Soil & Sediment Contamination, 13:375–390, 2004
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ISSN: 1058-8337 print / 1549-7887 online
DOI: 10.1080/10588330490466021

Column Leaching using Dry Soil to Estimate Solid-Solution Partitioning Observed in Zero-Tension Lysimeters. 2. Trace Metals

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The fundamental questions revolving around research into trace metals in soils are how much, and in what form, do metals exist in soil solutions. The mobile phase of soil solutions can be sampled by lysimeters, but cannot be consistently and accurately reproduced in laboratory extractions. We used a column leaching method developed specifically to produce solutions that were similar to those of lysimeters from northern forest podzolic soils. We hoped to yield reasonable estimates of the partitioning of Cd, Cu, Ni, Pb and Zn between the solid and solution phases observed in the field. The column leaching method produced solutions that were similar to lysimeter solutions in the concentrations of metals in solution. Partitioning coefficients (log K_d) calculated from average lysimeters solution concentrations ranged from 2.8 to 3.9 for Cd, 3.5 to 4.2 for Cu, 3.1 to 4.3 for Ni, 3.9 to 5.1 for Pb and 2.8 to 3.6 for Zn. Laboratory extractions produced very similar log K_d values ranging from 3.4 to 3.9 for Cd, 3.4 to 3.9 for Cu, 3.4 to 4.1 for Ni, 4.1 to 5.2 for Pb and 3.2 to 3.5 for Zn. According to a semi-mechanistic regression model based on observed lysimeter concentrations, the metal concentrations in solution were appropriate relative to known factors that

The authors would like to thank the National Science and Engineering Research Council of Canada for funding through the Research Grants program and through the Metals in the Environment Research Network and for a scholarship provided to D.M. The authors also gratefully acknowledge the assistance of Dr. Peter Campbell and the INRS-EAU for use of their laboratory facilities to carry out a portion of this research as well as the laboratory assistance of Hélène Lalande.

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influence metal partitioning in soils: pH and the concentrations of total metals and dissolved organic carbon. Partitioning coefficients based on laboratory extractions in the literature were on average an order of magnitude greater than those observed in lysimeters. When compared to the results of other laboratory extractions, the proposed extraction procedure appeared to be an effective method to estimate the chemistry of soil solutions in the field.

Keywords Soil solution extraction, miscible displacement, trace or heavy metals.

Introduction

Much of the concern in regions where trace metals have accumulated in soils revolves around the question of mobility, the time that metals will take to move through the ecosystem and the bioavailability of metals to organisms. Therefore, researchers' main concerns with respect to the soil solution are questions of "how much" metal is in solution and "in what form." The complexity of the mechanisms of adsorption of metals to the soil solid phase makes it difficult to evaluate how metals will be partitioned between the solid and solution phases of soils. Zero-tension lysimeters are used to directly sample the solution moving through the soil profile and are considered to provide an accurate sample of this mobile soil solution. Due to the time and expense required for the installation and sampling of lysimeters, it is not practical to use them to evaluate soils on a regional scale. Therefore, standardized laboratory procedures that provide *reasonable* estimates of the mobile fraction of trace metals in contaminated soils are needed.

A number of standard solution extraction methods have been used to estimate the partitioning of metals to soil solutions. These methods include saturation extracts, immiscible and miscible displacement of moist soils, centrifugation and batch extraction of the soil with water, or a salt solution (ex. $CaCl_2$ or KNO_3, 0.001 M to 0.01 M) at a variety of soil:solution dilutions from 1:1 to 1:20 (Campbell and Beckett, 1988; Holm *et al.*, 1995; Keller, 1995; Goody *et al.*, 1995; Romkens and Salomons, 1998; Fotovat and Naidu, 1998; Salam and Helmke, 1998; Tack *et al.*, 1998; Sauvé, 1999). However, concentrations in these solutions cannot be expected to be comparable to lysimeter solutions. We would not expect that a 0.01 M salt extraction, for example, would provide solutions comparable to lysimeters in forest soils where concentrations of cations rarely exceed 100 μM (Foster *et al.*, 1992; Bélanger *et al.*, 2002).

Concentrations of trace metals in solution are correlated with soil factors such as soil organic matter (SOM), total metals, soil pH, and cation exchange capacity (CEC) (Celardin, 1995; Romkens and Salomon, 1998; Sauvé *et al.*, 2000). Also, ligands such as dissolved organic carbon (DOC) will increase the concentration of metal in solution, particularly in organic horizons where dissolved organic complexes bind significant amounts of metals (Keller and Domergue, 1996; Wang and Benoit, 1996). These studies demonstrate that the partitioning of metals to solution is dependent on the nature of the soil solid phase and the speciation and composition of the soil solution. Consequently, to succeed in accurately reproducing metal partitioning, soil solution extractions must also succeed in reproducing the major characteristics of the soil solution.

The study of the speciation of soil solutions also requires solutions with reasonable concentrations of the different ligands and competing cations that may influence the distribution of chemical species (ex. Me^{2+}, MeDOC, MeOH, where Me is a given trace metal, DOC is dissolved organic substances and MeOH is a hydrolyzed metal species) and provide enough solution for analyses that often require large solution volumes. Since the role of DOC in complexing trace metals is known (Harter and Naidu 1995; Christenson *et al.*, 1999), the ability to produce solutions that have reasonable concentrations of DOC, major cations and pH at environmentally relevant ionic strengths, is necessary to obtain a realistic distribution of metal species.

We examined the concentration of metals in solutions collected by lysimeters installed beneath forest floors with a range of concentrations of the trace metals Cd, Cu, Ni, Pb and Zn. Trace metal concentrations are elevated in these soils due to emissions from metal smelters. We evaluated the leaching procedure outlined in MacDonald *et al.* (2004) to see if it would provide an estimate of the concentrations of metals in solution that were similar to concentrations observed in lysimeter solutions. The results of the leaching procedure were compared to the concentrations observed in lysimeter solutions and the concentrations predicted by a semi-mechanistic regression model developed by Sauvé *et al.* (2000) from a range of different soil solution extraction procedures.

Materials and Methods

Sampling and Site Description

Soils were sampled during the installation of lysimeters in sites located at increasing distances from two point sources of trace metal emissions, the smelting centers of Rouyn, Quebec, Canada, and Sudbury, Ontario, Canada. Six samples were taken from each of the six sites in 1999 to evaluate the average concentration and the variation in metal concentrations and soil characteristics within each experimental plot.

Samples were air dried, homogenized and sieved to 2 mm and digested according to EPA 3051 (USEPA, 1998). Digests were analyzed by flame atomic absorption spectrometry (FAAS) or when below flame detection limits by inductively coupled plasma atomic emission spectrometry (ICP AES, axial torch) including NIST quality control 2711. Metal recovery was 99%, 103%, 105%, 96%, 96% and 102% for Zn, Cu, Cd, Ni, Mn, and Pb, respectively, according to NIST quality controls. Organic carbon was analyzed using a modified Walkley Black method (Tiessen and Moir, 1993), and pH analyzed in water (Hendershot *et al*., 1993). Twenty percent of the chemical analyses carried out on each soil were duplicated to ensure the consistency of analytical results.

Lysimeters were allowed to equilibrate during the year of 1999 and lysimeter solutions were collected monthly during the summers of 2000 and 2001. Solutions were analyzed for pH and electrical conductivity (EC) and then filtered through 0.4 μm polycarbonate filters. A sub-sample was acidified to 0.2% HNO_3 for metal analyses. Major cations and trace metals were analyzed by ICP AES, or when below ICP AES detection limits, by graphite furnace atomic absorption spectrometry (GFAAS). All analyses were carried out using Environment Canada, National Water Research Institute, trace metal series inter-laboratory comparison samples as quality controls. Measured concentrations were within 10% of published values. Dissolved organic carbon was analyzed on a Shimadzu TOC analyzer.

Leaching Procedures

Leaching procedures were carried out according to the method outlined in MacDonald *et al.* (2004), with the exception that suction was applied to the soil column with a peristaltic pump instead of the syringe extractor. The use of a peristaltic pump allowed complete acid washing of the extraction system as solutions were collected in acid washed bottles thus avoiding contact with rubber seals in the syringes used in the syringe extractor.

Briefly, soil columns, maintained at 4 to 6°C, were pre-treated by washing with 30 ml aliquots of de-ionized water at 30 ml hr^{-1} allowing 2–3 hours between washes until the EC was below 50 μS cm^{-1}. Following pre-treatment, three leaching procedures were tested. In the first test, triplicate columns of the soil from Site 2 in Rouyn were leached using an 80 μM $CaCl_2$-$CaSO_4$ mixture at 24-hr intervals. In the second test, six columns of the same soil were leached with 80 μM $CaCl_2$-$CaSO_4$; leachates from two of the columns were retained for analysis while the leachates from the other four were passed through the columns again. Then leachates from two of the columns were retained for analysis while the leachates from the other two were passed through the columns a third time and then kept for analysis. In the third test, triplicate soil columns prepared using soils from the six experimental sites were washed and then leached with 80 μM $CaCl_2$-$CaSO_4$; the leachates from Day 3 were kept for analysis, then the columns were incubated for a further 3 days and leached a final time with 80 μM $CaCl_2$-$CaSO_4$. The leachate solutions were filtered and analyzed using the same procedures as the lysimeter solutions.

Statistical Analysis

Bulk solution results are presented as box plots analyzed using SYSTAT©10 (Wilkinson, 2000). Boxes represent 50% of observed values and whiskers are 1.5 times the inter-quartile range. The boxes and whiskers provide a visual presentation of the range of concentrations of different elements in lysimeter solutions.

Regressions were carried out using the mixed regression feature in SYSTAT©10. The regression model is based on the competitive ion adsorption model of Sauvé (1999):

$$-\log \mathrm{Me}^{2+} = \log K - \log\left(\frac{[\mathrm{S}-\mathrm{OMe}]}{[\mathrm{S}-\mathrm{OH}]}\right) + y \cdot \mathrm{pH} \qquad (1)$$

where Me is the metal, S is a surface site, and K is the equilibrium constant equivalent to $K_{Me} * K_H$. In acidic soils it is assumed that the majority of trace metals in solution will be either in the form of Me^{2+} or complexed as MeDOC (Yin *et al.*, 2002). Therefore we modified the regression model to include DOC:

$$\begin{aligned} -\log \mathrm{Me}_{\mathrm{solution}} &= -\log(\mathrm{Me}^{2+} + \mathrm{MeDOC}) \\ &= \log K - \log\left(\frac{[\mathrm{S}-\mathrm{OMe}]}{[\mathrm{S}-\mathrm{OH}]}\right) + y \cdot \mathrm{pH} + a \cdot \log \mathrm{DOC} \qquad (2) \end{aligned}$$

where MeDOC is a function of total DOC. Furthermore, we assume that in organic horizons (or forest floors) S-OH is a function of the percentage soil organic carbon (SOC) content and S-OMe is a function of the total metals. Therefore the regression model becomes:

$$\log \mathrm{Me}_{\mathrm{solution}} = d + c \cdot \log\left(\frac{[\mathrm{TotalMe}]}{[\mathrm{SOC}]}\right) + b \cdot \mathrm{pH} + a \cdot \log \mathrm{DOC} \qquad (3)$$

Mixed regressions were carried out using pH and DOC as fixed variables and the ratio of total Me to % SOC as the random variable.

Results and Discussion

Site Description

Table 1 provides the basic characteristics of the forest floor samples used in the leachate procedure. A gradient in total Cd, Cu, Pb and Zn concentrations was observed in Rouyn and Cu and Ni in Sudbury. The sites provided a range in pH between 3.7 to 4.7. Humus types were mors to moders.

Validation of Method

The soil taken from site 2 in Rouyn responded to pre-treatment washing and a series of leaching steps in a similar manner to soils in MacDonald *et al.* (2004) (Figure 1). Electrical conductivity decreased below levels typically observed in lysimeter solutions, as did the concentrations of other elements in the solution including trace metals. Trace element concentrations in the initial wash solutions were much higher than concentrations typically observed in lysimeters and, during the pre-treatment washing, decreased to concentrations slightly lower than those observed in lysimeter solutions.

Evaluation of Steady-State Conditions of Columns

We considered the possibility that the speed of the desorption reaction of trace metals was controlling leachate solution concentrations. To evaluate if solutions were a result of a steady state between the solid and solution phase, the soil solutions were reintroduced into the columns. It was assumed that if the observed solution concentrations were a result of reaction kinetics, concentrations would increase as contact time with the soil increased.

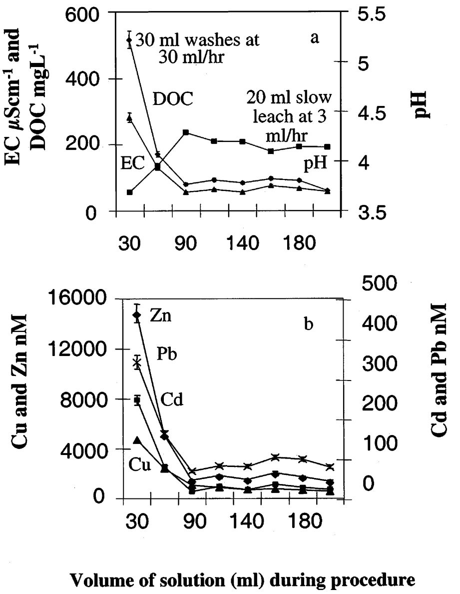

Figure 1. Concentrations of major solution components (a) and trace metals (b) in leachates from a soil from Site 2 in Rouyn during washing pre-treatment and four leaching steps at 24-hr intervals.

Table 1
Characteristics of soil in experimental sites in which lysimeters were established (average values)

	Distance (km) from smelter	Latitude/Longitude	pH	% Organic Carbon	Cd (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Sudbury Site 1	10	46° 35′ 47.9″ N 80° 49′ 53.8″ W	4.7	17	3.6	1500	1200	200	54
Sudbury Site 2	25	46° 35′ 52.7″ N 80° 37′ 21″ W	3.62	32	1.8	700	970	250	65
Sudbury Site 3	51	46° 35′ 11.4″ N 80° 49′ 34.4″ W	4.35	29	0.9	72	92	90	63
Rouyn Site 1	7	48° 17′ 4.4″ N 78° 54′ 22.5″W	3.65	36	15.9	1300	11	370	200
Rouyn Site 2	15	48° 18′ 46.8″ N 78° 51′ 16.0″ W	3.81	37	14.6	500	22	670	390
Rouyn Site 3	40	48° 32′ 31″ N 78° 39′ 39″ W	3.95	31	6.2	100	21	250	110

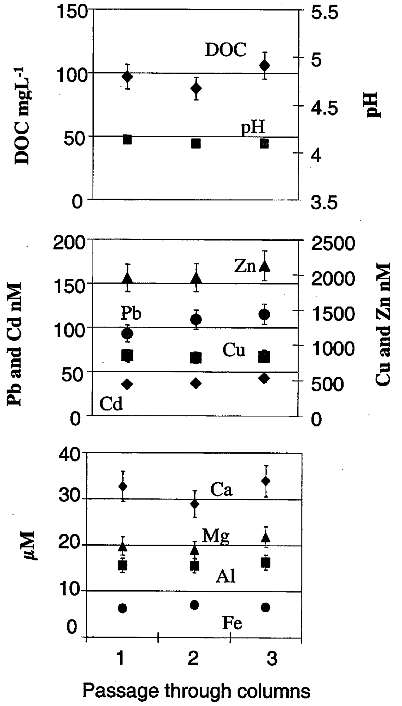

Figure 2. Concentrations of elements in leachates from a soil from Site 2 in Rouyn as extracted solutions are reintroduced to the soil column once, and a second time.

Figure 2 demonstrates that the first soil leachates appeared to be in a steady state with the soil solid phase. The concentrations in the soil solutions remained the same when the leachates were re-passed through the soil columns, with the exception of the slight increase in DOC. Dissolved organic carbon concentrations were typically the most variable component in soil solutions. These results support the hypothesis that the chemistry of the solutions are controlled by exchange reactions between the soil solid and the soil solution phases as was suggested by MacDonald *et al.* (2004).

Comparison to Lysimeter Solutions

The relationship between chemistry of lysimeter solutions and laboratory leachates is shown in Figure 3. Variability was large in the lysimeter solutions at these sites. The majority of solution characteristics (concentrations of divalent cations, pH, EC, and DOC) in the leachate solutions fell within the distribution of values indicated by the box and whiskers of lysimeter box plots. As was the case in MacDonald *et al.* (2004), median concentrations in lysimeter solutions were not reproduced exactly, but concentrations were generally within a factor of 2 of the observed median lysimeter concentrations. Notable exceptions are sites 1 and 3 in Rouyn. The leaching procedure underestimated Ca and Mg (in the case of site 3) concentrations by 3- to 4-fold. Leachates of Sudbury soils are also more acidic than lysimeter solutions particularly in sites 1 and 2 where differences were as great as 0.7 pH units. Furthermore, median values of DOC concentrations in site 2 of both Rouyn and Sudbury were greater in leachates by as much as a factor of 2.5.

It must be noted that three of the six sites have been influenced by the deposition of trace metals as well as SO_2 from the point sources. Sites 1 and 2 in Sudbury, in particular,

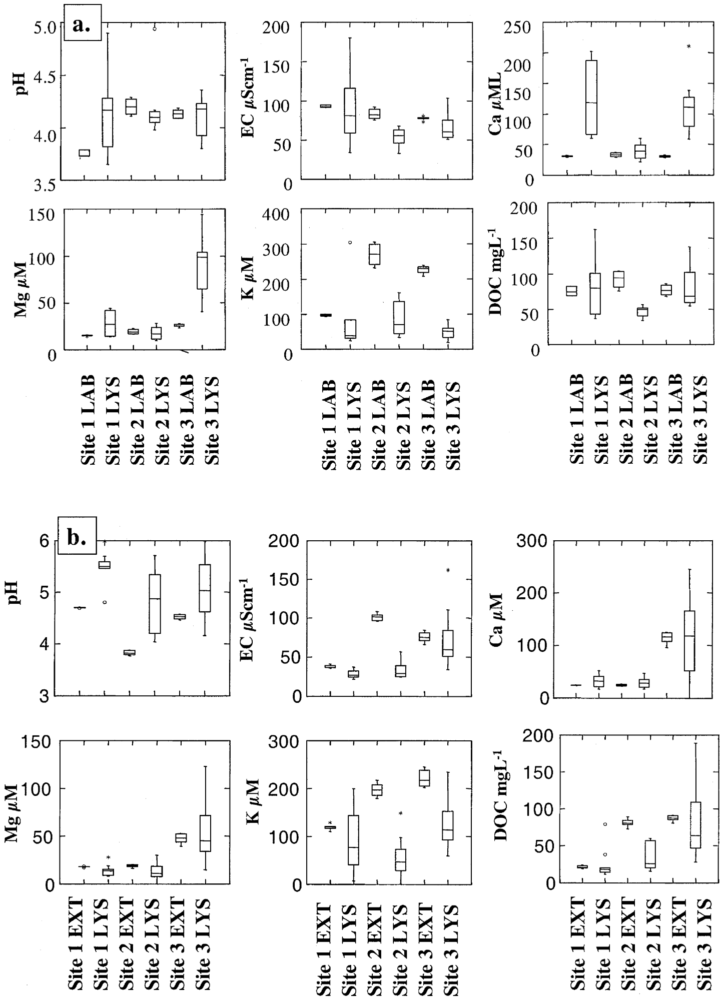

Figure 3. Comparison of the concentrations of major solution components in lysimeters (LYS) and in laboratory leachates (LAB) from soils collected at experimental sites in Rouyn (a) and Sudbury (b).

are characterized by shallow forest floors and vegetation has been severely affected by past emissions. Soil pH, organic matter concentration and metal concentrations were extremely variable at these sites (MacDonald and Hendershot, in revision). All sites are also currently influenced by depositions of a wide variety of elements from the point sources. Therefore, it is not surprising that lysimeter solutions from these sites were less similar to the solutions produced through the leaching procedure than what was observed in MacDonald *et al.* (2004).

Trace Metal Concentrations

Typical trace metal concentrations in lysimeters established under organic soils in pristine forest sites vary between 1.8 and 9 nM for Cd, 80 to 500 nM for Cu, 450 to 3000 nM for Zn, 5 to 70 nM for Pb and 17 to 170 nM for Ni (Heinrichs and Mayer, 1982; Bourg and Vedy, 1986; Bergkvist *et al.*, 1989; Keller and Domergue, 1996; Wang and Benoit, 1996). Close

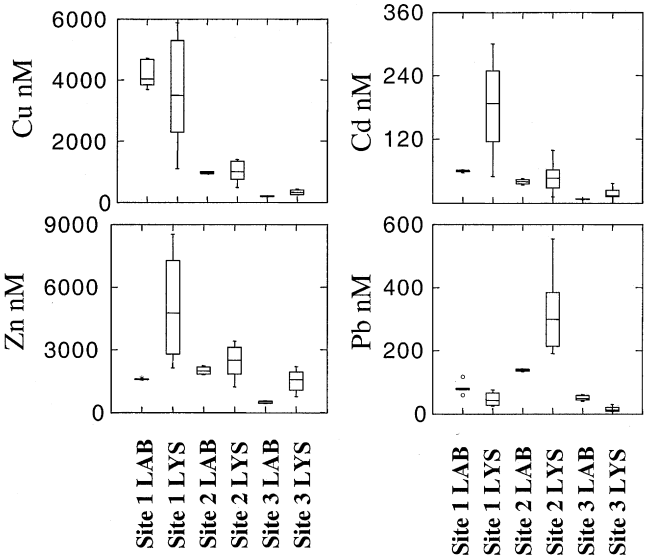

Figure 4. Boxplots comparing the concentrations of trace metals in lysimeters (LYS) and in laboratory leachates (LAB) from soils collected at experimental sites in Rouyn.

to point source emitters, concentrations can be as high as 8000 nM for Cu, 7000 nM for Ni and 5500 nM for Zn (Derome and Nieminen, 1998). At distances from a point-source emitter in northern Europe similar to our study, Nikonov *et al.* (2001) reported ranges of concentrations of 137 nM to 5700 nM Ni and 500 to 3000 nM, Cu. Concentrations that we observed in lysimeters are consistent with these data.

As was the case with other solution characteristics, the concentrations of trace metals in leachates did not mirror lysimeter solutions. They were, however, generally within a factor of 0.5 to 2.5 times the median lysimeter concentrations though there were exceptions (Figures 4 and 5). Sites 1 and 2 in Sudbury showed the greatest differences between contaminant trace metals in lysimeters and laboratory leachates. For example, the leaching procedure overestimated lysimeter median Cu concentrations by 3- to 4-fold. On the other hand, site 1 in Rouyn underestimated Zn and Cd concentrations by a factor of 2.5 to 3.

Overestimation in Sudbury is probably due to the nature of the sites themselves. Sites 1 and 2 in Sudbury have shallow forest floors and lysimeter solutions could be prone to dilution by rainfall events. In most cases, however, concentrations of leachates from the columns were lower than lysimeter concentrations. The underestimation in Rouyn may be due to the quantity of metal removed from the soil particle surfaces during the washing process or to less effective competition by Ca alone in acting to displace trace metals in the leachates. Throughfall solutions from this area contain other trace metals, as well as Fe and Al, that may provide stronger competition for surface sites than the Ca in the leaching solution. Trace metals may require stronger competition to displace them from the particle surfaces than is provided by Ca in the leaching solution.

Does the Leaching Method Produce Reasonable Estimates of Mobile Metals?

Semi-empirical regression models have been used to integrate the influence of soil solid phase and solution characteristics to predict concentrations of dissolved metals (Celardin,

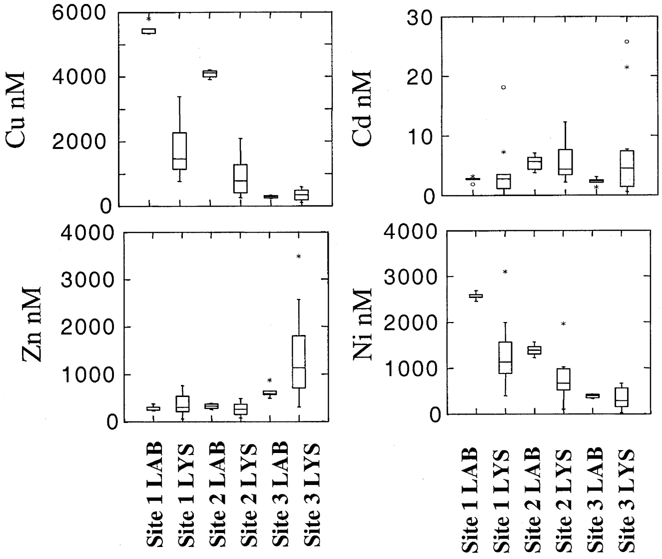

Figure 5. Boxplots comparing the concentrations of trace metals in lysimeters (LYS) and in laboratory leachates (LAB) from soils collected at experimental sites in Sudbury.

1995; Sauvé *et al.*, 2000). We used the lysimeter data for 2000 and 2001 to calibrate regression equations that identify the relationships between soil characteristics, solution characteristics and concentrations of trace metals in solution. The pH, DOC, and the ratio of total metals to organic carbon were observed to be significant factors in influencing the concentrations of metals in lysimeter solutions. These results correspond closely to what Yin *et al.* (2002) observed in batch extractions carried out in the laboratory. Table 2 demonstrates the parameters and the significance of the different factors used in developing regression models to calculate the expected metal concentrations in lysimeter solutions.

The leachates produced in the laboratory had a variety of different combinations of total metal concentrations, DOC and pH. To account for the combined effect of the differences in solution composition, we used the regression models described in Table 2 to predict what the concentration of contaminant trace metals would be expected in the leachates as a function of DOC and pH in the leachates and the concentration of metals and SOM in the soil sample. In Figure 6, we have super-imposed these calculated concentrations over the lysimeter data used to develop the regression equations. Regressions for Pb were not significant and are not presented in Figure 6.

In the case of Cd, Cu, Ni and Zn, the majority of the soil samples followed the relationships between total metals in solution, total metal on the solid phase, pH and DOC as observed in lysimeter solutions. Notable exceptions that fell outside the error of the regression were site 1 in Sudbury, in which the leaching procedure over-estimated the concentrations of Cu, and site 1 and site 3 in Rouyn, in which the concentration of Zn and Cd respectively were under-estimated. In the majority of the cases, Zn and Cd were under-predicted in the extractions though they were either on the border or within the 95% confidence interval of the regressions.

Table 2

Coefficients and standard error for parameters used in linear regressions to calculate concentrations in lysimeter solutions

Dissolved metal		Total metal (mg/kg)/% OC			PH			DOC (mg/kg)			Intercept				
μg/L		Coefficient	SE^b (+/−)		Coefficient	SE		Coefficient	SE		Coefficient	SE	R^2	SEE^a	N
Cd	=	0.867**	0.134	+	−0.422*	0.091	+	0.623***	0.208	+	2.742***	0.628	0.72	0.32	53
Cu	=	0.819***	0.057	+	−0.173***	0.036	+	0.594***	0.104	+	1.77***	0.316	0.88	0.15	56
Ni	=	0.540***	0.097	+	−0.047$^{\text{ns}}$	0.087	+	0.387*	0.204	+	1.664**	0.556	0.59	0.24	53
Zn	=	1.312***	0.126	+	−0.135**	0.049	+	0.842***	0.109	+	1.316***	0.349	0.85	0.20	56

[a] Standard error of estimate (SEE).

[b] Standard error (SE).

Statistical significance $^{*}p < 0.1$, $^{**}p < 0.01$, $^{***}p < 0.001$, ns: not significant.

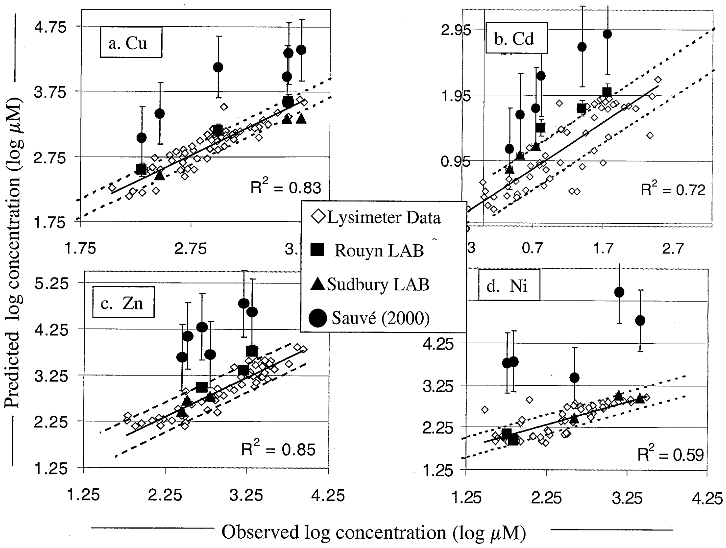

Figure 6. Observed concentrations versus concentrations predicted using regression equations. Super-imposed on lysimeter results (clear diamonds) are predicted versus experimental values for laboratory leachates, and the predicted values from the regression of Sauvé *et al.* (2000). Dotted lines indicate the standard error of estimate of the lysimeter regression equations.

These results suggest that the chemistry of laboratory leachate solutions are the result of similar, but not identical, reactions as produced the lysimeter solutions. In fact, the exceptions demonstrate the complexity of the mechanisms producing lysimeter solutions. The solutions are reasonable reproductions of lysimeter solutions with respect to the overall chemical composition of the solutions and they are not due to simple dilution of sampling artifacts.

Concentrations of Metals in Soil Solution Extractions, Literature Values

Sauvé *et al.* (2000) provided a complete review of the partitioning of trace metals in solution extracts from contaminated soils. Their work integrated soil characteristics (SOM and pH) together with metal loading to provide predictions of metal partitioning between the solid and solution phases of soils. This review combined a wide variety of solution extractions; batch extraction, water extracts, centrifugation, weak salt batch extractions, saturation extracts and lysimeter data. We used these regressions to calculate the expected concentrations of solutions produced by the leaching procedure relative to metal partitioning observed in other studies. The results are also super-imposed in Figure 6. Error bars are based on the observed standard error of estimate from the regression equations in Sauvé *et al.* (2000).

It is evident from the position of these points that the majority of solutions produced in past studies were more concentrated than what we have observed in our data in both laboratory leachates and lysimeter solutions. Average concentrations are typically a full order of magnitude greater than concentrations observed in our study. Our results were found to fall on the lower extreme of the error bars of these equations. Differences between literature values and lysimeter solutions are more evident when presented as partitioning coefficients (log K_d). Table 3 presents log K_d values calculated from the observed concentrations in lysimeter solutions, the laboratory leachates and the regression equations from Sauvé *et al.*

Table 3
Log Kd values calculated from the concentrations observed in lysimeters, laboratory leachates and from regression equations based on literature values

	log K_d values calculated from metal concentrations in lysimeters					log K_d values calculated from metal concentrations in leachates					log K_d values calculated from regression of Sauvé *et al.* (2000)				
	Cd	Cu	Ni	Pb	Zn	Cd	Cu	Ni	Pb	Zn	Cd	Cu	Ni	Pb	Zn
Sudbury Site 1	3.86	4.15	4.20	5.10	3.34	4.07	3.63	3.89	5.20	3.46	2.74	3.15	1.31	3.99	1.89
Sudbury Site 2	3.45	4.10	4.28	3.93	3.64	3.47	3.43	4.08	4.07	3.49	2.48	2.96	0.43	3.63	1.38
Sudbury Site 3	2.75	3.54	3.64	4.07	2.86	3.48	3.60	3.61	4.33	3.19	2.81	3.03	1.38	3.70	2.17
Rouyn Site 1	2.94	3.83	3.14	4.72	2.83	3.37	3.68	3.43	4.33	3.28	2.46	2.99	0.92	3.72	1.74
Rouyn Site 2	3.40	3.90	3.87	4.07	3.36	3.51	3.91	3.60	4.36	3.48	2.55	3.00	1.03	3.90	1.88
Rouyn Site 3	3.25	3.62	3.17	4.81	2.93	3.86	3.89	3.80	4.37	3.53	2.58	2.96	1.12	3.75	1.79

(2000). The latter are typically close to a full order of magnitude higher than those observed in this study. While any estimate of partitioning of elements to solution is at best a rough estimate, it is nonetheless important that estimates are on the same order of magnitude as field solutions. Order of magnitude differences may result in large over-estimates of toxicity and mobility of trace metals.

The differences between the regression results of Sauvé *et al.* (2000) and our results are due to a number of factors. Typically, laboratory solution extractions have been observed to be more concentrated than lysimeter solutions in all elements and the results vary significantly depending on sample manipulation and the type of extraction (Bartlett and James, 1980; Qian and Wolt, 1990; Sheppard *et al.*, 1992; Keller, 1995; Heinrichs *et al.*, 1995; Geisler *et al.*, 1996). The data used for the regressions in Sauvé *et al.* (2000) also included metal spiked soil data, which may have artificially increased solution concentrations. The differences could also be attributed to differences in the soils, i.e., we studied organic horizons that typically have stronger affinities for metals (McBride, 1994). Finally, some of the data came from studies where dilute salt solutions (i.e., 0.01 M) were used, resulting in higher concentrations of trace metals in solution; it also makes analysis somewhat easier. It is important, however, to be conscious of the fact that these extractions are probably not representative of mobile metals in the soils. From Figure 6, we may conclude that estimates of mobile soil solution chemistry may be better reproduced through the use of an extraction method such as is proposed in MacDonald *et al.* (2004).

Conclusion

Washing air-dried soils before leaching with a solution with environmentally relevant Ca concentration resulted in solutions similar in composition to field lysimeter solutions. Concentrations of cations, including contaminant trace metals in solutions produced by the leaching procedure, were not exact reproductions of lysimeter solutions. However, based on a simple regression model, the solutions were, for the most part, plausible reproductions of lysimeter solution chemistry with respect to metal concentrations and other factors known to influence metal partitioning and speciation.

In cases where field data are not available, the proposed method shows promise for providing estimates of partitioning coefficients for use in transport modeling, and for providing estimates of metal speciation for use in toxicity studies. The method also shows promise for preparing soil columns for use in metal adsorption-desorption experiments under conditions similar to those observed in the field. In general, this method has a number of advantages over possible alternatives. It uses air-dried and homogenized soil samples and yields a relatively large quantity of soil solution. A number of similar solutions can be produced over time from different sub-samples of the same soil. Also, the washing protocol provides a means of identifying the appropriate amount of water to use that will result in a reasonable estimate of field solutions if no knowledge of field solutions is available. By carrying out the leaching procedure with dilute salt solution after the electrical conductivity of the wash solution has begun to stabilize, we insure that constituents of the soil solution are a result of a steady state between the soil solution and the soil solid phase rather than simple dissolution of artifacts accumulated on the soil surface during the process of sample preparation. Researchers are cautioned as the methodology has only been tested on a single soil type and should be further validated in soils with a wide variety of chemical characteristics. The errors observed in the results also emphasize the complexity of the chemistry of trace metals in soils. The validity of results of extractions depend on the validity of the assumptions that field solutions are a result of steady state chemical exchange between the soil surface and the soil solution. Researchers must also be cautioned as to the validity of these assumptions. Evidently there is no real substitute for field data.

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