1 **Using isotopes to trace freshly applied**
2 **cadmium through mineral phosphorus fertilization in**
3 **soil-fertilizer-plant systems**
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26 **Abstract**

27 Applications of mineral phosphorus (P) fertilizer can lead to cadmium (Cd)
28 accumulation in soils and can increase Cd concentrations in edible crop parts.
29 To determine the fate of freshly applied Cd, a Cd source tracing experiment was
30 conducted in three soil-fertilizer-wheat systems by using a mineral P fertilizer
31 labeled with the radio isotope ^{109}Cd and by exploiting natural differences in Cd
32 stable isotope compositions ($\delta^{114/110}\text{Cd}$). Source tracing with stable isotopes
33 overestimated the proportion of Cd in plants derived from the P fertilizer,
34 because the isotope ratios of the sources were not sufficiently distinct from
35 those of the soils. Despite indistinguishable extractable Cd pools between
36 control and treatments, the addition of P fertilizer resulted in a more negative
37 apparent isotope fractionation between soil and wheat. Overall, the radio
38 isotope approach provided more robust results and revealed that 6.5 to 15 % of
39 the Cd in the shoot derived from the fertilizer. From the introduced Cd, a
40 maximum of 2.2 % reached the wheat shoots, whilst 97.8 % remained in the
41 roots and soils. The low recoveries of the fertilizer derived Cd suggest that
42 continuous P fertilizer application in the past decades can lead to a build-up of a
43 residual Cd pool in soils.

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47 **Key Words:** Cadmium, mineral P fertilizer, radio isotopes, source tracing, stable
48 isotopes, wheat, pot experiment

1. Introduction

The toxic element Cd occurs naturally in soils, but it has been additionally released into the environment through human activities. A major concern is posed by the unintended input of Cd into arable soils through mineral P fertilization (Jiao et al., 2012). Cadmium can substitute for Ca^{2+} in apatite ($\text{Ca}_{10-n}(\text{PO}_4)_6(\text{OH},\text{F})$, Fedoroff et al., 1999; Pan and Fleet, 2002; Sery et al., 1996). The latter is used to produce P fertilizer that contains, compared to the initial product, readily soluble $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and/or CaSO_4 and unintentionally also soluble Cd (Fedoroff et al., 1999; Prochnow et al., 2008). In Switzerland, the average Cd concentrations of P fertilizers are about 22 times higher than in arable soils (Bigalke et al., 2016; FOAG, 2015). Consequently, application of P fertilizer can lead to Cd accumulation in arable top soils (Bigalke et al., 2016) and to an increase of Cd in staple food products (Grant et al., 2013). In human nutrition, Cd poses a threat since it has a long biological half-life of about 10 years and damages organs such as the kidney (Godt et al., 2006). In this context, the fate of fertilizer-derived Cd and its impact on Cd transfer from soil to edible plant parts needs to be well understood in order to characterize the risk of Cd transfer into the food chain.

Isotope source tracing techniques are commonly used to investigate the fate of nutrients that were applied with fertilizer (e.g., Bosshard et al., 2009; McBeath et al., 2013; Nanzer et al., 2014). Compared to nutrient mass balances, isotope tracing of freshly applied nutrients provides further insights into the fate of nutrients by not only taking into account inputs- and outputs of soil-fertilizer-

72 plant systems but also the fluxes and dynamics within these systems. However,
73 to our knowledge only one study used isotopes (the radio isotope ^{109}Cd) to trace
74 fertilizer-derived Cd in soil-plant systems (Jensen and Mosbæk, 1990). It
75 revealed that 4 to 16 % of the Cd added to the soil-lettuce system with NPK-
76 fertilizer reached the plants, such that the majority of the applied Cd remained
77 in the soil. To date, no such study exists for wheat although it often receives Cd
78 through mineral P fertilizers and wheat is one of the main Cd contributors in the
79 diet of western European countries (Filippini et al., 2018; Vromman et al.,
80 2010).

81 Recent advances in metal stable isotope analysis enabled the use of isotope
82 ratios at natural abundance to trace sources of metals in the environment
83 (Wiederhold, 2015). The application of isotope ratios at natural abundances is
84 particularly interesting since the element sources of the investigated system do
85 not need to be additionally processed for Cd labeling, so that one manipulation
86 step that potentially creates artifacts can be skipped. Furthermore, the approach
87 does not require the purchase of isotope spikes, which significantly increase
88 costs depending on the size of the experiment and the scale of observation.
89 However, the contribution of different sources (e.g., soil, fertilizer) to a sink
90 (e.g., grain) can only be determined with confidence if (i) the sources have
91 distinct isotope ratios, (ii) the extent of isotope fractionation that occurs in the
92 system (e.g., during plant uptake and transport processes) is known or
93 negligible relative to the isotopic difference between the sources and (iii)
94 additional sources can be excluded. Two recent studies reported on the use of

95 stable isotopes at natural abundance to determine the impact of past
96 anthropogenic Cd inputs on the current Cd stocks in soils. Salmanzadeh et al.
97 (2017) showed that the Cd stock of arable soils can be dominated by past
98 applications of mineral P fertilizers. This finding is based on distinct isotope
99 ratios of old and new mineral P fertilizers, which governed the Cd isotope
100 compositions in the soils of a long-term field trial in New Zealand. Imseng et
101 al. (2018) measured Cd isotope ratios for all relevant inputs- (atmospheric
102 deposition, mineral and organic fertilizer, weathering), outputs (crop offtake,
103 leaching) and sinks (soil) of three arable cropping systems. Cadmium mass
104 balances and isotope ratios revealed that long-term processes such as soil
105 weathering and soil-plant cycling determined the current distribution of Cd
106 isotopes in soils whilst recent anthropogenic Cd inputs played a minor role.

107 Cadmium isotope ratios at natural abundance may also provide novel insights
108 into the fate of freshly applied Cd in soil-fertilizer-plant systems. Recent studies
109 have shown that the Cd isotope ratios of mineral P fertilizers ($\delta^{114/110}\text{Cd}$) range
110 between -0.15 ‰ and 0.15 ‰ (Imseng et al., 2018) while the plant-available Cd
111 pool (obtained using $\text{Ca}(\text{NO}_3)_2$ extraction) of arable Swiss soils ranged from
112 0.12 ‰ to 0.54 ‰ (Wiggenhauser et al., 2016). Furthermore, no or only minor
113 Cd isotope fractionation was observed between the plant-available Cd pool of
114 the arable soils and whole wheat plants ($\Delta^{114/110}\text{Cd}_{\text{whole plant-extractable}}$ -0.21 to
115 0.03 ‰). Thus, a source tracing approach using stable isotopes at natural
116 abundance would be applicable to selected soil-fertilizer-wheat systems, if the

117 addition of soluble mineral P fertilizer shifts the plant-available Cd pool
118 towards lighter isotopes.

119 In this study, Cd was freshly applied with a mineral P fertilizer and traced in
120 soil-wheat systems. This was achieved both with the aid of a Cd radio isotope
121 and stable isotope ratios at natural abundance, which were both employed in Cd
122 mass balances calculations. We aimed to (i) test if the natural variation of Cd
123 stable isotopes in the Cd sources of the plant (soil, fertilizer) can be used to
124 trace the distribution of freshly applied Cd in a closed soil-fertilizer-wheat
125 system and (ii) to quantify the fate of freshly applied Cd derived from mineral P
126 fertilization in soil-wheat systems.

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128 **2. Material & Methods**

129 **2.1. Soil-fertilizer-wheat systems**

130 Three soils from Oensingen (Oen), Wiedlisbach (Wied) and Landquart (LQ)
131 were selected to represent typical arable soils for wheat production in
132 Switzerland. The soils have distinct properties (Table A1) such as pH, texture
133 and C concentration which influence the size of the plant-available Cd pool
134 (Smolders and Mertens, 2013). For two of the three soils (Oen, Wied), Cd mass
135 balances at the field scale were determined recently (Imseng et al., 2018). The
136 third soil from LQ was chosen because of its comparatively high pH (7.1). In
137 Oen, we measured stable isotopes in soils and wheat that had received
138 unlabeled mineral P fertilizer. The wheat cultivar (*Triticum aestivum* L., cv.
139 “Fiorina”) has been commonly cultivated in the past years in Switzerland. A

commercially available mineral P fertilizer (triple super phosphate, TSP) was chosen with a Cd concentration of 19 mg kg⁻¹ Cd per kg of dry weight (equivalent to 92 mg kg⁻¹ P) which is at the upper end of Cd concentrations for mineral P fertilizers applied to Swiss agricultural soils (FOAG, 2015). We applied 500 mg mineral P fertilizer with 9.5 µg Cd (Table A2) to 1 kg of soil. This represents a P fertilization of 230 kg ha⁻¹ y⁻¹, an amount of P that is about 10 times larger than the current average P-fertilization of arable soils in Switzerland. However, P fertilization in Switzerland peaked in the 1970s and was then reduced by 80 % until 2005 (Spiess, 2011). Thus, the chosen model soil-fertilizer-wheat system can be considered as a worst-case scenario for Swiss farming practice in terms of unintended Cd addition to soils.

2.2. Fertilizer labeling

We adapted the protocol of Jensen and Mosbæk (1990) to label mineral P fertilizer with a radioactive Cd isotope. The P fertilizer (6.5g) was dissolved in deionized water (130mL, >18.2 MΩ) and continuously stirred. Afterwards, carrier-free ¹⁰⁹Cd (CdCl₂ in 0.5M HCl, 6MBq, radio isotope center POLATOM) was added to the mineral P fertilizer suspension, stirred for 10 min and evaporated slowly to dryness on a hotplate. The labeled fertilizer was then carefully ground and split into 13 portions, each containing 0.5 g of labeled fertilizer. Twelve portions were used for the pot experiment and one portion was used to measure the specific activity of the mineral P fertilizer added to each pot. For characterization, we compared the mineralogy of the inorganic crystallized species in the original mineral P fertilizer with the evaporated

163 fertilizer using Powder X-ray Diffraction (XRD, Bruker AXS D8 Advance).
164 The comparison revealed that the described procedure did not alter the Ca
165 speciation of the fertilizer (Fig. A1). Furthermore, the Cd water solubility of the
166 fertilizer was determined before and after evaporation. To this end, a solid to
167 liquid ratio of 1:10 with deionized H₂O (>18.2 MΩ) as extractant was used, the
168 reaction time was 2h on a horizontal shaker, where after the suspension was
169 passed through a paper filter (ashless filter, No. 42, Machery-Nagel). The
170 results showed that the labeling process did not change the water solubility of
171 Cd in the mineral P fertilizer (Table A2).

172 To test if the fertilizer addition to the soil changed the Cd isotope composition
173 of the plant-available Cd pool, a 0.05M Ca(NO₃)₂ extract was applied to soils
174 that had received mineral P fertilizer following the protocol reported previously
175 (Wiggenhauser et al., 2016).

176 **2.3. Pot experiment and sample processing**

177 Wheat was cultivated in the same way and period as published previously
178 (Wiggenhauser et al., 2016). Briefly, the pots where filled with 1 kg of dry soil,
179 macro and micro nutrients were added to ensure regular plant growth before the
180 wheat was sown. For the treatments that received mineral P fertilizer, we added
181 the finely ground mineral P fertilizer to the soils and homogenized soil and
182 fertilizer thoroughly before the wheat was sown. The ¹⁰⁹Cd-labeled mineral P
183 fertilizer was added to half of the pots. The other half received unlabeled
184 mineral P fertilizer that was processed in the same manner, following the
185 protocol outlined in section 2.2. Results for wheat that was grown on the same

186 soils without receiving fertilizer (control) were obtained for wheat grown in the
187 same period and are already published in Wiggenhauser et al. (2016). For each
188 soil and treatment, three (control, fertilizer with stable isotopes) or four
189 (fertilizer with radio isotope) replicates were prepared. Only three replicates
190 were prepared for treatments designated for stable isotope analyses because of
191 the time-consuming sample preparation that is required for these measurements.
192 For the control treatment of Oen, one of the four plants died (Wiggenhauser et
193 al., 2016).

194 For safety reasons, we did not collect root samples from the ^{109}Cd treatments.
195 Based on previous findings (Jensen and Mosbæk, 1990), we expected that most
196 of the ^{109}Cd remains in the soil and roots. Thus, the removal of soil from roots
197 would have produced a dust enriched in ^{109}Cd , which has a long radioactive
198 (462 d) and biological half-life (~10 y, Godt et al., 2006). Consequently, we
199 harvested only straw and grains from the ^{109}Cd -TSP treatment.

200 With the harvested plant parts, we were able to determine the Cd input to the
201 food chain (grain), the total Cd export from the soil after harvest (shoot = straw
202 + grain) and the Cd that could be in some cases returned to the soils with straw.
203 After harvest, the plant samples were milled and digested with HNO_3 in a single
204 reaction chamber microwave system (turboWave, MWS microwave systems,
205 Wiggenhauser et al., 2016). Radioactive Cd samples were milled in a fume hood
206 while wearing a protective mask.

2.4. Concentration and isotope measurements

Cadmium concentrations were determined using a quadrupole ICP-MS (Agilent 7500ce). The ^{109}Cd activity was measured using the 88 keV photon emission line by means of an intrinsic high-resolution Ge gamma spectrometer equipped with the spectrum software Interwinner (version 7.1.). For the determination of stable isotope ratios, Cd was first separated and purified using a three-stage column chemistry procedure and then analyzed using a double-spike technique by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS, Nu Plasma HR, Wiggenshauser et al., 2016).

2.5. Calculations and Statistics

The fraction of Cd in wheat derived from the fertilizer (Cd_{dff}) was calculated with Eq. 1:

$$\text{Cd}_{\text{dff}} = \frac{\text{SA}_{\text{wheat}}}{\text{SA}_{\text{fertilizer}}} \times 100 \quad (1)$$

where SA denotes the specific activity [$\text{Bq } (\mu\text{g Cd})^{-1}$] of the fertilizer or in a specific wheat part (straw, grain, shoot). The specific activity was calculated with Eq. 2:

$$\text{SA} = \frac{{}^{109}\text{Cd}}{\text{Cd}} \quad (2)$$

where ^{109}Cd denotes the radioactivity [$\text{Bq } (\text{g dry matter [DM]})^{-1}$] of the straw, grain, or shoot and the denominator represents the Cd concentration [$\mu\text{g Cd } (\text{g DM})^{-1}$] of the plant parts. Equations 1 and 2 can be used to calculate the Cd mass in straw and grains derived from the fertilizer with Eq. 3:

$$Cd_{mass.dff} = \frac{Cd_{dff}}{100} \times Cd_{mass} \quad (3)$$

where Cd_{mass} denotes the Cd mass [$\mu\text{g Cd (g DM plant)}^{-1}$] in straw, grain, or shoot. Finally, knowing the fertilizer-derived Cd mass in these plant parts, the fertilizer recovery [%] can be calculated with Eq. 4:

$$Cd_{recovery} = \frac{Cd_{mass.dff}}{Cd_{mass.added}} \times 100 \quad (4)$$

where $Cd_{mass.added}$ denotes the Cd mass [$\mu\text{g Cd (g DM soil)}^{-1}$] introduced into the soil-wheat systems for the fertilizer application.

Stable isotope ratios were used to calculate Cd_{dff} [%] with an end member-mixing model in the soil-fertilizer-wheat systems of Oen (Eq. 5):

$$Cd_{dff.shoot} = \frac{(\delta_{shoot.ferti} - \Delta_{corr.shoot}) - \delta_{soil.ctrl}}{\delta_{fertilizer} - \delta_{soil.ctrl}} \times 100 \quad (5)$$

The calculated $Cd_{dff.shoot}$ values can be further applied to Eq. 3 and 4. In Eq. 5, all δ values refer to $\delta^{114/110}\text{Cd}$ [‰], which was expressed relative to the NIST SRM 3108 isotope reference material (Abouchami et al., 2013). The $\delta_{fertilizer}$ and $\delta_{shoot.ferti}$ values denote the Cd isotope ratios of the mineral P fertilizer and the shoots that were grown with fertilizer added, respectively. To calculate Cd_{dff} for straw and grain, isotope ratios with the index “shoot” need to be replaced accordingly. $\delta_{soil.ctrl}$ represents the Cd isotope ratio for the plant-available Cd in the control pot. In Oen, this soil pool is well represented by the $\delta^{114/110}\text{Cd}$ value of the $\text{Ca}(\text{NO}_3)_2$ soil extract (Wiggenhauser et al., 2016). Furthermore, any

247 apparent Cd isotope fractionation within the soil-wheat system was corrected
248 with Eq. 6:

$$249 \quad \Delta_{corr.shoot} = \delta_{shoot.ctrl} - \delta_{soil.ctrl} \quad (6)$$

250 where $\Delta_{corr.shoot}$ [‰] denotes the apparent Cd isotope fractionation between the
251 shoot and the soil δ_{soil} that is represented by the $\text{Ca}(\text{NO}_3)_2$ soil extract. Eq. 6 can
252 also be used to calculate the apparent isotope fractionation between shoot-root
253 and grain-straw. The calculations thereby assume that the addition of mineral P
254 fertilizer did not change the Cd isotope fractionation in the soil-wheat system.
255 This assumption was tested by comparing the apparent isotope fractionation
256 between the wheat shoot and the extractable Cd in the soil pool ($\Delta^{114/110}\text{Cd}_{shoot-}$
257 extractable) and between the analyzed shoot parts for samples from both fertilized
258 and control pots.

259 We also calculated the apparent fertilizer use efficiency (AUE, Muñoz et al.,
260 2004) for Cd. The AUE [%] expresses the relative increase of the Cd mass in
261 the wheat from the addition of Cd with the mineral P fertilizer (Eq. 7):

$$262 \quad AUE = \frac{Cd_{wheat.ferti} - Cd_{wheat.ctrl}}{Cd_{ferti}} \times 100 \quad (7)$$

263 where $Cd_{wheat.ferti}$ and $Cd_{wheat.ctrl}$ denotes the Cd mass [$\mu\text{g} (\text{kg soil})^{-1}$] in the shoot,
264 straw, or grain of a fertilized (non labeled) or unfertilized control plant,
265 respectively. Cd_{ferti} denotes the Cd mass [$\mu\text{g} (\text{kg soil})^{-1}$] that was added to the
266 pots with the mineral P fertilizer.

267 To test if the observed mean Cd concentrations, masses, $\delta^{114/110}\text{Cd}$ values, Cd_{diff}
268 and $Cd_{recovery}$ were significantly different from each other, an ANOVA procedure

269 followed by a Tukey HSD post-hoc test were applied. If required, the response
270 variable was $\log_{10}$, square root, or $1/x$ transformed to produce homogeneity of
271 variance and normal distribution of the residuals.

3. Results

3.1. Dry matter production and Cd concentrations in wheat shoots

Wheat shoot DM production differed among the soils (Table 1). Shoot DM production was significantly higher in Wied (15.8 to 16.4 g) compared to Oen (10.1 to 14.9 g) and LQ (13.2 to 15.8 g). Significantly less shoot DM was produced in the treatments that did not receive mineral P fertilizer (10.1 to 15.8 g) compared with the wheat that had received ^{109}Cd -labeled mineral P fertilizer (14.9 to 18.4 g).

The different soil properties significantly influenced Cd concentrations of the wheat shoots (Table 1). Cadmium concentration in the shoots were higher in Oen (95 to 127 ng g^{-1}) than Wied (72 to 98 ng g^{-1}) and higher in Wied than in LQ (37 to 59 ng g^{-1}). The fertilizer addition had no significant impact on Cd concentrations in the shoot, straw and grain, except in Oen, where the Cd concentration was higher in plants treated with labeled or unlabeled P fertilizer (127 to 144 ng g^{-1} for shoots) than for the control treatment (95 ng g^{-1}). Furthermore, the accumulated Cd mass in the shoot varied strongly among the soils (average: LQ $0.63 \pm 0.08 \mu\text{g}$, Oen $1.61 \pm 0.56 \mu\text{g}$, Wied $1.38 \pm 0.22 \mu\text{g}$, Table 1) but was less influenced by the mineral P fertilizer addition (average: control $0.96 \pm 0.22 \mu\text{g}$, mineral P fertilizer $1.13 \pm 0.63 \mu\text{g}$).

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**Table 1: Dry matter (DM)
production, Cd
concentration and Cd mass
in wheat shoots**

Treatment ^a	DM						Cd concentration						Cd mass					
	LQ ^c		Oen ^c		Wied ^c		LQ ^c		Oen ^c		Wied ^c		LQ ^c		Oen ^c		Wied ^c	
	mean	sd ^b	mean	sd ^b	mean	sd ^b	mean	sd ^b	mean	sd ^b	mean	sd ^b	mean	sd ^b	mean	sd ^b	mean	sd ^b
	g		g		g		ng g ⁻¹		ng g ⁻¹		ng g ⁻¹		μg		μg		μg	
Control ^f	13.2 ± 4.34 ab		10.1 ± 3.77 b		15.8 ± 0.91 ab		58.5 ± 25.6 cd		95.1 ± 26.2 bc		72.4 ± 5.34 cd		0.72 ± 0.212 cd		1.03 ± 0.589 b-d		1.14 ± 0.079	
Shoot ¹⁰⁵ Cd P fertilizer	15.8 ± 1.35 ab		14.9 ± 1.05 ab		18.4 ± 0.46 a		36.8 ± 4.01 d		144 ± 11.8 a		76.3 ± 4.96 cd		0.58 ± 0.035 d		2.14 ± 0.154 a		1.41 ± 0.125	
P fertilizer	13.4 ± 3.66 ab		13.1 ± 1.22 ab		16.4 ± 0.89 a		44.9 ± 8.12 d		127 ± 11.1 ab		98.4 ± 35.7 bc		0.59 ± 0.101 d		1.67 ± 0.203 ab		1.60 ± 0.526	
Control ^f	7.34 ± 2.53 ab		5.98 ± 2.32 b		8.39 ± 0.43 ab		25.9 ± 9.70 c		63.4 ± 14.2 b		27.0 ± 1.73 c		0.17 ± 0.025 d		0.40 ± 0.209 bc		0.23 ± 0.025	
Grain ¹⁰⁵ Cd P fertilizer	9.38 ± 0.58 ab		9.49 ± 0.56 ab		10.3 ± 0.55 a		20.7 ± 1.59 c		99.9 ± 16.8 a		39.0 ± 3.77 c		0.19 ± 0.012 d		0.95 ± 0.160 a		0.40 ± 0.052	
P fertilizer	7.65 ± 2.07 ab		7.88 ± 0.83 ab		9.15 ± 0.39 ab		23.3 ± 5.32 c		69.8 ± 3.40 ab		37.3 ± 4.79 c		0.17 ± 0.023 d		0.55 ± 0.047 ab		0.34 ± 0.056	
Control ^f	5.84 ± 1.81 a-c		4.11 ± 1.46 c		7.42 ± 0.85 ab		100 ± 57.6 bc		142 ± 56.7 a-c		125 ± 15.3 bc		0.54 ± 0.229 b-d		0.63 ± 0.383 a-d		0.92 ± 0.055	
Straw ¹⁰⁵ Cd P fertilizer	6.38 ± 0.81 a-c		5.39 ± 0.59 bc		8.10 ± 0.99 a		60.8 ± 9.81 c		222 ± 10.1 a		124 ± 8.10 bc		0.38 ± 0.025 d		1.19 ± 0.095 a		1.00 ± 0.175	
P fertilizer	5.73 ± 1.60 a-c		5.26 ± 0.44 bc		7.21 ± 0.80 ab		73.8 ± 11.4 c		212 ± 28.0 ab		177 ± 84.1 ab		0.41 ± 0.080 cd		1.12 ± 0.160 ab		1.25 ± 0.542	

^aP-fertilizer and ¹⁰⁵Cd P-fertilizers refers to the stable and radio isotope approaches, respectively. I and II refer to Cd recovery values that were calculated with and without outlier, respectively (see text for details). The data from control treatment was taken from Wigganhauser et al. 2016.

^bsd denotes standard deviation of n = 3 (stable isotope, AUE) and n = 4 samples (radio isotopes). Small letters denote significant differences between the mean determined with a two-way ANOVA (y ~ soil | 3 * fertilizer | 2) and Tukey HSD post-hoc test.

^cLQ, Oen, and Wied refer to the origin of the arable soils used for the pot trial, i.e. the Swiss villages of Landquart, Oensingen and Wiedlisbach, respectively.

3.2. Source tracing of Cd using the P fertilizer labeled with ^{109}Cd

The proportion of Cd in straw and grains of wheat that derived from the mineral P fertilizer labeled with ^{109}Cd (Cd_{dff} , Eq.1) differed significantly among the soils (Figure 1a). The Cd_{dff} values were highest in Wied ($14.9 \pm 0.73 \%$), followed by LQ ($8.1 \pm 1.31 \%$) and Oen ($6.5 \pm 0.23 \%$). Furthermore, Cd_{dff} was higher in straw (7.9 to 16.7 %) than in the grains (4.7 to 10.6 %) for all soils (Figure 1a).

From the total Cd introduced into the soil-wheat systems by the mineral P fertilizer, only a minor part ($< 2.2 \%$) was recovered in straw and grains of wheat (Figure 1b). Among the soils, most Cd was recovered in the shoots in Wied ($2.2 \pm 0.10 \%$), followed by Oen ($1.5 \pm 0.03 \%$) and LQ ($0.50 \pm 0.05 \%$, Figure 1b). Among the shoot organs, less Cd was recovered in the grains (0.12 to 0.47 %) compared to the straw (0.40 to 1.7 %) on all soils.

Figure 1: a) Fraction of Cd in straw and grains of wheat that was derived from the fertilizer (Cd_{dff}) calculated with radio isotopes. b) Fraction of Cd introduced with the fertilizer that was recovered in straw and grains of wheat (Cd_{recovery}). Brown circles and green triangles denote grain and straw, respectively. LQ, Oen, and Wied denote the arable soils used. Error bars denote standard deviation of n = 4 replicates. Small letters denote significant differences between the means of straw and grains of all soils (two-way ANOVA and Tukey HSD post-hoc test)

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311 3.3. Source tracing of Cd applied with mineral P fertilizer using the 312 stable isotopes and mass balance

313 The fertilizer addition altered the apparent isotope fractionation of Cd between
314 the whole plant and the Ca(NO₃)₂ extractable soil pool in Oen. Specifically, the
315 fractionation $\Delta^{114/110}\text{Cd}_{\text{wholeplant-extractable}}$ was $-0.04 \pm 0.07 \text{ ‰}$ for the control plants
316 and $-0.28 \pm 0.07 \text{ ‰}$ for the plants treated with the P fertilizer (Figure 2a).
317 However, the Cd extractable soil pools had identical isotope compositions
318 within error, with results of $\delta^{114/110}\text{Cd}_{\text{control}} = 0.50 \pm 0.01 \text{ ‰}$ (Wiggenhauser et al.,

2016) and $\delta^{114/110}\text{Cd}_{\text{fertilizer}} = 0.56 \pm 0.06 \text{ ‰}$ (Table A1). The $\delta^{114/110}\text{Cd}$ values of shoots, straw and grains from the control and fertilizer treatments also did not differ significantly from each other (Figure 2b). However, wheat shoots, as well as grains and straw, appear to have slightly lower $\delta^{114/110}\text{Cd}$ for the fertilizer (0.37 to 0.40 ‰) than the control treatment (0.52 to 0.62 ‰, Figure 2b). Whilst this difference was not significant, it markedly influenced the results of the Cd_{diff} calculations that were based on the stable isotope mass balance (E1. 5; see details in section 4.1).

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Figure 2: Stable isotope results obtained for soil-wheat systems from Oen (no results are available for the other locations). a) Apparent Cd isotope fractionation in different compartments of soil-wheat systems. b) Cd isotope ratios of straw and grains of soil-fertilizer-wheat systems. Different shapes and colors of the symbols denotes soil-wheat systems that received (green triangles) or did not receive mineral P fertilizer (blue circles). Error bars denote standard deviation of $n = 3$ replicates. Small letters denote significant differences between the paired means. Plant- available Cd was extracted from the bulk soil using $\text{Ca}(\text{NO}_3)_2$. The Oen control data were taken from Wiggerhauser et al. 2016.

331 Source tracing calculations that employ stable isotopes revealed that $36 \pm 5 \%$
332 of the Cd in the Oen wheat shoots were derived from the fertilizer (Figure 3).
333 To test the sensitivity of the Cd_{dff} calculation using stable isotopes (Eq. 5), we
334 recalculated the mean $\Delta_{corr.shoot}$ (Eq. 6) following removal of the outlier in the
335 control treatment, which was strongly enriched in heavy isotopes compared to
336 the other treatments due to the low DM production and, as a consequence,
337 limited Cd uptake from the soil (Table 1). The recalculated results, illustrated in
338 Figure 3 as “stable isotopes II”, feature lower Cd_{dff} values (22 to 24 %) than the
339 original ‘stable isotope I’ data. Source tracing based on the natural stable Cd
340 isotope composition of the system hence resulted in significantly higher Cd_{dff}
341 values (22 to 30 %) than source tracing calculations for the radio label. As a
342 consequence, the stable isotope data suggest a significantly higher recovery of
343 the fertilizer-derived Cd in the wheat ($Cd_{recovery}$) than the radio isotope results
344 (Table 2).

345 In addition, the Cd recovery was also calculated based on the AUE, which is a
346 completely non-isotope mass balance approach (Eq. 7; Table 2). Calculations
347 with the AUE method produce significantly higher Cd recoveries for the shoots
348 (3.16 to 6.71 %) than the radio isotope approach ($1.46 \pm 0.06 \%$) and are also
349 somewhat lower than the stable isotope results (4.31 to 7.37 %). Importantly,
350 the standard deviations of the stable isotope and AUE $Cd_{recovery}$ data ($sd = 0.84$
351 to 3.77 %) are more than one order of magnitude larger compared to the radio
352 isotope results, which have sd values of 0.06 to 0.09 % (Table 2).

353

Figure 3: Comparison of methods to calculate the fraction of Cd derived from the mineral P fertilizer in shoot, straw and grains of wheat (Cd_{dff}) grown on soils from Oen (no results are available for the other locations). Different shapes and colors of the symbols denote different calculation methods: red circles = stable isotopes I, light green triangles = stable isotope II, dark green rectangles = radio isotopes. The stable isotope I and II were calculated either including or excluding a single outlier in the data reduction, respectively (see text for details). Error bars denote standard deviation of $n = 3$ replicates. Small letters denote significant differences of the mean for each box. The Oen control data that were used to calculate the stable isotope based Cd_{dff} values are from Wiggerhauser et al. (2016).

Table 2: Comparison of the Cd recovery from freshly applied mineral P fertilizer calculated with radio isotopes, stable isotopes and mass balance (Apparent Use Efficiency, AUE)

Method ^a	Shoot recovery		Straw recovery		Grain recovery	
	(%)	sd ^b	(%)	sd ^b	(%)	sd ^b
Radio isotope	1.46	± 0.06 b	0.99	± 0.07 b	0.47	± 0.09 b
Stable isotope I	7.37	± 3.77 a	4.24	± 2.43 ab	3.13	± 1.33 a
Stable isotope II	4.31	± 3.05 ab	3.00	± 2.11 ab	1.31	± 0.94 ab
AUE I	6.71	± 2.39 a	5.09	± 2.01 a	1.62	± 0.84 ab
AUE II	3.16	± 2.38 ab	2.78	± 2.01 ab	0.38	± 0.84 b

^aI and II refer to Cd recoveries that were calculated with and without outlier, respectively (see text for details).

^bsd denotes standard deviation of $n = 3$ (stable isotope, AUE control) and $n = 4$ samples (radio isotopes, AUE fertilized). Small letters denote significant differences between the mean within each column.

4. Discussion

4.1. Comparison of Cd source tracing methods

The Cd_{diff} and the $Cd_{recovery}$ values that were determined for wheat based on stable isotope data or a mass balance (AUE) approach are significantly higher compared to the radio isotope results, which were obtained using a mineral P fertilizer labeled with ^{109}Cd (Figure 3).

For the stable isotope calculations, the removal of the outlier from the control treatment data produced markedly lower Cd_{diff} values, by up to -26% (Figure 3). This demonstrates that even small changes or uncertainties in the isotope compositions of the sources and sinks have a significant impact on the calculated Cd_{diff} results. Furthermore, the $\delta^{114/110}Cd$ values of the sources range from 0.02 to 0.50 ‰. For this range, a 1% contribution of P fertilizer-derived Cd to the shoot changes the isotope composition of the shoot by only 0.005 ‰. In comparison, the external reproducibility of the isotope measurements was $\pm 0.083\text{‰}$ (2sd, Wiggerhauser et al., 2016), which is equivalent to an uncertainty of about $\pm 16\%$ for the final Cd_{diff} values. As such, our data do not fulfill the prerequisite that the isotope compositions of the two Cd sources for the plants (mineral P fertilizer and soil) are sufficiently distinct to enable precise source tracing (Wiederhold, 2015).

In addition, any change of the apparent isotope fractionation between soil and wheat also influences the source tracing results. The application of mineral P fertilizer did not significantly change the isotope composition of the $Ca(NO_3)_2$ extract (considering the analytical uncertainty; Table A1), but it did alter the

386 isotope fractionation between the extract and the shoot. This suggests that the
387 mineral P fertilizer, comprised mainly of Ca^{2+} , PO_4^{3-} and SO_4^{2-} ions (Fig. A1),
388 might have altered the speciation of the extractable and plant-available Cd,
389 thereby also affecting the isotope compositions of the Cd pool that was
390 transferred to the wheat shoot. Consequently, the shift in $\delta^{114/110}\text{Cd}$ for the wheat
391 shoots was partly due to stable isotope fractionation and not exclusively a
392 consequence of mixing Cd derived from the two relevant sources.

393 The addition of a radio isotope to a mineral P fertilizer can potentially create
394 artifacts. For example, labeling of a fertilizer with an isotope requires that the
395 introduced radio isotopes are homogeneously distributed (Frossard et al., 2011).
396 In this study, a qualitative XRD analysis showed that the labeling process did
397 not alter the Ca speciation during the labeling procedure (Fig. A1).
398 Furthermore, the water- soluble Cd fraction of the mineral P fertilizer (~ 40 %)
399 was not changed by the labeling procedure (Table A2). Thus, it is therefore
400 likely that the introduced, carrier-free ^{109}Cd could readily formed inorganic
401 complexes with PO_4^{3-} and / or replaced native Cd, Ca or other metal cations that
402 were present in the mineral P fertilizer and in particular, its water-soluble pool.
403 Furthermore, Prochnow et al. (2008) showed that a part of the Ca present in
404 mineral P fertilizers is still hosted in weakly soluble minerals, such as apatite,
405 which accounted for about 3.1 to 6.4 % of the fertilizer mass. This suggests that
406 the radio labeling procedure used here might not have accessed and exchanged
407 with insoluble Cd pools within the fertilizers. As worst case scenario, the added
408 ^{109}Cd would have only exchanged with the water soluble pool which represents

409 41.3 % of the total Cd of the P-fertilizer (Table A2). If this scenario is applied to
410 Eq. 1-4, Cd_{recovery} values decrease from initially 0.50 to 2.2 % to 0.21 to 0.90 %.
411 Notably, such corrections would further increase the difference between the
412 results of the radio isotope and the stable isotope approach.

413 The AUE mass balance approach to determine the Cd recovery in wheat shoots
414 also produced higher Cd recovery values and larger standard deviations than the
415 radio isotope approach (Table 2). The high Cd_{recovery} results might reflect the
416 small observed differences in the Cd masses of the control and fertilized wheat
417 shoots, which significantly impacts the precision of the AUE method. The AUE
418 mass balance approach is therefore less suitable for systems with low recoveries
419 and more precise for nutrients with high recovery rates such as N and P (e.g.,
420 recovery higher than 30% for mineral fertilizer in similar soil-plant systems;
421 Bosshard et al., 2009; Nanzer et al., 2014)

422 In summary, among the three approaches applied in this study, the radio isotope
423 approach provides most robust results and these are applied in the following to
424 constrain and discuss the fate of fertilizer-derived Cd in soil-wheat systems.

425

426 **4.2. The fate of freshly applied Cd through P-fertilization**

427 The Cd mass in the shoot is equal to the Cd mass exported from the soil during
428 harvesting, if no straw is left at the soil surface (Figure 4). The export of Cd
429 from soil to shoot varied significantly among the soils (Oen and Wied > LQ)
430 and was lowest for the soil with the highest pH (Figure 4). This finding is in
431 accordance with the results of previous studies and reflects that the solubility of

Cd increases with decreasing pH (Gray et al., 1999; Guttormsen et al., 1995) through proton-Cd exchange and less specific sorption (Loganathan et al., 2012). The export of Cd from soil to shoot was less influenced by the addition of mineral P fertilizer (Table 1), although the dose and Cd concentration of the added material represents a worst-case scenario for Cd input via fertilizer into Swiss agricultural systems (FOAG, 2015; Spiess, 2011). The strong influence of soil properties on Cd export into the shoot is in agreement with previous observations of a field study at the same sites (Imseng et al., 2018). However, the observed difference for the exported Cd between Oen and Wied was larger in the field study (Oen 2.6 times higher than Wied) than in the current pot study (1.5). The larger difference that observed in the former might reflect that Cd losses with seepage water were larger in the sandy soils of Wied ($0.99 \text{ g h}^{-1} \text{ y}^{-1}$) than in the clay rich Oen soils ($0.02 \text{ g h}^{-1} \text{ y}^{-1}$, Imseng et al., 2018). Such losses did not occur in the pot trial of this investigation, as this featured a completely closed soil-fertilizer-wheat system, with no Cd losses or additions after sowing.

Figure 4: Cadmium mass balances in three soil-fertilizer-wheat systems. Bold letters indicate origin of the soils from Landquart (LQ), Oensingen (Oen) and Wiedlisbach (Wied). The size of the boxes indicate the Cd mass in the individual compartments (brown = soil, blue = plant-available Cd, light red = mineral P fertilizer, green = wheat shoot). The size of the arrows (black) are not proportional to the box size but proportional to each other. Cd_{rec} denotes Cd recovery in the wheat shoots. The pie chart inset denotes the mass fraction of Cd in the wheat shoot derived from the P-fertilizer (Cd_{dff}). Data in brackets next to the soil names summarize soil properties: total Cd in soil, soil pH and cation exchange capacity (CEC). Data in brackets in the soil pool and mineral P fertilizer boxes represent the proportion of Cd relative to the total Cd mass in the soil. Soil data was taken from Wiggenhauser et al. (2016).

449 Although the addition of mineral P fertilizer generally did not increase the
 450 export of Cd from soil to wheat, up to 17 % and 11 % of the Cd in the straw and
 451 grains was derived from the fertilizer, respectively (Figure 1a). Moreover, Cd_{dff}
 452 differed significantly between the soils whereby higher Cd_{dff} was observed if
 453 more Cd was added to the soil, relative to the total soil Cd stock already present
 454 (Figure 4), in accord with previous results for soil-fertilizer-lettuce systems

455 (Jensen and Mosbæk, 1990). This suggests that the fertilizer-derived Cd was
456 diluted by Cd already present in the soils.

457 The comparatively low Cd recoveries found here are, however, in good
458 agreement with Cd recoveries determined for soil-fertilizer-lettuce systems (4
459 to 16%, Jensen and Mosbæk, 1990). The low recoveries suggest that the
460 continuous applications of mineral P fertilizers over the past decades probably
461 led to the accumulation of residual Cd. Field data obtained for arable soils of
462 Switzerland supports this hypothesis. In particular, two recent studies attributed
463 Cd accumulation in top- compared to subsoils at arable farming sites at least in
464 part to the past use of mineral P fertilizer (Bigalke et al., 2016; Imseng et al.,
465 2018). The build-up of a residual Cd pool might thereby have started as early as
466 in the 1950s (Spiess, 2011). From that time until now, P-fertilization in
467 Switzerland peaked in the 1970s and was then reduced by 80 % until 2005.
468 Thus, it is likely that the rate at which Cd was added by mineral P fertilizers
469 was higher in the past, provided that the Cd concentrations of the fertilizers
470 were similar in the past and present (FOAG, 2015). Furthermore, a residual Cd
471 pool would not only change the total Cd stock of the soils, but also increase the
472 total concentration of plant-available Cd (Gray et al., 2016; Hamon et al.,
473 1998). As such, the residual mineral P fertilizer derived Cd pool would impact
474 the transfer of Cd from soils to plant.

475 To constrain the size and the impact of a possible residual fertilizer-derived Cd
476 pool in soils on current fluxes of Cd in soil-plant systems, it is desirable to
477 conduct source tracing study of fertilizer-derived Cd for soils that differ only in

478 their fertilization history. As it was previously demonstrated for P, such an
479 investigation can distinguish between contributions of geogenic soil-derived
480 Cd, residual Cd in soil and Cd from mineral P fertilizer (Gallet et al., 2003).
481 Such a study would thus help to improve the relationships between past
482 P fertilizer applications and current Cd fluxes in arable soil systems.

483 **5. Conclusion**

484 Radio isotope methods provided the most robust approach for tracing Cd that
485 was applied with mineral P fertilizer to soil-wheat systems. The application of
486 natural Cd stable isotope data for this purpose provided estimates of the Cd that
487 derived from the fertilizer and the Cd recovery in the wheat that were imprecise
488 and too high because the isotope compositions of the two Cd sources (soil and
489 fertilizer) were too similar. Cadmium source tracing using radioactive ^{109}Cd
490 revealed that only a small fraction ($< 3\%$) of the Cd that was applied with
491 mineral P fertilizer reached the wheat shoots. The majority of the Cd that was
492 added to soils with mineral P fertilizer hence remained in the soil and might
493 contribute to the build-up of a residual Cd pool. We hypothesize that the past
494 build-up of such a residual Cd pool in soils may significantly impact the current
495 fluxes of Cd in soil-plant systems.

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