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Concentration and Distribution of Six Trace Metals in Northern Kentucky Soils

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Concentration and distribution of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) were determined in 26 soil profiles (n = 78) of northern Kentucky in response to environmental concerns about increasing anthropogenic inputs in a fast-paced urbanizing area. The selected sites represent alluvial, glacial till or residual soils that have not received any biosolid- or industrial-waste applications. Mean concentrations of Zn (53.8 mg kg^{-1}) and Ni (25.9 mg kg^{-1}) were the highest in the soil profile, whereas Cd (0.21 mg kg^{-1}) was present only in trace amounts. All metals were within the low to middle range of baseline concentrations reported for US soils, suggesting minimal anthropogenic inputs. The distribution of Cu, Cr, Ni, and Zn increased with soil depth, whereas Cd and Pb concentrations were unaffected throughout the soil profile. Alluvial soils had the highest overall metal accumulations, particularly in surface soil horizons, indicating potential metal enrichment through depositional processes. The presence of a fragipan horizon or depth to bedrock did not significantly affect metal retention. Single correlation and multiple regression analyses indicated OM and pH as the most influential soil parameters for metal retention, followed by cation exchange capacity (CEC) and CEC/clay. Single correlations among metals suggested strong covariance of Zn with most metals throughout the soil profile, but weaker for Pb and Ni.

Keywords Trace metals, background levels, parent material, soil depth, fragipan.

Introduction

Elevated concentrations of trace metals in the environment are known to endanger ecosystems and put human health at risk. Metals can leach into surface and ground waters, enter the food chain, and through deposition of hazardous wastes can contaminate residential, recreational, and ecologically sensitive areas. The major problem areas associated with trace metal contamination are landfills, industrial discharges, animal wastes, fossil fuel burning emissions, mining activities, and municipal treatment plants. Research has demonstrated that the increasing contribution of these pollution sources to elevated metal concentrations can only be understood if trace metal background concentrations have been established as a basis for comparison (Chen *et al.*, 1999).

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In the US, surveys for background trace metals are pursued on both the national (Holmgren *et al.*, 1993) and the state levels. Shacklette and Boerngen (1984) found a regional geochemical distribution pattern of metals, with generally lower concentrations in soils of the eastern US than in soils of the western US. Lee *et al.* (1997) reported elevated concentrations of Zn throughout the soil depth of Oklahoma soils, followed by Ni, Pb, Cu, and Co. A similar survey in Minnesota found Cd, Pb, and Zn to be largely associated with the surface horizons, whereas Cr, Cu, and Ni were more abundant in the subsoil and the parent material. However, most metals showed a greater association with the parent material rather than with soil variables, such as clay and organic matter content (Pierce *et al.*, 1982). Metal distribution in Florida soils indicated the highest metal concentrations in Ultisols and the lowest in Spodosols. Elevated concentrations of As, Cu, Cr, Pb, Ni, Zn, and Fe, were observed in Bt and Bh horizons as a result of higher amounts of clay and organic matter, respectively (Ma *et al.*, 1997). Levy *et al.* (1992) also reported increased levels of Cu, Cd, and Pb in surface horizons of uncontaminated Colorado soils, but stable concentrations of Zn throughout the soil profile.

Research on trace metal background levels has also been conducted on an international basis, with more emphasis on agricultural and forested areas rather than urban areas. Johnson *et al.* (1996) surveyed a designated region in Jamaica to establish a database of naturally occurring metal levels for environmental, agricultural, and human health purposes. A large- scale survey was also conducted in China to compare background trace metals from mainland China to those measured in other countries of the world. This program also compared regional differences in metal content due to parent material (Chen *et al.*, 1991). Similar surveys have also been conducted in several western European countries to address concerns related to long-term health effects from acid deposition and widespread land application of biosolid and industrial wastes (Berrow and Reaves, 1986; Angelone and Bini, 1992; Kelly *et al.*, 1996).

Naturally occurring metal concentrations depend on weathering, deposition, sedimentation, and erosion processes, but also on soil variables such as organic matter, oxides, and clays that offer high affinity sites for metal adsorption (Cannon, 1978; Laxen, 1985; Lo *et al.*, 1992; Tack *et al.*, 1997). Metal retention and distribution in soils is also influenced by pH, particle size distribution, CEC, mineralogy and their covariant effects that dictate soil behavior as a sink or source of metals (Msaky and Calvet, 1990; Dissing-Nielsen, 1990; Lee *et al.*, 1997). Although large scale surveys are useful for developing preliminary inventories of baseline metal concentrations, a better understanding of factors affecting metal distributions and approaches of discriminating natural from anthropogenic inputs can be obtained though local or regional surveys. Research to establish background concentrations of naturally occurring trace metals in Kentucky was initiated by Karathanasis and Seta (1993). However, this study provided only preliminary data from 29 soil sites scattered throughout the state. With increasing urbanization and increasing pollution sources around residential areas, communities and environmental protection agencies have been calling for more intensive investigations of environmentally sensitive areas (Chen, 1997).

This study seeks to contribute a preliminary database from an area in northern Kentucky undergoing rapid urban development in hopes of providing a baseline reference to monitor potential increases in trace metal deposition from pollution sources. The objectives of the study were to: (i) determine total trace metal concentrations of Cd, Cr, Cu, Ni, Pb, and Zn in representative soils of the studied area, and (ii) identify soil factors and parameters influencing the distribution of the metals in the soil profile.

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 urbanization 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.

Twenty-six soil sites were sampled across the survey area. Samples were chosen from different landscape positions and included eight major soil series (Table 1). The samples were collected from undisturbed sites, predominantly pastures, which had not previously received any waste applications. A probe truck was used to collect the soil samples. Triplicate cores were taken from each site and divided according to horizon designations. All three samples were combined at the sampling site. Samples were air dried, ground with a mortar and pestle and sieved through a 2-mm stainless steel sieve. Three groups of genetic horizons, 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, were sampled for laboratory analyses. The sampled soil depth zones covered approximately the range of 0–35 cm for the surface, 30–70 cm for the middle, and 70–150 cm or to a lithic or paralithic contact if present for the lowest layer.

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

Analytical Characterizations

Trace metal concentrations were determined by using an extraction procedure adopted from USEPA (1994) for the determination of metals in environmental samples. One gram of soil sample was mixed with 4 ml of 50% HNO_3 and 10 ml of 20% HCl. The samples were placed on a shaker for 30 minutes and then heated to 95°C for 30 minutes with periodical mixing of acids and residue during the heating process. Vigorous boiling was avoided. After cooling, the samples were centrifuged for 30 minutes at 3000 rpm. The supernatants were analyzed for Cd, Cr, Cu, Ni, Pb, and Zn using the IL S-11 atomic absorption spectrophotometer, following proper dilutions. All extractions were conducted in duplicate. The glassware used was soaked in 14% HNO_3 (v/v) for 24 hours prior to the procedure. In order to minimize matrix effects, multilevel standards and blanks were prepared in the same matrix as the extracting reagents for each fraction. After every six samples the spectrophotometer was standardized and after every 20 samples the burner head was cleaned to remove salt buildup that could affect the accuracy of the readings. To support the validity of the results, the concentrations were compared to the detection limits for each metal analyzed by the atomic absorption spectrophotometer. The detection limits for the metals were as follows: Cd (0.15 $\mathrm{mg\,kg^{-1}}$), Cr (0.10 $\mathrm{mg\,kg^{-1}}$), Cu (0.05 $\mathrm{mg\,kg^{-1}}$), Ni (0.10 $\mathrm{mg\,kg^{-1}}$), Pb (0.1 $\mathrm{mg\,kg^{-1}}$), and Zn (0.02 $\mathrm{mg\,kg^{-1}}$). All metal concentrations were above the detection limits, except for a few samples that were near or slightly below the Cd detection limit.

Soil physicochemical properties of all soil samples included in this study were determined through methods described by NRCS (1996). All samples were air-dried and passed through a 2 mm stainless steel sieve. The organic matter content was determined by combustion using a LECO 2000 C-N analyzer. 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% of NaCl at pH 3 (NRCS, 1996). The mineralogical composition of the designated horizons was determined by X-ray diffraction using 200 mg samples. A Phillips PW 1840 diffractometer and PW 1729 X-ray generator were used for the X-ray analysis and procedures were applied as described by Karathanasis and Hajek (1982). The diffractometer was equipped with a cobalt X-ray tube that operated at 40 kV and 30 mA. The scanning rate was 0.05° 2θ per minute from 2° to 40° and a scattering slit of 0.1°.

Statistical Analyses

Single correlation and multiple linear regression analyses were conducted to develop significant relationships between trace metal concentrations and soil physicochemical parameters. A Least Significant Difference (LSD) analysis was applied to determine differences ($\alpha < 0.10$) of mean metal concentrations in soils derived from different parent materials (alluvium, glacial till, and residuum). The F-test was first applied to reject or accept H_o, and then each pair-wise difference was tested using an α-level (<0.10) t-test, employing a Statistix® software program. The Pearson single correlation procedure was used to find relationships between metal content and soil variables, and relationships among metals.

Results and Discussion

For determination of means of soil properties and means of metal concentrations, soils were grouped based on the nature of parent material and whether or not a fragipan was present. Soils from the same parent material were grouped together because they did not show significant differences ($p < 0.05$).

Total Metal Distribution in the Soil Profile

Figure 1 shows mean metal concentrations of Cd, Cr, Cu, Ni, Pb, and Zn in the entire soil profile and the individual soil depths sampled. For all soil depths combined, the highest concentrations were observed for Zn and Ni, while Cd was found only in trace amounts. Overall, Zn was the most abundant metal, exceeding Ni by a factor of two and Cr, Cu, and Pb by almost threefold. Figure 2 demonstrates the distribution of metal concentrations as a function of the three soil depth zones sampled. The metals Cu, Cr, Zn, and Ni showed an increasing trend with soil depth, suggesting inherent influences from the parent materials, while Cd and Pb remained constant throughout the soil profile, indicating minimal redistribution with depth.

The high concentrations (52–64 mg kg^{-1}) of Zn throughout the soil profile probably indicate a Zn-enriched parent material. These concentrations are on the high end of those reported in the literature for limestone soils and sedimentary deposits (Kabata-Pendias and Pendias (1992)) but within the range of baseline concentrations reported for US soils (Shacklette and Boerngen, 1984). The high variability around the mean, particularly in the lowest soil depth, are indicative of the diversity of the parent materials studied, while the increasing trend of Zn with soil depth is probably due to elevated clay contents. Zinc is known to have high affinity for clay- and sesquioxide surfaces, which are more abundant in the middle and the lowest soil zones (Table 2) (Lindsay, 1979).

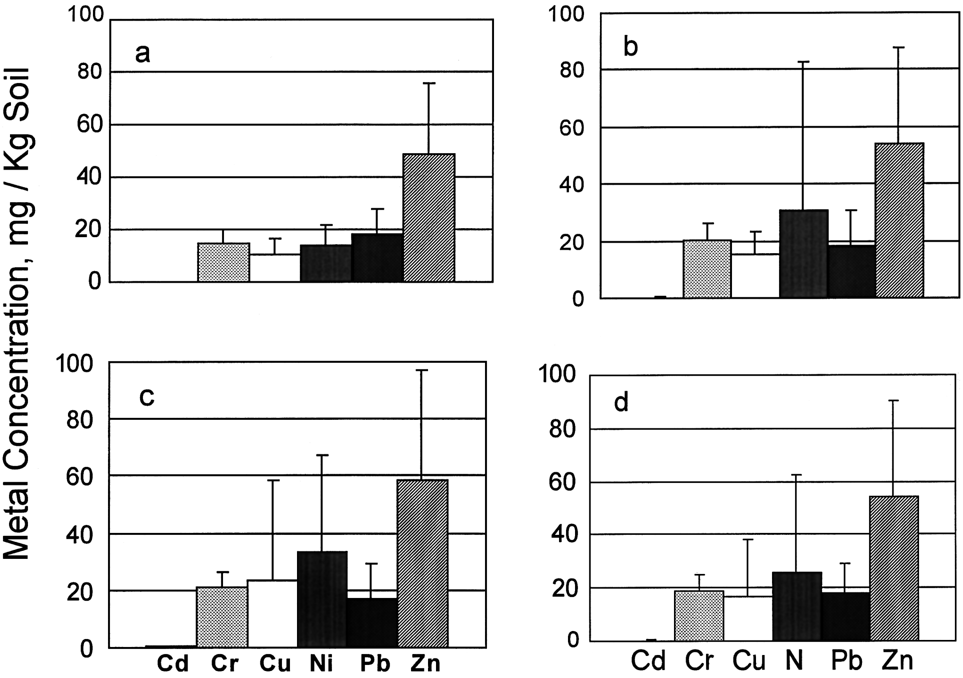

Figure 1. Mean concentration of metals in surface soil depths (a), middle soil depths (b), lowest soil depths (c), and the entire soil profile (d).

Table 2

Means ± 1SD 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.

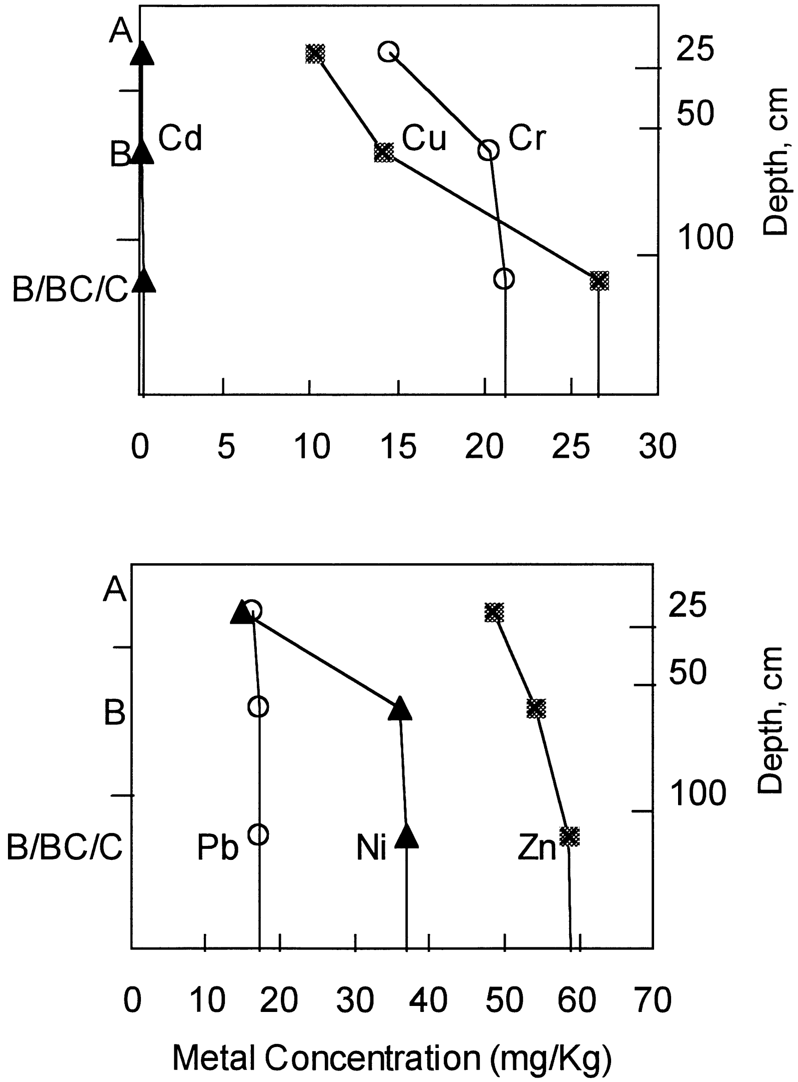

Figure 2. Distribution of metals as a function of soil depth and soil horizons sampled.

Copper showed the most dramatic increases with soil depth, from 10.7 mg kg^{-1} in the upper soil to 23.1 mg kg^{-1} in the lowest soil depth (Figure 2). These levels are within the range of background concentrations reported by Kabata-Pendias and Pendias (1992) for limestone-derived soils (5–20 mg kg^{-1}) and the baseline concentration range of US soils (Shacklette and Boerngen, 1984). According to Lindsay (1979), soil Cu concentrations in the range of 20–30 mg kg^{-1} are mostly associated with sorbed species onto mineral and organic matter surfaces or co-precipitated phases with sesquioxide and silicate minerals. Therefore, Cu increases with soil depth in this study can be explained by clay and sesquioxide accumulations in lower soil zones and translocation of Cu-organic complexes, which outweigh the organically bound Cu fraction in surface horizons (Lo *et al.*, 1992; Logan *et al.*, 1997).

Nickel concentrations averaged 21.2 mg kg^{-1} in the upper soil depth and increased to 33.4 mg kg^{-1} in the lowest soil depth. Chromium showed a similar increasing trend with depth with average concentrations of 14.5 mg kg^{-1} and 21.2 mg kg^{-1}, respectively (Figs. 1 and 2). Cannon (1978) listed average Cr and Ni concentrations for soils derived from limestone in the 10 mg kg^{-1} to 20 mg kg^{-1} range, while Ure and Berrow (1982) reported average values as high as 84 mg kg^{-1} and 34 mg kg^{-1} for Cr and Ni, respectively. These concentrations are in the low to middle range of baseline levels reported for US soils (Shacklette and Boerngen, 1984). McGrath and Loveland (1992) found positive correlations between elevated concentrations of Cr and Ni and increasing soil clay contents. This trend was also evident in our study, where clay increases from 20% in the upper soil depth to 42% in lower depths were associated with respective increases in Cr and Ni concentrations (Table 2 and Figure 2). Accumulation of sesquioxides in the subsoil zones may have also contributed to the elevated Cr and Ni concentrations below the soil surface (Berrow and Reaves, 1986).

Since Pb is considered insoluble and relatively immobile (Alloway, 1995), its stable distribution throughout the soil profile demonstrates parent material effects. Potential increases with depth as a result of increasing clay content have been probably balanced by higher organic matter contents in the upper soil depth (Merry *et al.*, 1983). Lead concentrations in this study ranged from 18.5 mg kg^{-1} in the upper soil depth (A) to 17.2 mg kg^{-1} in the lowest depth. These concentrations are consistent with average levels of 17–29 mg kg^{-1}, reported in other uncontaminated soils and considerably lower than the upper range of 71 mg kg^{-1} found in limestone soils (Davies, 1990).

Similarly, the steady distribution of Cd throughout the soil profile can be due to parent material influence. Considering the higher ability of Cd to leach down the profile after atmospheric deposition (Holmgren *et al.*, 1993), the observed low concentrations suggest very little or no anthropogenic input. Cadmium concentrations in the investigated soils ranged from 0.15 to 0.31 mg kg^{-1}, which are near the analytical detection limit employed. These concentrations are on the low end of the background range reported by Kabata-Pendias and Pendias (1992), and much lower than the range (0.3–11.0 mg kg^{-1}) found in soils derived from sedimentary rocks (Alloway, 1995).

Parent Material Effects

Grouping the soils by parent material (Table 2) showed higher concentrations of Cr, Cu, and Ni in the surface horizon of alluvial soils, while Zn was significantly higher at all three depths compared to soils derived from glacial till and residuum materials (Table 3). This could be the result of sediment deposition by metal-enriched flowing waters. Alluvial soils contained greater amounts of OM content throughout the soil profile, which has a high metal sorption affinity (Lo *et al.*, 1992). Comparing mean metal concentrations in the entire soil profile, alluvial soils also showed significantly ($\alpha = 0.10$) higher values for Cr, Pb, and Zn compared to glacial till and residual soils. Significantly elevated ($\alpha = 0.10$) values for Cd, Cr, Cu, Ni, and Zn were also observed in all surface soil horizons, as well as for Cu, Pb, and Zn in middle soil depths.

Elevated concentrations of Cr and Ni in surface horizons of alluvial soils were directly related to their high soil pH and OM content (Table 2). Increased Cu and Zn concentrations were strongly correlated to soil OM, while Cd levels were correlated with pH alone. Lo *et al.* (1992) attributed the high metal sorption capacity of OM to its higher CEC compared to clay, particularly at higher pH levels. Ionized functional groups associated with soil humus

Table 3

Statistical comparisons (LSD) of metal concentrations[†] at different soil depths as a function of parent material

Parent Material	Soil Depth	Cd	Cr	Cu mg kg^{-1}	Ni	Pb	Zn
Alluvium	Surface	0.28**a**	17.7**a**	18.3**a**	22.4**a**	22.0NS	75.2**a**
	Middle	0.34NS	22.8NS	21.6**a**	25.3NS	25.3**a**	86.7**a**
	Lowest	0.44NS	22.8NS	25.0NS	26.3NS	22.6NS	88.7**a**
	All	0.35NS	21.1**a**	21.6NS	24.7NS	23.3**a**	83.5**a**
Glacial till	Surface	0.15**ab**	11.8**b**	6.62**c**	9.57**b**	14.2NS	44.6**b**
	Middle	0.18NS	17.3NS	12.4**b**	45.2NS	12.6**b**	46.0**b**
	Lowest	0.18NS	19.3NS	33.0NS	40.9NS	16.2NS	55.5**b**
	All	0.17NS	16.2**b**	17.3NS	31.9NS	14.3**b**	48.7**b**
Residuum	Surface	0.09**b**	15.1**ab**	10.5**b**	13.0**b**	20.4NS	40.7**b**
	Middle	0.12NS	21.2NS	15.5**ab**	22.1NS	19.8**ab**	46.6**b**
	Lowest	0.35NS	21.9NS	14.9NS	30.6NS	15.7NS	48.5**b**
	All	0.19NS	19.4**a**	13.6NS	21.9NS	18.6**ab**	45.3**b**

[†] Metal averages within a column for a certain soil depth followed by different letters are significantly different at the 90% level of confidence (for example Cd concentration in the surface of alluvium materials is significantly different than for residuum materials, but Cd concentration in the glacial till materials is not statistically different from that of alluvium or residuum materials); NS implies no statistical differences between averages for the specified soil depth.

can increase dramatically with increasing soil pH resulting in CEC changes from ~200–300 cmol$_c$/kg at pH around 4.5 to 400–600 cmol$_c$/kg, at pH 7 (Bowen, 1966). Therefore, the increased OM and pH of alluvial soils may have contributed to formation of greater amounts of metal-organic complexes and therefore to greater metal immobilization and accumulation. The effect of OM on metal concentration can be seen clearly when comparing Cu content in surface horizons to OM and CEC/clay ratio, which decrease in the sequence alluvial > residual > glacial till soils (Tables 2 and 3). Dissing-Nielsen (1990) suggested that sandy soils with increased OM content and high CEC/clay ratios can effectively outcompete clayey soils in metal sorption capacity. The stronger relationship of Cu with OM compared to other metals can be explained by its higher organic complexation potential even at relatively low pH levels (Msaky and Calvet, 1990). Elevated Cd concentrations were associated solely with pH increases because Cd does not have a high affinity to form organic complexes, but instead is forming predominantly inner sphere complexes and covalent bonds that decrease metal mobility (Logan *et al.*, 1997). There were no significant differences between glacial till and residual soils in Cd, Cr, Ni, and Zn concentrations, except for Cu, which was considerably lower in the glacial till.

In the middle soil depth, alluvial soils showed significantly ($\alpha = 0.10$) higher concentrations for Cu, Pb, and Zn compared to soils derived from glacial till (Table 3). Copper and Pb concentrations in residual soils were intermediate but not significantly different than those found in alluvial and glacial till soils. The elevated OM content and pH of the alluvial soils, and therefore their higher metal complexation capacity, apparently contributed to the increased metal concentrations (Table 2). In contrast, the middle depths of glacial till soils had the lowest pH, OM, and CEC/clay ratio, which could not be compensated by considerable clay increases. Residual soils had intermediate OM, pH, and CEC/clay levels, which maintained their metal sorption capacity comparable to that of alluvial soils except for Zn.

In the lowest soil depth, Zn was the only metal to show a significantly higher concentration in alluvial soils over the other parent materials. This was associated mainly with the higher OM content and CEC/clay ratio of alluvial soils, in spite of the nearly two-fold higher clay content and the similar pH of glacial till and residual soils (Table 2). Another factor may have been the increased sesquioxide concentrations in the sand and silt fraction of alluvial soils, which has considerable metal adsorption potential. Dissing-Nielsen (1990) found a good correlation between Cu adsorption and the specific adsorption of Zn. This is evident in the distribution of these two metals with depth in all soils, suggesting a strong parent material influence. The distribution of trace metals was also analyzed by grouping soils according to their depth to bedrock, but no significant differences were observed, either for combined or individual soil depths.

The effect of fragipan horizons on metal distribution was also investigated. Eight of the 26 soils studied had fragipans distributed evenly between middle and lowest soil depths. However, fragipans were present only in glacial till- and residuum-derived soils, not in soils formed from alluvial parent materials. No significant differences in metal concentration and distribution were observed between fragipan and non-fragipan horizons. Potential differences in metal concentration gradients between fragipan and non-fragipan horizons may have been subdued because of the narrow range and the low metal levels encountered in glacial till and residual soils. Assuming that the low permeability of fragipans had an effect on metal concentration, it should have been materialized through maximum metal accumulations within or above the fragipan depth. However, no such trend was evident as metal concentrations increased gradually with soil profile depth in all soils with or without fragipans. There were significant differences ($\alpha = 0.10$) in total soil profile metal concentrations between soils with and without fragipans. Zinc, Cu, and Cd levels in soils without fragipans were 59.6 mg kg^{-1}, 19.3 mg kg^{-1}, and 0.27 mg kg^{-1} compared to 39.0 mg kg^{-1}, 10.0 mg kg^{-1}, and 0.08 mg kg^{-1} in soils with fragipans, respectively. These differences however, may have been skewed from the high metal levels of the alluvial soils that did not have fragipan horizons.

Statistical Relationships

Total metal concentrations of all 26 soils were correlated to six soil variables (pH, OM, CEC, clay%, silt% and CEC/clay). Additional statistical analyses included single correlations of soil variables to metal concentrations in surface, middle, and lowest soil depths.

Organic matter and pH were the only soil parameters that showed significant positive correlations with all metals in surface soil horizons and middle soil depths with the exception of Ni (Table 4). In the lowest soil depths, only Cr, Ni, and Zn showed positive correlations with pH and Cd, Cr, and Zn with OM content. Clay and CEC had significant effects only on the concentration of Cr, Ni, Pb, and Cu throughout the soil profile (Table 4), suggesting that these metals had stronger associations with the finer soil fraction. This was corroborated by the negative correlations of the silt fraction with Cu, Ni, Pb, and Zn.

Even though all metals have the ability to form organic complexes, different metals have variable affinity for organic matter depending on pH. Copper has relatively high affinity, Ni, and Cr moderate affinity, whereas Cd and Zn have the lowest affinity (Gluskoter *et al.*, 1977; Msaky and Calvet, 1990; Lo *et al.*, 1992). The pH level dictates the solubility and mobility of different metal species in the soil environment (Kabata-Pendias and Pendias, 1992). Zinc is able to bind to three different sites of humic acid molecules, but it can be very

Table 4

Correlation coefficients of metal content with soil parameters in surface, middle, and lowest soil depths, as well as the total soil profile

Metal	pH	OM†	CEC†	clay%	silt%	CEC/clay
			Surface soil depth ($n = 26$)			
Cd	0.42**	0.31*	NS	NS	NS	NS
Cr	0.33**	0.38**	NS	0.26*	NS	NS
Cu	0.40**	0.57***	NS	0.38**	−0.53***	−0.26*
Ni	0.28*	0.47***	0.28*	NS	−0.42**	NS
Pb	0.51***	0.58***	0.35**	0.35**	−0.30*	NS
Zn	0.36**	0.52***	NS	NS	−0.44**	NS
			Middle soil depth ($n = 26$)			
Cd	0.54***	0.78***	NS	NS	NS	NS
Cr	0.50***	0.74***	NS	NS	NS	0.36**
Cu	0.59***	0.83***	NS	NS	NS	NS
Ni	NS	NS	NS	NS	−0.26%	NS
Pb	0.39**	0.62***	NS	NS	−0.37**	NS
Zn	0.41**	0.88***	NS	NS	NS	0.42**
			Lowest soil depth ($n = 26$)			
Cd	NS	0.40**	NS	NS	0.28*	NS
Cr	0.27*	0.27*	NS	NS	NS	NS
Cu	NS	NS	NS	NS	NS	NS
Ni	0.29*	NS	0.32*	0.33**	NS	NS
Pb	NS	0.51***	NS	NS	NS	0.41**
Zn	0.31*	0.54***	NS	NS	0.26*	0.28*
			Total soil profile ($n = 78$)			
Cd	0.33***	0.25**	NS	NS	NS	NS
Cr	0.36***	NS	0.21**	0.35***	−0.26***	−0.29***
Cu	0.25**	NS	0.15*	0.29***	−0.25**	NS
Ni	NS	NS	0.23**	0.30***	−0.29***	NS
Pb	0.30***	0.46***	NS	NS	NS	NS
Zn	0.37***	0.45***	NS	NS	NS	NS

*,**,*** $p < 0.10$, <0.05, and <0.01, respectively; NS = non-significant.

†OM denotes organic matter, and CEC denotes cation exchange capacity.

easily leached when the pH drops below 5 (Logan *et al.*, 1997). On the other hand, Pb and Cu are particularly associated with humus and are more difficult to leach (Lo *et al.*, 1992). The most significant correlations of pH with metal concentrations found in this study were with Pb and Cu in surface horizons and Zn, Cr, and Cu in middle soil depths (Table 4). The effect of pH on metal concentrations was not apparent in the lowest soil depths in spite of the higher pH values, because of the narrow range encountered (6.3–6.5). However, OM was still relatively high and variable enough in the lowest depths to have a significant effect on metal retention (Table 2).

The mineralogical components vermiculite (V), smectite (SM), and their hydroxy-interlayered members present in the soil samples studied were also used in the statistical analysis because of their known interactions with metals. However, no statistically significant correlations could be established, apparently because of similarities in the mineralogical composition between samples or synergistic effects with CEC values. Influences on metal retention also derive from the presence of Fe, Al, and Mn oxides, which exist as nodules, concretions, and coatings on clay particles (Ma *et al.*, 1997). They retain metals by adsorption or co-precipitation processes. Since the correlations between metal concentration and silt fractions were either negative or not significant in this study, the effect of sesquioxides on metal retention must have been realized only through the coatings of clay particle surfaces, and therefore it is incorporated in the overall clay effect.

For all soil depths combined (Table 4), Zn showed the strongest correlations with Cd (0.60 ***), Cr (0.58***), and Pb (0.47***). In surface horizons (Table 4) the strongest associations were those of Zn with Ni (0.78***) and Cu (0.60***); Ni with Cd (0.62***) and Cr (0.57***); and Pb with Cu (0.57***). In middle soil depths (Table 4), Zn was strongly correlated with Cu (0.78***), Cr (0.77***), and Cd (0.73***). Strong associations were also observed between Cu and Cr (0.79***), and between Pb and Cu (0.62***). Finally, in the lowest soil depths (Table 4), Zn showed strong associations with most metals including, Cd (0.62***), Pb (0.60***), Cr (0.59***), and Ni (0.50***). Other significant correlations in this depth were those between Cu and Ni (0.53***), and between Cr and Pb (0.50***). The strong correlation between Cu and Zn is explained by their similar ionic radii and geochemical behavior during pedogenesis (Kabata-Pendias and Pendias, 1992). The correlation between Cr, Ni, and Pb may also suggest similar adsorption behavior to clay or clay-humus particle surfaces, since they belong to the same metal group (II) (Laxen, 1985). The correlation of Cd with Zn and Cr is mainly due to their strong association with clay mineral surfaces and sesquioxide coatings. Finally, correlations between Cu, Pb, Ni, and Zn are probably associated with OM and pH interactions. According to Lo *et al.* (1992) the metal adsorption sequence onto organic matter can be described in terms of very strong fixation for Pb and Cu, fair fixation for Cd and Ni, and slight fixation for Zn.

Multiple linear regression relationships using soil properties as predictors of metal accumulation in surface, middle, and lowest soil depths were not always consistent with single correlations. Among metals, Pb appeared to have the most consistent predictability for most soil properties in all soil depths. In surface horizons pH, OM, and clay content explained 48% of the variability in Pb content, in middle soil depths OM, CEC, and silt content accounted for >50% of the variability, while in the lowest depths OM, CEC/Clay, and silt content explained 53% of the variability in Pb concentrations (Table 5). This is consistent with the findings of Davies (1990), suggesting that Pb is mainly associated with

Table 5

Selected multiple linear regression relationships between metal concentrations and soil parameters explaining more than 40% of the variability around the mean

Depth	Metal	Equation	R^2
Surface	Pb	$= -21.45 + 4.57$ pH $+ 2.35$ OM $+ 0.20$ clay%	0.48***
Middle	Cr	$= 9.44 + 3.01$ OM $+ 0.35$ CEC/Clay	0.66***
	Pb	$= 26.20 + 4.99$ OM $+ 0.25$ CEC $- 0.34$ silt%	0.52***
Lowest	Pb	$= -2.74 + 5.73$ OM - 0.20 silt% + 40.03 CEC/clay	0.53***
	Zn	$= -8.24 + 16.87$ OM $+ 83.95$ CEC/clay	0.42***

$^{***}P < 0.01$.

clay-humus complexes. Organic matter and pH explained 42% of the variability in Zn concentration in the lowest soil depths, while OM and CEC/Clay accounted for 66% of the variability in Cr concentrations in middle soil depths. Similar results have been reported by Kiekens (1995), indicating sorption to clay mineral and organic particle surfaces as a function of pH to be the main mechanism for Zn immobilization. Negative contributions of CEC or pH in the presence of OM in some multiple regression models may be indicative of synergistic or antagonistic effects of these soil parameters under the broad range of pH and OM conditions experienced in this study. Finally, the negative impact of the silt fraction on metal accumulation corroborates the low association of metals with coarse soil particles and the absence of nodular or concretionary sesquioxide effects.

Conclusions

Total metal concentrations in three different soil depths showed levels in the low to middle range of baseline concentrations reported for US and world soils, suggesting no significant anthropogenic inputs in the studied area. Zinc and Ni had the highest concentrations throughout the profile. Metal distribution in the soil profiles indicated Cr, Cu, Ni, and Zn increases with depth, but stable levels of Cd and Pb throughout the soil profile. Organic matter, pH, and CEC or clay content were strongly associated with metal retention, with OM and pH being the dominant parameters in surface and middle soil depths. Correlation coefficients for all soil samples combined between metal content and soil parameters showed a strong pH effect for Cr, Pb, and Zn, and a prominent association of Pb and Zn with OM content. The amount of clay had a positive effect on Cr and Ni retention, whereas silt showed a negative effect on Cr, Cu, and Ni concentrations. Multiple regression analysis suggested OM as the most important soil variable influencing metal retention throughout the soil profile. Cation exchange capacity was the second most influential parameter, followed by clay content and CEC/clay.

Alluvial soils contained significantly higher metal concentrations, especially Zn, compared to glacial till and residual soils, and Cr and Pb compared to glacial till soils. Elevated concentrations of Cr, Cu, Ni, and Zn in surface horizons of alluvial soils may indicate metal enrichment through depositional processes, while metal increases with soil depth suggest parent material and pedogenic influences. No significant effects of fragipan horizon presence or soil-depth to bedrock on metal distribution were evident. Single correlations among metals showed close associations of Zn with Cd, Cr, Cu, and Pb in all soil depths sampled.

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