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Journal of Contaminant Hydrology 48 (2001) 189–212

JOURNAL OF
Contaminant
Hydrology

www.elsevier.com/locate/jconhyd

Evaluating non-equilibrium solute transport in small soil columns

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Received 27 July 1999; received in revised form 7 June 2000; accepted 25 August 2000

Abstract

Displacement studies on leaching of bromide and two pesticides (atrazine and isoproturon) were conducted under unsaturated steady state flow conditions in 24 small undisturbed soil columns (5.7 cm in diameter and 10 cm long) each collected from two sites differing in soil structure and organic carbon content in North Germany. There were large and irregular variabilities in the characteristics of both soils, as well as in the shapes of breakthrough curves (BTCs) of different columns, including some with early breakthrough and increased tailing, qualitatively indicating the presence of preferential flow. It was estimated that one preferential flow column (PFC) at site A, and four at site B, contributed, respectively to 11% and 58% of the accumulated leached fraction and to more than 80% of the maximum observed standard deviation (SD) in the field-scale concentration and mass flux of pesticides at two sites. The bromide BTCs of two sites were analyzed with the equilibrium convection–dispersion equation (CDE) and a non-equilibrium two-region/mobile–immobile model. Transport parameters of these models for individual BTCs were determined using a curve fitting program, CXTFIT, and by the time moment method. For the CDE based equilibrium model, the mean values of retardation factor, R , considered separately for all columns, PFCs or non-preferential flow columns (NPFCs) were comparable for the two methods; significant differences were observed in the values of dispersion coefficients of two sites

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using the two estimation methods. It was inferred from the estimated parameters of non-equilibrium model that 5–12% of water at site A, and 12% at site B, was immobile during displacement in NPFCs. The corresponding values for PFCs of two sites were much larger, ranging from 25% to 51% by CXTFIT and from 24% to 72% by the moment method, suggesting the role of certain mechanisms other than immobile water in higher degrees of non-equilibrium in these columns. Peclet numbers in PFCs of both sites were consistently smaller than five, indicating the inadequacy of the non-equilibrium model to incorporate the effect of all forms of non-equilibrium in PFCs. Overall, the BTCs of individual NPFCs, PFCs and of field average concentration at the two sites were better reproduced with parameters obtained from CXTFIT than by the moment method. The moment method failed to capture the peak concentrations in PFCs, but tended to describe the desorption and tail branches of BTCs better than the curve fitting approach. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Solute transport; Pesticides; Breakthrough curves; Preferential flow; Time moments; Convection dispersion equation

1. Introduction

Preferential flow is a generic term used to describe a range of physical non-equilibrium flow processes occurring under a variety of circumstances. In fine-textured soils, macropores (e.g. shrinkage cracks, earthworm channels, and root holes) operate as high-conductivity flow pathways and cause rapid movement of solutes through soil to occasionally induce severe groundwater contamination (Beven and Germann, 1982). Preferential flow is not confined to heavy clay soils, which have significant structural voids, although they represent the worst case. Based on the evidence of dye tracer studies of Kung (1990a,b), Ghodrati and Jury (1990) and Flury et al. (1994), it seems that preferential flow may also occur in unstructured sandy soils due to textural variations in horizons, solute funneling around small discrete lenses of coarse sand spread within the finer sand matrix, or by water repellency. This type of flow may also arise from fluid instabilities created by density or viscosity differences between the resident and invading fluids (Krupp and Elrick, 1969; Hillel and Baker, 1988) or due to local variations in the rate of water and solute input at the soil surface. Such flows are unpredictable, since these are triggered by small-scale heterogeneity, difficult to be captured by conventional sampling methods in the unsaturated zone.

Under field conditions, an application of a tracer pulse often produces a wide spectrum of solute breakthrough curves (BTCs) displaying small or pronounced tailing, and sometimes double or multiple peaks (Butters et al., 1989; Ellsworth et al., 1991; Roth et al., 1991). Field-scale solute transport studies are, however, scarce because of difficulty in precisely quantifying the mass balance for the considered control volume and limitation of available measurement devices to characterize in situ transport and retention properties in soil, besides huge data and funding requirements. Undisturbed soil columns collected at a certain grid from an experimental site and used for displacement studies in the laboratory have often been used to characterize the field-scale solute behavior. In this approach, the concentration distribution and associated transport parameters of individual (local) BTCs are assumed to encompass the variability in space

and time, while the field-scale solute transport is derived by statistically averaging the local BTCs or transport parameters (Gelhar and Axness, 1983). Most of the laboratory studies under unsaturated conditions have been conducted in soil columns of small (sometimes < 10 cm) lateral dimension. Studies with columns of larger diameter have only recently become popular (Jardine et al., 1988; Bootlink and Bouma, 1991; Singh and Kanwar, 1991; Tindall et al., 1992; Sassner et al., 1994).

Asymmetric BTCs with early peaks and increased tailing in laboratory column or field studies reflect qualitatively the occurrence of preferential flow. Such features are often attributed to non-equilibrium mass exchange between regions of different mobility (Kissel et al., 1973) and are simulated by models which divide the dissolved phase into a mobile and immobile region. The transport parameters of these models, derived from BTCs of laboratory column studies by applying a non-linear least squares inversion program CXTFIT (Parker and Van Genuchten, 1984; Toride et al., 1995) or time moment analysis (Jury and Sposito, 1985), are generally used for interpretation of the results at the field-scale.

In this study, the soil column approach was used to study the movement of bromide and pesticides in two soils differing in soil structure and organic carbon. Assuming that a large number of (even) small columns will sample the heterogeneity of a field better than a small number of large columns, displacement studies under unsaturated steady state flow conditions were conducted in 24 undisturbed small soil columns (5.7 cm in diameter and 10 cm long) each collected from two sites at a regular grid. Columns with preferential flow features were isolated and their contribution to field-scale transport of bromide and pesticides were evaluated. The bromide BTCs of two sites were analyzed with the classical equilibrium convection–dispersion equation (CDE) and a non-equilibrium two-region/mobile–immobile model (Van Genuchten and Wierenga, 1976). Transport parameters of these models were determined for individual BTCs using CXTFIT, and by time moment method and were analyzed separately for all columns, preferential flow columns (PFCs) or non-preferential flow columns (NPFCs). Specifically, results relating to the contribution of PFCs to overall variance of the field-scale solute concentration and mass flux and comparison of parameters of two models estimated by curve fitting (CXTFIT) and moment methods are discussed in this paper.

2. Material and methods

2.1. Time moment analysis

The classical equilibrium model for one-dimensional solute transport during steady state flow in a homogeneous porous medium can be expressed in dimensionless form of a CDE as

$$R \frac{\partial C}{\partial T} = \frac{1}{P} \frac{\partial^2 C}{\partial X^2} - \frac{\partial C}{\partial X} \quad (1)$$

where C is the dimensionless concentration, X is dimensionless distance, T is dimensionless time (pore volumes), R is the retardation factor, and P is the column Peclet number as follows:

$$C = c/c_0, \quad (2a)$$

$$X = z/L, \quad (2b)$$

$$T = vt/L = qt/\theta L \quad (2c)$$

$$R = 1 + \rho k_d/\theta, \quad (3a)$$

$$P = vL/D \quad (3b)$$

where c and c_0 are the solute concentration as a function of time and space and input concentration, respectively ($M L^{-3}$), z and L are distance and column length (L), t is time (T), $v (= q/\theta)$ is the mean pore water velocity ($L T^{-1}$), q is Darcy water flux ($L T^{-1}$), ρ is soil bulk density ($M L^{-3}$), k_d is the linear adsorption coefficient (LM^{-3}), θ is the volumetric water content ($L^3 L^{-3}$), and D is the dispersion coefficient ($L^2 T^{-1}$). The equilibrium model, henceforth referred to as model I, contains two parameters, R and P (or related D).

The non-equilibrium model assumes the liquid phase to be partitioned into a mobile and an immobile region, with water flow restricted to the mobile region. Solute exchange between mobile and immobile regions is modeled as a first-order diffusion process. The model (Van Genuchten and Wierenga, 1976) in dimensionless form can be given by

$$\beta R \frac{\partial C_m}{\partial T} + (1 - \beta) R \frac{\partial C_{im}}{\partial T} = \frac{1}{P_m} \frac{\partial^2 C_m}{\partial X^2} - \frac{\partial C_m}{\partial X} \quad (4a)$$

$$(1 - \beta) R \frac{\partial C_{im}}{\partial T} = \omega (C - C_{im}) \quad (4b)$$

where

$$P_m = v_m L/D_m \quad (5a)$$

$$\beta = (\theta_m + \rho f k_d)/(\theta + \rho k_d) \quad (5b)$$

$$\omega = \alpha L/q \quad (6)$$

The subscripts m and im in Eqs. (4a), (4b), (5a) and (5b), refer to the mobile and immobile regions, respectively, v_m is the mean pore water velocity of the mobile region ($v_m = q/\theta_m$), f is the fraction of adsorption sites in the mobile region (dimensionless), α is the first-order mass transfer coefficient between mobile and immobile region (T^{-1}), D_m is the dispersion coefficient of the mobile region, while θ_m and θ_{im} are the volumetric water contents of the mobile and immobile regions, respectively ($\theta = \theta_m + \theta_{im}$). All concentrations C , C_m , and C_{im} are relative concentrations normalized with respect to the input concentration c_0 . The non-equilibrium model, further denoted as model II, contains four parameters R , P_m (or related D_m), β and ω , and simplifies to the first model in absence of immobile water. Following Nkedi-Kizza et al. (1983) and Wierenga and Van Genuchten (1989), among others, we assumed equal retardation

factors for the two regions and the fraction f equal to θ_m/θ . Under these assumptions, β and $1 - \beta$ denote the relative fractions of mobile and immobile water, respectively.

Time moment analysis was applied to characterize experimental BTCs in terms of mean breakthrough time and degrees of spreading and asymmetry. The approach has been used earlier to test the validity of the local equilibrium assumption (Valocchi, 1985), and to study the effect of binary and ternary exchange (Leij and Dane, 1992) and soil layering and inlet boundary conditions (Leij and Dane, 1991) on solute transport. In dimensionless form, the temporal moments, M_p , are defined as

$$M_p = \int_0^{\infty} T^p c(Z, T) / c_0 dT \quad p = 0, 1, 2, \dots \quad (7)$$

where Z is the dimensionless space coordinate, T is the dimensionless time expressed as pore volumes ($T = vt/L$), v is the average pore water velocity ($L T^{-1}$), t is the time (T), L is the column length (L), c and c_0 are solute concentrations in the liquid phase and of the influent solute pulse, respectively ($M L^{-3}$). The subscript p is the order of the moment. The zeroth moment, M_0 , equals the mass of solute eluted from the column, while the first, second, third, and fourth moments can be used to characterize the mean, variance, skewness, and kurtosis, respectively of the BTCs. In addition to the absolute moments defined above, normalized, μ'_p , and central moments, μ_p , are often used.

$$\mu'_p = M_p / M_0 \quad (8)$$

$$\mu_p = \frac{1}{M_0} \int_0^{\infty} (T - \mu'_1)^p C(Z, T) / C_0 dT \quad p = 0, 1, 2, \dots \quad (9)$$

The first normalized moment, μ'_1 , yields the mean breakthrough time. The second central moment, μ_2 , quantifies the variance, a measure of the average spread of the BTC relative to the mean breakthrough time. The third central moment characterizes the asymmetry of the BTC. The degree of asymmetry can also be expressed in terms of a non-dimensional parameter, skewness S , defined as

$$S = \mu_3 / \mu_2^{3/2} \quad (10)$$

A positive value of skewness signifies a distribution with an asymmetrical tail extending towards the right, i.e. higher values of T , while a negative value signifies a distribution whose tail extends towards lower values of T . Kurtosis is another parameter combining the effect of μ_2 , μ_3 and μ_4 .

Valocchi (1985) derived theoretical moments for several transport models, including the two discussed above, by differentiating the solution of Eqs. (1), (4a) and (4b) in the Laplace transform subject to a Dirac (δ) tracer input. Jacobsen et al (1992) modified these expressions for pulse type tracer input to yield results for model I and II, as shown in Table 1. These expressions were used in the present study to determine theoretical moments of BTCs with a pulse type input. A third-type inlet boundary condition involving flux-averaged concentrations (Van Genuchten and Parker, 1984), a zero concentration gradient at infinity and an initially solute-free soil profile were considered.

Table 1
Time moments at depth L for models I and II for pulse input of duration T_0

Moment	Model I	Model II
μ_1	$R + (1/2T_0)$	$R + 1/2T_0$
μ_2	$(2R^2/P) + (1/12T_0^2)$	$(2R^2/P_m) + [(2(1-\beta)^2)/\omega] + (1/12)T_0^2$
μ_3	$(12R^3)/P^2$	$(12R^3/P_m^2) + [(12(1-\beta)^2R^3)/(P_m\omega)] + [(6(1-\beta)^3R^3)/\omega^2]$

2.2. Leaching experiments

Both experimental sites were situated in Northern Germany. Site A was cropped with spruces; no tillage was performed 5 years prior to sampling. Conversely, site B was subjected to conventional cultivation practices and received a mold-board ploughing once a year. At both sites, 24 undisturbed soil columns (5.7 cm in diameter and 10 cm long) were collected for leaching experiments at a uniform grid spacing of 15 m from 5 to 15 cm surface layer. Sampling was performed in late autumn when two-thirds of the sampled area at site B was covered with winter rape. Adjacent to each core, a second undisturbed soil column (5.7 cm in diameter and 5 cm long) was taken for conducting saturated hydraulic conductivity (K_s) tests. Bulk soil samples were collected from around all columns for analysis of additional soil properties for texture and organic carbon. Bulk density and water contents of soil of individual columns were measured subsequent to the leaching tests. Details of the methodology for determining these properties have been presented by Lennartz et al. (1997). Mean values and coefficient of variation (CV) of the selected properties of two soils are presented in Table 2. Statistical evaluation of soil parameters of two experimental sites revealed frequency distributions which were tested for normality using Kolmogorov–Smirnov criterion. The null (normal) hypothesis was not rejected at 0.15 level of significance. Organic carbon (OC) content at site B failed to satisfy the normality criterion; all other parameters (sand, silt, clay, bulk density, moisture content) exhibited a normal frequency distribution. Site A had a silty loam soil with subangular structure and high organic carbon (mean 3.7%), while site B was a loamy sand with relatively low organic carbon (mean 1.5%) and crumb structure. Increased organic carbon at site A resulted perhaps from occasional waterlogging and subsequent reduced biological activity. The average bulk density of the soil at site A was slightly higher, and soil water content at time of sampling lower, than those of site B. The frequency distributions of field moisture content, soil bulk density and texture parameters of both sites had a CV less than 50%.

Table 2
Mean values of the selected properties at two sites

Site	Structure	Sand (%)	Silt (%)	Clay (%)	Texture	Org.C (%)	Bulk density (g/cm ³)	Moisture (cm ³ /cm ³)
A	Subangular	54.4 (18.5) ^a	35.9 (29.9)	9.7 (44.0)	SiL	3.7 (20.0)	1.67 (7.9)	0.26 (13.5)
B	Crumb	63.3 (22.5) ^a	26.2 (40.9)	10.3 (49.4)	LS	1.5 (23.1)	1.53 (4.1)	0.30 (10.5)

^a Figures in parenthesis indicate the percent coefficient of variation of respective soil properties.

Displacement studies were conducted in all columns under unsaturated steady state flow conditions using a laboratory apparatus described by Rambow and Lennartz (1993). The apparatus (Fig. 1) can simulate a wide range of conditions on rainfall and soil water tension to study the leaching behavior of soil-applied chemicals in undisturbed/disturbed soil columns. Unsaturated water flow was induced by applying suction at the lower end of the sample, while the soil surface remained under atmospheric pressure. Lower boundary holding the sample consisted of a porous glass plate covered with a Nylon membrane, through which suction was applied. Leachate was drawn through the

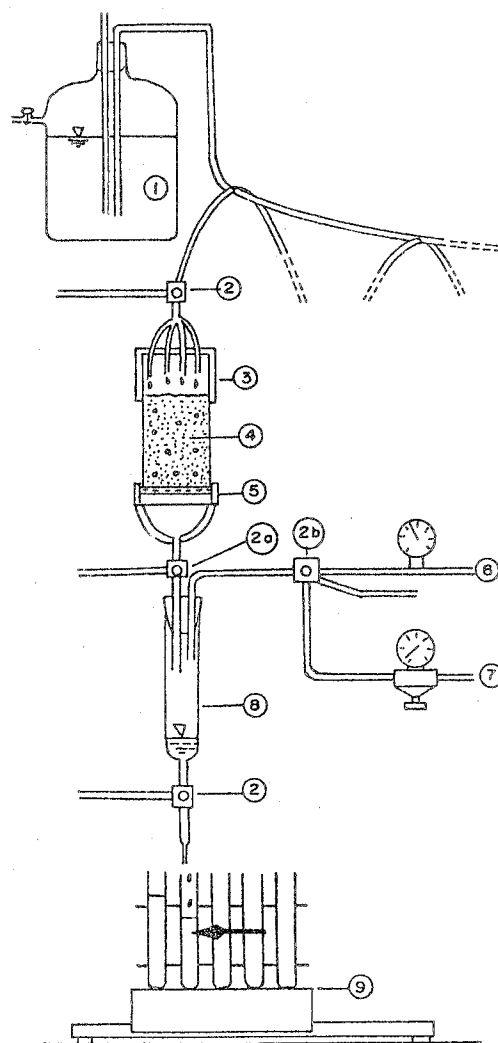


Fig. 1. Schematic diagram of laboratory apparatus showing: (1) Mariotte vessel; (2, 2a, 2b) magnetic valves; (3) sprinkler; (4) soil column; (5) porous glass plate with nylon membrane; (6, 7) vacuum tank with vacuum pump; (8) vacuum lock; (9) fraction sampler.

suction port via vacuum lock equipped with three magnetic valves. This lock allowed sampling of leachate with minor changes in the vacuum level. Four hypodermic needles formed the sprinkler unit for applying the standardized solute-free solution with ionic composition similar to the naturally occurring rainwater. Sprinkler supply from a Mariotte vessel was arranged by gravity, while irrigation was controlled by magnetic valves. Regulation of matrix suction or water content was not possible during the test since samples were not equipped with tensiometers or similar specific probes.

Twenty-four columns were simultaneously mounted on the experimental set-up and the applied suction was -3 kPa for every batch. Prior to application of solute pulse, samples were adjusted to steady state water flow conditions for at least 48 h with a Darcy flux of 0.8 cm/day. The flux rate and applied suction were chosen, based on experience of conducting similar tests in large undisturbed soil columns collected from same sites and fitted with tensiometers, which indicated a uniform distribution of matrix potential in the column under these flux and suction conditions. Bromide in the form of KBr was used as a non-reactive tracer in the column experiments. Transport of bromide and atrazine was investigated in columns of site A during August 1994, while leaching of bromide and isoproturon was studied in site B columns during May, 1994. Following a pulse application of bromide and pesticides at the soil surface of the columns, effluent volumes were measured at regular intervals to determine the flux density of water. The leaching test failed in one column of site B and further analysis was confined to 23 columns; all columns functioned properly at site A. Pesticide concentrations in the leachate were analyzed by UV-VIS HPLC with online solid phase extraction, while bromide concentrations were determined by ion chromatography.

Prior to the above reported studies for site B, bromide displacement studies were conducted in the same columns during April, 1994 as Test 1 for testing the apparatus for conducting leaching studies under unsaturated steady state conditions in 24 small columns. After completion of Test 1, leaching of bromide and two pesticides, as discussed above, was studied during May, 1994 in the same columns as Test 2. The results of two tests for bromide leaching were compared to evaluate the ability of small columns to capture field-scale soil heterogeneity and maintain the persistence of preferential flow pathways over subsequent wetting cycles. Lennartz and Kamra (1998) presented detailed results on these aspects, and concluded that despite variations in the water fluxes, flow velocities, pulse size and pulse duration in columns of two tests, the general shapes of individual preferential and non-preferential columns were maintained during two tests. The double peak behavior of field-averaged BTCs was also maintained over two tests, suggesting that the preferential flow, apparently an intrinsic property of the soil under consideration, remained time-invariant in small columns used in this study. Only the results of Test 2 of site B, and columns of site A, have been discussed in detail in subsequent sections of this paper.

2.3. Data treatment

The shape and features of experimental BTCs were analyzed in terms of the solute (bromide or pesticide) concentration c ; mass flux of solute per unit cross-sectional area $s \equiv cq$, in which q is the volumetric water flux; and accumulated mass of solute M ,

defined as the time integral of s (Sassner et al., 1994). Solute concentration c and mass flux s were normalized with respect to the surface load of the applied solute ρ_A , defined as the mass of solute applied per unit cross-sectional area of the column. The field-scale concentration \hat{c} ; solute flux \hat{s} and accumulated mass \hat{M} were derived by statistically averaging the corresponding quantities in individual columns on lines suggested by Gelhar and Axness (1983). Experimental moments μ'_1 , μ_2 and μ_3 of individual columns and field average BTCs of two sites were determined by numerical integration of Eqs. (7)–(9) using the trapezoidal rule. Skewness, S was subsequently determined using Eq. (10). The features of PFCs were characterized in terms of these moments and their contribution to field-scale leaching of bromide and pesticides was evaluated.

For estimation of transport parameters of equilibrium (model I) and non-equilibrium two-region (model II) models, bromide concentrations were expressed in dimensionless form, $c(T)/c_0$, with $T = vt/L$. Transport parameters of these models were determined by using CXTFIT (Toride et al., 1995), and by the time moment analysis. CXTFIT is a nonlinear least square inversion program of curve fitting in which the parameter values are varied arbitrarily to best fit the analytical solutions of Eqs. (1), (4a) and (4b) to the observed BTCs. The tracer pulse length was kept constant during the fitting procedure after correction for mass recovery. The velocity, measured independently during the experiment, was also kept constant while R and D were the fitting parameters for equilibrium model. The equilibrium assumption of model I results in an effective R , which is independent of the non-equilibrium phenomenon under specific column and flow conditions. This is also corroborated by the expression for μ'_1 in Table 1. To reduce the number of variables, the solution for model II was therefore fitted to the data by keeping R , as determined for equilibrium model, constant while D , ω and β were the fitting parameters. For estimation of transport parameters of model I by the moment method, expressions for theoretical moments of Table 1 were equated with the corresponding experimental values and solved for the model parameters. For model II, R obtained with the moment method for model I and D_m (related to P_m by Eq. (5a)) obtained for model II by CXTFIT was used, while β and ω were obtained by solving the system of equations given in Table 1. The constraints $0 \leq \theta_m \leq \theta$, $D > 0$ and $\alpha > 0$ were imposed for the parameter estimation with both methods.

3. Results and discussion

3.1. Column and field-scale BTCs

The results on leaching behavior of bromide and atrazine in 24 columns of site A, and of bromide and isoproturon in 23 columns of site B, have been included in this section. The representative texture, bulk density, organic carbon and soil moisture contents at the time of sampling at two sites have been presented in Table 2, while the water flow characteristics (including the CV) of leaching studies are summarized in Table 3. It is seen that despite textural differences, there was reasonable uniformity in the water flow characteristics of the two soils. This was due to the fact that water flux during displacement studies was adjusted by applying a suction of -3 kPa and by

Table 3

Mean and coefficient of variation, CV (in percent) of water flow characteristics of soils at two sites during leaching studies

Site	Solute	Test duration (h)	Water content (cm ³ /cm ³)		Water flux (cm/day)		Pore water velocity (cm/day)	
			Mean	CV	Mean	CV	Mean	CV
A	Bromide	129	0.33	7.4	0.79	6.9	2.40	16.1
	Atrazine	582	0.33	7.4	0.83	6.6	2.48	11.4
B	Bromide	160	0.33	8.0	0.77	1.2	2.38	11.9
	Isoproturon	352	0.33	8.0	0.62	1.6	1.92	18.0

regulating the inflow. The ratios of the maximum values of volumetric water content (θ), water flux (q) and pore water velocity (v) to corresponding minimum values in different columns ranged between 1.3 and 1.7. Flow in most columns of site A was close to steady state, though marginal increases in flux density were observed in some columns during the later stages when pesticide leaching was in progress. Water flux in columns of site B, however, reduced significantly during the later stages of the test (Table 3). It may be mentioned that the experimental set up was designed to treat a large number of samples simultaneously, rather than to achieve a very high level of accuracy of water flux in individual columns. Still, the CV among Darcy fluxes and water contents of both sites were less than 10%, while pore velocities were less than 20%. It was also observed that columns indicating preferential flow features (like rapid transport of high concentration of solute during early stages of the breakthrough) had smaller values of water flux and pore water velocity at both sites, though one would expect relatively higher velocities in such columns.

The soil columns at both sites displayed large and irregular variability in solute transport properties, including some showing typical features of preferential flow, like early breakthrough and extensive asymmetry in the BTCs. Lennartz et al. (1997) grouped the bromide BTCs of two sites into two broad categories: non-preferential type I and preferential type II curves. Type I curves included the BTCs having maximum concentration between 0.4 and 0.8 pore volumes of effluent, followed by a more or less pronounced tailing. The shape of type II BTCs was characterized by preferential flow features like an early breakthrough (with peak concentration more than those in Type I curves) at about 0.2 pore volumes, followed by a steep decrease in concentration and a long tail at larger pore volumes. BTCs with irregular features, like a double peak or a very broad shape, were also grouped with type II BTCs. One such PFC for site A, and four for site B were identified. As discussed earlier, the individual experimental BTCs were analyzed in terms of normalized solute concentration c (1/cm), mass flux s (1/h) and accumulated leached mass fraction M . The field-scale concentration \hat{c} , solute flux \hat{s} and accumulated mass \hat{M} were estimated as the arithmetic average of the corresponding quantities in individual columns. The contribution of PFCs to field-scale leaching behavior of bromide and pesticides was studied by excluding their contribution and taking the arithmetic average of NPFCs. Fig. 2 compares the normalized field-scale concentration, mass flux and accumulated mass fraction of atrazine for all 24 columns

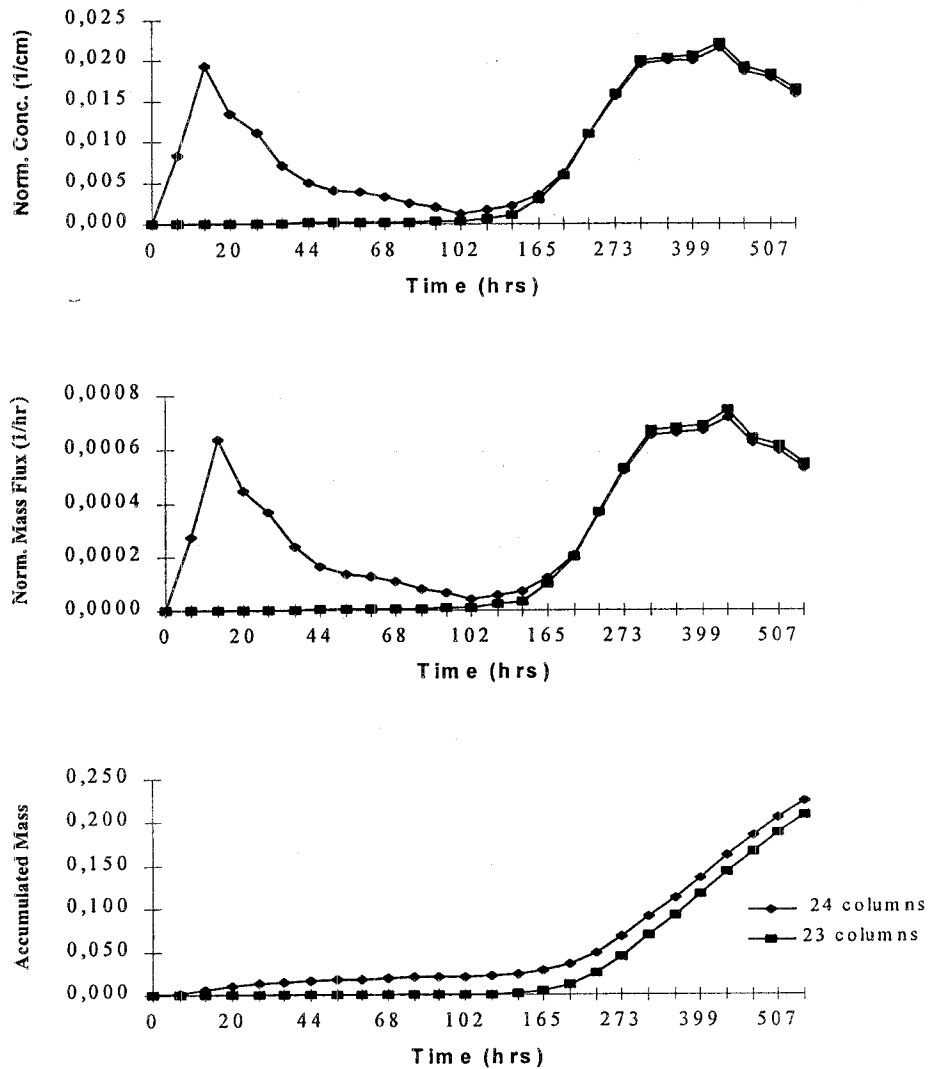


Fig. 2. BTCs in terms of normalized field-scale concentration, mass flux and accumulated mass of atrazine at site A considering the contribution of all 24 columns or 23 non-preferential flow columns.

and 23 NPFCs of site A. It is seen that one PFC contributed significantly during early stages of leaching to the field-scale concentration and mass flux of atrazine, resulting in double peaks of these parameters.

Large-scale solute movement can be described in terms of resident or flux-averaged concentrations (Kreft and Zuber, 1978; Parker and van Genuchten, 1984; Destouni and Cvetkovic, 1991). The large-scale flux averaged concentration is defined as $c_f \hat{=} s \hat{/} q \hat{}$, where $s \hat{}$ and $q \hat{}$ are the arithmetic averages of the solute flux and the specific discharge of water, respectively. $c_f \hat{}$ represents the concentration in water that crosses a

control plane at an arbitrary depth below soil surface (column length in our case) in unit time. The large-scale resident concentration is the area averaged concentration in an elementary volume of fluid at a given depth and can be estimated as the mean of the local resident concentrations. In this study, the concentrations were measured in the leaching effluent and represent local flux concentrations. The difference between local resident and flux concentrations depends upon local dispersion (Kreft and Zuber, 1978; Parker and Van Genuchten, 1984); the two concentrations are approximately equal for small values of dispersion. The two field-average concentrations, \hat{c} and \hat{s}/q , of bromide for two sites, are illustrated in Fig. 3. It is seen that two types of concentration including matching of two peaks are almost identical for site A, while \hat{c} for site B are smaller than \hat{s}/q in the rising phase and at two peaks of BTC but are larger than \hat{s}/q in the tail.

In addition to the mean field behavior, standard deviations (SD) of the field-scale parameters were calculated to provide a quantitative measure of the variability between columns. In Fig. 4, the large-scale mass flux of bromide, $s(t)$, is depicted along with the corresponding SD for columns of site B. It is seen that the shapes of the field-scale mass flux and SD curves followed similar patterns for the total as well as for the NPFCs.

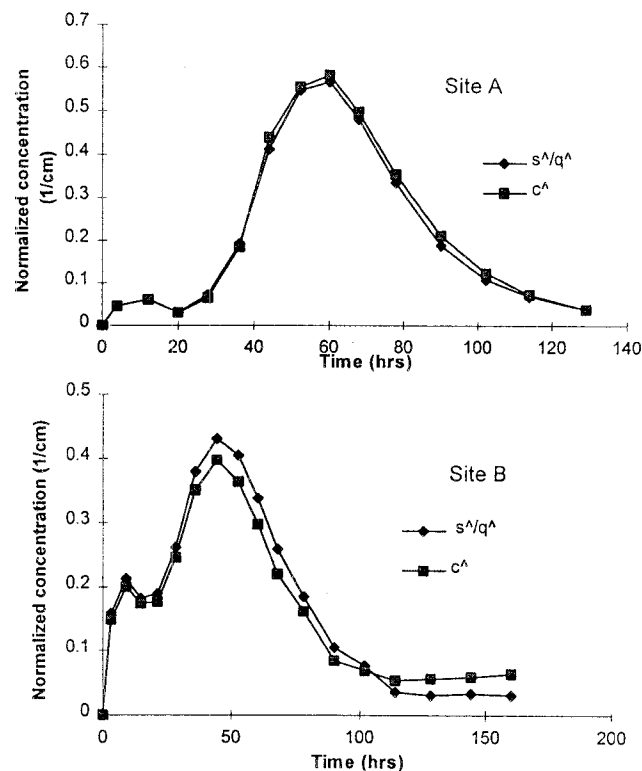


Fig. 3. Comparison between two field-averaged normalized concentration models: \hat{c} and \hat{s}/q for site A (a) and site B (b).

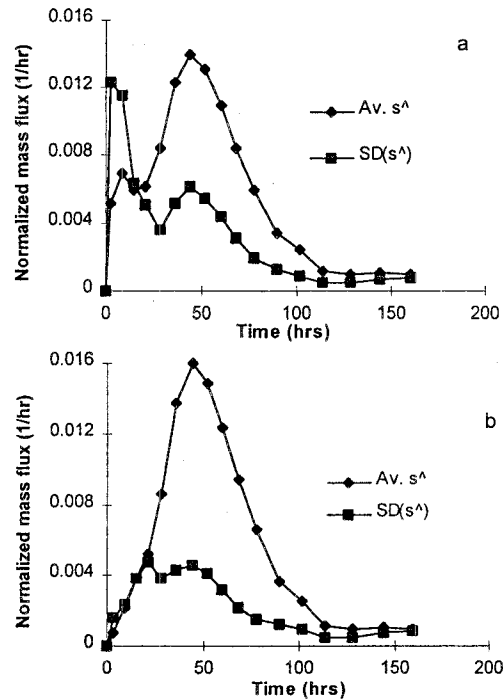


Fig. 4. The large-scale bromide flux (s^A) along with standard deviation of the bromide flux SD (s^A) at site B considering the contribution of all 23 columns (a) or 19 non-preferential flow columns (b).

Though the maximum observed mass fluxes in both cases were similar, the preferential flow introduced almost three times larger SD during initial stages in the mean breakthrough behavior than under non-preferential flow conditions. The first steep peak in the SD resulted due to 4 PFCs which exhibited significantly earlier peak arrival times than the remaining 19 columns. The second peak in the SD curve was smaller, but like the first peak it also occurred when the slope of the mean mass flux was steep. It was also estimated that more than 80% of the maximum observed SD in the field-scale concentration and mass flux of pesticides at two sites could be attributed to a small number of PFCs (Table 4). One PFC at site A and four PFCs at site B contributed to 11% and 58% of the field-scale accumulated leached fraction of atrazine and isotopuron, respectively.

3.2. Parameter estimation by CXTFIT and moment method

The transport parameters of model I and model II for individual bromide BTCs were estimated by CXTFIT (Toride et al., 1995) and with time moment analysis (Jury and Sposito, 1985) and are reported below.

3.2.1. Model I

The values of R , D (and related P) of model I, determined by CXTFIT and moment method for two sites, are presented in Tables 5 and 6 along with means and variance

Table 4
Contribution of preferential flow columns (PFCs) to variability in field-scale concentration, mass flux and accumulated mass of bromide and pesticides

Chemical	% contribution to maximum SD			% contribution to M^{\wedge}
	C^{\wedge}	s^{\wedge}	M^{\wedge}	
<i>Site A (1 PFC)</i>				
Bromide	8	6	3	1
Atrazine	87	84	15	11
<i>Site 2 (4 PFCs)</i>				
Bromide	63	61	6	2
Isoproturon	86	86	59	58

Table 5
Retardation factors (R), dispersion coefficients (D) and Peclet numbers (P) of model I of different columns of site A estimated by CXTFIT and moment method

Column	R_{mom}	R_{cxt}	D_{mom} (cm^2/day)	D_{cxt} (cm^2/day)	P_{mom}	P_{cxt}
A1	0.64	0.63	0.79	0.79	26.25	26.35
A2	0.69	0.68	0.62	0.57	34.98	37.94
A3	0.64	0.64	0.77	0.78	31.67	31.18
A4	0.63	0.64	1.08	1.05	20.10	20.77
A5	0.59	0.60	0.89	0.95	23.14	21.56
A6	0.55	0.56	1.29	1.43	15.92	14.44
B1	0.68	0.69	1.58	1.48	16.50	17.64
B2	0.81	0.82	0.79	0.80	27.72	27.37
B3	0.69	0.69	1.20	1.20	19.33	19.37
B4	0.62	0.63	0.63	0.74	29.46	25.16
B5	0.54	0.56	0.97	1.03	18.42	17.33
B6	0.54	0.55	0.94	1.20	20.52	16.18
C1	0.81	0.81	1.16	1.13	28.80	29.57
C2	0.64	0.63	0.72	0.58	33.93	41.95
C3	0.76	0.75	0.95	0.62	30.02	46.02
C4	0.79	0.78	1.01	0.75	27.76	37.58
C5	0.71	0.73	1.64	1.93	14.19	12.08
C6	0.58	0.56	2.00	1.50	12.85	17.18
D1	0.67	0.67	0.86	0.73	32.07	38.04
D2	0.69	0.68	1.06	0.86	25.73	31.64
D3	0.65	0.65	1.04	0.79	29.11	38.50
D4	0.70	0.69	0.89	0.75	29.38	35.02
D5	0.67	0.68	1.31	1.35	18.06	17.44
D6	0.26	0.16	10.02	6.80	2.14	3.15
<i>Mean</i>						
24 columns	0.65	0.64	1.43	1.24	23.67	25.98
NPFCs	0.67	0.67	1.05	1.01	24.61	26.97
<i>Variance</i>						
24 columns	0.013	0.016	3.46	1.52	63.37	118.34
NPFCs	0.006	0.006	0.11	0.12	44.25	99.02

Table 6
Retardation factors (R), dispersion coefficients (D) and Peclet numbers (P) of model I of different columns of site B estimated by CXTFIT and moment method

Column	R_{mom}	R_{cxt}	D_{mom} (cm^2/day)	D_{cxt} (cm^2/day)	P_{mom}	P_{cxt}
A1	0.65	0.66	2.47	2.52	12.07	11.83
A2	0.61	0.57	1.57	1.50	17.92	18.75
A3	0.71	0.68	1.56	1.69	16.38	15.12
A4	0.57	0.64	4.55	6.21	5.71	4.18
A5	0.68	0.66	2.06	2.18	12.12	11.45
B1	0.70	0.62	3.26	2.84	8.72	10.01
B2	0.74	0.70	1.90	2.06	14.25	13.14
B3	0.72	0.66	1.79	1.95	14.41	13.23
B4	0.60	0.60	1.74	2.67	12.88	8.40
B5	0.62	0.68	2.58	3.95	9.71	6.34
B6	0.54	0.70	4.14	10.33	5.48	2.20
C1	0.69	0.66	2.14	2.59	11.59	9.57
C2	0.57	0.74	2.89	8.21	7.64	2.69
C3	0.68	0.62	2.03	2.13	12.67	12.08
C4	0.64	0.74	2.96	6.06	8.42	4.11
C5	0.74	0.71	2.91	3.02	8.73	8.41
D1	0.66	0.60	2.48	2.04	10.53	12.80
D2	0.54	0.68	4.74	12.07	5.20	2.04
D3	0.54	0.67	3.09	4.37	6.85	4.84
C6	0.34	0.45	6.59	16.45	2.99	1.20
D4	0.43	0.48	6.00	7.90	3.21	2.44
D5	0.19	0.18	15.98	19.56	1.21	0.99
D6	0.32	0.34	9.97	22.94	2.15	0.93
<i>Mean</i>						
23 columns	0.59	0.61	3.89	6.32	8.99	7.69
NPFCs	0.64	0.66	2.68	4.13	10.41	9.01
PFCs	0.32	0.36	9.64	16.71	2.27	1.39
<i>Variance</i>						
23 columns	0.02	0.018	10.88	37.2	20.74	27.6
NPFCs	0.005	0.002	0.92	9.46	13.07	22.98
PFCs	0.009	0.019	20.95	41.54	0.82	0.50

separately for all columns, PFCs and NPFCs. For site A, only one column (D6) out of 24 columns was having preferential flow characteristics, while four columns (C6, D4, D5, D6) out of 23 were preferential for site B. R was not fixed at 1.0, during optimization of D , primarily because the apexes of Br BTCs had appeared at significantly less than one pore volume. For NPFCs, the average value of estimated R at both sites were about 0.65, much less than unity expected for non-reactive tracers like Br. Retardation factors smaller than unity for non-reactive tracers have been reported in a number of studies (Gaudet et al., 1977; Schulin et al., 1987; Veeh et al., 1994) to indicate negative adsorption ($K_d < 0$). The later phenomenon can be attributed either to anion exclusion (Schulin et al., 1987) or to a reduction in flow cross-sectional area caused by immobile water regions not participating in solute transport (Gaudet et al.,

1977; Seyfried and Rao, 1987; Lennartz and Meyer-Windel, 1995). Following the procedure of Veeh et al., (1994), Lennartz et al. (1997) reported the anion exclusion volumes resulting from negatively charged clay surfaces to be 3.7% and 3.6% of the water content for the sites A and B, respectively. Since these are not large percentages, immobile water contributed mainly to occurrence of small values of R in columns of both sites. Immobile soil–water was expected to occur under the chosen flow (unsaturated) and soil (undisturbed) conditions. The extent of immobile regions in a soil varies with flow velocity, water content and aggregate size (Van Genuchten and Wierenga, 1977; Nkedi-Kizza et al., 1983). In the present study, the water content of soil columns during leaching was relatively low (Table 3) which caused reduction in R -values of all columns to considerably less than unity. It is also clear from Eq. (3a) that small errors in determination of volumetric water content would have a strong effect in the calculation of R . Gaudet et al., (1977) also found the relative amount of stagnant water to increase with decreasing water content, while lower R values at higher pore water velocities were reported by Nkedi-Kizza et al. (1983). It appears that at higher pore water velocities, mixing is less complete and the solutes move faster through the porous medium.

R values for PFCs were less than 0.5 with a lowest value of 0.16 for one PFC of site A. Besides anion exclusion and immobile water, to which the most occurrences of non-equilibrium phenomena are usually attributed to, certain additional mechanisms seem to be operational to result in such low values of R . In fact, the complexity of the soil system exceeds that manifested by the mobile–immobile concept, since water may be intercepted in discontinuous macropores, which may be viewed as mobile in the traditional two-region concept (Bootink and Bouma, 1991). Further, model I assumes uniform pore-size distribution and flow conditions, which is nothing but a simplistic view of the real soil system. The PFCs of this study increased the variance among R values of all columns, two and up to nine times over those of NPFCs at sites A and B, respectively. The two computation methods, CXTFIT and the moment method, gave comparable mean values of R with respect to the whole population of samples, NPFCs at both sites and four PFCs at site B. The correlation coefficient " r^2 " between R values estimated by two methods for all columns, was 0.99 for site A and 0.84 for site B.

There were significant differences in the values of dispersion coefficients (D) of two sites and two estimation methods. The correlation coefficient, r^2 , among D values of combined columns in two methods was 0.99 at site A, and 0.87 for site B, and slightly lesser for NPFCs. The mean values of D estimated by both methods for total and NPFCs of site B were two to five times the mean values for site A, which could probably be attributed to differences in soil structure and organic carbon contents of the two sites. It is known that soil structure and geometry of the interfaces may induce differential mass transfer limitations to equilibrium between the dissolved and sorbed phases in different soils. Depending upon the estimation method, the value of D for one PFC at site A was 6–10 times the corresponding mean values for NPFCs. At site B, the mean D values of four PFCs estimated by two methods were about four times the mean value of D for NPFCs and 2.5 times the mean value for combined population. Further, the mean values of D estimated by CXTFIT for total, NPFCs or PFCs of site B were approximately 1.6 times the values obtained by moment method; the differences were

small for columns of site A. The variance in D of total population (due to PFCs) vis-a-vis the variance in D of NPFCs was much more for moment method (30 and 10 times) than by CXTFIT (12 and 4 times) for sites A and B, respectively. It is seen that one PFC at site A contributed much more to variance of D than four columns at site B, reflecting the need to define the extent or degree of preferential flow in individual PFCs instead of just qualitatively grouping them together.

The Peclet number, P , combining the variations in D and pore velocities (v), had much less variance and consequently better correlation ($r^2 = 0.91$ and 0.94 , respectively) between P values estimated by two methods for the two sites. Model I provided good to excellent fit to the Br BTCs for all column where r^2 values averaged 0.975, 0.980 and 0.985 for all, NPFCs and PFC of site A. The corresponding values of r^2 for site B were 0.91, 0.91 and 0.88, respectively. The r^2 values lower than these mean values were not necessarily confined to PFCs.

3.2.2. Model II

The classical two-parameter CDE (model I) provides unimodal distribution for solute transport and generally cannot explain the bimodal or highly asymmetric behavior of BTCs (Ma and Selim, 1995) which may result due to rapid transport of solute through a small fraction of the total soil water. Although the immobile water phase may be one of the several mechanisms contributing to the occurrence of preferential flow in the field soils, model II has been found capable of explaining the early breakthrough and extensive tailing in BTCs of non-reactive tracers like tritium and bromide (Van Genuchten and Wierenga, 1977; Yasuda et al., 1994). Consequently, we also estimated parameters of model II for local BTCs of the two sites by CXTFIT and the moment method to quantify the immobile water. In CXTFIT, four parameters of model II (R , D_m or P_m , β and ω) can be estimated simultaneously, but the resultant parameters may be relatively imprecise. Consequently R was taken equal to retardation factor estimated for model I (R_{eq}) and kept fixed while D_m or P_m , β and ω were estimated by CXTFIT. In the moment method, model parameters were determined by equating the experimental moments to the theoretical expressions given in Table 1 and solving the ensuing set of equations. First, the retardation factor, R , was computed from μ'_1 . The three independent parameters P_m , β and ω for model II could be estimated, at least theoretically, from μ_2 , μ_3 , and μ_4 . However, the use of higher order moments resulted in unrealistic estimates of parameters due to the predominant effect of experimental errors in the tail of the BTC. Still to get estimates for β and ω with moments, P_m (or D_m) values obtained with CXTFIT were used to calculate the values for β and ω from μ_2 and μ_3 according to Table 1. This approach of estimating transport parameters of model II by moment method, using D_m values obtained with CXTFIT, has also been reported by Leij and Dane (1991,1992) in respect of laboratory column studies. Table 7 lists the range, mean and the variance of D_m , P_m , β and ω values obtained by CXTFIT and also of β and ω estimated by the moment method separately for total, NPFCs and PFCs of the two sites.

Since the moment method provided estimates of β and ω only, the results for the dispersion coefficient, D_m , and Peclet number, P_m , estimated by CXTFIT were compared vis-a-vis the values obtained for model I at two sites (Tables 5 and 6). The range,

Table 7

Range, mean and variance of parameters of model II estimated by CXTFIT and moment method for two sites

	CXTFIT ($R = R_{eq}$)				Moment method ($R = R_{mom}$, $D_m = D_{cxl}$)	
	D_m (cm ² /day)	P_m	β	ω	β	ω
<i>Site A</i>						
Range	0.43–4.10	5.2–61.1	0.61–1.0	0.0–1.7	0.28–1.0	0.01–114
<i>Mean</i>						
24 columns	0.96	31.3	0.94	0.35	0.86	11.4
NPFCs	0.82	32.4	0.95	0.35	0.88	11.8
PFC	4.09	5.2	0.75	0.31	0.28	1.9
<i>Variance</i>						
24 columns	0.51	171.7	0.01	0.30	0.07	681.0
NPFCs	0.06	147.3	0.01	0.31	0.06	707.6
<i>Site B</i>						
Range	1.0–17.6	1.2–25.9	0.06–0.94	0.06–4.6	0.05–1.0	0.01–417
<i>Mean</i>						
23 columns	4.91	10.8	0.80	0.81	0.86	24.1
NPFCs	3.36	12.6	0.87	0.57	0.88	29.1
PFCs	12.3	2.0	0.49	1.95	0.76	0.5
<i>Variance</i>						
23 columns	23.3	65.9	0.040	1.27	0.09	7858
NPFCs	8.0	59.7	0.004	0.49	0.07	9454
PFCs	34.9	1.2	0.105	4.29	0.23	1.01

mean values and variance of dispersion coefficient of model II were smaller for all types of columns at both sites than the corresponding values of model I. For both models, the value of P was less than 20 for most columns of site B, a limit above which fitted values of D (or P) become more or less independent of the estimation method (Van Genuchten and Wierenga, 1986). The Peclet number for model II expectedly had larger means and variance than those of model I for all groups of columns at both sites due to an implicit incorporation of the solute spreading due to non-equilibrium into the Peclet number of model I.

The remaining two parameters β and ω of model II could be compared on the basis of the estimation method. These parameters govern the degree of non-equilibrium which increases with a decrease in β or ω . The parameter β represents the fraction of solute present in the mobile region under equilibrium conditions while ω represents the ratio between hydrodynamic residence time and a characteristic time of solute movement in the immobile region. Under simplifying assumption of f being equal to θ_m/θ and R being independent of concentration of non-reactive bromide, it can be derived from Eq. (5b) that β equals θ_m/θ . On this premise, it is observed from Table 7 that the mean mobile water fraction estimated by CXTFIT for NPFCs was 0.95 for site A and 0.87 for site B; the corresponding β values derived with moment method being 0.88 and 0.88, respectively. Thus, on an average, about 5–12% of water at site A, and 12% at site B was immobile during displacement in NPFCs. The mean β values in PFCs (ranging at two sites between 25% and 51% by CXTFIT and between 24% and 72% by moment

method) were very large as compared to average values in NPFCs. Such large fractions of immobile water in PFCs reflect high degrees of non-equilibrium caused by certain mechanisms other than only immobile water. The mean estimates of β for PFCs by two methods differed significantly at both sites; the variance for all types of columns was in general, much larger in moment method than in curve fitting method. Another approach for estimating the amount of immobile water involved interpretation of β obtained from the fit of Br BTCs to the bicontinuum model with R fixed at 1.0 rather than equal to R obtained from model I. Using this approach with CXTFIT, the mean values of immobile water for NPFCs and PFCs were estimated as 34% and 84%, respectively, for site A, and 39% and 52% for site B.

The dimensionless ω of the two-region model showed the highest degree of uncertainty of all parameters (Table 7). The ω estimates by CXTFIT were generally less than unity and much smaller than mean estimates obtained by moment method. Even the higher ω estimates of moment method were much less than 100, a limit indicating the absence of non-equilibrium (Brusseu et al., 1989) and consequently the ineffectiveness of applying model II. The constraints of $0 \leq \beta \leq 1$ and $\omega > 0$, implicitly defined in CXTFIT, were also applied in moment method, which helped to take care of certain absurd values of β (negative or more than 1) and ω (negative or extremely large values). Problems associated with the use of model II in conserving mass have been discussed in detail by Parker and van Genuchten (1984). These authors have noted that the BTCs derived by this model diverge, especially when $P < 5$. P values obtained in this study with model II, in particular for PFCs (Table 7), were smaller than five indicating the inadequacy of the mobile-immobile water concept of model II to account for the encountered range of pore water velocities in the mobile water regions and incorporate the effect of other forms of non-equilibrium in PFCs.

3.3. Simulated BTCs

Fig. 5 presents the observed and simulated BTCs for field-averaged concentration distribution and one PFC (D6) of site A and two PFCs (C6 and D5) of site B. The simulated BTCs were derived using transport parameters obtained with CXTFIT, with respect to model I and model II, and by the moment method (MM) with respect to model I. The field-averaged BTC of site A was characterized by a double peak behavior, in which the first peak resulted due to preferential flow effect of one PFC. Though fitted BTCs using CXTFIT and moment method adequately described the second peak and the tail of the observed BTC, all failed to capture the first peak. Furthermore, perhaps because of introduction of errors due to averaging of relatively unstable parameters of model II, model I (with estimated parameters by curve fitting or moment method) better described the peak concentration in fitted BTCs. The parameters of the moment method provided marginally better description of desorption phase of field averaged BTC than the parameters of curve fitting approach.

For PFCs of both sites, the following observations can be made: (i) the observed BTCs were better reproduced with parameters obtained from curve fitting than from the moment method, (ii) the moment method failed to capture the peak concentrations in PFCs, but described the desorption and tail branch of BTCs better than the curve fitting

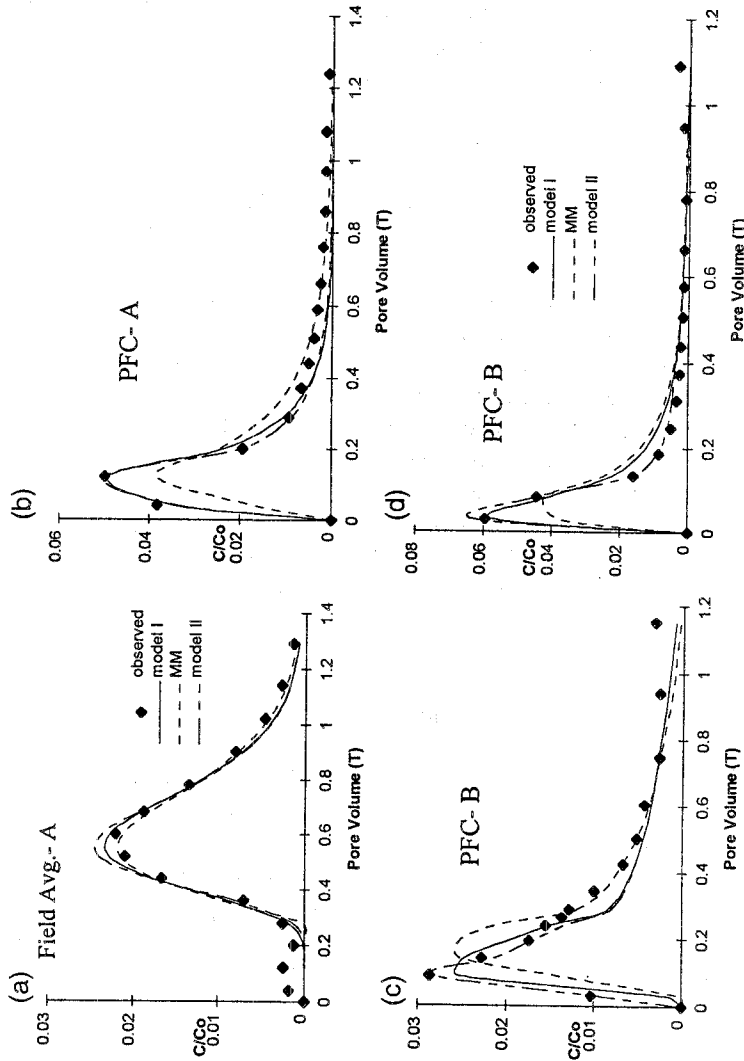


Fig. 5. Observed and simulated BTCs using parameters estimated by CXTFIT for model I and model II and by moment method (MM) for model I for field-average concentration of site A (a), a PFC D6 of site A (b), and PFCs C6 (c) and D5 (d) of site B.

approach, (iii) overall, model II provided a superior fit for NPFCs and PFCs than model I, especially its ability to describe the steep initial rise and tailing. The average correlation coefficient (r^2) values between observed and simulated BTCs of model II using CXTFIT derived parameters for all columns, NPFCs and PFCs (0.99, 0.98, 0.99 for site A; 0.95, 0.92, 0.93 for site B) were better than corresponding values of model I. The better fit with CXTFIT than the MM can be explained by greater flexibility of the former method to describe the BTC. The moment method, in contrast to CXTFIT, produces a unique set of parameters for a BTC which may adversely affect the estimation of remaining parameters if the experimental data are poorly described by the model used. In CXTFIT, the parameter values are varied arbitrarily to best describe the experimental BTCs. Particularly if the selected model does not exactly describe the transport processes like the unsure validity of CDE model for preferential flow conditions, CXTFIT is likely to provide better estimates of parameters. Another disadvantage of the moment method (MM) is the instability of solutions obtained using higher order moments. In spite of these limitations, the moment method is a useful means to characterize experimental BTCs in terms of mean travel time (u_1'), spreading (u_2) and asymmetry (S) and to theoretically analyze transport, even if parameter estimation is done with curve fitting.

4. Summary and conclusions

Displacement studies on leaching of bromide and two pesticides were conducted under unsaturated steady state flow conditions in 24 small, undisturbed soil columns each collected from two sites in north Germany. The field-scale BTCs were derived as the arithmetic average of the BTCs of individual columns and the contribution of PFCs to field-scale leaching of bromide and pesticides was evaluated. The bromide BTCs were analyzed with a CDE-based equilibrium model and a non-equilibrium mobile-immobile model, the transport parameters were determined using a curve fitting program, CXTFIT, and by the time moment method. Based on the results of this paper, the following salient observations and conclusions can be drawn:

(1) Large variability and double peak behavior in the field-scale concentration and mass flux of bromide and pesticides was induced due to a small number of PFCs at two sites. One PFC at site A, and four at site B contributed, respectively to 11% and 58% of the field-scale accumulated leached fraction, and to more than 80% of the maximum observed SD in the field-scale concentration and mass flux of pesticides at two sites.

(2) The field-scale mass flux and SD curves of bromide followed similar patterns; the double peaks in the SD curve occurred when the slope of the mean mass flux was steep.

(3) For CDE-based equilibrium model, the mean values of retardation factor, R , considered separately for all columns, PFC's or NPFC's were comparable for two methods; significant differences were observed in the values of dispersion coefficients, D , of two sites and two estimation methods. Two to five times higher values of D in columns of site B, vis-a-vis columns of site A, was attributed to differences in soil structure and organic carbon contents of two sites.

(4) The range, mean values and variance of dispersion coefficient of the non-equilibrium model were smaller for all types of columns at both sites than corresponding values obtained with equilibrium model. Peclet numbers of PFCs at both sites and for both models were consistently smaller than five, indicating the inadequacy of non-equilibrium models to incorporate the effect of all forms of non-equilibrium in PFCs.

(5) The estimated parameters of the non-equilibrium model indicated that 5–12% of water at site A, and 12% at site B was immobile during displacement in NPFCs. Immobile water fractions were much larger in PFCs, ranging at two sites between 25% and 51% by CXTFIT and from 24% to 72% by moment method, suggesting the contribution of certain mechanisms (other than immobile water) to higher degrees of non-equilibrium in these columns.

(6) Overall, the observed BTCs of individual NPFCs, PFCs and field average BTCs of two sites were better reproduced with parameters obtained from curve fitting than by the moment method. The moment method failed to capture the peak concentrations in PFCs, but tended to describe the desorption and tail branches of BTCs better than the curve fitting approach. Despite these limitations, the moment method is a useful tool for characterizing the experimental BTCs and to quantify the contribution of different mechanisms to field-scale solute transport, even if parameter estimation is done with curve fitting.

Acknowledgements

A major part of this study was conducted during the first author's stay at the Institute for Water Management and Landscape Ecology, University of Kiel, Herman-Rhodewald Str. 9, 24098 Kiel, Germany, as an Alexander von Humboldt fellow during June 1995–January 1997. The financial and logistic support of Alexander von Humboldt Stiftung, Jean-Paul-Straße 12, D-53173 Bonn (Germany) is gratefully acknowledged.

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