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1 **Plant-Soil-water interactions: implications from U-Th-Ra isotope analysis in**
2 **soils, soil solutions and vegetation (Strengbach CZO, France)**

3

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22 *Keywords:* ²³⁸U-²³⁴U-²³⁰Th-²²⁶Ra radioactive disequilibria, ²³⁰Th/²³²Th activity ratios,
23 soils, soil solutions, vegetation, Strengbach catchment.

24 **ABSTRACT**

25 This study presents U-Th-Ra isotope data for soils, soil grain size fractions, soil
26 solutions, throughfall, rainwater and tree samples from two experimental plots
27 under spruce and beech trees, in the Strengbach catchment (France) that highlight
28 the importance of the ^{238}U - ^{234}U - ^{230}Th - ^{226}Ra nuclides and the ($^{230}\text{Th}/^{232}\text{Th}$) for the
29 tracing of biogeochemical cycles in the plant-soil-water system of the critical zone
30 (CZ).

31 The results highlight the very contrasting impact of trees on the U-Th and Ra (Ba)
32 budgets in forest ecosystems with Ra-Ba being strongly and U-Th very little cycled
33 by vegetation, leading to high ($^{226}\text{Ra}/^{230}\text{Th}$) and ($^{226}\text{Ra}/^{238}\text{U}$) in trees. Thorium-
34 Ra(Ba) fractionations in soil solutions and soils are therefore strongly influenced by
35 tree uptake and litter decay but U-Th fractionations are little influenced. Compared
36 to other classical isotope systems such as Sr or Nd that are routinely used in the
37 study of the CZ and significantly affected by vegetation cycling, U-Th isotopes are
38 probably among the few tracers to be specific tracers of water-rock interactions in
39 the CZ. The Th activity ratios of soil minerals, especially of minor and secondary
40 mineral phases, show a large range of variation, from 0.7 to 5 in the Strengabch case.
41 These different characteristics give Th activity ratio an important role for tracing
42 the sources of chemical fluxes in soils, soil solutions and vegetation that is currently
43 under-exploited. The Strengbach study illustrates the utility of this approach and
44 the methodology is further strengthened by the combination of U, Th activity ratios
45 and Sr isotope ratios, which also provides additional constraints on the weathering
46 processes affecting the Strengbach bedrocks and the nature of the reservoirs
47 involved in the plant-soil-water transfers. The results emphasize that minor mineral
48 phases such as zircon, sulfate and phosphate are important sources of the U-Th
49 fluxes transiting soil solutions and significantly control the U and Th budget of the
50 Strengbach soil samples and their Th activity ratios. Furthermore, the comparison of
51 the U-Th-Sr isotopic characteristics of soil solutions and soil grain size fractions
52 allows the recognition of two stages of weathering of the bedrock i.e. 1- dissolution
53 of the primary minerals and formation of the secondary ones in the deep soil
54 horizons, and 2- dissolution of both primary and secondary minerals mainly from
55 the finest soil grain size fractions in the nearest surface soil horizons. The latter
56 might be related to recent modifications of the weathering processes in the

57 catchment, stronger and older under the spruce than the beech plot. We propose
58 that degree of weathering modification is related to the nature of tree cover because
59 spruce plantations have caused an increase of soil acidity and hence of weathering
60 intensity of some minerals and likely also of Ca leaching from the Ca-poor
61 Strengbach soils over the past decades. The U-Th-Sr results of this study also point
62 to the occurrence of isotopically different reservoirs of these elements for trees and
63 gravity soil solutions collected by lysimetric plates. This further suggests that for the
64 Strengbach watershed the gravity soil solutions cannot be the main tree nutrient
65 reservoir.

66

67

68 **1. INTRODUCTION**

69 Soil horizons play a key role in the evolution of the critical zone, as dynamic and
70 porous interfaces that connect the atmosphere, vegetation, rocks, groundwaters and
71 surface waters (Banwart et al., 2017; 2019). Precise knowledge of the relationships
72 and inter-relationships between the different components of this highly complex
73 system is necessary when one seeks, for instance, to model precisely the soil and
74 critical zone evolution (Banwart et al., 2019) or the chemical composition of stream
75 and surface waters (e.g., Li et al., 2017; Lucas et al., 2017; Ackerer et al., 2018).
76 Knowledge of key parameters including the nature and extent of weathering
77 processes active in the soil horizons and the interplay between biological processes,
78 water circulation and water-rock interactions, is certainly still insufficient. Advances
79 in the description/understanding of the main key hydro-biogeochemical reservoirs
80 and processes that are active in the surface soil horizons are still required.

81 Geochemical and especially isotopic approaches have been developed to address
82 these issues, both to specify the sources of elements and constrain their pathways in
83 plant-soil-water systems (e.g., Blum and Erel, 2005; Bouchez et al., 2013; Bullen and
84 Kendall, 1998; Kendal and Doctor, 2005). Significant efforts have been made over
85 recent decades to evaluate the potential of using geochemical proxies for
86 hydrogeochemical processes and biogeochemical cycles active within the soil
87 system. Understanding the parameters and processes that control the behavior of
88 geochemical tracers during plant-soil-water interactions has progressed from
89 studies conducted at the experimental watershed scale down to the laboratory
90 experiment scale. Such studies have included a large number of geochemical tools:
91 trace elements, traditional and non-traditional stable isotopes, and radioactive and
92 radiogenic isotopes (e.g., Akerman et al., 2014; Aubert et al., 2001; 2002; Babcsányi
93 et al., 2014; 2016; Braun et al., 1998; Bouchez et al., 2013; Bullen and Eisenhauer,
94 2009; Chabaux et al. 2015a,b; Cividini et al., 2010; Ladouche et al., 2001; Laveuf and
95 Cornu, 2009; Ma et al., 2011; Négrel et al., 2018; Opfergelt and Delmelle, 2012;
96 Opfergelt et al., 2014; Schmitt et al., 2003, 2012; 2013; Steinmann and Stille, 1997;
97 2009; Stille et al., 2006; 2009; 2011; Viers et al., 2015; Voinot et al., 2013).

98 These different studies have emphasized the potential of using these geochemical
99 tools to characterize biogeochemical cycles and hydrogeochemical transfer in plant-
100 soil-water systems. These studies also clearly demonstrated interest in coupling

101 geochemical proxies in water, soils and vegetation to understand the critical zone
102 processes and their dependence on environmental conditions (e.g., Sullivan et al.
103 2016 and references therein).

104 In the framework of these efforts, little attention has been paid so far to ^{238}U - ^{234}U -
105 ^{230}Th - ^{226}Ra nuclides and to Th isotope ratios as potential proxies/tracers of critical
106 zone function. To date, studies on U-series nuclides in soils, surface waters and
107 sediments have been mainly undertaken to determine the time constants of
108 alteration and erosion processes in the critical zone (e.g., Ackerer et al., 2016;
109 Bourdon et al., 2009; DePaolo et al., 2006; 2012; Dequincey et al., 2002; Chabaux et
110 al., 2003a,b; 2012; 2013; Gontier et al., 2015; Maher et al., 2006; Pelt et al., 2008;
111 Dosseto et al., 2008; 2014; Dosseto and Schaller, 2016; Ma et al., 2010; 2012; 2013;
112 Vigier et al., 2001). However, few studies have suggested the potential of using ^{238}U -
113 series nuclides to trace hydro- and biogeochemical transfers in watershed and soils.
114 For instance, the coupling between U and Sr isotopes has successfully elucidated the
115 hydrogeochemical fluxes in watershed and soil solutions (Riotte and Chabaux, 1999;
116 Bagard et al., 2011; Chabaux et al., 2001; Riotte et al., 2003; Durand et al., 2005;
117 Pierret et al. 2014; Schaffhauser et al., 2014; Prunier et al., 2015; Tricca et al., 2001).
118 The ($^{230}\text{Th}/^{232}\text{Th}$) activity ratios (hereafter, activity ratios will be noted in brackets)
119 in the different rock minerals were also observed to span a large range of values
120 (Bosia et al., 2016; 2018) that could thus, once combined with Sr or Nd isotopes, be
121 relevant to characterize the mineralogical source of elements in watersheds. Finally,
122 several studies have indicated the potential impact of vegetation on the Ra
123 geochemical cycle (e.g., Cerne et al., 2010; Gerzabeck et al., 1998; Greeman et al.,
124 1999; Jeambrun et al., 2012; Million et al., 1994; Pourcelot et al., 2017; Rihs et al.,
125 2011; 2016; Soudek et al., 2004; Lascar, 2019). These results suggest that ^{238}U - ^{234}U -
126 ^{230}Th - ^{226}Ra nuclides and ($^{230}\text{Th}/^{232}\text{Th}$) ratios are anticipated to be relevant for
127 tracing sources of elements, weathering processes and hydrogeochemical pathways
128 in the plant-soil-water system. So, in this study these nuclides along with the
129 ($^{230}\text{Th}/^{232}\text{Th}$) were analysed in the soils, soil solutions and trees of the Strengbach
130 Critical Zone Observatory (<http://ohge.unistra.fr>) in order to constrain better their
131 contribution to our understanding of the plant-soil-water system. The Strengch CZO
132 is an instrumented watershed, very well suited for this type of work, as already
133 illustrated for other geochemical tools, because it allows for the different

134 hydrogeological and biological components involved in plant-soil-water transfers to
135 be sampled (e.g., Aubert et al., 2004; Gangloff et al., 2014; Lemarchand et al., 2010;
136 Stille et al., 2006; 2009; 2011; 2012; Tricca et al., 1999; Cenko-Tok et al., 2009;
137 Cividini et al., 2010; Lemarchand et al., 2010; Lemarchand et al., 2012; Schmitt et al.,
138 2003; 2017; 2018).

139

140 **2. SITE AND SAMPLING**

141

142 **2.1. Site description**

143 The uppermost Strengbach watershed (0.8 km²) is situated in the Vosges mountains
144 (northeastern France) at altitudes between 880 and 1150 m (a.m.s.l.) and has
145 relatively steep slopes (mean 15°) (Fig. 1). This area is an instrumented
146 environmental observatory (<http://ohge.unistra.fr>) involved in the French critical
147 zone observatories network OZCAR (French network of Critical Zone Observatories:
148 Research and Applications) (<http://www.ozcar-ri.org>), where meteorological,
149 hydrological and water chemistry data have been collected since 1986 (e.g., Viville
150 et al., 2012; Pierret et al., 2014; 2018 for additional details). It was recently used to
151 carry out a study of in-situ dissolution rates of silicate minerals in the critical zone
152 (Wild et al., 2019). The climate is temperate oceanic mountainous with an average
153 rainfall of 1400 mm.yr⁻¹, with ≈20% under snowfall. Forest covers 90% of the
154 geographical area of the watershed. The forest area is composed of 80% spruces
155 (*Picea abies L.*) and 20% beeches (*Fagus sylvatica*).

156 The bedrock is mainly composed of Hercynian base-poor granites (the Brezouard
157 granite Massif), locally marked by petrological and mineralogical variabilities linked
158 to the polyphased history of these granites. As detailed in Hasalova et al. (2015) and
159 Tabaud et al. (2015), granites are derived from two main generations of granitic
160 magmas: a first and extensive K-Mg granitoid magmatism around 340 Ma, followed
161 by magmatic events occurring at ca. 325 Ma, which produced a large amount of
162 felsic anatectic melts, which pervasively intruded and compositionally and
163 texturally reworked previously formed granitoids (in Hasalova et al., 2015). Such a
164 magmatic history in the Strengbach watershed results in a continuum between
165 porphyritic granites with large feldspars and plagioclase phenocrysts, which were
166 formed during the first magmatic stage, to fine-grained more isotropic granites,

167 which were formed by crystallization of the late felsitic magmas, via intermediate
168 granites where the two magmatic assemblages are recognizable. Such a magmatic
169 history can lead to the coexistence of different types of K-feldspars in the same rock,
170 with Ba-rich K-feldspars crystallized from the primary magmas and Ba-poor K-
171 feldspars recrystallized from secondary anatectic magmas (Hasalova et al., 2015).
172 The granitic bedrock has undergone late hydrothermal alterations, which are more
173 important on the northern slope of the catchment than on the southern slope
174 (Fichter et al., 1998 a,b). Field observations also indicate the occurrence of more or
175 less developed veinlets of secondary minerals, including Fe and Mn oxyhydroxides,
176 quartz, and barite, which can be related to hydrothermal or meteoritic alterations.
177 Some of the meteoritic alterations might be of ante-Triassic age (Wyns et al., 2004;
178 Dewandel et al., 2006).

179 A sandy saprolite, which can reach several meters of thickness, usually separates
180 soil and granite. The soils are 80-100 cm deep and vary from Dystric Cambisol to
181 Albic Podzol (brown acidic to ochreous brown podzolic) (WRB 2014). The soils are
182 very coarse-grained, sandy and rich in gravel (Fichter et al., 1998a,b). The shallow
183 soils (upper 50 cm) under spruce (VP site) and beech (HP site) are acidic (pH=3.7-
184 4.5) (Aubert et al., 2001; Solovitch-Vella et al., 2007). Distric Cambisols are mainly
185 located on the northern slope, and Albic Podzols are located on the southern slope.
186 This soil difference likely results from the differences in the lithology, vegetation
187 cover and local climate between the north- and south-facing slopes (e.g., Pierret et
188 al., 2014).

189

190 **2.2. Sampling**

191 Samples were collected between 2004 and 2006 from two experimental sites: one
192 under spruce trees that were planted between 1890 and 1900, which is locally
193 named the VP site and hereafter the “spruce site”, and the other under beeches that
194 were planted between 1860 and 1870, hereafter named HP or the “beech site”
195 (Location Fig. 1). The beech site is developed on the gently hydrothermally altered
196 granite, while the spruce site has a bedrock that has undergone a much more
197 intense hydrothermal alteration (e.g., Fichter et al., 1998). Fine earth (<2 mm) from
198 two soil layers (30-40 cm and 90-100 cm), which were marked by the highest and
199 weakest root density in the two soil profiles, was collected and separated into four

200 particle size fractions: < 2 μm (clay), 2-50 μm (silt), 50-100 μm (fine sand) and
201 1600-2000 μm (coarse sand). Soil solutions were collected by zero-tension
202 lysimeter plates at -5, -10, -30 and -60 cm (noted VP-5, VP-10, VP-30 and VP-60)
203 next to the VP spruce soil profile and at -10 and -70 cm (noted HP-10 and HP-70)
204 next to the HP beech soil profile (see caption Fig. 1). Different parts of spruce and
205 beech trees (sapwood, roots, branches and needles or leaves) and litters from the
206 VP spruce and HP beech sites were collected from 2004 to 2007. Throughfall and
207 rainwater samples were also collected.

208

209 **3. ANALYTICAL METHODS**

210 **3.1. Grain size fractions and granite rocks**

211 Before crushing the fine earth fractions of the four sampled soil horizons, a
212 representative subsample (100 g) was dispersed for 30 min in a cylindrical Pyrex
213 container with 750 ml of ultrapure water to disaggregate the soil and separate the
214 different grain size fractions. The dispersion was sieved at 50 μm through a nylon
215 sieve. The nonpassing fraction was dried at 60°C and used to separate the fine sand
216 (50-100 μm) and coarse sand (1600-2000 μm) fractions using a set of nylon sieves.
217 The clay fraction (<2 μm) and the silt fraction (2-50 μm) was separated from the
218 50 μm -passing fraction via sedimentation in deionized ultrapure water based on
219 Stokes law, followed by centrifugation at 3500 rpm, as detailed in Prunier et al.
220 (2015).

221 Bedrocks and coarse sands (> 100 μm) of the two soil samples were crushed in an
222 agate disk mill. The major and trace element concentrations of these different
223 samples were measured by ICP-AES (Jobin Yvon) and ICP-MS (VG Plasma Quad
224 Thermo Electron), respectively, after lithium tetraborate fusion. The analytical
225 uncertainty was <3% for major element concentrations and <10% for trace element
226 concentrations at 2σ (Dequincey et al., 2005; Chabaux et al., 2012). For isotopic
227 measurements, an aliquot of approximately 100 mg of granite and particle size
228 fraction powders were spiked with ^{233}U and ^{229}Th tracers and digested by ultrapure
229 HF, HNO_3 , HClO_4 , HCl and H_3BO_3 acids (Pelt et al., 2013). After separation and
230 purification using Biorad AG1x8 anionic resin (e.g., Pelt et al., 2008; Granet et al.,
231 2010), the U-Th concentrations and ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{232}\text{Th}$) ratios were
232 measured by thermal ionization mass spectrometry (TIMS, Thermo-Scientific

233 Triton) using ^{233}U and ^{229}Th tracers. $^{87}\text{Sr}/^{86}\text{Sr}$ was determined after separation and
234 purification following chromatographic standard procedures on a VG Sector mass
235 spectrometer using a dynamic multicollection (Lahd Geagea et al., 2007). ^{226}Ra
236 concentration measurements were performed by TIMS (Triton Thermo-Scientific)
237 from another powder aliquot using a ^{228}Ra -enriched spike after digestion,
238 separation and purification according to the protocol given in Pelt et al. (2013) and
239 adapted from previous works by Chabaux et al. (1994) and Ghaleb et al. (2004).
240 Blanks ranged between 30 and 171 pg for U and 160 and 190 pg for Th and were <
241 0.1 fg for Ra and <1 ng for Sr; thus, the blanks were negligible compared to the Sr
242 and U-Th-Ra amounts analyzed in the samples. The repeatability of the Sr, Th and U
243 isotopic analyses was tested by repeated measurements of three solution standards,
244 NBS 987, Th105 and HU1. The mean value of $^{87}\text{Sr}/^{86}\text{Sr}_{\text{NBS987}}$ was 0.71027 ± 0.00002
245 ($n=22$, 2SD (Standard Deviation)), that of $^{232}\text{Th}/^{230}\text{Th}_{\text{Th105}}$ was 217080 ± 2400
246 ($n=37$, 2SD) and $(^{234}\text{U}/^{238}\text{U})_{\text{HU1}} = 0.999 \pm 0.004$ ($n=72$, 2SD). In addition, repeated
247 analyses of the AThO rock standard yielded a mean U activity ratio value of $1.000 \pm$
248 0.004 ($n=10$, 2SD) and a $^{232}\text{Th}/^{230}\text{Th}$ isotopic ratio of 182840 ± 1238 ($n=6$, 2SD). All
249 these data are consistent within errors with previously published data (Pelt et al.,
250 2013 and references therein). The ^{226}Ra concentration of the ^{228}Ra -spike was
251 regularly calibrated against the AThO rock standard assuming secular equilibrium
252 for the ^{226}Ra - ^{230}Th isotopes. The analysis of the $(^{226}\text{Ra}/^{230}\text{Th})$ ratios of the BEN rock
253 standard gives a value of 1.002 ± 0.017 (2SD) that is entirely consistent with the
254 assumed secular equilibrium value (Pelt et al., 2013).

255 **3.2. Vegetation samples**

256 Each sample was first washed with deionized ultrapure water in an ultrasonic
257 tank/bath to remove soil and airborne particles. The samples were then dried at
258 60°C until a constant mass was reached and finally crushed within a specific agate
259 disk mill. Two aliquots of 2 to 10 g of plant material powder were digested on a
260 hotplate in conventional PFA Teflon[®] beakers successively using a HNO_3 - H_2O_2
261 mixture and HNO_3 -HF (a) to determine $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios, U-Th
262 concentrations and U-Th activity ratios using the same protocol as described above
263 for the soil samples and (b) to determine ^{226}Ra concentrations. To avoid
264 interference by Ca during TIMS measurements, excess Ca was removed from the

265 samples using a pretreatment based on manganese complexation according to a
266 protocol adapted from Ghaleb et al. (2004). After complete sample mineralization,
267 the residue was dissolved in 1 to 2 ml of 6N HCl bidistilled and 150 ml of ultrapure
268 water. Approximately 150 μ l of 0.5 N KMnO_4 was added to oxidize the residual
269 organic matter. The solution was heated for 10 min at 80°C before adjusting the pH
270 to 10-11 with 1 M NaOH. Next, 200 μ l of 0.5 N $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was added to initiate Mn-
271 oxide precipitation, onto which Ra sorbed, while most Ca remained in solution. The
272 mixture was heated at 110°C for 15 min, cooled and centrifuged at 4000 rpm for 10
273 min. The precipitate was washed with hot ultrapure water, centrifuged and
274 dissolved in 5 to 10 ml of 6N HCl. After evaporation, the residue was dissolved with
275 2 N HCl to separate and purify the Ra fraction according to the protocol detailed
276 above for rocks. All blank procedures ranged between 7 and 41 pg for U, 0.7 and 162
277 pg for Th, <0.04 fg for Ra and < 1 ng for Sr, which are negligible compared to the Sr
278 and U-Th-Ra amounts analyzed in the samples.

279

280 **3.3. Soil solutions, rainwaters and throughfalls**

281 Water samples, i.e., soil solutions, rainwater and throughfalls, were filtered through
282 a 0.45 μ m cellulose acetate membrane filters in the laboratory a few hours after
283 sampling. Each water sample was subdivided into two aliquots: one acidified with
284 bidistilled 13.5 N HNO_3 to $\text{pH} \approx 1$ for trace element and isotopic analyses; another
285 one, not acidified, for measurement of pH, conductivity, and for analysis of major
286 element and dissolved organic carbon (DOC) concentrations following the standard
287 procedures used in the laboratory (e.g., Lucas et al., 2010; Schaffhauser et al., 2014;
288 Gangloff et al., 2014) and detailed in Prunier et al. (2015). Trace element
289 concentrations were determined by ICP-MS with an uncertainty better than 10%.
290 The precision and accuracy of the results were checked by regular analyses of the
291 SLRS-4 riverine standard. For Sr isotopic analyses and U-Th-Ra disequilibria
292 determination, between 10 and 2000 ml of water samples were used to reach 5 to
293 20 ng of U, 300 to 400 ng of Th, 100 ng of Sr and 2 to 40 fg of Ra, which are
294 necessary for precise isotope determinations. Samples poor in U and Th were
295 preconcentrated by coprecipitation with Fe hydroxide (Chabaux et al., 1995; 1997)
296 or by total evaporation if the DOC concentration was too high. Blanks ranged

297 between 12 and 55 pg for U, 150 pg for Th, < 0.07 fg for Ra and < 1 ng for Sr. These
298 quantities are negligible compared to those in the samples.

299

300 **4. RESULTS**

301 Major and trace element concentrations and the U and Sr isotope ratios were
302 presented and discussed in Prunier et al. (2015). Therefore, the present work
303 focuses on the U-Th-Ra isotope data, which, combined with Sr isotope ratios and
304 major and trace element concentrations, allow for emphasizing the potential of
305 using U-Th-Ra systematics in soils, soil solutions and trees to better constrain the
306 sources and pathways of element transfers involved in the biogeochemical cycles in
307 forest ecosystems. The main data used and discussed in this study are given in Table
308 1a-d. The complete dataset of the major and trace element concentrations, including
309 REE concentrations, is provided in Supplementary Material Tables EA1-2-3.

310

311 **4.1. Mineralogy**

312 In line with previous works on the soils in the Strengbach catchment (Ficher et al.,
313 1998a, 1998b; Aubert et al., 2001; Stille et al., 2009), Prunier et al. (2015) showed
314 that the main minerals of bulk soil samples are quartz, feldspars (orthoclase and
315 albite), muscovite and clay minerals. Biotite and traces of apatite were observed in
316 both soil profiles, while hematite (< a few %) was detected by XRD in only the
317 spruce soil profile. The 2 µm grain size fractions of the samples from the spruce and
318 beech profiles were composed of kaolinite and illite, with interstratified illite-
319 vermiculite and/or illite-smectite and traces of goethite, which were more abundant
320 in the spruce samples than in the beech samples. The minor minerals detected by
321 SEM were zircons, monazites and apatites.

322 The new SEM observations of the grain size fractions in the present study
323 emphasized that some zircons have blunted or fractured surfaces, which could be
324 evidence of weak surface weathering of zircons (Fig. EA1a). In addition, some Ba
325 and Sr sulfates were observed in the 2-50 µm and 50-100 µm fractions of the VP 90-
326 100 horizon (Fig. EA1b). SEM observations have also shown that the “so-called” <2
327 µm fraction of the HP90-100 horizon, used in Prunier et al. (2015), clearly
328 encompasses much larger particles than expected, most likely due to separation
329 problems. This fraction was therefore not considered in the present study.

330

331 **4-2: U and Th concentrations in grain size fractions**

332 As recognized by Prunier et al. (2015), the comparison of U concentrations with
333 major and trace elements in the different grain size fractions showed that the U
334 budget in these soils is strongly controlled by secondary minerals and minor
335 primary minerals such as phosphates. A more thorough comparison of the
336 variations in U and Th concentrations with major and trace element concentrations
337 in the different soil samples and grain size fractions allows for a better constraint of
338 the nature of the minor mineral phases controlling the U and Th budget in these
339 soils and their varied influences in the two plots and the different fractions. The
340 covariations between the U-Th concentrations and Zr concentrations (Fig. 2)
341 confirm that the U and Th budgets in the 2-50 μm and 50-100 μm grain size
342 fractions are at least partly controlled by zircons. In the beech (HP) plot samples, the
343 correlations between U, Th and Fe_2O_3 and P_2O_5 concentrations for the coarse grain
344 size fractions (Fig. 2) indicate that U and Th in the HP soils are also tightly
345 associated with phosphate and Fe-bearing phases. However, in the spruce (VP) plot
346 samples, U and Th concentrations were better correlated with Zr than with P
347 concentrations, suggesting that zircon is likely one of the main carriers of U and Th
348 in spruce plots but not in beech plots. The comparison of the Ba concentration with
349 the U and Th concentrations in the grain size fractions extracted from the different
350 soil horizons (Fig. EA2) indicates that some Ba-rich mineral phases also control the
351 U and Th budgets in the spruce soil horizons, especially in the 2-50 μm and 50-100
352 μm grain size fractions, while this control is much less present in the beech soil
353 horizons. Sulfate minerals, observed by SEM, and Ba-rich K-feldspars also observed
354 in Strengbach granitic rocks are among the possible Ba-carrying minerals, as well as
355 Mn oxyhydroxides (Palumbo et al., 2001, Vaniman et al., 2002, Ghaleb et al., 2004).
356 The VP spruce soil horizons had higher Ba levels than the HP soil horizons, implying
357 that the abundance of these Ba-rich minerals was low in the HP sites. This difference
358 can be related to the weak hydrothermal overprint of the bedrock from the southern
359 slope where the beech plot stands, which is thus likely less marked by hydrothermal
360 mineralizations that contain barites and oxyhydroxide minerals.

361 Together, these data emphasize the importance of secondary minerals as well as
362 minor primary minerals (zircons, sulfates and phosphates minerals) in the U and Th
363 budget in the soil of the two experimental plots in the Strengbach catchment.

364

365 **4.3. Th isotopic ratios and U-Th-Ra disequilibrium in grain size fractions**

366 The present data show important variations between the ($^{230}\text{Th}/^{232}\text{Th}$) ratios and
367 U/Th chemical ratios in the different grain size fractions and between the different
368 plots (Table 1a) with systematically lower values in the spruce (VP) than in the
369 beech (HP) plots. The <2 μm fraction of the HP (30-40 cm) soil horizon shows the
370 highest ($^{230}\text{Th}/^{232}\text{Th}$) ratio [$(^{230}\text{Th}/^{232}\text{Th}) = 4$] of all the grain size fractions analyzed
371 in this study, with a value close to that of apatite (≈ 5 from U/Th ratios given in
372 Aubert et al., 2004; 2001) (Fig. 3). The 2-50 μm and 50-100 μm grain size fractions
373 from the spruce site exhibit the lowest ($^{230}\text{Th}/^{232}\text{Th}$) ratio (0.71-0.75). The
374 correlation between ($^{230}\text{Th}/^{232}\text{Th}$) and ($^{238}\text{U}/^{232}\text{Th}$) ratios and Zr concentrations
375 observed for the VP grain size fractions (Fig. 4), as well as with Ba concentrations
376 (Fig. 5), highlights the low U/Th and Th activity ratios of the zircons and the Ba-
377 bearing minerals, which are much lower than the Th activity ratios of the other
378 primary granite minerals (apatite, biotite, muscovite and albite) as estimated from
379 the U/Th ratio given in Aubert et al. (2001; 2004). For the HP plot, all the grain size
380 fractions, except the two 1.6-2 mm fractions, show a very good covariation between
381 ($^{230}\text{Th}/^{232}\text{Th}$) and P_2O_5 contents ($R=0.972$) (Fig. 6).

382 The ^{238}U - ^{234}U - ^{230}Th - ^{226}Ra data (Tab. 1a) show that all grain size fractions are
383 marked by systematic ^{238}U - ^{230}Th disequilibrium with ($^{238}\text{U}/^{230}\text{Th}$) <1. The
384 comparison of the ^{238}U - ^{234}U - ^{230}Th - ^{226}Ra disequilibria in the different grain size
385 fractions indicates the higher ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{234}\text{U}$) ratios in the beech plot
386 grain size fractions than in the spruce plot as well as the higher ratios for a given
387 plot in the < 2 μm fractions than in the other fractions (Fig. 7a,b). This systematic
388 disequilibrium is, however, not observed for the ^{226}Ra - ^{230}Th disequilibria. With the
389 exception of the two <2 μm fractions from the VP plot, which are marked by
390 relatively high ($^{226}\text{Ra}/^{230}\text{Th}$) ratios (1.42, 1.6), all other grain size fractions show
391 rather similar ($^{226}\text{Ra}/^{230}\text{Th}$) ratios scattering between 0.88 and 1.13 (Fig. 7b) that
392 are unrelated to the size of the fractions or the depth of the analyzed horizons. At
393 the scale of the spruce plot, however, the ($^{226}\text{Ra}/^{230}\text{Th}$) and ($^{230}\text{Th}/^{234}\text{U}$) ratios

394 decrease in the following order: <2 μm fraction, 2-50 μm fraction and other
395 fractions. For the beech plots, such a systematic disequilibrium is not apparent for
396 the ($^{226}\text{Ra}/^{230}\text{Th}$) ratio, but it is still observed for the ($^{230}\text{Th}/^{234}\text{U}$) ratio.

397

398 **4.4. U-Th-Ra and Ba in soil solutions**

399 As for the grain size fractions, and as already noted in Prunier et al. (2015), the soil
400 solution data point to significant geochemical differences between the soil solutions
401 collected at the two experimental plots in both major and trace element
402 concentrations. The soil solutions from the VP spruce plot have higher TDS and
403 conductivities and lower pH values than those from the HP beech plot. The soil
404 solutions from the VP spruce plot are also 5 to 10 times richer in Mg, K and Ca than
405 those from the HP plot (data in supplementary materials Tab EA3). Our data show
406 that such differences are also seen in the U-Th-Ra systematics and that Ba has a
407 distinct compartment compared to Sr and Ca elements.

408

409 - Alkaline-earth elements

410 The trace element concentrations of the soil solutions show higher alkaline-earth
411 (Sr, Ba) concentrations under spruces than under beeches (Fig. EA3). Within a plot,
412 the Ca and Sr concentrations are higher in the surface soil solutions than in the deep
413 layers, which is certainly related to root absorption of these elements by the trees,
414 as evidenced by Ca isotopes (Cenki-Tock et al., 2009; Schmitt et al., 2017).
415 Compared to Sr and Ca, Ba shows different behavior in the spruce plot (Fig. EA3),
416 where the highest Ba concentrations are observed for soil solutions from 30 cm
417 depth, with a negative correlation with the sulfate contents (Fig. EA3). A negative
418 correlation is also observed for the -60 cm soil solution data but with a different
419 slope (Fig. EA3). The observation that positive, linear correlations passing through
420 the origin can be defined between the Ba and $1/\text{SO}_4$ concentrations for these two
421 soil solutions (Fig. EA3) likely indicates BaSO_4 saturation, meaning that the Ba and
422 SO_4 concentrations at depths of 30 cm and 60 cm are controlled by the precipitation
423 of BaSO_4 . The SEM observation of Ba sulfate precipitates in soil solutions collected at
424 depths of 30 cm and 60 cm supports this interpretation (Fig. EA1c). The atypical Ba
425 concentrations of the 30 cm soil solutions are clearly evidenced in a Ba vs Mg
426 concentration diagram, which indicates a specific source of Ba at this depth, but not

427 at 60 cm. The positive trend between the K and Ba concentrations in 30 cm soil
428 solutions likely suggests that the Ba input in these soil solutions results from the
429 dissolution of Ba-rich K-feldspars, at a sufficiently high level to cause a BaSO₄
430 precipitation. For the 60 cm soil solutions, the correlation between Mn and Ba (Fig.
431 EA3) suggests the dissolution of other minerals, such as Mn oxides and likely
432 sulfates, which are often associated with Mn oxides in hydrothermal veins
433 intersecting granitic rocks. The dissolution of sulfate minerals can thus control the
434 BaSO₄ saturation of the 60 cm soil solutions. Such a dissolution at 60cm depth and
435 not a 30cm depth can also account for the observation of a correlation between the
436 Sr and 1/SO₄²⁻ concentrations in only the 60 cm depth soil solutions (Fig. EA₃),
437 suggesting that the supply of sulfate is sufficient to also cause the saturation of
438 SrSO₄ in these waters or also of (SrBa)SO₄. Furthermore, dissolution of SO₄²⁻ bearing
439 mineral phases at 60 cm depth readily explains why the soil solutions from 60 cm
440 depth at the spruce plot are the only water reservoir in the Strengbach catchment
441 whose SO₄²⁻ concentrations did not decrease from 1990-2010 (Fig. EA₄ and Ackerer
442 et al., 2018).

443

444 - Th activity ratios and U-Th-Ra systematics

445 The (²³⁰Th/²³²Th) ratios of the (HP) beech plot soil solutions are significantly higher
446 than those of the (VP) spruce plot and those of most of the corresponding grain size
447 fractions (Fig. 3). Only the <2 μm grain size fraction of the HP (30-40 cm) soil layer
448 and apatite had higher (²³⁰Th/²³²Th) ratios. Compared to the grain size fractions and
449 the granite-derived primary minerals, the soil solutions of the beech plot exhibit
450 relatively high Th isotope ratios, namely, (²³⁰Th/²³²Th) of 4 and 3.7 for the HP-10 cm
451 and HP-70 cm soil solutions, respectively. These ratios are close to the (²³⁰Th/²³²Th)
452 of the <2 μm fraction but with different U/Th ratios depending on their depth of
453 collection. In the (²³⁰Th/²³²Th) vs. (²³⁸U/²³²Th) diagram (the so-called isochron
454 diagram), the surface solution (-10 cm) plot is relatively close to the <2 μm grain
455 size fraction, while the deep solution plot is much closer to the equiline (1:1 line in
456 the isochron diagram) (Fig. 3). In the spruce plot, the Th activity ratios were
457 analyzed in the soil solutions from the depths of only -5 cm and -10 cm due to the
458 very low Th concentrations in the deeper soil solutions. As apparent in Fig. 3, these
459 soil solutions have very similar (²³⁰Th/²³²Th) (1.6) but relatively scattered

460 ($^{238}\text{U}/^{232}\text{Th}$) ratios (0.7-1.04). The Th activity ratios in these solutions are higher
461 than those analyzed in the corresponding grain size fractions.

462 Based on the available ($^{226}\text{Ra}/^{230}\text{Th}$) ratios in both the beech and spruce plots, the
463 soil solutions have higher ($^{226}\text{Ra}/^{230}\text{Th}$) ratios than the corresponding soil fractions
464 (Table 1a-b). Furthermore, in the ($^{226}\text{Ra}/^{238}\text{U}$) vs ($^{234}\text{U}/^{238}\text{U}$) diagram (Fig. 8a), the
465 (VP) spruce plot soil solutions from depths of 10 cm, 30 cm and 60 cm define a
466 positive correlation with the lowest ($^{226}\text{Ra}/^{238}\text{U}$) ratios in the 30 cm soil solutions.
467 Moreover, the <2 μm and 2-50 μm grain size fractions from the VP 30-40 cm soil
468 horizon are aligned together with the soil solution collected from a depth of 30 cm
469 (Fig. 8b).

470

471 **4.5. Geochemical and isotopic characteristics of the vegetation samples.**

472 The geochemical and isotopic data of the vegetation samples are given in Table 1c.
473 These data show concentration variations, which vary from one tree to another and
474 within a tree between its different compartments. Uranium and Th concentrations
475 are higher in the roots than in the aerial parts of trees, which is not the case for Ba
476 and ^{226}Ra . This may indicate a possible fixation of U and Th on roots without real
477 transport within the aerial parts of trees at the difference of Ba and Ra. Compared to
478 soil solutions, soil samples and grain size fractions, trees are enriched in Ca, Sr, Rb
479 and K, as well as in Ba (Table 1). The data also point to high variability in the relative
480 concentrations of these elements between the different parts of the trees, even for
481 the elements from the same chemical family, such as the alkaline-earth Ca, Sr, Ba.
482 The Ca/Sr and Ba/Sr ratios vary by a factor of 5 or more in the beech trees and by a
483 factor of 10 in spruce. Compared to U and Th, Ra is also highly enriched in the trees,
484 with ($^{226}\text{Ra}/^{230}\text{Th}$) ratios as high as 5 and ($^{226}\text{Ra}/^{238}\text{U}$) ratios ranging from 1.12 up
485 to 79 in spruce. In beech, ($^{226}\text{Ra}/^{238}\text{U}$) ratios range from 21.5 to 1413, and
486 ($^{226}\text{Ra}/^{230}\text{Th}$) ratios range from 19.8 to 164.4.

487 The vegetation samples show $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios similar to those of the
488 corresponding soil solutions (Fig. 9). As noted in Prunier et al. (2015), the
489 ($^{234}\text{U}/^{238}\text{U}$) ratios of the beech samples are similar to those of the corresponding soil
490 solutions and soil samples, while they are systematically higher in the vegetation
491 samples from the spruce plot, with ($^{234}\text{U}/^{238}\text{U}$) ratios ≥ 1 in spruce samples for
492 ($^{234}\text{U}/^{238}\text{U}$) ratios ≤ 1 in the soil solution samples (Fig. 10, and Prunier et al., 2015).

493 The beech and spruce samples have ($^{238}\text{U}/^{230}\text{Th}$) ratios close to equilibrium
494 [$(^{230}\text{Th}/^{238}\text{U})\approx 1$] and hence plot along the equiline in the isochron diagram, with
495 ($^{230}\text{Th}/^{232}\text{Th}$) ratios ranging between 1 and 1.4 for beech and close to 1 for spruce,
496 which is very different from those of the corresponding soil solutions (Fig. 3).

497

498 **5. DISCUSSION**

499

500 ***5-1 U-Th-Ra fractionation by vegetation***

501 The comparison of the vegetation chemical data with the soil and soil solution data
502 points to an important enrichment of Ba and ^{226}Ra relative to U and Th in trees,
503 which suggests that trees can have a much greater impact on the Ra (Ba) budget
504 than the U and Th budgets in forest ecosystems. This impact is made clear when the
505 uptake of U, Th, Ba, Ra by tree roots and their respective recycling through litter
506 degradation are compared with their drainage by soil solutions (Tab. 2a,b). The
507 uptake fluxes can be estimated using the Ca uptake fluxes given in Poszwa et al.
508 (2000) for the Strengbach beeches and spruces and the U/Ca, Th/Ca, Ba/Ca and
509 $^{226}\text{Ra}/\text{Ca}$ ratios measured in the present study in the different tree organs (Tab.2a).
510 These chemical ratios can vary within a tree, such as Ca/Sr ratios (e.g., Poszwa et al.
511 2000; 2003; Wiegand et al., 2005; Blum et al., 2008; Drouet et Herbauts 2008),
512 leading to a relatively large uncertainty in the calculated uptake fluxes. However, the
513 data clearly indicate that the U and Th uptake fluxes are low compared to the
514 drainage by soil solutions (Tab. 2b), while they are comparable for Ba and Ra.
515 Similarly, the comparison of the maximum calculated U and Th fluxes coming from
516 litter degradation with those drained by the soil solutions demonstrates the very
517 low contribution of litter degradation on the U and Th budgets of soil solutions,
518 which is not the case for Ba and Ra (Tab. 2b). These results demonstrate that Ra and
519 Ba are highly cycled by vegetation, which is the opposite for U and Th, and that root
520 uptake and litter degradation can be important actors in Ra-Th and Ra-U
521 fractionation in soils and soil solutions (see also Rihs et al., 2011). This result is
522 clearly illustrated by the U-Th-Ra disequilibria variations in the soil solutions of the
523 beech plot at 10 cm depth (Fig. 11). The distribution of the data points in the
524 ($^{230}\text{Th}/^{234}\text{U}$) vs ($^{226}\text{Ra}/^{230}\text{Th}$) diagram indicates a more important Ra contribution
525 from litter decay to the soil solution in March 2005 than in May 2006, which mainly

526 impacts the ($^{226}\text{Ra}/^{230}\text{Th}$) ratios of the soil solutions and has much less of an impact
527 on the ($^{230}\text{Th}/^{234}\text{U}$) ratios. The data also show that this type of vegetation impact is
528 visible at 10 cm depth but is not visible at 70 cm depth, which indicates that tree-
529 related fractionation is confined to superficial soil and soil solutions. The ^{238}U -Ba-
530 ^{226}Ra data of soil solutions under spruces supports this conclusion. For the spruce
531 plot, the soil solution data collected at 10, 30 and 60 cm and the data from the $<2\ \mu\text{m}$
532 and $2\text{-}50\ \mu\text{m}$ grain size fractions of the 30-40 cm soil horizon define two linear
533 trends that converge towards the values of the 30 cm soil solutions in the
534 ($^{238}\text{U}/^{226}\text{Ra}$) vs ($^{234}\text{U}/^{238}\text{U}$) diagram (Fig. 7a). The latter soil solutions have the
535 lowest ($^{234}\text{U}/^{238}\text{U}$) and ($^{226}\text{Ra}/^{238}\text{U}$) ratios measured at the site (<1), which cannot
536 be explained by the contributions of U and Ra fluxes from vegetation recycling, as all
537 vegetation samples are marked by ($^{226}\text{Ra}/^{238}\text{U}$) $\gg 1$. Based on the ^{238}U - ^{234}U - ^{226}Ra -Ba
538 systematics, it is also difficult to invoke a variable vegetation contribution from one
539 soil solution sample to another to explain the ($^{226}\text{Ra}/^{238}\text{U}$) and ($^{234}\text{U}/^{238}\text{U}$)
540 differences among the soil solutions from depths of 30 cm and 60 cm. If this would
541 have been the case, a correlation between the Ba/U and ($^{226}\text{Ra}/^{238}\text{U}$) ratios of these
542 soil solutions should have been observed, which is not the case (Fig. 7b). Thus, the
543 geochemical end-member with ($^{234}\text{U}/^{238}\text{U}$) and ($^{226}\text{Ra}/^{238}\text{U}$) ratios <1 likely
544 represents a weathering end-member resulting from the destabilization of
545 secondary minerals contained in the finest grain size fractions of the 30-40 cm soil
546 horizon. The covariations observed in the ($^{226}\text{Ra}/^{238}\text{U}$) vs ($^{234}\text{U}/^{238}\text{U}$) and
547 ($^{226}\text{Ra}/^{238}\text{U}$) vs Ba/U diagrams between the 30 and 60 cm soil solutions (Fig. 7a, b)
548 likely reflect the control by different mineral fractions in each of these soil solutions.
549 For the 30 cm soil solution, a high contribution of a mineral fraction with high Ba/U
550 ratios but depleted in ^{234}U and ^{226}Ra relative to ^{238}U was observed. This mineral
551 fraction likely explains the low ($^{234}\text{U}/^{238}\text{U}$) and ($^{226}\text{Ra}/^{238}\text{U}$) ratios of the $2\text{-}50\ \mu\text{m}$
552 fractions of the 30-40 cm soil horizon. The $2\text{-}50\ \mu\text{m}$ fractions of the 30-40 cm soil
553 horizon are the most Ba enriched. Thus, mobilization of weathering products of Ba-
554 rich phases, such as Ba-rich K-feldspar evidenced in § 4-4, likely controls the U-Ba-
555 Ra characteristics of the 30 cm deep soil solutions. For the 60 cm deep soil solutions,
556 other minerals or less contribution of these Ba-rich minerals must be invoked to
557 explain their U-Ra-Ba characteristics, which is consistent with the proposition for

558 these soil solutions of a specific weathering flux from oxides and sulfate minerals
559 (see section 4-4).

560

561 However, regardless of the precise origin of weathering fluxes explaining the U, Ba,
562 Ra systematics within the deep soil solutions of the spruce plots, the results clearly
563 show that the impact of vegetation on U-(Th)-Ba and -Ra fractionations is visible
564 mainly in the surface soil horizons and soil solutions and much less in the deeper
565 ones. This conclusion is consistent with the demonstration that the ($^{226}\text{Ra}/^{230}\text{Th}$)
566 ratios in the shallowest soil layers can be affected by vegetation changes/types over
567 short timescales (Rihs et al., 2016). Moreover, this conclusion supports the
568 assumption of Ackerer et al. (2016) and the suggestions of Gontier et al. (2015) and
569 Rihs et al. (2016) that the deeper part of the weathering profiles below the zone of
570 vegetation influence is certainly the most adapted zone to apply the U-series
571 nuclides methodology classically developed for recovering regolith production rates
572 (e.g., Dequincey et al., 2002; Dosseto et al., 2008; Chabaux et al., 2013). The highly
573 contrasted behaviors of Ra and U-Th regarding vegetation cycling also has
574 implications for the interest in these elements and their isotopic ratios for tracing
575 biogeochemical cycles and water-rock interactions in forest ecosystems. Thus, being
576 highly absorbed by trees, Ra and its isotopic ratio ($^{228}\text{Ra}/^{226}\text{Ra}$) should become a
577 useful tracer of the impacts of vegetation on the geochemical cycles in the
578 biosphere. Moreover, the very different half-lives of ^{228}Ra (5.75 a) and ^{226}Ra (1600
579 a) should make Ra also a potential chronometer of the litter degradation rate, in
580 addition to being relevant for constraining the chemical element residence time in
581 the vegetation (e.g., Baeza et al., 1999). The second important implication of the
582 results is linked to the small impact of vegetation cycling on the U and Th budgets in
583 soils and soil solutions. These elements are therefore mostly controlled by water-
584 rock interactions. This finding is certainly the main difference between these
585 isotopic ratios and $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{143}\text{Nd}/^{144}\text{Nd}$, as Sr and Nd are two significantly
586 biocycled chemical elements (e.g., Stille et al., 2006; 2009). The Sr and Nd isotopic
587 ratios in soils and soil solutions thus represent an integration of lithogenic fluxes
588 directly derived from water-rock interactions with recycled and hence “delayed”
589 fluxes due to Sr and Nd vegetation cycling. Uranium and thorium are probably
590 among the few geochemical elements to be controlled by only direct water-rock

591 interactions and therefore to be specific tracers of these interactions. The
592 combination of this property with (a) the large range of the variations in the
593 ($^{230}\text{Th}/^{232}\text{Th}$) ratios in the soil minerals, especially in secondary and minor minerals
594 (this study; Bosia et al., 2016; 2018) and (b) the low contributions of rainwater and
595 atmospheric deposits on U and Th soil and soil solution budgets on granitic lithology
596 (e.g., Chabaux et al., 2005; 2013) indicates that the Th activity ratio has the potential
597 to become a powerful tracer of the sources of the chemical fluxes in the soils, soil
598 solutions and vegetation. Such an interest is illustrated in the following two sections.
599

600 **5-2 U-Th tracing weathering fluxes in soil solutions**

601 Previous studies have shown that Sr and Nd isotopes in soil solutions and streamlets
602 in the Strengbach watershed principally result from apatite and feldspar dissolution
603 (Aubert et al., 2001, Stille et al., 2006, 2009). The proximity of the soil solution HP-
604 70 (beech plot) to the ($^{230}\text{Th}/^{232}\text{Th}$ - $^{238}\text{U}/^{232}\text{Th}$) equiline between the apatite and the
605 feldspars data points (Fig. 3) is consistent with this interpretation. The soil solution
606 HP-10, however, clearly suggests a contribution of a third flux in addition to the two
607 previous fluxes with a U-Th signature close to that of the $<2\ \mu\text{m}$ grain size fraction,
608 which is also true when looking at the data in the ($^{230}\text{Th}/^{232}\text{Th}$) vs $^{87}\text{Sr}/^{86}\text{Sr}$ diagram
609 (Fig. 12).

610 The covariation between ($^{230}\text{Th}/^{232}\text{Th}$) and P_2O_5 contents in the grain size fractions
611 of the beech plot samples (Fig. 6) implies that Th isotopes are essentially controlled
612 by the presence of phosphate minerals with high Th activity ratios. Therefore, the
613 high Th activity ratios of the $<2\ \mu\text{m}$ fraction are imposed by phosphate minerals,
614 which in turn are those that controlled the U-Th-Sr weathering fluxes from the <2
615 μm fractions. As in the grain size fractions of the beech plot, the P_2O_5 contents do
616 not correlate with the corresponding Ca contents (not shown), it is not apatite but
617 probably other phosphate-rich, apatite replacement phases that control the
618 covariation between P_2O_5 contents and the ($^{230}\text{Th}/^{232}\text{Th}$) ratios in such a system.
619 Furthermore, as the ($^{238}\text{U}/^{232}\text{Th}$) ratio of the $<2\ \mu\text{m}$ grain size fraction from the HP
620 plot (<1.48) is significantly lower than that of apatite (5.07) and has relatively low
621 Sr concentrations relative to Fe, the formation of such secondary minerals from the
622 dissolution of apatite during weathering caused mobilization of not only Ca (Stille et
623 al., 2009) but also apparently apatite-derived-U and Sr (Fig. EA2). Such a difference

624 in the mobilization of U-Th-Sr during the weathering of apatite and formation of
625 secondary phosphate phases readily explains why the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.85) of the
626 $<2\ \mu\text{m}$ grain size fraction from the HP plot (30-40 cm) is significantly higher than
627 that of primary apatite (0.716), while the $(^{230}\text{Th}/^{232}\text{Th})$ ratio of this fraction (4.085)
628 remains close to that of apatite (5).

629 Altogether, these data indicate that in the beech plot, the dissolution of secondary
630 phosphates in the $<2\ \mu\text{m}$ fraction controls an important part of the U-Th-Sr chemical
631 budget of the surface soil solutions. These secondary minerals and their U-Th-Sr
632 isotopic signatures must therefore be inherited from a weathering process anterior
633 to the process controlling the present-day U-Th-Sr isotopic signature of the surface
634 soil solutions. Based on these data, a two-step weathering scenario can thus be
635 proposed for the beech plot: (a) predominant dissolution of primary minerals in the
636 deep soil horizons and the formation of secondary minerals partially maintain the
637 isotopic signature of the weathered primary minerals; (b) dissolution of these
638 secondary minerals, in particular those contained in the finest grain size fractions, in
639 the surface soil horizons. Schmitt et al. (2017) showed that the Sr isotope ratios of
640 the soil solutions increased from 2006 to 2011 in the beech plot at 10 cm depth but
641 not at 70 cm depth, which indicates that the contribution of the secondary minerals
642 to the chemical budget of the surface soil solution increased over this period and
643 hence could be a relatively recent process. This result is consistent with the results
644 of Rihs et al. (2011), who concluded based on short half-lived radionuclides of the
645 ^{232}Th -series that the surface soils under the beech plot have been affected by recent
646 ($<30\text{a}$) weathering processes.

647 For the spruce (VP) plot, the scattering of the 5 cm and 10 cm deep soil solution data
648 in the isochron diagram (Fig. 3), i.e., similar $(^{230}\text{Th}/^{232}\text{Th})$ ratios but variable
649 $(^{238}\text{U}/^{232}\text{Th})$ ratios, cannot be explained by the varying tree contributions to the U-
650 Th budget of the different soil solutions, as tree samples are marked by
651 $(^{230}\text{Th}/^{232}\text{Th})$ ratios lower than those measured in the surface soil solutions. For this
652 reason, and in line with the low contribution of tree cycling to the U and Th budget,
653 it is proposed that the U-Th budget of the spruce surface soil solutions (VP plot) is
654 controlled, as occurs in the beech plot, by a mixture of U-Th coming from the
655 dissolution of secondary minerals with $(^{230}\text{Th}/^{238}\text{U}) < 1$ and high $(^{230}\text{Th}/^{232}\text{Th})$ ratios
656 and more “equilibrated” U-Th coming from the dissolution of primary minerals.

657 However, unlike the beech plot, none of the analyzed grain size fractions in the
658 spruce plot show U-Th signatures similar to that of the surface soil solutions. In
659 particular, all of the grain size fractions have much lower ($^{230}\text{Th}/^{232}\text{Th}$) ratios than
660 those in the solutions, which can be explained in two ways. First, the U-Th signature
661 of the 30-40 cm grain size fractions are not representative of the 10 and 5 cm deep
662 fractions because of the local lithological heterogeneities (cf section 4-4). Second,
663 the weathering processes in the spruce plot were initially similar to those in the HP
664 plot, but this plot is now in a much more advanced weathering stage. Thus, it can
665 now be proposed that a large part of the minerals carrying the apatite signature has
666 been leached much more intensively under spruce than under beech, causing an
667 important loss of these minerals and hence a significant decrease in the
668 ($^{230}\text{Th}/^{232}\text{Th}$) ratios of the grain size fractions. This scenario, which is favored by the
669 more acidic conditions under the spruce plot, is also supported by the observation
670 of an earlier increase in the Sr isotopic ratios in the soil solutions of the VP spruce
671 plot than that in the HP beech plot: between 1997 and 2006 for the spruce plot
672 (Prunier et al., 2015) and between 2006 and 2011 for the beech plot (Schmitt et al.,
673 2017) (Fig. 9).

674 Thus, based on these results, the weathering scenario retained for the spruce plot
675 (VP) is similar to that invoked for the beech plot (HP) but with a slightly different
676 mineralogical composition and a much more advanced degree of alteration of the
677 fine grain size fractions of the VP surface soil horizons. This scenario, which is also
678 consistent with the B isotope data in the Strengbach catchment (Lemarchand et al.
679 2012), not only accounts for the earlier modification of the Sr isotope ratios in the
680 soil solutions of the spruce plot but also explains why the $<2\ \mu\text{m}$ and $2\text{-}50\ \mu\text{m}$
681 fractions are more depleted in Sr, Ca, U, Th and REE (Fig. EA2) for equivalent Fe
682 contents in the spruce (VP) than in the beech (HP) plot. This scenario is also
683 consistent with the weathering indexes calculated in Prunier (2008) following the
684 approaches proposed in Kronberg and Nesbeitt (1981). Such a difference between
685 the degree and timing of the destabilization of the beech and spruce plots is likely
686 the consequence of a larger chemical export by soil solutions under the spruce than
687 the beech plot. Climatic differences exist between the two slopes (e.g., Viville et al.,
688 1993; 2012), with longer and more intense sunshine duration on the VP south-
689 facing slope, which may explain part of this difference. But, this difference is also

690 certainly related to the difference in the pH of the soil solutions under these two
691 plots, which is clearly linked to the differences in vegetation cover. The more acidic
692 soil solutions under spruces allowed for stronger leaching of the soils in the spruce
693 (VP) plot than allowed by the less acidic soils in the beech (HP) plot. The fast-
694 growing spruces found in the VP plot were planted for forest exploitation. These
695 trees generally induce both a strong acidification of soils and soil solutions via the
696 decomposition of the needles and a high nutrient export flux that is much greater
697 than that induced by trees naturally growing on the site (fir - beech) (e.g., Binkley
698 and Valentine, 1991; Alriksson and Eriksson, 1998; Augusto et al., 2015; Berger et
699 al., 2009; Cremer and Prietzel, 2017). The cause of soil depletion and irreversible
700 modification of the tree nutrient carrier phases by vegetation have not been
701 sufficiently considered until now. The vegetation could play an important role and
702 may be equivalent or even more important than the effects of acid rain. For the
703 Strengbach catchment, we propose that the artificial change in vegetation explains
704 much of the differences in soil destabilization states between the beech and spruce
705 plots.

706

707 **5-3 U-Th, tracing the source of elements in the water-tree system.**

708 The Sr-U-Th isotopic characteristics of soil solutions and trees are different. Soil
709 solutions have Sr isotopic ratios that are relatively close to those of trees, which is
710 consistent with the biorecycled behavior of Sr. Nevertheless, Sr isotopic ratios in
711 trees are systematically slightly less radiogenic than those in soil solutions (Fig. 9).
712 The difference between soil solutions and trees is more marked in the spruce plot
713 than in the beech plot and increases with time (Fig. 9). As discussed in the previous
714 section (§ 5.2), this difference might be related to the higher or lower degree of
715 modifications of the water-rock-vegetation system in these two plots, as the
716 alteration processes have been more intensively modified in the spruce (VP) plot
717 than in the beech (HP) plot. This difference may also point to the occurrence of Sr
718 fluxes in soil solutions, which are different from those taken up by the tree and,
719 therefore, different from those recycled by vegetation. The observations that the U
720 activity ratios are higher in trees than in soil solutions in the spruce (VP) plot and
721 that the Th ratios are systematically different between trees and soil solutions in
722 both plots support such an interpretation (Fig. 13). The beech plot soil solutions are

723 entirely consistent with the three-end-member mixing model proposed in the
724 previous sections, between (1) the $<2 \mu\text{m}$ grain size fractions marked by a high
725 $(^{230}\text{Th}/^{232}\text{Th})$ ratio and a strong ^{234}U - ^{238}U disequilibrium, (2) an apatite end-
726 member with a high Th activity ratio and ^{238}U - ^{234}U equilibrium and (3) a third end-
727 member marked by a low $(^{230}\text{Th}/^{232}\text{Th})$ ratio and a $(^{234}\text{U}/^{238}\text{U})$ ratio close to
728 equilibrium. However, the very contrasted values of soil solutions and tree samples
729 indicate that beech trees absorb U and Th and probably also other nutrients not
730 directly from the gravitational soil solutions collected in this study but from other
731 reservoirs marked by different chemical and isotopic compositions, i.e. water-
732 reservoir - like bounded waters, or possibly also directly from solids, as trees can
733 uptake nutrients from solids without going through soil solutions (in Morgan and
734 Connolly, 2013). The relatively low $(^{230}\text{Th}/^{232}\text{Th})$ ratios of trees can be derived from
735 primary minerals, most likely biotite but also possibly apatite or feldspar, to account
736 for the scattering of the Th activity ratios in the beech trees. The ^{234}U - ^{238}U
737 disequilibria in the tree samples are consistent with an uptake of U enriched in ^{234}U
738 (by alpha recoil) from primary minerals. The absence of ^{238}U - ^{230}Th fractionation
739 suggests that during nutrient uptake, U and Th are not significantly fractionated.
740 This conclusion of different U and Th sources for vegetation and soil solutions has
741 also to be proposed for the spruce plot on the basis of the $(^{230}\text{Th}/^{232}\text{Th})$ vs
742 $(^{234}\text{U}/^{238}\text{U})$ and vs $^{87}\text{Sr}/^{86}\text{Sr}$ diagrams (Fig. 13 and Fig. 12). In the $(^{230}\text{Th}/^{232}\text{Th})$ vs
743 $(^{234}\text{U}/^{238}\text{U})$ diagram, the spruce plot soil solutions confirm the suggestion (§ 5-2)
744 that the U-Th budget of spruce soil solutions is controlled by minerals with
745 $(^{234}\text{U}/^{238}\text{U}) < 1$ and low $(^{230}\text{Th}/^{232}\text{Th})$ ratios, i.e., the U-Th characteristics of Ba-rich
746 and Zr-rich minerals in the spruce soils. On the other hand, spruce data in the
747 $(^{230}\text{Th}/^{232}\text{Th})$ vs $(^{234}\text{U}/^{238}\text{U})$ diagram suggest that the U and Th sources for spruces
748 might not be very different from those for beech, confirming that these trees absorb
749 nutrients from a distinct reservoir to that controlling the U-Th budget in solutions
750 collected by zero-tension lysimetric plates. The Strengbach results thus underscore
751 an interest, certainly not anticipated so far, of the use of the U-Th systematics in the
752 critical zone to constrain the nutrient source of the plants.

753

754 **CONCLUSIONS**

755 ^{238}U - ^{234}U - ^{230}Th - ^{226}Ra nuclide data and ($^{230}\text{Th}/^{232}\text{Th}$) ratios of soil minerals, soil
756 solutions and trees from the two instrumented spruce and beech plots of the
757 Strengbach catchment, yield new constraints on the sources and transfer pathways
758 of these elements within the plant-soil-water system. It has been demonstrated that
759 these are clearly important geochemical parameters for tracing biogeochemical
760 processes in the critical zone.

761 The results highlight the highly contrasting impact of trees on U-Th and Ra (Ba)
762 budgets in forest ecosystems with Ra-Ba being highly and U-Th only slightly cycled
763 by vegetation. Thus, tree uptake and litter decay can be a cause of Th-Ra(Ba)
764 fractionations in soil solutions and soils, especially in the surface soil horizons. In
765 contrast these processes have much less impact on U-Th fractionation, which is
766 mainly controlled by water-rock interaction. Therefore, due to the strong cycling by
767 trees, Ra together with its ($^{228}\text{Ra}/^{226}\text{Ra}$) isotopic ratio might become a powerful
768 tracer and chronometer of the biogeochemical cycles in forest ecosystems and the
769 processes they involve. On the other hand, due to the small impact of vegetation on
770 the U and Th budget in soils and soil solutions, U and Th isotopes are probably
771 among the few tracers to be specific indicators of water-rock interactions in the CZ
772 markedly contrasting with classical isotope systems such as Sr or Nd, routinely used
773 in the study of the CZ and significantly affected by vegetation cycling. Therefore, the
774 characteristics of Th along with its fairly large range of activity ratios in soil
775 minerals, especially in secondary and minor mineral phases, makes it a powerful
776 and specific tracer of the sources of chemical fluxes in soils, soil solutions and
777 vegetation. The Strengbach data emphasize this point but also highlight the utility of
778 combining analysis of U, Th activity and Sr isotope ratios to constrain the source of
779 these elements in soils and soil solutions. This approach places new constraints on
780 the weathering processes affecting the Strengbach bedrocks and the nature and
781 evolution of the reservoirs involved in (nutrient) element transfer at the plant-soil-
782 water interface. It has been shown that minor mineral phases such as zircons,
783 sulfates and phosphates significantly control the U and Th chemical budget and Th
784 activity ratios of the soil samples and also the U-Th fluxes transiting in the soil
785 solutions. The comparison of the U-Th-Sr isotopic characteristics of soil solutions
786 and soil grain size fractions also allows the recognition of two stages of weathering
787 with (a) dissolution of primary minerals and formation of secondary ones in the

788 deep soil horizons and soil solutions and (b) dissolutions of both primary and
789 secondary mineral phases in the finest soil grain size fractions of the nearest surface
790 soil horizons. The latter process might be related to recent modifications of
791 weathering in the catchment which is stronger and older under the spruce
792 compared to the beech plot. We propose that the artificial change in vegetation over
793 the past decades through planting of spruces significantly contributed to the current
794 differences in soil weathering between the beech and spruce plots. Spruce
795 plantation in the Strengbach catchment increased soil acidity, which accelerated
796 weathering of some minerals and likely also increased Ca leaching and the depletion
797 of the nutrient pool in the Ca-poor soil-vegetation system of the Strengbach
798 catchment. The U-Th-Sr results of this study point to the occurrence of isotopically
799 different reservoirs of these elements for trees and gravity soil solutions collected
800 by lysimetric plates. This further suggests that, in the case of the Strengbach
801 watershed, the gravity soil solutions cannot be the main, or even an important, tree
802 nutrient reservoir, which emphasizes that the U-Th systematics in the critical zone
803 can offer useful constraints on the nutrient source of the plants.

804

805

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815

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1241

1242 **Table Captions**

1243 Table 1 a-c: Major and trace element concentrations, $^{87}\text{Sr}/^{86}\text{Sr}$ and $(^{238}\text{U}/^{234}\text{U})$
1244 isotopic ratios, and U-Th-Ra activity ratios in soil grain size fractions (1a); soil
1245 solutions, rainwaters and throughfalls (1b); and litter and tree samples (1c).

1246 Table 2a: Mean annual (2004-2006) Ba, U, Th, Ra uptake fluxes by trees for the two
1247 experimental plots of the catchment.

1248 Table 2b: Mean annual (2004-2006) Ba, U, Th, Ra fluxes brought by litter deposition
1249 and throughfall and circulating in the soil solutions for the two experimental
1250 plots of the catchment.

1251

1252 **Figure Captions:**

1253 Figure 1: Left side: geological map of the Strengbach catchment (from El Gh'Mari,
1254 1995) showing the locations of the spruce (VP) and beech (HP) plots and the
1255 precipitation sampling sites (PPT). Right side: schematic presentation of the
1256 beech and spruce soil profiles, with the locations of the soil horizons analyzed
1257 in this study and the position of the lysimeter plates used to collect the soil
1258 solution samples. The surface lysimeter plates allow for sampling soil
1259 solutions in zones of high root density (0-30cm) and the deepest lysimeter
1260 plates the soil solution below the root zone as in both plots nearly all the fine
1261 root biomass resides in the organic layer and upper 0–70 cm of mineral soil.
1262 Descriptions of the beech (HP) and spruce (VP) soil profiles can be found in
1263 Aubert et al. (2001, 2004), Fichter et al. (1998a, 1998b) and Prunier et al.
1264 (2015): the beech soil profile is composed of a ≈ 2 cm thick “O” horizon, a \approx
1265 20–30 cm thick “A” horizon, which recovers a “B” horizon, whose transition
1266 with the saprolite is at ≈ 90 –100 cm depth; the spruce soil profile is marked by
1267 a ≈ 2 cm thick “O” horizon, a ≈ 30 –40 cm thick “A” topsoil horizon, and a B
1268 horizon, which reaches the granitic saprock at ≈ 1 –1.2 m depth.

1269 Figure 2: Variations in the U concentration as a function of Fe_2O_3 (A), P_2O_5 (B) and
1270 variations in the U (C) and Th (D) concentrations as a function of Zr
1271 concentrations for the soil size fractions from the spruce and beech soil
1272 samples.

1273 Figure 3: Plot of the data in the isochron diagram, $(^{230}\text{Th}/^{232}\text{Th})$ vs $(^{238}\text{U}/^{232}\text{Th})$,
1274 with the different mixing lines discussed in the text. The Th activity ratios of
1275 the primary minerals are calculated by assuming they are at secular
1276 equilibrium [$(^{230}\text{Th}/^{232}\text{Th}) = (^{238}\text{U}/^{232}\text{Th})$].

1277 Figure 4: Variations in the $(^{230}\text{Th}/^{232}\text{Th})$ and $(^{238}\text{U}/^{232}\text{Th})$ ratios as a function of Zr
1278 concentrations for the soil size fractions from the spruce and beech soil
1279 samples.

1280 Figure 5: Variations in the $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{232}\text{Th})$ ratios as a function of Zr
1281 concentrations for the soil size fractions from the spruce and beech soil
1282 samples.

1283 Figure 6: Variation in the $(^{230}\text{Th}/^{232}\text{Th})$ ratio as a function of P_2O_5 concentrations for
1284 the soil size fractions from the spruce and beech soil samples.

1285 Figure 7: Variations in the ($^{234}\text{U}/^{238}\text{U}$) (7a) and ($^{226}\text{Ra}/^{230}\text{Th}$) (7b) ratios as a
1286 function of ($^{230}\text{Th}/^{234}\text{U}$) ratios for the soil size fractions from the spruce and
1287 beech soil samples. Nota Bene: ($^{234}\text{U}/^{238}\text{U}$) ratios of 3 dusts analyses on the site
1288 are given in Prunier et al. (2015). Their U activity ratios range between 0.988
1289 and 1.04, and cannot explain the atypical U activity ratios (i.e. ≈ 0.9) of the
1290 deepest soil solutions.

1291 Figure 8a: Plot of the spruce site data in the ($^{226}\text{Ra}/^{238}\text{U}$) vs ($^{234}\text{U}/^{238}\text{U}$) diagram. As
1292 detailed in the text, the soil solution data collected at 10, 30 and 60 cm and
1293 those of the $<2\ \mu\text{m}$ and 2-50 μm grain size fractions of the 30-40 cm soil
1294 horizon define two linear trends that converge towards the values of the 30
1295 cm soil solutions.

1296 Figure 8b: Plot of the spruce site data in the ($^{226}\text{Ra}/^{238}\text{U}$) vs Ba/U diagram.

1297 Figure 9: Depth variations in the Sr isotope ratios of the soil solutions from the
1298 spruce (VP) and beech (HP) sites. The 0 cm sample points correspond to the
1299 throughfall values. The ranges of the vegetation and atmospheric dust values
1300 for Sr (data from Guéguen et al., 2012) are also shown. The apatite data are
1301 from Aubert et al. (2001). The Sr isotope data for the soil solutions for 1998-
1302 1998 are from Aubert et al. (2001), the data from 2004-2006 are from this
1303 study; and the data from 2011-2012 are from Schmitt et al. (2017).

1304 Figure 10: ($^{234}\text{U}/^{238}\text{U}$) vs $^{87}\text{Sr}/^{86}\text{Sr}$ diagram for the soil solutions, soil grain size
1305 fractions, vegetation samples and atmospheric deposits from the beech (HP)
1306 and spruce (VP) sites. The albite and apatite Sr data are from Probst et al.
1307 (2000) and Aubert et al. (2001), respectively. The curves are the theoretical
1308 mixing curves between end-members with U–Sr characteristics similar to
1309 those of the 2 μm fractions of the HP beech 30-40 cm soil horizon and the
1310 apatite and the albite end-members (see text for details).

1311 Figure 11: Plot of the data in the ($^{230}\text{Th}/^{234}\text{U}$) vs ($^{226}\text{Ra}/^{230}\text{Th}$) diagram. The
1312 ($^{230}\text{Th}/^{234}\text{U}$) ratio variations between depths of 10 cm and 70 cm cannot result
1313 from the variable contributions of U and Th from litter decay.

1314 Figure 12: Plot of the data in a diagram of the ($^{230}\text{Th}/^{232}\text{Th}$) ratios against
1315 ($^{87}\text{Sr}/^{86}\text{Sr}$) isotopic ratios with the different mixing lines discussed in the
1316 text.

1317 Figure 13: Plot of the data in the ($^{230}\text{Th}/^{232}\text{Th}$) vs ($^{234}\text{U}/^{238}\text{U}$) diagram. The lines in
1318 the figure represent possible mixing lines between the different end-members
1319 invoked to account for the dispersion of the (HP) beech plot data points in the
1320 diagram (see text).

1321

1322 **Supplementary Materials**

1323 Table EA1a-d: Major and trace element concentrations in the soil solutions from the
1324 spruce (1a) and beech (1b) plots, throughfall (1c) and rainwater (1d) for
1325 2003-2006.

1326 Table EA2a: Major (oxide %) and trace element concentrations (mg/kg) in the
1327 bedrock (granite), in soil ($< 2\ \text{mm}$) and the soil grain size fractions from the

1328 spruce and beech plots.
1329 Table EA2b: Major and trace element concentrations in the litter and different parts
1330 of tree samples.
1331 Table EA3a-e: REE concentrations in soil solutions from the spruce plot (a), from the
1332 beech plot (b), in throughfalls (c), in the granitic bedrock, in soil (< 2 mm)
1333 and soil grain size fractions (d) and in vegetation samples (e).
1334
1335 Figure EA1: SEM observations of zircons with evidence of blunted or fractured
1336 surfaces (1a), sulfate minerals in VP spruce soils (1b) and soil solutions (1c)
1337 Figure EA2: Variations in some major and trace element concentrations as a
1338 function of Fe₂O₃ concentrations for the soil size fractions from the spruce and
1339 beech soil samples. Fe₂O₃ concentrations increase with the decrease in the
1340 grain size fraction.
1341 Figure EA3: Plot of soil solution data in binary concentration diagrams (Mn, K vs. Ba;
1342 Ba, Ca vs. Mg; Sr, Ba vs. 1/SO₄²⁻)
1343 Figure EA4: Chloride, nitrate and sulfate concentrations of the soil solutions from
1344 (a) 10 cm and 70 cm depths at the spruce (HP) site and (b) 5 cm, 10 cm, 30 cm
1345 and 60 cm depths at the beech (VP) site for 1992–2010.

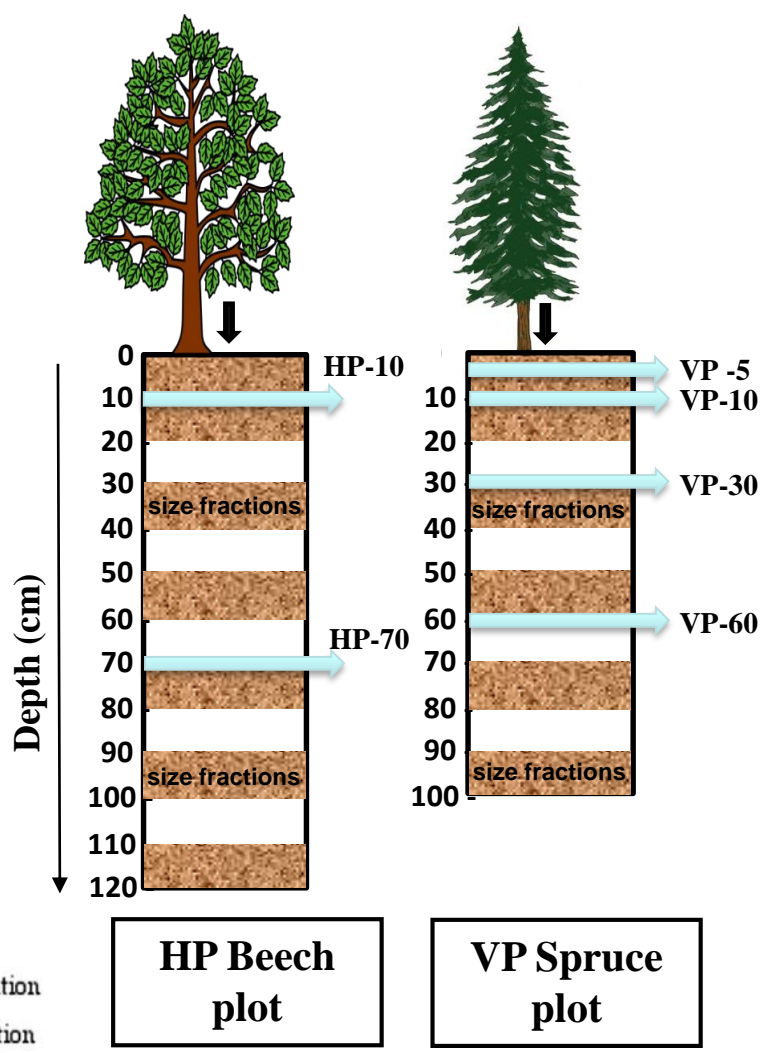
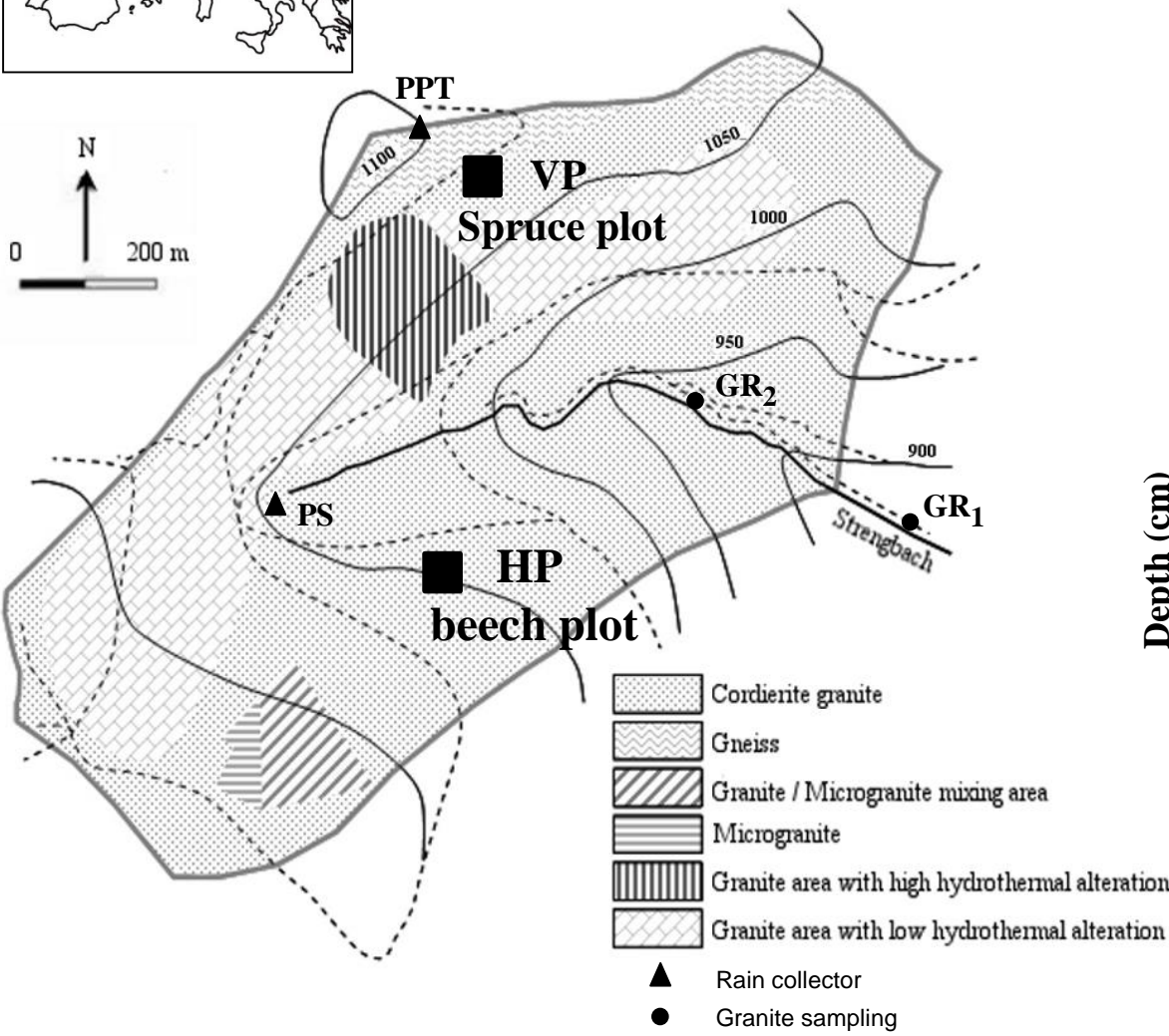
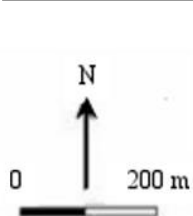


Fig.1

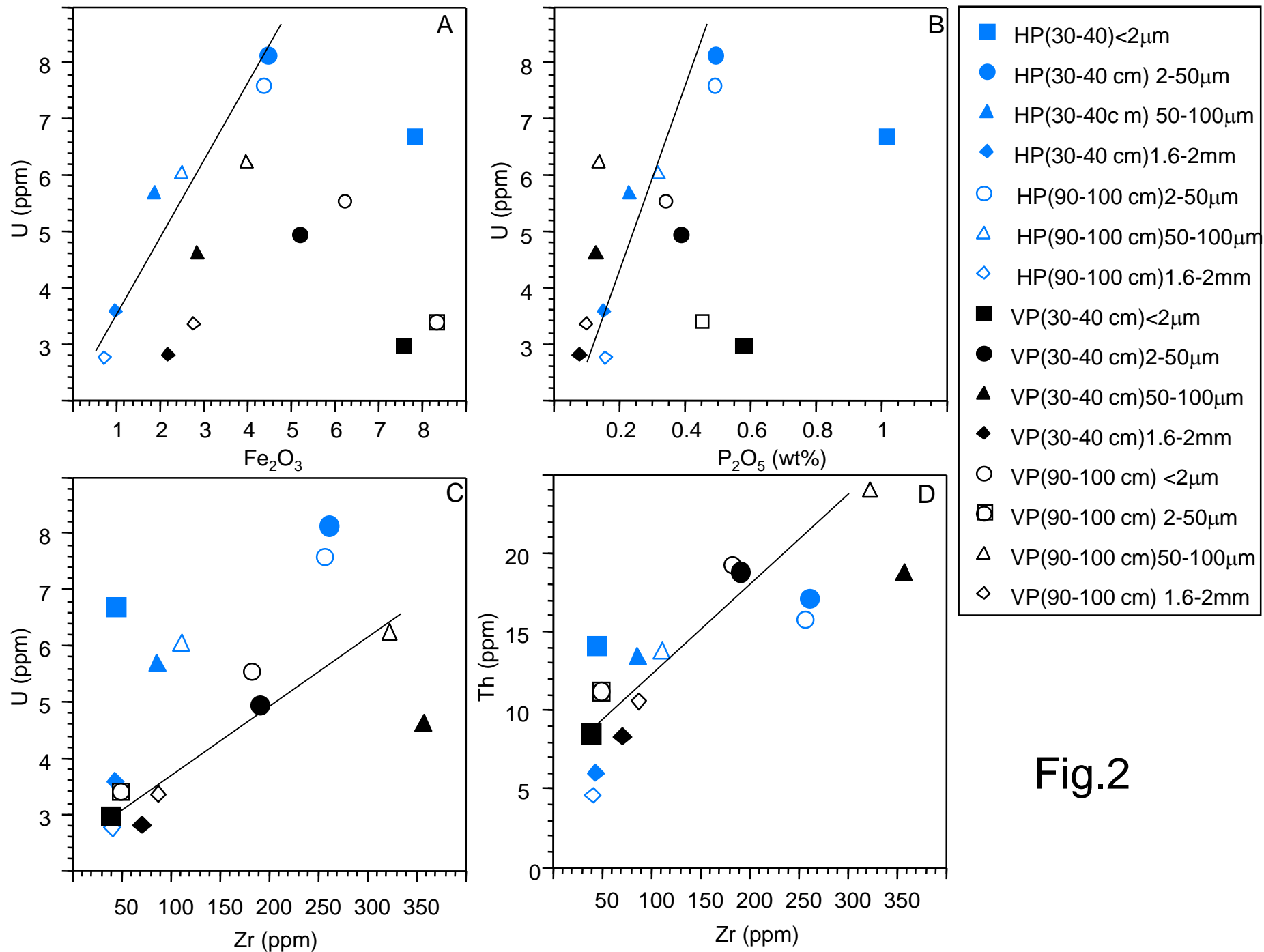


Fig.2

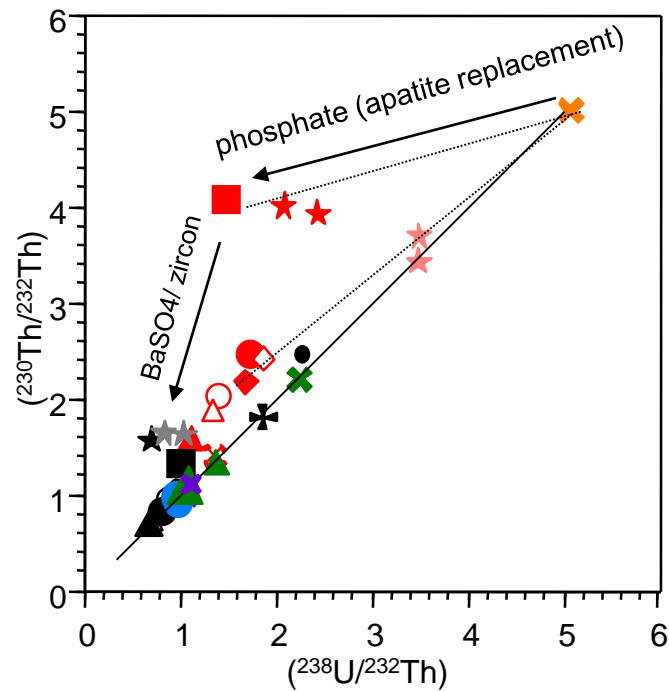
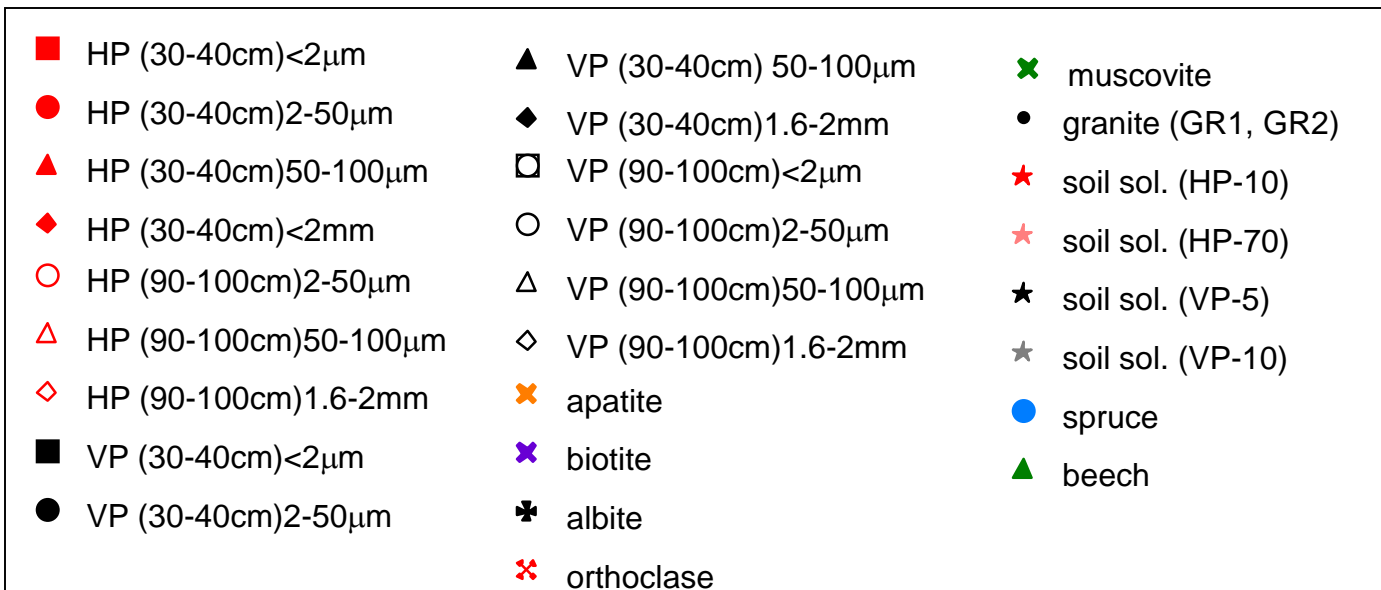


Fig.3



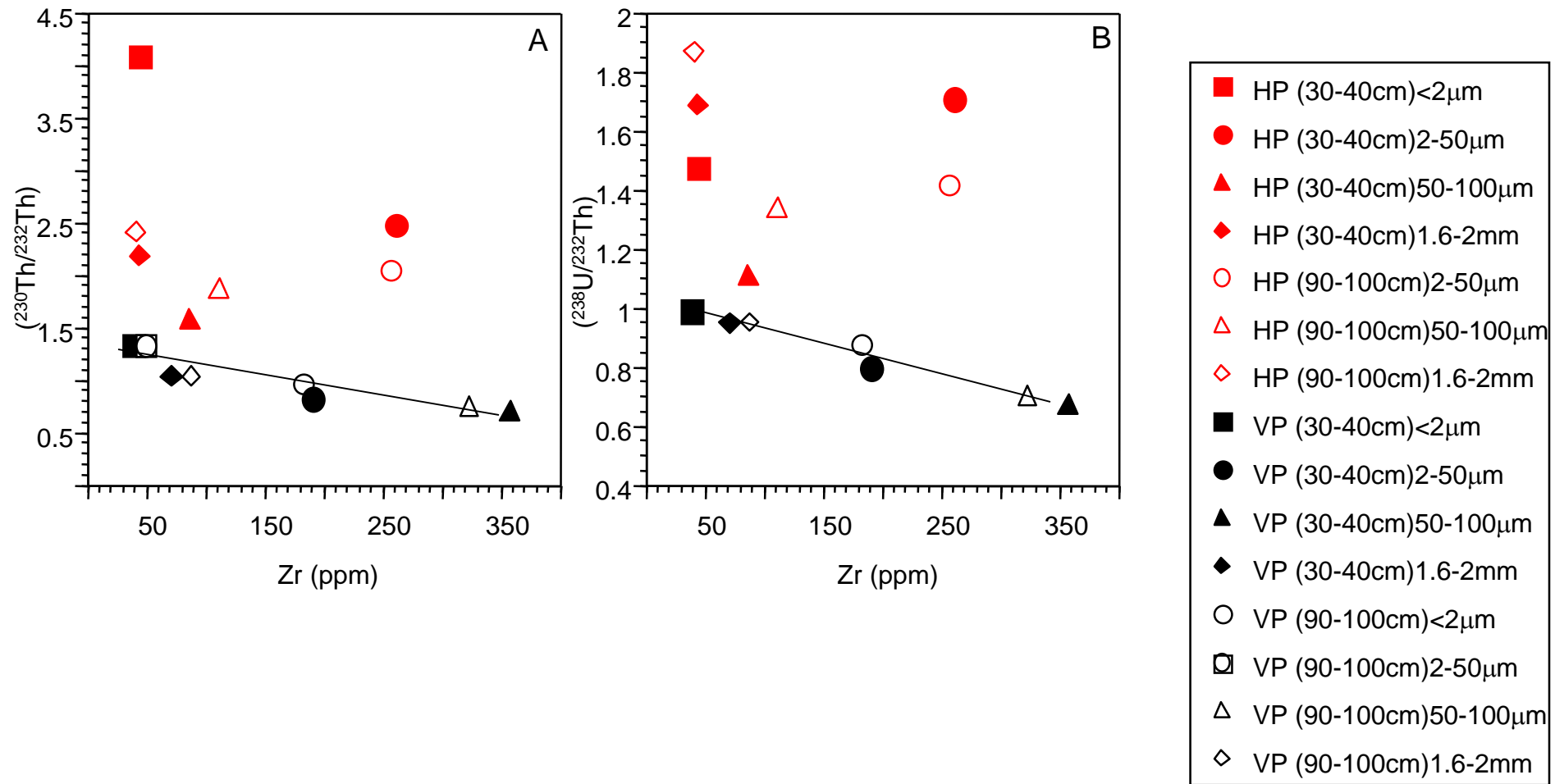


Fig.4

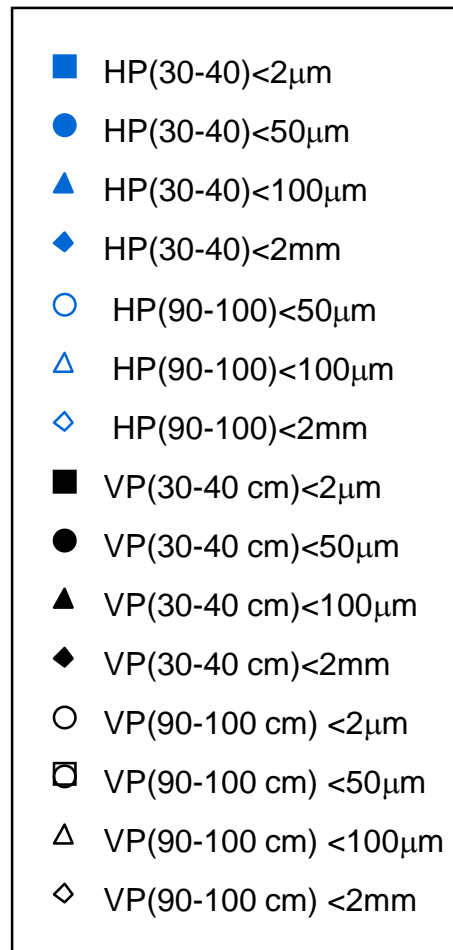
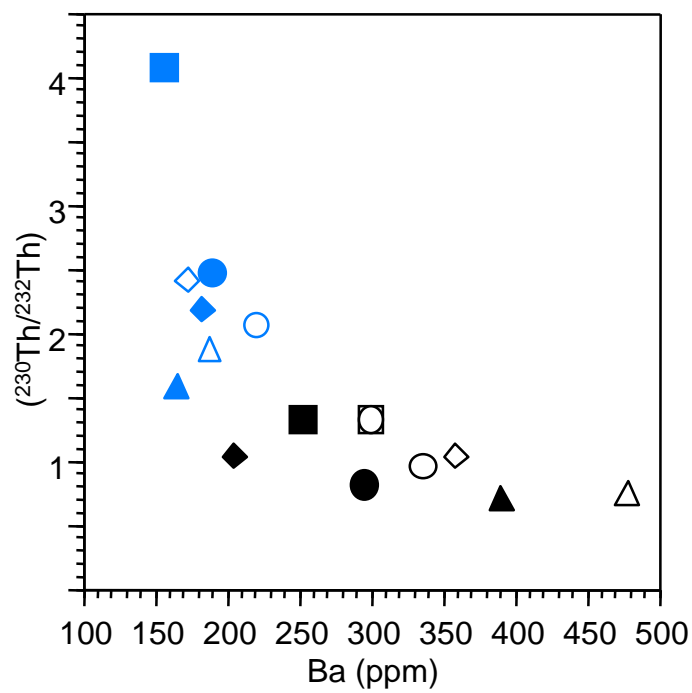
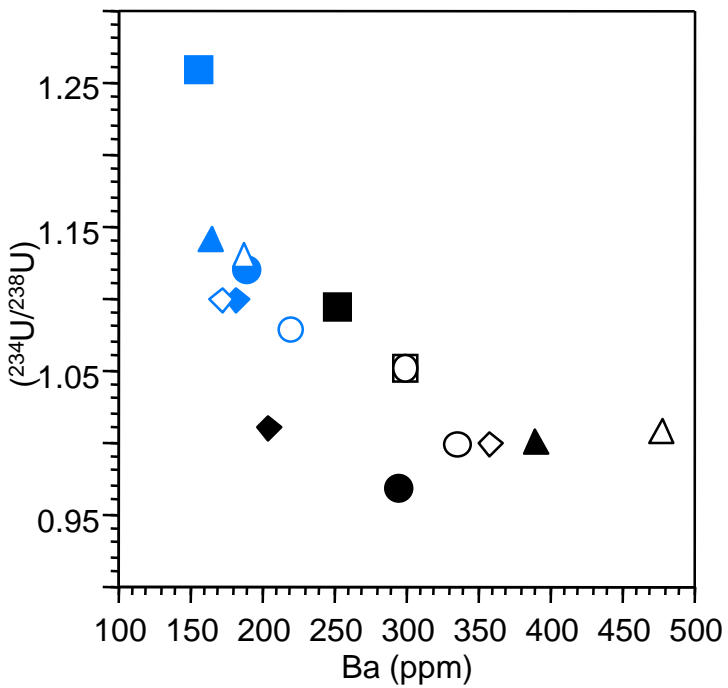
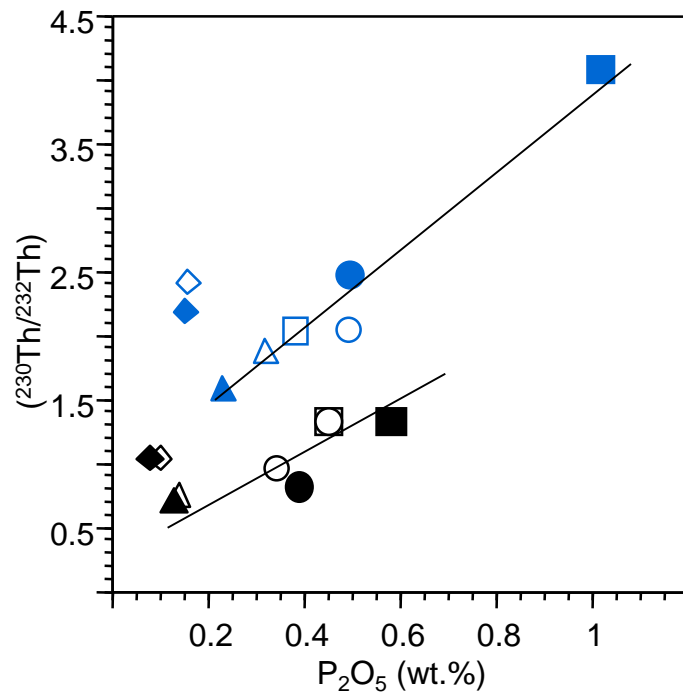


Fig.5



- HP(30-40)<math><2\mu\text{m}</math>
- HP(30-40)<math><50\mu\text{m}</math>
- ▲ HP(30-40)<math><100\mu\text{m}</math>
- ◆ HP(30-40)<math><2\text{mm}</math>
- HP(90-100)<math><50\mu\text{m}</math>
- △ HP(90-100)<math><100\mu\text{m}</math>
- ◇ HP(90-100)<math><2\text{mm}</math>
- VP(30-40 cm)<math><2\mu\text{m}</math>
- VP(30-40 cm)<math><50\mu\text{m}</math>
- ▲ VP(30-40 cm)<math><100\mu\text{m}</math>
- ◆ VP(30-40 cm)<math><2\text{mm}</math>
- VP(90-100 cm) <math><2\mu\text{m}</math>
- ◻ VP(90-100 cm) <math><50\mu\text{m}</math>
- △ VP(90-100 cm) <math><100\mu\text{m}</math>
- ◇ VP(90-100 cm) <math><2\text{mm}</math>

Fig.6

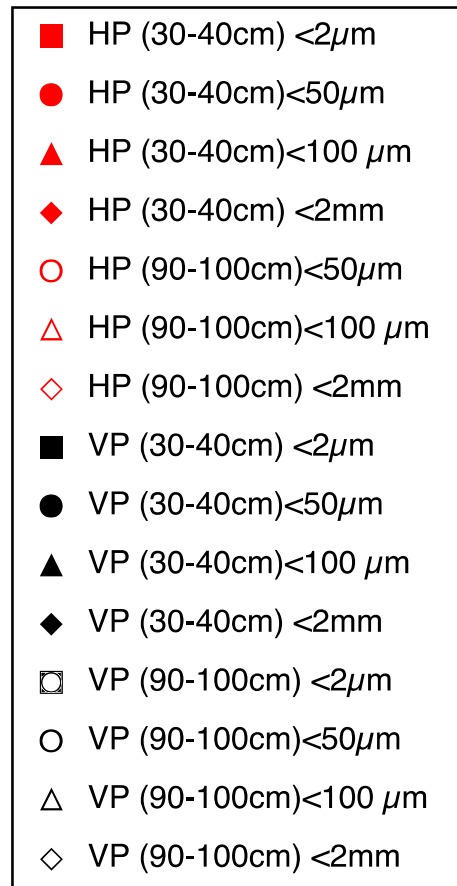
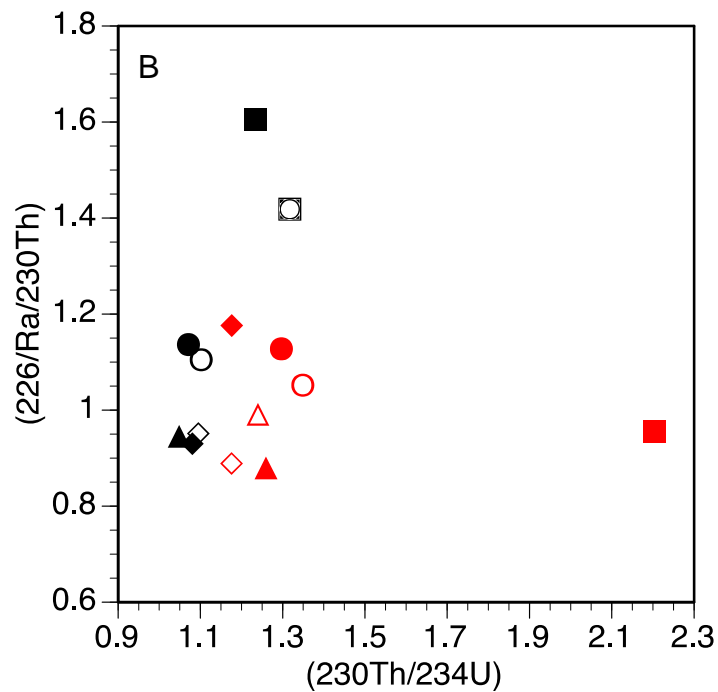
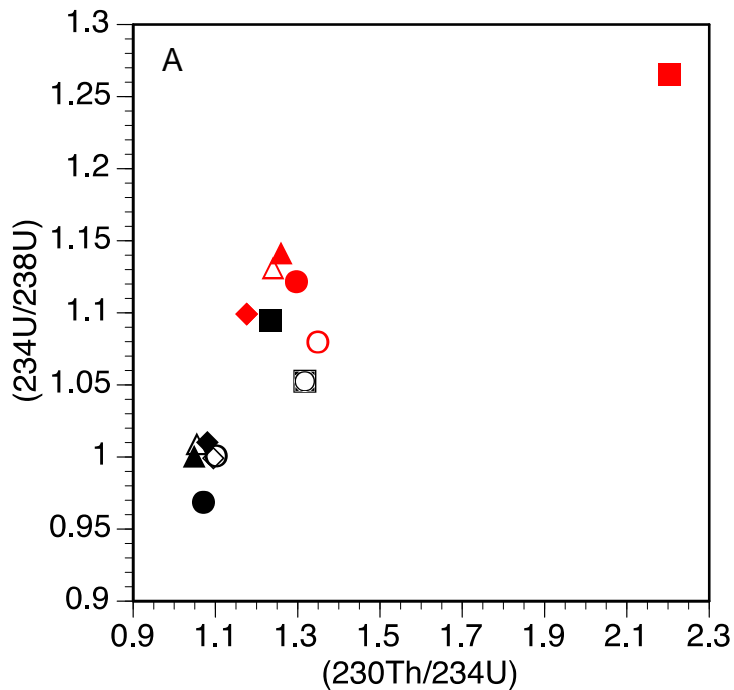
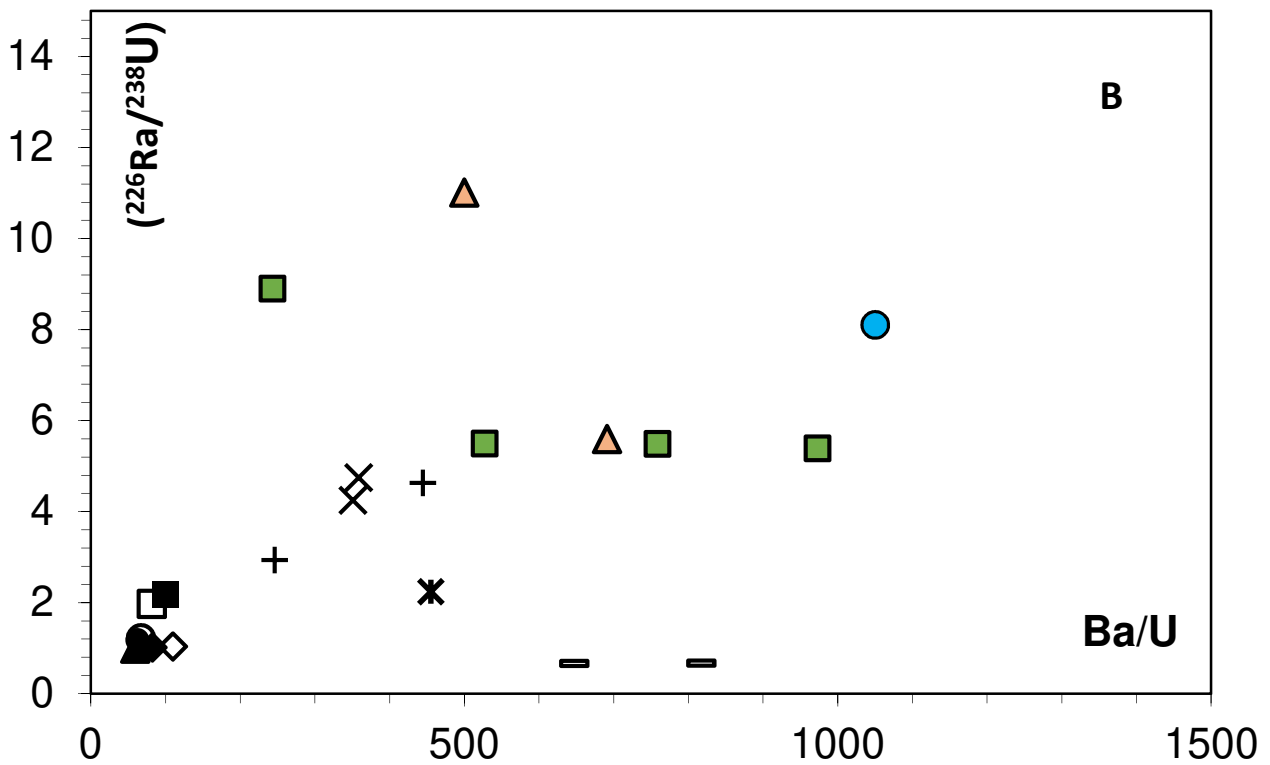
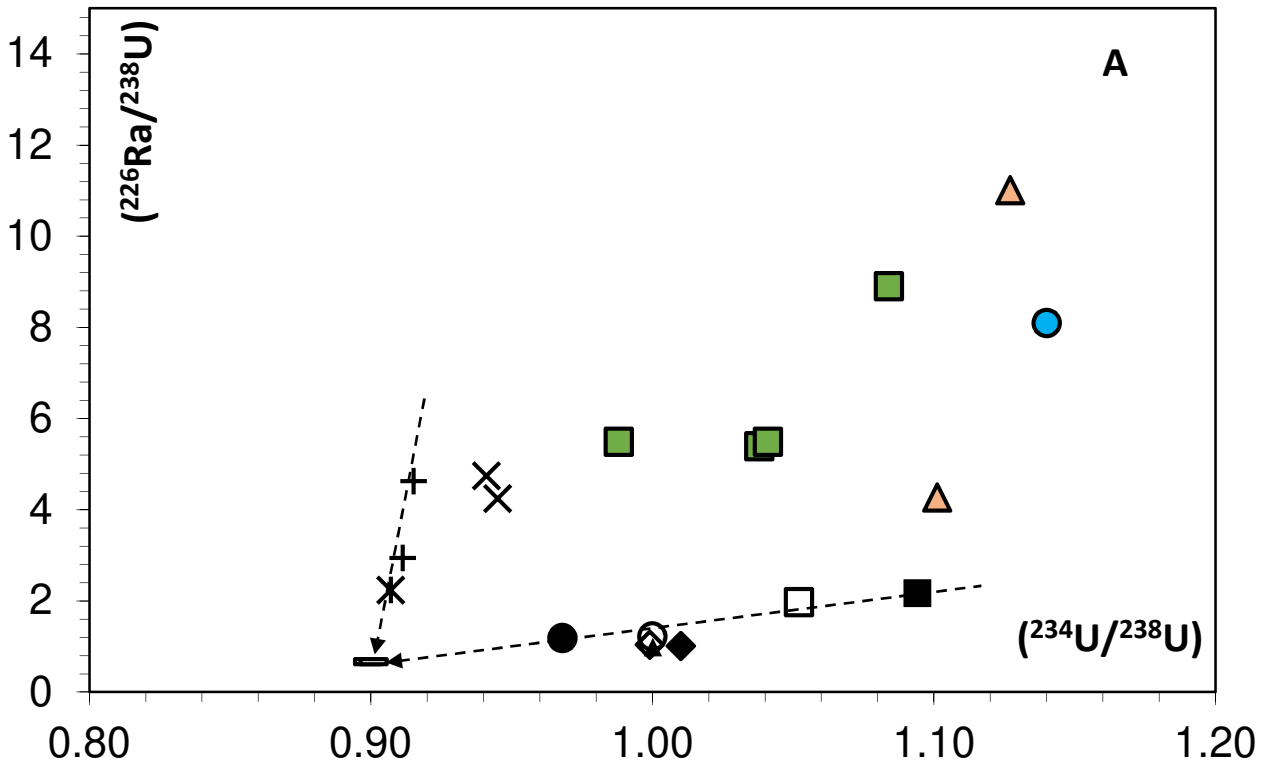


Fig.7



- Rain water
- 2-50 μm (VP 30-40)
- <2 μm (VP 90-100)
- vegetation
- soil sol. -30cm
- ▲ throughfalls
- ▲ 50-100 μm (VP 30-40)
- 50-100 μm (VP 90-100)
- × Soil sol. -5cm
- × soil sol. -60cm
- <2 μm (VP 30-40)
- ◆ 1.6 - 2 mm (VP 30-40)
- ◇ 1.6 - 2 mm (VP 90-100)
- + soil sol. -10cm

Figure 8

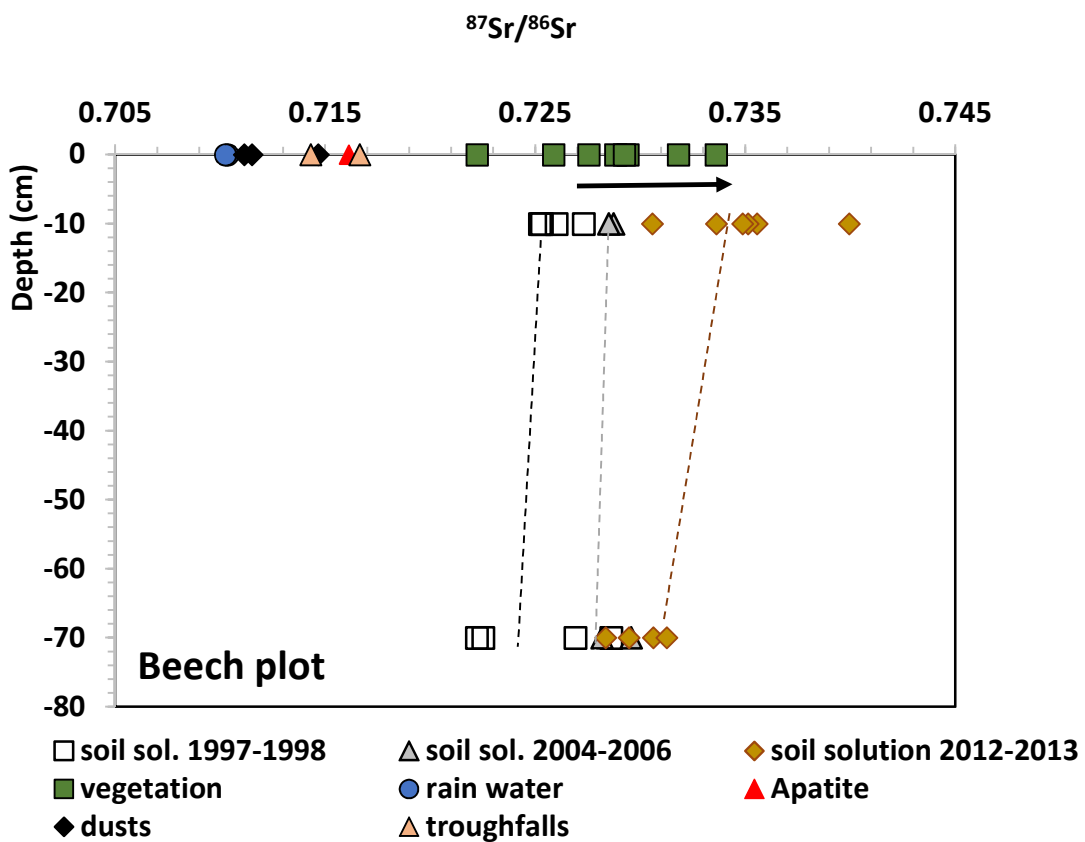
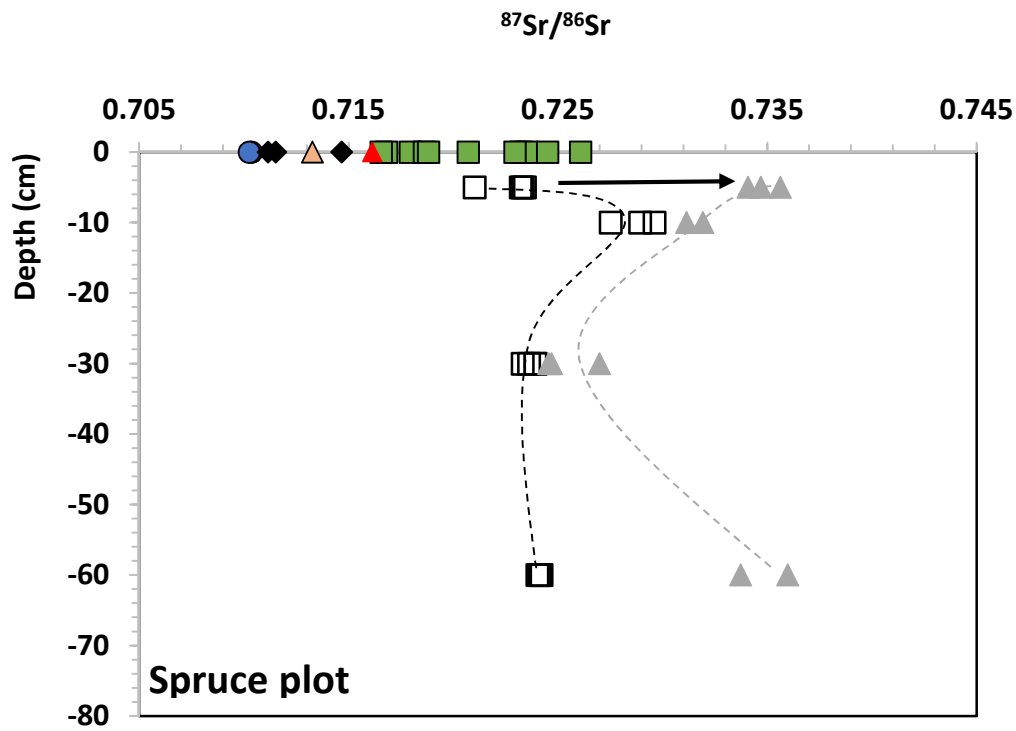


Figure 9

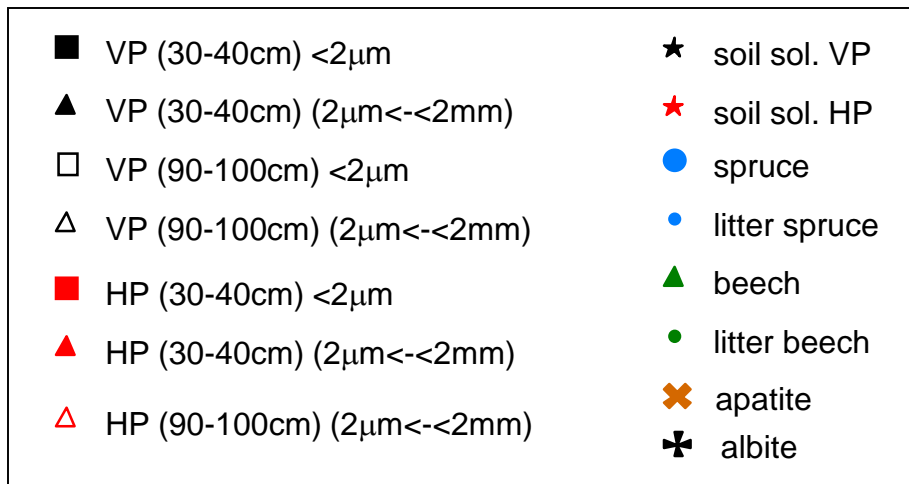
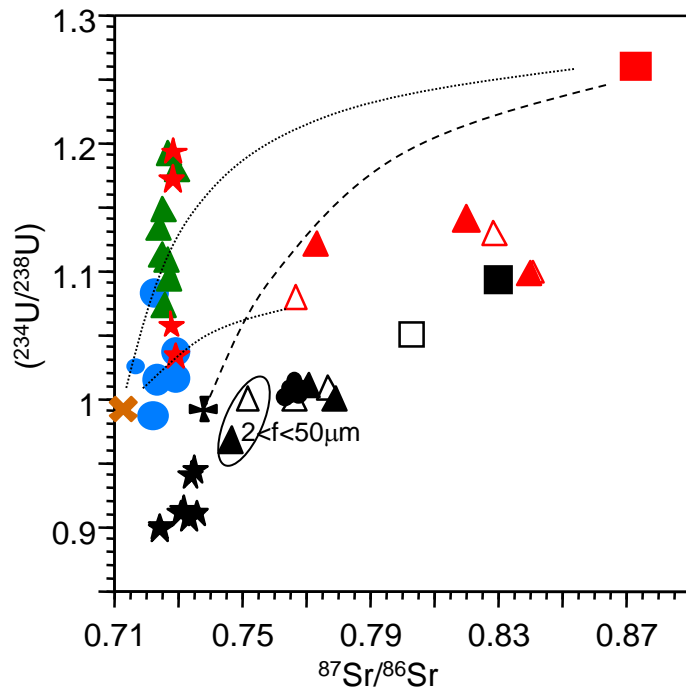


Fig.10

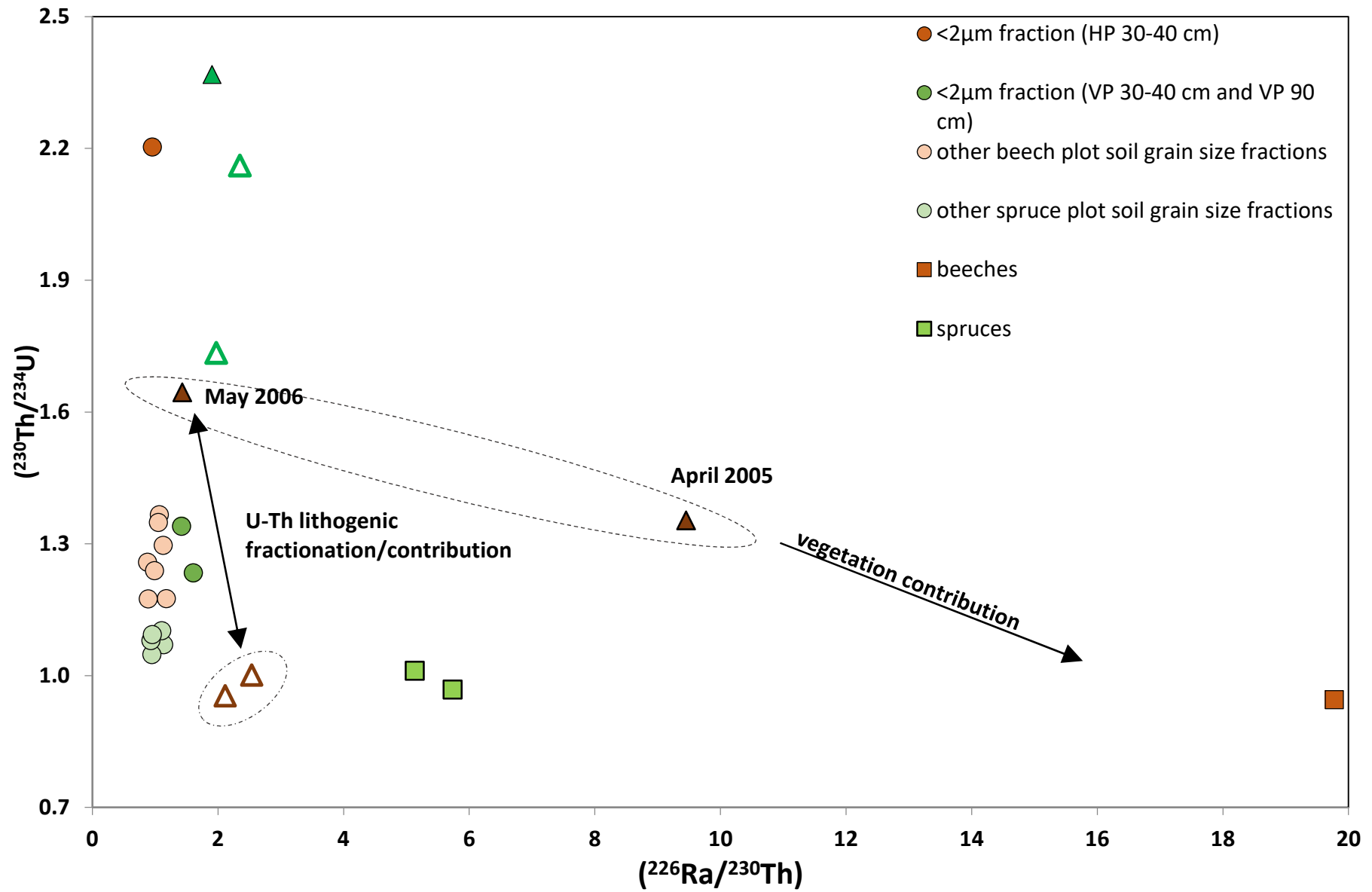
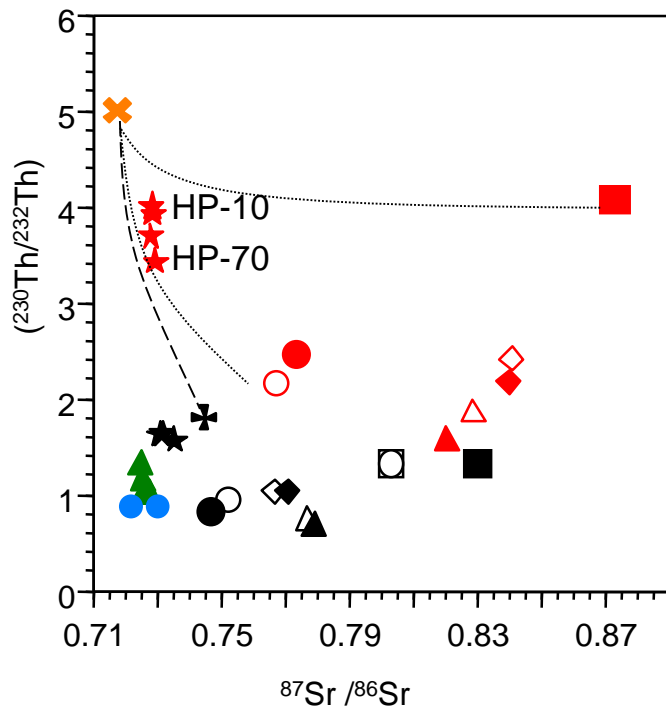
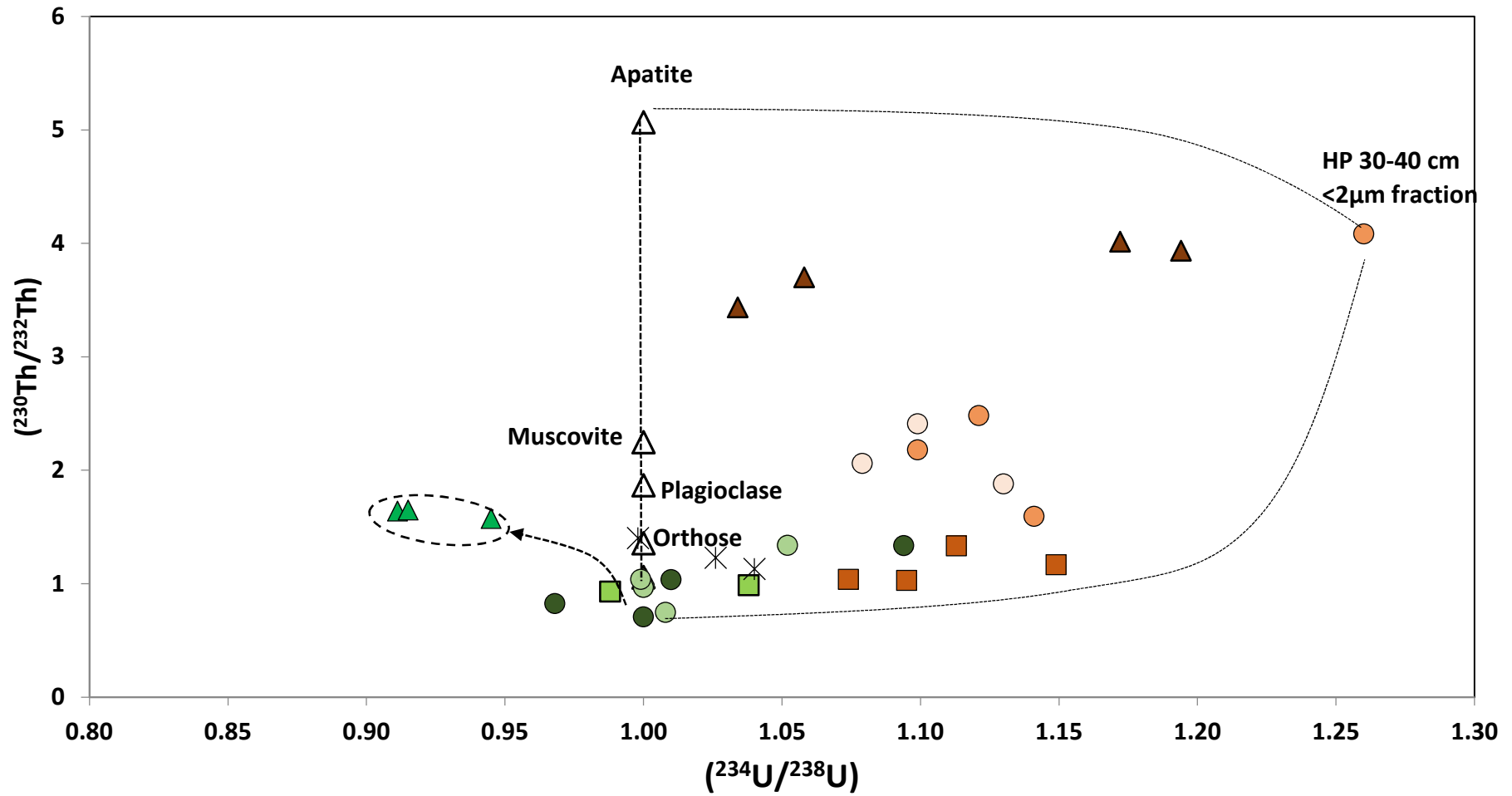


Figure 11



- HP (30-40cm)<2 μm
- HP (30-40cm)<50 μm
- ▲ HP (30-40cm)<100 μm
- ◆ HP (30-40cm)<2mm
- HP (90-100cm)<50 μm
- △ HP (90-100cm)<100 μm
- ◇ HP (90-100cm)<2mm
- VP (30-40cm)<2 μm
- VP (30-40cm)<50 μm
- ▲ VP (30-40cm)<100 μm
- ◆ VP (30-40cm)<2 μm
- VP (90-100cm)<2 μm
- VP (90-100cm)<50 μm
- △ VP (90-100cm)<100 μm
- ◇ VP (90-100cm)<2mm
- ✕ apatite
- ✦ plagioclase
- ★ soil sol. HP
- ★ soil sol. VP
- spruce
- ▲ beech

Fig.12



- ▲ spruce plot soil solution
- ▲ beech plot soil solution
- spruces
- beeches
- × dust
- ▲ primary minerals
- spruce plot soil grain size fractions (30-40 cm)
- spruce plot soil grain size fractions (90 cm)
- beech plot soil grain size fractions (30-40 cm)
- beech plot soil grain size fractions (90 cm)

Figure 13

Table 1 a : Major and trace element concentrations, $^{87}\text{Sr}/^{86}\text{Sr}$ and U-Th-Ra activity ratios in soil grain size fractions of two horizons 30-40 cm and 90-100 cm from spruce (VP) and beech (HP) profiles.

Site	Depth (cm)	Sample name	Size of the soil grain fractions	Fe ₂ O ₃ wt %	MnO ₂ wt %	P ₂ O ₅ wt %	Ba mg/kg	Zr mg/kg	Pb mg/kg	Sr mg/kg	U mg/kg	Th mg/kg	Ra pg/kg	$^{87}\text{Sr}/^{86}\text{Sr}$ (2σ)	$^{234}\text{U}/^{238}\text{U}$ (2σ)	$(^{230}\text{Th}/^{232}\text{Th})$ (2σ)	$(^{238}\text{U}/^{232}\text{Th})$ (2σ)	$(^{226}\text{Ra}/^{238}\text{U})$ (2σ)	$(^{226}\text{Ra}/^{230}\text{Th})$ (2σ)
VP spruce site	30-40	VP-F1A	<2 μm	5.89	0.115	0.580	251	39.0	99.6	36.5	2.508	7.635	1820	0.83003 ± 2	1.094 ± 3	1.34 ± 1	0.99 ± 1	2.17 ± 3	1.60 ± 2
		VP-F2A	2-50 μm	4.04	0.086	0.390	295	190	85.3	133	4.717	17.83	1858	0.74672 ± 2	0.968 ± 3	0.826 ± 8	0.797 ± 8	1.18 ± 2	1.14 ± 2
		VP-F3A	50-100 μm	2.22	0.032	0.130	390	358	49.3	66.1	6.587	29.31	2183	0.77931 ± 1	1.000 ± 3	0.710 ± 7	0.677 ± 7	0.99 ± 2	0.94 ± 1
		VP-F4A	1.6-2 mm	1.71	0.049	0.080	205	71.0	53.9	47.1	2.488	7.884	844.9	0.77082 ± 1	1.010 ± 3	1.04 ± 1	0.95 ± 1	1.01 ± 2	0.93 ± 1
	90-100	VP-F1B	< 2μm	6.47	0.156	0.450	299	49.0	40.7	36.9	3.653	11.37	2402	0.80289 ± 1	1.052 ± 3	1.34 ± 1	0.97 ± 1	1.96 ± 3	1.42 ± 2
		VP-F2B	2-50 μm	4.85	0.155	0.340	335	183	51.0	102	4.965	17.01	2022	0.75209 ± 1	1.000 ± 3	0.97 ± 1	0.879 ± 9	1.22 ± 2	1.10 ± 2
		VP-F3B	50-100 μm	3.10	0.112	0.140	478	323	132	72.3	5.464	23.33	n.d	0.77721 ± 1	1.008 ± 3	0.750 ± 8	0.706 ± 7	n.d	n.d
		VP-F4B	1.6-2 mm	2.16	0.188	0.100	359	88.0	50.6	55.8	3.271	10.35	1139	0.76657 ± 8	0.999 ± 3	1.04 ± 1	0.95 ± 1	1.04 ± 2	0.95 ± 1
HP beech site	30-40	HP-F1A	< 2μm	6.09	0.076	1.02	155	44.2	38.0	20.9	6.404	13.12 (12.09)	5674	0.87288 ± 2 (0.87289±2)	1.260 ± 3 (1.265±3)	4.09 ± 4 (4.10 ± 4)	1.47 ± 2	2.65 ± 4	0.95 ± 1
		HP-F2A	2-50 μm	3.48	0.042	0.494	188	260.6	22.9	57.3	7.425	13.10	4071	0.77335 ± 2	1.121 ± 3	2.48 ± 3	1.71 ± 2	1.64 ± 3	1.13 ± 2
		HP-F3A	50-100 μm	1.46	0.018	0.231	165	86.6	20.8	45.7	5.286	14.34	2234	0.82036 ± 2	1.141 ± 3	1.60 ± 2	1.11 ± 1	1.26 ± 2	0.88 ± 1
		HP-F4A	1.6-2 mm	0.77	0.032	0.154	183	43.9	20.4	31.7	3.253	5.803	1424	0.8402 ± 2	1.099 ± 3	2.18 ± 2	1.69 ± 2	1.31 ± 2	1.18 ± 2
	90-100	HP-F2B	2-50 μm	3.40	0.038	0.490	219	256	41.9	71.6	7.425	15.79	3799	0.76688 ± 1	1.079 ± 3	2.06 ± 2	1.42 ± 2	1.53 ± 2	1.05 ± 2
		HP-F3B	50-100 μm	1.94	0.036	0.320	188	111	70.5	49.8	5.809	13.02	2692	0.82885 ± 1 (0.82882±4)	1.130 ± 3	1.88 ± 2	1.34 ± 1	1.38 ± 2	0.99 ± 2
		HP-F4B	1.6-2 mm	0.57	0.013	0.160	172	41.0	42.3	34.7	3.401	5.487	1307	0.84092 ± 2	1.099 ± 3	2.41 ± 2	1.87 ± 2	1.15 ± 2	0.89 ± 1

U-Th-Ra data were determined by isotope dilution (n.d.: no defined). Replicates in brackets.

Table 1b: Major and trace element concentrations, $^{87}\text{Sr}/^{86}\text{Sr}$ and U-Th-Ra activity ratios in soil solutions, rainwaters and throughfalls from the Strengbach catchment.

Site	Sample name	Depth (cm)	date	SO ₄ ²⁻ mmol/L	DOC mg/kg	Fe mg/kg	Ba µg/kg	Sr µg/kg	U µg/kg	Th µg/kg	Ra fg/kg	$^{87}\text{Sr}/^{86}\text{Sr}$ (2σ)	(²³⁴ U/ ²³⁸ U) (2σ)	(²³⁰ Th/ ²³² Th) (2σ)	(²³⁸ U/ ²³² Th) (2σ)	(²²⁶ Ra/ ²³⁸ U) (2σ)	(²²⁶ Ra/ ²³⁰ Th) (2σ)
VP spruce site (7°1983 E, 48°216N)	VP-5 (soil solution)	-5	29/03/2005	0.040	16.7	0.470	14.3	4.18	0.0400	0.0740	63.38	0.73407 ± 2	0.941 ± 3	n.d	n.d	4.75 ± 7	n.d
		-5	22/05/2006	0.030	26.6	0.690	13.9	4.24	0.0379	0.1620	54.00	0.73561 ± 2	0.945 ± 4	1.58 ± 2	0.704 ± 7	4.25 ± 6	1.90 ± 3
	VP-10 (soil solution)	-10	29/03/2005	0.038	10.9	0.270	10.9	2.33	0.0444	0.1230	44.14	0.73114 ± 5	0.9112 ± 8	1.64 ± 2	1.04 ± 1	2.94 ± 4	1.97 ± 3
		-10	22/05/2006	0.030	13.7	0.290	14.3	3.17	0.0321	0.1160	49.80	0.73191 ± 2	0.915 ± 4	1.65 ± 2	0.838 ± 8	4.63 ± 7	2.35 ± 4
	VP-30 (soil solution)	-30	29/03/2005	0.045	4.38	0.026	30.3	3.09	0.0370	0.0350	8.300	0.72468 ± 2	0.899 ± 3	n.d	n.d	0.670 ± 1	n.d
		-30	22/05/2006	0.037	4.97	0.024	19.3	2.11	0.0298	0.0440	6.700	0.72455 ± 2	0.901 ± 1	n.d	n.d	0.667 ± 1	n.d
	VP-60 (soil solution)	-60	02/11/2004	0.049	2.61	0.003	17.8	2.65	0.0120	0.0070	n.d	0.73597 ± 2	0.911 ± 4	n.d	n.d	n.d	n.d
		-60	29/03/2005	0.052	1.76	0.008	13.7	3.22	0.0300	0.0050	22.64	0.73372 ± 2	0.907 ± 4	n.d	n.d	2.24 ± 3	n.d
HP beech site (7°1963 E, 48°211 N)	HP-10 (soil solution)	-10	29/03/2005	0.031	5.74	0.200	4.38	1.44	0.0380	0.0470	194.5	0.72872 ± 2	1.194 ± 3	3.94 ± 4	2.44 ± 2	15.1 ± 2	9.4 ± 1
		-10	22/05/2006	0.012	12.93	0.470	3.03	1.05	0.0740	0.1080	68.70	0.72850 ± 2	1.172 ± 2	4.02 ± 4	2.08 ± 2	2.76 ± 4	1.43 ± 2
	HP-70 (soil solution)	-70	29/03/2005	0.027	2.26	0.009	4.52	0.68	0.0290	0.0253	26.08	0.72817 ± 2	1.058 ± 3	3.70 ± 4	3.50 ± 4	2.68 ± 4	2.53 ± 4
		-70	22/05/2006	0.038	2.78	0.010	5.03	1.05	0.0310	0.0260	21.30	0.72956 ± 2	1.034 ± 4	3.44 ± 3	3.49 ± 4	2.09 ± 3	2.11 ± 3
Top of watershed	PPT (rain water)		31/05/2005	0.018	0.81	0.003	0.63	0.90	0.0006	n.d	1.100	0.71024 ± 4	1.140 ± 3	n.d	n.d	5.25 ± 8	n.d
	PS (rain water)		03/05/2005	0.013	0.72	0.007	3.19	0.81	0.0006	n.d	1.600	n.d	n.d	n.d	n.d	8.1 ± 1	n.d
VP spruce site (7°1983 E, 48°216N)	VP-PL5 (Throughfall)		29/03/2005	0.202	19.0	0.050	27.8	16.0	0.0028	<i>0.006</i>	27.97	n.d	n.d	n.d	n.d	21.9 ± 3	n.d
			31/05/2005	0.025	4.1	0.030	11.0	2.77	0.0029	<i>0.001</i>	4.100	0.71327 ± 2	1.101 ± 3	n.d	n.d	4.27 ± 6	n.d
HP beech site (7°1963 E, 48°211 N)	HP-PLH (Throughfall)		29/03/2005	0.041	4.47	0.010	4.14	5.26	0.0060	<i>0.007</i>	11.32	n.d	n.d	n.d	n.d	6.00 ± 8	n.d
			31/05/2005	0.033	9.04	0.010	0.510	0.56	0.0010	<i>0.005</i>	3.800	0.71664 ± 3	1.127 ± 4	n.d	n.d	11.0 ± 2	n.d

U-Th-Ra italic data were determined by ICP-MS and the others by isotope dilution (n.d.: no defined). Replicates in brackets.

Table 1c : Major and trace element concentrations, $^{87}\text{Sr}/^{86}\text{Sr}$ and U-Th-Ra activity ratios in litter and in different parts of tree samples.

Site	Sample	Sample name	Date	Ca mg/kg	K mg/kg	Mn mg/kg	Ba mg/kg	Sr mg/kg	U $\mu\text{g}/\text{kg}$	Th $\mu\text{g}/\text{kg}$	Ra pg/kg	$^{87}\text{Sr}/^{86}\text{Sr}$ (2 σ)	($^{234}\text{U}/^{238}\text{U}$) (2 σ)	($^{230}\text{Th}/^{232}\text{Th}$) (2 σ)	($^{238}\text{U}/^{232}\text{Th}$) (2 σ)	($^{226}\text{Ra}/^{238}\text{U}$) (2 σ)	($^{226}\text{Ra}/^{230}\text{Th}$) (2 σ)
VP spruce site	Litter	VP-LT	21/06/2004	3487	992.5	1038	13.8	7.17	<i>19.6</i>	<i>59.0</i>	n.d	0.71653 \pm 2	1.026 \pm 5	n.d	n.d	n.d	n.d
	Sapwood	VP-SW	23/05/2006	594	338.8	1117	28.4	6.25	0.3830	1.154	10.13	0.72915 \pm 4	1.017 \pm 4	n.d	n.d	79 \pm 1	n.d
	Tree roots ($\varnothing = 2\text{-}5$ mm)	VP-MR	23/05/2006	2647	3415	81.1	29.55	5.89	56.01	173.3	102.9	0.72195 \pm 3	0.988 \pm 3	0.932 \pm 9	0.97 \pm 1	5.49 \pm 8	5.73 \pm 9
	Top tree branches ($\varnothing = 2\text{-}5$ mm)	VP-TB	15/05/2007	2148	5140	91.6	9.32	5.25	9.583	30.67	17.29	0.71934 \pm 3	1.038 \pm 3	0.99 \pm 1	0.941 \pm 9	5.39 \pm 8	5.13 \pm 8
	Needles ($> 1\text{yr}$)	VP-ON4	15/05/2007	1736	4080	88.6	1.42	1.20	1.876	<i>5.92</i>	0.7057	0.72345 \pm 3	1.016 \pm 3	n.d	n.d	1.12 \pm 2	n.d
	Needles ($< 1\text{yr}$)	VP-YN1	15/05/2007	458	11293	141	0.601	0.36	2.467	<i>5.91</i>	7.349	0.72222 \pm 2	1.084 \pm 3	n.d	n.d	8.9 \pm 1	n.d
HP beech site	Litter	HP-LT	21/06/2004	5766	2043	757	16.3	12.7	<i>15.5</i>	<i>35.2</i>	n.d	n.d	1.049 \pm 4	n.d	n.d	n.d	n.d
	Sapwood	HP-SW	21/09/2005	182	273.2	16.2	7.41	2.69	0.234	1.089	110.8	0.72977 \pm 2	1.179 \pm 11	n.d	0.648 \pm 6	1413 \pm 21	n.d
	Buds	HP-B	05/05/2005	5057	21872	533	11.7	7.28	1.104	3.495	80.19	0.72726 \pm 8	1.192 \pm 5	n.d	0.95 \pm 1	217 \pm 3	n.d
	Leaves (180 cm high)	HP-L2	13/09/2005	6698	9520	743	17.1	9.86	3.365	9.036	170.2	0.72744 \pm 3	1.095 \pm 4	1.03 \pm 1	1.12 \pm 1	151 \pm 2	164 \pm 2
	Top leaves	HP-SL	21/09/2005	5460	11253	738	7.63	5.82	2.449	7.380	<i>71.97</i> (72.47)	0.72577 \pm 1	1.074 \pm 4	1.04 \pm 1	1.00 \pm 1	88 \pm 1	84 \pm 1
	Tree roots ($\varnothing = 2\text{-}5$ mm)	HP-MR	13/09/2005	2965	2324	108	27.7	10.6	7.307	16.82	262.2	0.72433 \pm 3	1.133 \pm 4	n.d	1.31 \pm 1	107 \pm 2	n.d
	Tree roots ($\varnothing = 1\text{-}1.5$ cm)	HP-SR	13/09/2005	1229	2114	67.1	13.0	5.38	16.75	47.09	120.8	0.72550 \pm 2	1.149 \pm 3	1.17 \pm 1	1.08 \pm 1	21.5 \pm 3	19.8 \pm 3
	Fine rootlets	HP-FR	13/09/2005	1419	2651	107	24.7	7.96	68.28	148.9	687.7	0.72518 \pm 1	1.113 \pm 3	1.34 \pm 1	1.38 \pm 1	30.1 \pm 5	31.1 \pm 5
Top tree branches ($\varnothing = 2\text{-}5$ mm)	HP-TB	21/09/2005	2954	2311	290	22.8	8.92	0.879 (0.892)	2.070	70.46	0.72664 \pm 1 (0.72672 \pm 8)	1.109 \pm 4 (1.118 \pm 6)	n.d	1.28 \pm 1	239 \pm 4	n.d	

U-Th-Ra italic data were determined by ICP-MS and the others by isotope dilution (n.d. : no defined). Replicates in brackets

Table 2a

	Ca Flux kg/m ² /a	(Ba/Ca) µg/g	(U/Ca) µg/g	(Th/Ca) µg/g	(Ra/Ca) pg/g	Ba flux µg/m ² /a	U flux µg/m ² /a	Th flux µg/m ² /a	Ra flux µg/m ² /a
Spruce Plot	12	0.8 - 4	1 - 5.3	3 - 15	4 - 16	900 - 1500	0.7 - 6	2 - 17	4.10 ⁻⁶ - 2. 10 ⁻⁵
Beech Plot	17.6	1.4 - 7.7	0.3 - 0.5	0.7 - 1.3	13 -25	2000 - 13000	0.5 - 1	1 - 2.3	2.10 ⁻⁵ - 4.5 10 ⁻⁵

Ba, U, Th and Ra fluxes are calculated by using the Ca flux given in Poszwa et al. (2000) and the range of Ba/Ca, U/Ca, Th/Ca and Ra/Ca concentrations ratios estimated for aerial parts (needles, leaves and branches) of trees analysed in each plot.

Table 2b

	Flux kg/m ² /a	(U) µg/kg	(Th) µg/kg	(Ba) µg/kg	(Ra) µg/kg	U flux µg/m ² /a	Th flux µg/m ² /a	Ba flux µg/m ² /a	Ra flux µg/m ² /a
<i>Spruce (VP) plot : Litter^a</i>	0.3	2.2/19	5.9/59	10.1/13.8 10 ³	4	0.7/5.7	1.8/17.7	3/4.1 10 ³	0.62 10 ⁻⁵
Throughfall	1322	0.015±0.01	0.009±0.006	6±5	16	5.5±4	12±8	10±8 10 ³	2.1 10 ⁻⁵
soil solution (-5cm)	1246	0.03±0.01	0.11±0.05	13±6	59	37±17	137±65	16.6±8 10 ³	7.3 10 ⁻⁵
soil solution (-10cm)	1185	0.03±0.01	0.11±0.04	14±8	50	41±15	136±45	17.5±9.5 10 ³	5.6 10 ⁻⁵
soil solution (-30cm)	1119	0.03±0.01	0.04±0.01	30±9	7.5	32±7	48±11	35.±10.5 10 ³	0.8 10 ⁻⁵
soil solution (-60cm)	1107	0.012±0.01	0.005±0.004	10±4	22.6	13±10	6±4	11.3±4.2 10 ³	2.5 10 ⁻⁵
<i>Beech (HP) Plot : Litter^b</i>	0.4	3/15	8.2/35	12.3/16 10 ³	140	1.2/3	3.3/14	4.9/6.5 10 ³	17 10 ⁻⁵
Throughfall	1376	0.01±0.005	0.01±0.005	1.24±1	7.55	7±6	9±7	2±1.5 10 ³	1.03 10 ⁻⁵
soil solution (- 10cm)	1295	0.065±0.02	0.1±0.03	4.3±1.5	132	84±30	118±40	5.5±2 10 ³	17 10 ⁻⁵
soil solution (- 70cm)	1160	0.024±0.01	0.021±0.01	4.8±1.2	24	28±9	24±9	5.6±1.4 10 ³	2.7 10 ⁻⁵

A daily water balance model developed by Granier et al. (1999) has been used to estimate the soil drainage at different depths. This model simulates the dynamics of soil water depletion and recharge, and predicts the main components of forest water balance (at $\approx \pm 10\%$). ^a Litter Flux in Ignatova and Dambrine, 2010 ; ^b Litter flux in Rihs et al., 2011. The U, Th, and Ba concentrations are the 2004-2006 mean annual concentrations and the standard deviation from data given in Table EA 1. The Ra concentration data are the average of the few analyses obtained in the present study. For the litters, the fluxes are calculated with the concentrations analyzed in the litter samples, which can contain some soil materials. If using leaf or needle data (in italic in table), the calculated U and Th fluxes would be \approx one order of magnitude lower for U and Th.