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1 Reconstruction of uranium and plutonium isotopic signatures in
2 sediment accumulated in the Mano Dam reservoir, Japan, before
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4

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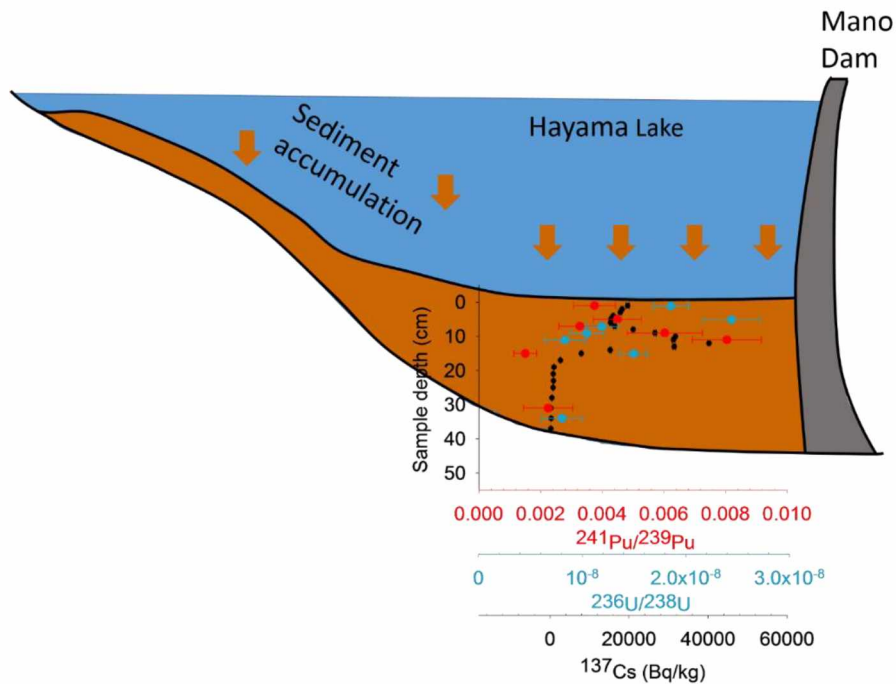
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24 **Abstract**

25

26 The Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident in Japan resulted in a major release of
27 radionuclides into the environment. Compared to others elements, few studies have investigated the
28 emission of actinides. Accordingly, this research investigates the Pu composition in soil samples
29 collected in nearby paddy fields before and after the accident. Furthermore, the vertical distributions
30 of Pu and U isotopic signatures, along with ^{137}Cs activities, were measured in a sediment core
31 collected in 2015 in the Mano Dam reservoir, in the Fukushima Prefecture. These signatures were
32 used to quantify changes in the relative contributions of the major actinide sources (global fallout or
33 FDNPP derived fallout) in sediment deposited in the reservoir. The distinct peak observed for all Pu
34 isotope ratios ($^{240}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$) and for ^{137}Cs concentrations in the sediment
35 core was attributed to the Fukushima fallout, and coincided with the maximum atomic contribution
36 of only $4.8\pm 1.0\%$ of Pu from the FDNPP. Furthermore, $^{236}\text{U}/^{238}\text{U}$ ratios measured in the sediment core
37 remained close to the global fallout signature indicating there was likely no U from the FDNPP
38 accident in the sediment core. More research is required on the environmental dynamics of trace
39 actinides in landscapes closer to the FDNPP where greater abundances of FDNPP-derived Pu and U
40 would be anticipated.

41 **Abstract art**



42

43

44 **Introduction**

45

46 The 2011 Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident released significant volumes of
47 radionuclides into the environment. In particular, various venting operations and explosions occurred
48 at the FDNPP and triggered the release of volatile fission products (^{131}I , ^{132}Te , ^{134}Cs and
49 ^{137}Cs)(Schneider et al., 2017). Accordingly, numerous studies were conducted to investigate the
50 distribution and the fate of the gamma-emitting isotopes, including radiocesium, after the
51 accident(Buesseler et al., 2016; Cao et al., 2016; Tanaka et al., 2015; Yamamoto et al., 2012; Zheng et
52 al., 2014). Erosion and remobilisation of particle-bound radiocesium contamination was investigated
53 through field monitoring(Evrard et al., 2016; Yamashiki et al., 2014) and model simulations(Kitamura
54 et al., 2016; Kitamura et al., 2014). These studies reported a rapid export of the particle-bound
55 radioactive contamination by the coastal rivers to the Pacific Ocean, with the preferential
56 remobilisation of fine sediment particles enriched in radiocesium. This process was shown to be

57 exacerbated during heavy typhoons, because of the strong hillslope-to-river sediment connectivity
58 observed, particularly with paddy fields that were found to be one of the main sources of
59 radiocesium shortly after the accident(Chartin et al., 2017; Laceby et al., 2016; Lepage et al., 2016).
60 Importantly, dams and reservoirs were demonstrated to store significant quantities of contaminated
61 sediment in the region and their management represents a significant challenge for the regional
62 authorities(Chartin et al., 2013; Yamada et al., 2015).

63 Although radiocesium sources have been extensively researched, less information is available in the
64 literature regarding the fate of other radionuclides such as U or Pu. Non-volatile Pu isotopes
65 including ^{239}Pu ($T_{1/2}=24,110$ y, alpha-decay), ^{240}Pu ($T_{1/2}=6,563$ y, alpha-decay), ^{241}Pu ($T_{1/2}=14.35$ y,
66 beta-decay) and ^{242}Pu ($T_{1/2}=376,000$ y, alpha-decay)(Evrard et al., 2014; Xu et al., 2016; Yamamoto et
67 al., 2014; Zheng et al., 2012b) and U isotopes including ^{238}U ($T_{1/2}=4.469\times 10^9$ y, alpha-decay), ^{235}U
68 ($T_{1/2}=7.038\times 10^8$ y, alpha-decay), ^{234}U ($T_{1/2}=245,500$ y, alpha-decay) and ^{236}U ($T_{1/2}=23.42\times 10^6$ y, alpha-
69 decay)(Sakaguchi et al., 2014; Schneider et al., 2017; Shinonaga et al., 2014; Yang et al., 2016), were
70 also detected in environmental samples collected in the Fukushima Prefecture. These radionuclides
71 may originate from two main sources: the global fallout associated with the nuclear atmospheric
72 weapon tests(Yamamoto et al., 2014) and the FDNPP accident. Additionally, ^{238}U , ^{235}U and ^{234}U
73 isotopes are naturally present in the environment. As Pu ($^{240}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$) and
74 U ($^{236}\text{U}/^{238}\text{U}$) isotope ratios may vary significantly depending on their source(Muramatsu et al., 2003;
75 Schneider et al., 2017), their precise measurement in sediment could provide powerful fingerprints
76 for source identification. Accordingly, investigating the changes in the Pu and U signatures with
77 depth in lacustrine sediment cores should provide information for reconstructing the changes in the
78 respective contributions of these radionuclide sources in lacustrine sediment.

79 To the best of our knowledge, the analysis of Pu isotopes in continental sediment deposited in
80 reservoirs following the FDNPP accident has been restricted to that of cores collected in the Lake
81 Inba, located 200 km south of the FDNPP site (i.e. outside of the main radioactive plume)(Cao et al.,
82 2017). Although the measured $^{134}\text{Cs}/^{137}\text{Cs}$ ratios indicated there was fallout from the FDNPP accident,

83 the $^{239+240}\text{Pu}$ activity and the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio remained similar to the global fallout signature,
84 suggesting that FDNPP-derived Pu did not reach the Lake Inba basin in significant quantities.

85 In this study, the global fallout signature was first refined for the study region through the analysis of
86 soil samples collected before the accident. Soils collected after the accident were analysed to
87 characterise the initial spatial pattern of Pu deposited in this area and to compare it with the well-
88 documented ^{137}Cs deposition pattern. Then, the vertical distribution of Pu and U isotope ratios was
89 characterised in a sediment core. These distributions were compared to that of ^{137}Cs concentrations
90 measured in the core, and the contributions of the different sources of Pu in this region (global
91 fallout vs. FDNPP) were quantified through the analysis of Pu isotope ratios. Implications regarding
92 the fate and the geochemical behaviour of actinides in the catchments draining the main radioactive
93 plume in the Fukushima Prefecture are then discussed.

94

95 **Materials and methods**

96

97 **Soil and sediment sampling**

98

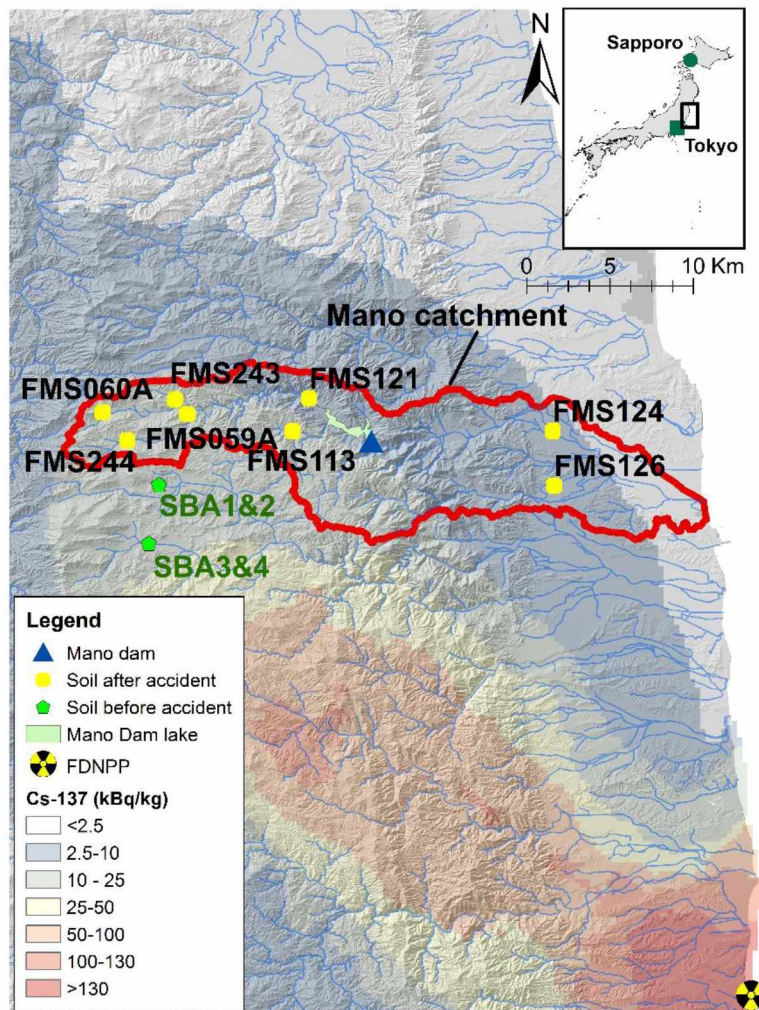
99 In order to provide the local signature of the Pu global fallout in this region, four soil samples
100 collected before the accident (in 2007 and in 2010, see Table S1) were first analysed. These samples
101 were taken at two different locations in cultivated paddy fields (12 km to the south-west of the Mano
102 Dam, see Figure 1) and at two different depths (ploughed and underlying layers). To characterise the
103 initial deposition of FDNPP-derived Pu, soil samples collected shortly after the accident (in November
104 2011, November 2012 and April 2012, see Table S2) were also analysed. Soil samples were taken
105 from a range of ^{137}Cs fallout levels to be representative of potential FDNPP fallout (see Figure 1).
106 Sampling methods are described elsewhere (Jaegler et al., 2018). In brief, soil samples are composed

107 of 10 soil scrape subsamples, taken with a plastic trowel, that were thoroughly homogenized prior to
108 analyses.

109

110 A sediment core collected in Lake Hayama, which is located 39 km to the northwest of the FDNPP in
111 the Mano River catchment, was analysed. This lake corresponds to the artificial Mano Dam reservoir,
112 with an area of 1.75 km², a water volume of 36,200 ×10³ m³ and a retention time of 0.48
113 year(Fukushima and Arai, 2014; Matsuda et al., 2015).

114 Researchers have investigated the radioactive contamination of sediment accumulated in this lake,
115 although they restricted their analysis to radiocesium concentrations. Matsuda *et al.*(2015)
116 measured the radiocesium concentration in bottom sediment and in lake water samples in 2012 and
117 2013, and they observed respective concentration decreases of 57% and 43% between the
118 successive sampling campaigns. Huon *et al.*(2018) measured the vertical distribution of ¹³⁷Cs
119 activities in four sediment cores sampled across the lake. Three of these four cores showed a distinct
120 peak likely corresponding to the initial radiocesium wash-off and migration phase following the
121 FDNPP accident. In the current study, one of these sediment cores (referred to as 'DD1') located in
122 the downstream section of the lake and composed of fine sediment material(Huon et al., 2018) was
123 selected to characterise variations of Pu and U isotope ratios with depth. More details on the core
124 sampling and the radiocesium analyses are provided in Huon *et al.*(2018). In brief, the sediment core
125 was collected on April 24, 2015 (37°43'25.75"N, 140°49'49.84"E) using a gravity core sampler, under
126 approximately 45 m of water. The sediment core was 37 cm long and was then divided into 1-cm
127 increments from 0 to 15 cm depth, 2 cm from 15 to 25 cm depth and, finally, 3 cm from 25 to 37 cm
128 depth. ¹³⁷Cs content was measured by gamma spectrometry in each subsample in order to
129 investigate the distribution of ¹³⁷Cs in the core(Huon et al., 2018).



130

131 Figure 1: Location of the soil samples analysed in this current research in the Mano catchment delineated in
 132 red. The main radiocaesium contamination plume is also located in the background map derived from Chartin
 133 *et al.*(2013).

134

135 Chemical preparation and separation of plutonium and uranium

136

137 Core sections were grouped by pairs to provide sufficient material (~5 g) for the actinide analyses.
 138 Samples were placed in an electric furnace at 450 °C for ~15 h to decompose the organic matter.
 139 After cooling to room temperature, they were transferred in Savillex® PFA Teflon® beakers. ~100 fg
 140 of ²⁴⁴Pu (diluted solution prepared from the certified isotopic reference material IRMM-042a, Geel,
 141 Belgium) was added as an isotopic dilution tracer. Chemical blanks were spiked as well. Digestion of

142 the samples was carried out through several acid leaching steps. Only partial dissolution protocol was
143 performed as it was shown that this partial leaching was sufficient to dissolved actinide contained in
144 samples(Lee et al., 2005,Liao, 2008 #532,Jaegler, 2018 #970). Moreover, total dissolution required
145 use of concentrated HF acid, which is known to contain more impurities than concentrated HCl and
146 HNO₃ acid.

147 50 mL concentrated HNO₃, 50 mL aqua regia and 50 mL concentrated HCl. Between each leaching
148 step, the solutions were dried in a closed evaporation system (Evapoclean®, Analab, Hoenheim,
149 France) at 110 °C until complete dryness. This device allows evaporation in a closed medium to
150 prevent any lab contamination. Samples were then recovered with 2M HCl and filtrated with a
151 disposable 0.45 µm Nalgene filtering unit (Thermo Scientific, Rochester, NY, USA). Dissolved fractions
152 were transferred in clean Savillex® PFA Teflon® beakers and evaporated to dryness in closed media.
153 Samples were then recovered with 50 mL of concentrated HNO₃ and a few mg of NaNO₂ were added
154 to stabilize the (+IV) oxidation state of Pu and evaporated to dryness. Samples were finally recovered
155 with 30 mL of 8M HNO₃ before Pu separation on chromatographic columns. The first column was
156 composed of a Dowex AG1X8 anion-exchange resin filled with ~10 mL of 50-100 mesh AG1X8 resin
157 and ~10 mL of 100-200 mesh AG1X8 resin, conditioned with 8 M HNO₃. After loading the sample
158 onto the column, U was first eluted with 8M HNO₃. Then, Th was eliminated with 10 M HCl. Pu was
159 finally eluted with NH₄I (1.5%) – 12 M HCl.

160 The same protocol was repeated twice on the Pu fraction with 2 mL Dowex AG1X4 anion-exchange
161 resin (100-200 mesh) to reduce as much as possible sample matrix elements, which can potentially
162 generate polyatomic (mainly PbO₂⁺, ²³⁸UH⁺) and isobaric (²⁴¹Am⁺) interferences. After evaporation of
163 the eluate, samples were recovered and evaporated to dryness several times with concentrated
164 HNO₃ to eliminate chlorides. Finally, the last recovery was performed with 2% HNO₃ + 0.01M HF for
165 ICP-MS measurements. The two consecutive purifications of the Pu fraction with Dowex resins
166 allowed a complete elimination of Am(Trémillon, 1965). However, PbO₂⁺ and UH⁺ interferences
167 persisted during ICP-MS measurements and required raw data corrections. The U fraction collected

168 with the first Dowex AG1X8 was further purified with a second column of 2 mL UTEVA extraction
169 resin (100 – 150 µm), conditioned with 4M HNO₃. U was directly eluted with 0.01M HNO₃. After
170 evaporation to dryness of this eluted solution, the U fraction of samples was finally recovered with
171 2% HNO₃ for ICP-MS measurements. At least two chemical blanks were systematically prepared with
172 sample treatments. **The sample preparation and Pu and U separation protocol efficiency was confirm**
173 **by analysing certified reference materials in a previous study (Jaegler et al., 2018).**

174 **Plutonium measurements by mass-spectrometry**

175
176 Pu isotopic composition in the samples were measured with a Multi-Collector Inductively Coupled
177 Plasma Mass Spectrometer (MC-ICP-MS) (Neptune Plus, Thermo Fisher Scientific Inc., Bremen,
178 Germany) equipped with eight Faraday cups and five ion counters for the simultaneous detection of
179 ion beams. All measurements were performed using Aridus II (Cetac) as introduction system, high-
180 efficiency sampler and skimmer cones, reinforced pumping in the interface to enhance the sensitivity
181 by a factor of ~10 (approximately 10⁸ counts/s per µg/L of ²³⁸U), compared to the standard
182 configuration.

183 Two certified reference materials, IRMM 186 and IRMM 057 (both reference materials were
184 provided by the Institute for Reference Materials and Measurements, Geel, Belgium), were
185 measured on a regular basis throughout each analysis sequence and used to correct interferences
186 and biases: instrumental mass fractionation, peak tailing at M+1 and M+2, and hydride formation
187 (mainly ²³⁸UH⁺) were determined. **Lead polyatomic interferences (PbO₂⁺) were corrected by**
188 **measuring three pure mono-elemental solutions of Pb at the end of the procedure. Measurement of**
189 **these standards in the chemical blanks shows that main lead interferences are instrumental induced**
190 **(PbAr) rather than induced by the chemical protocol (PbCl). Moreover, as levels of interferences as**
191 **similar in the blanks and in the sample, it shows that Pb is originating from the reagents added during**
192 **radiochemical protocol and not contained in the sample.** All these corrections were applied to a

193 solution of the Pu isotopic certified material CRM128 (NBL, US DOE) for verification. Finally, all Pu
194 compositions were corrected for tracer impurities according to the certificate of the isotopic
195 reference material IRMM-042a, decay-corrected to March 15, 2011 and for blank levels (average of
196 total Pu in the blanks: 3.4 ± 1.2 fg).

197

198 **Uranium measurements by mass spectrometry**

199

200 Precise ^{236}U measurements were performed twice in two different laboratories: at CEA/LANIE
201 (“Commissariat à l’Energie Atomique et aux Energies Alternatives/ Laboratoire de développement
202 Analytique Nucléaire, Isotopique, Élémentaire”) and at IRSN/LELI (“Institut de Radioprotection et de
203 Sureté du Nucléaire / Laboratoire sur le devenir des pollutions des sites radioactifs”) using two ICP-
204 MS/MS (Agilent 8800, Agilent Technologies, Tokyo, Japan) instruments well-suited for the
205 measurement of extremely low $^{236}\text{U}/^{238}\text{U}$ isotope ratios (Tanimizu et al., 2013; Yang et al., 2016). Two
206 analyses on each sample were conducted to provide more confidence in the results. The strategy
207 followed in both laboratories was based on the mass shift mode (through the detection of the oxide
208 form, U^{16}O^+) as described by Tanimizu *et al.* and Yang *et al.* (2013; 2016). This strategy allowed for
209 reducing ^{238}U and ^{235}U peak tailing and hydride formation from ^{235}U at $m/z=236$ opening up the
210 possibility to measure very low $^{236}\text{U}/^{238}\text{U}$ isotope ratios. Owing to these strong interferences, the
211 measurement of very low $^{236}\text{U}/^{238}\text{U}$ ratios by MC-ICP-MS is limited.

212 Both laboratories are equipped with the same ICP-MS/MS instrument and used desolvating
213 introduction systems in order to increase sensitivity and to reduce the formation of hydrides.
214 However, desolvating devices and measurement procedures showed significant differences.

215 The LANIE laboratory used the Aridus (Cetac Technologies, Omaha, NE, USA) introduction system.
216 The $^{236}\text{U}/^{238}\text{U}$ in the samples was deduced through the measurement of $^{236}\text{UO}^+ / ^{235}\text{UO}^+$ using the
217 natural $^{238}\text{U}/^{235}\text{U}$ (137.88) ratio (as ^{238}U and ^{235}U are mostly originating from natural uranium).

218 $^{236}\text{UO}^+ / ^{235}\text{UO}^+$ ratio was corrected for hydride formation ($^{235}\text{UOH}^+ / ^{235}\text{UO}^+$) and for the chemical
219 blanks. The instrumental mass fractionation was internally corrected using the $^{234}\text{UO}^+ / ^{235}\text{UO}^+$ ratios of
220 the samples, compared with the $^{234}\text{U} / ^{235}\text{U}$ isotope ratio also determined with another ICP-MS
221 instrument.

222 The LELI laboratory used the Apex-HF (Elemental Scientific, Omaha, NE, USA) introduction system. In
223 order to acquire signals only with the pulse counting mode during the analysis, the $^{236}\text{UO}^+ / ^{235}\text{UO}^+$
224 ratio was measured and the $^{236}\text{U} / ^{238}\text{U}$ was deduced using the natural $^{238}\text{U} / ^{235}\text{U}$ (137.88) ratio.
225 Instrumental mass fractionation was corrected by a standard bracketing method using the measured
226 $^{234}\text{U} / ^{235}\text{U}$ ratio of an IRMM186 certified solution. A hydride correction factor was calculated using the
227 $^{238}\text{UOH}^+ / (^{235}\text{UO}^+ \times 137.88)$ ratio and applied to the ^{236}U measurements to correct for the $^{235}\text{UO}^+$
228 hydride formation.

229 **Pu and U source term signatures**

230

231 Pu deposition on soils of this region may originate from two main sources: the global fallout and the
232 FDNPP accident. Pu fuel isotopic compositions at the moment of the accident were estimated to be
233 0.373 ± 0.044 (2σ) for $^{240}\text{Pu} / ^{239}\text{Pu}$, 0.1874 ± 0.0081 (2σ) for $^{241}\text{Pu} / ^{239}\text{Pu}$, and 0.0637 ± 0.0026 (2σ) for
234 $^{242}\text{Pu} / ^{239}\text{Pu}$ (Kirchner et al., 2012; Nishihara et al., 2012; Schwantes et al., 2012).

235 The global fallout signatures provided in the literature were measured worldwide (Kelley et al., 1999)
236 including various locations across Japan (Momoshima et al., 1997; Muramatsu et al., 2003; Ohtsuka et
237 al., 2004; Zhang et al., 2010). As the range of these Pu signatures is relatively wide (Table S3), there is
238 a need to refine the global fallout signatures for this specific sampling location in the Fukushima
239 Prefecture. In this study, the measurements conducted on the bottom sediment sample layer in the
240 core and on the soil samples collected before the accident were used to provide the local signatures
241 of the global fallout.

242 Unlike Pu, U is also naturally present in the environment with two primordial isotopes (^{238}U and ^{235}U)
243 and one radiogenic isotope (^{234}U) originating from the ^{238}U -decay. Moreover, these isotopes are
244 relatively abundant in soils and sediment, with the U concentration being 6 to 9 orders of magnitude
245 higher than that of Pu (Bu et al., 2017). On the contrary, the ^{236}U isotope has an extremely low
246 abundance in natural-occurring U present in environmental samples ($<10^{-13}$). However, ^{236}U is also
247 produced in significant quantities in nuclear reactors (by the capture of a neutron by the fissile
248 nuclide ^{235}U), which may result in $^{236}\text{U}/^{238}\text{U}$ ratios locally higher in those samples collected in the
249 close vicinity of some nuclear installations. For the U ratio representative of the FDNPP signature,
250 only Nishihara *et al.* (2012) estimated the $^{236}\text{U}/^{238}\text{U}$ in the nuclear fuel ratio at the time of the
251 accident, being $(3.20 - 3.71) \times 10^{-3}$ (mean $(3.42 \pm 0.52) \times 10^{-3}$, 2σ). Nevertheless, the main
252 contribution of ^{236}U in soils is, as for Pu isotopes, the global fallout associated with the nuclear
253 weapon atmospheric tests.

254 The representative $^{236}\text{U}/^{238}\text{U}$ ratios for the global fallout signature in Japan were previously measured
255 in a soil core (n=3) sampled in the Ishikawa Prefecture (Sakaguchi et al., 2009) ($1.85 \times 10^{-8} - 1.09 \times 10^{-7}$,
256 mean $(5.31 \pm 0.12) \times 10^{-8}$, 2σ). However, Schneider *et al.* (2017) recently determined even lower
257 $^{236}\text{U}/^{238}\text{U}$ ratios in the range of 10^{-9} in soil samples collected at various locations within the exclusion
258 zone nearby the FDNPP, and reported this signature as that of 'undisturbed uranium'. Currently, this
259 ratio remains poorly constrained with values varying between 10^{-10} and 10^{-7} .

260 The potential occurrence of U contamination following the FDNPP accident in the environment has
261 been examined in very few studies (Sakaguchi et al., 2014; Schneider et al., 2017; Shinonaga et al.,
262 2014; Yang et al., 2016) (See Table S4). Most of these samples reported $^{236}\text{U}/^{238}\text{U}$ ratios between 10^{-8}
263 and 10^{-7} , which suggests a global fallout origin (Sakaguchi et al., 2010). Shinonaga *et al.* (2014)
264 measured ratios of 10^{-6} in aerosol filter samples collected at 120 km from the FDNPP shortly after the
265 accident. However, as early as in April 2011 U ratios measured in aerosols collected at the same
266 location returned to the global fallout level. These results suggested that U was only released in trace
267 amounts during the FDNPP accident.

268

269 Accordingly, in the current research, the U isotope compositions were only analysed in the sediment
270 core, as the soil erosion and sediment transport processes are known to be selective and to mobilize
271 preferentially the finest and most contaminated particles(Evrard et al., 2015; Laceby et al., 2017).
272 Furthermore, ²³⁶U concentrations in the soil samples collected before and after the accident would
273 likely be too low to be detectable by ICP-MS with the chemical processes followed in this study.

274

275 **Quantifying source contributions**

276

277 The proportions of each source of Pu were determined using a binary mixing model(Kelley et al.,
278 1999). To this end, the isotopic abundance of ²⁴¹Pu in each source term and in each sediment sample
279 and each soil sample collected after the accident was calculated. ²⁴¹Pu abundance was used owing to
280 its relatively short half-life resulting in this isotope providing the best discrimination between
281 emissions from the global fallout or the FDNPP accident. Atomic abundance of each term
282 $Ab(^{241}\text{Pu})_{\text{sample}}$, $Ab(^{241}\text{Pu})_{\text{GF}}$ or $Ab(^{241}\text{Pu})_{\text{FDNPP}}$ is given in Equation 1:

$$Ab(^{241}\text{Pu})_i = \frac{(^{241}\text{Pu}/^{239}\text{Pu})_i}{1 + (^{240}\text{Pu}/^{239}\text{Pu})_i + (^{241}\text{Pu}/^{239}\text{Pu})_i + (^{242}\text{Pu}/^{239}\text{Pu})_i} \quad (1)$$

283 where i stands for “sample” or “GF” or “FDNPP”.

284 Abundance for FDNPP source $Ab(^{241}\text{Pu})_{\text{FDNPP}}$ as estimated at $(1.15 \pm 0.12) \times 10^{-2}$ based on results
285 published by Nishihara et al.(2012), Kirchner et al.(2012) and Schwantes et al.(2012). Other end-
286 member abundances were derived from our measurements. Then, the proportions of each source
287 term were deduced using a mixing equation with two sources (Equation 2):

$$Ab(^{241}\text{Pu})_{\text{FDNPP}} \times X_{\text{FDNPP}} + Ab(^{241}\text{Pu})_{\text{GF}} \times (1 - X_{\text{FDNPP}}) = Ab(^{241}\text{Pu})_{\text{sample}} \quad (2)$$

288 It is important to note that X_{FDNPP} is defined based on the total plutonium counting rates (equation
289 3):

$$X_{\text{FDNPP}} = \frac{({}^{239}\text{Pu} + {}^{240}\text{Pu} + {}^{241}\text{Pu} + {}^{242}\text{Pu})_{\text{FDNPP}}}{({}^{239}\text{Pu} + {}^{240}\text{Pu} + {}^{241}\text{Pu} + {}^{242}\text{Pu})_{\text{sample}}} \quad (3)$$

290

291 These proportions, based on the atomic ratio, were converted into mass proportions to determine
292 the Pu concentrations originating from the FDNPP relative to those derived from the global fallout.

293 Although no source contribution could be modelled for U, theoretical ${}^{236}\text{U}$ concentrations released
294 from the FDNPP were estimated based on the results of plutonium concentrations found in the
295 samples analysed in the current research. First, the corresponding theoretical
296 ${}^{236}\text{U}/({}^{239}\text{Pu} + {}^{240}\text{Pu} + {}^{241}\text{Pu} + {}^{242}\text{Pu})$ isotope ratios were estimated to be $0.46 \pm 0.12 (2\sigma)$ (Nishihara et al.,
297 2012), based on literature data. Then, the concentration of FDNPP-derived ${}^{236}\text{U}$ (${}^{236}\text{U}_{\text{FDNPP}}$) was
298 estimated based on the estimations of the FDNPP-derived Pu concentrations found in the soil
299 samples, and compared with the global fallout derived ${}^{236}\text{U}$ concentration.

300 Results and discussion

301

302 Refining the Pu global fallout signature in soils and sediment of the Fukushima Prefecture

303

304 In the sediment core collected in the Hayama Lake, the ${}^{240}\text{Pu}/{}^{239}\text{Pu}$, ${}^{241}\text{Pu}/{}^{239}\text{Pu}$ and the ${}^{242}\text{Pu}/{}^{239}\text{Pu}$
305 isotope ratios measured in the bottom layer (31 cm, MD7) were within the range of values for the
306 global fallout reported in the literature. Accordingly, it is assumed that these actinides in the bottom
307 layer of the core were likely supplied by the global fallout.

308 In the soil samples collected before the accident, no Pu was detected in the SBA4 sample (Table 1).

309 Pu isotope ratios found in other samples are surprisingly higher and more heterogeneous than the

310 values previously published in the literature, particularly for the $^{241}\text{Pu}/^{239}\text{Pu}$ ratio, which ranged from
 311 0.0023 to 0.0117 (mean 0.0061 ± 0.0010 , 2σ). The relative proximity of the sites where Chinese
 312 nuclear weapons were tested between 1964 and 1980 may have resulted in these high values.
 313 However, the maximum $^{241}\text{Pu}/^{239+240}\text{Pu}$ activity ratio measured in the current study is 61 ± 12 (SBA2,
 314 decay-corrected to the date of the main test on November 17, 1976), which is higher than that
 315 measured in the Chinese test debris (11 according to Zhang *et al.*, (2010) and Hirose *et al.* (2001)).
 316 More research is required to investigate these high pre-FDNPP accident plutonium isotope ratio
 317 values and their heterogeneity.

318

319 Table 1: ^{137}Cs activities and Pu isotope ratios measured in the soil samples collected before the accident.
 320 $^{241}\text{Pu}/^{239}\text{Pu}$ is decay-corrected to March 15, 2011. Uncertainties are extended with a coverage factor of 2.

Sample label	^{137}Cs (Bq/kg)	$^{240}\text{Pu}/^{239}\text{Pu}$	$^{241}\text{Pu}/^{239}\text{Pu}$	$^{242}\text{Pu}/^{239}\text{Pu}$	Pu concentration (fg/g)
SBA1	5.0 ± 1.4	0.182 ± 0.012	0.0044 ± 0.0017	0.0056 ± 0.0010	48.1 ± 5.9
SBA2	3.7 ± 0.8	0.179 ± 0.007	0.0117 ± 0.0023	0.0071 ± 0.0006	29.5 ± 1.1
SBA3	3.1 ± 1.2	0.179 ± 0.013	0.0023 ± 0.0005	0.0052 ± 0.0013	22.4 ± 1.8
SBA4	< 2.8	-	-	-	< 0.5

321

322 To model the source contributions of Pu in the samples, the Pu isotope ratios characterising the local
 323 signature of the global fallout in the Mano River catchment was calculated based on those results
 324 obtained for samples exposed only to the global fallout: the pre-accident soil samples (SBA1, SBA2
 325 and SBA3) and the bottom layer of the sediment core (MD7). Accordingly, the mean plutonium
 326 isotope ratios characterising the global fallout signature in the study area are: $^{240}\text{Pu}/^{239}\text{Pu} = 0.180 \pm$
 327 0.010 ; $^{241}\text{Pu}/^{239}\text{Pu} = 0.0052 \pm 0.0017$ and $^{242}\text{Pu}/^{239}\text{Pu} = 0.0054 \pm 0.0022$ (uncertainties are extended
 328 with a coverage factor of 2.)

329

330 **Initial surface deposition of plutonium in the Mano catchment**

331

332 Pu isotope ratios were measured in eight soil samples collected in the catchment after the accident
333 (Table 2). Results showed that Pu isotope ratios remained generally close to the global fallout
334 signature: the atomic proportions of Pu from the FDNPP in these soils were estimated to be lower
335 than 7 % (see Table 2, Table S5). Sample FMS243 provides an exception to this rule, as it contained
336 more than 40 % of Pu from the power plant. On the contrary, low isotope ratios were measured in
337 sample FMS113, in particular the $^{240}\text{Pu}/^{239}\text{Pu}$ isotope ratio (0.160 ± 0.011). The relevance of this value
338 is confirmed by the measurement of similar ratios in Japanese soils: Muramatsu *et al.*(2003)
339 observed a ratio of 0.155 ± 0.003 in a forest soil sample collected before 2002, and Zheng *et*
340 *al.*(2012b) found a ratio of 0.144 ± 0.006 in a soil sample collected in 2011 at 32 km from the FDNPP.
341 Moreover, no correlation ($p < 0.001$) could be observed between ^{137}Cs activities and Pu isotope ratios
342 in these samples. This confirms that Pu deposition on soils was locally heterogeneous (Salbu, 2011 ;
343 Schneider *et al.*, 2013). It may also reflect the occurrence of different processes of aerial transport of
344 radiocesium and Pu from the FDNPP to the study area.

345 Table 2: ^{137}Cs activities and Pu isotope ratios measured in the soil samples collected after the FDNPP accident across the Mano River catchment. Uncertainties are extended
 346 with a coverage factor of 2.

Sample label	^{137}Cs (kBq/kg)	$^{240}\text{Pu}/^{239}\text{Pu}$	$^{241}\text{Pu}/^{239}\text{Pu}$	$^{242}\text{Pu}/^{239}\text{Pu}$	Pu concentration (fg/g)	Fraction of Pu from FDNPP (%)
FMS059A	18.70 ± 0.94	0.177 ± 0.014	0.0033 ± 0.0017	0.0048 ± 0.0019	112.1 ± 6.1	1.4 ± 1.2
FMS060A	30.59 ± 1.50	0.184 ± 0.017	0.0075 ± 0.0045	0.0059 ± 0.0016	45.8 ± 3.9	4.4 ± 3.3
FMS243	19.40 ± 0.97	0.285 ± 0.049	0.0666 ± 0.0178	0.0488 ± 0.0029	75.6 ± 9.6	40.6 ± 11.4
FMS244	65.72 ± 3.30	0.188 ± 0.019	0.0069 ± 0.0009	0.0057 ± 0.0010	78.4 ± 6.0	3.9 ± 0.8
FMS113	13.37 ± 0.67	0.160 ± 0.011	0.0058 ± 0.0018	0.0075 ± 0.0029	61.0 ± 6.2	3.2 ± 1.4
FMS121	0.19 ± 0.01	0.184 ± 0.011	0.0027 ± 0.0017	0.0057 ± 0.0007	48.0 ± 3.5	0.9 ± 1.3
FMS124	3.28 ± 0.16	0.197 ± 0.013	0.0113 ± 0.0062	0.0116 ± 0.0008	67.4 ± 5.4	7.0 ± 4.5
FMS126	0.84 ± 0.04	0.187 ± 0.016	0.0094 ± 0.0010	0.0124 ± 0.0022	26.1 ± 2.0	5.7 ± 1.0

347

348

349 **Temporal variations of radiocesium in the sediment core**

350

351 The ^{137}Cs activities in the sediment core demonstrated that the lowest activity (mean = 0.58 ± 0.03 Bq/g)
352 was found in the bottom of the core (at 31 – 37 cm depth). The maximum activity was observed at 11 –
353 12 cm (40.24 ± 2.01 Bq/g) before decreasing in the upper part of the core (at 0-7 cm depth) to a mean of
354 16.96 ± 0.85 Bq/g (Table 3). The maximum of activity corresponds to the deposition of strongly
355 contaminated sediment in the reservoir shortly after the FDNPP accident. This increase of the activity
356 likely reflects the radiocesium wash-off and migration phase during the six first months that followed the
357 FDNPP accident(Huon et al., 2018).

358

359 Table 3: ^{137}Cs activities and Pu isotope ratios and Pu concentrations measured in the Mano Dam sediment core.

360 Uncertainties are extended with a coverage factor of 2.

Sample depth (cm)	Sample ID	^{137}Cs (kBq/kg)	$^{240}\text{Pu}/^{239}\text{Pu}$	$^{241}\text{Pu}/^{239}\text{Pu}$	$^{242}\text{Pu}/^{239}\text{Pu}$	Pu concentration (fg/g)
0-1	MD1	19.67 ± 0.98	0.180 ± 0.002	0.0038 ± 0.0007	0.0043 ± 0.0003	155.5 ± 11.3
1-2		18.27 ± 0.91				
2-3	-	17.77 ± 0.89	-	-	-	-
3-4	-	15.99 ± 0.80	-	-	-	-
4-5	-	15.39 ± 0.77	-	-	-	-
5-6	MD2	15.31 ± 0.77	0.172 ± 0.002	0.0045 ± 0.0008	0.0060 ± 0.0004	233.8 ± 21.0
6-7		16.35 ± 0.82				
7-8	MD3	21.06 ± 1.05	0.174 ± 0.002	0.0033 ± 0.0007	0.0042 ± 0.0003	170.3 ± 25.3
8-9		26.55 ± 1.33				
9-10	MD4	31.76 ± 1.59	0.184 ± 0.002	0.0060 ± 0.0012	0.0054 ± 0.0005	123.0 ± 12.6
10-11		31.23 ± 1.56				
11-12	MD5	40.24 ± 2.01	0.182 ± 0.002	0.0080 ± 0.0011	0.0062 ± 0.0003	77.5 ± 12.1
12-13		31.43 ± 1.57				
13-14	-	15.22 ± 0.76	-	-	-	-
14-15	-	7.91 ± 0.40	-	-	-	-
15-17	MD6	2.64 ± 0.13	0.159 ± 0.001	0.0015 ± 0.0004	0.0034 ± 0.0005	209.1 ± 32.5
17-19		0.99 ± 0.05				
19-21	-	0.81 ± 0.04	-	-	-	-
21-23	-	0.88 ± 0.04	-	-	-	-
23-25	-	0.77 ± 0.04	-	-	-	-
25-28	-	0.48 ± 0.02	-	-	-	-
28-31	-	0.24 ± 0.01	-	-	-	-
31-34	MD7	0.29 ± 0.01	0.175 ± 0.002	0.0022 ± 0.0008	0.0037 ± 0.0003	84.1 ± 11.4
34-37		0.21 ± 0.01				

361

362 Change of plutonium isotopic composition with depth

363

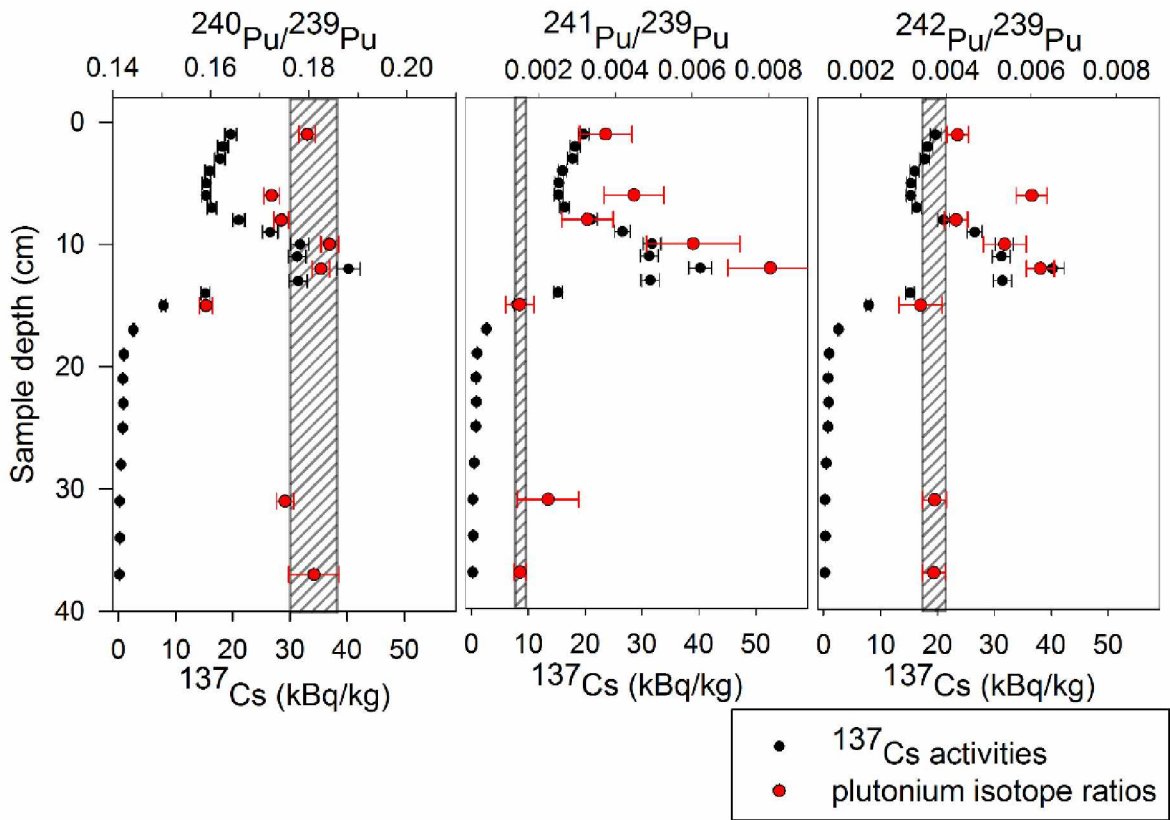
364 The evolution of the Pu isotopic composition with depth showed a similar pattern as ^{137}Cs activity (see
365 Table 3 and Figure 2). All isotope ratios ($^{240}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$) had a low value at the
366 bottom of the core. Then, all ratios increased up to maximum values found at 11-12 cm depth, which
367 corresponds to the peak in the ^{137}Cs activity. The variations on the sediment core with depth clearly

368 reflect changes in the origin of Pu(Evrard et al., 2014; Jaegler et al., 2018), ranging between the global
369 fallout signature and the FDNPP signature (see Figure S1), with the exception of the $^{240}\text{Pu}/^{239}\text{Pu}$ isotope
370 ratio measured in one sample (see below).

371

372 For $^{240}\text{Pu}/^{239}\text{Pu}$ ratios, all values remained in the range of the global fallout (Figure 2) although the
373 highest ratios corresponded to the maximum ^{137}Cs activity observed in the 11-12 cm depth layer. A
374 surprisingly low ratio value of 0.159 ± 0.001 was found in the layer MD6 (15 – 19cm depth). Similar ratios
375 lower than or equal to 0.16 were previously reported in Japan: Muramatsu *et al.*([2003](#)) and Zheng *et*
376 *al.*([2012b](#)), and Evrard *et al.*([2014](#)), who measured a ratio of 0.150 ± 0.005 in a sediment sample
377 collected in 2012. For those $^{241}\text{Pu}/^{239}\text{Pu}$ atom ratios, all isotope ratios measured in sediment samples
378 collected between 0 and 10 cm depth in the core were significantly higher than the upper limit of the
379 global fallout signature updated in the current study, showing a clear influence of the FDNPP inputs. A
380 good correlation was observed between this ratio in particular and the ^{137}Cs activities (correlation
381 coefficient of 0.90, p -value < 0.001). Finally, when examining $^{242}\text{Pu}/^{239}\text{Pu}$ values, they were slightly higher
382 than the upper limit of the global fallout, demonstrating a very low, although clear, impact of the FDNPP
383 fallout.

384



385
 386 Figure 2: Evolution of ^{137}Cs activities (black dots), $^{240}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$ atom ratios (red dots) with
 387 depth in the Mano Dam sediment core. The dashed zones provide the corresponding range of values reported for
 388 the global fallout, according to the literature (Kelley et al., 1999; Momoshima et al., 1997; Muramatsu et al., 2003;
 389 Ohtsuka et al., 2004; Zhang et al., 2010). Uncertainties are extended with a coverage factor of 2.

390
 391 **Sources of plutonium in the sediment core**
 392
 393 The maximum isotope ratio (MD5) corresponded to a maximum FDNPP atomic contribution estimated to
 394 be 4.3 ± 1.0 %. The measurement conducted on the deeper MD6 sediment layer showed the absence of
 395 contribution from FDNPP (0.0 ± 0.7 %). This result suggested that the migration of Pu with depth in the
 396 sediment profile was negligible.

397 Although detectable, the release of Pu from the FDNPP remained low in the sediment accumulated in
398 the Mano Dam (Table S6). Accordingly, the Pu detected in the sediment samples was mainly supplied by
399 the global fallout.

400 The shape of the three Pu isotopes profiles shows the occurrence of large variations, which were not
401 observed for the ^{137}Cs activity profile. No correlation ($p=0.015$) was found between ^{137}Cs and Pu
402 concentrations, as the main source that supplied these two radionuclides strongly differed: ^{137}Cs was
403 mainly supplied by the FDNPP releases, whereas Pu mainly originated from the global fallout. The
404 variations of Pu in the core likely reflect the heterogeneity of the Pu isotope ratios derived from the
405 global fallout as the global fallout Pu concentration was shown to be strongly heterogeneous (Kelley et
406 al., 1999) due to the particulate form of deposition (Salbu, 2011).

407

408 **Evolution of the ^{236}U isotopic signature in the sediment core**

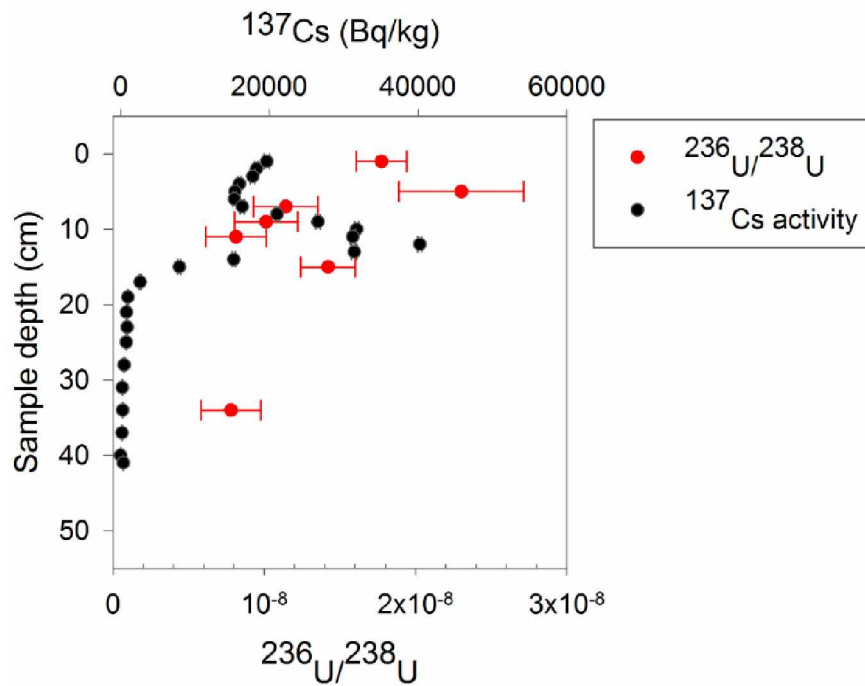
409

410 Data obtained with the two analytical methodologies were in very good agreement ($R^2 = 0.99$, slope of
411 linear regression = 0.99) (Figure S2). The measured $^{236}\text{U}/^{238}\text{U}$ isotope ratios ranged between
412 $(7.33 \pm 2.20) \times 10^{-9}$ and $(2.70 \pm 0.37) \times 10^{-8}$ (see Figure 3). These ratios were similar to the global fallout
413 values ($10^{-10} - 10^{-7}$) (Sakaguchi et al., 2009; Schneider et al., 2017), relative to the FDNPP range
414 $((3.42 \pm 0.52) \times 10^{-3})$ (Nishihara et al., 2012). The increase in $^{236}\text{U}/^{238}\text{U}$ values observed in the upper
415 section of the core is difficult to interpret because it may either reflect a slight impact of FDNPP derived
416 U releases or a local heterogeneity of the U concentration in the environment. Nevertheless, it may be
417 deduced from these measurements that the isotopic signature of U in these samples remained well
418 within the range of global fallout so that the potential fallout from the FDNPP is not detectable in these
419 samples. A part of U released from the FDNPP may also have been slowly incorporated into the bottom

420 sediment, which could explain the slight increase of the $^{236}\text{U}/^{238}\text{U}$ isotope ratio observed in the upper
 421 part of the core and the absence of a peak similar to that recorded for radiocesium and Pu. Moreover,
 422 the geochemical behaviour of U may be different from that of radiocesium as it is likely contained in UO_2
 423 microparticles from the nuclear fuel in association with Pu impurities. The absence of the detection of
 424 FDNPP –derived U suggested that the concentrations in actinide released from the power plant were
 425 lower than those already prevailing in the environment before the accident.

426

427



428

429 Figure 3: Evolution of the mean $^{236}\text{U}/^{238}\text{U}$ atom ratios (red dots) and ^{137}Cs activities (black dots) with depth in the
 430 Mano Dam sediment core. Uncertainties are extended with a coverage factor of 2. The uranium global fallout
 431 signature ($10^{-10} - 10^{-7}$) falls beyond the range of the X-axis.

432

433

434 **Detectability of uranium releases from the FDNPP**

435

436 Although it was not possible to calculate the U source contributions as it was done for Pu, theoretical
437 FDNPP-derived ^{236}U concentrations ($^{236}\text{U}_{\text{FDNPP}}$) in the samples analysed in the current study were
438 estimated, based on the $^{236}\text{U}/\text{Pu} = (0.46 \pm 0.12)$ ratio determined from the literature data (Nishihara et al.,
439 2012). The maximum FDNPP-derived Pu concentration in soil samples analysed here reached 30.7 ± 9.4
440 fg/g (Table S5). Accordingly, the theoretical ^{236}U concentration from the FDNPP was estimated to a
441 maximum of 14.1 ± 5.6 fg/g. Assuming a natural U concentration in Japanese soils of 1.9 ± 1.2
442 $\mu\text{g/g}$ (Yoshida et al., 1998; Yoshida et al., 2000), the estimation of the theoretical $^{236}\text{U}_{\text{FDNPP}}/^{238}\text{U}$ (i.e. the
443 potential impact of the FDNPP releases on the $^{236}\text{U}/^{238}\text{U}$ measured in the samples) was $(7.6 \pm 5.2) \times 10^{-9}$.
444 This theoretical calculation demonstrates that the occurrence of FDNPP-originating fallout is not
445 detectable in the analysed samples, because there is no significant difference between the $^{236}\text{U}_{\text{FDNPP}}/^{238}\text{U}$
446 ratio in these sediment samples and the $^{236}\text{U}/^{238}\text{U}$ isotope ratio associated with the very heterogeneous
447 global fallout signal ($10^{-10} - 10^{-7}$).

448 Similar calculations were performed to estimate the theoretical ^{236}U concentrations in the sediment
449 core, based on the FDNPP-derived Pu measurements in these samples. The resulting concentration
450 amounts to 1.7 fg/g, which demonstrates that the FDNPP-originating U fallout did not reach the region
451 of interest located at ~ 40 km from the power plant. Nevertheless, the potential occurrence of U
452 emissions by the FDNPP accident needs further investigations. In particular, similar analyses should be
453 performed in more contaminated areas such as in sediment accumulated in lakes located closer to the
454 FDNPP, where uranium may have been released in larger quantities.

455

456

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458

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465

466

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