 2016a; Humez et al., 2016b; Humez et al., 2019; McIntosh et al., 2019; Osborn et al., 2011) and the natural patterns of salinity in the potentially impacted freshwater aquifers (Bondu et al., submitted; Down et al., 2015; Harkness et al., 2017; Warner et al., 2012). The complexities of retrospective geochemical baseline assessment e.g. in areas of intense past and present conventional and unconventional hydrocarbon exploitation have been extensively discussed (McIntosh et al., 2019; Reimann and Garrett, 2005; Vengosh et al., 2014). Uncertainties on EBA are much reduced in pristine regions, where unconventional hydrocarbon potential exists but where no exploration or exploitation activities are conducted to date.

The Paris Basin constitutes one of these areas. In spite of the fact that oil has been extracted from the Triassic and Dogger layers for more than one century, no non-conventional exploitation of the hydrocarbons has ever occurred nor have the potential shale oil resources been seriously investigated or evaluated (Anthonsen et al., 2016; Hoelzer et al., 2016; Leteurtrois et al., 2012) due to the French moratorium on hydraulic fracturing. Overlying the potential host rocks, (the Lower Jurassic shales), deep freshwater aquifers are potentially endangered by gas or saline fluid leaks. Thus, this study aims at establishing a natural baseline of the Albian aquifer, against which can be tested any leak of deep saline fluids in case of a hypothetic non-conventional exploitation of the Liassic hydrocarbons as hydrocarbon source rocks or other uses of the deep subsoil in the Paris Basin.

The Albian aquifer of the Paris Basin has been largely exploited since the XIXth century through artesian wells for drinking water and landscape design (waterfall of the Bois de Boulogne park). Due to the overexploitation of the water resource, a drastic management policy has been established in the mid-XXth century. The Albian aquifer is now classified as a strategic groundwater resource. It is utilized as a drinking water resource, and fountains providing free drinking water (after treatment) are at the disposal of the Paris citizens. Also, the temperature (typically around 30°C in Paris) allows geothermal heating of buildings, like the French national broadcasting corporation.

In this context, isotopic fingerprinting can help in assessing potential naturally occurring leakage of groundwaters from the Dogger aquifer (sometimes further referred as Dogger waters) to the Albian aquifer, through the interlayered aquifers of Upper Jurassic and Lower Cretaceous, especially the Oxfordian aquifer. In addition to well established isotope tracers (δ^2H and δ^{18}O of the water molecule, δ^{13}C of DIC (Dissolved Inorganic Carbon), isotopic composition of dissolved sulfated (δ^{34}S, δ^{18}O) and strontium (^{87}Sr/^{86}Sr) isotopic compositions, advanced tracer methods based on the isotopic composition of boron (^{11}B/^{10}B), lithium (^{7}Li/^{6}Li) and uranium (^{234}U/^{238}U) have been also tested in the present study.

2. Geological and hydrogeological background

The Paris Basin features several aquifer formations, including the deep Dogger and Albian aquifers. The Dogger limestones are one of the deepest aquifers of the sedimentary basin only underlain by the black shales of Lower Jurassic, and then by the different Triassic sandstone aquifers. Then, upwards in the sedimentary sequence, the Dogger limestones are overlain by the Callovo-Oxfordian marlstone aquiclude, then the Upper Oxfordian (or Lusitanian) aquifer of Upper Jurassic. The latter is topped by the aquiclude of the Kimmeridgian marls, then by the Neocomian (Lower Cretaceous) aquifer, clayey Aptian deposits and finally the Albian aquifer (Fig. 1). In spite of the occurrence of the Aptian clays, these two aquifers are not clearly separated and behave as a single hydrological unit (Vernoux et al., 1997 and references therein).

The Dogger aquifer has been extensively studied in the center of the Paris basin, especially east of the Paris region (Brie area) for the following reasons. Firstly, it includes oil reservoirs, some of them still being exploited. The parent rock are the black shales of Lower Jurassic. The oil migrates either upwards into the Dogger limestones, or downwards to the Triassic sandstones (Gély, Hanot, et al., 2014, and references therein). Secondly, waters from the Dogger aquifer constitute a geothermal resource (e.g., Michard and Bastide, 1988; Rojas et al., 1989) and are also exploited for low-enthalpy geothermal energy. The complex origin of the Dogger saline waters has been emphasized during the 1990's (Fouillac et al., 1990; Matray and Fontes, 1990; Fontes and Matray, 1993; Matray et al., 1994).

Several studies have been carried out through time in order to assess the hydrological model of the Albian aquifer (Lemoine et al., 1939; Vuillaume, 1971; Raoult et al., 1997; Vernoux et al., 1997; Raoult, 1999; Hydroexpert, 2000). Old, possibly questionable, ^{14}C dates are available in Vuillaume et al. (1971). Although the groundwater circulation is not perfectly constrained yet, it is classically considered that the renewing of groundwaters of the Albian aquifer (sometimes further referred as Albian groundwaters) occurs mainly through recharge processes at Albian outcropping areas (Southeast of the Paris basin), but also through drainage processes from both

overlying (chalk) and underlying (Neocomian) aquifers. Furthermore, some studies suggest an influence of the deeper Upper Jurassic aquifer (Raoult, 1999).

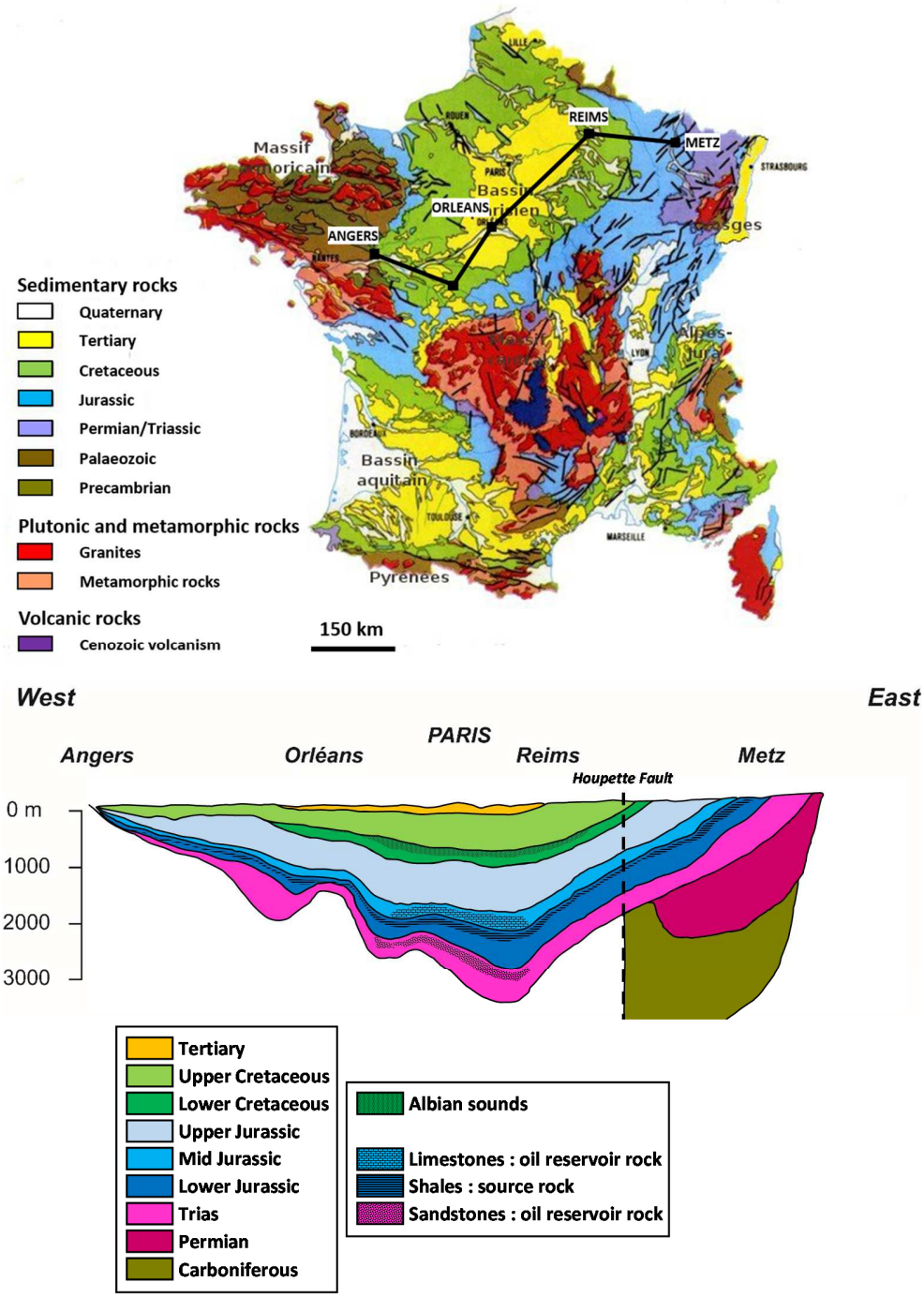

Figure 1 : West-East schematic cross-section of the Paris Basin (after Gély, Hanot et al., 2014). The analyzed waters refer to the middle Jurassic (Dogger) and lower Cretaceous (Albian).

This scheme has been strongly challenged very recently (Dentzer, 2016), on the basis of a study on the thermal regime of the Paris basin. Temperature heterogeneities between the northern and the southern part of the Paris region (Ile-de-France) in the Dogger saline waters are attributed to the overpumping in the Albian aquifer, resulting in a groundwater leakage occurring through fault systems affecting the whole sedimentary pile of the Paris basin. This makes possible connections between the strategic Albian aquifer and deeper groundwaters such as the Dogger aquifer containing saline waters that are exploited at present as a geothermic and oil-bearing resource.

Hence this study aims at investigating the behaviour of different isotopic systems, in order to determine which of them could best depict any leakage process between the different water masses, those that might naturally exist or be induced by current or future human influence on the flow patterns. The identified key parameters could be as such part of the environmental baseline of a hypothetic non-conventional exploitation of hydrocarbons.

3. Sampling and analytical techniques

Twelve groundwaters from the Albian aquifer were sampled throughout the whole Paris Basin. In addition, six Dogger saline waters were recovered from geothermal sites in the centre of the Paris Basin. No deep sampling point in the Lusatianian aquifer was accessible. The location of the sampling points is given in Figure 2.

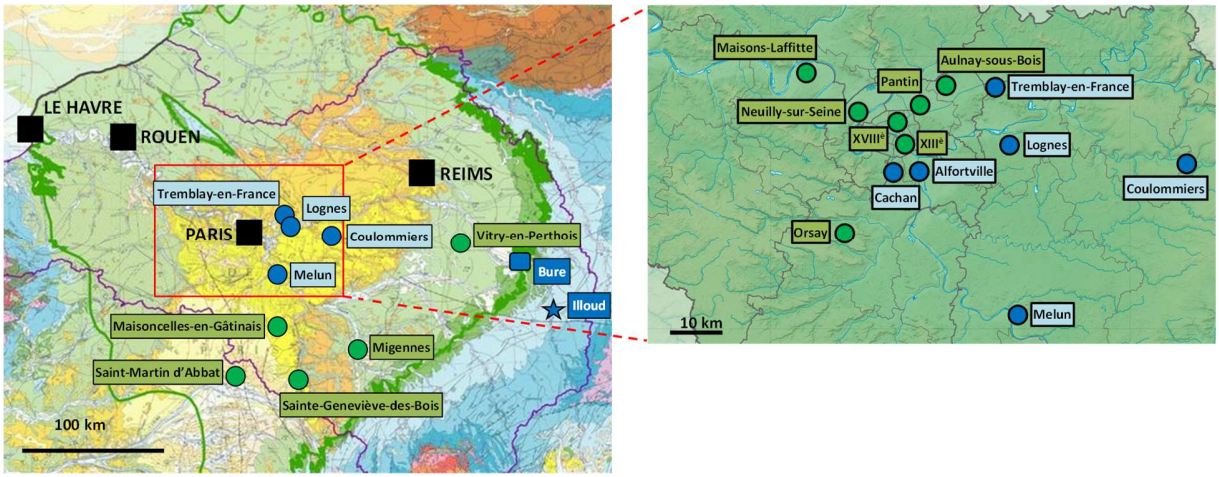

Figure 2 : Schematic geographic map of the Paris Basin showing sample locations. Blue disks : Dogger waters, green disks : Albian waters. Also, the location site of the Bure laboratory has been marked as a blue square and of the sampling site of the Illoud springwater as a blue star. Detailed explanations are given in the text.

Major and trace elements, oxygen and hydrogen isotopes of the water molecule, carbon isotopes of DIC, sulfur and oxygen isotopes of dissolved sulfates, strontium, lithium and boron isotopes, and finally uranium activity ratios were measured in the BRGM laboratories.

Physical and chemical parameters (T°, pH, Eh, conductivity, dissolved O_2) were determined directly in the field, and the alkalinity in the laboratory immediately after the field sampling campaign.

Concentrations in major cations (Ca, Mg, Na, K) have been determined by ICP-OES on waters previously filtered at 0.45 µm and acidified at pH~2 on site, in order to avoid precipitation,

element adsorption on the bottle walls, and also the development of bacterial flora. Major anions (Cl, SO_4) and ammonia were analyzed on 0.45 µm filtered waters (on site) by ionic chromatography. Bicarbonate contents have been derived from alkalinity. Results are reported in Table 1.

Sample	pH	T°C	Eh (mV)	Conductivity (µS/cm)	Dissolved O_2 (%)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	NH_4 (mg/l)	HCO_3 (mg/l)	Cl (mg/l)	SO_4 (mg/l)
Dogger													
Lognes	6.15	72.0	-111.8	37900		1212	224	7917	139	26.2	301	15029	941
Cachan	6.37	61.8	-138.0	24800		676	157	4978	81.7	19.3	321	9401	810
Coulommiers	6.24	58.9	-120.5	46800		1635	293	9792	151	31.1	239	19262	1357
Melun	6.14	69.0	-159.7	20600		552	145	4147	66.9	17.8	297	7544	724
Tremblay-en-France	6.21	52.5	-136.9	36100		1049	263	7469	116	24.8	291	13102	1055
Alfortville	6.12	68.2	-182.1	33300		869	190	6308	94.3	23.4	304	11916	907
Albian													
Saint-Martin d'Abbat	7.65	20.1	72.2	280	42	40.3	3.8	5.4	6.1	0.11	138	7.1	12.6
Vitry-en-Perthois	7.62	17.0	133.5	519	43	69.7	21.0	5.2	6.3	0.38	285	3.3	41.5
Sainte-Geneviève-des-Bois	6.51	25.6	91.3	200	11	24.8	3.4	3.1	2.7	0.00	86	5.7	7.5
Maisoncelles-en-Gâtinais	6.51	25.5	97.4	172	1.8	19.7	3.5	2.9	4.2	0.07	66	4.4	15.7
Maisons-Laffitte	7.64	26.0	271.0	317	23	27.5	8.3	16.0	11.2	0.31	165	6.2	9.6
Paris Verlaine square (XIIIè)	8.34	18.6	480.5	317	100	32.9	9.1	13.0	10.2	0.00	174	5.2	9.8
Paris Madone square (XVIIIè)	8.29	17.0	474.6	302	100	20.0	6.9	24.6	13.2	0.00	153	9.8	11.5
Aulnay-sous-Bois	7.74	31.6	50.0	360	16	22.0	6.8	32.8	15.5	0.52	190	7.0	13.0
Pantin	7.73	26.4	141.0	425	35	31.5	10.2	34.6	15.1	0.49	252	6.9	4.1
Neuilly-sur-Seine	7.89	27.5	139.0	282	36	25.9	7.9	12.4	10.8	0.28	150	5.5	10.4
Orsay	7.93	30.6	84.1	249	66	28.1	6.4	5.7	8.6	0.16	128	5.0	11.4
Migennes	8.14	15.5	170.0	295	86	45.3	6.1	3.9	5.0	0.12	156	7.0	20.2

Table 1 : Physico-chemical and major element data for the analyzed groundwaters. Analytical uncertainties are 5% for major element data. Albian water that is available at the Paris fountains is treated by municipal authorities to remove iron. Hence, waters sampled at the Verlaine and the Madone squares display a high pH value, resulting from the treatment.

Oxygen and hydrogen isotopes were measured in the groundwaters by Isotope Ratio Mass Spectrometry (IRMS) using the equilibration method : H_2 for hydrogen and CO_2 for oxygen, respectively.

For sulfur and oxygen isotopes of dissolved sulfates, waters were first stabilized in the field using cadmium acetate, then filtered in the laboratory. Finally, sulfates were precipitated using barium chloride, and analyzed by CF-IRMS. For $\delta^{13}C$, waters were acidified using H_3PO_4, then the obtained CO_2 was extracted under vacuum and purified before analysis by IRMS.

B, Li, and Sr concentrations have been also measured on 0.45 µm filtered and acidified waters on a X-Series Quadrupole ICP-MS (Thermo). Strontium and lithium isotopes have been measured on acidified and filtered waters. For boron isotopes, waters were also filtered, but not acidified. These three elements were then extracted from the matrix using techniques described in Millot et al. (2011a). B and Sr have been analyzed by Thermal Ionization Mass Spectrometer (TIMS), on a Finnigan MAT 261 for B, and on a Finnigan MAT 262 for Sr. Li has been measured on a Thermo Neptune MC-ICPMS plasma source magnet mass spectrometer (Millot et al., 2011a). All isotopic data, together with corresponding element concentrations, are reported in Table 2. Analytical techniques for the measurement of U concentrations and activity ratios are described in Millot et al. (2011a).

Sample	δD_{SMOW} (‰)	$\delta^{18}O_{SMOW}$ (‰)	$\delta^{13}C_{PDB}$ (‰)	$\delta^{34}S_{CDTsulfates}$ (‰)	$\delta^{18}O_{CDTsulfates}$ (‰)	Sr (µg/l)	$^{87}Sr/^{86}Sr$	2σ	B (µg/l)	$\delta^{11}B$ (‰)	Li (µg/l)	$\delta^{7}Li$ (‰)	U (ng/l)	$(^{234}U/^{238}U)$	2σ
Dogger															
Lognes	-31.5	-3.8	1.7	24.9	10.9	63492	0.707944	0.000008	13925	22.28	2724	9.70	1.92	1.504	0.031
Cachan	-33.0	-4.0	2.2	27.3	12.6	38473	0.707875	0.000006	10395	21.84	1843	9.60	1.19	1.946	0.028
Coulommiers	-31.3	-3.8	3.4	24.9	12.8	69588	0.707902	0.000007	15414	21.22	3142	9.70	1.34	6.202	0.051
Melun	-33.9	-4.0	2.7	26.2	13.0	34531	0.707779	0.000007	9081	20.50	1505	10.50	0.625	2.214	0.050
Tremblay-en-France	-33.0	-3.7	3.5	31.2	13.9	58588	0.707831	0.000007	12043	21.65	2404	10.90	1.53	1.207	0.030
Alfortville	-28.1	-3.0	1.8	26.7	12.4	50725	0.707911	0.000008	12328	22.13	2278	9.50	1.04	2.043	0.185
Albien															
Saint-Martin d'Abbat	-59.7	-8.8	-10.6	-2.7	7.3	356	0.707851	0.000006	12.9	1.95	10.9	6.90	0.334	5.588	0.139
Vitry-en-Perthois	-60.8	-8.8	-10.4	-7.4	9.0	3162	0.707421	0.000005	38.5	-0.46	5.91	16.90	4.67	15.974	0.094
Sainte-Geneviève-des-Bois	-54.1	-8.0	-11.1	-20.9	3.4	137	0.708693	0.000008	13.3	3.24	12.3	1.70	0.390	9.387	0.170
Maisoncelles-en-Gâtinais	-60.8	-8.9	-9.5	-22.4	2.1	219	0.708614	0.000006	15.5	2.37	12.3	4.60	0.688	1.670	0.035
Maisons-Laffitte	-56.7	-8.4	-11.5	-8.6	8.2	632	0.707735	0.000007	84.0	12.44	10.7	11.50	0.398	20.795	0.147
Paris Verlaine square (XIIIè)	-57.0	-8.4	-11.1	-4.3	11.5	1011	0.707692	0.000009	71.1	1.72	8.37	12.00	0.868	7.651	0.091
Paris Madone square (XVIIIè)	-57.0	-8.4	-12.3	-9.3	9.3	575	0.707657	0.000007	39.6	3.65	18.1	11.40	0.192	6.437	0.290
Aulnay-sous-Bois	-57.1	-8.4	-11.6	-12.9	7.8	854	0.707604	0.000006	76.0	8.23	11.7	10.90	0.474	18.222	0.187
Pantin	-56.5	-8.4	-8.9	34.9	10.5	1073	0.707636	0.000011	330	25.56	11.0	14.00	2.18	7.236	0.101
Neuilly-sur-Seine	-57.0	-8.4	-12.6	-15.7	6.6	715	0.707715	0.000007	49.8	1.93	10.8	12.10	0.359	20.043	0.295
Orsay	-57.7	-8.5	-13.7	-18.8	5.0	454	0.707967	0.000007	21.3	0.98	8.84	10.60	0.444	15.375	0.160
Migennes	-56.7	-8.4	-12.3	-20.5	4.8	486	0.707866	0.000007	27.0	3.10	13.2	12.90	66.3	3.940	0.017

Table 2 : Isotopic and trace element data for the analyzed groundwaters. Uncertainties on the delta values are estimated at 0.1‰ for $\delta^{18}O$, 0.8 ‰ for δD, 0.1‰ for $\delta^{13}C$, 0.3‰ for $\delta^{34}S$, 0.5‰ for $\delta^{7}Li$ and 0.3‰ for $\delta^{11}B$. Uncertainties on U concentrations are 1%, and 5% for B, Li and Sr concentrations.

4. Results and discussion

4.1. Physical and chemical parameters, major and trace elements

Groundwaters recovered from the Albian aquifer are very dilute, with conductivities not higher than 520 µS/cm (Tab. 1). Temperatures range from 15°C close to the outcrop (Mignennes) but may reach values higher than 31.6°C Northeast and West of Paris (Aulnay-sous-Bois, Orsay ; Tab. 1) Reported in a Piper diagram (Fig. 3), they fall into an overall calcium – bicarbonate facies, although a clear trend towards an alkaline (Na) facies can be evidenced from the cation triangle, especially in some waters sampled in the northern district of Paris and northeast of the city (Paris XVIII^{è}, Aulnay-sous-Bois, Pantin ; Fig. 3). It is also noticeable that the groundwater from Pantin provides much higher B concentration than the other Albian waters (330 µg/l, Tab. 2)

The six Dogger saline waters had temperatures high conductivities (Tab. 1), and temperaturesranging from 53°C to 72°C, with a negative Eh values (reducing waters, Tab. 1). In the Piper diagram, they all have a typical chloride – alkaline facies (Fig. 3).

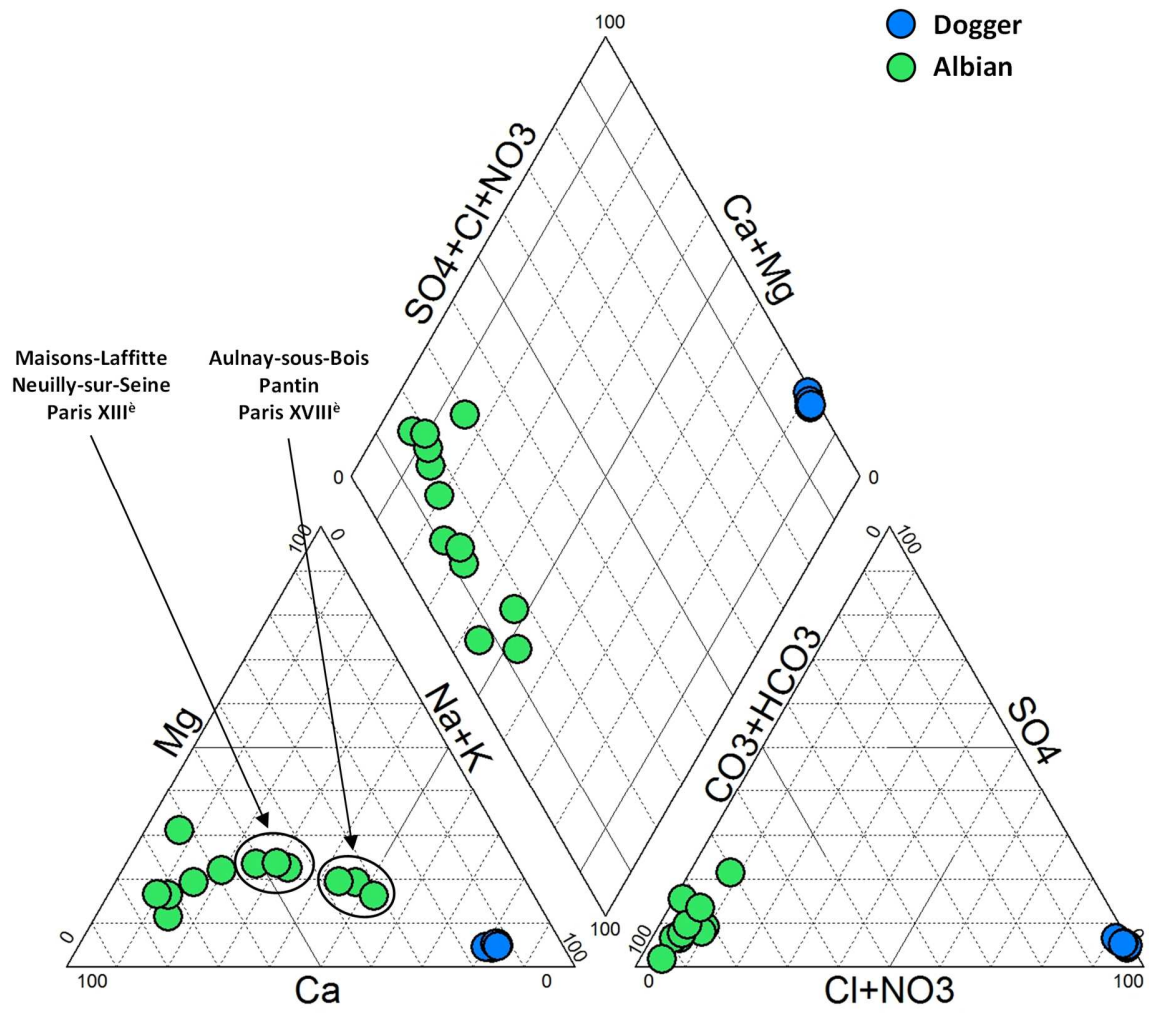

Figure 3 : Piper diagram for the analyzed waters. Same legend than in Figure 2.

4.2. Oxygen and hydrogen isotopes

The isotopic signatures of the stable isotopes of the water molecule indicate that Albian waters have a meteoric origin, as they follow the global meteoritic waters line (GMWL ; Craig, 1961).

Their isotopic signatures are closely clustered, ranging approximately from -9‰ to -8‰ for $\delta^{18}O$, and from -60‰ to -54‰ for δD (Fig. 4). Such values are lower than those of present-day rainwaters from Orléans (-7.6‰ and -50.4‰ in average between 1996 and 2003, Millot et al. 2010), and conversely higher than those from Thonon-les-Bains (-10.8‰ and -78.6‰ in average between 1996 and 2002, Millot et al. 2010).

All points in the Albian are located in the confined part of the aquifer, the points at Migennes and Vitry-en-Perthois being the closest to the potential recharge zone, a few km upstream (Grenet et al., 1996). Modern recharge in the investigated part of the Paris Basin shows $\delta^{18}O$ values from -7.5 ‰ to 7‰ (Millot et al., 2010), in accordance with those measured in the pre-Pleistocene groundwaters from the Albian sands (Dray et al., 1998). The ^{18}O-depletion of all groundwaters in the confined Albian sands in our study corresponds to the signatures observed for parts of the aquifer with glacial recharge, with mean residence times > 25 ky, varying between -7.5‰ and -8.5‰ (Dray et al., 1998).

In contrast, saline waters of the Dogger aquifer display much higher isotopic signatures, varying between -4‰ and -3‰ for $\delta^{18}O$, and between -34‰ and -28‰ for δD (Fig. 4). Furthermore, they plot away from the GMWL. According to Matray et al. (1994), this would result from dissolution processes of halite of the Triassic aquifer by percolating meteoritic waters, followed by mixing with residual primary brines, and finally migration of these saline waters through vertical faults into the overlying Dogger aquifer.

A review, as exhaustive as possible, of available $\delta^{18}O$ - δD data on groundwaters from both the Upper Trias (Keuper – Rhétien) and Dogger deep aquifers of the Paris Basin has been carried out. Data on the Triassic waters come from Matray (1988), Fontes and Matray (1993) and Millot et al. (2011a), whereas isotopic data on the Dogger waters are derived from Matray (1988), Rojas et al. (1989), Fontes and Matray, (1993) and Matray et al. (1994). In addition, isotopic data of the water molecule obtained on Dogger groundwaters from the eastern part of the Paris basin (Fig. 2) have been measured: waters from the Bure area (underground research laboratory for studying the feasibility of a geological disposal of radioactive waste, Fig. 2) (Rebeix et al.,

2011), and a spring water from Illoud, east of the Paris basin, within the recharge zone of the Dogger aquifer (Innocent et al., submitted).

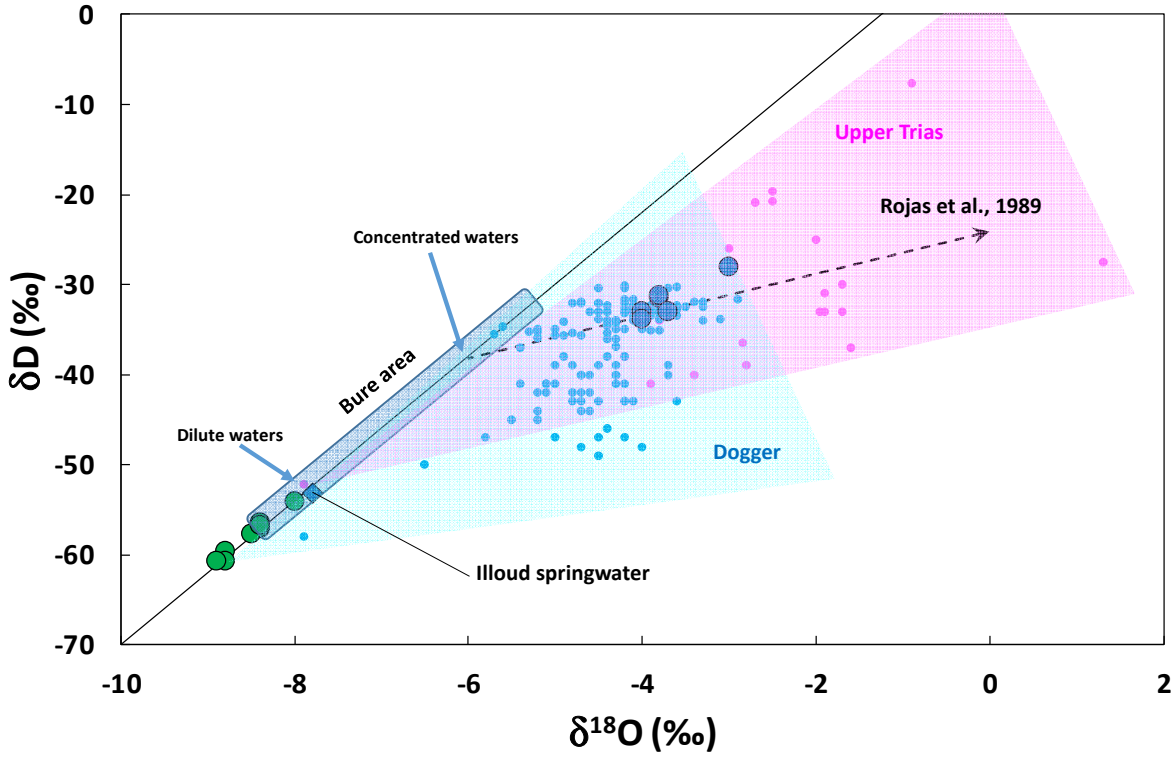

Figure 4 : δD_{SMOW} vs. $\delta^{18}O_{SMOW}$ diagram for the analyzed waters. Same legend than in Figure 2. The plain line corresponds to the GMWL (Craig, 1961). Available data on upper Triassic (pink points) and Dogger waters (blue points) from Rojas et al. (1989) have been reported. The blue field corresponds to Dogger waters from the Bure area (Rebeix et al., 2011). Finally, data obtained on a Dogger springwater from the Lorraine region (Innocent et al., submitted) has been plotted as a blue diamond.

Figure 4 clearly emphasizes that the isotopic compositions of groundwaters from both the Upper Triassic and the Dogger aquifer are very scattered when groundwaters from the whole Paris basin are taken into account. This indicates that the evolution processes are different from one saline groundwaters to the other, depending on the sampling site. However, the intersection with

the GMWL suggests that the isotopic signature of the meteoritic component would not be very different from that of the Albian groundwaters (Fig. 4). This is reinforced by the $\delta^{18}O$ - δD measured on the dilute springwater of Illoud, Such a result does not support the hypothesis of Rojas et al. (1989), who derived isotopic signatures of $\delta^{18}O$ = - 6‰ and δD = -38.3‰ for recharge waters.

Dogger groundwaters from the Bure area (Rebeix et al., 2011) have been also reported in Figure 4. They plot on the GMWL, with isotopic signatures scattering approximately from -8‰ to -5 ‰ for $\delta^{18}O$, and from -60 ‰ to -30 ‰ for δD. Groundwaters having the less negative isotopic signatures display also the highest Cl contents, and those displaying the most negative signatures are conversely the most dilute waters (Rebeix et al., 2011). These dilute waters have isotopic signatures close to both the Dogger limestone groundwaters in the recharge area (Matray et al., unpublished) and the Illoud springwater (Innocent et al., submitted), and represent the modern recharge component, whereras the more concentrated ones would correspond to the "end-member" derived by Rojas et al. (1989) (Fig. 4).

4.3. Carbon isotopes

The saline waters of the Dogger aquifer have $\delta^{13}C$ greater than 0. Two scenarios are envisageable to explain this: (1) Gaseous CO_2 input from deep sources (thermal cracking of marine carbonates, magmatic) enriched in ^{13}C with subsequent congruent dissolution of carbonates(Blavoux and Dazy, 1990; Lions et al., 2014), or (2) biogenic CO_2 interacting with carbonates first through congruent and then through incongruent dissolution (Wigley et al., 1978). However, the values are all slightly higher than the value of marine carbonates. (Mangenot et al., 2018) have measured $\delta^{13}C$ values of different carbonate generations in the Dogger aquifer, ranging between + 0.9 and +3.2‰. Slightly positive ^{13}C have been measured in the ancient waters of some karst aquifers (Gonfiantini and Zuppi, 2003), under similar conditions as in the Dogger aquifer (Mégnien, 1980).

Equilibrium calculations in PHREEQC (Lions et al., 2014), based on the approach of Deines et al. (1974), indicate rather high partial CO_2 pressures for the Dogger aquifer, log pCO_2 exceeding -1.2 (Fig. 5A). Marine carbonate dissolution under open system conditions by dissolved CO_2 with slightly negative $\delta^{13}C$ may explain the observed values (Fig. 5B). Congruent open or closed system dissolution of marine carbonates by a biogenic CO_2 will not shift $\delta^{13}C$ of DIC higher than around -10‰. Subsequent incongruent dissolution(Wigley et al., 1978), will further enrich DIC in ^{13}C, over longer time scales (Gonfiantini and Zuppi, 2003), but the final values would stay below the $\delta^{13}C$ of carbonates (Kloppmann et al., 1998).

On the other hand, the waters of the Albian aquifer have equally relatively homogeneous $\delta^{13}C$, but in the negative range, from -8.9‰ to -13.7‰ (Tab. 2). Such values are typical of groundwater, highlighting the double origin of carbon: dissolution of organic carbon from soils, with a very negative isotopic signature (Clark and Fritz, 1997), and then dissolution by this acid water of mineral carbonates of marine origin that are present in the sandy aquifer (Humez, 2012). Humez (2012) found, for the water of Maisoncelles-en Gâtinais, a carbon isotopic signature identical (-9.5‰) to that of the present study (Tab. 2). Alcalinity and pH data suggest closed system dissolution of carbonates at a log pCO_2 of -1.8. Most measured Albian groundwaters are saturated in calcite, except Maisoncelles-en-Gâtinais and Sainte-Geneviève-des-Bois that seem less evolved than the other waters. $\delta^{13}C$ of DIC for the Albian Groundwaters are compatible with dissolution of marine carbonates under closed system conditions by dissolved and dissociated CO_2 of biogenic origin ($\delta^{13}C$ -25 to -19‰, Fig. 5B). $\delta^{13}C$ and $\delta^{18}O$ of HCO_3^- of both aquifers fall in two distinct fields with no intermediate values indicating mixing. However, it has to be stated that isotope compositions of DIC are far from conservative and cannot be used for simple mixing calculations.

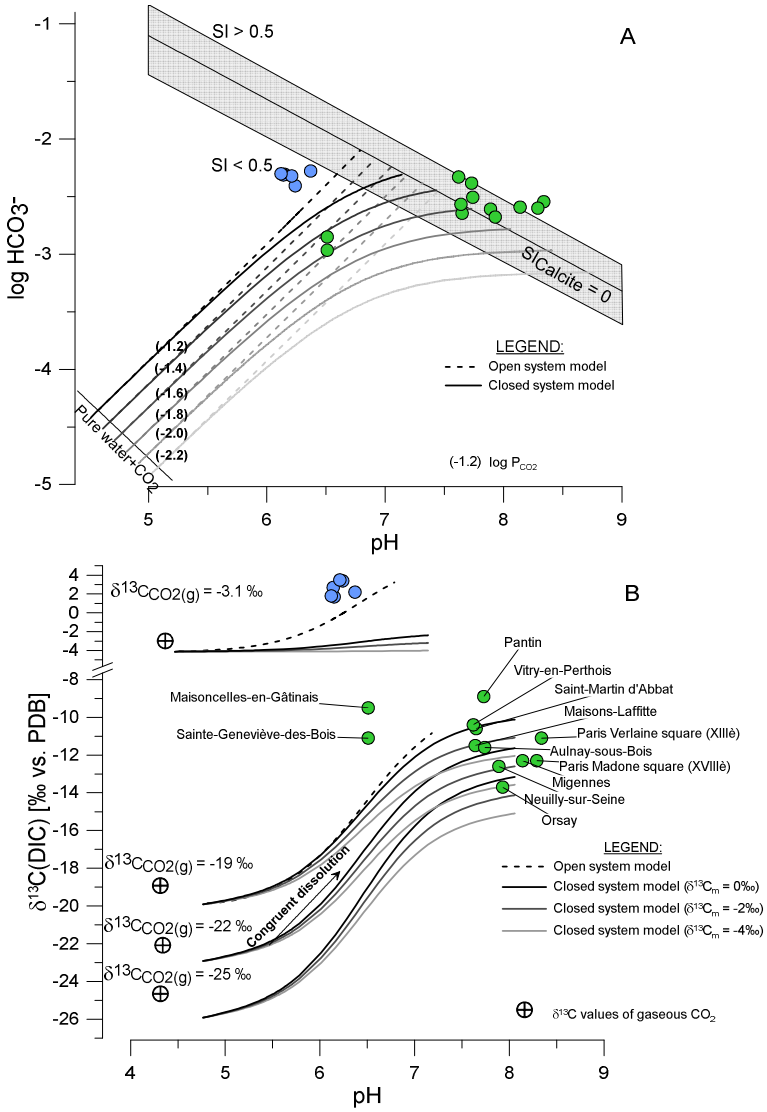

Figure 5 :$\delta^{13}C_{PDB}$ vs. $\delta^{18}O_{SMOW}$ diagram for the analyzed waters. Same legend than in Figure 2.

4.4. Sulfate-dissolved sulfur and oxygen isotopes

$\delta^{34}S$ of dissolved sulfates of groundwaters from the Albian aquifer are in most cases very low. In the $\delta^{18}O$ - $\delta^{34}S$ diagram (Fig. 6), most groundwaters plot along a straight line, which can be interpreted as a mixing line between two end-members representing two different sources of

sulfates : (i) sulfates derived from the abiotic oxydation of pyrites that are present in the aquifer, and (ii) atmospheric sources. In addition, a third end-member (the outcropping crust) may be involved to explain the isotopic signature of one groundwater (Fig. 6). This indicates that gypsitic minerals, that are also present in the aquifer, do not contribute significantly to the sulfur isotopic signature of these waters.

In contrast, the groundwater recovered at Pantin displays a much higher $\delta^{34}S$, with a $\delta^{18}O$ that remains in the range of the other Albian waters. Also, it has the lowest sulfate concentration of the whole Albian dataset (Tab. 1). Such characteristics are compatible with the effect of a bacterial reduction in a confined environment. However, the other Albian groundwater collected northeast of Paris (Aulnay-sous-Bois) does not seem to have undergone this kind of reduction process, as it plots in the field of the Albian groundwaters (straight line in Fig. 6). Hence, another possible hypothesis is that the isotopic signature of the dissolved sulfates in the Pantin groundwater could derive from interaction processes with saline waters coming from underlying aquifers, namely the Dogger aquifer, as suggested by Figure 6.

Groundwaters from the Dogger aquifer display both higher $\delta^{34}S$ and $\delta^{18}O$ compared to the Albian waters. Sulfur isotopic signatures are significantly higher than the domain of the Triassic evaporites (Fig. 6), as well as the global seawater isotopic signatures of both elements during the Triassic period (Claypool et al., 1980). Fouillac et al. (1990) concluded, based on older $\delta^{34}S$ - $\delta^{18}O$ data obtained on Dogger saline waters from the central part of the Paris basin (plotted in Figure 6) that the high $\delta^{34}S$ signatures derived from bacterial reduction processes, especially north of Paris ($\delta^{34}S$ as high as + 49‰). The authors observed that $\delta^{18}O$ remained uniform, though. South of Paris, overall sulfur isotopic signatures were lower, due to a higher flow rate of groundwaters (Fouillac et al., 1990).

More recently, oxygen and sulfur isotopes of dissolved sulfates have been also studied on more dilute Dogger groundwaters, originating from the Bure area, this is to say near the recharge zone (Rebeix et al., 2011). Overall $\delta^{18}O$ signatures are comparable to those of saline Dogger waters – a few being slightly higher, however - (Fig. 6), with $\delta^{34}S$ not higher than + 36‰. The two

groundwaters having the lowest isotopic signatures of both elements fall into the field of the Triassic evaporites (Fig. 6). The authors conclude that the dissolved sulfates derive from gypsum dissolution with a possible contribution of solutions of marine origin. In addition, they point out that the $\delta^{34}S$ signatures suggest the occurrence of partial reduction processes and/or successive dissolution/precipitation steps.

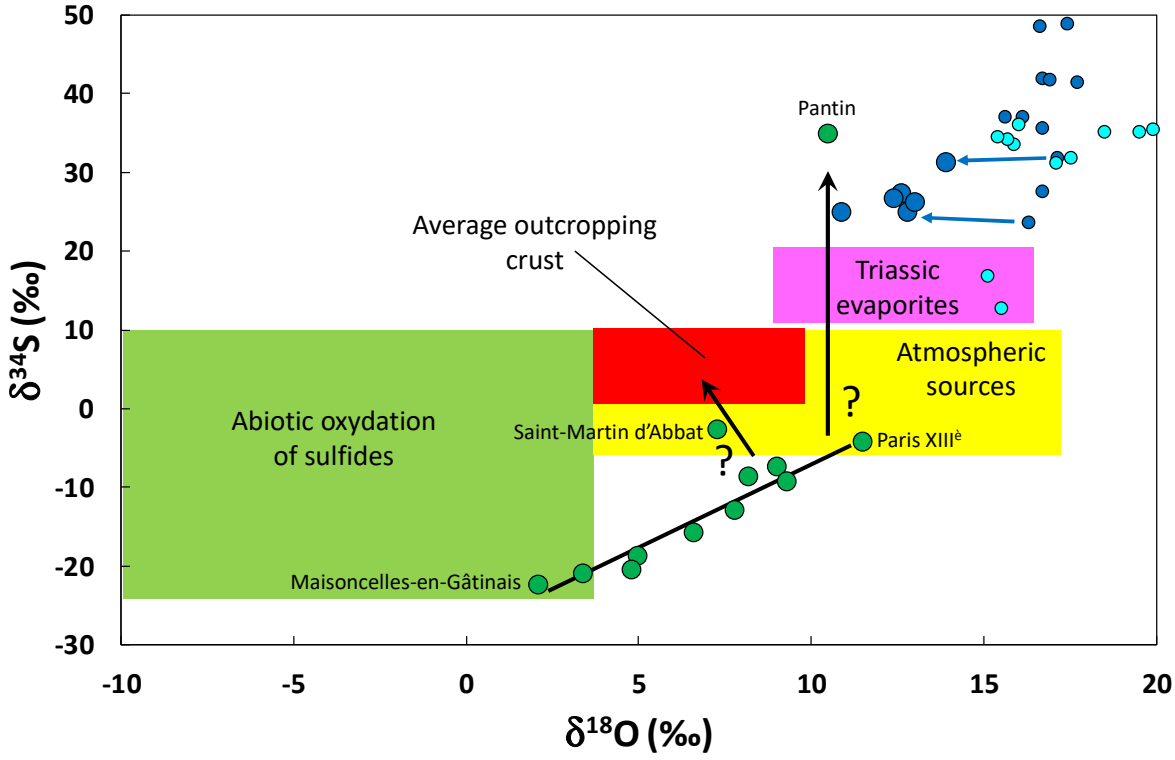

Figure 6 : $\delta^{34}S_{CDT}$ vs. $\delta^{18}O_{CDT}$ diagram measured in the dissolved sulfates of the analyzed waters. Same legend than in Figure 2. Available data on Dogger and waters from the Bure area (Rebeix et al., 2011) have been reported as small light blue disks, and data on Dogger waters from the center of the Paris Basin (Fouillac et al., 1987; 1990) as small dark blue disks. The two blue arrows represent the evolution of $\delta^{18}O$ signatures between Fouillac et al. studies and the present work for similar wells (Coulommiers and Tremblay-en-France). All domains come from Krouse and Mayer (2000), except that of the average outcropping crust (Berner et al., 2002; Pawellek et al., 2002).

4.5. B and Sr isotopes

Dogger waters have very homogeneous strontium and boron isotope signatures (Tab. 2). As regards Sr isotope ratios, they are identical to the previously published data available in Rojas et al. (1989). On the other hand, the Sr isotopic compositions of the waters of the Albian aquifer are more dispersed, ranging from 0.7076 to 0.7087 (Tab. 2). Above all, the boron isotope signatures are extremely variable, with $\delta^{11}B$ values ranging from very slightly negative to above +25‰ (Tab. 2). The coupling of these two isotopic tracers in a mixing diagram (Fig. 7) confirms that the Dogger waters are concentrated in a very restricted field. Their boron isotopic signature is of the same order of magnitude as that of the Dogger water in the Bure region, and greater than that of the overlying Oxfordian water in the same region (Millot et al., 2011b) (Fig. 7). In contrast, their Sr isotopic ratios are slightly higher than those measured for the two aquifers in the Bure region (Rebeix et al., 2011) (Fig. 7).

Most of the Albian waters are distributed according to a simple mixing curve (green-brown in Fig. 7), with the two end-members appearing to correspond to the isotopic characteristics of the two types of lithology constituting the aquifer. The lowest strontium isotope ratios are identical to those of the world ocean in the Albian epoch (Koepnick et al., 1985), as well as to those of the fraction of non-exchangeable strontium calculated from available geochemical and isotopic data for Albian glauconites (Humez, 2012). The second end-member, less well constrained and characterized by more radiogenic strontium isotope ratios, with lower Sr concentrations (Tab. 2), may correspond to the more distinctly clastic facies of the aquifer. For all these waters, boron isotope signatures remain close to 0 or slightly positive (Fig. 7).

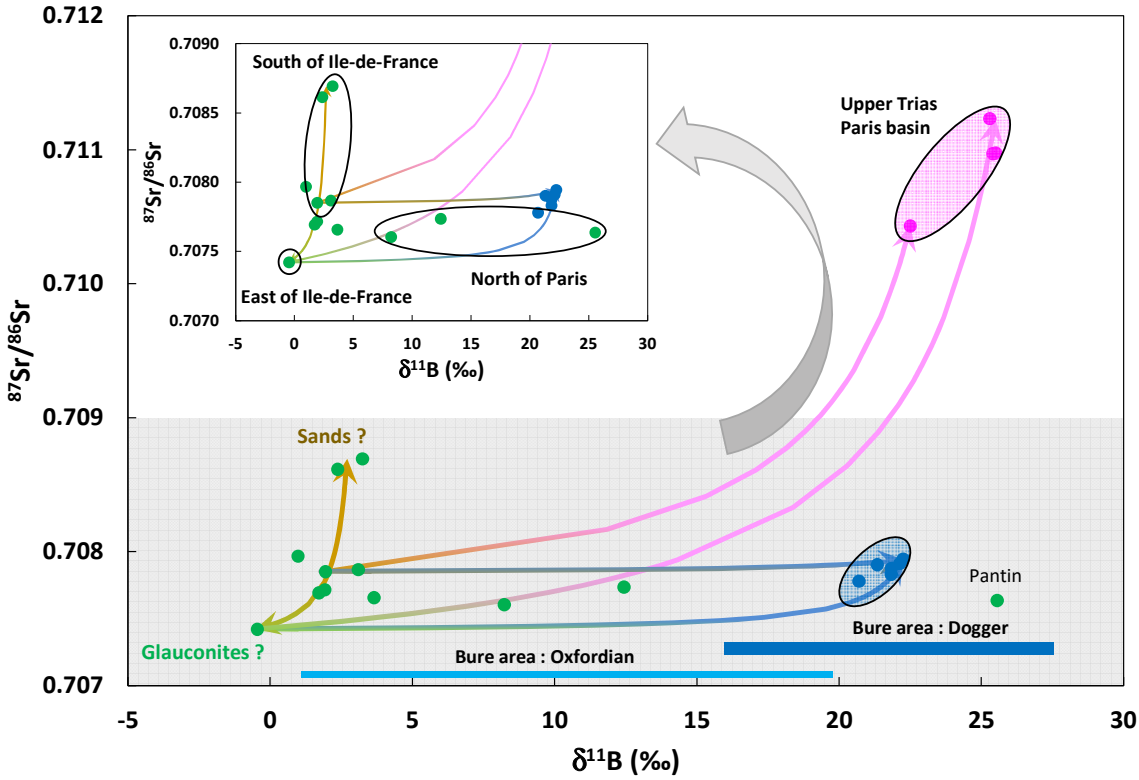

Figure 7 : $\delta^{11}B$ vs. $^{87}Sr/^{86}Sr$ for the analyzed waters. Same legend than in Figure 2. The domains of Dogger and Oxfordian waters from the Bure area are from Casanova et al. (2006), Rebeix et al. (2011) and Millot et al. (2011b). The domain of upper Triassic waters comes from Millot et al. (2011a).

Four of the waters from the Albian aquifer are significantly enriched in ^{11}B, up to 25‰ for Pantin water, already remarkable for the isotopic signatures of its dissolved sulfates (Fig. 6). These waters, collected in the Ile-de-France region, north and/or west of Paris, clearly deviate from the green-brown mixing curve (Fig. 7).

Such B isotopic signatures may originate from water/rock interaction processes, more precisely desorption of exchangeable boron of argillaceous minerals, which would result in both higher $\delta^{11}B$ and B concentrations in the groundwater (Pennisi et al., 2006). However, this would indicate it is not in equilibrium with the matrix.

Alternatively, such features may reveal the involvement of another source of strontium and boron. This source could correspond to the saline waters of the Dogger aquifer, or even to the deeper waters of the Upper Triassic (Millot et al., 2011a), with, in this case, much higher strontium isotope ratios (Fig. 7). Mixing curves have been calculated, with Upper Triassic (pink) and Dogger (blue) waters to try to account for the observed boron and strontium isotope signatures. If none of them completely explains the Pantin isotope ratios, these boron signatures, especially for the Pantin water, plead for a geochemical influence of the very deep aquifers waters on those of the Albian in this sector, supporting the mixing hypothesis based on S and O isotopes. In addition, Sr isotopic ratios higher than those reported in Figure 7 have been reported for Upper Triassic waters (Fontes and Matray, 1993). Unfortunately, no B isotopic signatures are available for these water. However, the contribution of saline waters would be very low (a few ‰ at most), which explains the absence of impact on the geochemistry of the major elements, contrarily to boron contents of Pantin water (Tab. 1; Tab. 2)

Whatever, the isotopic study would corroborate or at least does not contradict (in case of non-equilibrium water/rock interaction processes) the results recently obtained by Dentzer (2016), who concludes from both geothermal flux measurements and seismic profiles that the whole sedimentary pile of the Paris Basin is fractured North of Paris. This strongly suggests the occurrence of interaction of deeper groundwaters on the Albian aquifer.

4.6. Li isotopes

The Li contents are very comparable from one water to another for each of the aquifers. The concentrations in the Albian groundwaters are between 6 and 18 µg/l, approximately (Tab. 2), while those in the saline waters of the Dogger are much more concentrated, from 1.5 to 3 mg/l, approximately.

The isotope signatures of the Albian waters are quite variable (Fig. 8.). The lowest δ^7Li values are found in waters from the south of Ile-de-France, and are correlated with the most radiogenic

Sr isotope compositions (Fig. 8b). These results are perfectly consistent with the hypothesis of a sandier aquifer in this area (Fig. 7), since the mean δ^7Li of the silicate crust is low and close to 0‰ (Teng et al., 2004). On the other hand, in the East of Ile-de-France, the water of Vitry-en-Perthois has a higher δ^7Li with a lower $^{87}Sr/^{86}Sr$, perhaps reflecting the more glauconitic character of the aquifer in this sector, as Sr that is released from green clay minerals (glauconite, celadonite) through leaching processes in displays a low isotopic ratio (e.g.; Clauer et al., 1992; Hart and Staudigel, 1986; Innocent et al., 1997). The other waters of the Albian cluster more or less around a correlation curve between these two end-members.

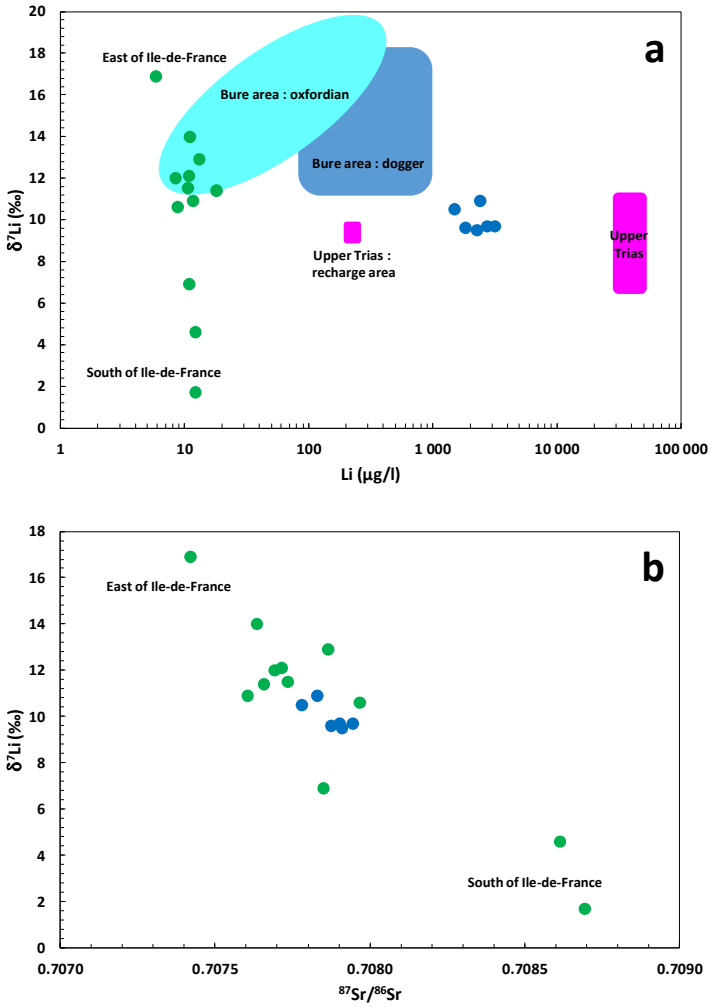

Figure 8 : (a) Higher panel : δ^7Li vs. Li concentrations for the analyzed waters. Same legend than in Figure 2. The domains of Dogger and Oxfordian waters from the Bure area are from Casanova et al. (2006) and Millot et al. (2011b). The domain of upper Triassic waters comes from Millot et al. (2011a) ; (b) Lower panel : δ^7Li vs. ^{87}Sr/^{86}Sr for the analyzed waters. Same legend than in Figure 2.

The waters of the Dogger aquifer show almost constant Li isotopic signatures, between +9.5 and +11‰ (Tab. 2, Fig. 8). It should be noted that they lie on the correlation trend defined by Li vs. Sr isotope compositions for the Albian waters in Figure 8b.

Putting the data obtained in a more general hydrogeological context (Fig. 8a), it appears that the Dogger waters analysed here have lighter Li isotope signatures than those of the same

hydrogeological level in the Bure region (Millot et al., 2011b), accompanied by higher Li contents. These δ^7Li values are consistent with those obtained from the saline waters of the underlying Upper Triassic aquifer (Millot et al., 2011a).

The Oxfordian groundwaters in the Bure sector have Li contents globally higher than those of the Albian water, with δ^7Li values close to those of the Dogger of Bure, and intersecting the tendancy defined by the Albian water in Figure 8a at δ^7Li signatures of the order of +12 to +14‰. However, the Li isotope data do not allow us to conclude that there is any interaction between these two aquifers. The isotope signatures of Li in groundwaters reflect both the processes of fluid-rock interaction and the contributions of the geochemical reservoirs involved (Hogan and Blum 2003; Négrel et al., 2010; 2012; Meredith et al., 2013; Pogge von Strandmann et al., 2014; Bagard et al., 2015). It has been shown that during water/rock interactions, ^{6}Li is preferentially retained into secondary mineral phases (clays and oxides) leading to higher δ^7Li signatures in the dissolved load.

4.7. Uranium activity ratios

Uranium activity ratios measured in the saline waters of the Dogger are above the secular equilibrium value (Tab. 2, Fig. 9), but, with one exception, do not exceed 2. Such values are of the same order of magnitude as those measured in the Upper Triassic waters in the centre of the Paris Basin (Millot et al., 2011a). On the other hand, they differ markedly from Dogger waters in the Bure region (Millot et al., 2011b), the latter generally having activity ratios below the secular equilibrium value, with generally higher U contents (Fig. 9).

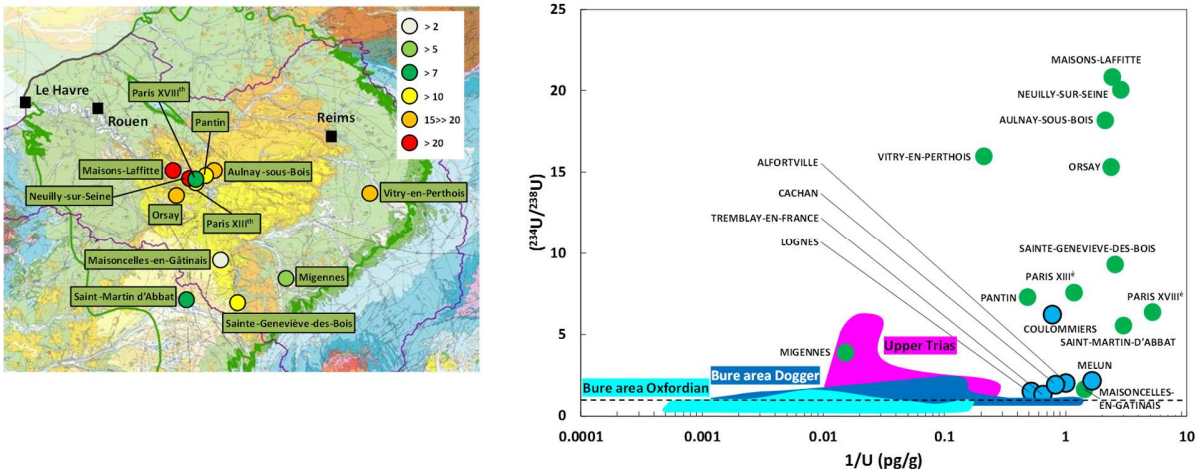

Figure 9 : ($^{234}U/^{238}U$) activity ratios vs. 1/U concentrations for the analyzed waters. Same legend than in Figure 2. The domains of Dogger and oxfordian waters from the Bure area are from Casanova et al. (2006) and Millot et al. (2011b). The domain of upper Triassic waters comes from Millot et al. (2011a).

For the Albian waters, activity ratios can reach very high values, sometimes above 20 (Tab. 2, Fig.

9). Such signatures are found in the vicinity of recharge areas, and reflect the passage of water from an oxidizing to a reduced milieu, near the redox front (Ivanovitch et al., 1991, and references therein). Indeed, the U contents of the Albian waters remain very low, which would be expected for reducing groundwaters(Cowart, 1980), with one exception (Tab. 2, Fig. 9). However, this is in apparent contradiction with the fact that none of the analysed Albian waters are reducing (Tab. 1). Indeed, Humez et al. (2013) reported anoxic conditions in the central confined part of the Albian sandstone with high iron concentrations. Thus the reported values for redox potential and dissolved oxygen might not reflect in-situ conditions, possibly due to atmospheric contamination during pumping or sampling.

It should also be noted that the Oxfordian (carbonate) groundwater in the Bure sector, close to the groundwater recharge area, has activity ratios generally below 1 (Millot et al., 2011b), with higher U contents. This reflects the difference in the behaviour of the element U between the waters present in these two types of aquifers.

However, the highest activity ratios are found north-west of Paris, close to the zone where drains between the Albian aquifer and the underlying aquifers (Dentzer, 2016, this study) have been identified even if the water of Pantin is not the most enriched in ^{234}U, the waters showing the highest activity ratios being located a little further west (Fig. 9). The measured U concentrations and activity ratios are the results of multiple processes within the Albian sandstone, redox-driven and dominated by water-rock interaction, superposed to potential mixing with deep fluids, so that the behaviour of uranium is highly non-conservative. This makes it not usable for unequivocally evidencing drainage processes.

5. Conclusions

This study focused on two of the deep aquifers (Dogger and Albian) within the multi-layered sedimentary aquifer system of the Paris Basin. The isotopic data emphasize, for the Albian aquifer, the possibility of a local geochemical influence of waters similar to those encountered in the underlying saline aquifers, especially Northeast of Paris, in agreement with recent geophysical studies. This contribution remains minor and does not induce significant shifts of salinity, major elements or the stable isotopes of the water molecule. The non-linear nature of isotope mixing for dissolved elements makes them a much more sensitive tracer then the aforementioned parameters. The isotopes of strontium and boron proved to be the most discriminating, even allowing a rough quantification of the contribution of these saline waters. Sulphur and oxygen isotopes of dissolved sulphates made it possible to clearly distinguish the different end-members involved. The behaviour of Li isotopes seems at first glance to be linked to that of Sr, but, as is often the case for this element, it is difficult to disentangle groundwater mixing processes from water-rock interactions. The same is true for uranium activities, whose very high ratios in most of the Albian groundwaters are clearly related to redox-driven water/rock interaction processes.

This work demonstrates also that selected isotopic tracers can be highly sensitive indicators of admixture of brines or saline groundwater to freshwater-bearing aquifers even for low drainage fluxes not inducing any detectable salinity anomalies. It also shows the possibility of drainage from deeper formations into the strategic Albian freshwater resource that needs to be taken into account in the assessment of the environmental baseline against which the impact of the different potential uses of the deep saline aquifers or aquicludes is evaluated. Any drilling through multi-aquifer/aquiclude systems like in the Paris Basin may create hydraulic shortcuts leading to fluid migration (Vernoux and Manceau, 2017). However, this raises the question of the involvement of the intermediate Oxfordian aquifer, for which geochemical and isotopic data are available in

the Bure transposition area only, but whose geochemical characteristics remain at present almost completely unknown in the center of the Paris Basin.

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