

A simple dynamic method to estimate anion retention in an unsaturated soil

Une méthode dynamique simple pour estimer la rétention anionique dans un sol non saturé

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(Received 30 March 1999, accepted 26 April 1999)

Abstract — The anions Br^- and NO_3^- are commonly adsorbed non-specifically by the highly weathered soils found in tropical regions. We used a simple dynamic technique to determine their retention, using the so-called "Perroux tube", and we compared these results with those obtained from leaching experiments. The method was tested on a ferrallitic soil from New Caledonia which is rich in aluminium and iron oxides. From the resident concentrations observed, we obtained retardation values of 1.1 and 1.15 for bromide and nitrate respectively, using respective input concentrations of 0.025 and 0.1 M. A numerical model using these results predicted the flux concentrations obtained from the leaching experiments quite well, thereby proving the utility of this simple technique. (© Académie des sciences / Elsevier, Paris.)

nitrate retention / Perroux tube / ferrallitic soil

Résumé — Les anions NO_3^- et Br^- sont généralement adsorbés non-spécifiquement par les sols très évolués des régions tropicales. Nous avons utilisé une technique simple, appelée « tube de Perroux », pour déterminer leur rétention et comparer les résultats à ceux obtenus à partir d'expériences de lixiviation. Cette méthode a été testée sur un sol ferrallitique de Nouvelle-Calédonie, riche en oxydes de fer et d'aluminium. À partir des concentrations résidentes observées, nous avons obtenu un retard de 1,1 et 1,15 pour le bromure et le nitrate respectivement, en utilisant des concentrations incidentes respectives de 0,025 et 0,1 M. Un modèle numérique utilisant ces résultats prédit assez bien les concentrations de flux obtenues à partir des expériences de lixiviation, montrant la validité et l'intérêt de cette technique simple. (© Académie des sciences / Elsevier, Paris.)

rétention du nitrate / tube de Perroux / sol ferrallitique

Version abrégée (voir p. 762)

Note communicated by Ghislain de Marsily.

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C. R. Acad. Sci. Paris, Sciences de la terre et des planètes / Earth & Planetary Sciences
1999. 328, 759-764

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1. Introduction

Improved knowledge of the transport mechanisms operating in the soil is essential to develop sustainable strategies for better management of the environment and to prevent chemical contamination of the underlying groundwater. Solute transport is strongly affected by sorption mechanisms between the soil solution and the soil matrix. These mechanisms have to be taken into account to predict the fate of anions such as nitrate.

Often anion retardation is not taken into account. However, the highly weathered soils of tropical regions often exhibit a substantial anionic exchange capacity (AEC). Retardation of non-specifically adsorbed anions such as NO_3^- , Cl^- and Br^- by these soils is well known: Kinjo and Pratt (1971), Wong et al. (1990), Bellini et al. (1996), Katou et al. (1996).

These studies used either batch experiments (Kinjo and Pratt, 1971) which are known to overestimate the exchange because of the breakdown of soil aggregates (Wong et al., 1990), or column leaching experiments (Bellini et al., 1996) which are laborious to conduct. We present here a simple methodology using horizontal, sectionable columns, to measure some of the parameters that characterize anion transport during an unsteady flow in an unsaturated soil. Some authors have already used this resident concentration technique for reactive cation transport in a silt-loam soil (Clothier et al., 1988), for ion transport in a clay soil (Bond and Phillips, 1990), and for competitive anion transport in an Andisol (Katou et al., 1996). We also carry this out here, but furthermore, we validate the method by comparing the results to those obtained from the flux concentration of the leachate collected at the bottom of column experiments that simulate field conditions. The sorption of NO_3^- and Br^- is compared. Bromide is often used to evaluate nitrate mobility, assuming similarity of their mobility.

We apply our methodology on a ferrallitic-allitic soil from the Loyalty Islands in New Caledonia. This soil is variably-charged. More intensive agricultural practices are being developed on these islands with an increasing use of nitrogen fertilizers (Duwig, 1998). The environmental consequences of these practices need to be assessed.

2. Theory

2.1. Water movement

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

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left[D_w(\theta) \frac{\partial \theta}{\partial x} \right] \quad (1)$$

where x is the horizontal distance (m), θ the water content ($\text{m}^3 \cdot \text{m}^{-3}$), t the time (s), and D_w the soil water diffusivity function ($\text{m}^2 \cdot \text{s}^{-1}$).

The sorptivity S ($\text{m} \cdot \text{s}^{-1/2}$), which is a measure of the soil capillarity, is given by (Philip, 1969):

$$S = \int_{\theta_n}^{\theta_s} \frac{x}{t^{1/2}} d\theta = \int_{\theta_n}^{\theta_s} \lambda_B d\theta \quad (2)$$

where $\lambda_B(\theta) = x(\theta)/t^{1/2}$ is the Boltzman variable.

2.2. Solute movement

The convection dispersion (CDE) for one-dimensional transport of reactive anions under transient conditions is (Kutilek and Nielsen, 1994):

$$\frac{\partial \theta C_r}{\partial t} + \frac{\partial(\rho A)}{\partial t} = \frac{\partial}{\partial x} \left(\theta D_s \frac{\partial C_r}{\partial x} \right) - \frac{\partial(v \theta C_r)}{\partial x} \quad (3)$$

where C_r is the resident solute concentration ($\text{mol} \cdot \text{m}^{-3}$), ρ the soil bulk density ($\text{kg} \cdot \text{m}^{-3}$), A is the amount of solute adsorbed ($\text{mol} \cdot \text{kg}^{-1}$), D_s the diffusion-dispersion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$) and v the pore water velocity ($\text{m} \cdot \text{s}^{-1}$).

The adsorption of anions by the soil was modelled using a simple linear isotherm of the form:

$$A = K_d C_r \quad (4)$$

with the distribution coefficient K_d ($\text{m}^3 \cdot \text{kg}^{-1}$) taken to be a constant, which can be linked to a retardation factor, $R(-)$, by:

$$R = 1 + (\rho K_d / \theta). \quad (5)$$

• For the short-duration *horizontal* experiments of about 1 800 s, where the water velocity is high enough, molecular diffusion of the solute can be ignored as compared to dispersion. The hydrodynamic dispersion coefficient can thus be written as: $D_s = \alpha v$ where α is the dispersivity (m) and v is the pore water velocity ($\text{m} \cdot \text{s}^{-1}$). The CDE (equation (3)) for a reactive solute transport into horizontal column, with uniform water content, can then be given as:

$$\frac{\partial C_r}{\partial t} = \alpha' \frac{\partial}{\partial x} \left(v \frac{\partial C_r}{\partial x} \right) - v' \frac{\partial C_r}{\partial x}, \quad (6)$$

where $\alpha' = \alpha/R$ and $v' = v/R$.

By using the Boltzman variable, Watson and Jones (1981), found an approximate expression for the normalized resident concentration C after a step input of solution of concentration C_1 :

$$C = \frac{C_r - C_0}{C_1 - C_0} = \frac{1}{2} \operatorname{erfc} \left[\frac{(\lambda_B - \lambda'_B) t^{1/4}}{2 (\alpha' \lambda'_B)^{1/2}} \right], \quad (7)$$

where C_0 is the initial concentration in the soil solution and λ'_B the retarded position of the centroid of the reactive solute front in terms of the Boltzman variable.

By considering complete displacement of the antecedent solution by the invading solute (Smiles and Philip, 1978), it is possible to locate the centroid, λ_B^* , of the front of invading water as:

$$\int_{\theta_n}^{\theta_s} \lambda_B d\theta = \int_0^{\lambda_B^*} \theta d\lambda_B \quad (8)$$

The retarded position of the centroid of the reactive solute is given by (Clothier et al., 1988):

$$\lambda'_B = \lambda_B^* / R. \quad (9)$$

• Vertical soil column flux experiments were used to validate this method. The details of those experiments are described in Vogeler et al. (1999). An analytical solution (Kreft and Zuber, 1978) of the CDE (equation (3)) for flux concentration was fitted on the breakthrough curve to determine the dispersivity α and the distribution coefficient K_d .

The appropriate initial and boundary conditions for a steady rainfall are given in Vogeler et al. (1999).

3. Materials and methods

3.1. Soil

The soil used is a ferrallitic-allitic soil from Maré in the Loyalty Islands, New Caledonia. Selected chemical properties of the soil are presented in the table (Duwig et al., 1998). The soil pH is usually slightly acid in the topsoil and decreases with depth. The ΔpH difference ($\text{pH}_{\text{H}_2\text{O}} - \text{pH}_{\text{KCl}}$) is positive in the surface samples but becomes negligible in deeper horizons, suggesting that the negative charges predominate near the surface but tend to balance positive charges in deeper horizons. Cation exchange capacity is highly correlated to organic matter levels ($r = 0.98$) which can reach up to 15 %. The AEC is due to the high levels of iron and aluminium oxides. The crystalline fraction is mainly present as boehmite and gibbsite for aluminium oxides, and goethite for iron oxides (Latham and Mercky, 1983).

Table. Selected analytical properties of the soil.

Principales propriétés du sol.

Depth cm	$\text{pH}_{\text{H}_2\text{O}}$	pH_{KCl}	Org.C g·kg ⁻¹	Exchangeable cations		Total elements		
				Ca cmol·kg ⁻¹	Mg cmol·kg ⁻¹	SiO ₂	Al ₂ O ₃ g·kg ⁻¹	Fe ₂ O ₃
0–7	6.78	6.37	80.9	15.4	11.6	10.1	583.7	324.0
7–20	6.69	6.26	43.2	6.4	5.4	9.4	592.6	332.0
20–40	6.29	6.06	33.8	3.8	3.5	7.9	596.6	334.2

3.2. Horizontal 'Perroux tube' experiments

Soil from the ploughed horizon (0–20 cm), moistened with distilled water, was packed to a bulk density of 0.84 (± 0.005) Mg·m⁻³ in sectionable acrylic columns, so called 'Perroux tube', of 25 cm length and 20 mm of internal diameter (Smiles and Philip, 1978). One-dimensional, horizontal, free-water adsorption experiments were carried out using only water, or a solution of either NO₃⁻ (0.025 M), or Br⁻ (0.025 and 0.1 M). The invading solution was supplied from a Mariotte bottle to

the proximal end of the column. The wet front position, and the water level in the reservoir were recorded frequently. After terminating each invading experiment, the Perroux tube was rapidly sectioned in samples of different lengths (ranging from 0.42 to 2.57 cm) and the samples were weighed and oven dried for determination of the water content. Samples for nitrate were not oven dried. Samples were then used for determination of the resident concentration of bromide and nitrate. 5 g soil was extracted with 25 mL of a KCl (2 M) solution and the resident concentrations were analysed in the supernatants. As the soil was saturated with KCl, the absorbed Br⁻ and NO₃⁻ were replaced by Cl⁻.

3.3. Vertical soil column experiments

The same soil was packed into a large column (30 cm high and 30 cm in diameter) to the bulk density of 0.8 Mg·m⁻³. The column, left bare, was placed on an inverted tension infiltrometer to ensure unsaturated flow at the base, and yet allow regular sampling of the effluent. A rainfall simulator was used to apply the water at a steady state of 36 mm·h⁻¹. When steady-state flow was reached, 72.5 mL of a bromide pulse (0.047 M) was sprayed onto the soil surface and leached through the column by four pore volumes of water. This was followed by a nitrate pulse (0.047 M) of the same volume, under the same leaching conditions. The effluent samples from both experiments were analysed for NO₃⁻ and Br⁻.

4. Results

4.1. Perroux tube

The water content (a), and normalized concentration profiles of Br⁻ and NO₃⁻ (b) as well as a numerical solution of the water content profile are shown in figure 1. The sorptivity calculated using equation (2) was $S = 2.4 (\pm 0.15) \text{ mm}\cdot\text{s}^{-1/2}$. The centroid of the front of invading water (equation (8)) was found to be at $\lambda_B^* = 3.67 (\pm 0.19) \text{ mm}\cdot\text{s}^{-1/2}$.

The centroid of the front of solute was $\lambda'_B = 3.3 \text{ mm}\cdot\text{s}^{-1/2}$ for bromide and 3.2 mm·s^{-1/2} for nitrate. The retardation factor between the reactive solute front and the convective front, given by equation (9), is 1.1 for the bromide and 1.15 for the nitrate. So in terms of anion exchange the K_d values (equation (5)) are $1.2\cdot 10^{-4}$ and $1.8\cdot 10^{-4} \text{ m}^3\cdot\text{kg}^{-1}$ respectively. The dispersivity found by fitting was 1.5 mm.

4.2. Vertical column

The flux concentrations of Br⁻ and NO₃⁻ measured in the effluent at the base of the large column are shown in figure 2. The best fit of an analytical solution of the CDE (equation (3)) gives dispersivities of 3 and 4 mm, and retardation values of 1.3 and 1.2 for bromide and nitrate respectively mm (not shown here). Predicted analytical solutions of the CDE using the retardation values obtained

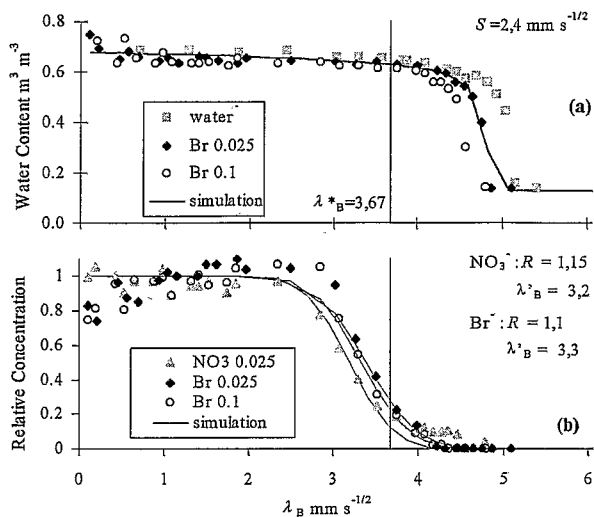


Figure 1. Water content (a) and normalized resident concentration profiles (b).

Profils de teneur en eau (a) et de concentrations résidentes adimensionnelles (b).

by the Perroux tube are also shown in figure 2. These predictions are relatively satisfying showing that the two methods give comparable results.

5. Discussions and conclusions

Significant retardation of the anions bromide and nitrate occurs in this ferrallitic soil. Anions such as NO₃⁻, Cl⁻ and Br⁻ are commonly adsorbed in soils high in amorphous inorganic material content (Singh and Kanehiro, 1969; Kinjo and Pratt, 1971; Black and Waring, 1979). The adsorption sites are the positively charged surfaces of ferric and other oxides.

Version abrégée

Connaître le transport des solutés à travers le sol est essentiel afin de développer des stratégies sûres pour une bonne gestion de l'environnement. Le transport des solutés est grandement affecté par leur sorption avec les constituants solides du milieu poreux qu'ils traversent.

Les sols fortement évolués des régions tropicales ont souvent une capacité d'échange anionique (CEA) importante. L'adsorption non spécifique d'anions tels que NO₃⁻, Cl⁻ et Br⁻ a été mentionnée par plusieurs auteurs : Kinjo et Pratt (1971), Wong et al. (1990), Bellini et al. (1996), Katou et al. (1996). Dans ces articles, elle a été mesurée soit par expériences en *batch*, connues pour surestimer la CEA, soit par expériences de lixiviation à travers une colonne de sol, laborieuses à mener.

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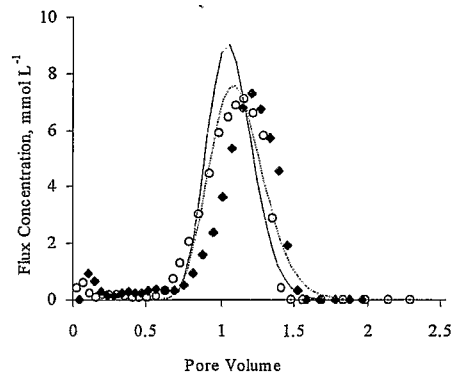


Figure 2. Measured and predicted breakthrough curves of the flux concentration of bromide (♦, solid line) and nitrate (o, broken line) in the leachate.

Concentrations de flux en bromure (♦, ligne continue) et en nitrate (o, ligne pointillée), mesurées et prédites dans les percolats.

K_d values found from the Perroux tube experiments gave good predictions of the leaching experiments. The best-fit of the breakthrough curve of the vertical columns gave only slightly higher K_d values. This can be explained by dilution of the anion peak through the soil column. According to Bellini et al. (1996), when the input concentration of anion increases, retardation decreases in spite of the increase in AEC that would result from higher electrolyte concentrations. This would be expected for input concentrations of Cl⁻ that were in excess of the equilibrium concentration that would saturate the AEC.

We have validated the Perroux tube method proposed here, and it could be easily used to determine the whole isotherm of a reactive solute, if the dynamic experiments were done at different initial concentrations.

The solute transport parameters determined in this study have already been used to predict nitrate transport through the soil from Maré in the Loyalty Islands (New Caledonia) to assess the consequences of intensive agricultural practices on the soil and water resources of these islands (Duwig, 1998).

Nous présentons ici une méthode simple à mettre en œuvre, fondée sur la mesure de la concentration résidente dans des tubes horizontaux sectionnables, et validons les résultats par comparaison avec l'analyse de la concentration de flux dans les percolats à la base d'une colonne verticale de sol. Nous appliquons cette méthode à un sol ferrallitique allitique des îles Loyauté en Nouvelle-Calédonie.

Théorie

L'équation (1) décrit l'écoulement de l'eau mono-directionnel quand une colonne de sol horizontale s'imbibe d'une solution, en condition transitoire non saturée, où x est la

distance horizontale à la source (m), θ la teneur en eau ($\text{m}^3 \cdot \text{m}^{-3}$), t le temps (s) et D_w la fonction de diffusivité ($\text{m}^2 \cdot \text{s}^{-1}$). Le transport d'un soluté réactif en condition transitoire est décrit par l'équation de convection-dispersion (3), où C_r est la concentration résidente du soluté ($\text{mol} \cdot \text{m}^{-3}$), ρ la masse volumique du sol sec ($\text{kg} \cdot \text{m}^{-3}$), A la quantité de soluté adsorbé ($\text{mol} \cdot \text{kg}^{-1}$), D_s le coefficient de dispersion-diffusion ($\text{m}^2 \cdot \text{s}^{-1}$) et v la vitesse de l'eau dans les pores ($\text{m} \cdot \text{s}^{-1}$). On suppose que l'adsorption non spécifique du soluté suit une isotherme linéaire. Ainsi, le facteur retard R (-), peut être déterminé grâce à l'équation (5), où K_d est le coefficient de distribution ($\text{m}^3 \cdot \text{kg}^{-1}$). L'équation (3), pour le transport d'un soluté réactif à travers une colonne de sol horizontale, dont la teneur en eau initiale est uniforme, se transforme en l'expression (6), où $\alpha' = \alpha/R$ et $v' = v/R$, α étant la dispersivité (m). Watson et Jones (1981) ont trouvé une solution approximative de cette équation, en fonction de la variable de Boltzman, décrivant l'évolution de la concentration adimensionnelle C , après un apport de soluté de concentration C_i pendant un temps très court (7). C_0 est la concentration initiale de soluté dans la colonne de sol et λ'_B la position du centre du front d'infiltration du soluté réactif. La position du front d'infiltration de l'eau λ_B est donnée par l'équation (8) ; le facteur retard peut donc être calculé grâce à l'équation (9).

Matériel et méthodes

Le sol étudié est un sol ferrallitique allitique des Iles Loyauté en Nouvelle-Calédonie. Ses principales caractéristiques sont présentées dans le *tableau* (Duwig et al., 1998).

Un échantillon de sol, prélevé dans l'horizon labouré (0–20 cm), a été compacté après séchage et tamisage à la masse volumique sèche de $0,84 \text{ Mg} \cdot \text{m}^{-3}$, dans un tube sectionnable, appelé tube de Perroux, de longueur 25 cm et de diamètre interne 2 cm. Quatre expériences, mono-directionnelles, horizontales, ont été réalisées, correspondant à l'imbibition d'eau, puis de nitrate (0,025 M) ou de bromure (0,025 et 0,1 M). L'évolution du front d'infiltration a été enregistrée et, en fin d'expérience, la colonne de sol a été découpée en tranches de longueurs différentes (entre 0,42 et 2,57 cm), sur lesquelles ont été déterminées la teneur en eau (sauf pour l'infiltration avec le nitrate), et la concentration résiduelle en solutés. Celle-ci a été mesurée dans le surnageant, après mélange de 5 g de sol à 25 mL d'une solution de KCl (2 M).

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C. R. Acad. Sci. Paris, Sciences de la terre et des planètes / *Earth & Planetary Sciences* 1999. 328, 759–764

L'expérience en colonne verticale, utilisant le même sol, est décrite dans Vogeler et al. (1999). Un simulateur de pluie a été utilisé pour appliquer à la surface un flux de $36 \text{ mm} \cdot \text{h}^{-1}$. Après obtention du régime permanent, 72,5 mL d'une solution concentrée de bromure (0,047 M) ont été pulvérisés à la surface du sol et lixiviés par l'équivalent de 4 volumes poreux. Ensuite, une solution de nitrate (0,047 M) de même volume a été appliquée et lixiviée dans les mêmes conditions. Les percolats ont été analysés pour déterminer leur concentration en nitrate ou en bromure.

Résultats

Les profils de teneur en eau (a) et de concentrations résidentes adimensionnelles en Br^- et NO_3^- (b) sont présentés sur la *figure 1*. La position du front d'infiltration de l'eau (équation (8)) est $\lambda_B = 3,67 (\pm 0,19) \text{ mm} \cdot \text{s}^{-1/2}$. La comparaison entre le front convectif λ_B et le front λ'_B des profils de concentration montre qu'il y a adsorption du nitrate et du bromure. Le facteur de retard obtenu par l'équation (9) est 1,1 pour le bromure et 1,15 pour le nitrate, soit, d'après l'équation (5), des K_d de $1,2 \cdot 10^{-4}$ et $1,8 \cdot 10^{-4} \text{ m}^3 \cdot \text{kg}^{-1}$ respectivement.

La *figure 2* montre les concentrations de flux en NO_3^- et Br^- mesurées dans les percolats collectés à la base de la colonne verticale. Le meilleur ajustement (non présenté ici) d'une solution analytique de l'équation de convection-dispersion (3) donne des facteurs retard de 1,2 et 1,3 pour le nitrate et le bromure respectivement. La même solution analytique, avec les facteurs retards obtenus par les tubes de Perroux, prédit de façon relativement satisfaisante les concentrations de flux en bromure et nitrate (*figure 2*), ce qui permet de conclure que les deux méthodes donnent des résultats comparables.

Conclusion

Les deux méthodes donnent des résultats similaires, validant ainsi la plus simple, utilisant les tubes de Perroux. Ils montrent une rétention non négligeable du bromure et du nitrate dans ce sol ferrallitique de Nouvelle-Calédonie. Le taux élevé d'oxydes de fer et d'aluminium est en grande partie responsable de la présence de charges positives induisant une adsorption non spécifique des anions tels que bromure et nitrate.

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