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Measurement of Reactive Chemical Transport through Soil

Mesure du transport de solutés réactifs à travers le sol

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Maré is an uplifted coral atoll with a variably-charged soil that is a Geric Ferralsol derived from weathered volcanic ejecta and ash. This soil is very permeable, and even though it is a soil with a degree on anion exchange, the intensity of tropical rainfall can induce leaching of nitrate. This poses a threat to the underlying fresh water lenses. Here we describe experiments that detail the mechanisms of nitrate transport in this ferralsol. One soil column growing mustard allowed us to study the impact of roots on the velocity of water and solute transport. The results show that despite a high initial nitrate concentration, and a nitrate exchange capacity with K_D†=†0.1 to 0.2 L kg^{-1}, it only takes 2 tropical storms of 200 mm, to push nitrate completely beyond the rooting depth of 300†mm. This mobility stresses the need to apply fertilizers frequently in small amounts, to maximise the opportunity for root uptake and to minimize the risk of nitrate leaching.

Keywords : Geric Ferralsol, anion transport, nitrate, groundwater
Mots clés : Geric Farrasol, transport d’anions, nitrates, nappe phréatique

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Introduction

As with developing countries, the islands of the South Pacific must increase their agriculture production. The use of fertilizers is often the first means to achieve this improvement.

The Loyalty Islands (New Caledonia), and especially MarÈ, are not spared this imperative because of demographic and economic pressures. MarÈ is an uplifted coral atoll with a Geric Ferralsol derived from volcanic ejecta and ash. The soil is very permeable with a saturated hydraulic conductivity in excess of 100 mm h^{-1}, and a very shallow soil less than 1 m deep, which sits atop a coral rock. At 50 to 100 meters deep, fresh water lenses inside this fractured coral rock float on the underlying salt water. The climate of MarÈ is characterized by a wetter season early in the year, during which frequent tropical storms of high intensity can occur. This description draws a picture of a very fragile ecosystem, where the major risk of using fertilizers is the pollution of those lenses that constitute the sole source of drinking water. A field study has confirmed the possibility of high nitrate leaching (Duwig *et al.*, 1997).

To achieve better understanding of the detailed mechanisms of solute transport in the rootzone, we carried out experiments with MarÈan soil with different devices such as sectionable columns, and soil cores instrumented with Time Domain Reflectometry (TDR). This allowed us to monitor, within the column, the passage of nitrate and bromide, as well as to carry out an analysis of the effluent at the base. These characterisation procedures also allow parametrisation of transport models for water and nitrate transport which include the solute exchange capacity of the soil.

Theory

For one-dimensional, transient and unsaturated inbibition into a horizontal soil column, the equation appropriate for the water flow is (Clothier *et al.*, 1988) :

$$\frac{\partial\theta}{\partial t}=\frac{\partial}{\partial x}\left[D(\theta)\frac{\partial\theta}{\partial x}\right], \qquad [1]$$

where x is the horizontal distance (m), θ the water content (m^3 m^{-3}) and t the time (s). We assume the soil water diffusivity function $D(\theta)$ (m^2 s^{-1}) to be of an exponential form (Brutsaert, 1979) :

$$D(\theta)=\frac{\gamma S^2}{(\theta_s-\theta_n)^2}\exp\left[\frac{\beta(\theta-\theta_n)}{\theta_s-\theta_n}\right] , \qquad [2]$$

where γ and β are interdependent constants, θ_n and θ_s the antecedent and saturated water content respectively, and S (m $s^{-1/2}$), the sorptivity, given by (Philip, 1969)†:

$$S=\int_{\theta_n}^{\theta_s}\frac{x}{t^{1/2}}d\theta . \qquad [3]$$

The convection-dispersion equation, for a reactive solute transport into a horizontal column, with an uniform water content, is given by :

$$\frac{\partial c}{\partial t}=\alpha'\frac{\partial}{\partial x}\left(\frac{\nu\partial c}{\partial x}\right)-\nu'\frac{\partial c}{\partial x}, \qquad [4]$$

where $\alpha' = \alpha/R$ and $\nu' = \nu/R$, with ν the pore-water velocity (m s^{-1}), α the dispersivity (m), and c the solute concentration (M L^{-1}). Solute exchange has been linearised so that the retardation factor R applies to a linear isotherm: $R = 1+(\rho K_D/\theta)$, where K_D is the distribution coefficient (L kg^{-1}) and ρ the bulk density (kg m^{-3}).

By using the Boltzman variable, $\lambda(\theta) = x(\theta)/t^{1/2}$, Watson and Jones (1981) found an approximate expression for the normalised concentration C after a step input of solution†:

$$C=\frac{1}{2}\operatorname{erfc}\left[\frac{(\lambda-\lambda')t^{1/4}}{2(\alpha'\lambda')^{1/2}}\right]. \qquad [5]$$

By considering complete displacement of the antecedent solution by the invading solute (Smiles and Philip, 1978), it is possible to locate the centroid, λ^*, of the front of invading water as : $\int_{\theta_n}^{\theta_s}\lambda\, d\theta=\int_0^{\lambda^*}\theta d\lambda$, [6]

The relative position of the centroid of the reactive solute front is given by (Clothier *et al.*, 1988) : $\lambda' = \lambda^*/R$. [7]

The theory used for the vertical soil column experiments is fully described in Vogeler *et al.* (1998).

Materials and methods

Experiments were carried out with Geric Ferralsols from MarÈ (Loyalty Islands, New Caledonia), using only material from the first 20 cm that was collected in a cultivated area which was relatively rich in organic matter. Table 1 presents relevant chemical characteristics of this top layer.

Table 1 : Selected properties of the top layer

pH H_2O	organic matter (g kg^{-1})		Exchangeable bases (cmol kg^{-1})				CEC	Total elements (%)		
	C	N	Ca	Mg	Na	K	pH 7	SiO_2	Fe_2O_3	Al_2O_3
6.6	78.6	6.1	16.0	11.6	0.3	0.7	33.1	1.1	21.1	37.6

The texture is very fine as particles smaller than 20 µm represent 70 to 80 %. However, this ìclay and fine siltî fraction consists mainly of aluminium and iron oxides. This mineralogical composition implies specific characteristics such as small nutrient reserves (except in phosporus), a fragile structure, and a high permeability.

The soil was first air dried, and then sieved to obtain homogeneous material. Two sets of experiments were carried out with this soil :

(1) Horizontal ìPerroux tubeî experiments

Soil, moistened with distilled water, was packed to a bulk density of 0.84 (±0.005) Mg†m^{-3} in sectionable acrylic columns of 20 mm of internal diameter, so called Perroux tubes (Smiles and Philip, 1978). One dimensional, horizontal, free-water adsorption experiments were carried out using only water, or a solution of either NO_3^- (0.025*M*), or Br^-(0.025 and 0.1*M*). The invading solution was supplied from a Marriotte bottle to the proximal end of the column. After terminating each invading experiment, the Perroux tube was rapidly sectioned and the samples weight and oven dried for determination of the water content, except for those with nitrate. The wet front position, and the water level in the reservoir were recorded frequently, to obtain the sorptivity, the water diffusivity function (Eq. [2]) and the solute retardation.

(2) Vertical soil column experiments

Air-dried, sieved soil was packed into a core, with both diameter and length of 300 mm, to a mean bulk density of 0.8 Mg m^{-3}. Mustard was sown, and fertilizers were added for nutrient supply of the plants. After 3 weeks, the roots had invaded the entire column length. The mustard was then allowed to dry down the soil over several days, to a water content of 0.25 m^3 m^{-3}. The core was then placed on an inverted tension infiltrometer, to ensure unsaturated flow at the base, yet allow regular sampling of the effluent. By then, the mustard had grown to a height of 300 mm. Three-wire TDR probes were inserted horizontally at depths of 50, 150 and 250 mm and these were monitored regularly for both the soilís water content q (m^3 m^{-3}), as well as its bulk soil electrical conductivity σ (S m^{-1}).

A concentrated pulse of $CaBr_2$, equivalent to a nitrogen-nitrate application rate of 100 kg ha^{-1} (47 mM), was sprayed onto the soil surface. The solute pulse was leached with 4 pore volumes of distilled water, using a rainfall simulator with a flow rate of 46 mm h^{-1}. Then, another concentrated pulse, but $Ca(NO_3)_2$ at the same concentration, was sprayed onto the soil surface while the steady-state rainfall was maintained. The effluent samples were analysed for NO_3^- and Br^-.

After this experiment, the soil was air-dried (q_n = 0.1) and sieved before packing into another soil column of length 280 mm. However, this column was kept bare. The TDR probes were installed at 30, 130 and 230 mm depths. On this column, a rainfall intensity of q_w = 30 mm h^{-1} was applied. When a steady-state flow was reached, a bromide pulse of again 100 kg ha^{-1} was sprayed and then leached with 4 pore volumes. A nitrate pulse was again applied under steady-state flow and leached with another 4 pore volumes. The two chemical tracers were hence sprayed here under the same conditions of q and q_w.

These two experiments allowed to assess the effect of initial water content and the impact of plants and their roots on anion transport through the unsaturated rootzone.

Results

ìPerroux tubeî experiments

The water content, and normalised concentration profiles of Br^- and NO_3^- are shown in Fig. 1. Values for the inter-dependent constants of the water diffusivity were found by comparing simulations, using a numerical model, to the measured q(l) profile. We found values of b = 12 and g = 3.57 x 10^{-5}. The sorptivity calculated from Eq. [3] was 2.4 (± 0.15) mm $s^{-1/2}$.

The centroid of the front of invading water l * (Eq. [6]) was found to be at 3.67 (± 0.19) mm $s^{-1/2}$. The comparison between the convected front and the C(l) profiles shows that there is adsorption of both bromide and nitrate. The retardation given by Eq. [7] is 1.1 for bromide and 1.15 for nitrate, or the K_D is 0.12 and 0.18 L kg^{-1} respectively.

In Eq. [5], a dispersivity value of a = 1.5 mm gave a satisfactory reproduction of the shape of the C(l) profiles. This value is reasonable considering the really fine structure of MarÈan soil. Clothier *et al.* (1988) found that a = 2 mm is appropriate for inert tracers in fine, repacked soil.

Bromide and nitrate are weakly adsorbed in this ferralsol, with a K_D of 0.12 and 0.18 L†kg^{-1} respectively. The high levels of well crystallized, poorly ordered Al and Fe oxides in this soil (Dubus *et al.*, 1998) can explain this adsorption. Kinjo and Pratt (1971) also found nitrate adsorption on oxisols, that seems to be related to the amount of amorphous inorganic materials present. Katou *et al.* (1996) found nitrate affinity in their Japanese andisol containing allophane and other poorly crystalline materials, with retardations of around 1.4-1.7.

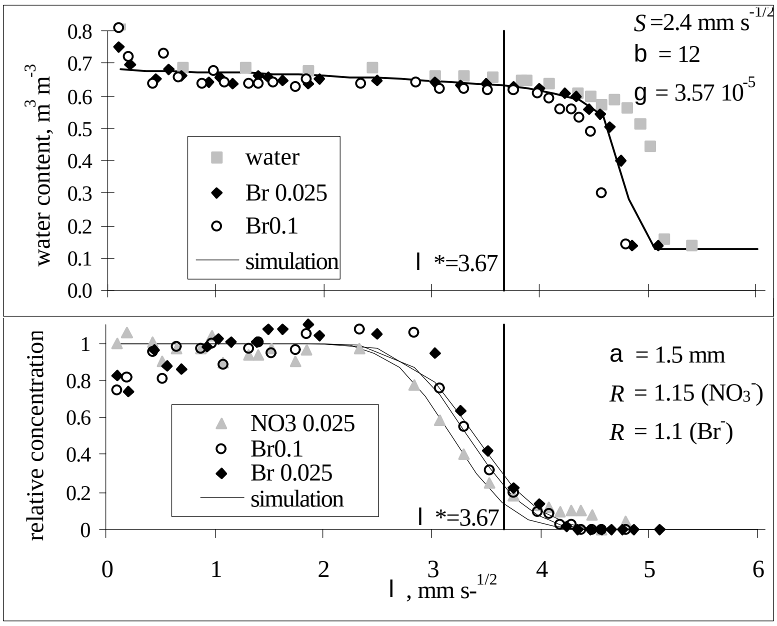

Figure 1: Water content and normalised concentration profiles, along with the plane of separation l^*.

Soil column experiments

For the soil column experiment under mustard, a maximum rainfall intensity of only 46 mm†h^{-1} could be applied, although in the field the saturated hydraulic conductivity is higher than 100 mm†h^{-1}. Sieving and packing the soil has highly changed the porosity of this weakly structured soil. Under bare soil, we even had to decrease the flow rate down to 30 mm h^{-1}. A light crust at the soilís surface probably developed due to the impact of heavy rainís drops.

The water content was recorded with TDR probes on both the mustard and the bare soil columns (Fig. 2). The water front velocity through the soil could thus be calculated from the wet front arrival times at the various depths. Under mustard, the velocities are 181 and 194 mm h^{-1} between the sets of probes, and under bare soil 91 and 79 mm h^{-1}.

If we assume that the soil behaves like a Green and Ampt soil (KutÌlek and Nielsen, 1994), the water front velocity can also be calculated using $v_f = i/(q_o - q_i)$, where i is the rainfall rate (mm h^{-1}), q_i and q_o are the initial and final water content. This analysis gives velocities of 115 to 125 mm h^{-1} under mustard and 50 to 66 mm h^{-1} under bare soil. These two ranges were calculated considering that the flow rate was decreased after the beginning of the experiment from 50 to 46 mm h^{-1} on mustard and from 40 to 30 mm h^{-1} on bare soil. Irrespective of the Green and Ampt assumption, the measured and calculated water velocities are quite different and might be due to preferential flow which seems to be even more pronounced under mustard. The more unusual shape of $q(t)$ under mustard also confirms this (Fig. 2a). The incident rainfall thus appears to have been focussed by the umbrella-like presence of the mustard leaves, which led to the creation of preferential flow paths in the soil. The wetting front is thus not moving like a piston as might be assumed for a Green and Ampt soil, but rather it is disturbed by the leaves, the roots, and their interaction with the soilís structure.

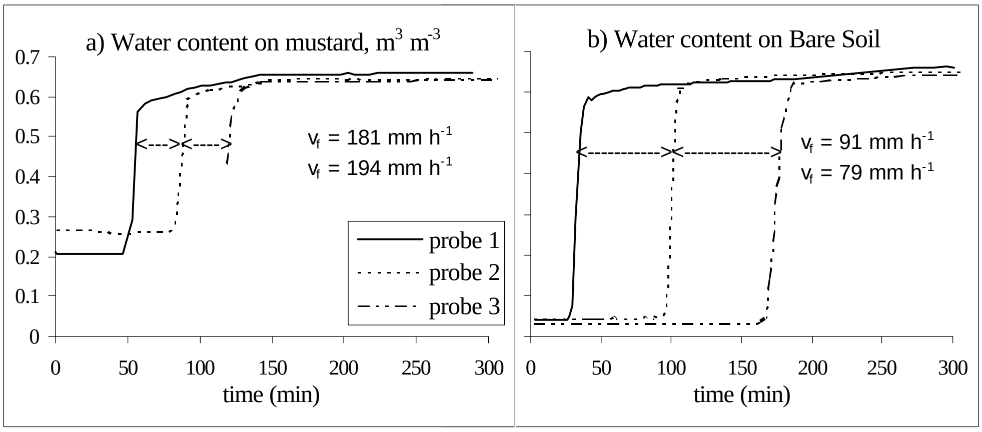

Figure 2 : Water content vs. time for the mustard and bare soil column experiment

Fig. 3 shows the bulk soil electrical conductivity measured by TDR for nitrate leaching under both mustard and bare soil, as well as the N-NO_3 concentration in the effluent at the bottom of the soil column. The same data are available for bromide (Vogeler *et al.*, 1998) but not presented here. Some noteworthy points are discussed.

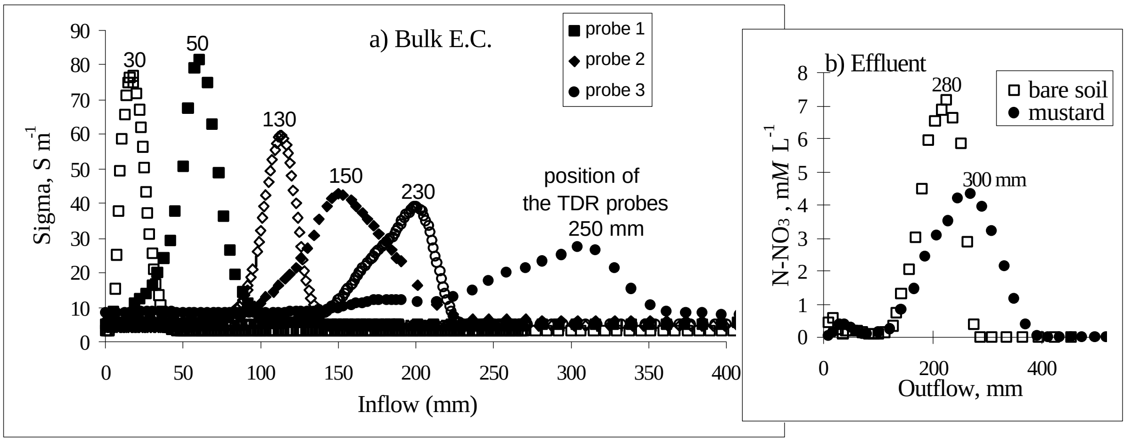

Figure 3 : Bulk conductivity (a) and nitrate concentration measured in the effluent (b) both for mustard (solid symbols) and bare soil (open symbols).

One pore-volume (200 mm) was enough to leach through the maximum concentration of nitrate, and after 2 pore volumes, all the applied nitrate had leached beyond a depth of 300 mm. The peaks are more dispersed under mustard than under bare soil. Therefore the plants and root system seem to increase the dispersion of the solute peak, an interaction that was also found for the vector of the passage of water through the soil. The retardation calculated from the TDR and effluents data are detailed and discussed in Vogeler *et al.* (1998).

Conclusion

The experiments with the ìPerroux tubeî allowed us to determine hydraulic and chemical transport characteristics for use in modelling leaching experiments on soil columns. Anion adsorption for both bromide and nitrate was found, in this ferralsol, to be described by adsorption coefficients of 0.1 to 0.2 L kg^{-1}. Despite this soil having an affinity of nitrate, the high rainfall rates which are common in this tropical climate, coupled with the soilís high permeability, mean that nitrate is quite mobile. The soil column experiments showed that one rainfall of 200 mm, which can happen in a single day in MarÈ, is enough to leach most of the applied nitrate out of the rootzone. Furthermore, when a crop is growing, the roots create preferential flow pathways to solute. Thereby, it increases the soilís dispersivity and the water and solute velocities. To miminise risks of nitrate leaching towards the underlying water lenses, it is necessary to apply fertilizers in split applications.

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