

## MOVEMENT OF HEAVY METALS THROUGH UNDISTURBED AND HOMOGENIZED SOIL COLUMNS

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### ABSTRACT

Soils accumulate heavy metals when sewage sludge is applied to land for disposal or intended beneficial use. Because of the concern over the environmental danger that these sludge-borne metals could represent if mobilized, many studies have been performed in an attempt to clarify the different factors that contribute to metal solubility, plant uptake and leachability. The objectives of this study were to determine if two independent factors - soluble organic chelators and preferential flow paths - enhanced metal mobility through soil.

Dilute solutions containing CdCl<sub>2</sub>, ZnCl<sub>2</sub>, CuCl<sub>2</sub>, and Pb(NO<sub>3</sub>)<sub>2</sub> were applied to soil columns with a rainmaker, and leachate metals and chloride concentrations were measured. For four columns, the input metal concentrations (mg L<sup>-1</sup>) were 7.25 Cd, 4.55 Zn, 3.51 Cu, and 13.85 Pb. With four other columns, the solution also contained dissolved organic matter so that the metals were organically-complexed, and input metal concentrations (mg L<sup>-1</sup>) were 6.30 Cd, 4.11 Zn, 3.19 Cu, and 12.55 Pb. For each treatment, two of the four soil columns were undisturbed and two were constructed from homogenized soils. The rate of continuous solution application was approximately 3 cm/day.

The undisturbed soil columns treated with organically-complexed metals had peak effluent concentrations, expressed as percent of influent, of 30, 26, 28, and 27% for Cd, Zn, Cu, and Pb, respectively. Peak effluent concentrations for undisturbed columns treated with metals in water were 30 and 23% of influent concentrations for Cd and Zn, but only 15 and 12% for Cu and Pb, respectively. However, the four homogenized soil columns retained all added metals, whether the metals were added in water or as organic complexes. The results indicate that previous laboratory metal leaching studies performed on homogenous soils might greatly underestimate metal mobility in the field, and that preferential flow, both alone and in combination with organic-facilitated transport, can accelerate metal leaching through soils.

### KEYWORDS

Heavy metals, cadmium, zinc, copper, lead, preferential flow, undisturbed soil, mobility

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## INTRODUCTION

The application of sewage sludge to land is, in principle, an effective disposal method. Not only does it provide a solution to the sludge disposal problem, but it can prove to be beneficial to agricultural productivity (Chang et al. 1978; Higgins 1984). The presence of heavy metals, such as Cd, Zn, Cu, Ni, Cr and Pb, is the most critical long-term hazard when applying sludge to land (Logan and Chaney 1983). Short-term benefits from sludge nutrients may then be negated by long-term deleterious effects on crop yield and quality, or, in the case of Cd, direct human toxicity. While it has generally been assumed that these metals are immobile in managed agricultural soils (McBride 1995), factors that enhance mobility could result in more plant uptake or leaching of the metals to the groundwater. These factors include the properties of the metals in question, the quantity and type of soil binding sites, pH, the concentration of complexing anions (organic and inorganic), and competing cations in soil solution (Tyler and McBride 1982).

Metals can bind to soil through the processes of ion exchange and chemisorption. Oxides of Fe, Al, and Mn can provide chemisorption sites for metals. Soil organic matter also plays a key role in complexing and retaining metals. McLaren and Crawford (1973) showed how Cu was strongly bound to the soil organic matter. Layer silicate minerals provide exchange sites for cations, and a few chemisorption sites at crystal edges. Kuo et al. (1985) showed that Cd retention was greater in fine-textured soils with high cation exchange capacity (CEC) compared to coarse-textured soils with lower CEC. McBride et al. (1981) showed that Cd retention was most closely related to the exchangeable base content of the soil. Many metals at high soil contamination levels will form precipitates with oxides, hydroxides and carbonates (Jenne 1968), especially at higher soil pH.

Organic matter, both soluble and insoluble, forms complexes with metals by exchange and chemisorption reactions. Metals bond with carboxyl, phenol, alcohol, carbonyl and methoxyl functional groups. When two or more functional groups bind with a single metal ion, the resulting five or six member chelation ring holds the metal very strongly (Snoeyink and Jenkins 1980). Chelation is pH dependent, because at low pH the metals must compete with H<sup>+</sup> ions for coordination sites on the functional groups.

This experiment examined the mobility of four metals: Cd, Zn, Cu and Pb. Of these, Cu and Pb form stronger complexes with surfaces and soluble organics than do Cd and Zn. This tends to make them less mobile in soils, but also provides a greater opportunity for facilitated transport by soluble organics (if present). Numerous studies (Elliott et al. 1986; Tyler and McBride

1982) have shown the relative mobility of these elements in soil is typically Cd > Zn > Cu > Pb.

Knowledge of the movement of these metals is primarily based on homogenized soil column studies, and under these conditions none of these metals is considered to be mobile (especially when applied via sewage sludge) except perhaps in very acid or coarse-textured soils. A laboratory study (Gerritse et al. 1982) showed that the relative velocity of these metals was about 0.01 to 0.1% of the velocity at which water moved through soil, even for a sandy loam soil with a CEC of only 0.16 cmol kg<sup>-1</sup>. Studies performed by Emmerich et al. (1982) and Giordano and Mortvedt (1976) further confirmed the immobility of these metals in conventionally-homogenized laboratory soil columns. Although the sludge-applied metals were taken up by plants, they did not leach through the soil below the depth of incorporation.

Other studies done on field sludge application sites have concluded that metals are strongly bound in the topsoil, since little or no metals accumulate in the soil below the depth of incorporation (Chang et al. 1984; Williams et al. 1987). However, when doing a mass balance of the metals at these sites, Williams et al. (1987), and several other researchers, could not account for all the metals that had been applied. McGrath and Lane (1989) found that 68% of the metals applied to the field site they were studying could not be accounted for. They blamed most of this loss on lateral movement of soil due to mechanical cultivation or erosion. Dowdy et al. (1991) claimed that some metal extraction methods used did not fully recover the metals from the interior of soil minerals or strong sorption sites. While this could cause metal balances to be inaccurate, this is an unlikely explanation because of the vigorous soil digestion methods used in most studies. They also mentioned the possibility that metals are transported to lower depths in the soil through cracks and macropores in a process they call non-matrix water flow, more generally known as preferential flow.

Preferential flow has been shown to greatly increase the mobility and velocity of solute movement to the groundwater (Steenhuis et al. 1995). Various forms of preferential flow exist. In homogeneous sandy soils, preferential flow is caused by instability at the wetting front (Glass et al., 1989) or by sloping textural interfaces (Kung, 1990). In finer soils, structural cracks, wormholes, plant root channels and other high conductivity paths form the network for preferential flow. Water added to the soil can rapidly flow through this preferential network, bypassing most of the soil matrix. In contrast, conventional laboratory leaching studies have generally considered soil to be a homogeneous mixture (and, by experimental design, force it to be the case) where

infiltrating water will travel through the entire soil matrix. The possibility that water and solutes can bypass much of the soil matrix via preferential flow paths has therefore been ignored. It has been demonstrated that preferentially-transported pesticides can rapidly reach groundwater, despite conventional model predictions to the contrary (Steenhuis, et al. 1994). It is therefore conceivable that preferential transport could also increase metal movement.

Another factor that could enhance metal mobility is transport of metals incorporated in soluble metal-organic complexes. While metal-organic complexation generally leads to decreased mobility, metal-organic complexes can become soluble at pH's above 7 (McBride 1994). Also, as the organic matter in soil decomposes, it could release soluble metal-organic complexes. This was demonstrated by Lund et al. (1976). Metal movement below sludge disposal ponds was correlated with soil chemical oxygen demand, suggesting that the metals were transported through the soil as metal-organic complexes. Van Erp and van Lune (1991) in a 14 year study of sludge-amended soil, found that concentrations of Cd and Zn in the leachate decreased over time while Cu and Pb concentrations increased. This was attributed to the fact that Pb and Cu are strongly bound to organic matter and would be slowly-released over time as the organic matter of the sludge decomposed. Cd and Zn are not as strongly bound to organic matter and therefore would not be as greatly affected by sludge decomposition. This slow release of metals is a potential "time bomb" effect that sludges have because of their high organic matter content (McBride 1995).

The literature shows that metals movement through soil is still not well understood. The roles of preferential flow paths and soluble organic matter are especially unclear. The objective of this study was to examine the effects (separately and in combination) of preferential flow paths and soluble organics on the mobilities of Cd, Zn, Cu and Pb through soil columns. To do this we carried out an experiment wherein metals in solution (in water or in an organic solution) were applied to both conventional and undisturbed soil columns. Leachates were monitored to determine metal transport. The extent of preferential water flow was characterized with chloride tracer.

## MATERIALS AND METHODS

### Treatments

Eight soil columns were used for this experiment. Four of the columns were prepared by extracting undisturbed soils in the field, and four were prepared from homogenized samples of the same soils.

Undisturbed soil columns were obtained from a

pasture (grass sod) at Cornell University in Ithaca, NY. Previous undisturbed soil extractions carried out at this site revealed conspicuous wormholes and root channels present in the soil. Soil was hand-excavated to expose a 20 cm (8 in.) diameter 35 cm (14 in.) high undisturbed column. A 35 cm (14 in.) length of commercially-available polyethylene culvert pipe with inner diameter of 20 cm (8 in.) was placed around the column, and expandable foam (Great Stuff polyurethane) was injected between the soil and the pipe. The foam was allowed to cure overnight and the bottom of the column was dug out the next day. The column was placed on a plastic-lined base with a central leachate drain and collection system.

Soil for disturbed columns was excavated from the same site, but the soil was pulverized to break up any aggregates before being placed into the columns. The soil was packed in layers to simulate the bulk density and horizonation of the undisturbed soil.

The soil used was Arkport silty loam (coarse loamy, mixed, mesic Psammentic Hapludalf). During excavation the presence of earthworms and extensive wormholes was noted. Soil sampling was conducted by sampling the column periphery prior to foaming at depths of 0-10 cm (upper) and 10-20 cm (lower). Organic matter, determined by loss on ignition for 2 hours at 500°C (Storer, 1984), was 4.1% in the upper layer and 2.0% beneath. Soil pH in water (Page, 1982) was 7.3 in the upper layer and 6.8 beneath. CEC for Arkport soils<sup>3</sup> is typically 9 cmol kg<sup>-1</sup>. [J.M. Galbraith, 1996. Personal communication. Cornell Univ., Ithaca, NY.]

Soil column treatments are summarized in Table 1. Metal salts were dissolved in distilled water for application to half of the undisturbed and homogenized columns. For the other half of the columns, the metal salts were added to a dilute solution of soluble organics. The organic solution was made by upflow leaching of tap water up through a drum filled with sphagnum peat moss (Premier Co. Lite Way Organic Peat, 98% organic matter), retained with a top layer of sand. The solution was collected in a polyethylene holding tank.

In order to determine the complexing capacity of the solution, the Chemical Oxygen Demand (COD) was used as an indication of the organic content in the water, measured by the Accu-TEST<sup>TM</sup> spectrophotometric method (Bioscience, Inc.).

Metal concentrations for both solutions were controlled by the need to ensure that all metals added to the organic solution would be complexed by the soluble organics while consuming only a small fraction of the potential binding capacity (estimated from humic and fulvic acid stoichiometry). Based on this, target metal salt additions were 10.1 mg L<sup>-1</sup> CuCl<sub>2</sub>, 13.7 mg L<sup>-1</sup> CdCl<sub>2</sub>, 24.8 mg L<sup>-1</sup> Pb(NO<sub>3</sub>)<sub>2</sub>, and 10.2 mg L<sup>-1</sup> ZnCl<sub>2</sub>.

Measured initial concentrations of chloride, metals and pH in the input solutions are shown in Table 2. Differences in the metal concentrations were caused by errors in estimating the volume of organic solution, or possibly from incomplete analytical recoveries.

### Rainfall Simulator

The eight columns were placed in a rainfall simulator (Andreini and Steenhuis 1990) set for an application rate of 3 cm/day. The simulator had three moving needles, each with a uniform flow rate. The organic-metal solution and the metal salt solution were stored in separate reservoirs and applied with peristaltic pumps. Additional pumps were used to keep the reservoirs circulating to prevent the metals from settling out of solution. The rain simulator was calibrated using rain gauges to obtain the desired flow rate. There was, however, some variation in the amount of rainfall intercepted by each column, which resulted in differences in total throughput for each column. The columns were placed under it and the respective solutions (but without metals added) were applied until the columns reached equilibrium flow conditions. At that point, application of the solutions with added metals began and continued for 31.5 days.

### Sampling

Column leachates were collected in individual glass flasks. The sampling frequency varied over the duration of the experiment. For the first two days the leachate was sampled every hour. For the next two weeks it was sampled every 4 hours, and finally every 8 hours for the remainder of the experiment. Samples (15 mL) were frozen within an hour of sampling for later analysis, and 15 mL of input solution was sampled and stored approximately every eight hours.

Chloride analysis was performed first with a digital chloridometer (Buchler Instruments) on all samples in order to obtain chloride breakthrough curves and determine flow velocities. Chloride concentrations for organic solution column leachates were corrected for the initial background chloride content. Samples were then chosen at five day intervals for a screening metal analysis. Based on this representative sampling, additional samples were analyzed in order to get a more detailed view of the metal breakthrough. Samples were acidified with 5% HCl and analyzed by ICP spectroscopy at the Fruit and Vegetable Science Analytical Laboratory, Cornell University.

### Calculations

Water velocities were estimated from the chloride breakthrough data using the advection-dispersion equation (Fetter 1993):

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad (1)$$

where:

- $D$  = Dispersion coefficient
- $C$  = Concentration
- $x$  = Distance
- $v$  = Velocity
- $t$  = Time

Chloride breakthrough data were fitted to Eq. (1) through the use of the CXTFIT computer program (Parker and van Genuchten 1984). The flux type boundary condition was applied with the retardation coefficient set at 1 and decay rate of zero. Velocities were then calculated using the following formula:

$$v = \frac{QL}{P_v} \quad (2)$$

where:

- $Q$  = average flux of water through columns
- $L$  = column length
- $P_v$  = pore volume

The average flux of water through each column was obtained by dividing the total throughput volume by 31.5 days (the length of the experiment). Significance of differences in mean velocities was tested at the 95% level of confidence with the ANOVA/Duncan test, as implemented in the WinSTAR statistical program (Anderson-Bell Corporation, Arvada, CO).

## RESULTS AND DISCUSSION

### Chloride Breakthrough

Chloride, as a non-retained anion, was used to characterize the flow characteristics of the different columns. The homogenized column breakthrough curves were typical of homogenous soil media (Fig. 1), indicating matrix flow. Breakthrough curves for the undisturbed columns, however, were distinctly different from the homogeneous columns, and were surprisingly uniform. Breakthrough was characterized by an initial rapid rise to 40-50% of  $C_0$ . This  $C/C_0$  level was maintained until it again increased after approximately 7.5 cm of throughput.

The shape of undisturbed soil breakthrough curves suggests a flow pattern in which the initial breakthrough is associated with macropore flow. At the first plateau ( $C/C_0 = 0.4$  to  $0.5$ ), approximately half of the flow is contributed by the macropores at the same chloride concentration as the input solution, while the balance is

from the soil matrix where breakthrough has not occurred yet and the chloride concentration is zero. The second increase in the  $C/C_0$  curve is associated with the appearance of chloride transported through the soil matrix until the effluent chloride concentration equals the input solution. Column UO1 behaved slightly differently in that it did not display a distinct first plateau. This difference in flow pattern could have been due to earthworm activity in the column, closing and opening pores during the course of the run.

Determining the velocity of the water in the columns is helpful to characterize the type of flow (preferential or matrix), which has implications for metal transport. Calculated pore volumes, flow velocities, moisture contents and correlation coefficients for the four homogenized soil columns are shown in Table 3. The moisture content was obtained by dividing the pore volume calculated by CXTFIT by the total volume of each column. A sample fit of the advection-dispersion equation with a single average velocity shows that the matrix flow model fits the observations well, as do the correlation coefficients in Table 3 (Fig. 2). (Note: initial near-zero readings for chloride concentration were below the detection limits of the chloridometer. Therefore, positive values observed before the initial chloride breakthrough were assumed to be zero.)

Velocities for the undisturbed soil columns can be obtained by separating the column into two separate regions similar to Pivetz and Steenhuis (1995). CXTFIT was used to fit both the preferential breakthrough and the matrix breakthrough of each column. Some temporary fitting points had to be assumed for the upper portion of the preferential curve and lower portion of the matrix curve where there was no experimental data, since CXTFIT will not fit incomplete curves. The temporary points were chosen such that the fitted result would closely follow the observed values. A sample curve is shown in Fig. 2. The parameter values that were used to obtain a fit are shown in Table 4.

The moisture content of each column was again obtained by dividing the calculated pore volume by the total volume of the column. The fraction of soil pore volume involved in preferential flow was calculated by dividing the preferential flow pore volume by the total (preferential plus matrix) pore volume. Equation (2) was used to obtain the respective component velocities.

The mean velocities for the homogenized columns ( $9.4 \text{ cm day}^{-1}$ , Table 3) and the matrix flow component in the undisturbed columns ( $14.9 \text{ cm day}^{-1}$ , Table 4) were not significantly different at the 95% confidence level, indicating that the matrix component of the undisturbed soil columns acts similarly to that of the homogenized columns. In contrast, the mean  $81.8 \text{ cm day}^{-1}$  preferential flow component velocity in Table 4 is

significantly higher than both the undisturbed matrix component and homogenized column velocities. (This preferential component velocity might actually be much higher because, as Fig. 2 indicates, the preferential flow velocities could be underestimated.)

Comparing the results of Table 4 with the undisturbed soil column chloride breakthrough (Fig. 1) shows that the preferential flow paths, because of their high velocity, account for 40-50% of the total transport while taking up only 16% of the total flow. This ratio is slightly narrower than what is reported in the literature (Parlange et al. 1988), and could be due to the long duration rainfall in this experiment. In short duration events, preferential flow could actually account for 100% of solute transport.

### Metal Breakthrough

As shown in Figs. 3 and 4, the homogenized columns completely retained all the metals that were added. All four undisturbed soil columns showed metals in the leachate, and breakthrough curves in the four columns differed both from the chloride breakthrough and from each other.

In the homogenized columns, there is intimate contact between the percolating water and the soil and, therefore, ample opportunity for metal adsorption and retention. The homogenized columns HO1 and HO2 may have stripped the metals from the organic chelating solution (Fig. 4), since soluble organics appeared in the leachate but the metals did not. The organic content of the water, as measured by COD, decreased somewhat passing through the homogenized columns, indicating that some of the organics were adsorbed, physically trapped or otherwise retained, possibly retaining complexed metals in the process. However, the fact that no metals passed through, while approximately half of the organic matter ( $\text{COD } C/C_0 = 0.43$ ) did, demonstrated a metal complexation capacity.

The preferential flow paths in the undisturbed columns, on the other hand, allowed metals to bypass the soil matrix and pass through the soil profile. Unlike the chloride breakthrough, however, the metal breakthrough differed in each of the four columns. Column UO1 did not show a significant metal breakthrough until about 108 cm of water had been applied to the column, much slower than the chloride breakthrough. This was possibly due to some matrix component (i.e., flow through soil between non-connected macropores) in the overall preferential flow path, which could be easily overcome by chloride but not by the metals, which would adsorb to some degree during the brief matrix flow.

Column UW2 also showed a delay between when the chloride broke through and when the metals appeared.

It is much less pronounced than column UO1, but could again be due to matrix components of the preferential flow paths. Columns UO2 and UW1 did not show any significant delay between chloride and metal breakthroughs.

These results demonstrate how difficult it is to characterize preferential flow paths. The four undisturbed soil columns all showed substantially different initial breakthrough response to the metal additions. Although the non-adsorbing chloride tracer was not sensitive to any flow path differences in the columns, adsorbable metals behaved quite differently among replicate soil columns. This variability makes it difficult to model preferential transport by conventional methods.

Regardless of the differences in the initial breakthroughs, all four undisturbed columns reached similar steady state or final metal concentrations (Table 5), indicating that there may be some consistency in longer-term preferential flow phenomena (if the soil remains wet for long periods of time). Table 5 also demonstrates that soluble organics have an effect on metal transport. In columns UW1 and UW2, which had the metals added in distilled water, the order of mobility was  $Cd > Zn > Cu > Pb$ , as would be expected from previous studies. However, in columns UO1 and UO2, which had the metals added as organic complexes, the order of mobility was  $Cd \approx Cu > Zn \approx Pb$ . The organic chelating agents increased the mobility of Cu and Pb, normally considered immobile in soil, to the point of being comparable to Cd and Zn.

Based on the homogenized soil column results, one would expect that the portion of the total water volume that flowed through the soil matrix in the undisturbed soil columns would be free from metals. Furthermore, the fact that the preferential flow paths account for approximately 40-50% of the transport through the undisturbed columns (based on chloride breakthrough) suggests that the overall effluent metal concentrations would be 40-50% of the input concentration. However, the observed effluent metal concentrations of 25% or less (Table 5) indicates that, even with preferential flow, the metals still interact with the soil binding sites on the preferential flow paths. The observed effluent metals concentrations, are, however, far higher than would be expected from the advection-dispersion equation, which is based on and only valid for homogenous flow in soils.

## CONCLUSIONS

The results obtained from this experiment demonstrate that preferential flow plays a crucial role in transporting metals through a soil profile, as illustrated by the fact that the homogenized matrix flow columns adsorbed all

applied metals while the undisturbed preferential flow columns allowed some of the metals through. Judgments about mobility can not be made solely on the basis of conventional assessments of soil characteristics. The Arkport soil used in this study had, as demonstrated with homogenized columns, sufficient binding capacity to adsorb all of the added metals, but preferential flow paths in the undisturbed columns allowed some metals to bypass the binding sites and leach from the column. Laboratory experiments based on homogenized soils that conclude that metals are immobilized in the zone of incorporation should be understood to represent a specific soil situation which most likely does not represent field conditions, and are likely to be overly optimistic in terms of metal retention. The degree of variation in metal breakthroughs among the undisturbed columns underscores the heterogeneity of preferential flow phenomena in soils, indicating that multiple replicates would be needed to attempt to quantify potential metal mobilities.

The presence of soluble organics had less of an effect on overall metal transport. There was no enhancement of mobility in the homogenized columns. However, soluble organics in the preferential flow columns allowed Cu and P, which have strong affinities for complexation, to leach at rates comparable to Cd and Zn, which were unaffected by the presence of organics.

Preferential flow and the presence of soluble metal-organic complexes could both contribute to the unexplained loss of metals in the field studies cited earlier (i.e. Dowdy, et al. , 1991), by potentially allowing mobilized metals to rapidly move below the depth of sampling. Even if a fraction of migrating metals are subsequently re-adsorbed on the walls of preferential flow paths within the depth of sampling, the re-adsorbed metals be difficult to detect since they will not contribute much to the bulk soil metal concentration. (Preferential flow paths represent a small portion of the total soil volume).

While this study demonstrates that preferential flow paths in undisturbed make a considerable difference when considering solute transport through soil, it may not be directly applicable to sludge-applied metals. Metals applied in this experiment were soluble metal salts, whereas metals in sewage sludge would not necessarily react in a similar matter, since the high organic content of sludges strongly retains metals (at least initially). Field moisture conditions fluctuate, in contrast to the equilibrium conditions used in this experiment. Nevertheless, there is opportunity for limited transport of soluble metal-organic complexes which may occur in sludge-amended soil, and preferential flow may increase the velocity and depth of transport. Ongoing research is extending this work by

examining the mobility of metals in both field situations and in sludge products applied to undisturbed columns.

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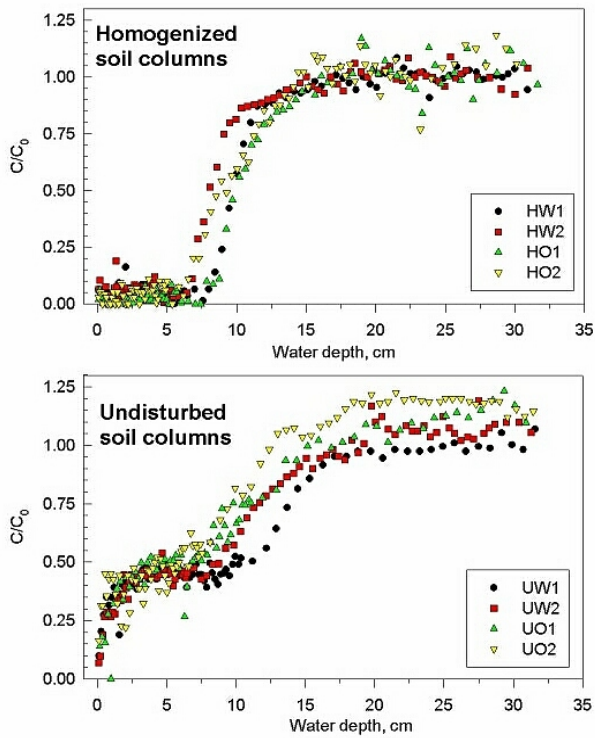


Figure 1. Chloride breakthrough curves for undisturbed and homogenized columns.

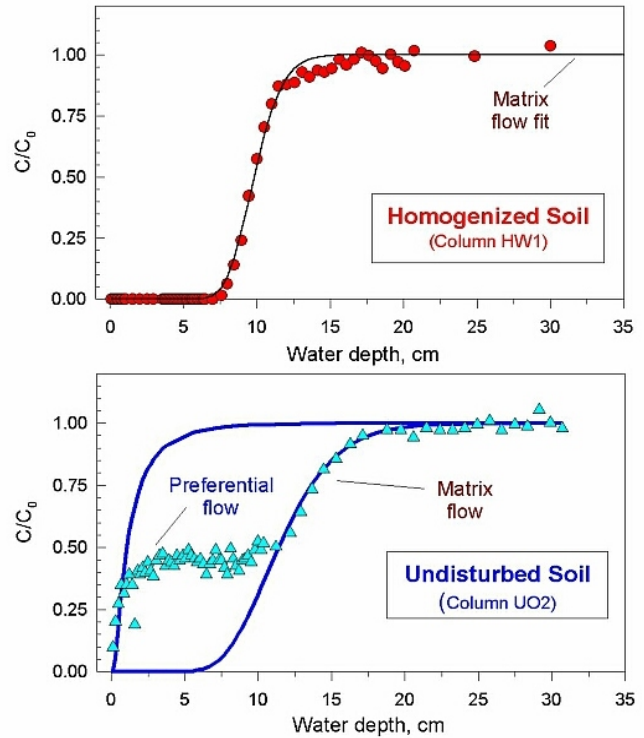


Figure 2. Sample fits of the advection-dispersion equation using CXTFIT for homogenized and undisturbed column chloride breakthrough data.

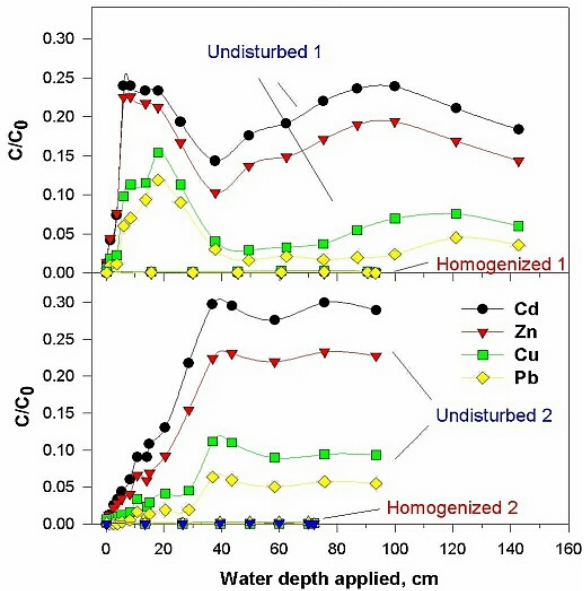


Figure 3. Metal breakthrough curves for undisturbed and homogenized columns applied with metals in distilled water.

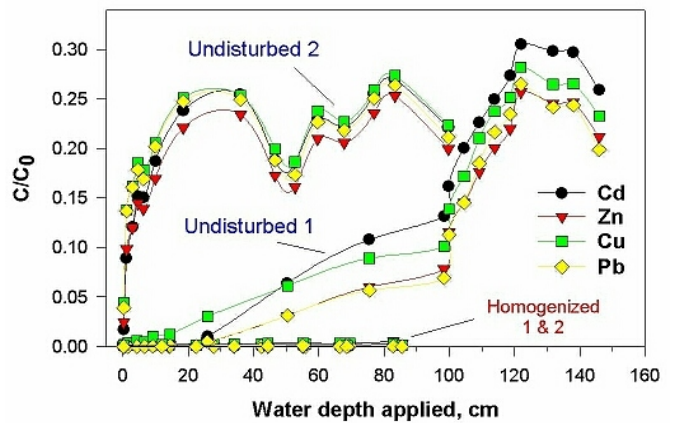


Figure 4. Metal breakthrough curves for undisturbed and homogenized columns applied with metals in organic solution.



Table 1. Summary of column treatments.

| Soil Column Type | Metals Applied in |                  |
|------------------|-------------------|------------------|
|                  | Distilled Water   | Organic Solution |
| Undisturbed      | UW1, UW2          | UO1, UO2         |
| Homogenized      | HW1, HW2          | HO1, HO2         |

Table 2. Mean measured input solution pH, chloride and metal concentrations, mg L<sup>-1</sup>.

| Analyte         | Organic Solution C <sub>0</sub> | Distilled Water C <sub>0</sub> |
|-----------------|---------------------------------|--------------------------------|
| pH              | 7.6                             | 5.2                            |
| Cl <sup>-</sup> | 14.5                            | 15.90                          |
| Cd              | 6.30                            | 7.25                           |
| Zn              | 4.11                            | 4.55                           |
| Cu              | 3.19                            | 3.51                           |
| Pb              | 12.6                            | 13.8                           |

Table 3. Homogenized columns calculated pore volumes, flow velocities, moisture contents and CXTFIT correlation coefficients.

| Column | Pore Volume (mL) | Velocity (cm day <sup>-1</sup> ) | Moisture Content | R <sup>2</sup> |
|--------|------------------|----------------------------------|------------------|----------------|
| HW1    | 3220             | 10.6                             | 0.28             | 0.99           |
| HW2    | 2730             | 9.7                              | 0.24             | 0.99           |
| HO1    | 3380             | 9.2                              | 0.29             | 0.98           |
| HO2    | 3060             | 8.2                              | 0.26             | 0.99           |
| Mean:  | 3100             | 9.4                              | 0.27             | -              |

Table 4. Undisturbed columns calculated pore volumes, flow velocities, moisture contents and CXTFIT correlation coefficients.

| Column                             | Pore Volume<br>(mL) | Flow Velocity<br>(cm day <sup>-1</sup> ) | Fraction Volume<br>Through Component | Moisture<br>Content |
|------------------------------------|---------------------|--|--------------------------------------|---------------------|
| <u>Preferential Flow Component</u> |                     |  |                                      |                     |
| UO1                                | 813                 | 67.8                                     | 0.22                                 | 0.07                |
| UO2                                | 364                 | 103.7                                    | 0.12                                 | 0.03                |
| UW1                                | 528                 | 101.7                                    | 0.12                                 | 0.05                |
| UW2                                | 656                 | 54.0                                     | 0.17                                 | 0.06                |
| Mean:                              | 590                 | 81.8                                     | 0.16                                 | 0.05                |
| <u>Matrix Flow Component</u>       |                     |  |                                      |                     |
| UO1                                | 2820                | 19.6                                     | 0.78                                 | 0.24                |
| UO2                                | 2610                | 14.4                                     | 0.88                                 | 0.23                |
| UW1                                | 3830                | 14.0                                     | 0.88                                 | 0.33                |
| UW2                                | 3110                | 11.4                                     | 0.83                                 | 0.27                |
| Mean:                              | 3090                | 14.9                                     | 0.84                                 | 0.27                |

Table 5. Mean metal concentrations ( $C/C_0$ ) in undisturbed column percolates following initial breakthrough.

| Column | Cd   | Zn   | Cu   | Pb   |
|--------|------|------|------|------|
| UO1    | 0.29 | 0.24 | 0.26 | 0.24 |
| UO2    | 0.23 | 0.21 | 0.23 | 0.23 |
| UW1    | 0.20 | 0.16 | 0.05 | 0.03 |
| UW2    | 0.29 | 0.23 | 0.10 | 0.06 |