Copper and Calcium Transport through an Unsaturated Soil Column

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ABSTRACT

To determine the relative importance of the physical and chemical factors that influence the movement of heavy metals through soils, leaching experiments were carried out under conditions of constant molarity during unsaturated steady-state water flow through a Manawatu fine sandy loam (a Dystric Fluventic Eutochrept). The movement and exchange of copper was studied in a binary Cu–Ca system. The movement of the associated anions, namely chloride and sulfate, was also monitored. The measurements were compared with predictions from the convection–dispersion equation (CDE), linked with cation exchange theory. The agreement between the measured and predicted breakthrough of sulfate and copper was good. This indicates that copper retardation in the Manawatu soil is closely related to the cation exchange capacity, and that exchange between Ca and Cu is the main process of Cu retardation in the Manawatu soil. However, copper appeared slightly later in the effluent than predicted, indicating that non-exchange processes are also involved in copper transport. Measurements of suction cups could also be used to obtain the parameters for the CDE to describe sulfate movement through the soil. Time domain reflectometry (TDR) measurements of the bulk-soil electrical conductivity could be used to monitor the movement of both sulfate and copper. This indicates that TDR can also be used to monitor cation transport and exchange through the soil, provided the percolating solution causes a sufficient change in the electrical conductivity.

Leaching of heavy metals resulting from intensified use of fungicides, application of sewage sludge, waste from timber preservation industry, and acid mine wastes has become an important area of environmental research. The development and parameterization of models for simulating heavy metal transport are key components for environmental impact assessment, because it can take decades for ground water contamination to become measurably apparent. To discern whether or not there is a chemical "time-bomb" in the soil, we need to rely on models. Furthermore, models can suggest strategies for mitigating contamination risks.

The movement of heavy metals through soil is strongly affected by adsorption processes. These exchange mechanisms depend on soil properties such as the cation exchange capacity (CEC), and exchange selectivity coefficients for the various cations and heavy-metal cations in the soil system. Many studies have been carried out to quantify these properties using batch experiments (e.g., Fic and Isenbeck-Schröter, 1989; Harter, 1992). Despite increasing concern with respect to heavy metal leaching into the ground water, few studies have been carried out to determine quantitatively the factors influencing the transport of heavy metals under unsaturated flow conditions (Abd-Elfattah and Wada, 1980; Dudley et al., 1991). Various models, based on adsorption equations or ion exchange, have been used with mixed success to describe cadmium and zinc movement through soils (Selim et al., 1992; Hinz and Selim, 1994; Buchter et al., 1996; Streck and Richter, 1997).

The use of TDR for studying chemical transport has been shown for inert solutes (Kachanoski et al., 1992; Wraith et al., 1993), and for reactive solutes provided that the adsorption was due to an increase in the anion exchange capacity (Vogeler et al., 1996). However, the use of TDR to monitor ion exchange has not yet been demonstrated.

To get a better understanding of heavy metal transport through soils under unsaturated conditions, the movement of copper through a repacked soil column of Manawatu fine sandy loam was studied. The convection–dispersion equation, coupled with ion exchange, was used to simulate the measured breakthrough curve of copper. Also, the movement of the associated anions is described briefly. The use of TDR for monitoring sulfate and copper movement and exchange was also investigated. This employed a relationship between the TDR-measured bulk electrical conductivity and the solute resident concentration that we had determined previously (Vogeler et al., 1997a). The TDR method relies on the fact that the electrical conductivity of 0.012 M $CuSO_4$ is 13% less than that of $CaSO_4$.

THEORY

Solute Transport

Reactive-solute transport during steady-state vertical flow through homogeneous soil is often described by the CDE. In terms of the cumulative infiltration depth of water, Q (m), the CDE is given by (Vogeler et al., 1998):

$$R\theta\frac{\partial C}{\partial Q} = \lambda\frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} \qquad [1]$$

where R is the dimensionless retardation factor, C is the concentration in the soil solution (mol m^{-3}), λ is the dispersivity (m), θ is the volumetric water content (m^3 m^{-3}), and z is the depth (m).

Retention of cations is generally assumed to depend on exchange reactions between cations adsorbed on the solid phase and those in the soil solution. Here we consider only a binary homovalent system with the cation species Ca^{2+} and Cu^{2+}. The total amount of adsorbed cation charge (X_{CEC}) can then be expressed as:

$$X_{CEC} = X_{Ca} + X_{Cu} \qquad [2]$$

where X denotes the charge concentration of adsorbed cations (mol$_c$ kg^{-1}), and the subscripts represent calcium and copper. Similarly, the total solution concentration,

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Abbreviations: BTC, breakthrough curve; CEC, cation exchange capacity; CDE, convection–dispersion equation; TDR, time domain reflectometry.

C_T (mol$_c$ m^{-3}), is given by:

$$C_T = C_{Ca} + C_{Cu} \qquad [3]$$

where and C_{Ca} and C_{Cu} are the concentrations of calcium and copper in the soil solution (mol m^{-3}).

It is assumed that cation exchange reactions are instantaneous and reversible, so equilibrium equations can be used to describe the relationship between the cation species in the soil solution, and those on the exchange sites. For homovalent exchange, such as Ca^{2+} and Cu^{2+}, the equilibrium equation can be written as (Bohn et al., 1985):

$$K_{\text{Ca-Cu}} = \frac{C_{Ca}X_{Cu}}{C_{Cu}X_{Ca}} \qquad [4]$$

where $K_{\text{Ca-Cu}}$ is the dimensionless selectivity coefficient, here assumed constant and so independent of concentration.

The experiment was performed under a constant total-solution concentration (C_T). Thus, the retardation factor for copper transport, assuming that nonpreferential exchange between Ca^{2+} and Cu^{2+} occurs ($K_{\text{Ca-Cu}}$ = 1), is given by (Selim et al., 1987):

$$R = 1 + \frac{\rho_b X_{CEC}}{\theta C_T} \qquad [5]$$

where ρ_b is the bulk density of the soil (Mg m^{-3}).

The boundary and initial conditions relevant to the study described here are for the soil to be initially free of the ion of interest (Cu^{2+}). Then, when Q equals zero, the flux concentration changes to $C = C_o$ in the infiltrating solution. Thus, the appropriate initial and boundary conditions are:

$$\begin{aligned} C &= 0 \qquad && z \geq 0;\ Q = 0 \\ -\lambda q\frac{\partial C}{\partial z} + qC &= qC_o \qquad && z = 0;\ Q \geq 0 \end{aligned} \qquad [6]$$

For the lower boundary, it is assumed that the soil column was part of an effectively semi-infinite system, as suggested by van Genuchten and Wierenga (1986).

At some depth L, we are interested in the flux and resident soil solution concentrations, C_f and C_r, as a function of cumulative infiltration. So the solutions we require are (van Genuchten and Wierenga, 1986):

$$\frac{C_f(Q, L)}{C_o} = \frac{1}{2}\operatorname{erfc}\left(\frac{RL - Q/\theta}{2(QR\lambda/\theta)^{1/2}}\right) + \frac{1}{2}\exp\left(\frac{L}{\lambda}\right)\operatorname{erfc}\left(\frac{RL + Q/\theta}{2(QR\lambda/\theta)^{1/2}}\right) \qquad [7]$$

and

$$\frac{C_r(z, Q)}{C_r(z, \infty)} = \frac{1}{2}\operatorname{erfc}\left(\frac{Rz - Q/\theta}{2(QR\lambda/\theta)^{1/2}}\right) + \left(\frac{Q}{\pi\theta R\lambda}\right)^{1/2}\exp\left(\frac{-(Rz - Q/\theta)^2}{4QR\lambda/\theta}\right) - \left(1 + \frac{z}{\lambda} + \frac{Q}{R\lambda\theta}\right)\exp\left(\frac{z}{\lambda}\right)\operatorname{erfc}\left(\frac{Rz + Q/\theta}{2(QR\lambda/\theta)^{1/2}}\right) \qquad [8]$$

QuickBASIC computer programs (similar to CXTFIT by Toride et al., 1995) were used to fit the analytical solutions for flux and resident concentrations to the observed data by the least sum of square method (Elprince and Day, 1977).

Time Domain Reflectometry

The theory of monitoring solute transport using TDR has been described previously (Vogeler et al., 1996). Only the salient features are repeated here. The estimation of the solute resident concentration in the soil is based both on the measurement of the water content (θ) and the bulk electrical conductivity (σ [S m^{-1}]) of the soil. The water content can be inferred from the universal relationship given by Topp et al. (1980). Meanwhile, the bulk electrical conductivity can be derived from the TDR-measured impedance, Z (Ω), using:

$$\sigma = K_G Z^{-1} f_t \qquad [9]$$

where K_G is a geometric probe constant and f_t is a temperature-correction coefficient.

The conductivity of the soil solution, σ_w (S m^{-1}), can then be estimated from the bulk electrical conductivity after calibration, using the equation considered by Vogeler et al. (1997a):

$$\sigma_w = \frac{\sigma - (a\theta - b)}{(c\theta - d)} \qquad [10]$$

where a, b, c, and d are soil-specific constants.

If the ionic species are known, the solute concentration can be calculated from the soil-solution electrical conductivity, and vice versa. The relationship depends on the particular salt used, and its concentration (Dean, 1985, p. 6–38 to 6–43). For a CuSO$_4$ solution ranging from 0.005 to 0.05 M, Dean gave data implying that:

$$\ln L_s = 3.44 - 0.18 \times \ln C \qquad [11]$$

where L_s is the equivalent conductance (Ω^{-1} cm^2 equiv^{-1}), which is related to the electrical conductivity of the solution by:

$$\sigma_w = \frac{L_s C}{10} \qquad [12]$$

For a CaCl$_2$ solution ranging from 0.005 to 0.05 M, Dean gave data implying that:

$$\ln L_s = 4.36 - 0.06 \times \ln C \qquad [13]$$

while for a CaSO$_4$ solution ranging from 0.001 to 0.01 M, the relationship is given by:

$$\ln L_s = 3.77 - 0.13 \times \ln C \qquad [14]$$

Thus, for example, the electrical conductivity of a 0.012 M CuSO$_4$ solution is only 87% of the conductivity of a 0.012 M CaSO$_4$ solution, and only 62% of that of a 0.012 M CaCl$_2$ solution.

MATERIALS AND METHODS

A solute-transport experiment was carried out on a repacked soil column under conditions of unsaturated flow. The soil used was Manawatu fine sandy loam (Dystric Fluventic Eutrochrept). The soil has a CEC of 0.111 mol$_c$ kg^{-1} (NH$_4$OAc) with Ca^{2+} as the dominant cation, and an organic matter content of about 3%. The sand (2–0.02 mm), silt (0.02–0.002 mm), and clay (<0.002 mm) fractions are 63, 21, and 16%, respectively. The dominant clay types are mica, chlorite, smectite, kaolinite, and halloysite, and the field pH is 5.4 (measured in water). The soil was sieved and then packed to a bulk density of 1.2 Mg m^{-3} in a column that was 300 mm in diameter and 280 mm in length. A rainfall simulator (for details see Vogeler et al., 1997b) was used to apply the various solutions at a rate of about 5 mm h^{-1}. The column was placed on an inverted tension infiltrometer made from plexiglass. This infiltrometer was maintained at a head of −50 mm to ensure unsaturated flow at the base, and yet allow regular sampling of the effluent (for details see Magesan et al., 1995). Three-wire TDR probes were installed horizontally at depths of 30, 130, and 230 mm. The TDR probes were 150 mm long with a wire diameter of 2 mm, and an interwire spacing of 12.5 mm. The probes were connected, via a multiplexer, to a Tektronix (Beaverton, OR) 1502C cable tester. A laptop computer controlled the settings of the TDR and the multiplexer, and it also recorded and analyzed the waveform. Contemporaneous measurements of both θ and σ were taken regularly. At the beginning, the TDR-measured water content for the probes at 30, 130, and 230 mm was 0.12, 0.19, and 0.17 m^3 m^{-3}, and at the end 0.32, 0.41, and 0.38 m^3 m^{-3}. The average volumetric water content (determined gravimetrically) measured at the end was 0.478 m^3 m^{-3}. The deviation between the gravimetrically determined and TDR-measured water content is probably due to the copper, as the two different methods have been shown to give similar results in this soil before (Vogeler et al., 1997a). At the same depth as the TDR probes, ceramic suction cups (made of vinyl chloride; Daiki Co., Tokyo, Japan) 100 mm in length and 3 mm in diameter were installed horizontally. During leaching with $CuSO_4$, suction was applied via syringes, and samples were collected twice a day in aliquots ranging from 3 to 7 mL.

The column was pre-equilibrated by leaching with about 1 liquid-filled pore volume of 0.015 *M* $Ca(NO_3)_2$. At a mean flow rate of 5 mm h^{-1} a pore volume infiltrates through the column in about 29 h. The pH of the solution was 5.4. Then 4 pore volumes of 0.013 *M* $CaCl_2$ (pH of 5.6) were applied to saturate the exchange sites of the soil with Ca^{2+}. Thereafter, the invading solution was changed to 0.012 *M* $CuSO_4$ (pH of 4.7), and a further 15 pore volumes were leached through the column. The change in concentration of $CaCl_2$ and $CuSO_4$ was not intended but considered in the modeling. Finally, the column was sectioned into 25-mm-thick layers. Subsamples of the soil from each layer were used to determine the gravimetric water content, the pH, and the resident concentrations of Cu^{2+}, Ca^{2+}, Mg^{2+}, Na^+, and K^+. The CEC at the soil's pH was obtained by adding the amounts of K^+, Na^+, Ca^{2+}, and Mg^{2+} measured in the soil prior to the experiment. The effluent quitting the base of the column was analyzed for Cl^-, SO_4^{2-}, Ca^{2+}, K^+, and Mg^{2+} using high performance liquid chromatography (HPLC) (Dionex [Sunnyvale, CA] 500, Column AG11, 2 mm), and Cu^{2+} was analyzed by atomic absorption (GBC [Australia] 904 atomic absorption spectrophotometer). The suction-cup samples were analyzed for SO_4^{2-}, Ca^{2+}, and Cu^{2+}. The electrical conductivities of the effluent and suction cup samples were measured with an electrical conductivity meter, and the pH was measured electrometrically (Multiline P3/LF Set; WTW, Weilheim, Germany).

RESULTS

Anion Movement: Effluent Concentrations

The breakthrough curves (BTCs) of chloride and sulfate measured in the effluent after leaching started with either 0.013 *M* $CaCl_2$ or 0.012 *M* $CuSO_4$ are shown in Fig. 1. The BTCs are quite similar, indicating that sulfate is not adsorbed by this soil. Also shown are the fitted curves using the CDE (Eq. [7]) and least-squares optimization. Dispersivity values of 2 and 4 mm were found for Cl^- and SO_4^{2-}, respectively, which are typical for repacked soil (Wagenet, 1983). The fitted values found for the retardation (*R*) were 0.88 and 0.94, respectively, suggesting some anion exclusion from the double layer.

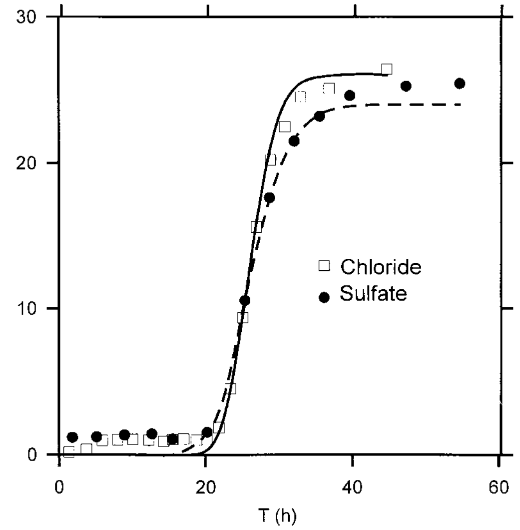

Fig. 1. Measured, and fitted breakthrough data as a function of time using the convection–dispersion equation (CDE) for Cl^- (□, and solid line) and SO_4^{2-} (●, and broken line).

Anion Movement: Suction Cup Concentrations

The sulfate concentrations measured in the suction cup samples at the three different depths are shown in Fig. 2. Also shown are the predictions of the flux concentrations (C_f) at these depths using the CDE (Eq. [7]). Dispersivities found from these data ranged from

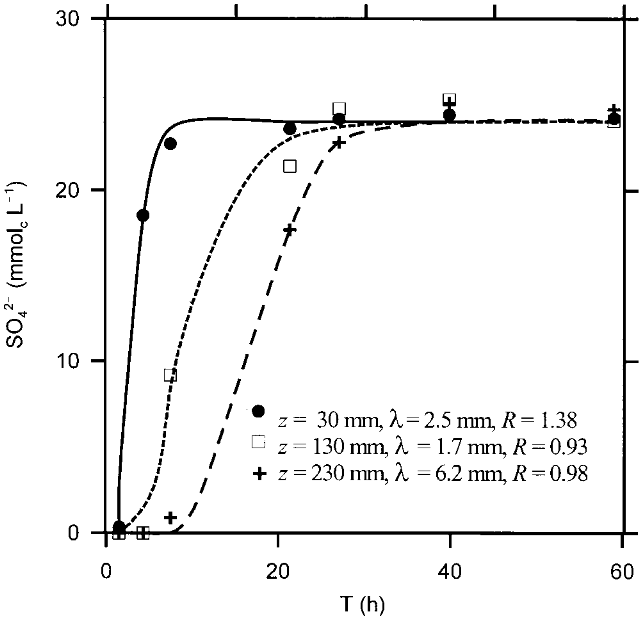

Fig. 2. Measured and fitted SO_4^{2-} data from the suction cups at 30 mm (●), 130 mm (□), and 230 mm (+) as a function of time.

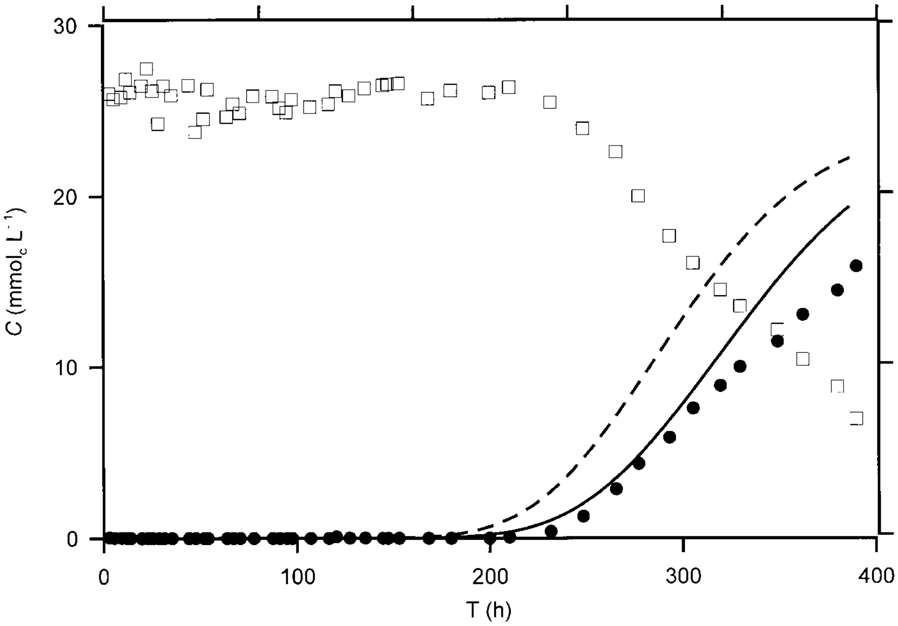

Fig. 3. Effluent concentrations of Ca^{2+} (□) and Cu^{2+} (●) as a function of time. Also shown are the predictions for Cu^{2+} from the convection–dispersion equation (CDE) using *R* values of 12.6 (broken line) and 14 (solid line).

2 to 6 mm. The *R* values ranged from 0.93 to 1.38. Apart from the *R* found for the upper suction cup, the values are similar to those found from the effluent data. Those results indicate that the suction cup data could be used to obtain the parameters needed to describe sulfate movement through the soil.

Cation Movement: Effluent Concentrations

The concentrations of Ca^{2+} and Cu^{2+} in the effluent after leaching started with $CuSO_4$ are shown in Fig. 3. Here, the small amount of Mg^{2+}, K^+, and Na^+ measured in the leachate have been added to the Ca^{2+} concentrations. Due to exchange between the calcium initially adsorbed onto the exchange sites, and the invading Cu^{2+}, the initial cation in the effluent is Ca^{2+}. Only once the Ca^{2+} has been leached out of the soil does Cu^{2+} appear in the leachate. In our case, this was after about 1200 mm of infiltration. Also shown, as the broken line, are the simulated concentrations for Cu^{2+}, using Eq. [6] and [7]. A dispersivity of 4 mm was used, as found for SO_4^{2-} transport. The retardation factor in Eq. [5] was calculated to be 12.6. The agreement between the measured and predicted Cu^{2+} concentrations is reasonable. This suggests that the movement of Cu^{2+} is closely related to the CEC. Similarly, Shuman (1975) found that the CEC was responsible for Zn^{2+} sorption. There is more retardation than expected from the CEC alone. A fit to the BTC data yields an *R* value of 14, shown as the solid line in Fig. 3. It seems that non-exchange processes, as suggested by Harter (1992) for Ca^{2+}–Cu^{2+} exchange, might also have been involved. Non-exchange sorption processes could be mineral edge complexation, as suggested by Quirk and Posner (1975) for Zn^{2+} sorption, or complexation at carboxylate or phenolic groups (Boyd et al., 1981; Piccolo and Stevenson, 1982). In all cases, complexation is associated with displacement of protons from hydroxyl groups, which results in a change in the solution pH. This is consistent with our pH measurements, which showed a decrease from 4.7 in the input solution to 4.6 in the effluent.

Cation Movement: Suction Cup Concentrations

The equivalent concentrations of Cu^{2+} measured in the suction cup samples are shown in Fig. 4. Also shown are the flux concentrations at the suction cup depths calculated from Eq. [6], using the dispersivity of 4 mm found from the effluent SO_4^{2-} data. A retardation value of 14 as obtained from the effluent data was used. The agreement is reasonable for all depths, which is consistent with the effluent data for Cu^{2+}. Again it appears that Cu^{2+} is not only adsorbed onto cation exchange sites, but that also some complexation of Cu^{2+} occurs.

Solute Movement: Time Domain Reflectrometry Measurements

The TDR-measured bulk-soil electrical conductivities (σ), once leaching with $CaCl_2$ started, for the three different depths are shown in Fig. 5. At the beginning, σ was nearly constant. After 92.5 h of leaching with $CaCl_2$, the solution was changed to $CuSO_4$. This resulted in a sharp drop in σ. The application of $CuSO_4$ to the Ca-saturated soil would have resulted in exchange between the Ca^{2+} adsorbed onto the soil surface and the invading Cu^{2+} solution. Consequently, a $CaSO_4$ solution would be moving through the soil. This drop in σ is due to the conductivity of a 0.012 *M* $CaSO_4$ solution being only 66% of the conductivity of a 0.013 *M* $CaCl_2$ solution. This drop appears slightly later in the second and third TDR probes, reflecting the movement of sulfate through the soil.

Another slight drop in σ can be seen from about 100

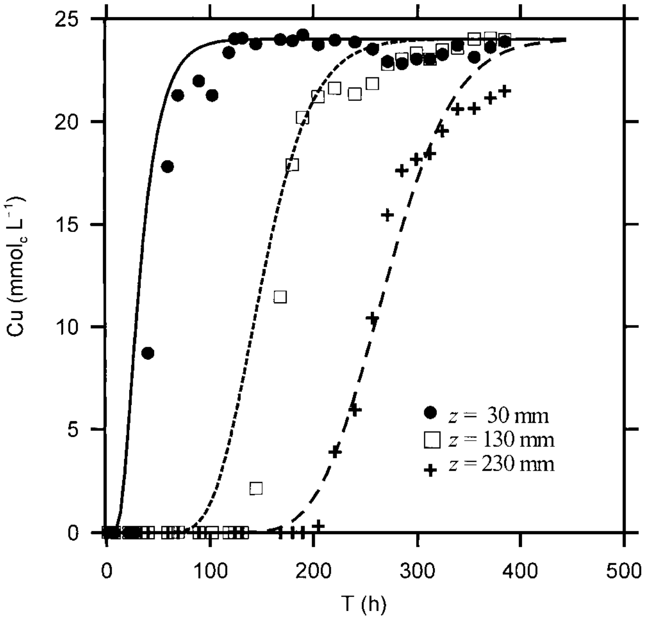

Fig. 4. Concentrations of Cu^{2+} from suction cups at 30 mm (●), 130 mm (□), and 230 mm (+). Also shown are the predictions using the convection–dispersion equation (CDE) and an *R* value of 12.6.

to 200 h in the TDR probe at 30 mm. This second drop is much more gradual and is due to a slow change of the solution from $CaSO_4$ to $CuSO_4$, resulting from the exchange between Cu^{2+} and Ca^{2+}. A 0.012 *M* $CuSO_4$ solution only has a conductivity of 87% of that of a 0.012 *M* $CaSO_4$ solution. The inset of Fig. 5 shows an enlarged view of the drop in σ during exchange between Ca^{2+} and Cu^{2+}. The increase of σ in the TDR probe at 30 mm just before 300 h is due to a slight increase in the water content. This might have been due to a change in hydraulic properties of the soil due to the copper or to a slight increase in the application rate by the rainfall simulator. The increase in water content has a large effect on the TDR-measured σ. This second drop in σ can be seen in the second TDR probe from about 200 to 350 h, and in the TDR probe at 230 mm from about 300 to 450 h. The σ measured by the second and third TDR probes were more constant than those of the first probe. There the water content remained almost constant.

Also shown in Fig. 5 are the σ predictions from the CDE using Eq. [8] and [10] through [14]. Here an *R* value of 14 was assumed. The predictions of σ are of the same magnitude as the TDR-measured σ. This suggests that the direct calibration described in Vogeler et al. (1996, 1997a) can be used in an inverse sense to estimate solute concentrations. The drop in σ due to the $SO_4{}^{2-}$ moving through the soil was described accurately by the model, suggesting that TDR can be used to monitor the movement of nonreactive anion transport through the soil. The absolute final values of TDR-measured σ and those modeled only agreed for the TDR probe at 230 mm. The reason for the disagreement between the measured and modeled values for the other two TDR probes are not known. However, the agreement between the simulated and measured duration of the second drop was reasonable for all three TDR probes. So TDR can also be used to monitor cation transport and exchange through soils, but only if the two cations considered in the system possess a different electrical conductivity.

CONCLUSIONS

Copper movement could be simply described using the convection–dispersion equation linked to cation exchange equations. Copper adsorption and retarded transport were found to be related closely to the CEC of the soil. Since Cu^{2+} appeared slightly later in the breakthrough than predicted from the CEC alone, nonexchangeable processes seemed also to be involved in Cu^{2+} retardation. This was not accounted for in the model. Also, suction cups could be used to monitor the movement of both SO_4^{2-} and Cu^{2+} through the soil. These results gave similar values for the transport parameters, such as the dispersivity and the retardation of Cu^{2+}.

Although exchange of Cu^{2+} with Ca^{2+} was closely related to the CEC, it must be borne in mind that the leaching experiment was carried out with high Cu^{2+} concentrations. As exchange and redistribution between various exchange sites depends on time and loading rate (McLaren and Ritchie, 1993; Han and Banin, 1997), exchange might be quite different if Cu^{2+} solutions are applied over the long term at lower concentrations. Furthermore, competition with other heavy metals might affect the sorption of Cu^{2+}. This was not accounted for.

These results indicate that in our soil, Cu^{2+} would begin to leach beyond 30 cm after about 1200 mm of drainage. The time when leaching occurs also depends on the CEC of the soil, and the Cu^{2+} concentration of the applied contaminant. As noted, in this experiment the concentration of $CuSO_4$ was quite high at 0.012 *M*. However, solutions used for timber treatment in New Zealand also have high concentrations of $CuSO_4$, up to 0.028 *M* (Carey et al., 1996). Thus, care must be taken to avoid spilling these solutions on shallow soils with a low CEC. Furthermore, it must be taken into account that this experiment was performed on a repacked soil column. In undisturbed soils, preferential flow can often result in more rapid leaching of copper.

Time domain reflectrometry-measured bulk-soil electrical conductivities also could be used to monitor sulfate and copper transport through the soil. This was because the various solutions had a different electrical conductivity, resulting in a change in bulk conductivity. The drop in σ due to the movement of SO_4^{2-} could be seen clearly. The influence of the copper was slight, as the electrical conductivity changed by only 13%. Thus, TDR seems to be a valuable tool for studying cation and heavy metal transport and exchange through soil, provided that high solution concentrations are used. I plan to carry out further experiments using TDR to investigate cation and heavy metal transport through soil. I intend to use $CaCl_2$ and $CdCl_2$ solutions, which differ in conductivity at 0.025 *M* by about 63% (Dean, 1985, p. 6–38 to 6–43).

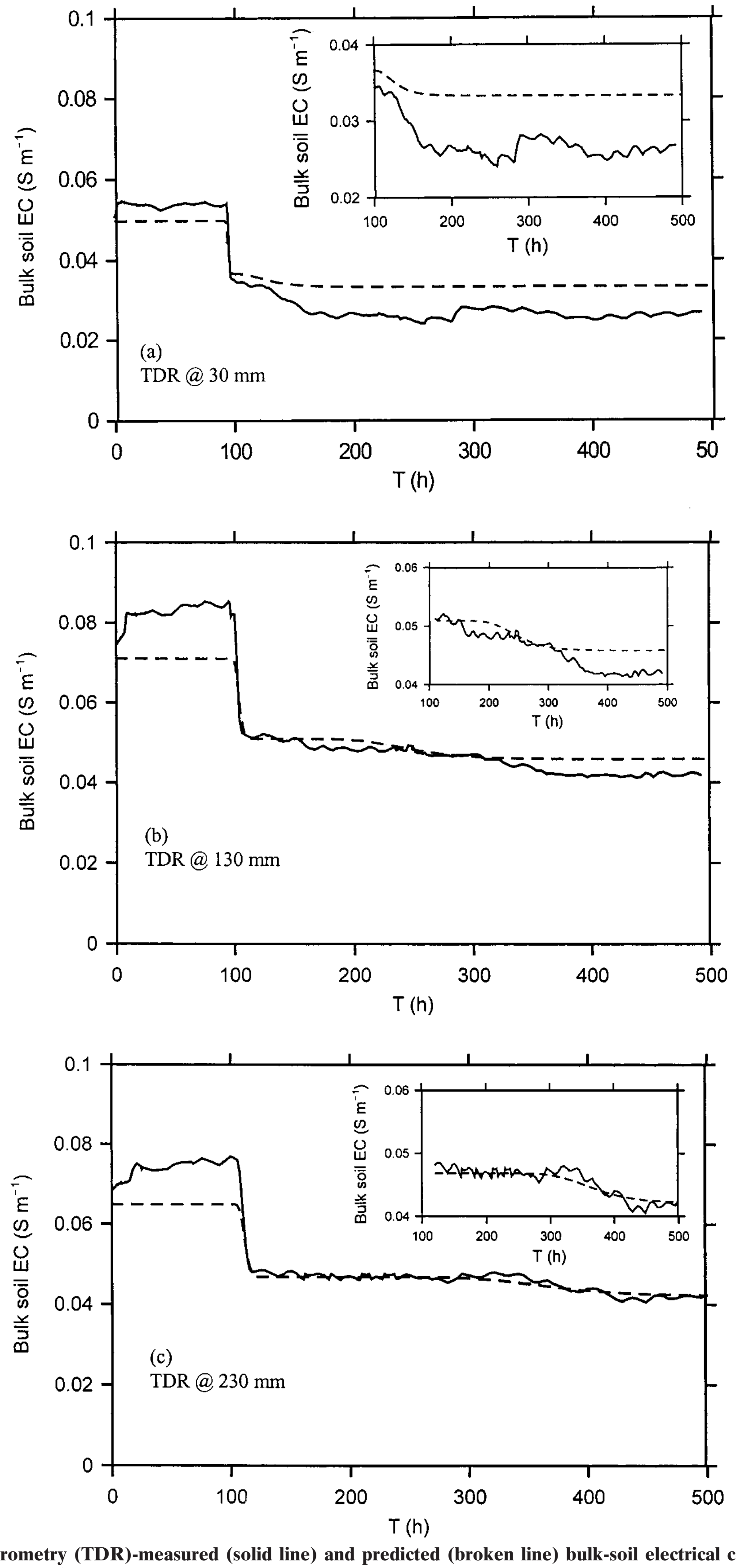

Fig. 5. Time domain reflectrometry (TDR)-measured (solid line) and predicted (broken line) bulk-soil electrical conductivity as a function of time for depths of (*a*) 30 mm, (*b*) 130 mm, and (*c*) 230 mm. The prediction was calculated using the convection–dispersion equation (CDE) and an *R* value for Cu^{2+} of 14.

APPENDIX

Parameters

C, concentration in soil solution (mol m^{-3}); C_{Ca}, concentration of calcium in soil solution (mol m^{-3}); C_{Cu}, concentration of copper in soil solution (mol m^{-3}); C_{T}, constant total solution concentration (mol m^{-3}); C_{o}, input concentration (mol m^{-3}); C_{f}, flux concentration (mol m^{-3}); C_{r}, resident concentration (mol m^{-3}); $K_{\mathrm{Ca\text{-}Cu}}$, selectivity coefficient; K_{G}, geometric TDR-probe constant; L, depth (m); L_{s}, specific conductance (Ω^{-1} cm^2 equiv^{-1}); Q, cumulative infiltration depth of water (m); R, retardation factor; X_{CEC}, total amount of cation charge (mol$_{\mathrm{c}}$ kg^{-1}); X_{Ca}, amount of adsorbed calcium (mol$_{\mathrm{c}}$ kg^{-1}); X_{Cu}, amount of adsorbed copper (mol$_{\mathrm{c}}$ kg^{-1}); z, depth (m); Z, impedance (Ω); λ, dispersivity (m); θ, volumetric water content (m^3 m^{-3}); ρ_{b}, bulk density (Mg m^{-3}); σ, bulk soil electrical conductivity (S m^{-1}); σ_{w}, conductivity of soil solution (S m^{-1}).

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