

Column Leaching Using Dry Soil to Estimate Solid-Solution Partitioning Observed in Zero-Tension Lysimeters. 1. Method Development

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In order to understand the reactions taking place between the soil solid phase and the soil solution, we require knowledge of the chemistry of the soil solution as it occurs in the field. This knowledge allows us to conduct experiments with environmentally relevant concentrations of macro and microelements in solution. Zero-tension lysimeters directly sample the mobile fraction of soil solutions. Unfortunately, they are expensive to sample and require long equilibration periods. Other solution extraction methods do not provide solutions similar in concentration to lysimeters, either because they sample a different fraction of the soil solution or due to the impacts of the sampling process. The processes that produce lysimeter solutions cannot be emulated; however, to estimate lysimeter solution chemistry, we developed a standard protocol to produce solutions that resemble lysimeter solutions from podzolic soils using air-dried samples. We washed air-dried soil columns sequentially with de-ionized water until the electrical conductivity (EC) of the leachates stabilized and then leached the columns using an environmentally relevant concentration of a weak salt solution. We hypothesize that the stabilization point of the EC of the soil solution is indicative of the point at which soluble salts and organic material precipitated during sampling and storage are removed from the soil surface. Solutions produced by leaching, once the EC of wash solutions had stabilized, were

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comparable to lysimeter solutions from the area where samples were collected with respect to the concentrations of divalent cations, pH, EC and DOC.

Keywords Soil solution extraction, miscible displacement, field solution.

Introduction

The physical transport and the uptake of nutrients and contaminants or their toxicity to biota are all related to the chemistry of the soil solution. However, the soil solution that is studied by researchers is operationally defined. Different extraction methods produce solutions that are chemically different and these differences are augmented by sample treatment. The influence of extraction method on soil solution chemistry is well documented (Litoar, 1989; Ross and Bartlett, 1990; Zabowski and Ugolini, 1990; Sheppard *et al.*, 1992; Marques *et al.*, 1996; LaZerte and Scott, 1996; Geisler *et al.*, 1996; Ludwig *et al.*, 1999). The differences are often explained as the fraction of the soil solution, i.e., the “mobile” fraction, or the “available” fraction (Ludwig *et al.*, 1999; Lawrence and David, 1996) defined by the force of the extraction method, or these differences are the result of changes in the soil solid phase during the process of sampling or storage (Bartlett and James, 1980; Qian and Wolt, 1990; Walworth, 1992; Kohut and Dudas, 1994; Courchesne *et al.*, 1995; Ludwig *et al.*, 1999; Marquis *et al.*, 1999).

With the advent of numerical modeling of contaminant fate and transport as well as risk assessment, there is a need for reasonably accurate estimates of soil solution chemistry, to calculate the partitioning of elements between the solution and solid phases. Furthermore, in order to understand the soil chemical processes we need to be able to carry out laboratory studies under conditions similar to those in the field. The ionic strength, pH and concentrations of ligands, especially dissolved organic carbon, influence the reactions that release elements to solution, as well as the chemical characteristics of the surface of the soil solid phase. The ability to homogenize and store soils, and subsequently reproduce solutions that are similar to field solutions would be a great benefit for experiments on solid-solution partitioning.

Zero-tension lysimeters are used to sample the mobile fraction of soil solutions, i.e., solutions that move freely through the soil profile (Lawrence and David, 1996; Ludwig *et al.*, 1999). Unfortunately, zero-tension lysimeters require equilibration periods of up to one year before they are stable, and are expensive to install and sample. Furthermore, since they are installed in undisturbed soil columns, it is difficult to describe the soil that is producing the solution without destroying the lysimeter itself.

Soils are altered when they are sampled and brought to the laboratory. The sampling method, storage, drying and homogenization of soil samples all alter soil chemistry. Typical observations include the acidification of particle surfaces (Qian and Wolt, 1990), changes in the solubility of certain solids (Comfort *et al.*, 1991), increases in soluble organic material (Bartlett and James, 1980; Walworth, 1992), inconsistent changes in pH (Courchesne *et al.*, 1995) and large increases in microbial activity (Qian and Wolt, 1990). Cell lysis, after the cutting and drying of fungal hyphae and fine roots, as well as the death of microbial organisms during the sampling and drying process, may also contribute to increases in soluble salts and soluble organic carbon (Jones and Edward, 1993).

Theory

The soil solution observed in lysimeters is a result of combinations of chemical, physical and biological reactions. Before they are sampled, soils are in steady state with their environment,

i.e., the concentration of cations in solution is a function of the charge of the soil surface, the cations that make up the exchange complex, biological demand for essential nutrients, leaching losses and the concentration of cations added to the soil via canopy leaching, organic matter decomposition and mineral weathering.

Sampling and treatment of soils, particularly air-drying, results in the accumulation of soluble salts and organic material on soil particle surfaces. We believe the main reason for the change in solution chemistry is the presence of these soluble salts and soluble organic material on the soil particle surface. Nonetheless, exchangeable cations are measured on dry soils by ion displacement so it is assumed that sampling, air-drying and homogenization does not significantly modify the *overall* chemical makeup of the soil exchange complex. We suggest that by sequentially washing a soil, excess soluble material can be removed. Since the soil particle surface is charged, it retains a defined amount of cations necessary to neutralize its negative charge while excess cations may be easily leached from the soil. The amount of pore water retained in the soil column also controls the quantity of ions retained in a soil column but not held by soil surface charge. These ions may be removed through dilution. Once the excess soluble material has been removed, concentrations of elements observed in percolating solutions, passing through soil columns should be controlled by exchange reactions with the soil exchange complex. Leaching with a concentration of cations similar to the solution entering the soil horizon (in throughfall or from upper soil horizons) should produce soil solutions similar in chemistry to that observed in lysimeter solutions.

This paper describes the development of a protocol for pre-treatment and steady-state leaching of dried and homogenized soils. This pre-treatment was developed to reproduce the partitioning of Ca and Mg as well as soil solution components such as pH, ionic strength and dissolved organic carbon (DOC) observed in lysimeter solutions from forest soils that have been monitored for several years. The protocol described here was later used to study the partitioning of trace metals in contaminated forest soils with similar intrinsic characteristics (MacDonald *et al.*, 2004).

Material and Methods

Site Description, Field Study and Sampling

The study site is located in the Hermine watershed, 80 km north of Montréal, Quebec, Canada. Lysimeter and throughfall data are from a continuous watershed monitoring program carried out by McGill University and l'Université de Montréal. Results presented are based on data gathered every two weeks from 1994 to 2000. The site, established in 1993, has been extensively described in Bélanger *et al.* (2002). The forest floor is a moder humus form; the soils are classified as Orthic Humo-Ferric Podzols formed on glacial till (Expert Committee on Soil Survey, 1998) and vegetation is dominated by sugar maple, red maple and American beech. The St-Hippolyte research site consists of nine experimental plots, in a 6-ha watershed, grouped in a 3 by 3 experimental design. Experimental plots are 15 meters in diameter in which vegetation, soil and soil solutions, rainfall and throughfall are sampled. Near the center of each plot there are two lysimeters, one that samples soil solutions leaving the forest floor and one that samples the soil solution leaving the rooting zone at 50-cm depth. The forest floor lysimeter is installed below the humus layer of the forest floor at the organic-mineral interface. Plots in each group of 3 are approximately 80 meters apart (center to center). The samples used in this study consist of three 1-kg samples of the forest floor, one gathered, between plots 7 and 8 (roughly 25 meters from the lysimeters) and two others between plots 8 and 9. Two mineral soil samples were also collected by

digging soil pits and gathering (using a hand spade) 1-kg samples at a depth of 40-50 cm in the soil profile, one between plots 7 and 8 and one between plots 8 and 9.

Solution Analysis

Electrical conductivity (EC) and pH were measured before filtering solutions through 0.4 μm Millipore polycarbonate filters. Cations were analyzed using flame atomic absorption spectrometry (FAAS) and anions using a Waters ion chromatograph. Dissolved organic carbon concentrations in solutions were first measured using the method described by Moore (1985) and were thereafter estimated using linear relationships between the absorbance at 254 nm and the DOC concentrations in mg L^{-1} . All solution analyses were carried out using external quality controls (LRTAP, Inter-laboratory study, Environment Canada).

Method Description

Solution extractions were carried out using a column miscible displacement method. The soil columns were prepared by loosely packing 5 g of forest floor or 15 g of mineral soil into a syringe barrel. High-density polyethylene frits encased the soil in the syringes. A second syringe barrel, to hold the solutions being added, was inserted into the middle syringe (see Figure 1). Suction was applied to the soil column by a Centurion 100 syringe extractor and solutions contained in the upper syringe dripped slowly into the soil columns and then out into the lower syringe. Columns were maintained at 4 to 6°C at all times.

Figure 2 describes the sequence of pre-treatments and the three different leaching procedures used in this study. Briefly, the pre-treatment was carried out by introducing aliquots of de-ionized water to the upper syringe. The water was then drawn through the soil column at 30 ml/hr. Two to three hours were allowed between washes; 30 ml aliquots were used in all the organic forest floor leaching experiments, but 20 ml aliquots were used in one preliminary test on mineral soil horizon samples. The total amount of water used for the pretreatment of forest floor and mineral soil samples was 120 ml and 80 or 90 ml respectively. Using this amount of water decreased the electrical conductivity of wash solutions to 50 $\mu\text{S cm}^{-1}$ in the case of organic soils and 20 $\mu\text{S cm}^{-1}$ in the case of mineral soils, which are typical of field observations.

After pre-treatment with de-ionized water, the soil columns were leached with either 20 ml of de-ionized water or an 80 μM $\text{CaCl}_2\text{-CaSO}_4$ mixture, at a rate of 2 to 3 ml hr^{-1} . In the two first leaching procedures solutions were extracted at 24-hour intervals for three and four days. In the third leaching procedure columns solutions were extracted by leaching the

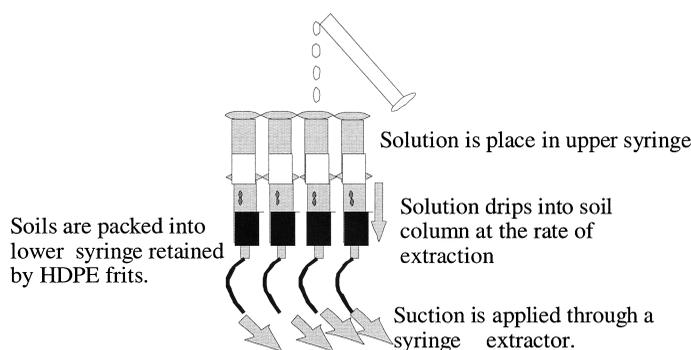


Figure 1. Experimental set-up.

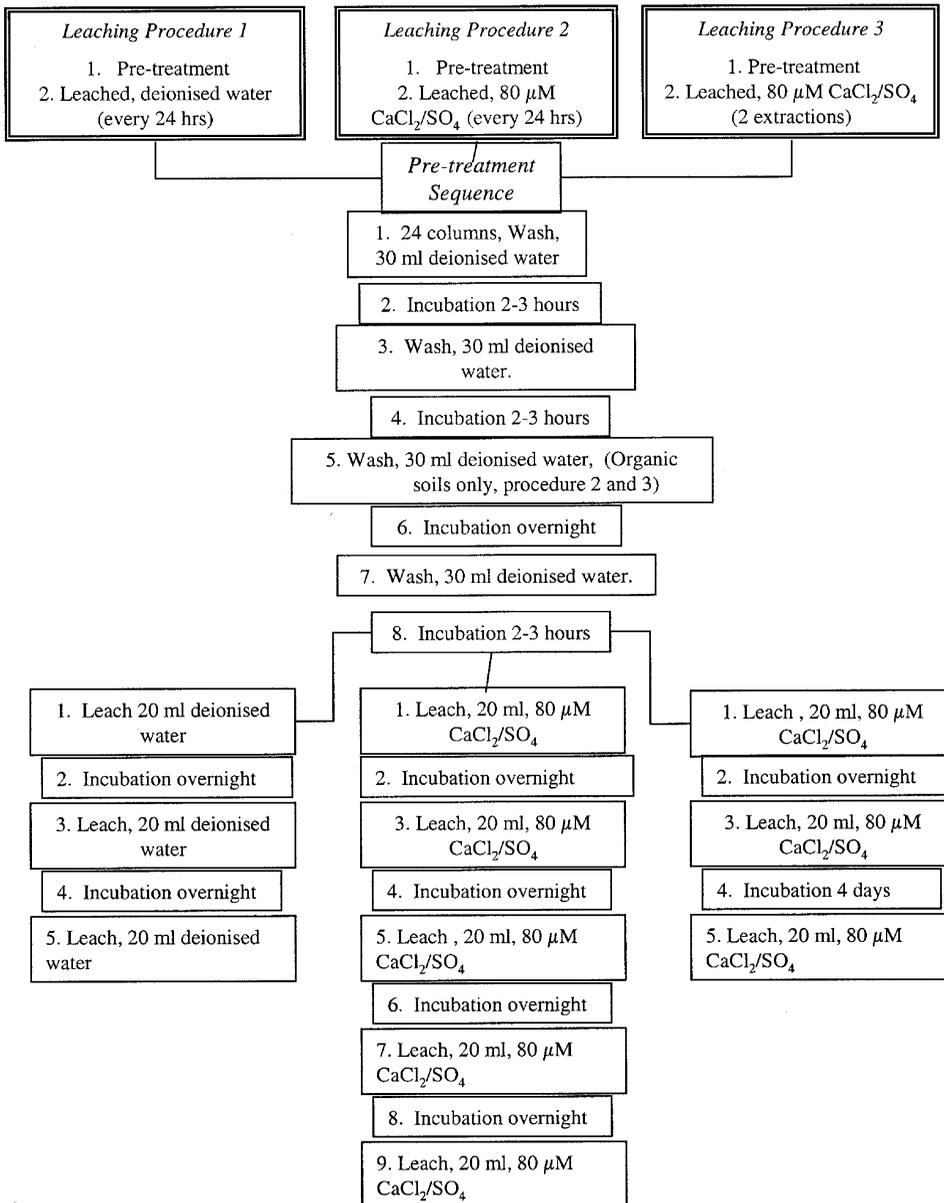


Figure 2. Organigram of methodology of extractions.

soil columns with the 80 μM $\text{CaCl}_2\text{-CaSO}_4$ mixture on day 3 of the procedure and after an incubation period of 4 days to attempt to simulate incubation times observed between rainfall events.

Modeling

To model the process of sequential washing of a charged surface in the presence of CaCl_2 , we used the permanent charge electrostatic adsorption (Guoy-Chapman) model in MINTEQA2 v. 4 released by the US EPA (Allison *et al.*, 1991) with a Windows graphical interface

Table 1
Summary of modeling scenarios using MINTEQA2 v. 4

	Initial conditions	Action and comments
Scenario 1	16.5 mM CaCl ₂ , 30 mmols surface charge.	7 sequential wash steps, assumes 25% water retention capacity. 75% of equilibrium solution and all Ca in this solution is removed at each wash step.
Scenario 2	15 mM CaCl ₂ , 30 mmols surface charge.	7 sequential wash steps (as above)
Scenario 3	16.5 mM CaCl ₂ , 30 mmols surface charge.	7 sequential wash steps (as above) At fourth through seventh step 80 μM CaCl ₂ is added to the suspension.

(Gustaffson, 1999). The surface is modeled as a suspension in a fixed volume of liquid and after each equilibration period the majority of the theoretical solution is removed from the preceding model calculations. The model assumes a pore water volume of 25% was carried over from each simulated leaching step to the subsequent step.

Table 1 describes the three modeling scenarios that were carried out. Sequential washing was simulated with a negatively charged surface of 30 mmol equilibrated with (1) 16.5 mM CaCl₂ cations (10% in excess of the negative charge of the surface) or (2) 15 mM CaCl₂ (positive charge supplied by cations equal to negative charge of surface). In the third scenario, a weak CaCl₂ solution (80 μM) was supplied to the suspension after four washings.

Statistical Analysis

We used the non-parametric statistical methods provided in SYSTAT© 10 (Wilkinson, 2000) to test if soil solution concentrations fell within a reasonable range of error that is defined by spatial and seasonal variation of soil solution chemistry observed in lysimeters. Leachate solutions produced during the third leaching procedure were compared to lysimeter results (collected bi-weekly from the three lysimeters in the same area over 4 years) using notched box plots that create confidence intervals around the median. Each box represents 50% of observed values and whiskers 1.5 times the inter-quartile range. While boxplots may be interpreted with respect to their statistical significance, we recognize the inherent differences in the solutions that we are comparing. Boxplots are presented as a means of judging the relative similarity of laboratory extractions versus lysimeter solutions (the similarity of median values) while also taking into account their variability (the distribution provided by the box and whiskers). General statistics for the data in St-Hippolyte were also calculated (mean, median and coefficient of variation) for the lysimeters installed at the site.

Results and Discussion

Modeling Results

Soils are composed of charged material and function in a similar fashion to charged surfaces. Examining how simple surfaces react to sequential washing provides insight into how soils should react. Figure 3a illustrates the results of modeling scenarios 1 and 2 using the fixed charge surface in MINTEQA2. In scenario 1 (the suspension has excess Ca²⁺

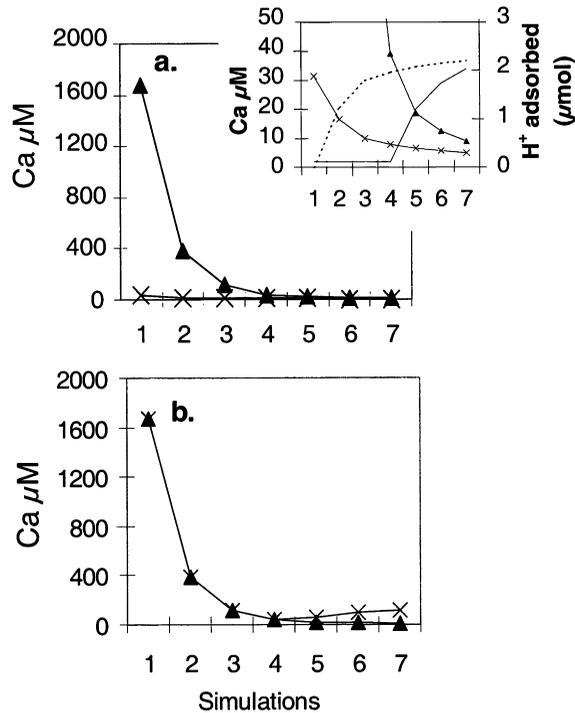


Figure 3. Model simulations of Ca concentrations in solution with a charged surface: (a) Scenario 1 (▲) and Scenario 2 (X); (b) Scenario 1 (▲) and Scenario 3 (X). Inset graph is a close-up of last four simulations and H^+ bound to the charged surface (dotted and solid lines) for the two modeled scenarios.

relative to the negative surface charge) the removal of excess Ca occurred after three washes of the charged surface and was recognizable as a plateau in the concentrations of Ca in solution. Concentrations of Ca in solution quickly decreased to concentrations observed in the suspensions that originally began with the positive charge of Ca in the suspension equal to the negative charge of the surface (scenario 2). The plateau is representative of an equilibrium occurring between H^+ and Ca at the fixed pH of 5.5. We observed that when there was no longer an excess of Ca^{2+} in solution, H^+ adsorbed to the surface and displaced Ca^{2+} (inset of Figure 3a).

In Figure 3b, scenario 1 is compared to scenario 3 in which a weak $CaCl_2$ electrolyte was introduced at step 4 after the excess Ca^{2+} was removed. The surface rapidly established a steady state in which the concentration of the output solution was equal to the concentration of the input solution.

There are two points to be taken from this modeling example. First, when there is an excess of base cations in solution, relative to the charge on the surface, the cations will remain in solution and can be easily leached. If there is a deficit of base cations, then the cations will be held strongly by the charged surface and can only be leached if another cation (such as H^+) is available to neutralize the surface charge. Also, the modeling demonstrates that when the particle surface has a water retention capacity, excess cations must be removed through sequentially diluting the solution held on the soil particle surfaces. The water retention capacity, or pore water volume, will influence the number of sequential leaching steps required to dilute the excess ions retained within the liquid phase of the soil.

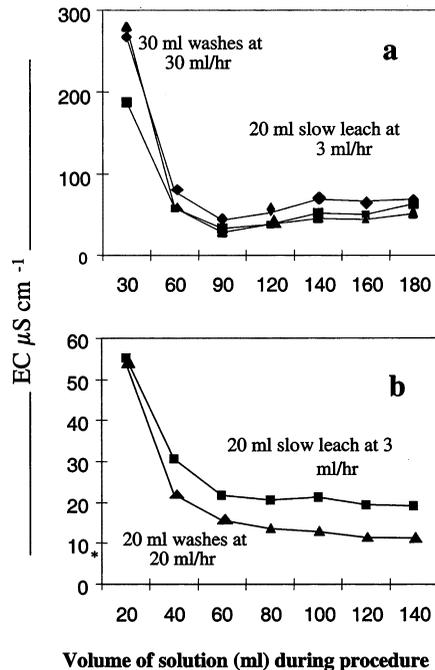


Figure 4. Electrical conductivity of leachates when using deionized water of (a) forest floors (◆ Sample A ▲ Sample B ■ Sample C), and (b) mineral soils (■ Sample D ▲ Sample E). *note that the wash procedure differed; smaller volumes were used (20 ml aliquots for mineral soils as opposed to 30 ml for organic soils).

Pre-Treatment of Soils

If we assume that sampling and drying of soils result in the accumulation of soluble salts and organic material on the soil particle surface, the soils should react in a manner similar to a charged surface in the presence of excess cations (model scenario 1). The EC of soil solutions is a measure of the total concentration of dissolved ions. Figure 4 shows that during pre-treatment of our soils, the EC of leachates decreased rapidly and stabilized after three washes with de-ionized water. After the initial three washes the EC values were similar but lower than those typically observed in lysimeter solutions ($50 \mu\text{S cm}^{-1}$ for forest floor, $20 \mu\text{S cm}^{-1}$ for mineral soil). The soils never reached steady state; there was a slight increase in EC in two of the three forest floor samples when they were left overnight (between 90 and 120 ml on Figure 4a). The mechanisms that produced soil solutions in the soil columns are more complex than the simple modeling example and involve a variety of chemical reactions subject to reaction kinetics, as well as physical and biological processes. Nonetheless, the observed decrease in EC in the wash solutions appears to be due to the dilution of excess soluble material in the samples. The EC fell to values that are similar to values observed in the field and remained roughly constant thereafter.

Introduction of a Weak Electrolyte

When a weak electrolyte was introduced to the soil columns, we observed an increase in the electrical conductivity, particularly in the case of the mineral soil samples (Figure 5). The EC of forest floor samples was very similar to what was observed when the soils were

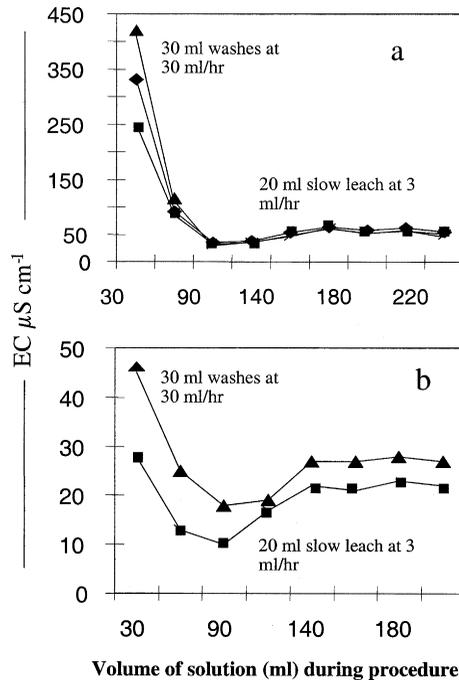


Figure 5. Electrical conductivity of leachates when using $80 \mu\text{M CaCl}_2/\text{SO}_4$ solution at 24-hour intervals after the wash step of (a) forest floors (◆ Sample A ▲ Sample B ■ Sample C), and (b) mineral soils (■ Sample D ▲ Sample E).

leached with de-ionized water alone. However, the concentrations of Ca were higher in the solutions extracted when using the weak electrolyte; concentrations in de-ionized water extractions were below $30 \mu\text{M}$ (not shown), whereas concentrations with the electrolyte ranged from 30 to $70 \mu\text{M}$. A weak electrolyte was required in order to initiate exchange reactions at the surface and produce solutions that were similar in composition to field solutions. A solution of $80 \mu\text{M CaCl}_2\text{-SO}_4$ was chosen because this concentration is similar to the EC of throughfall and soil solutions leaving the soil profile at 50 cm in St-Hippolyte and other northern hardwood forests (Foster *et al.*, 1992; Lawrence and David, 1996; Bélanger, 2000). Calcium was used as the cation due to its higher affinity for soil surfaces in comparison to other base cations such as Na or K (McBride, 1994) and its relative abundance in field solutions (Foster *et al.*, 1992; Bélanger, 2000). We have attempted to keep the protocol as simple as possible, but input solutions could be modified to meet the needs of different studies.

Figure 6 illustrates typical examples of the changes in the different elements of the soil solutions observed throughout the leaching process. The EC, pH and K concentrations were maintained over four leachings at 24 h intervals with a solution of $80 \mu\text{M CaCl}_2\text{-SO}_4$ from the fifth washing on. In mineral soils, the concentration of Mg in the leachates decreased during the leaching with the Ca solution due to the exhaustion of Mg on the exchange complex (Figure 6d). While the washing procedure removed only 5% of exchangeable Mg from forest floor samples, it removed up to 20% of exchangeable Mg in the case of mineral soil samples. Two extractions with Ca solution alter the makeup of the exchange complex sufficiently to reduce the amount of Mg released to solution. Therefore only the first two leachates, after the washing procedure, are representative of the soil solution.

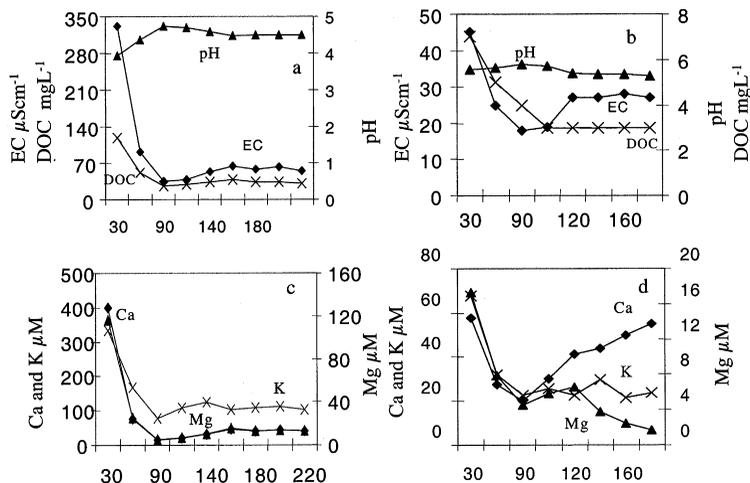


Figure 6. Elements in leachates using $80 \mu\text{M}$ at 24-hour intervals of a forest floor sample (a and c) and mineral soil sample (b and d).

Lysimeters versus Laboratory Leaching

Laboratory leachates produced during leaching procedure three, which included a 4-day incubation period, are compared to lysimeter solutions in Figures 7 and 8 and in Table 2. The laboratory solutions were not identical to field lysimeter solutions, but were similar in terms of pH, DOC, Mg, Ca and EC. The boxplots in Figures 7 and 8 can be interpreted statistically. Notches in the boxes represent the 95% confidence interval and the overlap of notches suggests that the solutions are statistically similar. If we interpret the boxplots in this way, some properties of the solutions are not statistically different from the lysimeters and some are statistically different. However, the lysimeters are not statistically indistinguishable according to this interpretation either; therefore, it is not surprising that extractions from

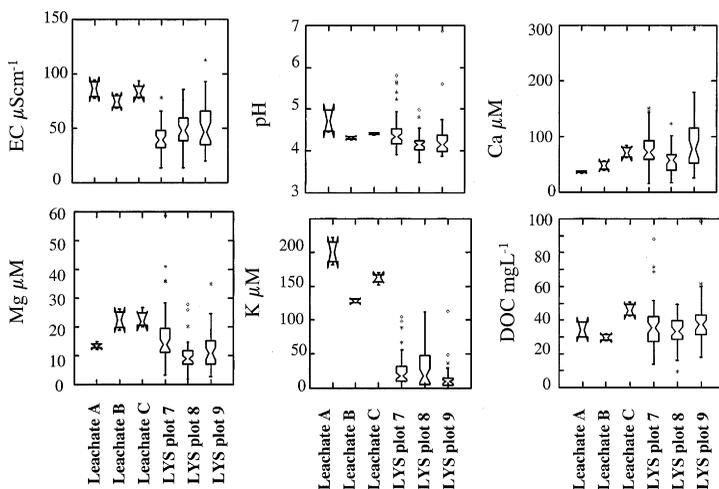


Figure 7. Boxplots comparing final two leachate solutions from leaching procedure 3 with a 4-day incubation (Leachate) to yearly lysimeter data (LYS) using forest floor samples A to C collected in St-Hippolyte.

Table 2

Lysimeter data and the average of concentrations in leachate solutions from Day 3 (24 hours after washing soils) and after 4 day incubation

	In Lab Column Extraction Method				St. Hippolyte Lysimeter		
	Sample A	Sample B	Sample C	Mean	Mean	Median	^A CV
A. Forest floor							
EC $\mu\text{s/cm}$	75	84	86	82	46	43	0.39
pH	4.31	4.41	4.7	4.47	4.29	4.2	0.59
DOC mgL^{-1}	29.6	46	34.3	36.6	36.3	34.9	0.36
Ca μM	48.2	71.4	36.1	51.9	74.1	62.5	0.6
Mg μM	22.5	22.7	13.4	19.5	13.2	11.5	0.64
K μM	128	162	201	164	24.8	14.4	1.25
NH ₄ μM	236	306	262	268	11.8	7.8	1.32
NO ₃ μM	0	3.54	6.9	3.48	4.18	0	1.52
Cl μM	113	112	80	102	15.1	10.5	0.9
SO ₄ μM	47.6	52.8	51.6	50.7	35.9	29.4	0.73
B. Mineral soils							
	Sample D	Sample E	Mean	Mean	Median	^A CV	
EC $\mu\text{s/cm}$	21.9	17.2	19.5	19.5	19.8	0.12	
pH	5.24	5.46	5.35	5.56	5.54	1.93	
DOC mgL^{-1}	2.98	2.15	2.57	2.48	2.43	0.32	
Ca μM	42.5	37.7	40.1	40.5	41.4	0.11	
Mg μM	15	6.38	10.7	9.8	9.47	0.21	
K μM	6.46	5.24	5.85	3.3	0	3.51	
NH ₄ μM	14.7	12.6	13.7	2.2	0	2.7	
NO ₃ μM	2.57	2.65	2.61	2.33	0	4.7	
Cl μM	77.9	78.2	78.1	10.9	9.8	0.47	
SO ₄ μM	26.7	11.4	19.1	55.4	56.4	0.11	

^ACoefficient of variation.

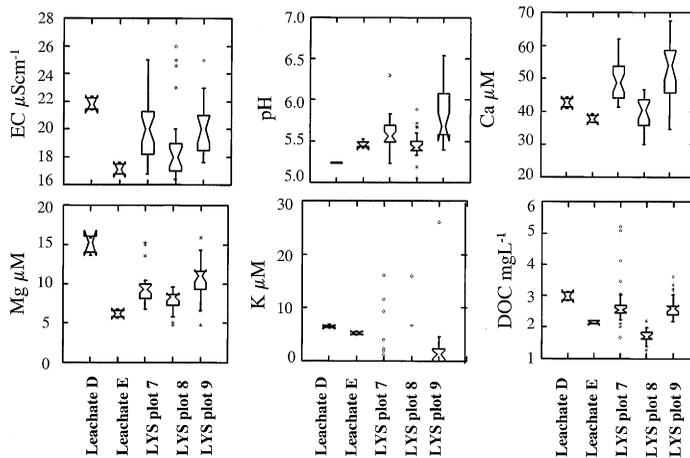


Figure 8. Boxplots comparing final two leachate solutions from leaching procedure 3 with a 4-day incubation (Leachate) to yearly lysimeter data (LYS) using mineral soil samples D and E collected in St-Hippolyte.

single soil samples collected at one time of the year are not statistically indistinguishable from the lysimeter results.

The median concentrations of these elements in leachates did not exceed median concentrations in lysimeters by factors of greater than two. With the exception of Mg, the solutions of the mineral soil samples fell within the whiskers of the box plots in Figure 8. Concentrations of monovalent macro elements such as K and NH_4 in the laboratory leachates were higher than in lysimeter solutions, particularly in forest floor samples. Forest floor solutions also had high EC values, probably due to the high concentration of monovalent cations in solution.

Incubating the columns for four days increased the range of solution characteristics. In mineral soils, the effect of incubation was minimal. Forest floor leachate solutions increased in concentrations of base cations and DOC by between 10 and 23%, the maximum difference being observed in an increase in Ca concentration in "forest floor sample C." In the case of "forest floor sample A," the pH decreased with incubation from 4.9 to 4.5.

The columns evidently are not entirely stable over time. However, the notches on boxplots for lysimeters in Figure 7 demonstrate that 95% confidence intervals around the median encompass concentration variations of up to 25%. Initial wash solutions of soil columns contained concentrations of Ca, Mg and DOC of 4 to 10 times lysimeter median values. With incubation concentrations do not return to concentrations observed in initial wash solutions, but vary on the same order of magnitude to the variation observed in lysimeter solutions.

In the only other effort to calibrate a solution extraction method to lysimeter solutions that we have observed, Lawrence and David (1996) proposed a complex treatment method for moist soils intended to be carried out in the field. An artificial throughfall solution was introduced to the soil and all liquid not retained against gravitational potential was removed. Interstitial solution was then extracted using low pressure applied by a syringe (i.e., essentially washing the soil using an artificial throughfall solution before displacing solution by pressure). Their washing procedure did not appear to adequately remove the effects of sampling. Furthermore, solutions from the disturbed soils were considerably more concentrated than lysimeter solutions, even with a low-pressure extraction; for example, concentrations of ions and DOC were 2 to 10 times greater than in lysimeter solutions.

Centrifugation and pressure are common methods of extracting soil solutions from field-moist soil samples, both of which require large amounts of soil for minimal amounts of solution. The results of these methods are not directly comparable to lysimeters, generally being more concentrated (total ions) and having DOC concentrations 2- to 3-fold those in lysimeters and having different ratios of ions in solution (Zabowski and Ugolini, 1990; Heinrichs *et al.*, 1995; Ludwig *et al.*, 1999). The use of dry soils increases differences. Ludwig *et al.* (1999) used a simple 2:1 dilution of a dry soil and observed similar total cation concentrations but concentrations of DOC five times that in lysimeters. While our results are not perfect reproductions of lysimeter solutions, they appear to be as good as other methods with the added advantages of using dried, homogenized soils, providing a relatively large volume of solution and being relatively simple and reproducible.

Conclusions

Lysimeter solutions cannot be reproduced in the laboratory. Nonetheless, we believe that soil solution chemistry is controlled by a steady state between the input solution and the soil exchange complex. Without field data, there is no way to guarantee that a solution is representative of lysimeter solution data. However, we have observed that the EC of

percolating soil solutions stabilizes at approximately the same value as EC's observed in field solutions. After soils were pre-treated to remove soluble salts and organic material precipitated on the soil particle surface during sampling and drying, laboratory leaching using a solution with environmentally relevant concentrations of Ca provided reasonable estimates of concentrations of DOC, Ca and Mg, pH and electrical conductivity typically found in lysimeters from the same area of northern hardwood forests. Though we feel the methodology is theoretically sound, the method was developed specifically with podzolic soils of northern hardwood forests and requires further validation on a wider variety of soils where lysimeter solutions are available. Nonetheless, the fact that this method uses dried homogenized soil samples that are easy to store, and that solutions may be replicated, makes it a practical option for studying a variety of chemical reactions taking place between the solid and solution phases of soils. Furthermore, it provides enough solution to run a range of analyses and is relatively simple compared to extractions that require undisturbed columns and complex experimental setups.

References

- Allison, J.D., Brown, D.S., and Nova-Gradac, J.D. 1991. MINTEQ/PROFEDQ, A geochemical assessment model for environmental systems. US Environmental Agency, Athens Georgia, EPA/600/3-91/021.
- Bartlett, R. and James, B. 1980. Studying dried, stored soil samples—some pitfalls. *Soil Sci. Soc. Am. J.* **44**, 721–724.
- Bélanger, N., Courchesne, F., Côté, B., Fyles, J.W., Warfvinge, P., and Hendershot, W.H. 2002. Simulation of soil chemistry and nutrient availability in a forested ecosystem of southern Quebec. Part II. Application of the SAFE model. *Env. Model. Software* **17**, 447–465.
- Bélanger, N. 2000. Investigating the long-term influence of atmospheric acid deposition and forest disturbance on soil chemistry and cation nutrient supplies in a forested ecosystem of southern Quebec. Doctoral Thesis, McGill University, Montreal, Canada.
- Comfort, S.D., Dick, R.P., and Baham, J. 1991. Air-drying and pretreatment effects on soil sulfate sorption. *Soil Sci. Soc. Am. J.* **55**, 68–973.
- Courschesne, F., Savoie, S., and Dufresne, A. 1995. Effects of air-drying on the measurement of soil pH in acidic forest soils of Quebec, Canada. *Soil Sci.* **160**, 57–67.
- Expert Committee on Soil Survey. 1998. *The Canadian Soil Classification System*, 3rd ed. Research Branch, Agriculture Canada, Publication 1646.
- Foster, N.W., Mitchell, M.J., Morrison, I.K., and Shepard, J.P. 1992. Cycling of acid and base cations in deciduous stands of Huntington Forest, New York, and Turkey Lakes, Ontario. *Can. J. For. Res.* **22**, 167–174.
- Geisler, R., Lundstrum, U.S., and Grip, H. 1996. Comparison of soil solution chemistry assessment using zero tension lysimeters or centrifugation. *Eur. J. Soil Sci.* **47**, 395–405.
- Gustafsson, J.P. 1999. Visual MINTEQ version 2.12, For Win95/98/NT. <http://amov.ce.kth.se/people/gustafjp/Vminteq/index.htm>.
- Heinrichs, H., Botcher, G., Brumsack, H., and Pohlman, M. 1995. Squeezed soil-pore solutes—a comparison to lysimeter samples and percolation experiments. *Wat Air Soil Pollut.* **89**, 189–204.
- Jones, D.L. and Edwards, A.C. 1993. Effect of moisture content and preparation technique on the composition of soil solution obtained by centrifugation. *Commun. Soil Sci. Plant Anal.* **24**, 171–186.
- Kohut, C. and Duda, M.J. 1994. Comparison of immiscibly displaced soil solutions and saturated paste extracts from saline soils. *Can. J. Soil Sci.* **74**, 409–419.
- Lawrence, G.B. and David, M.B. 1996. Chemical evaluation of soil-solution in acid forest soil. *Soil Sci.* **161**, 298–313.
- LaZerte, B.D. and Scott, L. 1996. Soil water leachate from two forested catchments on the Precambrian Shield, Ontario. *Can. J. For Res.* **26**, 1353–1365.

- Litoar, I. 1989. Review of soil solution samplers. *Wat. Res. Res.* **24**, 727–733.
- Ludwig, B., Meiwes, K.J., Khanna, P., Gehlen, R., Fortmann, H., and Hildebrand, E.E. 1999. Comparison of different laboratory methods with lysimetry for soil solution composition-experimental and model results. *J. Plant Nut. Soil Sci.* **162**, 343–351.
- MacDonald, J.D., Bélanger, N., and Hendershot, W.H. 2004. Column leaching using dry soil reproduces solid-solution partitioning observed in zero-tension lysimeters. 2. Trace Metals. *Soil Sedim. Cont.* **13**(4), 375–390.
- Marques, R., Ranger, J., Gelhaye, D., Pollier, B., Ponnette, Q., and Gædert, O. 1996. Comparison of chemical composition of soil solutions collected by zero-tension plate lysimeters with those from ceramic-cup lysimeters in a forest soil. *Eur. J. Soil Sci.* **47**, 407–417.
- Marquis, F., Camire, C., and Lachance, M. 1999. Basic cation and Al distribution in Ahe soil solution of fertilized maple stand: representativeness of saturation extracts (French). *Can. J. Soil Sci.* **79**: 47–55.
- McBride, M. 1994. *Environmental Chemistry of Soils*. Oxford University Press. New York.
- Moore, T.R. 1985. The spectrophotometric determination of dissolved organic carbon in peat waters. *Soil Sci. Soc. Am. J.* **49**, 1590–1592.
- Qian, P. and Wolt, J.D. 1990. Effects of drying and time of incubation on the composition of displaced soil solution. *Soil Sci.* **149**, 367–374.
- Ross, D.S. and Bartlett, R.J. 1990. Effects of extraction methods and sample storage on properties of solutions obtained from forested spodosols. *J. Environ. Qual.* **19**, 108–113.
- Sheppard, M., Thibault, D.H., and Smith, P.A. 1992. Effect of extraction techniques on soil pore water chemistry. *Commun. Soil Sci. Plant Anal.* **23**, 1643–1662.
- Walworth, J.L. 1992. Soil drying and rewetting, or freezing and thawing, affects soil solution composition. *Soil Sci. Soc. Am. J.* **56**, 433–437.
- Wilkinson, L. 2000. Systat Version 10? SPSS Inc., Chicago, IL.
- Zabowski, D. and Ugolini, F.C. 1990. Lysimeter and centrifuge solutions: seasonal differences between methods. *Soil Sci. Soc. Am. J.* **54**, 1130–1135.