

ZINC AND CADMIUM DISTRIBUTION AND LEACHING IN A METALLIFEROUS PEAT

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Abstract. Peat soils with a gradient of naturally high Cd and Zn (up to 190 and 70,000 mg/kg, respectively) were sampled at several depths from a wetland overlying Zn-rich dolomitic bedrock. Total concentrations of Zn, Cd and S were generally much higher in the seasonally water-saturated subsoils than at the surface. Leaching studies with intact soil columns showed the subsoils generally have a greater tendency to release Zn, Cd and S than the topsoils. Zn and Cd leaching were correlated to sulfate dissolution, with 6 successive leaching events removing up to 4% and 13% of the total Zn and S, respectively, from the most metal-rich subsoils. Relative leaching losses were less from the surface soils, not exceeding 1% and 3% of total Zn and S. Because Zn was relatively more soluble and extractable by 0.01 M CaCl₂ than Cd, Zn/Cd ratios in column leachates and field-sampled groundwater were higher than the soil Zn/Cd ratios. Consequently, the potential for loss of Zn from the soil by leaching was higher than that of Cd, particularly from the subsoil. Nevertheless, some soil layers of the profile were enriched in total Zn relative to Cd, indicated by Zn/Cd ratios well above that of the Cd-rich sphalerite in the parent dolomitic rock. This enrichment may be explained by historical migration and re-immobilization of Zn as sulfides. The low solubility of Cd in the peats despite high total Cd suggests preferential immobilization of this metal by organic sulfur or sulfide.

Keywords: cadmium, leaching, metal sulfides, mobilization, peat, soil organic matter, sulfur oxidation, zinc

1. Introduction

Fluctuating groundwater levels in wetland soils and sediments can lead to the oxidation of labile iron and heavy metal sulfides, increasing the concentrations of sulfate and chalcophilic metals, particularly Zn and Cd, in groundwater during periods when groundwater levels are low (Van den Berg *et al.*, 1998; Dollar *et al.*, 2001). Evidence for Zn sulfide phases in seasonally flooded soils has been obtained from synchrotron X-ray absorption spectroscopy (XAS) (Hesterberg *et al.*, 1997) and from electron microprobe (EDX) analysis, the latter showing a close association of elevated concentrations of Zn and S (Martinez *et al.*, 2002; Van den Berg *et al.*, 1998). Initial studies of unusually metalliferous peat soils from western New York revealed extremely high Zn and Cd in the topsoil in localized patches, evidently concentrated by weathering of sphalerite crystals from the relatively Zn and Cd-rich

dolomite bedrock followed by immobilization in wetlands (Cannon, 1955). Zn and Cd re-mobilization and leaching as a result of sulfur oxidation and soil acidification can be substantial when these metalliferous peat topsoils are exposed to aerobic conditions (Qureshi *et al.*, 2003). Since many of these soils have been drained for agricultural use, it is likely that their potential to release Zn and Cd into drainage water and surface waters of the region has been increased by this anthropogenic activity. However, groundwater analyses and greenhouse crop studies revealed that Cd is relatively less mobile and bioavailable than Zn in the metalliferous peats (Martinez *et al.*, 2002). Laboratory measurements of the partitioning coefficients of Cd and Zn in these peats reveal stronger binding of Cd than Zn (Martinez *et al.*, 2002), providing a chemical explanation for the lower availability and mobility of Cd.

Since the evidence suggests that Cd and Zn should have different degrees of mobility in the soil, which could be expected to produce different patterns of biogeochemical accumulation of these metals, a more detailed study of the lateral and vertical distribution of Cd and Zn in the peat profiles at and near an anomalously high-zinc area was undertaken. It was expected that the spatial distribution patterns would provide evidence for processes that mobilize and redistribute Cd and Zn over long time periods. In addition, soils from different depths in the peat profiles, and with widely different total Zn, Cd and S concentrations, were subjected to repeated aerobic leaching in the laboratory in order to assess the potential for metal mobilization and loss as a result of S oxidation.

2. Methods

2.1. SOIL TRANSECT SAMPLING

A location with extremely high Zn concentration in a cultivated peat field was selected as the central soil sampling location, with 4 additional sampling locations on an east-west transect at 80 m intervals away from this high-Zn site. The equidistant sampling locations are labeled 1, 2, 3, 4, 5 for convenience, with 1 and 5 being the sites furthest west and east, respectively, and 3 centered near the high-Zn location described by Martinez *et al.* (2002).

Soils were sampled in May 2004 at 20 cm depth intervals at each location using a Dutch auger until the marl underlying the peat was reached. The soils were saved in the field-moist state for pH determination (5 g. soil +5 ml. distilled water) and air-dried prior to extraction by 0.01 M CaCl₂ for soluble and exchangeable metals (3 g. soil + 30 ml. CaCl₂ solution). A portion of each sample was oven-dried at 105 °C before reverse aqua-regia digestion on a hot plate prior to determination of total Cd, Zn, Cu and S in the digests by axial-view inductively coupled plasma (ICP) spectrometry. Groundwater from each sampling bore hole at the level of the marl was collected at the same time by a hand-pump system, double-filtered using

Whatman #42 paper, and analysed for pH by electrode and dissolved Cd, Zn, Cu and S by axial-view ICP spectrometry.

2.2. LARGE COLUMN SAMPLING FOR LEACHING STUDIES

A set of three large intact peat columns from within and near the high-Zn toxic field site was obtained in 2002 by driving 1 m long aluminum tubes into the peat soil to just below the depth of the marl layer. The tubes were then pulled from the soil, and refrigerated until they could be cut open and sectioned. Small (10 cm long by 5 cm diameter) plexiglass tubes were pushed into the undisturbed peat column at 10 cm depth intervals, thereby sampling the complete vertical profile of each peat column. In addition, the soils were sampled at 5 cm intervals along the length of the columns for total Zn, Cd and S analysis. Total soil sulfur analyses were done by high-temperature combustion using an infrared detector to measure SO₂ generation (ASTM D4293-02). The soils were digested by a standard nitric-perchloric acid ashing method followed by analysis of the digests for Zn and Cd by ICP spectrometry. The 3 sampling sites were selected in order to obtain a wide range of surface soil Zn concentrations, and are labeled C1 (low Zn), C2 (medium Zn) and C3 (high Zn). As Figures 1A, B and C show, however, Zn and Cd concentrations were much higher in the subsoils for all 3 columns, and the highest subsoil Zn was actually measured in the C1 (low Zn) profile.

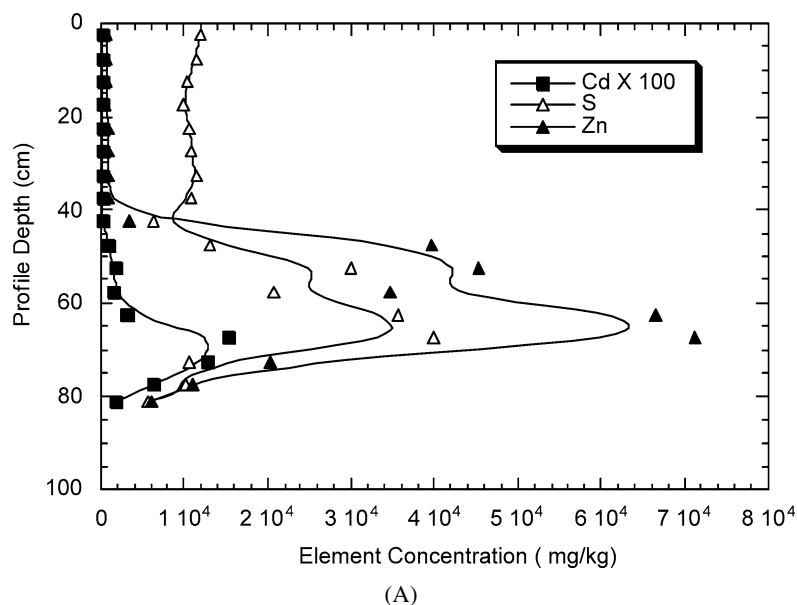


Figure 1. Concentrations of total Zn, Cd and S (mg/kg) as a function of depth in the peat soil profiles (A) C1, (B) C2 and (C) C3.

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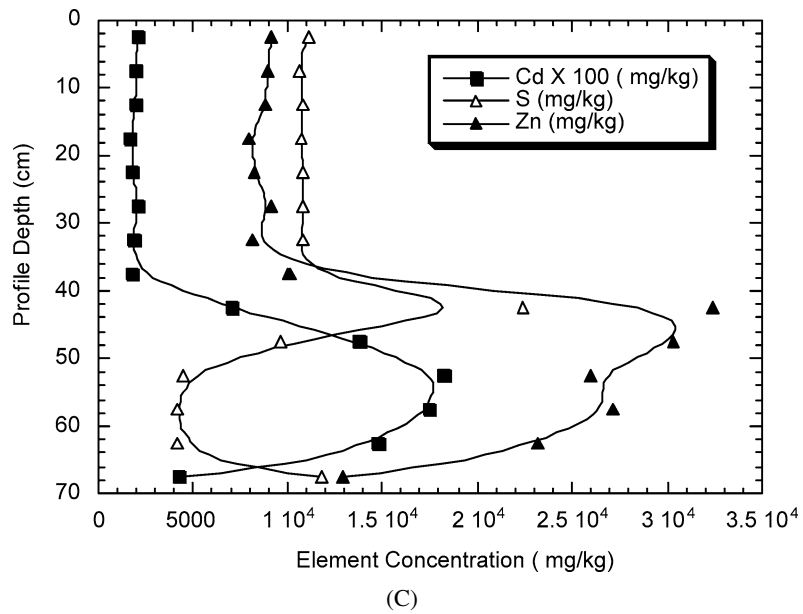
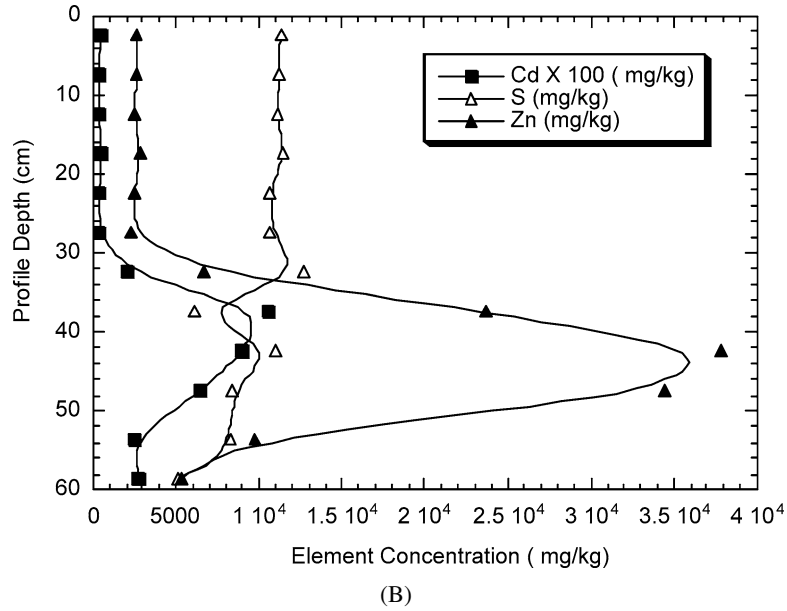


Figure 1. (Continued)

The small undisturbed peat columns were kept moist by sealing in plastic wrap and refrigerating until laboratory leaching experiments could be conducted. The leaching studies were done by first lining the bottom of each column with a double layer of Whatman #42 filter paper, then mounting each column on a Buchner funnel

with a 250 ml. beaker positioned beneath to collect the leachate. Distilled water was applied to the peat column surface at a rate of 1.5 ml/min using a peristaltic pump until 100 ml. of leachate was collected in the beaker. The pH and optical absorbance (at 450 nm) of the leachates were measured immediately after collection, the latter measurement used as an estimate of dissolved organic carbon (Yacobi *et al.*, 2003). Finally, 0.5 ml of concentrated HNO₃ (ultrapure grade) was added to the leachates prior to storage at 4 °C.

Five successive leachings were done at 2 week intervals on selected small columns from several depths of the large columns C1, C2 and C3. Following the 5th leach, all small columns were allowed to air dry in the laboratory for 1 month, and a final leach was done to determine the effect of drying on release of metals and sulfate.

All collected leachates were analysed for dissolved Zn, Cd, Cu and S by axial-view ICP spectrometry. The cumulative losses of the metals and sulfur from the columns were calculated from the total amounts of these elements measured in the leachates, and these losses were calculated as fractions of the total amounts of these elements measured initially in the soils.

3. Results

3.1. CONCENTRATIONS OF Zn, Cd AND S ALONG THE FIELD TRANSECT

As shown by the data for total soil Zn and S in Table I, soil Zn and S concentrations decrease with distance away from sampling site 3, which is near the center of the highly phytotoxic area. However, the lateral decrease in soil S is much less abrupt than that of Zn, with the consequence that soils further away from the most toxic area have lower Zn/S ratios, potentially an important factor in limiting Zn toxicity. The concentrations of both Zn and S tend to increase with depth in the profiles until the marl layer is reached, with S and Zn decreasing again in this mineral layer below the peat. At sampling site 3, soil Cd follows the trend of Zn, increasing with depth until the marl layer is reached, where there is an abrupt decrease in Cd. At the other sampling sites outside the toxic area, total soil Cd was less than 1 mg/kg (Table I).

Groundwater metal concentrations along the transect did not perfectly reflect the pattern of total Zn, Cd and S, with the highest dissolved Zn and S found at site 2, but the only detectable dissolved Cd found at site 3, where total soil Cd and Zn were highest. The pH of the groundwater was generally in the 6.7–7.1 range, reflecting the influence of the calcareous marl on groundwater chemistry. Soil pH values (data not shown) were in the range of 5.0–5.5 in the surface (0–40 cm), increasing to near 6.0 in the 40–60 cm depth, and approaching 7.3–7.7 in the underlying marl. This pattern of pH with depth was consistent for all sampling sites.

TABLE I
Total Zn, Cd and S concentrations in the peat soils (mg/kg) and shallow groundwater (mg/L) along the east-west 1–5 sampling transect

Sample	1	2	3	4	5
Zinc					
0–20 cm	131	123	7060	433	397
20–40 cm	68.8	149	7710	273	347
40–60 cm	181	3314	13,800	669	563
60–80 cm	108	–	12,800	2818	294
80–100 cm	61.9	1144	978		
Groundwater	0.052	5.27	3.12	1.24	0.40
Cadmium					
0–20 cm	<1	<1	36.1	<1	<1
20–40 cm	<1	<1	37.5	<1	<1
40–60 cm	<1	<1	157	<1	<1
60–80 cm	<1	–	176	<1	<1
80–100 cm	<1	<1	<1	–	–
Groundwater	n.d.	n.d.	0.005	n.d.	n.d.
Sulfur					
0–20 cm	5740	6790	8920	7370	6540
20–40 cm	5500	8550	9170	7630	6440
40–60 cm	7440	11,800	12,130	9460	7280
60–80 cm	1380	–	14,310	1768	2180
80–100 cm	2000	3480	7270	–	–
Groundwater	150	287	31.7	192	192

Bold numbers indicate soil samples that are predominantly marl rather than organic.

The CaCl₂-extractable Zn generally followed the trend of total soil Zn with depth, reaching the highest level in the peat at 40–60 cm depth, and decreasing abruptly in the marl layer. The fairly close correspondence between extractable Zn and total soil Zn is shown in Figure 2. The CaCl₂-extractable S followed a less clear pattern, but tended to be higher at the soil depth highest in exchangeable Zn. However, there was no correlation between CaCl₂-extractable S and total soil S. CaCl₂-extractable Cd was only at detectable levels in the profile at site 3, and reached its highest level (0.54 mg/kg) at the 60–80 cm depth, above the marl (data not shown). However, a later sampling of the soil along an east-west transect (June 2004) within 30 m of the most toxic site produced a greater number of soil samples with high Cd (up to 188 mg/kg in one soil from the 30–45 cm depth). For this set of 20 soil samples, CaCl₂-extractable Cd was significantly correlated to total Cd,

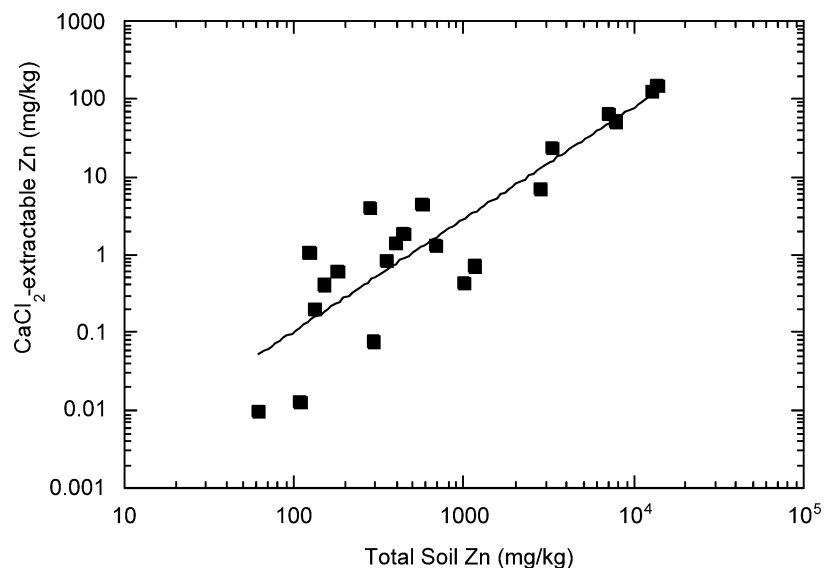


Figure 2. Relationship of CaCl_2 -extractable Zn to total soil Zn for all soil depths sampled along the 1–5 field transect.

according to the equation:

$$\begin{aligned} \text{Cd (CaCl}_2\text{-extracted)(mg/kg)} \\ = 0.072 + 0.0146 (\text{Soil Cd})(\text{mg/kg}) \quad r^2 = 0.86 \end{aligned}$$

The equation shows that the CaCl_2 extraction dissolves only about 1.5% of the total Cd in the high-Cd soils, with the analogous best-fit equation for Zn revealing that about 1.0% of the Zn in the high-Zn soils was extracted by CaCl_2 .

Figure 3 reveals that, for the toxic site C, the ratio of total Zn to total Cd in the soil is consistently lower throughout the profile than the ratio of CaCl_2 -extractable (soluble and exchangeable) Zn to Cd. The implication of this result is that Zn is relatively more soluble and mobile than Cd, confirming evidence from an earlier study that showed Cd to have a higher K_d than Zn in these peat soils (Martinez *et al.*, 2002).

Overall, soil total Cd was correlated positively to total Zn, as expected from the geochemical association between these two chalcophiles in minerals and soils, but there was a great deal of variability in the Zn/Cd ratio at different depths of each soil horizon sampled. A detailed description of Zn/Cd ratios was possible in the peat columns C1, C2 and C3, as total Zn and Cd was measured at 5 cm intervals throughout the profile into the marl layer. As shown in Figure 4, there was a clear pattern of Zn enrichment relative to Cd at 40–65 cm depth in C1, the low-Zn profile. In contrast, there was not a similar enrichment of Zn in C2 (not shown) or

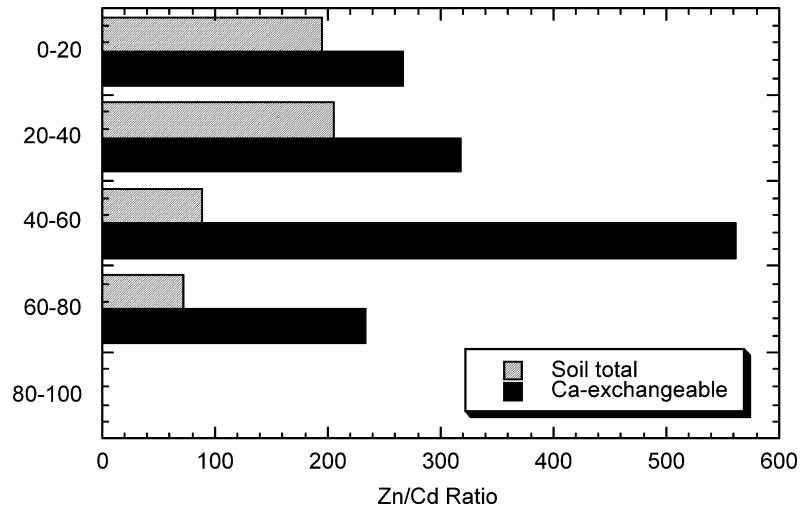


Figure 3. Ratio of Zn to Cd (by weight) in soils and CaCl_2 -extracts of soils sampled at several depths of site C of the 1-5 field transect.

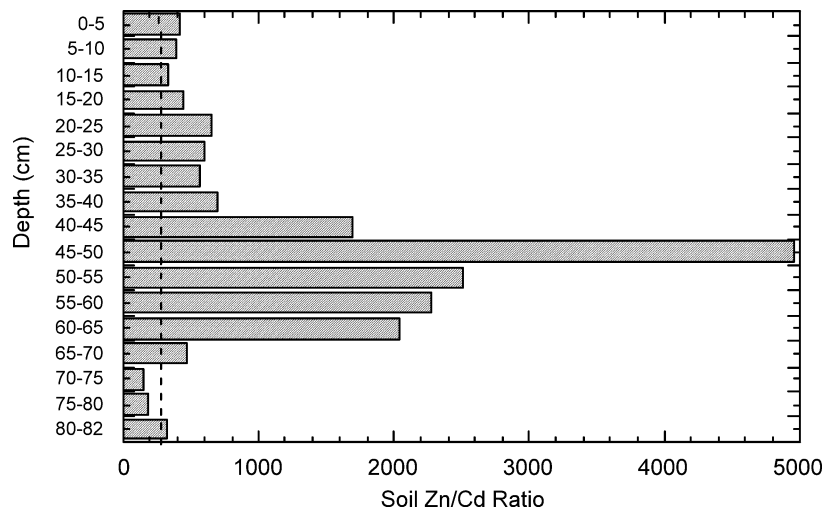


Figure 4. Ratio of Zn to Cd (by weight) as a function of depth in the soil profile C1. The broken line marks the Zn/Cd ratio of sphalerite in the parent dolomitic rock of the site.

C3 (Figure 5), but rather some depletion of Zn at this depth. It seems reasonable to suggest that, at C1, Zn selectively leaching downward from the surface soil may have been immobilized in the 40–65 cm layer by reduction of sulfate and formation of Zn sulfide at that depth. This process does not, however, explain the relative Zn depletion (Cd enrichment) at depth in the C2 and C3 profiles. Since C2 and C3 have lower total S at depth than C1 (see Figures 1A, B, C), one possibility is that

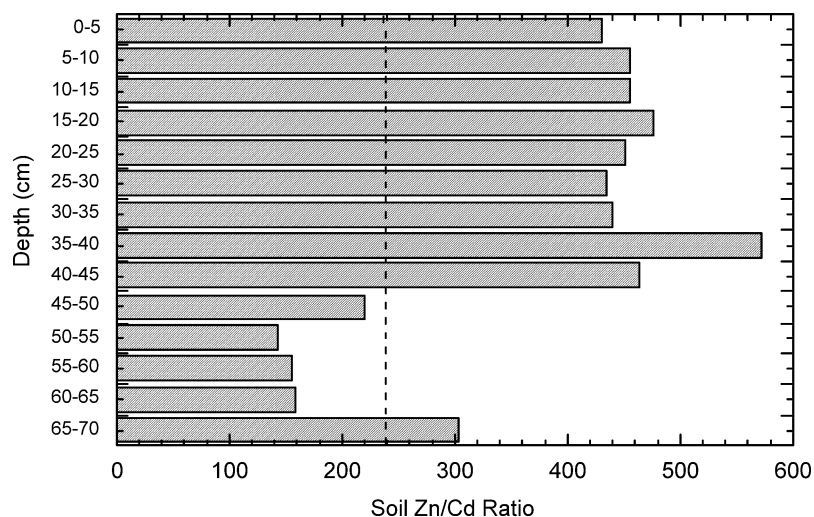


Figure 5. Ratio of Zn to Cd (by weight) as a function of depth in the soil profile C3. The broken line marks the Zn/Cd ratio of sphalerite in the parent dolomitic rock of the site.

Zn was too high in concentration relative to S at those sites to be immobilized by sulfides. However, as Cd forms a less soluble sulfide than Zn, it may have been more efficiently retained. Also, because the site with high surface Zn (C3) is in a slight depression in the field, there may be lateral flow of high-Zn water into the surface layer at C3, thereby tending to produce some surface enrichment in Zn relative to Cd.

Enrichment in Zn relative to Cd in the peats can be referenced to the Zn/Cd ratio of the original parent material at this site, the Silurian Dolomite. An analysis of sphalerite crystals found in exposed dolomite at the site produced a Zn/Cd ratio of 233 ± 8 on three separate samples. In Figures 4 and 5, the 233 ratio is marked as a broken line, showing the high degree of Zn enrichment in the subsoil at C1 (Figure 4), a feature that is not evident at C3 (Figure 5).

3.2. LEACHING OF Zn, Cd AND S

Small soil columns from several depths of the C1, C2 and C3 peat profiles (0–10 cm, 30–40 cm, 40–50 cm, 50–60 cm and 70–80 cm) were tested for leachability of Zn, Cd, and S. Generally, the highest concentrations of Zn, Cd and S were measured in the first leaching event; concentrations decreased with each subsequent leach. In addition, the leachate pH was lowest with the first leach (as low as 3.8), and increased with subsequent leachings to values between 5 and 6. pH was generally lower in the leachates from the surface soils. Thus, there was no indication of strong acidification in the high-S subsoils resulting from oxidation of metal sulfides. The trend for Zn,

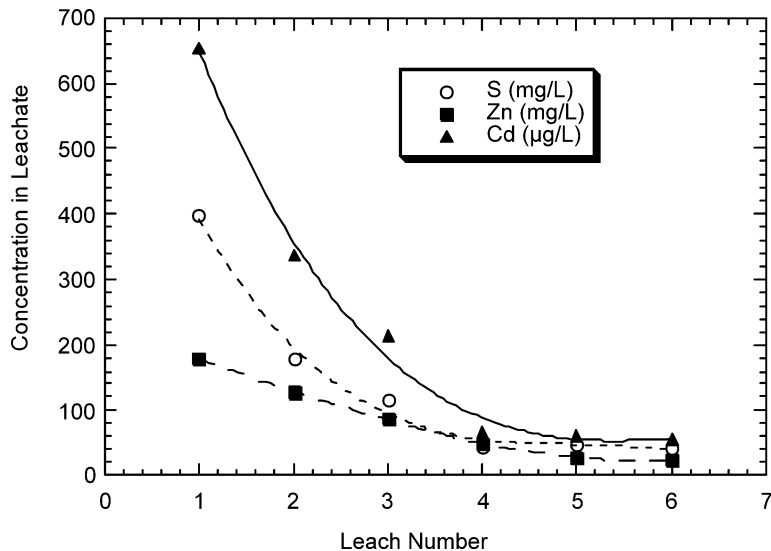


Figure 6. Leachate concentrations of Zn, Cd and S as a function of the number of times the peat column C1 (70–80 cm depth) was leached.

Cd and S in the leachates to decrease upon successive leachings is shown in Figure 6 for a deep layer (70–80 cm) of the C1 profile. This particular soil layer released the highest concentrations of all three elements; leachates from most of the soil layers had Cd concentrations well below 50 $\mu\text{g/L}$ after the first leaching event. Zn and Cd concentrations were highest in leachates from the deeper peat layers (40–80 cm), a result expected from the higher total Zn and Cd deeper in the profiles (see Figures 1A, B and C). However, much higher Zn and Cd concentrations leached from the deep layers of C1 and C2 than C3. Soluble Zn and Cd in subsoil leachates reached concentrations as high as 178 mg/L and 0.65 mg/L, respectively (from the 70–80 cm depth of C1 on the first leach). Dissolved S (presumed to be sulfate) also tended to be high in leachates from the deeper peat layers for both C1 and C2 (150–400 mg/L), whereas the deeper layers of C3 failed to leach high concentrations of S. Thus, site C3 showed a consistent pattern of lower Zn, Cd and S release from subsoil layers upon leaching, despite having the highest Zn concentration in leachates from the surface (0–10 cm), accounting for the phytotoxicity to field crops at the C3 site.

Drying the peat columns after 5 successive leaching cycles did not have any marked effect on metal or sulfate release, as the leaching event following the drying period produced leachate with generally somewhat lower Zn, Cd and S than that measured in the prior leaching event.

A consistent observation from the leaching experiments was the greater Zn/Cd ratios in the leachate than in the peat from which these metals were leached. One

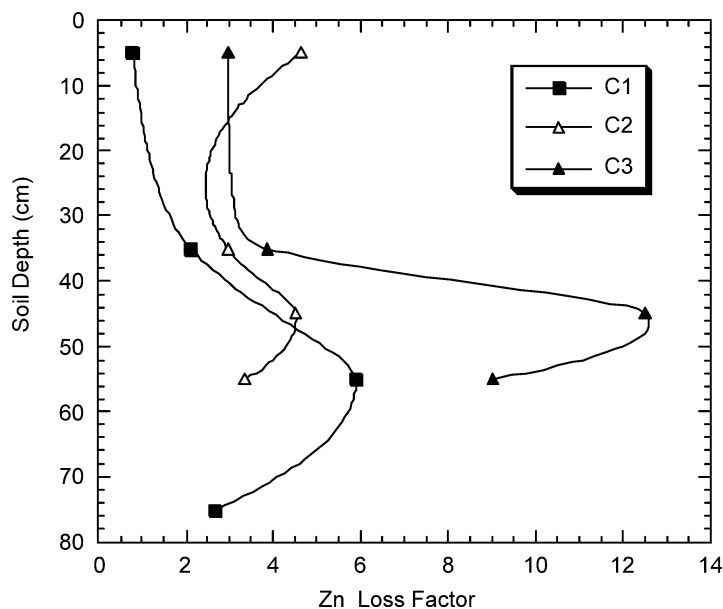


Figure 7. The calculated Zn loss factor (relative to Cd) for soil profiles C1, C2 and C3.

way to express the tendency of Zn to be lost by leaching relative to Cd, is to define a Zn Loss Factor as:

$$\text{Zn Loss Factor (ZLF)} = \frac{(\text{Zn})_{\text{sol}}/(\text{Cd})_{\text{sol}}}{(\text{Zn})_{\text{peat}}/(\text{Cd})_{\text{peat}}}$$

where the average concentrations of Zn and Cd in the leachates obtained from 6 leaching cycles are symbolized by $(\text{Zn})_{\text{sol}}$ and $(\text{Cd})_{\text{sol}}$ and the initial peat total concentrations of Zn and Cd are symbolized by $(\text{Zn})_{\text{peat}}$ and $(\text{Cd})_{\text{peat}}$. A ZLF greater than unity indicates that leaching is depleting the peat soil of Zn relative to Cd. Figure 7 shows the ZLF values for the C1, C2 and C3 peat profiles. It is clear that Zn is being preferentially leached throughout the profiles, but the most pronounced selectivity of Zn leaching is observed at about the 40–60 cm depth. This suggests a strong mechanism for Cd retention at depths where S is at particularly high concentrations, again implicating a role for sulfides in Cd immobilization. The greatest ZLFs are measured in the deeper layers of C3, the peat from the toxic site where metal and S dissolution were inhibited during the leaching experiments.

The data obtained on the leachates for all 6 leaching cycles (pH, optical absorbance, concentrations of Cd, Zn, Cu and S) were subjected to regression tests to determine if the soluble metal concentrations tended to be correlated to pH, dissolved sulfate, or dissolved organic matter. For both Zn and Cd, dissolved metal concentration (mg/L) was not correlated to leachate pH or color intensity (optical absorbance at 450 nm), but leachate S concentration (mg/L) was strongly correlated

to metal solubility:

$$(\text{Zn}) = -4.24 + 0.434(\text{S}) \quad r^2 = 0.838 \quad (p < 0.0001)$$

$$(\text{Cd}) = -0.025 + 0.001(\text{S}) \quad r^2 = 0.607 \quad (p < 0.0001)$$

In contrast, for leachate Cu, neither pH nor soluble S had a significant correlation to Cu concentration (mg/L), but optical absorbance at 450 nm (OA_{450}) was correlated:

$$(\text{Cu}) = 0.003 + 0.151\text{OA}_{450} \quad r^2 = 0.588 \quad (p < 0.0001)$$

These results are consistent with the hypothesis that sulfur oxidation (but not concomitant acidification) is the critical process releasing both Zn and Cd into soluble forms, whereas Cu dissolution and leaching is not predominantly by this mechanism but by complexation with dissolved organic matter.

The total cumulative losses of Zn and S from the peat columns were calculated from leachate concentrations averaged over all leaching events. These results are given in Table II as both absolute quantities of Zn and S lost from the columns (mg) and percentages of the initial soil Zn and S lost. The results reveal that the greatest absolute and relative losses of Zn and S were from the deep horizons of C1 and C2, whereas C3 lost substantially less of these elements. The results suggest that the oxidation of S and associated dissolution of Zn was inhibited in the deeper horizons of site C3. A closer analysis of the total element profiles of the 3 columns presented in Figure 1A, B and C shows that a feature of C3 that distinguishes it from the other 2 columns is the relatively high subsoil Cd (at 45–65 cm depth). Possibly at this

TABLE II

Cumulative absolute and percentage losses of Zn and S from the peat columns by 6 successive leaching events

Column	Zn loss (mg)	Zn loss (%)	S loss(mg)	S loss (%)
C1 0–10 cm	0.69	1.0	29.9	2.9
C1 30–40 cm	0.91	1.1	10.4	0.93
C1 50–60 cm	15.8	0.33	37.9	1.2
C1 70–80 cm	49.1	3.3	82.2	8.4
C2 0–10 cm	0.95	0.44	18.1	2.0
C2 30–40 cm	6.90	0.62	20.2	2.9
C2 40–50 cm	20.1	0.77	43.5	6.2
C2 50–60 cm	23.0	4.1	67.8	13.5
C3 0–10 cm	3.31	0.51	16.8	2.2
C3 30–40 cm	2.64	0.31	11.0	1.1
C3 40–50 cm	3.29	0.12	14.7	1.1
C3 50–60 cm	2.17	0.075	14.5	3.1

depth in C3, Cd is more toxic to microbes. However, because the Cd/S mole ratio at this depth is approximately 0.01, it is reasonable to expect that much of the Cd is immobilized in sulfides, and an alternative explanation for inhibition of sulfur oxidation in C3 subsoils may have to be sought.

The generally low concentrations of Cd measured in leachates from most of the soil layers during repeated leaching (data not shown) suggests the involvement of reduced S, possibly sulfides or thiol groups, in Cd retention. It is now known that a substantial fraction of the total S in cultivated peat soils is in the reduced state (Martinez *et al.*, 2002; Xia *et al.*, 1999), and that Cd selectively bonds with reduced sulfur ligands in organic matter (Karlsson *et al.*, 2005). Thiol groups in organic matter are expected to bond Cd more strongly than Zn (Xia *et al.*, 1999; Xu and Allard, 1991). It is likely, however, that complexes between heavy metals and reduced S ligands are not thermodynamically stable in aerobic soils, but oxidize slowly. Sulfides of Cd and Zn could, nevertheless, limit metal solubility in aerobic soils as they are substantially slower to oxidize than Fe sulfide (Simpson *et al.*, 1998), and additionally could be protected physically or chemically from oxidation in soil environments.

Acknowledgments

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