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1  **$^{210}\text{Po}$  sequential extraction applied to wetland soils at uranium mining sites**

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3

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10

11 **Abstract**

12 Former uranium mining activities have led to the presence of naturally occurring nuclides  
13 embedded in soil. Such activities have also modified the secular equilibrium between  
14 radionuclides in  $^{238}\text{U}$  decay series. The objective of this paper is to quantify the long-term  
15 effect of former uranium mining activities on the behavior of the final radionuclide in the  
16  $^{238}\text{U}$ -series, i.e. polonium-210 ( $^{210}\text{Po}$ ), present in soils. Soil samples are extracted from two  
17 uranium sites in France, specifically a quarried site and a natural site. The polonium  
18 distribution is studied within the various soil fractions, namely: water soluble, exchangeable,  
19 bound to carbonates, bound to iron/manganese oxides, bound to organic matter, and residual.  
20  $^{210}\text{Po}$  is mainly found in the residual fraction of both study sites (87-90%), followed by the  
21 carbonates fraction (5-9%). The  $^{210}\text{Po}$  activity in the other fractions is very small in  
22 comparison with total activity.

23

24 **Keywords**

25 Polonium-210, Sequential extraction, Soils, Uranium mining.

26

## 27           1. Introduction

28   Over 200 uranium mines sites exist in France, some of which had been in operations until the  
29   beginning of the 1990's (Ielsch *et al.*, 2017). Their existence has led to the presence of  
30   naturally occurring nuclides embedded in soil. Given society's persistent concern about  
31   radioactivity in the environment, assessing the impact of radioactive metals on environmental  
32   compartments is necessary in order to adopt appropriate precautions. To quantify this impact  
33   and understand the behavior of radionuclides in the environment, the main scientific challenge  
34   calls for identifying the chemical mechanisms that control radionuclide mobility,  
35   bioavailability and ecotoxicity. The major scientific milestone consists of quantifying labile  
36   species in the ecosystem and then describing their speciation in terrestrial and aquatic  
37   environments.

38   Discovered in 1898 by Pierre and Marie Curie,  $^{210}\text{Po}$  is a natural radionuclide occurring in the  
39   environment, with its precursors, i.e. radon-222 and lead-210, being the penultimate daughter  
40   of natural uranium-238. Of the 33 polonium isotopes,  $^{210}\text{Po}$  is one of the most abundant. Due  
41   to its very high specific activity ( $1.66 \cdot 10^{14} \text{ Bq.g}^{-1}$ ),  $^{210}\text{Po}$  is a substance extremely toxic to  
42   humans. Just a few micrograms are sufficient to cause death. This metallic substance is some  
43   one million times more toxic than sodium or potassium cyanide (Al-Masri *et al.*, 2004;  
44   Ansoborlo *et al.*, 2012). The issue of its bioavailability is directly correlated with the species'  
45   chemical form, which depends on environmental characteristics (pH, Eh, organic carbon  
46   content, etc.). This correlation between speciation and bioavailability remains puzzling given  
47   the current state of knowledge on polonium behavior (notably as regards the limited  
48   thermodynamic databases describing surface complexation reactions).

49   In the literature, many studies (Al-Masri *et al.*, 2006; Ekdal *et al.*, 2006; Karunakara *et al.*,  
50   2000; Özden *et al.*, 2013; Strumińska-Parulska and Olszewski, 2018) demonstrate that  
51   anthropic activities, such as phosphate industries, heavy metal mining and oil drilling, can  
52   lead to a local 'overconcentration' of  $^{210}\text{Po}$ . The correlation with uranium mining (i.e. ore  
53   extraction) is most obvious, over the range of 0.014 to 22 kBq.kg<sup>-1</sup> on surface soil (Lapham  
54   and Millard, 1989; Sethy *et al.*, 2014; Thomas, 2000). None of these authors could determine  
55   whether the polonium present is labile. The fate of polonium in the environment will differ  
56   because its behavior and mobility in the soil depend on its physicochemical forms as well as  
57   soil characteristics (Blanco *et al.*, 2004; Jia *et al.*, 2006; Prakash *et al.*, 2017; Žemberyová *et*  
58   *al.*, 2006).

59 A sequential extraction methodology allows access to the geochemical partitioning of heavy  
60 metals or radionuclides within the various constituent solid phases of soils or sediments. This  
61 methodology is based on a successive treatment of specific solutions, each designed to  
62 solubilize a targeted mineralogical fraction (Vandenhove *et al.*, 2014). Despite problems such  
63 as re-adsorption, non-selectivity of extraction reagents and an incomplete dissolution of target  
64 phases (Schultz *et al.*, 1998), sequential extraction yields key information on the original  
65 properties of radionuclides.  $^{210}\text{Po}$  in mineral samples was speciated by applying sequential  
66 extraction in order to identify their sources (Al-Masri *et al.*, 2006; Jia *et al.*, 2006; Štok and  
67 Smodiš, 2012).

68 The aim of this study is to determine the distribution of  $^{210}\text{Po}$  in the various geochemical  
69 fractions of soil samples from two uranium sites in France, specifically an operational site  
70 (Rophin) and a natural site (Granges du Colonel). For this purpose, a six-step sequential  
71 extraction method has been applied. This methodology was validated using certified reference  
72 materials from the IAEA Agency.

73

74 **2. Materials and methods**

75 *2.1. Study sites*

76 The two selected sites are in two enriched uranium zones in France (see Fig. 1). The first,  
77 named 'Rophin', is located in the Puy-de-Dôme Department about 3.4 km northwest of the  
78 city of Lachaux. The surrounding landscape is hilly and composed of forests and meadows.  
79 The soil at the Rophin site is qualified as wet to marshy. Quarried from 1948 to 1957, the  
80 Rophin site produced 0.4 tons of uranium for 2,000 tons of ore actually mined. This site now  
81 serves as a storage depot for uranium waste and has not been remodeled since its inception in  
82 the 1950's.

83 A mechanical or washing plant was built in 1948 on the mine itself in order to treat the  
84 extracted material. The objective of this facility was to concentrate uranium ores from local  
85 mining operations before processing.

86 The Rophin site is currently used to store ore processing residues and dismantling products  
87 from laundries. The actual storage location lies on the former mining tile of the Rophin mine  
88 and contains 30,000 tons of waste. Moreover, since this site has not been remodeled since its  
89 initial construction in the 1950's, it is now naturally vegetated.

90 The second site, named 'Granges du Colonel', lies roughly 7 km northeast of Belvédère in the  
91 Alpes-Maritimes Department. As part of the search for uranium resources in France, the  
92 granitic massif in this department was prospected during the years 1956-58. The occurrences  
93 of uranium here are mainly confined to the Permian lands, with the Granges du Colonel site  
94 offering some of the highest indices. Yet this site has never been quarried, due perhaps to its  
95 remote location and lack of accessibility or to local opposition. Samples from this site were  
96 collected in order to compare the impact of human activities on the behavior of polonium in  
97 the soil.

98

99 *2.2. Samples, sampling protocol, pretreatment*

100 **Certified material reference: IAEA-385**

101 The protocol validation and reproducibility steps were performed using the certified material  
102 standard IAEA-385 with a given value of  $^{210}\text{Po}$ . The material was collected in the Irish Sea by  
103 the Centre for the Environment, Fisheries and Aquaculture Science (CEFAS), Lowestoft,  
104 U.K. in 1995. It was then dried, sieved through a 250- $\mu\text{m}$  mesh and homogenized by mixing

105 in a nitrogen atmosphere. This sample received International Atomic Energy Agency (IAEA)  
106 certification (Pham *et al.*, 2005). The IAEA-385 sediment was subjected to the recognized  
107 analysis procedure before application to our environmental samples.

108

### 109 **Gamma Cartography**

110 Gamma cartography was conducted at the study sites in order to identify areas of high  
111 activity. Two gamma ray maps of the sites were derived from a gamma ray sensor with a  
112 Colibri device (Canberra, Inc.). The data were acquired automatically every five seconds.  
113 These measurements were recorded in May 2017 for the ‘Granges du Colonel’ site and in  
114 November 2017 for ‘Rophin’. The gamma mapping images and photographs were  
115 superimposed using the QGIS (Quantum Geographic Information System) software.

116

### 117 **Sampling and Sample Preparation**

118 Soil samples were collected in wetlands (denoted RW and GW for Rophin Wetland and  
119 Granges du Colonel Wetland, respectively) with soil traps placed at a depth of 15 cm. After  
120 sampling and storage in a plastic bag, the samples were dried in the oven at 50 °C for 10 days  
121 followed by cooling at room temperature. Stones, pebbles, plant materials and roots were  
122 manually removed. The samples were then sieved through a 2-mm screen sieve before being  
123 crushed in a ceramic pestle and mortar to obtain a homogeneous mixture that was stored until  
124 analysis.

125

### 126 *2.3. Analysis of soil properties*

#### 127 **Soil pH**

128 The soil pH was measured by a method specified in NF ISO 10390 (AFNOR 1994b).  
129 Measurements were carried out in two different media, i.e. distilled water or a 1 M KCl  
130 solution (the cations in these solutions displace the protons absorbed on the soil ion  
131 exchangers with as much quantitative precision as possible). Five grams of dry soil samples  
132 were vigorously shaken with 25 ml of the corresponding solution for 5 minutes. The  
133 suspension was then left to rest at least 4 hours before measurement with a pH meter  
134 (SevenCompact™ METTLER TOLEDO).

#### 135 **Carbonate and organic matter quantification**

136 The organic and carbonate matter contents in the soils were determined according to the LOI  
137 (Loss On Ignition) method (Heiri *et al.*, 2001). Approximately 1 g of dried soil sample was  
138 introduced into the oven at 50 °C overnight. Next, the soil samples were heated at 550 °C for  
139 5 h in the muffle furnace (Nabertherm) to burn the organic matter. In a subsequent step, they  
140 were heated to 950 °C for 2 h to burn the carbonate matter. Between each step, the samples  
141 were cooled in a desiccator and weighed.

142 The organic content (%OM) was calculated using the following equation:

$$143 \quad \%OM = \frac{DW_i - DW_{550}}{DW_i} \times 100 \quad \text{Eq. 1}$$

144 For carbonate content (%CO<sub>3</sub><sup>2-</sup>), the calculation proceeded as follows:

$$145 \quad \%CO_3^{2-} = \frac{DW_{550} - DW_{950}}{DW_i} \times 100 \times 1.36 \quad \text{Eq. 2}$$

146 where  $DW_i$  denotes the dry weight of the sample before combustion,  $DW_{550}$  the dry weight of  
147 the sample after heating at 550°C, and  $DW_{950}$  the dry weight of the sample after heating at  
148 950°C (all in g). The weight loss at 950°C multiplied by 1.36 (ratio of carbonate to carbon  
149 dioxide mass) equals the weight of the carbonate in the original sample.

150

#### 151 2.4. <sup>210</sup>Po analysis

##### 152 **Determination of total <sup>210</sup>Po activity in the soil**

153 0.5 g of soil with 40 mBq of an added <sup>209</sup>Po (Eckert Ziegler) tracer was digested with 10 ml of  
154 hydrofluoric acid (39%) in a microwave (Ethos Easy). The microwave cycle was set with two  
155 steps: the first one raised the temperature to 200 °C for 20 minutes, while the second step  
156 stabilized this temperature for 120 minutes. After cooling at room temperature, the  
157 hydrofluoric acid was evaporated to dryness at 50 °C. Then, 10 ml of concentrated nitric acid  
158 (65%) were added and then heated again with the same microwave cycle of mineralization.  
159 Then, it is evaporated to dryness at 50 °C. For spontaneous polonium deposition onto a silver  
160 disc, the residue was dissolved in a 0.5 M HCl solution before adding ascorbic acid (1 g for  
161 10 ml HCl 0.5 M) (Nelson *et al.*, 2017; Özden *et al.*, 2013). The contact time was set for 24 h  
162 at room temperature. The deposition was carried out in a nearly enclosed environment in  
163 order to reduce the loss by evaporation (Jia *et al.*, 2006). The disc was then washed using  
164 demineralized water and air-dried. Lastly, the polonium activity was measured by means of

165 alpha spectrometry. Triplicate samples were prepared to ensure the quality of the analysis  
166 performed.

167

### 168 **Sequential Extraction Procedure**

169 The distribution of  $^{210}\text{Po}$  in soil fractions was studied using a sequential extraction protocol  
170 developed by Tessier *et al.* (Tessier *et al.*, 1979) and Al-Masri *et al.* (Al-Masri *et al.*, 2006).

171 This six-step procedure isolates the following fractions: water soluble, exchangeable, bound-  
172 to-carbonates, bound-to-iron/manganese oxides, bound-to-organic matter, and residual  
173 fraction. Triplicate samples were prepared in order to ensure analytical quality.

174 One gram of each soil sample was introduced into centrifuge cones (50 ml) and stirred at  
175 room temperature for the first five steps. After each step, the suspension was centrifuged  
176 (Sigma<sup>TM</sup> 10223) at 4,000 rev/min for 20 min. The supernatant was removed and filtered  
177 through a 0.45- $\mu\text{m}$  pore size cellulose filter. The extracted solutions were evaporated to  
178 dryness at 50 °C. The residue in the centrifuge tube was then extracted by the reagent from  
179 the next steps according to the following procedure.

#### 180 *Fraction 1: Water soluble*

181 The samples were first extracted using 20 ml of demineralized water for 24 h in order to  
182 release water-soluble  $^{210}\text{Po}$ .

#### 183 *Fraction 2: Exchangeable*

184 The residue from Fraction 1 was leached with 20 ml of 1 M  $\text{NH}_4\text{OAc}$  for 24 h. The  $^{210}\text{Po}$   
185 adsorbed on mineral surfaces, capable of exchanging with an ion widely introduced into the  
186 solution ( $\text{NH}_4^+$ ), is released.

#### 187 *Fraction 3: Bound-to-Carbonates*

188 The residue from Fraction 2 was contacted with a 20 ml buffered  $\text{NaOAc}/\text{HOAc}$  solution (pH  
189  $5.2 \pm 0.1$ ) for 6 h. At this pH, elements precipitated or co-precipitated with the carbonates, as  
190 well as those that bind to the surfaces of solids by pH-dependent bonds, are released in  
191 solution (Cornu and Clozel, 2000).

#### 192 *Fraction 4: Bound-to-iron and manganese oxides*

193 The residue from Fraction 3 was contacted with 20 ml of 0.04 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  for 24 h in  
194 order to free  $^{210}\text{Po}$ , which had been bound to iron and manganese oxides.

195

196

197 *Fraction 5: Bound-to-organic matter*

198 The residue from Fraction 4 was contacted with 15 ml of 30%  $\text{H}_2\text{O}_2$  acidified to pH 2 by 0.02  
199 M  $\text{HNO}_3$  for 24 h; afterwards, 5 ml of 3.2 M  $\text{NH}_4\text{OAc}$  was added before separation so as to  
200 avoid sorption. This extraction step destroys the organic materials in order to release the  
201 complex or adsorbed metals.

202 *Fraction 6: Residual fraction*

203 Once the first five fractions had been removed, the residue consisted of the primary and  
204 secondary minerals, i.e. the most difficult to extract (Rodgers *et al.*, 2015). The residue from  
205 Fraction 5 was transferred to a Teflon tube and mineralized by the same procedure to  
206 determine the total  $^{210}\text{Po}$  activity concentration under the section 'Determination of total  $^{210}\text{Po}$   
207 activity in the soil'.

208  $^{209}\text{Po}$  was added to the filtrate resulting from each leaching step before evaporating to dryness  
209 at 50 °C. The residue obtained was then dissolved using 0.5 M hydrochloric acid. The  $^{210}\text{Po}$   
210 activity concentration in each fraction could be determined by alpha spectrometry after the  
211 spontaneous deposition of polonium on the silver disc.

## 212 **Polonium quantification**

213  $^{209}\text{Po}$  and  $^{210}\text{Po}$  were quantified using dual alpha spectrometers EG&G Ortec 576A equipped  
214 with boron-implanted silicon detectors offering a 450 mm<sup>2</sup> active area and an alpha resolution  
215 (FWHM) of 20 keV at 5.47 keV. Pulses were analyzed with a multichannel buffer analyzer  
216 (Spectrum Master Ortec 919) and spectra with the Vision software. The efficiency was  
217 determined by means of calibrated discs electroplated with known amounts of tracer, while  
218 the background noise was being controlled regularly. The average efficiency of the detector  
219 was  $22 \pm 2\%$ . The lower limit of detection for the method employed was 0.2 mBq (Leclercq  
220 *et al.*, 2014).

221

### 222 3. Results and discussion

#### 223 3.1. Total $^{210}\text{Po}$ activity in soil

224 The soil mineralization procedure using the microwave oven was performed with the IAEA-  
225 385 sediment standard in order to validate this protocol. The recommended specific activity of  
226  $^{210}\text{Po}$  for IAEA-385 was  $28.0 \text{ Bq.kg}^{-1}$ , with a confidence interval ranging from 23.8 to 36.6  
227  $\text{Bq.kg}^{-1}$  dry weight. Table 1 shows the results of the total  $^{210}\text{Po}$  activity concentration for the  
228 standard IAEA-385 obtained from this work. The average activity found equals:  $27 \pm 3$   
229  $\text{Bq.kg}^{-1}$  dry weight. This value lies within the confidence interval reported by IAEA, thus  
230 showing good agreement between the determined values and IAEA values ( $28.0 \text{ Bq.kg}^{-1}$ ). The  
231 results of replicated measurements attest to the reproducibility of the procedure used.  
232 Consequently, analyses of the standard IAEA-385 confirm that the recommended  
233 mineralization procedure to determine total  $^{210}\text{Po}$  amount yields reliable results.

234 Figure 2 presents the gamma ray map for both the Rophin (A) and Granges du Colonel (B)  
235 sites. At Rophin, a stream flows down a gradient of the uranium mining zone and  
236 subsequently merges with a north-south watercourse. The combined outflow of the two  
237 currents is named the Terrasson stream. A radionuclide accumulation zone was identified  
238 through this gamma mapping adjacent to the Terrasson stream 150 m after the confluence.  
239 Gamma radiation activity in this area reaches  $3500 \text{ c.s}^{-1}$ , which is 7 times higher than the site  
240 background level. The gamma irradiation levels at the Granges du Colonel site are much  
241 lower than at Rophin.

242 A soil sample denoted RW (for Rophin Wetland) was extracted from a wetland where  
243 radionuclide activity was locally at its highest level. A Granges du Colonel wetland soil  
244 sample (GW) was also extracted for comparative purposes. Both samples were taken at depths  
245 of 15 cm.

246 This mineralization protocol was then applied to the RW and GW samples. Table 1 reports  
247 their respective  $^{210}\text{Po}$  activity concentration ( $\text{Bq.kg}^{-1}$  dry weight) levels. In the RW sample,  
248 the  $^{210}\text{Po}$  level was more than 40 times greater than that of GW, i.e. the  $^{210}\text{Po}$  activity  
249 concentrations in the GW and RW soil samples are  $82 \pm 4 \text{ (Bq.kg}^{-1}\text{)}$  and  $3,461 \pm 148 \text{ (Bq.kg}^{-1}\text{)}$ ,  
250 respectively. These results are consistent with output from the gamma maps (Fig. 2). The  
251 much higher  $^{210}\text{Po}$  activity concentration of the Rophin sample can be explained by the  
252 presence of a high radiation background emanating from the uranium storage facility at  
253 Rophin.

254 3.2. *Sequential Extraction Studies*

255 According to Tessier *et al.* (Tessier *et al.*, 1979) and Al-Masri *et al.* (Al-Masri *et al.*, 2006), a  
256 modified procedure was performed in order to detect the  $^{210}\text{Po}$  distribution within the  
257 geochemical fraction. The IAEA-385 standard was studied for  $^{210}\text{Po}$  speciation using the  
258 procedure of sequential extraction; results are shown in Table 2. It can be noticed that the  
259  $^{210}\text{Po}$  fraction proportion of the sample equals: 1.24% in water-soluble form, 1.71% in  
260 exchangeable form, 5.61% bound to carbonates, 2.92% bound to iron and manganese oxides,  
261 1.09% bound to organic matter, and 87.4% bound to residue. In other words,  $^{210}\text{Po}$  was almost  
262 entirely found in the last fraction, thus indicating an association with the insoluble mineral  
263 phases. The sum of  $^{210}\text{Po}$  activity concentrations in these six each individual sequential  
264 extraction fractions is equal to  $25 \pm 3 \text{ Bq.kg}^{-1}$ . This is in good agreement with the total  $^{210}\text{Po}$   
265 activity measured in the unfractionated sample of  $27 \pm 3 \text{ Bq.kg}^{-1}$ . According to results  
266 obtained from the standard sediment IAEA-385, this sequential extraction procedure has  
267 successfully identified the  $^{210}\text{Po}$  distribution in the various soil fractions.

268 This extraction procedure was then applied to GW and RW samples. The  $^{210}\text{Po}$  activity  
269 concentrations in the different soil fractions are presented in Table 2. Sequential extraction  
270 results from the GW and RW samples are similar to those of the IAEA-385 sample.  $^{210}\text{Po}$  was  
271 mainly found in the residual fraction, followed by the carbonate fraction. The sum of  $^{210}\text{Po}$   
272 activity in the four other fractions is relatively low, not exceeding 8% of total activity.

273 In a water-soluble and exchangeable fraction, the quantity of  $^{210}\text{Po}$  was very small in  
274 comparison with the other fractions. It can be concluded that polonium mostly attaches to  
275 insoluble compounds in the atmosphere after the decay of radon gas (Al-Masri *et al.*, 2006).  
276 The  $^{210}\text{Po}$  was then deposited onto the ground as dry and wet deposition, which constitutes  
277 their main source in surface soil (Karunakara *et al.*, 2000).

278 Apart from the residual fraction,  $^{210}\text{Po}$  is mainly present in the carbonate fraction. However,  
279 the percentage of  $^{210}\text{Po}$  in the carbonate fraction of RW is much higher than that of GW, i.e.  
280 88% and 43% respectively, by comparing it with the sum of the first five fractions. While the  
281 carbonate content of both samples is equal (1.8% dry weight - Table 3). The uranium mining  
282 activities promoted the exhalation of radon. This phenomenon has consequently modified the  
283 secular equilibrium between radionuclides in the  $^{238}\text{U}$  decay series. Radiochemical  
284 disequilibrium points to the radionuclide mobilization and transport processes (Bister *et al.*,  
285 2015). Elevated levels of  $^{210}\text{Po}$  activity in the carbonates fraction can result from the decay of

286 unsupported radon-222; therefore, uranium mining activities at the Rophin site may indeed  
287 influence the geochemical distribution of  $^{210}\text{Po}$ . The increase in hydrogen ion concentration  
288 changes the mobilization intensity of heavy metals. A low soil pH value, in addition to  
289 mobilizing heavy metals, affects the activity of metal ions in the water contained in soil pores,  
290 thus also altering their bioavailability (Fijałkowski *et al.*, 2012). The pH value of RW is less  
291 than that of GW (Table 3), which may explain the higher portion of  $^{210}\text{Po}$  found in the  
292 carbonate-bound fraction in the RW sample.

293  $^{210}\text{Po}$  displays a low percentage (less than 1%) when  $\text{NH}_2\text{OH}\cdot\text{HCl}$  was introduced during the  
294 fourth step of the procedure, which would suggest that this element is only slightly associated  
295 with iron and manganese oxides.

296 As regards the organic fraction, numerous studies (Avadhani *et al.*, 2005; Narayana *et al.*,  
297 2006; Özden *et al.*, 2013) have shown a positive correlation between organic matter content  
298 and  $^{210}\text{Po}$  activity: the higher the organic matter content, the greater the level of  $^{210}\text{Po}$  activity.  
299 In contrast with these observations, results from the sequential extraction in this study reveal  
300 that  $^{210}\text{Po}$  activity concentration in the organic fraction remains very small, 0.16% and 3.43%  
301 for RW and GW, respectively, whereas the organic matter content in RW and GW amounts to  
302 respectively 22.7% and 9.2%. Prakash *et al.* found that the lower the organic matter  
303 percentage in the soil samples, the higher the level of  $^{210}\text{Po}$  activity and *vice versa* (Prakash *et*  
304 *al.*, 2017). The organic matter and  $^{210}\text{Po}$  were detected in the same location, i.e. on the soil  
305 surface, yet they remain uncorrelated. According to Vaaramaa,  $^{210}\text{Po}$  in the organic layer most  
306 probably originated in large part from atmospheric depositions, and no systematic correlation  
307 appeared between these two elements (Vaaramaa *et al.*, 2010).  $^{210}\text{Po}$  can indeed stem from  
308 two activity sources: supported  $^{210}\text{Po}$  from decay of the remaining radon-222 in the soil  
309 matrix, and unsupported  $^{210}\text{Po}$  due to the deposition of radon decay products from the  
310 atmosphere (Matthews *et al.*, 2007; Özden *et al.*, 2013; Persson, 2014). Upon reaching the  
311 soil surface as fallout from the atmosphere,  $^{210}\text{Po}$  is rapidly adsorbed by the surface soil,  
312 which accounts for the principal source of  $^{210}\text{Po}$  in surface soil (Avadhani *et al.*, 2005; Jia *et*  
313 *al.*, 2006). On the other hand, the soil surface is also a place where organic substances are  
314 primarily found. This initial layer of soil is mainly composed of decomposed plant debris and  
315 humic substances. The surface soil layer is also known to be the zone in which most  
316 biological activity occurs.

317 The highest  $^{210}\text{Po}$  portions were dissolved in mineral acids, with observed values equaling  
318 90% and 87% for the RW and GW samples, respectively. This finding reflects immobilization

319 of the particular radionuclide, which is due to the fact that  $^{210}\text{Po}$  has been incorporated into  
320 crystalline silicates. The low  $^{210}\text{Po}$  availability leads to the conclusion that its presence in the  
321 environment is not hazardous for ingestion pathways, but only for inhalation of the particulate  
322 materials (Desideri *et al.*, 2008).

323

324 **4. Conclusion**

325 The total  $^{210}\text{Po}$  activity concentration in soil samples extracted from two wetland areas near  
326 French uranium mining sites has been determined. The sample taken near a uranium storage  
327 facility reveals a significant level of total  $^{210}\text{Po}$  activity; this finding is correlated with the high  
328 radiation background. To study the distribution of  $^{210}\text{Po}$  in soils, a sequential extraction  
329 procedure was developed, validated with the certified reference material (IAEA-385) and then  
330 applied to soil samples from the two study sites. From these sequential extraction analyses,  
331 the  $^{210}\text{Po}$  found was almost entirely in the residual fraction of both sites. Apart from the  
332 residual fraction,  $^{210}\text{Po}$  is mainly present in the carbonate-bound fraction; however, the  
333 percentage of  $^{210}\text{Po}$  in the RW sample exceeds that of GW even though the carbonate content  
334 of both samples is equal. Elevated levels of  $^{210}\text{Po}$  activity in the carbonate-bound fraction may  
335 result from the decay of unsupported  $^{222}\text{Rn}$ . Underground mining operations can thus provide  
336 drains for the circulation of radon gas. This phenomenon modifies the secular equilibrium  
337 between radionuclides in  $^{238}\text{U}$  decay series.

338

339

340 **Acknowledgement**

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441

442 **Figure and Table captions**

443 Fig. 1: Map of the mean uranium content of geological units in France from (Ielsch *et al.*,  
444 2017), with identification of our two experimental sites

445

446 Fig. 2: Gamma cartography of the "Rophin" site (A) and the "Granges du Colonel" site (B)

447

448 Fig. 3: Distribution of  $^{210}\text{Po}$  (%) in six fractions from the sequential extraction of IAEA-385,  
449 RW and GW samples

450

451 Table 1: Total  $^{210}\text{Po}$  activity concentration ( $\text{Bq.kg}^{-1}$  dry weight)

452

453 Table 2: Fractionation of  $^{210}\text{Po}$  in the study samples ( $\text{Bq.kg}^{-1} \pm \text{SD}$ )

454

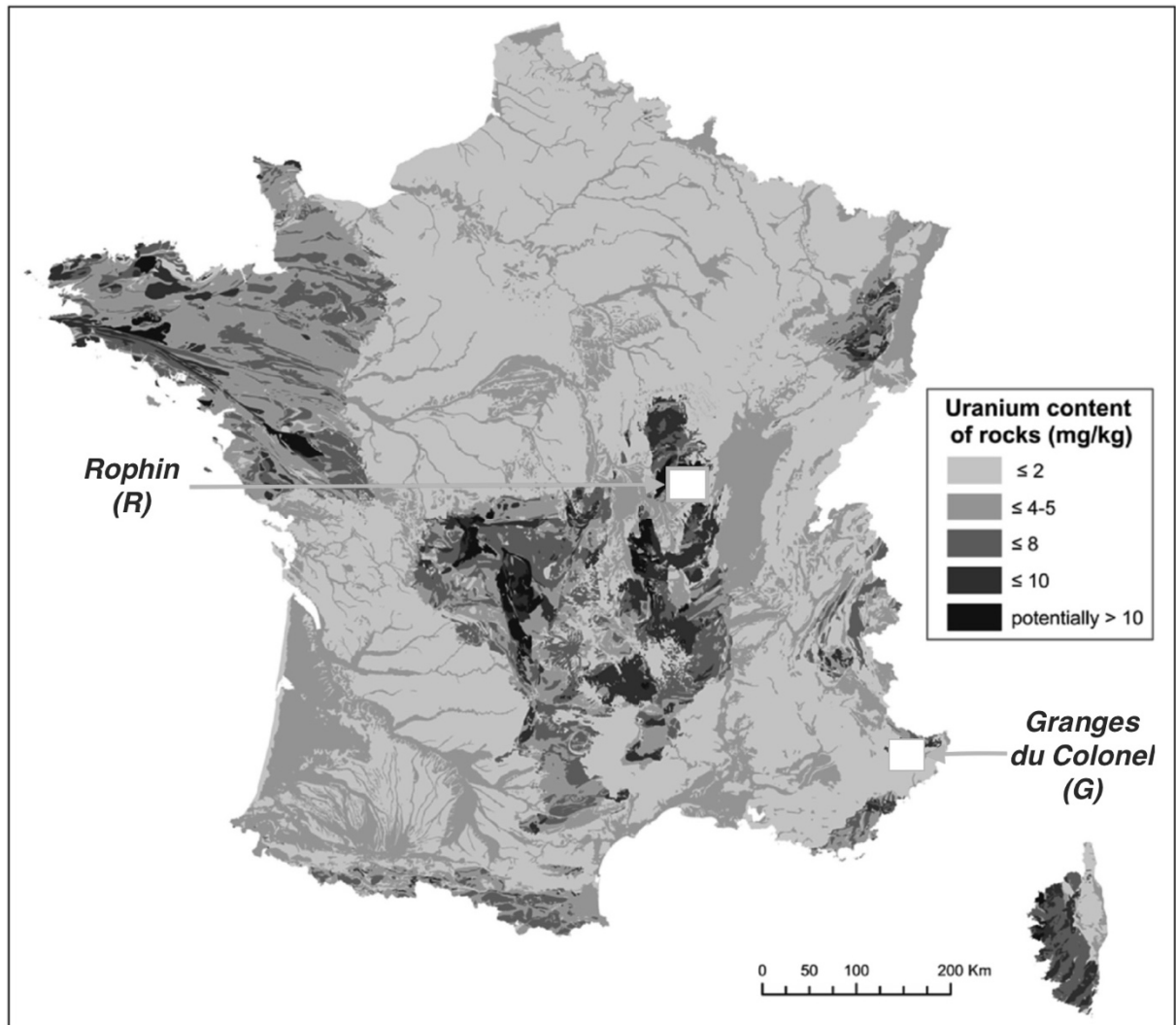
455 Table 3: Properties of the studied soil samples

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458 **List of figures and table**

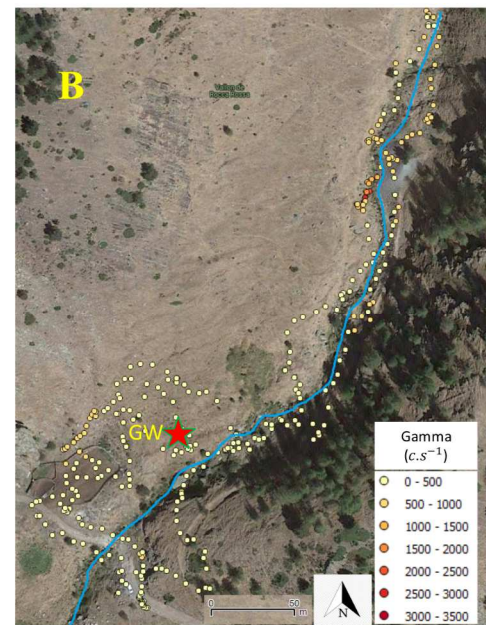
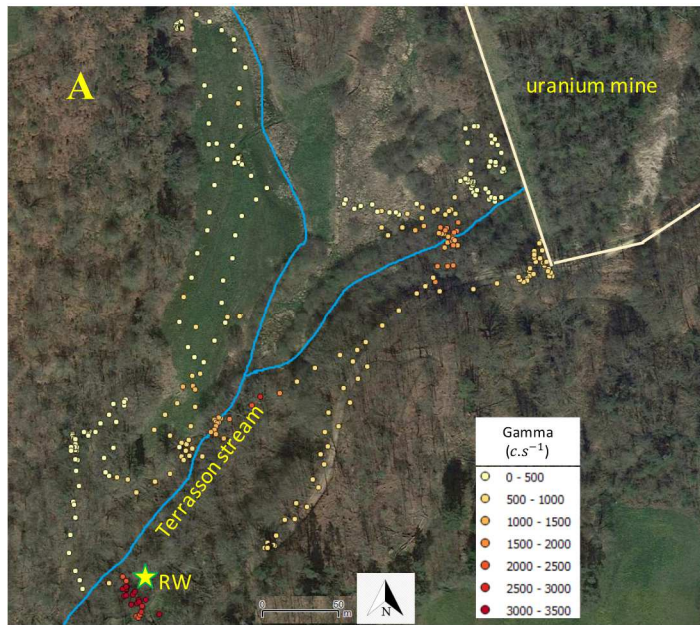
459 Fig. 1:



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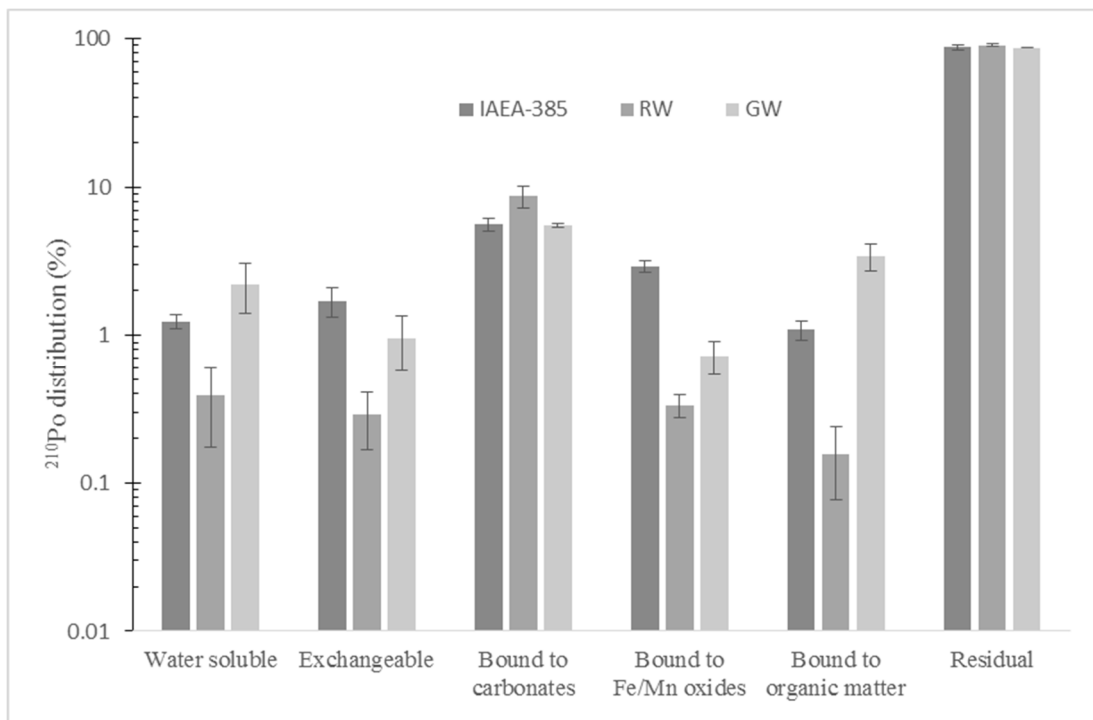
462 Fig. 2:



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465 Fig. 3:



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468 Table 1:

Sample	Activity concentration $\pm$ SD
IAEA-385*	$27 \pm 3$
RW	$3,461 \pm 148$
GW	$82 \pm 4$

469 \*Information value of  $^{210}\text{Po}$ :  $28.0 \text{ Bq.kg}^{-1}$  with a confidence interval from 23.8 to  $36.6 \text{ Bq.kg}^{-1}$  dry weight

470

471 Table 2:

Fraction	IAEA-385	RW	GW
Water soluble	$0.32 \pm 0.03$	$12 \pm 7$	$1.8 \pm 0.6$
Exchangeable	$0.43 \pm 0.09$	$9 \pm 4$	$0.8 \pm 0.3$
Bound to carbonates	$1.42 \pm 0.2$	$266 \pm 51$	$4.4 \pm 0.3$
Bound to Fe/Mn oxides	$0.72 \pm 0.06$	$10 \pm 2$	$0.6 \pm 0.1$
Bound to organic matter	$0.28 \pm 0.06$	$5 \pm 3$	$2.8 \pm 0.7$
Residual fraction	$22 \pm 2$	$2,762 \pm 71$	$70 \pm 3$

472

473

474 Table 3:

Sample	pH (H <sub>2</sub> O)	pH (KCl)	%OM	%CO <sub>3</sub> <sup>2-</sup>
RW	5.51	3.96	22.7	1.8
GW	5.61	4.52	9.2	1.8

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