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Supplementary material

Interpretation of heavy metal speciation in sequential extraction using geochemical modelling

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Table S1. NICA (Non-Ideal Competitive Adsorption)–Donnan model parameters for generic humic and fulvic acids[1,2]

V_D, Donnan volume; *I*, ionic strength; *b*, a constant; Q_{max}, site density on humic or fulvic acid; *p*, heterogeneity parameter of humic or fulvic acid; *n*, ion-specific non-ideality parameter; *K*, median affinity. Subscripts 1 and 2 respectively relate to the carboxylic and the phenolic type of sites on humic or fulvic acids

Generic humic acids				
b value in $\log V_D = b \log I - b - 1$ – 0.49				
	Carboxylic site		Phenolic site	
Site density Q_{max} (mol kg^{-1})	3.15		2.55	
Heterogeneity *p*	0.62		0.41	
Ion specific parameters	$\log K_1$	n_1	$\log K_2$	n_2
H	2.93	0.81	8.00	0.63
Ca	–1.37	0.78	–0.43	0.75
Mg	–0.6	0.77	0.6	0.59
Al	–1.05	0.40	8.89	0.30
Fe^{III}	5.00	0.30	17.5	0.25
Cu	2.23	0.56	6.85	0.34
Cd	–0.20	0.73	2.37	0.54
Zn	0.11	0.67	2.39	0.27
Ni	–0.26	0.64	1.0	0.55
Pb	1.26	0.60	4.86	0.69
Generic fulvic acids				
b value in $\log V_D = b \log I - b - 1$ – 0.57				
	Carboxylic site		Phenolic site	
Site density Q_{max} (mol kg^{-1})	5.88		1.86	
Heterogeneity *p*	0.59		0.70	
Ion specific parameters	$\log K_1$	n_1	$\log K_2$	n_2
H	2.34	0.66	8.60	0.76
Ca	–2.17	0.85	–3.29	0.83
Mg	–2.10	0.77	–2.40	0.59
Al	–4.11	0.42	12.16	0.31
Fe^{III} [A]	4.0	0.25	20	0.19
Cu	0.26	0.53	8.24	0.36
Cd	–0.99	0.68	0.73	0.50
Zn	–3.84	0.67	–0.73	0.61
Ni	–2.07	0.65	2.03	0.53
Pb	–1.22	0.60	6.87	0.70

[A]Parameters from Vega and Weng.[3]

Table S2. CD-MUSIC (charge distribution–multi-site complexation) model parameters of goethite[4–7]

110 face: surface area: 4.5×10^4 m^2 kg^{-1}, $FeOH^{-0.5}$ site: 3.0 nm^{-2}, $Fe_3O^{-0.5}$ site: 3.0 nm^{-2}. 021 face: surface area: 5×10^3 m^2 kg^{-1}, $FeOH^{-0.5}$ site: 3.75 nm^{-2}, $Fe_hOH^{-0.5}$ site: 3.75 nm^{-2}. C_1 = 1.02 F m^{-1}; C_2 = 5 F m^{-1}. log*K*, affinity constant; site 1 and site 2, number and type of the site involved; 0-, 1- and 2-plane, charge attributed to the corresponding electrostatic planes

		Species parameters				
surface species	log *K*	site 1	site 2	0-plane	1-plane	2-plane
$FeOH^{-0.5}$	0	$1FeOH^{-0.5}$		0	0	0
$FeOH_2^{+0.5}$	9.2	$1FeOH^{-0.5}$		1	0	0
$FeOHK^{+0.5}$	–1.0	$1FeOH^{-0.5}$		0	0	1
$FeOH_2NO_3^{-0.5}$	8.2	$1FeOH^{-0.5}$		1	0	–1
$Fe_3O^{-0.5}$	0	$1Fe_3O^{-0.5}$		0	0	0
$Fe_3OH^{+0.5}$	9.2	$1Fe_3O^{-0.5}$		1	0	0
$Fe_3OK^{+0.5}$	–1.0	$1Fe_3O^{-0.5}$		0	0	1
$Fe_3OHNO_3^{-0.5}$	8.2	$1Fe_3O^{-0.5}$		1	0	–1
$Fe_hOH^{-0.5}$	0.0	$1Fe_hOH^{-0.5}$		0	0	0
$Fe_hOH_2^{+0.5}$	9.2	$1Fe_hOH^{-0.5}$		1	0	0
$Fe_hOHK^{+0.5}$	–1.0	$1Fe_hOH^{-0.5}$		0	0	1
$Fe_hOH_2NO_3^{-0.5}$	8.2	$1Fe_hOH^{-0.5}$		1	0	–1
$FeOHCa^{+1.5}$	3.55	$1FeOH^{-0.5}$		0.2	1.8	0
$(FeOH)_2Mg^{+1}$	4.52	$2FeOH^{-0.5}$		0.72	1.28	0
$(FeOH)_2MgOH^0$	–6.78	$2FeOH^{-0.5}$		0.72	0.28	0
$(Fe_hOH)_2Mg^{+1}$	4.52	$2Fe_hOH^{-0.5}$		0.72	1.28	0
$FeOPO_3^{-2.5}$	20.8	$1FeOH^{-0.5}$		0.25	–2.25	0
$(FeO)_2PO_2H^{-1}$	35.7	$2FeOH^{-0.5}$		0.9	–0.9	0
$(FeO)_2PO_2^{-2}$	29.4	$2FeOH^{-0.5}$		0.39	–1.39	0
$(Fe_hO)_2PO_2H^{-1}$	35.7	$2Fe_hOH^{-0.5}$		0.9	–0.9	0
$(Fe_hO)_2PO_2^{-2}$	29.4	$2Fe_hOH^{-0.5}$		0.39	–1.39	0
$FeOHCu^{+1.5}$	8.62	$1FeOH^{-0.5}$		0.83	1.17	0
$FeOHCuOH^{+0.5}$	3.03	$1FeOH^{-0.5}$		0.83	0.17	0
$Fe_hOHCu^{+1.5}$	8.62	$1Fe_hOH^{-0.5}$		0.83	1.17	0
$Fe_hOHCuOH^{+0.5}$	3.03	$1Fe_hOH^{-0.5}$		0.83	0.17	0
$(FeOH)_2Cd^{+1}$	6.98	$2FeOH^{-0.5}$		0.71	1.29	0
$(FeOH)_2CdOH^0$	–2.94	$2FeOH^{-0.5}$		0.71	0.29	0
$(Fe_hOH)_2Cd^{+1}$	6.98	$2Fe_hOH^{-0.5}$		0.71	1.29	0
$(Fe_hOH)_2CdOH^0$	–0.32	$2Fe_hOH^{-0.5}$		0.71	0.29	0
$(FeOH)_2Pb^{+1}$	9.75	$2FeOH^{-0.5}$		1.15	0.85	0
$(Fe_hOH)_2Pb^{+1}$	9.75	$2Fe_hOH^{-0.5}$		1.15	0.85	0
$(FeOHFe_3O)Zn^{+1}$	8.01	$1FeOH^{-0.5}$	$1Fe_3O^{-0.5}$	0.83	1.17	0
$(FeOHFe_3O)ZnOH^0$	–1.0	$1FeOH^{-0.5}$	$1Fe_3O^{-0.5}$	0.83	0.17	0
$(Fe_hOH)_2Zn^{+1}$	6.63	$2Fe_hOH^{-0.5}$		0.83	1.17	0
$(Fe_hOH)_2ZnOH^0$	–2.38	$2Fe_hOH^{-0.5}$		0.83	0.17	0

Table S3. Amounts of metal extracted in selective sequential extraction (SSE)

Sum/total strong acid is the ratio of the sum of metals extracted in the SSE to the metals extracted in strong acids. In some cases, this ratio is larger than 100 %, which can be caused by uncertainties in the measurement (especially at low metal concentrations) or by a higher extraction efficiency of the SSE compared to the strong acid extraction

Soil	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
	Step 1 (mg kg^{-1})				Step 2 (mg kg^{-1})				Step 3 (mg kg^{-1})			
1	9.7	0.1	7.2	191.5	1.7	1.3	11.6	48.0	1.9	6.0	43.4	155.1
2	36.9	0.2	6.0	691.2	4.6	0.7	7.4	98.2	6.6	4.9	45.8	544.6
3	0.6	0.2	3.8	37.3	0.3	1.9	7.8	11.0	0.1	3.6	17.5	39.2
4	40.5	0.2	9.5	567.8	8.2	0.7	13.7	121.1	10.9	0.6	88.4	652.3
5	57.8	1.1	16.1	697.8	6.4	2.9	12.1	85.1	15.5	16.6	144.2	925.4
6	78.0	1.4	13.4	1102.5	6.9	4.1	12.9	118.4	21.0	23.2	182.2	1338.2
7	0.2	5.1	0.7	5.2	0.0	44.3	5.4	1.5	0.0	27.0	12.1	4.0
8	0.04	15.2	3.8	1.5	0.0	30.9	3.7	0.1	0.0	18.7	9.1	0.1
9	0.6	0.2	6.8	30.6	0.1	1.1	4.9	6.6	0.1	0.9	21.0	93.4
10	5.3	2.9	0.8	33.8	2.2	18.7	31.8	144.1	3.4	10.9	169.3	1563.3
11	12.1	0.9	41.3	101.6	0.9	3.3	15.3	9.7	2.2	5.3	119.0	131.0
12	0.4	0.3	0.3	8.2	0.2	2.4	1.4	2.6	0.2	2.2	7.9	22.8
13	4.2	1.7	0.02	27.3	1.4	10.9	3.4	118.3	1.6	12.0	19.7	1869.1
14	4.9	22.1	5.9	17.0	0.4	53.0	2.7	2.6	0.5	22.4	19.4	61.9
15	11.9	3.9	644.8	204.0	1.1	13.8	71.3	24.2	1.6	11.8	329.3	602.9
16	10.7	0.7	198.9	107.7	5.3	45.5	1068.9	920.1	3.0	4.9	1106.0	2605.4
	Step 4 (mg kg^{-1})				Residual (mg kg^{-1})				Sum/total strong acid (%)			
1	0.4	9.8	14.5	49.6	6.1	6.9	14.5	153.6	103	94	94	97
2	1.1	13.2	23.4	159.0	19.1	12.0	23.4	645.1	105	87	98	104
3	0.1	9.2	10.2	7.1	1.5	6.2	10. 2	42.2	96	98	115	102
4	2.1	22.6	38.1	229.3	17.3	16.3	38.1	647.1	105	90	106	101
5	2.7	66.4	58.6	273.3	25.2	55.3	58.6	833.7	106	87	118	93
6	4.3	45.3	68.2	269.0	28.7	77.0	68.2	451.6	115	96	107	122
7	0.0	21.5	3.7.7	1.7	0.0	15.4	3.7	0.2	145	90	130	135
8	0.0	15.5	30	0.2	0.0	13.7	3.0	1.3	148	91	131	129
9	0.0	12.5	11.0	24.0	0.3	15.7	11.0	91.3	102	117	117	124
10	0.5	176.1	62.8	425.4	4.0	139.1	62.8	375.2	89	93	101	85
11	0.4	26.6	35.9	67.1	5.1	11.1	35.9	127.4	101	100	96	88
12	0.0	4.4	2.2	5.1	0.8	25.5	2.2	42.3	100	92	106	100
13	0.3	59.8	6.2	258.9	1.5	42.9	6.2	164.5	84	86	93	119
14	0.1	193.0	10.2	30.7	2.8	116.9	10.2	68.3	102	86	111	113
15	0.8	69.0	125.2	528.4	4.7	61.6	125.2	753.7	95	109	101	102
16	2.6	191.9	166.3	1298.0	14.0	125.4	166.3	1782.8	92	89	112	92

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Table S4. Dissolved organic carbon (DOC) concentration in $CaCl_2$ extraction and pH, DOC and soluble Fe concentration in the first three steps of the sequential extraction

Soil	$CaCl_2$-extraction (soil : solution = 1 : 10)	Step 1 (soil : solution = 1 : 8)			Step 2 (soil : solution = 1 : 8)			Step 3 (soil : solution = 1 : 20)		
	DOC (mg L^{-1})	pH	DOC (mg L^{-1})	Fe (mg L^{-1})	pH	DOC (mg L^{-1})	Fe (mg L^{-1})	pH	DOC (mg L^{-1})	Fe (mg L^{-1})
1	30.9	3.68	45.5	1.15	4.75	210	37.8	2.27	263	180
2	46.5	3.82	68.6	1.94	4.71	400	89.3	2.39	129	369
3	25.1	3.56	31.4	1.95	4.77	177	27.7	2.13	328	58.5
4	49.7	3.72	65.9	1.81	4.65	240	46.7	2.44	180	283
5	44.7	3.70	61.4	2.89	4.67	374	98.4	2.49	56.4	503
6	51.0	3.81	71.8	2.66	4.65	402	98.3	2.57	57.8	576
7	24.7	4.18	28.8	3.50	4.80	45.6	10.5	2.06	215	74.4
8	33.2	3.15	44.5	5.95	4.80	74.5	18.9	1.98	224	71.1
9	94.3	3.28	102	7.55	4.61	638	66.9	2.58	1197	186
10	37.4	6.01	39.4	3.69	4.75	114	49.5	2.59	183	245
11	22.3	3.34	32.1	3.93	4.71	413	97.6	2.40	192	271
12	4.9	4.45	4.8	4.32	4.76	8.25	1.03	2.17	79.6	132
13	22.9	6.35	28.1	4.64	5.17	43.6	11.1	2.50	141	129
14	15.8	3.89	9.0	4.02	4.73	70.8	48.6	2.31	6.64	208
15	29.1	3.53	22.5	2.90	4.77	28.6	25.7	2.25	88.8	211
16	8.6	6.26	14.5	4.06	4.94	265	22.7	2.23	8.24	73.5

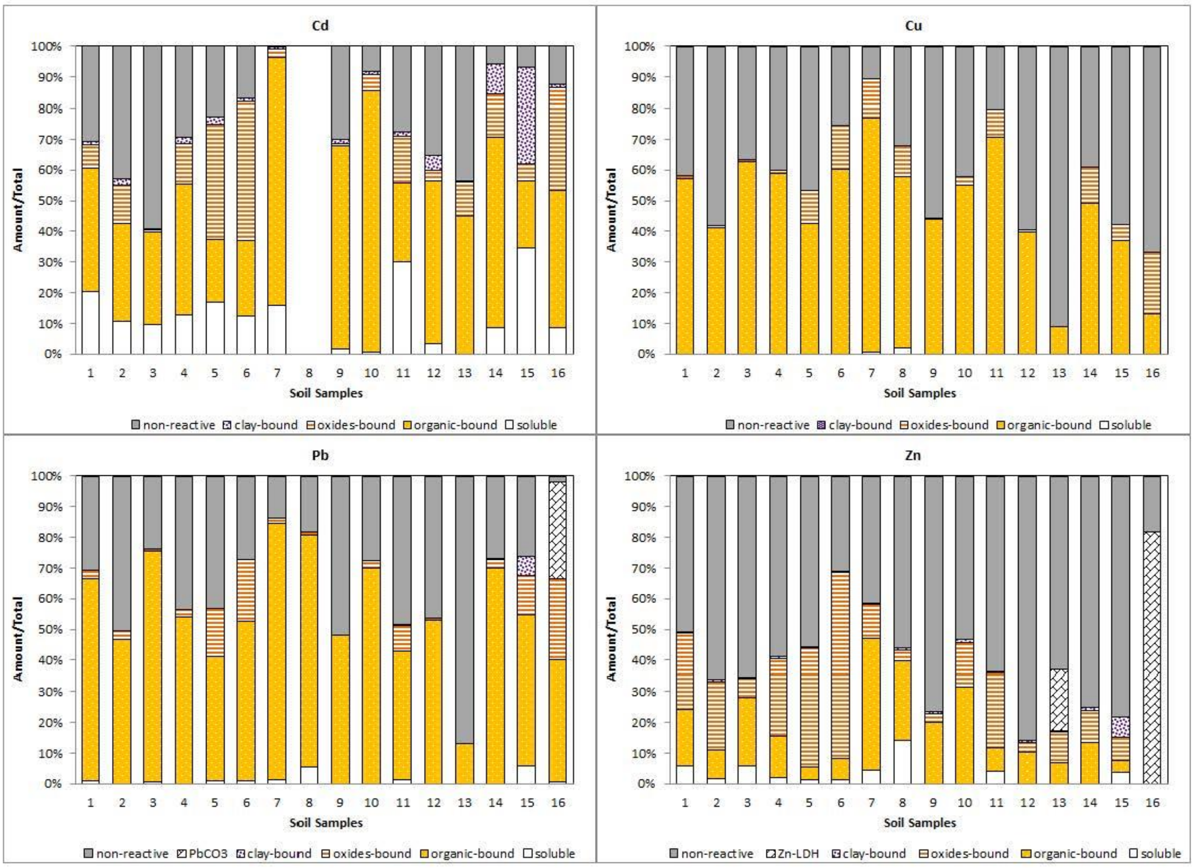

Fig. S1. Metal fractionation based on multi-surface modelling. The calculation was conducted for the conditions of the 0.01 M $CaCl_2$ extraction using metals in HNO_3 extraction as the total amount of reactive metal. The total metal concentration (100 %) used in making this figure was based on the strong acids digestion (Table 2 in the main text). The difference between total metal in strong acids extraction and metal–HNO_3 was called non-reactive. Soluble refers to soluble metal in 0.01 M $CaCl_2$ extraction. Cd distribution in Soil 8 was not calculated because the very low Cd concentration present in the soil made the model input very unreliable.

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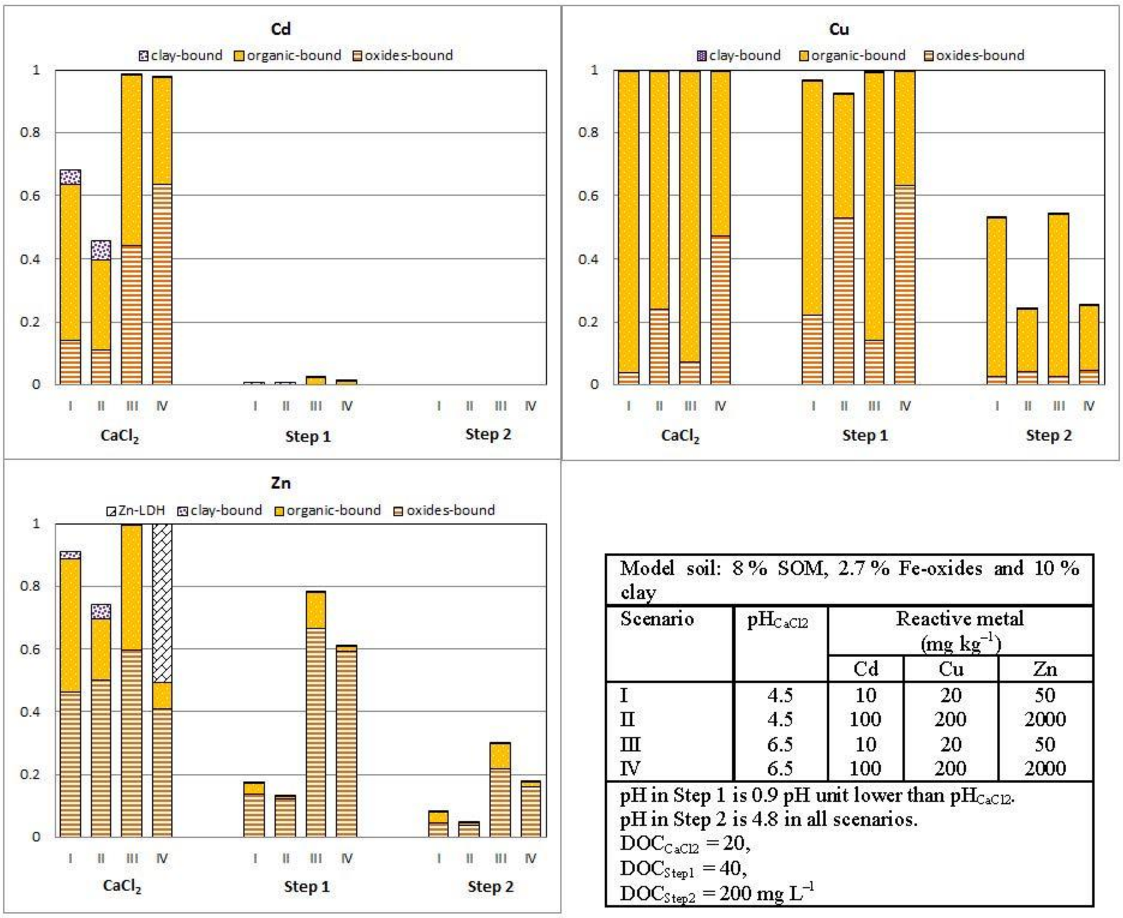

Model soil: 8 % SOM, 2.7 % Fe-oxides and 10 % clay				
Scenario	pH_{CaCl2}	Reactive metal ($mg\ kg^{-1}$)		
		Cd	Cu	Zn
I	4.5	10	20	50
II	4.5	100	200	2000
III	6.5	10	20	50
IV	6.5	100	200	2000
pH in Step 1 is 0.9 pH unit lower than pH_{CaCl2}. pH in Step 2 is 4.8 in all scenarios. DOC_{CaCl2} = 20, DOC_{Step1} = 40, DOC_{Step2} = 200 mg L^{-1}				

Fig. S2. Model prediction of Cd, Cu and Zn speciation in the solid phase originally (as in the 0.01 M $CaCl_2$ suspension) and in Step 1 and 2 of selective sequential extraction (SSE) for four scenarios (I, II, III and IV) for the 'model' soil. (In this graph, the reference point for 100 % is the amount of reactive metal. The gap between the amount shown in the graph and 100 % is soluble metal or metal extracted).

To better illustrate the modelling results and effects of pH and metal loading, a model simulation was carried out for a 'model' soil, with SOM = 8 %, Fe-oxides = 2.7 % and clay = 10 %. The simulation was done for four scenarios: I, low pH and low metal loading; II, low pH and high metal loading; III, high pH and low metal loading; IV, high pH and high metal loading. The low and high pH is respectively pH_{CaCl2} = 4.5 and 6.5. The simulation was carried out for Cd, Cu and Zn. The low metal loading is equivalent to a total reactive metal content of 10 mg kg^{-1} Cd, 20 mg kg^{-1} Cu and 50 mg kg^{-1} Zn, whereas it is 100 mg kg^{-1} Cd, 200 mg kg^{-1} Cu and 2000 mg kg^{-1} Zn for the high metal loading. The calculation was made under the same conditions as in the 0.01 M $CaCl_2$, Step 1 and Step 2 extractions respectively. The dissolved organic carbon (DOC) concentration used in the calculation was respectively 20, 40 and 200 mg L^{-1} for these three extractions. Based on the experience (Table S4), it was assumed that pH in Step 1 is 0.9 pH units lower than pH_{CaCl2} (i.e. pH = 3.6 or 5.6). For Step 2, the pH was fixed at 4.8 for all scenarios.

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