

Chloride and Lithium Transport in Large Arrays of Undisturbed Silt Loam and Sandy Loam Soil Columns

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ABSTRACT

The transport of Cl^- and Li^+ was investigated in 90 undisturbed soil columns (28-cm diam., 35 cm deep) representing two soil series: structured silt loam (Hudson; fine, illitic, mesic Glossoaquic Hapludalfs) and unstructured sandy loam (Arkport; coarse-loamy, mixed, active, mesic Lamellic Hapludalfs). The columns had previously been operated with two cropping cycles, including two applications of a variety of sewage sludges (biosolids) at agronomic rates. With soil columns at field capacity and with no crops present, a pulse of 3.55 mM LiCl was added in the equivalent of 5.8 cm of water over the surface of the columns, followed by several irrigations (11.6 cm total depth) of deionized water and multiple subsequent irrigations with synthetic acid rain. Tracer concentrations in the outflow water increased almost immediately after application, with the Li^+ concentrations an order of magnitude less than Cl^- . Although there was a great deal of variation in initial Cl^- concentrations among the individual columns, the overall pattern was consistent for each soil after the initial 10 cm of flow (when variable preferential flow effects dominated) and was independent of the sludge applications. Outflow Li^+ concentrations were extremely variable among columns. Lithium adsorption partition coefficients (k_a) from batch equilibrations were lower than those derived from outflow concentrations. Solute losses were described with a simple preferential flow model. Apparent water contents fit a normal distribution for Cl^- while Li^+ apparent k_a values were lognormally distributed. Outliers (i.e., columns with transport parameters very different from the mean) had transport velocities that were slower than would be predicted by the respective distributions. Probabilistic approaches can be used to select the number of experimental columns required to meet a desired level of probability that soils columns with a meaningful range of transport velocities will be represented in the experimental set.

MANY RECENT STUDIES have found rapid increases in concentrations of surface-applied agrochemicals in subsurface tile drainage lines or shallow groundwater shortly after application (Gish et al., 1991; Klavdivko et al., 1991; Edwards et al., 1997; Mohanty et al., 1998). These findings often differ substantially from model predictions (Jury and Flühler, 1992; Steenhuis et al., 1994b). In other studies, travel times of adsorbed and nonadsorbed chemicals have been found to be the same (Camobreco et al., 1996) contrary to predictions based on the convective-dispersive equation (CDE). Kung (1990) observed that preferential flow rapidly transported pesticides and a tracer (independent of the adsorption characteristics) to a great depth, resulting in

a “few hot spots” without leaving a trace at intermediate depths. Richards et al. (1998) measured significant leaching of trace metals from an old sludge application site (also McBride et al., 1999) with—contrary to conventional expectations—no detectable readsorption in the subsoil, due to transport occurring as less reactive complexes moving through preferential flowpaths.

Research on quantifying the preferential flow paths in undisturbed soils (Gelhar and Axness, 1983; Germann et al., 1984; Sollins and Radulovich, 1988; Andreini and Steenhuis, 1990; Ghodrati and Jury, 1990; Yasuda et al., 1996; Jorgenson et al., 1998; Forrer et al., 2000) has indicated three main causes for preferential flow: (i) macropores comprised of burrows, root cavities, cracks, and interpedal faces in structured soils (Lawes et al., 1882; McCoy et al., 1994; and many others); (ii) unstable wetting front or “finger” flow (Hill and Parlange, 1972; Bauters et al., 1998); and (iii) sloping layered soils resulting in funnel or focused flow (Kung, 1990). These studies concluded that solute transport is both highly variable in undisturbed soil and can occur at rates lower than the saturated conductivity. Spatial and temporal quantification of the movement of solutes under field conditions is difficult due to the large standard deviation in solute velocity and concentration (Nielsen et al., 1973). The coefficient of variation for solute concentrations have been reported to range from 13 to 260% (Jury et al., 1991).

Laboratory experiments with undisturbed cores have the advantage that the solute concentrations in the outflow water can be measured. Since a few high velocity paths are sufficient to pollute groundwater (Parlange et al., 1988), these laboratory studies should contain a sufficient number of soil cores with high solute velocities. To estimate the number of soil cores needed in experiments so that the high velocity paths are included we will use the probability theory originally developed for predicting floods (Singh, 1991). Let us assume that there is a probability, p , that a solute velocity V is exceeded in the field. The probability, P , of having one or more columns in a set of n columns in which the solute velocity is at least V is

$$P = 1 - (1 - p)^n \quad [1]$$

Probability theory shows that for a normally distributed flow field, the probability P of a velocity V that differs from the mean by one standard deviation is 0.158. For two and three standard deviations, p is 0.022 and 0.0014, respectively. The probability P that V is exceeded in one or more columns in a set of n experimental columns can be calculated with Eq. [1] and is plotted in

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Abbreviations: CDE, convective-dispersive equation.

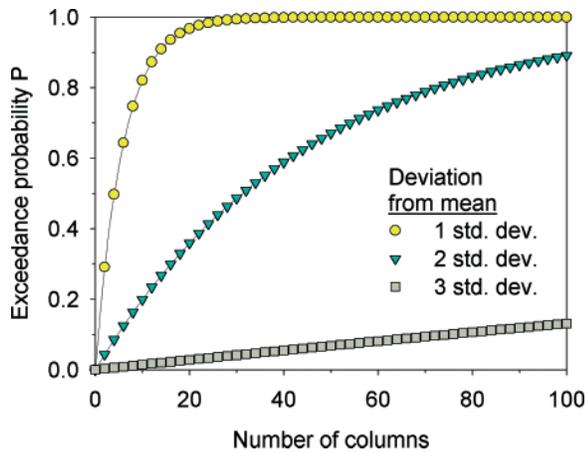


Fig. 1. Probability (P) that a velocity V (with probability, p) is exceeded in at least one experimental column as a function of the total number of columns used in a given experiment. Lines are probability that a column set contains at least one column with velocities that are 1 (circles, $P = 0.158$), 2 (triangles, $P = 0.022$), or 3 (squares, $P = 0.0014$) standard deviations from the mean value.

Fig. 1. The three lines in Fig. 1 represent the exceedance probability as a function of the number of soil columns for V at 1, 2, or 3 standard deviations from the mean. For example, for an experiment with 10 replicate columns, the probability is 82% that one or more columns have a velocity V of at least one standard deviation from the mean. There is only a 20% probability that one of these 10 columns has a solute velocity that is more than two standard deviations from the mean. Thus, most laboratory studies (such as by Skopp and Gardner, 1992; Camobreco et al., 1996; Djodjic et al., 1999; Ogden et al., 1999) with 10 or fewer columns have only a small probability that the fastest flowing pores (with V more than two standard deviations from the mean) present in the field are represented in the experimental columns. It is obvious that increasing the number of columns increases the likelihood that the preferential flow component can be accurately described in the laboratory.

For the current study, we used a large array of 90 undisturbed cores from two soil series (39 sandy loam and 51 silt loam, comprised of 39 regular and 12 old sludge application site cores), the number and design of soil columns governed by the experimental treatment matrix of a larger sewage sludge application study (described in detail in Richards et al., 2000). Note from Fig. 1 that with 39 columns of a given soil type there is a 60% probability that at least one of these columns has a solute velocity greater than two standard deviations above the mean. Because of the unique opportunity afforded by the large array of undisturbed soil columns, we examined the variability (among columns) of the transport of nonadsorbed anion (Cl^-) and adsorbable cation (Li^+) tracers. We used the nonadsorbed Cl^- tracer to determine the variability of movement of water through the columns, while the adsorbable Li^+ tracers allowed us to examine variability of adsorption among the soil columns. We used a simple preferential flow model to simulate the observed Cl^- and Li^+ movement and used the model parameters to characterize the variability of preferential transport among the replicate col-

umns. Our objectives were thus to examine the range and distribution of transport characteristics of Cl^- and Li^+ in this large array of soil columns.

MATERIALS AND METHODS

This study used 90 undisturbed columns that were part of a larger study of trace element mobility from land-applied sewage sludge products (Richards et al., 2000). The soil types selected, the number of soil columns, the sludge and soil pH treatments, and the use of synthetic acid rain were all governed by the experimental matrix of the sludge study, as described in greater detail in Richards et al. (2000). As will be shown below, the small amount of sludge applied up to that stage of the experiment did not affect observed tracer mobilities.

Soil Columns

The 90 undisturbed columns came from three sites representing two soil series, a silt loam and a sandy loam. Sites were within a 0.5-km radius on college farmland adjacent to the Cornell University (Ithaca, NY) campus. All sites had similar elevation and were nearly level or sloped slightly northward, and the soils were virtually free of rocks or gravel. Columns of soil (28-cm diam., approximately 33 cm tall) were hand-excavated in as close proximity to each other as possible, and a 35-cm length of corrugated polyethylene culvert pipe (30.5-cm i.d.) was placed around each soil column. Commercially available expanding polyurethane foam was injected to fill the voids between the soil and pipe. The foam was allowed to cure overnight, and the columns were removed the next day. Each column was placed on a support base (Fig. 2), with a central drain hole to allow free drainage. The column rested on two (1.2-m diam.) circles of black polyethylene film, which were drawn up and secured around the column. A circle of foam padding (2 cm thick) under the black plastic ensured contact between the plastic and the base soil. To direct leachate toward the central drain hole, a ridge of foam weatherstripping (1.3 cm thick) was placed around the outer edge of the foam base, and radial notches were cut into the foam base. PVC fittings threaded together through the drain hole both secured the plastic film to the base and provided a watertight seal. Leachate was directed through plastic tubing connected to the elbow to a polyethylene storage jug, with both tubing and jug darkened to retard algal growth.

The water application mode and pattern was the same as that used during regular cropping cycles of the larger experiment (Richards et al., 2000). To dispense water to each soil column, individual reservoirs (Fig. 2) were filled (volume = 3.3 L, equivalent to 5.8 cm depth over the entire column). Synthetic acid rain (pH 4–4.5; Richards et al., 2000) used during cropping cycles, designed to represent acid rainfall in the region, was prepared from deionized water and a concentrate of acids and salts. The rate of inflow was moderated to approximately 1.0 cm h^{-1} (which resulted in nonponded conditions during application for all but four columns) by fitting each reservoir with a constant-head device and a short piece of narrow-diameter tubing to serve as an in-line flow restrictor. A network of short fiberglass wicks was used to distribute the flow evenly across the soil surface of each column.

The 90 soil columns included (i) 39 columns of Hudson silt loam from a site with an unimproved pasture for a minimum of 25 yr (Hudson Meadow Site), (ii) 12 columns of the same Hudson soil but from a separate site in an adjacent apple orchard (Hudson Old Sludge Site) where a heavy loading of sludge was applied nearly 20 yr earlier (Richards et al., 1998;

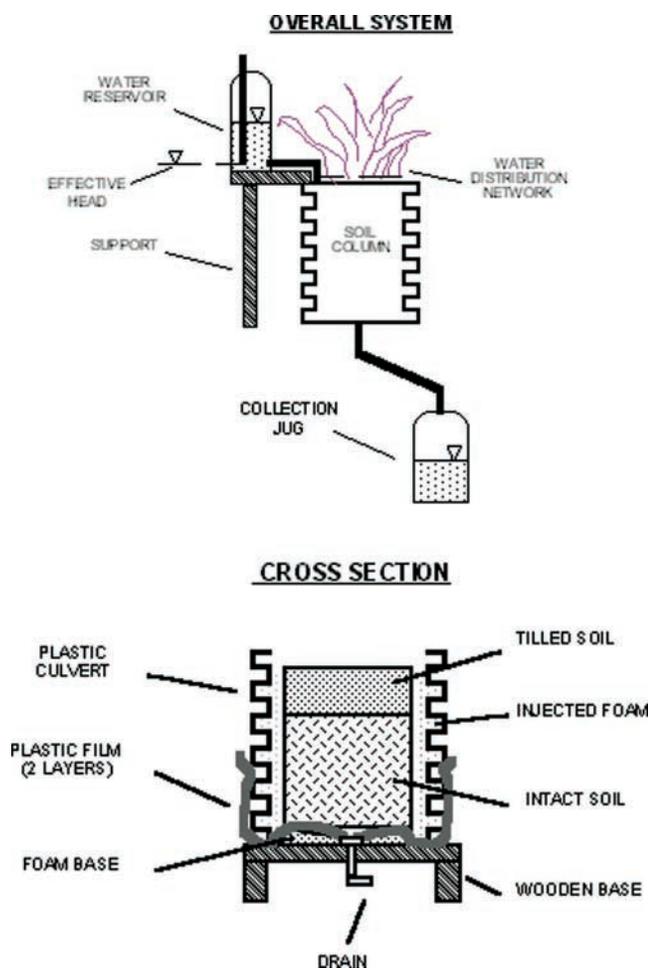


Fig. 2. Soil column and leachate collection system configuration.

McBride et al., 1999), and (iii) 39 columns of Arkport fine sandy loam from a site that was also in unimproved pasture for a minimum of 25 yr (Arkport Meadow Site). The Hudson consisted of a silt loam epipedon underlain by a silty clay loam subsoil. The Arkport had a sandy loam epipedon underlain by a variety of subsoil horizons varying from loamy sand to silty sand. The columns at one end of the column excavation area generally had a thin silty subsoil horizon that was absent in the other end. Earlier experiments have shown a well-defined macropore network for both soils (Steenhuis et al., 1994a, 1994b; Ogawa et al., 1999). The Hudson subsoil matrix is extremely dense, practically allowing flow to occur only in intrapedal cracks, root channels, and worm burrows, whereas the Arkport subsoil matrix is coarse, allowing substantial unsaturated flow in the matrix even when no flow occurs in the many worm burrows.

Prior Soil Column Treatments

Columns were stored indoors, sparingly watered to prevent desiccation, and covered with black plastic to kill weeds. Columns were placed in the greenhouse in the summer of 1994, and the upper 10 cm of the majority of columns was tilled and adjusted to initial pH levels of 6.5 to 7 (neutral) and 5.0 (low). Two sludge application-cropping cycles were performed before the tracer experiments described here. For each cycle, the upper 10 cm of the soil was tilled to simulate plowing and agronomic loadings of sludge (equivalent to 7.5 Mg ha⁻¹ dewatered sludge dry matter per cycle) were added. Sludge

products were (i) anaerobically digested dewatered sludge (the source feedstock for all other sludge products listed; Richards et al., 1997), (ii) dried pelletized sludge, (iii) alkaline-stabilized sludge (N-Viro™), (iv) composted sludge, and (v) incinerated sludge ash. Each sludge product was applied to three soil columns from each soil pH level for both the Arkport and Hudson soils. No-sludge control treatments included all Hudson Old Sludge Site columns as well as Arkport and Hudson soils at pH levels of 5, 6.5, and natural (unadjusted). During the 15- to 16-wk cropping cycles, the columns were watered once weekly with 5.8 cm of the simulated acid rain. Oat (*Avena sativa* L., Cycle 1) and romaine lettuce (*Lactuca sativa* L., Cycle 2) were grown. At harvest, the aboveground plant parts were removed, and root systems were tilled under following Cycle 1.

It is important to note that the columns had been leached at least 15 times since the last sludge application in Cycle 2. As we will show below, the sludge addition and pH adjustment treatments had no significant effect on analyte breakthrough when compared with the natural soil variation. This was expected in view of the low application rates of the sludge products.

Chloride and Lithium Breakthrough Study

The movement of Cl⁻ and Li⁺ ions through the soil columns was studied by adding a pulse of LiCl followed by multiple irrigations. The pattern of addition was intended to mimic the regular watering procedures used during cropping cycles. Before the LiCl addition, the final weekly watering of Cycle 2 was added on 17 July 1997; all percolation ceased and jugs were emptied on 19 July. On 20 July, 3.6 L (equivalent to 5.8 cm) of a solution of 3.55 mM LiCl in deionized water was added at a rate of about 1 cm h⁻¹ (which resulted in ponding at the surface of four of the 90 columns). This was followed by irrigation of 5.8 cm deionized water on 25 July and 1 August. Six rounds of sampling were conducted during the first 3 d following the LiCl pulse, and one round on the fifth day. Three rounds were collected in the 2 d following the first deionized water addition, and two rounds were collected in the 3 d following the second deionized watering. It should be noted that due to varying flow patterns, collected volumes varied markedly among columns. Practical considerations involved with simultaneous operation of 90 columns made collection of equal leachate volumes impossible.

Cropping Cycle 3 of the overall sludge application project followed the LiCl experiment. Much heavier applications of sludge products in Cycle 3 rendered any subsequent percolate concentrations invalid for the columns receiving sludge, but analysis was continued for percolates collected from the 24 no-sludge control columns (6 each of the Hudson and Arkport Meadow soils plus 12 Hudson Old Sludge Site); those columns experienced only a tillage of the upper 10 cm at the beginning of Cycle 3, so their percolate results—appearing at 35 to 40 cm cumulative depth in subsequent figures—were deemed useful.

Chloride was determined on all samples with a Buchler Instruments (Haake Buchler Instruments, Saddlebrook, NJ) digital chloridometer. The initial experimental design called only for Cl⁻ analysis, with Li determined later on archived samples using a Perkin Elmer (Wellesley, MA) atomic absorption spectrometer in emission mode. Lithium was determined only for the first three irrigations (the LiCl pulse followed by two deionized water irrigations) because the remaining runs had insufficient archived sample volumes.

Batch Adsorption Tests

The soil Li⁺ adsorption coefficients (k_d) were determined from adsorption isotherms developed through batch experi-

ments. Soil from the Ap (0–15) and Bw (15–40 cm) horizons of each soil type was passed through a 2-mm sieve. Ten grams of soil was equilibrated with 10-mL aqueous solutions containing 0, 10, 20, 50, 100, 250, 500, 1000, and 1200 mg L⁻¹ Li, separately, in three replicates. The suspension was gently hand mixed, allowed to stand for 24 h at room temperature, filtered (0.45- μ m nominal membrane porosity), and analyzed. The amount of Li added but not recovered in the solution was assumed to be adsorbed. Results were fitted to Freundlich isotherms.

Models

There are a number of models of varying complexity used to simulate solute flow in the vadose zone, including MACRO (Logsdon et al., 2002; Jarvis et al., 1991), USDA's Root Zone Water Quality Model (RZWQM; Ahuja, 1991), and LEACHEM (Hutson and Wagenet, 1995). The approach taken by the well-known CDE model assumes that water and solutes statistically sample all pore spaces, resulting in an equation where the water and solutes move at an average velocity with dispersion around the front. In contrast, preferential flow models assume there is limited involvement of the matrix in the transport process. In this paper, we tested the single fitting parameter preferential flow model developed by Steenhuis et al. (1994a). Testing of the CDE (both one and two domain; Parker and van Genuchten, 1984; Toride et al., 1995) was also performed but is not shown. Applicability of the CDE was compromised by transient water applications and the fact that the flow field had two distinct flow velocities representing both rapid preferential breakthrough as well as a portion of the solute moving slowly through the soil matrix. The CDE assumes a single average velocity with dispersion around the front, and cannot simultaneously fit both a rapid initial breakthrough and a long tail. The CDE algorithm is thus forced to assign an apparent velocity of zero and attributes all solute movement to impossibly large dispersivity values.

Most preferential flow models assume that a surface layer (termed the *distribution layer*) distributes water and solutes into the macropores (Ahuja, 1991; Jarvis et al., 1991; Ritsema and Dekker, 1994; Stagnitti et al., 2001; Steenhuis et al., 1994a; 1994b). The main differences among the various preferential flow models involve assumptions concerning the exchange of solutes in the preferential path with the soil matrix along the pore walls. Several models include some matrix–flowpath interaction (Wallach and Steenhuis, 1998; Stagnitti et al., 2001; Zhang et al., 1998). Ahuja (1991) assumed that some solutes end up in dead-end pores while in the MACRO models (Logsdon et al., 2002; Jarvis et al., 1991), water and solute exchange in the two domains is coupled by empirical interaction terms. Even with this degree of complexity, models may not adequately predict observed leaching (Logsdon et al., 2002).

The simplest model (Steenhuis et al., 1994a) assumes that the flow through the macropores is fast and that no interaction takes place with the conveyance zone below the distribution zone. This model is used here because of its simplicity and the minimum amount of parameters needed to be fitted. The soil profile is separated into a distribution zone (typically the plow layer) and a conveyance zone (subsoil). Water flows downward through the distribution zone and is then funneled into relatively few preferential flow paths in the conveyance zone. Assuming that this flow process can be described with the linear reservoir theory (Gelhar and Wilson, 1974), the cumulative loss of solutes, L , in the preferentially moving water from a soil can be written as (Steenhuis et al., 1994a, 1994b)

$$L = M_0 \left[1 - \exp\left(-\frac{Y}{W}\right) \right] \quad [2]$$

where L is the cumulative loss of solutes from the soil (M), M_0 is the initial amount of solute applied (M), Y is the cumulative depth of percolation since the application of solute (L), and W is the apparent water content (L).

The apparent water content (W) is a function of the distribution layer depth and characteristics:

$$W = D(\rho k_d + \theta_s) \quad [3]$$

where D is depth of distribution zone (L), ρ is soil bulk density (M V⁻¹), k_d is adsorption partition coefficient (V M⁻¹), and θ_s is saturated moisture content (V V⁻¹).

Because the flow velocity in the preferential flowpaths is high and no interaction occurs with the preferential flowpaths in the conveyance zone, Eq. [2] can be used to describe the solute flux. This preferential flow model has been successfully used to predict the loss of Cl⁻, pesticides and blue dye (Steenhuis et al., 1994a, 1994b), and trace elements (Steenhuis et al., 1999) when the matrix flow in the vadose zone can be neglected. The apparent water content W corresponds to the apparent fraction of the soil distribution layer volume containing water and participating in flow. As W decreases for a given amount of percolation (represented by Y), the predicted extent of solute loss increases.

Parameter Estimation

To obtain parameters to describe solute flow, the cumulative solute losses, L , calculated from concentrations and cumulative volumes determined at each sampling point, were fitted against the model described above. To obtain the apparent water content in the preferential flow model (Eq. [3]), we employed a linear regression of the outflow solute data in the form of $y = mx$ (zero intercept):

$$\ln\left(1 - \frac{L}{M_0}\right) = -\frac{1}{W}Y \quad [4]$$

Thus, taking Y as the independent variable and $\ln(1 - L/M_0)$ as the dependent variable and regressing (without intercept) yields the apparent water content as the inverse of the slope. In some cases, two to three data points from the lower end were deleted to achieve a better fit, a procedure similar to the SAS NLIN procedure (SAS Institute, 1996), except that it was done manually, using maximum R^2 as the criterion for the best fit.

The apparent water contents in the distribution layer (Eq. [3]) determined for each analyte allow us to estimate the adsorption partition coefficient (k_d) for Li⁺. By dividing W_{Li} , by W_{Cl} , we find from the definition of each that

$$\frac{W_{Li}}{W_{Cl}} = \frac{D(\rho k_d + \theta_s)}{D\theta_s} = 1 + \frac{\rho k_d}{\theta_s} \quad [5]$$

where W_{Li} and W_{Cl} are the apparent water contents for Li⁺ and Cl⁻, respectively. This ratio is thus equal to the retardation factor, r , which is actually a misnomer because the factor affects the outflow Li⁺ concentration but does not retard the arrival time. Lithium adsorption partition coefficients (k_d) were calculated with Eq. [4] using a saturated moisture content (θ) of 0.5 m³ m⁻³ in the distribution zone and a soil bulk density (ρ) of 1.3 Mg m⁻³ (both values based on prior experience with these soils).

To demonstrate the effects of the observed range of transport parameters on predicted mobilities, the preferential flow model was used to predict losses from each column (using the

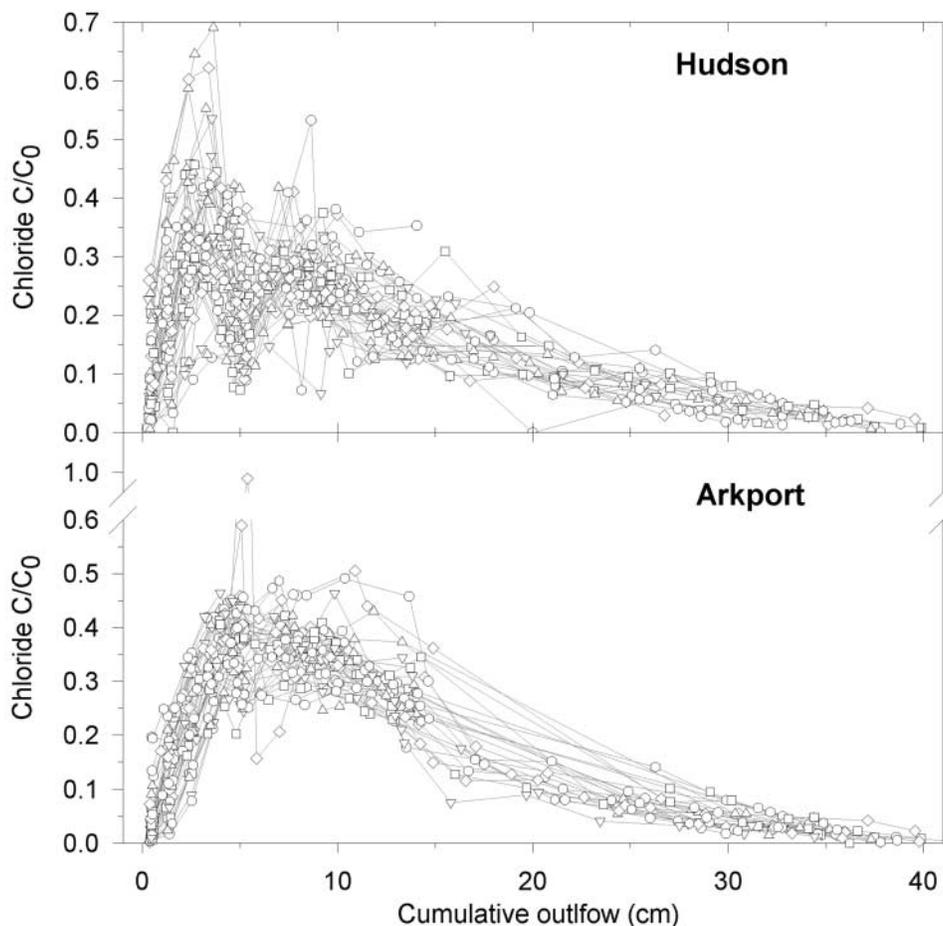


Fig. 3. Chloride concentration ratio C/C_0 in outflow water vs. cumulative effluent depth: 39 Hudson Meadow and 12 Old Sludge Site columns, 39 Arkport Meadow Site columns.

column's W_{Cl} and W_{Li} values) at various cumulative percolate depths (Y). At each cumulative depth (Y) simulated, the losses from individual columns were pooled so that we could calculate the solute loss from each column as a percentage of the loss from all columns.

Differences among soil column flow parameters were tested for interaction with prior sludge study treatments (sludge treatment, initial pH levels, and their interaction with soil type) using the SAS General Linear Model (SAS Institute, 1996).

RESULTS AND DISCUSSION

Chloride Breakthrough Curves

The relative Cl^- concentration (C/C_0) in the outflow water is plotted as a function of cumulative effluent depth for the Hudson (Fig. 3a) and the Arkport sites (Fig. 3b). Although there was, as expected, a large variation in Cl^- concentration among the 90 columns—especially for the first 5 cm of percolate—the overall concentration pattern near the end of the experiment for the two soils was surprisingly the same. In all cases, the concentration increased almost immediately after the tracer solution was applied. In most columns, $Cl^- C/C_0$ reached maxima at cumulative effluent depths of 2 to 5 cm, with the peak concentration occurring somewhat earlier for the Hudson columns. The rapid move-

ment of solute through preferential flow paths (especially in the Hudson) caused this early breakthrough. Although both soils reached background levels after 40 cm of percolation, the decrease in concentration differed for the two soil types. For the Hudson columns, a sharp decline in Cl^- concentration was noted first at about 5 to 6 cm and then, to a lesser degree, at 11 to 12 cm cumulative outflow depth (Fig. 3a), coinciding each time with the onset of the subsequent irrigation cycle, which suggests that preferential flow of the pure water caused this decline. The concentration in the drainage water then returned to approximately the same level before the sharp decrease. For the Arkport soil (Fig. 3b), the decrease in Cl^- concentration at 5 cm effluent depth was not as dramatic as for Hudson, with no “dip” in concentration at all at the end of the second irrigation cycle (11 cm of drainage). Overall, the Arkport had a more uniform response (Fig. 3b) with a smaller variation in concentrations.

Lithium Breakthrough Curves

As expected, the relative concentration of Li^+ in the drainage water (Fig. 4) was lower than that of Cl^- during the period when both analytes were measured. Most observed drainage concentrations were below 10% of

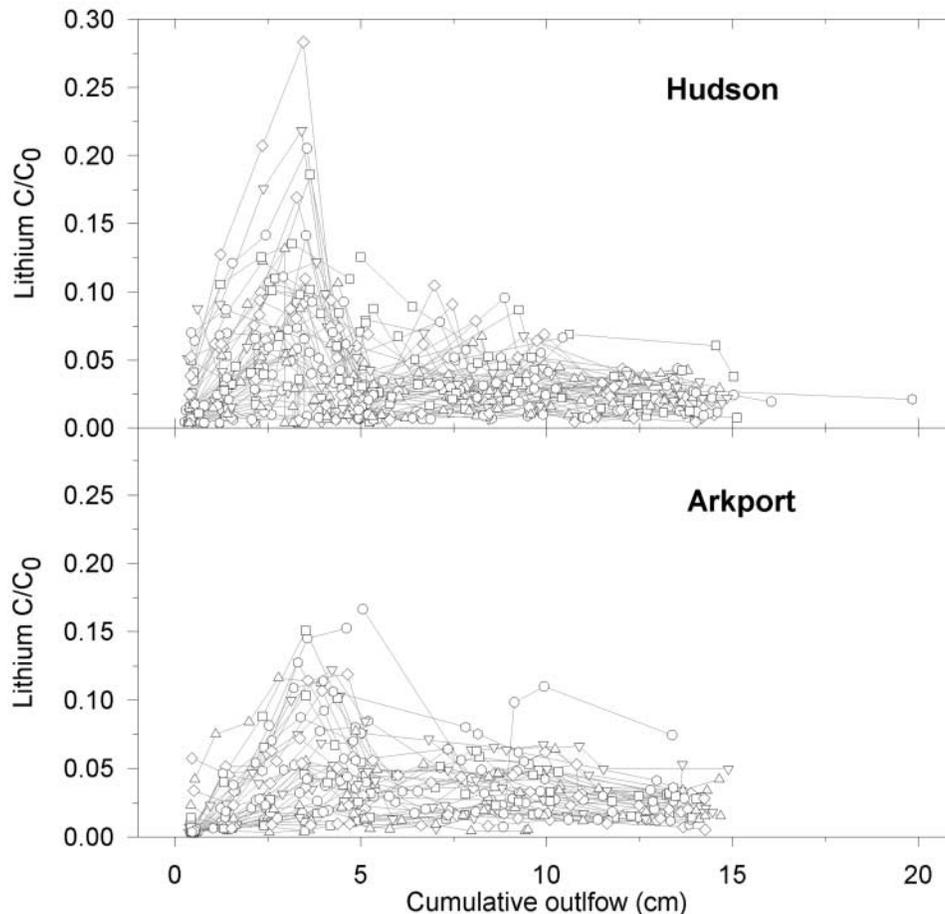


Fig. 4. Lithium concentration ratio C/C_0 in outflow water vs. cumulative effluent depth: 39 Hudson Meadow and 12 Old Sludge Site columns, 39 Arkport Meadow Site columns.

the input concentration. During the first irrigation (0–6 cm percolate), 36 Hudson and 25 Arkport columns had C/C_0 of 0.1 or higher. The relative variation in effluent Li^+ concentration was much larger (Fig. 4) than for Cl^- (Fig. 3), especially for Hudson columns. This means that the soil composition, together with the particular flow paths, affected cation transport in a different manner than the nonadsorbed anion (Jardine et al., 1988). Another remarkable characteristic for most columns was that Li^+ and Cl^- appeared in drainage water at the same time shortly after application (Fig. 4), contrary to the CDE approach where increased adsorption affects both the concentration as well as the velocity. Consequently, the CDE would have predicted a much greater velocity for Cl^- than for Li^+ .

Batch Adsorption Experiments

Figure 5 shows the results of the Li^+ batch adsorption results for the surface Ap (0–15 cm) and subsurface Bw (15–40 cm) horizons of both Hudson and Arkport soils. The adsorption characteristics of the Ap and Bw horizons were very similar, thus a single Freundlich isotherm was fitted to the combined concentration data from both layers for each soil type:

Hudson soil: $C_s = 1.50C^{0.80}$; $R^2 = 0.92$

Arkport soil: $C_s = 0.86C^{0.84}$; $R^2 = 0.98$

where C is the Li^+ concentration in solution (mg L^{-1}) and C_s is the Li^+ concentration adsorbed to soil (mg kg^{-1}).

Assuming that the linear adsorption coefficient can be represented by the tangent of the isotherm at the average concentration, we obtained k_d values of approximately $1.4 \text{ m}^3 \text{ Mg}^{-1}$ for the Hudson soil and $0.8 \text{ m}^3 \text{ Mg}^{-1}$ for the Arkport soil. The greater k_d in the Hudson

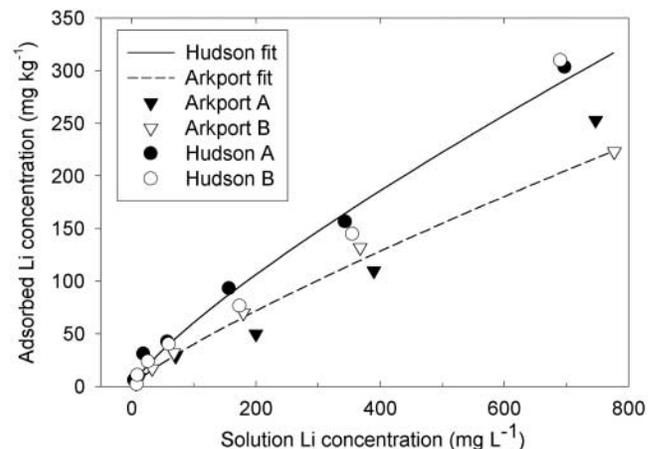


Fig. 5. Lithium batch adsorption isotherm results for the surface (Ap, 0–15 cm) and subsurface (Bw, 15–40 cm) horizons for Hudson and Arkport soils, with Freundlich fits.

Table 1. Preferential flow model parameters. W_{Li} and W_{Cl} are apparent water contents for Li^+ and Cl^- , respectively; R^2 is the regression correlation coefficient; r is the retardation factor (W_{Li}/W_{Cl}); and k_d is the adsorption partition coefficient ($m^3 Mg^{-1}$).

Sludge	Prior treatments	Cl^-		Li^+			
		Soil pH	W_{Cl}	R^2	W_{Li}	R^2	r
		cm		cm			
		Hudson Old Sludge Site					
No sludge	5	14.6	0.98	100	0.98	6.8	2.2
	7	17.9	0.97	180	0.98	10.2	3.5
	Natural	17.7	0.98	140	0.98	8.0	2.7
	>7	16.0	0.97	120	0.97	7.9	2.7
		Hudson Meadow Site					
Digested	5	21.8	0.93	540	0.98	25.9	9.6
	7	13.8	0.98	160	0.93	10.9	3.8
Compost	5	14.3	0.98	160	0.93	10.7	3.7
	7	15.6	0.97	220	0.95	14.0	5.0
Alk. stabilized	5	16.8	0.99	180	0.96	10.5	3.7
	7	13.2	0.99	110	0.95	8.2	2.8
Pelletized	5	15.6	0.99	100	0.95	6.0	1.9
	7	15.5	0.99	270	0.96	16.6	6.0
Ash	5	20.2	0.97	225	0.98	10.1	3.5
	7	17.1	0.98	190	0.98	11.2	3.9
Control	5	13.5	0.98	170	0.98	15.3	5.5
	7	17.7	0.98	160	0.95	8.7	3.0
	Natural	19.1	0.98	90	0.89	5.0	1.5
		Arkport Meadow Site					
Digested	5	11.2	0.95	110	0.95	3.2	9.9
	7	10.5	0.96	160	0.97	5.1	15.4
Compost	5	10.5	0.92	110	0.98	3.4	10.5
	7	15.0	0.95	230	0.98	5.2	15.5
Alk. stabilized	5	13.4	0.95	300	0.94	7.6	22.2
	7	14.3	0.94	290	0.96	6.6	19.5
Pelletized	5	13.2	0.88	190	0.96	4.8	14.5
	7	10.9	0.97	90	0.97	2.6	8.3
Ash	5	11.3	0.96	120	0.97	3.4	10.5
	7	13.2	0.90	370	0.94	9.4	27.3
Control	5	12.6	0.90	160	0.95	4.3	13.2
	7	14.3	0.97	280	0.95	6.5	19.3
	Natural	10.4	0.96	120	0.93	3.8	11.6

was likely caused by the greater adsorption capacity associated with finer texture (greater silt and clay content).

Model Assessment

In this section we describe how well the observed percolate Cl^- and Li^+ concentrations were fitted by the preferential flow model. Although results are tabulated based on sludge treatments from the overall sludge study, no distinction is made among treatments in the figures because statistical analysis found that only differences between soil types were significant ($p \geq 0.05$), with no significant differences resulting from the various sludge or initial soil pH treatments.

Chloride

The preferential flow model parameters, obtained by transforming and regressing the values according to Eq. [3], are shown for individual sludge–initial soil pH treatments in Table 1 and are summarized by soil type in Table 2. According to Eq. [3], the inverse of the slope of the regression line of $\ln(1 - L/M_0)$ vs. the cumulative outflow yields the apparent water content, W . For Cl^- the mean apparent water content (W_{Cl}) was 16.5 cm for all Hudson soils, with no distinction between old sludge site and Hudson meadow columns. The mean W_{Cl} was

Table 2. Preferential flow model parameters summarized by soil type (Hudson Old Sludge Site and Meadow Site presented separately and as a Hudson composite): W_{Li} and W_{Cl} are apparent water contents for Li^+ and Cl^- , respectively; R^2 is the regression correlation coefficient; r is the retardation factor (W_{Li}/W_{Cl}); and k_d is the adsorption partition coefficient ($m^3 Mg^{-1}$).

	Cl^-		Li^+			
	W_{Cl}	R^2	W_{Li}	R^2	r	k_d
	cm		cm			
	Hudson Meadow Site					
Mean	16.5	0.98	198	0.95	11.8	4.14
SD	3.8		171		9.5	3.64
CV	0.23		0.86		0.80	0.88
Median	16.2		133		7.9	2.65
Geometric mean					9.1	3.02
	Hudson Old Sludge Site					
Mean	16.6	0.98	135	0.98	8.2	2.77
SD	2.8		44		2.4	0.91
CV	0.17		0.32		0.29	0.33
Median	17.1		125		7.4	2.47
Geometric mean					7.9	2.63
	All Hudson					
Mean	16.5	0.98	183	0.96	10.9	3.82
SD	3.6		153		8.5	3.27
CV	0.22		0.84		0.78	0.86
Median	16.5		132		7.9	2.65
Geometric mean					8.8	2.92
	Arkport Meadow					
Mean	12.4	0.94	196	0.96	15.2	5.46
SD	2.0		132		9.0	3.45
CV	0.16		0.68		0.59	0.63
Median	12.3		143		12.5	4.43
Geometric mean					13.1	4.61

12.4 cm for Arkport soil. Using the SAS General Linear Model (SAS Institute, 1996), we found that only the difference among soil types was significant ($p \geq 0.05$), with no significant difference among the various sludge treatments or initial pH levels nor with their interaction with soil type.

The preferential flow model fit the data well, as indicated by mean R^2 values of 0.98 for Hudson columns and 0.93 for Arkport columns. The good fit to the preferential flow model for each column is also obvious from Fig. 6 where the natural log of Cl^- mass remaining in the column is plotted against the cumulative outflow for the 51 Hudson columns (Fig. 6a) and the 39 Arkport columns (Fig. 6b). The Cl^- outflow data from the Hudson columns (Fig. 6a) were linear, indicating that the preferential flow model fits the data well, with some increase in scatter at the end of the experiment. Though still a reasonably linear fit, the Arkport cumulative Cl^- loss plot had a slightly concave form. Unlike the Hudson subsoil's low matrix conductivity, the Arkport soil has a much higher matrix conductivity. Thus, while for the Hudson soil virtually no exchange of solutes takes place between macropores and matrix (as assumed in the preferential flow model; Steenhuis et al., 1994a), this was not true for Arkport, causing the observed deviation from the linear fit. As expected for both the Hudson and Arkport soils, the data departed from the linear fit during the initial 2 to 4 cm when the outflow concentrations were increasing. This is due to the model's assumptions of instantaneous mixing and no delay in traveling

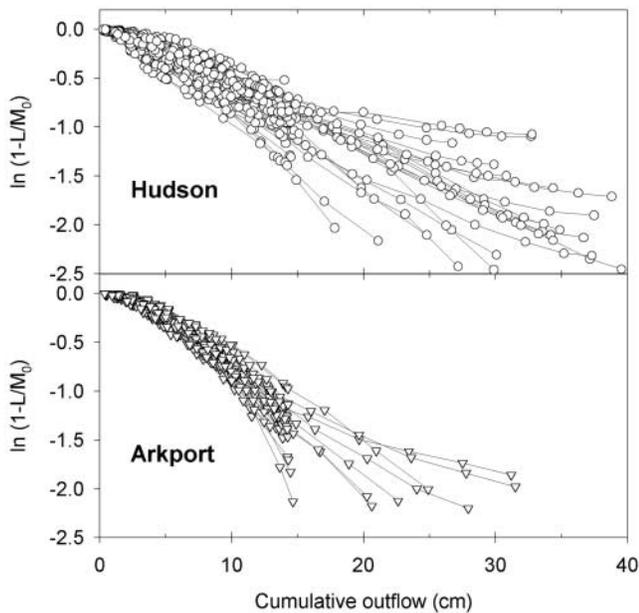


Fig. 6. Chloride preferential flow model regression: $\ln(1 - L/M_0)$ vs. cumulative flow with zero intercept for 51 Hudson Meadow and Old Sludge Site columns and 39 Arkport Meadow Site columns.

from the distribution zone to the bottom of the column, hence the initial deviation from the straight line.

Lithium

The preferential flow $\ln(1 - L/M_0)$ vs. cumulative flow plots for Li^+ are shown in Fig. 7. At first glance, the spread of the data for each soil was much larger than for Cl^- . The individual columns from the Hudson Old Sludge Site had significantly ($p > 0.05$) greater R^2 than the Hudson Meadow Site and the Arkport soils, indicating better individual straight line fits. The variability in the amount of Li^+ (Fig. 7) made it difficult to

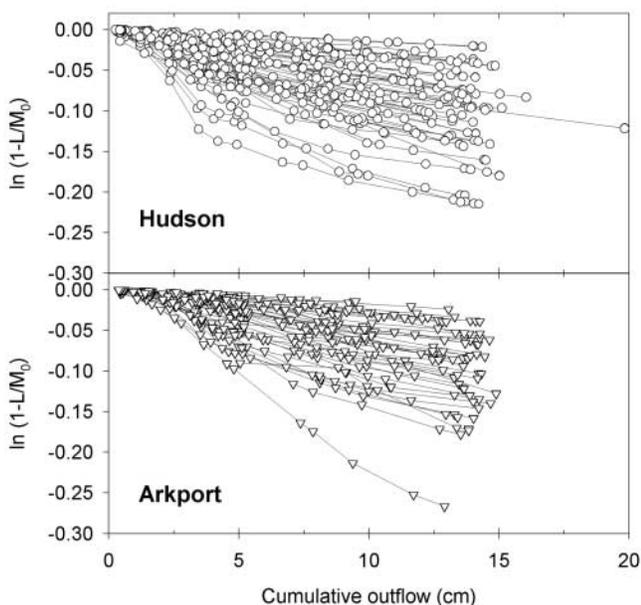


Fig. 7. Lithium preferential flow model regression: $\ln(1 - L/M_0)$ vs. cumulative flow with zero intercept for 51 Hudson Meadow and Old Sludge Site columns and 39 Arkport Meadow Site columns.

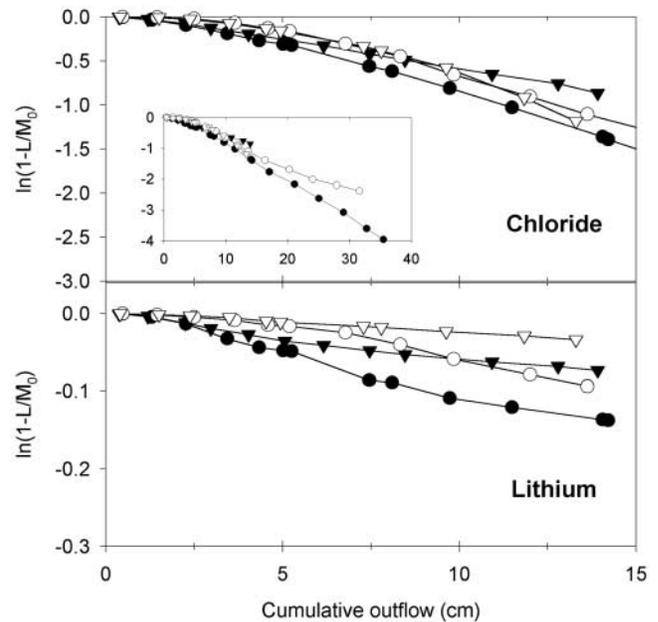


Fig. 8. Chloride and Li^+ remaining in columns as a function of cumulative outflow for two Hudson Meadow (filled symbols) and two Arkport Meadow (open symbols) soil columns (inset shows full scale for Cl^-).

discern losses from individual columns. Examples of typical Li^+ losses from four representative columns are given in Fig. 8, with Cl^- data shown for comparison. While the Cl^- plots are similar (Fig. 8a), the Li^+ breakthrough plots are somewhat linear after the first few centimeters of outflow but with widely differing slopes (Fig. 8b), indicating differing adsorption partition coefficients. This difference is not due to sludge type because, as shown below, the apparent water contents (which include an implicit determination of the Li^+ adsorption partition coefficient) differed significantly only between soil types.

The mean apparent water content W_{Li} was 135 cm for the Hudson Old Sludge Site, 198 cm for the Hudson Meadow Site, and 196 cm for the Arkport Meadow Site (Table 1). For both soils, the standard deviation of W_{Li} was much greater than for W_{Cl} . Statistical analyses indicated that W_{Li} values were not statistically differentiable by soil type, sludge treatment, initial soil pH, nor by any of their interactions. Nevertheless, it is interesting to note that the outflow concentrations of both Li^+ and Cl^- were more closely clustered for the 12 Hudson Old Sludge Site columns, which received no sludge applications in the study, compared with the Hudson and Arkport meadow soils, as indicated by the W_{Cl} vs. W_{Li} plot in Fig. 9. Although it is tempting to conclude that the Cycle 1 and 2 sludge applications had a significant effect on the variability of W_{Li} (and, as shown below, the Li^+ k_d coefficient) more evidence would be needed before the conclusion could be made.

Values of k_d calculated from W_{Cl} and W_{Li} using Eq. [4] for the various treatments are presented in Table 1, with mean values in Table 2. The average adsorption partition coefficient for the 12 columns from the Hudson Old Sludge Site was $2.8 \text{ m}^3 \text{ Mg}^{-1}$, ranging between 1.5

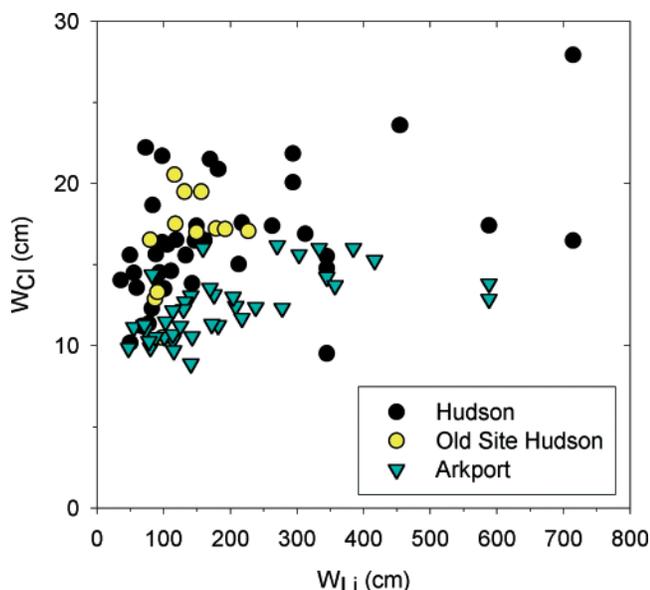


Fig. 9. Apparent water contents: Cl^- vs. Li^+ .

and $4.7 \text{ m}^3 \text{ Mg}^{-1}$ with a standard deviation of 0.9, a median around 2.5, and a geometric mean (discussed below) of $2.6 \text{ m}^3 \text{ Mg}^{-1}$. For the 39 columns of the Hudson Meadow Site, average k_d was $4.1 \text{ m}^3 \text{ Mg}^{-1}$ with a much greater range, varying between $0.2 \text{ m}^3 \text{ Mg}^{-1}$ and as high as $16 \text{ m}^3 \text{ Mg}^{-1}$. The standard deviation was 3.7, with a median of 2.6 and a geometric mean of 3.0. These central values are almost double the batch-derived value of $1.4 \text{ m}^3 \text{ Mg}^{-1}$. The fitted k_d values for the Arkport were generally higher than for the Hudson with an average of $5.4 \text{ m}^3 \text{ Mg}^{-1}$ and median of $4.4 \text{ m}^3 \text{ Mg}^{-1}$, with a standard deviation about the mean of 3.4 and a geometric mean of $4.6 \text{ m}^3 \text{ Mg}^{-1}$.

The fitted adsorption partition coefficients derived from the preferential flow model can be compared with the mean linear batch-determined values (approximately $1.4 \text{ m}^3 \text{ Mg}^{-1}$ for Hudson and $0.8 \text{ m}^3 \text{ Mg}^{-1}$ for Arkport soil). The fact that the k_d values derived from the preferential flow model are greater than the batch values are likely due to two factors. First, the batch experiment results were determined by *adsorption* of Li^+ to the soil matrix, while the preferential flow results were measured during *desorption*. Desorption k_d values are typically greater than adsorption values because of hysteresis in adsorption phenomena (Steenhuis et al., 1994a). Second, the preferential flow model assumes no adsorption of Li^+ below the distribution zone; any subsoil absorption will be reflected in greater calculated k_d values. Although the Arkport soil had a coarser texture than Hudson, the calculated adsorption partition coefficient was greater. This was due, as noted with Cl^- , to a more conductive matrix in the Arkport subsoil, which led to more subsoil interaction and opportunity for adsorption, raising the apparent k_d . In Fig. 10, measured Li^+ concentrations are plotted against Cl^- concentrations. Almost all points fall below the 1:2 line (corresponding an effective adsorption partition coefficient of at least $2 \text{ m}^3 \text{ Mg}^{-1}$) and most are below the 1:4 line (effective $k_d \geq 4$). Thus, the k_d values calculated from

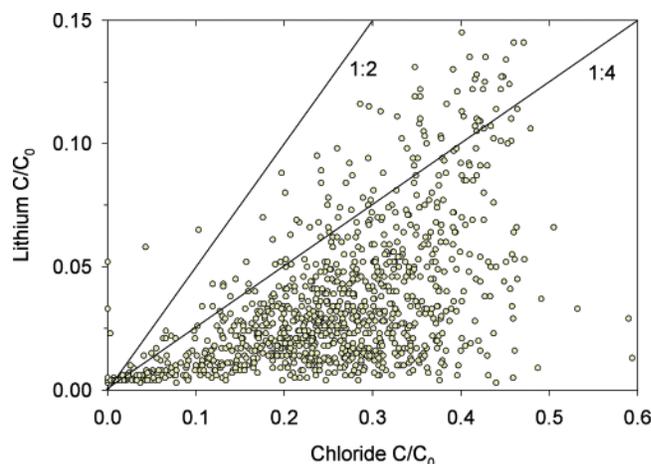


Fig. 10. Scatter diagram of Li^+ and Cl^- outflow concentrations: The 1:2 and 1:4 lines correspond to k_d of 2 and $4 \text{ m}^3 \text{ Mg}^{-1}$, respectively.

the preferential flow parameters reflect not only the inherent adsorption strength of the soil but also the extent of subsoil flowpath interaction. While the preferential flow model simulated experimental data well using W_{Li} (and, by extension, the derived k_d), the type and extent of subsoil flowpath interaction should be included in the model if *laboratory-derived equilibrium* k_d values are used to predict transport of adsorbable solutes.

Soil Column Variability

The distribution of preferential flow parameters for Cl^- (W_{Cl}) and Li^+ (k_d) were examined by testing goodness-of-fit to normal and lognormal distributions, which have been shown to define the spatial variability of most soil transport properties (Rao et al., 1979; Boll et al., 1997). Ranked distributions of Cl^- apparent water content (W_{Cl}) and Li^+ partition coefficient (k_d) results are presented in Fig. 11 and 12, respectively, with insets showing the corresponding probability plots. As shown in Table 3, Cl^- W_{Cl} values were normally distributed (r^2 of 0.96 and 0.98 for Hudson and Arkport, respectively). The lognormal distribution fit was nearly as good for Arkport (r^2 of 0.97); Rao et al. (1979) noted that both distributions could adequately describe data sets when coefficients of variation are low (<0.4), which was the case with the Arkport W_{Cl} ($CV = 0.16$). For Li^+ k_d measurements (Fig. 12), goodness-of-fit values were slightly greater for the lognormal distributions (r^2 of 0.87 and 0.97 for Hudson and Arkport, respectively) than for normal distributions.

Deviations from the linear fits shown in the probability plots tended to be greatest at the upper end of the parameters, most notably the maximum Hudson W_{Cl} value, which was nearly three standard deviations from the mean (Fig. 11), as well as the clustering of four Arkport W_{Cl} values near the maximum value (Fig. 11). These values were greater (reflecting slower potential transport) than would be predicted by the respective distributions, corresponding to transport in the "slowest" columns being even slower than predicted. It could be argued that these deviations are of little practical

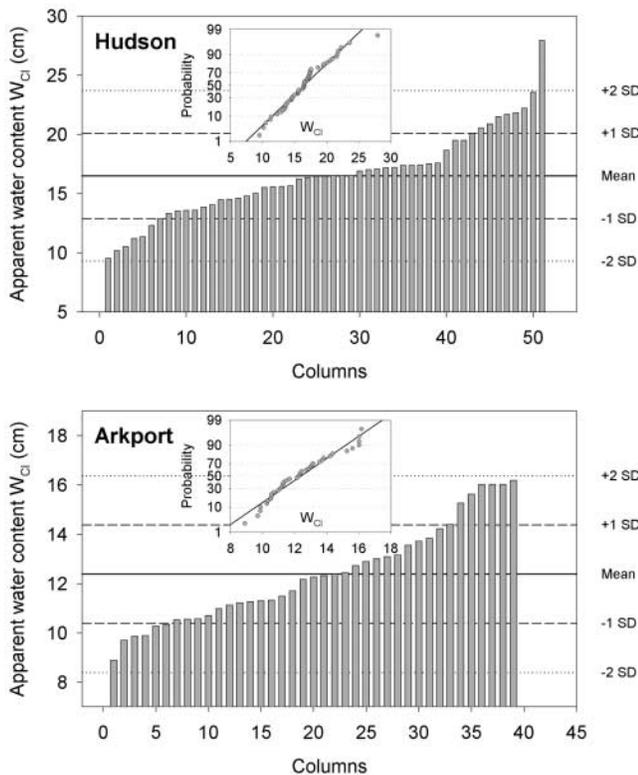


Fig. 11. Ranked distribution of Cl^- apparent water content (W_{Ci}) with mean and standard deviations: all Hudson columns and Arkport columns. Insets show normal probability plots ($r^2 = 0.96$ Hudson, 0.98 Arkport).

concern for transport, since the slowest columns are affected. Of greater concern are risks of mischaracterizing the transport potential of the higher rate columns. The minimum Arkport W_{Ci} values were somewhat greater (again implying lower transport potential) than predicted by a linear fit (Fig. 11), with only one value approaching two standard deviations below the mean. This trend could also be viewed as conservative, with actual results indicating lower transport velocities among the most rapid outliers than would be predicted by a normal distribution. The fact that the experimental results from our relatively large arrays of columns fit normal (nonadsorbed Cl^- W_{Ci}) or lognormal (Li^+ apparent k_d) distributions implies that probabilistic approaches (such as in Eq. [1] and Fig. 1) can be used to select the number of experimental columns required to meet a desired level of probability that the planned experimental array will include columns with transport velocities that are “ x ” standard deviations above or below the mean. In this experiment, we did not test the effects of scale (i.e., soil column diameter). Among-column variability could be expected to vary inversely with column diameter, with larger columns better representing mean conditions, being less susceptible to the effects of containing far more or far fewer macropores.

As stated above, the preferential flow model was used to predict losses from each column (using the column’s W_{Cl} and W_{Li} values) at various cumulative percolate depths (Y). The losses from each column were pooled at each level of Y to express solute loss from each col-

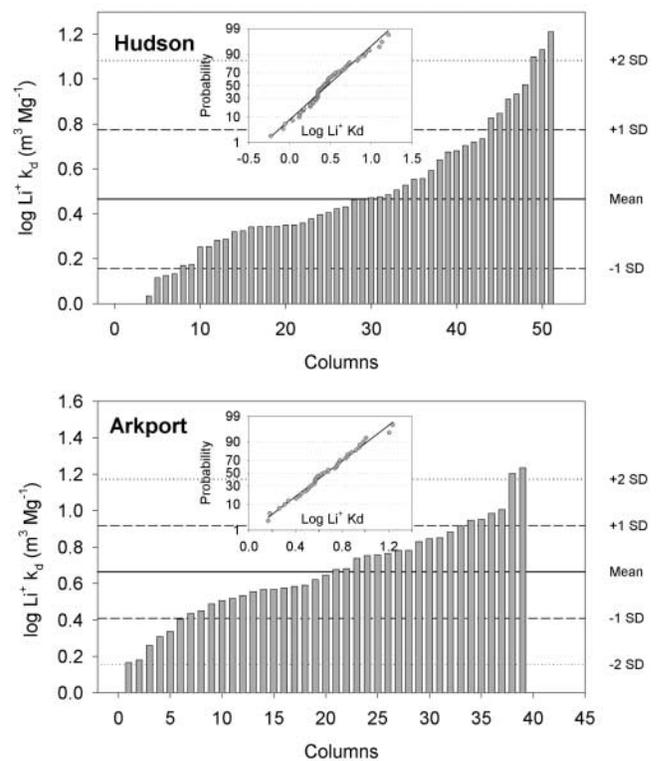


Fig. 12. Ranked distribution of Li^+ adsorption partition coefficient (k_d) with mean and standard deviations: all Hudson columns and Arkport columns. Insets show log-normal probability plots ($r^2 = 0.87$ Hudson, 0.97 Arkport).

umn as a percentage of the total system (all columns of each soil type) loss. Figure 13 summarizes results for the distribution of predicted Cl^- loss, with columns ranked from most rapid mobility to the least (as in Fig. 11 and 12). The horizontal line in each graph indicates the mean value (equal to $100/n$ columns) that would be achieved when loss is complete from all columns (at very large Y). The inset graphs show the total system loss of solute as a function of cumulative percolate depth (Y). During the initial stages of leaching (low values of Y), the columns with rapid transport contribute substantially to overall losses, with losses from the most rapid individual column to two (Arkport) to three (Hudson) greater than the slowest columns. This disparity in contribution diminishes as Y increases and allows the slower columns to “catch up.” The disparity in early contribution was even greater for Li^+ (Fig. 14), where an order of magnitude separated the fastest and slowest columns. The early contributions of the most rapid preferential flow paths (represented by the most rapid soil columns) can be significant: for both the Arkport and Hudson columns, the predicted early loss ($Y = 10$) of Li^+ from the

Table 3. Goodness-of-fit (as reflected by r^2) of preferential flow model parameters W_{Cl} and $\text{Li}^+ k_d$ to normal and lognormal distributions.

Parameter	Hudson		Arkport	
	Normal	Lognormal	Normal	Lognormal
W_{Cl}	0.96	0.73	0.98	0.97
$\text{Li}^+ k_d$	0.85	0.87	0.95	0.97

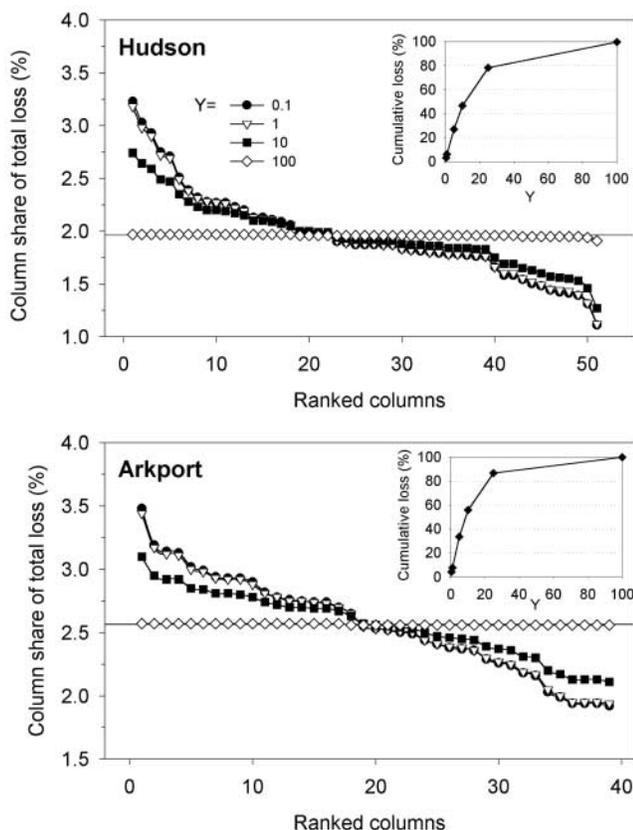


Fig. 13. Predicted relative contribution of individual columns (ranked by W_c) to overall loss of Cl^- as a function of cumulative percolate depth (Y): Hudson columns ($n = 51$), and Arkport columns ($n = 39$). Insets show cumulative system loss of Cl^- as a function of Y . Horizontal lines indicate the mean contribution per column ($100/n$) when loss is complete.

three most rapid columns amounted to 0.5 to 0.6% of total Li. The rapid early transport takes place before adsorption or, in other cases, degradation can occur. For some contaminants (fertilizer nutrients) this degree of loss is negligible, but for others (such as pesticides) this degree of loss of surface-applied materials would be sufficient to contaminate groundwater.

Related Experiments

Finally, it is of interest to compare these results with related work with undisturbed cores or in the field. Using similar intact soil columns, Akhtar et al. (2003) found that preferential flow of soluble P through soil was a function of soil structure and flow rate. During unsaturated flow, only Hudson soil columns experienced preferential transport of dissolved orthophosphate, while Arkport and several other soil types (all less strongly structured than Hudson and with greater matrix flow components) did not. Under ponded flow conditions, all soil types tested experienced preferential breakthrough of orthophosphate (Akhtar et al., 2003). In a field study near the same site from which the Hudson columns were extracted, solutes and water were collected with wick pan and gravity pan lysimeters (Steenhuis et al., 1994a). Under field conditions and with a lower rainfall rate, it was found that the preferen-

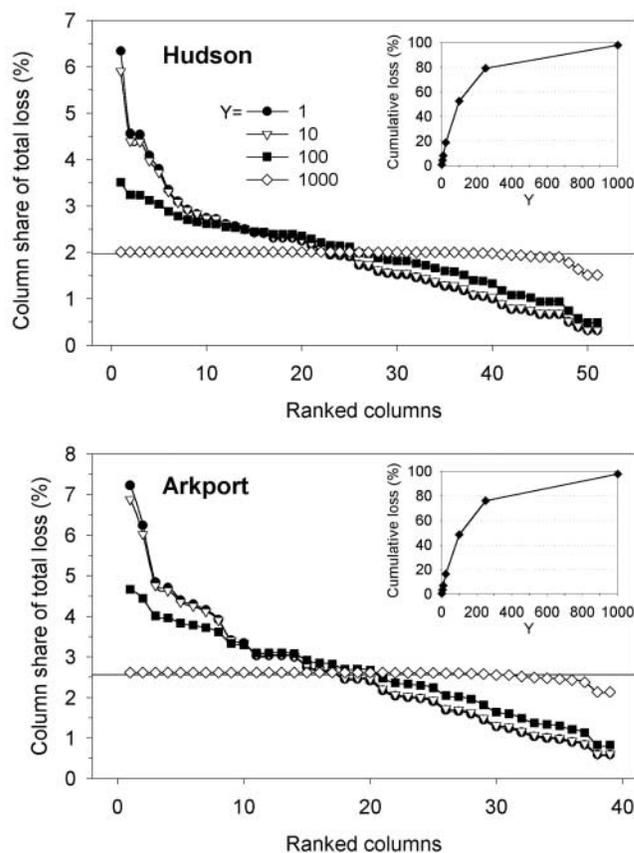


Fig. 14. Predicted relative contribution of individual columns (ranked by $\text{Li}^+ k_d$) to overall loss of Li^+ as a function of cumulative percolate depth (Y): Hudson columns ($n = 51$) and Arkport columns ($n = 39$). Insets show cumulative system loss of Li^+ as a function of Y . Horizontal lines indicate the mean contribution per column ($100/n$) when loss is complete.

tial model worked equally well for simulating transport of Cl^- and blue dye (FD&C Blue #1). The apparent water content of the distribution layer for Cl^- was lower than was observed for the soil columns in our study. This was probably due to the greater flow rate in this study, which resulted in less mixing and a higher apparent water content of the distribution zone (i.e., more water is needed to leach out the solutes). We are currently investigating how flow rate affects apparent water contents; initial results seem to support the hypothesis that greater flow rates lead to greater apparent water contents.

SUMMARY AND CONCLUSIONS

A leaching study was performed with 90 undisturbed columns that were part of a larger wastewater sludge application study. As determined by statistical testing, our results were not affected by the preceding sludge or soil pH treatments from the larger study. Preferential transport was evident in all columns, with rapid appearance of both nonadsorbed Cl^- and, at lower concentrations, adsorbable Li^+ . The preferential flow model fitted to about 80 of these columns with R^2 of 0.95 or better (Table 1). Though still significant, the difference in model precision was not as pronounced for the Arkport

soil, due to subsoil interaction and adsorption, which is assumed in the preferential flow model to be negligible.

Despite great differences among individual columns, the overall pattern of Cl^- loss was very similar among columns after the initial 10 cm of flow (when variable preferential flow effects dominated). The similarity in overall loss is a direct consequence of the drainage water concentration being a function of the amount of solutes in the distribution layer. Thus, stated simply, if a large amount of Cl^- is lost initially, less is available for subsequent loss; conversely, when the initial losses are relatively small, subsequent samples will have a relatively high concentration, ultimately minimizing the differences in cumulative loss among columns.

Lithium adsorption partition coefficients (k_d) calculated from preferential flow parameters (W_{Cl} and W_{Li}) were greater than those determined in batch equilibrium testing. This was attributed to subsoil interaction not accounted for in the preferential flow model, in addition to adsorption-desorption hysteresis effects. Lithium k_d values varied widely among columns, again attributed to differences in subsoil flow paths.

Experimental results from our large arrays of columns fit a normal distribution for Cl^- W_{Cl} and a lognormal distribution for Li^+ apparent k_d , although for Arkport soils the two distributions appeared nearly equally valid. Trends among outliers were conservative, with results indicating lower transport velocities among the most rapid outliers than would be predicted by the corresponding distributions. Probabilistic approaches can be used to select the number of experimental columns needed to meet a desired level of probability that columns with a meaningful range of transport velocities will be represented in the experimental array.

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