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## An integrated approach combining soil profile, records and tree ring analysis to identify the origin of environmental contamination in a former uranium mine (Rophin, France)

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1 **An integrated approach combining soil profile, records and tree ring analysis**  
2 **to identify the origin of environmental contamination in a former uranium**  
3 **mine (Rophin, France)**

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## 20 **Highlights**

- 21 • Origin of contamination near Rophin tailings storage site: natural vs. anthropogenic
- 22 • A whitish silt loam soil layer in a wetland was associated with a high U content.
- 23 • Dating and records indicate that U was deposited during previous mining activities.
- 24 • U mineral particles transported by turbid waters were deposited in a wetland.
- 25 • Dendroanalysis shows an uptake of  $^{238}\text{U}$  linked to the mining activity period.

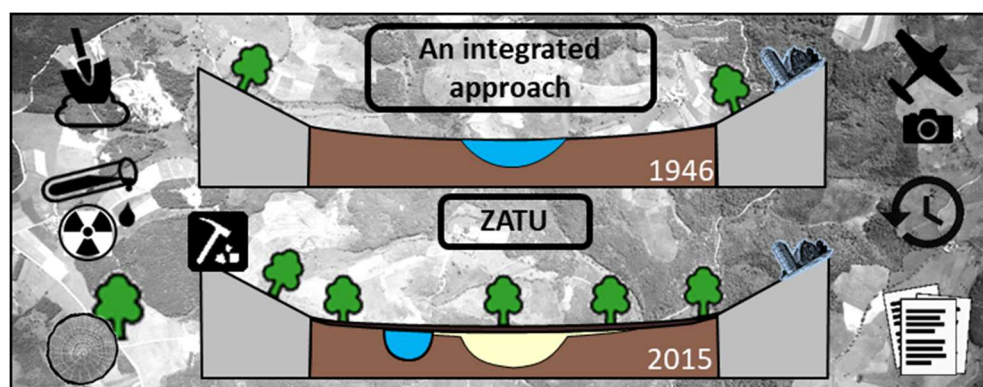
## 26 **Abstract**

27 Uranium mining and milling activities raise environmental concerns due to the release of  
28 radioactive and other toxic elements. Their long-term management thus requires a  
29 knowledge of past events coupled with a good understanding of the geochemical  
30 mechanisms regulating the mobility of residual radionuclides. This article presents the  
31 results on the traces of anthropic activity linked to previous uranium (U) mining activities in  
32 the vicinity of the Rophin tailings storage site (Puy de Dôme, France). Several  
33 complementary approaches were developed based on a study of the site's history and  
34 records, as well as on a radiological and chemical characterization of soil cores and a  
35 dendrochronology. Gamma survey measurements of the wetland downstream of the Rophin  
36 site revealed a level of  $1,050 \text{ nSv}\cdot\text{h}^{-1}$ . Soil cores extracted in the wetland showed U  
37 concentrations of up to  $1,855 \text{ mg}\cdot\text{kg}^{-1}$ , which appears to be associated with the presence of a  
38 whitish silt loam (WSL) soil layer located below an organic topsoil layer. Records,  
39 corroborated by prior aerial photographs and analyses of  $^{137}\text{Cs}$  and  $^{14}\text{C}$  activities, suggest the  
40 discharge of U mineral particles while the site was being operated. Moreover, lead isotope  
41 ratios indicate that contamination in the WSL layer can be discriminated by a larger  
42 contribution of radiogenic lead to total lead. The dendroanalysis correlate U emissions from

43 Rophin with the site's history. Oak tree rings located downstream of the site contain  
44 uranium concentrations ten times higher than values measured on unaffected trees.  
45 Moreover, the highest U concentrations were recorded not only for the operating period,  
46 but more surprisingly for the recent site renovations as well. This integrated approach  
47 corroborates that U mineral particles were initially transported as mineral particles in  
48 Rophin's watershed and that a majority of the deposited uranium appears to have been  
49 trapped in the topsoil layer, with high organic matter content.

50

## 51 Graphical abstract



52

## 53 Keywords

54 Uranium mining, wetland, records, dendroanalysis, radiochronology, U decay chain.

## 55 1. Introduction

56 Uranium (U) is a key resource that has been mined in France for use in the nuclear energy  
57 industry from 1948 to 2001. Uranium mining and milling activities, as well as mineral  
58 processing plants, raise environmental concerns due to the possible release of radioactive  
59 and other potentially toxic elements (Ljungberg and Öhlander, 2001; Lottermoser and

60 Ashley, 2005). The impact of U release into the environment is governed by the U speciation,  
61 which influences its solubility, mobility and bioavailability (Abdelouas, 2006). In areas  
62 unaffected by human activity, the inflow of U is considered to be primarily related to its  
63 dissolved or colloidal species; in the vicinity of mines on the other hand, its transport can  
64 also occur in the form of U mineral particles. Even though in Western Europe most U mines  
65 were shut down over the course of the past few decades, these former mines and especially  
66 their associated tailings storage sites are subject to continuous environmental monitoring  
67 (Ballini et al., 2020). In addition to the environmental monitoring of storage sites, it is also  
68 critical to consider the environment potentially contaminated near the mines. This  
69 consideration becomes even more important since the land may now be privately owned  
70 (Mangeret *et al.*, 2018).

71 In the vicinity of U mines, wetlands prove to be particular natural zones since they act as  
72 physical particle and metal traps. Numerous studies have indeed found highly increased U  
73 concentrations in wetlands, extending into the several thousand mg.kg<sup>-1</sup>; this observation  
74 has been recorded in areas affected by mining activities (Li et al., 2014; Mangeret et al.,  
75 2018; Schöner et al., 2009; Wang et al., 2014) as well as areas with granitic bedrock  
76 subjected to naturally elevated U concentrations in groundwater (Mikutta et al., 2016; Owen  
77 and Otton, 1995; Regenspurg et al., 2010; Zielinski et al., 1986). The accumulation of U is  
78 explained by complexation with organic matter (OM) present at high concentrations in  
79 wetlands (Bordelet et al., 2018) and/or by reduction of U(VI) to scarcely soluble U(IV) due to  
80 strongly reducing conditions related to the bacterial degradation of plant material (Alessi et  
81 al., 2012; Cumberland et al., 2016; Lovley et al., 1991; Nakashima et al., 1984; Newsome et  
82 al., 2015). However, it must be noted that the observed contaminations may be of natural

83 origin, without the involvement of any human action. Weathering and erosion of the local  
84 bedrock, which is often granitic in the case of French U mines, can also play a major role in  
85 increasing these concentration levels. High U contents have in fact already been  
86 documented at sites not heavily impacted by mining activities, such as Alpine soils (up to  
87 4,000 mg.kg<sup>-1</sup>), or by ground and surface waters, where the surrounding bedrock mainly  
88 consists of crystalline rocks that commonly contain trace amounts of U (Gourgiotis *et al.*,  
89 2020).

90 It is essential to not only report any past contamination linked to uranium mining, but also  
91 trace the origin of such contamination over these sites, i.e. natural vs. anthropogenic. This  
92 question corresponds to the focus of this article combining different approaches, featuring  
93 both direct knowledge of past events and an analysis of the records or characterization of  
94 environmental indicators like soil and vegetation.

95 In the absence of first-hand recollections of details surrounding the period of operations (Le  
96 Berre and Bretesché, 2019), the knowledge of past contaminations requires a rigorous study  
97 of historical evidence, mostly documents (regulatory and technical reports) and, ideally, a  
98 direct consultation of various records like raw data without operator interpretation. For  
99 example, a study of site history combined with satellite images or previous aerial  
100 photographs has been used to determine how tailings were deposited in ponds, e.g. disposal  
101 of tailings at the Cominak mine in Niger (Déjeant *et al.*, 2016) or at the Bois Noirs mine in  
102 France (Chautard *et al.*, 2020).

103 Concerning the soil analysis, an initial possibility consists of correlating the observed  
104 contaminations with dating approaches, i.e. <sup>137</sup>Cs and/or <sup>14</sup>C (Cuvier *et al.*, 2016). It should  
105 be noted that excessive use of <sup>210</sup>Pb is unfortunately impossible in a U mining context (Reyss

106 *et al.*, 2016). The origin of these U markings, whether natural or anthropogenic, can then  
107 also be traced by means of lead isotopy (Bollhöfer, 2012; Bollhöfer *et al.*, 2006; Cuvier *et al.*,  
108 2016; Gourgiotis *et al.*, 2020).

109 Concerning vegetation, past contaminations can be retrieved through dendroanalysis. This  
110 step consists of measuring the distribution of trace elements in the annual growth rings of  
111 trees; it is based on the assumption that trace elements remain immobile once deposited in  
112 the stem. Such a premise has raised controversy in the literature (Hagemeyer, 2000; Nabaisa  
113 *et al.*, 1999). The method has been implemented on a variety of tree species in order to  
114 correlate trace metal concentrations with the pollution history at various locations  
115 (Beramendi-Orosco *et al.*, 2013; Pearson *et al.*, 2005; Watmough and Hutchinson, 1996). The  
116 Cornish oak, *Quercus petraea*, has been repeatedly reported as a suitable indicator of  
117 changes in bioavailable trace metal concentrations in an environment with trees over time  
118 (Cutter and Guyette, 1993; Jonsson *et al.*, 1997; Perone *et al.*, 2018). Furthermore, oak tree  
119 rings have been tested for use in biomonitoring uranium (Edmands *et al.*, 2001), specifically  
120 in the vicinity of former mining activities (Märten *et al.*, 2015; Monticelli *et al.*, 2009). This  
121 approach however accounts for contamination by soluble, hence bioavailable, metals with  
122 root capture generally being predominant (Lepp, 1975).

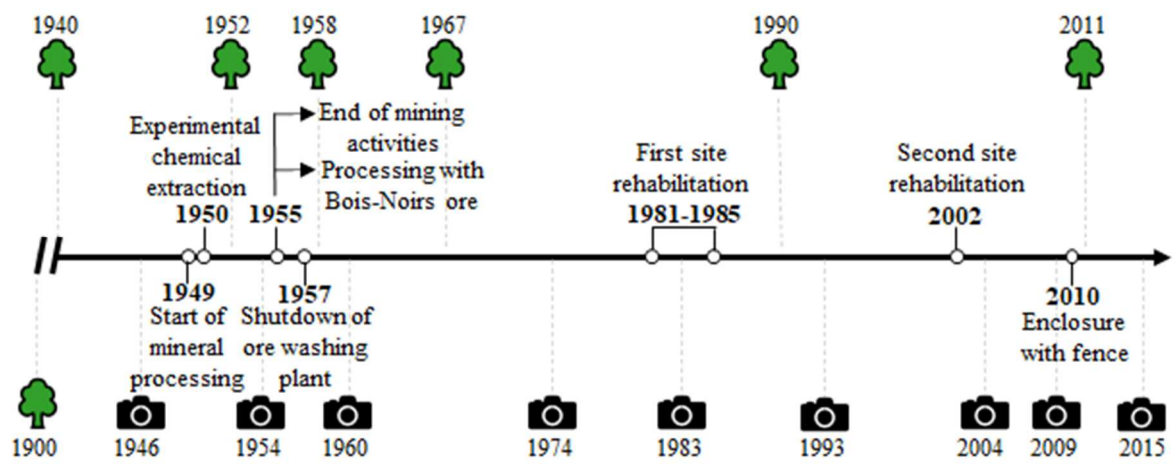
123 In summary, several complementary approaches are possible, each providing information, to  
124 characterize the origin of past contaminations. The ambition of this work is therefore to  
125 combine all these approaches to assess the origin of a contaminated wetland around the  
126 Rophin site (Puy-de-Dôme, France). Among the 16 sites chosen to store U waste in France  
127 (IRSN, 2018) and, as such, classified as an ICPE installation necessitating environmental  
128 protections, it was recently integrated into France's network of pilot study zones, under the

129 ZATU (*Zone Atelier Territoires Uranifères*) created in 2015. This network is part of the Long-  
130 Term Ecosystem Research ongoing in Europe (Bretagnolle et al., 2019). In this work, the  
131 results obtained from surface gamma surveys are compared with soil core analyses (lead  
132 isotopy, dating approaches, uranium and decay products) and dendrochronology, as well  
133 with information obtained from mine operating history through reliance on different sources  
134 in order to reconstitute the events leading to the current state of the Rophin site and its  
135 immediate environs.

## 136 2. Study site

137 The Rophin site lies within the Forez range east of the Limagne Graben, in the northeastern  
138 part of the Puy de Dôme department, close to the city of Lachaux (Fig. S1) and was among  
139 several mines referenced as Western Lachaux ore bodies (Fig. S2). In this area, the mean  
140 annual, temperature is 10.1°C with mean annual precipitations of 800 mm  $\gamma^{-1}$  (Météo-  
141 France, [www.meteofrance.com](http://www.meteofrance.com)). In the global context, Western Lachaux ore bodies appear  
142 as exceptional due to the predominance of parsonsite ( $\text{Pb}_2(\text{UO}_2)(\text{PO}_4)_2, 2\text{H}_2\text{O}$ ) under a  
143 workable deposit rather than an alteration product of pitchblende. The ore bodies are  
144 hosted by coarse-grained peraluminous granite of the alkaline type, like “Bois Noirs” granite,  
145 situated at the end of Variscan orogeny (Fig. S1). These bodies consist of low-temperature  
146 silica/quartz containing uranyl phosphate minerals, mainly parsonsite and, at the oxidized  
147 ore surface, both autunite ( $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2, 8-12 \text{H}_2\text{O}$ ) and tobernite ( $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2, 12\text{H}_2\text{O}$ )  
148 (Greffoy and Sarcia, 1955; Himeur and Andres, 2012). The principal events in the history of  
149 the Rophin mine have been summarized in a timeline (Fig. 1) with further details in Fig. S3.





150

151 Fig. 1: Timeline of Rophin mine operations with time-stamped aerial photographs (Fig. S6)  
 152 and the sampling strategy for tree ring analysis

153 To treat the materials extracted in the Western Lachaux sector, a mechanical ore washing  
 154 plant was built in 1948 next to the Rophin mine (Fig. S4 and Fig. S5). At first, ore treatment  
 155 was gravimetric with a vibrating table, crushing machines and a flotation circuit that  
 156 included 3 settling ponds to retain U particles (Himeur and Andres, 2012). In all, fewer than  
 157 30 tons of U were extracted from mine tailings, at a mean concentration rate of 0.7‰, and  
 158 then exported as 4.4% concentrates. Over 30,000 tons of mine and mill tailing waste were  
 159 stored on the site of the former processing plant (ICPE, see hachured area in Fig. 2).

160 Nowadays, the storage site is covered by vegetated soil, and forest vegetation is growing at  
 161 the top of the mine waste storage heap. Periodic water effluents from the underground  
 162 galleries are collected in a trench located in the western part of the Rophin ICPE. These  
 163 effluents join the “Le Gourgeat” stream heading in a NW-S direction; the stream is  
 164 connected to the five local ore bodies in the same watershed and moreover contributes to  
 165 the formation of a local wetland 200 m downstream of the Rophin site (Fig. S4). During the  
 166 period of mining operations, the Gourgeat watershed was closed 2 km downstream of the  
 167 Rophin site by a dam used as a water storage reservoir for water supply of the upper ore

168 washing plant before its ultimate connection with the Terrasson stream. A general map of  
169 the Gourgeat watershed, with other former U mines, is presented in Fig. S2. A biannual  
170 control of the uranium and radium concentrations in the effluent waters was set up as part  
171 of the ICPE site supervision program. Moderately high aqueous U concentrations have been  
172 detected in the trench collecting effluent waters running inside the ICPE, with values at  
173 times reaching 200  $\mu\text{g.L}^{-1}$  (Himeur and Andres, 2012).

174 The former Rophin mine has been chosen as study site for a variety of reasons. It is now  
175 uninhabited where vegetation grows on mine tailings, stored *in situ*, coupled with the  
176 presence of a creek (Gourgeat) running in the watershed and a wetland downstream of the  
177 storage area. The site offers a framework for conducting multidisciplinary scientific  
178 investigations on life under natural radioactivity in ZATU context.

## 179 3. Materials and Methods

### 180 3.1. Methodology for studying the history of mining operations

181 Generally speaking, French U mine operations have often been overlooked by residents (Le  
182 Berre and Bretesché, 2019), and former operators (CEA, COGEMA, AREVA and now ORANO)  
183 owned most of the records. In an effort to retrace the history of site operations as accurately  
184 as possible, several data sources were consulted:

185 (i) A compilation of data retracing the site history through: the operator's archivist and mine  
186 specialists (Guiollard, 2002), regulatory reports on environmental monitoring (Himeur, 2010;  
187 Himeur and Andres, 2012), technical reports on mine operations (Greffoy and Sarcia, 1955),  
188 and other independent environmental associations (Commission for Independent Research  
189 and Information on RADiation and the Puy de Dôme environment association).

190 (ii) A direct consultation of the records held by the Auvergne-Rhône-Alpes DREAL (Regional  
191 Directorate for the Environment, Land Planning and Housing) made available for onsite  
192 consultation in February and March 2017. These documents contain raw uninterpreted data  
193 from operators, including administrative and regulatory documents, inspection reports,  
194 correspondence between operators and oversight agencies, press articles and documents  
195 relative to mine operations (map, fees, etc.). A summary of the documents consulted,  
196 arranged in chronological order, is available in Fig. S3, Fig. S5 and Table S14.

197 (iii) A collection of aerial photographs available from the "Geoportail" database (National  
198 Geographic Institute (IGN)), allowing for observations of the site before, during and after  
199 mining operations (Fig. S6). Nine archived aerial photographs, with a spatial resolution of 50  
200 cm.pixel<sup>-1</sup> and a planimetric accuracy of less than 2 m, were projected into a WGS84 (World  
201 Geodetic System 1984) using QGIS (Quantum Geographic Information System).

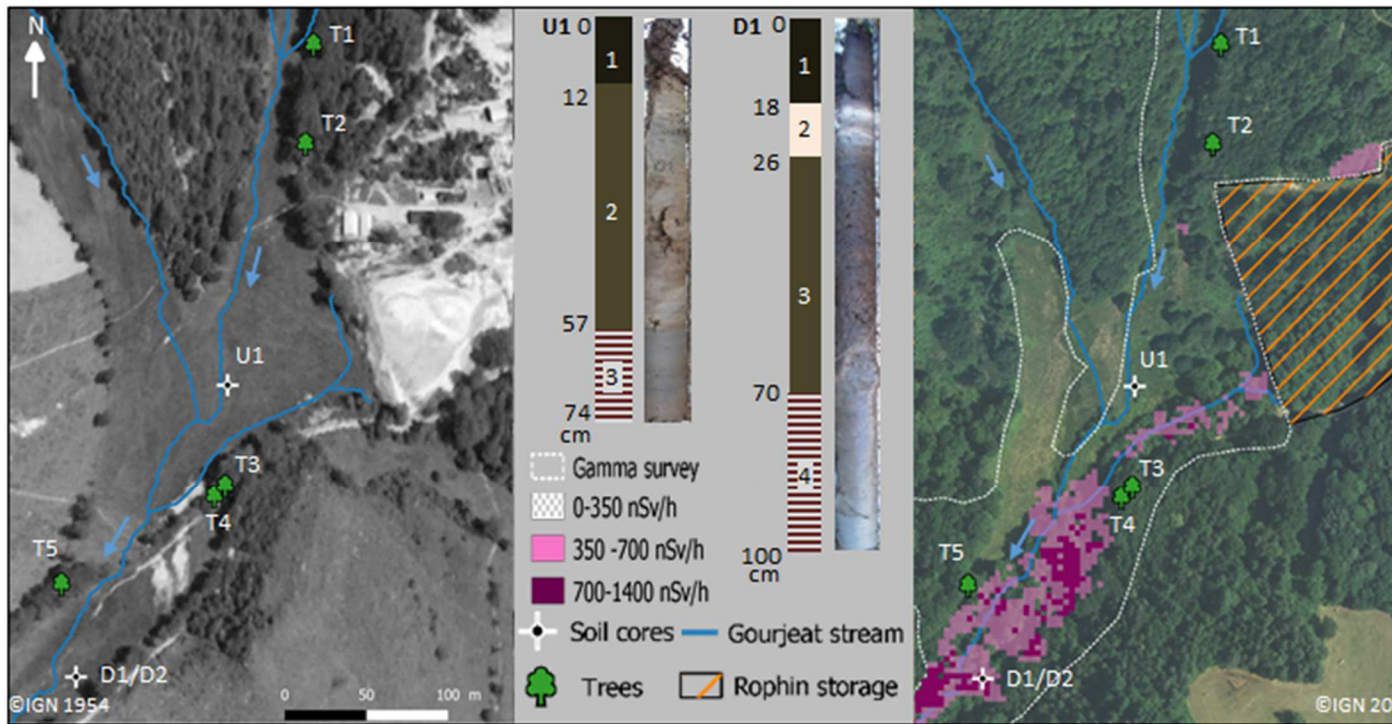
202 The results from the analysis of these selected documents, that enable tracing the history of  
203 site operations, will be summarized in the following section (3.1). These data will then be  
204 discussed in light of field measurement results obtained from our two centers of interest, i.e.  
205 wetland soils and tree rings.

### 206 3.2. *Sampling strategy*

207 An environmental monitoring and sampling campaigns were carried out between 2014 and  
208 2018 (Fig. 2).

209

210



211

212 Fig. 2: Overview of the Gourgeat watershed with sampling locations. Left: Aerial photograph (1954)  
213 with the Rophin mine processing plant. Right: Aerial photograph (2015) of the ICPE site with  
214 interpolated gamma dose rates. Center: Photographs and soil profile descriptions of cores U1 and D1  
over 74 and 100 cm. A second core (D2) with a higher vertical resolution was collected in April 2018.

### 215 3.2.1. Gamma survey

216 A radiological survey of the Gourgeat watershed was performed to provide an overview of  
217 the dose rate distribution at the periphery of the ICPE site open to the public. Dose-rate  
218 mapping (Fig. 2 and Fig. S4) was obtained with SG-2R gamma-ray sensors (Canberra, Inc.).  
219 The device used coupled the gamma-ray sensor (energy range: 59 keV to 1.5 MeV, and  
220 measurement range: 10 nSv.h<sup>-1</sup> to 1 mSv.h<sup>-1</sup>) with a Colibri<sup>®</sup> device (Canberra, Inc.) featuring  
221 an integrated GPS. Data were acquired automatically every 5 s or 30 s directly in dose rate,  
222 and the sensors were placed approx. 1 m above ground. The measurements were conducted  
223 during 5 field campaigns, from December 2014 to June 2018, across different areas. The  
224 measured data points, reported in nSv.h<sup>-1</sup> (80 - 1,050 nSv.h<sup>-1</sup>), were interpolated with the

225 inverse distance weighting method (distance coefficient = 5) using the QGIS software  
226 interpolation tool.

### 227 **3.2.2. Soil sampling**

228 Two soil cores were collected in January 2016 at locations upstream (Core U1) and  
229 downstream (Core D1) of the hydraulic system (Fig. 2) in place to assess the environmental  
230 footprint of the Rophin site with a Russian corer 100 cm long and 5 cm in diameter  
231 (Eijkelkamp). Cores U1 and D1 were brought back to the laboratory, subsampled with a  
232 cleaned ceramic blade the next day into 2-cm sections under laboratory atmosphere and  
233 lyophilized for gamma spectrometry analysis, <sup>14</sup>C dating and lead isotopy. A second  
234 downstream core (D2) with a greater vertical resolution (Fig. 2) was collected in April 2018  
235 close to the D1 location (Fig. S5c) with an in-house corer developed to protect the sample in  
236 a plastic tube (8.5-cm inner diameter, Fig. S7). After extraction, the core was stored at -20°C  
237 in a mobile freezer. Once back in the laboratory, the frozen core was cut into 1-cm slices by  
238 means of a bandsaw. Two subsamples from core D2 were analyzed by Scanning Electron  
239 Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) according to the  
240 methodology explained in Fig. S8 to determine location of U within minerals.

241 In addition, a total of 17 cores, called the M-series, were extracted in April 2018 (Russian  
242 corer, 50 cm, Eijkelkamp) over a distance of about 300 m alongside the main creek running  
243 from the storage site in order to provide an overview of the soil profile in the wetland (Fig.  
244 S9). Following core extraction, 2 to 4 sections of approx. 5 cm were selected depending on  
245 the soil profile, subsampled with the same protocol than for D1 core, and then stored in 250-  
246 mL plastic jars for gamma spectrometry analysis.

247 **3.2.3. Tree sampling**

248 Tree ring samples were collected from five oak trees (*Quercus petraea*), chosen for their age  
249 estimated at more than 100 years (T1 to T5) and located between 50 and 200 m from the  
250 former uranium mining and storage residue (Fig. 2). Trees T1 and T2, located upstream in  
251 the vicinity of the storage residue, are not influenced by the Gourgeat watershed due to an  
252 elevation difference exceeding 10 m. Trees T3 and T4, growing downstream of the storage  
253 residue, are located in the watershed very close to the site of water runoff from the storage  
254 residue. The last tree sampled, T5, is located further away, 200 m downstream of the  
255 storage residue, and has no apparent connection with the watershed due to elevation  
256 difference (Fig. 2, Fig. 6 and Table S10).

257 Tree rings were collected on each tree using an increment borer (Pressler; inner diameter 5  
258 mm). The selected trees were healthy, grew under similar surrounding natural conditions  
259 and belonged to the same cohort. The samples were extracted from the trunk at roughly 1.5  
260 m above ground in July 2015. Sampling was performed with great care so as to avoid any  
261 cross-contamination, i.e. the borer was washed with ethanol and Milli-Q water between  
262 each extraction. After sampling, all cores were immediately sealed in plastic tubes and  
263 transported to the laboratory for dendroanalysis. The samples were dried at room  
264 temperature and polished with sandpaper to improve visibility of the growth rings. To avoid  
265 any cross-ring contamination, the samples were cleaned by removing any dust with  
266 compressed air. Tree ring samples were then scanned (1,600 dpi), and the Coorecorder  
267 software (Larsson, 2016) was run for age determination with a final uncertainty of  $\pm 1$  year.  
268 The period covered by the tree rings ranged between 118 and 176 years (Table S10). Seven  
269 different years were selected for U analysis (Fig. 1): years 1900 and 1940 were chosen to

270 represent the period before mining activity; 1952 for the period of operations; 1958 for the  
271 mine's closure; and 1967, 1990 and 2011 for the period subsequent to specific site  
272 rehabilitation works.

### 273 3.3. Analysis

#### 274 3.3.1. Gamma spectrometry

275 Soil radionuclide contents from the  $^{238}\text{U}$  decay chain ( $^{234}\text{Th}$ ,  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$ ) were analyzed by  
276 means of gamma spectrometry. These analyses were carried out in filled petri dishes (5 cm  
277 diameter, 1.5 cm thick) sealed in a radon protection membrane (Petri-Seal<sup>(TM)</sup>). The samples  
278 were first analyzed for 3 hours and then 10 hours for those with low activity. The gamma  
279 spectrometry was performed using HPGe-detectors (Canberra, BE4823/S) with a high purity  
280 germanium detector (Ge-crystal, 7500SL cryostat, 2002CPSL pre-amplifier) and a multi-  
281 channel analyzer (MCA). Energy calibration by a  $^{152}\text{Eu}$  certified source (peak energy range:  
282 122 to 1408 keV) has been coupled to a certified multigamma mixture for efficiency (peak  
283 energy range: 60 to 1,836 keV). A multigamma mixture ( $^{241}\text{Am}$ ,  $^{109}\text{Cd}$ ,  $^{57}\text{Co}$ ,  $^{139}\text{Ce}$ ,  $^{51}\text{Cr}$ ,  $^{113}\text{Sn}$ ,  
284  $^{85}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$ ,  $^{88}\text{Y}$ ) has been proportionally introduced so that the counts for each of the  
285 energies are equivalent. The self-absorption of gamma lines in materials was taken into  
286 account in the Labsocs software using the composition and density of a typical soil sample.  
287 All radionuclide concentrations are expressed with uncertainties at  $2\sigma$ . These concentrations  
288 ( $^{234}\text{Th}$ ,  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$ ) with LD ( $^{210}\text{Pb}$ ) = 35.2 Bq.kg<sup>-1</sup>; LD ( $^{226}\text{Ra}$ ) = 52.0 Bq.kg<sup>-1</sup>; LD ( $^{234}\text{Th}$ ) = 34.6  
289 Bq.kg<sup>-1</sup>) were respectively determined with the following energy signals: 63.3 keV, 186.1  
290 keV, and 46.5 keV. The  $^{238}\text{U}$  sample concentrations were determined by assuming a secular  
291 equilibrium in the head of the decay chain between  $^{234}\text{Th}$  and  $^{238}\text{U}$ . The resulting  $^{238}\text{U}$   
292 concentrations were calculated with a specific activity of 12,350 Bq.g<sup>-1</sup>.

293 The 186.1 keV energy signal of  $^{226}\text{Ra}$  interferes with the 185.7 keV energy signal of  $^{235}\text{U}$ ; this  
294 effect is corrected by introducing the  $^{235}\text{U}$  concentration predicted by the natural isotopic  
295 ratio from  $^{238}\text{U}$  concentrations. The  $^{226}\text{Ra}$  values were verified for a few samples by  
296 measuring radiochemical equilibrium with its daughter nuclide  $^{214}\text{Pb}$  (295.2 keV, 351.9 keV;  
297  $\text{LD} = 13.2 \text{ Bq.kg}^{-1}$ ) and  $^{214}\text{Bi}$  (609.3 keV, 1120.3 keV, 1764.5 keV;  $\text{LD} = 81.4 \text{ Bq.kg}^{-1}$ ) by using  
298 sealed samples (to prevent radon from escaping) stored for at least 3 weeks. Equilibrated  
299 samples were used for the  $^{210}\text{Pb}$  activity determination. In addition to analyzing the  $^{238}\text{U}$   
300 decay chain, the  $^{137}\text{Cs}$  (661.7 keV) was measured for 24 h in a low-background environment,  
301 according to the protocol developed by Tedjani et al., (2016) in order to both achieve a  
302 lower limit of detection ( $2 \text{ Bq.kg}^{-1}$ ) and perform soil dating over the depth.

### 303 **3.3.2. Water and soil organic matter content**

304 Water and soil organic matter (SOM) contents of soil samples were simply determined by  
305 loss on ignition; this procedure relied on the protocol found in Heiri et al., (2001). Between 5  
306 and 10 g of homogenized wet samples were introduced into porcelain crucibles and first  
307 dried at  $105^\circ\text{C}$  overnight in a furnace (Nabertherm, Inc.), then heated at  $550^\circ\text{C}$  for 4 h to  
308 burn the organic matter. After each heating step, the crucibles were cooled to room  
309 temperature in a desiccator and weighed. SOM content was expressed relative to dry soil  
310 content, in contrast with water content, that account for the entire sample mass. The  
311 uncertainty for both measurements, expressed as a confidence interval ( $2\sigma$ ), was calculated  
312 at less than 10%.

### 313 **3.3.3. $^{14}\text{C}$ dating**

314 Several samples from core D1 were analyzed by applying the Accelerator Mass Spectrometry  
315 (AMS) radiocarbon dating technique after graphitization. Results (in age calBP) were



316 obtained by running the software OxCal V4.3.2 (Ramsey, 2017) using the IntCal13  
317 atmospheric curve (Reimer et al., 2013). More detailed information is available in Table S11.

#### 318 **3.3.4. Soil sample preparation and Pb HR-ICP-MS analysis**

319 Lead isotope ratios were analyzed on a single-collector high-resolution ICP-MS instrument  
320 (ELEMENT XR, Thermo Scientific, Bremen, Germany) after chemical purification of the lead in  
321 soil samples using a Dowex 1x8 (100-200 mesh) anion exchange resin in bromide form.

322 Prior to analysis, 100 mg of soil sample were acid digested using a microwave oven (ETHOS  
323 Easy, Milestone) in accordance with the EPA 3051A method drawn from the Milestone  
324 application book. Concentrated nitric acid (70% HNO<sub>3</sub>, Fisher Scientific) and hydrochloric  
325 acid (37% HCl, Fisher Scientific) were purified with the Savillex DST-1000 sub-boiling  
326 distillation system. The insoluble residue obtained after sample mineralization (leaching and  
327 incomplete digestion) was discarded by centrifugation while the supernatant was  
328 evaporated to dryness in a clean environment using the EvapoClean® device (Analab®). The  
329 sample was dissolved with 2 mL of 0.5 M HBr prepared from a high purity, concentrated HBr  
330 acid (Optima grade, Fisher Scientific), centrifuged and loaded onto the 1.2-mL ion exchange  
331 column to separate major cations with additional HBr and 0.5 M HCl, plus the elution of lead  
332 with 2 mL of 6 N HCl into a 5-mL Savillex vial. The average procedural Pb blank of  $1.0 \pm 1.6$  ng  
333 ( $2\sigma$ , n=12) is lower by a factor ranging from 1,500 to 75,000 relative to the amount of Pb  
334 derived from soil samples. Preliminary quantitative Pb analyses of the collected sample  
335 fractions were carried out in order to prepare sample solutions at a Pb concentration of 2 ng  
336 mL<sup>-1</sup> in 2% HNO<sub>3</sub> (v/v) for Pb isotope measurements performed by means of HR-ICP-MS.

337 All stable lead isotopes (<sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb, <sup>208</sup>Pb) and mercury isotopes (<sup>201</sup>Hg, <sup>202</sup>Hg) were  
338 measured with the operating and data acquisition parameters detailed in Table S12. The

339 analysis sequence consisted of five replicate analyses of the unknown sample solution  
340 bracketed by five replicate analyses of a  $2 \mu\text{g}\cdot\text{L}^{-1}$  Pb solution of the NIST SRM981 Pb isotope  
341 standard with, between them, the 2%  $\text{HNO}_3$  (v/v) blank solution analysis. The isobaric  
342 interference from  $^{204}\text{Hg}$  on  $^{204}\text{Pb}$  was corrected using the measured signal intensity of  $^{202}\text{Hg}$ ,  
343 and the abundance ratio  $^{202}\text{Hg}/^{204}\text{Hg}$  equaled 4.35. Special attention was paid by measuring  
344 the additional  $^{201}\text{Hg}$ , yielding the ratio of signal intensity of both isotopes with respect to the  
345 abundance ratio  $^{202}\text{Hg}/^{201}\text{Hg}$  and showing evidence of spectral interference free Hg isotopes.  
346 The Pb isotope ratios ( $^{204}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{206}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$ ) were corrected for instrumental  
347 mass discrimination using the exponential law (Fig. S13). The mass bias factor applied to the  
348 five replicate analyses of an unknown sample is the average of such factors calculated from  
349 analyses of the NIST SRM981 Pb both before and after the sample analyses. The errors  
350 calculated on Pb isotope ratios in soil samples correspond to two standard deviations from  
351 the mean ( $2\sigma$ ) based on five replicate analyses of the same sample solution.

### 352 **3.3.5. Tree sample preparation and U HR-ICP-MS analysis**

353 Individual rings were cut out using a sterilized scalpel that was washed with high purity  
354 ethanol and 5%  $\text{HNO}_3$  (v/v); this step was followed by a Milli-Q wash in between cuts. The  
355 obtained sample weights varied from 10 to 40 mg. The digestion procedure has been  
356 described elsewhere (Hassan Loni et al., 2019) and proves to be suitable for low-mass  
357 samples. The wood sections were washed in 0.1 M  $\text{HNO}_3$  for about an hour and then dried in  
358 an oven for 7 h at  $70^\circ\text{C}$  (until achieving constant weight). Next, the samples were weighed  
359 and deposited in a 5-mL Savillex container, with 1 mL of concentrated  $\text{HNO}_3$  being added.  
360 The containers were placed in an oven at  $80^\circ\text{C}$  for one day; 0.5 mL of ultrapure 30%  $\text{H}_2\text{O}_2$   
361 were added and the samples placed back in the oven for one more day. The solutions were  
362 then cooled and diluted in 2%  $\text{HNO}_3$  (v/v) using the  $^{205}\text{Tl}$  internal standard working solution

363 prepared at a concentration of 50 ng.L<sup>-1</sup>. The suitability and accuracy of this method were  
364 tested through a digested standard reference material, i.e. SRM NIST 1570a spinach leaves  
365 (U content = 0.155 ± 0.023 mg.kg<sup>-1</sup>) according to the same procedure.

366 The U concentrations in tree ring sample solutions obtained after digestion were measured  
367 by means of the HR-ICP-MS. The optimized ICP-MS operating conditions are given in Table  
368 S12. The calibrated U standards were prepared from 1,000 mg.L<sup>-1</sup> uranium ICP standard  
369 solution (SCP Science). Typical standard calibration curves could be obtained from  
370 measurements of the 2% HNO<sub>3</sub> (v/v) blank solution and U standard solutions of 10, 20, 30  
371 and 50 ng.L<sup>-1</sup>. The correlation coefficient (R<sup>2</sup>) values over the study duration were between  
372 0.999 and 1.00. <sup>205</sup>Tl and <sup>238</sup>U were measured at low resolution in E-scan acquisition mode,  
373 with the detector in triple mode. The limits of detection ranged from 0.002 to 0.2 ng.kg<sup>-1</sup>,  
374 and the relative standard deviation (2σ) was < 15%.

## 375 4. Results

### 376 4.1. *Records and maps*

#### 377 4.1.1. *Records*

378 Given this setting where mining operations previously encompassed the entire Gourgeat  
379 watershed, further details into what actually happens during mining can be gleaned from a  
380 study of several records. From selected correspondence, a description of the extracted  
381 minerals and residue could be clarified. Some ore bodies contain kaolinite clays, which were  
382 detrimental to the ore washing plant process during the sedimentation step and resulted in  
383 a loss of U mineral particles with mine tailings (Table S14, 29/06/1948). The discharge waters  
384 into the Gourgeat stream after the settling ponds were turbid due to an excess capacity  
385 limitation and inadequate maintenance of the facility (i.e. a mix of mud and sand never  
386 emptied) (Table S14, 27/10/1950, 21/04/1952, 20/10/1952, 27/07/1953, 26/06/1954). From  
387 these letters (Table S14, 12/01/1951, 27/07/1953 and 26/06/1954), we learned that a white  
388 coloration of the Terrasson and Vauziron streams over a distance of several kilometers was  
389 reported due to fine particles clogging the filters for the abstraction of drinking water to  
390 supply the City of Chateldon.

#### 391 4.1.2. *Maps*

392 A study of the 9 available prior aerial photographs from 1946 to 2015 (Fig. S6) has  
393 highlighted the changes induced by mining activities on the watershed as regards the  
394 timeline events (Fig. 1). Before the mine was founded in 1946, the head of the watershed  
395 was a grassland dedicated to breeding with a small stream running through the center. On  
396 the 1954 photograph showing mining operations, the footprint of mine installations with  
397 settling ponds is clearly visible. A large white deposit in the watershed some 200 m

398 downstream of the hydraulic output of the Rophin settling ponds can be noticed. Moreover,  
399 the small stream is highlighted by a white color, in comparison with the photographs from  
400 1946. The mine was then abandoned and overrun by vegetation (Fig. S6, 1960 and 1974).  
401 The first site rehabilitation is visible on the 1983 picture, with a large forest clearing on the  
402 mine for the purpose of dismantling the former installations. This step was repeated (visible  
403 in the 2004 photo) for the erection of a fence in 2015 in order to secure the ICPE installation.  
404 Since 1960, the vegetation growing in the watershed downstream of the mine has now  
405 become forestland.

#### 406 4.2. *Gamma survey results*

407 Results from the gamma survey are reported in Fig. 2 as a gamma cartography with 3  
408 radioactivity levels. The measured gamma dose rates range from 80 to 1,050 nSv.h<sup>-1</sup> in  
409 following a Gaussian distribution pattern for values between 80 and 350 nSv.h<sup>-1</sup>. Regarding  
410 the wider area under investigation, this pattern was assumed to be the local geological  
411 background (GB) of the Rophin area, with a mean value of 210 nSv.h<sup>-1</sup>, which aligns with a  
412 regional background between 201 and 250 nSv.h<sup>-1</sup> measured by IRSN, (2014). From this  
413 initial observation, two additional radioactivity levels were defined as 1-2 times and 2-4  
414 times the geological background (i.e. 350-700 and 700-1,400 nSv.h<sup>-1</sup>) in order to facilitate the  
415 reading of interpolated results on the gamma cartography.

416 The northern part of the ICPE area and the two creeks running from the north, which supply  
417 water to the wetland area, show values around the level of the GB. In the eastern part of the  
418 map, from the effluent waters discharged by the ICPE, a level of 1-2 GB was measured. The  
419 gamma radiation level then increases to 1-4 GB (maximum at 1,050 nSv.h<sup>-1</sup>) in the watershed  
420 after the confluence of the Gourgeat creek from the north and ICPE effluent waters (Fig. 2).

421 This high gamma dose rate level was localized on the valley floor, characteristic of a wetland,  
422 along the stream within a wide surrounding area without any clear pattern for maximum  
423 values. This gamma survey served as the basis for implementing the soil sampling strategy.

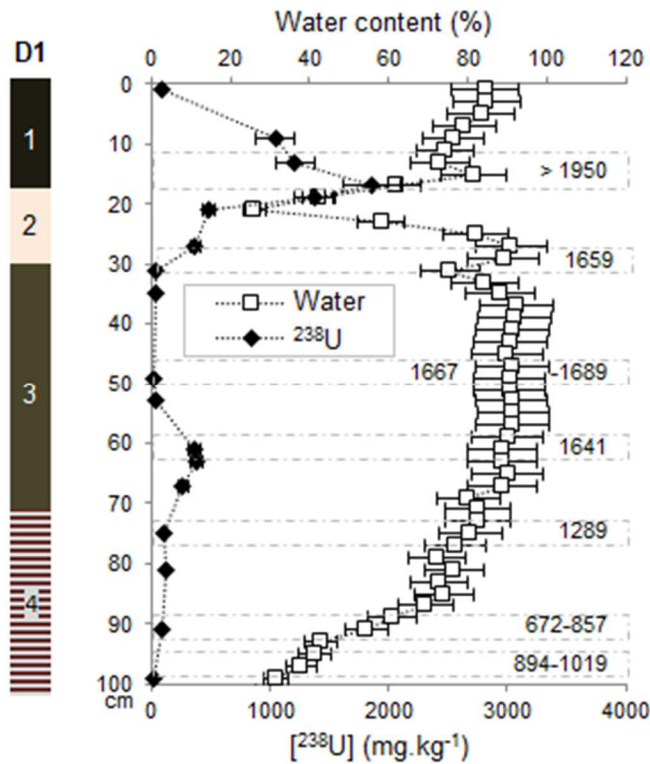
#### 424 **4.3. Soil analysis**

##### 425 **4.3.1. Soil properties**

426 The U1 soil core was sampled in the upstream grassland, whereas D1 and D2 were sampled  
427 in a wooded wetland fully saturated by water during a high flow period (Fig. 2).  
428 Consequently, these soil layers were considered at their maximum water holding capacity.

429 By observation of the D1 core (Fig. 2 and Fig. 3), 4 layers can be distinguished, based on  
430 visual criteria and soil organic matter (SOM) content. The top of the core (D1-1; 0-18 cm)  
431 consists of black soil composed of fibrous material and roots with a very high water content  
432 (78% of total mass) and SOM (34% of dry mass). At a depth between 18 and 30 cm (D1-2),  
433 the soil layer features a whitish color with a silt loam texture, a low organic content (8%) and  
434 a water content dropping to minimum value of 26%. The next layer (D1-3; 30-70 cm) is  
435 characterized by a brown color and a high organic carbon content (45%), which suggests a  
436 more heavily decomposed organic matter than in the D1-1 layer. The last brown-gray soil  
437 layer (D1-4; 70-100 cm) comprises a mix of organic and mineral characteristics, with a low  
438 level of SOM (7%), an apparent silt loam texture and a decreasing water content with depth  
439 (from 83% to 18%). The water and SOM contents of core D2 at the centimeter scale (Fig. 4)  
440 corroborate the differences between the first 3 layers as well as the correlation between  
441 SOM and water, i.e. the higher the content of water, the higher the content of SOM. Layers  
442 D1-2 and D2-2, displaying the same characteristics, will be referenced as the WSL (whitish

443 silt loam) layer. Note that this particular WSL layer was not observed in the U1 soil core (Fig.  
 444 2).

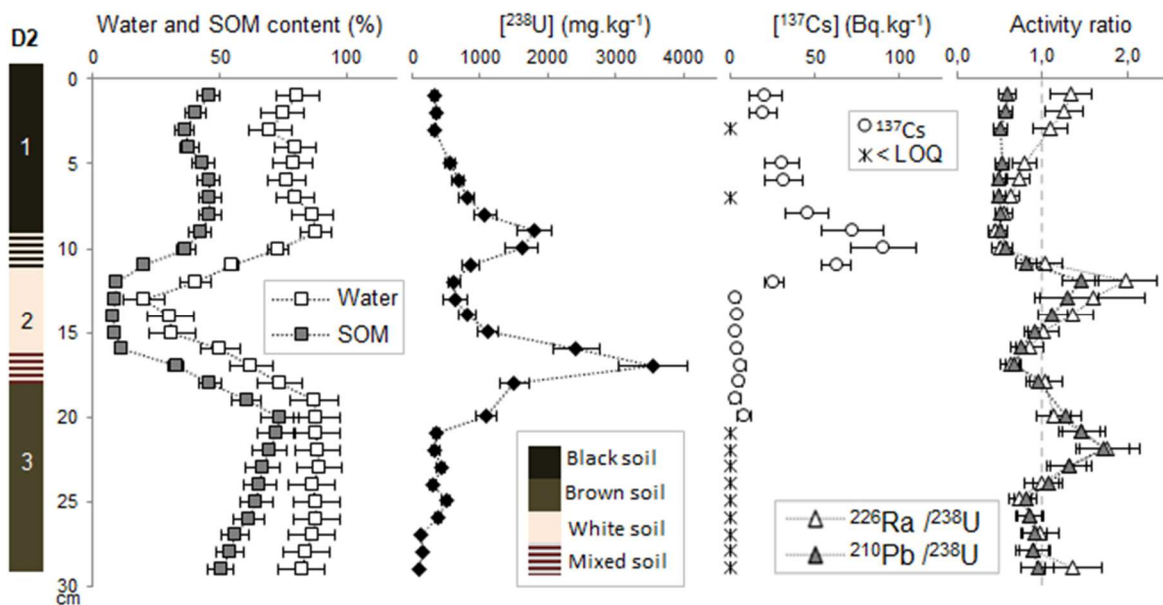


445  
 446 Fig. 3: Simplified soil profile description of core D1 (100 cm) with water content, <sup>238</sup>U concentrations  
 447 in dry mass and with <sup>14</sup>C dating.

#### 448 4.3.2. Uranium depth profiles and distribution in the watershed

449 The U concentrations determined range from 8.9 to 3,560 mg.kg<sup>-1</sup> in dry mass for cores D1  
 450 and D2 (Fig. 3 and Fig. 4). An analysis of the U soil profile for the D1 core reveals a U  
 451 concentration increase between the D1-1 and D1-2 layers (10-20 cm) for the highest  
 452 concentration (i.e. 1,855 mg.kg<sup>-1</sup>) and a smaller rise at the end of the D1-3 layer (379 mg.kg<sup>-1</sup>).  
 453 The D1-4 layer exhibits a low U concentration of around 10 mg.kg<sup>-1</sup>, which is in agreement  
 454 with the local geological background (11-59 mg.kg<sup>-1</sup>, from (Salpeteur and Angel, 2010)).  
 455 Layers D1-3 and D1-4 can thus be considered as the soil reference before the period of  
 456 mining operations. The higher spatial resolution of core D2 over 30 cm highlights two U

457 peaks at the interface between D2-1/2, in accordance with D1 results, and in the lower part  
 458 of D2-2 (not visible on D1 results), with respective intensities of 1,800 mg.kg<sup>-1</sup> and 3,560  
 459 mg.kg<sup>-1</sup>. By considering the density and water content of each soil layer, the highest mass of  
 460 U is primarily stored in the WSL layer (D1-2 and D2-2), with a tendency to accumulate locally  
 461 at the interface with the topsoil layers (D1-1 and D2-1) characterized by a high SOM content.



462

463 Fig. 4: Simplified soil profile description of core D2 (30 cm) with water and SOM contents, <sup>238</sup>U  
 464 concentrations in dry mass, <sup>137</sup>Cs activity in dry mass (LOQ : Limit of Quantification) and activity ratios  
 465 of <sup>226</sup>Ra and <sup>210</sup>Pb to <sup>238</sup>U.

466 This correlation between U stock and WSL layer was confirmed by the M-series of 50-cm  
 467 cores in the area (Fig. S9), which also indicated the presence of the WSL layer, mainly in the  
 468 center of the watershed downstream of the mine discharge location. Moreover, the U soil  
 469 profile concentrations of the U1 core (not shown here) reveal a single increase in U  
 470 concentration, from 51 to 77 mg.kg<sup>-1</sup>, in the organic topsoil layer (0-7 cm); this result is  
 471 consistent with the absence of the characteristic WSL layer in the first 30 cm.

472 The measured (<sup>226</sup>Ra/<sup>238</sup>U) and (<sup>210</sup>Pb/<sup>238</sup>U) activity ratios range from 0.46 to 2.00 and from  
 473 0.50 to 1.73, respectively (Fig. 4). Due to the highly distinct mobility of the “long-life”



474 radionuclides of the  $^{238}\text{U}$  decay chain ( $^{238}\text{U}$ ,  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$ ), an activity ratio close to the  
475 secular equilibrium highlights a collective transport of radionuclides mainly in particle form  
476 (Zielinski et al., 1986), whereas a deviation stands out for an output (by migration) or input  
477 (of various origins) of one radionuclide from the decay chain. The ratio value close to 1 at the  
478 end of D2-3 is in line with a natural U geological background in secular equilibrium. If we  
479 look closely at the results, the second U peak in the lower part of D2-2 correlates with a ratio  
480 close to 1, thus suggesting past transport in particulate form. However, an excess of  $^{226}\text{Ra}$   
481 and  $^{210}\text{Pb}$  observed in the middle of the WSL layer could suggest a depletion in U. The D2-1  
482 layer with the first U peak shows a continuous deviation from 0.46 at 10 cm to 1.34 at the  
483 soil surface for the  $^{226}\text{Ra}/^{238}\text{U}$  ratio, in comparison with the  $^{210}\text{Pb}/^{238}\text{U}$  ratio of around 0.5.  
484 This difference in behavior combined with the deviation from a ratio of 1 signifies a rupture  
485 in the decay chain between  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  and a non-equilibrium with  $^{238}\text{U}$ . The  $^{226}\text{Ra}/^{238}\text{U} <$   
486 1, at the end of the D2-1 layer, may highlight the input of  $^{238}\text{U}$  into this soil layer by means of  
487 a vertical migration from the WSL layer (D2-2).

488 In addition, SEM has revealed the presence of a large number of U-rich particles with  
489 diameters between 1 and 20  $\mu\text{m}$  in the D2-1 and D2-2 layers of the core (Fig. S6). The EDS  
490 spectra show the presence of U at contents as high as 50% and an association with other  
491 elements (Pb, Fe, Cu, Al, Si and O).

#### 492 **4.3.3. Tracers: $^{14}\text{C}$ , $^{137}\text{Cs}$ and stable lead isotopy**

493  $^{14}\text{C}$  dating results on core D1, as detailed in Table S11 and summarized in Fig. 3, show a post-  
494 1950 age for the depths 12-14 and 16-18 cm. The sample at depths of 20-22 cm (aliquoted in  
495 WSL) could not be dated by the  $^{14}\text{C}$  dating technique since it was devoid of carbon. From 30

496 to 100 cm, older ages of up to 1 millennium are involved. The dating step has been refined  
497 over the first 30 cm via  $^{137}\text{Cs}$  on core D2 (Fig. 4).

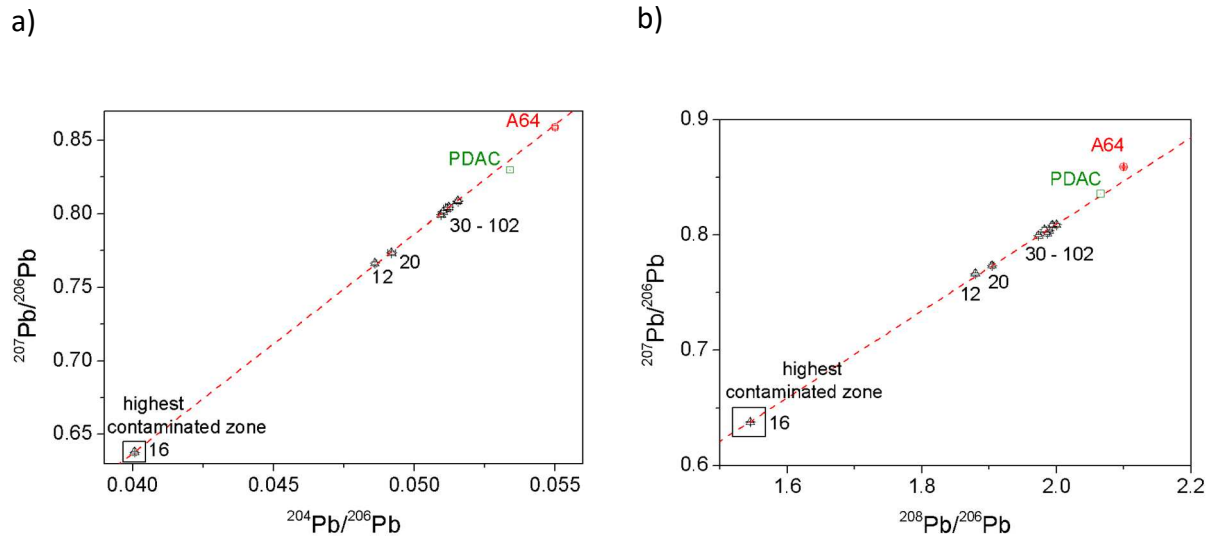
498 Cesium makes it possible to date sediments by their  $^{137}\text{Cs}$  activity caused by nuclear fallout  
499 (IAEA, 1998, p.6) combined with their limited mobility properties. The specific  $^{137}\text{Cs}$  activity in  
500 the D2-1 layer reaches an intermediate value of  $31.7 \text{ Bq.kg}^{-1}$  at 6 cm, and a maximum of 91  
501  $\text{Bq.kg}^{-1}$  was observed right at the D2-1/2 interface (Fig. 4). The values then decrease to  
502 roughly  $3.4 \text{ Bq.kg}^{-1}$  for the lower parts of the D2-2 and D2-3 layers. Below 20 cm, the values  
503 were less than the limit of detection. Since the main peak of  $^{137}\text{Cs}$  activity in the D2 core is  
504 located directly above the WSL layer and only very low values were detected below, it seems  
505 safe to assume that this layer was deposited before the peak in nuclear weapons testing at  
506 the beginning of the 1960's (IAEA, 1998, p.45). Moreover, this finding is consistent with  $^{14}\text{C}$   
507 dating for this layer (post-1950 age).

508 The benefit of using stable lead isotopes (Fig. 5) is to both highlight the existence of an  
509 environmental marker related to the presence of U and discriminate between anthropogenic  
510 (uranium stemming from mining and milling activities) and natural input (uranium from the  
511 geochemical background). Most stable Pb isotopes are indeed present in the decay chains of  
512 naturally occurring radionuclides ( $^{238}\text{U} \rightarrow ^{206}\text{Pb}$ ,  $^{235}\text{U} \rightarrow ^{207}\text{Pb}$  and  $^{232}\text{Th} \rightarrow ^{208}\text{Pb}$ ) and  
513 moreover  $^{204}\text{Pb}$  is non-radiogenic.

514 Our data are shown in a three-isotope diagram ( $^{207}\text{Pb}/^{206}\text{Pb}$  vs.  $^{204}\text{Pb}/^{206}\text{Pb}$ , Fig. 5a), thus  
515 showcasing the mixing processes between various pollution sources. For purposes of  
516 comparison, the A64 sample (Loire surface sediment  $47^{\circ}17'17''\text{N} - 02^{\circ}10'54''\text{W}$  (Péron *et al.*,  
517 2016), which is not under the influence of mining discharges) was used as the geochemical  
518 background end-member with a  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio ( $0.859 \pm 0.001$ ) close to the Present Day

519 Average Crustal (PDAC)  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio estimated at 0.83 (Cumming and Richards, 1975;  
520 Stacey and Kramers, 1975). As observed in Figure 4a, the alignment of the samples ( $R^2 =$   
521 0.9999) confirms a binary mixing between the U-ore particles and the geochemical  
522 background. This outcome clearly highlights an anthropogenic signature in the recent core  
523 layers, in comparison with the PDAC and A64, which are consistent with a post-mining  
524 context. In order to calculate the radiogenic Pb contribution in the core samples, a precise  
525 determination of the Pb end-members is of great importance. The A64 sample was used for  
526 the geochemical background end-member and for the intercept of the linear regression in  
527 Figure 4a as the  $^{207}\text{Pb}/^{206}\text{Pb}$  radiogenic end-member. By applying the mixing model and  
528 taking the Pb atomic abundances into account, it is possible to correctly calculate the  
529 contribution of radiogenic lead ( $k$ , in %) to the total lead for each sample (Gourgiotis et al.,  
530 2020).

531 The 6 soil samples at a depth below 30 cm (D1-3 and D1-4 layers) present similar  $^{207}\text{Pb}/^{206}\text{Pb}$   
532 ratio values, ranging from  $0.7664 \pm 0.0009$  to  $0.808 \pm 0.001$ , with  $1.4 \pm 0.07\% < k < 1.7 \pm$   
533  $0.07\%$  corresponding to a slight U enrichment signature. The soil samples at 12-14 cm (D1-1)  
534 and 20-22 cm (top of D1-2) display an intermediate value for both ratios and  $k = 3 \pm 0.07\%$   
535 and  $k = 2.7 \pm 0.08\%$ , respectively. However, the lowest  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{204}\text{Pb}/^{206}\text{Pb}$  ratios  
536 were found for the 16-18 cm sample with values of respectively  $0.6378 \pm 0.0005$  and  
537  $0.04007 \pm 0.00005$ . This sample, with  $k = 8.6 \pm 0.07\%$ , is located at the interface between the  
538 D1-1 and D1-2 layers in the highest contaminated zone of core D1 ( $[\text{U}]_{\text{soil}}$  between 1,210 and  
539  $1,850 \text{ mg.kg}^{-1}$ ). These results are in agreement with the  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios obtained for U-  
540 contaminated soils and isotopic background in (Cuvier et al., 2016), at 0.6578 and 0.8305,  
541 respectively.



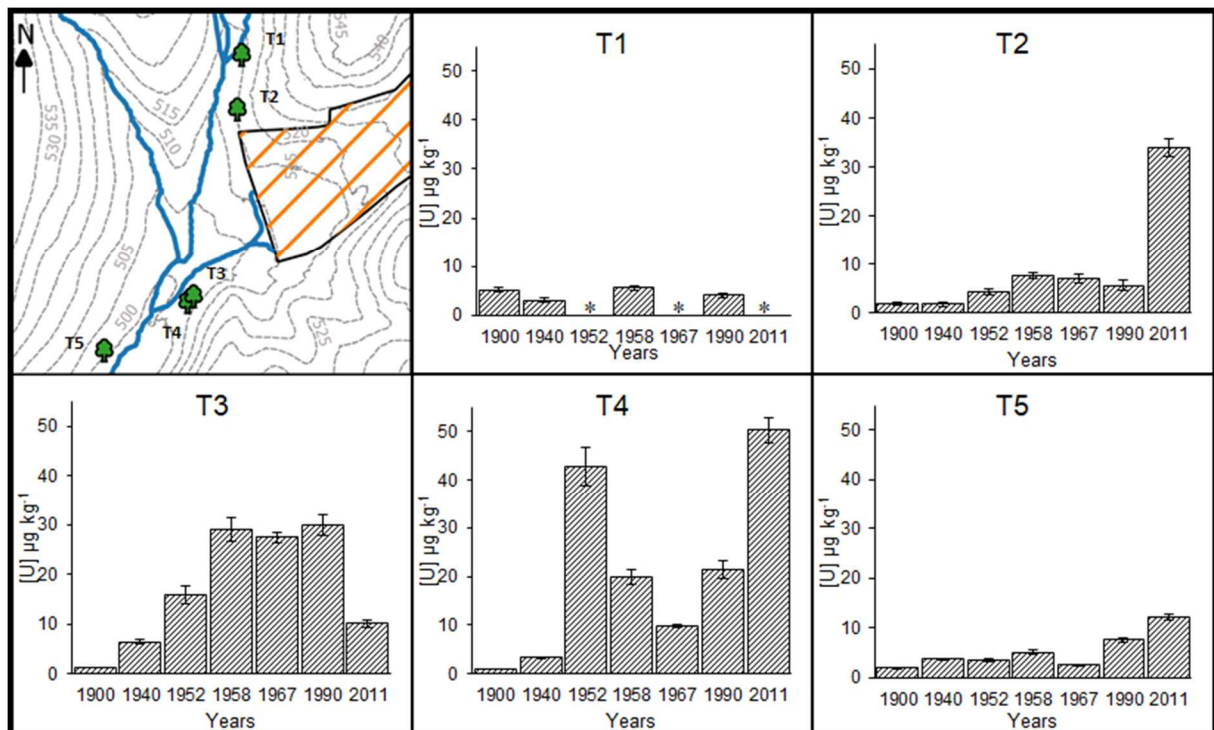
543 Fig. 5: a)  $^{207}\text{Pb}/^{206}\text{Pb}$  vs.  $^{204}\text{Pb}/^{206}\text{Pb}$  isotope ratios, and b)  $^{207}\text{Pb}/^{206}\text{Pb}$  vs.  $^{208}\text{Pb}/^{206}\text{Pb}$  isotope ratios of  
 544 core D1. In addition, **A64**, Loire Surface sediment and **PDAC** (Present Day Average Crustal Ratios)  
 545 (Cumming and Richards, 1975; Stacey and Kramers, 1975) have been plotted. The dashed line  
 546 represents the linear regression. The uncertainties ( $2\sigma$ ) are included in the plot. The values indicated  
 547 under the points correspond to the depths (in cm). The 30-102 cm range includes 6 sampling depths,  
 548 namely 30, 48, 60, 74, 90 and 102 cm.  
 549

550 The  $^{207}\text{Pb}/^{206}\text{Pb}$  vs  $^{208}\text{Pb}/^{206}\text{Pb}$  plot (Fig. 5b) confirms the presence of environmental  
 551 contamination, mainly due to the presence of U-bearing phases from the U mine, which  
 552 underscores the absence of thorogenic  $^{208}\text{Pb}$  in the U-ore. This observation is consistent with  
 553 the U-ore minerals of Rophin previously described, which are lacking in  $^{232}\text{Th}$ . The linear  
 554 regression ( $R^2 = 0.9996$ ) indeed indicates binary mixing with no supply of  $^{208}\text{Pb}$  in the highest  
 555 contaminated zone. The highest contaminated zone (16-18 cm sample) has the lowest  
 556  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio:  $1.5451 \pm 0.0009$ . In a post-U mining context, the results are consistent  
 557 ( $^{238}\text{U}$  to  $^{206}\text{Pb}$ ) with the geochemical background A64  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio:  $2.100 \pm 0.001$ . These  
 558 results are also in agreement with the isotopic background ( $^{208}\text{Pb}/^{206}\text{Pb} = 2.09$ ) and U-  
 559 contaminated soils ( $^{208}\text{Pb}/^{206}\text{Pb} = 1.620$ ) obtained in (Cuvier et al., 2016). The  $^{208}\text{Pb}/^{206}\text{Pb}$   
 560 ratio indicates that the enrichment matches with an uraniumogenic and not thorogenic Pb. The

561 other depths, which correspond to a slight U enrichment signature, present intermediate  
 562  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio values ranging from  $1.8795 \pm 0.0009$  to  $2.000 \pm 0.001$ .

563 **4.4. Tree ring analysis**

564 Uranium concentrations measured in the tree rings by HR-ICP-MS are given in Fig. 6;  
 565 concentrations were detected and quantified in all tree rings analyzed. The distribution  
 566 patterns of these tree samples reveal different trends.



567  
 568 Fig. 6: Locations of the oak trees with contour lines in the Gourgat watershed (upper left) and  
 569 uranium concentrations measured in the sampled annual rings

570 For T5, located far from the former mine without any apparent connection to the watershed  
 571 due to an elevation difference (Fig. 6), U values ranging from 2 to 12  $\mu\text{g.kg}^{-1}$  were obtained  
 572 (with low variations over time). For the upstream trees, T1 and T2, U concentrations did not  
 573 increase over time or only very slightly (except T2 in 2011). The U concentrations found for  
 574 T1 and T2 during the various years analyzed are of the same order of magnitude, i.e. ranging

575 from 2 to 7  $\mu\text{g.kg}^{-1}$  and up to 34  $\mu\text{g.kg}^{-1}$  for T2 in 2011. The values for trees T3 and T4,  
576 located downstream of the storage site, fluctuate strongly over time, from 1 to 50  $\mu\text{g.kg}^{-1}$   
577 with two distinct temporal trends. For T3, the concentration gradually increases until 1990  
578 and declines for 2011. For T4, after a maximum concentration measured in 1952, the  
579 concentration decreases until 1967 and starts increasing again in 2011.

580 Knowing that the mine was discovered in 1924, the low U concentration values for the year  
581 1900 (ranging from 1 to 5  $\mu\text{g.kg}^{-1}$ ) are expected to represent the local tree ring background.  
582 These backgrounds however are higher than other values given in the literature for oak trees  
583 (between 0.3 and 1  $\mu\text{g.kg}^{-1}$ ) (Edmands et al., 2001; Monticelli et al., 2009). This finding may  
584 be explained by the naturally increasing U levels in the soil (10  $\text{mg.kg}^{-1}$ ) of areas with granitic  
585 bedrock, especially near U deposits.

## 586 5. Discussion

587 A data integration approach is proposed in this section in order to offer insight into what has  
588 actually happened in the Gourgeat watershed. The gamma survey results indicate a  
589 contamination in the Gourgeat watershed downstream of the ICPE facility, in contrast with  
590 the upstream of the watershed. This finding has been confirmed by the high U  
591 concentrations measured in the topsoil (< 30 cm) of cores D1, D2 and the M series. More  
592 specifically, the highest U concentrations measured in the soil profiles of cores D1 and D2  
593 were localized around the WSL layer (D1-2 and D2-2); this layer with a specific texture, a low  
594 water and organic matter content and a high U content was not observed in the U1 core.  
595 Such an observation has led to the hypothesis that this contaminated WSL soil layer  
596 originated from a natural source or anthropogenic activities located near the current ICPE  
597 site. The overlap of gamma survey results with the 1954 aerial photograph (Fig. 2) shows a

598 partial correlation with a large white surface deposit, visible in the watershed around 200 m  
599 downstream of the hydraulic output of the former Rophin settling ponds (deposit not  
600 observable in 1946, see Fig. S6). The hypothetical contamination scenario can therefore be  
601 refined to a diffuse distribution of natural radionuclides from mine operations transported  
602 by water. In other words, the WSL layer could have been deposited in the wetland during a  
603 flooding event or else by slow sedimentation as a covering layer of mining materials. This  
604 scenario is supported by evidence in the records of: i) ore bodies containing kaolinitic clays  
605 (fine particles), ii) malfunction and inadequate maintenance of the settling ponds, and iii)  
606 turbid waters with a white coloration in the Gourgeat, Terrasson and Vauziron streams.  
607 Moreover, the dating of soil cores D1 and D2 by  $^{14}\text{C}$  and  $^{137}\text{Cs}$  corroborates the deposit of the  
608 WSL post-1950 (for  $^{14}\text{C}$ ) and before the beginning of the 1960's (for  $^{137}\text{Cs}$ ), which is in  
609 agreement with the timeline (Fig. 1) and the end of mining activities in 1957. In addition,  
610 lead isotope ratios indicate that contamination at a depth below 30 cm is slightly influenced  
611 by U-mine material (compared to PDCA and A64), while contamination at around 12-22 cm  
612 can be distinguished between intermediate and high enrichment signatures with a greater  
613 contribution of radiogenic lead to total lead ( $k = 8.6 \pm 0.07\%$ ) at 16 cm. Similarly, the  
614 enrichment factors, calculated from the mean geochemical background in the D1-3 and D1-4  
615 layers dated prior to 1700 ( $[\text{U}]_{\text{GB, soil}} = 101 \mu\text{g}\cdot\text{kg}^{-1}$ ), range from 3.7 to 35.4 in the WSL layer  
616 and from 0.9 to 18.4 in topsoil layers. The WSL layer may thus be used in future studies as a  
617 visual tracer during field sampling and as an indicator of a mining activity footprint.  
618 Combining this U marking of the wetland with the  $^{14}\text{C}$  dating technique, it can be assumed  
619 that the wetland is an accumulation area for natural U and its radioactive daughter for up to  
620 1,000 years. This information clearly demonstrates the recent impact of anthropic mining  
621 activities not only in the WSL layer but in topsoil layers as well. Following this assessment,

622 some questions arise, regarding for example the form of transport, and the migration  
623 behavior and bioavailability of the radionuclides. The means of transporting radionuclides by  
624 turbid waters in the watershed suggests migration in particulate form and most likely as ore  
625 particles given the poor efficiency of the ore washing plant process being applied (mainly  
626 paronsite in 1949-1954 and pitchblende in 1955-1957). The measured ratios of the activities  
627 of  $^{238}\text{U}$  to  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  for the U second peak in the lower part of the D2-2 layer (Fig. 4)  
628 correlates with a ratio value close to 1, which confirms partial transport as non-altered ore  
629 particles. Moreover, SEM (Fig. S8) revealed the existence of U-rich particles in this layer, but  
630 the stoichiometry determined by EDS cannot be confirmed with the ore composition of  
631 paronsite or pitchblende. It is therefore assumed that at least a portion of the deposited U  
632 mineral particles have dissolved over time. However, disequilibrium in the decay chain for  
633 the topsoil layer (D2-1) might suggest an enrichment of U by the migration of U as aqueous  
634 species and sorption on SOM. Two hypothesis can be formulated: i) a slow dissolution of U  
635 particles contained in the WSL layers over decades, followed by an accumulation in the  
636 topsoil layer associated with a seasonal change of water level in the wetland; or ii) a regular  
637 inflow over the decades of U dissolved by water from the Gourgeat creek altered by mine  
638 water effluent even after ICPE site rehabilitations. Such an accumulation mechanism in the  
639 wetland has been detected and similarly described for other sites affected by U mining  
640 (Bister et al., 2015; Mangeret et al., 2018). At the same time, the fact that U concentrations  
641 quickly decrease below the WSL in cores D1 and D2 suggests that the mobility of the U  
642 deposited by diffusion has been rather low under the conditions prevailing during the last 50  
643 years. In conclusion, the wetland, enriched in SOM, acts as a radionuclide trap for natural or  
644 anthropogenic U emissions observed at the Rophin site over the decades.



645 In this study, the dendroanalysis has served to correlate the U emissions from Rophin with  
646 the site history using oak tree rings as a suitable bioindicator of changes in bioavailable U  
647 concentrations. Considering the local tree ring background observed in 1900, two U  
648 concentration variations between 1940 and 2011 can be concluded. First, the maximum U  
649 values were observed between 1949 and 1958 for the T3 and T4 trees. This increase in U  
650 concentration in tree rings coincides with the period of mining activities (1949-1957) with an  
651 extended period of influence for T3. This result confirms the past transport of U into the  
652 hydraulic system in a bioavailable form. Moreover, by comparing U concentrations in the  
653 tree rings of T5 (no hydraulic influence) and T1 and T2 (located upstream) with the T3 and T4  
654 results (located downstream of the former mine and near the effluent waters) for this same  
655 period, it is reasonable to assume that this increase could be attributed to mining  
656 operations. Such anthropogenic activities could have generated bioavailable U  
657 concentrations, via the documented effluent waters and/or particle deposits (WSL layer),  
658 accumulated by the roots of trees growing in the wetland. Let's note that U concentrations  
659 in tree rings did not return to the local background level even after mining operations ceased  
660 (in 1958). Although an influence on T3 and T4 trees is observed, the concentrations  
661 identified are still very low compared to those obtained by Märten et al., (2015) (around 400  
662  $\mu\text{g.kg}^{-1}$  for the maximum U concentration). This difference is probably due to both the length  
663 of time the site had been in operation (including the processing period) and the quantity of  
664 ore extracted. The Rophin site was in fact only operated for 8 years (vs 40 years for "Reuster  
665 Forst"), including one year of shutdown (in 1951) for economic reasons. This "short"  
666 operating period has certainly helped mitigate the impact of these mining activities on plants  
667 growing in this region. Second, a large increase in U concentration (more than 20 times the  
668 background level) was observed in 2011 for trees T2 and T4. This trend is also slightly visible

669 for the non-influenced T5 tree (6 times). This particular period coincides with the major soil  
670 transformations of the Rophin site in 2002 and 2010 (Fig. 1 and Fig. S3), which are visible on  
671 the aerial photographs from 1993 to 2015 (Fig. S6). Since the variation was observed on both  
672 upstream (T2) and downstream (T4) trees in the vicinity of the ICPE site (and slightly on T5  
673 located further away), the hypothesis of an atmospheric contamination during the  
674 transformation is indeed possible. The transfer of elements within tree rings is a complex  
675 process that depends on a variety of parameters, such as soil pH, soil organic matter,  
676 bioavailability, concentrations in the environment, and the uptake capacity of trees (Cutter  
677 and Guyette, 1993). Atmospheric contamination during mining is thus one of the pathways  
678 of metal transport into trees (Lepp, 1975; Sansone et al., 2001). This determination  
679 corresponds mainly to foliar uptake, with subsequent export from the leaf via the phloem,  
680 followed by a lateral movement from this tissue into the xylem. However, the relationship  
681 between these levels of deposition and the levels in leaves and in other plant parts is  
682 presently unknown. On the other hand, this hypothesis is counterbalanced by the T3 tree  
683 results, which showed a higher U concentration in 1990 than in 2011.

684 Thanks to our methodology, which employs an integrated approach with a study of records,  
685 a gamma survey, and soil and tree ring analyses, it has been possible to trace the  
686 contamination history at the Rophin site. Beyond the interest in this methodology, the  
687 results of this work will provide the basis for future projects taking place in a ZATU workshop  
688 context. Further studies are being planned to better understand the processes taking place  
689 in the soil layers in order to derive predictions of the overall dynamics occurring at the site.  
690

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