A Simple Approach to Determine Reactive Solute Transport Using Time Domain Reflectometry

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ABSTRACT

Time domain reflectometry (TDR) possesses potential for determining solute-transport parameters, such as dispersion coefficients and retardation factors for reactive solutes. We developed a simple method based on peak-to-peak measurements of water and solute velocities through the soil using TDR. The method was tested by carrying out unsaturated leaching experiments in the laboratory on two soil columns packed with a South Pacific soil from Maré, which is a ferrasol with variable surface charge. One column was left bare and the other was planted with mustard. Pulses of $CaBr_2$ and $Ca(NO_3)_2$ were applied to the surface of either wet or dry soil and then leached by water from a rainfall simulator applied at a steady rate of between 30 and 45 mm h^{-1}. Water and solute transport were monitored by collecting the effluent. Contemporaneous in situ measurements of the water content and electrical conductivity were made using TDR. Transport parameters for the convection–dispersion equation, with a linear adsorption isotherm, were obtained from the flux concentration and the solute resident concentrations measured by TDR. Anion retardations between 1.2 and 1.7, and dispersivities between 1 and 9 mm, were found. Retardations also were calculated using our simple approach based on TDR-measured water and solute front velocities. These used TDR measurements of soil water content and bulk soil electrical conductivity with time, and were similar to those obtained from the effluent. The agreement suggests TDR could be a valuable in situ technique for obtaining the parameters relating to reactive solute transport through soil.

L ACK OF ADEQUATE INSTRUMENTATION limits in situ measurements of transport processes of water and chemical movement in the unsaturated zone. Within the last decade TDR has become widely used for measuring soil water content. Now TDR is seen as a means by which the changing concentration of electrolyte in the soil solution can also be observed. The ability to take such measurements continuously and automatically, in a nondestructive way, makes TDR a valuable tool for observing solute transport in situ. So far application of this technique to monitor solute transport has been limited to soils in which anions such as nitrate are considered to be nonreactive solutes (Kachanoski et al., 1992; Vanclooster et al., 1993; Mallants et al., 1994). However, many soils around the Pacific region, and elsewhere in volcanic regions, carry variable surface charge and are known to adsorb anions. Therefore these soils need to be managed differently, because adsorption critically controls the depth and pattern of leaching. The degree of anion adsorption depends on the exchange capacity of the soil, which is generally determined from batch experiments. Limitations of batch techniques include breakdown of soil aggregates, disturbance of flow pathways, and the use of soil-to-solution ratios that are much smaller than in natural soil systems. This results in inappropriate estimates of the exchange characteristics (Bond and Phillips, 1990). Alternatively, exchange characteristics can be inferred from leaching experiments on undisturbed soil columns using fitting procedures to the concentration of the effluent (Vogeler et al., 1997a). However, such leaching experiments are laborious and cannot be used for in situ measurements in the field.

The objective of this study was to develop a simple method by which anion retardation of soils can be inferred from TDR measurements of water content and bulk soil electrical conductivity. We present some measurements of bromide and nitrate movement through a ferrasol. The soil has a variable surface charge that adsorbs anions and therefore retards their movement through the soil. We studied anion transport through a bare soil column and a column growing mustard. The mustard was used to study the impact of the presence of roots on the velocity on solute movement. Nitrate and bromide transport were measured by collecting the effluent exiting at the base of the column and monitoring the change in water content and electrical conductivity as measured by TDR probes installed at various depths within the soil column. These measurements are compared to the results generated from a numerical solution of the convection–dispersion equation (CDE), in which soil water transport is predicted using Richards's equation. Parameters describing chemical transport obtained in situ from TDR-measured peak-to-peak velocities of water and solutes fronts are compared with those obtained from the flux concentration in the effluent. Although the TDR technique was used to obtain the transport parameters for repacked soil columns in the laboratory, the approach should also be suitable for in situ measurements in the field.

THEORY

The Transport Model

One-dimensional transient water flow into a uniform unsaturated soil can be described by Richards's equation. Assuming that root water uptake is negligible, this equation can be written as

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[D_w(\theta)\frac{\partial \theta}{\partial z}\right] - \frac{dK_w}{d\theta}\frac{\partial \theta}{\partial z} \qquad [1]$$

where θ is volumetric water content (m^3 m^{-3}), D_w is soil water

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Abbreviations: CDE, convection–dispersion equation; PV, pore volumes; TDR, time domain reflectometry.

diffusivity (m^2 s^{-1}), K_w is hydraulic conductivity (m s^{-1}), t is time (s), and z is depth (m) (Kutílek and Nielsen, 1994). For the purpose of modeling the water flow we assume that diffusivity can be described using an exponential function (Brutsaert, 1979), and that conductivity can be described using a power law function (Quadri et al., 1994). The appropriate initial and boundary conditions for unsaturated flow into a soil column under steady rainfall are

$$\theta = \theta_i(z) \qquad t = 0 \qquad 0 \le z \le l,$$
$$q_w = q_0 \qquad z = 0 \qquad t > 0 \qquad [2]$$

where θ_i is initial water content (m^3 m^{-3}), q_w is water flux density (m s^{-1}), l is column length (m), and q_0 is the constant flux imposed at the surface (m s^{-1}).

The convection–dispersion equation (CDE) for one-dimensional transport of reactive anions under transient conditions is

$$\frac{\partial(\theta C_r)}{\partial t} + \frac{\partial(\rho S_A)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D_s \frac{\partial C_r}{\partial z}\right) - \frac{\partial(q_w C_r)}{\partial z} \qquad [3]$$

where C_r is solute concentration in the resident soil solution (mol m^{-3}), S_A is the amount of solute adsorbed (mol kg^{-1}), and ρ is the bulk density of the soil (kg m^{-3}) (Kutílek and Nielsen, 1994). We assume that D_s, the diffusion dispersion coefficient (m^2 s^{-1}), is given by

$$D_s = \alpha \nu + \tau D_m \qquad [4]$$

where α is dispersivity [m], ν is average pore water velocity of q_w/θ (m h^{-1}), τ is the tortuosity factor, and D_m is the molecular diffusion coefficient in a free solution (10^{-10} m^2 s^{-1}).

For the purpose of modeling solute transport we assume that the soil is initially free of the solute of interest. A solute pulse with a concentration C_0 was applied to the soil surface over a very short time interval, $0 < t < t_i$. This was followed by a continuous application of solute-free water at a steady water flow. Thus, for the solute the appropriate initial and boundary conditions are (van Genuchten and Wierenga, 1986)

$$C_r = 0 \qquad 0 \le z \le l \qquad t = 0$$
$$-\theta D_s \frac{\partial C_r}{\partial z} + q_w C_r = q_0 C_0 \qquad z = 0; 0 < t < t_i$$
$$-\theta D_s \frac{\partial C_r}{\partial z} + q_w C_r = 0 \qquad z = 0; t > t_i \qquad [5]$$

For the lower boundary condition it was assumed that the soil column was part of an effectively semi-infinite system, as suggested by van Genuchten and Wierenga (1986, p. 1034). The adsorption of anions by the soil was modeled using a simple linear isotherm of the form

$$S_A = K_D C_r \qquad [6]$$

with distribution coefficient K_D (L kg^{-1}) taken to be constant. For a linear isotherm, any anion adsorption retards the solute front by the factor R defined as

$$R = 1 + \frac{\rho K_D}{\theta} \qquad [7]$$

As part of our modeling procedures, Eq. [1] through [7] were solved numerically using a fully implicit Newton–Raphson iteration for the water flow equation and a time-centered Crank–Nicholson scheme for the solute flow (Green, 1997). Soil hydraulic properties were determined from one-dimensional, free-water adsorption experiments, using horizontal sectionable columns (Duwig, 1998). The value found for the saturated conductivity was $K_s = 1.56 \times 10^{-2}$ mm s^{-1},

with the constants for the $D_w(\theta)$ function $\gamma = 3.847 \times 10^{-5}$ and $\beta = 12$, sorptivity $S = 2.4$ mm $s^{-1/2}$ for the transient case, and the saturated water content $\theta_s = 0.69$ m^3 m^{-3}.

Time Domain Reflectometry

Here we describe a simple method to determine the soil's solute transport properties based on TDR measurements of soil water content and bulk soil electrical conductivity. For a Green–Ampt soil (that is, a soil possessing a Dirac-δ diffusivity function $D_w[\theta]$), the invading water enters the soil as a rectangular wet front and rides atop the initial water content θ_i. Thus, the wet front, z_f (m), at any time is located at

$$z_f = \frac{I}{(\theta_0 - \theta_i)} \qquad [8]$$

where I is the cumulative depth of water infiltrated (m) and θ_0 is the final water content (m^3 m^{-3}) (Clothier, 1998). The velocity of the wet front ν_f is therefore given by

$$\nu_f = \frac{\partial z_f}{\partial t} = \frac{i}{(\theta_0 - \theta_i)} \qquad [9]$$

where i is the infiltration rate (m h^{-1}). By monitoring $\theta(t)|_z$ with TDR probes installed horizontally at sequential depths z it should be possible to measure ν_f as the wet front passes the probes. Frequent measurements using an automated system are therefore required.

We use a similar approach to analyze the solute movement. Assuming the soil water is fully mobile, and that solute dispersion and diffusion can be ignored, the solute front, because of this complete invasion of the wetted pore space, will be located at a depth of

$$s_f = \frac{I}{\theta_0} \qquad [10]$$

The peak concentration will also be at the depth s_f for a pulse application of solute, even if dispersion and diffusion occur.

The solute velocity is given by

$$\nu_s = \frac{\partial s_f}{\partial t} = \frac{i}{\theta_0} \qquad [11]$$

Using the TDR to monitor changes in the bulk soil electrical conductivity should also allow measurement of ν_s. It follows that

$$\nu_s = \nu_f \frac{(\theta_0 - \theta_i)}{\theta_0} \qquad [12]$$

Both the wet front velocity and solute front velocity can be inferred simply from peak-to-peak measurements of $\theta(t)|_z$ and $\sigma(t)|_z$ as measured by TDR. If the measured solute velocity, ν_s^*, is smaller than the ν_s calculated using Eq. [12], then anion adsorption must have occurred. This anion adsorption must be related to a change in anion adsorption capacity with change in soil solution concentration, as TDR would not detect solute retardation due to anion exchange. For simplicity we assume that this change in anion adsorption capacity with soil solution concentration is linear, and thus Eq. [7] applies. The retardation will simply be given by ν_s/ν_s^*. For an excluded anion, the measured solute velocity will likewise be greater than the predicted one. This analysis requires that there be complete invasion of the wetted pore space by the invading solute. Should this not be the case, then the denominator in Eq. [10]–[12] will be the mobile water fraction θ_m. The tech-

nique will then also require a sample of the resident concentration so that θ_m can be determined (Clothier et al., 1992).

This simple approach of obtaining the retardation and anion exchange parameters was tested under controlled conditions on repacked soils in the laboratory, which are known to have no immobile water. The approach will be compared to results obtained from breakthrough curves.

MATERIALS AND METHODS

Use of Time Domain Reflectometry

The TDR technique for measuring soil water content (θ) and solute resident concentration (C_r) is based on the measurement of the soil's dielectric constant (ϵ) and bulk soil electrical conductivity (σ). The dielectric constant is calculated from Topp et al. (1980) as

$$\epsilon = \left[\frac{ct}{2l_t}\right]^2 = \left[\frac{l_a}{l_t\, v_p}\right]^2 \qquad [13]$$

where c is the propagation velocity of an electromagnetic wave in free space (3×10^8 m s^{-1}), t is travel time (s), l_t is the real length of the transmission line (m), l_a is the apparent length (m) as measured by a cable tester, and v_p is the relative velocity setting of the instrument.

Following the thin-sample theory of Giese and Tiemann (1975), the electrical conductivity of the soil σ can be described by Topp et al. (1988) as

$$\sigma = \frac{1}{120\pi l_t}\frac{Z_0}{Z_u}\left(\frac{2V_0}{V_f} - 1\right) \qquad [14]$$

where Z_0 is the characteristic impedance of the probe (Ω), Z_u is the characteristic impedance of the TDR system (50Ω), V_0 the voltage of the incident step, and V_f the final reflected voltage. The probe impedance Z_0 was calculated using Topp et al. (1988):

$$Z_0 = 60 \ln\!\left(\frac{2s}{d}\right) \qquad [15]$$

where s is the rod spacing (m) and d the rod diameter (m).

We assume the soil to be initially solute free with an initial bulk soil electrical conductivity of σ_i. If a steady state water flux, i, has already been established, and a pulse with a total mass of M (mol m^{-2}) is applied to the soil surface, then

$$M = i\!\int_0^\infty C_r\,(t)\mathrm{d}t = i\!\int_0^\infty C_f\,(t)\mathrm{d}t$$
$$= ia\int_0^\infty (\sigma(t) - \sigma_i)\mathrm{d}t \qquad [16]$$

where C_f is the flux concentration as measured in the effluent (mol m^{-3}), C_r is the resident concentration (mol m^{-3}) as measured by TDR at a depth z, and a is an empirical constant that provides an integrally correct interpretation of the conductivity measurements.

Soil Material

The soil material used was a Geric Ferrasol from Maré (Loyalty Islands, New Caledonia), derived from volcanic ejecta and ash. Details of chemical and mineralogical properties of the soil are given in Duwig (1998) and Duwig et al. (1998). Only material from the upper 20 cm of a cultivated area was used. The soil is variably charged, relatively rich in organic matter (about 13%), and primarily composed of Al and Fe oxides.

Time Domain Reflectometry Water Content Calibration

The determination of the water content from the TDR-measured dielectric constant was based on a third-order polynomial equation fitted to calibration measurements carried out with the same soil material (Duwig, 1998). The equation is given as

$$\theta = -0.17 + 6.3 \times 10^{-2}\,\epsilon - 1.7$$
$$\times 10^{-3}\,\epsilon^2 + 1.6 \times 10^{-5}\,\epsilon^3 \qquad [17]$$

This equation deviates by up to 0.2 m^3 m^{-3} from the curve suggested by Topp et al. (1980) for mineral soils. The deviation is probably due to the combination of high organic matter content and the low bulk density of the soil (Jacobsen and Schønning, 1993).

Laboratory Soil Column Transport Experiments

Oven-dried soil was sieved and packed in columns to the field bulk density of 0.8 Mg m^{-3}. Two soil columns were used, one with a diameter of 300 mm and length of 280 mm, the other with a diameter of 300 mm and length of 300 mm. One had a bare soil surface and the other had mustard growing on it. The columns were placed on inverted tension infiltrometers (Magesan et al., 1995) to ensure unsaturated flow at the base, yet also allow regular sampling of the effluent. Time domain reflectometry probes were installed at depths of 30, 130, and 230 mm into the bare soil column and at 50, 150 and 250 mm into the mustard column. Three-wire TDR probes, 150 mm long, with a wire diameter of 2 mm, and a spacing of 12.5 mm, were used. The probes were connected via a multiplexer (similar in design to that of Heimovaara and Bouten [1990]), to the Tektronix cable tester (1502C, Tektronix, Beaverton, OR). A laptop computer controled the settings of the TDR and also recorded and analyzed the waveforms using software developed in the laboratory, based on curve-fitting algorithms described by Baker and Allmaras (1990). Measurements of both θ and σ were taken every 5 min at the beginning and every 30 min after the fourth hour. A rainfall simulator (Vogeler et al., 1997b) was used to apply the water at a steady rate to each column. The experimental setup is shown in Fig. 1.

Mustard Experiment

In the mustard column, the roots had invaded the entire column length after 3 wk. To study the effect of the initial water content at the soil surface prior to solute application, the mustard was used to dry the soil down to a water content of 0.25 m^3 m^{-3}. A pulse of CaBr$_2$, equivalent to a nitrate–nitrogen application of 100 kg N ha^{-1}, was then sprayed onto the dry soil surface. The column was subsequently leached with four pore volumes (PV) of distilled water applied via the rainfall simulator. To mimic tropical rainfall intensities, a water flux density of initially 50 mm h^{-1} was used. Because ponding on the surface occurred, the intensity was decreased to 46 mm h^{-1}. After the 4 PV a concentrated pulse of Ca(NO$_3$)$_2$ at the same concentration was sprayed onto the soil surface while the steady-state rainfall was maintained.

Bare Soil Experiment

The bare soil column was first leached with distilled water using the rainfall simulator. Initially, the water was applied at a water flux density of 40 mm h^{-1}. Because ponding on the bare soil column occurred at this rate, the rate was dropped to 36 mm h^{-1}. When steady state flow was reached, a bromide
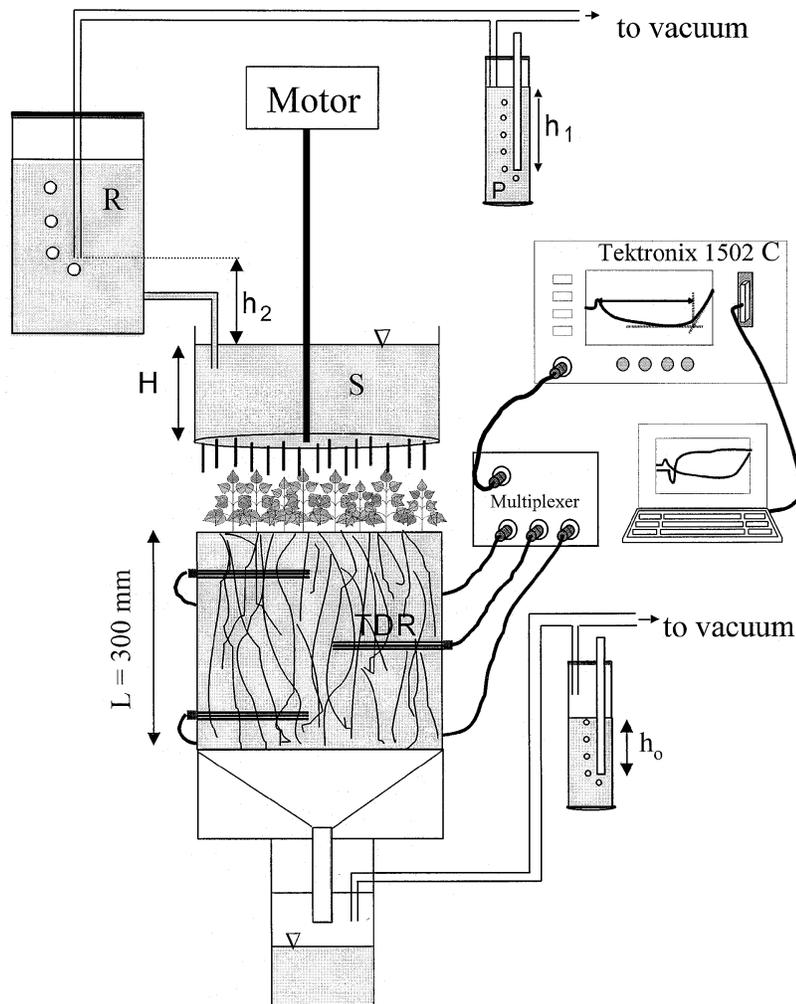
Fig. 1. Experimental setup with sprinkler reservoir (S), pressure head regulator (P), and water reservoir (R). The pressure potential h_1 (= h_2) controls the water head (H) in the sprinkler reservoir and the pressure potential h_0 controls the pressure potential at the base of the soil column.

pulse, again an anion equivalent to 100 kg N ha^{-1}, was sprayed on the soil surface and leached with 4 PV of water. This was followed by a nitrate pulse, again leached under the same steady-state water flow. The effluent samples from both experiments were analyzed for NO_3^- and Br^-.

RESULTS AND DISCUSSION

Effluent Concentrations

The flux concentrations of bromide and nitrate measured in the effluent from the bare soil and the mustard column are shown in Fig. 2 as a function of cumulative infiltration Q (mm). Note that the bromide pulse in the mustard column was applied to a dry soil surface. Also shown are fitted numerical solutions of the water and solute flow equations (Eq. [1] through [7]). Dispersivities ranging from 3 to 9 mm were found (Table 1), giving K_D values ranging from 0.11 to 0.4 L kg^{-1}. This implies R values of 1.2 to 1.5 (Eq. [7]), which are within the 1.4–1.7 range of R values found by Katou et al. (1996) for their andisol from Japan. The effect of plant roots and the initial water content of the soil surface on anion movement and retardation seems negligible.

Time Domain Reflectometry Measurements of Water Content

Figure 3a shows the measured water contents at various depths with time, as measured by TDR during the infiltration of water into the bare soil column. Figure 3b shows the same, but following an application of bromide onto mustard. The early part of the $\theta(t)$ signal of the
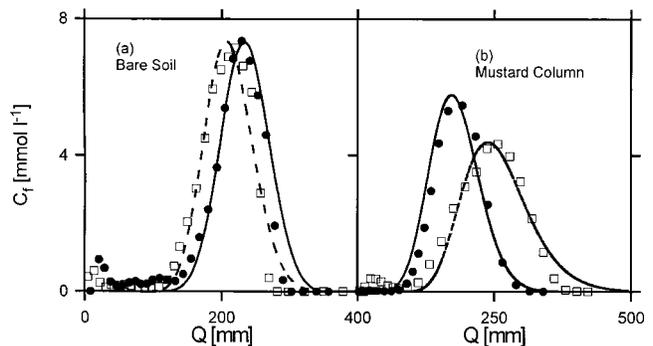

Fig. 2. Measured and predicted (using the CDE model) breakthrough curves of bromide (● and solid line) and nitrate (□ and broken line) for (a) bare soil column and (b) column with mustard. C_f denotes the flux concentration.

Table 1. Column data and model parameters obtained from the convection–dispersion equation†. The hyphen indicates a missing value and the semicolon separates replicates.

q_w	θ	α (mm)		R			ν_f		ν_s^*		MR TDR
		BTC-fitted	TDR-fitted	TDR-peak-peak	TDR-fitted	BTC-fitted	ν_r^*	ν_f	ν_s^*	ν_s	
mm h⁻¹	m³ m⁻³						————— mm h⁻¹ —————				%
Bare soil: bromide pulse on wet soil, steady-state water flow											
36.4	0.663	3	2	1.4	1.3	1.3	91	50	38	55	105
			1		1.4		79	66	38		104
Bare soil: nitrate pulse on wet soil, steady-state water flow											
29.7	0.663	4	3	1.4	1.2	1.2			32	45	116
			1	1.3	1.3				34		131
Mustard: bromide pulse on dry soil, transient water flow											
43.6	0.625	4	–	1.9	–	1.5	181	115	55	105	172
							194	125	–		
Mustard: nitrate pulse on wet soil, steady-state water flow											
44.5	0.625	9	1	1.4	1.7	1.4			52	71	94
			2	2.4	1.6				30		70

† q_w = water flux density, θ = volumetric water content, α = dispersivity, R = retardation factor, ν_r = water front velocity, ν_s = solute front velocity, MR = mass recovery, BTC = breakthrough curve, TDR = time domain reflectometry.

deepest probe was eliminated due to water falling outside the core onto the external connector of the TDR probe. Water front velocity through the soil could thus be calculated from the wet front arrival times at the various depths. For the bare soil we determined velocities ν_f^* of 91 and 79 mm h⁻¹, while under mustard velocities were 181 and 194 mm h⁻¹ (Table 1).

From Eq. [9] we calculated wet front velocities (ν_f) for the bare soil of 65 and 64 mm h⁻¹, based on an initial flow rate i of 40 mm h⁻¹. For the mustard column we calculated water front velocities ν_f of 128 and 135 mm h⁻¹, based on an initial i of 50 mm h⁻¹. The measured and calculated velocities are quite different. This might be due to preferential water flow or nonuniform wetting of the soil, which could have occurred because of water ponding on the soil surface, or a nonuniform water content in the horizontal plane (caused by nonuniform water uptake). This nonuniform wetting can be seen in the

TDR measurements of the water content in Fig. 3b, where there is a slow rise in θ to the final water content. A certain degree of hydrophobicity, which seems to be widespread in this soil, might be the overall cause. The wetting front is thus not moving as a rectangle as prescribed by the Green and Ampt assumption, but rather is affected by the soil structure and texture and plant leaves and roots. This, however, did not affect solute transport as the solute front lags behind the water front due to the initial water content. Furthermore, ponding of water occurred only at the beginning of the experiment, before the solute was applied.

Time Domain Reflectometry and Solute Transport

The TDR-measured electrical conductivity of the bulk soil (σ) following the various pulses of bromide and nitrate is shown in Fig. 4a and 4b. From these peak-
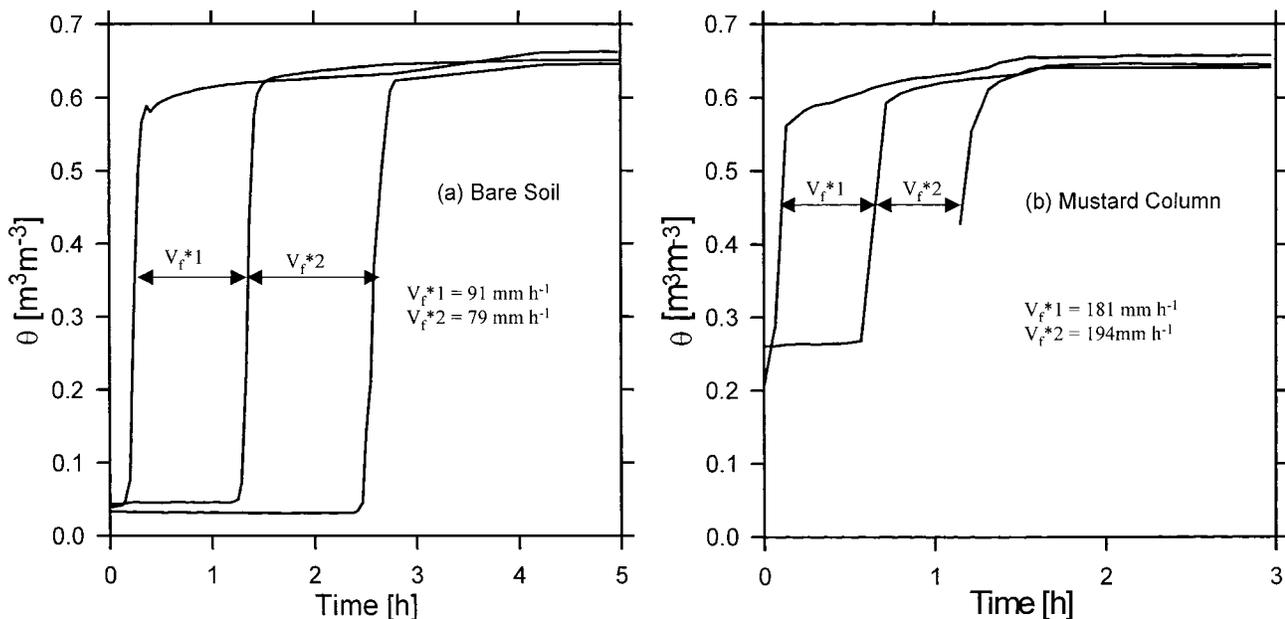

Fig. 3. Time domain reflectometry–measured water content for (a) bare soil column and (b) column with mustard.
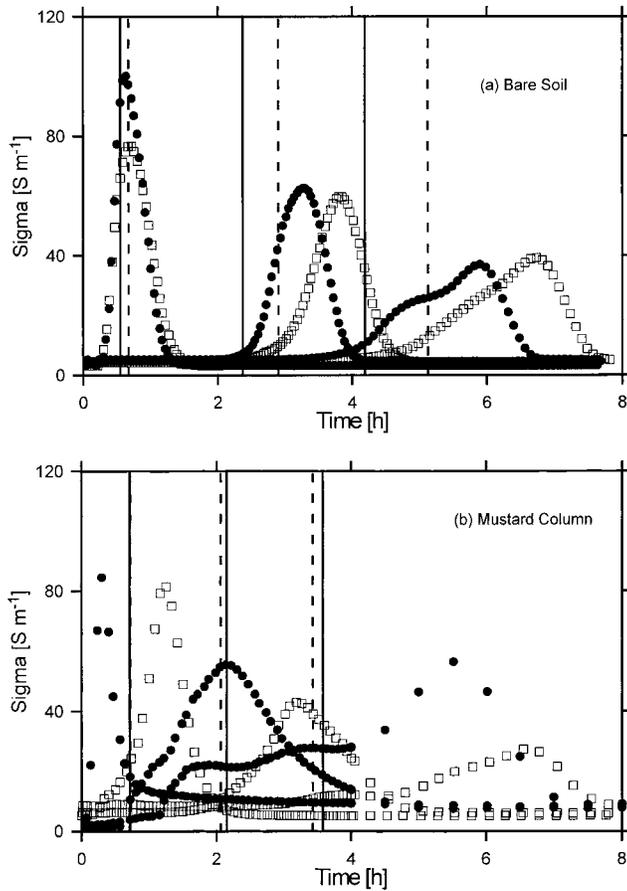
Fig. 4. Time domain reflectometry–measured bulk soil electrical conductivity for (a) bare soil column and (b) column with mustard, following a pulse of bromide (●) and nitrate (□). Also shown are the times for one pore volume for each probe and for bromide (solid lines) and nitrate (broken lines).

Fig. 5. Bromide (●) and nitrate (□) concentrations, obtained from time domain reflectometry–measured bulk soil electrical conductivities for (a) bare soil column and (b) a column with mustard. Also shown are the predictions using the convection–dispersion equation for the upper two TDR probes for bromide (solid line) and nitrate (broken line).

to-peak velocities (v_s^*) were calculated (Table 1). For the transient case only the peaks of the upper two probes could be used, because the lower TDR probe gave inexplicable measurements of σ. This confirms the problem caused by local heterogenities around TDR probes.

Predicted solute velocities (v_s) using Eq. [12] were in all cases higher compared to v_s^*. Because we know that all the soil water is mobile, this disparity suggests an increase in anion adsorption capacity with increasing soil solution concentration that effectively retards the downward movement of bromide and nitrate. R values ranged from 1.3 to 2.4. The highest R value from the peak-to-peak measurements following the nitrate pulse on the mustard column is probably due to a misinterpretation of the unusual third peak. A slight increase in water content measured by the lower two TDR probes might also have caused a delayed increase in σ. Apart from the transient flow case, all other R values are similar to those obtained from the flux concentration in the effluent. Implicit in the use of this TDR approach for obtaining retardation factors during invasion of water into a dry soil is the assumption that the soil behaves like a Green-Ampt soil with a rectangular wetting profile of complete invasion. However, as shown by the $\theta(t)|_z$ measurements (Fig. 3) and discussed above, this
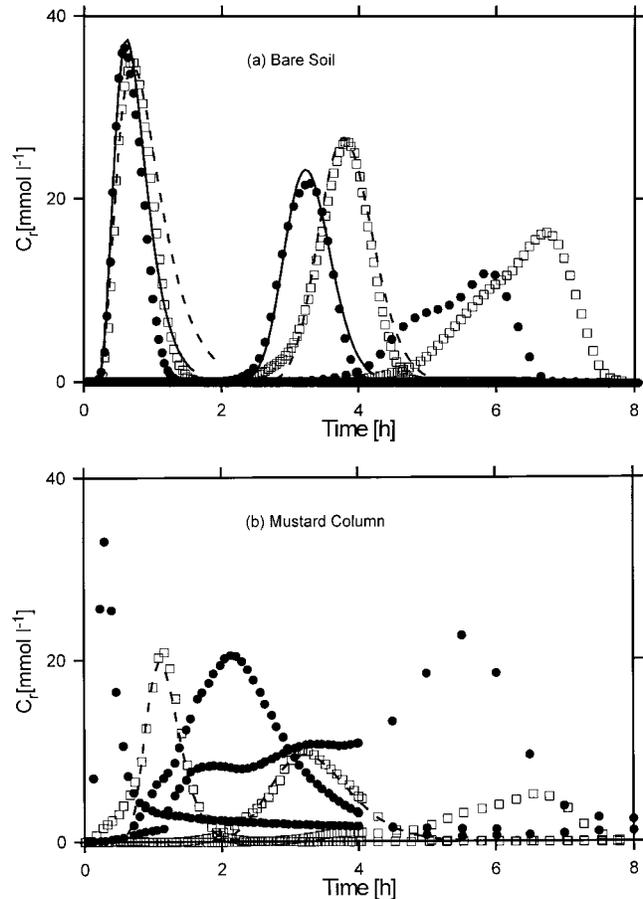
soil does not seem to behave like an ideal Green-Ampt soil. It is worthwhile to explore the impact that nonideal behavior might have on this technique, because in the field such simplicity is unlikely to be encountered.

Time Domain Reflectometry and Modeling of Solute Transport

For modeling solute transport from TDR measurements, the measured bulk soil electrical conductivities (σ) of the upper probe were converted into concentrations using Eq. [16]. The values of a found for each pulse application were then used to convert measured σ values of the other two TDR probes into concentrations.

Mass recoveries for steady-state water flow cases calculated from these concentrations ranged from 94 to 116% for the middle TDR probes and from 70 to 130% for the lower TDR probes. The mass recoveries for the effluent ranged between 97 and 107%. Reasons for the poorer recoveries for the lower TDR probes, as well as the secondary peaks observed in the measurements of σ for the lower TDR probes, are not clear. For the transient flow case, again only the upper two TDR probes were used, but a recovery of 172% for the second

probe was obtained. This is probably again due to non-uniform wetting. If the water content still changes while the solute front passes the TDR probe, the assumption of a unique value of a (Eq. [16]) does not hold. Thus, for modeling purposes, only the two upper probes were used and the measurements for the transient flow case were not used at all.

The converted TDR-measurements are shown in Fig. 5a and 5b. Also shown for the steady-state flow cases are fitted numerical solutions for Eq. 1 through 7. Dispersivities range from 1 to 3 mm and are slightly lower than those obtained from the effluent. Similar observations were made by Hart and Lowery (1998), when TDR was used to measure transport of a bromide tracer. They found that their simulated dispersion, using the LEACHM model, was greater than that measured by TDR. They argued that the low electrolyte concentration in combination with the low moisture content of their sandy soil might have biased the TDR measurements. However, in our study, electrolyte concentrations were high enough for detection by TDR, as evidenced by the relatively good mass recoveries. Retardation factors between 1.2 and 1.7 were found for the steady-state flow cases. These are again similar to those obtained from the effluent, indicating that TDR is a promising tool for obtaining solute transport parameters in situ.

CONCLUSIONS

Our study has demonstrated that TDR is a useful tool for monitoring the transport of not only inert solutes, but also reactive solutes provided that the soil inhibits an increase in anion adsorption capacity with increasing soil solution concentration. A simple theory was used to obtain retardation factors from peak-to-peak measurements of the bulk soil electrical conductivity obtained by TDR. This method was not quite accurate for estimating water front velocities because of nonuniform wetting of the soil. However, it did not affect the TDR-estimated solute transport parameters, which were comparable to those obtained from breakthrough curves and by directly fitting the TDR measurements to the CDE. This means that the proposed TDR method should be a simple and nondestructive way for determining solute transport parameters of not only conservative, but also reactive chemicals such as nitrate in variably charged soils.

The TDR technique for obtaining retardation factors was demonstrated under controlled conditions in the laboratory and should now be tested on undisturbed soil columns. If immobile water fractions need to be taken into account, as is common in the field, then it may also be necessary to take an independent measure of the resident concentration.

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