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Solid-Phase Chemical Fractionation of Selected Trace Metals in Some Northern Kentucky Soils

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The fractionation and distribution with depth of Cd, Cr, Cu, Ni, Pb, and Zn in 26 soils of Northern Kentucky were determined through a sequential extraction procedure in response to environmental concerns about increasing anthropogenic inputs in a fast-paced, urbanizing area. The selected sites have not received any biosolid- or industrial-waste applications. Average total concentrations per metal in soil profiles derived from alluvial, glacial till, and residual materials ranged from 0.43 to 56.00 mg kg^{-1} *in the sequence Zn > Ni > Pb > Cr > Cu > Cd, suggesting relatively small anthropogenic inputs. The distribution of Cu, Cr, Ni, and Zn increased with soil depth, whereas Cd and Pb remained stable, indicating a strong geological or pedogenic influence. Residual forms were most important for the retention of Cu, Zn, and Ni. Cadmium and Pb exhibited a strong affinity for the Fe-Mn oxide fraction, while Cr showed the strongest association with the organic fraction. In terms of metal mobility and toxicity potential inferred from metal concentrations in labile fractions, Cd posed the greatest risk, followed by Cr ∼ Pb > Ni > Zn > Cu. Soil pH, OM, and clay content were the most important parameters explaining the partitioning of metals in labile and residual fractions, emphasizing the importance of metal fractionation in soil management decisions. Alluvial soils generally contained the highest total and labile metal concentrations, suggesting potential metal enrichment through anthropogenic additions and depositional processes. These environments exhibit the highest risk for metal mobilization due to drastic changes in redox conditions, which can destabilize existing metal retention pools.*

Keywords Sequential extraction, metal distribution, soil depth, parent material.

Introduction

Expanding urbanization and industrialization have caused an increasing awareness of potential soil pollution problems by metals released from emissions or processed wastes. Proper assessment and remediation of associated environmental issues require a thorough understanding of the factors affecting metal accumulation in soils and the conditions and mechanisms contributing to their remobilization into the soil solution. Today it is generally recognized that the particular behavior of trace metals in the environment is determined mostly by their specific physicochemical fractionation and speciation, rather than by their total concentration (Tack and Verloo, 1995). Total metal concentrations appear to be insufficient for the evaluation of exposure risks and the determination of toxic effects because only a specific fraction of the metal may have adverse effects on the environment. On the other hand, chemical speciations provide more important information about the behavior

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and fate of the metals in terms of mobility, bioavailability, toxicity, and chemical reactivity (Winistörfer, 1995).

While soil solution metal speciations are generally more analytically reliable, solid phase speciations are mostly operationally defined due to the complexity of the sorption and precipitation reactions controlling metal phase formation and distribution (Brumner, 1986). Therefore, all experimental techniques used for chemical speciation analysis of metals suffer from their own limitations, conceptual, technical, operational, or analytical (Tack and Verloo, 1995). One of the most widely used procedures involves a series of sequential extractions with various reagents separating the metal forms into exchangeable, acid soluble or carbonate-bound, reducible or oxide-bound, organically complexed, and residual or silicate-bound (Tessier *et al.*, 1979; Calvet *et al.*, 1990). However, selecting different extractants in each sequential step to accommodate various samples and variable extraction times has rendered the results not directly comparable (Msaky and Calvet, 1990). In spite of these limitations, sequential extraction procedures have proved to be quite useful in better understanding and predicting the environmental behavior of metals (Brumner, 1986). Application examples include: (a) assessing retention, mobility, and biocycling patterns in impacted agricultural and forest ecosystems (Belanca *et al.*, 1996; Johnson and Petras, 1998; Cabrera *et al.*, 1999); (b) fingerprinting anthropogenic metal sources (Krumgalz, 1993); (c) identifying critical pools and pathways of metal mobilization (Patterson and Passino, 1986); (d) identifying soil and environmental parameters enhancing or inhibiting metal remobilization and redistribution (Elejalde *et al.*, 1992; Andersen *et al.*, 2002); and (e) establishing metal bioavailability and toxicity indices (Weng *et al.*, 2004).

This study seeks to contribute a preliminary database of soil metal speciation for an area in Northern Kentucky, which has been recently declared by US-EPA (2004) as having a high pollution risk due to increased emissions from accelerated urbanization and industrialization. The results will hopefully provide a baseline reference for monitoring potential increases in trace metal deposition and fingerprinting anthropogenic pollution sources. The objectives of the study were to: (i) determine the speciation and distribution of Cd, Cr, Cu, Ni, Pb, and Zn in representative soils of the area; and (ii) establish relationships between metal speciation and selected soil physicochemical and geomorphological properties.

Materials and Methods

Area Description and Soil Sampling

The survey area included major parts of Boone and Kenton Counties, two of Kentucky's most northern counties, located directly south to southwest of Cincinnati, Ohio, in the Outer Bluegrass Region of Kentucky. Because of increasing development from a mainly rural to a rapidly growing suburban area over the past 20 years, the area has drawn special interest. Increasing interstate and transportation corridors and residential growth due to the close proximity to Cincinnati, increased traffic at the Greater Cincinnati Airport, and the operation of several coal-fired electric power plants have generated concerns about potential heavy metal contamination in the region (US-EPA, 2004).

Twenty-six soil pedons were collected from sites across the survey area. Samples were chosen from different landscape positions and included the following major soil series: Cynthiana, Eden, Faywood, Huntington, Jessup, Nicholson, Rossmoyne, and Wheeling. These soils were selected because of their areal extent and diverse parent material (Table 1).

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Table 1

Soil series, classification, number of pedons sampled and parent material of the soils studied

Soil series	Taxonomic classification	# of pedons	Parent material
Rossmoyne	Fine-silty mixed, superactive, mesic Aquic Fragiudalfs	5	Glacial till
Jessup	Fine, mixed, mesic Typic Hapludalfs	4	Glacial till
Nicholson	Fine-silty, mixed, active, mesic Oxyaquic Fragiudalfs	3	Residuum
Cynthiana	Clayey, mixed, mesic, Lithic Hapludalfs	2	Residuum
Eden	Fine, mixed, active, mesic Typic Hapludalfs	3	Residuum
Faywood	Fine, mixed, active, mesic Typic Hapludalfs	4	Residuum
Wheeling	Fine-loamy, mixed, acive, mesic Ultic Hapludalfs	3	Alluvium
Huntington	Fine-silty, mixed, active, mesic Fluventic Hapludolls	2	Alluvium

The samples were collected from undisturbed sites that had been on pasture for at least 15 years without receiving any waste applications. A Guiddings probe was used to collect triplicate core samples from an area of about 400 m^2 within each site and described by soil horizon. Similarly designated horizons from each core sample were combined to form composite samples from three designated soil depth zones (A, B, and C), representing the surface (Ap), the middle subsoil (Bt/Bw/Btx), and the lowest subsoil or parent material (Bt/Btx/Bw/BC/C) profile section, above a lithic or paralithic contact. These soil depth zones encompassed approximately the range of 0–35 cm for A, 30–70 cm for B, and 70–150 cm for C.

Sequential Extractions

Cadmium, Cr, Cu, Ni, Pb, and Zn were extracted following the sequential procedure developed by Tessier *et al.* (1979) to recover the operationally defined fractions: exchangeable, carbonate-bound, Fe-Mn oxide-bound, organic-bound, and residual. The fractionation scheme employed involved the following steps:

1. *Exchangeable Fraction*. One gram of soil was extracted with 8 ml of pH 7, unbuffered, 1.0 M $MgCl_2$. Samples were placed on a reciprocating shaker for 1 hour at 25°C before centrifugation.
2. *Carbonate-Bound Fraction*. The residue left following the removal of the exchangeable fraction was extracted with 8 ml of 1.0 M NaOAc, and adjusted to pH 5 with acetic acid (HOAc). Samples were then placed on shaker for 6 hours at 25°C before centrifugation.
3. *Fe-Mn Oxide-Bound Fraction*. The residue left after the removal of the carbonate fraction was extracted with 20 ml of 0.04 M NH_2OH-HCl in 25% HOAc (v/v). Samples were heated for 6 hours in a water bath at 96 ± 3°C with occasional agitation before centrifugation.
4. *Organic-Bound Fraction*. The residue left following the separation of the Fe-Mn oxide-bound fraction was extracted with 3 ml of 0.02 M HNO_3 + 5 ml of 30% H_2O_2 adjusted to pH 2 with HNO_3. Samples were heated for 2 hours to 85 ± 2°C with occasional agitation. An additional 3 ml of pH 2, 30% H_2O_2 was added and samples were heated at 85 ± 2°C for 3 more hours with occasional agitation. After cooling, 5 ml of 3.2 M NH_4OAc in 20% (v/v) of HNO_3 was added. Sample volume was brought to 20 ml with de-ionized water and placed on the shaker for 30 minutes before centrifugation.

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5. *Residual Fraction.* The residue left after the removal of the organic-bound fraction was digested with 4 ml of 50% HNO_3 and 10 ml of 20% HCl (US-EPA, 1994). The samples were placed on a shaker for 30 minutes and then heated to 95°C for 30 minutes with periodic mixing of acids and residue. They were allowed to cool down to room temperature before centrifugation.

After each fractionation step the samples were centrifuged for 30 min at 3000 rpm (X 2,500 *g*). Supernatants were pipetted into 100 ml volumetric flasks and brought to 100 ml with de-ionized water. The remaining residue was washed twice with 8 ml de-ionized water following vigorous hand shaking before adding the extractant for the next metal fraction. All glassware was soaked in 14% HNO_3 (v/v) for 24 hours prior to the procedure. All extractions were conducted in duplicate samples.

Analytical Characterizations

Metal concentrations in the supernatants recovered from each fraction were analyzed for Cd, Cr, Cu, Ni, Pb, and Zn, using a Shimadzu GFA-EX7 graphite furnace atomic absorption spectrometer (GFAAS, Kyoto, Japan). In order to minimize matrix effects, multilevel reference standards and de-ionized water blanks were prepared in the same matrix as the extracting reagents for each fraction. The reference standards were prepared from metal chloride reagents of >99% purity obtained from Aldrich Chemicals, Milwaukee, WI. Every six samples the spectrometer was standardized and every 20 samples the burner head was cleaned to remove impurities such as salts that could affect the accuracy of the readings. The detection limits of the GFAAS for the metals studied on a mg kg^{-1} of soil basis were: 0.10 for Cr, Ni, and Pb; 0.05 for Cu; and 0.02 for Cd and Zn.

Soil physicochemical properties of all soil samples included in this study were determined through methods described by the Natural Resources Conservation Service (NRCS, 1996). All samples were air-dried and passed through a 2-mm stainless steel sieve. The organic matter content was determined with a LECO 2000 C-N analyzer, using 0.25-g samples and reference soil standards with known OM content. Soil pH was determined from a 1:1 soil-water suspension with an equilibration period of one hour and the particle size distribution was determined using the pipette method. For the CEC determination, the soil samples were extracted with NH_4OAc at pH 7 and then leached with 10% NaCl at pH 3 (NRCS, 1996).

Statistical Analysis

Multiple linear regression analyses were conducted to develop significant relationships between trace metal speciation and soil physicochemical parameters. Least Significant Difference (LSD) analysis was applied to determine differences of means ($\alpha = 0.10$) in soil profile cumulative total metal concentrations and metal fractions of soils derived from different parent materials (alluvium, glacial till, and residuum).

Results and Discussion

Soil Properties

The means of selected soil properties as a function of profile depth grouped by parent material are shown in Table 2. Generally, there was a tendency for pH and OM content to

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Table 2
Means ± SD for selected soil parameters of the sites studied grouped by parent material

Parent material	Number of pedons	Soil depth	pH	OM[†] %	Sand %	Silt %	Clay %	CEC[‡] cmol_c/kg	CEC/Clay
Alluvium	5	Surface	6.6 ± 0.5	4.08 ± 1.2	26.8 ± 12.5	54.8 ± 10.9	18.4 ± 3.7	19.9 ± 4.5	1.57 ± 0.31
		Middle	6.9 ± 0.4	2.80 ± 0.8	16.8 ± 7.8	59.4 ± 11.7	23.7 ± 4.2	16.0 ± 4.3	0.74 ± 0.23
		Lowest	6.5 ± 0.4	1.70 ± 0.4	13.4 ± 7.5	61.1 ± 9.7	25.5 ± 4.0	16.0 ± 3.5	0.67 ± 0.20
		All	6.7 ± 0.4	2.86 ± 0.8	18.8 ± 9.2	58.9 ± 10.2	22.5 ± 4.0	17.3 ± 4.2	0.99 ± 0.24
Glacial till	9	Surface	5.8 ± 0.2	3.26 ± 0.5	12.1 ± 5.6	71.0 ± 7.6	16.9 ± 5.4	17.3 ± 3.7	1.07 ± 0.27
		Middle	5.1 ± 0.6	0.43 ± 0.3	9.8 ± 3.8	55.6 ± 6.3	34.5 ± 7.2	19.8 ± 3.1	0.59 ± 0.18
		Lowest	6.3 ± 0.4	0.60 ± 0.3	8.8 ± 4.1	41.6 ± 6.3	49.6 ± 6.7	28.2 ± 2.5	0.57 ± 0.21
		All	5.7 ± 0.5	1.43 ± 0.4	10.3 ± 4.5	56.0 ± 6.8	33.6 ± 6.5	21.8 ± 3.1	0.74 ± 0.19
Residuum	12	Surface	5.9 ± 0.7	3.69 ± 0.4	13.0 ± 4.7	64.1 ± 7.2	22.8 ± 3.5	21.8 ± 2.9	1.02 ± 0.25
		Middle	5.9 ± 0.5	1.01 ± 0.2	7.8 ± 3.3	53.3 ± 7.8	38.9 ± 9.2	23.3 ± 3.8	0.63 ± 0.17
		Lowest	6.5 ± 0.3	1.32 ± 0.2	10.4 ± 4.1	45.7 ± 6.4	43.9 ± 7.3	22.9 ± 5.6	0.52 ± 0.13
		All	6.1 ± 0.5	2.01 ± 0.3	10.4 ± 4.0	54.4 ± 7.0	35.2 ± 7.2	22.7 ± 4.1	0.72 ± 0.18

[†] Organic matter.

[‡] Cation exchange capacity.

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be lowest in glacial till soils and highest in alluvial soils, while clay content and CEC were highest in residual soils and lowest in alluvial soils. Organic matter was highest in surface depth zones, while pH and clay content usually increased with depth. Soils from the same parent material were grouped together because they did not show statistically significant differences ($p < 0.05$).

Metal Fractionation and Distribution with Depth

Mean concentrations ± standard deviation (mg kg^{-1}) of different metal species by soil depth zone for all 26 pedons combined are shown in Table 3. The percent contribution of each metal fraction to the total concentration of the metal (expressed as the sum of all fractions) in the soil in each depth zone is reported in Table 4. Multiple linear regressions between selected soil parameters and the most mobile metal fractions explaining more than 60% of the variability in their distribution at different soil depth zones are listed in Table 5. Since most of the soils studied were lacking carbonates, this fraction may account for metal

Table 3

Average metal concentrations (mg kg^{-1}) and standard deviations in various fractions[†] extracted at different soil depths[‡] and average cumulative totals for the total soil profile (TSP)[§]

	Cd	Cr	Cu	Ni	Pb	Zn
EXCH						
A	0.07 ± 0.11	0.14 ± 0.14	BDL[#]	1.03 ± 1.50	1.26 ± 2.36	0.50 ± 0.50
B	0.05 ± 0.11	0.13 ± 0.13	BDL[#]	0.73 ± 1.21	1.68 ± 3.13	0.23 ± 0.38
C	0.07 ± 0.18	0.14 ± 0.13	BDL[#]	0.90 ± 1.34	0.75 ± 1.66	0.24 ± 0.34
ABC	0.06 ± 0.14	0.14 ± 0.13	BDL[#]	0.89 ± 1.35	1.23 ± 2.81	0.33 ± 0.43
CARB						
A	0.03 ± 0.06	0.11 ± 0.08	0.06 ± 0.19	0.22 ± 0.30	0.88 ± 0.63	1.75 ± 5.45
B	0.07 ± 0.12	0.13 ± 0.18	0.19 ± 0.39	0.45 ± 0.69	1.22 ± 1.08	2.23 ± 4.36
C	0.11 ± 0.16	0.15 ± 0.19	0.22 ± 0.44	0.71 ± 0.81	1.79 ± 1.74	1.04 ± 3.91
ABC	0.07 ± 0.12	0.13 ± 0.16	0.16 ± 0.36	0.46 ± 0.66	1.30 ± 1.28	1.29 ± 4.57
FMOX						
A	0.13 ± 0.11	2.35 ± 1.26	1.03 ± 0.63	3.38 ± 3.39	8.90 ± 3.19	7.77 ± 4.84
B	0.14 ± 0.19	3.94 ± 2.83	2.49 ± 0.85	4.62 ± 6.11	6.17 ± 6.43	4.95 ± 5.56
C	0.16 ± 0.23	3.22 ± 1.84	2.66 ± 1.12	7.24 ± 5.65	5.75 ± 7.38	7.26 ± 6.12
ABC	0.14 ± 0.18	3.17 ± 2.16	2.06 ± 1.15	5.08 ± 5.37	6.94 ± 6.03	6.66 ± 5.60
ORG						
A	0.05 ± 0.15	8.24 ± 5.83	1.58 ± 2.50	4.28 ± 6.65	2.81 ± 2.02	8.67 ± 20.20
B	BDL[#]	8.31 ± 6.61	1.57 ± 3.27	4.30 ± 7.28	2.29 ± 2.50	7.97 ± 26.30
C	0.03 ± 0.14	7.20 ± 6.33	1.24 ± 3.07	5.49 ± 6.99	2.68 ± 3.20	8.35 ± 24.00
ABC	0.03 ± 0.12	7.92 ± 6.20	1.46 ± 2.93	4.69 ± 6.91	2.59 ± 2.59	8.33 ± 23.30
RES						
A	0.14 ± 0.37	5.58 ± 3.90	8.56 ± 6.10	9.74 ± 5.72	8.97 ± 5.88	33.10 ± 12.90
B	0.16 ± 0.43	12.50 ± 17.20	15.00 ± 11.90	17.20 ± 11.10	12.10 ± 7.76	41.20 ± 16.10
C	0.10 ± 0.27	10.01 ± 5.97	15.70 ± 13.60	19.60 ± 14.00	10.10 ± 5.89	43.90 ± 18.40
ABC	0.13 ± 0.36	9.39 ± 11.00	13.10 ± 11.30	15.50 ± 11.20	10.40 ± 6.61	39.40 ± 16.40
TSP[§]	(0.43 ± 0.18^{d})	(20.75 ± 3.93^{bc})	(16.81 ± 3.16^{c})	(26.62 ± 5.10^{b})	(22.46 ± 3.86^{bc})	(56.01 ± 10.06^{a})

[†] EXCH = Exchangeable; CARB = "Carbonate"; FMOX = Fe-Mn; ORG = Organic; RES = Residual.

[‡] A = surface horizons; B = middle horizons; C = lowest horizons; ABC = all horizons.

[§] TSP = Average cumulative total metal concentrations ± SD in all fractions of A, B, and C soil depths (values followed by a different letter are significantly different at $\alpha = 0.10$).

[#] BDL = Below Detection Limit.

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Table 4
Percent contribution of each fraction to the total metal concentration

	Cd	Cr	Cu	Ni	Pb	Zn
EXCH[†]						
A[‡]	16.7	0.9	0.0[#]	5.5	6.5	1.0
B	11.9	0.6	0.0[#]	2.7	7.2	0.4
C	14.9	0.7	0.0[#]	2.7	3.6	0.4
ABC	14.0	0.7	0.0[#]	3.3	5.5	0.6
CARB						
A	7.1	0.7	0.5	1.2	3.9	3.4
B	16.7	0.5	1.0	1.6	5.2	3.9
C	23.4	0.7	1.1	2.1	8.5	1.7
ABC	16.3	0.6	1.0	1.7	5.8	3.0
FMOX						
A	31.0	14.2	9.2	18.1	39.0	15.0
B	33.3	15.7	12.9	16.9	26.3	8.7
C	34.0	15.5	13.4	21.5	27.3	11.9
ABC	32.6	15.3	12.3	19.2	30.9	11.8
ORG						
A	11.9	50.2	14.1	22.9	12.3	16.7
B	0.0[#]	33.2	8.1	15.8	9.8	14.1
C	6.4	34.6	6.2	16.4	12.7	13.7
ABC	7.0	38.2	8.7	17.6	11.5	14.8
RES						
A	33.3	34.0	76.2	52.3	38.3	63.9
B	38.1	50.0	77.8	63.0	51.5	72.9
C	21.3	48.5	79.1	57.3	47.9	72.3
ABC	30.1	45.2	77.8	58.2	46.3	69.8

[†] EXCH = Exchangeable; CARB = "Carbonate"; FMOX = Fe-Mn; ORG = Organic; RES = Residual.

[‡] A = surface horizons; B = middle horizons; C = lowest horizons; ABC = all horizons.

[#] Fractions with metal concentrations below the detection limit were assumed to have 0 contribution.

associations with sulfate, sulfide, chloride and phosphate minerals (Tessier *et al.*, 1979). However, the term "carbonate fraction" was retained in this discussion for consistency with the method employed.

Cadmium. Cadmium exhibited by far the lowest overall total concentrations among the metals, averaging <1.0 mg kg^{-1} in the soil profile. The highest amounts of Cd were associated with the Fe-Mn-oxide-bound and the residual fraction, making up about 2/3 of the overall total Cd content (Tables 3 and 4). Cadmium distribution followed the sequence, Fe-Mn-oxide = residual > "carbonate" = exchangeable > organic fraction, which is consistent with the findings of Jenne (1968) and Shuman (1979). The Fe-Mn oxide-bound Cd fraction was evenly distributed with depth, while residual Cd was lowest in the C depth zone. Cadmium in the Fe-Mn fraction was mainly correlated to pH in the A soil zone, and

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Table 5

Multiple linear regression relationships between metal concentration in the relatively mobile fractions and soil parameters explaining more than 60% of the variability at different soil depths

Fraction	Metal	Equation	R^2
Surface horizon			
Exchangeable	Cd	$= 0.02 + 0.06\,\text{pH} - 0.003\,\text{clay\%} - 0.004\,\text{silt\%}$	0.62^{***}
Fe-Mn oxide	Cd	$= 0.24 + 0.07\,\text{pH} - 0.006\,\text{CEC} - 0.006\,\text{silt\%}$	0.73^{***}
	Ni	$= 12.70 + 2.19\,\text{pH} - 0.31\,\text{CEC} - 0.25\,\text{silt\%}$	0.87^{***}
	Zn	$= -3.05 + 1.48\,\text{pH} + 2.07\,\text{OM} - 0.28\,\text{CEC}$	0.63^{***}
Organic	Cu	$= 13.00 + 1.13\,\text{OM} - 0.32\,\text{CEC} - 0.14\,\text{silt\%}$	0.89^{***}
	Ni	$= 16.44 + 2.65\,\text{OM} - 0.36\,\text{clay\%} - 0.22\,\text{silt\%}$	0.76^{***}
	Pb	$= -8.72 + 1.76\,\text{pH}$	0.70^{***}
	Zn	$= 49.07 - 5.24\,\text{OM} - 0.72\,\text{silt\%} + 22.15\,\text{CEC/clay}$	0.96^{***}
Middle horizon			
Exchangeable	Cd	$= 0.09 - 0.04\,\text{pH} + 0.08\,\text{OM} + 0.005\,\text{CEC}$	0.87^{***}
	Ni	$= -1.13 + 0.50\,\text{OM} + 0.06\,\text{CEC}$	0.67^{***}
	Zn	$= 0.81 - 0.20\,\text{pH} + 0.25\,\text{OM} + 0.46\,\text{CEC/clay}$	0.92^{***}
Fe-Mn oxide	Cd	$= -0.18 + 0.09\,\text{OM} + 0.34\,\text{CEC/clay}$	0.90^{***}
	Cr	$= 12.07 - 1.79\,\text{pH} + 1.98\,\text{OM}$	0.80^{***}
	Ni	$= -4.66 + 3.31\,\text{OM} + 0.16\,\text{clay\%}$	0.84^{***}
	Pb	$= 25.09 - 4.28\,\text{pH} + 5.20\,\text{OM}$	0.93^{***}
	Zn	$= 1.31 + 3.15\,\text{OM}$	0.89^{***}
Organic	Ni	$= -1.28 + 2.53\,\text{OM} - 0.25\,\text{silt\%} + 25.87\,\text{CEC/clay}$	0.93^{***}
	Pb	$= -2.08 + 1.04\,\text{OM} + 4.99\,\text{CEC/clay}$	0.85^{***}
	Zn	$= 197.47 - 0.38\,\text{CEC} - 2.20\,\text{clay\%} - 1.91\,\text{silt\%}$	0.70^{***}
Lowest horizon			
Exchangeable	Cd	$= -0.14 - 0.04\,\text{pH} + 0.11\,\text{OM} + 0.57\,\text{CEC/clay}$	0.82^{***}
	Ni	$= -2.28 + 0.36\,\text{OM} + 4.87\,\text{CEC/clay}$	0.66^{***}
	Zn	$= 1.40 - 0.26\,\text{pH} + 0.22\,\text{OM} + 0.47\,\text{CEC/clay}$	0.82^{***}
Fe-Mn oxide	Cd	$= -0.40 + 0.12\,\text{OM} + 0.74\,\text{CEC/clay}$	0.82^{***}
	Cr	$= -3.42 + 0.83\,\text{OM} + 0.04\,\text{clay\%} + 6.80\,\text{CEC/clay}$	0.73^{***}
	Ni	$= -27.23 + 3.90\,\text{pH} + 0.19\,\text{CEC} + 8.86\,\text{CEC/clay}$	0.74^{***}
	Pb	$= 6.14 - 2.91\,\text{pH} + 4.57\,\text{OM} + 23.04\,\text{CEC/clay}$	0.86^{***}
	Zn	$= -19.30 + 2.21\,\text{pH} + 1.50\,\text{OM} + 18.74\,\text{CEC/clay}$	0.71^{***}
Organic	Cd	$= -0.33 + 0.07\,\text{OM} + 0.49\,\text{CEC/clay}$	0.84^{***}
	Cu	$= -6.94 + 1.51\,\text{OM} + 11.38\,\text{CEC/clay}$	0.84^{***}
	Pb	$= -5.76 + 1.32\,\text{OM} + 12.19\,\text{CEC/clay}$	0.78^{***}

$^{***}, ^{**}, ^{*} = P < 0.01$, <0.05, and <0.10, respectively.

OM or CEC/clay in the lower (B and C) depth zones. Cadmium adsorption by Mn-oxides has been reported to increase linearly with pH, while organic coatings present on Fe-Mn particle surfaces may enhance metal retention (Manceau *et al.*, 1992). However, significant associations of Cd with the organic and "carbonate-bound" fraction have been observed only in soils with >50 mg kg^{-1} total Cd content (Lindsay, 1979; Ma and Rao, 1997). In contrast, adsorption onto clay and Fe-Mn oxide particle surfaces is a more important Cd

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retention mechanism in non-polluted soils (Alloway, 1995). Because of the low overall Cd concentrations and their main association with the Fe-Mn and the residual fraction, toxicity problems attributed to Cd are not expected to occur, unless deterioration in drainage conditions causes the reduction of Fe or Mn and result in Cd mobilization. In spite of relatively low exchangeable levels, Cd showed a stronger association with the exchangeable fraction than any other metal (Hickey and Kittrick, 1984). This association was generally higher in A and C depth zones as a result of pH changes and organic matter or clay increases, as was indicated by multiple regression analysis (Table 5). These factors have been shown to play significant roles in specific Cd adsorption (Kuo *et al.*, 1983; Alloway, 1995). Considering that the exchangeable Cd fraction is also regarded as a sensitive indicator of plant uptake and bioavailability, the Cd concentrations found in this study are considerably lower than the lowest reported toxic soil levels (8 mg kg^{-1}), suggesting low toxicity risks in the soil environment (Kabbata-Pendias and Pendias, 1972; Stover *et al.*, 1976). Cadmium was also the only metal to have relatively high contributions to the "carbonate fraction," with an increasing trend with soil depth. In spite of the low overall levels of Cd in the soil profile, its mobility and toxicity potential was the highest among the metals since the non-residual metal fraction accounted for nearly 70% of the total Cd concentration.

Chromium. Chromium was the fourth overall metal in abundance after Zn, Ni, and Pb, averaging 20.8 mg kg^{-1} in the soil profile. The most common and stable forms of Cr in natural environments are Cr(III) and Cr(VI) (Lindsay, 1979). The latter exists in anionic form, and therefore it is easier to extract and more toxic than Cr(III), which as a cation shows a tendency to precipitate and a greater affinity for retention by the soil matrix (Alloway, 1995). In the soils studied, Cr was found in highest concentrations in the organic and residual fraction, with average contributions to the total Cr concentrations between 38 and 45%, respectively. The distribution of Cr in the residual fraction showed an increasing trend with depth, while the highest amounts of organic-bound Cr were found in the soil surface (Tables 3 and 4). In natural soil environments, Cr is present as a structural impurity in a variety of alumino-silicate minerals, or chromite, a resistant Cr-oxide mineral account for most of the residual Cr fraction (Kabata-Pendias and Pendias, 1992). Chromium also showed the highest affinity for the organic fraction (Tables 3–5), which is related to its strong chelating capacity, and the role played by the organic matter as an electron donor in the reduction of Cr^{6+} to Cr^{3+} (Kabata-Pendias and Pendias, 1992). The Fe-Mn-oxide fraction was the third largest contributor to Cr retention, averaging $\sim$15% of the total Cr concentration and being distributed relatively evenly throughout the soil profile. Chromate ions can be easily sorbed to hydrous oxide surfaces at pH levels >4, while Cr^{3+} tends to coprecipitate with Fe- or Al-hydroxides because its ionic size and geochemical properties are very similar to those of Fe^{3+} and Al^{3+} (Kabata-Pendias and Pendias, 1992). This is supported by multiple regression analysis showing a strong dependence of the Fe-Mn-oxide-bound Cr on pH, OM, and clay content, particularly in B and C soil depth zones (Table 5). Very small amounts of Cr were found in the exchangeable and the "carbonate-bound" fraction. This is not surprising because at the soil pH levels encountered (5.8–6.4), Cr^{3+} precipitates readily (McGrath and Cegarra, 1992), while carbonate minerals were absent in most soils studied. High contributions of Cr in the organic fraction may raise concerns about its bioavailability and toxicity, particularly under conditions of accelerated OM decomposition. Furthermore, Cr can be mobilized to lower soil depths through chelation by humic acids. Chromium was the second overall metal after Cd in mobility and toxicity potential, considering that nearly 55% of the total concentration was present in the non-residual fraction. However, the oxidation state of Cr must be defined before reliable Cr toxicity assessments can be made.

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Copper. Total Cu concentrations in the soil profile averaged 16.8 mg kg^{-1}, being the second lowest metal after Cd (Table 3). Copper exists mainly as Cu^{2+} in natural environments. In spite of the general perception that Cu is usually associated with organic and inorganic particle surfaces (Harter, 1979; Hickey and Kittrick, 1984), nearly 78% of Cu in this study was found in the residual fraction with a noticeable increase with depth (Table 4). High concentrations of Cu in the residual fraction reported by Gupta and Chen (1975), and Shuman (1979), were attributed to Cu-Al substitutions in the structure of alumino-silicate minerals (Harter, 1979). The Fe-Mn oxide and organic fractions were the other two significant contributors, but with significantly lower Cu concentrations compared to the residual fraction. The association of Cu with Fe-Mn oxides is attributed to Cu^{2+}-Fe^{2+} competitive sorption or co-precipitation processes (Taylor, 1965), while the increasing trend with depth is explained by the enrichment of lower soil depths with concretionary material. Copper associated with the organic fraction decreased with soil depth following the organic carbon distribution pattern. Organic matter, pH, and CEC or CEC/clay showed significant correlations with the retention of Cu to the organic fraction, emphasizing the importance of chelation and complexation reactions for Cu retention in soils (Kabata-Pendias and Pendias, 1992). The participation of Cu in the exchangeable and "carbonate" fractions was either negligible or not detectable. Since Cu was mainly associated with the residual and the Fe-Mn oxide fractions, which are relatively insoluble under natural conditions, its status in the soils studied is considered stable. Copper bound to the Fe-Mn oxide fraction could be mobilized if the soil drainage conditions deteriorate causing Fe and Mn reduction, but Cu toxicity problems are unlikely to occur.

Nickel. Nickel was the second highest metal in abundance (after Zn), averaging 26.6 mg kg^{-1} in the soil profile. As was the case for all metals except Cd, the residual fraction was the main sink of Ni, accounting for 58.2% of the total Ni concentration in the soil profile (Tables 3 and 4) (Hickey and Kittrick, 1984). Residual Ni concentrations in subsoil horizons were nearly double of those in the soil surface, probably due to the general trend of pH increases with depth (McGrath and Cegarra, 1992). According to Gupta and Chen (1975) and Tessier *et al.* (1980), the origin of Ni in natural soil environments is mainly detrital, where it is usually found as an occlusion in the structure of weathering silicate minerals (Norrish, 1975). This association was supported in this study by significant correlations between residual Ni concentrations and clay content, which increased substantially with depth (Table 2). The Fe-Mn oxide fraction was the next most important Ni retention contributor, with an average soil profile contribution of 19.2% of the total Ni concentration. This trend is consistent with the findings of other investigators reporting that hydrous Fe and Mn oxides are of secondary importance after the residual fraction as a sink of Ni, accounting for about 20% of the total soil Ni content (Hickey and Kittrick, 1984; McGrath and Cegarra, 1992). Multiple regression analysis showed that pH was the main soil parameter controlling Ni retention in the Fe-Mn oxide fraction, while OM, clay content, and CEC were secondary contributors. The sorption of Ni on Fe-Mn oxide surfaces usually occurs through Ni^{2+} substitutions of Mn, which must have been enhanced by the elevated pH of subsoil horizons (Jenne, 1968; McKenzie, 1979). This is consistent with the findings of other investigators suggesting that Ni mobilized during weathering processes is mainly co-precipitated with Fe-Mn oxide minerals (Kabata-Pendias and Pendias, 1992). The organic matter effect is attributed to the presence of organic coatings on the Fe-Mn oxide surfaces, which offer additional metal binding sites. Similarly, Fe-Mn oxide coatings present on clay particle surfaces may explain the Ni contributions of clay and CEC in the Fe-Mn oxide fraction. These trends are supported by the concurrent increases of clay, CEC,

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and Ni in the Fe-Mn oxide fraction with depth (Table 3). The organic fraction also contained significant Ni concentrations accounting for 17.6% of total Ni in the soil profile. Although the % contributions to the total Ni fraction were highest in soil surface horizons, actual Ni concentrations in the organic fraction peaked in the lowest soil depth (C), possibly due to association with illuviated organic colloidal particles. Multiple regression analysis suggested OM as the main predictor of organic-bound Ni concentrations, while silt, clay, and CEC had a negative influence on the association (Table 5). In spite of the small amounts of Ni contained in the exchangeable and "carbonate fraction," they were the second (after Pb) and third (after Pb and Zn) largest, respectively, compared to other metals (Table 3). Organic matter and CEC as the main contributors to the total soil exchangeable charge were good predictors of Ni concentrations in the exchangeable fraction (Table 5). The mobility and bioavailability potential of this metal should be of concern in the soils studied, particularly if the soil pH drops significantly or OM-Ni complexes are subjected to induced oxidation conditions.

Lead. Although Pb was the third overall metal in abundance after Zn and Ni, it was the only metal with average soil profile concentrations >1 mg kg^{-1} in every fraction. As with most metals the highest amounts of Pb were associated with the residual fraction, accounting for nearly half of the total Pb concentration (Tables 3 and 4). Residual Pb concentrations peaked in the middle soil depth (B), correlating well with increases in clay, CEC and pH, although similar increases were also observed in lower soil depths (C) (Table 2). Lead exists predominantly as Pb^{2+} in the environment, but when oxidized to Pb^{4+} it can be incorporated in clay mineral and Fe-Mn oxide structures (Norrish, 1975; Kabata-Pendias and Pendias, 1992). The Fe-Mn oxide fraction was the second most important sink for Pb, averaging >30% of the total Pb concentration in the soil profile (Tables 3 and 4). Levy *et al.* (1992) listed the Fe-Mn oxide fraction as playing a dominant role for Pb retention, but they did not analyze the residual Pb fraction. Unlike the distribution of other metals associated with the Fe-Mn oxide fraction, Pb showed the highest levels in the soil surface and a gradual decrease with depth. Multiple regression analysis suggested that lower pH and higher OM in the soil surface may be responsible for this trend (Table 5). The organic-Pb fraction accounted for 11.5% of the total Pb concentration, showing the highest levels in the surface and the lowest soil depth, where OM or clay content were the highest. Multiple regression analysis suggested a positive pH effect on Pb-OM associations in the surface, apparently as a result of pH-dependent charge increases. Increases in organic-Pb concentrations in subsoil horizons may be attributed to the presence of organic coatings on clay surfaces or the migration of organic colloidal particles. This is supported by the results of multiple regression analysis, indicating OM and CEC/clay as good predictors of organic-bound Pb (Table 5). The exchangeable and "carbonate" Pb fractions averaged 1.3 mg kg^{-1}, accounting for about 5.5% each of the total Pb concentration in the soil profile. Exchangeable Pb concentrations peaked in the middle soil depth (B), while "carbonate-bound" Pb levels increased gradually with depth. Although neither fraction was significantly correlated with any soil parameters, their distribution with soil depth is probably influenced by soil pH levels, which were generally lower in middle soil depths, particularly in glacial till and residual soils. According to Ullrich *et al.* (1999), a threshold pH of 6 or less is required before significant increases in Pb or Zn can be detected in the exchangeable fraction. The elevated concentrations of Pb found in the relatively labile fractions (exchangeable, "carbonate," organic) of these soils suggest an increased risk for potential toxicity problems as a result of acidification from natural weathering or anthropogenic deposition processes.

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Zinc. Zinc was the most abundant metal in the soils studied with average total concentrations of 56.0 mg kg^{-1}. Like most other metals, the majority of Zn was present in the residual fraction, accounting for nearly 70% of the total concentration in the soil profile and with an increasing trend with soil depth (Tables 3 and 4). Dominantly residual associations of Zn in uncontaminated soils, particularly with clay minerals, have also been reported by Ma and Rao (1997), while $Zn(OH)_2$, $ZnCO_3$, and $Zn(PO_4)$ phases have been found mainly in contaminated soils (Gupta and Chen, 1975; Kabata-Pendias and Pendias, 1992). The organic and the Fe-Mn oxide fractions were the next most important contributors in Zn retention, accounting for ~15% and 12%, respectively, of the total Zn concentration in the soil profile. For both fractions the highest Zn concentrations were observed in the surface and lowest soil depths, suggesting strong associations with organic and clay particle surfaces (Kabata-Pendias and Pendias, 1992). The retention of Zn in the Fe-Mn oxide fraction is explained by the high stability constants of Zn oxides and the ability of Zn to replace Mn in the oxide surface (Ma and Rao, 1997). Multiple regression analysis suggested strong effects by pH and OM (apparently through pH-dependent charge increases and coatings) on Zn retention in the Fe-Mn oxide fraction (Table 5). The influence of CEC/clay is probably indirect through Fe-Mn coatings on clay particle surfaces. Relatively low levels of Zn were associated with the "carbonate fraction" (most likely phosphate-bound) and even lower with the exchangeable fraction, contributing 3% and 0.6%, respectively, in the total Zn concentration. Increases in exchangeable Zn were generally affected by pH decreases and elevated clay mineral and organic surface charge contributions (Table 5). Considering the low levels of Zn in the non-residual fraction of these soils, toxic effects are unlikely, unless significant acidification or accelerated organic matter decomposition takes place.

Parent Material Effects on Metal Speciation

Metal concentrations in different soil fractions for the entire soil profile and individual soil depths derived from different parent materials were compared statistically using the LSD

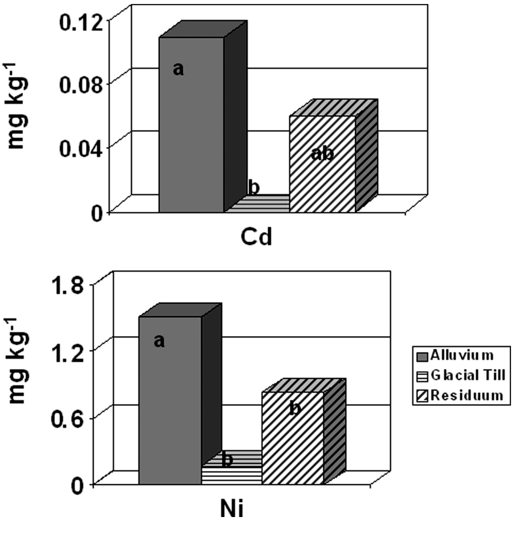

Figure 1. Average concentrations (mg kg^{-1}) for Cd and Ni in the exchangeable fraction of middle soil depths (B) and statistical differences ($\alpha = 0.10$) among parent materials.

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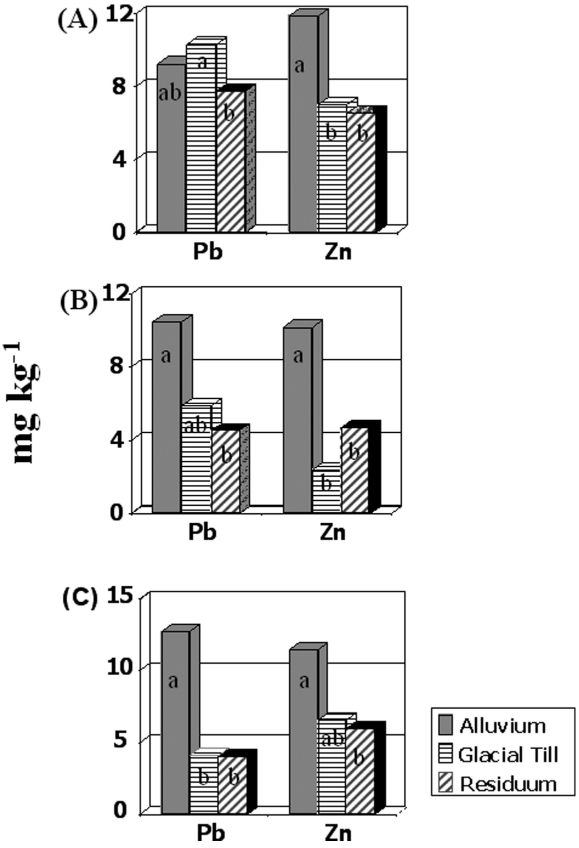

Figure 2. Average concentrations (mg kg^{-1}) for Pb and Zn in the Fe-Mn oxide fraction of surface soil horizons (A), middle soil depths (B), and the lowest soil depths (C), and statistical differences ($\alpha = 0.10$) among parent materials.

test at $\alpha = 0.10$ probability. As a general trend, alluvial soils showed significantly higher metal concentrations than other parent materials in most fractions (Figures 1–4). This may be evidence for anthropogenic influence since aquatic depositional processes constitute

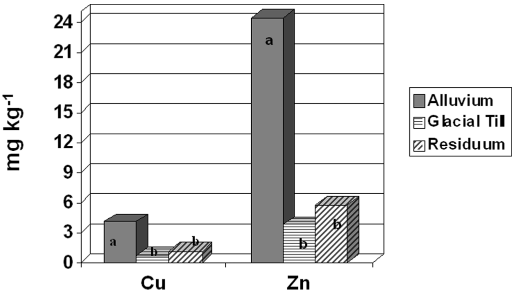

Figure 3. Average concentrations (mg kg^{-1}) for Cu and Zn in the organic fraction of surface soil horizons (A), and statistical differences ($\alpha = 0.10$) among parent materials.

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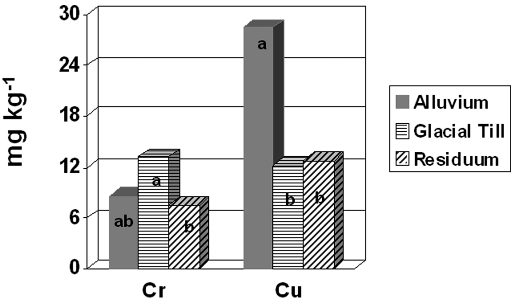

Figure 4. Average concentrations (mg kg^{-1}) for Cr and Cu in the residual fraction of the lowest soil depths (C), and statistical differences ($\alpha = 0.10$) among parent materials.

common avenues for non-point source pollution and depositional environments are some of the most vulnerable to contamination.

In the exchangeable fraction the most significant differences were observed for Cd and Ni retained in the middle soil depths (B), which were highest in alluvial soils and lowest in the glacial till-derived soils (Figure 1). Residual soils exhibited moderate exchangeable metal concentrations. This trend was clearer in middle rather than surface soil depths, most likely due to clay increases in conjunction with the maintenance of elevated organic carbon contents (Table 2). Another contributing factor may be the higher overall pH of middle soil depths in alluvial soils, which may enhance pH- dependent charge interactions. In the Fe-Mn oxide fraction parent material effects on metal speciation were more prominent between Pb and Zn distributions (Figure 2). In surface soil horizons Pb distribution was not that strikingly different between soils, but still higher in glacial till than in residual soils. However, Zn associated with Fe-Mn oxides in the soil surface was nearly twice as high in alluvial soils compared to other parent materials. Similar enrichments of the Fe-Mn oxide fraction in Pb and Zn were also evident in middle and lower depths of alluvial soils. Although this fraction is not one of the most labile when considering toxicity risks, alluvial soil environments are susceptible to drastic redox changes, which upon Fe and Mn reduction may cause significant mobilization of Pb and Zn. The parent material influence on Cu and Zn retention in the organic fraction was more evident in surface soil horizons, with the alluvial soils containing 3–4 times higher levels of Cu and Zn than other soils, respectively (Figure 3). Considering that alluvial soil environments are subject to considerable fluctuations in redox conditions, mobilization risks for these metals may increase during extended droughts through accelerated OM decomposition, or OM transport by flooding waters to better oxidized environments. Alluvial soils contained the highest levels of Cu in the residual fraction of the lowest soil depths, emphasizing the influence of depositional processes throughout the soil profile (Figure 4). In contrast, Cr retention in the residual fraction of lower soil depths was significantly higher in soils derived from glacial till compared to those formed in residual materials, probably associated with the highest amounts in clay content (Table 2).

Conclusions

Total metal concentrations in soil profiles derived from alluvial, glacial till, and residual materials were within the low to middle range baseline levels reported for US soils, with potential anthropogenic inputs in alluvial soils only. The distribution of Cu, Cr, Ni, and Zn

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increased with soil depth, whereas Cd, and Pb levels were steady throughout the soil profile. The residual was the largest overall fraction for the retention of Cu, Zn, and Ni, while $>50\%$ of Pb, Cr, and Cd was associated with labile metal fractions. In terms of metal mobility and toxicity potential, based on metal concentrations in the non-residual fraction Cd posed the greatest risk, followed by $\mathrm{Cr} \sim \mathrm{Pb} > \mathrm{Ni} > \mathrm{Zn} > \mathrm{Cu}$. Soil pH, OM, and clay content were the most important parameters explaining the partitioning of metals in labile and residual fractions, emphasizing the importance of metal fractionations in soil management decisions. While natural weathering processes have a relatively small and gradual impact on metal speciations, significant changes may occur as a result of fertilization, tillage, biosolid or industrial waste applications, mining activities, and emissions. In general, alluvial soils contained the highest total metal concentrations and considerably higher levels of Cd, Ni, Pb, Zn, and Cu in the non-residual fraction of most soil horizons. This suggests potential metal enrichment through alluvial depositional processes since fluvial environments often represent storage areas for potentially contaminated materials. These environments also exhibit the highest risk for metal mobilization and potential toxicity because they are subject to drastic redox potential changes that can destabilize exchangeable, carbonate, organic, and Fe-Mn oxide metal retention pools.

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