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Supplementary Material

A comparison of characterisation and modelling approaches to predict dissolved metal concentrations in soils

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Table S1. Locations and background information on soil sampling sites.

Sampling location	Latitude	Longitude	LCM2015 aggregate land class	Contamination–metal source notes	Mineralisation (England only)
388501	52.9903	–2.1302	Built up areas and gardens	Urban	
388911	53.0268	–2.1537	Built up areas and gardens	Urban	
403376	*53.6648*	*–0.6287*	*Arable*		
406408	*53.4125*	*–0.5036*	*Arable*		
407769	*53.2248*	*–1.8477*	*Semi-natural grassland*		*Ni, Pb, general*
408038	53.1116	–1.1289	Arable		
411227	*53.312*	*–0.0347*	*Arable*		
420444	52.9307	–1.3434	Improved grassland		
423618	*52.6901*	*–0.6948*	*Arable*		
427567	*52.6205*	*–0.3638*	*Arable*		
443361	52.4799	0.7022	Coniferous woodland		
449638	51.7039	0.0173	Arable		
500851	*50.6516*	*–4.0643*	*Semi-natural grassland*		*Cu, general*
600859	51.4879	–3.1995	Built up areas and gardens	Urban	
601363	51.6638	–3.8547	Built up areas and gardens	Urban	
601561	51.6216	–3.8774	Built up areas and gardens	Industrial	
601716	51.6626	–3.9051	Built up areas and gardens	Urban, historic copper processing	
601721	51.6717	–3.8983	Built up areas and gardens	Urban, historic copper processing	
Sampling location	Latitude	Longitude	LCM2015 aggregate land class	Contamination–metal source notes	NBC group (England only)
601884	51.6209	–3.9753	Built up areas and gardens	Urban	
601912	51.6804	–3.9132	Built up areas and gardens	Urban	
602069	51.6132	–3.9023	Coastal		
602114	51.5668	–3.9878	Coastal		
602734	52.6439	–2.4174	Built up areas and gardens	Industrial	
603020	53.7606	–0.2819	Built up areas and gardens	Urban	
603385	*53.7178*	*–0.4273*	*Built up areas and gardens*	*Industrial*	
603678	53.6074	–0.5979	Semi-natural grassland	Steel works	
603700	53.6126	–0.652	Arable	Steel works	
604213	53.4073	–1.4455	Built up areas and gardens	Urban	
604260	53.421	–1.447	Built up areas and gardens	Urban	
605002	53.5177	–1.1141	Built up areas and gardens	Urban	
605005	53.5228	–1.1261	Built up areas and gardens	Urban	
606148	53.1453	–1.1739	Built up areas and gardens	Urban	

606649	52.9175	–1.4972	Built up areas and gardens	Urban	
606664	52.9267	–1.4977	Built up areas and gardens	Urban	
606692	*52.9223*	*–1.4904*	*Built up areas and gardens*	Urban	
606805	52.9177	–1.4756	Built up areas and gardens	Urban	
606874	52.9221	–1.4682	Built up areas and gardens	Urban	
607736	*52.4991*	*–0.6638*	*Built up areas and gardens*	*Industrial*	
608099	52.5822	–0.2471	Built up areas and gardens	Urban	
990443	52.582	–2.1445	Built up areas and gardens	Urban	
990510	52.576	–2.1293	Built up areas and gardens	Urban	
990655	52.5636	–2.1295	Built up areas and gardens	Urban	
990666	52.5636	–2.1374	Built up areas and gardens	Urban	
990668	52.5643	–2.1667	Built up areas and gardens	Urban	

Sampling location	Latitude	Longitude	LCM2015 aggregate land class	Contamination–metal source notes	NBC group (England only)
AHF	51.1546	–0.8588	Improved grassland		
CG 1 H1	*57.1166*	*–3.8445*	*Coniferous woodland*		
CG 1 H2	*57.1166*	*–3.8445*	*Coniferous woodland*		
CG 2 H1	*57.1172*	*–3.8488*	*Coniferous woodland*		
CG 2 H2	*57.1172*	*–3.8488*	*Coniferous woodland*		
CG 3	*57.1172*	*–3.8488*	*Coniferous woodland*		
CM	50.5023	–4.4337	Improved grassland	Historic copper mining	Cu, general
CF	54.6883	–3.063	Semi-natural grassland	Historic lead, copper, arsenic and tungsten mining	Pb, general
CHM	53.4717	–2.4153	Arable	Historic application of urban waste	
CW	*53.1518*	*–1.6166*	*Broadleaf woodland*	*Historic lead and zinc mining*	*Ni, Cd, Pb, general*
Clydach	51.6956	–3.887	Built up areas and gardens	Nickel processing	
CY 1 H1	52.3533	–3.7636	Semi-natural grassland	Historic lead mining	
CY 1 H2	52.3533	–3.7636	Semi-natural grassland	Historic lead mining	
CY 2	52.3567	–3.7601	Semi-natural grassland	Historic lead mining	
DGC 1	50.5377	–4.2223	Coniferous woodland	Historic copper and arsenic mining	Cu, general
DGC 2	50.5373	–4.2182	Coniferous woodland	Historic copper and arsenic mining	Cu, general
DGC 3	50.5436	–4.2215	Coniferous woodland	Historic copper and arsenic mining	Cu, general
Drayton	52.1933	–1.7631	Arable		
DCM	52.4153	–3.8043	Semi-natural grassland	Historic lead, zinc and copper mining	
Ecton	53.1224	–1.8576	Improved grassland	Historic copper mining	Ni, Cd, Pb, general
GS 1 H1	56.9111	–2.5706	Mountain, heath, bog		
GS 1 H2	56.9111	–2.5706	Mountain, heath, bog		

GS 2 H1	56.9122	–2.5724	Mountain, heath, bog		
GS 2 H2	56.9122	–2.5724	Mountain, heath, bog		
GS 3 H1	56.8955	–2.5334	Improved grassland		
GS 3 H2	56.8955	–2.5334	Improved grassland		
Sampling location	Latitude	Longitude	LCM2015 aggregate land class	Contamination–metal source notes	NBC group (England only)
GS 4 H1	56.894	–2.5333	Improved grassland		
GS 4 H2	56.894	–2.5333	Improved grassland		
GS 4 H3	56.894	–2.5333	Improved grassland		
HW 1	54.1203	–2.107	Semi-natural grassland		Cd, Pb, general
HW 2	54.1232	–2.1	Semi-natural grassland		Cd, Pb, general
HW 3	54.131	–2.065	Improved grassland		Cd, Pb, general
HT 1 H1	57.3112	–2.9034	Mountain, heath, bog	Serpentine Soil	
HT 1 H2	57.3112	–2.9034	Mountain, heath, bog	Serpentine Soil	
HT 2 H1	57.3106	–2.9034	Mountain, heath, bog	Serpentine Soil	
HT 2 H2	*57.3106*	*–2.9034*	*Mountain, heath, bog*	*Serpentine Soil*	
HT 3 H1	*57.3118*	*–2.9035*	*Mountain, heath, bog*	*Serpentine Soil*	
HT 3 H2	57.3118	–2.9035	Mountain, heath, bog	Serpentine Soil	
JT 1	54.0026	–2.6927	Improved grassland		
JT 2	*54.0026*	*–2.6927*	*Improved grassland*		
Kegworth	52.8293	–1.2757	Arable	Roadside Contamination	
MH 1	54.6932	–2.3873	Mountain, heath, bog	Historic lead mining	Pb, general
MH 2	*54.6945*	*–2.387*	*Mountain, heath, bog*	*Historic lead mining*	*Pb, general*
MD 1	*57.0858*	*–2.94*	*Mountain, heath, bog*		
MD 2 H1	57.0864	–2.9435	Coniferous woodland		
MD 2 H2	*57.0864*	*–2.9435*	*Coniferous woodland*		
MD 2 H3	*57.0864*	*–2.9435*	*Coniferous woodland*		
MD 2 H4	*57.0864*	*–2.9435*	*Coniferous woodland*		
NW Ind	52.5845	–2.9582	Improved grassland	Historic lead mining	General
PM 1	53.3833	–4.3419	Improved grassland	Historic copper mining	
PM 2	53.3833	–4.3419	Improved grassland	Historic copper mining	
Sampling location	Latitude	Longitude	LCM2015 aggregate land class	Contamination–metal source notes	NBC group (England only)
PT 1	51.5548	–3.7456	Built up areas and gardens	Steel works	
PT 2	51.5476	–3.6771	Improved grassland	Steel works	
RG	52.5967	–2.982	Improved grassland	Historic lead mining	General
SHM 1	51.3115	–2.7922	Improved grassland	Historic lead and zinc mining	Cd, Pb, general

SHM 2	51.3314	–2.771	Improved grassland	Historic lead and zinc mining
Snowdon	53.0739	–4.0338	Semi-natural grassland	
SB	52.9616	–1.0472	Arable	Sewage Farm
SB 6B	52.9627	–1.0501	Arable	Sewage Farm
SB 7A	*52.9654*	*–1.0483*	*Arable*	*Sewage Farm*
SB 8B	52.9573	–1.0505	Arable	Sewage Farm
SB 8T	52.9572	–1.049	Arable	Sewage Farm
WM H1	52.3487	–3.8857	Semi-natural grassland	Historic lead and zinc mining
WM H2	52.3487	–3.8857	Semi-natural grassland	Historic lead and zinc mining
WV4	52.5729	–2.1154	Built up areas and gardens	Urban

Italicised results are for soils not used in modelling. Where soil names are differentiated by e.g. H1, H2, this indicates different soil horizons sampled at the same location. The LCM2015 aggregate land class is the dominant land cover class within the 1- x 1-km square containing the sampling location (Rowland *et al*. 2017). The Mineralisation column indicates where for Ni, Cu, Cd, Pb or for metals in general, the location falls within a mineralised domain (Johnson *et al*. 2012; British Geological Survey, 2012). Abbreviations: AHF, Alice Holt Forest; CG, Cairngorms; CM, Caradon Mine; CF, Carrock Fell; CHM, Chat Moss; CW, Clough Wood; CY, Cwmystwyth; DGC, Devon Great Consols; DCM, Dyffryn Castell Mine; GS, Glensaugh; HW, Hawkswick; HT, Hill of Towanreef; JT, Jubilee Tower; MH, Moor House; MD, Muir of Dinnet; PM, Parys Mountain; PT, Port Talbot; RG, Roman Gravels; SHM, Shipham Mine; SB, Stoke Bardolph; WM, Wemyss Mine; WV4, WV4 Urgent Project

Table S2. Total, EDTA-extractable and isotopically exchangeable concentrations of Ni, Cu, Zn, Cd and Pb in the studied soils (mol kg^{-1} ($\log_{10}$)).

Sampling location	$\{Ni\}_{Total}$	$\{Ni\}_{EDTA}$	$\{Ni\}_{E}$	$\{Cu\}_{Total}$	$\{Cu\}_{EDTA}$	$\{Cu\}_{E}$	$\{Zn\}_{Total}$	$\{Zn\}_{EDTA}$	$\{Zn\}_{E}$	$\{Cd\}_{Total}$	$\{Cd\}_{EDTA}$	$\{Cd\}_{E}$	$\{Pb\}_{Total}$	$\{Pb\}_{EDTA}$	$\{Pb\}_{E}$
388501	–3.95	–5.25	–5.23	–3.84	–4.43	–4.46	–3.30	–4.09	–4.01	–5.94	–6.15	–6.09	–3.78	–4.19	–4.23
388911	–3.10	–4.37	–4.44	–2.71	–3.14	–3.26	–2.25	–3.25	–3.24	–4.90	–5.28	–5.30	–2.80	–3.12	–3.30
403376	*–2.76*	*–4.02*	*–4.47*	*–3.45*	*–4.27*	*–4.19*	*–2.56*	*–3.90*	*–4.14*	*–5.46*	*–5.97*	*–6.22*	*–3.49*	*–4.16*	*–5.26*
406408	*–3.07*	*–4.21*	*–4.31*	*–3.52*	*–4.18*	*–4.16*	*–2.85*	*–4.41*	*–4.63*	*–5.54*	*–5.91*	*–6.06*	*–3.91*	*–4.38*	*–5.59*
407769	*–3.44*	*–5.04*	*–4.95*	*–3.56*	*–4.21*	*–4.15*	*–2.83*	*–4.23*	*–3.85*	*–5.06*	*–5.25*	*–5.23*	*–3.06*	*–3.38*	*–3.48*
408038	–3.99	–5.09	–5.07	–3.81	–4.24	–4.37	–3.03	–3.70	–3.73	–5.65	–5.82	–5.84	–3.62	–3.97	–4.04
411227	*–3.39*	*–5.45*	*–4.90*	*–3.73*	*–4.79*	*–5.42*	*–3.01*	*–4.53*	*–4.63*	*–5.37*	*–5.78*	*–5.77*	*–3.88*	*–4.73*	*–5.82*
420444	–3.28	–4.57	–4.56	–3.60	–4.25	–4.24	–2.81	–4.02	–3.94	–5.47	–5.67	–5.67	–3.65	–4.20	–4.45
423618	*–3.17*	*–4.88*	*–4.81*	*–3.48*	*–4.21*	*–4.13*	*–2.77*	*–4.57*	*–4.41*	*–5.78*	*–6.17*	*–6.17*	*–3.46*	*–4.02*	*–4.10*
427567	*–3.09*	*–4.33*	*–4.49*	*–3.57*	*–4.39*	*–4.28*	*–2.98*	*–4.49*	*–4.74*	*–5.38*	*–5.85*	*–6.02*	*–3.87*	*–4.40*	*–5.77*
443361	–3.88	–5.43	–5.43	–4.08	–5.22	–5.15	–3.21	–3.97	–3.93	–5.87	–6.20	–6.16	–3.75	–4.25	–4.25
449638	–2.15	–2.44	–2.50	–1.88	–2.06	–2.27	–1.49	–1.65	–1.92	–2.99	–3.19	–3.43	–2.70	–3.12	–3.93
500851		*–5.28*	*–5.21*	*–4.25*	*–5.03*	*–4.88*	*–3.56*	*–3.94*	*–3.89*	*–5.75*	*–5.89*	*–5.81*	*–3.67*	*–3.98*	*–3.91*
600859	–3.21	–4.65	–4.80	–3.05	–3.47	–3.64	–2.01	–2.61	–2.90	–4.75	–5.04	–5.22	–2.58	–2.72	–3.12
601363	–3.15	–4.35	–4.74	–2.65	–3.43	–3.64	–1.75	–2.91	–3.20	–4.84	–5.10	–5.11	–3.00	–3.39	–3.67
601561	–3.57	–4.58	–4.67	–2.73	–2.99	–3.24	–2.54	–3.17	–3.34	–5.28	–5.52	–5.58	–3.35	–3.67	–4.37
601716	–3.16	–4.35	–4.43	–2.59	–3.07	–3.18	–1.53	–2.18	–2.37	–3.97	–4.21	–4.29	–2.52	–2.75	–3.04
601721	–3.13	–4.06	–4.05	–2.69	–3.08	–3.09	–2.05	–2.72	–2.65	–4.21	–4.35	–4.31	–3.10	–3.44	–3.52
601884	–3.05	–4.55	–4.61	–2.73	–3.27	–3.48	–1.94	–2.78	–3.02	–4.93	–5.18	–5.27	–2.79	–2.99	–3.31
601912	–2.70	–3.58	–3.33	–2.57	–3.00	–2.98	–1.99	–2.70	–2.61	–4.53	–4.69	–4.70	–2.78	–2.88	–3.47
602069	–3.32	–4.57	–4.64	–3.09	–3.56	–3.60	–2.16	–2.93	–2.87	–4.60	–4.73	–4.72	–3.08	–3.37	–3.51
602114	–3.44	–4.90	–5.26	–2.73	–3.50	–3.68	–1.63	–2.80	–2.98	–5.21	–5.50	–5.51	–2.98	–3.30	–3.48
602734	–3.58	–5.07	–4.99	–3.82	–4.57	–4.55	–2.81	–3.77	–3.65	–4.99	–5.22	–5.14	–3.73	–4.26	–4.21
603020	–3.04	–4.33	–4.69	–2.42	–2.81	–2.98	–1.94	–2.59	–2.77	–5.09	–5.39	–5.49	–2.56	–2.80	–3.10
603385	–3.37	–4.51	–4.66	–3.22	–3.79	–3.88	–1.86	–2.41	–2.84	–5.41	–5.69	–5.87	–3.43	–3.58	–4.80
603678	–3.63	–4.76	–4.96	–3.63	–4.35	–4.50	–2.58	–3.36	–3.51	–5.35	–5.76	–5.92	–3.49	–3.93	–4.54
603700	–3.39	–4.35	–4.63	–3.39	–3.95	–4.04	–2.12	–2.82	–3.02	–5.02	–5.28	–5.37	–3.03	–3.31	–3.58
604213	–3.34	–4.56	–4.57	–3.26	–3.80	–4.14	–2.75	–3.64	–3.72	–5.38	–5.61	–5.69	–2.98	–3.40	–3.78
604260	–3.08	–4.48	–4.62	–2.37	–2.87	–3.03	–1.93	–2.65	–2.84	–4.76	–5.05	–5.13	–2.65	–2.82	–3.10
605002	–3.43	–4.71	–4.45	–3.11	–3.58	–3.71	–2.64	–3.54	–3.49	–5.29	–5.57	–5.59	–3.12	–3.40	–3.56
605005	–3.46	–4.52	–4.61	–2.89	–3.17	–3.34	–2.44	–2.94	–3.11	–5.03	–5.25	–5.29	–2.86	–3.07	–3.47
606148	–3.39	–4.58	–4.57	–3.02	–3.58	–3.74	–2.42	–2.78	–2.97	–5.18	–5.40	–5.52	–2.33	–2.86	–3.48
606649	–3.25	–4.42	–4.42	–2.99	–3.44	–3.53	–2.41	–3.15	–3.12	–4.78	–4.96	–4.95	–2.72	–2.85	–3.03
606664	–3.09	–4.40	–4.11	–2.70	–3.14	–3.26	–1.94	–2.44	–2.40	–4.91	–5.16	–5.24	–2.52	–2.65	–3.04
606692	*–3.22*	*–4.66*	*–4.98*	*–2.85*	*–3.37*	*–3.62*	*–2.29*	*–3.07*	*–3.48*	*–4.97*	*–5.30*	*–5.56*	*–2.46*	*–2.63*	*–2.98*
606805	–3.34	–4.34	–4.36	–3.04	–3.45	–3.57	–2.30	–2.78	–2.84	–4.81	–4.95	–5.02	–2.81	–2.98	–3.41
606874	–3.36	–4.47	–4.60	–3.29	–3.70	–3.77	–2.54	–3.35	–3.38	–4.92	–5.07	–5.12	–2.80	–2.97	–3.28

Sampling location	$\{Ni\}_{Total}$	$\{Ni\}_{EDTA}$	$\{Ni\}_{E}$	$\{Cu\}_{Total}$	$\{Cu\}_{EDTA}$	$\{Cu\}_{E}$	$\{Zn\}_{Total}$	$\{Zn\}_{EDTA}$	$\{Zn\}_{E}$	$\{Cd\}_{Total}$	$\{Cd\}_{EDTA}$	$\{Cd\}_{E}$	$\{Pb\}_{Total}$	$\{Pb\}_{EDTA}$	$\{Pb\}_{E}$
607736	*–3.21*	*–4.73*	*–4.69*	*–3.17*	*–4.21*	*–4.76*	*–2.52*	*–3.47*	*–3.61*	*–5.44*	*–6.05*	*–6.21*	*–3.76*	*–4.36*	*–5.24*
608099	–3.26	–4.45	–4.84	–2.78	–3.28	–3.53	–2.00	–2.50	–2.77	–4.85	–5.13	–5.28	–2.64	–2.80	–3.26
990443	–3.46	–4.80	–4.60	–2.85	–3.42	–3.56	–2.48	–3.28	–3.29	–5.29	–5.57	–5.64	–2.98	–3.23	–3.62
990510	–3.17	–4.40	–4.38	–2.67	–3.01	–3.02	–2.20	–2.91	–2.79	–4.88	–5.25	–5.19	–3.02	–3.41	–3.47
990655	–3.50	–4.46	–4.19	–3.01	–3.35	–3.37	–2.08	–2.53	–2.61	–4.95	–5.12	–5.15	–3.37	–3.66	–3.93
990666	–3.40	–4.71	–5.10	–3.08	–3.60	–3.83	–2.48	–3.05	–3.37	–5.16	–5.39	–5.53	–2.84	–3.44	–3.85
990668	–3.07	–4.50	–4.55	–2.19	–2.88	–2.92	–3.05	–3.06	–3.07	–4.59	–4.82	–4.81	–2.80	–3.15	–3.34
AHF	–3.42	–4.48	–4.45	–3.53	–4.38	–4.37	–3.04	–4.17	–4.09	–5.97	–6.10	–6.05	–3.98	–4.13	–4.18
CG 1 H1		*–4.94*	*–4.89*	*–4.25*	*–4.73*	*–4.57*	*–3.19*	*–3.27*	*–3.28*	*–5.40*	*–5.46*	*–5.46*	*–3.80*	*–4.03*	*–3.94*
CG 1 H2		*–5.34*	*–5.23*		*–5.50*	*–5.16*	*–3.36*	*–3.79*	*–3.71*	*–5.70*	*–5.97*	*–5.89*	*–3.95*	*–4.35*	*–4.31*
CG 2 H1		*–4.84*	*–4.79*	*–4.31*	*–4.73*	*–4.51*	*–3.18*	*–3.24*	*–3.19*	*–5.61*	*–5.90*	*–5.78*	*–4.15*	*–4.25*	*–4.24*
CG 2 H2		*–5.51*	*–5.42*		*–5.25*	*–5.05*	*–3.30*	*–4.66*	*–4.58*	*–5.90*	*–6.79*	*–6.73*	*–3.81*	*–4.83*	*–4.74*
CG 3			*–6.40*			*–5.63*	*–3.29*	*–5.32*	*–4.76*	*–6.16*	*–7.24*	*–7.02*	*–3.73*	*–5.24*	*–4.96*
CM	–3.74	–5.49	–5.41	–2.13	–2.50	–2.48	–2.94	–4.55	–4.45	–5.94	–6.74	–6.66	–3.44	–3.81	–3.74
CF	–3.40	–4.65	–4.61	–2.86	–3.42	–3.46	–2.09	–3.09	–2.97	–4.36	–4.85	–4.78	–2.42	–2.60	–2.71
CHM	–2.97	–4.11	–3.94	–2.37	–3.13	–3.08	–2.19	–2.84	–2.74	–4.72	–5.15	–5.04	–2.52	–3.06	–3.02
CW	*–2.70*	*–3.59*	*–3.65*	*–2.69*	*–3.17*	*–3.39*	*–1.03*	*–1.58*	*–1.78*	*–3.24*	*–3.48*	*–3.47*	*–1.08*	*–1.30*	*–1.46*
Clydach	–1.17	–2.28	–2.33	–1.91	–2.42	–2.42	–2.36	–2.92	–2.96	–4.74	–4.93	–4.92	–2.74	–2.92	–3.03
CY 1 H1	–3.72	–4.76	–5.10	–3.57	–4.06	–4.09	–2.79	–3.97	–3.92	–5.95	–6.31	–6.33	–2.32	–2.34	–2.40
CY 1 H2	–3.76	–5.65	–4.81	–3.65	–4.37	–4.03	–2.63	–4.52	–3.78	–5.85	–6.51	–6.25	–2.48	–2.67	–2.77
CY 2	–3.49	–5.24	–5.16	–3.09	–4.15	–4.08	–2.57	–4.20	–4.09	–5.34	–6.40	–6.33	–2.41	–2.66	–2.67
DGC 1	–3.25	–4.18	–4.12	–1.46	–1.69	–1.64	–2.45	–3.27	–3.15	–5.42	–5.79	–5.66	–2.82	–3.19	–3.17
DGC 2	–3.64	–5.76	–5.55	–1.77	–3.07	–2.87	–2.99	–5.02	–4.81	–5.84	–7.29	–7.20	–3.40	–4.74	–4.52
DGC 3	–3.30	–4.54	–4.53	–2.85	–3.38	–3.41	–2.59	–4.18	–3.84	–5.52	–5.77	–5.76	–3.43	–4.10	–3.94
Drayton	–3.16	–4.15	–4.20	–3.27	–3.83	–3.92	–2.62	–3.37	–3.46	–5.28	–5.59	–5.73	–3.80	–4.11	–4.65
DCM	–3.54	–4.64	–4.68	–2.84	–3.27	–3.30	–1.13	–1.60	–1.65	–3.71	–3.90	–3.90	–2.92	–3.21	–3.36
Ecton	–3.07	–3.73	–3.77	–0.81	–1.74	–1.91	–0.74	–1.04	–1.11	–2.96	–3.20	–3.23	–1.69	–2.09	–2.23
GS 1 H1	–3.38	–4.56	–4.51	–3.53	–4.10	–4.02	–3.06	–3.43	–3.37	–5.16	–5.31	–5.24	–3.27	–3.29	–3.20
GS 1 H2	–3.78	–4.88	–4.74	–3.78	–4.68	–4.47	–3.37	–4.22	–4.09	–5.67	–5.94	–5.79	–3.65	–4.16	–4.05
GS 2 H1	–3.83	–4.61	–4.56	–3.50	–4.15	–3.98	–3.33	–3.91	–3.85	–5.44	–5.57	–5.50	–3.12	–3.21	–3.20
GS 2 H2	–3.61	–4.81	–4.77	–3.72	–4.76	–4.67	–3.34	–4.77	–4.68	–5.87	–6.11	–6.03	–3.68	–4.11	–4.10
GS 3 H1	–3.86	–4.72	–4.72	–3.74	–4.56	–4.46	–3.16	–3.73	–3.70	–5.52	–5.64	–5.61	–3.07	–3.11	–3.13
GS 3 H2	–3.77	–5.32	–5.26	–3.70	–4.98	–4.81	–3.04	–4.61	–4.49	–5.77	–6.11	–6.03	–3.93	–4.38	–4.42
GS 4 H1	–3.56	–4.90	–4.89	–3.60	–4.72	–4.60	–1.84	–2.00	–2.02	–5.61	–5.75	–5.73	–3.50	–3.61	–3.73
GS 4 H2	–3.82	–4.70	–4.63	–3.72	–4.54	–4.21	–1.74	–1.74	–1.72	–5.40	–5.47	–5.37	–3.30	–3.44	–3.32
GS 4 H3	–4.08	–5.01	–5.02	–3.85	–4.85	–4.80	–1.91	–2.08	–2.09	–5.61	–5.77	–5.74	–3.72	–4.27	–4.30
HW 1	–2.91	–3.81	–3.90	–3.25	–3.79	–3.87	–1.51	–3.00	–3.02	–3.99	–4.23	–4.31	–2.40	–2.79	–3.28
HW 2	–3.19	–4.72	–4.67	–3.23	–3.94	–3.91	–1.44	–3.55	–3.46	–4.81	–5.22	–5.18	–2.36	–2.65	–2.90
HW 3	–3.61	–4.52	–4.57	–3.79	–4.26	–4.36	–2.47	–3.25	–3.33	–4.70	–4.89	–5.02	–3.28	–3.46	–4.34

Sampling location	$\{Ni\}_{Total}$	$\{Ni\}_{EDTA}$	$\{Ni\}_{E}$	$\{Cu\}_{Total}$	$\{Cu\}_{EDTA}$	$\{Cu\}_{E}$	$\{Zn\}_{Total}$	$\{Zn\}_{EDTA}$	$\{Zn\}_{E}$	$\{Cd\}_{Total}$	$\{Cd\}_{EDTA}$	$\{Cd\}_{E}$	$\{Pb\}_{Total}$	$\{Pb\}_{EDTA}$	$\{Pb\}_{E}$
HT 1 H1	–2.73	–2.89	–2.92	–4.07	–4.41	–4.36	–3.02	–3.18	–3.15	–5.21	–5.28	–5.25	–3.68	–3.76	–3.76
HT 1 H2	–1.84	–2.02	–2.03	–3.71	–4.26	–4.55	–2.97	–3.42	–3.41	–5.14	–5.21	–5.24	–3.40	–3.64	–4.14
HT 2 H1	–1.72	–2.08	–2.11	–3.79	–4.78	–4.86	–2.97	–3.91	–3.88	–5.51	–5.58	–5.57	–3.26	–3.48	–3.80
HT 2 H2	*–1.89*	*–3.06*	*–3.04*			*–5.30*	*–2.98*	*–4.90*	*–4.40*	*–6.06*	*–6.87*	*–6.89*		*–5.60*	*–5.58*
HT 3 H1	*–2.87*	*–3.35*	*–3.32*	*–3.33*	*–4.72*	*–4.65*	*–3.02*	*–3.45*	*–3.42*	*–5.59*	*–5.92*	*–5.81*		*–4.56*	*–4.49*
HT 3 H2	–2.36	–3.33	–3.25	–3.97	–5.28	–4.97	–2.97	–4.29	–4.17	–5.70	–6.24	–6.11	–3.51	–4.22	–4.13
JT 1	–4.24	–4.97	–4.95	–4.11	–4.64	–4.80	–3.43	–3.79	–3.85	–5.61	–5.72	–5.77	–3.72	–3.78	–4.10
JT 2	*–4.13*	*–4.96*	*–4.86*		*–4.89*	*–4.83*	*–3.61*	*–3.96*	*–3.92*	*–5.59*	*–5.76*	*–5.71*	*–3.71*	*–3.76*	*–3.94*
Kegworth	–3.08	–4.60	–4.73	–3.15	–3.57	–3.75	–2.55	–3.37	–3.49	–5.09	–5.32	–5.42	–2.88	–3.12	–3.42
MH 1	–4.20	–4.42	–4.39	–4.05	–4.54	–4.44	–2.42	–3.45	–3.43	–5.63	–5.65	–5.61	–3.37	–3.32	–3.41
MH 2		*–4.64*	*–4.63*	*–3.59*	*–4.14*	*–4.04*	*–2.95*	*–3.12*	*–3.12*	*–5.14*	*–5.22*	*–5.19*	*–2.59*	*–2.64*	*–2.66*
MD 1	*–3.68*	*–4.95*	*–4.90*		*–5.28*	*–4.97*	*–3.13*	*–4.07*	*–4.04*	*–5.85*	*–6.19*	*–6.14*	*–3.88*	*–4.44*	*–4.45*
MD 2 H1	–4.02	–4.60	–4.58	–3.95	–4.33	–4.24	–3.09	–3.33	–3.33	–5.43	–5.48	–5.46	–3.12	–3.20	–3.18
MD 2 H2		*–5.60*	*–5.58*	*–4.50*	*–5.27*	*–5.12*	*–3.81*	*–4.68*	*–4.68*	*–6.14*	*–6.28*	*–6.36*	*–3.48*	*–3.70*	*–3.71*
MD 2 H3		*–6.18*	*–6.04*			*–5.77*	*–3.56*	*–5.37*	*–5.30*	*–6.17*	*–6.88*	*–6.88*	*–3.87*	*–4.56*	*–4.58*
MD 2 H4	*–3.94*	*–6.15*	*–5.64*			*–5.37*	*–3.02*	*–5.23*	*–4.72*	*–6.09*	*–6.92*	*–6.57*	*–4.00*	*–5.27*	*–4.88*
NW Ind	–3.28	–3.92	–3.96	–2.58	–2.98	–3.20	–0.85	–1.23	–1.30	–3.02	–3.12	–3.11	–1.24	–1.40	–1.61
PM 1	–4.10	–5.76	–5.77	–1.19	–2.99	–2.98	–1.25	–3.56	–3.52	–4.16	–6.03	–6.07	–0.86	–1.96	–1.93
PM 2	–4.25	–4.94	–4.86	–1.56	–3.19	–3.18	–1.58	–2.47	–2.49	–4.42	–4.98	–4.98	–1.23	–2.10	–2.17
PT 1	–3.27	–4.76	–4.68	–3.13	–3.69	–3.79	–2.12	–3.12	–3.52	–4.96	–5.49	–5.73	–3.09	–3.57	–4.66
PT 2	–3.38	–4.38	–4.54	–3.32	–3.81	–3.95	–2.60	–3.62	–3.65	–5.32	–5.50	–5.65	–3.71	–4.20	–5.05
RG	–3.32	–4.46	–4.74	–2.61	–3.37	–3.51	–1.08	–1.76	–2.00	–3.52	–4.05	–4.05	–1.85	–2.11	–2.29
SHM 1	–3.07	–3.69	–3.83	–3.49	–4.07	–4.14	–1.21	–1.73	–1.75	–3.41	–3.59	–3.58	–2.16	–2.43	–2.56
SHM 2	–3.36	–4.17	–4.29	–3.12	–3.64	–3.79	–1.74	–2.41	–2.47	–3.98	–4.11	–4.19	–2.47	–2.83	–3.13
Snowdon	–3.39	–5.21	–5.07	–3.56	–4.12	–3.88	–2.72	–4.36	–4.21	–5.78	–6.19	–6.09	–3.42	–3.84	–3.76
SB	–2.09	–2.65	–2.47	–1.79	–2.32	–2.28	–1.37	–1.82	–1.92	–3.37	–3.77	–3.85	–2.39	–2.98	–3.12
SB 6B	–2.56	–2.97	–3.09	–2.26	–2.50	–2.63	–1.86	–2.12	–2.34	–3.87	–3.99	–4.22	–2.81	–3.00	–3.34
SB 7A	*–3.37*	*–4.01*	*–4.33*	*–3.20*	*–3.50*	*–3.63*	*–2.64*	*–3.20*	*–3.31*	*–5.16*	*–5.27*	*–5.43*	*–3.55*	*–3.81*	*–4.30*
SB 8B	–2.20	–2.44	–2.49	–1.99	–2.20	–2.32	–1.60	–1.82	–2.03	–3.42	–3.68	–3.94	–2.63	–2.88	–3.30
SB 8T	–2.19	–2.59	–2.55	–1.88	–2.19	–2.26	–1.49	–1.80	–1.91	–3.46	–3.74	–3.90	–2.56	–2.95	–3.23
WM H1	–3.49	–5.07	–4.73	–3.53	–4.30	–4.34	–1.74	–2.57	–2.09	–4.49	–5.16	–4.67	–2.38	–2.76	–2.78
WM H2	–3.26	–4.56	–5.06	–3.72	–4.18	–4.30	–1.93	–1.96	–2.51	–4.91	–4.56	–5.13	–2.67	–2.52	–2.77
WV4	–3.44	–4.62	–4.68	–2.99	–3.37	–3.51	–2.36	–2.82	–2.89	–5.18	–5.48	–5.54	–3.31	–3.45	–3.97

Italicised results are for soils not used in modelling. Abbreviations: AHF, Alice Holt Forest; CG, Cairngorms; CM, Caradon Mine; CF, Carrock Fell; CHM, Chat Moss; CW, Clough Wood; CY, Cwmystwyth; DGC, Devon Great Consols; DCM, Dyffryn Castell Mine; GS, Glensaugh; HW, Hawkswick; HT, Hill of Towanreef; JT, Jubilee Tower; MH, Moor House; MD, Muir of Dinnet; PM, Parys Mountain; PT, Port Talbot; RG, Roman Gravels; SHM, Shipham Mine; SB, Stoke Bardolph; WM, Wemyss Mine; WV4, WV4 Urgent Project.

Table S3. Parameters used for checking mineral saturation in soil supernatants, and the highest saturation index (SI) found by WHAM/Model VII speciation of the soil supernatants.

Mineral	Equilibrium	log K_{sp}	ΔH (kJ mol^{-1})	maximum log SI	Reference
$NiCO_{3\,(s)}$	$NiCO_{3\,(s)} \leftrightarrow Ni^{2+} + CO_3^{2-}$	–11.2	–41.589	–1.86	Allison *et al*. (1991); NIST (2001)
$Ni(OH)_{2\,(s,\,am)}$	$Ni(OH)_{2\,(s,\,am)} + 2H^+ \leftrightarrow Ni^{2+} + 2H_2O$	12.89	–95.96	–4.56	NIST (1990); NIST (2001)
$CuCO_{3\,(s)}$	$CuCO_{3\,(s)} \leftrightarrow Cu^{2+} + CO_3^{2-}$	–11.5	–	–2.98	NIST (2001)
$Cu(OH)_{2\,(s)}$	$Cu(OH)_{2\,(s)} + 2H^+ \leftrightarrow Cu^{2+} + 2H_2O$	9.29	–53.12	–2.36	NIST (2001)
Tenorite	$Cu(OH)_{2\,(s)} + 2H^+ \leftrightarrow Cu^{2+} + 2H_2O$	8.49	–64.687	–1.60	NIST (1993) NIST (1986)
Azurite	$Cu_3(CO_3)_2(OH)_{2\,(s)} + 2H^+ \leftrightarrow 3Cu^{2+} + 2CO_3^{2-} + 2H_2O$	–17.4	–40.6	–4.59	Preis and Gamsjäger (2001)
Malachite	$Cu_2CO_3(OH)_{2\,(s)} + 2H^+ \leftrightarrow 2Cu^{2+} + CO_3^{2-} + 2H_2O$	–5.469	–44.2	–2.05	Preis and Gamsjäger (2001)
$ZnCO_{3\,(s)}$	$ZnCO_{3\,(s)} \leftrightarrow Zn^{2+} + CO_3^{2-}$	–10.8	–	–2.00	NIST (2001)
Hydrozincite	$Zn_5(CO_3)_2(OH)_{6\,(s)} + 6H^+ \leftrightarrow 5Zn^{2+} + 2CO_3^{2-} + 6H_2O$	–236.5	9.407	–8.75	Preis and Gamsjäger (2001)
Smithsonite	$ZnCO_{3\,(s)} \leftrightarrow Zn^{2+} + CO_3^{2-}$	–10.9	–3.8	–1.92	Preis and Gamsjäger (2001)
Otavite	$CdCO_{3\,(s)} \leftrightarrow Cd^{2+} + CO_3^{2-}$	–12.01	6.8	–2.61	Preis and Gamsjäger (2001)
$Cd(OH)_{2\,(s)}$	$Cd(OH)_{2\,(s)} + 2H^+ \leftrightarrow Cd^{2+} + 2H_2O$	13.644	–94.62	–7.01	NIST (2001)
Cerrusite	$PbCO_{3\,(s)} \leftrightarrow Pb^{2+} + CO_3^{2-}$	–13.2	24.79	–2.93	NIST (1990); NIST (2001)
Hydrocerrusite	$Pb_3(CO_3)_2(OH)_{2\,(s)} + 2H^+ \leftrightarrow 3Pb^{2+} + 2CO_3^{2-} + 2H_2O$	–18.96	–	–8.09	NIST (2001)
$Pb(OH)_{2\,(s)}$	$Pb(OH)_{2\,(s)} + 2H^+ \leftrightarrow Pb^{2+} + 2H_2O$	8.15	–58.5342	–2.97	Allison *et al*. (1991)
$Pb_2OCO_{3\,(s)}$	$Pb_2OCO_{3\,(s)} + 2H^+ \leftrightarrow 2Pb^{2+} + CO_3^{2-} + H_2O$	–0.5578	–40.8199	–10.4	NIST (1990)
$Pb_3O_2CO_{3\,(s)}$	$Pb_3O_2CO_{3\,(s)} + 4H^+ \leftrightarrow 3Pb^{2+} + CO_3^{2-} + 2H_2O$	11.02	–110.5831	–16.8	Allison *et al*. (1991)

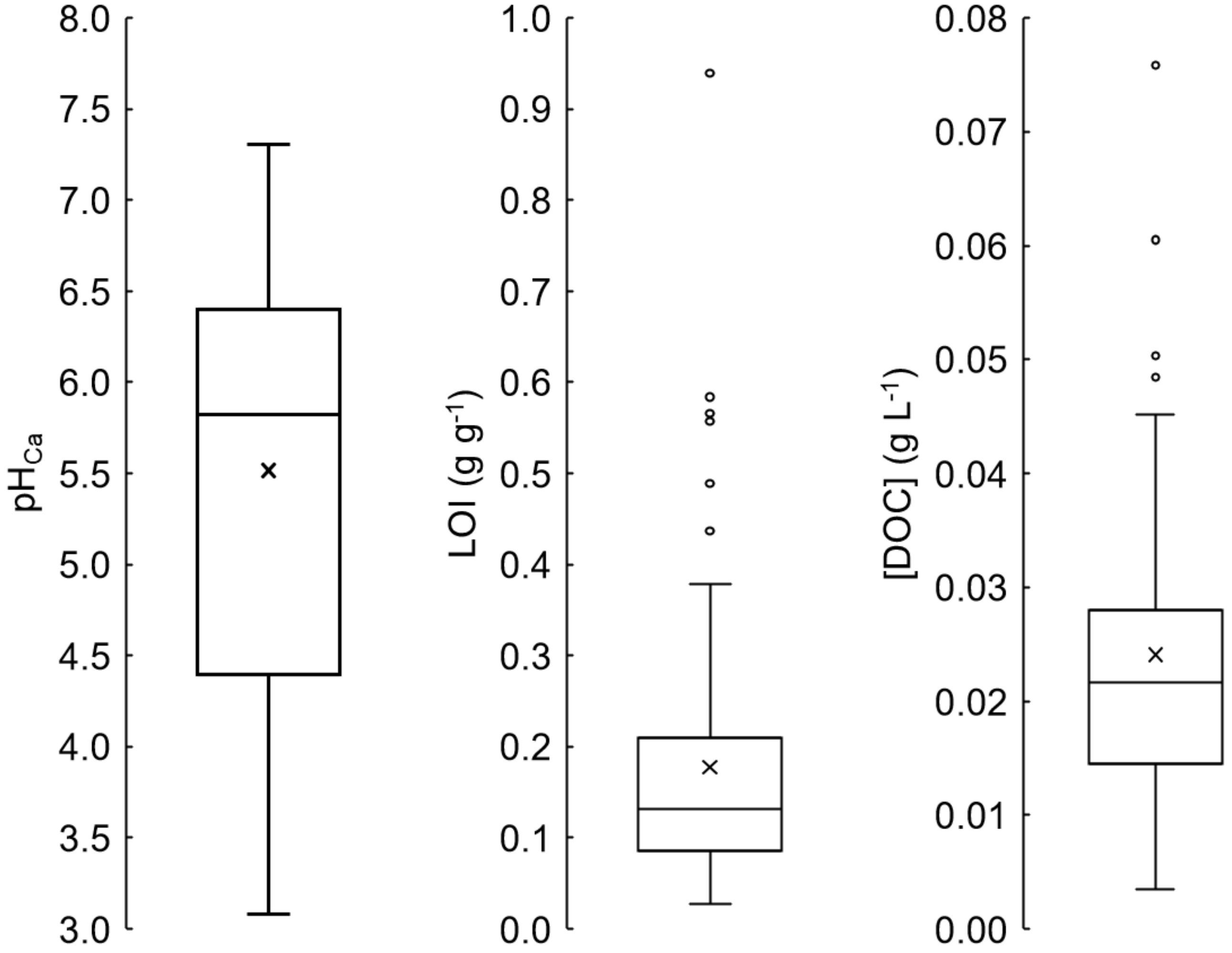

Fig. S1. Ranges of pH_{Ca}, LOI and [DOC] in the dataset. Line within box, median. Cross, mean. The box shows the interquartile range (25th to 75th percentile). Whiskers span from the smallest value that is greater than 1.5 times smaller than the 25th percentile, to the largest value that is less than 1.5 times greater than the 75th percentile. Values outside this latter range are shown as points.

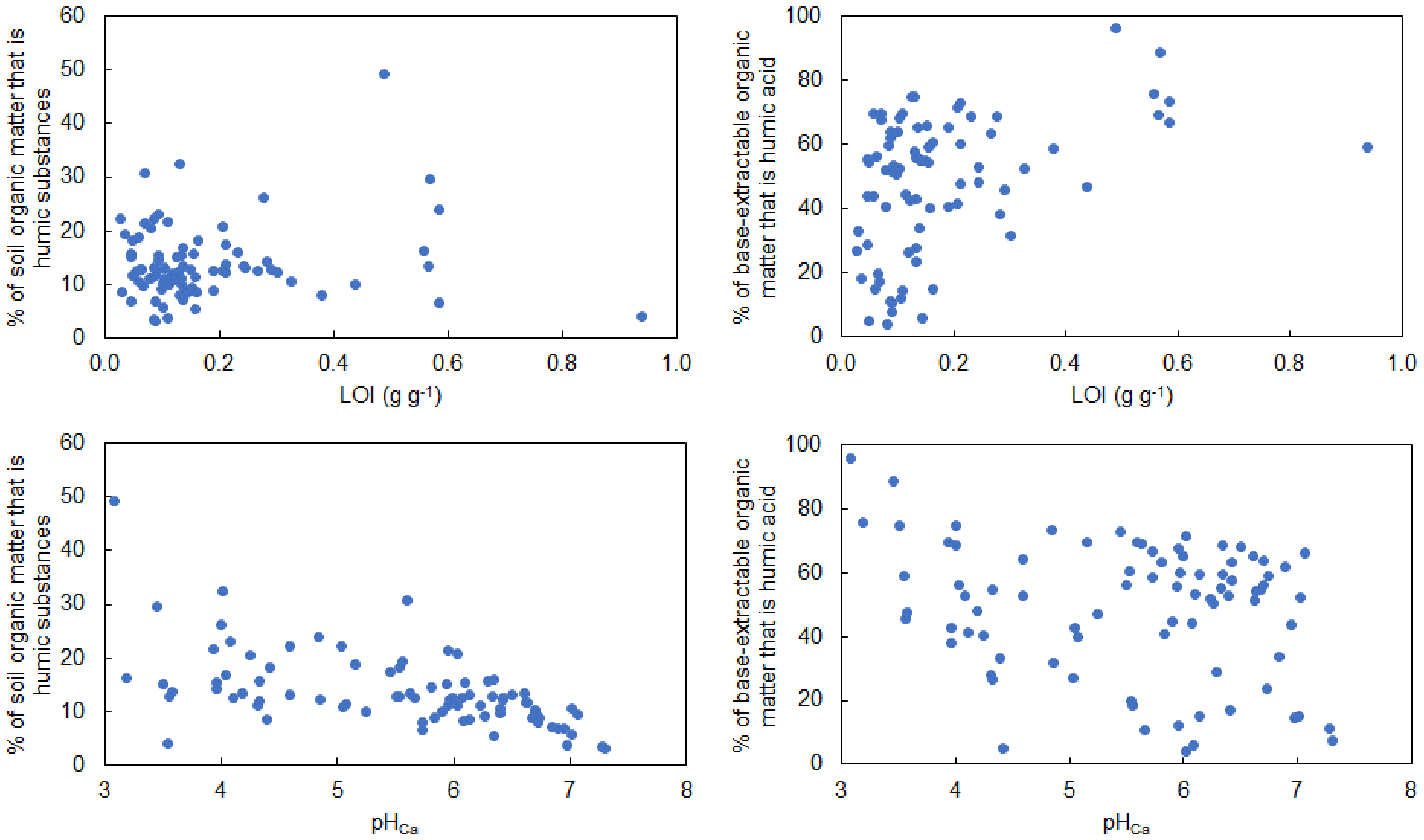

Fig. S2. Concentrations of humic substances in the soils dataset. Top left pane, percentage of soil organic matter (as loss on ignition) extractable as humic substances, plotted against loss on ignition (LOI). Bottom left pane, percentage of soil organic matter (as loss on ignition) extractable as humic substances, plotted against pH_{Ca}. Top right pane, percentage of base-extractable organic matter that is humic acid, plotted against LOI. Bottom right pane, percentage of base-extractable organic matter that is humic acid, plotted against pH_{Ca}.

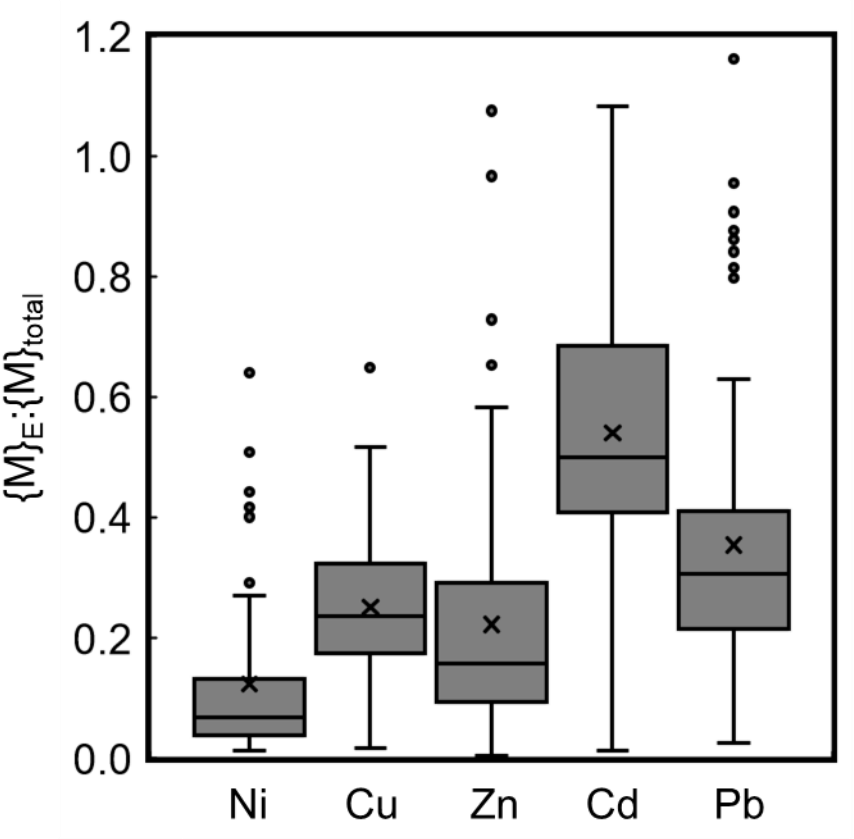

Fig. S3. Distributions of $\{M\}_E$:$\{M\}_{total}$ ratios for the metals. Crosses indicate the mean values.

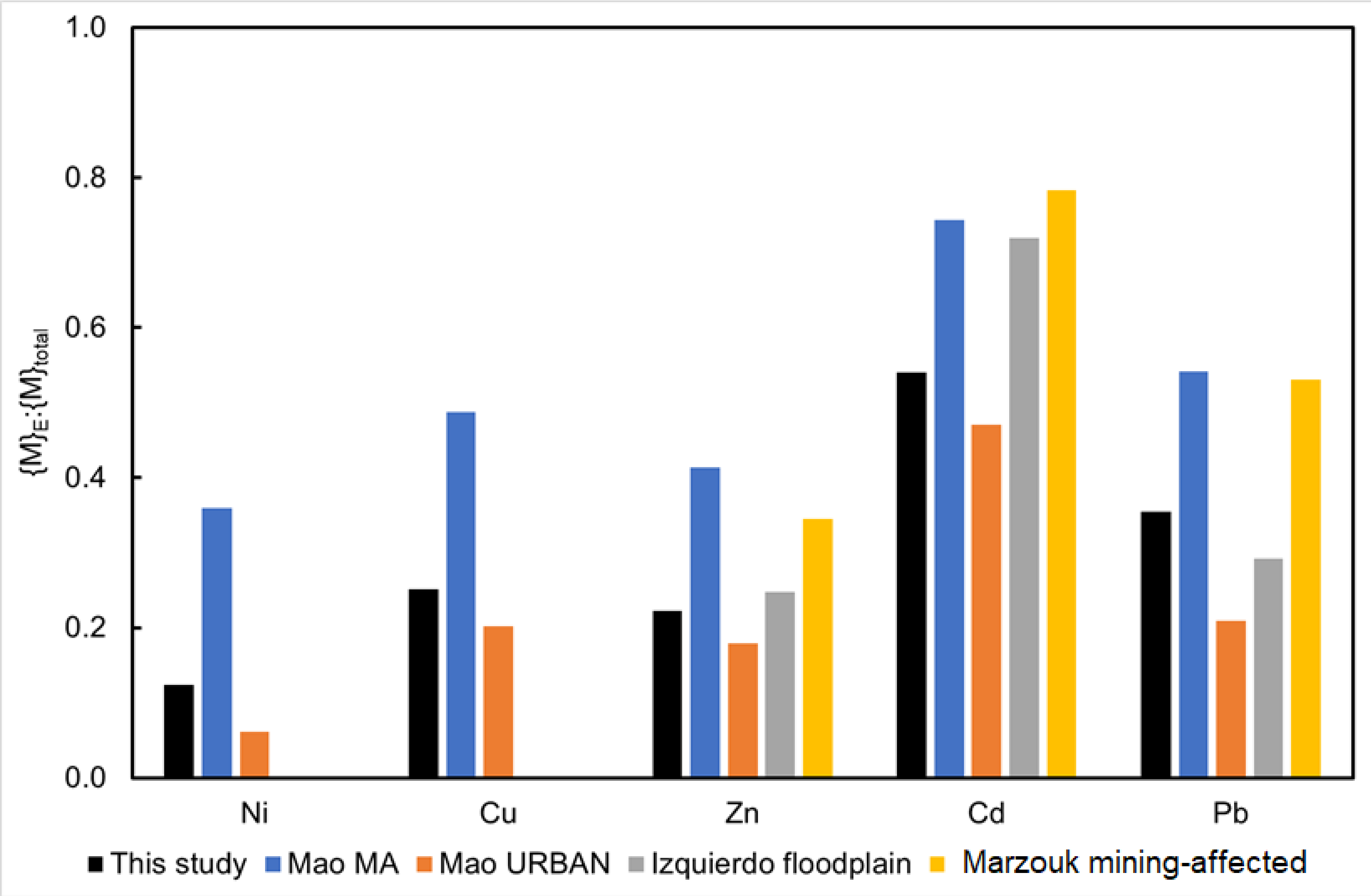

Fig. S4. Comparison of the mean $\{M\}_E$:$\{M\}_{total}$ ratio for each metal in this study with ratios from previous studies of isotopic lability in UK soils. Mao MA, Mao (2013) using soils of varying land use, amended 10 years previously with metal spikes; Mao URBAN, Mao (2013) using soils from urban areas including industrial, recreational and garden sites; Izquierdo floodplain, Izquierdo *et al*. (2013) using soil sampled from the floodplain of the River Trent; Marzouk mining-affected, Marzouk *et al*. (2013) using soils sampled from a catchment containing historic Pb–Zn mining activities.

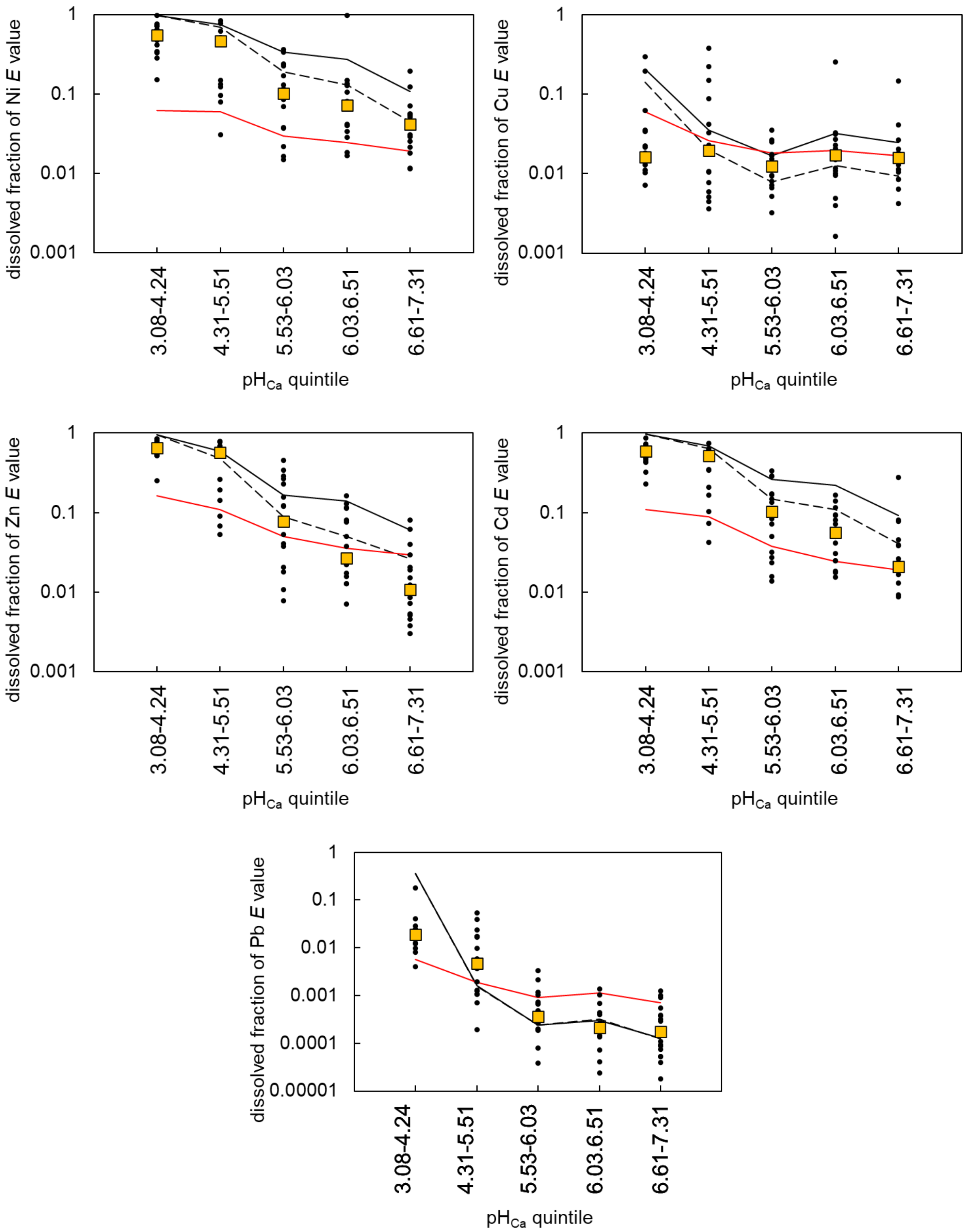

Fig. S5. The observed and modelled soluble fractions of isotopically labile metal within successive quintiles of pH_{Ca}. Black points, observed soluble fractions; yellow squares, median observed soluble fraction in each quintile; solid black lines, median predicted soluble fraction for the quintiles, using WHAM/Model VII and using measured soil HA and FA; dashed black lines, median predicted soluble fraction for the quintiles, using WHAM/ Model VII and assuming soil HA is 50% of LOI with no soil FA; red lines, median predicted soluble fraction for the quintiles, using POSSMs.

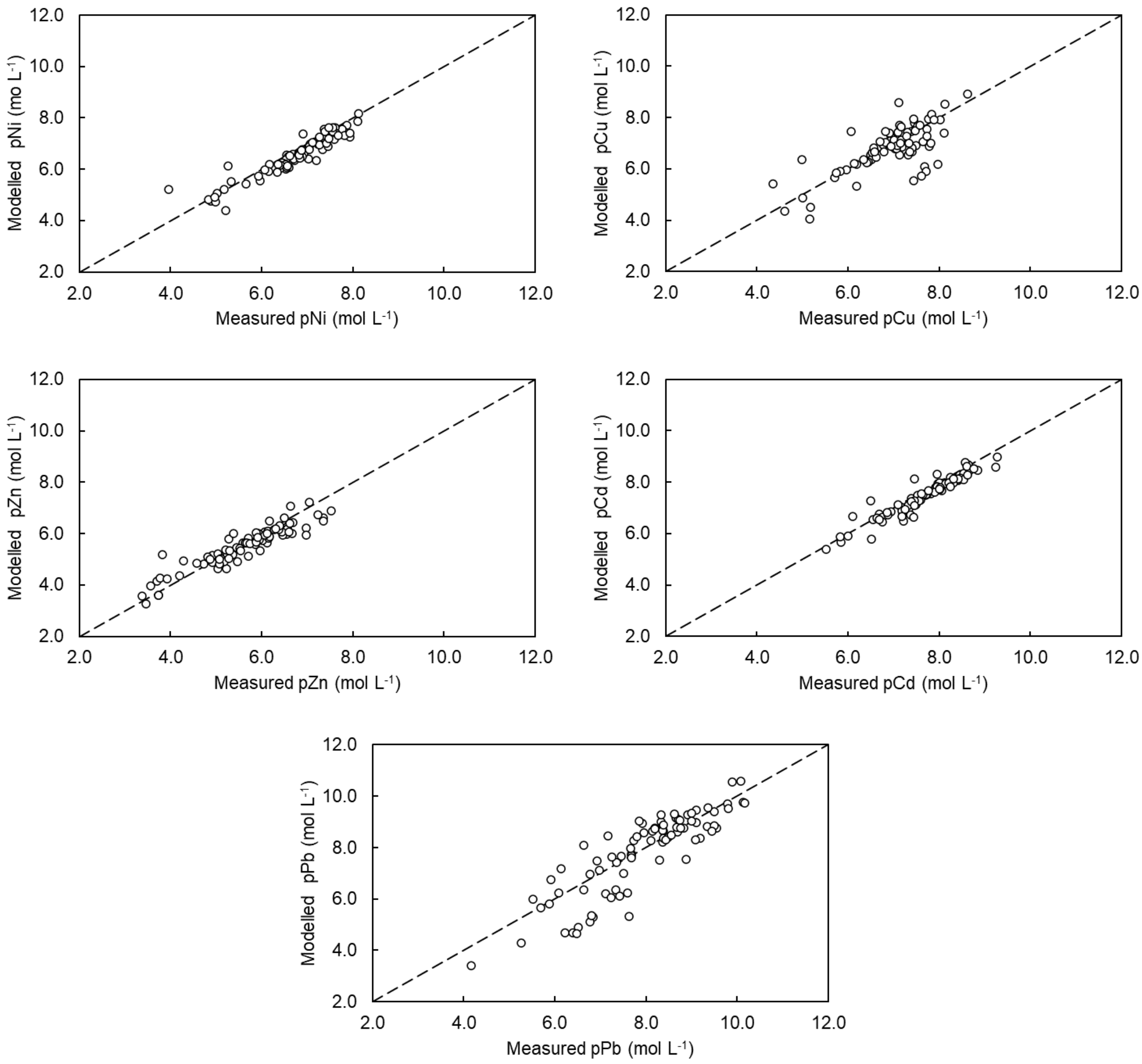

Fig. S6. Comparison of measured solution metal concentrations (mol L^{-1}; log_{10} scale) in 0.01 M $Ca(NO_3)_2$ soil suspensions with WHAM/Model VII outputs using $\{M\}_E$ as model inputs and assuming the soil organic matter to comprise 50% humic acid. The dashed lines indicate the 1:1 line.

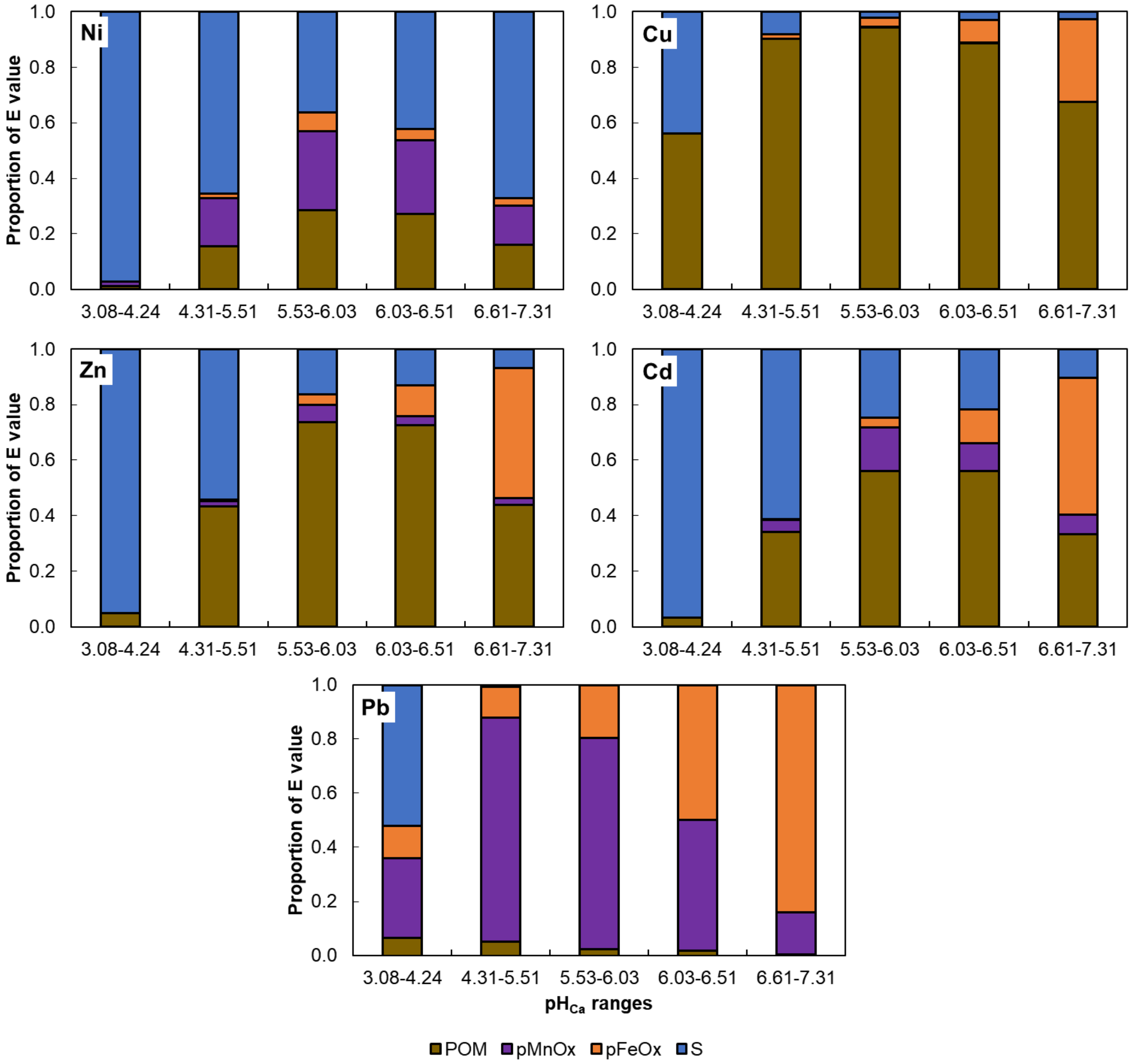

Fig. S7. WHAM/Model VII–predicted speciation of *E* value metal among solution and soil phases, as a function of quintiles of pH_{Ca}. POM, soil organic matter (humic acid + fulvic acid); pMnOx, particulate manganese oxide; pFeOx, particulate iron(III) oxide; S, solution.

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