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## Deciphering sources of U contamination using isotope ratio signatures in the Loire River sediments: exploring the relevance of $^{233}\text{U}/^{236}\text{U}$ and stable Pb isotope ratios

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1 Deciphering sources of U contamination using isotope ratio  
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4

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17

18

19 Abstract

20

21 A broad range of contaminants has been recorded in sediments of the Loire River over the last  
22 century. Among a variety of anthropogenic activities of this nuclearized watershed, extraction of  
23 uranium and associated activities during more than 50 years as well as operation of several nuclear  
24 power plants led to industrial discharges, which could persist for decades in sedimentary archives of  
25 the Loire River. Highlighting and identifying the origin of radionuclides that transited during the last  
26 decades and were recorded in the sediments is challenging due to i) the low concentrations which  
27 are often close or below the detection limits of routine environmental surveys and ii) the mixing of  
28 different sources. The determination of the sources of anthropogenic radioactivity was performed  
29 using multi-isotopic fingerprints ( $^{236}\text{U}/^{238}\text{U}$ ,  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$ ) and the newly developed  
30  $^{233}\text{U}/^{236}\text{U}$  tracer. For the first time  $^{233}\text{U}/^{236}\text{U}$  data in a well-dated river sediment core in the French  
31 river Loire are reported here. Results highlight potential sources of contamination among which a  
32 clear signature of anthropogenic inputs related to two accidents of a former NUGG NPP that  
33 occurred in 1969 and 1980. It is important to mention that the  $^{233}\text{U}$  and  $^{236}\text{U}$  levels measured in this  
34 work by recent high performance analytical methods are at ultra-trace levels and present a negligible  
35 radiological impact on health and on the environment. The determination of the mining activities by  
36 the use of stable Pb isotopes is still challenging probably due to the limited dissemination of the Pb-  
37 bearing material marked by the U-ore signature downstream to the former U mines.

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43 **Keywords:**  $^{233}\text{U}$ ,  $^{236}\text{U}$ , nuclear power plant, uranium mines, Loire River, lead isotopes

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## 46 Introduction

47

48 The Loire River is the longest French river with a linear distance of 1,012 km between its source  
49 (Mont Gerbier-de-Jonc) and its entrance into the estuary (Ancenis). Its watershed covers an area of  
50 117,800 km<sup>2</sup>, which represents 20% of the surface area of metropolitan France (Coularis, 2016;  
51 Dhivert, 2014). The Loire basin is geologically rich in uranium-bearing rocks and has been exploited  
52 for more than 50 years (since 1947) to extract the uranium necessary for the manufacture of nuclear  
53 fuel (IRSN, 2019). In the Loire watershed, 64,000 tons of uranium were produced between 1947 and  
54 2002, i.e., around 80% of total French production (IRSN, 2019). A total of 138 mining installations are  
55 located in the Loire basin, all located in the southern part of the basin, with the most uranium-rich  
56 rocks (Ielsch et al., 2017) (Figure 1). Moreover, the Loire River is one of the most nuclearized rivers in  
57 Europe since the 1960s, especially by the construction of Nuclear Power Plants (NPP) first equipped  
58 with reactors from the Natural Uranium Graphite Gas (NUGG) sector, then with Pressurized Water  
59 Reactors (PWRs). The NUGG reactors were set up along the Loire River between 1963 (Chinon) and  
60 1971 (Saint-Laurent-des-Eaux). In 1980, the first PWR was commissioned (Dampierre) and PWRs  
61 gradually replaced the NUGG reactors. In 1969 and 1980, two nuclear accidents took place at the  
62 former Saint-Laurent-des-Eaux NPP (NUGG reactors named SLA1 and SLA2 respectively). These  
63 events led to the fusion of fuel elements and plutonium was detected in water and sediment in the  
64 Loire River (Eyrolle et al., 2019; Guignard and Catoire, 2015; IRSN, 2016; Thomas, 1982). All NUGG  
65 reactors located on the Loire watershed were definitely stopped in 1992. Today, 4 NPPs are located  
66 along the Loire River and 1 NPP on the Vienne tributary (on the downstream part of the Loire River).  
67 These NPPs are equipped with PWRs and are currently in operation (Figure 1).

68 Operations in both U mining sites and NPPs can lead to radionuclide releases increasing their  
69 concentration in the environment. Several studies were performed in order to retrace the historical  
70 evolution and the origin of various radionuclides transiting along the Loire River during the last  
71 century (Copard et al., 2021; Eyrolle et al., 2019). Nevertheless, the uranium and lead from nuclear  
72 activities which were transferred along the Loire River since the beginning of the nuclear age remain  
73 poorly documented. This study was part of the PALYNO (NEEDS - Environment) and TRAJECTOIRE  
74 (ANR) projects which aim at establishing the socio-historical trajectories of key non-legacy  
75 contaminants (radionuclides, microplastics and ultra-rare metals) on the major French watersheds  
76 based on the observations (data sets) of the last decades. For this purpose, multi-isotopic tracers  
77 were determined in the same sediment core collected downstream the Loire River Basin and  
78 covering a large period of time, i.e. from the 1930s to present day. Four isotopic ratios were used to  
79 trace anthropogenic origins of uranium and lead:  $^{236}\text{U}/^{238}\text{U}$ ,  $^{233}\text{U}/^{236}\text{U}$ ,  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$ .

80 The  $^{236}\text{U}/^{238}\text{U}$  ratio is a powerful indicator to quantify the contributions of uranium from  
81 anthropogenic origin. The  $^{236}\text{U}$  is mainly produced by neutron capture on  $^{235}\text{U}$  and allow us to  
82 efficiently highlight small anthropogenic U contributions that are completely undetectable by using  
83 conventional methods based on naturally occurring U isotopes ( $^{238}\text{U}$ ,  $^{235}\text{U}$ ,  $^{234}\text{U}$ ) fingerprinting. Three  
84 main sources of  $^{236}\text{U}$  can be distinguished in the environment: global fallout from past nuclear  
85 testing, nuclear accidents and authorized discharges of spent nuclear fuel reprocessing plants. The  
86 global inventory and the relative contribution of these sources in the environment is still to be  
87 understood and some works have been involved in this effort (Casacuberta et al., 2014; Sakaguchi et  
88 al., 2009). The natural  $^{236}\text{U}/^{238}\text{U}$  ratios in the pre-anthropogenic environment range from  $10^{-14}$  to  $10^{-$   
89  $^{10}$ , the typical value of the  $^{236}\text{U}/^{238}\text{U}$  ratio for U-ores ranges between  $10^{-12}$  and  $10^{-10}$  (Steier et al.,  
90 2008; Wilcken et al., 2008). Areas influenced by anthropogenic  $^{236}\text{U}$  display  $^{236}\text{U}/^{238}\text{U}$  ratio values  
91 greater than  $10^{-9}$ : from  $10^{-6}$  to more than  $10^{-3}$  near the Chernobyl damaged NPP (Boulyga and Becker,  
92 2001; Hotchkis et al., 2000; Mironov et al., 2002), from  $10^{-8}$  to  $10^{-6}$  near the Fukushima one (Jaegler  
93 et al., 2019; Sakaguchi et al., 2014; Shinonaga et al., 2014; Yang et al., 2019, 2016), from  $10^{-6}$  to  $10^{-5}$   
94 in the sediments from the Irish Sea impacted by the Sellafield reprocessing plant (Hotchkis et al.,  
95 2000; Ketterer et al., 2003; Marsden et al., 2001; Srncik et al., 2011a) and about  $10^{-9}$  to  $10^{-6}$  in areas  
96 affected by the global fallout from past nuclear testing as is the case in the northern  
97 hemisphere (Quinto et al., 2013, 2009; Sakaguchi et al., 2010, 2009; Shao et al., 2019; Srncik et al.,  
98 2011b). Moreover, the  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio was widely used to trace water masses in  
99 oceans (Casacuberta et al., 2014; Christl et al., 2015; Sakaguchi et al., 2012). However, the large  
100 range of  $^{236}\text{U}/^{238}\text{U}$  variation can sometime lead to signature overlapping making thus difficult the  
101 identification of the U origin. Besides, it is worth mentioning that  $^{236}\text{U}/^{238}\text{U}$  variation depends also to  
102 natural variations of  $^{238}\text{U}$ .

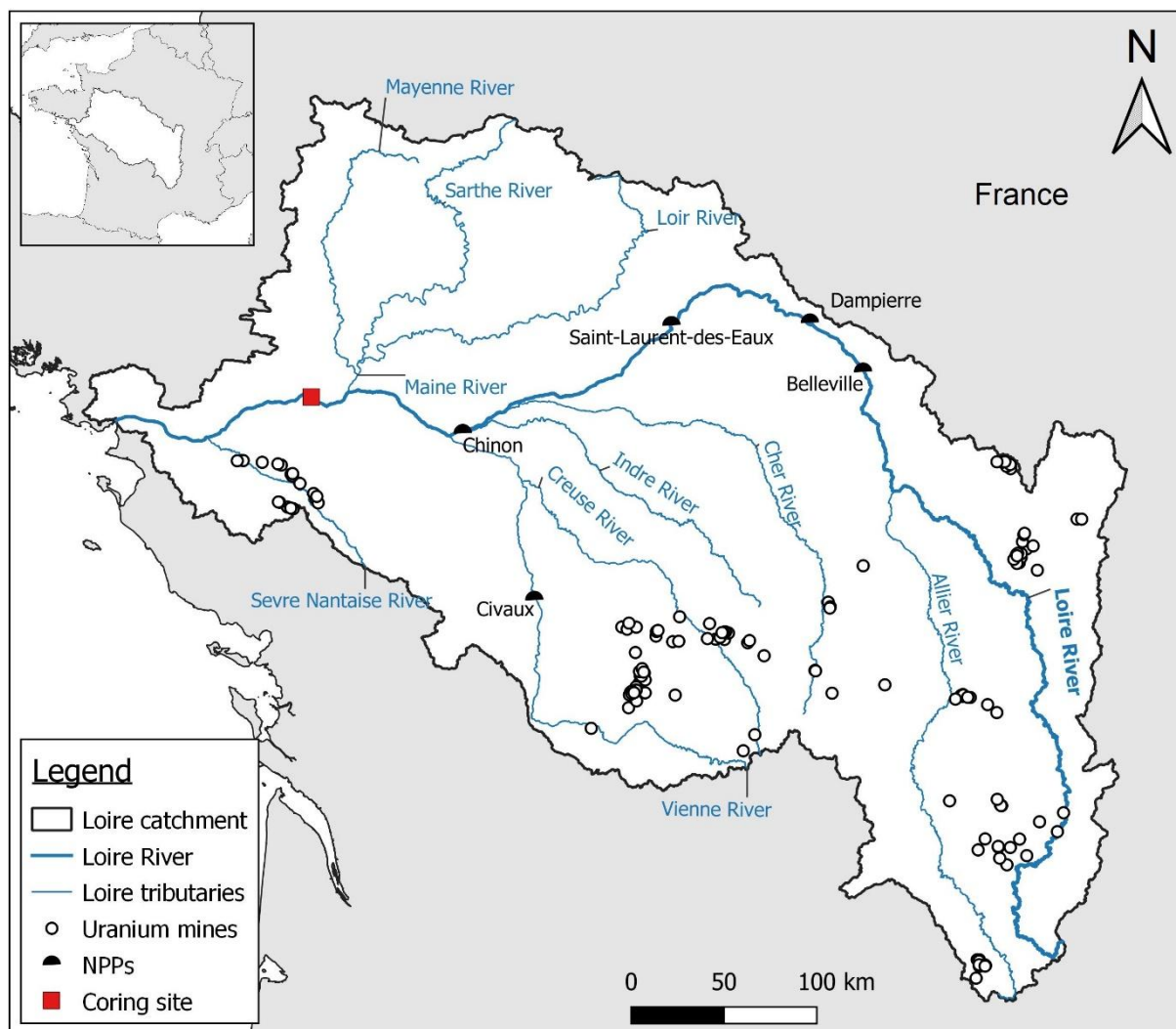
103 A second useful anthropogenic U isotope for environmental studies is  $^{233}\text{U}$ . This isotope has been  
104 measured by Accelerator Mass Spectrometry (AMS) in samples impacted by nuclear weapons and  
105 close to contaminated sites (Child and Hotchkis, 2013; Tumey et al., 2009). Recent pioneering works  
106 at the Vienna Environmental Research Accelerator (VERA) allowed very low-level measurements of  
107  $^{233}\text{U}$  in environmental samples by AMS (Hain et al., 2020, 2017). Thanks to these studies, the  
108  $^{233}\text{U}/^{236}\text{U}$  ratio became a new powerful tracer, combining two anthropogenic isotopes emitted  
109 simultaneously in different proportions from the above described sources, allowing to discriminate  
110 environmental emissions of civil nuclear activities from global fallout (Hain et al., 2020, 2017; Qiao et  
111 al., 2021, 2020). This tracer, independent of natural  $^{238}\text{U}$  variations, offers also new perspectives as a  
112 new oceanic tracer (Lin et al., 2021). In brief, the main source for anthropogenic  $^{233}\text{U}$  is nuclear  
113 weapons (global atmospheric fallout), either directly released by  $^{233}\text{U}$  fueled weapons or produced in

114 thermonuclear weapons by the  $^{235}\text{U}(n,3n)^{233}\text{U}$  reaction. This reaction requires fast neutrons and  
115 highly enriched U in contrast to nuclear power plants for which thermal neutrons are needed for the  
116 fission of  $^{235}\text{U}$ . On the other hand the  $^{236}\text{U}$  can be produced by both nuclear power plants and fission  
117 and thermonuclear weapons. Hain et al. (2020) estimated an average value of the  $^{233}\text{U}/^{236}\text{U}$  ratio  
118 from global fallout equal to  $(1.40 \pm 0.15) \times 10^{-2}$ . Reactor model calculations obtained for the fuel of  
119 pressurized water reactors give an average  $^{233}\text{U}/^{236}\text{U}$  close to  $\sim 10^{-7}$  (Naegeli, 2004). Therefore, any  
120 actual  $^{233}\text{U}/^{236}\text{U}$  atomic ratios below  $(1.40 \pm 0.12) \times 10^{-2}$  for natural samples would indicate the  
121 admixing of reactor-associated  $^{236}\text{U}$ . In the Irish Sea, an average  $^{233}\text{U}/^{236}\text{U}$  atomic ratio of  
122  $(0.12 \pm 0.01) \times 10^{-2}$  has been measured by Hain et al. (2020), reflecting a dominant reactor signal  
123 released from Sellafield. These results clearly show that this isotope ratio could be used to  
124 discriminate the different uranium sources in the environment.

125 Following the pioneering work of Clair Patterson on the identification of Pb air pollution sources (C.C  
126 Patterson and Settle, 1987; Clair C Patterson and Settle, 1987), lead isotopes have been widely used  
127 for environmental studies allowing identifying sources of lead pollution (Komárek et al., 2008). Lead  
128 isotopes have been also studied in a number of French rivers such as the Loire River (Négre and  
129 Petelet-Giraud, 2012) and the Seine River (Ayrault et al., 2012). Monna et al. (1997) identified Pb  
130 isotope ratio end-members of airborne particulate material in France. In the context of  
131 environmental impact assessment studies related to uranium mining activities, Pb isotopes  
132 constitute a relevant tracer. Indeed, the enriched  $^{238}\text{U}$  and  $^{235}\text{U}$  contents in U-ores lead to the  
133 production of radiogenic  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$  with  $^{206}\text{Pb}$  being the most abundant isotope. In contrast, the  
134 low Th contents of U-ores lead to a restricted production of  $^{208}\text{Pb}$ , generating thus a major contrast  
135 between the isotopic signatures of the U-ores and that of the Earth crust (hereafter, Present Day  
136 Average Crustal (PDAC) (Cumming and Richards, 1975; Stacey and Kramers, 1975)) for which  $^{208}\text{Pb}$  is  
137 the most abundant isotope. It is worth mentioning that the Pb isotope signature of U-ores is also  
138 markedly different from that of industrial lead and that from gasolines for which  $^{208}\text{Pb}$  is also the  
139 most abundant isotope.  $^{204}\text{Pb}$  is not a radiogenic isotope, and thus its concentration does not evolve  
140 on Earth over time. The isotopes of lead were used in several environmental impact assessment  
141 studies of uranium mining sites or unexploited uranium deposits (Bollhöfer, 2012; Bollhöfer et al.,  
142 2006; Bollhöfer and Martin, 2003; Dang et al., 2018; Frostick et al., 2011, 2008; Gulson et al., 1989;  
143 Kyser et al., 2015; Liu et al., 2018; Munksgaard et al., 2003; Santos and Tassinari, 2012; Vecchia et al.,  
144 2017) and although roughly 250 sites were operated in France (IRSN, 2019) only three published  
145 works deal with Pb isotopes (Cuvier et al., 2016; Gourgiotis et al., 2020; Martin et al., 2020). Mining  
146 activities (dewatering water, emission of dust, wastewaters from tailings storage basins, etc.) or even  
147 natural phenomena of weathering of the deposit, particularly in the case of unexploited deposits

148 (e.g. erosion, leaching), contribute also to the transport of Pb coming from the U-ore (hereafter  
149 marked as Pb\*) outside the deposit (Kister et al., 2004).

150 This work aims to investigate past major contamination events which occurred during the last  
151 seventy years of development of nuclear industries from mining to accidental releases of  
152 radionuclides by nuclear power plants. The originality of this study is to combine the newly  
153 developed  $^{233}\text{U}/^{236}\text{U}$  tracer,  $^{236}\text{U}/^{238}\text{U}$  and associated lead isotopes. Although the former Saint-  
154 Laurent-des-Eaux NUGG NPP accidents resulted in well-known contamination of waters and  
155 sediments of the Loire River by accidental discharges of plutonium (IRSN, 2016; Thomas, 1982), any  
156 study of these ratios had been carried out so far on this river. Data of  $^{233}\text{U}$  and  $^{236}\text{U}$  isotopes were  
157 explored to evaluate the relevance of this tracer to distinguish emissions of civil nuclear industry  
158 from weapons fallout while lead isotopes were used as a potential tracer to highlight uranium mining  
159 and milling activities.



160  
161 *Figure 1: Map of uranium mines, NPPs and coring site locations in the Loire River catchment in France.*

162

163 **Materials and methods**

164 **Sediment core sampling and dating.**

165 The sampling site is located at coordinates 47 ° 23'34.0 "N 0 ° 51'23.1" W, on an alluvial island in the  
166 town of Montjean-sur-Loire (France), which is located downstream all the Loire and Vienne NPPs and  
167 most of uranium mines (Figure 1), but upstream of the estuary thus outside the influence of the tides  
168 of the Atlantic Ocean. The coring site, at an altitude of 12 to 17 m, is submerged only during flood  
169 events for the last decade, when the flow of the Loire exceeds 2,500 m<sup>3</sup>/s (the average annual flow  
170 of the Loire at the station of Montjean-sur-Loire is 840 m<sup>3</sup>/s). This sampling area, described by  
171 Grosbois et al. (2012), is considered to be a coring site suitable for historical tracing of contamination  
172 due to the sedimentary accumulation of fine particles during flood episodes thanks to the presence  
173 of vegetation which slows down the currents and favours the deposition of fine material. To obtain  
174 the final master core, several one-meter sediment cores were collected in September 2016, using a  
175 percussion driller (Cobra TT, SDEC, France) with transparent PVC tubes (diameter 46 mm). Once in  
176 the laboratory, 5 cm slices were stored at -25°C and freeze-dried under dehydrated nitrogen flux in  
177 order to avoid any atmospheric exchange and sieved at 2 mm before analyses. The age model is  
178 based on <sup>137</sup>Cs concentrations and <sup>238</sup>Pu/<sup>239</sup>Pu activity ratio. Radiocesium concentrations show two  
179 major peaks at 92.5 cm and 37.5 cm related to the peak of radioactive emissions from atmospheric  
180 nuclear tests in 1963 and to the radioactive fallout from the Chernobyl accident in 1986 respectively.  
181 In addition, plutonium isotopes (<sup>238</sup>Pu/<sup>239+240</sup>Pu activity ratio) also show two peaks, the first one at  
182 77.5 cm and the second one at 52.5 cm. Although these isotopes were released during atmospheric  
183 nuclear tests over the 1945 - 1980 period and the explosion of the Transit 5 BN-3 satellite in 1964,  
184 plutonium isotopes ratios observed in the particular case of the Loire River are due to accidental  
185 liquid discharges of plutonium by the Saint-Laurent-des-Eaux NPP in 1969 (77.5 cm depth) and 1980  
186 (52.5 cm depth). It is important to note that in the case of fluvial environments, the sedimentation  
187 rate is variable over time contrary to lakes and quiet environments. Consequently, the <sup>210</sup>Pb<sub>xs</sub> dating  
188 method is not available in this study as previously mentioned in Grosbois et al. (2012), Eyrolle et al.  
189 (2019), Morereau (2020) and Copard et al. (2021). Hence, these identified chronological landmarks  
190 (1963, 1969, 1980 and 1986) allow obtaining a robust age model presenting two main periods with  
191 constant sedimentation rates, the 1963 – 1986 period with 2.4 ± 0.2 cm/y and the 1986 – 2016  
192 period with 1.3 ± 0.2 cm/y with uncertainties estimated to ± 2 years.

193

194 **Chemical preparation of samples.**

195 High-purity acids were obtained by distillation (Savillex® DST-1000 system) of hydrochloric acid (HCl,  
196 Merck, Emsure 37%), nitric acid (HNO<sub>3</sub>, VWR Chemicals, Normapur 68%). De-ionized water was



197 produced by a Millipore system (18.2 MΩ/cm resistivity). All sample dilutions and solutions for  
198 elemental and isotope analysis were performed with 0.5 mol/L (M) HNO<sub>3</sub>. This acid was also used as  
199 the blank and for instrument washing between standards and samples.

200 For isotopic analysis, ~ 10 g of finely ground dry samples were calcined in an oven at 480°C for 52h in  
201 view of the realization of chemical separations in order to extract uranium and lead prior to the  
202 measurement steps. After calcination, the samples were transferred to the Teflon vials (Savillex) and  
203 aqua regia has been added to the dry residue. The mix was heated at 90 °C for 10 h in closed vials  
204 and after it had cooled down, the solution was filtered using a disposable filter set of 0.45 μm  
205 porosity. The insoluble residue was discarded and the filtrate was collected to the same vials and  
206 evaporated to dryness before adding 2 mL of 3 M (mol/L) of HNO<sub>3</sub>. Then, the uranium was separated  
207 from the sample matrix using UTEVA resin (TrisKem International) previously conditioned in 3 M  
208 HNO<sub>3</sub> (Douville et al., 2010): after sample loading onto the columns, the resin was rinsed with 3 M  
209 HNO<sub>3</sub> to eliminate the sample matrix. This fraction was collected for Pb isotope analysis. Then the  
210 resin was rinsed with 3 M HCl for Th elution and U was finally eluted with 0.1 M HCl. U fractions were  
211 evaporated to dryness and then taken up in HNO<sub>3</sub> 0.05 M. Five selected U samples were split in two  
212 parts, one for ICP-MS/MS analysis and one for analysis by AMS. While samples are ready for ICP-  
213 MS/MS analysis then, AMS analysis requires the preparation of solid material from the sample  
214 aliquots.

215 For this aim, 1-2 mg of Fe and 1 mL NH<sub>3</sub> 20% (VWR, ultrapure, Pennsylvania, United States) were  
216 added to the solution. The precipitate is separated from the supernatant by centrifugation, then  
217 evaporated in an oven during 4h at 90°C. Iron oxide samples containing the uranium fractions were  
218 then placed in an electric furnace at 800°C during 3h. Finally, iron oxide samples were pressed into  
219 aluminum sample holders for AMS analyses (Lin et al., 2021; Steier et al., 2019).

220 Elution fractions containing Pb were evaporated to dryness and redissolved in 0.3 mL of HBr (0.5 M,  
221 Ultrapur) for Pb separation and purification by ion-exchange resin (Biorad, AG 1-X8, 200-400 mesh).  
222 The resin was previously washed (0.25 M HNO<sub>3</sub> and HCl 0.2 M) and conditioned with 0.5 M HBr. In  
223 short, the protocol (Manhes et al., 1984) consists of the sample load onto the column, a matrix wash  
224 with ~5 mL of HBr (0.5 M), and Pb elution with ~5 mL of HCl (0.2 M). Then, the samples were  
225 evaporated to dryness and taken up in HNO<sub>3</sub> 0.5 M for ICP-MS/MS analysis.

#### 226 Uranium and lead isotope analysis by ICP-MS/MS.

227 Lead and <sup>236</sup>U/<sup>238</sup>U isotope ratio measurements were performed using an Agilent 8800 ICP-MS/MS  
228 (Agilent Technologies, Tokyo, Japan) housed at the LELI laboratory of the French Institute of

229 Radiological Protection and Nuclear Safety (PATERSON mass spectrometry Platform, IRSN, Fontenay-  
230 aux-Roses, France).

231 In short, for  $^{236}\text{U}/^{238}\text{U}$  ratio analysis the ICP-MS/MS was coupled with an efficient desolvating module  
232 (APEX  $\Omega$ , Elemental Scientific) and all measurements were performed in MS/MS mass shift mode.  
233  $\text{N}_2\text{O}$  was introduced in the collision reaction cell and uranium was analyzed in  $\text{UO}^+$  form. This  
234 configuration significantly decreased uranium hydride formation ( $^{235}\text{UH}^+$ ) as well as  $^{238}\text{U}$  and  $^{235}\text{U}$   
235 peak tailing allowing an accurate determination of low  $^{236}\text{U}/^{238}\text{U}$  isotope ratios. Detailed information  
236 about  $^{236}\text{U}/^{238}\text{U}$  measurements by ICP-MS/MS can be found in Jaegler et al. (2020).

237 For lead isotope analysis ( $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$ ) the ICP-MS/MS was run in single quadrupole  
238 mode, and a Peltier-cooled ( $2^\circ\text{C}$ ) Scott-type spray chamber with a PFA nebulizer (0.33 mL/min, ESI,  
239 U.S.) was used as the introduction system. The self-aspiration mode was used for the sample  
240 introduction and all analyses were performed in pulse counting mode. More details about lead  
241 isotope ratio measurements can be found in Gourgiotis et al. (2020). ICP-MS/MS data can be found in  
242 Table 1.

#### 243 AMS analysis.

244 The AMS measurement of  $^{236}\text{U}/^{238}\text{U}$  and  $^{233}\text{U}/^{238}\text{U}$  atomic ratios was carried out at the Vienna  
245 Environmental Research Accelerator (VERA) facility at the University of Vienna. A detailed description  
246 of the method and configuration for the AMS measurement of  $^{236}\text{U}$  and  $^{233}\text{U}$  at VERA has been  
247 reported in Hain et al. (2020) and Steier et al. (2019). The overall detection efficiency of the system  
248 for U atoms in the sputter target was  $5 \times 10^{-4}$  (Steier et al., 2019) assuming complete consumption of  
249 the sputter material. The majority of the measurement time was dedicated to the less abundant  $^{233}\text{U}$ ,  
250 while  $^{236}\text{U}$  was measured shorter, and the whole material usually was not used up. In general,  $^{233}\text{U}$   
251 sample count rates are roughly one order of magnitude above instrumental and procedural blank.  
252 AMS data can be found in Table 1.

#### 253 Gamma spectrometry.

254 For the gamma spectrometry, samples were beforehand freeze-dried and packed into tightly closed  
255 plastic boxes (17-60 mL). They were placed under vacuum in a hermetically sealed bag preventing  
256 any exchange of air and light with the outside which could interfere with the secular equilibrium of  
257 the radionuclides. The gamma emitters were measured using high resolution and low-background  
258 Germanium Hyper pure detectors in the LMRE laboratory of the French Institute of Radiological  
259 Protection and Nuclear Safety in Orsay (Bouisset and Calmet, 1997). Only  $^{238}\text{U}$  was presented here  
260 which was measured from its decay products assuming secular equilibrium. Gamma spectrometry  
261 data can be found in Table 1.



263 Table 1: Isotope ratios, concentrations and activities of the samples of the sediment core. Uncertainties are expressed for a coverage factor  $k=2$ . Values of  
 264 ( $^{238}\text{Pu}/^{239+240}\text{Pu}$ ) in the sediment core and in atmospheric deposit are from Eyrolle et al. (2019). The PADC (Present Day Average Crustal) is from  
 265 Stacey and Kramers (1975).

| Average depth (cm) | Year | $^{236}\text{U}/^{238}\text{U}$ ( $\times 10^{-8}$ ) |            | $^{233}\text{U}/^{236}\text{U}$ ( $\times 10^{-2}$ ) | $^{238}\text{U}$             | $^{236}\text{U}$ ( $\times 10^{-8}$ ) | $(^{236}\text{U})$    | $(^{233}\text{U})$ | $^{204}\text{Pb}/^{207}\text{Pb}$ | $^{206}\text{Pb}/^{207}\text{Pb}$ | $^{208}\text{Pb}/^{207}\text{Pb}$ | $(^{238}\text{Pu}/^{239+240}\text{Pu})$ | $(^{238}\text{Pu}/^{239+240}\text{Pu})$ |
|--------------------|------|--|------------|--|------------------------------|---------------------------------------|-----------------------|--------------------|-----------------------------------|-----------------------------------|-----------------------------------|---|---|
|                    |      | ICP-MS/MS  | AMS        | AMS  | ( $\mu\text{g/g}$ gamma sp.) | (atoms/g)                             | ( $\mu\text{Bq/kg}$ ) |                    |                                   |                                   |                                   |   | Sediment core                           |
| 2.5                | 2011 | 0,94 ±0,07   | 0,96 ±0,07 | 0,29 ±0,13   |                              |                                       |                       |                    | 0,06419 ±0,0003                   | 1,182 ±0,004                      | 2,460 ±0,006                      |   | 0,031                                   |
| 17.5               | 2002 |  |            |  | 5,6 ±0,6                     |                                       |                       |                    |                                   |                                   |                                   |   | 0,032                                   |
| 27.5               | 1994 |  |            |  | 5,5 ±0,6                     |                                       |                       |                    |                                   |                                   |                                   | 0,0362                                  | 0,034                                   |
| 37.5               | 1986 | 1,32 ±0,09   | 1,18 ±0,12 | 0,78 ±0,11   | 5,6 ±0,6                     | 1,85 ±0,24                            | 174 ±22               | 199 ±37            | 0,06415 ±0,0004                   | 1,163 ±0,003                      | 2,441 ±0,007                      | 0,0362                                  | 0,036                                   |
| 42.5               | 1984 | 1,34 ±0,05   |            |  |                              |                                       |                       |                    |                                   |                                   |                                   |   | 0,037                                   |
| 47.5               | 1982 | 1,43 ±0,05   |            |  | 5,6 ±0,6                     | 2,05 ±0,23                            | 192 ±22               |                    |                                   |                                   |                                   | 0,0628                                  | 0,037                                   |
| 52.5               | 1980 | 1,83 ±0,09   | 1,86 ±0,15 | 0,23 ±0,05   | 5,7 ±0,6                     | 2,65 ±0,31                            | 249 ±29               | 83 ±20             | 0,06402 ±0,0004                   | 1,163 ±0,004                      | 2,440 ±0,008                      | 0,0782                                  | 0,038                                   |
| 57.5               | 1978 |  |            |  | 5,8 ±0,6                     |                                       |                       |                    |                                   |                                   |                                   | 0,0681                                  | 0,038                                   |
| 62.5               | 1976 |  |            |  | 5,9 ±0,6                     |                                       |                       |                    |                                   |                                   |                                   |   | 0,039                                   |
| 67.5               | 1973 | 2,28 ±0,09   |            |  | 6,0 ±0,6                     | 3,44 ±0,39                            | 322 ±37               |                    |                                   |                                   |                                   |   | 0,040                                   |
| 72.5               | 1971 |  |            |  | 5,9 ±0,6                     |                                       |                       |                    |                                   |                                   |                                   | 0,0449                                  | 0,039                                   |
| 77.5               | 1969 | 2,43 ±0,06   |            |  | 5,9 ±0,6                     | 3,61 ±0,39                            | 339 ±36               |                    |                                   |                                   |                                   | 0,0572                                  | 0,037                                   |
| 82.5               | 1967 |  |            |  | 5,8 ±0,6                     |                                       |                       |                    |                                   |                                   |                                   | 0,0506                                  | 0,030                                   |
| 87.5               | 1965 |  |            |  | 5,8 ±0,6                     |                                       |                       |                    |                                   |                                   |                                   | 0,0276                                  | 0,025                                   |
| 92.5               | 1963 | 2,15 ±0,16   | 2,20 ±0,47 | 0,44 ±0,15   |                              |                                       |                       |                    | 0,06393 ±0,0004                   | 1,170 ±0,003                      | 2,452 ±0,006                      |   | 0,025                                   |
| 102.5              | 1959 |  |            |  | 6,6 ±0,7                     |                                       |                       |                    |                                   | 1,181 ±0,004                      | 2,462 ±0,006                      | 0,0201                                  | 0,026                                   |
| 112.5              | 1954 |  |            |  | 6,2 ±0,6                     |                                       |                       |                    |                                   |                                   |                                   | 0,0180                                  |   |
| 122.5              | 1950 | 0,34 ±0,09   | 0,25 ±0,03 | 2,49 ±0,59   | 5,7 ±0,6                     | 0,49 ±0,14                            | 46 ±13                | 168 ±64            | 0,06417 ±0,0003                   | 1,177 ±0,003                      | 2,453 ±0,007                      |   |   |
| PDAC               |      |  |            |  |                              |                                       |                       |                    |                                   | 1.197                             | 2.472                             |   |   |

## 266 Results and discussion

267

268 The  $^{236}\text{U}/^{238}\text{U}$  shows anthropogenic sources of uranium.

269 The measurements of  $^{236}\text{U}/^{238}\text{U}$  isotope ratio were carried out onto 9 samples distributed mainly in  
270 the central core layers covering the period between 1950 and 1990. The top layer of the archive  
271 (2011) represents the reference value of the current levels and the sample of the bottom of the core  
272 (1950) the value before the NPPs activities in the Loire River (first reactors in the Loire River starting  
273 from 1963). Some of these samples were also analyzed by both ICP-MS/MS and AMS in order to  
274 validate the performance of the recently developed method for  $^{236}\text{U}/^{238}\text{U}$  ratio analysis by ICP-  
275 MS/MS (Jaegler et al., 2020). As can be seen in Figure 2, both techniques show similar results within  
276 analytical uncertainties.

277 Activity ratios of Pu from Eyrolle et al. (2019), have been used in this study in order to highlight the  
278 accidental releases that occurred in 1969 and 1980 from the former NUGG reactors of the Saint-  
279 Laurent des Eaux NPP. These values, higher than the theoretical background ( $^{238}\text{Pu}/^{239+240}\text{Pu}$ ) ratios as  
280 calculated by the authors, are clearly related to the two NUGG NPP events as mentioned above  
281 (Figure 2c) (Eyrolle et al., 2019).

282 The  $^{236}\text{U}/^{238}\text{U}$  ratios range between  $0.34 \times 10^{-8}$  and  $2.43 \times 10^{-8}$  (Figure 2a) and as  $^{238}\text{U}$  concentration  
283 remains almost constant in these sediment layers, this ratio fluctuation is due to  $^{236}\text{U}$  variation only  
284 (Figure 2b). It's worth mentioning that  $^{238}\text{U}$  concentrations are within natural values variation. The  
285 lowest value was measured at the 122.5 cm average depth of the core, dated back to 1950. This layer  
286 should be slightly influenced by anthropogenic  $^{236}\text{U}$  considering the small number of weapon tests  
287 before this year (only 9 tests performed (Mikhailov et al., 1999)) or by  $^{236}\text{U}$  downward migration in  
288 the core. Indeed, the lowest value, measured in 1950, doesn't reach expected pre-nuclear  
289 values  $< 10^{-12}$  (Steier et al., 2008).

290 From 1950 to 1969 a clear increase of the  $^{236}\text{U}/^{238}\text{U}$  ratio was observed with the maximum value in  
291 1969 ( $2.43 \times 10^{-8}$ ). This high value could correspond to the first event of the Saint-Laurent-des-Eaux  
292 NUGG NPP, as pointed out by Pu isotopes. Indeed, the fact that the  $^{236}\text{U}/^{238}\text{U}$  ratio in 1969 is higher  
293 than the value in 1963 (maximum contribution of the global fallout), indicates the possibility of a  
294 second source of  $^{236}\text{U}$ . From 1969 onwards, the  $^{236}\text{U}/^{238}\text{U}$  ratio decreases to reach the current value  
295 of  $9.4 \times 10^{-9}$  (2011) with a slope break in 1980 ( $1.83 \times 10^{-8}$ ) corresponding probably to the second  
296 NPP event according to the Pu isotopes (Figure 2a and 2c). Indeed, no more significant direct global  
297 fallout occurred and, thus, a second input of  $^{236}\text{U}$  should be considered in 1980. From 1983 onwards,  
298 the  $^{236}\text{U}/^{238}\text{U}$  ratio doesn't reach the value recorded in 1950 meaning that the additional  $^{236}\text{U}$  might  
299 originate from the redeposition of global fallout-derived uranium and/or uranium from the former

300 NUGG reactors of the Saint-Laurent-des-Eaux events which was deposited elsewhere and  
301 subsequently resuspended. In this case study it is worth mentioning that the  $^{236}\text{U}/^{238}\text{U}$  signature is  
302 not a relevant tracer to highlight U-mine inputs due to the high values of anthropogenic  $^{236}\text{U}$ .

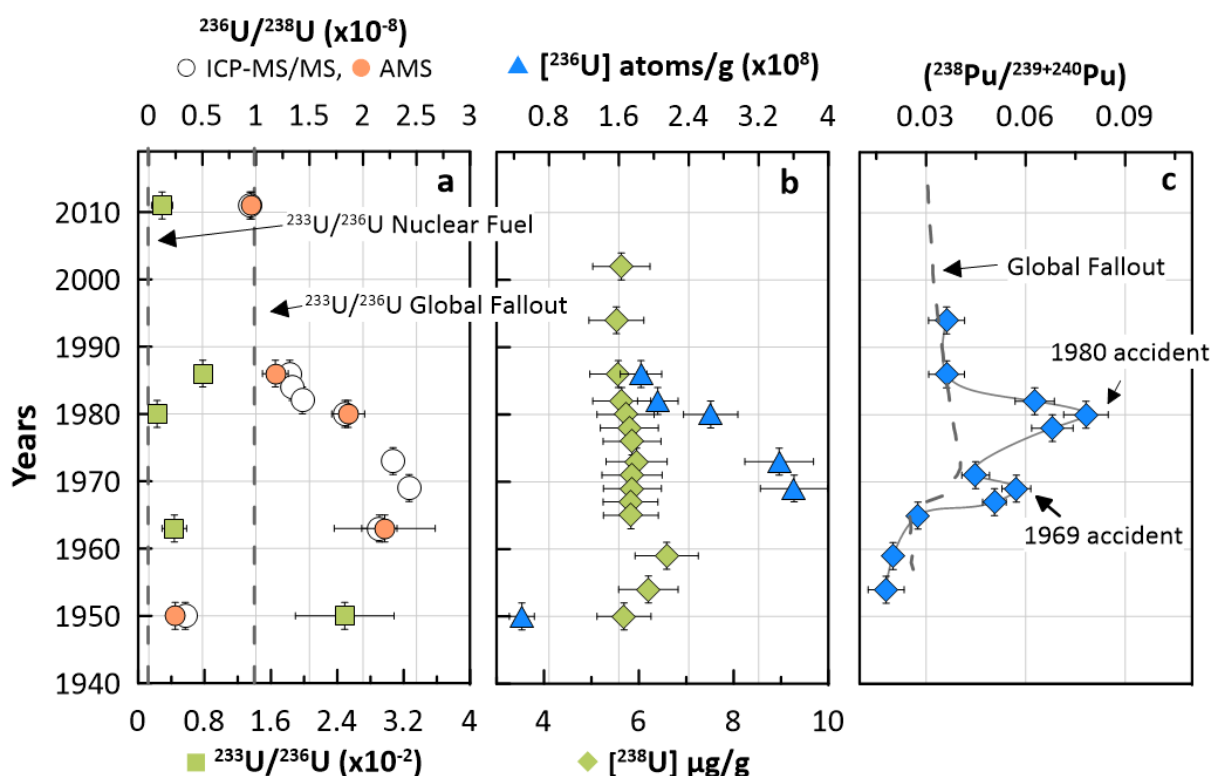
303 In systems affected by different anthropogenic sources (e.g. global fallout and NPP accident), the lack  
304 of a second anthropogenic uranium isotope is a disadvantage compared to plutonium for the source  
305 identification:  $^{236}\text{U}/^{238}\text{U}$  ratio variation depends on the dilution with natural U. For the Loire River, it  
306 is clear that the  $^{236}\text{U}/^{238}\text{U}$  ratio variation fits within the global fallout range ( $10^{-9}$  to  $10^{-6}$ ) (Alam et al.,  
307 2021; Liu et al., 2020; Quinto et al., 2013; Sakaguchi et al., 2010, 2009; Srncik et al., 2011a; Wang et  
308 al., 2021; Yang et al., 2019), thus making a reliable identification of possible other U emission sources  
309 challenging.

310 The  $^{233}\text{U}/^{236}\text{U}$  allows discriminating environmental emissions of civil nuclear activities from  
311 global fallout.

312 The  $^{233}\text{U}$  isotope was analyzed in order to explore the application of the  $^{233}\text{U}/^{236}\text{U}$  signature in the  
313 context of the present work. This isotope ratio stays undisturbed by chemical fractionation in the  
314 environment as well as during sample preparation, simplifying the interpretation of the  
315 measurement results in the presence of mixing and dilution processes (Child and Hotchkis, 2013). The  
316  $^{233}\text{U}/^{236}\text{U}$  ratio of the layer dated back to 1950 showed a value of  $(2.49 \pm 0.6) \times 10^{-2}$  which is higher  
317 compared to the average value for the global fallout  $(1.40 \pm 0.15) \times 10^{-2}$  (Hain et al., 2020) (Figure 2a).  
318 According to the work of Hain et al. (2020) two phases of nuclear weapon testing can be  
319 distinguished (1952-1958 and 1961-1962) and a  $^{233}\text{U}/^{236}\text{U}$  ratio of  $(5.1 \pm 1.1) \times 10^{-2}$  was obtained by  
320 the authors for the earlier phase. Higher values than the average  $^{233}\text{U}/^{236}\text{U}$  global fallout ratio have  
321 also been found in Baltic Sea sediments ( $^{233}\text{U}/^{236}\text{U} \approx 0.1$ ) (Lin et al., 2021) and in a sediment core  
322 taken at the continental slope of the Philippine Sea off Mindanao Island  
323 ( $^{233}\text{U}/^{236}\text{U}_{\text{max}} = (3.47 \pm 0.62) \times 10^{-2}$ ) (Qiao et al., 2022). Therefore, considering precision of the age  
324 model the age ( $\pm 2$  years), analytical uncertainties and also a potential slight downward migration of  
325 anthropogenic U ( $^{238}\text{U}$  detrital is not influenced by migration), this point fits with the earlier phase of  
326 the nuclear weapon testing. The other four points (from 1963 to 2011) indicate the influence of NPP-  
327 derived U. Even in the layer corresponding to the peak of the global fallout (1963), the isotope  
328 signature is clearly influenced by a NPP signature, probably due to a downward migration of the  $^{233}\text{U}$   
329 and  $^{236}\text{U}$  isotopes arising from the event in 1969. Similar processes of  $^{236}\text{U}$  downward migration have  
330 already been observed in an ombrotrophic peat core (Quinto et al., 2013) and in marine  
331 sediments (Qiao et al., 2022). It should be noted that for the NPP accidents, our values were  
332 compared with the  $^{233}\text{U}/^{236}\text{U}$  signature measured in sediments in the Irish Sea close to the  
333 reprocessing Sellafield plant as determined by Hain et al. (2020). This value was found to be equal to

334  $(0.12 \pm 0.01) \times 10^{-2}$  (marked by vertical dashed line in Figure 2a) and according to the authors reflect  
 335 a dominant reactor signal released from Sellafield.

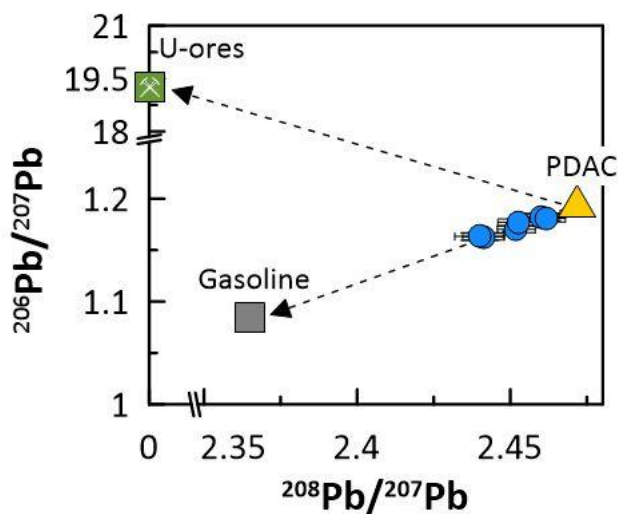
336 It is important to point out that thanks to the  $^{233}\text{U}/^{236}\text{U}$  tracer we can show that even after the  
 337 second event in 1980, a contribution of civil nuclear U completely “blind” to the  $^{238}\text{U}$  concentration  
 338 (Figure 2 b), is recorded in the sediment core in 1986. Civil nuclear U is also measured in 2011 and  
 339 this contribution may be explained, again, by: i) the resuspension of past contaminated particles  
 340 along the Loire River and/or ii) post-depositional upward anthropogenic U migration in the core.  
 341 However, based on the  $^{233}\text{U}/^{236}\text{U}$  ratio in 2011, the presence of a potential additional source of  
 342 anthropogenic U at ultra-trace level, i.e. far below the detection limit of conventional analytical  
 343 methods, cannot be excluded. As this hypothesis is based only on a single measurement point, future  
 344 studies are needed to further assess it, e.g. by analyzing surface sediments and river water in the  
 345 vicinity of NPPs. It is important to mention that the  $^{233}\text{U}$  and  $^{236}\text{U}$  levels measured in this work  
 346 present a negligible radiological impact on health and on the environment: the highest activities for  
 347  $^{233}\text{U}$  and  $^{236}\text{U}$  were found to be  $2 \times 10^{-4}$  Bq/kg and  $3.4 \times 10^{-4}$  Bq/kg, respectively. These activities are to  
 348 be compared with the natural  $^{238}\text{U}$  activity of the core which is  $\sim 68$  Bq/kg ( $\sim 5.5$  ppm).



349  
 350 Figure 2: Sediment core profiles of: a)  $^{236}\text{U}/^{238}\text{U}$  and  $^{233}\text{U}/^{236}\text{U}$  isotope ratios, b)  $^{236}\text{U}$  and  $^{238}\text{U}$  concentrations and c)  
 351  $(^{238}\text{Pu}/^{239+240}\text{Pu})$  activity ratios, modified from Eyrolle et al. (2019). The three dashed lines indicate the  $^{233}\text{U}/^{236}\text{U}$  average  
 352 ratios for the spent nuclear fuel and global fallout (Hain et al., 2020) (a) and the average  $(^{238}\text{Pu}/^{239+240}\text{Pu})$  activity ratios for  
 353 the global fallout Eyrolle et al. (2019) (c). Uncertainties are expressed for a coverage factor  $k=2$  and when they are not  
 354 visible, are included in the points.

355

356 Investigating the impact of the U-mining and milling activities using stable Pb isotope ratio.  
 357 Lead isotope ratios were plotted in a three isotope diagram (Figure 3) in which three end-members  
 358 were represented: the PDAC (Stacey and Kramers, 1975), the gasoline emissions in France (Monna et  
 359 al., 1997) and the U-ores from France. For the calculation of the U-ore end-member an age of  
 360  $\approx 280$  Ma, corresponding to an average value of the U deposition in the Loire watershed and in  
 361 particular in the study area, was used (Cathelineau et al., 1990). This age leads to a radiogenic  
 362  $^{206}\text{Pb}/^{207}\text{Pb}$  end-member equal to 19.27. As can be seen in Figure 3, the good alignment of the  
 363 samples confirms a binary mixing between the Pb from the PDAC and the Pb from gasoline emissions  
 364 without any significant influence from the U-mining and milling activities. This finding is in agreement  
 365 with previous works in the Loire River showing an important influence of Pb from gasoline  
 366 emissions (Négre and Petelet-Giraud, 2012). As radiogenic Pb is rather associated with particulate  
 367 bearing phases, the fact that no Pb marked by the U-ore signature was found highlights that U-  
 368 mining material dissemination was probably limited closer to mining sites (e.g. in (Cuvier et al., 2016;  
 369 Gourgiotis et al., 2020; Martin et al., 2020)). For this reason coring the sub-watershed of the former  
 370 U-mines may be more relevant to highlight signatures of U ore and associated mining activities in  
 371 sediments. This isotopic study shows that U-bearing minerals are poorly transported during  
 372 sedimentary cascade in the Loire basin.



373  
 374 *Figure 3: Lead isotope ratio measured in the sediment core collected in the Loire River (blue dots) in a three isotope plot. For*  
 375 *the gasoline (grey square) and the geochemical background (PDAC) endmembers, the values of Monna et al. (1997) and*  
 376 *Stacey and Kramers (1975) were used, respectively. For the U-ore endmember a ratio of  $^{206}\text{Pb}/^{207}\text{Pb}$  equal to 19.27 was used*  
 377 *corresponding to an average age of  $\approx 280$  Ma (Cathelineau et al., 1990).*

378  
 379 In Figure 4 the decrease of the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio between 1959 and 1986 highlights the increasing use  
 380 of lead in gasoline (Ayrault et al., 2012; Monna et al., 1997). Considering the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio dated  
 381 back to 1950 as the reference value (sediments not or slightly influenced by gasoline-derived Pb),



382 ratio values in recent years return back to the reference value pointing probably out the resilience  
383 time of the system.

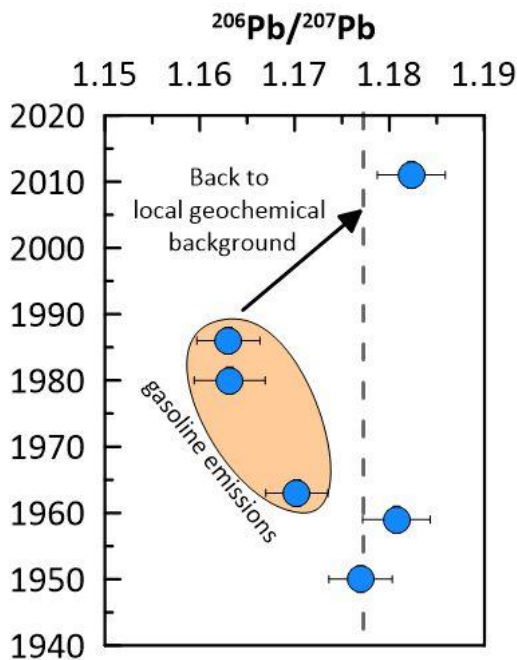
384 A binary mixing model taking into account the atomic abundances of Pb (Gourgiotis et al., 2020) has  
385 been used to determine the proportion of lead from gasoline:

386

$$Ab_{sample}^{206} = kAb_{gasoline}^{206} + (1 - k)Ab_{background}^{206}$$

387

388 Where  $Ab^{206}$  are the  $^{206}\text{Pb}$  atomic abundances of the sample, gasoline and geochemical background,  
389 respectively. For the gasoline and the geochemical background end-members the values of  
390 Monna et al. (1997) and of the core layer dated back to 1950 were used, respectively. Knowing these  
391 abundances, the  $k$  factor that expresses the proportion of the gasoline Pb to the Pb of the sample  
392 can be calculated. Results of this mixing model show that the gasoline contribution is about 1% in  
393 1959 and increases over time: 11% in 1963 15% in 1980 and 16% in 1986. In 2011, the  $^{206}\text{Pb}/^{207}\text{Pb}$   
394 ratio reaches the local geochemical background value, showing a resiliency of the system following  
395 the progressive replacing of leaded gasoline by unleaded gasoline, since 1990 in France. Indeed, the  
396 release of leaded gasoline in the atmosphere started decreasing around 1990 in France (Lestel et al.,  
397 2007)



398

399 *Figure 4: Profile of  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratio measured in the sediment core collected in the Loire River. The dashed line*  
400 *corresponds to the ratio value dated back to 1950 considered as the local geochemical background value.*

401

## 402 Conclusions

403

404 The first records of  $^{233}\text{U}$  and  $^{236}\text{U}$  in a well dated sedimentary archive collected in the Loire River were  
405 presented. Thanks to the recent capabilities of ultra-trace level measurements of  $^{236}\text{U}$  and in  
406 particular  $^{233}\text{U}$ , different potential sources of anthropogenic U transiting in the Loire River since the  
407 1950s were discussed. This work confirms the high sensitivity of the  $^{236}\text{U}/^{238}\text{U}$  ratio to highlight small  
408 anthropogenic inputs for which the naturally occurring U isotopes are completely “blind”. However,  
409 the very low levels of  $^{236}\text{U}$  in the samples made the identification of the emission sources quite tricky.  
410 The recently developed  $^{233}\text{U}/^{236}\text{U}$  tracer combining two anthropogenic isotopes, has made it possible  
411 to further consider NPP accident contributions *versus* the global fallout of  $^{236}\text{U}$ . These observations  
412 are consistent with the ( $^{238}\text{Pu}/^{239+240}\text{Pu}$ ) activity ratio peaks in 1969 and 1980. However, future  
413 studies are needed to profoundly explore the NPPs  $^{233}\text{U}/^{236}\text{U}$  ratio signature, e.g. by analyzing surface  
414 sediments and river water from the vicinity of different NPPs, in combination with data related to  
415 fuel source terms. The determination of the mining activities by the use of stable Pb isotopes is still  
416 challenging probably due to the limited dissemination of the Pb-bearing material marked by the U-  
417 ore signature downstream to the former U mines. However, thanks to the lead isotopes the impact  
418 of the gasoline atmospheric emissions was clearly highlighted and estimated. Further research is  
419 needed to identify the impact of mining and milling activities in the Loire River sediments involving  
420 new coring of the sub-watershed of the former U-mines and / or the use of additional relevant  
421 tracers (isotopic and elemental).

422

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430

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