

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 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 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 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 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.

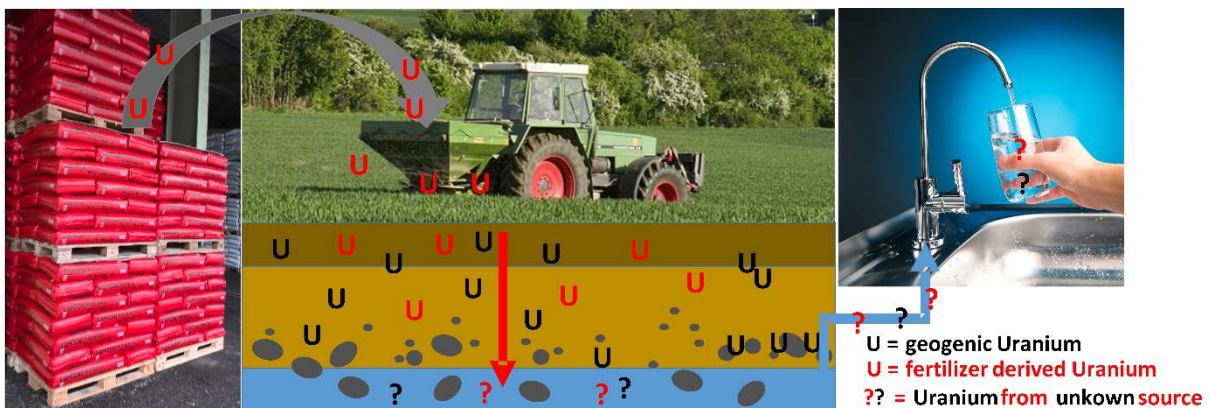
37 **Highlights:**

- 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).

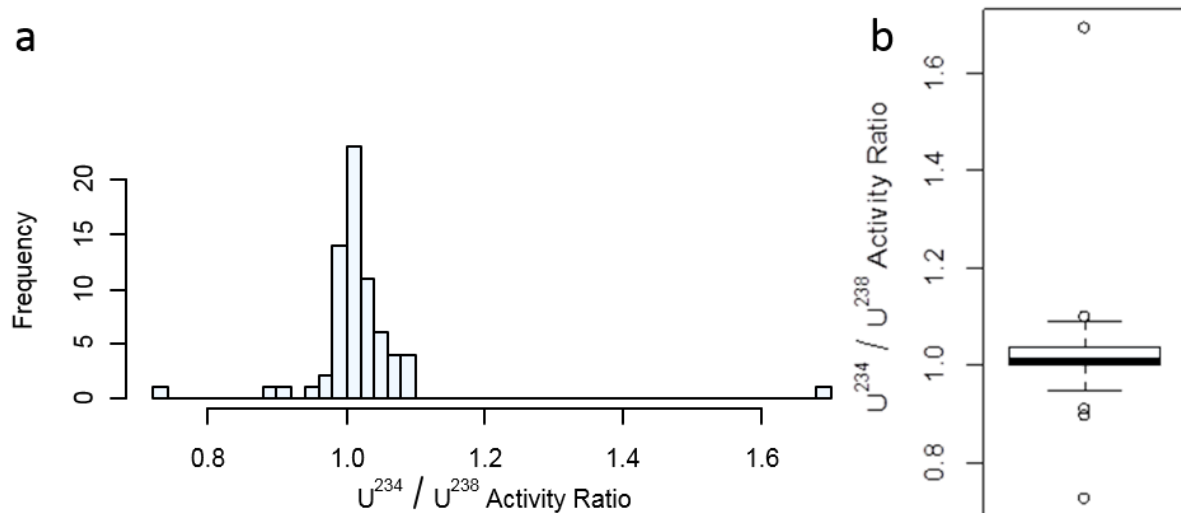
55 Mineral based phosphorous fertilizers are produced from phosphate rocks of igneous or
56 sedimentary origin. Depending on the source, sedimentary phosphorites are heavily enriched
57 in U (up to 280 mg kg⁻¹; McLaughlin et al., 1996). During the process of fertilizer production, U
58 is enriched in 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 (PO_4^{3-}), carbonates (CO_3^{2-}), sulphates (SO_4^{2-}), chlorides (Cl^-) or fluorides
86 (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 U^{4+} to U^{6+} during decay are
101 reasons for preferential leaching of ^{234}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). 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 ⁻¹])	Uranium concentration [$\mu\text{g L}^{-1}$]	^{234/238} 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 μm) and acidified (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 ≤ 2 mm using a stainless steel sieve. The pH was measured in 0.01-M 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 (NH_4NO_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 Ca^{2+} , Mg^{2+} , K^+ , Na^+ ,
187 Al^{3+} and 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 (Ca^{2+} , Mg^{2+} , K^+ and Na^+) of the ECEC.

189 For texture analysis an aliquot of the soil was oxidized by heating with H_2O_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 (C_{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 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 H₂O₂ (30%), 2 ml HF (40%) and 2 ml
207 HNO₃ (69%) at 200°C for 40 minutes. A second run was carried out after adding 10 ml of 6%
208 boric acid (H₃BO₃), at 180°C for 30 minutes to complex the remaining HF. Total digestions of
209 fertilizers were undertaken in 8 ml HNO₃ (69%) and 2 ml H₂O₂ (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 ¹⁰³Rh and ¹¹⁵In
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⁻¹, n = 4) and certified (1.69±0.19 mg kg⁻¹) 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 HNO₃ (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 HNO₃ (3:1
218 ratio) and evaporated. The samples were redissolved in 4 ml of 3 M HNO₃ 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⁻¹ 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). ¹⁰³Rh and ¹¹⁵In

234 were used as internal standards and ^{232}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 ± 0.004 , mean \pm SD, $n = 12$) agree well with the values of
240 1.000 ± 0.001 reported by Beier et al. (2010a, b) and of 1.001 ± 0.002 reported by Keech et al.
241 (2013). The overall reproducibility was similar for the BCR (± 0.004 , SD, $n = 12$), an in house
242 standard (± 0.004 , SD, $n = 6$) and repeated sample digests (± 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 (90th 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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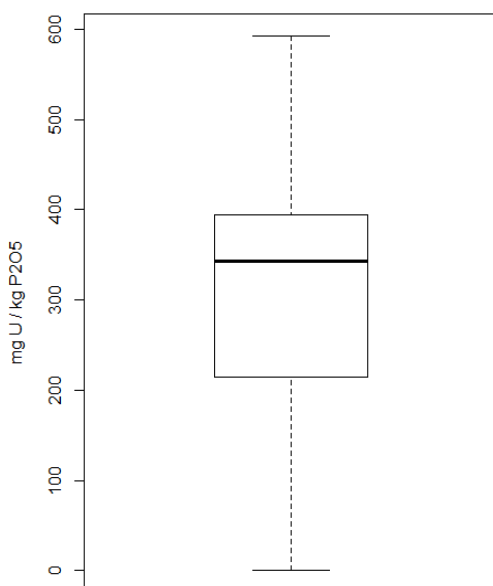
262 **Statistical Analysis and geochemical mass balancing**

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 τ -values following Brimhall et al. (1992)
267 using Ti as an immobile element. The τ -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 τ -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⁻¹ P₂O₅; the median value
280 was 343 mg kg⁻¹ P₂O₅ (Figure 2, Table S1). The lowest and highest U concentrations were
281 0.21 and 593 mg kg⁻¹ P₂O₅. The mean and median U concentrations compared to the dry
282 weight of fertilizer were 77.8 and 69.6 mg kg⁻¹, with a range of 0.11–188 mg kg⁻¹. Comparably

283 high concentrations were detected for PK (mean 386 mg kg⁻¹ P₂O₅; n = 4), superphosphate
 284 (mean 358 mg kg⁻¹ P₂O₅; n = 4) and NP-fertilizers (mean 348 mg kg⁻¹ P₂O₅; n = 4), whereas
 285 DAP U concentrations were one order of magnitude lower (mean 25.1 mg kg⁻¹ P₂O₅; 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⁻¹; 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⁻¹).

291

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

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

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_{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 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_{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 τ_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).

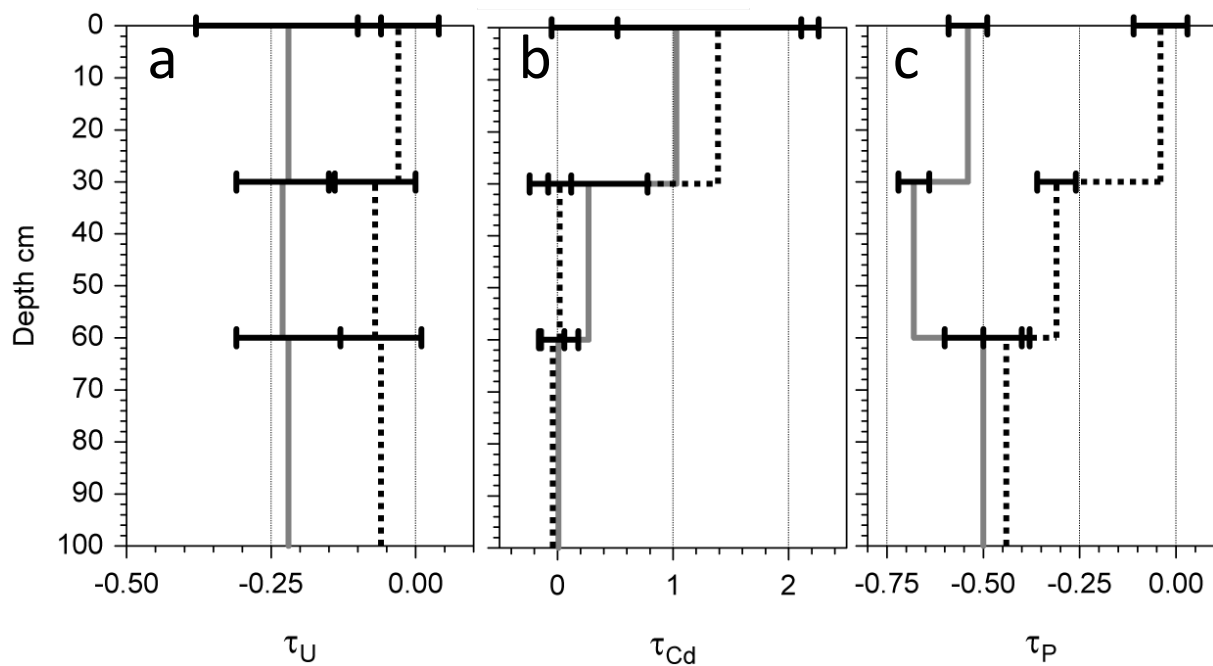
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Table 3 Soil properties, concentrations of selected elements and $^{234/238}\text{U}$ activity ratios of all soils.

Site	Field	Depth	pH	CEC	Base sat.	Clay	Silt	Sand	C _{org}	P	Cd	Th	U _{total}	U _{NaHCO₃}	$^{234/238}\text{U}$	SD
		[cm]		[mmol kg ⁻¹]			[%]				[mg kg ⁻¹]				Activity Ratio	
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 Rütli	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
Rock	-	-	-	-	-	-	-	-	372	0.04	7.12	1.98	-	0.954	0.001	



337

338 *Figure 3 The a) τ_U , b) τ_{Cd} and c) τ_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.

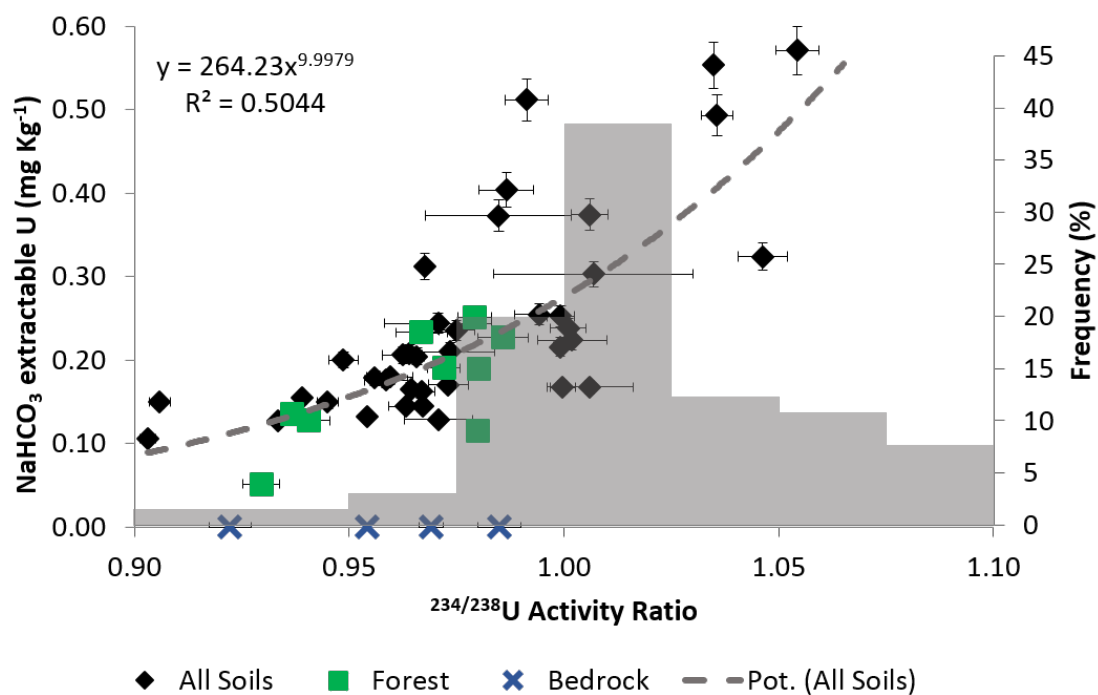
343 The possible effect of fertilizer-derived U on soils and leaching water has been assessed based
 344 on the U concentrations in the investigated mineral based fertilizers (Figure 2), official
 345 fertilization recommendations for different crop types, infiltration rates from the literature, and
 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⁻¹ (Kratz et al., 2008) and 2.8–16 g ha⁻¹ a⁻¹ (Uterman and Fuchs,
 349 2008) in Germany; 15 and 16 g ha⁻¹ a⁻¹ 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⁻¹ a⁻¹ 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 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 kg
360 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 NaHCO₃-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⁻¹ 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⁻¹ a⁻¹; 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 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, τ_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⁻¹. This is close to our (non-significant) mean difference of 0.15 mg kg⁻¹ between forest
434 and agricultural sites and to U enrichments reported in Swiss agricultural topsoil compared to
435 subsoils (mean 0.19 mg kg⁻¹; 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⁻¹ (Birke and Rauch, 2008;
445 Conceicao and Bonotto, 2003; Zielinski et al., 2006) but may reach up to 3.4 µg L⁻¹ 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⁻¹. 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 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, τ_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 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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