

# Uranium in agricultural soils and drinking water wells on the Swiss Plateau

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## Abstract

Mineral phosphorus fertilizers are regularly applied to agricultural sites, but their uranium (U) content is potentially hazardous to humans and the environment. Fertilizer-derived U can accumulate in the soil, but might also leach to ground-, spring and surface waters. We sampled 19 mineral fertilizers from the canton of Bern and soils of three arable and one forest reference sites at each of four locations with elevated U concentrations (7–28  $\mu\text{g L}^{-1}$ ) in nearby drinking water wells. The total U concentrations of the fertilizers were measured. The soils were analysed at three depth intervals down to 1 m for general soil parameters, total Cd, P, U and  $\text{NaHCO}_3$ -extractable U concentrations, and  $^{234/238}\text{U}$  activity ratios (AR). The U concentrations and AR values of the drinking water samples were also measured. A theoretical assessment showed that fertilizer-derived U may cause high U concentrations in leaching waters (up to approx. 25  $\mu\text{g L}^{-1}$ ), but normally contributes only a small amount (approx. 0–3  $\mu\text{g L}^{-1}$ ). The arable soils investigated showed no significant U accumulation compared to the forest sites. The close positive correlation of AR with  $\text{NaHCO}_3$ -extractable U ( $R = 0.7$ ,  $p < 0.001$ ) indicates that application of fertilizer can increase the extractable U pool. The lack of depth gradients in the soil U concentrations (1.5–2.7  $\text{mg kg}^{-1}$ ) and AR (0.90–1.06) ratios are inconsistent with the accumulation of U in the surface soil, and might indicate some leaching of fertilizer-derived U. The AR values in the water samples were close to 1, possibly suggesting an influence of fertilizer-derived U. However, based on findings from the literature and considering the heterogeneity of the catchment area, the agricultural practices, and the

30 comparatively long distance to the groundwater, we conclude that fertilizer-derived U makes  
31 only a minor contribution to the elevated U concentrations in the water samples.

32

33 **Keywords:** Uranium, mineral fertilizer, soil, water, activity ratio

34 **Capsule:** Mineral fertilizer application causes an increase of  $\text{NaHCO}_3$ -extractable U in soil,  
35 and might significantly contribute to U concentrations in waters at background levels, but is  
36 probably only a minor contributor at high U concentrations in the waters of the Swiss Plateau.

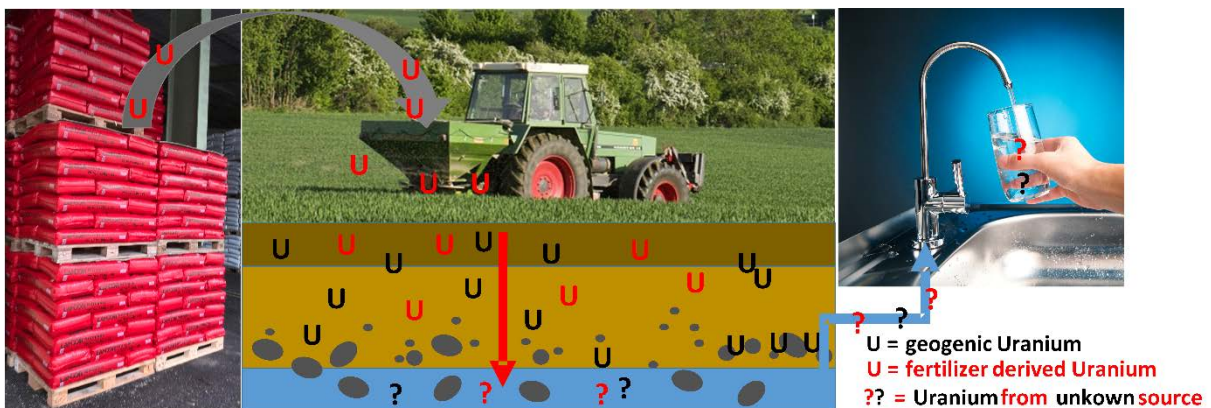
37 **Highlights:**

- 38 • Mineral P fertilizers contain high U concentrations.
- 39 • Mineral fertilization could cause high U concentrations in waters.
- 40 • The concentration of extractable U is linked to mineral fertilizer application.
- 41 • No accumulation in the surface soil might indicate partial leaching of U.
- 42 • Fertilizer-derived U is probably only of minor importance for water concentrations.

43

44

45 **Graphical Abstract**



## 49 **Introduction**

50 Mineral based phosphorous fertilizers are regularly applied to many agricultural sites, but often  
51 contain high concentrations of U. Depending on the soil conditions, fertilizer-derived U might  
52 be mobile and contaminate ground- and surface waters (Birke and Rauch, 2008; Huhle et al.,  
53 2008; Schnug and Lottermoser, 2013). Finally, the U may end up in drinking water, which is  
54 the major source for human uptake of toxic U (65%–95% of total U uptake; Schnug, 2012).

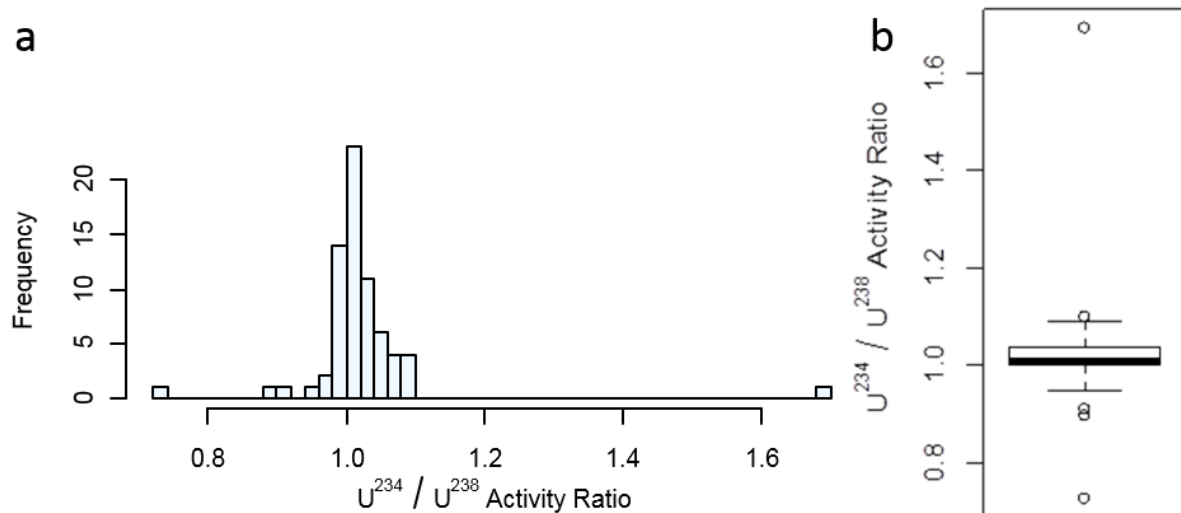
55 Mineral based phosphorous fertilizers are produced from phosphate rocks of igneous or  
56 sedimentary origin. Depending on the source, sedimentary phosphorites are heavily enriched  
57 in U (up to 280 mg kg<sup>-1</sup>; McLaughlin et al., 1996). During the process of fertilizer production, U  
58 is enriched in the fertilizers by up to 150% (Sattouf, 2007). Thus, different types of fertilizers  
59 (e.g. triple superphosphate and diammoniumphosphate) may have very different U contents  
60 (Table S1) depending on the source and type of production. When mineral based fertilizers  
61 are applied to soil, they are rapidly solubilized and the mobilized U can be sorbed to soil  
62 components, precipitated, or leached. Uranium binds to organic matter, Al and Fe oxides, clay  
63 minerals and soil organisms (Echevarria et al., 2001; Zheng et al., 2003; Zielinski et al., 2000).  
64 For soils with high clay and organic-matter content, U is anticipated not to migrate substantially  
65 (Rogasik et al., 2008). Accordingly, several studies have shown that long-term fertilization with  
66 mineral based P-fertilizers leads to substantial accumulation of U in soils, particularly topsoil,  
67 compared to unfertilized soils (Bigalke et al., 2017; Jones, 1992; Rogasik et al., 2008; Schipper  
68 et al., 2011; Takeda et al., 2005, 2006; Taylor, 2007; Wetterlind et al., 2012; Yamaguchi et al.,  
69 2009; Zielinski et al., 2006). In accordance with these findings, a number of authors have  
70 pointed to regional variations in concentrations of U in drinking water generally related to  
71 bedrock composition, even if the direct relationship might be complicated by groundwater flow  
72 through different rock formations (CCME, 2011; Stalder et al., 2012). However, a number of  
73 studies also found indications of U transfer from fertilizers to water bodies (Azouazi et al., 2001;  
74 Barisic et al., 1992; Conceicao and Bonotto, 2003; Huhle et al., 2008; Smidt et al., 2012;  
75 Zielinski et al., 2000). The influence of fertilizer-derived U inputs can be tested by comparing  
76 fertilized and unfertilized reference sites (Birke and Rauch, 2008; Huhle et al., 2008; Rogasik

77 et al., 2008) or from correlations between U and other fertilizer-derived components such as  
78 nitrate, K and B, especially in shallow drinking waters at agricultural sites (Knolle, 2008; Popit  
79 et al., 2004; Schäf et al., 2007; Smidt et al., 2012).

80 One important reason for the different findings in terms fertilizer U transfer to groundwaters is  
81 the U mobility in soils. The pH is one of the most important drivers of U mobility in soils  
82 (Echevarria et al., 2001; Tylor and Olsson, 2001). The lowest mobility of U is around pH 7 but  
83 mobility increases with decreasing pH because of decreasing number of binding sites and  
84 changes in U speciation. Depending on pH and the presence of organic and inorganic ligands  
85 such as phosphates ( $\text{PO}_4^{3-}$ ), carbonates ( $\text{CO}_3^{2-}$ ), sulphates ( $\text{SO}_4^{2-}$ ), chlorides ( $\text{Cl}^-$ ) or fluorides  
86 ( $\text{F}^-$ ) U forms stable complexes of different mobilities (Bourdon et al., 2003; Vandenhove et al.,  
87 2007). Especially under slightly alkaline and oxic conditions -as they are common in many  
88 Swiss agricultural fields- U is therefore quite mobile (Jacques et al., 2006). The presence of  
89 carbonates particularly increases the mobility of U in alkaline soils because U-carbonate  
90 complexes are predominantly neutral or negatively charged and have a low affinity for soil  
91 minerals (Echevarria et al., 2001; Read et al., 2008; Zheng et al., 2003). Besides pH and  
92 complexing agents the amount of possible binding sites (organic material, Fe oxides and clay)  
93 controls the possible U sorption (Rogasik et al., 2008). Depending on soil properties, U does  
94 or does not significantly accumulate in soils but is readily transferred to aquifers (Hamamo et  
95 al., 1995; Mortvedt, 1994), especially if the ground water table is close to the soil surface (Huhle  
96 et al., 2008) .

97 The  $^{234}\text{U}/^{238}\text{U}$  alpha activity ratio (AR) is a tool to relate U to its source directly. In an undisturbed  
98 closed system, as is assumed in a phosphate rock deposit, a secular equilibrium becomes  
99 established and AR levels approach 1 (Figure 1; Bourdon et al., 2003; Keith et al., 2007).  
100 Conversely, recoil processes and the spontaneous oxidation of  $\text{U}^{4+}$  to  $\text{U}^{6+}$  during decay are  
101 reasons for preferential leaching of  $^{234}\text{U}$  from soil, leaving it with  $\text{AR} < 1$  and the leaching water  
102 with  $\text{AR} > 1$  (Osmond and Cowart, 1976). The extent of  $^{234}/^{238}\text{U}$  disequilibrium depends on the  
103 characteristics of the disturbance and values of 0.8–10 in waterbodies, 0.8–8 in precipitation  
104 and 0.5–1.2 in soil have been reported (Keith et al., 2007). The contribution of fertilizer-derived

105 U to soils, surface and groundwater can therefore be recognized by a shift in AR towards 1,  
106 which has been successfully used in a number of studies to trace the sources of U in soil and  
107 water (Conceicao and Bonotto, 2003; Zielinski et al., 1997, 2000, 2006).



108

109 *Figure 1 a) Frequency distribution of AR in 65 mineral based P fertilizers; b) Boxplot of AR values of P*  
110 *fertilizers. The bold black line in the box, shows the median, the upper and lower end of the box show*  
111 *the upper and lower quantile. The whisker represent the lowest and highest value, which is still within*  
112 *1.5 times the interquartile range. Dots above and below the whiskers can be considered as outliers.*  
113 *Data from Baeza et al. (2011), Conceicao and Bonotto (2003), Gafvert et al. (2001), Guimond and*  
114 *Windham (1975), Makweba and Holm (1993), Mangini et al. (1979), Osmond and Cowart (1976),*  
115 *Sattouf (2007), Saueia and Mazzilli (2006), Taylor (2007) and Zielinski et al. (1997, 2000, 2006).*

116 To study the influence of fertilizer-derived U on concentrations in soils and its possible  
117 leaching, we sampled soils from four agricultural catchments that showed elevated U  
118 concentrations in drinking water wells. These areas are under intensive agricultural usage and  
119 there is no obvious source of the high U in the water wells. The aims of this study were to  
120 determine:

- 121 1. whether fertilizer-derived U has the potential to cause significantly elevated U  
122 concentrations in ground- and surface waters,
- 123 2. whether there is any indication of fertilizer-derived U enrichment in the agricultural soils  
124 and,
- 125 3. whether there is any indication of U leaching from the soils.

126

## 127 **Material and Methods**

### 128 **Study sites**

129 Four study locations in the canton of Bern, Switzerland were chosen because of the  
130 occurrence of elevated U concentrations in ground- and spring waters (Table 1) nevertheless  
131 the geology is very similar to other sites with low U in waters. The locations Oberwil bei Büren  
132 (pumping station at Rossmatt), Oberwil bei Büren (well at Rüti), Ins (well) and Walliswil (well)  
133 were selected. All locations are in the Swiss molasse basin (Figure S1). The agricultural fields  
134 and the nearby forest sites have similar underlying geology ([www.geo.admin.ch](http://www.geo.admin.ch)). The two  
135 locations in Oberwil bei Büren (Rossmatt and Rüti) are close to each other and the area is  
136 underlain by Quaternary unconsolidated rock, mainly till from the last glaciation (Würm). The  
137 forest at Rüti covers the same formation, and the forest at Rossmatt lies on the same formation  
138 but is close to Tertiary molasse (Lower Freshwater Molasse) of the Zinshölzli Formation under  
139 a thin Quaternary cover. The pumping station at Rossmatt pumps water from 40m depth. The  
140 water permeability is classified as normal for all fields, and the water-retention capacity is  
141 moderate to good. In Ins the agricultural fields and the forest site are situated on grey-green  
142 shell sandstones and marl of the Upper Marine Molasses. The springs are located on clayey  
143 marls, freshwater limestone and grey sandstones. The water permeability is characterized as  
144 normal with a good water-retention capacity. In Walliswil the area contains Quaternary  
145 unconsolidated rocks, probably from the last glaciation (Würm). The water permeability for the  
146 Walliswil sites is classified as excessive and the water-retention capacity as low. However, the  
147 forest site in Walliswil has a loose surface layer, the highest  $C_{org}$  concentrations, and a name  
148 indicating a historical peat land (Dängelmoos). In addition, local knowledge indicates that the  
149 forest site receives significant amounts of drainage water/surface runoff from other agricultural  
150 and forested sites. The water chemistry of all waters is dominated by dissolved  $Ca^{2+}$  (90-131  
151  $mg L^{-1}$ ) and  $Mg^{2+}$  (5.9-26.9  $mg L^{-1}$ ; total hardness 3.3 - 3.7  $mmol L^{-1}$ ), with less Na (3.3-16 and  
152 K (0.9-4.6 ) and has a neutral to slightly alkalic pH. The dominating soils are Cambisols, while  
153 at some sites also Luvisols might have formed (FAO, 2006). The depth of the ploughed surface  
154 horizon is between 25-30 cm, regular manure application is likely on most of the fields.  
155 Irrigation of the field sites is unlikely as mainly crops are grown which are not irrigated in this  
156 part of Switzerland (wheat, corn, grass etc.; Fuhrer 2014)

157

158 *Table 1: Uranium concentrations and AR in drinking water wells*

Location	Type of water (Concession volume [l min <sup>-1</sup> ])	Uranium concentration [ $\mu\text{g L}^{-1}$ ]	<sup>234/238</sup> U Activity Ratio
Rossmatt	Groundwater (101– 250)	27.97	1.22
Rüti	Spring tap 1 & 2 (315 & 370)	12.01	1.22
Walliswil	Groundwater (40)	7.4	-
Ins	Spring tap (40)	20.34	1.11
Ins Schlosshubel	Spring tap 1 (-)	8.13	1.05
	Spring tap 2 (40)	15.82	0.99
	Spring tap 3 (-)	12.39	1.06

159

160 **Sampling**

161 At each study site three agricultural fields and one forest were sampled. The arable sites were  
162 always located in the direct water protection area (inflow area) of the corresponding drinking  
163 water well. The information about the inflow areas are taken from the water protection maps  
164 (geoadmin.ch), and are mainly based on test with fluorescent tracers in the past (personal  
165 communication Bruno Schlup, responsible person for the Rüti Well). One nearby forest site  
166 was chosen at every location as an unfertilized reference site. At each of the sites soil was  
167 sampled with a soil auger down to 1 m depth in ten replicates evenly distributed over the sites.  
168 The samples from all sites were separated into subsamples from depths 0–30, 30–60 and 60–  
169 100 cm. In addition, for field C at Ins the last depth interval was subdivided because of obvious  
170 changes in colour and structure. One composited sample was prepared from the 10 replicates  
171 for each depth. In total twelve arable sites and four forest sites were sampled at three depth  
172 intervals. For analytical purposes nineteen commercially available fertilizers were bought from  
173 shops in the canton of Bern. In total six PK (phosphorous potassium), six superphosphates,  
174 six NP (nitrogen phosphorous) and one MKP (monopotassium phosphate) fertilizer were  
175 sampled. Water samples were collected from the pumping station and the water wells in plastic  
176 bottles, filtered (0.45 $\mu\text{m}$ ) and acidified ( $\text{HNO}_3$ ) directly after sampling.

177

178 **Soil characterization**

179 After sampling the 49 soils were dried at 40°C, aggregates were crushed and the sample was  
180 sieved to  $\leq 2$  mm using a stainless steel sieve. The pH was measured in 0.01-M  $\text{CaCl}_2$  with a  
181 soil solution ratio of 1:2.5 after 2 h using a glass pH electrode. To determine the effective cation  
182 exchange capacity (ECEC) and base saturation, 5 g of soil was extracted in 100 ml of 1 M  
183 ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) solution on a horizontal shaker for 1 h. The concentrations of  
184 calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), manganese (Mn) and aluminium  
185 (Al) were measured with flame atom absorption spectrometry (ZEE nit 700P, Analytik Jena).  
186 ECEC was then calculated as the sum of the charge of the exchangeable  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  
187  $\text{Al}^{3+}$  and  $\text{Mn}^{2+}$  ions, and is expressed in  $\text{mmol}_c \text{ kg}^{-1}$ . Base saturation was calculated as the  
188 percentage of the charge of basic cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$ ) of the ECEC.

189 For texture analysis an aliquot of the soil was oxidized by heating with  $\text{H}_2\text{O}_2$  to remove all  
190 organic material. Samples were then washed and finally dispersed in a sodium  
191 hexametaphosphate/sodium carbonate solution. Particle-size distribution was measured using  
192 a laser diffraction particle-size analyser (Mastersizer 2000, Malvern, Herrenberg, Germany).  
193 The average relative standard deviation of repeated samples was 8%. For total element  
194 concentrations and analysis of carbon, nitrogen and sulphur (CNS), an aliquot of each soil  
195 sample was ground in a ball mill in agate beakers (PM 200, Retsch GmbH, Haan, Germany).  
196 Rock samples were crushed using a jaw breaker and ground with the same ball mill. The CNS  
197 concentrations were analysed by elemental analysis (vario EL cube, Elementar  
198 analysesysteme, Hanau, Germany) on both 550°C-heated (only inorganic C) and untreated  
199 (organic and inorganic C) samples: the amount of organic C ( $\text{C}_{\text{org}}$ ) was calculated from the  
200 difference between the two values.

201

202 **U analysis**

203 The extractable U fraction was extracted in 0.5 mol  $\text{NaHCO}_3$  (pH 8.5) after 16 h of shaking at  
204 a soil/solution ratio of 1:60. After shaking the sample was filtered (Whatman, Grade 589/2) and  
205 the supernatant was analysed for U concentrations. Total digestions were performed in a



206 microwave oven with 0.1 g of pulverized sample, 0.5 ml H<sub>2</sub>O<sub>2</sub> (30%), 2 ml HF (40%) and 2 ml  
207 HNO<sub>3</sub> (69%) at 200°C for 40 minutes. A second run was carried out after adding 10 ml of 6%  
208 boric acid (H<sub>3</sub>BO<sub>3</sub>), at 180°C for 30 minutes to complex the remaining HF. Total digestions of  
209 fertilizers were undertaken in 8 ml HNO<sub>3</sub> (69%) and 2 ml H<sub>2</sub>O<sub>2</sub> (30%) in a microwave oven at  
210 200°C. Total element concentrations were measured using an inductively coupled plasma  
211 mass spectrometer (ICP-MS; 7700x, Agilent Technologies, Palo Alto, CA) with <sup>103</sup>Rh and <sup>115</sup>In  
212 as internal standards. The applied method was tested using standard reference material  
213 (BCR-2, United States Geological Survey, Reston, Virginia) and showed good agreement  
214 between measured (1.73±0.08 mg kg<sup>-1</sup>, n = 4) and certified (1.69±0.19 mg kg<sup>-1</sup>) values.

215 For the AR analysis, 0.1 g of the pulverized samples were weighed in Savillex beakers and  
216 heated on a hotplate in 2.4 ml HF (40%) and 0.8 ml HNO<sub>3</sub> (69%, 3:1 ratio) for 48 h. The digest  
217 was dried down and the remaining residues treated with 750 µl HCl and 250 µl HNO<sub>3</sub> (3:1  
218 ratio) and evaporated. The samples were redissolved in 4 ml of 3 M HNO<sub>3</sub> and purified  
219 following the method of Weyer et al. (2008) on UTEVA (Eichrom Technologies Inc.) U specific  
220 resin. We modified the method using 9 M HCl to convert the columns from the nitric to the  
221 chloric system as proposed by the manufacturer of the columns (Eichrom Technologies Inc.,  
222 2005). The purification procedure showed good separation of U (Figure S2). In total, 99% of  
223 the total eluted U was collected in the U fraction and the concentrations of Th and Fe were  
224 less than 0.1% of that of U. Recovery rates for the BCR-2 reference material after column  
225 purification were 90%±9% (n = 3), comparable to the results of Grinberg et al. (2005). The  
226 recoveries were considered sufficient because the isotope ratio is not affected by the  
227 separation process (Weyer et al., 2008). The total blank of the method was <0.4% of the lowest  
228 concentrations in a sample.

229 Isotope ratios were analysed on the same Quadrupole ICP-MS as was used for the element  
230 concentrations. Before analysis, all standards and samples were diluted to a concentration of  
231 12.5 µg L<sup>-1</sup> and the instrument settings were adjusted to allow highly accurate U isotope  
232 analysis (five replicates, 1000 sweeps/replicate, integration time 0.3, 0.3, 0.99, 50.01, 5.01  
233 and 0.99 seconds for mass 103, 115, 232, 234, 235 and 238, respectively). <sup>103</sup>Rh and <sup>115</sup>In

234 were used as internal standards and  $^{232}\text{Th}$  was monitored to detect possible interference. The  
235 isotope ratio was mass bias corrected using the standard bracketing method (Albarède and  
236 Beard, 2004). IRMM 3184 (Institute for Reference Materials and Measurements, Geel,  
237 Belgium) was used as the bracketing standard. The measured isotope ratios were transformed  
238 to activity ratios using the specific activity of each isotope. We repeatedly analysed BCR-2 for  
239 quality control. The results ( $1.000 \pm 0.004$ , mean  $\pm$  SD,  $n = 12$ ) agree well with the values of  
240  $1.000 \pm 0.001$  reported by Beier et al. (2010a, b) and of  $1.001 \pm 0.002$  reported by Keech et al.  
241 (2013). The overall reproducibility was similar for the BCR ( $\pm 0.004$ , SD,  $n = 12$ ), an in house  
242 standard ( $\pm 0.004$ , SD,  $n = 6$ ) and repeated sample digests ( $\pm 0.007$ , SD,  $n = 6$ ) and sufficient  
243 at the overall variation of AR in the samples (0.906-1.065).

244

#### 245 **Assessment of possible U leaching**

246 Using available information about fertilizer use in Switzerland (Agristat, 2013; BLW, 2014;  
247 GRUDAF, 2009) and the U concentrations in the fertilizers, estimates of U leaching were  
248 obtained on an annual basis. The estimate of the possible contribution of fertilizer-derived U  
249 to the U concentration in water was based on certain assumptions. Two scenarios were tested.  
250 The first scenario, the “average scenario”, was based on average values for fertilizer  
251 application (GRUDAF, 2009), U content in the fertilizer (Figure 2), leaching rate and infiltration  
252 rate (von Gunten, 2000). A second estimate was calculated using a “high scenario” with a high  
253 fertilizer application rate (for fodder beet, the culture with the highest P demand according to  
254 GRUDAF [2009]). A correction factor of 1.25 was applied, what means that 25% more fertilizer  
255 can be applied to compensate for lower than normal P concentrations in the soil. For the high  
256 scenario, a fertilizer with high U concentration (90<sup>th</sup> percentile, Figure 2), the maximum  
257 leaching rate and a high infiltration rate was assumed (von Gunten, 2000). The maximum  
258 correction factor for P fertilization according to GRUDAF (2009) was not applied because it  
259 seems unlikely that a P-demanding crop is cultivated on a field where such a correction factor  
260 would apply. The infiltration on the Swiss Plateau is  $250\text{--}700 \text{ mm a}^{-1}$  (Von Gunten, 2000).

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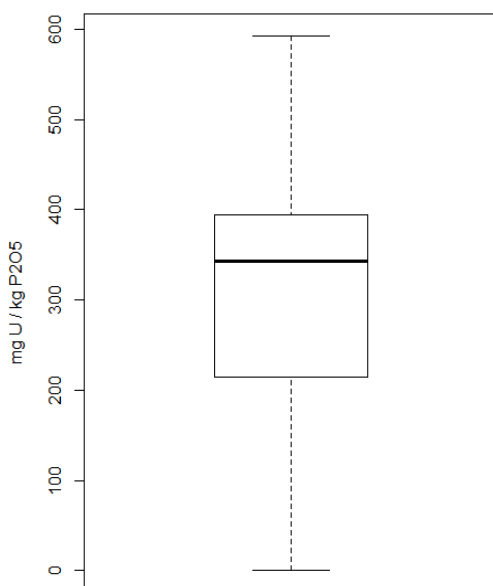
## 262 **Statistical Analysis and geochemical mass balancing**

263

264 Differences between groups (e.g., between forest and arable soils) were tested using a two  
265 sided t test.

266 Geochemical mass balances of U were calculated as  $\tau$ -values following Brimhall et al. (1992)  
267 using Ti as an immobile element. The  $\tau$ -value is a measure for the depletion (negative value)  
268 or enrichment (positive value) of an element in a soil relative to the bedrock and corrected with  
269 an immobile element. A  $\tau$ -value of 0.5 for example would indicate an enrichment of U by 50%  
270 compared to the bedrock.

271



272

273 *Figure 2: Boxplot of U concentrations in 19 mineral based P-fertilizers sampled in the canton of Bern.*  
274 *The bold black line in the box, shows the median and the upper and lower end of the box show the*  
275 *upper and lower quantile. The whisker represent the lowest and highest value, which is still within 1.5*  
276 *times the interquartile range.*

277

## 278 **Results**

279 The mean U concentration in the analysed fertilizers was 294 mg kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>; the median value  
280 was 343 mg kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub> (Figure 2, Table S1). The lowest and highest U concentrations were  
281 0.21 and 593 mg kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>. The mean and median U concentrations compared to the dry  
282 weight of fertilizer were 77.8 and 69.6 mg kg<sup>-1</sup>, with a range of 0.11–188 mg kg<sup>-1</sup>. Comparably

283 high concentrations were detected for PK (mean 386 mg kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>; n = 4), superphosphate  
 284 (mean 358 mg kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>; n = 4) and NP-fertilizers (mean 348 mg kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>; n = 4), whereas  
 285 DAP U concentrations were one order of magnitude lower (mean 25.1 mg kg<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>; n = 3).  
 286 The assessment of the possible contributions of fertilizer-derived U to the U concentrations of  
 287 leaching water indicated significant contributions (Table 2), compared to concentrations in  
 288 Swiss drinking waters (median 0.77 µg L<sup>-1</sup>; Stalder et al., 2012). However, even in the rather  
 289 unlikely high scenario, fertilizer-derived U does not cause exceedance of the World Health  
 290 Organisation (WHO) threshold level for drinking water (30 µg L<sup>-1</sup>).

291

292 *Table 2: Estimation of the possible contribution of mineral based P fertilizers to U in ground-*  
 293 *and well water.*

	<b>“Average” scenario</b>	<b>“High” scenario</b>
Mineral based fertilizer application rate	36.8 kg P <sub>2</sub> O <sub>5</sub> ha <sup>-1</sup>	150 kg P <sub>2</sub> O <sub>5</sub> ha <sup>-1</sup>
U concentration in fertilizer	294 mg kg <sup>-1</sup> P <sub>2</sub> O <sub>5</sub>	509 mg kg <sup>-1</sup> P <sub>2</sub> O <sub>5</sub>
U input via fertilization	10.8 g ha <sup>-1</sup>	76.4 g ha <sup>-1</sup>
Infiltration rate	600 mm a <sup>-1</sup>	300 mm a <sup>-1</sup>
Leaching amount	50%	100%
<b>U concentration in leaching water</b>	<b>1.80 µg L<sup>-1</sup></b>	<b>25.5 µg L<sup>-1</sup></b>

294

295

296 The forest soils showed generally lower pH and ECEC values than the arable soils. Only the  
 297 Walliswil arable sites exhibited lower pH and ECEC values than the forest site (Table 3). The  
 298 deviation in soil properties and AR in the Walliswil forest site can be explained by the fact  
 299 that the soil was located at slightly lower elevation than the arable area and probably  
 300 received leaching water that was enriched in nutrients, carbonate and U with AR > 1. High  
 301 soil moisture caused a relative accumulation of organic carbon (Table 3), which could lead to  
 302 U sorption to organic compounds or precipitation under anaerobic conditions in the peat  
 303 (Regenspurg et al., 2010). This was also confirmed by the visual impression of the site at the

304 time of sampling. The topsoil had quite a large organic overlay, probably caused by reduced  
305 decomposition under wet conditions. The name of the site (Dänglermoos) and personal  
306 communication with farmers indicate that the area is a former peatland. A cluster analysis  
307 based on the soil properties of all soils confirmed that the Walliswil forest site is different from  
308 all other soils. Because of these extraordinary features, the forest site at Walliswil was  
309 excluded from further comparison and is not included in Figures 3–4.

310 In contrast,  $C_{\text{org}}$  was always higher in the forest topsoils. Except for these differences, forest  
311 soils did not differ from agricultural soils. The difference in the mean U concentration between  
312 fields and forests of  $0.15 \text{ mg kg}^{-1}$  (Figure S3, S4) was statistically not significant ( $p = 0.21$ ),  
313 which might, however, also be attributable to the small number of samples (especially for the  
314 forest sites) and the variation between the individual sites. The  $U_{\text{NaHCO}_3}$  concentrations also  
315 exhibited a tendency to be higher at arable sites compared to forest soils, but this difference  
316 was not significant at all depths (Table 3). The  $\tau_U$  values tend to be lower in forests compared  
317 to agricultural fields at each individual site except Walliswil, although these differences are  
318 only marginally statistically significant ( $p = 0.07$ ). The difference was about 0.2 over the whole  
319 depth of the profile, indicating about 20% more loss of U at the forest sites (Figure 3a). In  
320 addition, Cd, which has a high concentration in mineral based P-fertilizers (McLaughlin et al.,  
321 1996), exhibited no significant enrichment in the arable sites compared to the forest ones ( $p =$   
322  $0.77$ ; Figure 3b), whereas this difference was highly significant for P down to 60 cm depth (0–  
323 30 cm,  $p = 0.001$ ; 30–60 cm,  $p < 0.001$ ; Figure 3c).

324 The AR values were generally not different or higher in agricultural topsoils compared to  
325 subsoils (Figure S5, S6, Table 3). Compared to forest soils, the AR values at the agricultural  
326 sites were only consistently higher in Rossmatt, but were overlapping in Ins and Rüti and  
327 clearly lower in Walliswil. Overall, there is a highly significant correlation ( $p < 0.001$ ) between  
328 the amount of extractable U and AR (Figure 4). However, for individual sites the correlation is  
329 significant for Rossmatt ( $p < 0.001$ ), Walliswil ( $p < 0.001$ ), and marginally significant for Ins ( $p$   
330  $= 0.08$ ) but not significant for Rüti ( $p = 0.62$ ; Figure S4). The AR values in the well water were  
331 between 0.99 and 1.22 (Table 1).

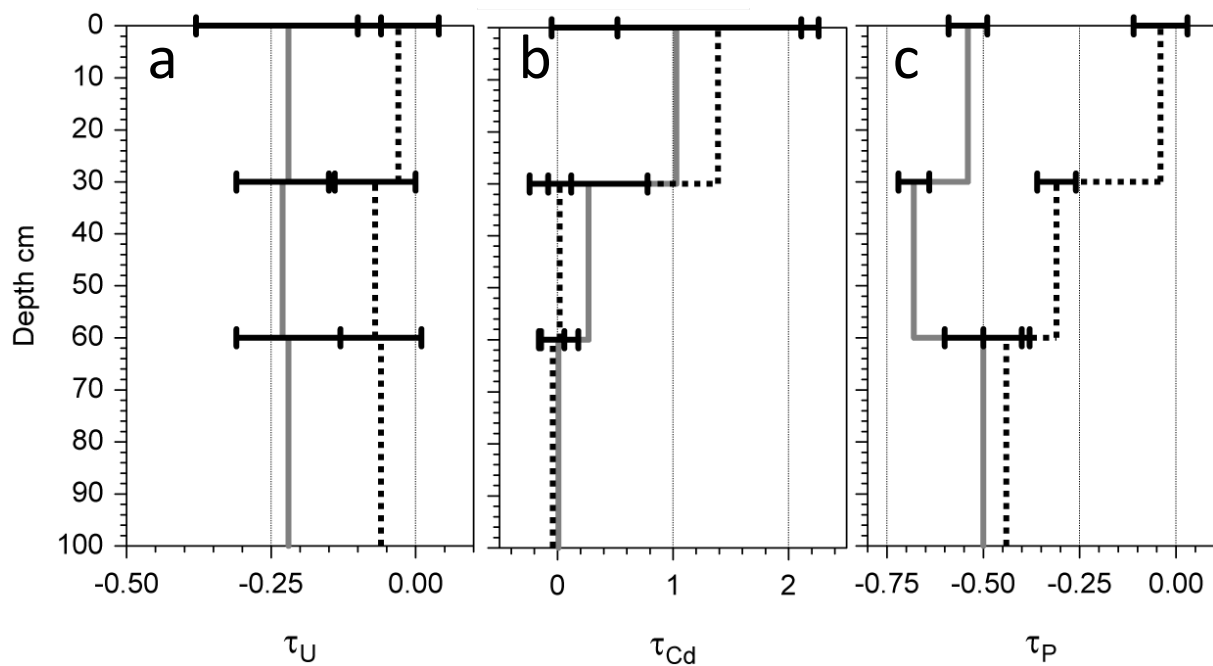
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Table 3 Soil properties, concentrations of selected elements and <sup>234/238</sup>U activity ratios of all soils.

Site	Field	Depth [cm]	pH	CEC [mmol kg <sup>-1</sup> ]	Base sat.	Clay	Silt	Sand	C <sub>org</sub>	P	Cd	Th	U <sub>total</sub>	U <sub>NaHCO<sub>3</sub></sub>	<sup>234/238</sup> U Activity Ratio	SD
Oberwil Rossmatt	Forest	0-30	3.9	34	42	10	35	56	1.70	389	0.14	6.85	2.02	0.13	0.940	0.005
		30-60	4.0	27	30	7	25	68	0.62	248	0.09	6.30	1.54	0.14	0.937	0.002
		60-100	6.4	151	100	9	31	60	0.26	304	0.11	7.66	1.68	0.05	0.930	0.004
	Field A	0-30	5.1	67	99	8	39	53	1.31	741	0.23	5.96	2.29	0.24	1.001	0.004
		30-60	5.4	74	99	7	37	56	0.83	511	0.17	6.29	2.17	0.25	0.994	0.006
		60-100	6.8	-	100	9	43	48	0.51	294	0.13	5.64	1.89	0.22	0.999	0.001
	Field B	0-30	5.5	64	99	8	35	57	1.24	708	0.20	6.08	1.99	0.30	1.007	0.023
		30-60	5.5	63	99	7	34	58	0.63	584	0.17	6.77	1.93	0.17	0.964	0.001
		60-100	5.5	68	100	6	30	64	0.34	582	0.17	6.75	1.86	0.14	0.967	0.001
	Field C	0-30	5.6	101	100	10	43	47	1.67	612	0.18	5.62	1.64	0.57	1.054	0.005
		30-60	5.8	81	100	9	37	55	0.96	532	0.17	6.21	2.06	0.32	1.046	0.006
		60-100	5.8	68	100	8	34	58	0.45	438	0.14	6.82	1.94	0.49	1.036	0.004
Rock	-	-	-	-	-	-	-	-	707	0.11	3.79	1.21	-	0.922	0.005	
Walliswil	Forest	0-30	6.2	-	100	7	38	55	4.36	903	0.40	5.81	2.03	0.37	1.006	0.004
		30-60	6.4	-	100	9	41	50	2.49	890	0.25	6.86	2.50	0.55	1.036	0.006
		60-100	6.4	-	100	9	45	46	1.52	806	0.26	7.02	2.52	0.69	1.065	0.007
	Field A	0-30	5.4	64	99	8	55	37	1.31	871	0.20	7.10	2.23	0.24	0.975	0.004
		30-60	5.1	52	100	9	58	33	0.75	758	0.18	8.50	2.21	0.18	0.956	0.001
		60-100	5.0	64	100	6	44	50	0.35	476	0.12	8.73	2.17	0.15	0.939	0.000
	Field B	0-30	5.2	75	99	10	40	51	2.53	1222	0.22	6.73	1.95	0.20	0.966	0.002
		30-60	5.1	51	100	8	34	58	1.37	814	0.17	6.77	1.76	0.18	0.959	0.005
		60-100	5.3	43	99	12	37	52	0.63	565	0.13	7.32	2.09	0.15	0.906	0.002
	Field C	0-30	5.5	72	100	10	41	49	1.81	1386	0.27	5.94	1.96	0.31	0.968	0.000
		30-60	5.0	37	99	9	34	57	1.04	792	0.20	6.16	1.85	0.21	0.962	0.005
		60-100	5.1	38	99	7	33	60	0.46	453	0.43	7.47	1.95	0.15	0.945	0.003
Rock	-	-	-	-	-	-	-	-	699	0.21	4.03	0.97	-	0.985	0.005	
Oberwil Rüti	Forest	0-30	4.3	41	83	7	40	53	1.50	303	0.14	6.37	1.82	0.19	0.980	0.003
		30-60	4.4	59	89	7	49	43	0.48	256	0.33	8.68	2.20	0.19	0.972	0.004
		60-100	4.8	86	93	6	51	43	0.16	423	0.19	9.57	2.38	0.11	0.980	0.002
	Field A	0-30	5.1	63	95	6	40	54	1.02	685	0.42	6.40	2.11	0.24	0.971	0.012
		30-60	5.4	82	93	7	43	51	0.32	395	0.16	8.18	2.40	0.17	0.973	0.005
		60-100	5.6	93	100	7	52	41	0.12	466	0.17	9.03	2.43	0.14	0.963	0.004
	Field B	0-30	6.0	91	100	8	52	40	1.27	737	0.39	7.43	2.33	0.20	0.949	0.003
		30-60	5.7	87	100	5	37	58	0.67	521	0.16	8.75	2.20	0.13	0.954	0.001
		60-100	6.9	89	100	8	55	37	0.23	607	0.17	5.19	1.97	0.11	0.903	0.002
	Field C	0-30	5.8	95	100	9	49	42	1.03	782	0.18	7.12	2.24	0.21	0.964	0.002
		30-60	5.9	94	100	8	45	47	0.33	713	0.18	7.65	2.21	0.18	0.959	0.005
		60-100	5.7	89	100	7	47	46	0.18	551	0.19	8.49	2.42	0.13	0.933	0.001
Rock	-	-	-	-	-	-	-	-	531	0.12	5.82	2.25	-	0.969	0.003	
Ins	Forest	0-30	3.9	59	47	10	47	44	1.69	341	0.31	5.24	1.89	0.23	0.986	0.006
		30-60	4.1	42	92	8	42	49	0.56	227	0.08	7.03	2.34	0.25	0.979	0.004
		60-100	4.6	92	99	10	45	44	0.26	482	0.10	9.42	2.64	0.23	0.967	0.006
	Field A	0-30	4.5	68	99	6	33	60	1.22	501	0.10	6.01	1.58	0.21	0.979	0.013
		30-60	5.1	76	99	6	34	60	0.81	540	0.08	7.66	1.79	0.16	0.965	0.004
		60-100	5.2	89	100	5	29	66	0.65	501	0.07	8.37	1.95	0.13	0.971	0.008
	Field B	0-30	5.7	91	100	8	39	53	0.95	641	0.15	5.85	2.19	0.37	0.976	0.021
		30-60	5.7	97	100	9	38	53	0.55	438	0.12	6.64	2.47	0.51	0.989	0.006
		60-100	5.9	-	100	9	41	50	0.29	362	0.10	7.52	2.69	0.40	0.987	0.006
	Field C	0-30	6.0	73	100	8	41	51	0.95	506	0.80	6.00	2.14	0.25	0.998	0.004
		30-60	5.9	66	100	10	42	48	0.63	371	0.10	6.05	1.96	0.22	0.993	0.001
		60-90	5.8	82	100	7	40	53	0.27	286	0.08	7.15	2.32	0.17	1.006	0.010
90-100	5.9	95	100	9	48	43	0.18	258	0.08	7.69	2.31	0.17	1.000	0.003		
Rock	-	-	-	-	-	-	-	-	372	0.04	7.12	1.98	-	0.954	0.001	



337

338 *Figure 3 The a)  $\tau_U$ , b)  $\tau_{Cd}$  and c)  $\tau_P$  values of the field and forest soils. Solid grey lines denote*  
 339 *forest sites; dotted black lines represent arable fields.*

340

## 341 Discussion

### 342 General assessment of the possible impact of fertilizer-derived U on drinking water.

343 The possible effect of fertilizer-derived U on soils and leaching water has been assessed based  
 344 on the U concentrations in the investigated mineral based fertilizers (Figure 2), official  
 345 fertilization recommendations for different crop types, infiltration rates from the literature, and  
 346 assumed leaching rates, for both an average and a high scenario (Table 2).

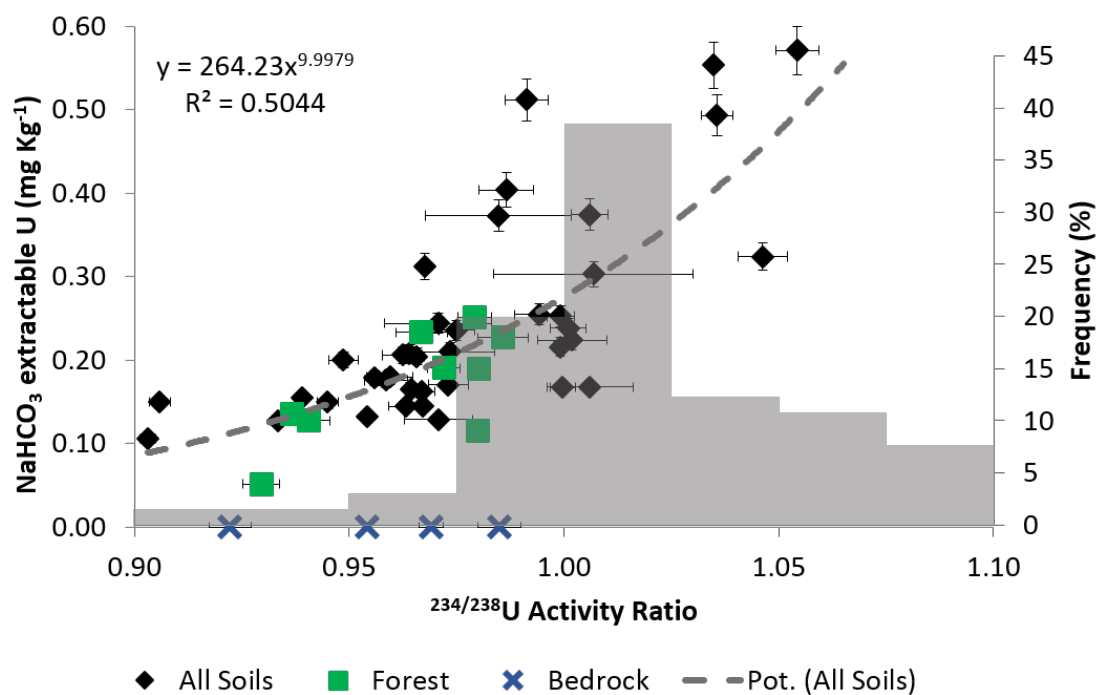
347 The assumed U input via fertilization for the average scenario falls well within the range of  
 348 literature values: 0.13–61 g ha<sup>-1</sup> (Kratz et al., 2008) and 2.8–16 g ha<sup>-1</sup> a<sup>-1</sup> (Uterman and Fuchs,  
 349 2008) in Germany; 15 and 16 g ha<sup>-1</sup> a<sup>-1</sup> at two sites in England and New Zealand (Rothbaum  
 350 et al., 1979). The values in the high scenario seem reasonable, as U application in Switzerland  
 351 has been reported to reach up to 110 g ha<sup>-1</sup> a<sup>-1</sup> for certain sites with high-P-demand crops and  
 352 purely mineral based fertilization in certain years (Bigalke et al., 2017). The most critical aspect  
 353 of the assessment of U concentrations in leaching water is surely the amount of U leached. In  
 354 this study, 50% or even 100% is probably an overestimation for most sites; however, the 100%  
 355 approach is taken to estimate the maximal possible fertilizer-derived U concentration in  
 356 leaching water.



357 Uranium output by plant uptake and crop harvesting was estimated to be less than  $1 \text{ g ha}^{-1}$   
358 (Kratz et al., 2008), leaving  $9.8\text{--}75 \text{ g ha}^{-1} \text{ a}^{-1}$  in either the soil or leachates (Table 2).  
359 Translating this into an increase in U concentration in the topsoils (30cm depth, density  $1 \text{ kg}$   
360  $\text{cm}^{-3}$ ) yields a value of  $3.3\text{--}25 \text{ }\mu\text{g kg}^{-1} \text{ a}^{-1}$ , in good agreement with the compiled annual U  
361 accumulation rates in topsoil (0-20 or 0-30 cm depth) of  $1\text{--}46 \text{ }\mu\text{g kg}^{-1}$  from long-term  
362 fertilization experiments (Rogasik et al., 2008, Taylor and Kim, 2008). This similarity of U inputs  
363 and enrichment in soil indicates that a considerable amount of the applied U is retained in the  
364 soil. However, Barisic et al. (1992) estimated that 20% of applied fertilizers are transported to  
365 drainage channels, whereas Conceicao and Bonotto (2003) assumed that 30%–43% of U in  
366 river water is derived from fertilizer application. Furthermore, Rogasik et al. (2008) detected  
367 strong differences in the accumulation rates related to different soil properties; conversely,  
368 certain soils did not immobilize U to the same extent as others. Therefore, estimation of  
369 leached U is quite difficult because of the high uncertainty and lack of measured values. The  
370 estimations (Table 2) illustrate that under extreme circumstances (e.g., shallow groundwater,  
371 sandy soil, high-P-demand crop, high U concentration in fertilizer) fertilizer-derived U might  
372 cause the U concentration in groundwater to be close to the WHO threshold value and to  
373 exceed the threshold for drinking water of some countries (e.g., Germany,  $10 \text{ }\mu\text{g L}^{-1}$ ). However,  
374 while we assume these extreme cases to be rare, under normal circumstances fertilizer-  
375 derived U will not reach values close to the Swiss threshold values but might however  
376 significantly contribute to U concentrations in normal Swiss groundwater (median values in  
377 Switzerland are  $0.77 \text{ }\mu\text{g U L}^{-1}$ ; Stalder et al., 2012).

378 Our results fit published results from the literature as an increase in U concentrations in ground  
379 water derived from fertilizers has also been shown also in a number of other studies (Azouazi  
380 et al., 2001; Barisic et al., 1992; Birke and Rauch, 2008; Conceicao and Bonotto, 2003; Huhle  
381 et al., 2008; Zielinski et al., 2000). As an example, near-surface groundwater is 3–17-fold  
382 enriched in U in agricultural areas (Huhle et al., 2008) and U concentrations in water in the  
383 former West Germany are reported to be higher than in water in the former East Germany  
384 ( $0.741$  and  $0.462 \text{ }\mu\text{g L}^{-1}$ , respectively). The latter has been explained by the lower intensity of

385 P-fertilization and lower U concentration (P from igneous rocks; Birke and Rauch, 2008; Schulz  
 386 et al., 2003). In a broad study of U concentrations in drinking water in Switzerland it was  
 387 determined that elevated concentrations (up to 100  $\mu\text{g L}^{-1}$ ) were only attributable to geological  
 388 factors (Stalder et al., 2012). However, for that study important cantons (e.g., Bern, where our  
 389 study sites are located) on the Swiss Plateau were not included and fertilizer-derived U was  
 390 not considered as a source of U. Other studies investigated high U concentrations in surface  
 391 waters and found geological factors to be responsible for the elevated concentrations (Banning  
 392 et al., 2013; Schott and Wiegand, 2003; Zielinski et al., 1995, 1997).



394 *Figure 4: Exponential relationship between AR and NaHCO<sub>3</sub>-extractable U fraction. The grey*  
 395 *bars are the frequency (%) histogram of fertilizer AR values (Figure 1).*

396

### 397 **Enrichment and sources of U in agricultural soils**

398 Although in our study area U was not significantly enriched at the arable sites (Figures S3),  
 399 comparable studies reported significant enrichments of 0.1–1.3 mg U kg<sup>-1</sup> in fertilized soils  
 400 (Ahmed et al., 2014; Bigalke et al., 2017; Huhle et al., 2008; Rogasik et al., 2008; Rothbaum  
 401 et al., 1979; Taylor, 2007). The reasons for the broad range might be different sampling depths,  
 402 different fertilization rates (up to 500–600 kg triple superphosphate ha<sup>-1</sup> a<sup>-1</sup>; Taylor, 2007),

403 different U concentrations in the fertilizers and different soil properties (pH, organic matter,  
404 redox conditions; Rogasik et al., 2008; Rothbaum et al., 1979). However, many of the soils in  
405 the studies received mineral based P-fertilizers annually, whereas in the studied soils, manure  
406 application might account for a significant part of the fertilization. Insignificant U accumulation  
407 in the surface soil at the studied sites might be partly attributable to surface erosion or leaching  
408 of U from the soil.

409 In Rossmatt, Rüti and Ins the AR values of the forest soils are close to those of the local  
410 bedrock, but some arable soils exhibit significant deviations (Figures S5, S6, Table 3).  
411 Although soil formation should normally lead to AR values smaller than that of the bedrock,  
412 this is only the case for Walliswil (except Walliswil forest soils) and Rüti. In contrast Rossmatt  
413 and Ins show higher AR compared to the bedrock, indicating higher proportions of fertilizer-  
414 derived U, which overcompensate for the weathering effect on the AR (Figures S5, S6).

415 The overall correlation between extractable U and AR indicates a link between high fertilizer  
416 U input and the amount of weakly bound U in the soil. As the  $\text{NaHCO}_3$ -extractable U has a  
417 higher mobility compared to the rest of the total U, this correlation indicates a contribution of  
418 fertilizer derived U to U leaching. The lack of correlation for the Rüti and Ins site might be  
419 caused by the topography of the sites. The sites are located on top- and midslope positions and  
420 erosion might eliminate clear patterns because of constant loss of surface soil. On the other  
421 hand lateral water flow down the slope might affect AR, because of leaching water with  $\text{AR} > 1$ ,  
422 which might be sorbed and increase AR of the soil at positions down the slope.

423

#### 424 **Leaching of U in fertilized soils**

425 The distributions of U concentrations,  $\tau_U$  values and AR values do not exhibit obvious depth  
426 gradients (Figures 3, 4, S3-S6). In contrast, the depth gradient is very significant for P, the  
427 main component of the mineral based P-fertilizers (Figure 3, Table S1). These differences  
428 might be attributable to the much higher P contents compared to the U contents of the  
429 fertilizers and the different background concentrations in the soil and to manure fertilization,  
430 with low U contents. Assessment of the possible U input in the topsoil (0-30 cm) from the P

431 enrichment in the topsoil, based on the mean U concentrations of the fertilizers (Figure 2)  
432 suggests the U enrichment in the topsoil compared to the subsoil would be around 0.25 mg  
433 kg<sup>-1</sup>. This is close to our (non-significant) mean difference of 0.15 mg kg<sup>-1</sup> between forest  
434 and agricultural sites and to U enrichments reported in Swiss agricultural topsoil compared to  
435 subsoils (mean 0.19 mg kg<sup>-1</sup>; Bigalke et al., 2017). However, while it is well known that high  
436 amounts of P are extracted from the soil by plant growth and exported from the soil via  
437 harvest, this is not the case for U. Conversely, manure can provide significant inputs of P  
438 without adding large amounts of U to the soil. The mean AR ratios show a tendency to be  
439 higher in the arable soils, but clearly overlap with the AR values of forest soils and bedrock.  
440 Overall, the lack of a U depth gradient indicates a lack of accumulation in the topsoil and thus  
441 might suggest U leaching or erosion. However, U might also be sorbed in deeper soil and  
442 rock layers, depending on the solution chemistry and speciation of U, and will not necessarily  
443 end up in ground- and spring water. In the literature, fertilizer-derived U concentrations in  
444 ground- and surface waters were mostly estimated to be <0.5 µg L<sup>-1</sup> (Birke and Rauch, 2008;  
445 Conceicao and Bonotto, 2003; Zielinski et al., 2006) but may reach up to 3.4 µg L<sup>-1</sup> in  
446 drainage water and near-surface groundwater directly in arable fields (Huhle et al., 2008;  
447 Zielinski et al., 2000). However, at our study sites the ground- and spring water reservoirs are  
448 comparatively deep (many sorption sites), some fertilization was in the form of manure, and  
449 not all of the catchment was covered by arable sites. Thus, we assume that contribution to  
450 groundwater would rather be lower than the average scenario we calculated (Table 2). From  
451 these assumptions, we roughly estimate that leaching of fertilizer-derived U to ground- and  
452 spring water is probably less than approx. 2 µg L<sup>-1</sup>. Comparing this value to the elevated U  
453 concentrations in the wells, it becomes clear that there must be additional sources for the  
454 elevated U concentrations.

455 The AR values in natural, unpolluted water samples are 1–4, while a value close to 1 might  
456 indicate fertilizer-derived U in the water (Zielinski et al., 1997, 2000, 2006). Thus, the AR  
457 values in the waters at our study sites (Table 1) might indicate fertilizer-derived U input, but  
458 also a geological basis cannot be excluded.

459

## 460 **Conclusions**

- 461 • Fertilizer-derived U can theoretically cause high U concentrations in waters under  
462 extreme conditions, but normally the contribution is rather low (approx.  $<2 \mu\text{g L}^{-1}$ ).  
463 Higher concentrations in waters are normally associated with geogenic inputs.
- 464 • The investigated arable sites showed no significant U accumulation compared to the  
465 forest sites. The close correlation of bulk soil AR with  $\text{NaHCO}_3$ -extractable U indicate  
466 that mineral based P-fertilizer application increases the extractable U pool, which  
467 might cause higher leachability.
- 468 • The lack of depth gradients of U concentrations,  $\tau_U$  and AR ratios are not consistent  
469 with accumulation of U in the surface soil, which might indicate leaching of fertilizer-  
470 derived U. However, based on the calculated U leaching and considering the  
471 heterogeneity of the catchment, agricultural practices, and the comparatively long  
472 distance to the groundwater, we assume only small contributions (few  $\mu\text{g L}^{-1}$ ) of the  
473 fertilizer-derived U to the elevated U concentrations in the water samples.

474 Based on the estimated contributions of fertilizer-derived U to U in leaching waters, the  
475 correlations of  $\text{NaHCO}_3$ -extractable U and AR, the absence of depth gradients and the AR in  
476 the water samples, it is considered likely that U is leached in the soil. However, while the  
477 leaching is in a concentration range that might be relevant at normal U concentrations in  
478 drinking water, it is only of minor importance at the high concentrations present in the  
479 investigated drinking water wells.

480

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486

487 **Appendix A. Supplementary data**

488 Supplementary data related to this article can be found online.

489

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