



**HAL**  
open science

## Elevated uranium concentration and low activity ratio ( $^{234}\text{U}/^{238}\text{U}$ ) in the Œuf river as the result of groundwater–surface water interaction (Essonne river valley, South of Paris Basin, France)

Mathilde Zebracki, Christelle Marlin, Thierry Gaillard, Josselin Gorny, Olivier Diez, Valérie Monange, Véronique Durand, Charlotte Lafont, Cyrielle Jardin

### ► To cite this version:

Mathilde Zebracki, Christelle Marlin, Thierry Gaillard, Josselin Gorny, Olivier Diez, et al.. Elevated uranium concentration and low activity ratio ( $^{234}\text{U}/^{238}\text{U}$ ) in the Œuf river as the result of groundwater–surface water interaction (Essonne river valley, South of Paris Basin, France). *Science of the Total Environment*, 2023, 876, pp.162537. 10.1016/j.scitotenv.2023.162537 . hal-04041118

HAL Id: hal-04041118

<https://hal.science/hal-04041118v1>

Submitted on 4 Apr 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

1 Title

2 Elevated uranium concentration and low activity ratio ( $^{234}\text{U}/^{238}\text{U}$ ) in the Œuf river as the result of  
3 groundwater – surface water interaction (Essonne river valley, South of Paris Basin, France)

4 Author names and affiliations

5 Mathilde Zebracki<sup>\*1</sup>, Christelle Marlin<sup>2</sup>, Thierry Gaillard<sup>3</sup>, Josselin Gorny<sup>1</sup>, Olivier Diez<sup>1</sup>, Véronique  
6 Durand<sup>2</sup>, Charlotte Lafont<sup>1</sup>, Cyrielle Jardin<sup>1</sup>, Valérie Monange<sup>3</sup>

7 <sup>1</sup>Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSE-ENV/SEDRE/LELI, 92260, Fontenay-aux-  
8 Roses, France

9 <sup>2</sup>Université Paris-Saclay, CNRS, GEOPS, 91405, Orsay, France

10 <sup>3</sup>Compagnie de Prospection Géophysique Française (CPGF)-HORIZON, 77210, Avon, France

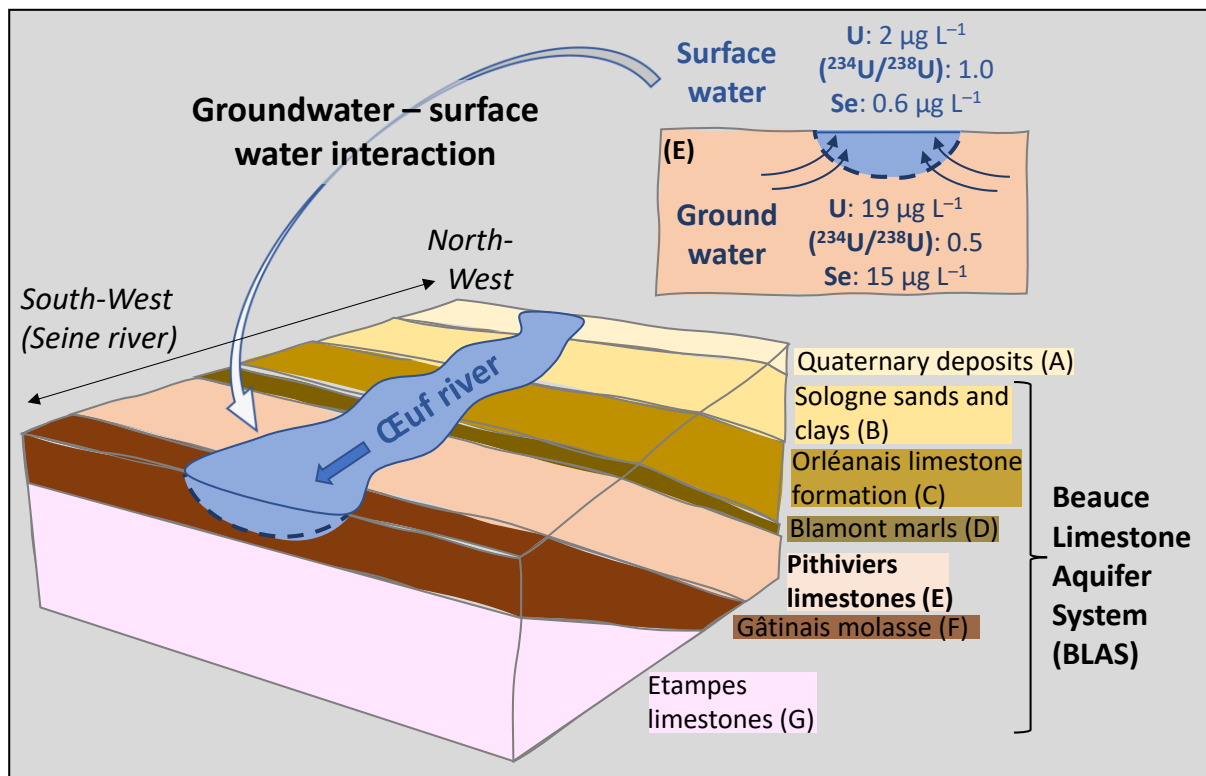
11 \*Corresponding author: [mathilde.zebracki@irsn.fr](mailto:mathilde.zebracki@irsn.fr)

12 Keywords

13 Uranium, ( $^{234}\text{U}/^{238}\text{U}$ ) activity ratio, river-groundwater interaction, selenium, Tertiary limestones,  
14 Beauce aquifer, Paris Basin, Essonne river

15 Abstract

16 Uranium (U) is a naturally occurring radioactive heavy metal widely distributed on Earth. Noticeable  
17 elevated U concentration and low activity ratio (AR) were occasionally detected in headwater stream  
18 of the Essonne river (Seine Basin, France), the namely Œuf river. This paper aims at providing new  
19 insight on geogenic U features in headwater streams and examines the role of river-groundwater  
20 interaction. The Œuf river was sampled four times in 2020 to investigate the influence of heterogenous  
21 geology and hydrological seasonality. The dissolved fraction of water samples was analyzed for a  
22 variety of chemical parameters (anion, major, minor and trace element concentrations, isotopes  $^{234}\text{U}$   
23 and  $^{238}\text{U}$ ). The Œuf river was shown to exhibit elevated U concentration up to  $19.3 \mu\text{g L}^{-1}$  (exceeding  
24 by 100-fold the value of  $0.19 \mu\text{g L}^{-1}$  known for riverine average) and low AR down to 0.41 (almost the  
25 third of the value expected in surface water, *i.e.*, 1.17). The Œuf river got enriched in U when receiving  
26 groundwater from Beauce Limestone Aquifer System. High U concentration (above  $15 \mu\text{g L}^{-1}$ ) was  
27 found in association with low AR (below 0.5) in the stream water when flowing in the outcrop zone of  
28 one BLAS unit. Taking advantage of changes in the stream flow conditions and the geochemical  
29 contrast between surface and ground waters, mixing volumes were calculated. This study first  
30 examined the potential of using U isotopes in combination with selenium as hydrogeochemical tracers  
31 of the river-groundwater continuum. In HWS, the aquifer discharge was shown to supply 12 to 59 % of  
32 the river water. This study demonstrates the key role played by the river-groundwater interaction on  
33 river water chemistry in small streams draining catchment with various geology setting. It also supports  
34 the use of combining redox sensitive trace elements to track the river-groundwater continuum.



36

### 37 1 Introduction

38 Uranium (U) is a naturally occurring radioactive heavy metal that is widely distributed on Earth, *i.e.*, in  
 39 rocks, sediments, soils and waters. In surface waters, U results from the weathering of soils and rocks  
 40 and its concentration generally reflects the lithology of the weathered bedrock (F Chabaux, Riotte, &  
 41 Dequincey, 2003; Ollivier, Radakovitch, & Hamelin, 2011; Zebracki et al., 2017). In worldwide riverine  
 42 water (Palmer & Edmond, 1993), the average U concentration is assessed to be  $0.19 \mu\text{g L}^{-1}$ . The  
 43 concentration of U was initially examined in large rivers to quantify flux to ocean and it showed low  
 44 fluctuations (Windom, Smith, Niencheski, & Alexander, 2000). Rivers draining small catchments are  
 45 more likely to record larger variations of U concentration (Windom et al., 2000). Typically U  
 46 concentration is reported below  $4 \mu\text{g L}^{-1}$  in river water (Smedley & Kinniburgh, 2023). In certain basins  
 47 (less than 1 %), streams show display natural elevated U concentration (Salminen et al., 2005) (above  
 48  $10 \mu\text{g L}^{-1}$ ), when draining specific areas containing U mineralization (Camacho et al., 2010; Salminen et  
 49 al., 2005; Smedley & Kinniburgh, 2023; Snow & Spalding, 1994). Little is known about the geogenic  
 50 fluctuations of U in small streams and increasing attention is given to U origin in agricultural draining  
 51 areas (Gardner et al., 2022; Lyons, Gardner, Welch, & Israel, 2020). In groundwater, U concentration  
 52 is reported to display much greater amplitude of variation with values ranging from 0.03 to  $120 \mu\text{g L}^{-1}$   
 53 (Mangini, Sonntag, Bertsch, & Müller, 1979). The level of U concentration in groundwater is  
 54 constrained by the oxidation-reduction potential, U being very soluble in oxidizing conditions and  
 55 insoluble in reducing conditions. The alkaline character of the limestone formations favours U mobility  
 56 in groundwater through the formation of stable U carbonate complexes (Banning, Demmel, Rude, &  
 57 Wrobel, 2013a). The weathering of geogenic source material and the desorption from mineral surfaces  
 58 are the principal mechanisms of U release into groundwater (Riedel & Kübeck, 2018). Anthropogenic  
 59 and geogenic causes might enhance U solubility in groundwater leading to the potential degradation  
 60 of water drinking quality (Rosen, Burow, & Fram, 2019). Nitrate is a common contaminant deriving  
 61 from surface-applied chemical fertilizer that fosters U mobility in groundwater (Nolan & Weber, 2015;

62 Riedel & Kübeck, 2018). In shallow aquifer, U mobility is favoured during the recharge of oxidizing  
63 water into the aquifer (Y. Wu, Wang, & Guo, 2019). Similarly, as U, selenium (Se) is trace element which  
64 mobility is also driven by redox conditions. The association of U and Se is typically found in U roll-front  
65 deposits (Bullock & Parnell, 2017; Howard III, 1977), which are produced by the groundwater  
66 transportation of dissolved elements from oxidized level to increasingly reduced and deep one. In  
67 sedimentary basin, deposits enriched in organic matter play an important role in U accumulation, in  
68 the forms of detrital material (Pregler et al., 2019), peat and lignite formations (Cumberland, Douglas,  
69 Grice, & Moreau, 2016; Pregler et al., 2019; Read et al., 1993). Argillaceous sediments enriched with  
70 organic matter and pyrite fulfilling karst cavities were shown to concentrate together U and Se (Bassil  
71 et al., 2016).

72 Uranium has three U isotopes which are commonly detected in rocks:  $^{238}\text{U}$  (half-life:  $4.47 \cdot 10^9$  y),  $^{235}\text{U}$   
73 ( $7.04 \cdot 10^8$  y) and  $^{234}\text{U}$  ( $2.46 \cdot 10^5$  y). Both  $^{238}\text{U}$  and  $^{235}\text{U}$  are primordial radionuclides present on Earth since  
74 its formation, while  $^{234}\text{U}$  has a radiogenic origin, being produced through the radioactive disintegration  
75 of  $^{238}\text{U}$ . This radiogenic fractionation yields to a preferential leaching of  $^{234}\text{U}$  relative to  $^{238}\text{U}$  during the  
76 rock chemical weathering (Fleischer, 1980; Kigoshi, 1971). Consequently, surface and ground waters  
77 generally display an enrichment of  $^{234}\text{U}$  with respect to  $^{238}\text{U}$ , with corresponding ( $^{234}\text{U}/^{238}\text{U}$ ) activity  
78 ratio (AR) above 1. Waters depleted in  $^{234}\text{U}$  indicate that the weathered solid surface is also depleted  
79 in  $^{234}\text{U}$  (Israelson, Bjrk, Hawkesworth, & Possnert, 1997; Mathieu, Bernat, & Nahon, 1995; Riotte &  
80 Chabaux, 1999). In soil leachates,  $^{234}\text{U}$  deficit indicates that surface or subsurface soil have already  
81 experienced  $^{234}\text{U}$  loss by leaching, as this has been pointed out in soil of river (Riotte & Chabaux, 1999)  
82 and lake (Israelson et al., 1997) catchments. The riverine value of AR is averaged 1.17 (François  
83 Chabaux, Riotte, Clauer, & France-Lanord, 2001). On a worldwide scale, the observation of  $^{234}\text{U}$  deficit  
84 regarding  $^{238}\text{U}$  (AR below 1) in freshwater is scarcely documented: single example is given by the  
85 Strengbach watershed (France) where a slight  $^{234}\text{U}$  deficit has been occasionally documented in a  
86 stream (Riotte & Chabaux, 1999) (minimum AR of 0.966) and a spring (Pierret, Stille, Prunier, Viville, &  
87 Chabaux, 2014) (AR of 0.819). Little is known about geogenic AR fluctuation in small streams.  
88 Groundwaters exhibit a larger range of AR variation than surface waters, AR values commonly ranging  
89 from 0.9 to 12 (Osmond & Cowart, 1976). Extreme low AR values nearby or below 0.5 were detected  
90 as single values in a variety of hydrogeological settings (Abdul-Hadi, Alhassanieh, & Ghafar, 2001; Chkir,  
91 Guendouz, Zouari, Hadj Ammar, & Moulla, 2009; El-Aassy et al., 2015; Grabowski & Bem, 2012;  
92 Kaufman, Rydell, & Osmond, 1969). This extreme deficit in  $^{234}\text{U}$  (with respect to  $^{238}\text{U}$ ) was taken as an  
93 indicator of specific hydrogeological areas with high permeability, rapid groundwater circulation and  
94 intense dissolution (Kaufman et al., 1969). The fractionation between  $^{238}\text{U}$  and  $^{234}\text{U}$  is specific of U and  
95 unique among the other heavy metals (Michel, Kraemer, & DeWayne Cecil, 2009; Osmond, Cowart, &  
96 Ivanovich, 1983). Taking advantage from this, U isotopes were shown to be relevant isotopic tracers in  
97 hydrological studies (Osmond & Cowart, 1976; Osmond, Rydell, & Kaufman, 1968), especially in  
98 tracking the groundwater circulation (F. Chabaux, Bourdon, & Riotte, 2008; Osmond & Cowart, 1976;  
99 Osmond, Kaufman, & Cowart, 1974; Rován et al., 2020). Based on U isotopes ability to distinguish  
100 different water sources, they were used in river catchments as tracers of the interactions between  
101 groundwater and surface waters (Huckle et al., 2016; Navarro-Martinez et al., 2017; Pierret et al., 2014;  
102 Ryu, Lee, Chang, & Cheong, 2009). Infrequently U isotopes were utilized to quantify the groundwater  
103 contribution to surface water in combination with other tracers, as strontium isotopes (Durand,  
104 Chabaux, Rihs, Düringer, & Elsass, 2005; Paces & Wurster, 2014; Riotte & Chabaux, 1999) and major  
105 elements (Navarro-Martínez, Sánchez-Martos, Salas García, & Gisbert Gallego, 2020).

106 At the head of the Essonne river valley (Seine Basin), in the namely Œuf river, a maximum U  
107 concentration of  $22 \mu\text{g L}^{-1}$  (100-fold the average riverine concentration) was occasionally detected in  
108 the framework of radiological national survey. In parallel, isotopes analyses conducted in the stream

109 river revealed AR values below 0.5, indicating a large deficit in  $^{234}\text{U}$  compared to  $^{238}\text{U}$ . So far, such low  
110 AR (half that of 1.17) has not been described in other surface waters around the world. The ground  
111 catchment of the Œuf river is part of the Beauce Limestone Aquifer System (BLAS), one of the major  
112 French aquifers in the Paris Basin. In this reservoir, high level of Se concentration (above  $10\ \mu\text{g L}^{-1}$ ) was  
113 occasionally found in groundwater for drinking water supply (Cary, Joulian, Battaglia-Brunet, &  
114 Decouchon, 2018). The presence of Se anomaly is of geogenic origin and was attributed to Ypresian  
115 lignite layer (Lower Eocene) which is known to concentrate Se in association with U (Chery & Rouelle-  
116 Castrec, 2004; Gaillard, 2017; Gaillard & Garnier-Séréno, 2017). The role of river-groundwater  
117 interaction was examined in this study to provide new insight on geogenic U characteristics in small  
118 streams and to improve the understanding of such atypical observations for freshwater. Here we  
119 presented the results of investigations on the interaction of the river with aquifer geology and the  
120 influence of hydrological seasonality. Prior to this work, no hydrogeochemical study was performed in  
121 streams of the Essonne river valley. This study also first examines the potential of using U isotopes in  
122 combination with Se as hydrogeochemical tracers of the river-groundwater continuum.

## 123 2 Regional settings

124 The Paris Basin refers to a large sedimentary basin covering almost the northern half of France (Figure  
125 1), whose deposits extend from Permian and Triassic at the base to Tertiary to Quaternary at the  
126 surface. It is drained by several rivers, amongst which the Seine River, being interconnected with large  
127 sedimentary aquifers.

128 The Essonne river is one of the major tributaries of the Seine river and it derives from the confluence  
129 of the Œuf river and the Rimarde river (Figure 1). The Œuf river originates as a small stream from the  
130 Grand Vau pond in the Orléans Forest located approximately 100 km south of Paris. The Œuf river  
131 flows through a South-West to North-East axis with a length pathway of approximately 32 km. The Œuf  
132 river drains a surface catchment of  $282\ \text{km}^2$  with elevations ranging from 129 to 88 m above the sea  
133 level (masl). The slope of the river is 1.3 ‰ in average.

134 The Œuf river displays a mean annual discharge of  $0.5\ \text{m}^3\ \text{s}^{-1}$  (water discharge measured over the  
135 1970 – 2010 period at Bondaroy station (Figure 1) ; data available from <http://hydro.eaufrance.fr/>).  
136 This river yearly exhibits two contrasted hydrological seasons: the high water season (HWS) from  
137 January to May and the low water season (LWS) from June to December.

138 The local geological formations typically comprise lacustrine limestones interbedded with detrital  
139 sedimentary formation. The riverbed consists in Quaternary alluvium, mainly clayey, and mostly  
140 covering Early and Middle Miocene geological formations. At the downstream river extremity,  
141 Oligocene geological formation starts outcropping. In detail, the Œuf river crosses upstream to  
142 downstream the following geological formations (Gigot, 1984) (A to F; Figure 1):

- 143 - From 0 to 3 km, the river starts as connected ponds (Grand Vau then Petit Vau) lying on  
144 Quaternary deposits “A”, Sologne sands and clays “B” (Late Langhian to Early Pliocene),  
145 Orléanais marls and sands C1 (Burdigalian);
- 146 - From 3 to 9.5 km, the river flows on Orléanais marls and limestones “C2” (Burdigalian);
- 147 - From 9.5 to 10.9 km, the river flows on Blamont marls “D” (Aquitanian);
- 148 - From 10.9 to 23.1 km, the river flows on Pithiviers limestones “E” (Aquitanian);
- 149 - From 23.1 to 32 km, the river flows on Gâtinais molasse “F” (Aquitanian).

150 The Œuf river ends when meeting the Rimarde river and that coincides with the outcrop of Etampes  
151 limestones G (Rupelian). The two Orléanais formations C1 and C2 are considered as lateral variation of  
152 Orléanais limestone formation unit; on Figure 1 they were distinguished based on the difference

153 reported between their lithological facies. Except for the Langhian and Burdigalian sandy deposits, this  
154 sedimentary pile of Tertiary lacustrine calcareous formations dating from Rupelian (Early Oligocene)  
155 to Aquitanian (Early Miocene) forms the upper part of the Beauce Limestone Aquifer System (BLAS).  
156 The BLAS (*sensu stricto*), approximately 75 m thick, comprises three main aquifer units, *i.e.*, Orléanais  
157 limestones, Pithiviers limestones and Etampes flinty limestones, separated by two aquitards, *i.e.*,  
158 Blamont marls and Gâtinais molasse.

159 South of the Œuf river catchment and below the Orléans Forest, the BLAS is overlaid by Orléanais marls  
160 and sands and by Sologne sands and clays (Figure 1). The geological formation of Sologne sands and  
161 clays is permeable at its top (due to the presence of sands) and more impermeable at its bottom  
162 (presence of clayey deposits), making the Sologne sand an additional aquifer in the studied area. The  
163 sandy texture of Orléanais formation is separated from Sologne sands by a paleosol containing a peat  
164 layer (Gigot, 1984). The Sologne detrital formation is known to come from the erosion of granite  
165 mountains located further south (Massif Central) (Rasplus, 1982). Based on the borehole cutting  
166 description (<https://infoterre.brgm.fr/>), the limestones of the Orléanais and the Pithiviers formations  
167 have a mudstone texture with pseudobreccia horizons.

168 At a larger scale, the BLAS is the upper part of the regional Beauce aquifer that comprises a thicker  
169 sedimentary series deposited from Eocene to Miocene (Ypresian to Burdigalian) above the Late  
170 Cretaceous Chalk (Martin, Giot, & Le Nindre, 1999). The Beauce aquifer is a 230 m-thick multi-layered  
171 aquifer of regional extension of *ca.* 9 – 10,000 km<sup>2</sup> that makes it one of the largest aquifers in France  
172 (Martin et al., 1999).

173 The Œuf river originates in the most western part of the Orléans Forest. Northwest to the Orléans  
174 Forest the Beauce Plateau consists in recent (Quaternary) fertile silts that are used for intensive  
175 agriculture, particularly of wheat. The hydrographic network on the Beauce Plateau displays a low  
176 density and a low elongation index of watercourses which correspond to the river headwaters either  
177 flowing to the Seine river (to the north) or to the Loire river (to the south) (Larue & Étienne, 2014). On  
178 the Beauce Plateau, the low density hydrographic network coupled with a moderate soil coverage, the  
179 presence of chasms (in the Orléans Forest) and an important karstic network (Lorain, 1973) (North of  
180 Orléans Forest, Pithiviers and Etampes limestone formations) lead to an important and rapid water  
181 infiltration to the aquifer (Desprez, 1983).

## 182 3 Materials and methods

### 183 3.1 River water

#### 184 3.1.1 Sampling and field measurement

185 Surface water samples were collected in the Œuf river stretches corresponding to the different  
186 formation outcrops and at the different hydrological seasons LWS and HWS. The Œuf river was  
187 sampled four times in 2020 in March (HWS), and in June, September, and December (LWS). To  
188 investigate the interaction between the Œuf river and the outcropping geological formations, twelve  
189 sampling sites were selected (R1 to R12, from B to F; Figure 1):

- 190 - R1 at 1.1 km and R2 at 1.6 km are in the outcrop zone of Sologne sands and clays followed by  
191 Orléanais marls and sands (B and C1, ending at 3 km),
- 192 - R3 at 4.9 km, R4 at 8.2 km and R5 at 9.2 km are in the outcrop zone of Orléanais marls and  
193 limestones (C2, from 3 to 9.5 km),
- 194 - R6 at 12.3 km, R7 at 14.1 km, R8 at 15.3 km, R9 at 16.3 km and R10 at 17.8 km are in the  
195 outcrop zone of Pithiviers limestones (E, from 10.9 to 23.1 km),
- 196 - R11 at 24.9 km and R12 at 29.5 km are in the outcrop zone of Gâtinais molasse (F, from 23.1  
197 to 32 km).

198 The most upstream sampling site (R1) is in the Petit Vau pond which is hydraulically connected to the  
199 Grand Vau pond (main spring). The most downstream sampling site (R12) is 2.5 km before the  
200 Œuf – Rimarde confluence. Four tributaries (T1 to T4) meeting the Œuf river at 1.5, 8.6, 10.0 and  
201 11.2 km respective distances from the spring were also sampled (Figure 1). During LWS, we noticed  
202 that the riverbed was dried out in the first 12.3 – 14.1 km of the Œuf river and in the four tributaries.  
203 On the contrary, we noticed that the spring area of the Œuf river (Grand Vau pond) was permanently  
204 filled.

205  
206 Single samples of river water were collected considering the water mass was homogeneous owing to  
207 the stream small size (approximately 2 m wide, 30 cm deep). In total, a set of 42 samples of river  
208 water was collected and stored in 50 mL-glass bottles and 1 L-polyethylene bottles in refrigerating  
209 conditions until they were transported to the laboratory (located approximately one hour's drive from  
210 the field, at Fontenay-aux-Roses, Paris south area), and prior to further treatment.

211 In parallel, physical and physico-chemical parameters were measured on field using a portable multi-  
212 parameter system (WTW Multi 3420) connected to single and specific probes for the determination of  
213 the temperature (T) and the electrical conductivity (EC; TetraCon 925), pH (SI Analytics ADA S7/IDS)  
214 and the oxidation-reduction potential (ORP; WTW Sentix). The ORP was measured with a reference  
215 electrode Ag/AgCl (3 M KCl), with a potential equal to 208 mV versus the Standard Hydrogen Electrode  
216 (SHE). All redox potential (Eh) values reported in the text are expressed versus the SHE electrode. For  
217 field measurement, the deviation was estimated at  $\pm 10\%$  for each probe.

### 218 3.1.3 Sample preparation

219 The sample preparation was performed within 24 hours after sampling at IRSN laboratory LUTECE  
220 (Laboratoire Unifié d'expérimentation Et de Caractérisation dans le domaine des dEchets). All water  
221 samples were filtrated (at 0.45 or 0.7  $\mu\text{m}$  threshold) and the dissolved fraction was subsequently  
222 analyzed.

223 For carbon analysis, the water sampled with glass bottle was filtrated through glass fibre filter at  
224 0.7  $\mu\text{m}$  (Whatman). The dissolved fraction was then collected in 30 mL-glass bottle and immediately  
225 analyzed for carbon measurement.

226 For other chemical species, the water sampled with polyethylene bottle was filtrated through cellulose  
227 acetate membrane at 0.45  $\mu\text{m}$  (Sartorius). The dissolved fraction was stored in 50 mL-polypropylene  
228 tube (VWR) then immediately analyzed for anion measurement; it was acidified with 0.3 M  $\text{HNO}_3$  then  
229 stored at 4 °C prior to elemental analyses.

230 For U isotope analysis, the sample preparation procedure was completed by spiking each sample with  
231 a double isotope reference standard (Richter et al., 2008) (IRMM 3636) and followed by a separation  
232 step using UTEVA extraction chromatographic resin (Horwitz et al., 1992) (Eichrom Technologies). An  
233 aliquote of each filtered and acidified water sample (5 mL) to pH 1 was analyzed to determine the  
234 required volume of filtered water sample. Additional filtration was only performed for water samples  
235 having U concentration lower than 5  $\mu\text{g L}^{-1}$ . The filtered water sample was then evaporated to dryness  
236 in 50 mL-polypropylene tube (VWR). The dry residue was dissolved in 4 mL 3 M  $\text{HNO}_3$  and mixed with  
237 10  $\mu\text{L}$  of IRMM 3636 double spike with a  $^{233}\text{U}/^{236}\text{U}$  isotope ratio of 1:1 and an initial  $^{236}\text{U}$  concentration  
238 at 8.67  $\text{ng g}^{-1}$ .

### 239 3.1.4 Chemical analyses

240 Only the dissolved fraction ( $< 0.45 \mu\text{m}$ ) of the water samples was analyzed and all analyses were  
241 performed at IRSN laboratory LUTECE. Analytical settings are detailed in Supplementary information –



242 Materials and methods. For each measurement, the uncertainty derives from the standard analytical  
243 deviation and is given at  $\pm 2 \sigma$ .

244 Concentration of anions  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{Br}^-$  and  $\text{PO}_4^{3-}$  was measured using ionic chromatography  
245 (Metrohm 930 Compact IC). Dissolved organic and inorganic carbon was measured using a carbon  
246 analyzer (Elementar TOC Vario). Concentration of the chemical elements Ca, Na, K, Si, Mg, Ba and Sr  
247 was determined using ICP-OES (Thermo Fisher Scientific iCAP 7600 Duo). The determination of U and  
248 Se concentrations and ( $^{234}\text{U}/^{238}\text{U}$ ) activity ratio was performed using Agilent 8800 Inductively coupled  
249 plasma-Tandem mass spectrometry ICP-MS/MS (Agilent Technologies, Tokyo, Japan) equipped with  
250 an octupole collision/reaction cell (CRC) situated between two mass-selecting analysers.

### 251 3.2 Groundwater

252 Groundwater of BLAS units was not sampled through the study. We extracted data from the French  
253 national web portal ADES on groundwater (<https://ades.eaufrance.fr/>). Four boreholes (GW1 to GW4)  
254 were available in the vicinity of the  $\text{C}\ddot{\text{e}}\text{u}f$  river (Figure 1), and for each one, the drilling settings were  
255 examined: GW1 extracts groundwater from Orléanais limestone formation, GW2 and GW3 from  
256 Pithiviers limestones, and GW4 from both Pithiviers and Etampes limestones. A dataset of monitoring  
257 data acquired over the 2001 – 2021 timespan was compiled, including EC, ORP, the concentrations of  
258  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , Ca, Mg, Se, U and the activities of isotopes  $^{238}\text{U}$  and  $^{234}\text{U}$  (allowing the computation of AR).

### 259 3.3 U speciation modelling

260 The choice of the thermodynamic database is known to impact the final speciation modelling of  
261 aqueous U in natural systems (Lartigue, Charrasse, Reile, & Descostes, 2020; Reiller & Descostes, 2020;  
262 X. Wang et al., 2019). In this study, we investigated the aqueous speciation of U in the presence of  
263 common inorganic ligands (Markich, 2002; Smedley, Smith, Abesser, & Lapworth, 2006), including  $\text{OH}^-$   
264 ,  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$  and  $\text{Br}^-$ . The thermodynamic modelling code PHREEQC version 3 was used  
265 to compute U speciation (Parkhurst & Appelo, 2013), using the MINTEQ.V4 database (Eary & Jenne,  
266 1992). The percentage of each U specie was based on its relative contribution to U concentration in  
267 water. The distribution of U aqueous species was calculated in the water samples displaying a complete  
268 chemical dataset only: R1 – R12 in March, R3 and R6 in June, R10 and R11 in September, and R1 – R3,  
269 R7, R8 and R10 – R12 in December.

## 270 4 Results

### 271 4.1 Stream water supply

272 Since we conducted a river survey at different times of 2020, we were able to observe differences in  
273 the river flow along the  $\text{C}\ddot{\text{e}}\text{u}f$  riverbed between LWS (March) and HWS (June, September and  
274 December).

275 In LWS, the water flow occurred permanently at R1 (1.1 km) which corresponds to the Grand Vau pond  
276 located nearby the spring of the  $\text{C}\ddot{\text{e}}\text{u}f$  river in the Orléans Forest. There, the geological formation of  
277 Sologne sands and clays is permeable at its top due to the presence of sands and more impermeable  
278 at its bottom due to the presence of clayey deposits. This is likely to explain the permanence of water  
279 at R1 that was attributed to the continuous discharge of Sologne sandy aquifer below the Orléans  
280 Forest. The  $\text{C}\ddot{\text{e}}\text{u}f$  riverbed was found occasionally dry in the outcrop zones of Orléanais formation  
281 (between R2 at 1.6 km to R5 at 9.2 km), indicating a loss of the stream water. Also, we noticed the  
282 absence of water in the four tributaries (T1 to T4) preventing from discharge into the main stream at  
283 1.5, 8.6, 10.0 and 11.2 km. Permanent water flow was seen from 14.1 km (R7), indicating a water  
284 supply through groundwater discharge once the river flows over the Pithiviers limestones  
285 (10.9 – 23.1 km). The intermittent flow observed at the beginning of Pithiviers limestones (R6 at  
286 12.3 km) indicates water table fluctuations with time. The zone where the stream flow became



287 continuous coincides with the disappearance of Blamont marls (aquitard) and the change of Pithiviers  
288 limestone aquifer from confined to unconfined (<https://infoterre.brgm.fr/>).

289 In HWS, the stream flow was permanent along the entire Œuf riverbed and its four tributaries,  
290 indicating that rainfall and its consecutive increasing water discharge is sufficient to maintain a  
291 continuous stream flow.

#### 292 4.2 Stream water chemistry

293 The chemical results of the water sampled in the Œuf river catchment were reported in Tables 1 – 4 in  
294 Supplementary information. The spatial and seasonal variations of the stream water chemistry were  
295 illustrated on Figure 2 (physical and chemical parameters), Figure 3 (anion concentration) and Figure  
296 4 (major, minor and trace element concentration).

297 Water ion balances were equilibrated for all sampling points with 10 % uncertainty. The Œuf river  
298 displayed pH values mostly comprised in the range 7 – 8, with lower values observed in LWS (7 – 7.5)  
299 compared to HWS (*ca.* 8). The pH of the stream water displayed circumneutral conditions, being in  
300 accordance with natural freshwater in carbonated environment. The ORP exhibited values mostly  
301 comprised in the range 330 – 550 mV, indicating the prevalence of oxidizing conditions being in  
302 accordance with water river conditions. Occasionally a low value (23 mV) was measured in December  
303 at 1.6 km when the stream water was shallow and stagnant.

304 Whatever the hydrological season (LWS or HWS), the dominant chemical species in the stream water  
305 were Ca (above 110 mg L<sup>-1</sup> and 50 mg L<sup>-1</sup> in LWS and HWS, respectively) and DIC (above 50 mg<sub>C</sub> L<sup>-1</sup> and  
306 20 mg<sub>C</sub> L<sup>-1</sup> in LWS and HWS, respectively). Therefore, the stream water referred as calcium bicarbonate  
307 water, that being confirmed by the Piper diagram (Suppl. Inf. Figure 2). Concentration of NO<sub>3</sub><sup>-</sup> was  
308 systematically above 30 mg L<sup>-1</sup> in LWS, thus exceeding the European guideline alert value (*i.e.*, 25 mg L<sup>-1</sup>;  
309 European Water Framework Directive 2000/60/EC).

310 Whatever the season, EC of the stream water globally increased downgradient, reflecting an  
311 increasingly degree of mineralization. The lowest values were seen at the most upstream site (R1 at  
312 1.1 km), and the range of variation was narrow (39 – 51 μS cm<sup>-1</sup>) whatever the hydrological season.  
313 The values increased up by a factor 20 downgradient, the highest values being found at the most  
314 downstream site (R12 at 29.3 km) where values varied almost 2-fold between LWS (898 μS cm<sup>-1</sup> in  
315 September) and HWS (545 μS cm<sup>-1</sup> in March).

316 Most chemical species and elements, including DIC (Figure 2), Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, Br<sup>-</sup> (Figure 3), Ca,  
317 Mg, Na, K, Sr, and Se (Figure 4), generally exhibited concentration with a downgradient increase  
318 whatever the hydrological season (LWS or HWS). When comparing the concentrations between the  
319 hydrological season, the main contrast was their amplitude of variation: low concentrations were seen  
320 in HWS and high ones in LWS. Noticeably, Cl<sup>-</sup>, Br<sup>-</sup>, Na and K showed a sharp increase of concentration  
321 downstream in the outcrop zone of Gâtinais molasse. The variation of EC (Figure 2) was found to be in  
322 good agreement with the variations of DIC, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Mg, Ca, and Sr (correlation coefficients of 0.97,  
323 0.91, 0.87, 0.96, 0.98 and 0.94, respectively; Suppl. Inf. Table 6).

324 The concentration of PO<sub>4</sub><sup>3-</sup> varied by 2 orders of magnitude from 0.004 (R2) to 0.62 mg L<sup>-1</sup> (R3). Also,  
325 it displayed differences between upstream and downstream, and between LWS and HWS: PO<sub>4</sub><sup>3-</sup>  
326 concentration was higher in LWS than HWS upstream (till 9.5 km, *i.e.*, in the outcrop zones of Sologne  
327 sands and clays and Orléanais formation), and lower in LWS than HWS downstream (from 12.3 km, *i.e.*  
328 in the outcrop zone of Pithiviers limestones followed by Gâtinais molasse).

329 The DOC values ranged from 16 to 25 mg<sub>C</sub> L<sup>-1</sup>, the highest values founded upstream in the outcrop  
330 zones of Sologne sands and clays and Orléanais marls and sands (0 – 3 km). The DOC values showed a  
331 general downgradient decrease with higher values in LWS compared to HWS. The DOC variations were  
332 found to be inversely correlated to DIC variations (correlation coefficient of – 0.94; Suppl. Inf. Table 6),  
333 indicating different carbon sources in the river.

#### 334 4.3 Stream water uranium

335 The spatial and seasonal variations of U concentration and AR in the Œuf river were illustrated on  
336 Figure 5. Data were reported in Suppl. Inf. Table 4.

##### 337 4.3.1 Spatial and seasonal variation

338 In the Œuf river, U concentration overall increased upstream to downstream, roughly varying by 3  
339 orders of magnitude between 0.02 µg L<sup>-1</sup> and 19.3 µg L<sup>-1</sup>. In parallel, AR decreased by half upstream  
340 (1.06) to downstream (0.41).

341 Firstly, the longitudinal variations of U concentration and AR found in the Œuf river during LWS (Low  
342 Water Season) were described. Upstream to downstream, the stream displayed various U features  
343 (Figure 5 **Erreur ! Source du renvoi introuvable.**):

- 344 - In the outcrop zone of Sologne sands and clays followed by Orléanais marls and sands (B+C1;  
345 0 – 3 km), U concentration was relatively low (0.02 – 0.9 µg L<sup>-1</sup>), and AR was less but close to  
346 1 (0.90 – 0.97);
- 347 - In the outcrop zone of Orléanais marls and limestones (C2; 3 – 9.5 km), U concentration  
348 increased and ranged from single (6.6 µg L<sup>-1</sup>) to double (12.4 µg L<sup>-1</sup>), and AR remained close to  
349 1 and slightly decreased (0.87 – 0.90);
- 350 - In the outcrop zone of Pithiviers limestones (E; 10.9 – 23.1 km), the stream exhibited the  
351 highest values of U concentration which varied in a narrow range (15.0 – 19.3 µg L<sup>-1</sup>) and AR  
352 significantly decreased (0.44 – 0.51);
- 353 - In the outcrop zone of Gâtinais molasse (F; 23.1 – 32 km), U concentration decreased and  
354 varied in a narrow range (12.2 – 13.7 µg L<sup>-1</sup>), and AR slightly decreased and displayed the  
355 lowest values (down to 0.41).

356 Secondly, U and AR longitudinal profiles were compared according to the hydrological season. While  
357 U concentration and AR exhibited similar longitudinal trends together in HWS and LWS, noticeable  
358 differences were shown based on the amplitude of their variations: U concentration was systematically  
359 lower in HWS than LWS, while AR showed the contrary. Upstream to downstream U concentration  
360 exhibited two peak values. In the outcrop zone of Orléanais marls and limestones (3 – 9.5 km), the  
361 maximum of U concentration was 12.4 µg L<sup>-1</sup> in LWS and 2.5 µg L<sup>-1</sup> in HWS (*i.e.*, 6 times less). In the  
362 outcrop zone of Pithiviers limestones (10.9 – 23.1 km), the maximum U concentration was 19.3 µg L<sup>-1</sup>  
363 in LWS and 11.5 µg L<sup>-1</sup> in HWS (*i.e.*, almost 2 times less). Also, a downgradient shift was observed  
364 between U peaks in HWS and LWS: first U peak occurred at 4.9 km in LWS and 8.2 km in HWS, and  
365 second peak U occurred at 14.1 km in LWS and 17.8 km in HWS. Similarly, the decrease of U  
366 concentration was observed from 17.8 to 24.9 km in LWS, and from 24.9 to 29.5 km in HWS.

367 The outcrop zone of Pithiviers limestones (10.9 – 23.1 km) was the river stretch that registered the  
368 greatest changes in both U concentration and AR whatever the hydrological season. In HWS, the  
369 observation of a sharp rise in U concentration (from 2.1 to 11.5 µg L<sup>-1</sup>) was inversely related to a sharp  
370 fall in AR (from 1.0 to 0.54). In LWS, U concentration displayed high values of U concentration and  
371 inversely low AR was soon as the stream water re-emerged (at 12.3 km in June and 14.1 km in  
372 September and December).

373 Regarding the four tributaries (T1 to T4) discharging in the Œuf river (in HWS only), U concentration  
374 and AR exhibited variations in the ranges 0.11 – 4.2  $\mu\text{g L}^{-1}$  and 0.81 – 1.0, respectively.

375 Whatever the hydrological season, U concentration was well correlated with several parameters and  
376 analytes (Suppl. Inf. Table 6): positively with EC, DIC,  $\text{NO}_3^-$ , Mg, Ca, Sr, Ba and Se (coefficient above  
377 0.8), and negatively with DOC and AR (coefficient below –0.8). The positive and good correlation  
378 coefficient between U and EC, DIC and Ca indicated that U occurrence in the stream water was related  
379 to carbonate dissolution, as expected in sedimentary basin (Smedley & Kinniburgh, 2023). The positive  
380 relationships of U to Se (0.93),  $\text{NO}_3^-$  (0.83) and to a lesser extent to  $\text{SO}_4^{2-}$  (0.48) suggested either a  
381 common origin in the river catchment (*e.g.*, a specific mineralization) or a concomitant transfer (the  
382 way they were supplied to the river is the same). The negative relationship of U to AR (–0.89) indicated  
383 that the more the water got enriched in U, the more U was depleted in  $^{234}\text{U}$ .

#### 384 4.3.2 U aqueous species

385 The results of U speciation modelling with PHREEQC are reported in Suppl. Inf. Table 7. In the Œuf  
386 river, U was found in its oxidized form U(VI) as expected in freshwater. Whatever the hydrological  
387 season, U was found to form inorganic complexes  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ,  $\text{UO}_2(\text{CO}_3)_4^{3-}$  and  $\text{UO}_2(\text{CO}_3)$ . In LWS only,  
388 U was occasionally found in forms of  $\text{UO}_2^{2+}$  and  $\text{UO}_2\text{OH}^+$ . These U aqueous species were in agreement  
389 with the ones expected in freshwater (Lartigue et al., 2020; Markich, 2002), *i.e.*, hydroxyl complexes  
390  $(\text{UO}_2(\text{OH})_n)^{(2-n)+}$  and carbonate complexes  $(\text{Ca}_n\text{UO}_2(\text{CO}_3)_3)^{(4-2n)-}$ . Also, U was found to complex with  
391 phosphate anion to form  $\text{UO}_2(\text{HPO}_4)_2^{2-}$ . Although phosphate is an inorganic ligand currently occurring  
392 in freshwater (Markich, 2002), the stability of complex with U under natural conditions is debated  
393 (Sandino & Bruno, 1992; X. Wang et al., 2019).

#### 394 4.4 Groundwater chemistry

395 The groundwater data relative to BLAS units are presented in Suppl. Inf. Table 5. Between the different  
396 BLAS units, EC values varied in a narrow range, between 691 and 554  $\mu\text{S cm}^{-1}$  (in average), that fitting  
397 well with European limestone aquifer (Wendland et al., 2008) (from 95 to 1,146  $\mu\text{S cm}^{-1}$ ). Also, Ca  
398 concentration varied in a narrow range, between 95 and 111  $\text{mg L}^{-1}$  (in average), which fitted well with  
399 the values expected in limestone aquifers (Wendland et al., 2008) (from 66 to 122  $\text{mg L}^{-1}$ ). The values  
400 of ORP were available in groundwater GW3 only, and it showed fluctuations with time (from 100 to  
401 268 mV).

402 Differences between BLAS units were seen regarding the anion concentration. The concentration of  
403  $\text{Cl}^-$  showed high values in the groundwater GW2 (49  $\text{mg L}^{-1}$  in average) compared to GW1, GW3 and  
404 GW4 (22 and 23  $\text{mg L}^{-1}$  in average). The concentration of  $\text{NO}_3^-$  was very low in GW4 (0.55  $\text{mg L}^{-1}$  in  
405 average), it showed much higher concentration in GW1 (29  $\text{mg L}^{-1}$  in average), and the highest values  
406 were found in GW2 and GW3 (44 and 45  $\text{mg L}^{-1}$  in average). In the water extracted from Pithiviers  
407 limestones (GW2 and GW3),  $\text{NO}_3^-$  concentration occasionally exceeded the WHO guideline for  
408 drinking-water purpose (50  $\text{mg L}^{-1}$ ).

409 In BLAS units of interest, U concentration ranged from 7.3 to 12  $\mu\text{g L}^{-1}$  (in average), this level of U  
410 concentration being in accordance with that expected in limestone aquifers (Bonotto & Andrews,  
411 2000; Smedley et al., 2006) (*i.e.*, below 15  $\mu\text{g L}^{-1}$ ). The values of AR were systematically below 0.5 (from  
412 0.32 to 0.45 in average).

## 413 5 Discussion

### 414 5.1 River-groundwater continuum

#### 415 5.1.1 Hydrogeological approach

416 In this section we examined the origin of the water supplied to the Œuf river according to the  
417 hydrogeological settings.

418 In LWS, the Œuf river was shown gaining or losing water when flowing above Orléanais formation  
419 (0 – 9.5 km) and at the beginning of the outcrop zone of Pithiviers limestones (before 14.1 km). The  
420 stream was only gaining water above Sologne sands and clays (0 – 3 km) and after Pithiviers limestones  
421 changed from confined to unconfined aquifer (from 14.1 km). The way the Œuf river interacted with  
422 these aquifers is typical of headwater streams flowing at head catchment and hydraulically connected  
423 to groundwater (Khan & Khan, 2019). In the period of negative efficient rainfall (rainfall level below  
424 evapotranspiration in LWS), the flow of the Œuf river was transient, thus depending on groundwater  
425 discharge and water table fluctuations. In HWS, the rainfall and the surface runoff led to maintain a  
426 continuous flow along the stream riverbed.

427 To characterize the interaction between the Œuf river flowing on the surface and the groundwater of  
428 the different BLAS units outcropping in the river catchment, we first examined the existing  
429 potentiometric lines (BRGM, 1995; Verley, Brunson, Verjus, & Cholez, 2003). Although available, this  
430 information was not appropriate to the space scale of our field observations. Based on our  
431 observations, we considered the Œuf river as an outlet for aquifer discharges from Sologne sands  
432 (0 – 3 km), Orléanais marls and limestones (3 – 9.5 km) and Pithiviers limestones (10.9 – 23.1 km).

#### 433 5.1.2 Geochemical approach

434 In this section, the influence of the geology and the hydrological season on the stream water chemistry  
435 of the Œuf river was examined.

436 The lower values and the lower amplitude observed for EC and major chemical specie concentrations  
437 (DIC,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , Ca) in HWS compared to LWS indicate a water supply being less mineralized. This  
438 decreasing degree of mineralization in HWS was attributed to the contribution of surface runoff and  
439 rainfall to the river water. To focus on the interaction between river and groundwater, the stream  
440 water chemistry in LWS was further examined only. The longitudinal profile of EC indicated a stream  
441 water increasingly mineralized upstream to downstream. The EC values were well and positively  
442 correlated with DIC and Ca, and the other alkaline earth elements Mg and Sr. When flowing on  
443 Orléanais marls and limestones (3 – 9.5 km) and Pithiviers limestones (3 – 23.1 km), the Œuf river got  
444 noticeably enriched in DIC and Ca. The Ca level in the stream water (above  $100 \text{ mg L}^{-1}$ ) fitted relatively  
445 well with the range of values found in the corresponding aquifer units ( $95 - 111 \text{ mg L}^{-1}$  in average in  
446 GW1, GW2 and GW3; Suppl. Inf. Table 5). Therefore, the observation of an increasing mineralized  
447 stream water gave the evidence of an aquifer discharge that mainly consisted in limestones and where  
448 carbonate dissolution took place. In the most downstream zone, *i.e.*, where outcrop Gâtinais molasse  
449 (23.1 – 32 km), the stream water records a sharp increase of  $\text{Cl}^-$ ,  $\text{Br}^-$ , Mg, Na, K and Sr concentrations.  
450 That change was attributed to the groundwater discharge from this geological formation, although it  
451 was only defined as an aquitard.

452 When plotting the molar ratios Mg/Ca vs Sr/Ca (Figure 6), differences were seen in the stream water  
453 depending on the geology. The stream water flowing in the outcrop zone of Sologne sands and clays  
454 followed by Orléanais marls and sands distinguished from that flowing downstream: the ratio Mg/Ca  
455 was relatively high (above 3) in this zone compared to others (Mg/Ca below 1.5). From Orléanais marls  
456 and limestones to Gâtinais molasse, the increasing trend of Mg and Sr concentrations indicated that  
457 water supplied to the stream got enriched in these alkaline earth metals. That possibly reflected an

458 ageing effect: the more the groundwater was aged, the more it contained elements that have been  
459 solubilized through the carbonate dissolution in limestone aquifer. That was evidenced by the  
460 difference observed between Mg/Ca molar ratio of the groundwater extracted from BLAS units (Suppl.  
461 Inf. Table 5): it was higher in Orléanais limestones deposited in Burdigalian (0.073 at GW1), compared  
462 to Pithiviers limestones dated from Aquitanian (0.083 at GW2).

463 The distribution between the dissolved carbon species gave additional information on the water origin  
464 in the stream. Nearby the spring located in the Orléans Forest, the highest DOC values indicated an  
465 enrichment of organic species attributable to the leaching of the surrounding forest soils (in form of  
466 soluble fulvic and humic substances, typically). Downgradient, as the stream water got enriched in DIC  
467 it got depleted in DOC (correlation factor of  $-0.94$ ; Suppl. Inf. Table 6). The DIC increase was taken as  
468 an indicator of groundwater discharge from the limestone aquifers interacting with the stream.  
469 Therefore, the inverse relationship between DIC and DOC gave an indication of the longitudinal  
470 variation of the water supply: upstream the stream water contained mostly soluble organic species  
471 inherited from the leachate of organic soils, while downstream the stream water acquired inorganic  
472 characteristics from the limestone aquifer discharge.

## 473 5.2 Origin of U in the Œuf river

### 474 5.2.1 Atypical feature of U

475 In the Œuf river, U concentration widely varied, almost by 3 orders of magnitude (from 0.02 to  
476  $19.3 \mu\text{g L}^{-1}$ ). The maximum value detected in the Œuf river exceeded by 100 times the worldwide  
477 riverine value (Palmer & Edmond, 1993) ( $0.19 \mu\text{g L}^{-1}$ ), it encompassed most of the natural waters  
478 (Salminen et al., 2005; Smedley & Kinniburgh, 2023) (generally U below  $4 \mu\text{g L}^{-1}$ ), including those  
479 impacted by anthropogenic U sources (Markich, 2002) (*e.g.*, mining activities). Important longitudinal  
480 fluctuations were found in headwater streams or small streams, as they were more liable to register  
481 hydrological fluctuations deriving from precipitations and groundwater discharge (Bagard et al., 2011;  
482 Durand et al., 2005; Navarro-Martínez et al., 2020). A 1000-fold variation in longitudinal U  
483 concentration was documented in areas displaying geological heterogeneities (Durand et al., 2005;  
484 Grzymko, Marcantonio, McKee, & Mike Stewart, 2007; Saari et al., 2007). The combination of  
485 longitudinal amplitude (up to 10 or 100-fold) with elevated U concentration (above  $20 \mu\text{g L}^{-1}$ ) has been  
486 occasionally observed in streams draining specific areas displaying localized U mineralization. This was  
487 the case of the Llobregat river (Spain) which got enriched in U when draining lignite formations  
488 (Camacho et al., 2010) (from  $1.6$  to  $21 \mu\text{g L}^{-1}$ ), another example was given by the Platte River in  
489 Colorado (United States) where headwaters got enriched in U by draining uraniumiferous rocks (Snow &  
490 Spalding, 1994) (from  $0.27$  to  $31.7 \mu\text{g L}^{-1}$ ). Similarities were found with U enrichment in streams  
491 affected by U release from anthropogenic activity. Examples were given by streams draining U mining  
492 areas in operation in Kazakhstan and Kyrgyzstan (Uralbekov et al., 2014) (U varied from  $1.9$  to  
493  $39.5 \mu\text{g L}^{-1}$ ), or being no longer in operation in France (Y. Wang et al., 2013) (U varied from  $2.9$  to  
494  $30.9 \mu\text{g L}^{-1}$ ).

495 In the Œuf river, AR values varied by almost 3-fold (from 0.411 to 1.06). In freshwaters, AR generally  
496 exceeds 1, the averaged riverine AR value being estimated at 1.17 (François Chabaux et al., 2001). The  
497 excess of  $^{234}\text{U}$  activity regarding  $^{238}\text{U}$  is a consequence of  $^{234}\text{U}$  production mode (alpha disintegration)  
498 leading to its preferential solubilisation during rock weathering. A single example of AR below 1 in a  
499 stream was reported, corresponding to the Strengbach headwaters (France), where AR displayed 0.996  
500 at the lowest (Riotte & Chabaux, 1999). The observation of extreme low AR values founded  
501 downstream in the Œuf river (AR below 0.6) has no equivalent in freshwater around the world. The  
502 scarcity of AR values below 1 reported for freshwater in literature is possibly due to a lack of U and AR  
503 investigations conducted in headwater streams.

504 The Œuf river is a small stream that receives water through groundwater discharge. In this section U  
505 characteristics were first examined in the groundwater of BLAS units that outcrop in the river  
506 catchment (Suppl. Inf. Table 5). For reminder, the groundwater data of BLAS units were acquired  
507 through a national survey program and not through the present study. Groundwater extracted from  
508 Orléanais formation and Pithiviers limestones exhibited AR below 0.4 (GW1 and GW3), indicating an  
509 extreme  $^{234}\text{U}$  deficit with respect  $^{238}\text{U}$ . The ubiquitous observation of extreme  $^{234}\text{U}$  deficit in three  
510 boreholes surrounding the Œuf river catchment (GW1, GW3 and GW4 in Figure 1) suggested that low  
511 AR might occurred at a regional scale and was a characteristic of BLAS reservoir. If so, that would differ  
512 from previous works which documented AR nearby 0.5 in groundwater at a local scale due to specific  
513 hydrogeological settings (Abdul-Hadi et al., 2001; Kaufman et al., 1969). Groundwater with AR nearby  
514 or below 0.5 was documented in a variety of hydrogeological settings (Abdul-Hadi et al., 2001; El-Aassy  
515 et al., 2015; Kaufman et al., 1969). To explain  $^{234}\text{U}$  deficit in groundwater, several factors were pointed  
516 out based on field settings or laboratory experiments (Andersen, Erel, & Bourdon, 2009; Bonotto &  
517 Andrews, 2000): a change in the redox conditions (Osmond & Cowart, 1976; Osmond et al., 1983), an  
518 increasing rate of weathering in karstic limestones (Kaufman et al., 1969), a lack of U renewal during  
519 rock weathering (Kumar et al., 2016) and a leaching of surface and subsurface horizons that already  
520 have experienced  $^{234}\text{U}$  loss (Israelson et al., 1997; Milena-Pérez et al., 2021; Riotte & Chabaux, 1999).  
521 The ground catchment of the Œuf river was likely to fulfil these conditions: karstic limestones are  
522 present at its top and groundwater is expected to oxidize when crossing the river-groundwater  
523 boundary. Regarding the Œuf river, the detection of low AR (below 0.5) in the outcrop zone of Pithiviers  
524 limestones supported the evidence of a stream hydraulically connected to aquifer.

525 The Œuf river received U when flowing in the outcrop zones of Orléanais marls and limestones and  
526 Pithiviers limestones. Regarding AR values, the feature of U contribution was different: U was highly  
527 depleted in  $^{234}\text{U}$  (AR below 0.5) in the zone of Pithiviers limestones, while it was slightly depleted in  
528 the zone of Orléanais marls and limestones (AR nearby 1). This difference was not seen when regarding  
529 groundwater characteristics since both aquifers displayed low AR (below 0.4). That AR difference in  
530 the stream water possibly took its origin in local and specific hydrogeochemical settings, as it has been  
531 seen in the vicinity of surface and subsurface soil horizons (Israelson et al., 1997; Riotte & Chabaux,  
532 1999). If considering that  $^{234}\text{U}$  depletion is the fate of U feature in BLAS groundwater, that AR difference  
533 would provide an age marker: the more the stream water is depleted in  $^{234}\text{U}$ , the more it is supplied  
534 by old groundwater.

### 535 5.2.2 Influence of geology and hydrology

536 The most elevated U concentrations were detected in the Œuf river when flowing on the Orléanais  
537 marls and limestones ( $12.4 \mu\text{g L}^{-1}$ ) and Pithiviers limestones ( $19.3 \mu\text{g L}^{-1}$ ). Regarding U concentration  
538 in these aquifers (Suppl. Inf. Table 5), Orléanais limestone formation (GW1) displayed similar U  
539 concentration ( $11 \mu\text{g L}^{-1}$  in average) and Pithiviers limestones (GW3) lower U concentration ( $7 \mu\text{g L}^{-1}$   
540 in average). In limestone aquifer, U concentration was expected to be rather low (Smedley &  
541 Kinniburgh, 2023; Smedley et al., 2006), not exceeding  $10 \mu\text{g L}^{-1}$ . However, if interacting with U  
542 mineralization, U concentration in the groundwater can be much higher (Smedley & Kinniburgh, 2023).  
543 In the aquifers interacting with the Œuf river, *i.e.*, Orléanais formation and Pithiviers limestones, U  
544 concentration was nearby or lower than in surface river and did not display noticeable U level.  
545 Therefore, the elevated U concentration founded in the stream waters could have resulted from  
546 specific hydrogeochemical settings (oxidizing conditions typically) in combination with localized U  
547 mineralization.

548 Field observations pointed out the dependence of the Œuf river flow to groundwater discharge and  
549 rainfall. In LWS, stream water was permanent nearby the stream spring area (presence of Sologne

550 sands) as well as in the area where Pithiviers limestone aquifer discharged water to form a continuous  
551 flow. The stream hydrology changed in HWS with rainfall, surface runoff and groundwater discharge  
552 maintaining a continuous flow along the entire riverbed. On the Beauce Plateau, the discharge rate of  
553 streams was mainly controlled by the water table level. The variation of U characteristics was taken as  
554 an indicator of the groundwater outflow into the  $\text{C}\text{Euf}$  river. In the zone where Pithiviers limestones  
555 changed from confined to unconfined groundwater, thus supporting river-groundwater interaction, in  
556 LWS the stream water displayed an hydrochemical facies typical of old water ( $\text{Ca} > 100 \text{ mg L}^{-1}$ ,  
557  $\text{EC} > 600 \mu\text{S cm}^{-1}$ ) with elevated U concentration ( $\text{U} > 15 \mu\text{g L}^{-1}$ ) and low AR (below 0.5). In HWS, the  
558 stream water chemistry indicated younger water ( $\text{Ca} < 70 \text{ mg L}^{-1}$ ,  $\text{EC} < 400 \mu\text{S cm}^{-1}$ ) with lower U  
559 concentration and an AR tending to 1.

560 In HWS, the influence of tributaries was examined by comparing U concentration upstream and  
561 downstream the first and last tributary intersection with the  $\text{C}\text{Euf}$  river (*i.e.*, at 8.2 and 12.3 km). In this  
562 river stretch, the concentration of U showed a slight decrease (from 2.52 to 2.10  $\mu\text{g L}^{-1}$ ). In parallel, AR  
563 remained similar and nearby 1 (from 1.03 to 1.00). Thus, the tributaries appeared to exert a minor  
564 control on U characteristics of the  $\text{C}\text{Euf}$  river. They rather diluted U concentration of the main stream  
565 and their role as potential U supplier was discarded. The systematic decrease of U concentration in  
566 stream waters indicated a dilution process attributable to precipitations as the rainwater is known to  
567 contain low U level (1.7  $\text{ng L}^{-1}$ ) (Tsumura, Okamoto, Takaku, & Yamasaki, 1995). This influence of  
568 hydrological season on U concentration is typical of small streams as they are more liable to register  
569 changes induced by rain (Saari, Schmidt, Huguet, & Lanoux, 2008).

570 In the outcrop zone of Pithiviers limestones (10.9 – 23.1 km), U was mainly present in the stream in  
571 form of  $\text{UO}_2^{2+} - \text{CO}_3^{2-}$  complexes (92.6 – 98.8 %; Suppl. Inf. Table 7). These highly soluble complex are  
572 typical of freshwater draining sedimentary basin made of limestones (F. Chabaux et al., 2008; Palmer  
573 & Edmond, 1993; Smedley & Kinniburgh, 2023), and leading to an enhancement of U mobility. The  
574 formation of highly soluble complexes of U with carbonates possibly favoured the occurrence of  
575 elevated level of U concentration and U mobility in the Essonne river valley.

### 576 5.2.3 U source(s) in the ground

577 In this section a review was done on the geological settings potentially involved in the observation of  
578 elevated U in the  $\text{C}\text{Euf}$  river. This examination was enlarged at the scale of the head catchment of the  
579 Essonne river valley, since elevated U concentration (10.5  $\mu\text{g L}^{-1}$ ) was also documented in another  
580 stream (Salpeteur, 2010), the Rimarde river. As the  $\text{C}\text{Euf}$  river, the Rimarde river originates in the  
581 Orléans Forest, it crosses the same geological sequence and intersects the  $\text{C}\text{Euf}$  river (the Essonne river  
582 originates from that confluence).

583 The source(s) of U were discussed regarding selenium (Se), another trace element that displays similar  
584 geochemical behaviour to U (*i.e.*, redox sensitive mobility), and for which an anomaly occurrence was  
585 reported in the Essonne valley. In the  $\text{C}\text{Euf}$  river, a good correlation coefficient is found between U and  
586 Se concentrations (0.93; Suppl. Inf. Table 6), indicating a common source. Both elements are generally  
587 found in association in organic rich materials (Bullock & Parnell, 2017; Meunier, Bruhlet, & Pagel,  
588 1992), where reducing conditions prevail and are favourable to sulphur precipitation. In the redox  
589 barrier (typically an aquifer area where occurs a change from aerobic to anaerobic conditions), U and  
590 Se tend to accumulate and can be found in form of uraninite ( $\text{UO}_2$ ) and ferrosilite ( $\text{Fe}_2\text{Se}$ ), respectively.  
591 The increasing  $\text{SO}_4^{2-}$  concentration in the stream water concomitantly with U and Se enrichment of the  
592 stream water evoked sulphur oxidation and consecutive mineral dissolution. It is likely that U and Se  
593 accumulated in organic rich deposits within the continental deposits constituting BLAS and that  
594 oxidizing conditions led to their release through the water-rock interaction within the aquifer.



595 Therefore, evidence or proof of U and Se accumulation in the ground and the aquifer hosted rock was  
596 searched in the documentation relative to BLAS and adjacent formations.

597 Regarding BLAS and its adjacent formations from deep to surface, a variety of organic materials have  
598 been evidenced within these continental formations thus providing good candidates to concentrate U  
599 and Se. At the basis of BLAS, Ypresian formation (lower stage of Eocene) consists in lignite layer where  
600 U and Se were shown to concentrate (Gaillard, 2017; Gaillard & Garnier-Séréno, 2017) : 18.5 and  
601 29  $\mu\text{g kg}^{-1}$  for U and Se, respectively. The occurrence of lignite was also reported in Etampes limestones  
602 (Chery & Rouelle-Castrec, 2004). Since both formations do not outcrop at the head of the Essonne river  
603 valley, they could not interact directly with the streams flowing on the surface, *i.e.*, the Œuf and  
604 Rimarde rivers. If U and Se derived from these deep formations, they have been necessarily  
605 transported upward through leakage transfer. At the head of the Essonne catchment, the formation  
606 of Sologne sands and clays is known to overlay a peat layer. The Sologne sands are of granitic detrital  
607 origin and consist in heavy minerals (Etienne & Larue, 2011; Gigot, 1984), possibly containing U at non  
608 negligible level. When infiltrating, meteoric water would have solubilized U by grain leaching and then  
609 the expected reducing peat layer would have trapped U and Se (Bullock & Parnell, 2017; Cumberland  
610 et al., 2016), in a way similar to roll-front mineralization (Campbell, Gallegos, & Landa, 2015; Meunier,  
611 Bruhlet, & Pagel, 1992; Van Berk & Fu, 2017). Below the peat layer, the limestone dissolution of  
612 Orléanais carbonate formation would have provided the carbonate that promoted highly soluble and  
613 easily mobilizable uranyl complexes. Therefore, the water table fluctuation would have been  
614 responsible of U and Se trapping and release to the stream water. The ground catchment of the Œuf  
615 river is known to display a significant karstic network (Lorain, 1973), that is confirmed by the presence  
616 of palaeokarsts inside the Pithiviers limestones (see boreholes B3 and B4 on the Suppl. Inf. Figure 1).  
617 These palaeokarsts are filled by sandy detrital material probably corresponding to Sologne sands that  
618 would have provided an additional U source within the carbonate formation.

619 Regarding AR values in the Œuf river and the groundwater of BLAS units, U depleted in  $^{234}\text{U}$  was present  
620 in both surface and ground waters. In general, a deficit of  $^{234}\text{U}$  in groundwater implies an intense  
621 dissolution in zones of high permeability where the preferential leaching of U leaves behind rocks with  
622  $^{234}\text{U}$  deficit regarding  $^{238}\text{U}$  (Abdul-Hadi et al., 2001; Kaufman et al., 1969). This could explain the  
623 observation of low AR ( $< 0.4$ ) founded in Orléanais and Pithiviers limestone aquifers. Also it can be  
624 interpreted in terms of lack of U renewal in U accumulation in ground material (Milena-Pérez et al.,  
625 2021; Osmond & Cowart, 1976; Osmond et al., 1974): ground material that experienced a loss in  $^{234}\text{U}$   
626 is not compensated by the arrival of undepleted material. That could explain the difference in  $^{234}\text{U}$   
627 observed upstream and downstream the Œuf river. Above Orléanais limestones the stream water got  
628 enriched in U ( $12.3 \mu\text{g L}^{-1}$ ) with AR nearby 1 (0.90), while it got enriched in U ( $19.3 \mu\text{g L}^{-1}$ ) with lower  
629 AR (0.46) above Pithiviers limestones (Suppl. Inf. Table 4). At the upstream part of Œuf river, AR nearby  
630 1 indicated that ground material had experienced moderate loss in  $^{234}\text{U}$  (in case of a common U source)  
631 or had been compensated by the renewal of undepleted U (in case of multiple U sources). In case of  
632 multiple U sources, the formation containing undepleted U is expected to be the Sologne sands and  
633 clays that overlays Orléanais marls and sands. Again, this granitic detrital sand consists in heavy  
634 minerals (Etienne & Larue, 2011; Gigot, 1984), thus possibly contains U available for leaching by  
635 meteoric water infiltration. The disappearance of this geological formation in the first km of the Œuf  
636 river ( $< 3 \text{ km}$ ) would have explained the lack of undepleted U renewal downstream.

#### 637 5.2.4 Influence of nitrate

638 Pending a direct identification of U source(s) in the ground catchment of the Œuf river, the other  
639 possible factors causing U enrichment in surface and groundwater were examined. Enrichment in U of  
640 surface and groundwater might have resulted from a direct contribution (of anthropogenic or geogenic

641 origin) or a change in U mobility owing to its redox sensitivity. The presence of nitrate is one of the  
642 factors leading to U enhancement in surface and groundwater, as it was shown in agricultural areas  
643 (Liesch, Hinrichsen, & Goldscheider, 2015; Lyons et al., 2020). Since nitrate displayed elevated level of  
644 concentration ( $> 20 \text{ mg L}^{-1}$ ) together in the surface and the ground waters of the Œuf river catchment,  
645 its influence was further discussed below.

646 In the Œuf river, the good and positive relationship of U to  $\text{NO}_3^-$  (correlation coefficient of 0.83; Suppl.  
647 Inf. Table 6) indicated a common source (synthetic nitrate fertilizer application) or was the result of a  
648 concomitant transfer to the stream (here aquifer discharge). In case of a common source, the  
649 application then solubilization of synthetic nitrate in soils would have released U in agricultural  
650 wastewater (Gardner et al., 2022). Although this was shown to generate detectable U enrichment in  
651 water up to a few micrograms per litre elsewhere (Lyons et al., 2020), it seemed unlikely to be the sole  
652 factor causing the observed U increase in the Œuf river (*i.e.*, 1000-fold increase, max.  $19.3 \text{ } \mu\text{g L}^{-1}$ ). To  
653 date, no evidence is given in literature to link  $^{234}\text{U}$  deficit to fertilizer application. It is even the contrary:  
654 AR is expected to tend to 1 in case of nitrate fertilizer influence (Böhlke, Verstraeten, & Kraemer, 2007;  
655 Milena-Pérez et al., 2021). Therefore, the hypothesis of fertilizer application as a direct U contribution  
656 of U in the Œuf river was discarded. Hence, the concomitant increase U and  $\text{NO}_3^-$  observed in LWS in  
657 the stream when flowing on Pithiviers limestones reflects a common water supply through  
658 groundwater discharge.

659 The presence of nitrate in groundwater is known to alter U solubility by oxidative dissolution of  
660 reduced U(IV) minerals present in aquifer materials (Nolan & Weber, 2015) or in subsurface soil  
661 horizons (Hee, Komlos, & Jaffé, 2007; W. M. Wu et al., 2010). Thereby,  $\text{NO}_3^-$  presence in groundwater  
662 induces U enrichment by modifying the redox conditions which in turn enhances U mobility (Banning,  
663 Demmel, Rude, & Wrobel, 2013b; Coyte, Singh, Furst, Mitch, & Vengosh, 2019). Generally, the causal  
664 relationship between  $\text{NO}_3^-$  and U concentrations in groundwater is not easy to establish (Coyte et al.,  
665 2018; Riedel & Kübeck, 2018; Rosen et al., 2019). In groundwater of BLAS units, Pithiviers limestones  
666 exhibited relatively high  $\text{NO}_3^-$  concentration in average ( $> 40 \text{ mg L}^{-1}$  in GW2 and GW3; Suppl. Inf. Table  
667 5). In BLAS shallow aquifers, the contamination by nitrogen (and other pesticides) is known since  
668 decades (Berger et al., 1976; Desprez, 1983). The presence of nitrate at elevated concentration level  
669 reflected the vulnerability of shallow groundwater to surface land utilization. The intensive agriculture  
670 requests application of large quantity of synthetic fertilizers containing nitrate. Thus, the presence of  
671 nitrate in shallow groundwater is a marker of surface water characteristics. Shallow aquifer displaying  
672 surface water features is possibly affected by oxidizing conditions during water recharge. The presence  
673 of nitrate indicates a lack of denitrification in the aquifer water during recharge. Therefore, the  
674 presence of nitrate is an indicator of groundwater oxidizing features. In the Œuf river ground  
675 catchment, a groundwater oxidization was likely to promote U solubilization from ground materials.  
676 When the stream received back groundwater, it also got enriched in nitrate and U.

677 In groundwater affected by nitrate inputs, the pyrite oxidation was shown to participate to the  
678 denitrification (Zhang et al., 2012). In case of U and Se association in U mineralization of roll-front type,  
679 Se is expected to follow U geochemical behaviour (Bullock & Parnell, 2017). In reducing organic  
680 materials, U and Se together concentrate in reducing barrier corresponding to sulphur precipitation.  
681 Sulphur oxidation due to nitrate presence possibly promotes the release of U and Se associated with  
682 sulphur (Houben, Sitnikova, & Post, 2017). In the Œuf river, the positive relationship of U to Se,  $\text{NO}_3^-$   
683 (correlation coefficient above 0.8; Suppl. Inf. Table 6) and  $\text{SO}_4^{2-}$  in a lesser extent (correlation  
684 coefficient of 0.43) supported the hypothesis of U and Se association in reducing organic ground  
685 material and their consecutive release due to nitrate presence. The Œuf river registered a decrease in  
686 U concentration and AR while  $\text{NO}_3^-$  was increasing when the stream was entering the outcrop zone of

687 Gâtinais molasse in LWS. The groundwater discharge in this zone was already discussed and was shown  
688 to be different from upstream, *i.e.*, in the outcrop zone of Pithiviers limestones: the discharged  
689 groundwater was shown to be more mineralized. Therefore, this change in U concentration and AR  
690 possibly indicated a specific feature of the aquifer discharge.

### 691 5.3 Tracking the aquifer discharge

692 In the Œuf river, the stream water was shown to derive from both groundwater discharge and surface  
693 runoff, the relative proportion of these two water components varying through time and along the  
694 river profile. In HWS, the variation of the stream water chemistry in the outcrop zone of Pithiviers  
695 limestones was shown to result from the river-groundwater interaction. Then this river stretch  
696 (10.9 – 23.1 km) was considered as a mixing zone between two water components: water component  
697 1 corresponding to the groundwater discharge, and water component 2 corresponding to the stream  
698 water coming from upstream (Table 1). The characteristics of the groundwater discharge (water  
699 component 1) were given by the stream water collected at R7 (14.1 km) in LWS, and the characteristics  
700 of the upstream stream water (water component 2) by the stream water collected at R6 (12.3 km) in  
701 HWS. Here the geochemical characteristics of the groundwater discharged in this zone were assumed  
702 to remain unchanged between LWS and HWS.

703 Several analytes measured in this study have shown their ability to track the influence of river-  
704 groundwater interaction on the stream water chemistry: EC, DIC, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Ca, Mg, Sr, Ba,  
705 Na, K, Se, U and AR. These indicators were tested to identify those suitable for quantifying groundwater  
706 supply in HWS based on the data acquired in March 2020. Amongst them, only U isotopes and Se have  
707 provided appropriate hydrogeochemical tools, as indicated by the linear distributions between the two  
708 water components 1 and 2 (Figure 7). Then the relative proportion of groundwater volume to the  
709 stream was calculated upstream to downstream: from 12 ± 1 % at 14.1 km (R7) to 59 ± 4 % at 17.8 km  
710 (R10), corresponding to U increasing rate of 13 % per km.

711 This study further supports the use of U isotopes to quantitatively track groundwater supply in stream  
712 water as it was already demonstrated elsewhere, in combination with the major elements Cl<sup>-</sup> and Na<sup>+</sup>  
713 (Navarro-Martínez et al., 2020), and Sr isotopes (Gardner et al., 2022; Riotte & Chabaux, 1999). By  
714 using U in combination with Se as tracers of the river-groundwater continuum, this study first  
715 demonstrates the suitability of combining two redox sensitive trace elements, *i.e.*, U and Se.

### 716 6 Conclusion

717 Atypical U characteristics were found in the headwater stream of the Essonne river, *i.e.*, the namely  
718 Œuf river: the stream water exhibited elevated U concentration up to 19.3 µg L<sup>-1</sup> (which exceeded by  
719 100-fold the average worldwide riverine concentration of 0.19 µg L<sup>-1</sup>), and low AR down to 0.41 (which  
720 was almost the third of the expected value in freshwater, *i.e.*, 1.17). By reporting these atypical U  
721 characteristics, this study gives new insight on geogenic U and AR fluctuations in natural rivers. The  
722 Œuf river was shown to get enriched in U when interacting with Beauce limestone aquifer. Elevated U  
723 concentration (above 15 µg L<sup>-1</sup>) was found in association with low AR (below 0.5) when the stream  
724 water was supplied by groundwater in the zone where limestone aquifer changed from confined to  
725 unconfined. Taking advantage of changes in the origin of water supplied to the stream (groundwater,  
726 surface runoff) and its contrasted U and Se characteristics, the groundwater contribution was  
727 quantified to the stream water: in March 2020, the groundwater supplied from 12 to 59 % of the total  
728 water flowing in the stream. Our results demonstrate the interest of investigating geogenic U  
729 fluctuations in small streams draining catchment where outcrop heterogeneous geology. By combining  
730 U and Se, this study promotes the use of trace element sensitive to redox conditions as suitable  
731 hydrogeochemical tools to characterize the river-groundwater continuum.

732 **Credit authorship contribution statement**

733 **M. Zebracki**: conceptualization, methodology, resources, writing-original draft preparation,  
734 supervision, funding acquisition; **C. Marlin**: conceptualization, writing-review; **T. Gaillard**:  
735 conceptualization, writing-review, visualization; **J. Gorny**: methodology, resources; **O. Diez**:  
736 methodology, resources; **V. Durand**: conceptualization, visualization; **C. Lafont**: methodology,  
737 resources; **C. Jardin**: methodology, resources; **V. Monange**: visualization.

738 **Declaration of competing interest**

739 The authors declare that the research was conducted in the absence of any commercial or financial  
740 relationships that could be construed as a potential conflict of interest.

741 **Acknowledgements**

742 The authors are grateful to Dr. Christelle Courbet, Dr. Caroline Simonucci, Damien Tournieux and Dr.  
743 Claire Gréau (IRSN) for sharing relevant information relative to the study area. The authors are  
744 particularly thankful to Dr. Alkiviadis Gourgiotis (IRSN) for kindly sharing his expertise in ICP-MS  
745 measurement. Special thanks are addressed to Evelyne Barker and Anthony Julien (IRSN) for their  
746 analytical assistance during the preliminary investigations. The authors thank Louise Darricau (IRSN)  
747 and Dr. Olivier Clarisse (Moncton University, Canada) for occasional help during field and laboratory  
748 works. The authors thank Dr. Charlotte Cazala and Christophe Debayle (IRSN) for proofreading. This  
749 work was funded by the French programme NEEDS as part of the UTOPIA project. This is PATERSON,  
750 the IRSN mass spectrometry platform, contribution n°17.

751 **Disclaim**

752 The present publication reflects only the authors' view. Responsibility for the information and views  
753 expressed therein lies entirely with the authors.

754 Reference list

- 755 Abdul-Hadi, A., Alhassanieh, O., & Ghafar, M., 2001. Disequilibrium of uranium isotopes in some  
756 Syrian groundwater. *Applied Radiation and Isotopes*, 55(1), 109–113.  
757 [https://doi.org/10.1016/S0969-8043\(00\)00369-9](https://doi.org/10.1016/S0969-8043(00)00369-9)
- 758 Andersen, M. B., Erel, Y., & Bourdon, B., 2009. Experimental evidence for <sup>234</sup>U-<sup>238</sup>U fractionation  
759 during granite weathering with implications for <sup>234</sup>U/<sup>238</sup>U in natural waters. *Geochimica et*  
760 *Cosmochimica Acta*, 73(14), 4124–4141. <https://doi.org/10.1016/j.gca.2009.04.020>
- 761 Bagard, M. L., Chabaux, F., Pokrovsky, O. S., Viers, J., Prokushkin, A. S., Stille, P., Rihs, S., Schmitt, A.  
762 D., & Dupré, B., 2011. Seasonal variability of element fluxes in two Central Siberian rivers  
763 draining high latitude permafrost dominated areas. *Geochimica et Cosmochimica Acta*, 75(12),  
764 3335–3357. <https://doi.org/10.1016/j.gca.2011.03.024>
- 765 Balcaen, L., Bolea-fernandez, E., Resano, M., & Vanhaecke, F., 2015. Inductively coupled plasma –  
766 Tandem mass spectrometry (ICP-MS/MS): A powerful and universal tool for the interference-  
767 free determination of (ultra) trace elements – A tutorial review. *Analytica Chimica Acta*, 894, 7–  
768 19. <https://doi.org/10.1016/j.aca.2015.08.053>
- 769 Banning, A., Demmel, T., Rude, T. R., & Wrobel, M., 2013a. Groundwater uranium origin and fate  
770 control in a river valley aquifer. *Environmental Science and Technology*, 47(24), 13941–13948.  
771 <https://doi.org/10.1021/es304609e>
- 772 Banning, A., Demmel, T., Rude, T. R., & Wrobel, M., 2013b. Groundwater uranium origin and fate  
773 control in a river valley aquifer. *Environmental Science and Technology*, 47(24), 13941–13948.  
774 <https://doi.org/10.1021/es304609e>
- 775 Bassil, J., Naveau, A., Fontaine, C., Grasset, L., Bodin, J., Porel, G., Razack, M., Kazpard, V., & Popescu,  
776 S. M., 2016. Investigation of the nature and origin of the geological matrices rich in selenium  
777 within the Hydrogeological Experimental Site of Poitiers, France. *Comptes Rendus - Geoscience*,  
778 348(8), 598–608. <https://doi.org/10.1016/j.crte.2016.08.004>
- 779 Berger, G., Bosch, B., Desprez, N., Letolle, R., Marce, A., Mariotti, A., & Mégnien, C., 1976. *Recherches*  
780 *sur l'origine des nitrates dans les eaux souterraines de la Beauce. Rapport sur la campagne de*  
781 *prélèvements et d'analyses du 1er semestre 1976. Rap. BRGM 76 SGN 444 BDP.*
- 782 Böhlke, J. K., Verstraeten, I. M., & Kraemer, T. F., 2007. Effects of surface-water irrigation on sources,  
783 fluxes, and residence times of water, nitrate, and uranium in an alluvial aquifer. *Applied*  
784 *Geochemistry*, 22(1), 152–174. <https://doi.org/10.1016/j.apgeochem.2006.08.019>
- 785 Bonotto, D. M., & Andrews, J. N., 2000. The transfer of uranium isotopes <sup>234</sup>U and <sup>238</sup>U to the  
786 waters interacting with carbonates from Mendip Hills area (England). *Applied Radiation and*  
787 *Isotopes*, 52(4), 965–983. [https://doi.org/10.1016/S0969-8043\(99\)00151-7](https://doi.org/10.1016/S0969-8043(99)00151-7)
- 788 BRGM. (1995). *Piézométrie du système aquifère de Beauce - Basses eaux 1994 (R38572).*
- 789 Bullock, L. A., & Parnell, J., 2017. Selenium and molybdenum enrichment in uranium roll-front  
790 deposits of Wyoming and Colorado, USA. *Journal of Geochemical Exploration*, 180(May), 101–  
791 112. <https://doi.org/10.1016/j.gexplo.2017.06.013>
- 792 Camacho, A., Devesa, R., Vallés, I., Serrano, I., Soler, J., Blázquez, S., Ortega, X., & Matia, L., 2010.  
793 Distribution of uranium isotopes in surface water of the Llobregat river basin (Northeast Spain).  
794 *Journal of Environmental Radioactivity*, 101(12), 1048–1054.  
795 <https://doi.org/10.1016/j.jenvrad.2010.08.005>
- 796 Campbell, K. M., Gallegos, T. J., & Landa, E. R., 2015. Biogeochemical aspects of uranium  
797 mineralization, mining, milling, and remediation. *Applied Geochemistry*, 57, 206–235.

- 798 <https://doi.org/10.1016/j.apgeochem.2014.07.022>
- 799 Cary, L., Joulian, C., Battaglia-Brunet, F., & Decouchon, E., 2018. Arsenic et Sélénium dans les eaux  
800 souterraines de Beauce et de Sologne - caractérisation des eaux souterraines sur 26 communes.  
801 In *BRGM/RP-67590-FR*.
- 802 Chabaux, F., Bourdon, B., & Riotte, J., 2008. Chapter 3 U-Series Geochemistry in Weathering Profiles,  
803 River Waters and Lakes. *Radioactivity in the Environment*, 13(07), 49–104.  
804 [https://doi.org/10.1016/S1569-4860\(07\)00003-4](https://doi.org/10.1016/S1569-4860(07)00003-4)
- 805 Chabaux, F., Riotte, J., & Dequincey, O., 2003. U-Th-Ra fractionation during weathering and river  
806 transport. *Reviews in Mineralogy and Geochemistry*, 52, 533–576.  
807 <https://doi.org/10.2113/0520533>
- 808 Chabaux, François, Riotte, J., Clauer, N., & France-Lanord, C., 2001. Isotopic tracing of the dissolved U  
809 fluxes of Himalayan rivers: Implications for present and past U budgets of the Ganges-  
810 Brahmaputra system. *Geochimica et Cosmochimica Acta*, 65(19), 3201–3217.  
811 [https://doi.org/10.1016/S0016-7037\(01\)00669-X](https://doi.org/10.1016/S0016-7037(01)00669-X)
- 812 Chery, L., & Rouelle-Castrec, M., 2004. Les occurrences de sélénium dans les forages d'alimentation  
813 en eau de la région parisienne: origine et perspectives d'étude. *Géologie et Hydrogéologie Du*  
814 *Bassin de Paris. Avancées et Perspectives*, 16-17 Novembre, 197–204.
- 815 Chkir, N., Guendouz, A., Zouari, K., Hadj Ammar, F., & Moulla, A. S., 2009. Uranium isotopes in  
816 groundwater from the continental intercalaire aquifer in Algerian Tunisian Sahara (Northern  
817 Africa). *Journal of Environmental Radioactivity*, 100(8), 649–656.  
818 <https://doi.org/10.1016/j.jenvrad.2009.05.009>
- 819 Condon, D. J., McLean, N., Noble, S. R., & Bowring, S. A., 2010. Isotopic composition (<sup>238</sup>U/<sup>235</sup>U) of  
820 some commonly used uranium reference materials. *Geochimica et Cosmochimica Acta*, 74(24),  
821 7127–7143. <https://doi.org/10.1016/j.gca.2010.09.019>
- 822 Coyte, R. M., Jain, R. C., Srivastava, S. K., Sharma, K. C., Khalil, A., Ma, L., & Vengosh, A., 2018. Large-  
823 Scale Uranium Contamination of Groundwater Resources in India. *Environmental Science and*  
824 *Technology Letters*, 5(6), 341–347. <https://doi.org/10.1021/acs.estlett.8b00215>
- 825 Coyte, R. M., Singh, A., Furst, K. E., Mitch, W. A., & Vengosh, A., 2019. Co-occurrence of geogenic and  
826 anthropogenic contaminants in groundwater from Rajasthan, India. *Science of the Total*  
827 *Environment*, 688, 1216–1227. <https://doi.org/10.1016/j.scitotenv.2019.06.334>
- 828 Cumberland, S. A., Douglas, G., Grice, K., & Moreau, J. W., 2016. Uranium mobility in organic matter-  
829 rich sediments: A review of geological and geochemical processes. *Earth-Science Reviews*, 159,  
830 160–185. <https://doi.org/10.1016/j.earscirev.2016.05.010>
- 831 Desprez, N. (1983). *Etude de la stratification chimique dans la partie libre de la nappe des calcaires de*  
832 *Beauce (Loiret). Rap. BRGM 83 SGN 115 CEN*.
- 833 Durand, S., Chabaux, F., Rihs, S., Düringer, P., & Elsass, P., 2005. U isotope ratios as tracers of  
834 groundwater inputs into surface waters: Example of the Upper Rhine hydrosystem. *Chemical*  
835 *Geology*, 220(1–2), 1–19. <https://doi.org/10.1016/j.chemgeo.2005.02.016>
- 836 Eary, L. E., & Jenne, E. A., 1992. *Version 4.00 of the MINTEQ geochemical code*. Retrieved from  
837 [doi:10.2172/7073252](https://doi.org/10.2172/7073252)
- 838 El-Aassy, I. E., El-Feky, M. G., Issa, F. A., Ibrahim, N. M., Desouky, O. A., & Khattab, M. R., 2015.  
839 Uranium and <sup>234</sup>U/<sup>238</sup>U isotopic ratios in some groundwater wells at Southwestern Sinai,  
840 Egypt. *Journal of Radioanalytical and Nuclear Chemistry*, 303(1), 357–362.

- 841 <https://doi.org/10.1007/s10967-014-3461-y>
- 842 Etienne, R., & Larue, J.-P., 2011. Contribution à l'étude des liaisons Loire-Seine: mise en évidence par  
843 l'étude des minéraux lourds de l'antécédence de la Loire en Sologne (Bassin Parisien, France).  
844 *Physio-Géo*, 5, 269–291. <https://doi.org/https://doi.org/10.4000/physio-geo.2181>
- 845 Fleischer, R. L., 1980. Isotopic Disequilibrium of Uranium : Alpha-Recoil Damage and Preferential  
846 Solution Effects. *Science*, 207, 979–981.
- 847 Gaillard, T., 2017. *Etude de sécurisation en eau potable de plusieurs communes du Sud-Est de*  
848 *l'Essonne. Résultats de la plateforme hydrogéologique de Maisse.*
- 849 Gaillard, T., & Garnier-Séréno, C., 2017. Intérêt des réseaux multi-profondeurs, exemple de la  
850 plateforme de Maisse (Essonne, France). *Géologues*, 195, 34–37.
- 851 Gardner, C. B., Wichterich, C., Calero, A. E., Welch, S. A., Widom, E., Smith, D. F., Carey A. E., & Lyons,  
852 W. B., 2022. Carbonate weathering , phosphate fertilizer, and hydrologic controls on dissolved  
853 uranium in rivers in the US Corn Belt : Disentangling seasonal geogenic- and fertilizer-derived  
854 sources. *Science of the Total Environment*, (November), 17.  
855 <https://doi.org/10.1016/j.scitotenv.2022.160455>
- 856 Gigot, C., 1984. *Notice explicative de la feuille Bellegarde-du-Loiret à 1/50000.*
- 857 Gourgiotis, A., Mangeret, A., Manhès, G., Blanchart, P., Stetten, L., Morin, G., Le Pape, P., Lefebvre P.,  
858 Le Coz, M., & Cazala, C., 2020. New Insights into Pb Isotope Fingerprinting of U-Mine Material  
859 Dissemination in the Environment: Pb Isotopes as a Memory Dissemination Tracer.  
860 *Environmental Science and Technology*, 54(2), 797–806.  
861 <https://doi.org/10.1021/acs.est.9b04828>
- 862 Grabowski, P., & Bem, H., 2012. Uranium isotopes as a tracer of groundwater transport studies.  
863 *Journal of Radioanalytical and Nuclear Chemistry*, 292(3), 1043–1048.  
864 <https://doi.org/10.1007/s10967-011-1558-0>
- 865 Gronbaek-Thorsen, F., Stürup, S., Gammelgaard, B., & Hyrup Moller, L., 2019. Development of a  
866 UPLC-IDA-ICP-MS/MS method for peptide quantitation in plasma by Se-labelling, and  
867 comparison to S-detection of the native. *Journal of Analytical Atomic Spectrometry*, 34, 375–  
868 383. <https://doi.org/10.1039/c8ja00341f>
- 869 Grzymko, T. J., Marcantonio, F., McKee, B. A., & Mike Stewart, C., 2007. Temporal variability of  
870 uranium concentrations and 234U/238U activity ratios in the Mississippi river and its  
871 tributaries. *Chemical Geology*, 243(3–4), 344–356.  
872 <https://doi.org/10.1016/j.chemgeo.2007.05.024>
- 873 Hee, S. M., Komlos, J., & Jaffé, P. R., 2007. Uranium reoxidation in previously bioreduced sediment by  
874 dissolved oxygen and nitrate. *Environmental Science and Technology*, 41(13), 4587–4592.  
875 <https://doi.org/10.1021/es063063b>
- 876 Horwitz, E. P., Dietz, M. L., Chiarizia, R., Diamond, H., Essling, A. M., & Graczyk, D., 1992. Separation  
877 and preconcentration of uranium from acidic media by extraction chromatography. *Analytica*  
878 *Chimica Acta*, 266(1), 25–37. [https://doi.org/10.1016/0003-2670\(92\)85276-C](https://doi.org/10.1016/0003-2670(92)85276-C)
- 879 Houben, G. J., Sitnikova, M. A., & Post, V. E. A., 2017. Terrestrial sedimentary pyrites as a potential  
880 source of trace metal release to groundwater e A case study from the Emsland , Germany.  
881 *Applied Geochemistry*, 76, 99–111. <https://doi.org/10.1016/j.apgeochem.2016.11.019>
- 882 Howard III, J. H., 1977. Geochemistry of selenium: formation of ferroselite and selenium behavior in  
883 the vicinity of oxidizing sulfide and uranium deposits. *Geochimica et Cosmochimica Acta*, 41(11),



884 1665–1678. Retrieved from [http://www.sciencedirect.com/science/article/B6V66-48C8JD2-](http://www.sciencedirect.com/science/article/B6V66-48C8JD2-VK/2/0e2f2b4c207daf16e957a55b8e63a952)  
885 [VK/2/0e2f2b4c207daf16e957a55b8e63a952](http://www.sciencedirect.com/science/article/B6V66-48C8JD2-VK/2/0e2f2b4c207daf16e957a55b8e63a952)

886 Huckle, D., Ma, L., McIntosh, J., Vázquez-Ortega, A., Rasmussen, C., & Chorover, J., 2016. U-series  
887 isotopic signatures of soils and headwater streams in a semi-arid complex volcanic terrain.  
888 *Chemical Geology*, 445, 68–83. <https://doi.org/10.1016/j.chemgeo.2016.04.003>

889 Israelson, C., Björck, S., Hawkesworth, C. J., & Possnert, G., 1997. Direct U-Th dating of organic- and  
890 carbonate-rich lake sediments from southern Scandinavia. *Earth and Planetary Science Letters*,  
891 (97).

892 Kaufman, M. I., Rydell, H. S., & Osmond, J. K., 1969. <sup>234</sup>U/<sup>238</sup>U Disequilibrium as an aid to hydrologic  
893 study of the Floridan aquifer. *Journal of Hydrology*, 9, 374–386.

894 Khan, H. H., & Khan, A., 2019. Groundwater and surface water interaction. In *GIS and Geostatistical*  
895 *Techniques for Groundwater Science*. <https://doi.org/10.1016/B978-0-12-815413-7.00014-6>

896 Kigoshi, K., 1971. Alpha-Recoil Thorium-234: Dissolution into Water and the Uranium-234/Uranium-  
897 <sup>238</sup>U Disequilibrium in Nature. *Science*, 173(5), 47–48.

898 Kumar, A., Karpe, R. K., Rout, S., Gautam, Y. P., Mishra, M. K., Ravi, P. M., & Tripathi, R. M., 2016.  
899 Activity ratios of <sup>234</sup>U/<sup>238</sup>U and <sup>226</sup>Ra/<sup>228</sup>Ra for transport mechanisms of elevated uranium  
900 in alluvial aquifers of groundwater in south-western (SW) Punjab, India. *Journal of*  
901 *Environmental Radioactivity*, 151, 311–320. <https://doi.org/10.1016/j.jenvrad.2015.10.020>

902 Lartigue, J. E., Charrasse, B., Reile, B., & Descostes, M., 2020. Aqueous inorganic uranium speciation  
903 in European stream waters from the FOREGS dataset using geochemical modelling and  
904 determination of a U bioavailability baseline. *Chemosphere*, 251, 126302.  
905 <https://doi.org/10.1016/j.chemosphere.2020.126302>

906 Larue, J.-P., & Étienne, R., 2014. Évolution quaternaire de la ligne de partage des eaux entre les  
907 bassins de la Seine et de la Loire, du Perche à la Puisaye : hydrographie, structure et tectonique.  
908 *Norois*, (230), 95–108. <https://doi.org/10.4000/norois.5044>

909 Liesch, T., Hinrichsen, S., & Goldscheider, N., 2015. Uranium in groundwater - Fertilizers versus  
910 geogenic sources. *Science of the Total Environment*, 536, 981–995.  
911 <https://doi.org/10.1016/j.scitotenv.2015.05.133>

912 Lorain, J., 1973. *Le Calcaire de Beauce: géologie, hydrogéologie, applications en construction routière*  
913 *et génie civil*.

914 Lyons, W. B., Gardner, C. B., Welch, S. A., & Israel, S., 2020. Uranium in Ohio, USA Surface Waters:  
915 Implications for a Fertilizer Source in Waters Draining Agricultural lands. *Scientific Reports*,  
916 10(1), 1–6. <https://doi.org/10.1038/s41598-020-61922-2>

917 Mangini, A., Sonntag, C., Bertsch, G., & Müller, E., 1979. Evidence for a higher natural uranium  
918 content in world rivers [5]. *Nature*, 278(5702), 337–339. <https://doi.org/10.1038/278337a0>

919 Markich, S. J., 2002. Uranium speciation and bioavailability in aquatic systems: an overview. *The*  
920 *Scientific World Journal*, 2, 707–729. <https://doi.org/10.1100/tsw.2002.130>

921 Martin, J.-C., Giot, D., & Le Nindre, Y. M., 1999. *Etudes préalables à la réalisation d'un modèle de*  
922 *gestion de la nappe de Beauce - Géométrie du réservoir et limites de la nappe de Beauce. Rap.*  
923 *BRGM R 40571*.

924 Mathieu, D., Bernat, M., & Nahon, D., 1995. Short-lived U and Th isotope distribution in a tropical  
925 laterite derived from granite (Pitinga river basin, Amazonia, Brazil): Application to assessment of  
926 weathering rate. *Earth and Planetary Science Letters*, 136, 703–714.

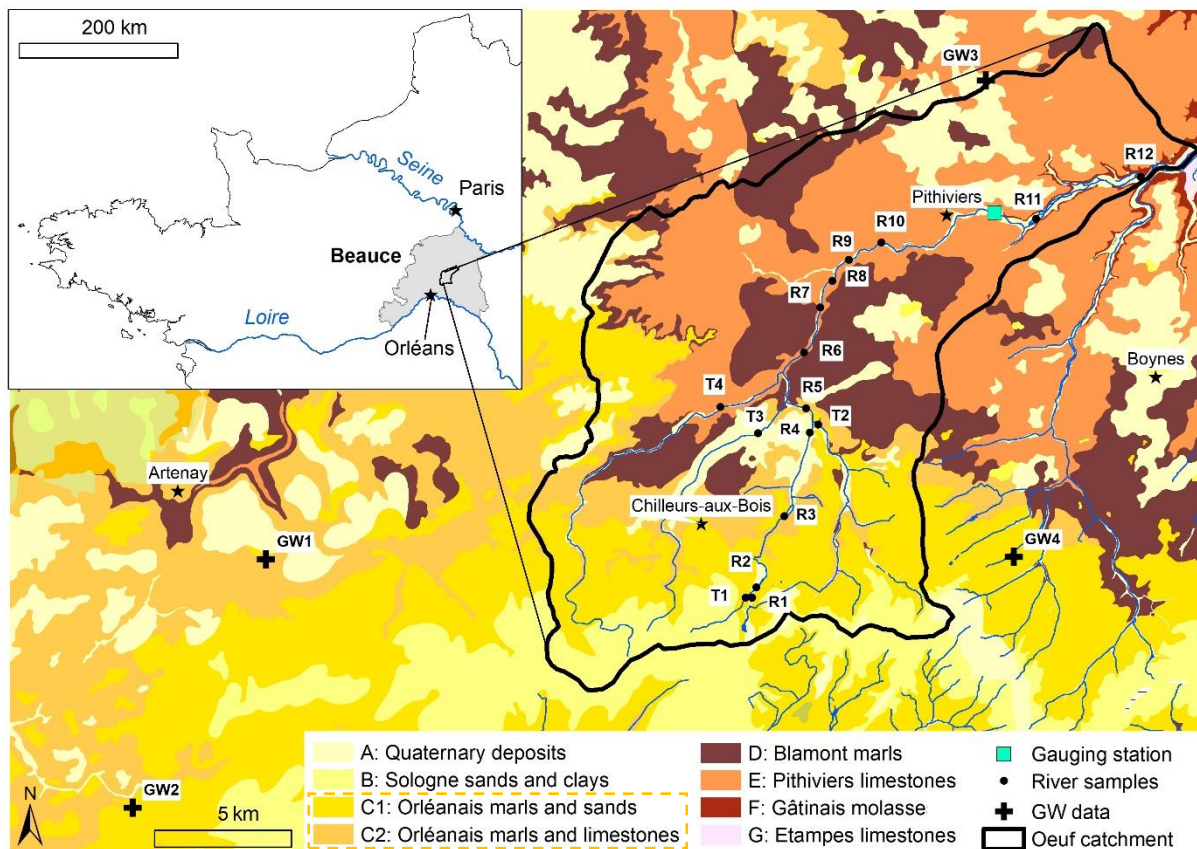
- 927 Meunier, J. D., Bruhlet, J., & Pagel, M., 1992. Uranium mobility in the sediment-hosted uranium  
928 deposit of Coutras, France. *Applied Geochemistry*, 7(2), 111–121. [https://doi.org/10.1016/0883-](https://doi.org/10.1016/0883-2927(92)90030-7)  
929 [2927\(92\)90030-7](https://doi.org/10.1016/0883-2927(92)90030-7)
- 930 Michel, R. L., Kraemer, T. F., & DeWayne Cecil, L., 2009. Chapter 5.1 Surface water, unsaturated zone,  
931 and glacial systems. In *Radioactivity in the Environment* (Vol. 16).  
932 [https://doi.org/10.1016/S1569-4860\(09\)01605-2](https://doi.org/10.1016/S1569-4860(09)01605-2)
- 933 Milena-Pérez, A., Piñero-García, F., Benavente, J., Expósito-Suárez, V. M., Vacas-Arquero, P., & Ferro-  
934 García, M. A., 2021. Uranium content and uranium isotopic disequilibria as a tool to identify  
935 hydrogeochemical processes. *Journal of Environmental Radioactivity*, 227(December 2020).  
936 <https://doi.org/10.1016/j.jenvrad.2020.106503>
- 937 Navarro-Martinez, F., Salas Garcia, A., Sánchez-Martos, F., Baeza Espasa, A., Molina Sánchez, L., &  
938 Rodríguez Perulero, A., 2017. Radionuclides as natural tracers of the interaction between  
939 groundwater and surface water in the River Andarax, Spain. *Journal of Environmental*  
940 *Radioactivity*, 180, 9–18. <https://doi.org/10.1016/j.jenvrad.2017.09.015>
- 941 Navarro-Martínez, F., Sánchez-Martos, F., Salas García, A., & Gisbert Gallego, J., 2020. The use of  
942 major, trace elements and uranium isotopic ratio ( $^{234}\text{U}/^{238}\text{U}$ ) for tracing of hydrogeochemical  
943 evolution of surface waters in the Andarax River catchment (SE Spain). *Journal of Geochemical*  
944 *Exploration*, 213(February), 106533. <https://doi.org/10.1016/j.gexplo.2020.106533>
- 945 Nolan, J., & Weber, K. A., 2015. Natural Uranium Contamination in Major U.S. Aquifers Linked to  
946 Nitrate. *Environmental Science and Technology Letters*, 2(8), 215–220.  
947 <https://doi.org/10.1021/acs.estlett.5b00174>
- 948 Ollivier, P., Radakovitch, O., & Hamelin, B., 2011. Major and trace element partition and fluxes in the  
949 Rhône River. *Chemical Geology*, 285(1–4), 15–31.  
950 <https://doi.org/10.1016/j.chemgeo.2011.02.011>
- 951 Osmond, J. K., & Cowart, J. B., 1976. The theory and uses of natural uranium isotopic variations in  
952 hydrology. *Atomic Energy Review*, 14(4), 621–679.
- 953 Osmond, J. K., Cowart, J. B., & Ivanovich, M., 1983. Uranium isotopic disequilibrium in ground water  
954 as an indicator of anomalies. *Nuclear Geophysics*, 34(1), 283–308. [https://doi.org/10.1016/0020-](https://doi.org/10.1016/0020-708X(83)90132-1)  
955 [708X\(83\)90132-1](https://doi.org/10.1016/0020-708X(83)90132-1)
- 956 Osmond, J. K., Kaufman, M. I., & Cowart, J. B., 1974. Mixing volume calculations, sources and aging  
957 trends of Floridan aquifer water by uranium isotopic methods. *Geochimica et Cosmochimica*  
958 *Acta*, 38(7), 1083–1100. [https://doi.org/10.1016/0016-7037\(74\)90006-4](https://doi.org/10.1016/0016-7037(74)90006-4)
- 959 Osmond, J. K., Rydell, H. S., & Kaufman, M. I., 1968. Uranium Disequilibrium in Groundwater : An  
960 Isotope Dilution Approach in Hydrologic Investigations. *Science*, 162, 997–999.
- 961 Paces, J. B., & Wurster, F. C., 2014. Natural uranium and strontium isotope tracers of water sources  
962 and surface water – groundwater interactions in arid wetlands – Pahrnagat Valley, Nevada,  
963 USA. *Journal of Hydrology*, 517, 213–225. <https://doi.org/10.1016/j.jhydrol.2014.05.011>
- 964 Palmer, M. R., & Edmond, J. M., 1993. Uranium in river water. *Geochimica et Cosmochimica Acta*,  
965 57(20), 4947–4955. [https://doi.org/10.1016/0016-7037\(93\)90131-F](https://doi.org/10.1016/0016-7037(93)90131-F)
- 966 Parkhurst, D. L., & Appelo, C. A. J., 2013. Description of Input and Examples for PHREEQC Version 3 –  
967 A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse  
968 Geochemical Calculations. In *U.S. Geological Survey Techniques and Methods*.  
969 <https://doi.org/10.1097/00000446-195210000-00005>

- 970 Pierret, M. C., Stille, P., Prunier, J., Viville, D., & Chabaux, F., 2014. Chemical and U-Sr isotopic  
 971 variations in stream and source waters of the Strengbach watershed (Vosges mountains,  
 972 France). *Hydrology and Earth System Sciences*, 18(10), 3969–3985.  
 973 <https://doi.org/10.5194/hess-18-3969-2014>
- 974 Pregler, A., Surbeck, H., Eikenberg, J., Werthmüller, S., Szidat, S., & Türlér, A., 2019. Increased  
 975 uranium concentrations in ground and surface waters of the Swiss Plateau: A result of uranium  
 976 accumulation and leaching in the Molasse basin and (ancient) wetlands? *Journal of*  
 977 *Environmental Radioactivity*, 208–209(June), 106026.  
 978 <https://doi.org/10.1016/j.jenvrad.2019.106026>
- 979 Rasplus, L., 1982. *Contribution à l'étude géologique des formations continentales détritiques du Sud-*  
 980 *Ouest du bassin de Paris.*
- 981 Read, D., Bennett, D. G., Hooker, P. J., Ivanovich, M., Longworth, G., Milodowski, A. E., & Noy, D. J.,  
 982 1993. The migration of uranium into peat-rich soils at Broubster, Caithness, Scotland, U.K.  
 983 *Journal of Contaminant Hydrology*, 13(1–4), 291–308. [https://doi.org/10.1016/0169-](https://doi.org/10.1016/0169-7722(93)90067-3)  
 984 [7722\(93\)90067-3](https://doi.org/10.1016/0169-7722(93)90067-3)
- 985 Reiller, P. E., & Descostes, M., 2020. Development and application of the thermodynamic database  
 986 PRODATA dedicated to the monitoring of mining activities from exploration to remediation.  
 987 *Chemosphere*, 251. <https://doi.org/10.1016/j.chemosphere.2020.126301>
- 988 Richter, S., Alonso-Munoz, A., Eykens, R., Jacobsson, U., Kuehn, H., Verbruggen, A., Aregbe, Y.,  
 989 Wellum, R., & Keegan, E., 2008. The isotopic composition of natural uranium samples –  
 990 Measurements using the new n(233U)/n(236U) double spike IRMM-3636. *International Journal*  
 991 *of Mass Spectrometry*, 269(1–2), 145–148. <https://doi.org/10.1016/j.ijms.2007.09.012>
- 992 Riedel, T., & Kübeck, C., 2018. Uranium in groundwater – A synopsis based on a large  
 993 hydrogeochemical data set. *Water Research*, 129, 29–38.  
 994 <https://doi.org/10.1016/j.watres.2017.11.001>
- 995 Riotte, J., & Chabaux, F., 1999. (234U/238U) activity ratios in freshwaters as tracers of hydrological  
 996 processes: The Strengbach watershed (Vosges, France). *Geochimica et Cosmochimica Acta*,  
 997 63(9), 1263–1275. [https://doi.org/10.1016/S0016-7037\(99\)00009-5](https://doi.org/10.1016/S0016-7037(99)00009-5)
- 998 Rosen, M. R., Burow, K. R., & Fram, M. S., 2019. Anthropogenic and geologic causes of anomalously  
 999 high uranium concentrations in groundwater used for drinking water supply in the southeastern  
 1000 San Joaquin Valley, CA. *Journal of Hydrology*, 577(July), 124009.  
 1001 <https://doi.org/10.1016/j.jhydrol.2019.124009>
- 1002 Rován, L., Lojen, S., Zuliani, T., Kanduč, T., Petrič, M., Horvat, B., Rusjan, S., & Štrok, M., 2020.  
 1003 Comparison of uranium isotopes and classical geochemical tracers in Karst Aquifer of Ljubljana  
 1004 River catchment (Slovenia). *Water (Switzerland)*, 12(7). <https://doi.org/10.3390/w12072064>
- 1005 Ryu, J. S., Lee, K. S., Chang, H. W., & Cheong, C. S., 2009. Uranium isotopes as a tracer of sources of  
 1006 dissolved solutes in the Han River, South Korea. *Chemical Geology*, 258(3–4), 354–361.  
 1007 <https://doi.org/10.1016/j.chemgeo.2008.10.039>
- 1008 Saari, H. K., Schmidt, S., Coynel, A., Huguet, S., Schäfer, J., & Blanc, G., 2007. Potential impact of  
 1009 former Zn ore extraction activities on dissolved uranium distribution in the Riou-Mort  
 1010 watershed (France). *Science of the Total Environment*, 382, 304–310.  
 1011 <https://doi.org/10.1016/j.scitotenv.2007.04.030>
- 1012 Saari, H. K., Schmidt, S., Huguet, S., & Lanoux, A., 2008. Spatiotemporal variation of dissolved 238U in  
 1013 the Gironde fluvial-estuarine system (France). *Journal of Environmental Radioactivity*, 99, 426–

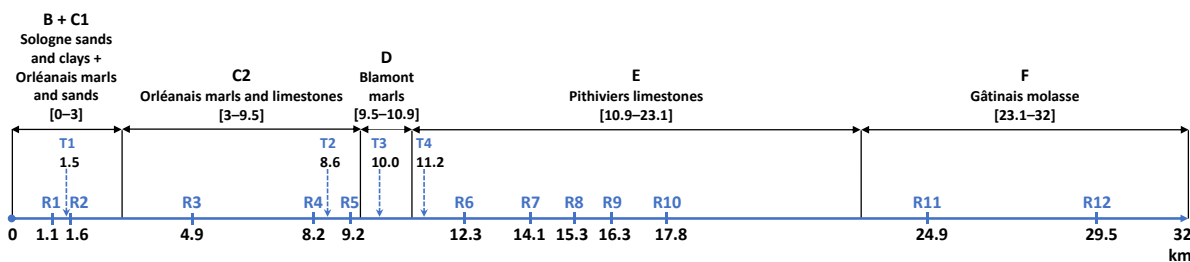
- 1014 435. <https://doi.org/10.1016/j.jenvrad.2007.11.016>
- 1015 Salminen, R., Batista, M. J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis,  
1016 A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis,  
1017 J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Å., Ottesen, R., Petersell, V.,  
1018 Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., & Tarvainen, T.,  
1019 2005. *Geochemical Atlas of Europe. Part 1 - Background Information, Methodology and Maps*.  
1020 Retrieved from <http://weppi.gtk.fi/publ/foregsatlas/index.php>
- 1021 Salpeteur, I., 2010. Valeurs de référence traces dans les eaux de rivières et les sédiments, obtenues  
1022 Atlas géochimique européen \* (I). *Environnement, Risques & Santé*, 9, 121–135.
- 1023 Sandino, A., & Bruno, J., 1992. The solubility of  $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{s})$  and the formation of U(VI)  
1024 phosphate complexes: Their influence in uranium speciation in natural waters. *Geochimica et*  
1025 *Cosmochimica Acta*, 56(12), 4135–4145. [https://doi.org/10.1016/0016-7037\(92\)90256-I](https://doi.org/10.1016/0016-7037(92)90256-I)
- 1026 Smedley, P. L., & Kinniburgh, D. G., 2023. Uranium in natural waters and the environment:  
1027 distribution, speciation and impact. *Applied Geochemistry*, 105534.  
1028 <https://doi.org/10.1016/j.apgeochem.2022.105534>
- 1029 Smedley, P. L., Smith, B., Abesser, C., & Lapworth, D., 2006. Uranium occurrence and behaviour in  
1030 British groundwater. *British Geological Survey Groundwater Programme Commissioned Report*  
1031 *CR/06/050N*, 48.
- 1032 Snow, D. D., & Spalding, R. F., 1994. Uranium isotopes in the Platte River drainage basin of the North  
1033 American High plains Region. *Applied Geochemistry*, 9(3), 271–278.  
1034 [https://doi.org/10.1016/0883-2927\(94\)90037-X](https://doi.org/10.1016/0883-2927(94)90037-X)
- 1035 Tsumura, A., Okamoto, R., Takaku, Y., & Yamasaki, S., 1995. Direct Determination of Uranium in  
1036 Rainwater by High Resolution ICP-MS with an Ultrasonic Nebulizer. *Radioisotopes*, 44(2), 85–92.  
1037 <https://doi.org/10.3769/radioisotopes.44.85>
- 1038 Uralbekov, B., Burkitbayev, M., Satybaldiyev, B., Matveyeva, I., Tuzova, T., & Snow, D., 2014. Spatial  
1039 and temporal variability of  $^{234}\text{U}/^{238}\text{U}$  activity ratios in the Shu River, Central Asia.  
1040 *Environmental Earth Sciences*, 72(9), 3635–3642. <https://doi.org/10.1007/s12665-014-3274-x>
- 1041 Van Berk, W., & Fu, Y., 2017. Redox Roll-Front Mobilization of Geogenic Uranium by Nitrate Input  
1042 into Aquifers: Risks for Groundwater Resources. *Environmental Science and Technology*, 51(1),  
1043 337–345. <https://doi.org/10.1021/acs.est.6b01569>
- 1044 Verley, F., Brunson, F., Verjus, P., & Cholez, M., 2003. *Nappe de Beauce - Piézométrie hautes eaux*  
1045 *2002*.
- 1046 Wang, X., Shi, Z., Kinniburgh, D. G., Zhao, L., Ni, S., Wang, R., ... Zhu, B., 2019. Effect of  
1047 thermodynamic database selection on the estimated aqueous uranium speciation. *Journal of*  
1048 *Geochemical Exploration*, 204(May), 33–42. <https://doi.org/10.1016/j.gexplo.2019.05.001>
- 1049 Wang, Y., Fruttschi, M., Suvorova, E., Phrommavanh, V., Descostes, M., Osman, A. A. A., Geipel, G., &  
1050 Bernier-Latmani, R. (2013). Mobile uranium(IV)-bearing colloids in a mining-impacted wetland.  
1051 *Nature Communications*, 4(May), 1–9. <https://doi.org/10.1038/ncomms3942>
- 1052 Wendland, F., Blum, A., Coetsiers, M., Gorova, R., Griffioen, J., Grima, J., Hinsby, K., Kunkel, R.,  
1053 Marandi, A., Melo, T., Panagopoulos, A., Pauwels, H., Ruisi, M., Traversa, P., Vermooten, J. S. A.,  
1054 & Walraevens, K., 2008. European aquifer typology: A practical framework for an overview of  
1055 major groundwater composition at European scale. *Environmental Geology*, 55(1), 77–85.  
1056 <https://doi.org/10.1007/s00254-007-0966-5>

- 1057 Windom, H., Smith, R., Niencheski, F., & Alexander, C., 2000. Uranium in rivers and estuaries of  
1058 globally diverse, smaller watersheds. *Marine Chemistry*, 68, 307–321.  
1059 [https://doi.org/10.1016/S0304-4203\(99\)00086-9](https://doi.org/10.1016/S0304-4203(99)00086-9)
- 1060 Wu, W. M., Carley, J., Green, S. J., Luo, J., Kelly, S. D., Van Nostrand, J., Lowe, K., Mehlhorn, T., Carroll,  
1061 S., Boonchayanant, B., Löffler, F. E., Watson, D., Kemner, K. M., Zhou, J., Kitanidis, P. K., Kostka,  
1062 J. E., Jardine, P. M., & Criddle, C. S., 2010. Effects of nitrate on the stability of uranium in a  
1063 bioreduced region of the subsurface. *Environmental Science and Technology*, 44(13), 5104–  
1064 5111. <https://doi.org/10.1021/es1000837>
- 1065 Wu, Y., Wang, Y., & Guo, W., 2019. Behavior and fate of geogenic uranium in a shallow groundwater  
1066 system. *Journal of Contaminant Hydrology*, 222(January), 41–55.  
1067 <https://doi.org/10.1016/j.jconhyd.2019.02.009>
- 1068 Zebracki, M., Cagnat, X., Gairoard, S., Cariou, N., Eyrolle-Boyer, F., Boulet, B., & Antonelli, C., 2017. U  
1069 isotopes distribution in the Lower Rhone River and its implication on radionuclides  
1070 disequilibrium within the decay series. *Journal of Environmental Radioactivity*, 178–179.  
1071 <https://doi.org/10.1016/j.jenvrad.2017.09.004>
- 1072 Zhang, Y., Slomp, C. P., Peter, H., Bostick, B., Passier, H. F., Böttcher, M. E., Omoregie, E. O., Lloyd, J.  
1073 R., Polya, D. A., & Cappellen, P. V., 2012. Isotopic and microbiological signatures of pyrite-driven  
1074 denitrification in a sandy aquifer. *Chemical Geology*, 300–301, 123–132.  
1075 <https://doi.org/10.1016/j.chemgeo.2012.01.024>
- 1076

1077 Figures



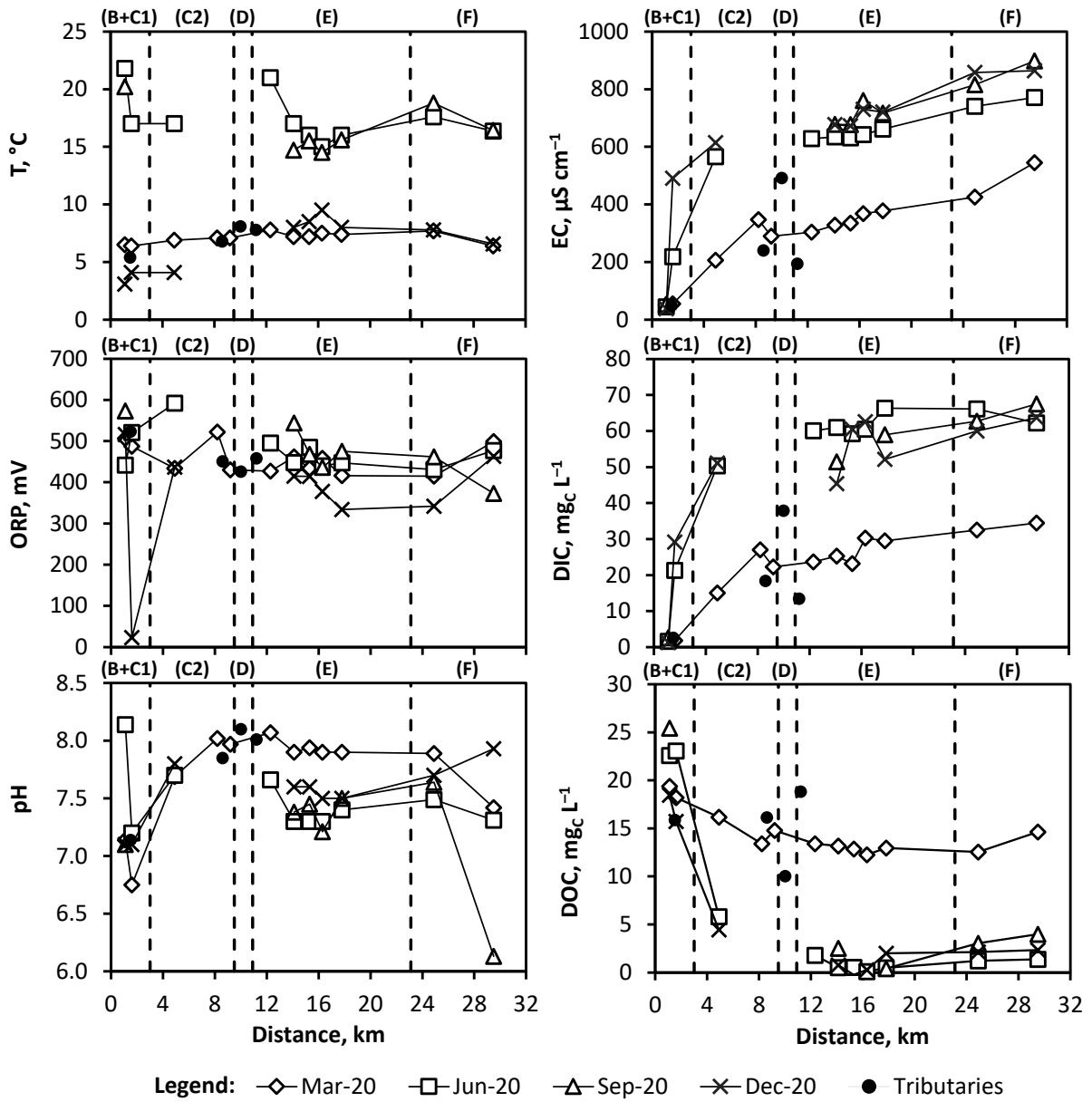
1078



1079

1080 Figure 1 : Maps of the study area with the sampling sites of surface water and groundwater, and the geological formations  
 1081 (using ArcGis, data available from <https://infoterre.brgm.fr/>). Below is given the longitudinal profile of the Oeuf river.

1082



1084

1085

1086

1087

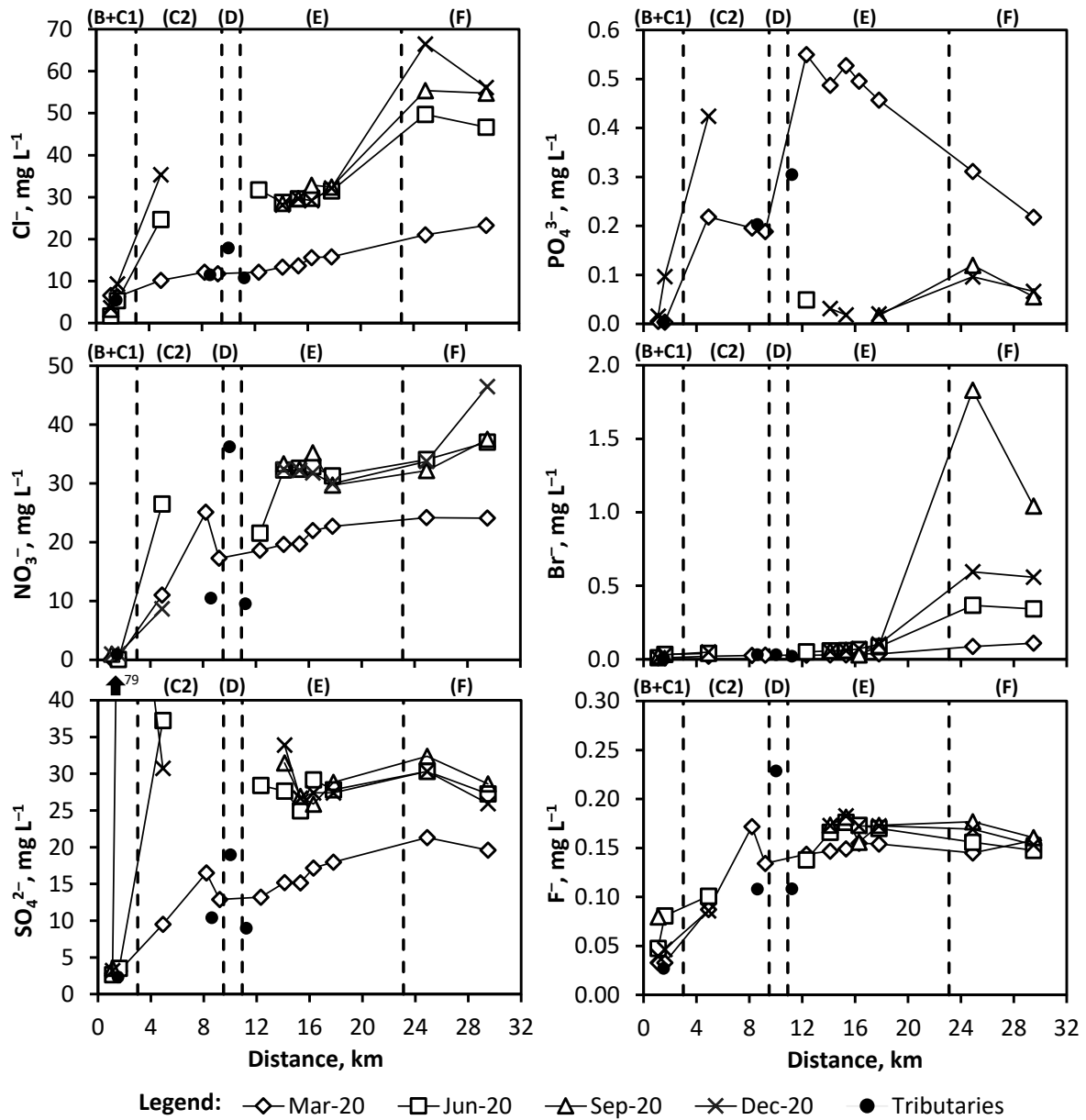
1088

1089

Figure 2 : Longitudinal and seasonal variations of the physical and physico-chemical parameters and the dissolved carbon concentration in the Œuf river and tributaries. The river zones where outcrop the geological formations are delineated, corresponding to (upstream to downstream): Sologne sands and clays followed by Orléanais marls and sands C1 (B+C1; 0–3 km), Orléanais marls and limestones (C2; 3–9.5 km), Blamont marls (D; 9.5–10.9 km), Pithiviers limestones (E; 10.9–23.1 km) and Gâtinais molasse (F; 23.1–32 km).

1090





1092

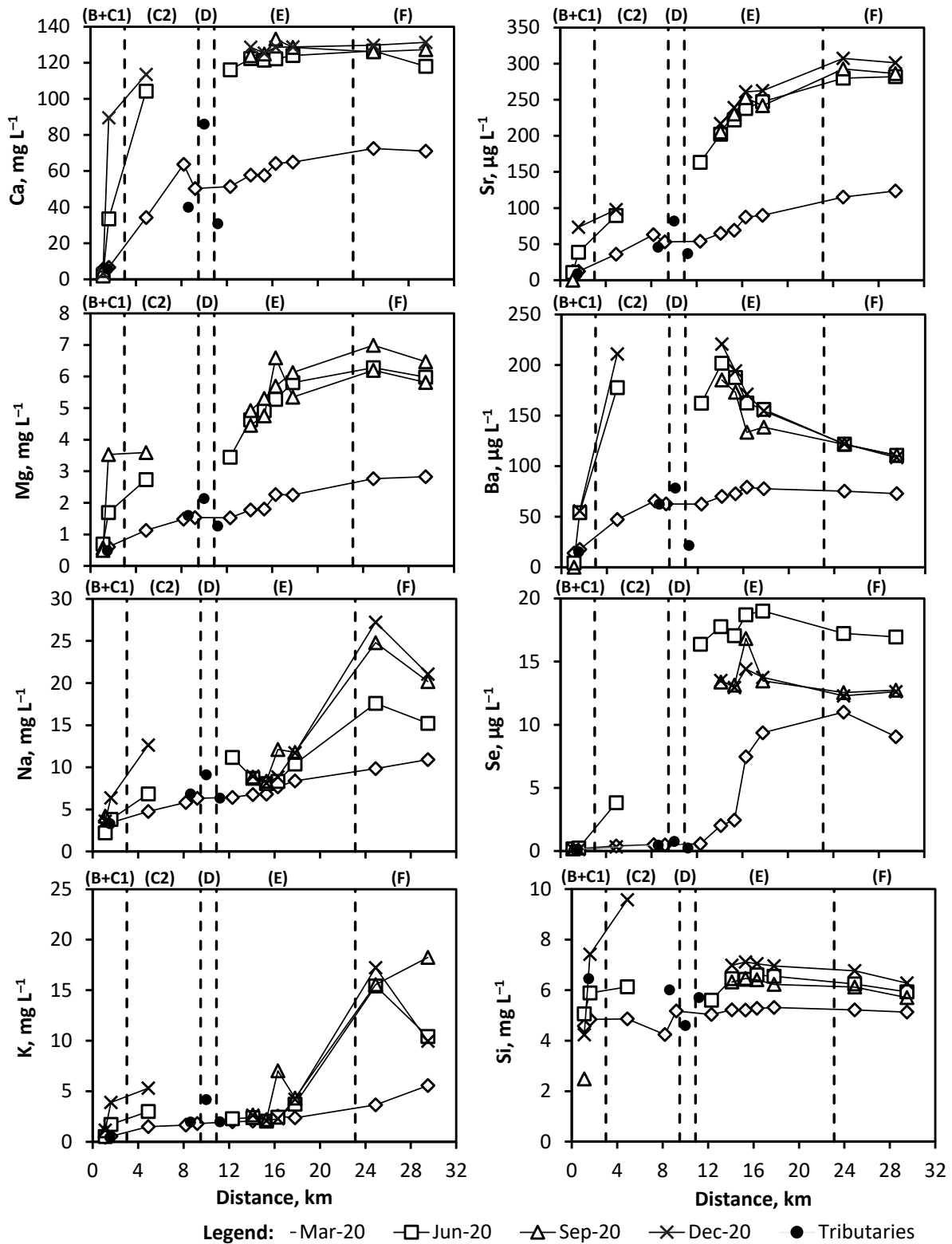
1093

1094

1095

1096

Figure 3 : Longitudinal and seasonal variations of anion concentrations in the Œuf river and tributaries. The river zones where outcrop the geological formations are delineated, corresponding to (upstream to downstream): Sologne sands and clays followed by Orléanais marls and sands C1 (B+C1; 0 – 3 km), Orléanais marls and limestones (C2; 3 – 9.5 km), Blamont marls (D; 9.5 – 10.9 km), Pithiviers limestones (E; 10.9 – 23.1 km) and Gâtinais molasse (F; 23.1 – 32 km).



1098

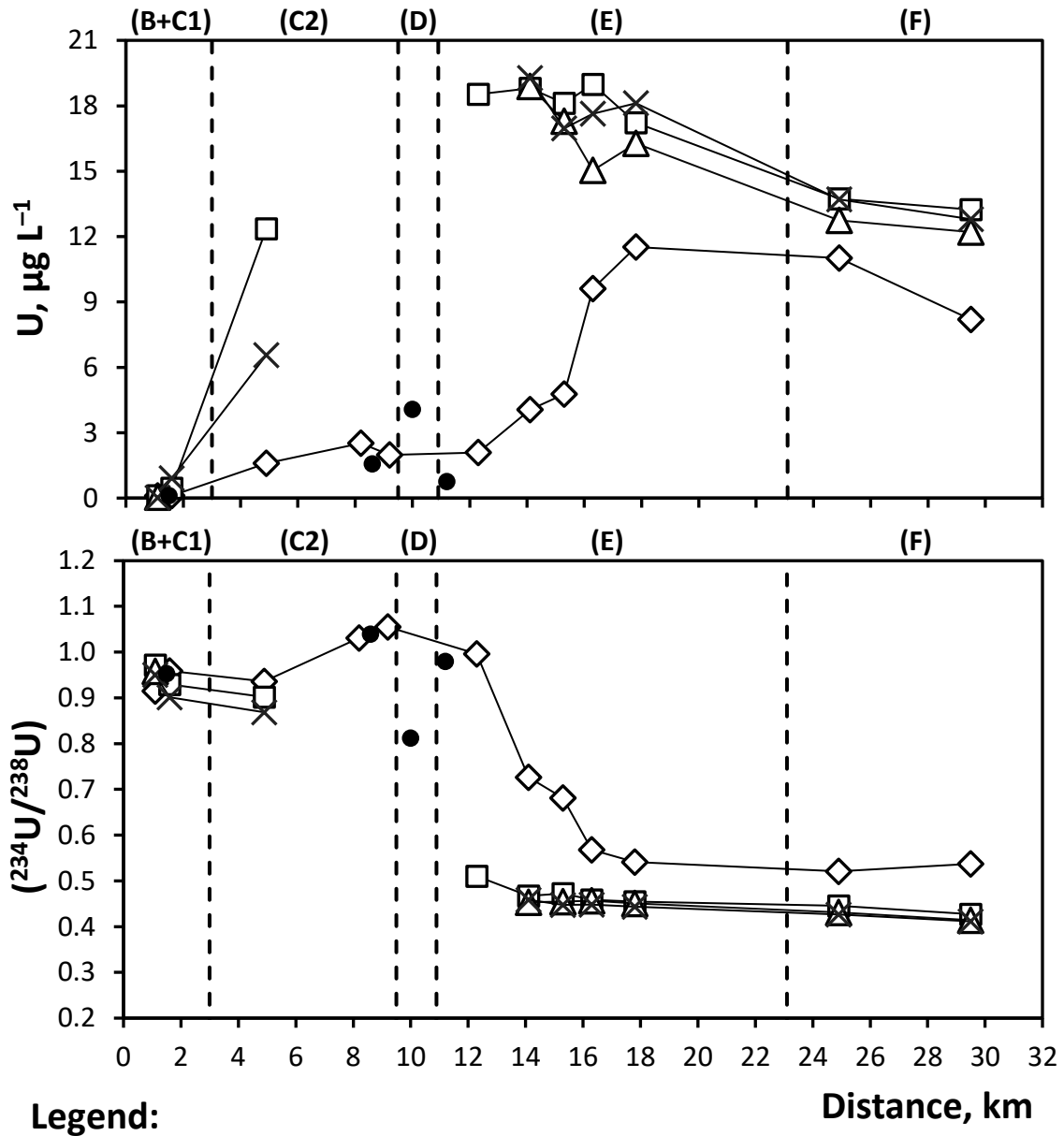
1099

1100

1101

1102

Figure 4 : Longitudinal and seasonal variations of the chemical element concentrations in the Cœuf river and tributaries. The river zones where outcrop the geological formations are delineated, corresponding to (upstream to downstream): Sologne sands and clays followed by Orléanais marls and sands C1 (B+C1; 0 – 3 km), Orléanais marls and limestones (C2; 3 – 9.5 km), Blamont marls (D; 9.5 – 10.9 km), Pithiviers limestones (E; 10.9 – 23.1 km) and Gâtinais molasse (F; 23.1 – 32 km).



**Legend:**  
 ◇ Mar-20   □ Jun-20   △ Sep-20   × Dec-20   ● Tributaries

1104

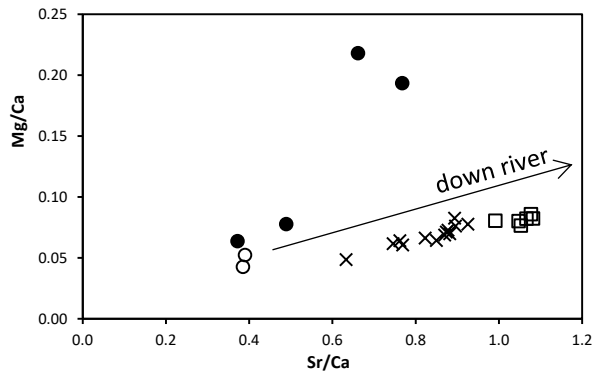
1105

1106

1107

1108

Figure 5 : Longitudinal and seasonal variations of U concentration and <sup>234</sup>U/<sup>238</sup>U in the Œuf river and tributaries. The river zones where outcrop the geological formations are delineated, corresponding to (upstream to downstream): Sologne sands and clays followed by Orléanais marls and sands C1 (B+C1; 0 – 3 km), Orléanais marls and limestones (C2; 3 – 9.5 km), Blamont marls (D; 9.5 – 10.9 km), Pithiviers limestones (E; 10.9 – 23.1 km) and Gâtinais molasse (F; 23.1 – 32 km).

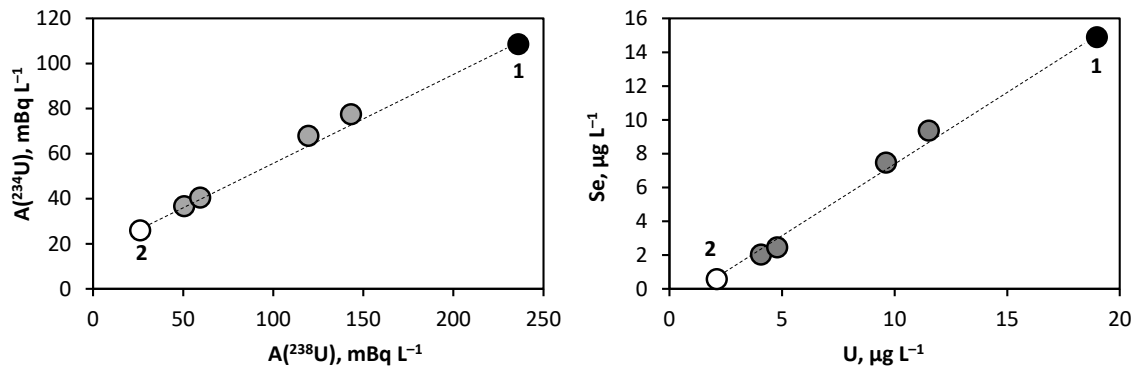


● Orléanais marls and sands (C1)    ○ Orléanais marls and limestones (C2)  
 × Pithiviers limestones (E)        □ Gâtinais molasse (F)

1109

1110 *Figure 6 : Plot of Mg/Ca versus Sr/Ca molar ratios in the Cēuf river in LWS. Stream data are grouped according to the outcrop*  
 1111 *geology zone.*

1112



1113

1114 *Figure 7 : On the left, plot of <sup>234</sup>U versus <sup>238</sup>U activities; on the right, plot of Se versus U concentrations. Water component 1*  
 1115 *corresponds to the groundwater supply and water component 2 to the stream water coming from upstream.*

1116

## 1117 Tables

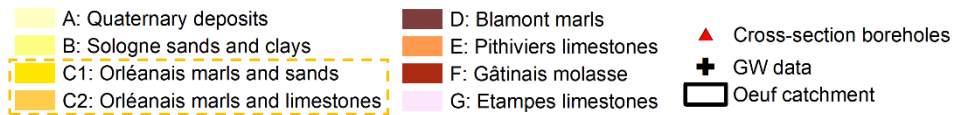
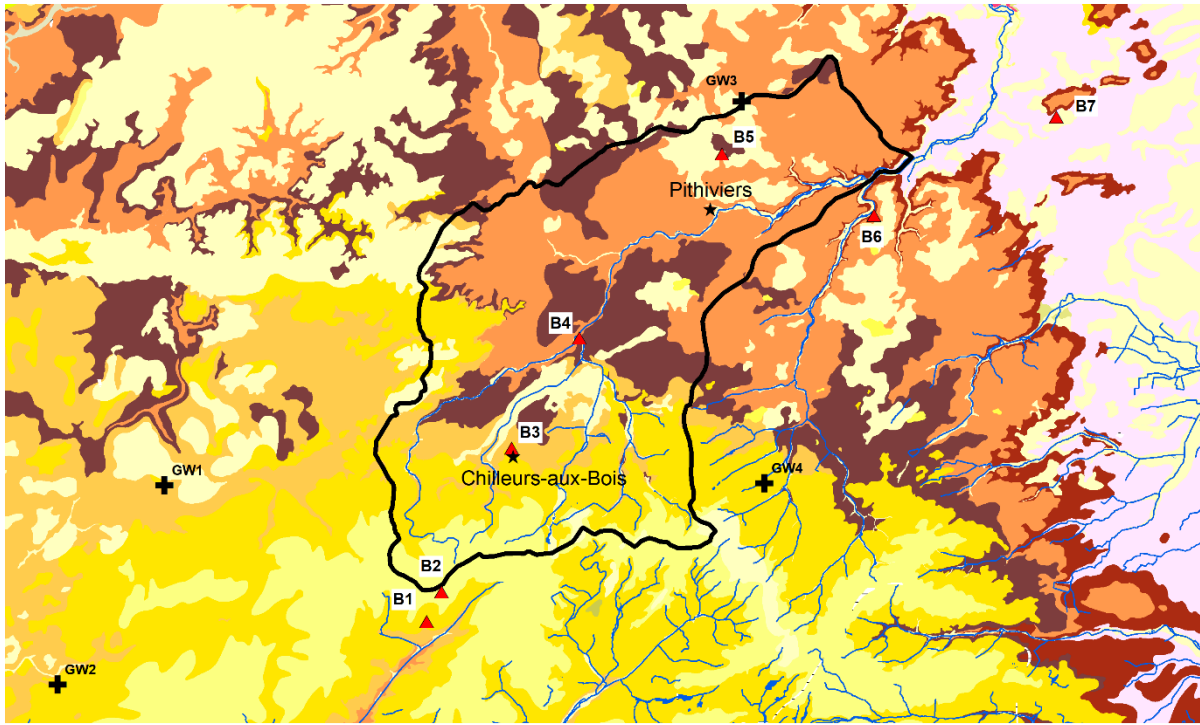
1118 *Table 1 : Characteristics of the two water components and calculation of the mixing water volume in the CEuf river stretch*  
 1119 *R7 – R10 (14.1 – 17.8 km) in high water season (04/03/2020).*

			23/06/20	21/09/20	10/12/20	Mean value	
<i>Characteristics of the water components 1 and 2</i>	<b>1 = water coming from the ground</b>	<sup>234</sup> U, mBq L <sup>-1</sup>	109	106	110	<b>109</b>	
		<sup>238</sup> U, mBq L <sup>-1</sup>	234	235	240	<b>236</b>	
		U, µg L <sup>-1</sup>	18.8	18.9	19.3	<b>19.0</b>	
		Se, µg L <sup>-1</sup>	17.8	13.4	13.5	<b>14.9</b>	
	<b>2 = water coming from upstream</b>			04/03/20			
		<sup>234</sup> U, mBq L <sup>-1</sup>		<b>26.0</b>			
		<sup>238</sup> U, mBq L <sup>-1</sup>		<b>26.1</b>			
		U, µg L <sup>-1</sup>		<b>2.1</b>			
						<b>0.6</b>	
<i>High water season (04/03/2020)</i>	Mix 1 + 2		R7	R8	R9	R10	
		<sup>234</sup> U, mBq L <sup>-1</sup>	36.7	40.5	67.9	77.5	
		<sup>238</sup> U, mBq L <sup>-1</sup>	50.5	59.4	120	143	
		U, µg L <sup>-1</sup>	4.1	4.8	9.6	11.5	
		Se, µg L <sup>-1</sup>	2.0	2.5	7.5	9.4	
<i>% Water volume</i>	% 1 to 2		<b>R7</b>	<b>R8</b>	<b>R9</b>	<b>R10</b>	
			<b>14.1 km</b>	<b>15.3 km</b>	<b>16.3 km</b>	<b>17.8 km</b>	
		<sup>234</sup> U	13	18	51	62	
		<sup>238</sup> U	12	16	44	56	
		U	12	16	44	56	
		Se	10	13	48	61	
		<b>Mean value</b>	<b>12</b>	<b>16</b>	<b>47</b>	<b>59</b>	
±	1	2	3	4			

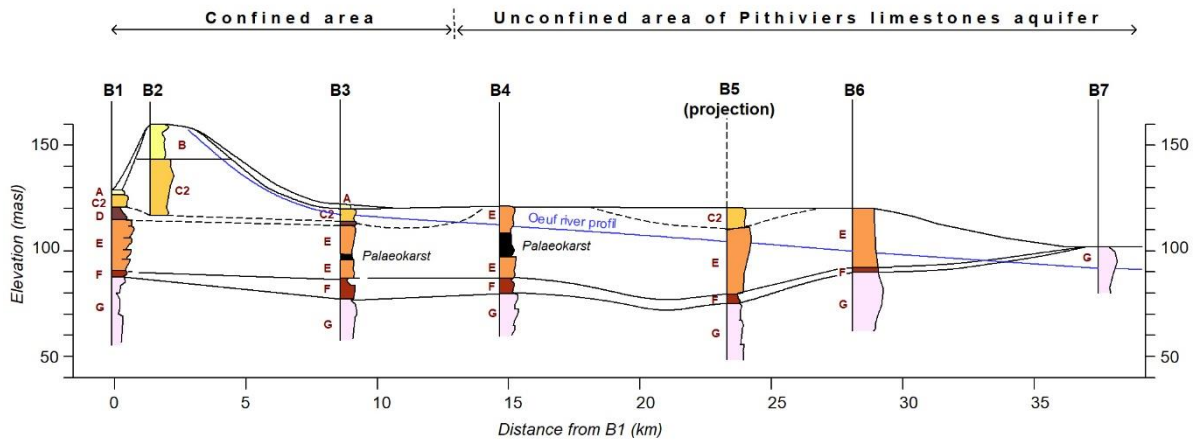
1120

1121

1122 Supplementary information – Figures



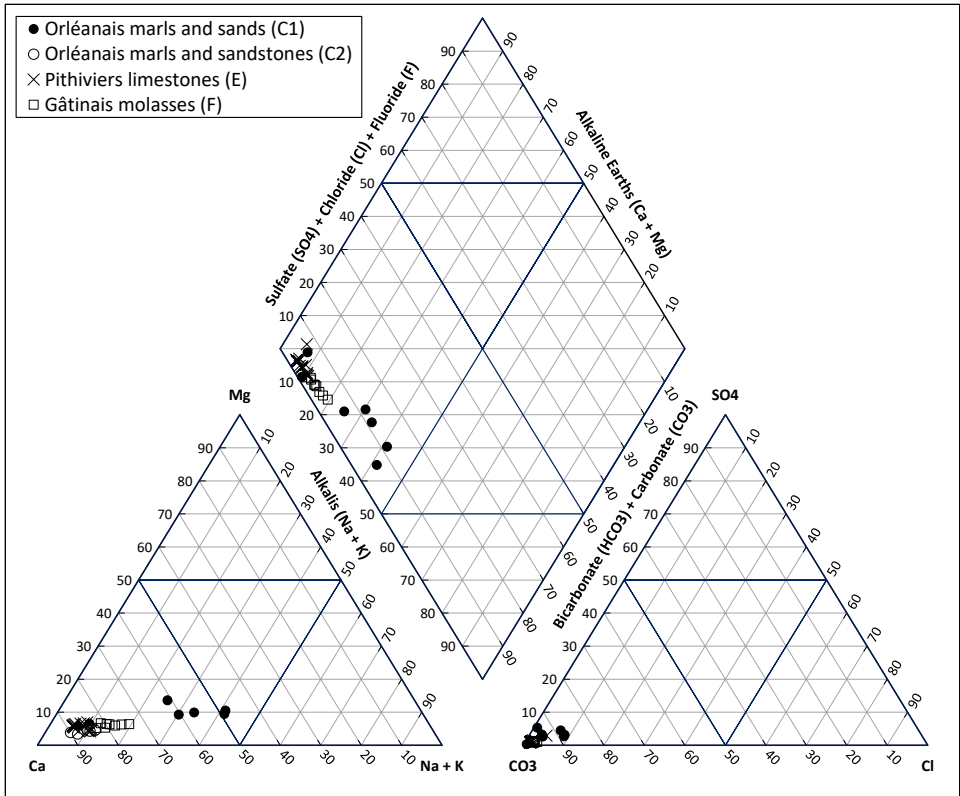
1123



1124

1125 *Suppl. Inf. Figure 1 : Geological map (top) and cross-section (bottom) of the Œuf river ground catchment (the figures were*  
 1126 *prepared using ArcGis and MapInfo). On the cross-section (bottom) are only reported the geological formations that outcrop*  
 1127 *in the Œuf river catchment. In the boreholes B3 and B4, sands and clays are described in the cuttings inside the Pithiviers*  
 1128 *formation and referred as palaeokarst. These deposits correspond to karst filling by materials coming from rivers flowing*  
 1129 *during the Holocene (Lorain, 1973). The national codes of the boreholes B1 to B7 are (<https://infoterre.brgm.fr/>):*  
 1130 *BSS001ABMF (B1), BSS001ABSB (B2), BSS000YDWS (B3), BSS000YFBV (B4), BSS000YEMU (B5), BSS000YETY (B6) and*  
 1131 *BSS000YEXV (B7).*

1132



1133

1134 *Suppl. Inf. Figure 2 : Piper diagram. Carbonate and bicarbonate correspond to the total dissolved inorganic carbon measured*  
 1135 *in the water samples.*

1136

1137



1138 **Supplementary information – Tables**

1139 *Suppl. Inf. Table 1 : Physical and physico-chemical parameters and dissolved carbon concentration measured in the Cœuf river*  
 1140 *and its tributaries. Carbon results are missing for R8 and R9 in September 2020 ("Not Determined"), as samples were lost*  
 1141 *during the step sample preparation.*

Sampling site	Distance km	Geology	Lat.	Long.	Date	T		pH		ORP		EC		TC		DIC		DOC		
						°C	±		±	mV	±	µS cm <sup>-1</sup>	±	mgc L <sup>-1</sup>	±	±	±	±	±	±
R1	1.1	C1	48.0357	2.1307	04/03/20	6.5	0.1	7.1	0.1	506	5	51.3	0.5	21.3	0.1	1.9	0.2	19.4	0.2	
			48.0357	2.1307	23/06/20	21.8	0.2	8.1	0.1	442	4	45.1	0.5	24.2	0.3	1.6	0.2	22.6	0.4	
			48.0357	2.1307	21/09/20	20.2	0.2	7.1	0.1	573	6	53.0	0.5	28.0	0.4	2.6	0.6	25.4	0.8	
			48.0357	2.1307	10/12/20	3.10	0.03	7.1	0.1	516	5	39.0	0.4	19.8	0.9	1.3	0.4	18	1	
R2	1.6	C1	48.0357	2.1307	04/03/20	6.4	0.1	6.8	0.1	487	5	55.2	0.6	20.0	0.1	1.8	0.1	18.2	0.1	
			48.0357	2.1307	23/06/20	17.0	0.2	7.2	0.1	521	5	219	2	44.4	0.5	21.3	0.6	23.1	0.8	
			48.0357	2.1307	10/12/20	4.10	0.04	7.1	0.1	23.0	0.2	491	5	45	1	29	1	16	2	
R3	4.9	C2	48.0553	2.1736	04/03/20	6.9	0.1	7.7	0.1	434	4	206	2	31.2	0.2	15.0	0.3	16.2	0.4	
			48.0553	2.1736	23/06/20	17.0	0.2	7.7	0.1	592	6	566	6	56.1	0.1	50	1	5.8	0.9	
			48.0553	2.1736	10/12/20	4.10	0.04	7.8	0.1	437	4	614	6	56	1	51	2	4	3	
R4	8.2	C2	48.1020	2.1889	04/03/20	7.1	0.1	8.0	0.1	522	5	347	3	40.4	0.1	27.0	0.4	13.4	0.4	
R5	9.2	C2	48.1044	2.1931	04/03/20	7.1	0.1	8.0	0.1	430	4	290	3	37.0	0.2	22.3	0.2	14.8	0.3	
R6	12.3	E	48.1282	2.1862	04/03/20	7.8	0.1	8.1	0.1	427	4	304	3	37.1	0.1	24	1	13	1	
			48.1282	2.1862	23/06/20	21.0	0.2	7.7	0.1	495	5	628	6	61.9	0.3	60	1	2	1	
R7	14.1	E	48.1429	2.1942	04/03/20	7.2	0.1	7.9	0.1	462	5	328	3	38.4	0.2	25.3	0.7	13.2	0.8	
			48.1429	2.1942	23/06/20	17.0	0.2	7.3	0.1	448	4	634	6	61.5	0.3	61	1		<1.4	
			48.1429	2.1942	21/09/20	14.7	0.1	7.4	0.1	544	5	678	7	53.9	0.7	51	2	3		
			48.1429	2.1942	10/12/20	8.0	0.1	7.6	0.1	415	4	677	7	46	1	45	2		<2.3	
R8	15.3	E	48.1517	2.2001	04/03/20	7.2	0.1	7.9	0.1	434	4	335	3	36.0	0.1	23.1	0.2	12.9	0.2	
			48.1517	2.2001	23/06/20	16.0	0.2	7.3	0.1	485	5	631	6	59.8	0.4	59	1		<1.1	
			48.1517	2.2001	21/09/20	15.5	0.2	7.5	0.1	468	5	677	7	19.9	0.4	ND		ND		
R9	16.3	E	48.1517	2.2001	10/12/20	8.5	0.1	7.6	0.1	414	4	673	7	60	2	60	2		<2.8	
			48.1587	2.2083	04/03/20	7.5	0.1	7.9	0.1	458	5	368	4	42.5	0.2	30.3	0.8	12.3	0.8	
			48.1587	2.2083	23/06/20	15.0	0.2	7.3	0.1	440	4	642	6	60.6	0.4	61	1		<1.2	
			48.1587	2.2083	21/09/20	14.5	0.1	7.2	0.1	436	4	760	8	39.7	0.5	ND		ND		
R10	17.8	E	48.1587	2.2083	10/12/20	9.5	0.1	7.5	0.1	378	4	730	7	63	2	63	3		<3.0	
			48.1643	2.2243	04/03/20	7.4	0.1	7.9	0.1	416	4	378	4	42.5	0.1	29.5	0.2	13.0	0.2	
			48.1643	2.2243	23/06/20	16.0	0.2	7.4	0.1	447	4	661	7	66.8	0.5	66.3	0.7	0.5	0.8	
R11	24.9	F	48.1643	2.2243	21/09/20	15.6	0.2	7.5	0.1	475	5	717	7	59.3	0.7	58.9	0.9		<1.1	
			48.1643	2.2243	10/12/20	8.0	0.1	7.5	0.1	334	3	720	7	54	1	52	2		<2.5	
			48.1722	2.3003	04/03/20	7.7	0.1	7.9	0.1	415	4	426	4	45.1	0.1	32.5	0.1	12.5	0.2	
			48.1722	2.3003	23/06/20	17.6	0.2	7.5	0.1	431	4	740	7	67.31	0.02	66.1	0.9	1.2	0.9	
R12	29.5	F	48.1722	2.3003	21/09/20	18.8	0.2	7.6	0.1	462	5	815	8	65.8	0.8	63	1	3	1	
			48.1722	2.3003	10/12/20	7.8	0.1	7.7	0.1	342	3	858	9	62	2	60	2		<2.9	
			48.1860	2.3519	04/03/20	6.4	0.1	7.4	0.1	499	5	545	5	49.1	0.2	34.4	0.3	14.6	0.4	
			48.1860	2.3519	23/06/20	16.4	0.2	7.3	0.1	477	5	771	8	63.6	0.2	62.2	0.7	1.4	0.7	
T1	1.5	C1	48.1860	2.3519	21/09/20	16.4	0.2	6.1	0.1	373	4	898	9	71.5	0.8	68	1	4	1	
			48.1860	2.3519	10/12/20	6.6	0.1	7.9	0.1	463	5	864	9	66	2	64	4		<4.0	
			48.0357	2.1307	04/03/20	5.4	0.1	7.1	0.1	523	5	49.1	0.5	18.44	0.05	2.6	0.1	15.9	0.1	
T2	8.6	C1	48.1044	2.1934	04/03/20	6.8	0.1	7.9	0.1	451	5	240	2	34.5	0.1	18.4	0.2	16.1	0.2	
T3	10.0	A	48.1013	2.1636	04/03/20	8.1	0.1	8.1	0.1	426	4	492	5	47.9	0.2	37.9	0.3	10.0	0.3	
T4	11.2	E	48.1101	2.1452	04/03/20	7.8	0.1	8.0	0.1	458	5	194	2	32.28	0.04	13.4	0.1	18.8	0.1	

1142

Sampling site	Distance km	Geology	Lat.	Long.	Date	F <sup>-</sup> ±		Cl <sup>-</sup> ±		Br <sup>-</sup> ±		NO <sub>3</sub> <sup>-</sup> ±		PO <sub>4</sub> <sup>3-</sup> ±		SO <sub>4</sub> <sup>2-</sup> ±		
						mg L <sup>-1</sup>												
R1	1.1	C1	48.0357	2.1307	04/03/20	0.0330	0.0005	6.58	0.03	0.0103	0.0001	0.126	0.001	0.0057	0.0004	2.82	0.03	
			48.0357	2.1307	23/06/20	0.048	0.005	1.74	0.04		<0.01		<0.01		<0.01	2.7	0.2	
			48.0357	2.1307	21/09/20	0.080	0.006	3.3	0.4	0.022	0.002	0.9	0.4			<0.01	3.5	0.4
			48.0357	2.1307	10/12/20	0.040	0.004	3.6	0.4	0.009	0.002	0.9	0.4	0.016	0.003	3.2	0.5	
R2	1.6	C1	48.0357	2.1307	04/03/20	0.0330	0.0005	6.32	0.03	0.0103	0.0001	0.39	0.03	0.0041	0.0004	3.1	0.1	
			48.0357	2.1307	23/06/20	0.081	0.006	5.364	0.004	0.032	0.005	0.040	0.004			<0.01	3.5	0.1
			48.0357	2.1307	10/12/20	0.047	0.004	9.4	0.5	0.032	0.002	1.0	0.4	0.097	0.005	79	4	
			48.0553	2.1736	04/03/20	0.087	0.002	10.21	0.02	0.020	0.001	10.97	0.02	0.219	0.003	9.5	0.1	
R3	4.9	C2	48.0553	2.1736	23/06/20	0.10	0.01	24.68	0.06	0.04	0.01	26.48	0.04	0.62	0.04	37	2	
			48.0553	2.1736	10/12/20	0.086	0.004	35	2	0.049	0.003	8.6	0.5	0.42	0.03	31	2	
			48.1020	2.1889	04/03/20	0.172	0.002	12.12	0.02	0.025	0.001	25.1	0.3	0.196	0.003	16.5	0.1	
			48.1044	2.1931	04/03/20	0.134	0.002	11.80	0.02	0.028	0.001	17.24	0.02	0.189	0.004	12.9	0.2	
R5	9.2	C2	48.1282	2.1862	04/03/20	0.144	0.002	12.15	0.08	0.027	0.001	18.60	0.02	0.55	0.03	13.2	0.1	
			48.1282	2.1862	23/06/20	0.14	0.01	31.76	0.04	0.05	0.01	21.50	0.04	0.05	0.04	28.4	0.2	
			48.1429	2.1942	04/03/20	0.147	0.002	13.37	0.02	0.029	0.001	19.61	0.02	0.49	0.03	15.2	0.2	
			48.1429	2.1942	23/06/20	0.17	0.01	28.74	0.04	0.06	0.01	32.28	0.05		<0.01	27.6	0.2	
R6	12.3	E	48.1429	2.1942	21/09/20	0.173	0.009	28	1	0.057	0.003	33.3	1.8		<0.01	31	2	
			48.1429	2.1942	10/12/20	0.173	0.009	28	1	0.055	0.003	32.4	1.7	0.032	0.003	34	2	
			48.1517	2.2001	04/03/20	0.149	0.002	13.63	0.09	0.029	0.001	19.71	0.02	0.53	0.03	15.1	0.1	
			48.1517	2.2001	23/06/20	0.18	0.01	29.64	0.04	0.06	0.01	32.55	0.04		<0.01	25.0	0.2	
R7	14.1	E	48.1517	2.2001	21/09/20	0.182	0.009	30	2	0.060	0.003	32.4	1.7		<0.01	27	1	
			48.1517	2.2001	10/12/20	0.183	0.009	30	2	0.059	0.003	32.2	1.7	0.019	0.003	27	1	
			48.1587	2.2083	04/03/20	0.155	0.002	15.64	0.02	0.037	0.001	21.97	0.02	0.50	0.03	17.2	0.2	
			48.1587	2.2083	23/06/20	0.17	0.01	29.73	0.04	0.07	0.01	32.84	0.04		<0.01	29.2	0.4	
R8	15.3	E	48.1587	2.2083	21/09/20	0.156	0.008	33	2	0.029	0.002	35.2	1.8		<0.01	26	1	
			48.1587	2.2083	10/12/20	0.172	0.008	29	1	0.070	0.004	31.8	1.6		<0.015	27	1	
			48.1643	2.2243	04/03/20	0.154	0.002	15.77	0.02	0.036	0.001	22.68	0.02	0.46	0.03	18.0	0.9	
			48.1643	2.2243	23/06/20	0.17	0.01	32	2	0.08	0.01	31.27	0.04		<0.01	27.8	0.9	
R9	16.3	E	48.1643	2.2243	21/09/20	0.173	0.009	32	2	0.092	0.005	29.7	1.6	0.017	0.001	29	2	
			48.1643	2.2243	10/12/20	0.173	0.009	32	2	0.103	0.006	30.0	1.5	0.021	0.003	27	1	
			48.1722	2.3003	04/03/20	0.145	0.002	21.05	0.02	0.0872	0.0005	24.2	0.3	0.311	0.005	21.3	0.2	
			48.1722	2.3003	23/06/20	0.16	0.05	49.7	0.5	0.37	0.03	34.1	0.8		<0.01	30.3	0.5	
R10	17.8	E	48.1722	2.3003	21/09/20	0.177	0.009	55	3	1.83	0.09	32.2	1.6	0.120	0.007	32	2	
			48.1722	2.3003	10/12/20	0.169	0.008	66	4	0.594	0.036	33.8	1.8	0.096	0.006	30	2	
			48.1860	2.3519	04/03/20	0.158	0.002	23.3	0.3	0.1098	0.0005	24.1	0.3	0.218	0.003	19.6	0.1	
			48.1860	2.3519	23/06/20	0.148	0.047	46.7	0.4	0.34	0.02	37.0	0.8		<0.01	27	1	
R11	24.9	F	48.1860	2.3519	21/09/20	0.161	0.009	55	3	1.04	0.05	37.5	2.0	0.055	0.003	29	2	
			48.1860	2.3519	10/12/20	0.153	0.007	56	3	0.56	0.03	46.4	2.4	0.066	0.004	26	1	
			48.0357	2.1307	04/03/20	0.0273	0.0005	5.49	0.02	0.0102	0.0001	0.88	0.03	0.0038	0.0004	2.36	0.03	
			48.1044	2.1934	04/03/20	0.108	0.002	11.55	0.02	0.030	0.001	10.46	0.02	0.203	0.003	10.4	0.1	
T2	8.6	C1	48.1013	2.1636	04/03/20	0.229	0.002	17.91	0.03	0.030	0.001	36.2	0.2	5.0	0.1	19.0	0.1	
T3	10.0	A	48.1101	2.1452	04/03/20	0.108	0.002	10.78	0.02	0.020	0.001	9.51	0.02	0.305	0.003	9.0	0.2	
T4	11.2	E																

1144

1145

Sampling site	Distance km	Geology	Lat.	Long.	Date	Si		Na		K		Mg		Ca	
						±	mg L <sup>-1</sup>	±		±		±		±	
R1	1.1	C1	48.0357	2.1307	04/03/20	4.6	0.1	3.631	0.005	0.45	0.03	0.60	0.05	5.7	0.2
			48.0357	2.1307	23/06/20	5.1	0.2	2.23	0.04	0.52	0.01	0.70	0.01	1.86	0.09
			48.0357	2.1307	21/09/20	2.5	0.1	4.22	0.03	1.09	0.02	0.58	0.03	4.86	0.09
			48.0357	2.1307	10/12/20	4.2	0.1	3.62	0.07	1.16	0.03	0.50	0.01	3.2	0.2
R2	1.6	C1	48.0357	2.1307	04/03/20	4.8	0.2	3.43	0.02	0.54	0.02	0.61	0.07	6.5	0.2
			48.0357	2.1307	23/06/20	5.9	0.1	3.81	0.04	1.71	0.02	1.69	0.01	33.5	0.9
			48.0357	2.1307	10/12/20	7.4	0.1	6.37	0.09	3.90	0.03	3.5	0.3	90	9
R3	4.9	C2	48.0553	2.1736	04/03/20	4.9	0.1	4.8	0.1	1.50	0.06	1.13	0.04	34.2	0.3
			48.0553	2.1736	23/06/20	6.1	0.1	6.8	0.1	3.01	0.05	2.73	0.04	104	2
			48.0553	2.1736	10/12/20	9.6	0.2	12.6	0.3	5.3	0.1	3.6	0.3	114	11
R4	8.2	C2	48.1020	2.1889	04/03/20	4.2	0.1	5.84	0.01	1.64	0.07	1.5	0.1	64	1
R5	9.2	C2	48.1044	2.1931	04/03/20	5.2	0.1	6.3	0.2	1.80	0.02	1.5	0.1	50	1
R6	12.3	E	48.1282	2.1862	04/03/20	5.0	0.0	6.43	0.02	1.98	0.01	1.5	0.1	51	1
			48.1282	2.1862	23/06/20	5.6	0.1	11.2	0.4	2.28	0.01	3.4	0.1	116.0	0.6
R7	14.1	E	48.1429	2.1942	04/03/20	5.2	0.1	6.8	0.1	2.04	0.02	1.8	0.1	58	1
			48.1429	2.1942	23/06/20	6.45	0.01	8.7	0.2	2.39	0.01	4.63	0.03	122	2
			48.1429	2.1942	21/09/20	6.3	0.1	8.9	0.1	2.65	0.02	4.5	0.2	124	3
			48.1429	2.1942	10/12/20	6.98	0.05	9.0	0.1	2.64	0.02	4.9	0.3	129	15
R8	15.3	E	48.1517	2.2001	04/03/20	5.2	0.1	6.83	0.03	2.07	0.03	1.8	0.1	58	1
			48.1517	2.2001	23/06/20	6.4	0.1	8.1	0.2	2.04	0.02	4.9	0.2	121.5	0.8
			48.1517	2.2001	21/09/20	6.5	0.1	8.3	0.1	2.18	0.02	4.8	0.2	125	3
			48.1517	2.2001	10/12/20	7.1	0.1	8.14	0.07	2.09	0.01	5.3	0.3	125	15
R9	16.3	E	48.1587	2.2083	04/03/20	5.3	0.1	7.68	0.01	2.55	0.09	2.3	0.1	64	1
			48.1587	2.2083	23/06/20	6.60	0.04	8.3	0.1	2.44	0.01	5.3	0.2	122	1
			48.1587	2.2083	21/09/20	6.4	0.1	12.1	0.1	7.03	0.09	6.6	0.1	133	1
			48.1587	2.2083	10/12/20	7.0	0.1	8.86	0.07	2.29	0.04	5.7	0.5	129	13
R10	17.8	E	48.1643	2.2243	04/03/20	5.3	0.1	8.4	0.2	2.36	0.03	2.3	0.1	65	1
			48.1643	2.2243	23/06/20	6.5	0.2	10.4	0.1	3.72	0.07	5.8	0.1	124	4
			48.1643	2.2243	21/09/20	6.2	0.1	11.8	0.2	4.32	0.06	5.4	0.2	129	1
			48.1643	2.2243	10/12/20	6.95	0.05	11.7	0.4	4.20	0.04	6.1	0.5	129	18
R11	24.9	F	48.1722	2.3003	04/03/20	5.22	0.04	9.86	0.04	3.66	0.04	2.8	0.1	72	1
			48.1722	2.3003	23/06/20	6.2	0.2	17.6	0.4	15.4	0.5	6.3	0.1	127	2
			48.1722	2.3003	21/09/20	6.1	0.1	24.8	0.4	15.5	0.1	6.2	0.1	126	3
			48.1722	2.3003	10/12/20	6.8	0.1	27.2	0.7	17.2	0.2	7.0	0.2	130	15
R12	29.5	F	48.1860	2.3519	04/03/20	5.1	0.1	10.93	0.03	5.56	0.09	2.8	0.1	71	1
			48.1860	2.3519	23/06/20	5.9	0.1	15.2	0.3	10.4	0.1	6.0	0.1	118	1
			48.1860	2.3519	21/09/20	5.70	0.03	20.2	0.7	18.3	0.3	5.8	0.1	127	5
			48.1860	2.3519	10/12/20	6.3	0.1	21.1	0.4	10.0	0.1	6.5	0.2	131	18
T1	1.5	C1	48.0357	2.1307	04/03/20	6.4	0.1	3.33	0.02	0.43	0.02	0.49	0.05	5.7	0.2
T2	8.6	C1	48.1044	2.1934	04/03/20	6.0	0.1	6.9	0.1	2.0	0.1	1.6	0.1	40	1
T3	10.0	A	48.1013	2.1636	04/03/20	4.6	0.1	9.1	0.1	4.2	0.1	2.1	0.1	86	1
T4	11.2	E	48.1101	2.1452	04/03/20	5.7	0.1	6.3	0.2	1.98	0.05	1.3	0.1	30.8	0.4

1149  
1150

Suppl. Inf. Table 4 : Chemical element concentration (continued) and (<sup>234</sup>U/<sup>238</sup>U) activity ratio measured in the Cēuf river and its tributaries.

Sampling site	Distance km	Geology	Lat.	Long.	Date	$\mu\text{g L}^{-1}$													AR	±
						Sr	±	Ba	±	Fe	±	Mn	±	Se	±	U	±			
R1	1.1	C1	48.0357	2.1307	04/03/20	12.3	0.3	13.9	0.5	186	1	21.7	0.2	0.18	0.02	<b>0.098</b>	0.001	<b>0.92</b>	0.02	
			48.0357	2.1307	23/06/20	<10	<10	1011	37	11.1	0.4	0.18	0.02	<b>0.111</b>	0.001	<b>0.97</b>	0.03			
			48.0357	2.1307	21/09/20	<10	<10	252	8	<10		0.18	0.03	<b>0.0517</b>	0.0004	<b>0.96</b>	0.03			
			48.0357	2.1307	10/12/20	<10	<10	750	20	23.0	0.6	0.15	0.03	<b>0.0197</b>	0.0001	<b>0.95</b>	0.05			
R2	1.6	C1	48.0357	2.1307	04/03/20	12.1	0.9	18	1	225	1	22.5	0.3	0.19	0.01	<b>0.111</b>	0.001	<b>0.96</b>	0.06	
			48.0357	2.1307	23/06/20	38.7	0.2	53.8	0.3	793	23	178	3	0.26	0.02	<b>0.451</b>	0.003	<b>0.93</b>	0.02	
			48.0357	2.1307	10/12/20	73	2	56	2	340	6	268	4	0.13	0.09	<b>0.914</b>	0.004	<b>0.90</b>	0.02	
			48.0553	2.1736	04/03/20	35.9	0.3	47	2	128	1	21.1	0.2	0.40	0.04	<b>1.59</b>	0.01	<b>0.94</b>	0.01	
R3	4.9	C2	48.0553	2.1736	23/06/20	89.4	0.3	178	1	28.7	0.9	18.5	0.4	3.8	0.1	<b>12.35</b>	0.04	<b>0.902</b>	0.002	
			48.0553	2.1736	10/12/20	98	2	211	4	<10		15.4	0.6	0.34	0.07	<b>6.55</b>	0.04	<b>0.87</b>	0.01	
			48.1020	2.1889	04/03/20	63.1	0.4	66	1	93	1	<10		0.51	0.03	<b>2.52</b>	0.02	<b>1.03</b>	0.01	
			48.1044	2.1931	04/03/20	52.9	0.1	63	3	104.4	0.3	10.2	0.1	0.49	0.02	<b>1.99</b>	0.01	<b>1.06</b>	0.02	
R6	12.3	E	48.1282	2.1862	04/03/20	54.0	0.7	62.3	0.4	105	1	<10		0.57	0.02	<b>2.10</b>	0.01	<b>1.00</b>	0.01	
			48.1282	2.1862	23/06/20	163	1	162	2	12.9	0.9	<10		16	1	<b>18.53</b>	0.07	<b>0.51</b>	0.01	
			48.1429	2.1942	04/03/20	65.0	0.4	70	1	85.4	0.5	<10		2.0	0.1	<b>4.06</b>	0.02	<b>0.73</b>	0.01	
			48.1429	2.1942	23/06/20	202	3	202	4	8.5	0.9	<10		17.8	0.2	<b>18.80</b>	0.09	<b>0.47</b>	0.01	
R7	14.1	E	48.1429	2.1942	21/09/20	205	5	185	5	11.7	0.4	<10		13.4	0.4	<b>18.89</b>	0.04	<b>0.45</b>	0.01	
			48.1429	2.1942	10/12/20	217	3	221	3	<10		<10		13.5	0.4	<b>19.27</b>	0.08	<b>0.459</b>	0.004	
			48.1517	2.2001	04/03/20	69.1	0.5	72.6	0.5	103.0	0.6	<10		2.5	0.1	<b>4.78</b>	0.02	<b>0.68</b>	0.01	
			48.1517	2.2001	23/06/20	222	2	188	1	10.1	0.5	<10		17.1	0.1	<b>18.12</b>	0.06	<b>0.473</b>	0.005	
R8	15.3	E	48.1517	2.2001	21/09/20	230	7	173	5	12	1	<10		13.1	0.3	<b>17.30</b>	0.04	<b>0.454</b>	0.005	
			48.1517	2.2001	10/12/20	239	2	194	2	<10		<10		13.0	0.3	<b>17.0</b>	0.1	<b>0.45</b>	0.01	
			48.1587	2.2083	04/03/20	87.4	0.3	79	1	88.1	0.9	<10		7.5	0.2	<b>9.61</b>	0.05	<b>0.57</b>	0.02	
			48.1587	2.2083	23/06/20	238	1	163	1	13.1	0.2	<10		18.7	0.3	<b>18.98</b>	0.10	<b>0.46</b>	0.01	
R9	16.3	E	48.1587	2.2083	21/09/20	253	5	133	4	12.5	0.8	<10		16.8	0.4	<b>15.04</b>	0.03	<b>0.46</b>	0.01	
			48.1587	2.2083	10/12/20	261	4	171	6	<10		<10		14.4	0.5	<b>17.64</b>	0.07	<b>0.45</b>	0.01	
			48.1643	2.2243	04/03/20	89.9	0.4	77.6	0.1	77.1	0.5	<10		9.4	0.1	<b>11.52</b>	0.06	<b>0.54</b>	0.01	
			48.1643	2.2243	23/06/20	247	1	156	2	13	1	<10		19.0	0.2	<b>17.22</b>	0.09	<b>0.45</b>	0.01	
R10	17.8	E	48.1643	2.2243	21/09/20	242	5	138	9	16.2	0.8	<10		13.5	0.5	<b>16.27</b>	0.04	<b>0.45</b>	0.01	
			48.1643	2.2243	10/12/20	262	3	155	2	22	1	<10		13.8	0.4	<b>18.11</b>	0.09	<b>0.444</b>	0.005	
			48.1722	2.3003	04/03/20	115.2	0.4	75	4	76.2	0.2	13.5	0.1	11.0	0.1	<b>11.01</b>	0.06	<b>0.52</b>	0.02	
			48.1722	2.3003	23/06/20	280	4	122	3	26.3	0.6	13.9	0.2	17	2	<b>13.73</b>	0.05	<b>0.45</b>	0.01	
R11	24.9	F	48.1722	2.3003	21/09/20	293	6	121	3	25	1	<10		12.6	0.3	<b>12.74</b>	0.04	<b>0.43</b>	0.01	
			48.1722	2.3003	10/12/20	307	3	122	2	49	1	18.3	0.4	12.3	0.4	<b>13.71</b>	0.09	<b>0.43</b>	0.01	
			48.1860	2.3519	04/03/20	123.5	0.4	72.8	0.4	94	1	16.5	0.3	9	1	<b>8.20</b>	0.04	<b>0.54</b>	0.02	
			48.1860	2.3519	23/06/20	282	4	111	2	26.0	0.7	<10		17.0	0.2	<b>13.24</b>	0.05	<b>0.43</b>	0.01	
R12	29.5	F	48.1860	2.3519	21/09/20	286	4	111	1	23.7	0.2	<10		12.7	0.3	<b>12.21</b>	0.03	<b>0.414</b>	0.003	
			48.1860	2.3519	10/12/20	301	3	108	2	41	1	<10		12.6	0.2	<b>12.79</b>	0.05	<b>0.41</b>	0.01	
			48.0357	2.1307	04/03/20	8.8	0.4	15	2	205	1	<10		0.16	0.01	<b>0.110</b>	0.001	<b>0.95</b>	0.03	
			48.1044	2.1934	04/03/20	46	1	62	3	117	1	13.8	0.3	0.48	0.02	<b>1.57</b>	0.01	<b>1.04</b>	0.02	
T2	8.6	C1	48.1013	2.1636	04/03/20	82	1	78	3	38.3	0.5	<10		0.78	0.04	<b>4.07</b>	0.02	<b>0.81</b>	0.01	
T4	11.2	E	48.1101	2.1452	04/03/20	36.9	0.3	21	2	275.9	0.4	<10		0.26	0.02	<b>0.76</b>	0.01	<b>0.98</b>	0.04	

1151

1152

Groundwater code	Borehole national code	BLAS unit	Dataset	$\sigma$ (25°C)	ORP	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Ca	Mg	Se	U	( <sup>234</sup> U/ <sup>238</sup> U)	
				$\mu\text{S cm}^{-1}$	mV	mg L <sup>-1</sup>		$\mu\text{g L}^{-1}$					
				2001–2020		1997–2020	1991–2020	1997–2020		1998–2020	2012–2018		
GW1	BSS001AAZQ	Orléanais limestone formation	Period	2001–2020		1997–2020	1991–2020	1997–2020		1998–2020	2012–2018		
			n	37		35	54	13	13		38	4	4
			min	543	ND	20	21	94	4		7	10	0.37
			MAX	631		25	36	109	5		15	11	0.38
			mean	572		23	29	103	5	11	11	0.38	
GW2	BSS001AAWC	Pithiviers limestones	Period	2005–2006		2001–2006							
			n	4	10	11	10	11	11				
			min	605	100	25	45	96	5			ND	
			MAX	800	268	71	54	121	6				
			mean	691	150	49	45	111	6				
GW3	BSS000YEJL	Pithiviers limestones	Period	2001–2021		1992–2021	1991–2021	1992–2020		1998–2021	2011		
			n	38		40	72	17	17		44	1	1
			min	503	ND	16	34	85	4.1		5	7.3	0.32
			MAX	585		28	55	102	5.3		12	7.3	0.32
			mean	554		23	44	95	5	9	7.3	0.32	
GW4	BSS000YFHV	Pithiviers limestones + Etampes limestones	Period	2001–2021		1991–2021				2010–2021	2009–2020		
			n	47		49	34	31	31		15	6	6
			min	532	ND	19	0.10	95	7		2	11	0.43
			MAX	646		24	1.1	112	8.3		3	12	0.47
			mean	586		22	0.55	102	7	2	12	0.45	

1153

1154

1155

Suppl. Inf. Table 5 : Characteristics of the groundwater extracted from the BLAS aquifer units featured in the *Œuf* river catchment. Data are available from the French national web portal ADES (<https://ades.eaufrance.fr/>).

1156

1157 *Suppl. Inf. Table 6 : Correlation coefficient between the analytes measured in the Cēuf river.*

T	pH	Eh	EC	TC	DIC	DOC	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	Si	Na	K	Mg	Ca	Sr	Ba	Fe	Mn	Se	U	AR	
<b>1.00</b>	-0.20	0.34	0.24	0.31	0.33	-0.28	0.18	0.24	0.29	0.34	-0.07	0.02	-0.06	0.14	0.19	0.27	0.24	0.49	0.43	0.02	-0.05	0.43	0.35	-0.27	T
	<b>1.00</b>	0.08	-0.10	-0.08	-0.08	0.01	0.21	-0.11	-0.17	0.15	0.55	-0.10	0.02	-0.06	-0.24	-0.17	-0.06	-0.22	-0.01	-0.42	-0.17	-0.06	-0.06	-0.14	pH
		<b>1.00</b>	-0.23	-0.15	-0.14	0.01	0.01	-0.12	-0.08	0.01	0.19	-0.65	-0.44	-0.18	-0.22	-0.28	-0.23	-0.10	0.10	0.004	-0.66	-0.04	-0.01	0.11	Eh
			<b>1.00</b>	<b>0.84</b>	<b>0.97</b>	<b>-0.91</b>	0.75	<b>0.91</b>	0.48	<b>0.87</b>	-0.21	0.67	0.68	0.79	0.66	<b>0.96</b>	<b>0.98</b>	<b>0.94</b>	0.71	-0.64	0.01	<b>0.81</b>	<b>0.83</b>	<b>-0.84</b>	EC
				<b>1.00</b>	<b>0.98</b>	<b>-0.87</b>	0.62	0.79	0.47	0.70	-0.11	0.56	0.56	0.70	0.60	0.79	<b>0.81</b>	0.74	0.57	-0.51	0.07	0.71	0.70	-0.68	TC
					<b>1.00</b>	<b>-0.94</b>	0.75	<b>0.86</b>	0.42	<b>0.85</b>	-0.15	0.61	0.67	0.71	0.57	<b>0.93</b>	<b>0.97</b>	<b>0.92</b>	0.78	-0.63	-0.05	<b>0.86</b>	<b>0.88</b>	<b>-0.82</b>	DIC
						<b>1.00</b>	-0.65	<b>-0.88</b>	-0.42	<b>-0.82</b>	-0.17	-0.54	-0.58	-0.76	-0.62	<b>-0.87</b>	<b>-0.94</b>	<b>-0.86</b>	<b>-0.84</b>	0.67	0.28	<b>-0.80</b>	<b>-0.88</b>	0.72	DOC
							<b>1.00</b>	0.61	0.26	<b>0.88</b>	0.09	0.30	0.32	0.51	0.33	0.69	0.76	0.69	0.55	-0.71	-0.30	0.75	0.78	-0.77	F <sup>-</sup>
								<b>1.00</b>	0.68	0.79	-0.26	0.47	0.53	<b>0.95</b>	<b>0.85</b>	<b>0.89</b>	<b>0.83</b>	<b>0.89</b>	0.49	-0.56	-0.26	0.72	0.68	-0.76	Cl <sup>-</sup>
									<b>1.00</b>	0.38	-0.23	0.20	0.10	0.79	<b>0.81</b>	0.47	0.34	0.51	0.02	-0.21	-0.19	0.26	0.17	-0.37	Br <sup>-</sup>
										<b>1.00</b>	-0.04	0.36	0.38	0.64	0.50	<b>0.83</b>	<b>0.85</b>	<b>0.86</b>	0.59	-0.74	-0.46	<b>0.83</b>	<b>0.83</b>	<b>-0.83</b>	NO <sub>3</sub> <sup>-</sup>
											<b>1.00</b>	-0.08	-0.06	-0.23	-0.22	-0.37	-0.17	-0.48	-0.09	-0.23	-0.20	-0.36	-0.21	0.26	PO <sub>4</sub> <sup>3-</sup>
												<b>1.00</b>	0.67	0.40	0.34	0.61	0.70	0.41	0.43	-0.40	0.56	0.41	0.48	-0.42	SO <sub>4</sub> <sup>2-</sup>
													<b>1.00</b>	0.39	0.26	0.66	0.74	0.47	0.73	-0.32	0.29	0.43	0.56	-0.45	Si
														<b>1.00</b>	<b>0.92</b>	0.77	0.67	0.75	0.25	-0.47	-0.20	0.55	0.48	-0.65	Na
															<b>1.00</b>	0.65	0.51	0.64	0.07	-0.31	-0.11	0.41	0.28	-0.49	K
																<b>1.00</b>	<b>0.94</b>	<b>0.98</b>	0.65	-0.54	0.04	<b>0.86</b>	<b>0.82</b>	<b>-0.86</b>	Mg
																	<b>1.00</b>	<b>0.91</b>	<b>0.83</b>	-0.67	0.05	<b>0.83</b>	<b>0.89</b>	<b>-0.82</b>	Ca
																		<b>1.00</b>	0.63	-0.53	-0.22	<b>0.87</b>	<b>0.82</b>	<b>-0.88</b>	Sr
																			<b>1.00</b>	-0.54	-0.25	0.66	<b>0.85</b>	-0.58	Ba
																				<b>1.00</b>	0.29	-0.58	-0.64	0.58	Fe
																					<b>1.00</b>	-0.28	-0.33	0.20	Mn
																						<b>1.00</b>	<b>0.93</b>	<b>-0.93</b>	Se
																							<b>1.00</b>	<b>-0.89</b>	U
																								<b>1.00</b>	AR

1158

1159

1160 *Suppl. Inf. Table 7 : Modelled speciation of U aqueous species in the Cēuf river.*

Sampling site	Distance km	Sampling date	U	U(IV)	U(VI)	UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	UO <sub>2</sub> (CO <sub>3</sub> ) <sub>4</sub> <sup>3-</sup>	UO <sub>2</sub> (CO <sub>3</sub> )	UO <sub>2</sub> (HPO <sub>4</sub> ) <sub>2</sub> <sup>2-</sup>	UO <sub>2</sub> OH <sup>+</sup>	UO <sub>2</sub> <sup>2+</sup>	Σ(U – CO <sub>3</sub> )	Σ(U – PO <sub>4</sub> ) %	Other U(VI)
mol L <sup>-1</sup>														
R1	1.1	04/03/20	4.2E-10	1.9E-28	4.2E-10	2.0E-12	4.3E-14	1.9E-12	4.2E-10	3.9E-14	8.6E-15	0.9	99.0	0
R2	1.6	04/03/20	4.6E-10	1.4E-25	4.6E-10	1.3E-10	1.1E-12	3.2E-10	0.0E+00	7.0E-12	3.8E-12	97.6	0	2.3
R3	4.9	04/03/20	6.7E-09	2.9E-27	6.7E-09	3.0E-11	2.4E-11	8.7E-13	6.6E-09	2.5E-15	1.7E-16	0.8	99.2	0
R4	8.2	04/03/20	1.1E-08	1.4E-29	1.1E-08	6.4E-10	2.5E-09	4.6E-12	7.5E-09	8.0E-15	2.6E-16	29.6	70.4	0
R5	9.2	04/03/20	8.4E-09	1.2E-26	8.4E-09	3.4E-10	8.9E-10	3.4E-12	7.1E-09	6.9E-15	2.4E-16	14.7	85.3	0
R6	12.3	04/03/20	8.8E-09	3.4E-27	8.8E-09	8.9E-11	3.0E-10	6.5E-13	8.4E-09	1.3E-15	3.5E-17	4.4	95.6	0
R7	14.1	04/03/20	1.7E-08	4.0E-28	1.7E-08	1.2E-10	3.2E-10	1.2E-12	1.7E-08	2.3E-15	9.5E-17	2.6	97.4	0
R8	15.3	04/03/20	2.0E-08	2.7E-27	2.0E-08	1.2E-10	3.2E-10	1.2E-12	2.0E-08	2.5E-15	9.4E-17	2.2	97.8	0
R9	16.3	04/03/20	4.0E-08	9.4E-28	4.0E-08	4.3E-10	1.4E-09	3.5E-12	3.9E-08	5.5E-15	2.3E-16	4.5	95.5	0
R10	17.8	04/03/20	4.8E-08	3.3E-26	4.8E-08	5.7E-10	1.8E-09	4.9E-12	4.6E-08	7.8E-15	3.2E-16	5.0	95.0	0
R11	24.9	04/03/20	4.6E-08	1.0E-25	4.6E-08	1.4E-09	5.1E-09	1.1E-11	4.0E-08	1.6E-14	6.7E-16	14.0	86.0	0
R12	29.5	04/03/20	3.4E-08	8.7E-29	3.4E-08	3.9E-10	5.5E-10	8.6E-12	3.4E-08	1.1E-14	1.5E-15	2.8	97.2	0
R3	4.9	23/06/20	5.2E-08	2.4E-32	5.2E-08	1.4E-09	3.4E-09	7.1E-12	4.7E-08	0	0	9.3	90.7	0
R6	12.3	23/06/20	7.8E-08	2.8E-28	7.8E-08	2.1E-08	5.4E-08	7.7E-11	2.1E-09	0	0	97.3	2.7	0
R10	17.8	21/09/20	6.8E-08	3.8E-27	6.8E-08	2.1E-08	4.7E-08	1.5E-10	8.4E-10	0	0	98.8	1.2	0
R11	24.9	21/09/20	5.4E-08	2.6E-27	5.4E-08	1.2E-08	3.3E-08	4.8E-11	8.9E-09	0	0	83.4	16.6	0
R12	29.5	21/09/20	5.1E-08	6.8E-23	5.1E-08	8.0E-09	9.0E-10	1.1E-09	4.1E-08	0	0	19.4	80.6	0
R1	1.1	10/12/20	8.3E-11	7.6E-30	8.3E-11	4.8E-14	7.9E-16	8.1E-14	8.2E-11	0	0	0.2	99.8	0
R2	1.6	10/12/20	3.8E-09	7.3E-13	3.8E-09	5.3E-11	3.9E-11	3.1E-12	3.7E-09	0	0	2.5	97.5	0
R3	4.9	10/12/20	2.8E-08	5.1E-27	2.8E-08	6.1E-10	4.5E-09	4.0E-12	2.2E-08	0	0	18.4	81.6	0
R7	14.1	10/12/20	8.1E-08	1.1E-24	8.1E-08	1.7E-08	5.8E-08	1.7E-10	6.0E-09	0	0	92.6	7.4	0
R8	15.3	10/12/20	7.1E-08	4.4E-25	7.1E-08	1.3E-08	5.7E-08	9.4E-11	8.6E-10	0	0	98.8	1.2	0
R10	17.8	10/12/20	7.6E-08	5.7E-22	7.6E-08	1.8E-08	5.5E-08	1.9E-10	2.9E-09	0	0	96.2	3.8	0
R11	24.9	10/12/20	5.8E-08	5.5E-23	5.8E-08	6.8E-09	4.2E-08	3.9E-11	8.4E-09	0	0	85.5	14.5	0
R12	29.5	10/12/20	5.4E-08	1.6E-27	5.4E-08	4.1E-09	4.9E-08	1.4E-11	9.4E-10	0	0	98.3	1.7	0

1161

1162

1163 **Supplementary information – Materials and methods**

1164 **Reagents, materials and solutions**

1165 All the solutions were prepared with deionized water (18.2 MΩ cm<sup>-1</sup> resistivity, Milli-Q water,  
1166 Millipore). High purity acids were obtained by distillation (Savillex DST-1000 system) from HCl (Merck,  
1167 Emsure 37 %) and HNO<sub>3</sub> (VWR Chemicals, Normapur 68 %). The following chemicals were used:  
1168 Na<sub>2</sub>CO<sub>3</sub> (VWR Chemicals, Analar Normapur), Na<sub>2</sub>CO<sub>3</sub> (VWR Chemicals, Analar Normapur), C<sub>8</sub>H<sub>5</sub>KO<sub>4</sub>  
1169 (VWR Chemicals, Analar Normapur), H<sub>3</sub>PO<sub>4</sub> (VWR Chemicals, Normapur 85 %), UTEVA resin (100-  
1170 150 μm mesh, Triskem international). The following standard solutions were used: uranium standard  
1171 solution (1 g L<sup>-1</sup>, matrix 2 % HNO<sub>3</sub>, CPACem), multi-element standard solution VIII (24 elements,  
1172 100 mg L<sup>-1</sup>, matrix 6 % HNO<sub>3</sub>, Supelco, Certipur), anion chromatography standard solution including Cl<sup>-</sup>  
1173 , Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> (100 mg L<sup>-1</sup>; matrix deionized water, CPACem).

1174 **Chemical analyses**

1175 Concentration of anions SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, Br<sup>-</sup> and PO<sub>4</sub><sup>3-</sup> was measured using ionic chromatography  
1176 (Metrohm 930 Compact IC) equipped with trap (Metrosep C; 37 – 74 μm particle diameter 4 mm i.d. ×  
1177 30 mm), guard column (Metrosep A Supp 5; 5 μm particle diameter, 4 mm i.d. × 5 mm) coupled with  
1178 analytical column (Metrosep A Supp 5; 5 μm particle diameter, 4 mm i.d. × 150 mm), a 250 μL PEEK  
1179 injection loop, a thermostatic column oven set at 35.0 ± 0.1°C, a mobile phase containing 3.2 mmol L<sup>-1</sup>  
1180 <sup>1</sup>Na<sub>2</sub>CO<sub>3</sub> and 1 mmol L<sup>-1</sup> NaHCO<sub>3</sub>, a MSM suppressor using regenerant solution containing 500 mmol L<sup>-1</sup>  
1181 <sup>1</sup>H<sub>3</sub>PO<sub>4</sub>, and a conductivity detector. The flow rate of mobile phase was fixed at 700 μL min<sup>-1</sup>. Standard  
1182 solutions were freshly prepared in deionized water.

1183 Total dissolved carbon (TC) was determined by measuring the CO<sub>2</sub> released after combustion at 850 °C,  
1184 using a carbon analyzer (Elementar TOC Vario). Dissolved inorganic carbon (DIC) was determined on  
1185 another aliquot by measuring the amount of CO<sub>2</sub> released after acidification with a 1 M H<sub>3</sub>PO<sub>4</sub> solution  
1186 (final pH < 2). Dissolved organic carbon (DOC) then was calculated by subtracting DIC from TC.

1187 Concentration of the chemical elements Ca, Na, K, Si, Mg, Ba and Sr was determined using ICP-OES  
1188 (Thermo Fisher Scientific iCAP 7600 Duo). Calibration standards were prepared in 0.3 M HNO<sub>3</sub> in the  
1189 range of 0.02 – 30 mg L<sup>-1</sup>.

1190 The determination of U and Se concentrations and (<sup>234</sup>U/<sup>238</sup>U) activity ratio was performed using  
1191 Agilent 8800 Inductively coupled plasma-Tandem mass spectrometry ICP-MS/MS (Agilent  
1192 Technologies, Tokyo, Japan) equipped with an octupole collision/reaction cell (CRC) situated between  
1193 two mass-selecting analysers. A Peltier-cooled (2 °C) Scott-type spray chamber with a MicroMist  
1194 nebulizer (*ca.* 400 μL min<sup>-1</sup>) was employed as introduction system. For Se concentration, ICP-MS/MS  
1195 analysis was conducted by using the MS/MS with pure oxygen (≥ 99.999 %, Air Products, Aubervilliers,  
1196 France) as reaction gas (Balcaen, Bolea-fernandez, Resano, & Vanhaecke, 2015; Gronbaek-Thorsen,  
1197 Stürup, Gammelgaard, & Hyrup Moller, 2019). The oxygen flow rate in CRC was fixed at 3.5 L min<sup>-1</sup>.  
1198 Selenium was measured in mass shift mode on *m/z* 94 (<sup>78</sup>Se<sup>16</sup>O<sup>+</sup>). Rhodium as internal standard was  
1199 added with a T-piece, and its initial signal on *m/z* 103 (<sup>103</sup>Rh<sup>+</sup>) was 50,000 – 70,000 cps. Standard Se  
1200 solutions (up to 10 μg L<sup>-1</sup>) were prepared in 300 mmol L<sup>-1</sup> HNO<sub>3</sub>. The single MS mode was used to  
1201 quantify U concentration in sample aliquots, following a measurement protocol already described  
1202 (Gourgiotis et al., 2020). The activity of U isotopes was calculated from the analytical response of the  
1203 double isotope reference standard (IRMM 3636) and was corrected from the instrumental mass bias  
1204 factor using the reference value (Condon, McLean, Noble, & Bowring, 2010; Richter et al., 2008).

1205