Scientific registration number : 138
Symposium n^{o} : 8
Presentation : oral

Modelling of reactive chemical transport through soil
Modélisation du transport de solutés réactifs à travers le sol

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To asses the ability of Time Domain Reflectometry for determation of solute transport parameters, unsaturated leaching experiments were carried out in the laboratory on two soil columns packed with Maréan soil, a ferrasol with variable surface charge. One of the 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 with a rainfall simulator at intensities of between 30 to 45 mm h^{-1}. Water and solute transport were monitored by collecting the effluent, and *in situ* by Time Domain Reflectometry. Transport parameters of the convection dispersion equation, with a linear adsorption isotherm, were obtained from the flux concentrations and used to predict the resident concentrations at several depth in the soil column, as measured by TDR. Anion retardations of between 1.2 to 1.5, and dispersivities between 3 to 9 mm were found. Retardations were also calculated using a simple approach based on water and solute front velocities. These used TDR measurements of the soil water content and bulk soil electrical conductivity with time. The agreement suggests TDR to be a valuable technique for obtaining *in situ* the transport parameters for reactive solutes.

Keywords : Time Domain Reflectometry, Retardation factors
Mots clés : Oxisol, échange d'anions, réfléctométrie, TDR, concentration des flux

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Introduction

Convection-dispersion models for simulating contaminant transport through the unsaturated zone are a key component for developing efficient and sustainable strategies of fertiliser application, and for environmental protection. These convection-dispersion models (CDE) however require quantification of various parameters, such as the dispersion coefficient and the retardation of reactive solutes. These parameter are generally obtained from column leaching experiments, often in the laboratory, using breakthrough curves (BTC's) of the flux concentration. This technique is, however, laborious, and cannot be used for *in situ* measurements in the field.

Time Domain Reflectometry has been widely used to monitor both the transport of water and nonreactive solutes under steady-state water flow in the laboratory, as well as in the field (Vanclooster *et al*., 1993; Kachanoski *et al*., 1992). Likewise, by monitoring the change in water content (q) and bulk soil electrical conductivity (s_s), following a pulse application of solute leached into either a wet, or a dry soil, it should also be possible to infer the retardation of a reactive solute from TDR measurements. This retardation should allow inference of the exchange characteristics.

We present some measurements of bromide and nitrate movement through a ferrasol with variable surface charge, which adsorbs anions. Transport through a bare soil column, and a column growing mustard, was studied. Chemical transport was measured both by collecting the effluent at the base of the column, and also by monitoring the change in water content and electrical conductivity by TDR probes installed at various depth within the soil column. These measurements are modelled using the CDE, in which soil water transport is predicted using Richards' equation. Chemical transport parameters obtained *in situ* from TDR are compared to those obtained from the flux concentration in the effluent. Although the TDR technique for obtaining transport parameters is here used under controlled conditions on repacked soil columns in the laboratory, the approach should also be suitable for *in situ* measurements in the field.

Also investigated is the impact of plant roots and the soil's initial water content on the leaching of surface applied fertilisers under tropical rainfall intensities. However, these issues are discussed in the accompanying paper (Duwig *et al.*, 1998).

Theory

Water and Solute Transport

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

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[D_{\mathrm{w}}(\theta) \frac{\partial \theta}{\partial z} \right] - \frac{\partial K_{\mathrm{w}}(\theta)}{\partial z} , \qquad [1]$$

where θ is the volumetric water content [$m^3\ m^{-3}$], D_{w} is the soil water diffusivity [$m^2\ s^{-1}$], K_{w} is the hydraulic conductivity function [$m\ s^{-1}$], q_{w} is the water flux density [$m\ s^{-1}$], t is the time [s], and z is the depth [m]. The diffusivity function is here assumed to be exponential (Brutsaert, 1979), and for the conductivity function a power-law function is used (Quadri *et al.*, 1994). The relevant initial and boundary conditions for unsaturated flow into a soil column under steady rainfall are

$$\begin{array}{lll} \theta = \theta_{\mathrm{i}}(z) & t = 0 & 0 \le z \le l \\ q_{\mathrm{w}} = q_{\mathrm{o}} & z = 0;\, t > 0 & \end{array} , \qquad [2]$$

where θ_{i} is the initial water content [$m^3\ m^{-3}$], l is the column length [m], and q_{o} 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,

$$\frac{\partial(\theta C_{\mathrm{r}})}{\partial t} + \frac{\partial(\rho S_{\mathrm{A}})}{\partial t} = \frac{\partial}{\partial z}\left(\theta D_{\mathrm{s}} \frac{\partial C_{\mathrm{r}}}{\partial z} \right) - \frac{\partial(q_{\mathrm{w}} C_{\mathrm{r}})}{\partial z} \qquad [3]$$

where C_{r} is the solute concentration in the resident soil solution [$mol\ m^{-3}$], S_{A} is the amount of solute adsorbed [$mol\ kg^{-1}$], and D_{s} is the diffusion-dispersion coefficient [$m^2\ s^{-1}$], which we assume to be given by

$$D_{\mathrm{s}} = \alpha v + \tau D_m \qquad [4]$$

where α is the dispersivity [m], v is the average pore water velocity of q_{w}/θ, τ is the tortuosity factor, and D_{m} is the molecular diffusion coefficient in a free solution.

For simplicity adsorption of anions by the soil is often described using a linear isotherm, $S_{\mathrm{A}} = K_{\mathrm{D}} C_{\mathrm{r}}$. The effect of anion adsorption is then to retard the solute front by the factor R defined as, $R = 1 + \dfrac{\rho K_{\mathrm{D}}}{\theta}$ [5]

where ρ is the bulk density [$kg\ m^{-3}$], and K_{D} is the distribution coefficient [$L\ kg^{-1}$].

Equations [1] through [5] were solved numerically using Newton-Raphson iteration for the water flow equation and for the solute flow a Crank-Nicholson scheme. Hydraulic properties were found from one-dimensional, free water adsorption horizontal experiments, using sectionable columns (Duwig *et al*., 1998). The values found were the saturated conductivity K_s = 1.56 x 10^{-2} mm s^{-1}, the slope of the $D_w(\theta)$ function β = 12, the sorptivity S = 2.4 mm $s^{-1/2}$, and the saturated water content θ_s = 0.69 m^3 m^{-3}.

Time Domain Reflectometry

For a Green-Ampt soil, that is a soil that possesses a Dirac-δ diffusivity, water enters the soil as a rectangular wet front and rides atop of the antecedent water content θ_i, such that the wet front x_f at any time can be found at (Clothier, 1997),

$$x_f = \frac{I}{(\theta_o - \theta_i)} \qquad [6]$$

where I is the cumulative amount of water infiltrated [m], and θ_o is the final water content [m^3 m^{-3}]. The velocity of the wet front v_f is therefore given by

$$v_f = \frac{\partial x_f}{\partial t} = \frac{i}{\left(\theta_o - \theta_i\right)} \qquad [7]$$

where i is the infiltration rate [m h^{-1}]. By monitoring $\theta(t)\big|_x$ with TDR-probes installed horizontally at sequential depths it should be possible to measure v_f.

Assuming that all the water is mobile, and that solute dispersion and diffusion can be ignored, the solute front considering complete invasion of the wetted pore space will be at depth, $s_f = \frac{I}{\theta_o}$ [8]

and the solute velocity by, $v_s = \frac{\partial x_s}{\partial t} = \frac{i}{\theta_o}$. [9]

TDR in electolytic tracer mode, should allow measurement of v_s. It follows that,

$$v_s = v_f \frac{(\theta_o - \theta_i)}{\theta_o} \qquad [10]$$

Under steady-state water flow the solute invasion equation simplifies to,

$$v_s = \frac{i}{\theta_o}. \qquad [11]$$

The solute velocity can simply be inferred from peak-to-peak measurements of $\sigma_s(t)\big|_x$ using TDR. If this measured solute velocity v_s^* is smaller then the v_s calculated using Eq. [10] or [11], anion adsorption must have occured. The retardation (Eq.[6])

will simply be given by v_s / v_s^*. For an excluded anion, the measured solute velocity will likewise be greater than the predicted one.

This simple approach of obtaining the retardations and anion exchange will here be tested under controlled conditions on repacked soils in the laboratory. The approach will be compared to results obtained from BTC's.

Methods and materials

Details of the experiments are given in Duwig *et al.* (1998). Briefly, column leaching experiments were carried out on repacked soil columns of Maréan soil, a ferrasol with variable charge. Two soil columns were used, with a diameter of 300 mm and one of length of 280 mm, the other 300 mm. One had a bare soil surface, the other growing mustard. Pulses of $CaBr_2$ and $Ca(NO_3)_2$, equivalent to a nitrogen-nitrate application of 100 kg ha^{-1} were sprayed onto either a dry or a wet soil surface, and then leached with distilled water using a rainfall simulator (Vogeler *et al.*, 1997). To mimic tropical rainfall intensities, water flux densities of between 36 and 45 mm h^{-1} were used. TDR probes of 150 mm length were installed at depth of 30, 130 and 230 mm into the bare soil column, and at 50, 150 and 250 mm into the mustard column. These TDR probes and the effluent collected at the base of the column were used to monitor water and solute transport.

Results

The flux concentrations of bromide and nitrate measured in the effluent from the bare soil, and the mustard column, are shown in Figs. 1a and b. Note that the bromide pulse in the mustard column was applied to a dry soil surface. Also shown are the best-fit numerical solutions of the CDE (Eq.1-5). Dispersivities ranging from 3 to 9 mm, and K_D values ranging from 0.11 to 0.4 L kg^{-1}were found (Table 1). This implies R values of 1.2 to 1.5. Neither the initial water content, nor the presence of the mustard, seemed to have a significant impact on solute transport under these high rainfall intensities.

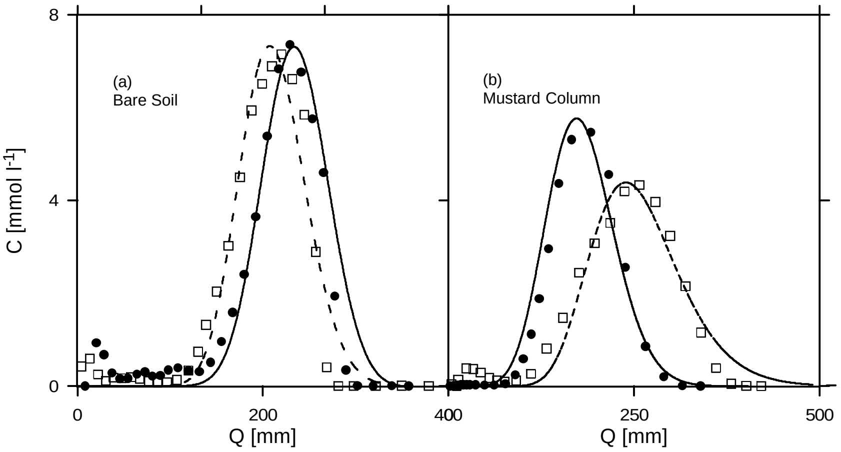

Fig. 1. Measured and predicted BTC's of bromide (● and solid line) and nitrate (□ and broken line).

Table 1. Column data and model parameters obtained from the CDE. The hyphen indicates a missing value, and the semicolon seperates replicates.

q_w [mm h^{-1}]	θ [m^3 m^{-3}]	α [mm]		R		K_D [L kg^{-1}]	
		BTC	TDR	BTC	TDR	BTC	TDR
Bare soil, Bromide pulse onto wet soil							
36.4	0.663	3	2; 1	1.3	1.4	0.21	0.32
Bare soil, Nitrate pulse onto wet soil							
29.7	0.663	4	3; 1	1.2	1.4; 1.3	0.11	0.32; 0.24
Mustard, Bromide pulse onto dry soil							
43.6	0.625	4	-	1.5	1.9	0.39	0.70
Mustard, Nitrate pulse onto wet soil							
44.5	0.625	9	1; 2	1.4	1.4	0.29	0.29

Fig. 2 shows, for the bare soil column, the bromide concentrations, calculated from the TDR-measured bulk soil electrical conductivity at depths of 30, 130 and 230 mm. Also shown are the predictions from the CDE using the values for a and *R* obtained from the effluent (solid lines). The model predicts almost the same peak arrival time as measured by TDR. For the two upper TDR probes the model predicts a more dispersed peak. The TDR measurements of the upper two probes were also fitted to the CDE (broken lines). Dispersivities of 1 and 2 mm were found, which are similar to the value found from the BTC. The values found for the other experiments are given in Table, and range from 1 to 3 mm. Although the CDE with independently obtained parameters (from the effluent) predicts more dispersed peaks than measured by TDR, direct fitting of the TDR-measured s_s results in similar values for the dispersivity. The reasons for the secondary peaks in the TDR measurements of s_s for the lower TDR probe are not clear, and show the problems, which sometimes occur with TDR.

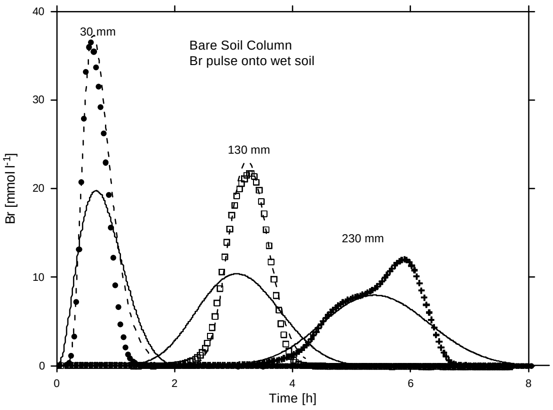

Fig.2 TDR-measured and predicted Br concentrations

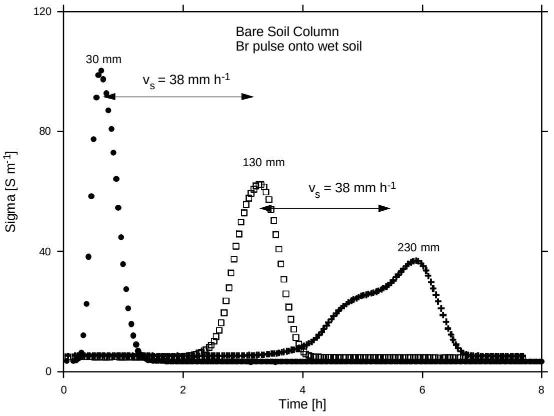

Fig. 3 TDR measured bulk-soil EC

The TDR-measured electrical conductivity of the bulk soil following a pulse of bromide under steady state water flow is shown in Fig. 3. Calculated peak-to-peak velocities were 38 mm h^{-1}, whereas a velocity of 55 mm h^{-1} was predicted using Eq. [11]. This suggests an *R* value of 1.4. The *R* values found for the other experiments under steady-state flow are given in Table 1, and these are between 1.3 and 1.4. In all cases the values are similar to those obtained from the effluent (Table 1).

For the transient flow cases, Fig 4a and b show the measured water contents and bulk soil electrical conductivities as measured by TDR following an application of bromide onto mustard. Using Eq.[7] wet front velocities of 181 and 194 mm h^{-1} are obtained from the position of the 3 wet fronts. For the calculation of the solute velocity only the peaks of the upper two TDR probes could be used, as the lower TDR probe gave inexplicable measurements of s_s. The peak-to-peak velocity is 55 mm h^{-1}, whereas the prediction using Eq [11] gives a v_s of 105 mm h^{-1} resulting in an *R* of 1.9. This *R* value obtained from TDR measurements is quite different to the value of 1.5 obtained from 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 retangular wetting profile. However, as shown by the $q(t)|_x$ measurements, and discussed in the accompanying paper (Duwig *et al*., 1998), this soil does not seem to behave like an ideal Green-Ampt soil.

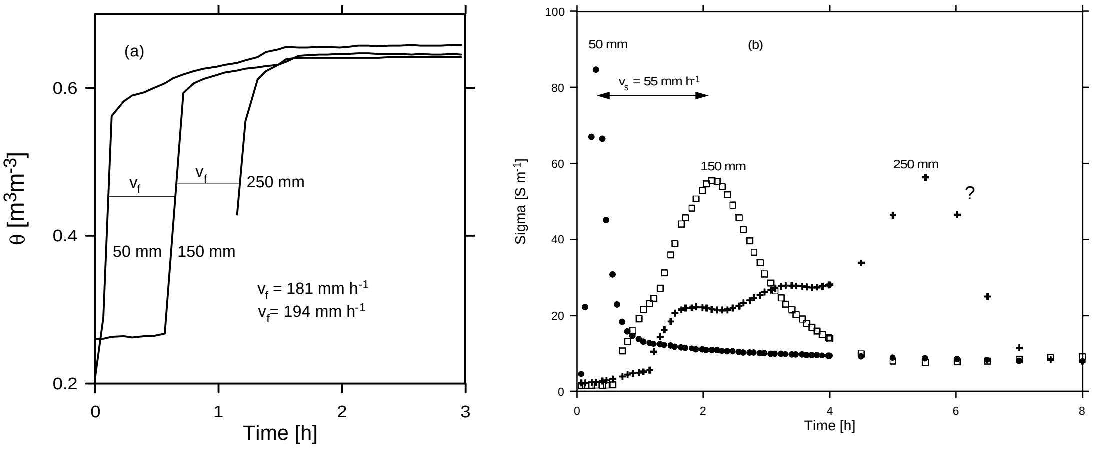

Fig. 5 (a) TDR measured water content and (b) bulk soil electrical conductivity.

Conclusions

Our study has demonstrated that TDR is a useful tool for monitoring the transport of not only inert solutes, but also reactive solutes, such as anions in variable-charge soils. A simple theory was used to obtain retardation factors from peak-to-peak measurements of the bulk soil electrical conductivity obtained by TDR. The values were similar to the values obtained from the effluent. The dispersivities obtained from TDR measurements at various depth within the soil column were also similar to those obtained from the BTC's.

Although the TDR technique for obtaining retardation factors was here demonstrated under controlled conditions in the laboratory, the approach should also be suitable for *in situ* observations in the field.

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