

Supplemental Information

Uranium and nickel partitioning in a contaminated riparian wetland

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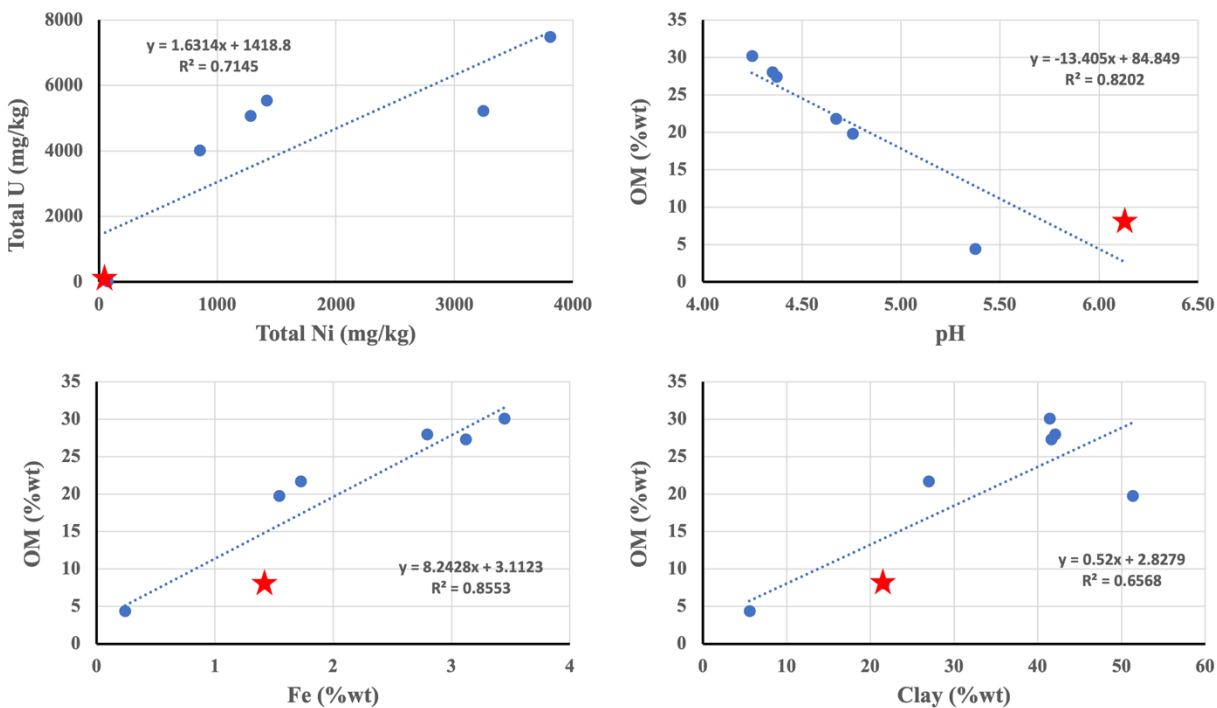


Figure S1. Observed correlation between different sediment properties in Tims Branch sediments. Red star denotes the #2306 sample collected from the upstream of Tims Branch.

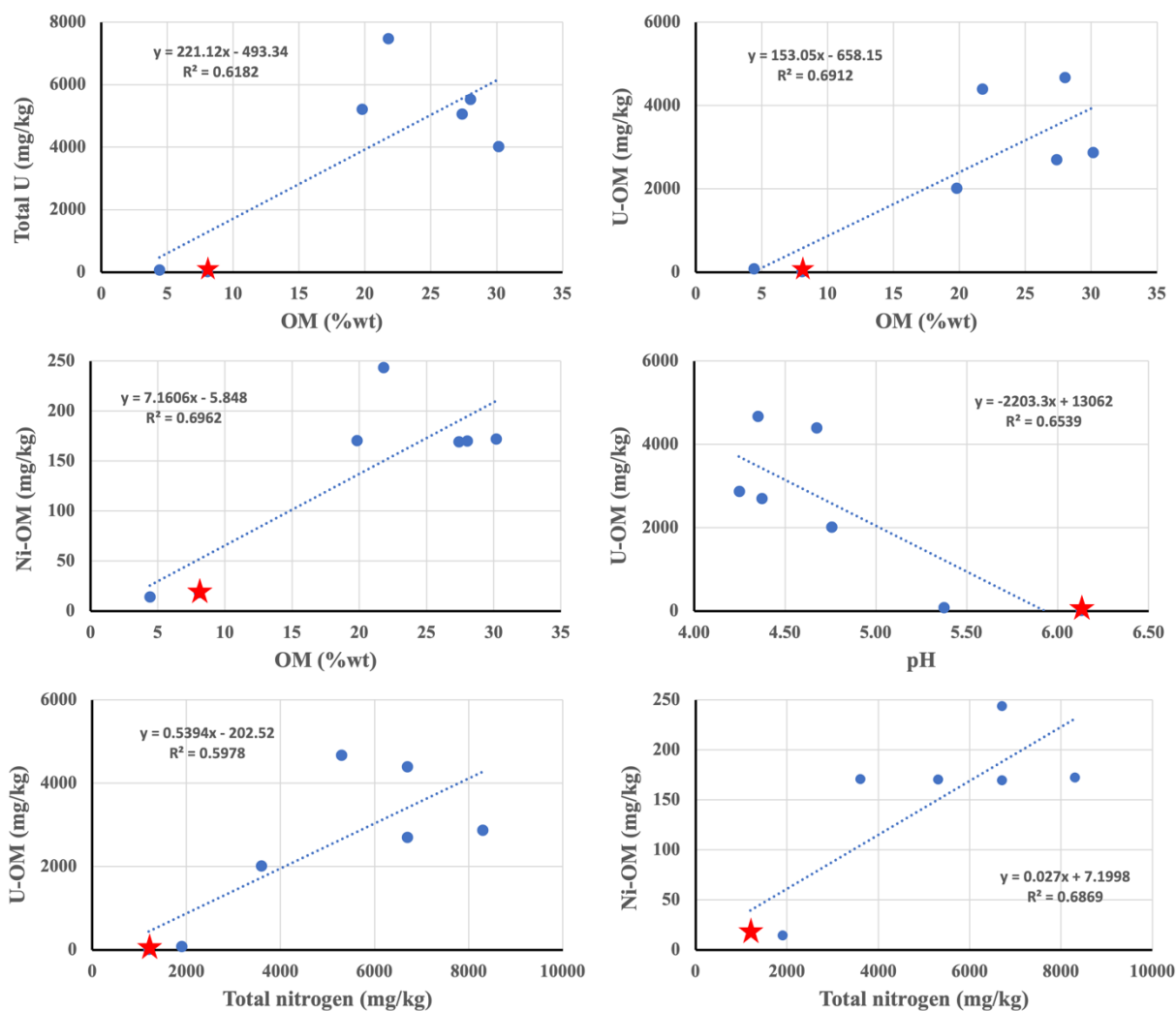


Figure S2. Observed correlation of sediment properties (pH, organic matter (OM), total nitrogen) with total U/Ni concentrations or U/Ni associated with the organic fraction in Tims Branch sediments. Red star denotes the #2306 sample collected from the upstream of Tims Branch.

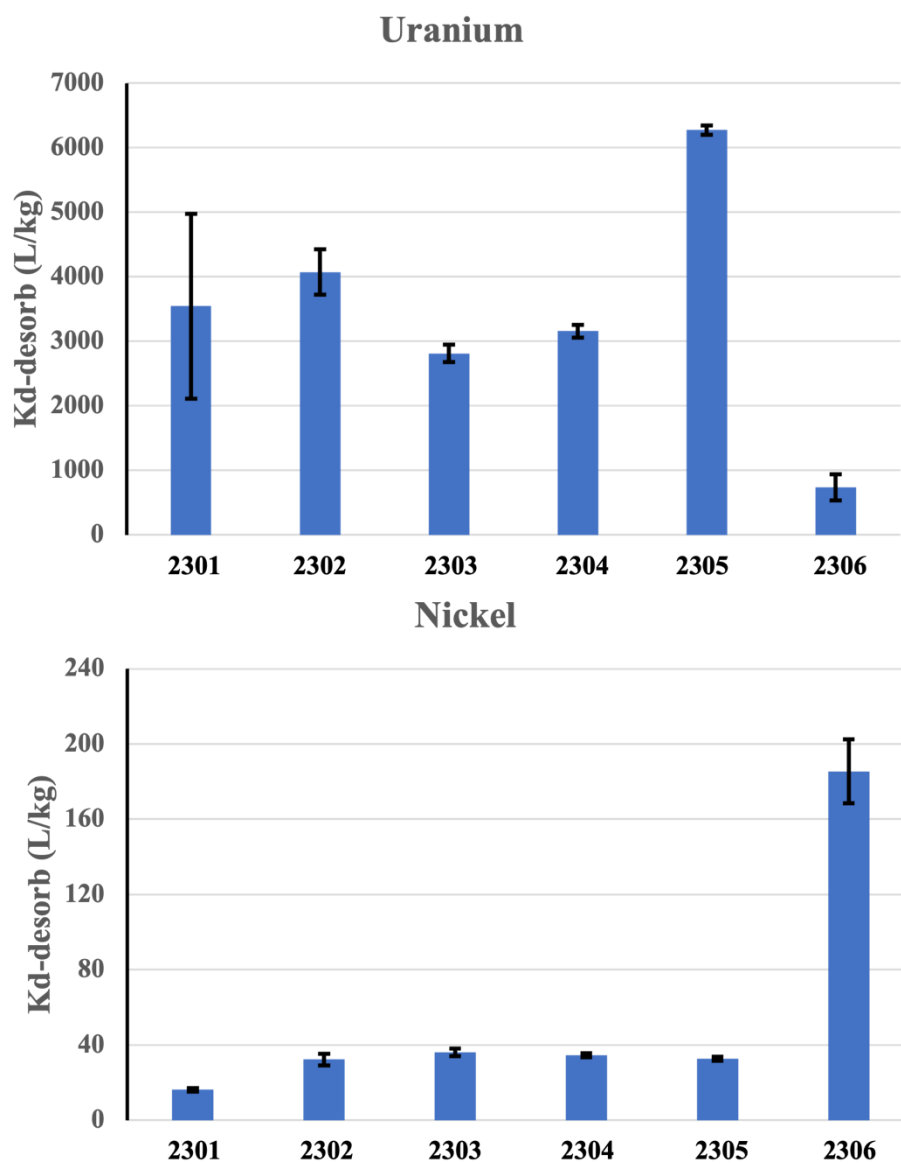


Figure S3. Desorption coefficient values (K_d -desorb) of U and Ni in the Tims Branch sediments.

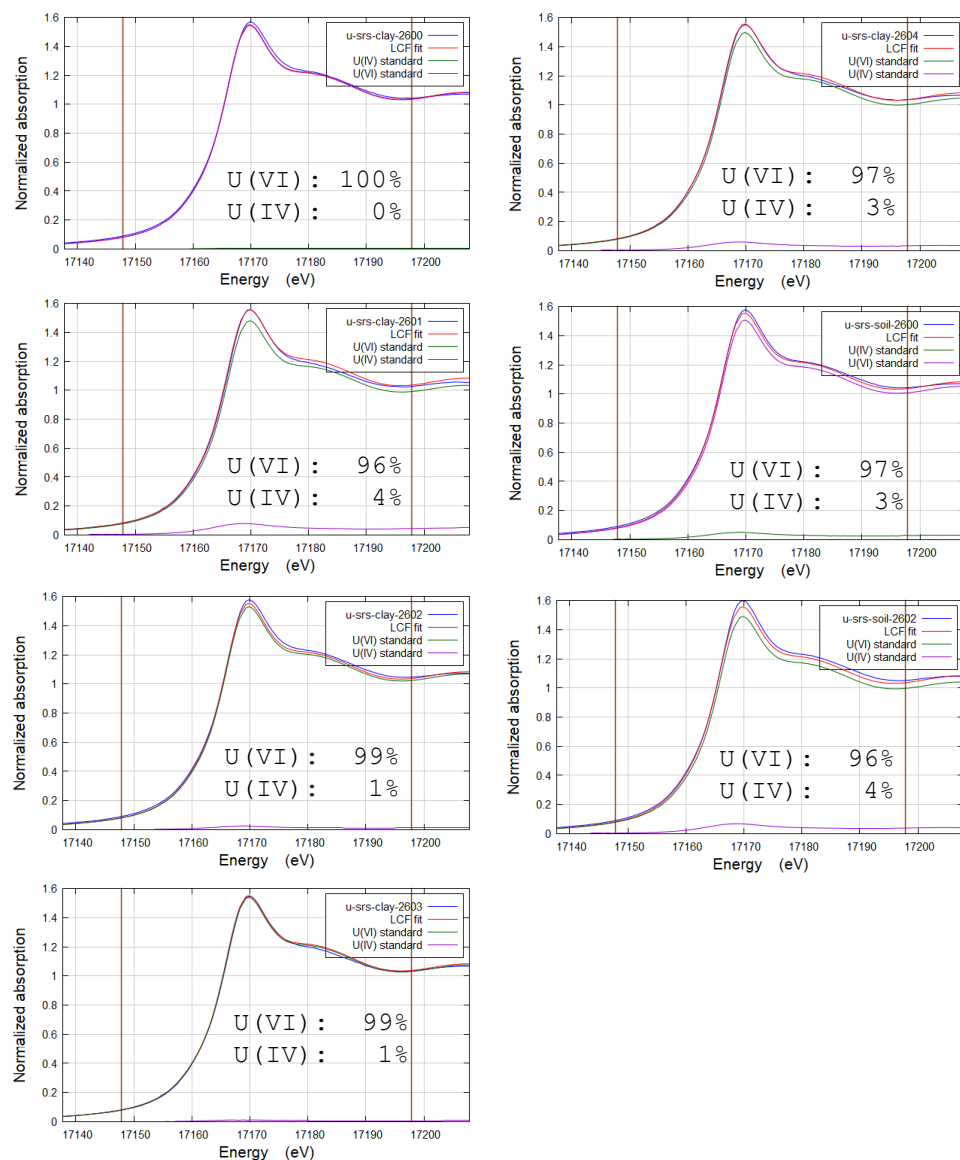
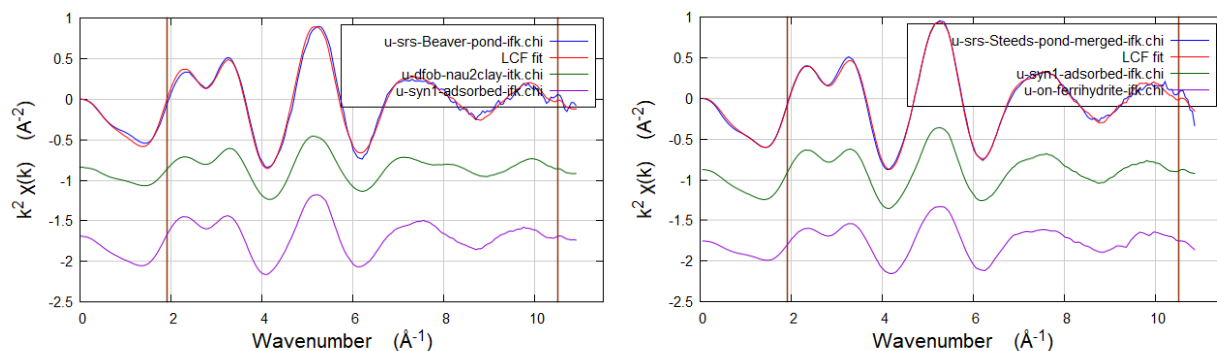


Figure S4: Linear combination analysis of the U XANES data from the sediments using a U(IV) standard (nanoparticulate uraninite; [64]) and a U(VI) standard (U(VI) complexed with DFOB and adsorbed to NAu-1 clay; [33]). The refined proportion of each standard spectrum is shown as % of total U in the solids. Uncertainty is estimated at $\pm 5\%$.



Fit components (standards)	Proportions in sample spectrum	
	Beaver pond (averaged)	Steed pond (averaged)
U ^{VI} adsorbed on montmorillonite clay	0.63	0.64
U ^{VI} complexed to DFOB on clay ^b	0.37	
U ^{VI} adsorbed on iron oxides ^c		0.36
R-factor (goodness of fit indicator)	0.0148	0.0062
χ^2 (goodness of fit indicator)	0.0022	0.0011

Reference: [a] = [30]; [b] = [33]; [c] = [65].

Figure S5: Best fits in the linear combination (LC) analysis of the U EXAFS data from the two sediment areas. The scaled fit components are plotted below the data and fit, the vertical lines indicate the fit range, and the table lists the refined scaling factors. Uncertainty is estimated at $\pm 5\%$. The goodness-of-fit parameters are those calculated by the program ATHENA [35] that was used to perform the LC fits.

Sequential Extraction Procedure

The sequential extraction method used in this study was taken from Miller et al. (1986) and is a modification of ASTM method D 5074-90 [66] and ASTM D-3974-81 [67]. Five extractions (Table S1) were made from each of the 6 sediments. The mass extracted in the first four extraction steps were used to calculate the desorption K_d values (described below).

In an attempt to quantify the fraction of contaminant associated with the mineral matrix, some researchers have used selective extraction techniques; however, these selective or sequential extraction techniques have experimental limitations. Problems with sequential extractions include incomplete extraction of trace elements on mineral surfaces, non-selectivity of extraction reagents for given soil phases, or re-adsorption of extracted contaminants onto other surfaces. Thus, individual sequential extraction “pools” may not adequately represent the discrete soil phase to which the contaminant is bound. The actual concentration extracted may only be assumed to be associated with a given operationally defined phase.

Table S1. Sequential Extraction Procedure

Extractant: Chemical Composition	Targeted Contaminant Fraction	Liquid: Solid	Contact Duration	Ref.
Saturated Paste Extract: D.I. water	Aqueous	0.4:1	1 week	[68]
Dilute-acid Extract: dilute acetic acid [0.44 M CH ₃ COOH + 0.1 M Ca(NO ₃) ₂]	Exchangeable	25:1	1 day	[69]
Organically Bound Extract: sodium pyrophosphate [0.1 M (Na ₄ P ₂ O ₇)]	Bound to Organic Fraction	25:1	1 day	[69]
Amorphous Fe-oxide Extract: acidified ammonium oxalate: pH 3 (0.175 M (NH ₄) ₂ C ₂ O ₄ + 0.1 M oxalic acid (H ₂ C ₂ O ₄)	Associated with amorphous Al- and Fe-oxide	25:1	30 min	[69]
Aqua Regia part HNO ₃ :3 parts HCl:1 part H ₂ O	Structural	24:1	60 °C for 6 hr	[69]

Table S2. Sediment characterization, including pH, organic matter abundance (OM), total organic carbon (TOC), total nitrogen (TN), total free Fe concentrations, and the clay/silt/sand distribution.

	Contaminated Area						
	Steed Pond (SP)				Beaver Pond (BP)		
	#2306	#2300	#2301	#2302	#2303	#2304	#2305
pH	6.13	4.67	5.37	4.75	4.25	4.35	4.37
OM (LOI), % wt	8	22	4	20	30	28	27
TOC, g/kg	22.5	68.4	28.4	43.4	119.9	73.3	103.7
TN, g/kg	1.2	6.7	1.9	3.6	8.3	5.3	6.7
Clay, %-wt	22	27	6	51	41	42	42
Silt, %-wt	37	11	5	7	13	9	17
Sand, %-wt	42	62	89	42	46	49	41
Total Free Fe, %-wt ^a	1.42	1.73	0.24	1.55	3.45	2.79	3.12
XRD Mineralogy ^b	Am>Kao> Qtz>>Gib> Goe>Hem	Kao>Am> Qtz>> Gib> Goe>Hem	Am>Qtz > Kao>>Gib> Goe>Hem	Am>Kao>> Qtz>Gib> Goe>Hem	Kao>Am>> Qtz>Gib > Goe>Hem	Am>Kao>> Qtz >Gib > Goe>Hem	Am >Kao> Qtz>>Gib > Goe>Hem

^a Total Free Fe is a measure of the amorphous and crystalline iron oxides, and it does not include Fe associated with the clay mineral phase.

^b XRD mineralogy represents a ranking of the relative mineral semi-quantitative concentrations. (Am = amorphous, Goe = goethite, Gib = gibbsite, Hem = hematite, Kao = kaolinite, Qtz = quartz). Quantitative results and some additional explanation regarding spectral analyses are provided in Table S3.

XRD Analysis

Goodness of Fit (GOF): The GOF is a measure of how well the modeled data fits the experimental data; a perfect fit has a GOF = 1. GOF does not always correlate to data accuracy because it is possible to produce a better fit by modifying the input parameters to the point at which the model no longer represents reality. There are several reasons why the GOF values are greater than 1 for the analyzed sediments, including:

- Inability to model all the identified phases due to lack of ICDD PDF crystal structure data (i.e., vermiculite and montmorillonite).
- Overlapping peaks.
- Preferred crystal orientation.
- Multiple amorphous phases.
- Fitting of low intensity peaks for minor/trace phases.

For complex natural sediments that have not been pretreated for iron and OM removal, a GOF of <2 may be considered a reasonable fit. For comparison, when performing Rietveld analysis on a fly ash sample for which all the crystalline phases are known, the GOF is still approximately 2.

Finally, the relative percentages reported in Table S2 are more accurate than the absolute percentages. For example, less confidence can be placed on asserting sample #2301 contains exactly 29.1 wt. % quartz, than can be placed on asserting that the wt. % of quartz in #2301 is approximately three times greater than that present in #2302. This distinction is based on the fact that the sample compositions, and therefore the scans, are similar and the same model inputs were used for the analysis of each sample.

Table S3. Mineral composition of the clay-size fraction from contaminated (#2300 - #2305) and upstream (#2306) sediments.

Phase	Weight %						
	#2300	#2301	#2302	#2303	#2304	#2305	#2306
<i>Amorphous</i>	37.9	38.0	41.6	38.4	49.3	40.1	41.3
<i>Gibbsite</i>	7.2	3.8	6.0	5.6	3.9	4.1	4.1
<i>Goethite</i>	3.6	2.1	3.2	4.7	2.8	2.2	2.2
<i>Hematite</i>	0.2	0.0	0.4	0.8	0.5	0.3	0.3
<i>Kaolinite</i>	39.6	27.0	38.4	43.8	35.7	28.7	28.1
<i>Quartz</i>	11.5	29.1	10.3	6.8	7.9	24.5	24.1
<i>Goodness of Fit</i>	1.89	2.13	1.80	1.89	1.71	1.75	1.75

Table S4. Total Ni and U concentrations and their accumulation in contaminated Tims Branch sediments, as well as the desorption coefficient values of U and Ni ($K_{d-desorb}$) and enrichment of Ni and U in clay fraction of sediments.

	Upstream	Contaminated Area					
		Steed Pond (SP)				Beaver Pond (BP)	
		#2306	#2300	#2301	#2302	#2303	#2304
Nickel							
Total Ni, mg-Ni/kg	72	3806	52	3243	850	1416	1278
Clay Ni, mg-Ni/kg-clay	213	3132	543	3016	925	1417	1343
Clay-fraction enrichment ^a	3.0	0.8	10.4	0.9	1.1	1.0	1.1
<i>K_{d-desorb}</i> , L/kg	185±17	-	16±1	32±3	36±2	35±1	33±1
Uranium							
Total U, mg-U/kg	22	7479	71	5218	4022	5535	5069
Clay U, mg-U/kg-clay	57	4952	517	4337	3754	4479	4424
Clay-fraction enrichment ^a	2.6	0.7	7.3	0.8	0.9	0.8	0.9
<i>K_{d-desorb}</i> , L/kg	737±203	-	3544±1430	4071±350	2812±138	3158±101	6275±71
^a Clay-fraction enrichment = C _{clay-U/Ni} / C _{total} ; where C _{clay-U/Ni} is the concentration of U or Ni in the clay fraction of sediments (mg/kg-clay) and C _{clay-U/Ni} is the total U or Ni concentration in the sediments (mg/kg).							

Table S5. Concentrations and solid phase distribution (in %) of different U and Ni fractions.

	Upstream	Contaminated area					
		Steed Pond (SP)				Beaver Pond (BP)	
		#2306	#2300	#2301	#2302	#2303	#2304
Uranium							
Total U, mg-U/kg	22	7479	71	5218	4022	5535	5069
Exchangeable, %	31.2	11.4	29.5	8.4	10.7	9.5	10.3
Organic fraction, %	64.4	58.8	68.5	38.6	71.5	84.4	53.3
Amorph. Fe-oxide, %	4.4	4.3	2.0	1.7	2.8	6.0	2.5
Structural fraction, %	0	25.5	0	51.2	15.0	0	33.9
Nickel							
Total Ni, mg-Ni/kg	72	3806	52	3243	850	1416	1278
Exchangeable, %	35.1	31.7	37.3	15.3	23.8	31.2	20.5
Organic fraction, %	25.8	6.4	27.3	5.3	20.3	12.0	13.3
Amorph. Fe-oxide, %	35.1	31.7	37.3	15.3	23.8	31.2	20.5
Structural fraction, %	4.1	30.1	0	64.1	32.1	25.6	45.8

“n.d.” denotes undetectable.

“-” denotes data is not available.

Additional details related to the sequential extraction procedure provided in Table S1.