

Appendix A. Supplementary data

**Thallium sorption and speciation in soils:
Role of micaceous clay minerals and manganese oxides**

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46 pages, 21 tables, 9 figures

Content

1. Site description.....	3
2. Physicochemical characterisation of soil samples	4
2.1 Inorganic and organic C contents and soil texture	4
2.2 Soil mineralogy	6
2.3 Total element contents and correlations.....	8
3. Exchangeable cations.....	11
4. Pseudo-porewater extracts.....	14
5. Distribution coefficients for exchangeable cations.....	17
6. Isotope exchange experiment	19
7. Sequential soil extractions.....	22
8. Adsorption and re-extraction experiment	26
8.1 Details on the different laboratory protocols.....	26
8.2 Behaviour of the pH and different cations during the experiment	27
8.3 Additional sorption plots.....	31
9. X-ray absorption spectroscopy	32
10. Predictions for Tl adsorption onto micaceous soil clay minerals.....	36
10.1 Geogenic Tl.....	36
10.2 Adsorption experiments	36
11. Experiment with Mn/Fe-depleted and Mn/Fe-enriched soil material	37
11.1 Site and soil profile description and soil sampling.....	37
11.2 Physicochemical characterization of the soil material	38
11.3 Tl adsorption experiments.....	41
11.4 XAS results	43
12. Estimates for Tl sorbed onto Mn oxides, Fe oxides and soil organic matter	44
13. References.....	46

1. Site description



Figure S1. Topsoils (0-20cm) from three soil profiles from the Erzmatt (compiled from images kindly provided by the Office for Environment and Energy, Kanton Basel-Landschaft, Switzerland).

2. Physicochemical characterisation of soil samples

2.1 Inorganic and organic C contents and soil texture

Table S1. Inorganic and organic C contents and texture results with their relative standard deviation (\pm).

sample	C_{inorg}		C_{org}		clay		silt		sand	
	wt%	\pm	wt%	\pm	wt%	\pm	wt%	\pm	wt%	\pm
A1	1.90	0.12	2.63	0.30	14.2	0.1	83.1	0.1	2.7	0.2
A2	0.02	0.00	3.31	0.28	11.0	0.1	87.7	0.0	1.3	0.0
A3	4.48	0.00	2.71	0.15	11.4	0.0	83.6	0.3	5.0	0.3
A4	3.51	0.02	4.15	0.23	8.9	0.0	88.0	0.1	3.1	0.1
A5	2.16	0.16	3.24	0.57	8.3	0.1	87.8	0.5	3.8	0.5
A6	0.21	0.02	3.10	0.30	11.1	0.1	85.2	0.8	3.6	0.9
B1	0.70	0.00	4.08	0.57	10.5	0.2	87.3	1.3	2.1	1.5
B2	1.23	0.01	4.07	0.28	6.9	0.1	87.6	0.7	5.5	0.8
B3	1.01	0.27	3.81	0.43	10.1	0.2	85.1	1.4	4.8	1.6
B4	1.99	0.31	2.89	0.38	8.8	0.1	87.5	0.9	3.6	1.0
B5	0.05	0.04	4.32	0.10	10.4	0.1	82.5	0.8	7.1	0.9
B6	10.84	0.09	1.04	0.13	7.3	0.0	92.6	0.0	0.1	0.0
C1	0.53	0.03	4.31	0.12	11.5	0.0	86.8	0.1	1.6	0.2
C2	0.29	0.06	2.04	0.08	14.2	0.0	84.1	0.1	1.7	0.1
C3	0.94	0.20	3.59	0.30	9.2	0.0	86.6	0.1	4.2	0.1
C4	0.03	0.03	4.84	0.28	13.2	0.1	77.0	0.5	9.7	0.6
C5	3.16	0.30	4.96	0.32	5.5	0.0	88.5	0.1	6.0	0.1
C6	9.57	0.27	1.66	0.32	9.2	0.1	89.8	0.1	1.0	0.1

Table S1. Continuation.

sample	C _{inorg}		C _{org}		clay		silt		sand	
	wt%	±	wt%	±	wt%	±	wt%	±	wt%	±
D1	0.21	0.09	3.09	0.09	15.1	0.2	82.4	1.0	2.6	1.1
D2	0.22	0.01	2.19	0.03	19.2	0.1	79.5	0.1	1.2	0.1
D3	4.14	0.14	5.09	0.15	7.2	0.1	86.3	0.6	6.4	0.6
D4	3.53	1.97	3.08	1.98	12.5	0.0	86.6	0.1	0.9	0.1
D5	0.20	0.02	4.29	0.02	9.9	0.0	82.5	0.2	7.6	0.2
D6	0.09	0.00	2.63	0.07	17.4	0.0	82.2	0.1	0.4	0.1
E1	0.02	0.03	5.10	0.18	8.2	0.2	85.2	1.1	6.6	1.3
E2	0.04	0.05	5.36	0.13	11.3	0.1	86.1	0.1	2.6	0.2
E3	0.16	0.02	3.21	0.12	13.3	0.0	85.7	0.2	1.0	0.3
E4	1.26	0.37	8.43	0.48	7.7	0.0	88.2	0.0	4.1	0.1
E5	0.00	0.01	4.16	0.26	11.6	0.0	85.5	0.3	2.9	0.3
E6	2.00	0.24	5.16	0.30	7.7	0.0	89.4	0.7	2.9	0.7
F1	0.00	0.00	5.25	0.18	10.9	0.0	87.0	0.1	2.1	0.2
F2	0.08	0.01	3.33	0.02	13.2	0.0	86.5	0.1	0.3	0.0
F3	0.03	0.03	4.95	0.29	10.1	0.0	88.2	0.1	1.7	0.1
F4	3.25	0.18	5.37	0.53	8.5	0.1	89.3	0.1	2.2	0.0
F5	0.16	0.02	3.63	0.28	13.9	0.1	83.0	0.2	3.1	0.3
F6	0.00	0.00	4.50	0.12	14.1	0.2	80.9	1.4	4.9	1.7

2.2 Soil mineralogy

The mineralogy of the six soil samples used for Tl adsorption / re-extraction experiments was determined on randomly oriented powder specimens with X-ray diffraction analysis. First, the samples were crushed <0.4 mm and homogenized. A representatively split aliquot of 2 g was milled in ethanol to a grain size below 20 µm with a McCrone micronizing mill. For frontloading preparation, about 1 g of the powdered material was filled in a frontloading sample holder. For packing, sample-height adjustment and forming a flat surface, a razor blade was used to minimize preferred orientation (Zhang et al., 2003). A second sample preparation was carried out producing oriented specimens for enhancement of the (001) basal reflexes of layer silicates to facilitate their identification. Changes in the reflex positions in the XRD patterns of oriented specimens by intercalation of different organic compounds (e.g. ethylenglycol) and after heating were used for identification in particular of smectite.

X-ray diffraction measurements were made with a Bragg-Brentano diffractometer (BRUKER AXS D8) using Co K α radiation with 40 kV and 35 mA. The instrument was equipped with an automatic theta compensating divergence and antiscattering slit, primary and secondary soller slits and a Sol-X solid state detector. The powder samples were step-scanned at room temperature from 2 to 80 °20 (step width 0.02 °20, counting time 4 s per step). The qualitative phase composition was determined with the software DIFFRACplus (BRUKER AXS). Based on the peak positions and their relative intensities, the mineral phases were identified in comparison to the PDF-2 data base (International Centre for Diffraction Data). The quantitative determination of the mineralogical composition was carried out by Rietveld analysis using the Rietveld program Profex/BGMN (Bergmann et al., 1998; Bergmann and Kleeberg, 1998; Döbelin and Kleeberg, 2015; Omotoso et al., 2006).

Table S2. Results of the mineralogical analysis for Erzmatt soils.

Mineral	A6		B4		C5		D1		D6		E6		average
	wt%	±3σ											
Quartz	38.7	0.7	37.0	0.6	34.6	0.6	39.7	0.7	41.5	0.6	31.6	0.5	37.2
K-feldspar	26.0	0.5	15.8	0.6	10.5	0.5	23.9	0.6	24.3	0.6	15.5	0.5	19.3
Na-plagioclase	4.3	0.4	3.4	0.3	2.5	0.2	2.1	0.3	3.2	0.3	3.3	0.3	3.1
Calcite	<0.3	-	0.9	0.2	1.0	0.2	<0.3	-	<0.3	-	13.5	0.3	5.1
Dolomite	2.6	0.2	19.4	0.5	32.2	0.5	2.8	0.2	2.0	0.2	14.1	0.3	12.2
Goethite	1.4	0.2	1.1	0.2	1.0	0.3	1.3	0.2	1.4	0.2	1.4	0.3	1.3
Anatase	0.6	0.2	0.3	0.1	0.3	0.1	0.7	0.1	0.6	0.1	0.6	0.1	0.5
Rutile	0.6	0.2	0.5	0.2	0.4	0.1	0.6	0.1	0.6	0.2	0.4	0.1	0.5
Total non-clay	74.1		78.4		82.5		71.1		73.6		80.4		76.7
Kaolinite	6.0	0.9	3.1	0.6	1.6	0.4	5.5	1.2	5.5	1.0	1.0	0.3	3.8
Muscovite 2M ₁	8.1	0.6	5.2	0.6	3.5	0.5	8.6	0.6	5.8	0.6	4.1	0.5	5.9
Illite 1M	9.2	0.6	10.4	0.6	10.3	0.7	11.3	0.7	12.2	0.6	11.8	0.6	10.9
Chlorite (trioctahedral)	2.5	0.5	2.9	0.6	2.1	0.3	3.4	0.8	2.8	0.3	2.7	0.3	2.7
Total clay/phyllosilicate	25.9		21.6		17.5		28.9		26.4		19.6		23.3

2.3 Total element contents and correlations

Table S3. Selected XRF results (in mg/kg) for all 36 topsoil samples.

Sample	Al	As	Ba	Ca	Fe	K	Mg	Mn	Pb	Rb	S	Si	Sr	Tl
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
A1	58000	25.3	305.5	52740	34900	29810	32000	1083.0	40.2	112.4	548.9	186000	171.3	2.8
A2	68330	37.9	296.7	5325	47620	17690	9880	887.8	34.1	86.3	703.8	228300	94.9	2.2
A3	46550	44.9	212.0	92360	26320	18840	47020	810.0	31.8	74.0	708.4	135900	358.6	2.6
A4	44540	26.8	248.6	72990	25960	23610	40200	887.6	37.6	86.4	719.2	148100	188.8	3.4
A5	48170	27.4	366.6	77730	27400	16500	17270	712.1	69.2	83.5	793.0	190900	145.0	3.0
A6	68410	46.5	340.0	9575	34540	39150	11160	1185.0	44.8	116.4	838.5	248700	464.7	3.1
B1	61580	69.3	307.0	21360	37260	24640	24630	931.7	38.1	96.8	821.6	213800	121.3	15.5
B2	57340	60.9	297.4	29640	32450	28610	21060	1487.0	122.6	107.3	990.4	214700	343.6	6.4
B3	60590	54.9	311.1	38800	36650	31080	25570	1243.0	45.3	114.8	783.2	195800	216.3	8.9
B4	57300	45.0	269.2	44330	30850	27190	27570	1066.0	43.8	100.8	671.6	198200	189.4	7.6
B5	65840	47.8	430.9	8556	40610	30460	28140	1044.0	47.3	133.1	783.9	207800	117.8	10.3
B6	9992	39.0	90.6	188700	7921	5456	104600	264.4	13.7	18.4	342.6	34640	133.1	9.7
C1	63890	86.3	299.4	17170	37350	32300	18700	1225.0	48.4	120.0	672.1	215800	282.5	21.9
C2	71210	89.6	343.4	11310	42020	32650	18380	998.2	45.8	126.0	506.1	237900	282.9	25.4
C3	56660	53.8	337.8	31610	36080	20740	22040	1025.0	51.9	86.7	777.4	208200	126.4	8.5
C4	67160	69.0	314.5	5383	36640	34780	15600	987.4	48.0	118.6	481.3	235500	282.8	23.8
C5	44350	114.2	261.3	71350	28230	18350	37870	909.7	49.9	73.8	1076.0	155900	161.1	27.2
C6	18490	86.3	121.9	167100	12410	8663	90110	411.3	17.5	34.9	484.0	59460	123.2	26.9

Table S3. Continuation.

Sample	Al	As	Ba	Ca	Fe	K	Mg	Mn	Pb	Rb	S	Si	Sr	Tl
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
D1	67790	235.7	363.8	10540	38730	38150	17020	1334.0	46.9	127.9	701.0	237200	266.4	72.7
D2	71130	308.6	353.5	8893	39610	40030	16640	1288.0	46.4	127.1	547.7	258100	288.8	70.5
D3	42260	226.9	212.6	117100	25910	19420	24950	698.7	46.6	76.9	825.4	138400	212.6	76.3
D4	46280	254.9	263.1	113000	27710	21380	36710	656.8	30.5	81.0	622.7	149000	197.4	78.3
D5	67930	280.5	411.3	11010	41980	33780	24170	1266.0	50.3	132.1	1001.0	216800	170.7	102.3
D6	70090	349.2	395.5	6390	40440	39060	17440	1237.0	45.3	129.7	613.3	249900	282.9	102.9
E1	64290	834.2	325.4	6298	41300	36610	14070	1082.0	45.6	111.2	1143.0	230300	348.0	245.4
E2	63990	690.8	319.4	7227	34210	40380	10820	828.5	47.5	103.2	858.5	249600	398.7	264.6
E3	68170	932.0	367.9	10490	40380	42720	11700	808.3	46.0	109.1	1078.0	260200	449.7	318.7
E4	55000	606.3	335.0	48770	35710	26310	12090	1045.0	60.6	102.6	1070.0	172400	300.3	294.6
E5	67680	1017.0	383.6	4412	45350	37250	15020	1394.0	52.1	118.9	1177.0	236900	329.2	348.6
E6	50720	702.4	281.9	76970	37170	23840	19940	1091.0	58.4	83.1	1177.0	190800	281.3	346.6
F1	66170	1808.0	392.5	3450	47880	36040	11520	1074.0	54.1	107.7	1558.0	231000	473.3	689.3
F2	70690	1332.0	378.4	8969	55320	38120	14310	1474.0	47.9	119.7	1079.0	238100	433.9	694.3
F3	64630	1744.0	335.3	7166	61000	35630	11700	1302.0	53.0	116.4	1371.0	221300	483.2	747.5
F4	48780	1956.0	254.4	61240	56800	22600	31040	1203.0	51.1	81.9	1427.0	147700	366.2	756.7
F5	71320	2068.0	415.1	7613	56040	39190	15110	1025.0	58.1	123.8	1450.0	239900	454.5	856.0
F6	68490	2384.0	370.2	4498	72550	34150	12270	1683.0	184.5	105.4	1422.0	216200	542.5	1026.0

Table S4. Correlation analysis for total element contents determined by XRF. Selected XRF data for Al, As, Ba, Ca, Fe, K, Mg, Mn, Pb, Rb, S, Si, Sr, and Tl are given in Table S3.

	Al	As	Ba	Ca	Cr	Cu	Fe	Ga	K	Mg	Mn	Ni	P	Pb	Rb	S	Si	Sr	Ti	Tl	V	Zn	Zr
Al	1.00																						
As	0.29	1.00																					
Ba	0.88	0.35	1.00																				
Ca	-0.97	-0.31	-0.87	1.00																			
Cr	0.88	0.02	0.76	-0.85	1.00																		
Cu	0.50	0.17	0.54	-0.53	0.49	1.00																	
Fe	0.73	0.78	0.68	-0.74	0.56	0.47	1.00																
Ga	0.93	0.24	0.90	-0.89	0.81	0.50	0.66	1.00															
K	0.87	0.39	0.78	-0.85	0.62	0.33	0.62	0.82	1.00														
Mg	-0.89	-0.32	-0.81	0.86	-0.81	-0.65	-0.69	-0.82	-0.74	1.00													
Mn	0.73	0.41	0.65	-0.74	0.55	0.69	0.75	0.65	0.67	-0.66	1.00												
Ni	0.87	0.36	0.75	-0.83	0.76	0.67	0.79	0.84	0.72	-0.79	0.85	1.00											
P	0.39	0.07	0.34	-0.43	0.40	0.66	0.30	0.30	0.27	-0.46	0.59	0.39	1.00										
Pb	0.31	0.46	0.35	-0.34	0.27	0.55	0.54	0.15	0.25	-0.40	0.62	0.50	0.36	1.00									
Rb	0.93	0.19	0.88	-0.89	0.79	0.50	0.62	0.95	0.89	-0.79	0.74	0.85	0.32	0.25	1.00								
S	0.32	0.85	0.43	-0.38	0.16	0.45	0.70	0.29	0.35	-0.46	0.47	0.38	0.39	0.48	0.23	1.00							
Si	0.96	0.24	0.86	-0.95	0.84	0.49	0.64	0.87	0.88	-0.90	0.66	0.76	0.42	0.29	0.88	0.29	1.00						
Sr	0.46	0.76	0.37	-0.46	0.20	0.25	0.63	0.36	0.66	-0.47	0.50	0.51	0.29	0.46	0.38	0.65	0.46	1.00					
Ti	0.97	0.21	0.85	-0.96	0.85	0.40	0.64	0.89	0.86	-0.85	0.65	0.74	0.40	0.21	0.89	0.26	0.97	0.39	1.00				
Tl	0.28	0.99	0.34	-0.30	0.02	0.20	0.78	0.23	0.37	-0.31	0.43	0.38	0.06	0.48	0.18	0.84	0.22	0.75	0.18	1.00			
V	0.83	0.23	0.69	-0.84	0.91	0.55	0.72	0.72	0.57	-0.75	0.73	0.82	0.50	0.44	0.72	0.36	0.74	0.30	0.79	0.22	1.00		
Zn	0.46	0.38	0.51	-0.48	0.42	0.81	0.58	0.41	0.33	-0.66	0.67	0.61	0.62	0.76	0.44	0.58	0.47	0.43	0.36	0.39	0.51	1.00	
Zr	0.61	-0.36	0.46	-0.65	0.73	0.31	0.14	0.49	0.33	-0.56	0.27	0.35	0.37	-0.03	0.49	-0.18	0.67	-0.19	0.69	-0.39	0.61	0.15	1.00

3. Exchangeable cations

Table S5. 1 M NH₄-exchangeable Tl, Rb, K, Ba, Mg, and Ca and 2 M KCl-exchangeable NH₄ (\pm = relative standard deviation; n = number of replicate extractions).

Sample	Tl			Rb			K			Ca			Mg			Ba			NH ₄		
	mmol/kg	\pm	n	mmol/kg	\pm	n	mmol/kg	\pm	n	mmol/kg	\pm	n	mmol/kg	\pm	n	mmol/kg	\pm	n	mmol/kg	\pm	n
A1	0.00030	0.00003	4	0.00668	0.00027	2	8.9	1.3	4	209	25	4	17.1	2.1	4	0.191	0.019	4	0.80	0.05	2
A2	0.00030	0.00004	4	0.00948	0.00006	2	5.7	1.0	4	94	11	4	22.3	2.8	4	0.213	0.013	4	0.93	0.00	2
A3	0.00026	0.00004	4	0.00303	0.00000	2	5.5	0.7	4	101	11	4	41.0	5.6	4	0.067	0.004	4	0.69	0.03	2
A4	0.00093	0.00011	6	0.01045	0.00008	2	6.7	0.9	6	136	14	6	44.6	5.9	6	0.116	0.008	6	0.96	0.01	2
A5	0.00042	0.00002	7	0.00483	0.00007	3	9.0	0.3	7	205	19	7	12.0	0.7	7	0.232	0.015	7	1.26	0.07	2
A6	0.00038	0.00004	6	0.00830	0.00023	2	6.6	0.7	6	92	7	6	37.8	3.7	6	0.095	0.003	6	0.87	0.01	2
B1	0.00254	0.00051	4	0.00827	0.00004	2	12.0	2.5	4	133	16	4	45.3	7.7	4	0.207	0.043	4	1.35	0.17	2
B2	0.00198	0.00075	5	0.01733	0.00807	3	13.3	2.3	5	125	15	5	51.5	8.8	5	0.084	0.030	5	1.16	0.06	2
B3	0.00202	0.00040	4	0.01107	0.00004	2	12.0	1.7	4	241	32	4	24.1	4.0	4	0.191	0.033	4	1.10	0.03	2
B4	0.00138	0.00041	5	0.00834	-	1	9.4	1.6	5	144	19	5	37.0	6.8	5	0.151	0.028	5	-	-	-
B5	0.00091	0.00022	6	0.00950	0.00008	2	12.0	1.8	6	185	21	6	36.7	6.2	6	0.580	0.083	6	0.96	0.04	2
B6	0.00124	0.00029	6	0.00062	0.00000	2	1.8	0.2	6	96	9	6	27.6	2.9	6	0.044	0.006	6	0.41	0.03	2
C1	0.00258	0.00021	4	0.01520	0.00003	2	7.4	1.3	4	123	10	4	60.1	9.9	4	0.153	0.010	4	0.92	0.02	2
C2	0.00315	0.00022	4	0.01601	0.00105	2	5.8	0.4	4	115	4	4	50.0	3.2	4	0.253	0.018	4	0.62	0.10	2
C3	0.00087	0.00004	5	0.00748	0.00011	3	7.5	1.4	5	169	14	5	25.5	2.8	5	0.188	0.008	5	0.96	0.11	2
C4	0.00372	0.00044	4	0.01430	0.00002	2	7.9	0.7	4	93	5	4	51.4	6.1	4	0.195	0.021	4	0.94	0.02	2
C5	0.00308	0.00039	3	0.00829	#DIV/0!	1	6.6	1.4	3	149	40	3	38.3	4.0	3	0.108	0.032	3	1.59	-	1
C6	0.00260	0.00015	4	0.00256	0.00013	2	4.7	1.4	4	113	34	4	33.7	2.5	4	0.074	0.018	4	0.53	0.03	2

Table S5. Continuation.

Sample	Tl			Rb			K			Ca			Mg			Ba			NH ₄		
	mmol/kg	±	n	mmol/kg	±	n	mmol/kg	±	n	mmol/kg	±	n	mmol/kg	±	n	mmol/kg	±	n	mmol/kg	±	n
D1	0.01123	0.00101	4	0.01147	0.00006	2	9.5	1.2	4	102	16	4	34.4	4.0	4	0.168	0.008	4	1.50	0.11	2
D2	0.00975	0.00070	4	0.00918	0.00002	2	7.5	0.2	4	88	4	4	29.6	1.2	4	0.182	0.013	4	0.99	0.08	2
D3	0.00452	0.00302	4	0.00356	0.00504	2	8.1	1.0	4	212	31	4	12.6	1.7	4	0.134	0.008	3	1.72	0.18	2
D4	0.00912	0.00089	4	0.00847	0.00015	2	3.8	0.5	4	198	10	4	10.3	0.9	4	0.130	0.012	4	0.64	0.00	2
D5	0.01443	0.00046	5	0.01100	0.00042	3	13.6	0.8	5	132	10	5	40.7	2.2	5	0.231	0.003	5	1.43	0.11	2
D6	0.01551	0.00047	4	0.01311	0.00026	2	7.1	0.2	4	84	2	4	32.1	0.4	4	0.219	0.006	4	0.81	0.01	2
E1	0.05395	0.00453	4	0.01410	0.00009	2	6.0	0.8	4	105	6	4	22.5	1.3	4	0.176	0.006	4	1.71	0.02	2
E2	0.05751	0.00411	4	0.01321	0.00022	2	5.4	0.3	4	107	4	4	26.4	1.2	4	0.118	0.005	4	1.38	0.02	2
E3	0.07850	0.00625	3	0.01503	#DIV/0!	1	3.0	0.3	3	130	18	3	21.7	1.8	3	0.139	0.010	3	1.20	0.00	2
E4	0.01130	0.00309	2	0.00753	#DIV/0!	1	3.3	0.1	2	286	11	2	17.6	0.6	2	0.209	0.001	2	-	-	-
E5	0.10459	0.01307	5	0.01357	0.00008	3	7.2	0.6	5	75	6	5	21.9	1.3	5	0.293	0.013	5	1.60	0.02	2
E6	0.07806	0.01005	4	0.01053	0.00002	2	4.6	0.4	4	211	24	4	14.4	1.0	4	0.161	0.015	4	1.25	0.01	2
F1	0.24729	0.02636	4	0.01034	0.00012	2	5.3	0.6	4	58	3	4	11.6	1.1	4	0.174	0.011	4	2.22	0.02	2
F2	0.20318	0.01247	4	0.01307	0.00019	2	3.5	0.1	4	126	1	4	18.2	1.1	4	0.198	0.005	4	1.09	0.00	2
F3	0.21901	0.02093	4	0.01256	0.00027	2	4.5	0.4	4	108	2	4	16.6	1.2	4	0.150	0.005	4	1.77	0.06	2
F4	0.10003	0.01227	4	0.01121	0.00012	2	4.3	0.5	4	136	11	4	64.2	9.5	4	0.119	0.010	4	1.92	0.65	2
F5	0.19729	0.01143	5	0.01443	0.00041	3	4.3	0.2	5	80	4	5	31.7	1.6	5	0.213	0.009	5	0.92	0.00	2
F6	0.26265	0.02103	4	0.00976	0.00020	2	3.6	0.5	4	71	5	4	19.8	1.8	4	0.207	0.013	4	1.64	0.09	2

Table S6. 1 M NH₄-exchangeable Tl in four consecutive extraction steps of six selected topsoil samples (A5, B2, C3, D5, E5, and F5).

Sample / Step	Tl		sum 1-4		Sample / Step	Tl		sum 1-4	
	mmol/kg	% of total	mmol/kg	% of total extracted		mmol/kg	% of total	mmol/kg	% of total extracted
A5/1	0.000293	2.00	0.0004875	60.2	D5/1	0.008966	1.79	0.0174469	51.4
A5/2	0.000108	0.73		22.1	D5/2	0.004731	0.95		27.1
A5/3	0.000061	0.41		12.5	D5/3	0.002429	0.49		13.9
A5/4	0.000026	0.17		5.2	D5/4	0.001320	0.26		7.6
B2/1	0.000954	3.05	0.0018290	52.2	E5/1	0.070339	4.12	0.1089811	64.5
B2/2	0.000467	1.49		25.5	E5/2	0.024331	1.43		22.3
B2/3	0.000262	0.84		14.3	E5/3	0.009819	0.58		9.0
B2/4	0.000146	0.46		8.0	E5/4	0.004492	0.26		4.1
C3/1	0.000663	1.59	0.0010475	63.3	F5/1	0.137957	3.29	0.2165826	63.7
C3/2	0.000222	0.53		21.2	F5/2	0.049108	1.17		22.7
C3/3	0.000107	0.26		10.2	F5/3	0.019615	0.47		9.1
C3/4	0.000055	0.13		5.3	F5/4	0.009903	0.24		4.6

4. Pseudo-porewater extracts

Table S7. pH_{CaCl₂} value and Tl, Rb, NH₄, K, Na, Ba, Mg, and Ca concentrations determined in 0.01 M CaCl₂ extracts (\pm indicates the relative standard deviation, and n the number of replicate extractions.

Sample	pH			Tl			Rb			NH ₄			K			Na			Ba			Mg			Ca		
		\pm	n	μM	\pm	n	μM	\pm	n	μM	\pm	n	μM	\pm	n	μM	\pm	n	μM	\pm	n	μM	\pm	n	μM	\pm	n
A1	7.2	0.3	6	0.00098	0.00028	2	0.0180	0.0015	4	28.6	6.3	5	190	10	6	30.3	4.1	6	0.6234	0.0532	6	751	31	6	9097	385	6
A2	5.6	0.2	6	0.00057	0.00002	2	0.0291	0.0014	4	46.8	8.2	5	157	12	6	64.2	3.7	6	0.8182	0.0543	6	1148	36	6	8390	391	6
A3	7.3	0.4	6	0.00075	0.00001	2	0.0180	0.0019	4	36.7	8.0	5	191	8	6	21.4	3.6	6	0.3286	0.0514	6	1601	83	6	8075	314	6
A4	7.2	0.3	6	0.00176	0.00004	2	0.0349	0.0033	4	58.2	12.2	5	138	7	6	24.2	3.2	6	0.3992	0.0546	6	1937	127	6	7837	676	6
A5	7.2	0.3	6	0.00161	0.00013	3	0.0343	0.0036	5	85.9	21.0	5	362	17	7	21.4	3.1	7	1.4906	0.1328	7	579	22	7	9393	626	7
A6	6.9	0.1	6	0.00113	0.00040	4	0.0309	0.0014	6	39.9	9.0	7	164	22	8	38.0	4.6	8	0.3333	0.0402	8	1932	158	8	8205	751	8
B1	6.8	0.2	5	0.00534	0.00026	4	0.0359	0.0009	2	89.6	5.3	3	288	16	4	20.7	1.7	4	0.8530	0.0326	4	1761	27	4	7883	342	4
B2	7.1	0.1	5	0.01047	0.01539	5	0.0705	0.0023	3	78.2	5.0	3	345	10	5	26.1	1.4	5	0.2743	0.0147	5	1954	63	5	7493	472	5
B3	7.0	0.3	5	0.00332	0.00008	4	0.0332	0.0005	2	70.5	3.2	3	207	8	4	39.6	1.0	4	0.5327	0.0238	4	854	19	4	8919	467	4
B4	7.2	0.1	5	0.00281	0.00144	5	0.0225	0.0012	4	31.9	6.8	5	200	14	6	26.3	3.1	6	0.4156	0.0136	6	1425	87	6	8542	615	6
B5	6.8	0.2	7	0.00105	0.00010	7	0.0170	0.0007	2	45.8	4.8	6	183	12	7	47.2	11.0	7	1.5568	0.1008	7	1200	150	7	8324	905	4
B6	7.6	0.2	5	0.00577	0.00047	4	0.0084	0.0000	2	22.8	2.5	3	103	9	4	12.9	1.1	4	0.2893	0.0155	4	659	46	4	8981	809	4
C1	7.0	0.1	5	0.00491	0.00035	4	0.0376	0.0006	2	50.7	1.4	2	125	6	4	25.6	1.3	4	0.3384	0.0331	4	2540	127	4	7352	355	4
C2	7.0	0.1	7	0.00292	0.00039	4	0.0209	0.0018	4	17.2	1.7	4	64	2	6	36.7	5.5	6	0.3486	0.0365	6	1869	53	6	7846	207	6
C3	7.1	0.1	9	0.00162	0.00024	8	0.0224	0.0015	5	64.7	10.8	7	180	9	10	22.7	3.6	10	0.5677	0.0438	10	994	98	10	8658	192	7
C4	5.8	0.1	8	0.00635	0.00111	7	0.0387	0.0013	2	46.8	3.1	5	148	20	7	31.4	8.5	7	0.6258	0.0918	7	2173	320	6	7384	404	4
C5	7.1	0.1	6	0.00972	0.00099	5	0.0435	0.0032	3	102.6	16.1	3	217	18	5	31.0	3.7	5	0.4552	0.0350	5	1564	67	5	8681	303	5
C6	7.3	0.2	5	0.00793	0.00046	4	0.0155	0.0005	2	35.8	0.3	2	153	12	4	16.9	1.8	4	0.3119	0.0328	4	1170	66	4	8599	245	4

Table S7. Continuation.

Sample	pH			Tl			Rb			NH ₄			K			Na			Ba			Mg			Ca		
		±	n	μM	±	n	μM	±	n	μM	±	n	μM	±	n	μM	±	n	μM	±	n	μM	±	n	μM	±	n
D1	7.0	0.0	5	0.0251	0.0018	6	0.0377	0.0035	4	67.6	43.2	4	220	16	6	24.5	2.9	6	0.5404	0.0785	6	1716	120	6	7899	611	6
D2	7.0	0.0	3	0.0183	0.0024	4	0.0265	0.0002	2	31.0	0.2	2	154	12	4	23.6	2.9	4	0.5199	0.0855	4	1464	68	4	7640	381	4
D3	7.2	0.1	6	0.0205	0.0033	7	0.0459	0.0005	2	110.2	30.2	5	275	30	7	77.0	15.7	7	0.5185	0.0598	7	573	87	7	9223	313	4
D4	7.5	0.2	3	0.0180	0.0020	4	0.0249	0.0003	2	66.6	2.0	2	94	7	4	25.8	3.3	4	0.3699	0.0366	4	518	23	4	9475	511	4
D5	6.8	0.1	3	0.0300	0.0017	5	0.0359	0.0014	3	32.1	1.7	2	317	10	5	26.6	2.5	5	0.8968	0.0642	5	1811	28	5	7799	309	5
D6	6.6	0.1	5	0.0239	0.0014	6	0.0262	0.0016	4	44.3	25.7	4	124	6	6	32.6	3.3	6	0.6018	0.0429	6	1754	60	6	8048	452	6
E1	6.0	0.2	6	0.1529	0.0149	7	0.0587	0.0015	2	93.8	6.7	6	142	9	7	45.3	3.9	6	0.7927	0.1141	7	1078	80	7	7996	599	4
E2	6.0	0.6	4	0.1931	0.0023	4	0.0588	0.0002	2	72.0	1.8	3	154	10	4	28.1	2.8	4	0.5285	0.0340	4	1371	90	4	7969	192	4
E3	6.8	0.1	3	0.1897	0.0360	3	0.0427	-	1	44.5	3.8	2	97	77	3	43.1	6.8	3	0.4336	0.1567	3	1254	340	3	8455	238	3
E4	7.1	0.0	2	0.1130	0.1281	2	0.0213	-	1	60.9	-	1	106	76	2	28.1	3.8	2	0.5159	0.0156	2	1110	560	2	8793	603	2
E5	5.5	0.1	4	0.2999	0.0395	5	0.0545	0.0022	3	81.6	2.4	3	183	4	5	39.7	2.1	5	1.6100	0.0911	5	1207	70	5	7979	181	5
E6	7.2	0.1	6	0.2407	0.0071	6	0.0431	0.0014	4	82.1	9.9	5	118	2	6	32.7	3.1	6	0.5943	0.0185	6	678	34	6	9401	446	6
F1	5.0	0.1	4	1.3227	0.0312	4	0.0677	0.0006	2	84.5	32.4	3	166	4	4	91.1	43.8	4	1.5052	0.0436	4	756	78	4	8470	373	4
F2	7.1	0.0	4	0.3148	0.0037	4	0.0241	0.0005	2	35.1	1.8	3	47	3	4	55.8	38.7	4	0.4322	0.0156	4	908	58	4	8753	381	4
F3	6.1	0.2	7	0.5869	0.0858	7	0.0446	0.0014	2	100.8	20.5	5	101	21	7	66.2	52.9	7	0.6053	0.0452	7	909	270	7	8572	309	4
F4	7.3	0.1	4	0.2586	0.0119	4	0.0391	0.0001	2	38.4	26.1	3	78	9	4	34.9	33.2	4	0.3265	0.0175	4	2619	37	4	7099	84	4
F5	6.4	0.1	4	0.3992	0.0175	5	0.0353	0.0018	3	51.8	14.1	3	93	5	5	36.1	30.0	5	0.7452	0.0381	5	1772	99	5	7727	410	5
F6	5.4	0.1	4	0.8417	0.1087	4	0.0311	0.0011	2	42.8	26.2	3	71	12	4	68.2	44.8	4	0.9120	0.1075	4	1260	147	4	8401	982	4

Table S8. Tl concentrations in four consecutive 0.01 M CaCl₂ extracts for six selected topsoil samples (A5, B2, C3, D5, E5, and F5).

Sample/Step	Tl		Sample/Step	Tl	
	µM	% of 1. step		µM	% of 1. step
A5/1	0.00172	100	D5/1	0.02850	100
A5/2	0.00088	51	D5/2	0.02123	75
A5/3	0.00076	44	D5/3	0.01684	59
A5/4	0.00067	39	D5/4	0.01440	51
B2/1	0.00333	100	E5/1	0.30164	100
B2/2	0.00232	70	E5/2	0.22385	74
B2/3	0.00176	53	E5/3	0.14507	48
B2/4	0.00181	55	E5/4	0.11366	38
C3/1	0.00160	100	F5/1	0.38233	100
C3/2	0.00118	74	F5/2	0.27420	72
C3/3	0.00099	62	F5/3	0.21235	56
C3/4	0.00090	57	F5/4	0.17624	46

5. Distribution coefficients for exchangeable cations

Table. S9. Log-transformed distribution coefficients for exchangeable geogenic Tl, Rb, K, Ba and Mg in all soils ($\log(^X\text{Tl}_{\text{d,geo}}/\text{L/kg})$; Eq. 1). Soil B6 with highest carbonate content and soil E4 with highest organic C content (marked in red) were not considered for the calculation of averages.

sample	Tl	Rb	K	Ba	Mg	sample	Tl	Rb	K	Ba	Mg
A1	2.49	2.57	1.67	2.49	1.36	D1	2.65	2.48	1.64	2.49	1.30
A2	2.72	2.51	1.56	2.42	1.29	D2	2.73	2.54	1.69	2.54	1.31
A3	2.55	2.23	1.46	2.31	1.41	D3	2.34	1.89	1.47	2.41	1.34
A4	2.72	2.48	1.69	2.46	1.36	D4	2.71	2.53	1.61	2.55	1.30
A5	2.42	2.15	1.40	2.19	1.32	D5	2.68	2.49	1.63	2.41	1.35
A6	2.53	2.43	1.61	2.46	1.29	D6	2.81	2.70	1.76	2.56	1.26
B1	2.68	2.36	1.62	2.38	1.41	E1	2.55	2.38	1.62	2.35	1.32
B2	2.28	2.39	1.59	2.49	1.42	E2	2.47	2.35	1.55	2.35	1.28
B3	2.78	2.52	1.76	2.56	1.45	E3	2.62	2.55	1.49	2.50	1.24
B4	2.69	2.57	1.67	2.56	1.41	E4	2.00	2.55	1.50	2.61	1.20
B5	2.94	2.75	1.82	2.57	1.49	E5	2.54	2.40	1.59	2.26	1.26
B6	2.33	1.87	1.24	2.18	1.62	E6	2.51	2.39	1.60	2.43	1.33
C1	2.72	2.61	1.77	2.65	1.37	F1	2.27	2.18	1.50	2.06	1.19
C2	3.03	2.89	1.96	2.86	1.43	F2	2.81	2.73	1.87	2.66	1.30
C3	2.73	2.52	1.62	2.52	1.41	F3	2.57	2.45	1.65	2.39	1.26
C4	2.77	2.57	1.73	2.49	1.37	F4	2.59	2.46	1.74	2.56	1.39
C5	2.50	2.28	1.48	2.37	1.39	F5	2.69	2.61	1.67	2.46	1.25
C6	2.52	2.22	1.49	2.37	1.46	F6	2.49	2.50	1.71	2.36	1.20

Table S10. Correlation coefficients for log (${}^X\text{K}_{\text{d,geo}}$ /(L/kg)) listed in Table S9 (excluding outliers B6 and E4; soil B6 with highest carbonate content; soil E4 with highest organic C content).

	<i>Tl</i>	<i>Rb</i>	<i>K</i>	<i>Ba</i>	<i>Mg</i>
<i>Tl</i>	1.00				
<i>Rb</i>	0.82	1.00			
<i>K</i>	0.76	0.85	1.00		
<i>Ba</i>	0.75	0.76	0.78	1.00	
<i>Mg</i>	0.32	0.09	0.21	0.41	1.00

6. Isotope exchange experiment

Table S11. Results from the isotope exchange experiment with ^{204}Tl in 0.01 M CaCl_2 and of the parallel inactive experiment for elemental analysis. Before spiking, the soil samples were conditioned with 0.01 M CaCl_2 for two hours (PreEq).

Sample	Time	CaCl_2						NH_4		^{204}Tl				
		Tl		Rb	NH_4	K	Mg	Ca	Tl	Log K_d	Log K_d	E (^{204}Tl)	%NH ₄	%E(t=0)
		μM	(%PreEq)	μM	μM	μM	μM	μM	mol/kg	L/kg	L/kg	mol/kg		
A6	PreEq	1.50E-03	93%	3.10E-02	27	193	2070	8810	3.80E-07	2.42				
	4 h	1.60E-03	100%	3.80E-02	48	194	2112	8790	3.80E-07	2.39	2.71	8.10E-07	209%	
	1 d	2.10E-03	135%	6.00E-02	152	200	2201	9057			2.55	7.60E-07		
	3 d	1.60E-03	101%	6.40E-02	191	212	2177	9117			2.53	5.40E-07		
	7 d	1.30E-03	82%	4.20E-02	61	208	2372	9462			2.64	5.70E-07		
	14 d	3.80E-04	24%	1.10E-02	1	171	2485	9734			3.16	5.50E-07		
	30 d	5.60E-04	35%	1.30E-02	<7	181	2656	9886			3.25	9.90E-07		
	90 d	4.60E-04	29%	1.20E-02	<7	148	2244	8818			3.28	8.80E-07		109%
B4	PreEq	4.00E-03	86%	2.30E-02	20	214	1533	9207	1.40E-06	2.54				
	4 h	4.60E-03	100%	2.70E-02	33	212	1518	9150	1.40E-06	2.47	2.75	2.60E-06	189%	
	1 d	4.70E-03	102%	4.20E-02	119	234	1616	9541			2.60	1.90E-06		
	3 d	5.20E-03	112%	5.10E-02	180	247	1663	9709			2.55	1.80E-06		
	7 d	4.90E-03	106%	5.10E-02	177	256	1774	9976			2.58	1.80E-06		
	14 d	1.10E-03	24%	1.00E-02	1	198	1826	10218			3.15	1.50E-06		
	30 d	1.60E-03	34%	1.10E-02	<7	214	1923	10624			3.23	2.60E-06		
	90 d	1.20E-03	26%	1.10E-02	<7	190	1914	10160			3.27	2.30E-06		88%

Table S11. Continuation.

Sample	Time	CaCl ₂						NH ₄		²⁰⁴ Tl			
		Tl		Rb	NH ₄	K	Mg	Ca	Tl	Log K _d	Log K _d	E (²⁰⁴ Tl)	%NH ₄
		μM	(%PreEq)	μM	μM	μM	μM	μM	mol/kg	L/kg	L/kg	mol/kg	%E(t=0)
C5	PreEq	1.10E-02	81%	4.20E-02	73	215	1621	8745	3.10E-06	2.46			
	4 h	1.30E-02	100%	5.60E-02	145	236	1661	8956	3.10E-06	2.37	2.48	4.00E-06	131%
	1 d	1.60E-02	122%	7.00E-02	348	209	1682	9003			2.33	3.50E-06	
	3 d	1.70E-02	125%	8.50E-02	587	254	1759	9249			2.30	3.30E-06	
	7 d	1.70E-02	125%	8.50E-02	593	294	1900	9690			2.27	3.10E-06	
	14 d	3.80E-03	29%	1.60E-02	9	197	2000	10390			2.93	3.20E-06	
	30 d	4.00E-03	31%	1.80E-02	<7	227	2094	10485			2.99	4.00E-06	
	90 d	2.80E-03	21%	1.30E-02	<7	192	2060	10216			3.18	4.20E-06	105%
D1	PreEq	2.50E-02	88%	3.50E-02	38	223	1846	8569	9.70E-06	2.66			
	4 h	2.80E-02	100%	4.10E-02	54	227	1832	8454	9.70E-06	2.60	2.76	1.60E-05	164%
	1 d	3.70E-02	133%	5.60E-02	131	245	1848	8477			2.67	1.70E-05	
	3 d	4.40E-02	156%	7.10E-02	209	269	1875	8767			2.55	1.60E-05	
	7 d	4.20E-02	148%	6.80E-02	201	263	2014	9109			2.55	1.50E-05	
	14 d	1.60E-02	58%	1.60E-02	2	214	2067	9239			3.09	2.00E-05	
	30 d	1.10E-02	40%	1.60E-02	<7	218	2170	9653			3.20	1.80E-05	
	90 d	1.10E-02	40%	1.50E-02	<7	190	2186	8744			3.29	2.20E-05	

Table S11. Continuation.

Sample	Time	CaCl ₂						NH ₄		²⁰⁴ Tl			
		Tl		Rb	NH ₄	K	Mg	Ca	Tl	Log K _d	Log K _d	E (²⁰⁴ Tl)	%NH ₄
		μM	(%PreEq)	μM	μM	μM	μM	μM	mol/kg	L/kg	L/kg	mol/kg	%E(t=0)
D6	PreEq	2.50E-02	83%	2.50E-02	17	127	1824	8407	1.60E-05	2.80			
	4 h	3.00E-02	100%	3.00E-02	30	148	1855	8548	1.60E-05	2.72	2.90	2.40E-05	152%
	1 d	3.70E-02	124%	3.80E-02	62	127	1835	8316			2.80	2.40E-05	
	3 d	4.80E-02	159%	5.30E-02	131	155	1898	8484			2.70	2.40E-05	
	7 d	4.80E-02	161%	5.60E-02	177	166	2009	8549			2.59	1.80E-05	
	14 d	9.50E-03	32%	1.10E-02	31	115	2163	8818			2.97	8.90E-06	
	30 d	9.20E-03	31%	1.00E-02	<7	116	2318	9051			3.42	2.40E-05	
	90 d	9.20E-03	31%	8.60E-03	<7	99	2261	8190			3.47	2.70E-05	115%
E6	PreEq	2.40E-01	93%	4.20E-02	56	116	694	9637	7.80E-05	2.52			
	4 h	2.50E-01	100%	4.50E-02	81	108	680	9622	7.80E-05	2.49	2.53	8.50E-05	109%
	1 d	4.20E-01	166%	7.80E-02	342	121	713	9793			2.36	9.70E-05	
	3 d	5.00E-01	198%	9.80E-02	564	160	769	10658			2.32	1.10E-04	
	7 d	5.50E-01	219%	1.10E-01	749	175	820	10969			2.30	1.10E-04	
	14 d	4.20E-01	165%	8.30E-02	720	156	846	10969			2.85	3.00E-04	
	30 d	8.80E-02	35%	1.50E-02	<7	111	938	11848			3.13	1.20E-04	
	90 d	6.70E-02	26%	1.20E-02	<7	106	977	11916			3.26	1.20E-04	

7. Sequential soil extractions

Table S12. Sequential extraction results for exchangeable (1 M NH₄-acetate, pH 6.8) and reducible Tl and Mn (0.1 M hydroxylamine / 1 M NH₄-acetate, pH 6.1) in 18 topsoils samples. In the three hydroxylamine extraction steps, less than 1% of the total Fe was extracted.

Soil	step	Mn			Tl			Tl/Mn mol/mol	$\log^{Tl} K_d$
		mol/kg	sum	%total	mol/kg	sum	%total		
A1	NH4 1.1	1.1E-04			2.3E-07				
	NH4 1.2	7.4E-05			5.5E-08				
	NH4 1.3	7.3E-05	2.5E-04	1.3	2.0E-08	3.1E-07	2.2		
	Hx 2.1	1.0E-02			1.3E-07				
	Hx 2.2	1.8E-03			3.1E-08				
	Hx 2.3	5.1E-04	1.3E-02	63.5	8.5E-09	1.7E-07	1.2	1.3E-05	5.1
A2	NH4 1.1	8.7E-04			2.1E-07				
	NH4 1.2	1.8E-04			3.6E-08				
	NH4 1.3	8.6E-05	1.1E-03	7.0	1.0E-08	2.5E-07	2.3		
	Hx 2.1	5.6E-03			3.4E-08				
	Hx 2.2	1.2E-03			9.5E-09				
	Hx 2.3	3.3E-04	7.1E-03	44.1	3.1E-09	4.7E-08	0.4	6.5E-06	5.0
A6	A6 NH4 1.1	2.3E-04			3.0E-07				
	A6 NH4 1.2	8.3E-05			7.0E-08				
	A6 NH4 1.3	6.0E-05	3.7E-04	1.7	2.6E-08	4.0E-07	2.6		
	A6 Hx 2.1	1.3E-02			2.3E-07				
	A6 Hx 2.2	3.4E-03			7.6E-08				
	A6 Hx 2.3	1.2E-03	1.8E-02	83.4	3.4E-08	3.4E-07	2.2	1.9E-05	5.2
B1	NH4 1.1	1.6E-04			1.5E-06				
	NH4 1.2	6.3E-05			3.3E-07				
	NH4 1.3	6.6E-05	2.9E-04	1.7	1.0E-07	2.0E-06	2.6		
	Hx 2.1	7.5E-03			6.2E-07				
	Hx 2.2	2.0E-03			1.9E-07				
	Hx 2.3	7.8E-04	1.0E-02	60.6	6.6E-08	8.8E-07	1.2	8.6E-05	5.2
B2	NH4 1.1	1.4E-04			1.1E-06				
	NH4 1.2	6.6E-05			3.1E-07				
	NH4 1.3	7.2E-05	2.8E-04	1.0	1.2E-07	1.5E-06	4.8		
	Hx 2.1	1.4E-02			5.4E-07				
	Hx 2.2	3.7E-03			1.5E-07				
	Hx 2.3	1.3E-03	1.9E-02	70.6	4.0E-08	7.2E-07	2.3	3.8E-05	4.5
B6	NH4 1.1	6.9E-05			7.2E-07				
	NH4 1.2	9.5E-05			1.3E-07				
	NH4 1.3	1.1E-04	2.7E-04	5.7	5.9E-08	9.1E-07	1.9		
	Hx 2.1	2.2E-03			9.3E-07				
	Hx 2.2	2.6E-04			1.4E-07				
	Hx 2.3	7.4E-05	2.5E-03	52.4	2.9E-08	1.1E-06	2.3	4.4E-04	5.8

Table S12. Continuation.

Soil	step	Mn			Tl			Tl/Mn mol/mol	$\log^{Tl}K_d$
		mol/kg	sum	%total	mol/kg	sum	%total		
C1	NH4 1.1	4.3E-04			2.1E-06				
	NH4 1.2	1.9E-04			4.7E-07				
	NH4 1.3	1.6E-04	7.8E-04	3.5	1.4E-07	2.7E-06	2.6		
	Hx 2.1	1.4E-02			2.0E-06				
	Hx 2.2	3.1E-03			4.2E-07				
	Hx 2.3	1.2E-03	1.8E-02	82.5	1.0E-07	2.5E-06	2.3	1.4E-04	5.4
C2	NH4 1.1	1.2E-04			2.4E-06				
	NH4 1.2	4.1E-05			4.2E-07				
	NH4 1.3	4.0E-05	2.1E-04	1.1	1.2E-07	2.9E-06	2.4		
	Hx 2.1	8.6E-03			1.0E-06				
	Hx 2.2	1.6E-03			2.5E-07				
	Hx 2.3	5.1E-04	1.1E-02	59.1	6.5E-08	1.4E-06	1.1	1.3E-04	5.6
C6	NH4 1.1	1.0E-04			1.5E-06				
	NH4 1.2	9.9E-05			2.4E-07				
	NH4 1.3	1.1E-04	3.1E-04	4.2	7.8E-08	1.8E-06	1.4		
	Hx 2.1	3.4E-03			5.7E-07				
	Hx 2.2	5.9E-04			1.1E-07				
	Hx 2.3	1.8E-04	4.1E-03	55.1	3.4E-08	7.2E-07	0.5	1.7E-04	5.3
D1	D1 NH4 1.1	8.0E-04			1.2E-05				
	D1 NH4 1.2	2.5E-04			2.1E-06				
	D1 NH4 1.3	1.8E-04	1.2E-03	5.0	5.2E-07	1.4E-05	4.0		
	D1 Hx 2.1	1.2E-02			4.6E-06				
	D1 Hx 2.2	3.1E-03			8.2E-07				
	D1 Hx 2.3	3.8E-03	1.9E-02	77.5	2.2E-07	5.6E-06	1.6	3.0E-04	5.0
D2	NH4 1.1	6.1E-04			8.3E-06				
	NH4 1.2	1.9E-04			1.7E-06				
	NH4 1.3	1.3E-04	9.3E-04	4.0	6.1E-07	1.1E-05	3.1		
	Hx 2.1	9.6E-03			1.4E-05				
	Hx 2.2	3.2E-03			6.8E-06				
	Hx 2.3	1.1E-03	1.4E-02	59.1	9.4E-07	2.1E-05	6.2	1.5E-03	5.9
D6	D6 NH4 1.1	3.3E-04			1.7E-05				
	D6 NH4 1.2	8.8E-05			2.7E-06				
	D6 NH4 1.3	5.2E-05	4.7E-04	2.1	7.3E-07	2.0E-05	4.0		
	D6 Hx 2.1	1.3E-02			7.4E-06				
	D6 Hx 2.2	2.8E-03			1.7E-06				
	D6 Hx 2.3	9.6E-04	1.7E-02	73.5	5.4E-07	9.6E-06	1.9	5.8E-04	5.3

Table S12. Continuation.

Soil	step	Mn			Tl			Tl/Mn mol/mol	$\log^{Tl}K_d$
		mol/kg	sum	%total	mol/kg	sum	%total		
E1	NH4 1.1	3.5E-04			4.3E-05				
	NH4 1.2	1.0E-04			7.7E-06				
	NH4 1.3	5.8E-05	5.1E-04	2.6	2.0E-06	5.3E-05	4.4		
	Hx 2.1	5.1E-03			8.7E-06				
	Hx 2.2	2.2E-03			4.5E-06				
	Hx 2.3	9.9E-04	8.2E-03	41.8	1.6E-06	1.5E-05	1.2	1.8E-03	5.0
E2	NH4 1.1	3.9E-04			4.7E-05				
	NH4 1.2	1.2E-04			8.3E-06				
	NH4 1.3	8.1E-05	5.9E-04	3.9	2.0E-06	5.7E-05	4.4		
	Hx 2.1	3.4E-03			8.3E-06				
	Hx 2.2	1.4E-03			2.7E-06				
	Hx 2.3	6.3E-04	5.5E-03	36.4	8.2E-07	1.2E-05	0.9	2.1E-03	5.0
E6	E6 NH4 1.1	1.7E-04			7.8E-05				
	E6 NH4 1.2	1.1E-04			1.4E-05				
	E6 NH4 1.3	1.1E-04	3.9E-04	1.9	3.5E-06	9.5E-05	5.6		
	E6 Hx 2.1	1.0E-02			3.5E-05				
	E6 Hx 2.2	2.5E-03			1.1E-05				
	E6 Hx 2.3	8.3E-04	1.3E-02	67.3	4.4E-06	5.0E-05	2.9	3.7E-03	5.1
F1	NH4 1.1	3.0E-04			2.1E-04				
	NH4 1.2	7.3E-05			3.2E-05				
	NH4 1.3	3.8E-05	4.1E-04	2.1	6.3E-06	2.5E-04	7.4		
	Hx 2.1	3.5E-03			3.6E-05				
	Hx 2.2	1.4E-03			2.3E-05				
	Hx 2.3	5.3E-04	5.5E-03	28.0	7.5E-06	6.7E-05	2.0	1.2E-02	4.9
F2	NH4 1.1	5.0E-05			1.6E-04				
	NH4 1.2	1.9E-05			3.0E-05				
	NH4 1.3	1.5E-05	8.4E-05	0.3	7.5E-06	2.0E-04	5.9		
	Hx 2.1	7.3E-03			8.2E-05				
	Hx 2.2	3.1E-03			3.6E-05				
	Hx 2.3	1.2E-03	1.2E-02	43.7	1.1E-05	1.3E-04	3.8	1.1E-02	5.5
F6	NH4 1.1	1.0E-03			2.1E-04				
	NH4 1.2	2.1E-04			4.1E-05				
	NH4 1.3	1.1E-04	1.3E-03	4.3	1.0E-05	2.6E-04	5.2		
	Hx 2.1	1.0E-02			4.6E-05				
	Hx 2.2	2.6E-03			1.6E-05				
	Hx 2.3	1.0E-03	1.4E-02	45.0	4.1E-06	6.6E-05	1.3	4.8E-03	4.7

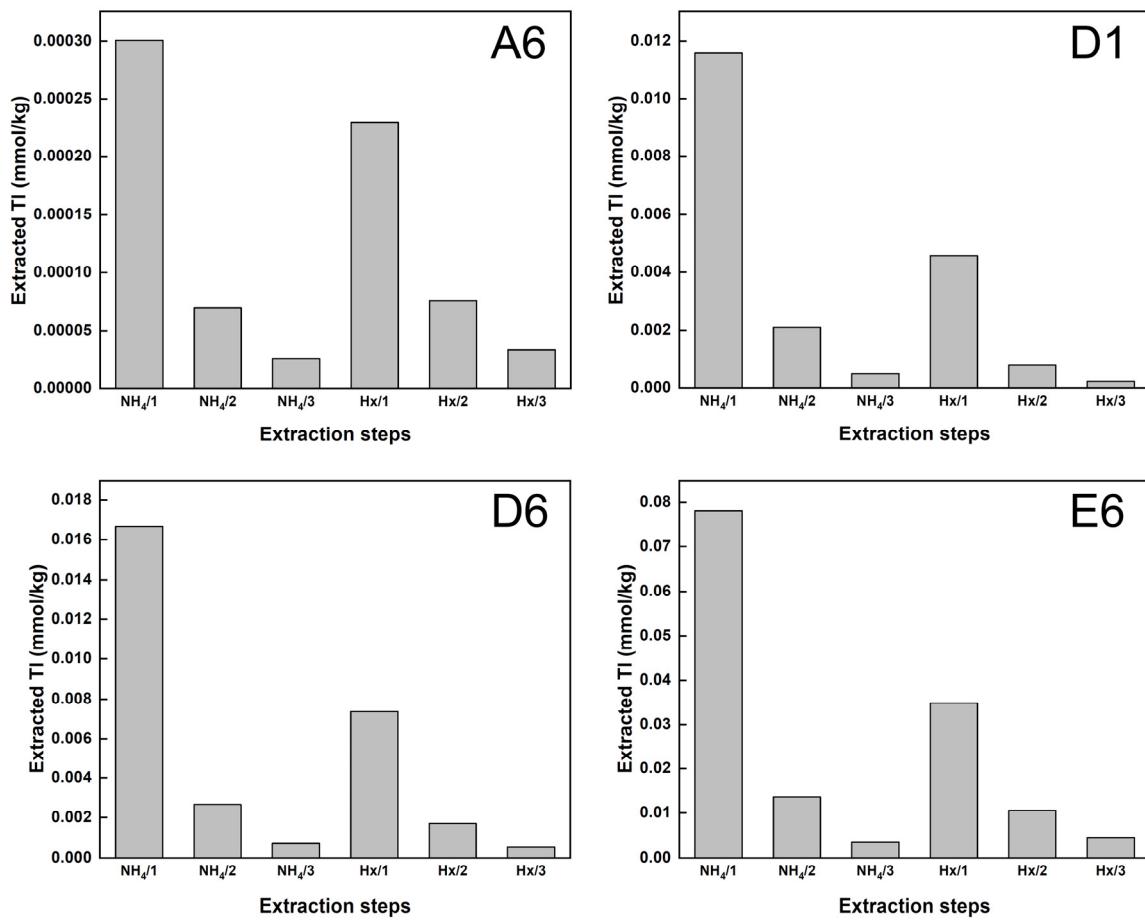


Figure S2. Extracted Tl (in mmol/kg) in the sequential soil extractions in 1 M NH₄-acetate (NH₄/1 to 3) and in 0.1 M hydroxylamine / 1 M NH₄-acetate (Hx/1 to 3) for four selected topsoil samples (A6, D1, D6, and E6).

8. Adsorption and re-extraction experiment

8.1 Details on the different laboratory protocols

In total, adsorption and re-extraction experiments were performed three times with different topsoil samples. The first time, the soil samples C5, D6, and E6 were used, the second time the samples B4, C5, and D6, and the third time the samples A6 and D1. The laboratory protocol used in the second and third time is described in the materials and methods section in the manuscript.

Nearly the same laboratory protocol was used the first time, with minor modifications. 5.0 g of dried soil was weighted in in 50 mL polypropylene tubes and conditioned two times with 50 mL 0.01 M $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$ / 0.0001 M KNO_3 solution for 2 h, recording the pH and measuring element concentrations in the conditioning solutions. For Tl adsorption, 0.01 M $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$ / 0.0001 M KNO_3 solutions were spiked with seven different Tl concentrations (ranging from $\sim 5.0 \times 10^{-7}$ to $\sim 5.0 \times 10^{-4}$ M) using 0.01 M, 0.001 M, and 0.0001 M TINO_3 (Sigma Aldrich) stock solutions. The wet soil materials were then suspended in 45 g (≈ 45 mL) of the Tl-containing electrolyte solutions and reacted for seven days on a table shaker (350 rpm) at room temperature. After reaction, the suspensions were centrifuged and the supernatant filtered (0.2 μm nylon membrane) and acidified (1% v/v HNO_3 suprapur) for the analysis of Mg, K, Ca, and Tl using ICP-MS. The solution pH was recorded in the suspension after solution sampling and resuspension. The residual wet soil materials were stored at 4°C in the dark. The difference between spiked and residual dissolved Tl was assumed to correspond to Tl adsorbed to the soil. The total amount of adsorbed Tl was calculated by adding the amounts of NH₄-exchangeable geogenic Tl in the individual soils prior to Tl adsorption to the amounts of freshly sorbed Tl (NH₄-acetate extraction of soils from sorption experiments without Tl spike).

After Tl adsorption, the reacted soils were first extracted with 46 g (≈ 46 mL) 0.01 M $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$ / 0.0001 M KNO_3 to determine pseudo-porewater concentrations. In a second step, the soils were extracted twice with 45 g (≈ 45 mL) 1 M NH₄-acetate to determine the amounts of NH₄-exchangeable Tl (as described above for geogenic Tl). After sorption and between the two extraction steps, supernatants were decanted as completely as possible and the wet soils were stored at 4 °C in the dark. Carryover of Tl or other elements from residual solution into the next extraction step and dilution of the extracts by residual solution was calculated from solution composition and the gravimetrically determined volume of residual solution.

Despite these differences in the experimental protocol, replicate experiments with soils C5 and D6 showed a good agreement and reproducibility in log-scale isotherm plots (not shown). In the manuscript, data for soil E6 are from the first experiment (with slightly modified protocol), data for the soils A6, B5, C5, D1, D6, from the second and third experiment (Fig. 3 and S3). In these two figures, experimental results are only shown for treatments where adsorbed and dissolved Tl concentrations were above the geogenic background.

8.2 Behaviour of the pH and different cations during the experiment

Table S13. Changes in pH and cation concentrations over the washing, adsorption and re-extraction steps for the blank samples (X0 level; no Tl addition in the adsorption step) of soils B4, C5, D6, and E6.

	Tl μM	Rb μM	K μM	Ba μM	Mg μM	Ca μM	pH
washing step 1							
B4	0.005	0.024	219	0.465	1370	8169	7.2
C5	0.007	0.043	237	0.500	1525	8386	7.2
D6	0.021	0.027	156	0.694	1725	8029	6.7
E6	0.235	0.043	155	0.591	679	9364	7.4
washing step 2							
B4	0.004	0.020	169	0.401	692	8663	7.3
C5	0.005	0.033	175	0.415	773	8830	7.3
D6	0.019	0.024	140	0.644	860	8737	6.6
E6	0.195	0.036	130	0.507	341	9339	7.4
adsorption step							
B4	0.007	0.037	176	0.446	557	9734	7.0
C5	0.013	0.078	189	0.550	609	9992	6.8
D6	0.044	0.052	156	0.695	650	9294	6.8
E6	0.481	0.102	178	0.847	274	10931	7.3
Ca-extraction step							
B4	0.001	0.018	81	0.234	247	8885	7.1
C5	0.006	0.032	71	0.255	254	8928	7.2
D6	0.025	0.028	77	0.448	288	8893	6.9
E6	0.142	0.025	36	0.288	48	9264	7.6

Table S14. Tl data for adsorption and re-extraction experiments.

Sample	levels	1. washing step	2. washing step	Adsorption				Ca-extraction	NH4-extraction		
		mol/L Tl	mol/L Tl	mol/L Tl	mol/kg Tl _{corr}	Tl adsorbed	K _d ads	mol/L Tl	mol/kg Tl	Tl extracted	K _d extr
		log	log	log	log	% of spiked	log	log	log	% of spiked	log
A6	X0	-9.45	-9.67	-9.05	-6.54	-	2.50	-9.28	-6.53	-	2.75
	X1	-9.59	-9.77	-8.00	-5.39	97.3	2.61	-8.24	-5.60	62.1	2.64
	X2	-9.64	-9.81	-7.44	-4.87	97.2	2.57	-7.71	-5.12	56.7	2.58
	X3	-9.62	-9.83	-6.86	-4.34	96.9	2.52	-7.13	-4.57	59.9	2.56
	X4	-9.58	-9.73	-6.38	-3.88	96.7	2.50	-6.63	-4.14	56.5	2.49
	X5	-9.61	-9.78	-5.77	-3.35	96.1	2.42	-6.04	-3.58	60.3	2.45
	X6	-9.54	-9.69	-5.16	-2.88	94.7	2.28	-5.38	-3.09	62.6	2.28
	X7	-9.58	-9.78	-4.42	-2.36	91.5	2.06	-4.60	-2.56	66.4	2.04
B4	X0	-8.33	-8.42	-8.18	-5.66	-	2.52	-8.32	-5.65	-	2.67
	X1	-8.38	-8.48	-7.88	-5.23	96.4	2.66	-8.11	-5.39	69.5	2.72
	X2	-8.63	-8.73	-7.51	-4.81	97.6	2.70	-7.78	-5.08	54.6	2.70
	X3	-8.74	-8.86	-6.99	-4.32	97.7	2.67	-7.27	-4.56	59.1	2.71
	X4	-8.73	-8.16	-6.46	-3.89	97.2	2.57	-6.73	-4.17	54.0	2.57
	X5	-7.55	-8.53	-5.81	-3.36	96.4	2.45	-6.09	-3.59	59.9	2.50
	X6	-8.73	-8.91	-5.22	-2.89	95.3	2.33	-5.47	-3.18	52.2	2.29
	X7	-8.76	-8.85	-4.48	-2.37	92.5	2.11	-4.70	-2.62	58.5	2.08

Table S14. Continuation.

sample	levels	1. washing step	2. washing step	Adsorption				Ca-extraction	NH ₄ -extraction		
		mol/L Tl	mol/L Tl	mol/L Tl	mol/kg Tl _{corr}	Tl adsorbed	K _d iso	mol/L Tl	mol/kg Tl	Tl extracted	K _d extr
		log	log	log	log	% of spiked	log	log	log	% of spiked	log
C5	X0	-8.17	-8.32	-7.87	-5.79	-	2.08	-8.16	-5.75	-	2.41
	X1	-8.19	-8.33	-7.53	-5.28	92.0	2.26	-7.84	-5.40	77.8	2.45
	X2	-8.15	-8.32	-7.12	-4.84	94.0	2.27	-7.45	-5.05	63.3	2.40
	X3	-8.20	-8.34	-6.65	-4.34	94.8	2.30	-6.97	-4.56	61.5	2.41
	X4	-8.14	-8.30	-6.17	-3.90	94.6	2.27	-6.50	-4.25	46.7	2.25
	X5	-8.18	-8.32	-5.60	-3.38	94.1	2.23	-5.91	-3.60	61.5	2.31
	X6	-8.14	-8.30	-5.00	-2.90	92.3	2.10	-5.29	-3.06	73.5	2.24
	X7	-8.14	-8.30	-4.28	-2.39	88.1	1.89	-4.55	-2.57	70.8	1.98
D1	X0	-7.68	-7.79	-7.49	-4.96	-	2.53	-7.73	-4.95	-	2.78
	X1	-7.69	-7.79	-7.31	-4.83	86.8	2.48	-7.56	-4.87	93.6	2.69
	X2	-7.70	-7.80	-7.16	-4.62	94.6	2.54	-7.41	-4.72	81.3	2.69
	X3	-7.69	-7.79	-6.81	-4.25	96.5	2.56	-7.06	-4.41	70.9	2.66
	X4	-7.67	-7.79	-6.41	-3.85	96.9	2.56	-6.64	-4.04	66.5	2.60
	X5	-7.65	-7.77	-5.84	-3.34	96.7	2.50	-6.08	-3.53	66.7	2.55
	X6	-7.70	-7.81	-5.26	-2.87	95.8	2.39	-5.47	-3.04	69.1	2.43
	X7	-7.67	-7.78	-4.53	-2.35	93.4	2.18	-4.70	-2.48	77.5	2.22

Table S14. Continuation.

sample	levels	1. washing step	2. washing step	Adsorption				Ca-extraction	NH ₄ -extraction		
		mol/L Tl	mol/L Tl	mol/L Tl	mol/kg Tl _{corr}	Tl adsorbed	K _d iso	mol/L Tl	mol/kg Tl	Tl extracted	K _d extr
		log	log	log	log	% of spiked	log	log	log	% of spiked	log
D6	X0	-7.67	-7.72	-7.36	-4.95	-	2.42	-7.60	-4.93	-	2.67
	X1	-7.66	-7.71	-7.26	-4.82	85.1	2.44	-7.43	-4.81	105.8	2.62
	X2	-7.66	-7.71	-7.15	-4.61	94.5	2.54	-7.41	-4.72	79.2	2.68
	X3	-7.65	-7.70	-6.86	-4.25	96.9	2.61	-7.11	-4.46	63.5	2.65
	X4	-7.67	-7.73	-6.48	-3.86	97.4	2.62	-6.72	-4.18	49.1	2.54
	X5	-7.61	-7.67	-5.87	-3.35	96.8	2.52	-6.12	-3.66	50.6	2.46
	X6	-7.65	-7.69	-5.33	-2.88	96.3	2.45	-5.55	-3.09	62.7	2.46
	X7	-7.64	-7.69	-4.59	-2.36	94.2	2.23	-4.79	-2.57	64.0	2.22
E6	X0	-6.57	-6.51	-6.30	-4.52	-	1.78	-6.59	-4.46	-	2.14
	X1	-6.59	-6.49	-6.28	-4.46	-	1.81	-6.55	-4.27	156.3	2.28
	X2	-6.56	-6.49	-6.17	-4.38	52.4	1.80	-6.35	-4.18	158.2	2.17
	X3	-6.59	-6.48	-6.08	-4.14	82.3	1.94	-6.33	-4.09	113.2	2.24
	X4	-6.59	-6.49	-5.82	-3.81	89.3	2.01	-6.02	-3.84	92.9	2.18
	X5	-6.60	-6.50	-5.36	-3.35	90.6	2.00	-5.59	-3.41	87.0	2.18
	X6	-6.59	-6.48	-4.86	-2.90	90.2	1.96	-5.07	-2.97	85.5	2.10
	X7	-6.58	-6.48	-4.26	-2.40	88.2	1.86	-4.43	-2.47	84.4	1.96

8.3 Additional sorption plots

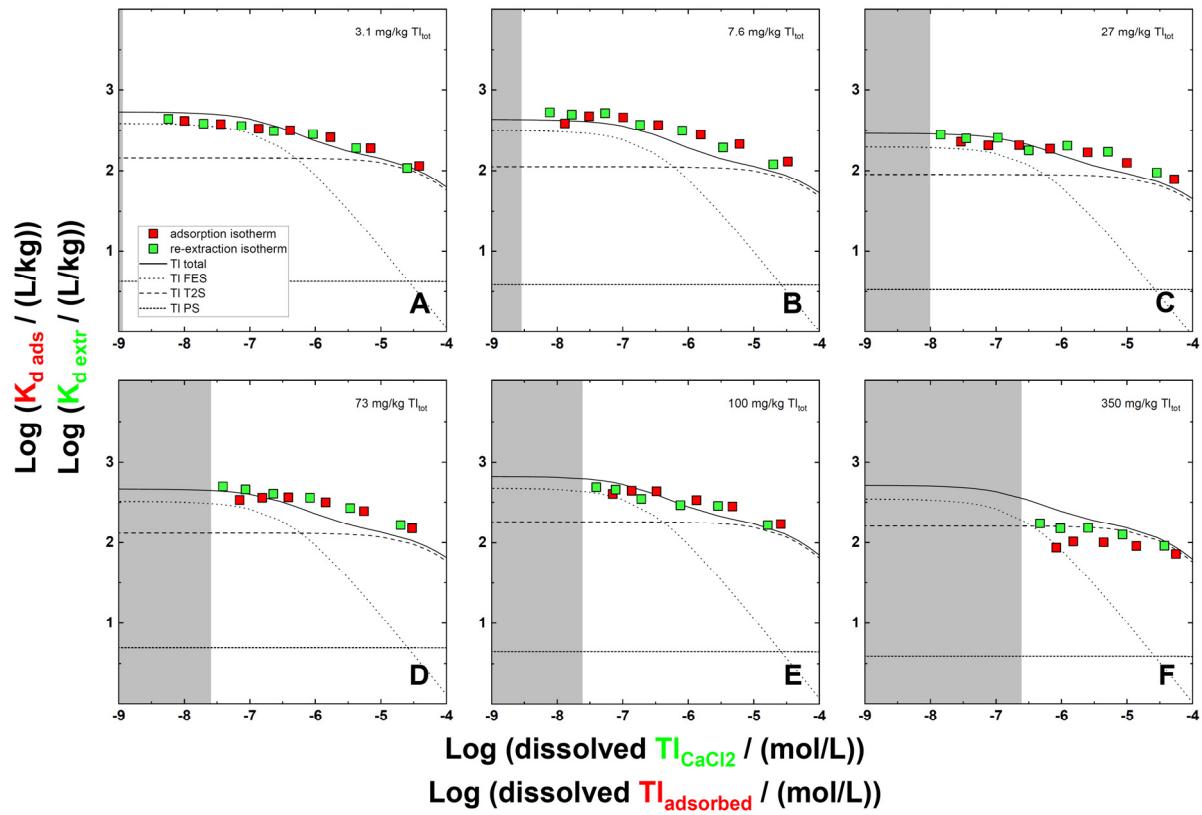


Figure S3. Log K_d -plots for adsorption isotherms and re-extraction results for six topsoil samples (A: A6; B: B4; C: C5; D: D1; E: D6; F: E6) with geogenic Tl contents from ~ 4 to ~ 400 mg/kg Tl spiked with up to 1000 mg/kg additional Tl.

9. X-ray absorption spectroscopy

For the interpretation of the Tl L_{III}-edge XANES spectra, a set of reference spectra was considered (Figure S4): **(i)** Tl(I)-acetate: carboxylate-complexed Tl(I) (Aldrich T8266, spectrum from Voegelin et al. (2015)). **(ii)** Tl(I)-ferrihydrite: 6300 mg/kg Tl(I) adsorbed onto synthetic 2-line ferrihydrite (pH 6.1, 0.1 M NaNO₃, 7 d reaction time; log (K_d/(L/kg)) = 1.7; spectrum recorded at beamline SAMBA; Synchrotron Soleil). **(iii)** Tl(I)-triclinic birnessite: triclinic birnessite with ~100'000 mg/kg adsorbed Tl(I) (pH 9.4, 0.1 M NaNO₃, 1 d reaction time; spectrum from Wick et al. (2019)). **(iv)** Tl(I)-smectite: Na-exchanged smectite with 9300 mg/kg adsorbed Tl(I) (spectrum from Voegelin et al. (2015)). **(v)** Tl⁺ (aq): 0.01 M aqueous Tl⁺ (from TlNO₃; spectrum recorded at SuperXAS beamline, Swiss Light Source). **(vi)** Tl(I)-illite: illite with Tl loading of 3800 mg/kg Tl (spectrum from Wick et al. (2018)). **(vii)** Tl(I)-muscovite: Ba-rich muscovite ("oellacherite") from Lengenbach (Switzerland) with ~200 mg/kg Tl(I). **(viii)** Tl(III)-δ-MnO₂: 0.021 Tl(III)/Mn sorbed onto Na-δ-MnO₂ (spectrum from Wick et al. (2019)). **(ix)** Tl₂O₃: Tl(III)-oxide (Aldrich 204617, avicennite based on XRD analysis, spectrum from Voegelin et al. (2015)). **(x)** Tl(I)-jarosite: synthetic Tl(I)-jarosite (from Dutrizac et al. (2005); kindly provided by S. Beauchemin (Natural Resources Canada)).

The spectra of Tl(I) sorbed onto ferrihydrite, triclinic birnessite and smectite closely match to the spectrum of aqueous Tl⁺, suggesting that Tl(I) is bound to these sorbents in hydrated form. The spectrum of solid Tl(I)-acetate looks slightly different, but also resembles the spectrum of aqueous Tl⁺. For Tl⁺ sorption onto humic acids and ferrihydrite, sorption studies indicated a low sorption affinity similar to K⁺ (Coup and Swedlund, 2015; Martin et al., 2020), in line with rather weak outer-sphere binding of hydrated Tl⁺. For these reasons, in the LCF analysis, the XANES spectrum of aqueous Tl⁺ was included to represent (hydrated) Tl⁺ sorbed onto natural organic matter, Fe oxides, Mn oxides or clay minerals.

The spectra of Tl(I)-illite and Tl(I)-muscovite clearly differ from the spectrum of hydrated aqueous Tl⁺, in line with the adsorption of dehydrated Tl⁺ at the frayed edges of micaceous clay minerals or its structural incorporation in the interlayer. While the overall shape of the two spectra was similar, spectral features appeared to be a bit sharper in the Tl(I)-muscovite than the Tl(I)-illite spectrum, probably because the coordination environment of Tl(I) in the interlayer is more ordered than of Tl(I) sorbed at the frayed edges of micaceous clay minerals. However, the spectral features were not distinct enough to allow for an unequivocal spectroscopic differentiation between Tl(I) adsorption or structural incorporation.

The Tl(III) reference spectra exhibit an edge shape distinctly different from the Tl(I) references. The spectrum of Tl(III)- δ -MnO₂ differs from the spectrum of Tl₂O₃. Yet, the spectral difference is not large enough to allow for a clear distinction of these compounds in sample spectra dominated by Tl(I).

The spectrum of dehydrated Tl⁺ in Tl(I)-jarosite is very characteristic. Preliminary LCF analysis of the sample spectra indicated that Tl(I)-jarosite was not a dominant species in the studied topsoil samples: Only for two sample spectra, inclusion of a minor fraction of Tl(I)-jarosite caused a minor improvement in the best LCF.

Based on the considerations above, the final LCF analysis of the sample spectra was based on four references: **(i)** Aqueous Tl⁺ as proxy for hydrated Tl⁺ sorbed onto soil organic matter, Fe or Mn oxides, or clay minerals. **(ii)** Tl(I)-illite and **(iii)** Tl(I)-muscovite as proxies for Tl(I) associated with micaceous clay minerals, either by incorporation into the interlayer or adsorption at the frayed edges. **(iv)** Tl(III)- δ -MnO₂ as proxy for Tl(III).

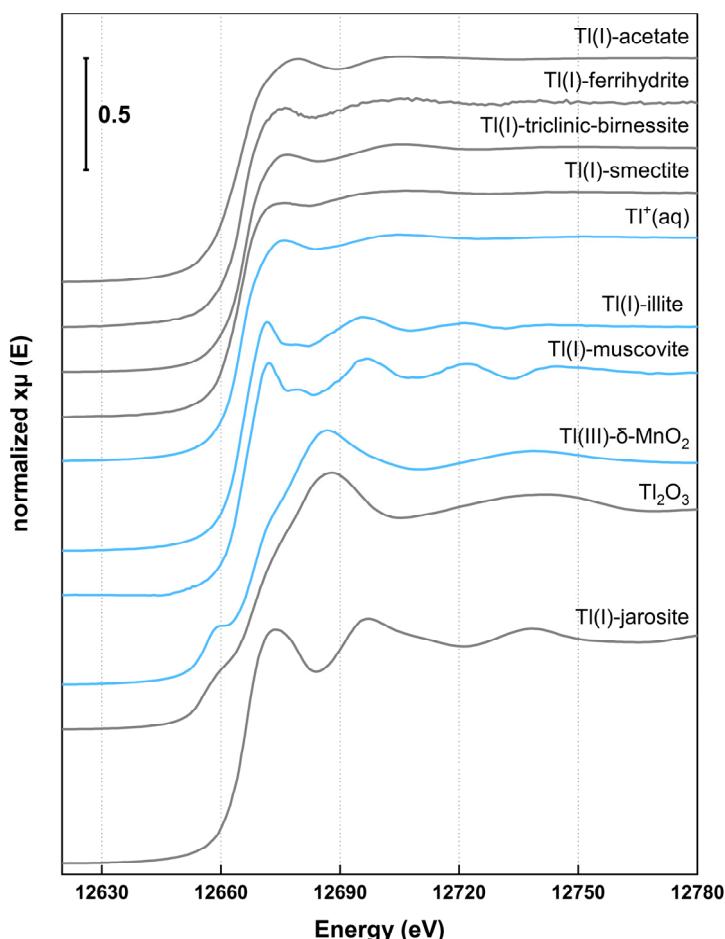


Figure S4. Tl L_{III}-edge XANES spectra of Tl(I) and Tl(III) reference compounds. The reference spectra used for the LCF analysis of sample spectra are displayed in blue.

Table S15. Linear combination fit (LCF) results for geogenic Tl in topsoil samples (B4 to F6) and a clay mineral isolate (P1 00-20 clay) and for soils with freshly adsorbed Tl (A6, D1). Fractions normalized to a sum of unity are listed together with the sum of the fitted fractions and the normalized sum of the squared residuals (NSSR).

Sample	Tl(I)-illite	Tl(I)-muscovite	Tl ⁺ (aq)	Tl(III)-δ-MnO ₂	Sum	NSSR
geogenic Tl						
B4	1.00	-	-	-	1.02	0.00040
B5 ^a	0.64	0.36	-	-	1.02	0.00020
B6	0.93	-	-	0.07	1.03	0.00025
C1	1.00	-	-	-	1.00	0.00018
C4	1.00		-	-	1.01	0.00046
C5	0.66	0.34	-	-	1.01	0.00022
C6	1.00	-	-	-	1.00	0.00017
D1	1.00	-	-	-	1.00	0.00012
D1 / 2nd	0.41	0.52	-	0.07	1.01	0.00003
D5	0.79	0.21	-	-	1.01	0.00011
D6	0.69	0.31	-	-	1.01	0.00010
E5	0.95	-	-	0.05	1.01	0.00009
E6	0.71	0.24	-	0.05	1.01	0.00006
F3	0.96	-	-	0.04	1.00	0.00008
F4	0.97	-	-	0.03	1.00	0.00007
F5 ^a	1.00	-	-	-	1.01	0.00012
F6	0.70	0.21	-	0.09	1.00	0.00009
P1 00-20 clay	0.73	0.27	-	-	1.00	
average (n=18)	0.84	0.14	-	0.02		
st.dev.	0.18	0.17	-	0.03		
freshly adsorbed Tl						
A6 +100 mg/kg Tl	0.41	0.25	0.26	0.09	0.99	0.00004
A6 +1000 mg/kg Tl	0.35	0.30	0.26	0.08	1.00	0.00003
D1 +1000 mg/kg Tl	0.28	0.36	0.28	0.08	1.00	0.00002
average (n=3)	0.35	0.30	0.27	0.08		
st.dev.	0.06	0.05	0.01	0.01		

^a For the soil samples B5 and F5, fits with Tl(I)-illite and Tl(I)-jarosite resulted in a ~10% lower NSSR relative to the listed fits (B5: 0.80 Tl(I)-illite + 0.20 Tl(I)-jarosite, NSSR 0.00018; F5: 0.90 Tl(I)-illite + 0.10 Tl(I)-jarosite, NSSR 0.00010).

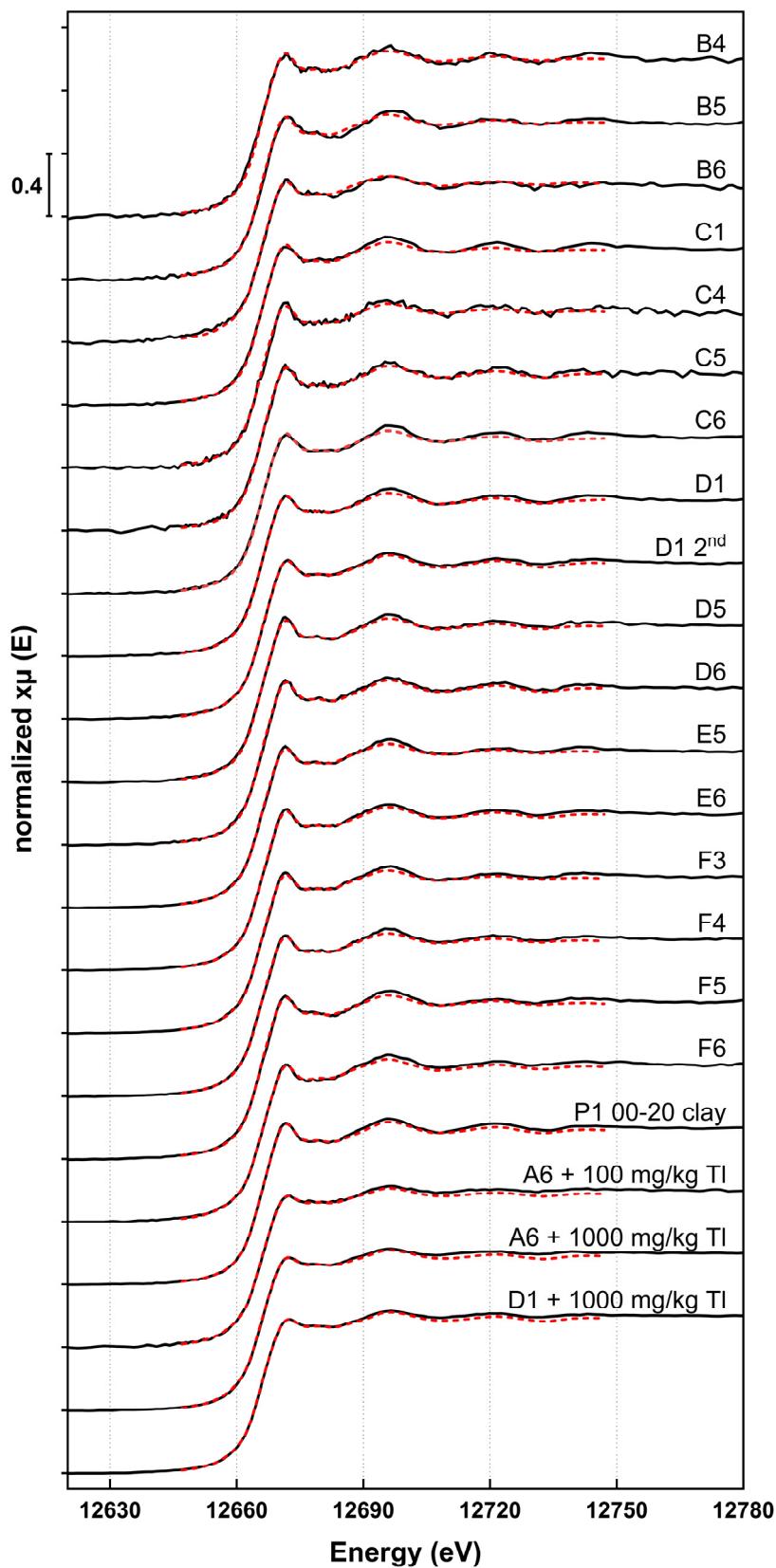


Figure S5. Tl L_{III}-edge XANES spectra of geogenic Tl in soil samples and a clay mineral isolate and of freshly spiked Tl in soil samples (black lines) and reconstructed LCF spectra (dashed red lines) based on LCF results in Table S15.

10. Predictions for Tl adsorption onto micaceous soil clay minerals

10.1 Geogenic Tl

Table S16. Averaged cation concentrations and pH in 0.01 M CaCl₂ used for the modelling of geogenic Tl in soils. The sum of all cations is charge balanced with NO₃⁻.

	Rb	NH ₄	K	Na	Mg	Ca	NO ₃ ⁻	pH
	μM	μM	μM	μM	μM	μM	mM	
Average	0.035	58.1	165	36.6	1357	8316	19.6	6.75
5 percentile	0.017	27.2	69	19.7	577	7376	16.0	5.45
95 percentile	0.061	101.3	324	70.4	2265	9395	23.8	7.37

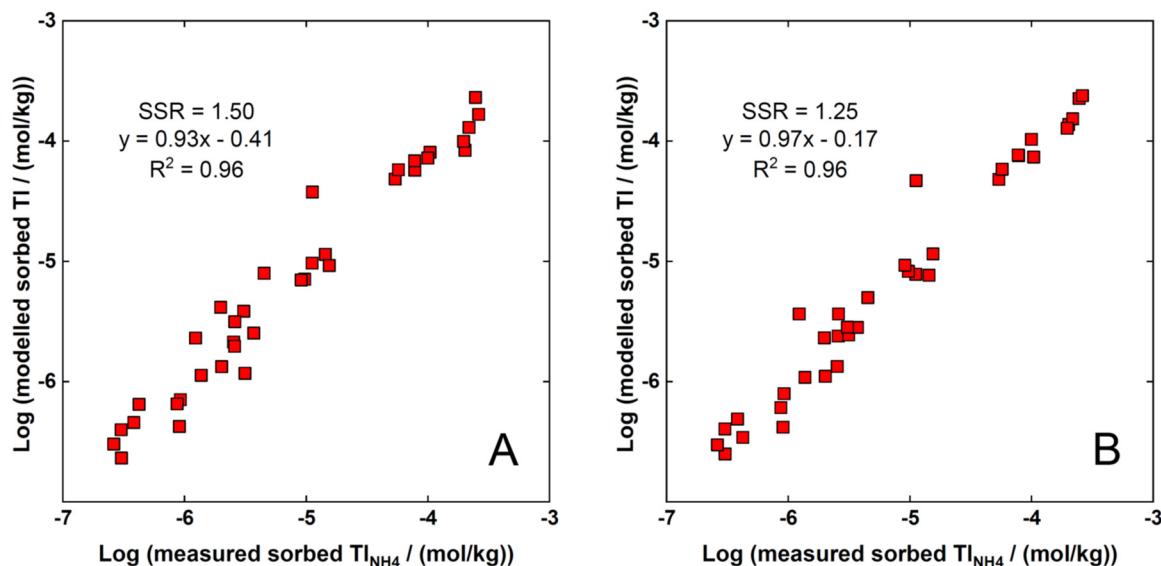


Figure S6. Modelled and measured adsorbed Tl amounts. In (A), the average cation concentrations were used (Table S16), in (B) the individual cation concentrations of each soil sample (Table S7).

10.2 Adsorption experiments

For the modelling of adsorption experiments, the individual pH and cation concentration of the pseudo-porewater extracts for each soil (A6, B4, C5, D1, D6, E6) were used. These values are listed in Table S7. As for the modelling of the geogenic Tl, the sum of the cations (Rb, NH₄, K, Na, Mg, Ca) was charge balanced by NO₃⁻.

11. Experiment with Mn/Fe-depleted and Mn/Fe-enriched soil material

11.1 Site and soil profile description and soil sampling

Mn/Fe-enriched (oxic), Mn/Fe-depleted (reduced) and bulk soil material was collected from the Sd horizon of an acidic pseudogley soil (Fig. S7) that exhibits bleached preferential flow paths and an oxidized soil matrix. The sampling site is located in Rafz in Northern Switzerland (Kanton Zürich; 47°37'20"N, 8°32'46"E). The soil has developed from loess deposited onto glacial till.

For soil sampling, the profile had to be drained first. Soil samples were collected from the main soil horizons, as well as from Mn/Fe-enriched and -depleted zones in the Sd horizon (German soil classification). In the laboratory, the samples were immediately air-dried at 40 °C in an oven, sieved to <2 mm and stored at room temperature in closed polyethylene vessels.

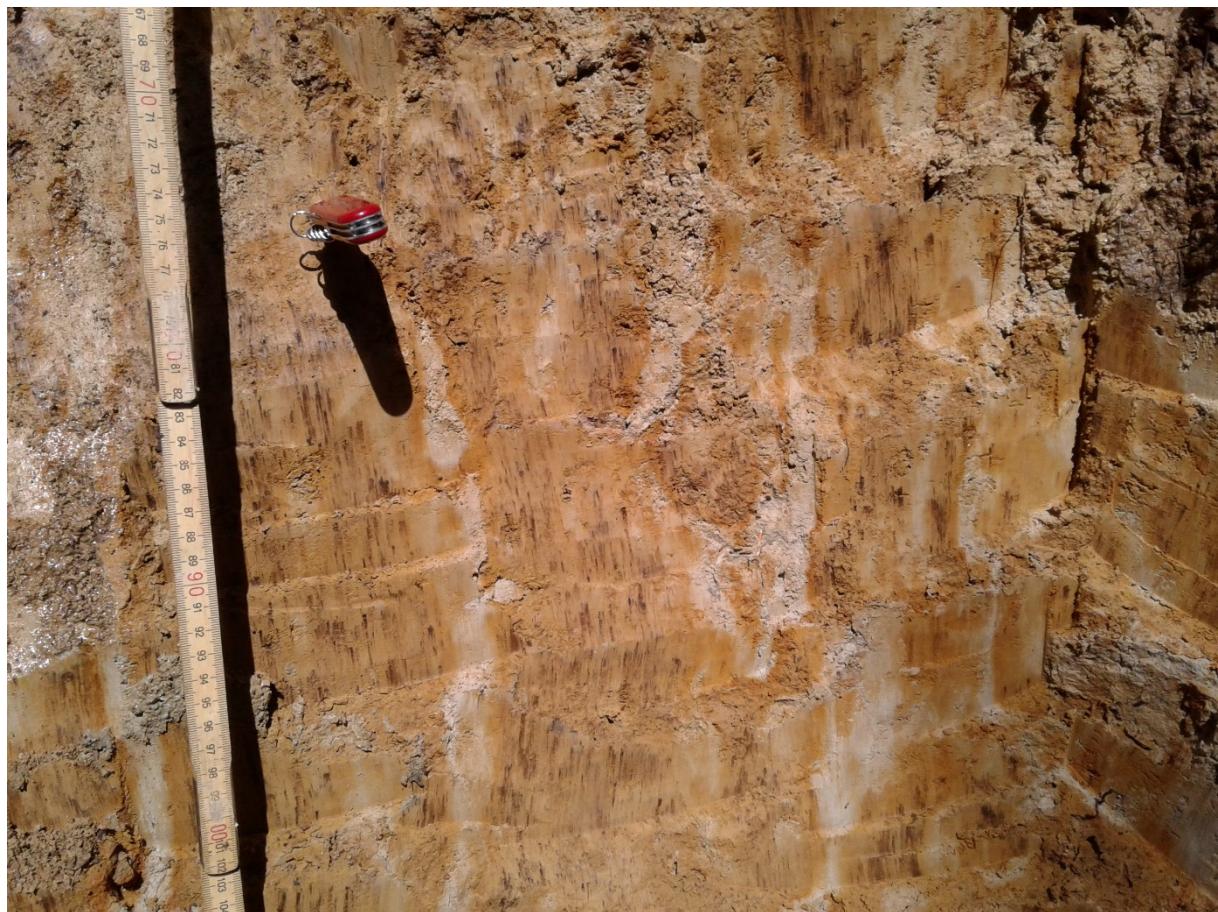


Fig S7. Image of the sampled Sd horizon exhibiting an oxidized soil matrix characterised by the brownish colour of Fe oxides and by black Mn concretions and grey zones corresponding to reductively bleached preferential flow paths. The homogenized bulk soil horizon as well as brownish and greyish material were sampled.

11.2 Physicochemical characterization of the soil material

The dried soil material was analysed for total element contents using XRF (Xepos+, SPECTRO Analytical Instruments GmbH, Germany), for total contents of carbon (C) and nitrogen (N) (CNS total element analyser, EuroVector), and for the contents of inorganic C (Coulomat, UIC, Inc.) (Table S17).

The mineralogy of Sd soil material (bulk, reduced, oxic) was determined on randomly oriented powder samples by XRD analysis (Table S18). X-ray diffraction measurements were made with a Bragg-Brentano diffractometer (BRUKER AXS D8) using Co K α radiation with 40 kV and 35 mA. The instrument was equipped with an automatic theta compensating divergence slit, primary and secondary Soller slits and a Lynx-Eye XE-T line detector. The powder samples were step-scanned at room temperature from 2 to 80 °2θ (step width 0.02 °2θ, counting time 1 s per step). The qualitative phase composition was determined with the software DIFFRACplus (BRUKER AXS). Based on the peak positions and their relative intensities, the mineral phases were identified in comparison to the PDF-2 data base (International Centre for Diffraction Data). The quantitative determination of the mineralogical composition was carried out by Rietveld analysis using the Rietveld program Profex/BGMN (Bergmann et al., 1998; Bergmann and Kleeberg, 1998; Döbelin and Kleeberg, 2015; Omotoso et al., 2006).

Table S17. Organic C content and elemental composition (XRF) of soil samples from Rafz. For the Sd horizon, total element contents confirm that the greyish zones are depleted in Mn and Fe (reduced) relative to the bulk soil and especially to the brownish soil matrix. Total and inorganic C were measured at least in duplicates. Since the soil samples contained no detectable inorganic C, total C was assumed to be organic C. Numbers in sample names indicate depth (in cm) in the soil profile.

sample	depth	C _{org}	Al	As	Ca	Fe	K	Mg	Mn	Na	Rb	Si
	cm	wt%	mg/kg									
Ah	0-3	4.59	43820	6	1998	14420	11100	4137	317.8	3748	50.4	292100
Sw-Bv	3-30	1.17	52840	5.4	2160	16710	13000	5440	894.5	4870	65.4	328600
Sw	30-55	0.37	59600	6.6	1968	20630	14380	7196	747.7	4175	75.6	318300
Sd bulk	55-100	0.13	69550	13.5	1869	31750	15200	9822	599.2	1882	88.5	287600
Sd oxic	55-100	0.10	71270	13.9	2025	33260	14870	10300	901.4	3104	85.5	295000
Sd anoxic	55-100	0.12	70640	5.5	2001	19390	15310	8816	151.7	2587	87.9	301400
C-Sd	100-140	0.10	68790	12.8	2397	30680	14300	9597	529.9	3297	81.3	297800

Table S18. Results of the mineralogical analysis of the Sd horizon of Rafz soil samples.

Mineral	Rafz bulk55_100		Rafz anoxisch 55_100		Rafz oxisch 55_100		average
	wt%	±3σ	wt%	±3σ	wt%	±3σ	
Quartz	54.5	1.1	56.1	1.0	53.8	1.0	54.8
K-Feldspar	5.6	0.4	6.0	0.4	5.2	0.4	5.6
Na-plagioclase	11.0	0.3	11.1	0.3	10.7	0.5	11.0
Calcite	-	-	-	-	-	-	-
Dolomite	-	-	-	-	-	-	-
Goethite	0.7	0.2	0.2	0.1	0.9	0.2	0.6
Hematite	<0.2	-	<0.2	-	<0.2	-	-
Rutile	1.2	0.2	1.1	0.2	1.0	0.2	1.1
Total Non-clay	73.1		74.5		71.6		73.1
Muscovite 2M ₁	9.0	0.3	9.5	0.4	9.3	0.4	9.3
Illite 1M	2.2		2.1		2.1		2.1
Chlorite (trioctahedral)	15.7	1.4	13.9	1.3	16.9	1.4	15.5
Total clay/phyllosilicate	26.9		25.5		28.4		26.9

11.3 Tl adsorption experiments

Tl adsorption experiments were performed with soil samples from the Sd horizon (55–100 cm depth), which was selectively probed for Mn-/Fe-enriched (oxic, red colour), Mn-/Fe-depleted (reduced, grey colour) and bulk soil material. 2.0 g of the dried soil material was weighted into 50 mL polyethylene tubes. In a first step, 0.01 M $\text{Ca}(\text{NO}_3)_2$ electrolyte was added and samples were shaken. In a second step different amounts of a 0.01 M TlNO_3 stock solution (in 0.01 M $\text{Ca}(\text{NO}_3)_2$ electrolyte) were added to reach target spike level. Total added volume of electrolyte and Tl stock solution was 20 mL resulting in a final solid to liquid ratio of 0.1 kg/L in all samples. The samples were shaken on a table shaker (300 rpm) for one day at room temperature. Subsequently, samples were centrifuged (10 min, 2700 g), filtered (0.2 μm nylon membrane), acidified (1% v/v HNO_3 suprapur), and analysed for Na, K, Ca, Mg, and Tl with an inductively coupled plasma mass spectrometer (ICP-MS; Agilent Triple Quadrupole 8900). pH was measured immediately in the remaining re-suspended supernatant.

Wet chemical results showed (Fig. S8; Table S19) only minor differences in Tl adsorption between the three soil sample series, indicating that high Mn and Fe contents did not markedly increase Tl adsorption. In fact, at the highest Tl loadings, the Mn-/Fe-depleted soil material even seems to bind Tl more strongly, possibly because Mn- and Fe-coatings in the oxic and bulk soil materials inhibit access to sorption sites on clay minerals. From log-transformed sorption data, linear regressions parameters were derived (Table S20).

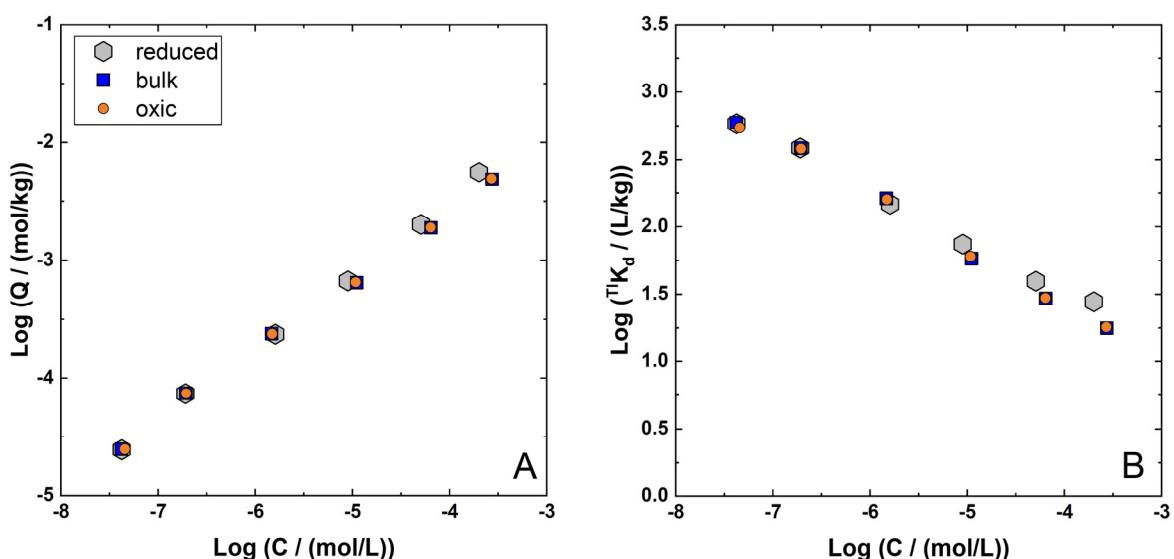


Fig. S8. Sorption isotherms for Rafz soils plotted as $\log Q$ (Q in mol/kg) versus $\log C$ (in mol/L) (A) and $\log K_d$ (K_d in L/kg) versus $\log C$ (B).

Table S19. Results of the Tl adsorption experiments with Rafz soil material including calculated log $K_{d, \text{ads}}$ (K_d in L/kg) and pH after sorption.

Sample	mol/L Tl	mol/kg Tl	Tl adsorbed	$K_{d, \text{ads}}$	pH
	log	log	% of spike	log	
bulk 1	-7.38	-4.60	98.3	2.77	3.9
bulk 2	-6.71	-4.13	97.4	2.58	3.9
bulk 3	-5.83	-3.62	94.1	2.21	3.9
bulk 4	-4.95	-3.19	85.3	1.76	3.9
bulk 5	-4.19	-2.72	74.5	1.47	3.9
bulk 6	-3.56	-2.31	63.9	1.25	3.9
ox 1	-7.34	-4.60	98.2	2.74	4.0
ox 2	-6.71	-4.13	97.4	2.58	4.0
ox 3	-5.83	-3.62	94.1	2.20	4.0
ox 4	-4.96	-3.19	85.7	1.78	4.0
ox 5	-4.19	-2.72	74.7	1.47	4.0
ox 6	-3.57	2.31	64.3	1.26	4.0
red 1	-7.37	-4.61	98.3	2.76	4.0
red 2	-6.72	-4.13	97.5	2.59	4.0
red 3	-5.79	-3.63	93.6	2.17	4.0
red 4	-5.05	-3.18	88.2	1.87	4.0
red 5	-4.29	-2.70	79.8	1.60	4.0
red 6	-3.70	-2.25	73.5	1.44	3.9

Table S20. Linear regression parameters log K_f and n_f with their standard errors (in brackets) of the adsorption experiment with Rafz soil material. n_{DP} indicates the number of data points and R^2 the coefficient of determination.

Sample series	n_{DP}	Log K_f	n_f	R^2
bulk	6	-0.26 (0.08)	0.58 (0.01)	1.00
ox	6	-0.22 (0.08)	0.59 (0.01)	1.00
red	6	0.01 (0.08)	0.62 (0.01)	1.00

11.4 XAS results

For XAS analysis, the Tl-sorbed soil samples were freeze-dried and prepared as 7-mm pellets with cellulose as binder. The XAS spectra of all analyzed samples (list) closely matched the spectrum of Tl(I) adsorbed on FES on illite (Fig. S9), suggesting that Tl was nearly completely adsorbed onto micaceous clay minerals. The spectra of Tl-sorbed pseudogley soil samples were recorded at the SAMBA beamline (French National Synchrotron Soleil, France).

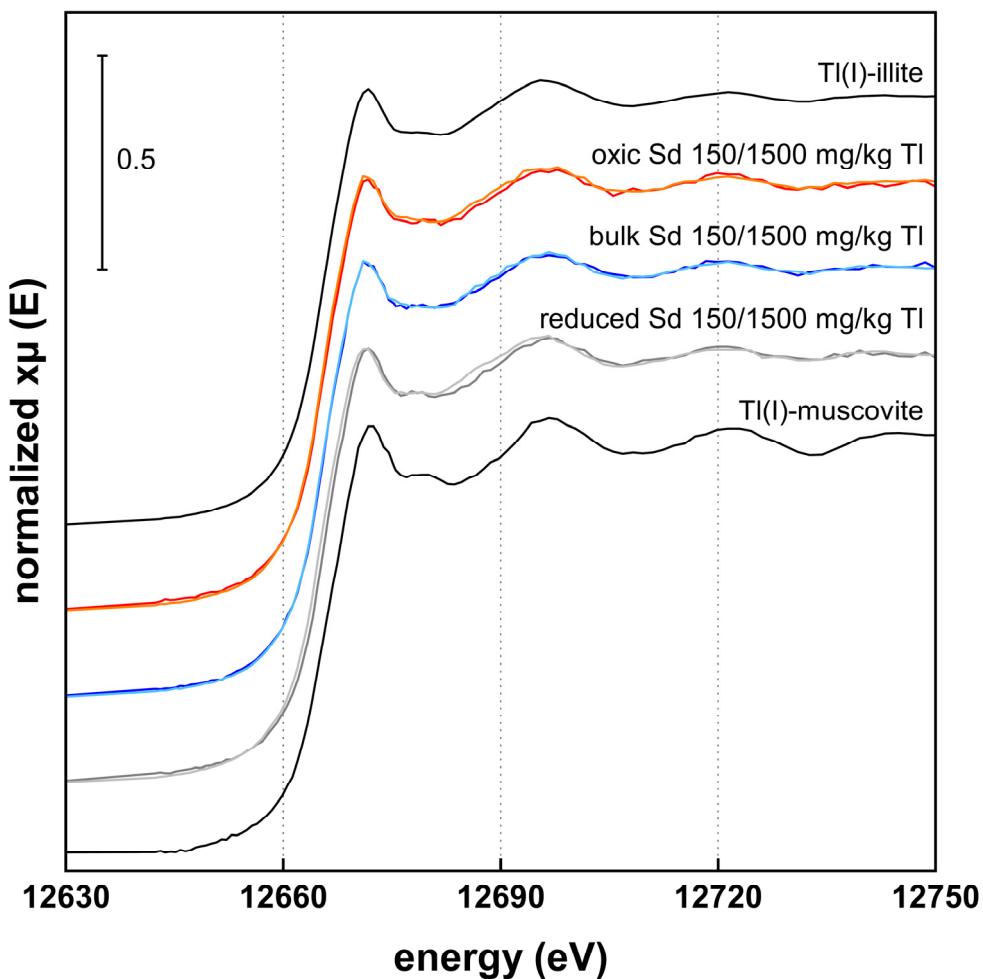


Fig. S9. Tl L_{III}-edge XANES spectra of Mn-/Fe-enriched (oxic), bulk, and Mn-/Fe-depleted (reduced) soil materials from Rafz with 150 or 1500 mg/kg spiked Tl (lighter color = higher loading) in comparison to reference spectra for Tl(I) adsorbed onto FES on illite (Tl(I)-illite) and of Tl(I) in interlayer of Ba-rich muscovite (Tl(I)-muscovite)).

12. Estimates for Tl sorbed onto Mn oxides, Fe oxides and soil organic matter

Tl sorption onto Mn oxides was estimated based on the assumption that all soil Mn was contained in triclinic birnessite (8.8 mol/kg Mn), using a linear regression equation describing Tl sorption onto triclinic birnessite in 0.1 M NaNO₃ electrolyte (Wick et al., 2019). For the calculation of the average of the percentages of total Tl, soil B2 was excluded.

Estimates for Tl sorption onto Fe oxides were based on the assumption that 15% of the total soil Fe (common fraction in acid oxalate extracts) (Voegelin et al., 2015) was ferrihydrite, and assuming a log (K_d/(L/kg)) of 3.6, as derived from published data for Tl sorption onto ferrihydrite at pH 7.8 in 0.01 M NaNO₃ electrolyte (Casiot et al., 2011).

Estimates for Tl sorption onto soil organic matter were based on the assumption that 50% of the organic carbon was contained in humic acid with a stoichiometry C₂H₂O, and based on an average log (K_d/(L/kg)) of 3.1 ± 0.2 (n=6) derived from data on Tl sorption onto two humic acids at pH 6, 7 and 8 (n=6) in 0.1 M NaClO₄ (Liu et al., 2011). All results of these calculations are given in Table S21.

Table S21. Estimated Tl sorption onto Mn oxides (triclinic birnessite), Fe oxides (ferrihydrite) and soil organic matter (humic acid) in Erzmatt soils based on published sorption data. Estimates for sample B2 and E4 were not considered for calculating the average and standard deviation. Calculated amounts of Tl sorbed onto Mn oxides are also given as percentage of total soil Tl, and calculated amounts of Tl sorbed onto Fe oxides and organic matter as percentage of the NH₄-exchangeable soil Tl.

soil	Mn oxides			Fe oxides			soil organic matter		
	Log K _d	Q		Log K _d	Q		Log K _d	Q	
		L/kg	mol/kg		L/kg	mol/kg		L/kg	mol/kg
A1	5.7	1.10E-06	8%	3.6	2.10E-08	7%	3.1	2.90E-08	9%
A2	5.8	6.00E-07	6%	3.6	1.60E-08	5%	3.1	2.10E-08	7%
A3	5.7	6.70E-07	5%	3.6	1.20E-08	4%	3.1	2.20E-08	9%
A4	5.6	1.40E-06	9%	3.6	2.70E-08	3%	3.1	8.00E-08	9%
A5	5.7	1.10E-06	7%	3.6	2.60E-08	6%	3.1	5.70E-08	14%
A6	5.7	1.30E-06	9%	3.6	2.30E-08	6%	3.1	3.90E-08	10%
B1	5.5	3.50E-06	5%	3.6	1.20E-07	5%	3.1	2.40E-07	9%
B2	5.5	9.20E-06	(29%)	3.6	2.00E-07	10%	3.1	4.70E-07	24%
B3	5.6	3.20E-06	7%	3.6	7.30E-08	4%	3.1	1.40E-07	7%
B4	5.6	2.40E-06	7%	3.6	5.20E-08	4%	3.1	8.90E-08	6%
B5	5.7	1.10E-06	2%	3.6	2.60E-08	3%	3.1	5.00E-08	5%
B6	5.5	1.00E-06	2%	3.6	2.70E-08	2%	3.1	6.60E-08	5%
C1	5.5	4.30E-06	4%	3.6	1.10E-07	4%	3.1	2.30E-07	9%
C2	5.6	2.30E-06	2%	3.6	7.30E-08	2%	3.1	6.60E-08	2%
C3	5.6	1.50E-06	4%	3.6	3.50E-08	4%	3.1	6.40E-08	7%
C4	5.5	4.20E-06	4%	3.6	1.40E-07	4%	3.1	3.40E-07	9%
C5	5.5	5.30E-06	4%	3.6	1.60E-07	5%	3.1	5.30E-07	17%
C6	5.5	2.10E-06	2%	3.6	5.90E-08	2%	3.1	1.40E-07	6%
D1	5.4	1.60E-05	5%	3.6	5.80E-07	5%	3.1	8.50E-07	8%
D2	5.4	1.20E-05	4%	3.6	4.30E-07	4%	3.1	4.40E-07	5%
D3	5.4	7.20E-06	2%	3.6	3.20E-07	7%	3.1	1.20E-06	25%
D4	5.4	6.10E-06	2%	3.6	3.00E-07	3%	3.1	6.10E-07	7%
D5	5.3	1.70E-05	3%	3.6	7.50E-07	5%	3.1	1.40E-06	10%
D6	5.4	1.40E-05	3%	3.6	5.80E-07	4%	3.1	6.90E-07	4%
E1	5.2	5.10E-05	4%	3.6	3.80E-06	7%	3.1	8.60E-06	16%
E2	5.2	4.70E-05	4%	3.6	3.90E-06	7%	3.1	1.10E-05	20%
E3	5.2	4.50E-05	3%	3.6	4.60E-06	6%	3.1	6.70E-06	9%
E4	5.2	3.90E-05	3%	3.6	2.40E-06	21%	3.1	1.00E-05	(93%)
E5	5.1	1.10E-04	6%	3.6	8.10E-06	8%	3.1	1.40E-05	13%
E6	5.1	7.30E-05	4%	3.6	5.30E-06	7%	3.1	1.40E-05	18%
F1	5.0	2.60E-04	8%	3.6	3.80E-05	15%	3.1	7.60E-05	31%
F2	5.1	1.20E-04	4%	3.6	1.00E-05	5%	3.1	1.20E-05	6%
F3	5.0	1.70E-04	5%	3.6	2.10E-05	10%	3.1	3.20E-05	15%
F4	5.1	8.50E-05	2%	3.6	8.80E-06	9%	3.1	1.50E-05	15%
F5	5.1	1.00E-04	2%	3.6	1.30E-05	7%	3.1	1.60E-05	8%
F6	5.0	2.90E-04	6%	3.6	3.60E-05	14%	3.1	4.20E-05	16%
Average			4.40%			6.30%			11.10%
St.Dev.			2.10%			3.90%			6.50%

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