

SUPPLEMENTARY MATERIAL

Thallium stable isotope ratios in naturally Tl-rich soils

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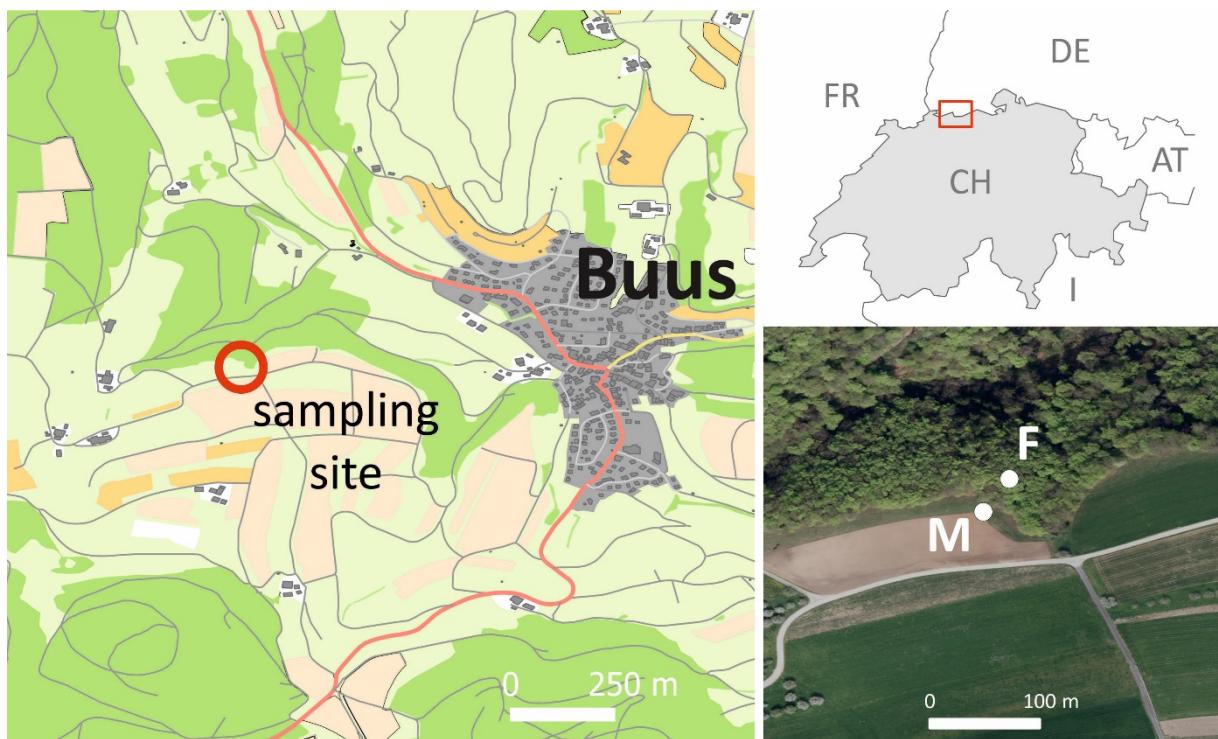


Figure S1. Location of the study area and the soil sampling sites; meadow (M) and forest (F) soil profiles – Buus, the Swiss Jura Mountains (Switzerland). The GPS coordinates of soil profiles were as follows: (M) N 47.505715, E 7.852667, and (F) N 47.505781, E 7.852798.

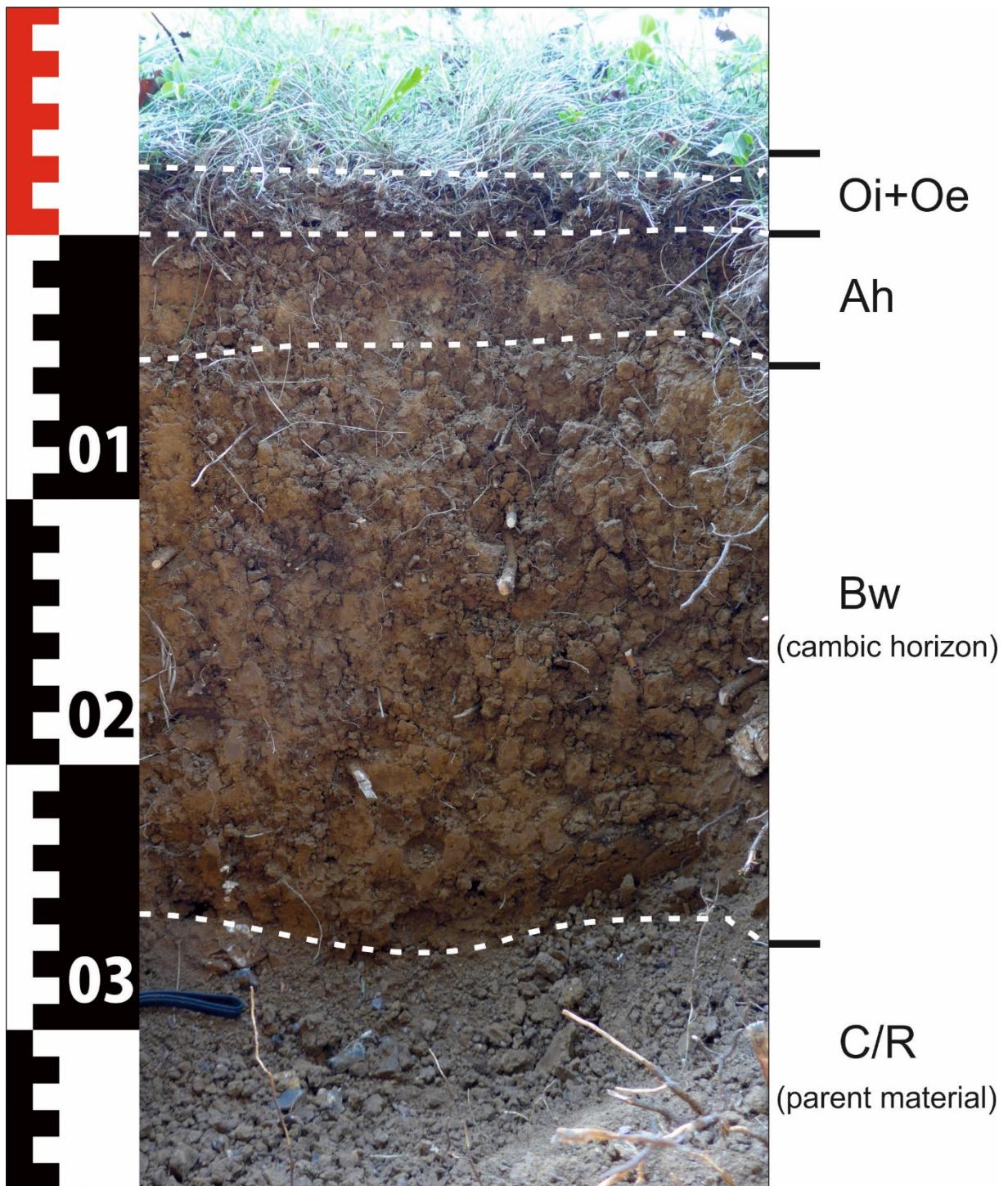


Figure S2. Meadow soil profile; Eutric Skeletic Cambisol (World Reference Base for Soil Resources, FAO).

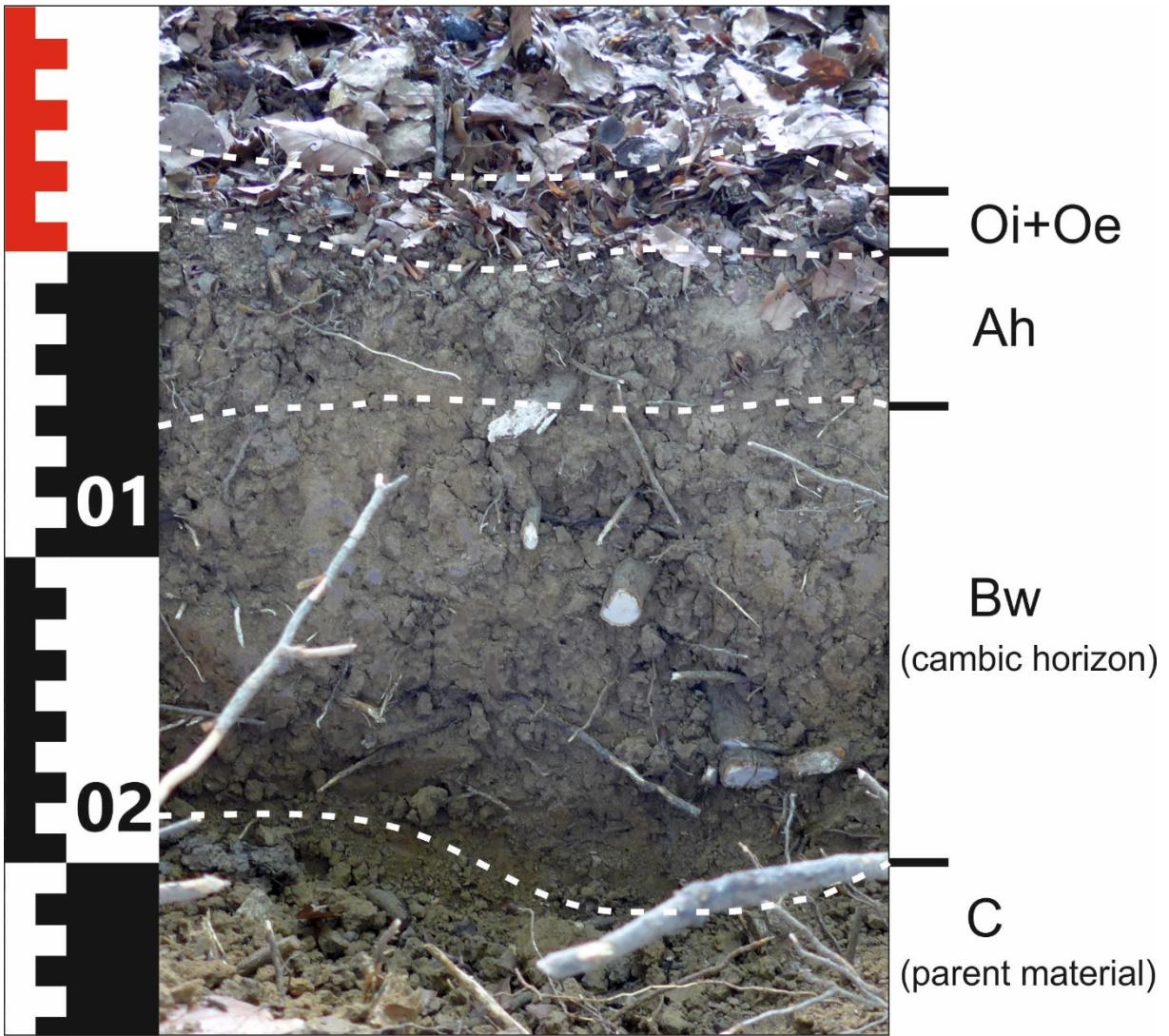


Figure S3. Forest soil profile; Eutric Hyperskeletal Cambisol (World Reference Base for Soil Resources, FAO).

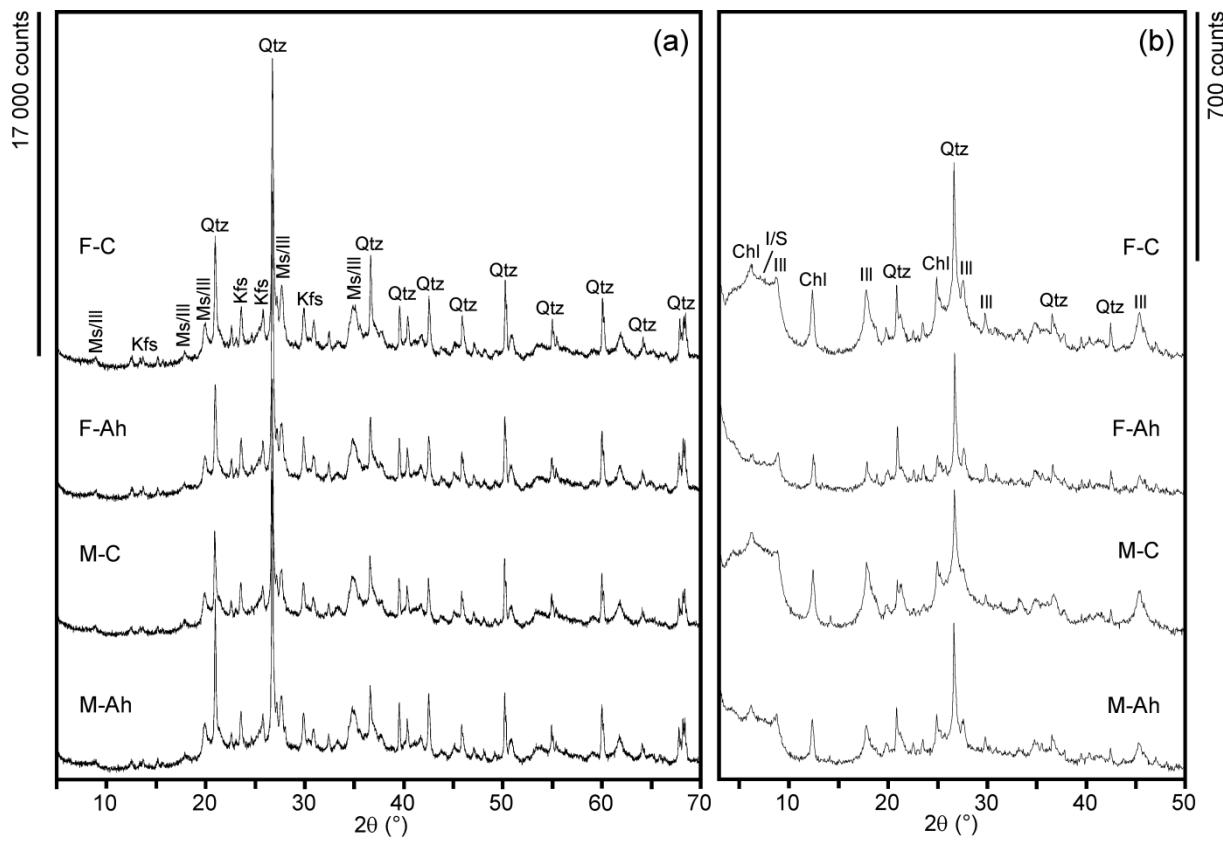


Figure S4. XRD patterns of bulk samples from upper/bottom horizons of meadow and forest soil profiles (a) and oriented clay-rich aggregates (b). Chl, chlorite; I/S, mixed-layered illite/smectite; Ill, illite; Kfs, K-feldspar; Ms/III, muscovite and/or illite; Qtz, quartz. Identification of mixed-layered illite/smectite is based on the ethylene glycol solvation.

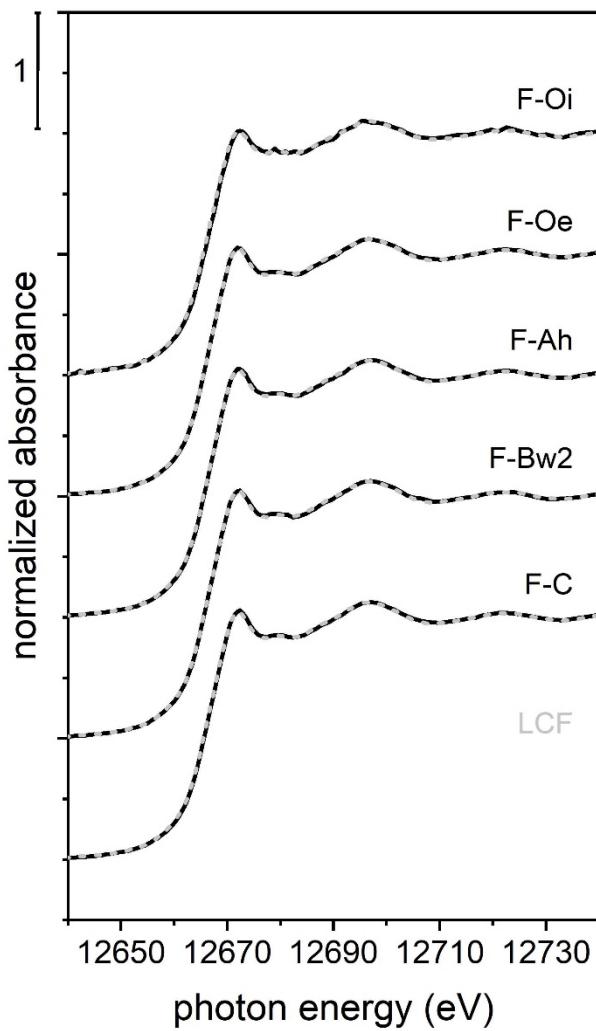


Figure S5. Tl L_{III}-edge XANES spectra of selected soil samples from the forest profile (F-Oi, F-Oe, F-Ah, F-Bw2, F-C). Gray dashed lines represent linear reconstruction spectra based on LCF results in Table 2.

Table S1. Measured and certified Tl values for standard reference material, NIST 2711 (Montana Soil) (National Institute of Standards and Technology, USA) The analysis was carried out in triplicate and depict mean \pm 1 SD.

	Measured (mg/kg)	Certified (mg/kg)
NIST 2711	2.30 ± 0.21	2.47 ± 0.15

Table S2. Measured and reference Tl concentration and Tl isotope data for USGS standard reference material, AGV-2 (Andesite).

	Tl ($\mu\text{g}/\text{kg}$)	2 SD	$\varepsilon^{205}\text{Tl}$	2 SD	n	Dissolutions	Reference
AGV-2	250	38	-2.6	0.8	3	3	This study
AGV-2	239	30	-3.2	0.6	2	2	¹
AGV-2	282	35	-2.8	0.7	2	1	²
AGV-2	245	32	-3.4	0.7	6	6	³

Table S3. Physico-chemical characteristics of the studied soils and bedrock sample.

Sample	Horizon	Depth	Clay ^a	pH		TC	TS	CEC	Fe _{oxal}	Mn _{oxal}	Al _{oxal}
		(cm)	(%)	KCl	H ₂ O	(%)	(%)	(cmol(+)/kg) ^b	(g/kg) ^b		
Meadow soil profile^c											
M-Oi	Oi	3-1	n.d.	5.5	6.3	36.6	0.71	59.3	1.1	0.5	0.7
M-Oe	Oe	1-0	n.d.	5.2	5.9	16.3	0.43	39.6	3.5	1.0	2.4
M-Ah	Ah	0-5	12	5.1	6.0	5.41	0.24	33.7	5.7	1.5	3.5
M-Bw1	Bw1	5-10	12	4.8	6.1	4.54	0.22	30.5	4.6	1.3	3.3
M-Bw2	Bw2	10-15	12	5.2	6.3	4.24	0.22	30.2	5.7	1.5	3.9
M-Bw3	Bw3	15-20	12	5.2	6.2	3.78	0.21	29.7	3.7	1.2	3.0
M-Bw4	Bw4	20-25	12	5.5	7.0	3.33	0.22	29.7	4.8	1.3	3.7
M-C	C	25-	12	5.6	6.7	3.27	0.21	30.6	4.2	1.3	3.3
M-R	R	--	n.d.	n.d.	n.d.	0.26	0.01	n.d.	n.d.	n.d.	n.d.
Forest soil profile^c											
F-Oi	Oi	2-1	n.d.	5.9	6.3	41.5	0.74	80.3	0.3	0.1	0.1
F-Oe	Oe	1-0	n.d.	6.1	6.7	17.4	0.43	51.2	1.2	0.4	0.7
F-Ah	Ah	0-5	15	5.9	6.8	6.00	0.24	37.7	2.5	0.8	1.7
F-Bw1	Bw1	5-10	15	5.8	7.0	3.88	0.18	29.0	2.8	0.9	1.8
F-Bw2	Bw2	10-15	15	5.6	7.1	3.19	0.17	25.9	3.0	1.0	2.1
F-Bw3	Bw3	15-20	15	5.5	6.9	2.83	0.17	27.2	3.4	1.0	2.2
F-C	C	20-	15	5.5	7.1	2.88	0.19	22.9	3.0	0.9	2.1

^a clay content was measured on a mixed sample (from A, B, and C horizons).

^b means of triplicate analysis of single extracts; RSD < 10%; Fe_{oxal}, Mn_{oxal}, Al_{oxal}: oxalate-extractable Fe, Mn and Al concentrations.

^c meadow: Eutric Skeletic Cambisol; forest: Eutric Hyperskeletal Cambisol.

n.d.: not determined.

Table S4. Reducible (reduc) and oxalate-extractable (oxal) Tl and Mn concentrations (mg/kg) and Tl/Mn ratios (mol/mol) in the studied soil profiles (n = 3).

Sample	Tl _{reduc} (mg/kg)	Mn _{reduc} (mg/kg)	Tl/Mn _{reduc} (mol/mol)	Tl _{oxal} (mg/kg)	Mn _{oxal} (mg/kg)	Tl/Mn _{oxal} (mol/mol)
M-Oi	34	405	0.023	36	520	0.019
M-Oe	71	850	0.022	44	974	0.012
M-Ah	72	837	0.023	49	1460	0.009
M-Bw1	75	885	0.023	46	1324	0.009
M-Bw2	72	830	0.023	48	1549	0.008
M-Bw3	77	905	0.023	39	1180	0.009
M-Bw4	81	900	0.024	49	1352	0.010
M-C	78	867	0.024	51	1273	0.011
F-Oi	7	118	0.016	2	143	0.004
F-Oe	28	453	0.017	9	400	0.006
F-Ah	43	627	0.018	23	820	0.008
F-Bw1	54	672	0.022	32	900	0.009
F-Bw2	60	733	0.022	31	996	0.008
F-Bw3	61	709	0.023	46	1027	0.012
F-C	60	708	0.023	32	926	0.009

Table S5. Operationally defined Tl fractionation in the studied soil profiles following a modified BCR sequential extraction procedure (n = 3).

Sample	Acid-ext. (%)	Reducible (%)	Oxidizable (%)	Residual (%)
M-Oi	2.4	6.7	12.2	78.7
M-Oe	0.5	9.1	3.4	87.0
M-Ah	0.4	8.6	2.6	88.4
M-Bw1	0.3	8.9	2.5	88.3
M-Bw2	0.1	7.9	2.2	89.8
M-Bw3	0.2	8.2	2.2	89.4
M-Bw4	0.2	8.2	2.0	89.6
M-C	0.2	8.0	2.1	89.7
F-Oi	1.2	5.6	10.8	82.4
F-Oe	0.3	5.3	4.9	89.6
F-Ah	0.2	6.5	2.4	90.8
F-Bw1	0.3	8.1	2.2	89.5
F-Bw2	0.2	8.9	2.1	88.7
F-Bw3	0.3	8.7	2.1	88.9
F-C	0.2	7.8	1.9	90.2

Table S6. Stable Tl isotope compositions ($\varepsilon^{205}\text{Tl}$) in selected mineral (bulk) soils and 1 M NH_4NO_3 leachates (exchangeable soil Tl fraction).

Sample	Bulk Soil	Exchangeable
	$\varepsilon^{205}\text{Tl} \pm 0.7$	$\varepsilon^{205}\text{Tl} \pm 0.7$
M-Oi	+3.62	n.d.
M-Oe	+4.84	n.d.
M-Ah	+7.18	n.d.
M-Bw1	+8.66	+4.60
M-Bw2	+5.57	+4.86
M-Bw3	+4.23	+4.67
M-Bw4	+3.58	+3.18
M-C	+2.60	n.d.
F-Oi	+2.53	n.d.
F-Oe	+2.72	n.d.
F-Ah	+3.26	n.d.
F-Bw1	+8.65	+4.61
F-Bw2	+8.06	+4.18
F-Bw3	+3.63	+4.36
F-C	+0.76	n.d.

n.d.: not determined.

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