

Cadmium isotope fractionation in soil-wheat systems

Supporting Information

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1. Materials and Methods (detailed information)

1.1. Plant growth experiment

To ensure regular plant growth, 100 mg N (80 mg N applied as $\text{Ca}(\text{NO}_3)_2$ and 20 mg as NH_4NO_3), 35 mg P (KH_2PO_4), 50 mg K (K_2SO_4), 25 mg Mg (MgSO_4), 5 mg Fe (Fe-EDTA) and 2 mg Zn (ZnSO_4) were added to each pot and mixed thoroughly.

The wheat plants were cultivated in a growth chamber with the following settings: photoperiod 16 h, illuminance 25 klx, temperature 24°C at daytime and 16°C at night, humidity 60%. The wheat was watered to maintain a range of 40 to 70% of the maximal water holding capacity (Table S2).

1.2. Sample preparation

The roots were rinsed with 6 mM NaNO_3 and transferred for 15 min into a 6 mM NaNO_3 cleaning bath followed by rinsing with the same solution. Cleaning bath (5 min) and rinsing were repeated up to three times until the roots and waste cleaning solution were visibly free of any soil particles. Sodium nitrate was chosen to disperse the clay minerals that adhered to the roots.¹ The concentration of the cleaning solution was adapted to the equivalent of the conductivity² in soil solutions obtained in currently running field studies at the same study sites (own, unpublished results).

To digest the plants in the high pressure single reaction chamber microwave system (turboWave, MWS microwave systems), 1 g portions of material were treated using 12 ml 8 M HNO_3 . The A and C horizon of the soils were digested using a mixture of 8 ml 16 M HNO_3 and 2 ml 24 M HF (Milestone, SK-10 high pressure rotor). Several digestion batches of one sample were combined to achieve a minimum quantity of 100 ng Cd for isotopic analysis.

1.3. Analyses and standard reference materials

Application of the double spike methodology for the Cd isotope analyses ensured that results were unbiased by any isotope fractionation induced by the Cd separation chemistry and enabled precise correction for the large instrumental mass bias incurred in MC-ICP-MS. Additionally, use of the double spike facilitated precise determination of Cd concentrations by isotope dilution (ID).³ To this end, an appropriate volume of the ^{111}Cd - ^{113}Cd double spike solution was equilibrated with the samples after digestion.⁴ Cadmium was then separated from the sample matrix using a three-stage separation chemistry that employs both anion exchange and extraction chromatography.^{4, 5} This was followed by a liquid-liquid extraction step for sample cleanup.⁵

Cadmium concentrations determined by ID-MC-ICP-MS for plant and soil samples ($n = 2-3$) were employed to investigate the relationship between Cd pool sizes and Cd isotope fractionation (Table 1, Figure 3, Figure S3). The Cd concentrations of all plant samples were also measured by quadrupole ICP-MS without prior matrix separation. These results exceeded the Cd abundances determined by ID-MC-ICP-MS by $7.5 \pm 2.0\%$ (1se). The quadrupole ICP-MS Cd data were used to compare the Cd concentrations and Cd quantities of plant samples ($n = 4$; Figure S1).

A number of standard reference materials (SRMs) were analyzed during the course of the study for quality control, with results summarized in Table S1. The performance of the MC-ICP-MS instrument was routinely monitored based on multiple analyses of SRM BAM I012 Cd. These measurements yielded $\delta^{114/110}\text{Cd} = -1.30 \pm 0.09$ (2sd, $n = 12$), in good agreement with the consensus value of -1.33 ± 0.04 .⁶

The Cd isotope compositions and contents of three geological and biological SRMs with matrices and Cd concentrations similar to those of the experimental samples were also analyzed. These were andesite rock USGS SRM AGV-2, soil NIST SRM 2709a, and wheat flour NIST SRM 1567b (Table S1). The Cd concentrations of the SRMs were determined using the added double spike for ID calculations.³ The Cd isotope data acquired for these SRMs showed good reproducibilities of

between 0.02‰ and 0.11‰ (2sd, n=2–6), as determined from multiple analyses of separately treated sample aliquots (Table S1). Isotopic reference data are unfortunately not available for these SRMs.

The Cd concentrations obtained for the SRMs are indicative of good Cd recoveries for soil NIST SRM 2709a ($96 \pm 3\%$, 2sd) and rock USGS SRM AGV-2. For the latter sample, recent independent analyses conducted at Imperial College yielded a Cd concentration of 67.7 ng g^{-1} (own, unpublished result), in excellent agreement with the present result of $66.6 \pm 0.03 \text{ ng g}^{-1}$ (2sd, n=2). Notably, other recent studies reported Cd contents of between about 60 and 3000 ng g^{-1} for this sample, indicating that Cd may be heterogeneously distributed in the powder.⁷ There is, however, a small but clearly resolvable discrepancy between the Cd concentration determined here for wheat flour NIST 1567b and the reference value. In detail, our analyses indicate a Cd recovery of only $88 \pm 8\%$ (2sd, n = 6). The Cd recovery for this SRM did not improve when initially undigested silicates were treated with HF for full dissolution. The low recovery may hence reflect a slightly erroneous reference value for this sample. This conclusion is based on the observation that the certified Cd concentration of $254 \pm 0.9 \text{ ng g}^{-1}$ was not determined on the actual NIST SRM 1567b material but adopted from the Cd concentration measured for the original NIST 1567a sample.⁸

2. Cadmium isotope compositions and concentrations of standard reference materials (SRMs)

Table S1: Summary standard reference materials

SRM	Type	$\delta^{114/110}\text{Cd} \pm 2\text{sd}^{\text{a}}$ (‰)	Reference (‰)	Cd conc. $\pm 2\text{sd}^{\text{a}}$ ($\mu\text{g g}^{-1}$)	Reference ($\mu\text{g g}^{-1}$)	n
NIST 2709a	Soil	-0.22 ± 0.02	-	0.356 ± 0.01	0.371	2
NIST 1567b	Wheat flour	0.93 ± 0.08	-	0.0216 ± 0.0019	0.0254	6
USGS AGV-2	Andesite rock	0.11 ± 0.11	-	0.0666 ± 0.0003	$0.063\text{--}0.34^{\text{c}}$	2^{b}
BAM-I012	Isotopic RM	1.30 ± 0.09	$-1.33 \pm 0.04^{\text{d}}$	-	-	12

^a $2\text{sd} = 2 \times$ standard deviation of n samples.

^b A single sample was digested and spiked and then split into two samples for which column chemistry and isotopic analyses were done separately.

^c Values summarized from GeoReM⁷

^d Mean value from Abouchami et al. (2013)⁶

3. Soil properties of Oensingen (Oen), Landquart (LQ) and Wiedlisbach (Wied).

Table S2: Soil properties

General information				A horizon ^a								C horizon ^b	
Origin	soil type ⁹	Land use	texture	max. water holding capacity	CEC	pH	C-content	total Cd		Ca(NO ₃) ₂ extractable Cd ^c		total Cd	
				g H ₂ O/g soil	mmol _c kg ⁻¹	(CaCl ₂)	g kg ⁻¹	ng g ⁻¹	se ^d	ng g ⁻¹	se ^d	ng g ⁻¹	se ^d
Oen	Cambisol	arable farming	silt loam	0.51	164	5.6	24	508	±20	20.4	±9.8	152	± 0.4
LQ	Fluvisol	arable farming	silt loam	0.60	217	7.1	57	287	±3	2.75	±0.25	129	± 4
Wied	Cambisol	arable farming	sandy loam	0.38	44	5.2	15	193	±40	39.6	±3.9	113	± 11

^a The A horizons were sampled from 0-20 cm.

^b The C horizons were provided by the Swiss National Soil Observation Program (NABO) from their archive.

^c Plant-available Cd was extracted using 0.05 M Ca(NO₃)₂.

^d se denotes standard error of the mean (n=2).

4. DM production, Cd concentration and Cd uptake of wheat

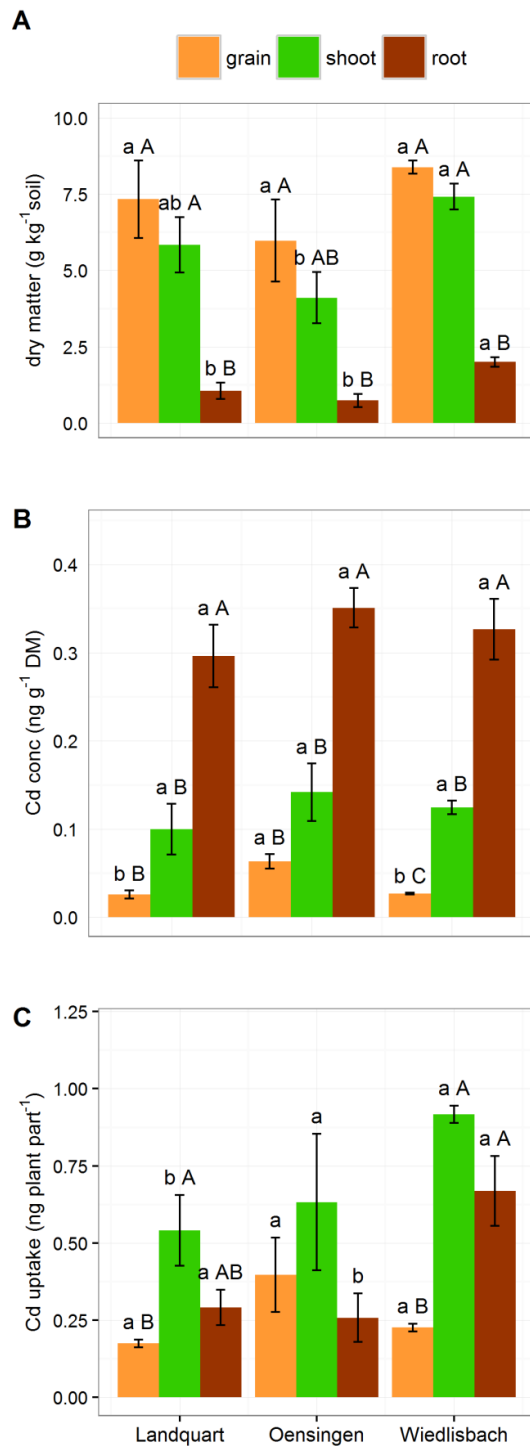


Figure S1 (A) Dry matter production, (B) Cd concentration and (C) Cd uptake of wheat grown on different soils under controlled conditions. Error bars indicate standard error (n=4 for LQ and Wied, n=3 for Oen). Upper case letters denote significant differences of the mean between different plant parts from wheat grown on the same soils. Lower case letters indicate significant differences between the same plant parts grown on different soils ($p < 0.05$).

5. Distribution of Cd, macro and micronutrients in wheat

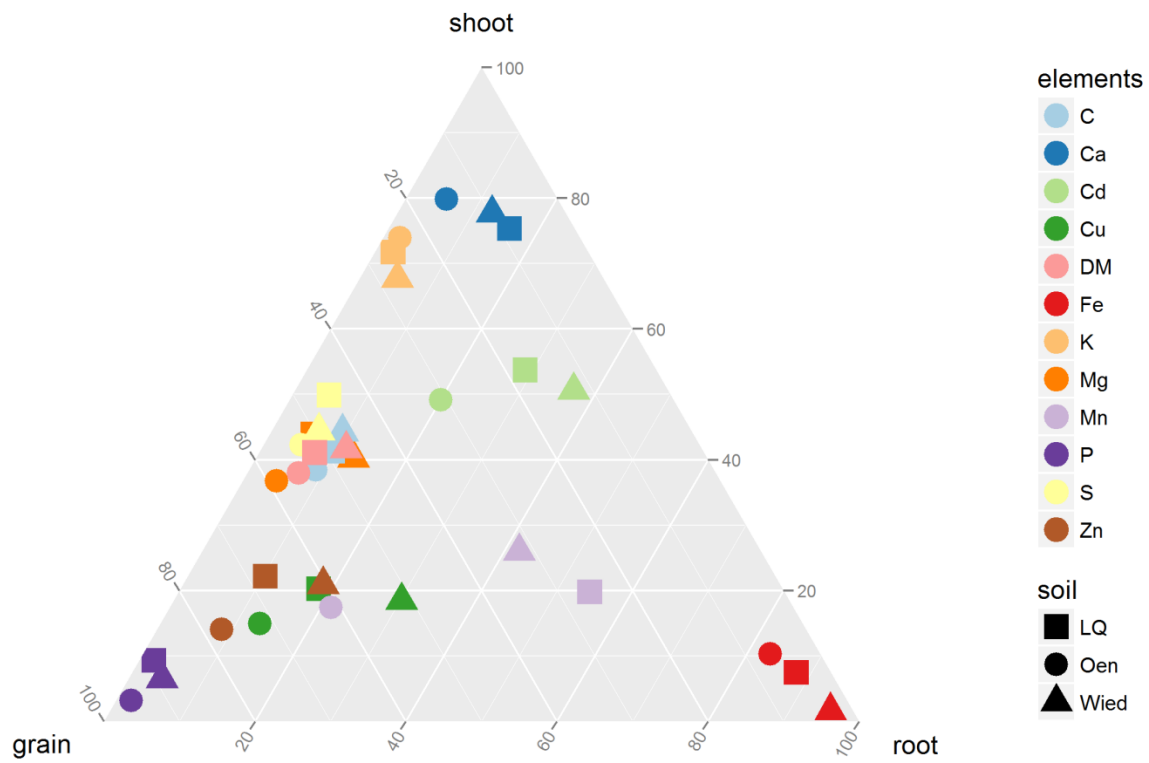


Figure S2: Relative distribution of Cd, macro and micronutrients in the analyzed plant parts of wheat. Colors represent the elements measured and shapes represent the different soils. The values are given in percent, as calculated from the mean values (quantity of element as ng per plant part, n=4). Cd, Cu and Zn were measured by ICP-MS; Ca, Fe, K, Mg, Mn and P were measured by ICP-OES; C and S by IRMS.

Table S3: Element concentrations measured in the different wheat parts.

element	unit	mean ^b	standard error ^a	soil	plant part
C	g/kg DM	416	1	LQ	grain
		414	2	Oen	
		417	0	Wied	
		439	3	LQ	straw
		441	1	Oen	
		451	1	Wied	
		415	1	LQ	root
		435	3	Oen	
		360	19	Wied	
Ca	g/kg DM	0.49	0.03	LQ	grain
		0.56	0.03	Oen	
		0.41	0.04	Wied	
		5.40	0.40	LQ	straw
		4.30	0.50	Oen	
		3.75	0.22	Wied	
		5.87	0.57	LQ	root
		1.72	0.13	Oen	
		2.25	0.17	Wied	
Cd	mg/kg DM	0.026	0.005	LQ	grain
		0.063	0.008	Oen	
		0.027	0.001	Wied	
		0.100	0.029	LQ	straw
		0.142	0.033	Oen	
		0.125	0.008	Wied	
		0.296	0.035	LQ	root
		0.351	0.022	Oen	
		0.327	0.035	Wied	
Cu	mg/kg DM	6.33	0.76	LQ	grain
		5.11	0.93	Oen	
		4.28	0.05	Wied	
		2.58	0.23	LQ	straw
		1.45	0.10	Oen	
		1.73	0.06	Wied	
		13.44	1.37	LQ	root
		6.97	0.43	Oen	
		10.49	0.61	Wied	
Fe	mg/kg DM	18	2	LQ	grain
		26	2	Oen	

element	unit	mean	standard error ^a	soil	plant part
Fe	mg/kg DM	35	1	Wied	grain
		42	16	LQ	straw
		46	20	Oen	
		23	6	Wied	
		2280	254	LQ	root
		2567	370	Oen	
		4708	392	Wied	
K	g/kg DM	3.9	0.4	LQ	grain
		4.8	0.4	Oen	
		4.0	0.2	Wied	
		13.9	1.3	LQ	straw
		21.2	1.8	Oen	
		11.4	1.2	Wied	
		2.5	0.4	LQ	root
		3.9	0.3	Oen	
		3.0	0.4	Wied	
Mg	g/kg DM	1.2	0.1	LQ	grain
		1.2	0.0	Oen	
		1.3	0.0	Wied	
		1.3	0.1	LQ	straw
		1.0	0.2	Oen	
		1.3	0.1	Wied	
		0.9	0.1	LQ	root
		0.8	0.1	Oen	
		1.5	0.1	Wied	
Mn	mg/kg DM	2.6	0.4	LQ	grain
		13	0.7	Oen	
		34	1.6	Wied	
		3.2	0.3	LQ	straw
		5.0	0.8	Oen	
		31	6	Wied	
		39	5	LQ	root
		40	7	Oen	
		185	10	Wied	
N	g/kg DM	20.2	1.5	LQ	grain
		20.0	0.9	Oen	
		18.2	0.3	Wied	
		7.6	0.4	LQ	straw
		6.3	1.0	Oen	
		6.9	0.0	Wied	

element	unit	mean	standard error ¹	soil	plant part
P	g/kg DM	3.53	0.52	LQ	grain
		2.74	0.47	Oen	
		3.16	0.09	Wied	
		0.48	0.12	LQ	straw
		0.12	0.01	Oen	
		0.26	0.02	Wied	
		0.55	0.07	LQ	root
		0.41	0.06	Oen	
		0.65	0.06	Wied	
S	g/kg DM	1.66	0.10	LQ	grain
		1.52	0.07	Oen	
		1.55	0.02	Wied	
		2.45	0.56	LQ	straw
		1.76	0.12	Oen	
		1.58	0.06	Wied	
		0.88	0.06	LQ	root
		0.92	0.02	Oen	
		0.83	0.03	Wied	
Zn	mg/kg DM	23.9	4.0	LQ	grain
		18.9	0.8	Oen	
		25.3	0.9	Wied	
		9.9	1.5	LQ	straw
		4.9	0.4	Oen	
		9.9	0.8	Wied	
		26.2	4.3	LQ	root
		17.6	1.6	Oen	
		32.0	2.1	Wied	
DM	g	7.3	1.3	LQ	grain
		6.0	1.3	Oen	
		8.4	0.2	Wied	
		5.8	0.9	LQ	straw
		4.1	0.8	Oen	
		7.4	0.4	Wied	
		1.1	0.3	LQ	root
		0.7	0.2	Oen	
		2.0	0.2	Wied	

¹Standard error of the mean of $n=4$ samples

^bCd, Cu and Zn were determined by ICP-MS; Ca, Fe, K, Mg, Mn and P were determined by ICP-OES; C, N and S by IRMS.

6. Apparent isotope fractionation between A horizon and $\text{Ca}(\text{NO}_3)_2$ extract

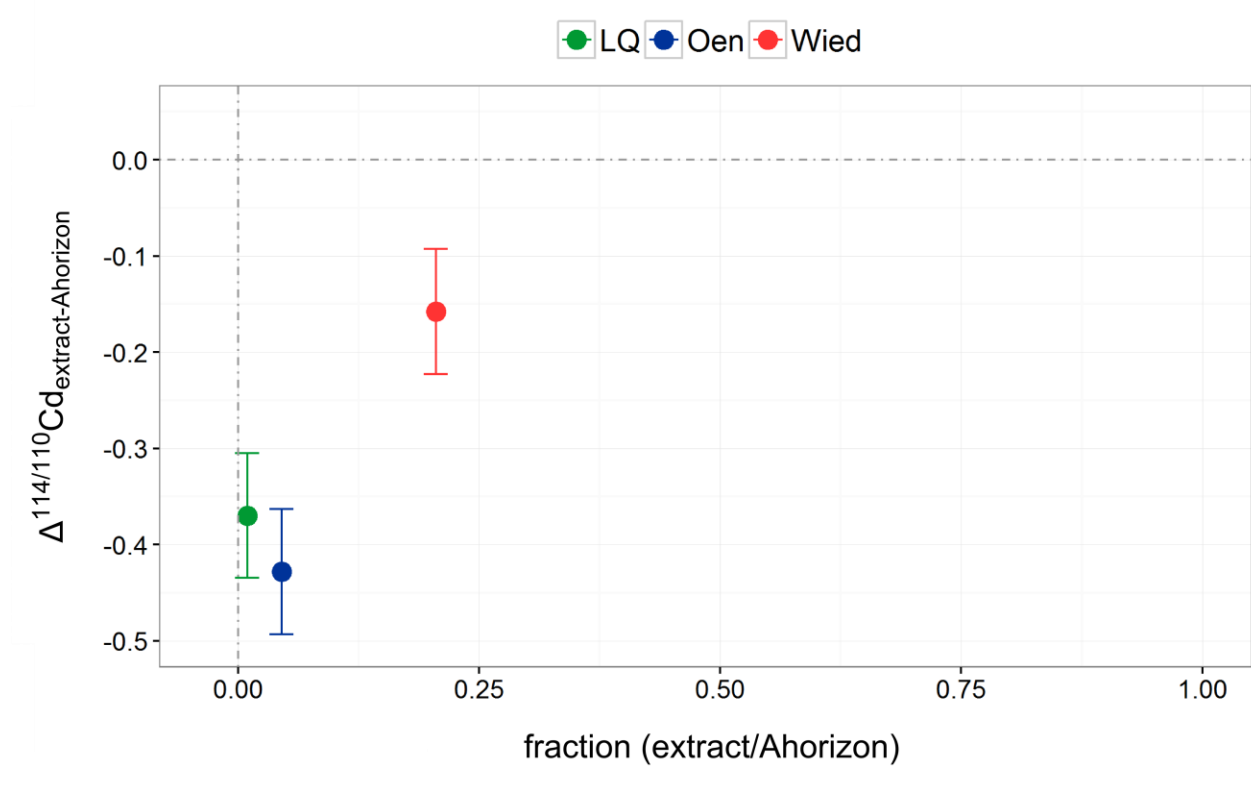


Figure S3: Relationship between the fractionation $\Delta^{114/110}\text{Cd}_{\text{extract-Ahorizon}}$ and the mass fraction of $\text{Ca}(\text{NO}_3)_2$ extractable Cd in soil (relative to the total mass of Cd in the A horizon)

7. Cd isotope compositions (as $\delta^{114/110}\text{Cd}$ values) of the soil–plant systems

Table S4: Cadmium isotope compositions (as $\delta^{114/110}\text{Cd}$) of the soil-wheat systems.

	Oen		LQ		Wied	
	$\delta^{114/110}\text{Cd}$	SE	$\delta^{114/110}\text{Cd}$	SE	$\delta^{114/110}\text{Cd}$	SE
	‰		‰		‰	
grain	0.62	±0.10	0.66	±0.04	0.59	±0.01
straw	0.52	±0.07	0.37	±0.04	0.09	±0.01
root	0.11	±0.05	0.13	±0.03	-0.12	±0.02
Ca(NO₃)₂ extractable	0.50	±0.05	0.54	±0.05	0.12	±0.05
A horizon	0.07	±0.01	0.09	±0.01	-0.04	±0.01
C horizon	0.04	±0.02	0.00	±0.02	-0.16	±0.02

SE = standard error of the mean, where $n = 3$ for plant samples and $n = 2$ for soil samples

8. Box model Oensingen

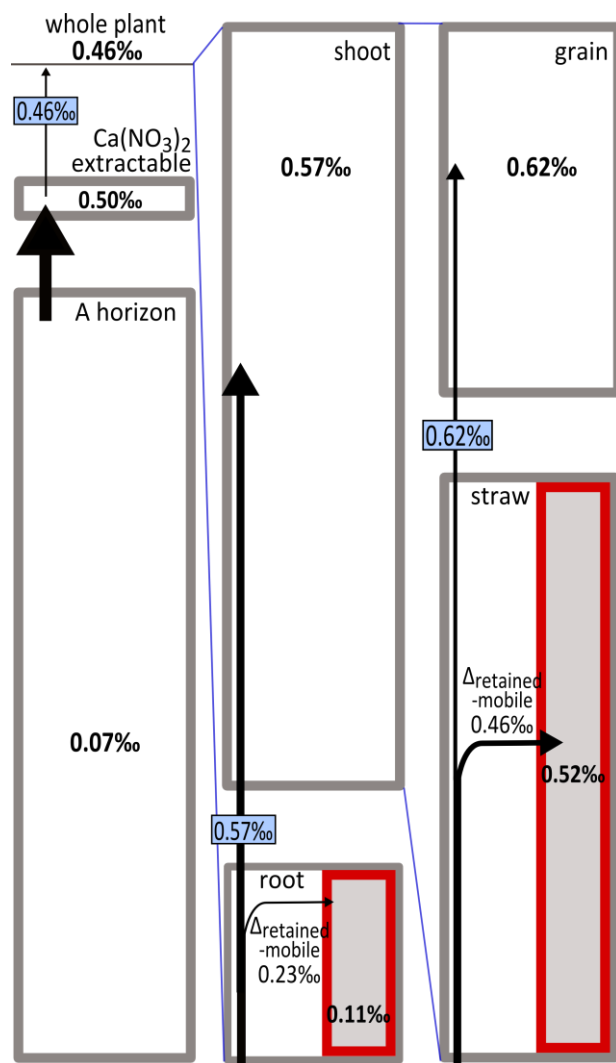


Figure S4: Box model that illustrates the Cd mass balance and isotope fractionation for the soil-wheat system at site Oensingen (Oen). Numbers in ‰ represent average $\delta^{114/110}\text{Cd}$ values. The δ -values in the blue boxes represent the exported δ -values from a soil pool or plant part (e.g., root) to the next soil pool or plant part (e.g., shoot). The exported δ -values are identical to the δ -value measured for the next soil pool or plant part (e.g., shoot). The $\Delta^{114/110}\text{Cd}$ values were modeled with data from Oen, but also Wied and LQ as shown in Figure 3 and represent the apparent Cd isotope fractionation that results from retention of Cd in the respective plant part. The width of the arrows and size of the boxes are adapted to denote the relative sizes of the Cd fluxes and Cd pools, respectively.

9. Box model Landquart

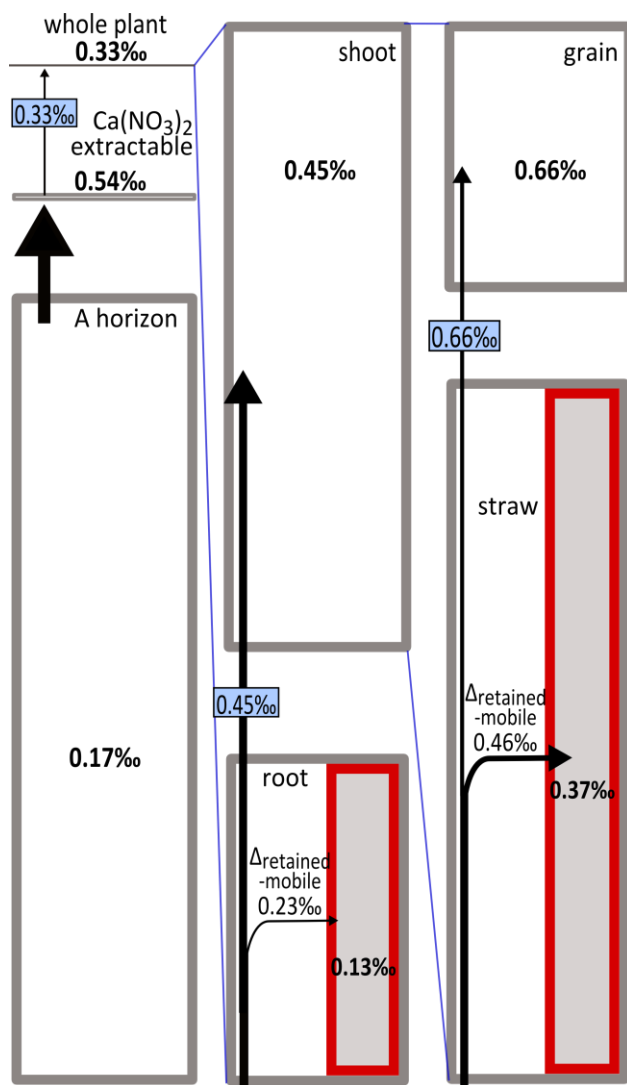


Figure S5: Box model that illustrates the Cd mass balance and isotope fractionation for the soil-wheat system at site Landquart (LQ). Numbers in ‰ represent average $\delta^{114/110}\text{Cd}$ values. The δ -values in the blue boxes represent the exported δ -values from a soil pool or plant part (e.g., root) to the next soil pool or plant part (e.g., shoot). The exported δ -values are identical to the δ -value measured for the next soil pool or plant part (e.g., shoot). The $\Delta^{114/110}\text{Cd}$ values were modeled with data from LQ, but also Wied and Oen as shown in Figure 3 and represent the apparent Cd isotope fractionation that results from retention of Cd in the respective plant part. The width of the arrows and size of the boxes are adapted to denote the relative sizes of the Cd fluxes and Cd pools, respectively.

10. Comparison with published Cd isotope data for terrestrial and aquatic environments

Figure S6 compares previously reported Cd isotope compositions for various terrestrial and aquatic environments with the plant data acquired in the present study. The comparison illustrates that rocks of the earth's mantle and crust, including fresh water sediments, show only limited isotopic variability with $\delta^{114/110}\text{Cd}$ values of about -0.4‰ and 0.4‰. In contrast, seawater and marine sediments and deposits show a much wider range in $\delta^{114/110}\text{Cd}$, with values from -0.45‰ to about 5‰. The most positive $\delta^{114/110}\text{Cd}$ values are found in surface seawater, where dissolved Cd concentrations are extremely low, due to the uptake and storage of isotopically light Cd by phytoplankton.^{3, 10-12}

In our study, samples in which Cd isotope fractionation was dominated by biological processes also showed a larger isotopic variation than samples in which Cd isotope fractionation was dominated by abiotic geological processes. The A and C soil horizons displayed a much smaller range of $\delta^{114/110}\text{Cd}$ (from -0.09 to -0.16‰) than the different wheat parts, which were characterized by $\delta^{114/110}\text{Cd} = -0.12$ to 0.97‰. An important additional source of Cd isotope variation in the investigated soil-plant systems is the apparent fractionation between the A horizon and the $\text{Ca}(\text{NO}_3)_2$ extractable Cd of the soil (Figure 1). Notably, published Cd isotope data for birch leaves¹³ and Cd-tolerant plants¹⁴ exhibit a similar range of $\delta^{114/110}\text{Cd}$ values (from -0.39 to 1.3‰) as were measured here for the plant parts (-0.12 to 0.97‰).

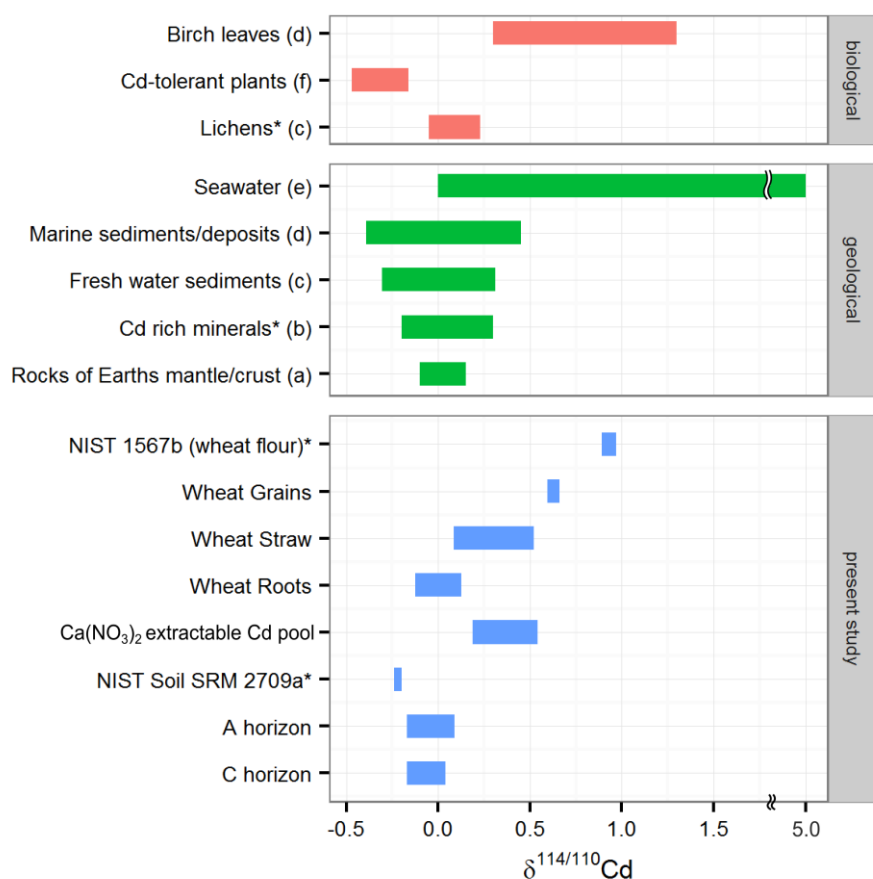


Figure S6: Summary of stable Cd isotope data ($\delta^{114/110}\text{Cd}$) for uncontaminated material in terrestrial and aquatic systems. Values are separated into biological and geological data and results obtained in the present study. Shown are the $\delta^{114/110}\text{Cd}$ ranges of the samples unless the material (Y-axis) is marked with an asterisks, which indicates that the standard deviation of the dataset is plotted. All results are given relative to $\delta^{114/110}\text{Cd}_{\text{NIST3108}} = 0$.¹² Small letters refer to the data sources.

Sources: (a) Schmitt et al.¹⁵, Rehkämper et al.¹⁶, (b) Schmitt et al.¹⁵, Rehkämper et al.¹⁶, Wombacher et al.¹⁷, Shiel et al.¹⁸, (c) Pallavicini et al.¹³, (d) Schmitt et al.¹⁵, Horner et al.¹⁹, (e) Ripperger et al.³, Lacan et al.¹⁰, Conway & John¹², Abouchami et al.²⁰, Xue et al.¹¹, Rehkämper et al.¹⁶, (f) Wei et al.¹⁴, Wei et al.²¹

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