Accumulation of cadmium and uranium in arable soils in Switzerland

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Abstract

Mineral phosphorus (P) fertilizers contain contaminants that are potentially hazardous to humans and the environment. Frequent mineral P fertilizer applications can cause heavy metals to accumulate and reach undesirable concentrations in agricultural soils. There is particular concern about Cadmium (Cd) and Uranium (U) accumulation because these metals are toxic and can endanger soil fertility, leach into groundwater, and be taken up by crops. We determined total Cd and U concentrations in more than 400 topsoil and subsoil samples obtained from 216 agricultural sites across Switzerland. We also investigated temporal changes in Cd and U concentrations since 1985 in soil at six selected Swiss national soil monitoring network sites. The mean U concentrations were 16% higher in arable topsoil than in grassland topsoil. The Cd concentrations in arable and grassland soils did not differ, which we attribute to soil management practices and Cd sources other than mineral P fertilizers masking Cd inputs from mineral P fertilizers. The mean Cd and U concentrations were 58% and 9% higher, respectively, in arable topsoil than in arable subsoil, indicating that significant Cd and U inputs to arable soils occurred in the past. Geochemical mass balances confirmed this, indicating an accumulation of 52% for Cd and 6% for U. Only minor temporal changes were found in the Cd concentrations in topsoil from the six soil-monitoring sites, but U concentrations in topsoil from three sites had significantly increased since 1985. Sewage sludge and atmospheric deposition were previously important sources of Cd to agricultural

soils, but today mineral P fertilizers are the dominant sources of Cd and U. Future Cd and U inputs to agricultural soils may be reduced by using optimized management practices, establishing U threshold values for mineral P fertilizers and soils, effectively enforcing threshold values, and developing and using clean recycled P fertilizers.

Capsule

Past accumulation of Cd and U and ongoing accumulation of U in agricultural soils, point to the need to use "clean" P fertilizers.

1. Introduction

Phosphate (P)-containing mineral fertilizers contain trace elements that are potentially hazardous to humans and the environment (Kratz et al., 2016; McLaughlin et al., 1996; Schnug and Lottermoser, 2013). Agricultural productivity and ecosystem services can be negatively affected by the use of phosphate-containing fertilizers because of the undesirable amounts of heavy metals added to soil in the fertilizers (Mar and Okazaki, 2012). Metals that are mobile and available to plants may be transferred to crops, groundwater, and surface water (McLaughlin et al., 1996; Schnug and Lottermoser, 2013; Wilcke and Dohler, 1995). Cadmium (Cd) and Uranium (U) may be important impurities in mineral P fertilizers, and there is particular concern about these metals being added to soil in fertilizer because they are toxic (Camelo et al., 1997; Mar and Okazaki, 2012; McLaughlin et al., 1996). Heavy metal concentrations in mineral P fertilizers vary widely depending on the origins of the phosphate rocks used to produce the fertilizers and the nature of the finished fertilizers. For example, Cd concentrations (per kilogram of P) from 1 to >640 mg kg^{-1} have been found in fertilizers (McLaughlin et al., 1996; Ulrich et al., 2014). Phosphate rocks are relatively insoluble in water, so they are processed to make fertilizers. Radionuclides and heavy metals become concentrated during these processes, and can reach 1.5 times the concentrations found in the unprocessed ore (Sattouf, 2007).

The problem of Cd in fertilizers accumulating in soils has been investigated in a number of studies in Sweden (Bengtsson et al., 2003), Germany (Boyson, 1992, Knappe et al., 2008; Wilcke and Döhler, 1995), the Netherlands (Moolenaar and Lexmond, 1998), England and Wales (Nicholson et al., 2003), Australia (Mann et al., 2002), New Zealand (Gray et al., 1999; Schipper et al., 2011) and its general implications for soil, environmental and human health (deVries et al., 2005; Moolenaar et al., 1997; Oborn et al., 2003) and plant uptake (Johnston and Jones, 1992) were assessed. It is well known that Cd in fertilizers can accumulate in agricultural topsoils and that the amount that accumulates depends on the fertilization rate, the crop rotation used, and the properties of the soil (Mann et al., 2002; McLaughlin et al., 1996). Mineral P fertilizer is the main source of Cd to a soil if the fertilizer is applied regularly (Keller

74 and Schulin, 2003; Moolenaar and Lexmond, 1998). Cd is also added to soil by the application

75 of manure and atmospheric deposition (Nicholson et al., 2003). In the past, the application of

76 sewage sludge may also have added Cd to soil (Kabata-Pendias and Mukherjee, 2007; Keller

77 et al., 2005), but applying sewage sludge to soil is now prohibited in many countries, and was

78 prohibited in Switzerland in 2006. Cd is predominantly removed from soil through the

79 harvesting of crops and, depending on the properties of the soil, the leaching of Cd to deeper

80 soil layers. It has recently been found that current Cd soil budgets in the European Union and

81 Norway are almost in balance (Six and Smolders, 2014). These authors suggested that Cd

82 concentrations in soils will decrease over the next few decades. However, this conclusion was

83 based on average values for Europe, and Cd concentrations in soils will not necessarily

84 decrease in areas with particular crop rotations and fertilization regimes.

85 Relatively little information is available on the behaviour of U in soils derived from P fertilizers.

86 U may become enriched in topsoils (Takeda et al., 2006; Wetterlind et al., 2012) but can be

87 mobile and leach into groundwater and surface water (Schnug and Lottermoser, 2013; Schnug

88 et al., 2005; Iurian et al., 2015). Mineral P fertilizer is the main source of U to agricultural soils,

89 and manure or sewage sludge application and atmospheric deposition are minor sources

90 (Bottcher et al., 2012; Kabata-Pendias and Mukherjee, 2007; Kratz et al., 2008). Kratz et al.

91 (2008) found that U inputs from manure or sewage sludge are 13%–45% of U inputs in mineral

92 P fertilizers containing the same amounts of P. Plants take up relatively little U from soil, but U

93 in soil can sorb to roots and enter the food chain in root vegetables (ATSDR, 2013; Kratz et

94 al., 2008). However, humans ingest negligible amounts of U in plant products, and it has been

95 suggested that drinking water is the main source of human U uptake (Schnug and Lottermoser,

96 2013; Schnug et al., 2005). While some studies stated that concentrations of U in drinking

97 water vary regionally and are generally related to the geological bedrock (CCME, 2011; Stalder

98 et al., 2012), other studies found that (depending on soil properties) fertilizer derived U will not

99 significantly accumulate in soils, but is readily transferred to aquifers (Birke and Rauch, 2008;

100 Huhle et al., 2008; Smidt et al., 2012).

101   A number of factors, listed below together with their trends, need to be considered when

102   assessing the importance of mineral P fertilizers in the accumulation of Cd and U in agricultural

103   soils.

104   1. As in many European countries the amount of mineral P fertilizer used has decreased

105   significantly since the 1990s in Switzerland (Spiess, 2011). For instance, 16562 t of

106   mineral P fertilizer was applied to agricultural land in Switzerland in 1990, reducing to

107   4206 t in 2013 (BLW, 2014).

108   2. Mineral P fertilizers are predominantly applied where crops with high P demands are

109   grown and insufficient animal manure is available to meet the P demands of the crops.

110   3. Several mineral P fertilizers contain high concentrations of Cd and U (Gisler and

111   Schwab, 2015; Nziguheba and Smolders, 2008). In a recent Swiss survey, 45% of all

112   the mineral P fertilizers analysed contained Cd concentrations higher than the Swiss

113   threshold (50 mg kg^{-1} P), and the highest concentration was 220 mg kg^{-1} (Gisler and

114   Schwab, 2015). No thresholds for U in fertilizers have yet been set. Swiss fertilizers

115   have been found to have relatively high median and maximum U concentrations, of 291

116   and 485 mg kg^{-1} P$_2$O$_5$, respectively (Gisler and Schwab, 2015).

117   In two recent studies, Fitzgerald and Roth (2015) and Roth and Fitzgerald (2015) concluded

118   that Cd concentrations in the fertilizers used in Switzerland need to be as low as possible

119   because some sections of the population already have Cd intakes close to the tolerable daily

120   intake. They also concluded, because of the toxicity of U, that U concentrations in fertilizers

121   should be more closely monitored than they are currently. Better information on the fates of

122   Cd and U in mineral fertilizers added to soils is needed than is currently available because

123   such information will be required to allow rational debates about managing fertilizer quality in

124   Switzerland and achieving long-term decreases in risks caused by agricultural activities.

125   In the study described here, we compared Cd and U concentrations in topsoil samples from

126   agricultural and grassland sites and in topsoil samples and subsoil layers (C horizon) at

127   agricultural sites. The aim was to determine whether Cd and U have accumulated in topsoils

128   at arable sites compared to topsoils at grassland sites to which smaller amounts or no mineral

129 P fertilizers have been added. In a second trial, topsoils of arable sites were compared to or

130 than in deeper soil layers at the same sites, to assess Cd and U accumulation by input from

131 the surface. We also determined Cd and U concentrations in archived soil samples from

132 selected soil monitoring sites in Switzerland that have, in the past, received regular mineral P

133 fertilizer, and calculated Cd and U budgets for the sites over a 25-year period. The aim of the

134 study was to attempt to answer the following questions.

135 I.   Are higher Cd and U concentrations found in arable soils than in grassland soils to

136   which little or no mineral fertilizer has been applied?

137 II. Are Cd and U more enriched in topsoils than in subsoils?

138 III. What are the main sources of Cd and U to the arable soils, and are Cd and U still being

139   accumulated appreciably?

140 IV. What political measures should be taken to decrease Cd and U inputs to soils from

141   mineral P fertilizers?

142

143 ## 2. Materials and methods

144 ### 2.1. Study sites

145

146 Cd and U concentrations in about 400 archived soil samples from Switzerland were

147 determined. The samples were from 216 agricultural sites in areas in which mineral P fertilizers

148 are used on arable land. The sites were chosen using georeferenced farm census data that

149 allowed areas containing arable farms to be identified (Figures 1 and S1). Arable farms do not

150 generally have access to sufficient animal manure to provide the nutrients required by arable

151 crops, so we presumed that mineral P fertilizers are predominantly applied on arable farms.

152 Archived soil samples were available from the Swiss soil monitoring network (NABO; from

153 which soil samples collected from 34 arable sites between 2005 and 2009 were available), the

154 Swiss biodiversity monitoring network (BMN; 65 arable sites and 38 grassland sites between

155 2011 and 2013), the Canton of Aargau (15 arable sites in 2006), the Canton of Solothurn (39

156 arable sites between 1995 and 2005), and the Canton of Fribourg (25 arable sites between

157 2007 and 2011). Except for the BMN samples, each archived soil sample was made up of at

158   least 25 individual topsoil (0–20 cm deep) cores from within a 10 m^2 x 10 m^2 square mixed

159   together (Hämmann and Desaules, 2003). Subsoil samples were obtained from soil profiles at

160   the soil monitoring network sites.

161   The BMN archive contained topsoil samples (individual 0–20 cm deep cores from within a

162   circle of radius 5 m at each site) but no subsoil samples. We therefore compared Cd and U

163   concentrations in topsoil samples from arable sites with Cd and U concentrations in topsoil

164   samples obtained from grassland sites (Figure S2), because little or no mineral fertilizer is

165   generally applied to grassland systems in Switzerland. We selected archived soil samples

166   from five soil surveys conducted at the same sites between 1985 and 2009 at six NABO sites

167   to allow temporal changes in Cd and U concentrations in topsoil to be evaluated. The surface

168   soil samples (0-20 cm) were taken every 5 years from the same 10 m^2 x 10 m^2 plot. Each

169   time, two composite samples were generated by mixing 25 individual topsoil cores equally

170   distributed over the plot, to account for the spatial variability of the soils. The mean value for

171   the two composite samples is reported. The mean relative standard deviation between the

172   metal concentrations in the two samples was 6.1% for Cd and 2.6 % for U and was within the

173   analytical error. Thus we assume that our sampling design was suitable to compensate for

174   spatial variations. Annual land management data (including fertilization practices) provided by

175   farmers were available for the NABO sites. The design of the NABO network was described

176   in detail by Gubler et al. (2015).
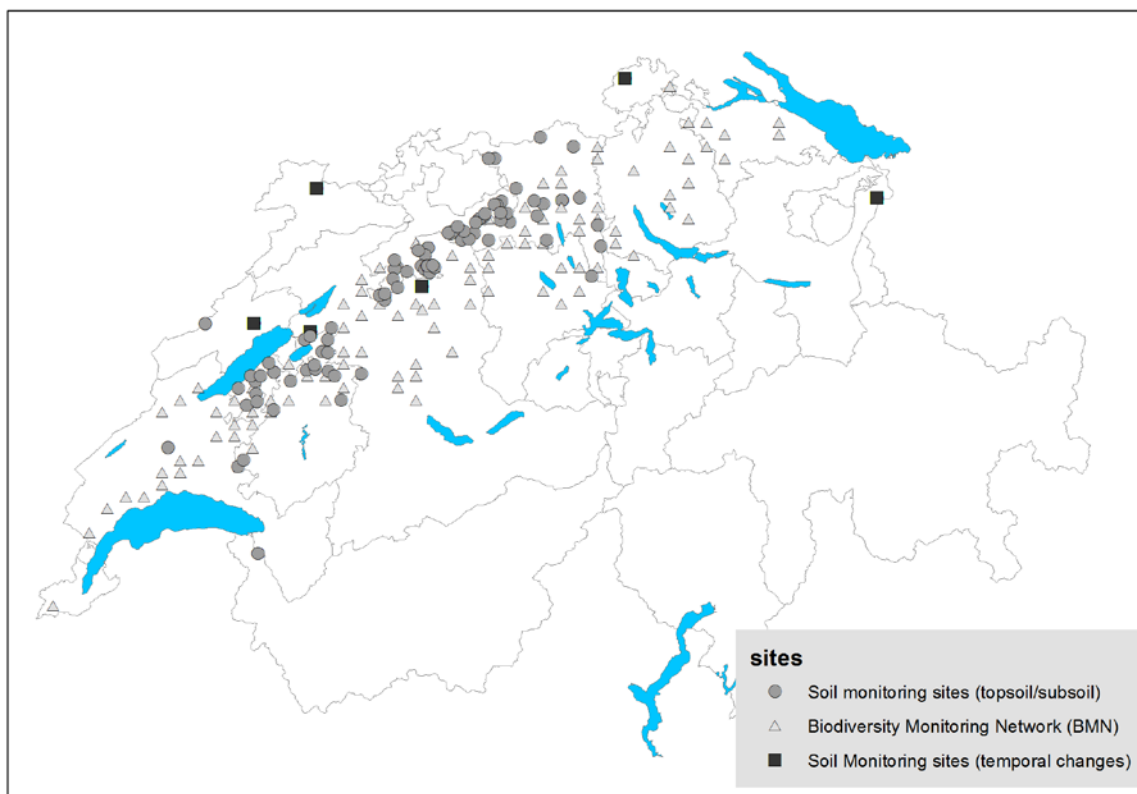
177
178 *Figure 1. Map of Switzerland showing the locations of the selected sites. The Cd and U*
179 *concentrations in topsoil and subsoil from the soil monitoring sites (circles) were compared, as*
180 *were the Cd and U concentrations in topsoil samples from the biodiversity monitoring network*
181 *arable sites and grassland sites (triangles). Temporal changes in the Cd and U concentrations*
182 *in soil samples collected from six soil monitoring sites (squares) between 1985 and 2009 were*
183 *evaluated. The study sites were on the Swiss plateau because little arable farming occurs in*
184 *the Jura mountains to the north or in the Alps to the south (see Figure S1).*

185

186 2.2. Analysis

187 Each soil sample was air dried and passed through a 2 mm sieve. A representative subsample
188 was then ground in an agate mortar. A 0.2 g aliquot was then digested in a mixture of 2 ml
189 69% HNO_3, 2 ml 48% HF, and 1.5 ml 30% H_2O_2 in a microwave oven at 200 °C, then 10 ml
190 6% H_3BO_3 was added and the sample was heated to 180°C to complex the residual HF. The
191 Cd and U concentrations in the digest were determined using an inductively coupled plasma
192 mass spectrometer (ICP-MS 7700X; Agilent Technologies, Frankfurt am Main, Germany)
193 using Rh and In as internal standards. The Ti concentration was analysed to allow a τ value to
194 be calculated. The τ value is the result of geochemical mass balancing calculations, which

8

195 accounts for natural weathering induced enrichment/depletion of an element (Brimhall et al.,

196 1992; more details in the supplementary material). The Cd and U detection limits were 7 and

197 2 μg kg^{-1}, respectively. The accuracy of the method was assessed by analysing the "San

198 Joaquin soil" reference material (NIST 2709a) 16 times, and the Cd, U, and Ti recoveries were

199 101%, 96%, and 93%, respectively. The reproducibility of the method was assessed by

200 digesting and analysing 11 soil samples between two and 16 times. The mean reproducibility

201 (as relative standard deviations) for Cd and U was 9.1% and 4.1%, respectively.

202 2.3.   Statistics and budget calculations

203 Geochemical mass balances (τ values) were calculated following the method described by

204 Brimhall et al. (1992). Annual Cd budgets were calculated for the NABO sites for the period

205 1985–2013 following the method described by Keller and Desaules (2004) and Keller et al.

206 (2005). The soil surface balances for the six selected NABO sites took into account Cd inputs

207 from animal manure, mineral fertilizers, atmospheric deposition, sewage sludge, and compost

208 and other outputs in harvested crops. The available land management data were described in

209 more detail by Della Peruta et al. (2014). We only calculated inputs of U from mineral fertilizers

210 because other sources of U, such as atmospheric deposition and animal manure, are negligible

211 (Sheppard and Sanipelli 2012). The leaching of U into subsoil and groundwater cannot

212 currently be estimated because reliable adsorption isotherms and measured leaching data are

213 unavailable. Estimating the leaching of U into groundwater will require an adsorption isotherm

214 similar to that derived by Elzinga et al. (1999) for Cd, to allow the mobility of U in the soil to be

215 estimated from the soil characteristics. The output of U from harvested crops was ignored

216 because very little U has been found to be removed in crops; in previous studies <0.1 and

217 <0.35 g ha^{-1} y^{-1} were found to be removed from rapeseed and sugarbeet, respectively

218 (ATSDR, 2013; Kratz et al., 2008). To test for differences between groups a t test for

219 independent (grass-vs. arable land) or dependent (top- vs subsoil) samples as well as a Mann-

220 Whitney U test (for Cd, no variance homogeneity) was performed. Significance levels were

221 highlighted with * (significant, 95%), ** (highly significant, 99%) and *** (very highly significant,

222   99.9%). The τ values calculation, statistical analyses, and element budgeting are all described

223   in greater detail in the supplementary material.

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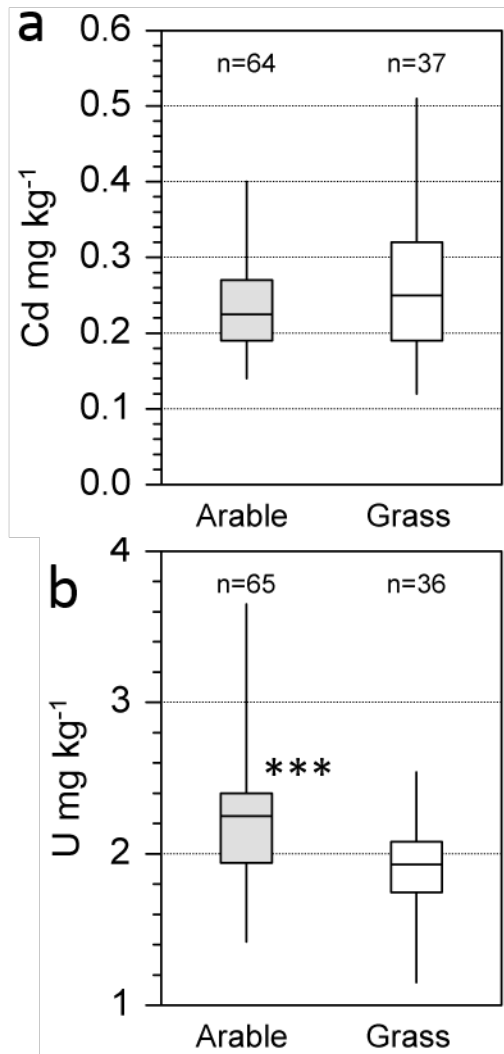
226   *Figure 2. Boxplots of the (a) Cd and (b) U concentrations in soil samples obtained from the Swiss*
227   *biodiversity monitoring network arable and grassland sites*
228

229   3. Results

230   While there was no significant difference between the Cd concentrations in the soil samples

231   obtained from the BMN arable and grassland sites, the U concentrations in the soil samples

232   were very significantly different (Figure 2). The median U concentration in the arable samples

233   was 2.25 mg kg^{-1}, which was 0.32 mg kg^{-1} (16%) higher than the median concentration in the

234 grassland samples (1.93 mg kg^{-1}). We conclude that U concentrations are higher in arable

235 topsoils to which mineral P fertilizers have regularly been added than in grassland topsoils.

236 The Cd and U concentrations in the topsoils and subsoils were very highly significantly different

237 (Figure 3). The mean and median Cd concentrations were 0.11 and 0.10 mg kg^{-1} (58% and

238 62%) higher, respectively, and the mean and median U concentrations were 0.19 and 0.16 mg

239 kg^{-1} (9% and 7%) higher, respectively, in the topsoils than in the subsoils.
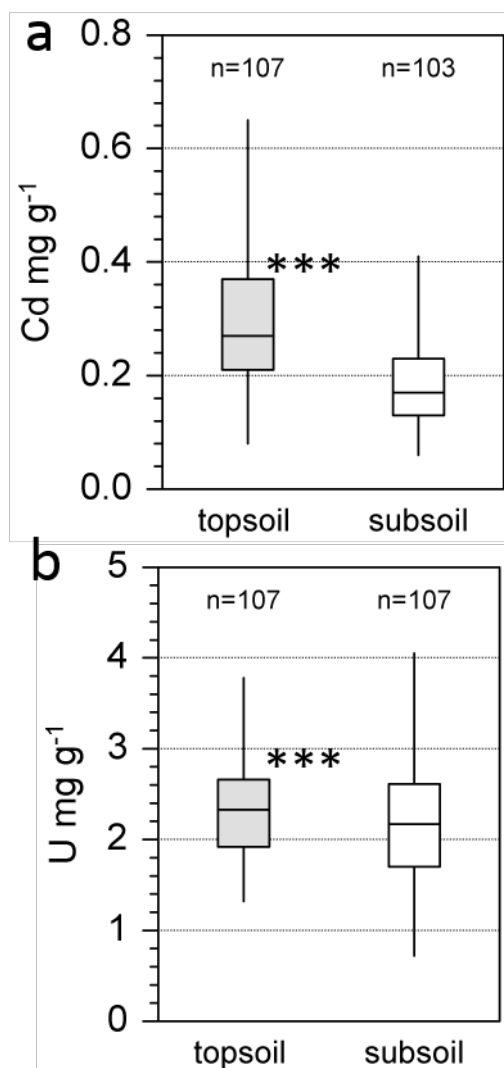
241 *Figure 3. Boxplots of the (a) Cd and (b) U concentrations in the topsoil and subsoil samples*

242
243 The correlation between the Cd concentrations in the topsoil and subsoil was highly

244 significantly, but the correlation coefficient was relatively small and the slope was only 0.31,

245 indicating that there were Cd inputs from sources other than the parent material. The same

246 was true for U, but the correlation coefficient and slope were both higher (Figure S3). The

correlation between the Cd and U concentrations in the topsoil and subsoil samples suggested that there were two main sources of Cd and U in the soils (Figure 4), namely mineral fertilizers increasing the Cd and U concentrations, and additional sources of Cd (e.g., sewage sludge and atmospheric deposition) increasing the Cd concentrations. The Cd and U τ values were very significantly different from zero (Figure 5), and indicated that Cd accumulation added 52% (mean) or 35% (median) and U accumulation added 6% (mean and median) to the concentrations found in the topsoil. Slightly higher enrichment values were found when the Cd and U concentrations in the topsoil and subsoil samples were compared directly than when the τ values were used, because natural enrichment during weathering was not taken into account in the direct comparison.
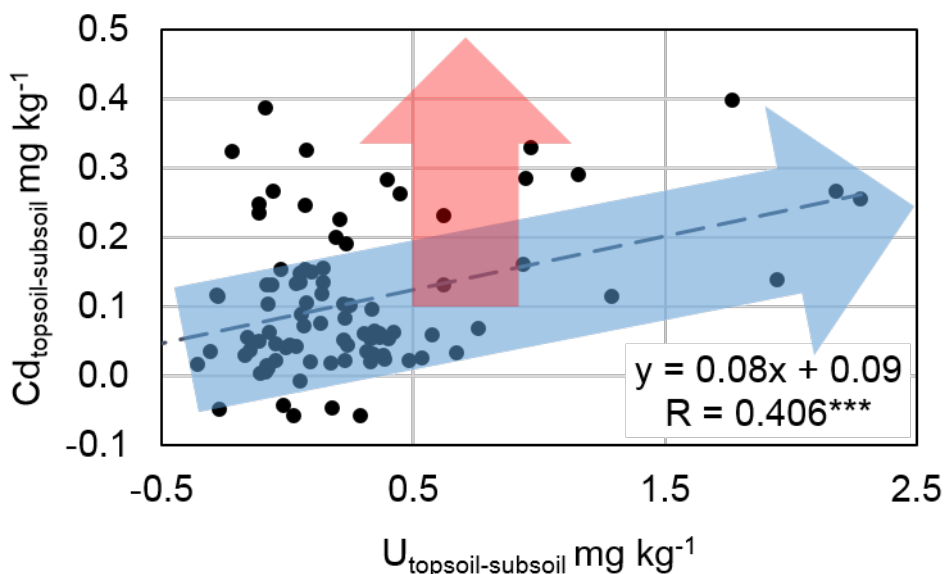
Figure 4. Relationships between the differences between the Cd concentrations in the topsoil and subsoil samples ($Cd_{topsoil}$–$Cd_{subsoil}$) and the differences between the U concentrations in the topsoil and subsoil samples ($U_{topsoil}$–$U_{subsoil}$). The blue arrow indicates areas in which Cd and U could have been added to the soil in fertilizer. The red arrow indicates possible contributions from other sources that add more Cd than U to the soil.
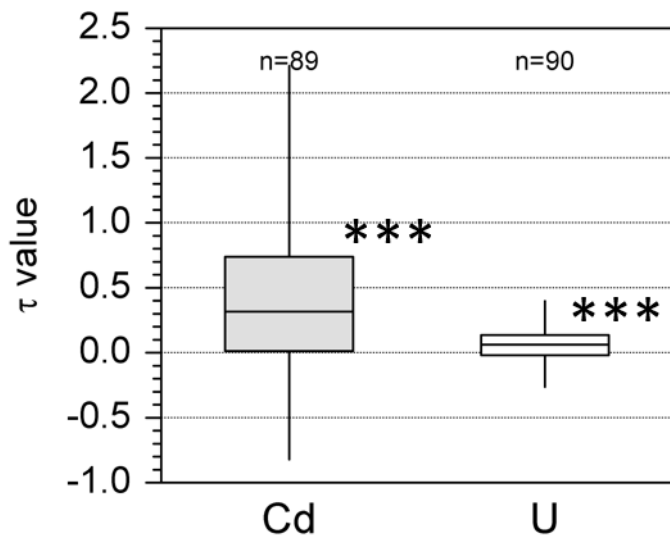
263
264 *Figure 5. Boxplots of the Cd and U τ values. A τ value of 0 indicates no change in the concentration of the element*
265 *during weathering, whereas a τ value of 0.5 indicates 50% enrichment and a value of −0.5 indicates 50% depletion*
266 *(see the supplementary material for further details). The Cd and U τ values were very significantly positive, indicating*
267 *that both had accumulated in the topsoil samples.*
268

269 The Cd balances for the six soil monitoring sites showed that Cd inputs in the period 1985–

270 2009 were between 2 and 20 g ha^{-1} y^{-1} (Figures S4–S9). The main source of Cd in the soil

271 was found to be mineral fertilizer. At one site, where triple P mineral fertilizer had regularly

272 been added, Cd inputs were 20–30 g ha^{-1} y^{-1}. Larger amounts of mineral fertilizers were

273 generally applied in the 1980s and 1990s than more recently. The net Cd balance was

274 generally positive, indicating a slight accumulation of Cd (around 0.02 mg kg^{-1} between 1985

275 and 2009) in the topsoils (Figure 6b). Overall, the surface balance indicated a slight

276 accumulation of Cd at three sites and that the Cd concentration remained stable at each of the

277 other three sites. Repeated soil measurements confirmed the estimated Cd budgets (Figure

278 6a). Overall, the Cd concentrations in the soil samples increased or decreased only a little

279 between 1985 and 2009.

280 Inputs of U through mineral P fertilizers at the six monitoring sites were mostly between 10 and

281 50 g ha^{-1} y^{-1} (Figures S4–S8), but were 100–120 g ha^{-1} y^{-1} at one site where triple P mineral

282 fertilizer was regularly applied. Using the bulk densities of the soil samples and assuming that

283 the added U remained in the topsoil, we calculated that the U concentration increased by 0.1–

284 0.7 mg kg^{-1} between 1985 and 2009 (Figure 6d), a result generally confirmed by the repeated

285 soil measurements (Figure 6c). The U concentrations at four of the six monitoring sites

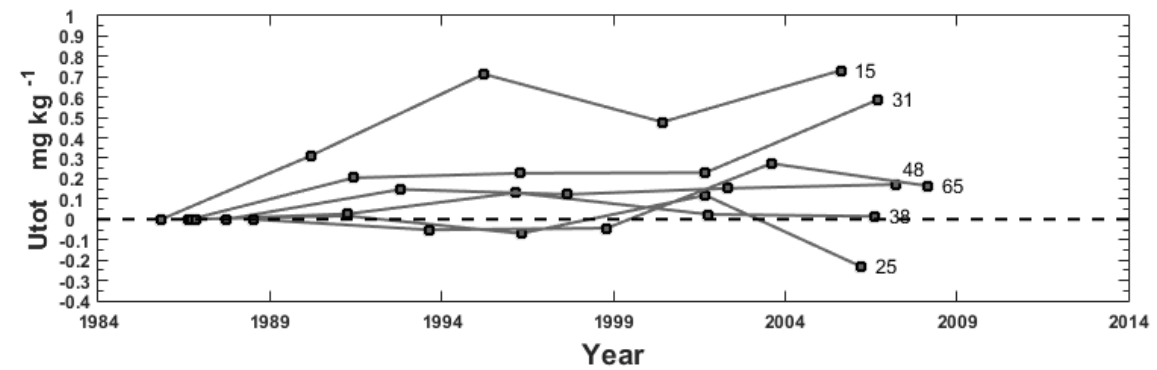286 increased by 0.1–0.7 mg kg^{-1}, remained constant at one site, and decreased at another.
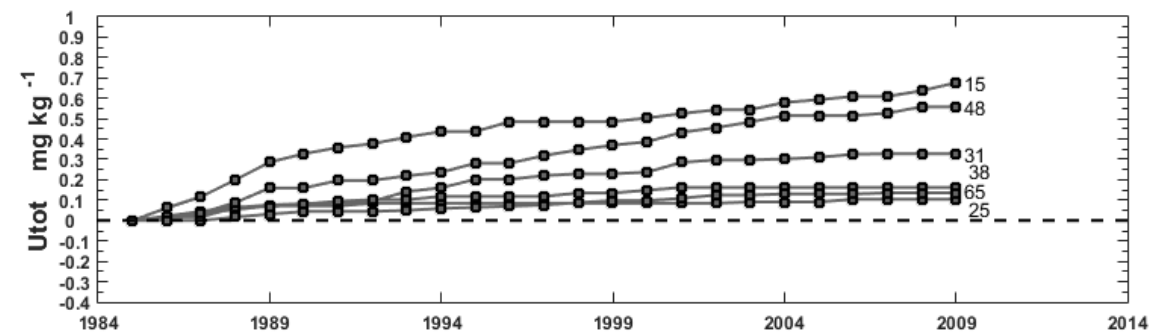
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293 d)
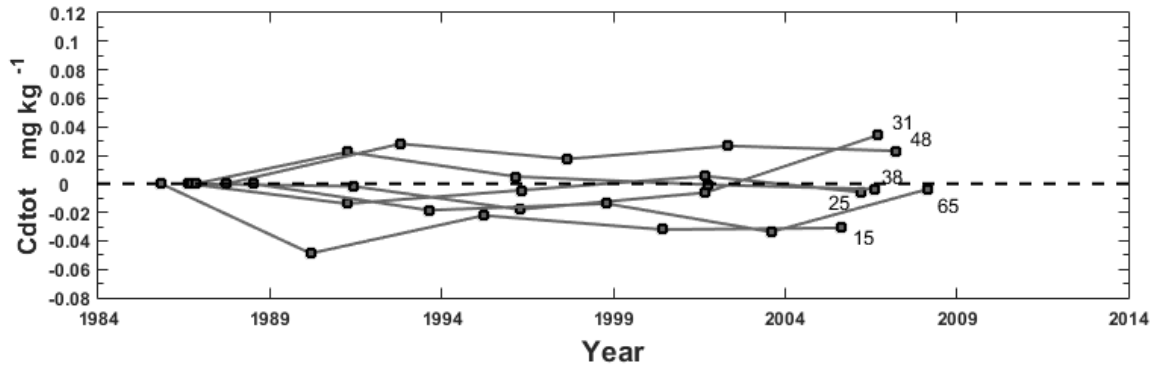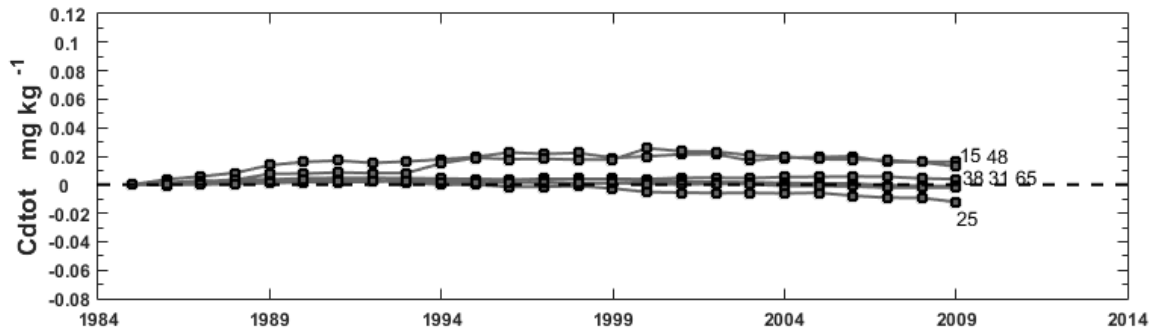
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295
296 *Figure 6. Temporal changes in the Cd and U concentration in topsoil (0–20 cm deep) from the six soil monitoring*
297 *sites. (a) Cd concentrations in soil samples collected every five years, (b) estimated Cd inputs based on farmers'*
298 *land management records, (c) U concentrations in soil samples collected every five years, and (d) estimated U*
299 *inputs in mineral fertilizers based on farmers' land management records.*

4. Discussion

4.1. Comparison of Cd and U enrichment in arable and grassland soils

The Cd concentrations in the 65 arable soil samples and 38 grassland soil samples were not significantly different, but U was significantly enriched in the arable topsoils relative to the grassland topsoils (Figure 2). There were a number of possible reasons why Cd was not enriched at the arable sites relative to the grassland sites. Ploughing dilutes Cd in the top soils of arable sites, while high levels of Cd inputs from the atmosphere at times when industrial emissions of Cd were important could have accumulated more effectively in grassland than in arable land. Manure and sewage sludge are more likely to be applied to grassland than arable land, and also smaller amounts of mineral fertilizers are likely to be applied to grassland than arable land, levelling the differences between grass- and arable land. Finally, Cd is taken up by plants, so it is mainly removed from agricultural soils when crops are harvested. This factor affects arable land more than grassland, with a more closed nutrient cycle (McLaughlin et al., 1996; Quezada-Hinojosa et al., 2015).

Negligible atmospheric deposition and plant uptake (and therefore loss through harvested crops) of U occur (ATSDR, 013; Kratz et al., 2008), so, due to the lack of any other credible source we assume that the higher U concentrations in arable topsoils than in grassland topsoils were caused by the long-term application of mineral P fertilizers containing U (Eriksson, 2001; Kratz et al., 2008). It should be noted that some mineral P fertilizer is generally applied to grassland in Switzerland, but much less is applied to grassland than to arable land (Flisch et al., 2009). The U concentrations may be affected by soil properties as grassland soils tend to have higher organic matter contents and lower pH values than arable soils and might sorb U stronger compared to arable soils (Rogasik et al., 2008). The effects of soil management systems, such as tillage, are also important. Ploughing arable land generally mixes the topsoil and subsoil, so enriched U in topsoil will be diluted to some degree depending on ploughing depth. However, this additional factors are probably only of minor importance compared to mineral fertilizer input.

327 The degree to which we found that U was enriched was similar to the enrichment seen in long-

328 term fertilizer experiments at the Rothamsted Research station in the UK (Rothbaum et al.,

329 1979). The Rothamsted Research experiments have been running since 1843, and in 1976 U

330 was found to be enriched in fertilized plots by a mean of 0.43 mg kg^{-1} relative to control plots.

331 Similar levels of U enrichment have been found in other long-term field experiments, although

332 the actual enrichment levels were somewhat lower because the fertilizer application periods

333 were shorter (Rogasik et al., 2008; Schipper et al., 2011; Taylor and Kim, 2008).

334 Taylor and Kim (2009) reported Cd and U to be enriched by a factor of 6.45 and 2.53 in arable

335 compared to background (forest) sites. Differences in selection of background sites

336 (grasslands vs. forests) as well as lower atmospheric deposition (Arimoto et al., 1990), but

337 higher Cd and U fertilizer concentrations in New Zeeland (Nauru deposits, McLaughlin et al.,

338 1996) might be the main reason much higher enrichments at the arable sites.

339

340 4.2.   Enrichment of Cd and U in agricultural topsoils

341 The Cd and U concentrations in the paired topsoil and subsoil samples clearly indicate the

342 enrichment of Cd and U in the arable topsoils. The enrichment of Cd in arable topsoils relative

343 to subsoils can mainly be attributed to the application of mineral P fertilizer, atmospheric

344 deposition, and in some cases, the historical application of sewage sludge. The atmosphere

345 currently causes only small amounts of Cd to soil, but before effective filters were used to

346 decrease industrial emissions, it provided much more (Heinrichs and Mayer, 1977; Kabata-

347 Pendias and Mukherjee, 2007; Nicholson et al., 1994). Significant amounts of Cd may have

348 been added to the soil at some sites in sewage sludge before the practice was banned in

349 Switzerland in 2006 (Eriksson, 2001; Kabata-Pendias and Mukherjee, 2007; Keller et al.,

350 2005). The Cd concentrations were 58% (mean) higher in the topsoils than in the subsoils, and

351 almost the same result (60% higher concentrations in topsoils than in subsoils) was found in

352 Sweden (Eriksson et al., 1997). The Cd and U concentrations in New Zealand farmed soils in

353 0-100 mm depth were reported to be enriched by a factor of 1.74 and 1.17 compared to 100-

354 200 mm depth, respectively (Taylor and Kim, 2009), which is a bit higher compared to our

findings. Our results also agreed well with the results of a study in Germany (Uterman and Fuchs, 2008), in which 392 arable, 206 grassland, and 367 forest soils were analysed. In that study, U was relatively more enriched in topsoils than in subsoils at arable sites compared to grassland and forest sites (the median differences between the topsoils and subsoils from arable, grassland, and forest sites were 0.11, 0.09, and -0.04 mg kg^{-1}, respectively). Several researchers have stated that U is predominantly added to agricultural soils in mineral P fertilizers (Bottcher et al., 2012; Kratz et al., 2008; Schnug and Lottermoser, 2013). Considerable amounts of U can be leached from soil, and this can decrease the difference between the U concentrations in topsoil and subsoil (Schnug and Lottermoser, 2013). The τ values confirmed that U was enriched in the topsoil relative to the subsoil (Figure 5). Cd and U are considered to be relatively mobile, so weathering might be expected to deplete these elements in soil. However, we found both to be significantly enriched in the topsoils relative to the subsoils. Given that mineral P fertilizer is the dominant source of Cd and U to soil, and assuming that Cd and U behave similarly during weathering, the degrees to which Cd and U are enriched in topsoil relative to subsoil should correlate. Indeed, we found a highly significant correlation (r=0.406; $p < 0.001$) between the differences between the topsoil and subsoil concentrations of Cd and U (Figure 4). However, two general patterns were found. The results for some sites appeared to follow the relationship described above (indicated by the blue arrow in Figure 4), indicating that the Cd and U that had accumulated in these topsoils had the same source. However, for a second group of sites, the differences between the Cd concentrations in the topsoils and subsoils were higher than the differences between the U concentrations in the topsoils and subsoils (indicated by the red arrow in Figure 4). The different degrees to which Cd and U accumulated at these sites could have been caused by differences in Cd inputs from the atmosphere and sewage sludge, different Cd and U concentrations in the fertilizers used, and differences in the dominant routes through which Cd and U were exported from the soils, Cd being predominantly removed in harvested crops and U through leaching (Kabata-Pendias and Mukherjee, 2007; Kratz et al., 2008; Schnug and Lottermoser, 2013).

382 The U concentrations in topsoils on arable land compared to topsoils on grassland were 16%

383 higher, but the topsoils of the arable land were only 6-9% higher than the subsoils. This

384 difference could indicate that U was lost from the topsoils through leaching to deeper soil

385 layers. This process would lower the difference between top- and subsoil, by decreasing topsoil

386 and increasing subsoil concentration. In the opposite in the comparison between topsoils of

387 arable land and grassland, leaching of U would happen at both sites to a similar degree and

388 thus the differences in U concentrations would be higher.

389 About 30% of the τ values are negative, indicating a net loss of U from the topsoil, even though

390 applying fertilizer added U to soil, being an additional indicator for U leaching. A negative τ

391 value could therefore result when U loss during soil development and U leaching are higher

392 than anthropogenic U inputs like P fertilizers.

393

394 4.3.   Budgets and trends

395 Cd inputs at all six sites were highest in the late 1980s, then decreased in the 1990s. Only

396 small increases in Cd concentrations were found at four of the six sites (Figure 6). In general,

397 smaller amounts of mineral fertilizers have been applied in Switzerland since the 1990s than

398 were applied before this (Spiess, 2011) because of new fertilizer regulations and agricultural

399 policies aimed at protecting the environment (Herzog et al., 2008). However, apart from this

400 overall trend, fertilization regimes at different sites depend mainly on the crop rotation used

401 and the nutrient requirements of the crops. The Cd and U inputs in mineral fertilizers at the six

402 sites varied greatly over the years (Figures S4–S9) but tended to decrease. This agrees with

403 the results of a study performed by Six and Smolders (2014), who assumed that current

404 environmental and fertilization practices would not lead to any net accumulation of Cd in

405 agricultural soil in the European Union. The temporal changes we found for the six monitoring

406 sites confirmed that little Cd is accumulating in soils in Switzerland. The predicted and

407 measured Cd and U concentrations in the soils generally agreed well except for Cd at site 15.

408 This discrepancy was attributed to the soil at site 15 having been ploughed deeply several

18

times during the study period. Deep ploughing dilutes the Cd in the topsoil and here caused the Cd concentration to decrease over time despite relatively large amounts of Cd being added. The application of mineral fertilizers caused U to accumulate to a considerable degree in soil at three of the six sites (Figure 6c). However, no other sources of U were considered and U export in harvested crops was assumed to be negligible. The U budget was limited by a lack of information on the leaching of U from soil and the sorption of U by soil. There are strong indications that U leaching might be relevant and that the amount of leaching that occurs depends on soil parameters such as the organic matter and clay content and pH (Rogasik et al., 2008). The studied soils show a wide variation in organic matter and clay content as well as in the pH (Table S1), which however did not seem to affect U concentrations in the soil, probably because of the very different amounts of mineral P fertilizers, which overprints differences in U sorption (Figure S4-9). The estimated budgets could therefore only be used to indicate general trends, and soil tillage and leaching were not taken into account. No dilution effect caused by deep ploughing at site 15 was found in the U budget, meaning either that U inputs overcompensated for dilution or that the topsoil and subsoil contained similar U concentrations (because of the natural distribution or leaching of U).

4.4. Measures to decrease Cd and U inputs in fertilizers

Mineral P fertilizers need to be applied efficiently according to the needs of plants, crop rotation, and soil nutrient status, to prevent Cd and U accumulating in agricultural soils. In Switzerland, most of the P requirements of plants are provided by animal manure. Imported mineral fertilizers provided only 15% of the 65,500 t of P_2O_5 applied to crops in 2013. The efficiency at which P is used increased from 22% in the 1980s to 60% in 2013 (BLW, 2013). While all Cd concentrations found in the topsoil samples were still well below the critical loads (mean 2.6 mg Cd kg^{-1} soil) calculated from soil pH and organic matter contents (de Vries et al. 2005), there is increasing evidence that Cd concentrations in arable soils and plants have to be kept as low as possible to minimize negative effects on human health (Clemens et al., 2013). For U no critical load approaches are available by now.

437   Ekardt and Stubenrauch (2013) stated that controlling the use of fertilizers and applying

438   sanctions to traders who do not comply with the law are major challenges to preventing the

439   use of fertilizers containing high concentrations of heavy metals. Laws need to be enforced

440   more strictly to prevent fertilizers that do not comply with the current Cd limits to be applied to

441   the soils (Gisler and Schwab, 2015). Threshold U concentrations for fertilizers may allow U

442   inputs at agricultural sites to be controlled and decreased more effectively than is currently

443   possible. Steps to recover Cd and U could be included in fertilizer production processes (Ulrich

444   et al., 2014). Switzerland is a small country with no sources of mineral P, so it depends entirely

445   on fertilizers produced elsewhere, where any limits for heavy metal concentrations in fertilizers

446   may not be sufficient for Swiss purposes. However, there is some impetus for change, and

447   proposed European Union fertilizer regulations (EC, 2016) will contain strict Cd concentration

448   limits for mineral P fertilizers. Mineral P fertilizers may be substituted with new, more

449   environmentally friendly products prepared from secondary P sources that contain lower heavy

450   metal concentrations than phosphate rock. Such fertilizers may be viable mid- to long-term

451   ways of decreasing Cd and U inputs to soils (Cordell et al., 2009; Hukari et al., 2016; Shepherd

452   et al., 2016). The European Union aims to increase the use of recycled P fertilizers (EC, 2016),

453   and Switzerland has passed a law requiring P to be recovered from P-rich waste, such as

454   wastewater, within the next 10 years (VVEA, 2016). However, depending on the sources and

455   the fertilizer production processes used, such fertilizers may still contain large amounts of

456   potentially toxic trace elements (Kratz et al., 2016; Kumpiene et al., 2016). Further research

457   into the production of sustainable recycled P fertilizers containing low concentrations of

458   pollutants is required.

459

5. Conclusions

461   1. Significantly (16%) higher U concentrations were found in arable soils than grassland soils

462   from Switzerland, and we attribute this mainly to the historical application of mineral P

463   fertilizers to arable soils. The Cd concentrations in arable and grassland soils were not

significantly different, probably because of a variety of sources of Cd and the different soil properties and management practices used at these sites.

2. The Cd and U concentrations were higher in topsoil than subsoil, consistent with surface application of Cd and U. While atmospheric deposition and sewage sludge and fertilizer application could have been the sources of Cd, mineral P fertilizer application would have been the main source of U.

3. Mineral fertilizers were likely the dominant sources of additional Cd and U above background levels in fertilized soils. The Cd and U concentrations in these soils remained constant or increased (mostly depending on the amounts of mineral fertilizer applied) between 1985 and 2009.

4. Further decreases in Cd and U inputs to agricultural soils should be enforced by optimizing fertilization practices, better enforcing existing Cd limits, developing new thresholds for U, and increasing the use of clean recycled P fertilizers.

We determined Cd and U concentrations and trends in Swiss arable topsoils for the first time. The results indicate that Cd and U are still accumulating in soils to which mineral P fertilizers are regularly applied. Sources of Cd inputs to agricultural soils and the long-term behaviour of Cd in soils have been investigated in a number of studies, but there is clearly a need for further research into the sources and long-term behaviour of U, particularly into the leaching of U from agricultural soils to groundwater and surface water.

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References

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495 Arimoto, R., Ray, B.J., Duce, R.A., Hewitt, A.D., Boldi, R., Hudson, A., 1990. Concentrations,
496   Sources, and Fluxes of Trace-Elements in the Remote Marine Atmosphere of New-
497   Zealand. J. Geophys. Res.-Atmos., 95(D13): 22389-22405.
498 ATSDR, 2013. Toxicological profile for uranium, Atlanta, Georgia.
499 Bengtsson, H., Oborn, I., Jonsson, S., Nilsson, I., Andersson, A., 2003. Field balances of some
500   mineral nutrients and trace elements in organic and conventional dairy farming - a case
501   study at Ojebyn, Sweden. Eur. J. Agron. 20, 101-116.
502 Birke, M., Rauch, U., 2008. Uranium in stream water of Germany. In: De Kok, L.J., Schnug,
503   E. (Eds.), Loads and fate of fertilizer derived uranium. Backhuys publishers, Leiden,
504   pp. 79-90.
505 BLW, 2013. Agrarbericht, in: Landwirtschaft, Bundersamt für Landwirtschaft, Bern.
506 BLW, 2014. Agrarbericht, in: Landwirtschaft, Bundersamt für Landwirtschaft, Bern.
507 Bottcher, G., Dau, A.-K., Ehrentreich, B., Hennings, U., Kape, H.-E., Kuhne, J., Lemke, G.,
508   Prohl, K., Puchert, W., Reuther, C., Schwerdtfeger, B., Stein, K., Voigt, B., 2012.
509   Bestandsaufnahme zur Klärung erhöhter Uran -Gehalte im Grund- und Trinkwasser in
510   Mecklenburg-Vorpommern. Landesamt für Umwelt, Naturschutz und Geologie, Güstrow.
511 Boyson, P., 1992. Schwermetalle und andere Schadstoffe in Düngemitteln, Forschungsbericht
512   107 01 016/01. Umweltbundesamt, Berlin.
513 Brimhall, G.H., Chadwick, O.A., Lewis, C.J., Compston, W., Williams, I.S., Danti, K.J., Dietrich,
514   W.E., Power, M.E., Hendricks, D., Bratt, J., 1992. Deformational mass-transport and
515   invasive processes in soil evolution. Science 255, 695-702.
516 Camelo, L.G.D., deMiguez, S.R., Marban, L., 1997. Heavy metals input with phosphate
517   fertilizers used in Argentina. Sci. Tot. Environ. 204, 245-250.
518 CCME, 2011. Scientific Criteria Document for the Development of the Canadian Water
519   Quality Guidelines for the Protection of Aquatic Life: Uranium. Canadian Council of
520   Ministers of the Environment, Winnipeg.
521 Clemens, S., Aarts, M.G.M., Thomine, S., Verbruggen, N., 2013. Plant science: the key to
522   preventing slow cadmium poisoning. Trends Plant Sci., 18(2): 92-99.
523 Cordell, D., Drangert, J.O. and White, S., 2009. The story of phosphorus: Global food
524   security and food for thought. Global Environ. Chang. 19, 292-305.
525 de Vries, W., Schütze, G., S., L., Tipping, E., Meili, M., Römkens, P., Groenenberg, J.E., 2005.
526   Calculation of critical loads for cadmium, lead and mercury, Alterra-report 1104,
527   Wageningen.
528 Della Peruta, R., Keller, A., Schulin, R., 2014. Sensitivity analysis, calibration and validation of
529   EPIC for modelling soil phosphorus dynamics in Swiss agro-ecosystems Environmental
530   Modelling & Software 62: 97-111.
531 EC (2016). Circular economy: New Regulation to boost the use of organic and waste-based
532   fertilisers. European Commission, Press Release. Available at:
533   http://europa.eu/rapid/press-release_IP-16-827_en.htm (accessed March 17, 2016)
534 Ekardt, F., Stubenrauch,J., 2013. Schadstoffanreicherungen in Böden als Governance und
535   Rechtsproblem – das Beispiel Cadmium Zugleich zu einigen Grundproblemen von

Ordnungsrecht. In: Hebeler, T., Hendeler, R., Proelss, A., Reiff, P. (eds). Jahrbuch des Umwelt- und Technikrechts 2013. Erich Schmidt Verlag, Berlin.

Elzinga, E.J., van Grinsven, J.J.M., Swartjes, F.A., 1999. Freundlich isotherms for cadmium, copper and zinc in soils. Eur. J. Soil Sci. 50:139–149.

Eriksson, J., 2001. Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertiliser, precipitation and in oil and crops, Report 5159. Swedish Environmental Protection Agency, Uppsala.

Eriksson, J., Andersson, A., Andersson, R., 1997. Current status of Swedish arable soils, rapport 4778. Naturvårdsverket.

FitzGerald, R., Roth, N., 2015. Cadmium in mineral fertilizers - human and environmental risk update. Report for the BLW. Swiss Center for Applied Human Toxicology, Basel.

Flisch R., Sinaj, S., Charles, R., Richner, W., 2009. GRUDAF 2009 — Grundlagen für die Düngung im Acker- und Futterbau. Agrarforschung 16:1–97

Gisler, A., Schwab, L., 2015. Marktkampagne Dünger 2011/2012 Kennzeichnung und Schwermetalle, Bundesamt für Landwirtschaft, Bern.

Gubler A., Schwab P., Wächter D., Meuli R. G., Keller A. 2015. Ergebnisse der Nationalen Bodenbeobachtung (NABO) 1985-2009. Zustand und Veränderungen der anorganischen Schadstoffe und Bodenbegleitparameter. Bundesamt für Umwelt, Bern.

Hämmann, M., Desaules, A., 2003. Manual: Sampling and sample pretreatment for soil pollutant surveys. Environment in practice (VU-4814-E). Federal Office for the Environment SAFEL,Bern.

Heinrichs, H., Mayer, R., 1977. Distribution and cycling of major and trace-elements in 2 central European forest ecosystems. J. Environ. Qual. 6, 402-407.

Herzog, F., Prasuhn, V., Spiess, E., Richner, W., 2008. Environmental crosscompliance mitigates nitrogen and phosphorus pollution from Swiss agriculture. Environ. Sci. Policy 11, 655–668.

Hukari, S., Hermann, L. and Nattorp, A., 2016. From wastewater to fertilisers - Technical overview and critical review of European legislation governing phosphorus recycling. Sci. Total Environ. 542, 1127-1135.

Huhle, B., Kummer, S., Stadler, S., Merkel, B.J., 2008. Mobility of uranium from phosphate fertilizers in sandy soils. In: De Kok, L.J., Schnug, E. (Eds.), Loads and fate of fertilizer derived uranium. Backhuys Publishers, Leiden pp. 47-55.

Iurian, A.-R., Phaneuf, M.O. and Mabit, L., 2015. Mobility and bioavailability of radionuclides in soils. In: Walther, C., Gupta, D.K. (Eds.), Radionuclides in the environment. Springer, Heidelberg, New York, Dordrecht, London.

Johnston, A.E., Jones, K.C., 1992. The cadmium issue - long-term changes in the cadmium content of soils and the crops grown on them. Phosphate Fertilizers and the Environment. Proceedings of an International Workshop 18, 255-269.

Jones, R.L., 1992. Uranium and phosphorus contents in morrow plot soils over 82 years. Commun. Soil Sci. Plan. 23, 67-73.

Kabata-Pendias, A., Mukherjee, A.B., 2007. Trace elements from soil to human. Springer, Berlin.

Keller, A., Desaules, A., 2004. Stoffbilanzen für Parzellen der Nationalen Bodenbeobachtung. Agrarforschung 11, 498-503.

Keller, A., Rossier, N., Desaules, A., 2005. Schwermetallbilanzen von Landwirtschaftsparzellen der nationalen Bodenbeobachtung. Agroscope FAL, Reckenholz.

Keller, A., Schulin, R., 2003. Modelling regional-scale mass balances of phosphorus, cadmium and zinc fluxes on arable and dairy farms. Eur. J. Agron. 20, 181-198.

585 Knappe F., Möhler S. A. Ostermayer, S. Lazar und C. Kaufmann. 2008. Vergleichende
586   Auswertung von Stoffeinträgen in Böden über verschiedene Eintragspfade.
587   Forschungsbericht 203 74 275 Umweltbundesamt. Dessau Germany. available at:
588   http://www.umweltbundesamt.de
589 Kratz, S., Knappe, F., Rogasik, J., E., S., 2008. Uranium balances in agroecosystems, in: de
590   Kok, L.J.a.S., E. (Ed.), Loads and fate of fertilizer derived uranium. Backhuys Publishers,
591   Leiden.
592 Kratz, S., Schick, J., Schnug, E., 2016. Trace elements in rock phosphates and P containing
593   mineral and organo-mineral fertilizers sold in Germany. Sci. Total Environ. 542, 1013-
594   1019.
595 Kumpiene, J., Brannvall, E., Wolters, M., Skoglund, N., Cirba, S. and Aksamitauskas, V.C.,
596   2016. Phosphorus and cadmium availability in soil fertilized with biosolids and ashes.
597   Chemosphere 151, 124-132.
598 Mann, S.S., Rate, A.W., Gilkes, A.J., 2002. Cadmium accumulation in agricultural soils in
599   Western Australia. Water Air Soil Poll. 141, 281-297.
600 Mar, S.S., Okazaki, M., 2012. Investigation of Cd contents in several phosphate rocks used
601   for the production of fertilizer. Microchem. J. 104, 17-21.
602 McLaughlin, M.J., Tiller, K.G., Naidu, R., Stevens, D.P., 1996. Review: The behaviour and
603   environmental impact of contaminants in fertilizers. Aust. J. Soil Res. 34, 1-54.
604 Moolenaar, S.W., Lexmond, T.M., 1998. Heavy-metal balances of agro-ecosystems in the
605   Netherlands. Neth. J. Agri. Sci. 46, 171-192.
606 Moolenaar, S.W., VanderZee, S.E.A.T.M., Lexmond, T.M., 1997. Indicators of the
607   sustainability of heavy-metal management in agro-ecosystems. Sci. Tot. Environ. 201,
608   155-169.
609 Nicholson, F.A., Jones, K.C., Johnston, A.E., 1994. Effect of phosphate fertilizers and
610   atmospheric deposition on long-term changes in the cadmium content of soils and crops.
611   Environ. Sci. Technol. 28, 2170-2175.
612 Nicholson, F.A., Smith, S.R., Alloway, B.J., Carlton-Smith, C., Chambers, B.J., 2003. An
613   inventory of heavy metals inputs to agricultural soils in England and Wales. Sci. Tot.
614   Environ. 311, 205-219.
615 Nziguheba, G., Smolders, E., 2008. Inputs of trace elements in agricultural soils via phosphate
616   fertilizers in European countries. Sci. Tot. Environ. 390, 53-57.
617 Oborn, I., Edwards, A.C., Witter, E., Oenema, O., Ivarsson, K., Withers, P.J.A., Nilsson, S.I.,
618   Stinzing, A.R., 2003. Element balances as a tool for sustainable nutrient management: a
619   critical appraisal of their merits and limitations within an agronomic and environmental
620   context. Eur. J. Agron. 20, 211-225.
621 Quezada-Hinojosa, R., Follmi, K.B., Gillet, F., Matera, V., 2015. Cadmium accumulation in six
622   common plant species associated with soils containing high geogenic cadmium
623   concentrations at Le Gurnigel, Swiss Jura Mountains. Catena 124, 85-96.
624 Rogasik, J., Kratz, S., Funder, U., Panten, K., Baumecker, M., Gutser, R., Lausen, P., 2008.
625   Uranium in soils of German long-term fertilizer experiments, in: De Kok, L.J.S, E (Ed.),
626   Loads and Fate of Fertilizer Derived Uranium. Backhuys Publishers, Leiden, pp. 135–146.
627 Roth, N., FitzGerald, R., 2015. Human and environmental impact of uranium derived from
628   mineral phosphate fertilizers. SCAHT report for BLW. Swiss Centre for Applied Human
629   Toxicology, Basel.
630 Rothbaum, H.P., Mcgaveston, D.A., Wall, T., Johnston, A.E., Mattingly, G.E.G., 1979. Uranium
631   accumulation in soils from long-continued applications of super-phosphate. J. Soil Sci. 30,
632   147-153.
633 Sattouf, M., 2007. Identifying the origin of rock phosphates and phosphorous fertilisers using
634   isotope ratio techniques and heavy metal patterns, in: Landbauforschung Völkenrode.

635 Schipper, L.A., Sparling, G.P., Fisk, L.M., Dodd, M.B., Power, I.L., Littler, R.A., 2011. Rates of
636   accumulation of cadmium and uranium in a New Zealand hill farm soil as a result of long-
637   term use of phosphate fertilizer. Agri. Ecosyst. Environ. 144, 95-101.
638 Schnug, E., Lottermoser, B.G., 2013. Fertilizer-Derived Uranium and its Threat to Human
639   Health. Environ. Sci. Tech. 47, 2433-2434.
640 Schnug, E., Steckel, H., Haneklaus, S., 2005. Contribution of uranium in drinking waters to the
641   daily uranium intake of humans - a case study from Northern Germany. Landbauforschung
642   Volkenrode 55, 227-236.
643 Schultheiß, U., Döhler, H., Roth, U., Eckel, H., Goldbach, H., Kühnen, V., Wilcke, W., Uihlein,
644   A., Früchtenicht, K., Steffens, G., 2004. Erfassung von Schwermetallströmen in
645   landwirtschaftlichen Tierproduktionsbetrieben und Erarbeitung einer Konzeption zur
646   Verringerung der Schwermetalleinträge durch Wirtschaftsdünger tierischer Herkunft in
647   Agrarökosysteme. Umweltbundesamt, Berlin.
648 Sheppard S.C., Sanipelli B., 2012. Trace elements in feed, manure and manured soils. J. Env.
649   Qual. 41: 1846:1856.
650 Shepherd, J.G., Sohi, S.P., Heal, K.V., 2016. Optimising the recovery and re-use of
651   phosphorus from wastewater effluent for sustainable fertiliser development. Water Res 94,
652   155-165.
653 Six, L., Smolders, E., 2014. Future trends in soil cadmium concentration under current
654   cadmium fluxes to European agricultural soils. Sci. Tot. Environ. 485, 319-328.
655 Smidt, G.A., Hassoun, R., Erdinger, L., Schäf, M., Knolle, F., Utermann, J., 2012. Uranium in
656   German tap and groundwater - Occurence and origins. In: Merkel, B.J., Schipper, M.
657   (Eds.), The New Uranium Mining Boom - Challenge and Lesson learned. Springer,
658   Berlin, Heidelberg.
659 Spiess, E., 2011. Nitrogen, phosphorus and potassium balances and cycles of Swiss
660   agriculture from 1975 to 2008. Nutr. Cycl. Agroecosys. 91, 351-365.
661 Stalder, E., Blanc, A., Haldimann, M., Dudler, V., 2012. Occurrence of uranium in Swiss
662   drinking water. Chemosphere 86, 672-679.
663 Takeda, A., Tsukada, H., Takaku, Y., Hisamatsu, S., Nanzyo, M., 2006. Accumulation of
664   uranium derived from long-term fertilizer applications in a cultivated Andisol. Sci. Tot.
665   Environ. 367, 924-931.
666 Taylor, M.D., Kim, N., 2008. The fate of uranium contaminants of phosphate fertilizer, in: De
667   Kok, L.J.S., E. (Ed.), Loads and Fate of Fertilizer Derived Uranium. Backhuys publishers,
668   Leiden, pp. 147–155.
669 Taylor, M.D., Kim, N.D., 2009. Dealumination as a mechanism for increased acid recoverable
670   aluminium in Waikato mineral soils. Aust. J. Soil Res., 47(8): 828-838.
671 Ulrich, A.E., Schnug, E., Prasser, H.M., Frossard, E., 2014. Uranium endowments in
672   phosphate rock. Sci. Tot. Environ. 478, 226-234.
673 Uterman, J., Fuchs, M., 2008. Uranium in German soils. in: De Kok, L.J.S., E. (Ed.), Loads and
674   Fate of Fertilizer Derived Uranium. Backhuys Publishers, Leiden, pp. 33-55.
675 VVEA, 2015, Verordnung über die Vermeidung und die Entsorgung von Abfällen, Schweizer
676   Bundesrat.
677 Wetterlind, J., Richer De Forges, A.C., Nicoullaud, B., Arrouays, D., 2012. Changes in uranium
678   and thorium contents in topsoil after long-term phosphorus fertilizer application. Soil Use
679   Manage. 28, 101-107.
680 Wilcke, W., Döhler, H., 1995. Schwermetalle in der Landwirtschaft. Landwirtschaftsverlag
681   GmbH, Munster-Hiltrup.