

Evaluating equilibrium and non-equilibrium transport of bromide and isoproturon in disturbed and undisturbed soil columns

S. Dousset^{a,*}, M. Thevenot^b, V. Pot^c, J. Šimunek^d, F. Andreux^b

^a UMR 5561-Biogéosciences, UFR Sciences Terre and Environnement, Université de Bourgogne, 6 Bd Gabriel, 21000 Dijon, France

^b UMR 1229-Microbiologie et Géochimie des Sols, UFR Sciences Terre and Environnement, Université de Bourgogne, 6 boulevard Gabriel, 21 000 Dijon, France

^c UMR INRA-INA-PG-Unité Environnement et Grandes Cultures-BP 01, 78850 Thiverval-Grignon, France

^d Department of Environmental Sciences, University of California, Riverside, California, USA

Received 31 July 2006; received in revised form 23 January 2007; accepted 1 July 2007

Available online 17 July 2007

Abstract

In this study, displacement experiments of isoproturon were conducted in disturbed and undisturbed columns of a silty clay loam soil under similar rainfall intensities. Solute transport occurred under saturated conditions in the undisturbed soil and under unsaturated conditions in the sieved soil because of a greater bulk density of the compacted undisturbed soil compared to the sieved soil. The objective of this work was to determine transport characteristics of isoproturon relative to bromide tracer. Triplicate column experiments were performed with sieved (structure partially destroyed to simulate conventional tillage) and undisturbed (structure preserved) soils. Bromide experimental breakthrough curves were analyzed using convective–dispersive and dual-permeability (DP) models (HYDRUS-1D). Isoproturon breakthrough curves (BTCs) were analyzed using the DP model that considered either chemical equilibrium or non-equilibrium transport. The DP model described the bromide elution curves of the sieved soil columns well, whereas it overestimated the tailing of the bromide BTCs of the undisturbed soil columns. A higher degree of physical non-equilibrium was found in the undisturbed soil, where 56% of total water was contained in the slow-flow matrix, compared to 26% in the sieved soil. Isoproturon BTCs were best described in both sieved and undisturbed soil columns using the DP model combined with the chemical non-equilibrium. Higher degradation rates were obtained in the transport experiments than in batch studies, for both soils. This was likely caused by hysteresis in sorption of isoproturon. However, it cannot be ruled out that higher degradation rates were due, at least in part, to the adopted first-order model. Results showed that for similar rainfall intensity, physical and chemical non-equilibrium were greater in the saturated undisturbed soil than in the unsaturated sieved soil. Results also suggested faster transport of isoproturon in the undisturbed soil due to higher preferential flow and lower fraction of equilibrium sorption sites.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Bromide; Isoproturon; Breakthrough curves; Modeling; HYDRUS-1D

1. Introduction

Isoproturon is one of the most widely used herbicides in France. It is used to control weeds in cereal crops and is one of the most frequently detected herbicides in surface and ground waters (IFEN, 2006). This herbicide

* Corresponding author. Université de Bourgogne, UFR Sciences Terre and Environnement, 6 boulevard Gabriel, 21 000 Dijon, France. Tel.: +33 3 80 39 68 88; fax: +33 3 80 39 63 87.

E-mail address: Sylvie.Dousset@u-bourgogne.fr (S. Dousset).

was measured in concentrations higher than $0.1 \mu\text{g L}^{-1}$, which is the European Community Council limit for water consumption (ECC, 1998), in numerous natural waters around Europe (House et al., 1997; Garmouma et al., 1998; Spliid and Koppen, 1998). Isoproturon is therefore one of the priority substances that are monitored in European natural waters (OJEC, 2001).

Numerous studies have provided evidence that preferential flow processes are the main mechanisms of isoproturon leaching in drained heavy clay soils (Haria et al., 1994; Johnson et al., 1994; Brown et al., 1995; Heppel et al., 1999). Biopores (worm holes) and mechanical pores (shrinkage cracks, and cracks resulting from ploughing) were identified as main vertical preferential flow paths (Harris et al., 1994). Preferential transport of isoproturon through earthworm burrows that bypass the soil matrix was shown at the field scale in lower clay content soils by Zehe and Flühler (2001). Their study emphasized the role of deep penetrating macropores interconnected with the soil surface for the occurrence of preferential flow events.

A better understanding of mechanisms controlling pesticide behavior in macroporous structured soils with by-pass flow thus remains a current issue. Conservative tracers such as bromide, chloride and dyes are traditionally used to determine the main physical transport processes in soils and to visualize flow pathways in field and/or laboratory studies (e.g., Seyfried and Rao, 1986; Andreini and Steenhuis, 1990; Flury and Flühler, 1994; Zehe and Flühler, 2001). A comparison of water flow and solute transport in sieved and undisturbed soil columns could help to better identify mechanisms affecting the transport of solutes. In particular, the importance of physical non-equilibrium transport stemming from physical heterogeneities (macropores) in structured soils could be identified. The accessibility of pesticide molecules to reactive solid surfaces in undisturbed soils, as compared to sieved soils, could also be assessed. Some studies that compared transport in undisturbed and disturbed soil columns suggest that Cl^- (Cassel et al., 1974; Starret et al., 1996) and atrazine (Zsolnay, 1991) move faster in undisturbed than in sieved soils. On the other hand, Veeh et al. (1994) showed that the transport of Br^- and chlorsulfuron is similar through undisturbed or sieved soil columns. Sadeghi et al. (2000) found a faster transport of atrazine in either the undisturbed or sieved soils depending upon the soil's physico-chemical properties. Finally, Griessbach et al. (1998) showed that the leaching of a silicone-polyether was lower in undisturbed than in sieved soil columns. These widely contrasting results have been reported in the literature, even for conditions where the soil texture and structure

were similar. In most studies, structured soil columns were prepared by pushing a PVC or metallic tube into the soil manually or with a hydraulic jack. Possible soil compaction resulting from the use of this method cannot be ignored and may partly explain these different observations (Dousset et al., 1995).

We performed bromide and isoproturon displacement experiments in both disturbed and undisturbed soil columns that were sampled from a silty clay loam soil in an intensively cultivated agricultural area (Citeaux, Côte d'Or, France). In addition, the dye tracer, Brilliant Blue FCF, was used to visualize and quantify potential macropore pathways used by water flow in undisturbed soil columns. Although several authors suggested that due to its charge Brilliant Blue FCF may sorb somewhat more strongly than expected to the clay (Perillo et al., 1998; Kasteel et al., 2002; Nobles et al., 2004) and organic carbon (Ketelsen and Meyer-Windel, 1999) fractions of the soil, Brilliant Blue FCF remains to be one of the best dye tracers available today for identifying water flow pathways (German-Heins and Flury, 2000).

Our objectives were (i) to assess the importance of preferential flow on isoproturon leaching in the silty clay loam soil of Citeaux and (ii) to evaluate whether a comparison of bromide and isoproturon leaching in disturbed and undisturbed soil columns could help identify different processes occurring during transport. Displacement experiments were analyzed using multi-process solute transport models that describe physical equilibrium transport using the convection–dispersion equation (CDE), and physical non-equilibrium transport using the dual-permeability (DP) model that also considers chemical equilibrium (instantaneous sorption) or non-equilibrium (kinetic sorption) processes. This work contributes to our understanding of non-equilibrium reactive solute transport processes in undisturbed and sieved laboratory soil columns and the use of numerical models accounting simultaneously for both physical and chemical non-equilibrium processes.

2. Materials and methods

2.1. Soils and column sampling

A silty clay loam soil (gleyic luvisol, FAO, 1998) was sampled from a fallow area of the INRA experimental site at Citeaux (Côte d'Or, France). Some young alfalfa plants (*Medicago sativa*) were growing on the fallow soil. Three undisturbed soil column monoliths (16-cm i.d., 20-cm long) were prepared by carefully excavating the surrounding soil using a shovel. A 25 cm-long polyvinyl chloride (PVC) pipe with an internal

diameter of 20 cm was then placed over the soil cylinder. A minimal-expansion foam was injected into the gap between the soil column and the PVC pipe to fill empty space and thus reduce possible sidewall flow. The foam was then allowed to harden overnight before the columns were removed by digging under the PVC pipe. A nylon mesh was placed at the bottom of the columns to retain the soil base. Three homogenized soil columns, were then prepared with the same soil collected from the 0–20 cm horizon. The soil was first air dried and then sieved through 5-mm and, subsequently, 1-mm sieves. The soil aggregates with equivalent diameters between 1 and 5 mm were packed in a 15-cm i.d. and 20-cm long PVC pipe. The 0–1 mm diameter aggregates were removed to avoid possible clogging of the soil columns. Soil analysis has shown that the physico-chemical properties of the 0–1 mm and the 1–5 mm aggregates were similar (Table 1). The 0–1 mm fraction represents 17% of the 0–5 mm soil fraction mass. Note that soil aggregates were not dispersed prior to sieving and aggregated structural properties of the soil were thus partially preserved.

Particle size distribution of the soil was analyzed by sieving and sedimentation after its dispersion in sodium hexametaphosphate (AFNOR X 31-107). The organic C concentration was determined by dry combustion (ISO 10694). The CaCO_3 concentration and $\text{pH}_{\text{H}_2\text{O}}$ were measured by following the ISO 10693 and ISO 10390 standards, respectively. All analyses were carried out at the Soil Analysis Laboratory INRA-Arras, France.

2.2. Chemicals

Analytical grade reagents were used for the experiments. Isoproturon (3-(4-isopropylphenyl)-1,1-dimethylurea) was purchased from Dr. Ehrenstorfer (Augsburg,

Germany). Its water solubility is 65 mg L^{-1} at $22 \text{ }^\circ\text{C}$ (Tomlin, 1997). Its half-life varies from 6.5 to 34 days in surface soils (Pieuchot et al., 1996; Walker et al., 2001). Its normalized adsorption coefficient (K_{oc}) varies from 43 to 225 L kg^{-1} in surface soil (0–30 cm) (Benoit et al., 1999; Lennartz, 1999; Spark and Swift, 2002). Large variations in K_{oc} values may be due to (i) different experimental conditions among reported studies, (ii) differences in the nature of the soil organic carbon in the analyzed soils, and (iii) isoproturon adsorption to the clay fraction (Pantani et al., 1997). Bromide was used in the form of KBr. Depending on pH, the Brilliant Blue FCF dye tracer is either neutral or dissociates into a mono- or bivalent anions ($\text{p}K_{\text{a}}=5.83$ and 6.58). The tracer is thus expected to be anionic in our soil with pH value of 8.

2.3. Soil column setup for displacement experiments

All soil columns were brought back to the laboratory held at a constant temperature of $20 \text{ }^\circ\text{C}$ and placed on a support base. The bottom of each column rested on a PVC plate perforated with 2-mm diameter holes. A glass fiber filter was placed on the soil surface to ensure homogeneous distribution of water over the soil surface. Distilled water was applied over 12 h to the top of each sieved and undisturbed soil column at a constant rate of 4 mL min^{-1} (1.3 cm h^{-1}) using a peristaltic pump (Ismatec MP 25) until steady-state flow was achieved. An influent aqueous solution (0.25% CH_3OH) with 20 mg L^{-1} of bromide and 3.5 mg L^{-1} of isoproturon was then applied at the same flow rate over 48 h, followed by an influent distilled water solution applied for 48 h to evaluate also the desorption process. Each undisturbed soil column was then leached with one pore volume of the dye at a concentration of 5 g L^{-1} . The soil cores were subsequently allowed to drain for 72 h, extracted from the PVC pipe, and then cut lengthwise into 2-cm thick soil slices with a knife. Digitized images of each slice were taken using the SONY DKC 5000 triCCD camera and treated using OPTIMAS 6.5 software in order to quantify the area dyed with the Brilliant Blue FCF. The dye coverage is a measure of the volumetric proportion of preferential flow paths, which can consequently be used to evaluate the mobile zone.

No degradation of isoproturon was detected in the influent solution during the injections at 0, 20 and 48 h. Effluents from the bottom of each soil column were collected every hour in glass vials using a Foxy 200 fraction collector. Leachate volumes were determined gravimetrically. The bromide and isoproturon breakthrough curves (BTCs) were constructed using the

Table 1
Main characteristics of the sieved and undisturbed soil (all data except pH values are in g kg^{-1})

	pH	Sand H_2O (50–2000 μm)	Silt (2–50 μm)	Clay (<2 μm)	Organic carbon	CaCO_3
<i>Undisturbed soil depth</i>						
0–5 cm	8.0	164	492	343	12	10.6
5–10 cm	8.0	163	486	349	10	12.6
10–15 cm	8.0	173	476	349	11	12.3
15–20 cm	8.0	165	488	347	11	12.6
<i>Sieved soil (1–5 mm fraction)</i>						
0–20 cm	8.0	181	459	361	11	16.1
<i>Sieved soil (0–1 mm fraction)</i>						
0–20 cm	8.0	172	474	354	11	15.1

concentrations measured in the leachates. Recoveries of bromide and isoproturon were calculated from the BTCs.

The porosity, w ($\text{cm}^3 \text{cm}^{-3}$) of the soil was calculated as follows (Danielson and Sutherland, 1986):

$$w = (1 - \rho_b / \rho_p) \quad (1)$$

where ρ_p is the particle density (g cm^{-3}) and ρ_b is the bulk density (g cm^{-3}). The bulk density of the undisturbed soil was obtained by averaging measured bulk densities of 20 soil core samples (100 cm^3 volume) collected in the field. The bulk density of the sieved soil was determined on small laboratory soil columns (6.8 cm diameter and 6 cm long). Mean bulk densities were $1.60 \pm 0.08 \text{ g cm}^{-3}$ and $1.07 \pm 0.02 \text{ g cm}^{-3}$ for the undisturbed and sieved soils, respectively. This large difference in bulk densities may be explained in part by the removal of the 0–1 mm aggregates from the sieved soil and by the compaction of the undisturbed soil by the agricultural machinery, as also previously reported by Renault et al. (1998) for the same soil. Assuming a particle density of 2.65 g cm^{-3} , the porosity was equal to $0.3956 \pm 0.0297 \text{ cm}^3 \text{cm}^{-3}$ and $0.5957 \pm 0.0066 \text{ cm}^3 \text{cm}^{-3}$ for the undisturbed and sieved soils, respectively. The gravimetric soil water content was measured on the same small sieved soil columns and on additional small undisturbed soil columns (6.8 cm diameter and 6 cm long) after 12 h of water irrigation at 1.3 cm h^{-1} . The volumetric water contents, θ , were $0.392 \pm 0.030 \text{ cm}^3 \text{cm}^{-3}$ and $0.447 \pm 0.005 \text{ cm}^3 \text{cm}^{-3}$ for the undisturbed and sieved soil columns, respectively. Volumes of water in the column, V_p ($=\theta\pi R^2 L$, where R is the inner diameter of the soil columns (cm) and L is the length of the soil column (cm)), were 1576.3 cm^3 and 1579.8 cm^3 for the undisturbed and sieved soil columns, respectively.

The potential anion exclusion volume for bromide in the soil columns was calculated using an average value of the clay surface area of $1.5 \times 10^5 \text{ m}^2 \text{kg}^{-1}$ and an average double layer thickness of 0.5 nm as reported by Veeh et al. (1994), resulting in an exclusion volume of $0.0375 \text{ cm}^3 \text{g}^{-1}$ of clay. The anion exclusion volume, V_{ex} , of Citeaux soil columns was estimated to be 3.23% and 5.35% of the pore volume for the sieved and undisturbed soils, respectively.

2.4. Chemical analysis

The column effluent samples were filtered through $0.45 \mu\text{m}$ cellulose nitrate membranes (Sartorius) and analyzed using a Waters HPLC equipped with a Diode Array Detector and a $25 \text{ cm} \times 4.6 \text{ mm}$ C18-column

packed with Kromasil $5 \mu\text{m}$ for isoproturon, and a $15 \text{ cm} \times 4.6 \text{ mm}$ Waters IC Pack Anion HC for Br^- . The mobile phase was acetonitrile–water at 60/40 v/v for isoproturon and a 30 mM KH_2PO_4 solution with 20% acetonitrile acidified to pH 2.8 for Br^- (Bowman, 1984). The flow rate of the mobile phase was 1 mL min^{-1} for isoproturon analysis, and 2 mL min^{-1} for Br^- analysis. Detection was performed at 242 nm for isoproturon and 205 nm for Br^- . Minimum detectable concentrations were 0.02 mg L^{-1} for isoproturon and 0.1 mg L^{-1} for Br^- .

2.5. Batch adsorption and degradation coefficients measurement

For the batch adsorption experiments, each sample consisted of 2 g of soil mixed with 10 mL isoproturon solution (soil/solution ratio: 1/5, w/v) in a 50 mL polycarbonate centrifuge tube. Herbicide concentrations ranged from 0.56 mg L^{-1} to 11.47 mg L^{-1} . The tubes were agitated on a rotary shaker for 36 h at $20 \text{ }^\circ\text{C}$ to achieve equilibrium. The suspensions were then centrifuged for 20 min at 4000 g (Beckman-Avanti J-25 centrifuge maintained at $20 \pm 1 \text{ }^\circ\text{C}$). Blanks without soil, otherwise prepared in the same way, showed no sorption to the polycarbonate tubes. The amount of adsorbed herbicide, x (mg), per mass of soil, m (kg), at equilibrium was determined by the difference between the initial and equilibrium herbicide concentrations in the solution, C_{eq} (mg L^{-1}). Sorption isotherms were obtained by plotting x/m against C_{eq} and described using the Freundlich equation (e.g., Fouqué-Brouard and Fournier, 1996; Benoit et al., 1999; Nemeth-Konda et al., 2002):

$$x/m = K_f C_{\text{eq}}^n \quad (2)$$

where K_f ($\text{mg}^{1-n} \text{L}^n \text{kg}^{-1}$) and n (–) are empirical sorption coefficients. Three replicates were conducted for each sample.

For the degradation experiments, 50-g portions of the 1–5 mm sieved soil were put in crystallizers (65 mm diameter). The soil moisture was brought to 42% with a 3.2 mg L^{-1} solution of isoproturon in water + methanol (99.75 + 0.25 by volume), quite similar to the maximum concentration in the soil columns. Each glass vessel was placed in a room at a constant temperature of $20 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$ for 16 days. Triplicate soil samples were incubated for 4, 10 and 16 days. The remaining isoproturon was extracted from the soil samples (50 g) with 100 mL of methanol–water solution (80/20; v/v) by three 12-hour rotary agitations. The slurries were then centrifuged at 8000 g for 10 min. The three extractions were first

combined, then evaporated to dryness with a rotovapor, and finally dissolved in methanol (5 mL) for analysis by HPLC. Isoproturon degradation was usually described using a first-order model (Walker et al., 1999):

$$C = C_0 \exp(-kt) \quad (3)$$

where C is the soil concentration of the parent molecule at time t (d), C_0 is the initial concentration at time 0, and k is the rate constant (d^{-1}).

2.6. Transport models

The modified one-dimensional transport model HYDRUS-1D (Šimůnek et al., 1998, 2003; Pot et al., 2005) was used to describe the transport of bromide and isoproturon in the soil columns. The dual-permeability (DP) model (Gerke and van Genuchten, 1993; Šimůnek et al., 2003) was used to describe the physical non-equilibrium transport. The liquid phase is in this model is assumed to consist of two mobile flow regions, named hereafter fracture and matrix regions, each with its own flow and transport properties. The total water content is defined as $\theta = w_f \theta_f + (1 - w_f) \theta_{\text{ma}}$, where θ_f and θ_{ma} are local volumetric water contents in the fracture and matrix regions, respectively. The water flux density, q (cm h^{-1}), is similarly defined as $q = w_f q_f + (1 - w_f) q_{\text{ma}}$, where q_f and q_{ma} are the water flux densities in the fracture and matrix regions, respectively. In both relations, w_f is the volumetric weighting factor (–) expressing the ratio of the fracture domain to the total soil volume. The total contribution of the fracture and matrix domain to the overall water content are calculated as: $\theta_f^c = w_f \theta_f$ and $\theta_{\text{ma}}^c = (1 - w_f) \theta_{\text{ma}}$, respectively.

Assuming that degradation is active only in the liquid phase, the transport equations for one-dimensional steady-state water flow conditions for the fracture (4) and matrix (5) regions are written as:

$$\theta_{\text{ma}} \frac{\partial C_{\text{ma}}}{\partial t} + \rho_b \frac{\partial S_{\text{ma}}}{\partial t} = \theta_{\text{ma}} D_{\text{ma}} \frac{\partial^2 C_{\text{ma}}}{\partial z^2} - q_{\text{ma}} \frac{\partial C_{\text{ma}}}{\partial z} + \alpha_s (C_f - C_{\text{ma}}) - \theta_{\text{ma}} \mu_1 C_{\text{ma}} \quad (4)$$

$$\theta_f \frac{\partial C_f}{\partial t} + \rho_b \frac{\partial S_f}{\partial t} = \theta_f D_f \frac{\partial^2 C_f}{\partial z^2} - q_f \frac{\partial C_f}{\partial z} - \alpha_s \frac{1 - w_f}{w_f} (C_f - C_{\text{ma}}) - \theta_f \mu_1 C_f \quad (5)$$

where t is time (h), z is the vertical coordinate (cm), $C_{\text{ma}(f)}$ is the solute concentration of the liquid phase in the matrix (fracture) region (mg L^{-1}), $S_{\text{ma}(f)}$ is the solute concentra-

tion of the solid phase in the matrix (fracture) region (mg g^{-1}), $D_{\text{ma}(f)}$ is the dispersion coefficient in the matrix (fracture) region ($\text{cm}^2 \text{h}^{-1}$), μ_1 is the coefficient of degradation in the liquid phase (h^{-1}), and α_s is the first-order mass transfer rate coefficient between the two regions (h^{-1}). Following Pot et al. (2005), the physical and chemical non-equilibrium transport model was described by combining the dual-permeability model and the two-site sorption model (Selim et al., 1977; van Genuchten and Wagenet, 1989). In this latter model, the sorption is assumed to be instantaneous on one fraction of the sorption sites (named hereafter type-1 sites) and to be a time-dependent, first-order kinetic process on the remaining fraction of the sorption sites (named hereafter type-2 sites). The governing equations for the matrix (6) and fracture (7) regions are written as:

$$\theta_{\text{ma}} \frac{\partial C_{\text{ma}}}{\partial t} + \rho_b f_{\text{ma}} \frac{\partial S_{\text{ma}}}{\partial t} = \theta_{\text{ma}} D_{\text{ma}} \frac{\partial^2 C_{\text{ma}}}{\partial z^2} - q_{\text{ma}} \frac{\partial C_{\text{ma}}}{\partial z} + \alpha_s (C_f - C_{\text{ma}}) - \theta_{\text{ma}} \mu_1 C_{\text{ma}} - \rho_b \alpha_k [(1 - f_{\text{ma}}) K_f C_{\text{ma}}^n - S_{k,\text{ma}}] \quad (6)$$

$$\theta_f \frac{\partial C_f}{\partial t} + \rho_b f_f \frac{\partial S_f}{\partial t} = \theta_f D_f \frac{\partial^2 C_f}{\partial z^2} - q_f \frac{\partial C_f}{\partial z} - \alpha_s \frac{1 - w_f}{w_f} (C_f - C_{\text{ma}}) - \theta_f \mu_1 C_f - \rho_b \alpha_k [(1 - f_f) K_f C_f^n - S_{k,f}] \quad (7)$$

where $S_{\text{ma}(f)}$ are the adsorbed concentrations on the type-1 sites in the matrix (fracture) domain (mg g^{-1}), $S_{k,\text{ma}(f)}$ are the adsorbed concentrations on the type-2 sites in the matrix (fracture) domain (mg g^{-1}), $f_{\text{ma}(f)}$ are the fractions of the type-1 sorption sites in the matrix (fracture) domain (–). In this work, we assumed that the equilibrium sorption process was described using the Freundlich isotherm.

2.7. Parameter estimation

The inverse problem was solved using the non-linear least-squares inversion method proposed by Marquardt (1963). Physical transport processes were first determined by analyzing the bromide BTCs. Then the chemical transport processes for isoproturon were determined by inverting the herbicide BTCs, using the physical transport parameters estimated for the bromide transport. For all inversions, the soil water content, θ , and the flux density, q , were fixed to measured values.

For bromide modeling, the molecular diffusion coefficient was set to $0.066 \text{ cm}^2 \text{h}^{-1}$ (Weast, 1985). Note that Parsons (1959) gives a value of similar order of

magnitude of $0.075 \text{ cm}^2 \text{ h}^{-1}$. Estimated transport parameters were q_{ma} , λ_{ma} , λ_{f} , w_{f} and α_{s} , while parameters θ_{f}^* , θ_{ma}^* , $q_{\text{f}} = (q - (1 - w_{\text{f}})q_{\text{ma}}) / w_{\text{f}}$, and the pore water velocities in the fracture ($v_{\text{f}} = q_{\text{f}} / \theta_{\text{f}}$) and matrix ($v_{\text{ma}} = q_{\text{ma}} / \theta_{\text{ma}}$) domains were calculated from the fitted parameters. Finally, anion exclusion (for bromide) was addressed by fixing the retardation factor, R , to 0.97 and 0.95 for the sieved and undisturbed soil columns, respectively, following Veeh et al. (1994).

For isotroturon modeling, we assumed that the herbicide underwent the same physical transport processes as bromide, so that dispersivities (λ_{ma} and λ_{f}), matrix and fracture contributions to the overall water content ($\theta_{\text{ma}}^{\text{c}}$ and $\theta_{\text{f}}^{\text{c}}$), a volumetric ratio of the fracture domain (w_{f}), and pore water velocities (v_{ma} and v_{f}) were fixed to values estimated for the bromide transport. The first-order mass transfer rate coefficient, α_{s} , was fixed to the bromide value corrected for the molecular diffusion coefficient of pesticides (taken as $0.0179 \text{ cm}^2 \text{ h}^{-1}$, Jury et al., 1983). Sorption related parameters, K_{f} and n , and the degradation rate, μ_1 , were either fixed to the batch values or fitted. Additional parameters f_{ma} , f_{f} , and α_{k} were estimated when considering the chemical non-equilibrium transport model.

3. Results and discussion

3.1. Batch adsorption and degradation experiments

The adsorption isotherm was well described using the Freundlich equation:

$$x/m = 1.06 C_{\text{eq}}^{0.88} (r^2 = 0.97). \quad (8)$$

The Freundlich adsorption coefficient ($K_{\text{d}} = 1.06$) is in agreement with K_{f} values published in the literature for batch conditions, which vary between 0.52 and $1.3 \text{ mg}^{1-n} \text{ L}^n \text{ kg}^{-1}$ (Fouqué-Brouard and Fournier, 1996; Benoit et al., 1999; Nemeth-Konda et al., 2002), with n values ranging from 0.51 to 0.77.

The incubation experiment on a soil treated with isotroturon showed that the pesticide degradation was negligible over 4 days; the isotroturon recovery was $93.3 \pm 1.3\%$ after 4 days of incubation, compared to $96.2 \pm 8.4\%$ at t_0 . The degradation of isotroturon was well described by a first-order kinetic equation:

$$x/m = 1.41 \exp(-0.055t) (r^2 = 0.93) \quad (9)$$

that resulted in the isotroturon half-life of 12.6 days. This is in agreement with half-lives between 6.4 and 34 days reported by Pieuchot et al. (1996) and Walker et al. (2001), and 19 days measured by Walker et al. (1999).

3.2. Displacement column experiments

3.2.1. Bromide breakthrough curves

Solute breakthrough curves are plotted using the relative concentration measured in the leachate versus the number of pore volumes eluted, defined as V/V_0 , where V is the flux-averaged volume of solute eluted (cm^3) and V_0 is the volume of water in the column (cm^3).

Prior to interpreting the results of the displacement experiments, we stress here that at the same rainfall intensity the displacement experiments occurred under saturated conditions for the undisturbed soil columns and under unsaturated conditions for the sieved soil columns. Thus contrary to the sieved soil, the macropores in the undisturbed soil column were water filled and involved in solute transport. The sieved columns were repacked with the soil which was sieved without first destroying the soil aggregates. Since the particles that fell through the 1-mm sieve were removed before packing the column, and only larger particles and aggregates were used to pack the column, the physical properties of disturbed and undisturbed columns were quite different. The disturbed soil columns thus did not have any macro-structural features, such as macropores, but retained micro-structural features, such as aggregates. The removal of the small particle fraction led to relatively high hydraulic conductivities in the sieved soil columns, while still allowing for non-equilibrium flow due to the presence of aggregates.

Fig. 1 shows that bromide breakthrough curves for both the sieved (Fig. 1a) and undisturbed (Fig. 1b) soil columns were shifted to the left relative to the theoretical curve predicted by the equilibrium transport model. This early arrival of bromide suggests the existence of preferential flow. The shape of bromide breakthrough curves was similar for the three sieved columns (Fig. 1a). While the BTCs shape was also similar for columns 1 and 2 in the undisturbed soil, it was different for column 3 (Fig. 1b). This difference could be explained by the spatial heterogeneity of the soil structure at the field scale. The average bromide recoveries were $97.5 \pm 0.2\%$ for the sieved soil and $90.8 \pm 0.6\%$ for the undisturbed soil. The latter value is similar to an average bromide recovery of 87% reported by Lennartz and Kamra (1998) in undisturbed loamy sand. Bromide concentrations in the column effluent did not reach inflow concentrations even after leaching of 2 pore volumes, but tended to increase over the whole application period without reaching inflow concentrations. Such tailing in the BTC of a tracer is an indication of physical-non-equilibrium. In contrast to the sieved soil, bromide was detected in the first effluent of the undisturbed soil,

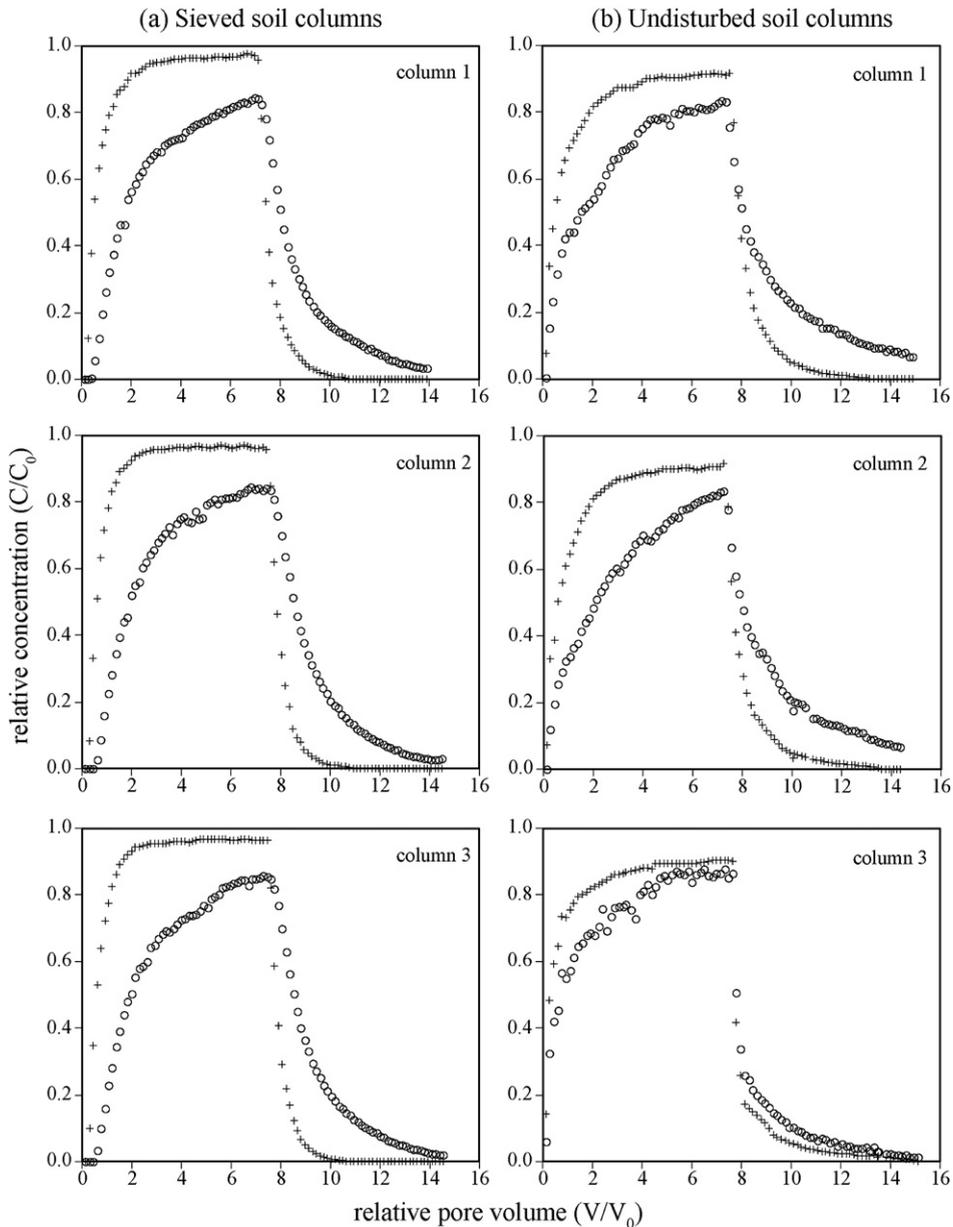


Fig. 1. Measured BTCs for bromide (+) and isoproturon (O) in the sieved (a) and undisturbed (b) soil columns.

indicating significant by-pass flow. The number of pore volumes eluted when the outflow concentration reached half of the input concentration was higher for the sieved soil (0.59 ± 0.03 pore volume) than for the undisturbed soil (0.47 ± 0.13 pore volume), indicating slower transport in the sieved soil. These observed differences emphasized the role of the soil structure and water saturation. Continuous macropores allowing for short-circuiting (recall that Br concentrations were found even in the first effluent samples) and rapid flow were likely

present in the undisturbed soil columns. The high biological activity due to earthworms and alfalfa roots that resulted in the presence of abundant macropores can explain the significant by-pass flow through the undisturbed soil columns. Indeed, the preferential flow pathways were highlighted using the brilliant blue dye, in soil slices from the undisturbed columns (Fig. 2). The dye was found mainly along the biopores, as similarly observed by Jorgensen et al. (2004). The bromide loss (10%) in the undisturbed soil, compared to the sieved

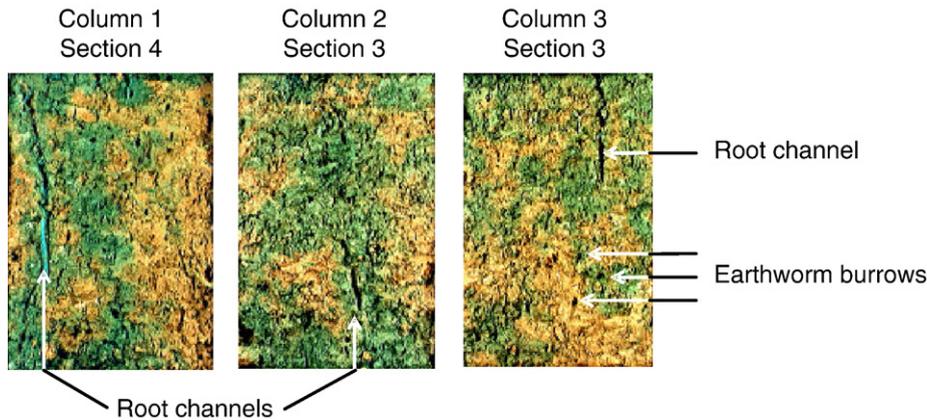


Fig. 2. Examples of vertical slices of the undisturbed soil in columns 1, 2 and 3 showing pathways stained by the brilliant blue dye.

soil, may be explained by bromide ‘trapped’ in surface-connected earthworm macropores that do not connect to the bottom of the undisturbed soil column.

The dual-permeability model (DP) was used to analyze the bromide BTCs. Note that the equilibrium transport model (CDE) failed to describe the bromide transport. The equilibrium transport model did not reproduce tailing for the sieved and undisturbed soil columns and provided unrealistically large dispersivities for the undisturbed soil columns (data not shown). The DP model described the bromide elution curves of the sieved soil columns well, whereas it overestimated the tailing of the bromide BTCs for the undisturbed soil columns (Fig. 3). We also tried to fit the bromide BTCs for the undisturbed columns with a more complex model (Pot et al., 2005), in which the liquid phase of the matrix region is further partitioned into mobile and immobile regions (data not shown). We could not, however, find better fits, although this model can in principle describe trapped bromide in the immobile region (Köhne et al., 2006) and thus explain the low recovery rates. The DP model was thus also used to describe the bromide transport in the undisturbed soil columns.

In both cases (sieved and undisturbed soil columns) the matrix conductivities were very small, indicating that the water fraction in the matrix domain was quasi stagnant. Note that, as in Pot et al. (2005), λ_{ma} was fixed to 1 cm. Average dispersivities in the fracture domain, λ_f , were 5.9 ± 1.1 cm and 10.9 ± 5.9 cm for the sieved and undisturbed soil columns, respectively (Table 2). Dispersivity values at the column scale are correlated with the pore-size distribution and the magnitude of the soil structure heterogeneity. High λ values indicate a heterogeneous pore system or long flow-path lengths (Shaw et al., 2000). Relatively lower λ values were estimated for the fracture region of the sieved soil columns,

indicating a relatively homogeneous porous medium. Pore-size distribution of these columns was indeed relative homogeneous since only 1–5 mm aggregates were used to pack the sieved soil columns. The difference in water saturation between the sieved and undisturbed soil columns could also explain these differences. Preferential flow significantly increased in the undisturbed soil columns, because biopores (mainly due to earthworm and alfalfa roots) were active for the water saturated conditions as indicated by patterns of the brilliant blue (Hutchinson et al., 2003). Higher dispersivities for the undisturbed soil columns were thus attributed to greater soil structure heterogeneity combined with a higher degree of water saturation.

Average values of w_f of 0.74 ± 0.03 and 0.44 ± 0.12 suggested that 26% and 56% of the total water were contained in the slow-flow matrix domains of the sieved and undisturbed soil columns, respectively, indicating a higher degree of non-equilibrium in the undisturbed soil. Our results are in agreement with findings of van Genuchten and Wierenga (1977), Nkedi-Kizza et al. (1984) and Veeh et al. (1994), who showed the presence of physical non-equilibrium transport also in sieved soil columns, contrary to other authors (e.g., Rao et al., 1979; Gamerdinger et al., 1990; Beigel and Di Pietro, 1999) who could describe their data using equilibrium models. The average value of the mass transfer rate coefficient α_s in the sieved (undisturbed) soil columns was $0.02 \pm 0.01 \text{ h}^{-1}$ ($0.10 \pm 0.05 \text{ h}^{-1}$), which resulted in a mean transfer time of the solute between the fracture and matrix domains (t_{α_s} , defined as $1/\alpha_s$) of 50 (10) hours. The mean travel time of the solute (t_t , defined as L/q) was 15 (16) hours for the sieved (undisturbed) soil columns. The longer transfer time of bromide (into the matrix domain) relative to its mean travel time in the column explained the tailing for the sieved soil columns.

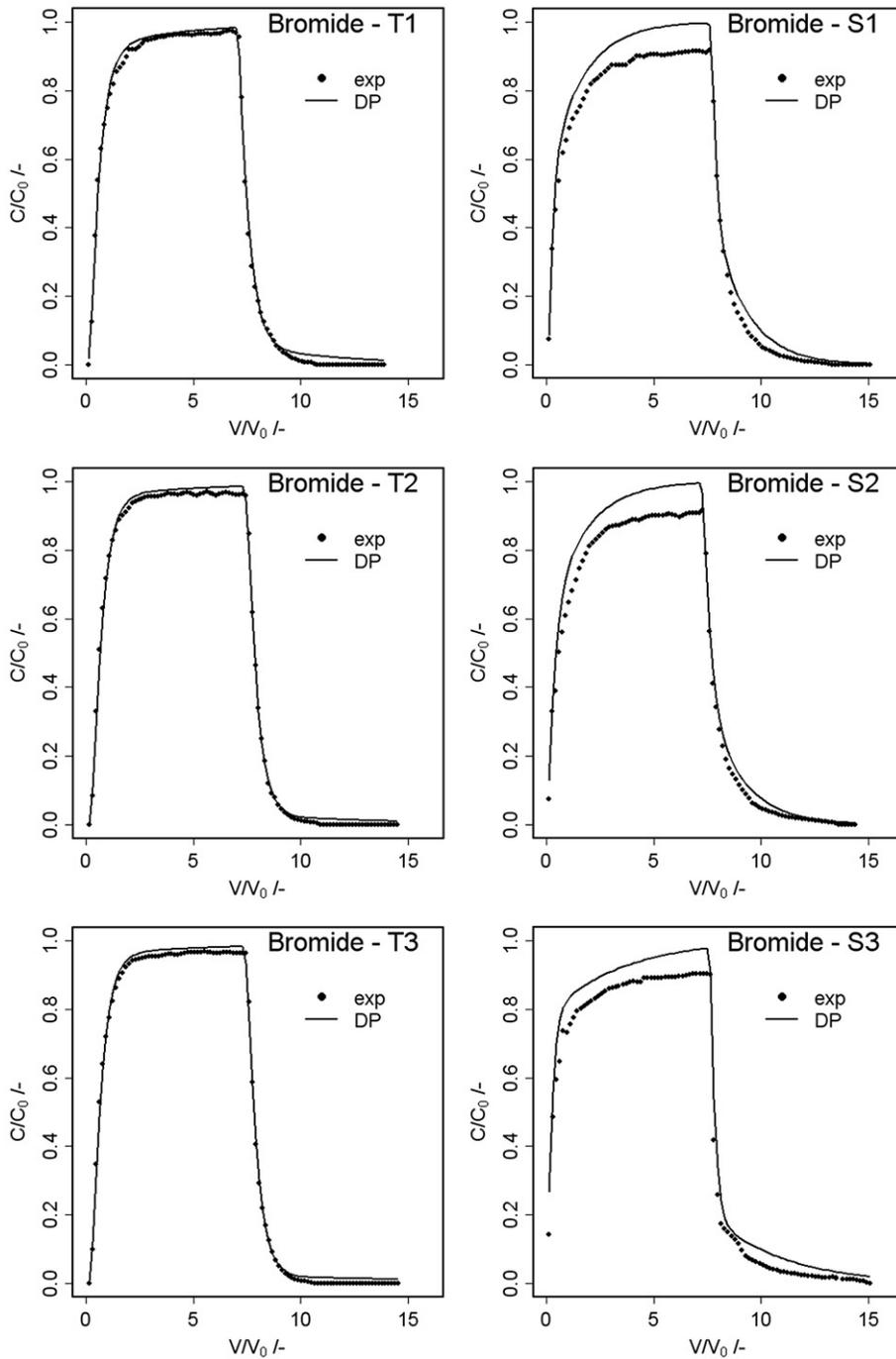


Fig. 3. Bromide BTCs measured and calculated for the sieved (T) and undisturbed (S) soil columns. Symbols are the experimental data and solid lines are the fits provided by the DP transport model.

Comparable solute transfer and mean travel times were found for the undisturbed soil columns, for which the tailing part of the BTCs was underestimated. In contact to the sieved soil, there was sufficient time for the bromide exchange from the fracture to the matrix domain in the undisturbed soil. This could partly be ex-

plained by water saturation of the undisturbed soil and the undersaturation of the sieved soil.

The basic assumption made in interpreting the dye patterns was that the more solution passes through a given point the more darkly stained that point is. Thus stained regions are interpreted as having relatively fast

Table 2

Predicted transport parameters (\pm Standard Error) for bromide using the dual-permeability model (DP) in HYDRUS-1D; * denotes fixed parameters, ** estimated parameters and *** parameters calculated from the estimated parameters

	q^* cm h ⁻¹	λ_{ma}^* cm	λ_f^{**} cm	θ_{ma}^{***} cm ³ cm ⁻³	θ_f^{***} cm ³ cm ⁻³	w_f^{**} –	α_s^{***} h ⁻¹	v_{ma}^{***} cm h ⁻¹	v_f^{***} cm h ⁻¹	$Q_{ma}^{***, a}$ –	$Q_f^{***, a}$ –	r^2
<i>Sieved soil columns, $\theta = 0.447$ cm³ cm⁻³</i>												
Column 1	1.294 (0.026)	1.00	7.24 (0.76)	0.129 (0.024)	0.318 (0.024)	0.7112 (0.053)	0.0301 (0.0450)	0.048 (0.556)	4.051 (1.730)	0.0048 (0.0048)	0.9952 (0.9988)	0.9988
Column 2	1.351 (0.016)	1.00	5.18 (0.38)	0.106 (0.005)	0.341 (0.005)	0.7621 (0.011)	0.0169 (0.0150)	0.149 (0.149)	3.920 (0.450)	0.0117 (0.0030)	0.9883 (0.2543)	0.9990
Column 3	1.353 (0.017)	1.00	5.33 (0.39)	0.119 (0.004)	(0.328)	0.7330 (0.0088)	0.0115 (0.0015)	0.180 (0.081)	4.064 (0.297)	0.0159 (0.0027)	0.9841 (0.1676)	0.9992
Mean	1.333 (0.034)	1.00	5.92 (1.15)	0.118 (0.012)	0.329 (0.012)	0.7354 (0.0255)	0.020 (0.010)	0.126 (0.069)	4.012 (0.080)	0.0108 (0.0056)	0.9892 (0.0056)	–
<i>Undisturbed soil columns, $\theta = 0.392$ cm³ cm⁻³</i>												
Column 1	1.270 (0.034)	1.00	5.31 (4.00)	0.220 (0.044)	0.172 (0.044)	0.4378 (0.1125)	0.1381 (0.1650)	0.051 (1.415)	7.335 (6.778)	0.0089 (0.0211)	0.9911 (2.3410)	0.9984
Column 2	1.212 (0.026)	1.00	17.03 (13.39)	0.174 (0.058)	0.218 (0.058)	0.5567 (0.1487)	0.1096 (0.1500)	0.170 (0.156)	5.419 (2.127)	0.0243 (0.0321)	0.9757 (1.2873)	0.9990
Column 3	1.273 (0.035)	1.00	10.39 (5.85)	0.266 (0.013)	0.126 (0.013)	0.3215 (0.0337)	0.0445 (0.0300)	0.171 (0.347)	9.740 (2.818)	0.0357 (0.0282)	0.9643 (0.7602)	0.9978
Mean	1.251 (0.036)	1.00	10.91 (5.88)	0.220 (0.046)	0.172 (0.046)	0.4386 (0.1176)	0.0974 (0.0480)	0.131 (0.069)	7.498 (2.165)	0.0230 (0.0134)	0.9770 (0.0134)	–

^a Q_{ma} and Q_f are the relative contributions of the matrix and fracture regions to the total flux, respectively.

flow, while unstained regions as having relatively slow flow. The volume of soil stained with the brilliant blue was estimated to be 51.7%, 55.4% and 49.7% for undisturbed soil columns 1, 2, and 3, respectively. Dye-stained areas were correlated with the ratio relating the mobile water content and the total water content by Shaw et al. (2000). Using their correlation, the ratios of the mobile water content to the total water content for undisturbed soil columns 1, 2, and 3 were calculated to be 0.46, 0.49 and 0.44, respectively. Thus, on average 54% of water may be assumed to be immobile in the undisturbed soil columns. This value was similar to the average value calculated from w_f values estimated using the DP model (56%, Table 2).

3.2.2. Isoproturon breakthrough curves

As for bromide, the isoproturon breakthrough curves observed in the undisturbed soil columns had earlier arrival times (0.2 ± 0.1 pore volume) than those observed in the sieved soil columns (0.5 ± 0.1 pore volume), confirming the faster solute transport in the undisturbed soil. The isoproturon BTCs were clearly asymmetric and exhibited significant tailing that indicated non-equilibrium transport processes. As in the bromide case, the shape of the isoproturon breakthrough curves was similar for the three sieved soil columns (Fig. 1a), and similar for columns 1 and 2 but different for column 3 in the undisturbed soil columns (Fig. 1b). The isoproturon average recovery rate was lower in the undisturbed soil

(79.0% \pm 0.9%) than in the sieved soil (86.1% \pm 2.4%), as similarly observed for bromide. Degradation and/or chemical non-equilibrium processes can explain lower recoveries for isoproturon than for bromide. Since the batch incubation experiments with the silty clay loam soil treated with isoproturon showed that degradation was negligible over 4 days, it can be hypothesized that isoproturon mass balance could be better explained by the slow diffusion of isoproturon into soil aggregates where it is less available for leaching and/or slow desorption (Beulke et al., 2004). In addition, the high sorption hysteresis found for isoproturon by several authors (Fouqué-Brouard and Fournier, 1996; Benoit et al., 1999; Boivin et al., 2005) may also explain lower recoveries for isoproturon than for bromide.

The dual-permeability models (DP) that either consider chemical equilibrium or chemical non-equilibrium were used to analyze the isoproturon BTCs. A first series of simulations was performed with the Freundlich adsorption (K_f , n) and degradation (μ) parameters fixed to their batch values (described in Section 3.1). The chemical equilibrium model did not describe the isoproturon BTCs well and it particularly failed in reproducing the early arrival (Fig. 4). The chemical non-equilibrium model provided rather good fits despite of systematically overestimating the adsorption and desorption tailings (Fig. 5, Table 4). In order to test both models, a second series of simulations was performed in which the Freundlich adsorption and degradation parameters were

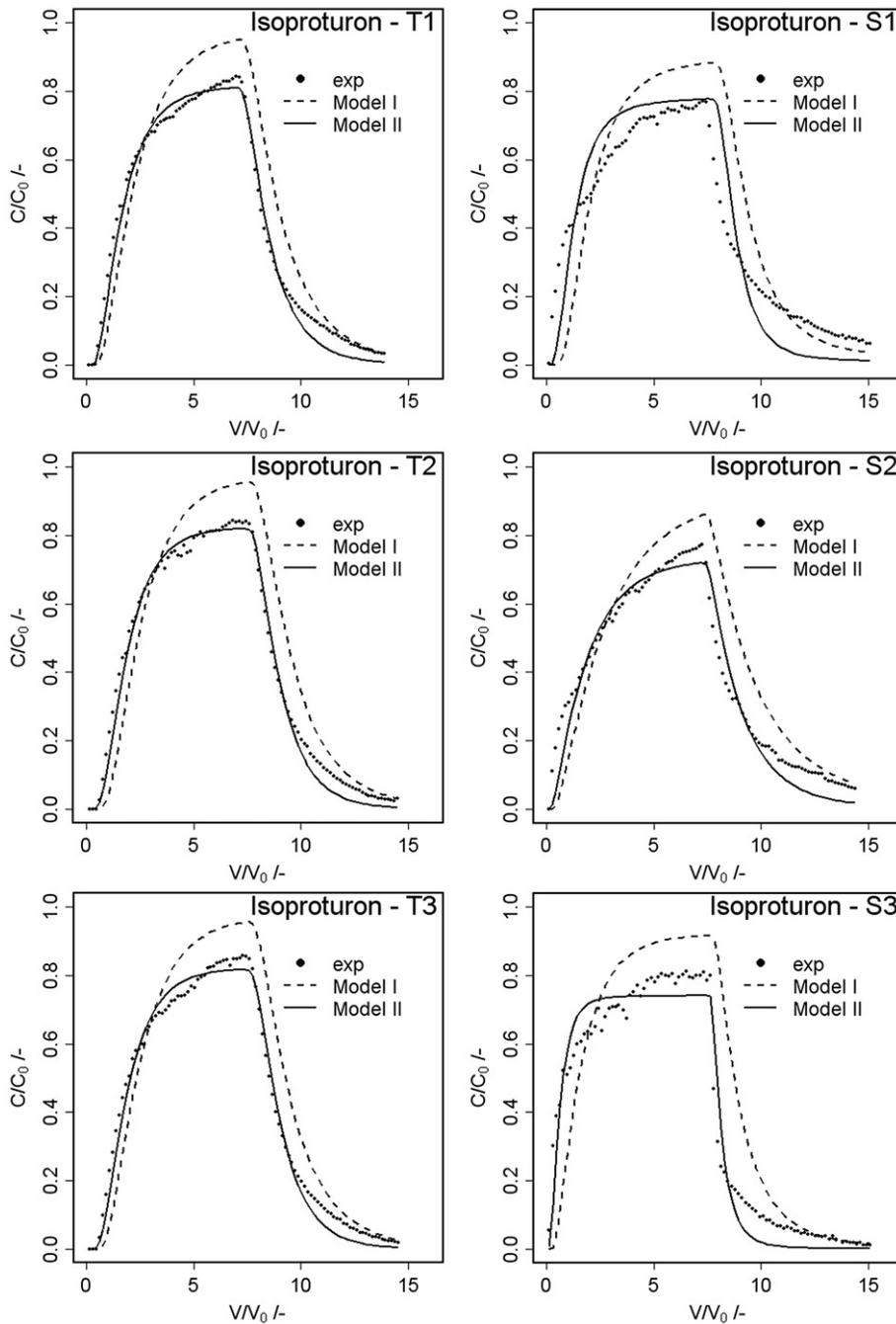


Fig. 4. Isoproturon BTCs measured and calculated for the sieved (T) and undisturbed (S) soil columns. Symbols are the experimental data, dashed lines and solid lines are the fits provided by the DP model combined with the equilibrium chemical model with K_f , n and μ_1 fixed to the batch values (Model I) and fitted (Model II), respectively.

optimized. Results showed that although the chemical equilibrium model was now able to reproduce the early arrival of isoproturon in the sieved soil columns, it underestimated the desorption tailing (Fig. 4, Table 3). The model could not reproduce the early solute arrival in the undisturbed soil columns, except for the third column

(Fig. 4, Table 3). The chemical non-equilibrium sorption model appeared to be the best model to describe isoproturon transport in both sieved and undisturbed soil columns (Fig. 5, Table 4). Comparing the estimated transport parameters, the chemical equilibrium model provided smaller K_f values than the batch data (Table 3).

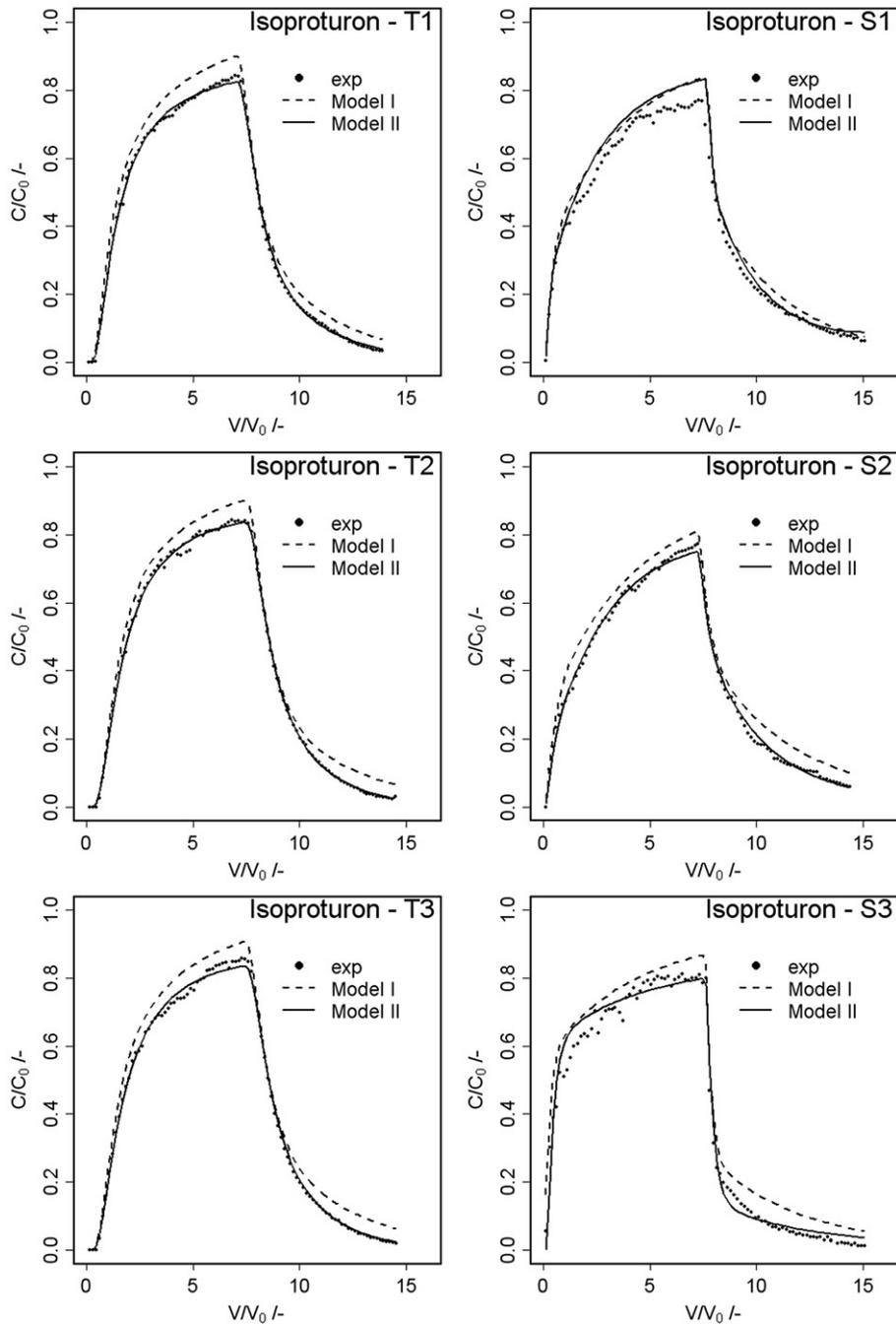


Fig. 5. Isoproturon BTCs measured and calculated for the sieved (T) and undisturbed (S) soil columns. Symbols are the experimental data, dashed lines and solid lines are the fits provided by the DP model combined with the non-equilibrium chemical model with K_f , n and μ_1 fixed to the batch values (Model I) and fitted (Model II), respectively.

Higher K_f values, although still smaller than the batch value, were estimated using the chemical non-equilibrium sorption model (Table 4). This was expected since the early arrival of isoproturon is explained in part by the non-equilibrium chemical transport processes. Lower estimated K_f values as compared to the batch value could be

explained by the fact that adsorption could not reach equilibrium under flow conditions, contrary to batch conditions.

The optimized degradation rate for both chemical equilibrium and non-equilibrium models was more than 10 times higher than the batch data value. This increase

Table 3

Predicted transport parameters (\pm Standard Error) for isotoproturon using the dual-permeability transport model in HYDRUS-1D combined with equilibrium chemical model and fitted sorption and degradation parameters; * denotes fixed parameters, ** estimated parameters and *** parameters calculated from the estimated parameters

	q^* cm h ⁻¹	K_f^{**} L kg ⁻¹	n^{**} –	μ_i^{**} h ⁻¹	DT_{50}^{***} d	r^2
<i>Sieved soil columns, $\theta = 0.447 \text{ cm}^3 \text{ cm}^{-3}$</i>						
Column 1	1.294 (0.026)	0.77 (0.02)	0.9185 (0.0400)	0.0393 (0.0016)	0.73 (0.03)	0.9942
Column 2	1.351 (0.016)	0.75 (0.01)	0.9544 (0.0350)	0.0363 (0.0014)	0.80 (0.03)	0.9952
Column 3	1.353 (0.017)	0.79 (0.01)	0.9606 (0.0383)	0.0377 (0.0015)	0.77 (0.03)	0.9931
Mean	1.333 (0.034)	0.77 (0.02)	0.9445 (0.0223)	0.0378 (0.0015)	0.77 (0.04)	–
<i>Undisturbed soil columns, $\theta = 0.392 \text{ cm}^3 \text{ cm}^{-3}$</i>						
Column 1	1.270 (0.034)	0.65 (0.03)	1.0016 (0.1386)	0.0584 (0.0077)	0.49 (0.07)	0.9503
Column 2	1.212 (0.026)	0.79 (0.02)	0.9817 (0.0541)	0.0705 (0.0046)	0.41 (0.03)	0.9749
Column 3	1.273 (0.035)	0.35 (0.03)	0.7752 (0.1440)	0.1185 (0.0075)	0.24 (0.02)	0.9705
Mean	1.251 (0.036)	0.60 (0.22)	0.9195 (0.1254)	0.0825 (0.0318)	0.38 (0.13)	–

allowed a better fit of the BTCs that were otherwise overestimated. Similar results were found with similar transport models in Pot et al. (2005) and Köhne et al. (2006). Since these models do not consider sorption

hysteresis, the degradation rate acts as a lumped parameter that encompassed both degradation and sorption that appears as irreversible at the time scale of the percolation experiments. Our modeling results may thus confirm the existence of sorption hysteresis for isotoproturon, which was also demonstrated in batch experiments by Benoit et al. (1999) and Boivin et al. (2005). Since the sorption hysteresis is not yet included in HYDRUS-1D, optimized degradation constants are often artificially increased, as also observed by Pot et al. (2005) and Köhne et al. (2006). The effect is particularly strong when chemical equilibrium is assumed. Altfelder and Streck (2006) and Sabbah et al. (2005) argued that sorption hysteresis is an artifact resulting from the use of an inadequate sorption model. Both Sabbah et al. (2005) and Altfelder and Streck (2006) demonstrated that the spherical diffusion model performed better than the first-order model when describing long-term desorption in batch experiments. Although the application of the spherical diffusion model could possibly lead to more realistic estimates of the degradation and sorption rate coefficients, we are not aware of any application, in which this model would be coupled with dual-permeability transport models.

Estimated transport parameters showed a higher degree of non-equilibrium sorption in the undisturbed soil than in the sieved soil. Indeed, a lower fraction of equilibrium sorption sites in the fracture region was found in the undisturbed soil columns ($f_r = 0.13 \pm 0.09$)

Table 4

Predicted transport parameters (\pm Standard Error) for isotoproturon using the dual-permeability transport model in HYDRUS-1D combined with non-equilibrium chemical model (instantaneous and first-order kinetic retention) with fitted sorption and degradation parameter; * denotes fixed parameters, ** predicted parameters and *** parameters calculated from the estimated parameters

	q^* cm h ⁻¹	K_f^{**} L kg ⁻¹	n^{**} –	f_{ma}^* –	f_r^{**} –	α_k^{**} h ⁻¹	μ_i^{**} h ⁻¹	DT_{50}^{***} d	r^2
<i>Sieved soil columns, $\theta = 0.447 \text{ cm}^3 \text{ cm}^{-3}$</i>									
Column 1	1.294 (0.026)	0.96 (0.02)	0.904 (0.015)	0.500	0.585 (0.010)	0.0741 (0.0053)	0.0275 (0.0008)	1.05 (0.03)	0.9980
Column 2	1.351 (0.016)	0.86 (0.01)	0.950 (0.012)	0.500	0.622 (0.010)	0.1001 (0.0066)	0.0273 (0.0005)	1.06 (0.02)	0.9976
Column 3	1.353 (0.017)	0.90 (0.01)	0.947 (0.018)	0.500	0.619 (0.016)	0.1072 (0.0107)	0.0284 (0.0008)	1.02 (0.03)	0.9975
Mean	1.333 (0.034)	0.91 (0.05)	0.934 (0.026)	0.500	0.609 (0.021)	0.0938 (0.0174)	0.0277 (0.0006)	1.04 (0.02)	–
<i>Undisturbed soil columns, $\theta = 0.392 \text{ cm}^3 \text{ cm}^{-3}$</i>									
Column 1	1.270 (0.034)	0.86 (0.01)	0.835 (0.003)	0.500	0.028 (0.005)	0.1339 (0.0055)	0.0196 (0.0008)	1.47 (0.06)	0.9969
Column 2	1.212 (0.026)	0.89 (0.01)	0.802 (0.021)	0.500	0.201 (0.019)	0.1411 (0.0081)	0.0437 (0.0018)	0.66 (0.03)	0.9964
Column 3	1.273 (0.035)	0.90 (0.41)	0.515 (0.057)	0.500	0.171 (0.061)	0.0465 (0.0099)	0.0510 (0.0188)	0.57 (0.21)	0.9894
Mean	1.251 (0.036)	0.88 (0.02)	0.717 (0.176)	0.500	0.133 (0.092)	0.1072 (0.0527)	0.0381 (0.0164)	0.90 (0.50)	–

than in the sieved soil columns ($f_f=0.61\pm 0.02$). Similar kinetic sorption rates were found in both sets of columns ($\alpha_k=0.09\pm 0.02\text{ h}^{-1}$ and $0.11\pm 0.05\text{ h}^{-1}$, respectively) (Table 4). This could be explained by a higher accessibility of sorption sites in the sieved soil due to the disrupted soil structure as well as due to shorter time transfer. Note that results were found to be insensitive to the fraction of equilibrium sorption sites in the matrix region, f_{ma} . The matrix region was a quasi stagnant region and thus chemical equilibrium sorption was sufficient in explaining sorption in the matrix. Attempts to estimate f_{ma} resulted in very broad confidence intervals and thus this parameter was fixed to a prescribed value of 0.5 as in Pot et al. (2005). Furthermore, irreversible sorption appeared to be more important in the undisturbed soil columns ($\mu_1=0.038\pm 0.016\text{ h}^{-1}$) than in the sieved soil columns ($\mu_1=0.028\pm 0.001\text{ h}^{-1}$).

4. Conclusion

The physical non-equilibrium dual-permeability model described the bromide BTCs for the three sieved soil columns very well. This model was also found to best approximate the bromide BTCs of the undisturbed soil columns. HYDRUS-1D analysis showed that the transport regime in the sieved soil with small sieved aggregates demonstrated more physical equilibrium with more available equilibrium sorption sites than the natural undisturbed soil. Physical non-equilibrium in the undisturbed soil columns was attributed to the heterogeneity of the soil structure and higher water saturation. Biopores were activated at higher saturations, as shown by both modeling and color patterns of the brilliant blue, and acted as preferential flow paths.

The isoproturon BTCs were also well modeled by the dual-permeability two-site sorption model. The optimized chemical transfer rates were the same for the disturbed and undisturbed soils, indicating that chemical characteristics did not change by sieving the soil. However, a higher degree of chemical non-equilibrium was found in the undisturbed soil columns than in the sieved soil columns. Optimized degradation rates were almost ten times higher in the soil columns than in the batch studies. This overestimation of optimized degradation rates may have several explanations. These include a) the existence of sorption hysteresis, b) the formation of non-extractable residues of isoproturon, or c) the inadequacy of the first-order rate sorption model as compared to the spherical diffusion model. The numerical model could thus be improved by including these processes and concepts to provide more realistic degradation rates.

Our laboratory column experiments carried out at similar rainfall intensities demonstrated larger physical and chemical non-equilibria in the saturated undisturbed soil columns than in the unsaturated sieved soil columns. The undisturbed soil exhibited more significant preferential flow and lower fraction of equilibrium sorption sites than the sieved soil, which resulted in faster transport of isoproturon through the undisturbed soil. In addition, the undisturbed soil columns reflected the spatial heterogeneity of the soil structure at the field scale. Experiments carried out on undisturbed soil columns may thus be irreproducible and may vary from column to column. Further investigations concerning the effects of the spatial heterogeneity at the field scale on the pesticides transport are thus needed.

Acknowledgements

This work was financed by the French Ministry of Research (Programme National de Recherche Sols et Erosion). The authors would like to thank Françoise Gasquez and Thérèse Choné of CNRS (Dijon, 21) for their technical contributions. The terrestrial Sciences Program of the Army Research Office (Terrestrial Processes and Landscape Dynamics and Terrestrial System Modeling and Model Integration) provided support to Dr. Jirka Simůnek.

References

- Altfelder, S., Streck, T., 2006. Capability and limitations of first-order and diffusion approaches to describe long-term sorption of chlortoluron in soil. *J. Contam. Hydrol.* 86, 279–298.
- Andreini, M.S., Steenhuis, T.S., 1990. Preferential paths of flow under conventional and conservation tillage. *Geoderma* 46, 85–102.
- Beigel, C., Di Pietro, L., 1999. Transport of triticonazole in homogeneous soil columns: influence of nonequilibrium sorption. *Soil Sci. Soc. Am. J.* 63, 1077–1086.
- Benoit, P., Barriuso, E., Vidon, Ph., Real, B., 1999. Isoproturon sorption and degradation in a soil from grassed buffer strip. *J. Environ. Qual.* 28, 121–129.
- Beulke, S., Brown, C.D., Fryer, C.J., van Beinum, W., 2004. Influence of kinetic sorption and diffusion on pesticide movement through aggregated soils. *Chemosphere* 57, 481–490.
- Boivin, A., Cherrier, R., Schiavon, M., 2005. A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. *Chemosphere* 61, 668–676.
- Bowman, R.S., 1984. Analysis of soil extracts for inorganic and organic tracer anions via high performance liquid chromatography. *J. Chromatogr.* 285, 467–477.
- Brown, C.D., Hodgkinson, R.A., Rose, D.A., Syers, J.K., Wilcockson, S.J., 1995. Movement of pesticides to surface waters from a heavy clay soil. *Pestic. Sci.* 43, 131–140.
- Cassel, D.K., Krueger, T.H., Shroer, F.W., Norum, E.B., 1974. Solute movement through disturbed and undisturbed soil cores. *Soil Sci. Soc. Am. Proc.* 38, 36–40.

- Danielson, R.E., Sutherland, P.L., 1986. In: Klute, A. (Ed.), *Methods of Soil Analysis, Part I. Physical and Mineralogical Methods*, 2nd edition. Agronomy monograph, vol. 9, pp. 443–461.
- Dousset, S., Mouvet, C., Schiavon, M., 1995. Leaching of atrazine and some of its metabolites in undisturbed field lysimeters of three soils relation to the physico-chemical properties of three soils. *Chemosphere* 30 (3), 511–524.
- European Community Council, 1998. Directive concerning the quality of water intended for human consumption. Official Journal of the European Communities, 98/83 EEC L330. Office for Official Publications of the European Communities, Luxembourg, L, pp. 32–54.
- FAO, 1998. World reference base for soil resources. ISSS-ISRIC-FAO, FAO, Rome, Italy. *World Soil Resources Reports*, vol. 84. 109 pp.
- Flury, M., Flühler, H., 1994. Brilliant blue FCF as a dye tracer for solute transport studies — a toxicological overview. *J. Environ. Qual.* 23, 1108–1112.
- Fouqué-Brouard, C.M., Fournier, J.M., 1996. Adsorption–desorption and leaching of phenyl-urea herbicides on soils. *Talanta* 43, 1793–1802.
- Gamerding, A.P., Wagenet, R.J., van Genuchten, M.Th., 1990. Application of two-site/ two-region models for studying simultaneous nonequilibrium transport and degradation of pesticides. *Soil Sci. Soc. Am. J.* 54, 957–963.
- Garmouma, M., Teil, M.J., Blanchard, M., Chevreuil, M., 1998. Spatial and temporal variations of herbicide (triazines and phenylureas) concentrations in the catchment basin of the Marne river (France). *Sci. Total Environ.* 224, 93–107.
- Gerke, H.H., van Genuchten, M.Th., 1993. A dual-porosity model for simulating the preferential movement of water and solutes in structured porous media. *Water Resour. Res.* 29, 305–319.
- German-Heins, J., Flury, M., 2000. Sorption of Brilliant Blue FCF in Soils as Affected by pH and Ionic Strength. *Geoderma* 97, 87–101.
- Griessbach, E.F.C., Copin, A., Deleu, R., Dreze, P., 1998. Mobility of a silicone polyether studied by leaching experiments through disturbed and undisturbed soil columns. *Sci. Total Environ.* 221, 159–169.
- Haria, A.H., Johnson, A.C., Bell, J.P., Batchelor, C.H., 1994. Water movement and isoproturon behavior in a drained heavy clay soil: 1. preferential flow processes. *J. Hydrol.* 163, 203–216.
- Harris, G.L., Nicholls, P.H., Bailey, S.W., Howse, K.R., Mason, D.J., 1994. Factors influencing the loss of pesticides in drainage from a cracking clay soil. *J. Hydrol.* 159, 235–253.
- Heppel, C.M., Burt, T.P., Williams, R.J., Haria, A.H., 1999. The influence of hydrological pathways on the transport of the herbicide, isoproturon, through an underdrained clay soil. *Water Sci. Technol.* 39, 77–84.
- House, W.A., Leach, D., Long, J.L.A., Cranwell, P., Smith, C., Bharwaj, L., Meharg, A., Ryland, G., Orr, D.O., Wright, J., 1997. Micro-organic compounds in the Humber rivers. *Sci. Total Environ.* 194/195, 357–371.
- Hutchinson, J.M., Seaman, J.C., Aburime, S.A., Radcliffe, D.E., 2003. Chromate transport and retention in variably saturated soil columns. *Vadose Zone J.* 2, 702–714.
- IFEN, 2006. Les pesticides dans les eaux. Données 2003 et 2004. Les dossiers, vol. 5. 38 pp.
- Johnson, A.C., Haria, A.H., Bhardwaj, C.L., Volkner, C., Batchelor, C.H., Walker, A., 1994. Water movement and isoproturon behavior in a drained heavy clay soil: 2. persistence and transport. *J. Hydrol.* 163, 217–231.
- Jorgensen, P.R., Hestrup, T., Urup, J., Seifert, D., 2004. Modeling of non-reactive solute transport in fractured clayey till during variable flow rate and time. *J. Contam. Hydrol.* 68, 193–216.
- Jury, W.A., Spencer, W.F., Framer, W.J., 1983. Behavior assessment model for trace organics in soil: I. model description. *J. Environ. Qual.* 12, 558–564.
- Kasteel, R., Vogel, H.J., Roth, K., 2002. Effect of non-linear adsorption on the transport behaviour of brilliant blue in a field soil. *Eur. J. Soil Sci.* 53, 231–240.
- Ketelsen, H., Meyer-Windel, S., 1999. Adsorption of brilliant blue FCF by soils. *Geoderma* 90, 131–145.
- Köhne, J.M., Köhne, S., Šimůnek, J., 2006. Multi-process herbicide transport in structured soil columns: experiments and model analysis. *J. Contam. Hydrol.* 85, 1–32.
- Lennartz, B., 1999. Variation of herbicide transport parameters within a single field and its relation to water flux and soil properties. *Geoderma* 91, 327–345.
- Lennartz, B., Kamra, S.K., 1998. Temporal variability of solute transport under vadose zone conditions. *Hydrol. Process.* 12, 1939–1949.
- Marquardt, D.W., 1963. An algorithm for least-squares estimation of nonlinear parameters. *J. Soc. Ind. Appl. Math.* 11, 431–441.
- Nemeth-Konda, L., Füleky, Gy., Morovjan, Gy., Csokan, P., 2002. Sorption behaviour of acetochlor, atrazine, carbendazim, diazinon, imidacloprid and isoproturon on Hungarian agricultural soil. *Chemosphere* 48, 545–552.
- Nkedi-Kizza, P., Biggar, J.W., Selim, H.M., van Genuchten, M.Th., Wierenga, P.J., Davidson, J.M., Nielsen, D.R., 1984. On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated oxisol. *Water Resour. Res.* 20, 1123–1130.
- Nobles, M.M., Wilding, L.P., McInnes, K.J., 2004. Submicroscopic measurements of tracer distribution related to surface features of soil aggregates. *Geoderma* 123, 83–97.
- Official Journal of the European Communities. 2001. Decision n° 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. L331, 1–5.
- Pantani, O.L., Dousset, S., Schiavon, M., Fusi, P., 1997. Adsorption of isoproturon on homoionic clays. *Chemosphere* 35, 2619–2626.
- Parsons, R., 1959. *Handbook of Electrochemical Constants*. Academic Press, New York. 113 pp.
- Perillo, C.A., Gupta, S.C., Nater, E.A., Moncrief, J.F., 1998. Flow velocity effects on the retardation of FD and C blue no 1 food dye in soil. *Soil Sci. Soc. Am. J.* 62, 39–45.
- Pieuchot, M., Perrin-Ganier, C., Portal, J.M., Schiavon, M., 1996. Study on the mineralization and degradation of isoproturon in three soils. *Chemosphere* 33, 467–478.
- Pot, V., Šimůnek, J., Benoit, P., Coquet, Y., Yra, A., Martinez-Cordon, M.J., 2005. Impact of rainfall intensity on the transport of two herbicides in undisturbed grassed filter strip soil cores. *J. Contam. Hydrol.* 81, 63–88.
- Rao, P.S.C., Davidson, J.M., Jessup, R.E., Selim, H.M., 1979. Evaluation of conceptual model for describing nonequilibrium adsorption–desorption of pesticides during steady-flow in soils. *Soil Sci. Soc. Am. J.* 43, 22–28.
- Renault, P., Mohrath, D., Gaudu, J.C., Fumal, J.C., 1998. Air pressure fluctuations in a prairie soil. *Soil Sci. Soc. Am. J.* 62, 553–563.
- Sabbah, I., Ball, W.P., Young, D.F., Bouwer, E.J., 2005. Misinterpretations in the modelling of contaminant desorption from environmental solids when equilibrium conditions are not fully understood. *Environ. Eng. Sci.* 22, 350–366.
- Sadeghi, A.M., Isensee, A.R., Shirmohammadi, A., 2000. Influence of soil texture and tillage on herbicide transport. *Chemosphere* 41, 1327–1332.

- Selim, H.M., Davidson, J.M., Rao, P.S.C., 1977. Transport of reactive solutes through multilayered soils. *Soil Sci. Soc. Am. J.* 41, 3–10.
- Seyfried, M.S., Rao, P.S.C., 1986. Solute transport in undisturbed columns of an aggregated tropical soil: preferential flow effects. *Soil Sci. Soc. Am. J.* 51, 1434–1444.
- Shaw, J.N., West, L.T., Radcliffe, D.E., Bosch, D.D., 2000. Preferential flow and pedotransfer functions for transport properties in sandy kandiudults. *Soil Sci. Soc. Am. J.* 64, 670–678.
- Šimůnek, J., Šejna, M., van Genuchten, M.Th., 1998. The HYDRUS-1D Software Package For simulating the One-dimensional Movement of Water, Heat, and Multiple Solutes in Variably-saturated Media. Version 2.0, *IGWMC-TPS-70*. International Ground Water Modeling Center, Colorado School of Mines, Golden, Colorado. 202 pp.
- Šimůnek, J., Jarvis, N.J., van Genuchten, M.Th., Gärdenäs, A., 2003. Review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone. *J. Hydrol.* 272, 14–35.
- Spark, K.M., Swift, R.S., 2002. Effect of soil composition and dissolved organic matter on pesticide sorption. *Sci. Total Environ.* 298, 147–161.
- Spliid, N.H., Koppen, B., 1998. Occurrence of pesticides in Danish shallow ground water. *Chemosphere* 37, 1307–1316.
- Starret, S.K., Christains, N.E., Austin, A.A., 1996. Comparing dispersivities and soil chloride concentrations of turfgrass-covered undisturbed and disturbed soil columns. *J. Hydrol.* 180, 21–29.
- Tomlin, C.D.S., 1997. *The Pesticide Manual*, 11th ed. British Crop Protection Council and The Royal Society of Chemistry, UK.
- van Genuchten, M.Th., Wagenet, R.J., 1989. Two-site/two-region models for pesticide transport and degradation: theoretical development and analytical solutions. *Soil Sci. Soc. Am. J.* 53, 1303–1310.
- van Genuchten, M.Th., Wierenga, P.J., 1977. Mass transfer studies in sorbing porous media II. Experimental evaluation with tritium ($^3\text{H}_2\text{O}$). *Soil Sci. Soc. Am. J.* 41, 272–285.
- Veeh, R.H., Inskeep, W.P., Roe, F.L., Fergusson, A.H., 1994. Transport of chlorosulfuron through soils columns. *J. Environ. Qual.* 23, 542–549.
- Walker, A., Turner, I.J., Cullington, J.E., Welch, S.J., 1999. Aspects of the adsorption and degradation of isoproturon in a heavy clay soil. *Soil Use Manage.* 15, 9–13.
- Walker, A., Jurado-Exposito, M., Bending, G.D., Smith, V.J.R., 2001. Spatial variability in the degradation rate of isoproturon in soil. *Environ. Pollut.* 111, 407–415.
- Weast, R.C., 1985. *Handbook of Chemistry and Physics*, 66th edition. CRC Press, Boca Raton, Florida.
- Zehe, E., Flüher, H., 2001. Preferential transport of isoproturon at a plot scale tile-drained site. *J. Hydrol.* 247, 100–115.
- Zsolnay, A., 1991. The use of small columns to estimate the effect of soil structure on transport. *Chemosphere* 23, 107–115.