

Parameter Determination for Chloride and Tritium Transport in Undisturbed Lysimeters during Steady Flow

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Breakthrough curves of Cl and $^3\text{H}_2\text{O}$ were obtained during steady unsaturated flow in five lysimeters containing an undisturbed coarse sand (Orthic Haplohumod). The experimental data were analyzed in terms of the classical two-parameter convection-dispersion equation and a four-parameter two-region type physical nonequilibrium solute transport model. Model parameters were obtained by both curve fitting and time moment analysis. The four-parameter model provided a much better fit to the data for three soil columns, but performed only slightly better for the two remaining columns. The retardation factor for Cl was about 10 % less than for $^3\text{H}_2\text{O}$, indicating some anion exclusion. For the four-parameter model the average immobile water fraction was 0.14 and the Peclet numbers of the mobile region varied between 50 and 200. Time moments analysis proved to be a useful tool for quantifying the breakthrough curve (BTC) although the moments were found to be sensitive to experimental scattering in the measured data at larger times. Also, fitted parameters described the experimental data better than moment generated parameter values.

Introduction

Many problems in agricultural management and subsurface pollution involve anion transport through unsaturated soils. Leaching of surface-applied NO_3 fertilizers through the unsaturated zone toward the ground-water table is just one obvious example. Anions tend to move faster through the soil than water because of their

exclusion by negatively charged soil particles (Corey *et al.* 1963). The extent of anion exclusion depends on the charge density of soil surfaces, the ambient concentration of the soil solution, and the valences of anions and cations in the soil solution (Krupp *et al.* 1972; James and Rubin 1986; Bond and Phillips 1990). The presence of immobile water in the form of dead-end pore water or water tightly adsorbed to soil solids, can also influence anion movement (Gaudet *et al.* 1977; van Genuchten and Wierenga 1977). Structured or aggregated soils in particular can contain relatively large fractions of immobile water (Rao *et al.* 1980; Nkedi-Kizza *et al.* 1983), a situation which can lead to asymmetrical or non-sigmoidal displacement and tailing phenomena in BTC's. We note that physical nonequilibrium has been observed also for stony soils (Schulin *et al.* 1987), as well as for seemingly uniform sandy soils (Gaudet *et al.* 1977; Wierenga and van Genuchten 1989).

Simulation models, rather than detailed but time-consuming and expensive field studies, are often used to forecast subsurface solute transport. The parameters needed in such models are mostly determined during saturated flow involving relatively small, disturbed soil laboratory columns. It is our objective to investigate anion transport in undisturbed soil columns of a size that allows interpretation of the results at the scale of field conditions.

Van Genuchten and Wierenga (1986) listed several methods for determining transport parameters from observed BTC's. Prominent among them is the non-linear least squares inversion program CXTFIT of Parker and van Genuchten (1984b) which may be used to fit the parameters in several equilibrium and non-equilibrium models to measured BTC's. Transport parameters can also be calculated with time moment analysis (Jury and Sposito 1985). Experimental spatial or temporal moments are convenient tools for summarizing BTC data (Skopp 1984), whereas theoretical moments are helpful for elucidating the effects of different transport processes on the predicted BTC (Valocchi 1985).

In this study, Cl and $^3\text{H}_2\text{O}$ displacement experiments were conducted to determine the effects of anion exclusion and physical nonequilibrium on anion transport through undisturbed soil monoliths during steady unsaturated flow. Model parameters were estimated with both CXTFIT and the moment method.

Theory

Transport Models

The classical equilibrium model for one-dimensional solute transport can be expressed in dimensionless form as

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

where

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- C - the concentration,
- Z - distance (depth),
- T - time,
- P - the column Peclet number, and
- R - the retardation factor.

The quantity $1-R$ may be viewed as the relative anion exclusion volume (van Genuchten and Wierenga 1986). These and other symbols are defined in the notation section at the end of the paper. The equilibrium model, referred to below as model I, contains the two experimental variables P and R .

The physical nonequilibrium model assumes that the liquid phase can be partitioned into a mobile and an immobile region, with water flow being restricted to the mobile region. Solute exchange between mobile and immobile regions is assumed to be proportional to the difference in concentrations between the two regions (van Genuchten and Wierenga 1976). In dimensionless form the model is given by

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

$$(1-\beta) R \frac{\partial C_m}{\partial T} = \omega (C_m - C_{im}) \quad (3)$$

in which, as before, T and Z are the independent variables. Following Nkedi-Kizza *et al.* (1983) and Wierenga and van Genuchten (1989), among others, we assumed equal retardation factors for the two regions. In this case β and $1-\beta$ denote the relative fractions of mobile and immobile water, respectively. The model given by Eqs. (2) and (3), further denoted as model II, contains four experimental variables. Model II is conceptually the same as the anion exclusion model by Krupp *et al.* (1972) if anion exclusion is restricted to the immobile water phase. Model II simplifies to model I in the absence of immobile water.

Analytical solutions to models I and II for an initially solute-free soil profile, subject to a pulse input of duration T_0 , and an effectively infinite outlet condition, have been reported by Lindstrom *et al.* (1967) and van Genuchten and Wierenga (1976), respectively. Since the observed effluent concentrations are considered to be flux averaged, a first- or concentration-type inlet condition must be used (Parker and van Genuchten 1984a).

Time Moments

Time moment analysis is a statistical technique for characterizing BTC's without bias towards a specific transport model (Skopp 1984). For linear transport models, experimental moments can be related to model parameters using properties of the Laplace transform (Aris 1958). Absolute time moments (m_n) are defined as

$$m_n = \int_0^\infty T^n c_m(Z, T) dT \quad n \equiv 0, 1, 2, \dots \quad (4)$$

where m_0 equals the total amount of mass applied to the soil. The normalized absolute moments are given by

$$\mu'_n = \frac{m_n}{m_0} \quad (5)$$

where the first normalized moment yields the mean breakthrough time. Central moments, μ_n , are defined by

$$\mu_n = \frac{1}{m_0} \int_0^\infty (T - \mu'_1)^n c_m(Z, T) dT \quad (6)$$

The second and third central moments quantify the variance and asymmetry of the BTC, respectively. A symmetry in the concentration distribution is frequently also expressed in terms of the skewness

$$S = \frac{\mu_3}{\mu_2^{3/2}} \quad (7)$$

Valocchi (1985) derived moments for several transport models, including models I and II, subject to a Dirac (δ) tracer input. His expressions for the moments can be readily adapted for general pulse inputs by using the relationships

$$\mu_1^f = \mu_1^\delta + v_1 \quad (8)$$

$$\mu_n^f = \mu_n^\delta + v_n \quad n \equiv 2, 3 \quad (9)$$

where the superscripts f and δ denote the general and Dirac input functions, respectively, v_1 is the first absolute moment of the normalized input function (Eq. (5)), and v_n is the n^{th} central moment of the input function (Eq. (6)). For a step

Table 1 - Time moment formulas at depth L for models I and II for step pulse input of duration T_0 .

Moment	Model I	Model II
μ'_1	$R + \frac{1}{2}T_0$	$R + \frac{1}{2}T_0$
μ_2	$\frac{2R^2}{P} + \frac{1}{12}T_0^2$	$\frac{2R^2}{P_m} + \frac{2(1-\beta)^2R^2}{\omega} + \frac{1}{12}T_0^2$
μ_3	$\frac{12R^3}{P^2}$	$\frac{12R^3}{P_m^2} + \frac{12(1-\beta)^2R^3}{P_m\omega} + \frac{6(1-\beta)^3R^3}{\omega^2}$

input of duration T_0 (as is the case in our experiments) we obtain $v_1 = T_0/2$, $v_2 = T_0^2/12$, and $v_3 = 0$. With these results the expressions by Valocchi (1985) could be modified immediately for step input conditions, to yield the results as shown in Table 1. Note that μ_1' is identical for both models; this indicates that nonequilibrium conditions do not affect the mean solute breakthrough time.

Methods and Materials

Five undisturbed cylindrical soil monolith lysimeters of 1.00 m height and 0.20 m diameter were sampled at the Jyndeved Research Station in Tinglev, Denmark. The PVC lysimeter containers were placed in a steel cylinder and slowly driven into the soil, while simultaneously excavating the soil surrounding the lysimeters. The soil was classified as a coarse-sandy, siliceous, mesic Orthic Haplohumod. Soil textural and hydraulic properties were reported by Jacobsen (1989): the topsoil had 4 % clay, 70 % coarse sand ($> 200 \mu\text{m}$), and 2.3 % organic matter; corresponding values for the subsoils were 2.5 %, 84 % and 0.4 %. Additional soil-physical data are listed in Table 2.

The experimental setup is schematically shown in Fig. 1. Water extracted from a well ($\text{EC}_e \approx 42 \text{ mmho/m}$ and $\text{pH} = 7.9$) was applied at a steady rate with a peristaltic pump through an assembly of 15 hypodermic needles. No anion adsorption is likely to have occurred at this relatively high pH. The background Cl and $^3\text{H}_2\text{O}$ concentrations were subtracted from the measured effluent BTC prior to data analysis. A ceramic plate with bubbling pressure of 1,000 hPa was placed at the bottom of the column to collect the effluent at a steady rate by applying a 100 hPa suction underneath the plate. Tensiometers were installed at depths of 10, 50, and 90 cm in each column to measure the soil water suction. The assumption of unit gradient in the hydraulic head, implying a uniform water content in a homogeneous soil, was met reasonably well. The measured average suctions are listed in Table 2. After establishing steady flow rates for the lysimeters (about 3 days) as listed in Table 2, solute pulses of about 0.4 mol CaCl_2 (0.08 mol CaCl_2 for column 3) and 40 μCi of $^3\text{H}_2\text{O}$ were applied to the five columns.

Total effluent volumes were determined at least daily, while subsamples were taken at regular times for Cl and $^3\text{H}_2\text{O}$ determinations. The subsamples were collected three times daily during breakthrough of the solute peaks. The time corresponding to a measured concentration was assumed to occur at the midpoint of each sampling period. Chloride was measured by potentiometric titration with AgNO_3 , whereas $^3\text{H}_2\text{O}$ activity was determined by liquid scintillation.

Upon completion of the leaching experiment, the columns were sliced into 5-cm long segments to determine water contents and bulk densities. All columns had very similar average water contents and bulk densities (Table 2). Fig. 1 shows the measured water content distribution for column 3. Notice that the water content in the topsoil (A-horizon) is more than twice as high as in the subsoil. Observed water

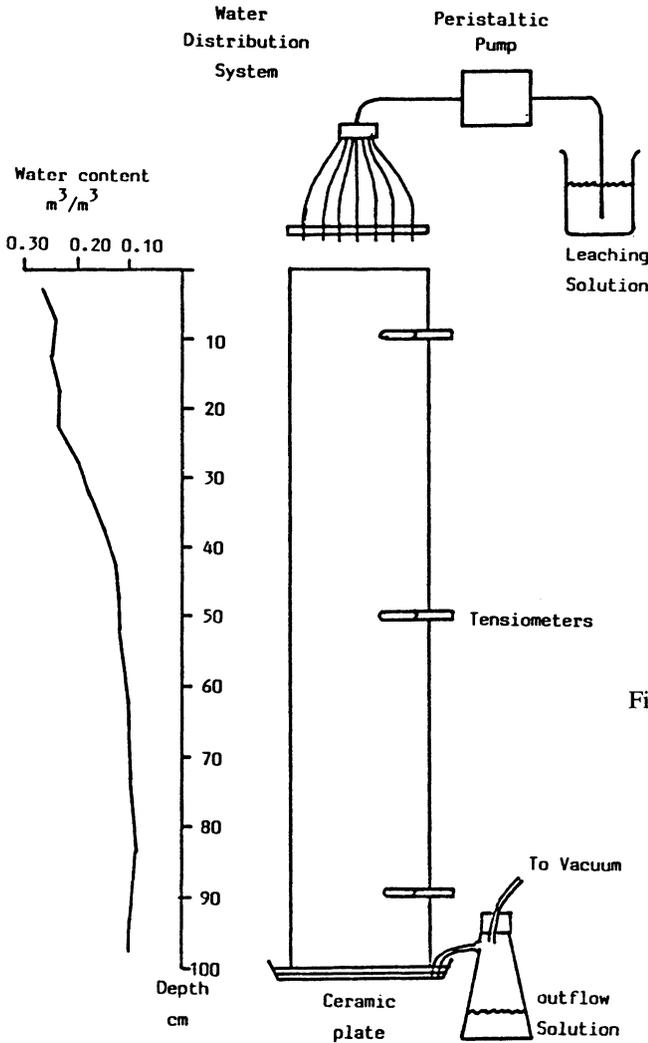


Fig. 1. Schematic diagram of experimental setup, and the volumetric water content profile for column 3.

Table 2 – Experimental conditions.

column No.	bulk density Mg/m ³	total porosity m ³ /m ³	average water content m ³ /m ³	average suction cm H ₂ O	<i>q</i> cm/day	<i>T</i> ₀
1	1.521	0.420	0.148	24	0.915	0.067
2	1.526	0.419	0.153	29	1.030	0.071
3	1.492	0.432	0.145	25	1.180	0.070
4	1.517	0.422	0.155	23	1.590	0.111
5	1.502	0.428	0.156	20	1.634	0.112

content profiles for the other columns were very similar. Clearly, the soil profiles are not homogeneous as is implicitly assumed when applying models I or II. Hence, the estimated model parameters must be viewed as effective bulk values for a particular depth (in this case 1 m). Although they may be valid only for that particular depth, we believe that the data are still useful for examining the general processes of anion exclusion and physical nonequilibrium during anion transport in undisturbed soil profiles.

Parameter Estimation

The nonlinear least squares inversion program CXTFIT (Parker and van Genuchten 1984b) was used to estimate the parameters in models I and II. The pulse time (T_0) was measured independently and kept constant during the curve fitting. To ensure mass recovery, c_0 was adjusted slightly to make the input concentration consistent with the mass balance $c_0 T_0 \equiv m_0$. Fitted parameters for model I are P and R , whereas P_m , R , β and ω are unknowns in model II. The dispersion coefficient D can be calculated from the Peclet number.

Experimental moments were calculated from the BTC's according to

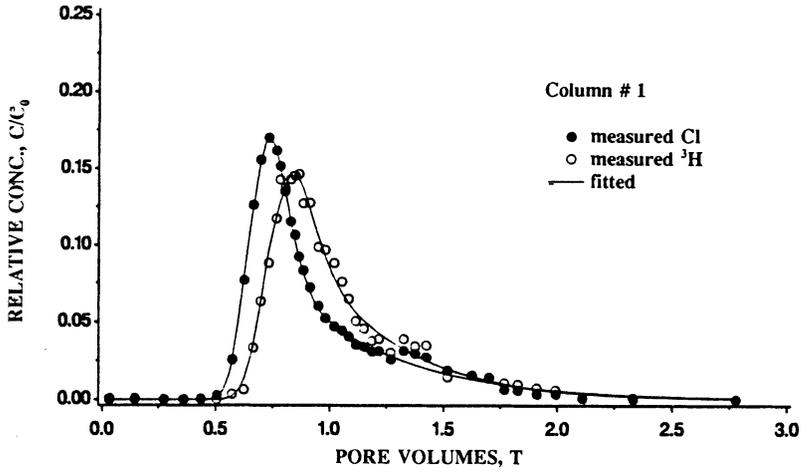
$$m_n \approx \sum_{k=1}^N (\bar{T}_k)^n \bar{c}_k \Delta T_k \quad (10)$$

Normalized absolute and central moments were obtained from Eq. (10) by applying Eqs. (5) and (6). Model parameters could subsequently be determined by equating the experimental moments to the theoretical expressions in Table 1, and solving the ensuing set of equations. First, the R -value in both models was computed from μ_1' . The Peclet number for model I is calculated from μ_2 . The three independent parameters P_m , β and ω for model II may be estimated, at least theoretically, from μ_2 , μ_3 , and μ_4 . However, the use of higher order moments often results in unstable or unreliable parameter estimates because of the predominant effects of relatively small experimental errors in the tail of the BTC. Still to get estimates for β and ω in model II with moments, we used the results for P_m from CXTFIT. Notice that for the higher order moments β and ω are not very sensitive to the value for P . With the fixed values for P_m , β and ω could be calculated from μ_2 and μ_3 according to Table 1.

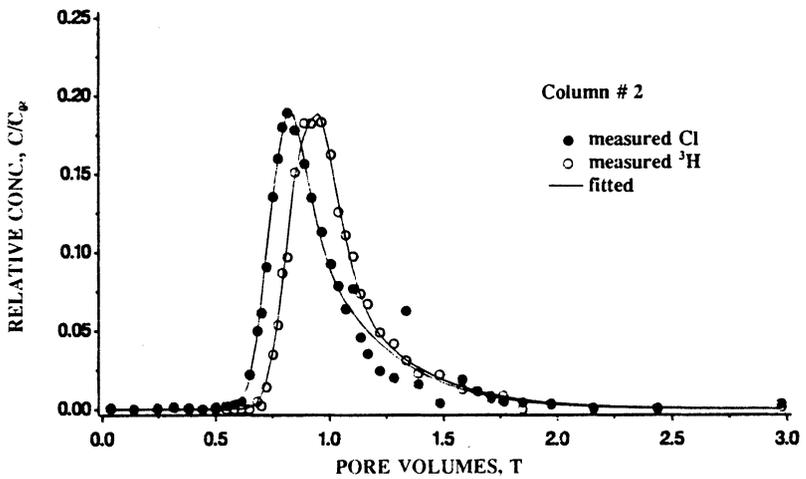
Results and Discussion

Figs. 2a-e show BTC's for Cl and $^3\text{H}_2\text{O}$ for the five experiments. Solid lines are fitted to the data points with CXTFIT according to model II. In all cases Cl appeared earlier in the effluent than $^3\text{H}_2\text{O}$, indicating some anion exclusion. The curves for columns 3 and 5 were fairly symmetrical whereas the BTC's for columns 1, 2 and 4 showed *tailing* for both Cl and $^3\text{H}_2\text{O}$, thus suggesting some degree of physical nonequilibrium.

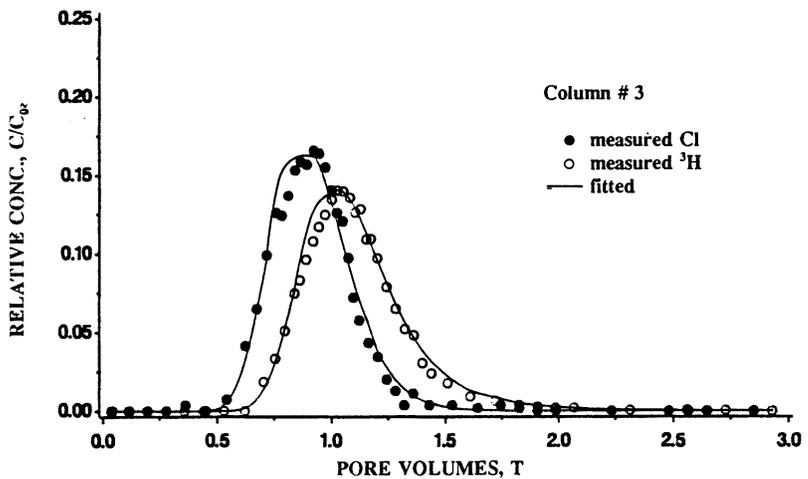
a)



b)



c)



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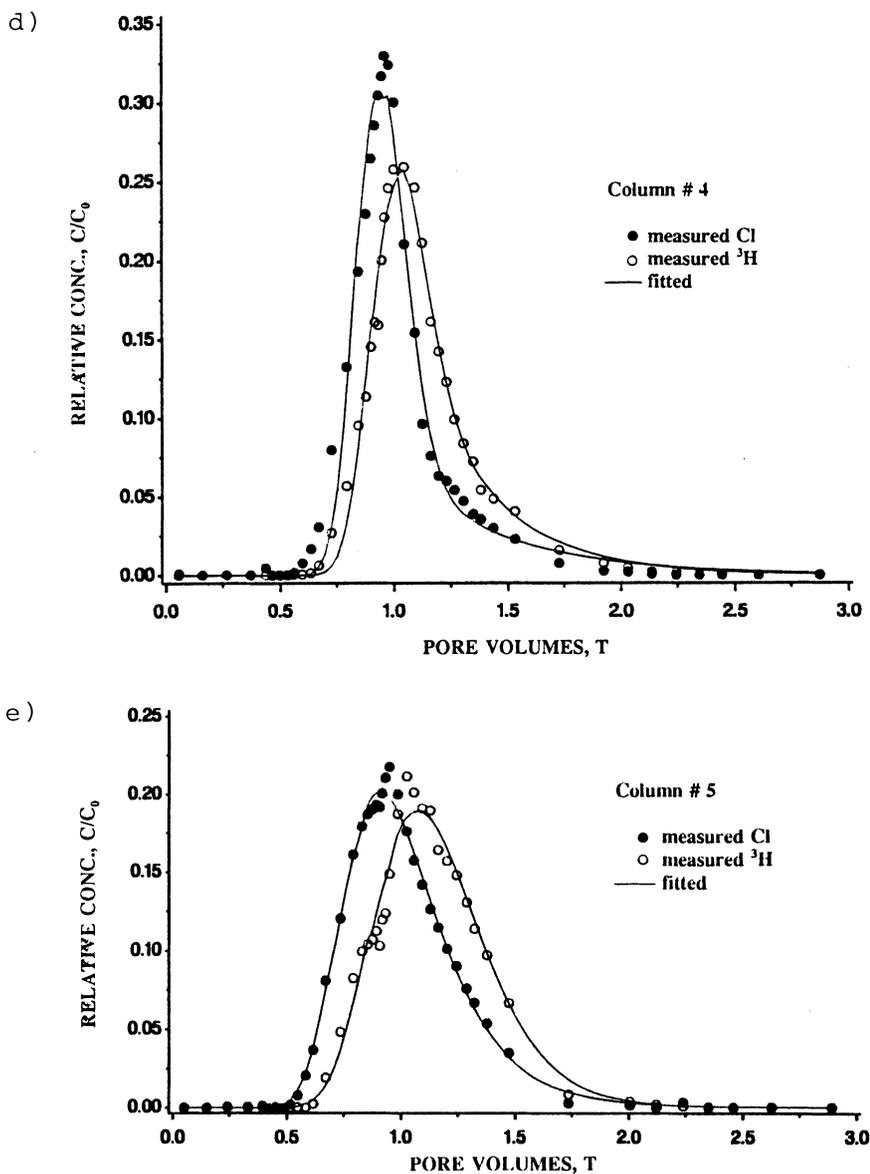


Fig. 2. Observed and fitted Cl and $^3\text{H}_2\text{O}$ distributions for the five soil columns. The solid line represents the BTC predicted according to model II using parameters obtained with CXTFIT.

Table 3 – Parameters obtained with CXTFIT according to model I and model II.

column no.	tracer	ν cm/d	Model I				Model II			
			P	R	r^2	P_m	R	β	ω	r^2
1	Cl	6.20	31	0.79	0.870	148	0.96	0.73	0.87	0.997
	³ H ₂ O		38	0.90	0.916	135	1.02	0.77	1.00	0.989
2	Cl	6.73	57	0.87	0.908	198	0.96	0.81	1.01	0.978
	³ H ₂ O		77	0.95	0.941	173	1.03	0.86	0.64	0.996
3	Cl	8.17	53	0.89	0.986	59	0.88	0.94	1.89	0.990
	³ H ₂ O		49	1.06	0.993	70	1.07	0.93	0.42	0.996
4	Cl	10.26	78	0.92	0.969	156	1.02	0.86	0.38	0.984
	³ H ₂ O		63	1.03	0.965	145	1.12	0.86	0.64	0.990
5	Cl	10.45	32	0.95	0.994	48	0.96	0.88	0.81	0.996
	³ H ₂ O		39	1.11	0.979	48	1.10	0.94	0.62	0.984

Table 3 summarizes the parameters determined with CXTFIT for models I and II. The correlation coefficients (r^2) for model I were quite high for columns 3 and 5, which showed relatively symmetrical curves. However, the r^2 values for model I were much lower for those columns which exhibited *tailing*. Values for P varied between 30 and 78, with a geometric mean of 47 for Cl and 51 for ³H₂O. These values correspond to a dispersivity of about 2 cm, which is reasonably small for undisturbed soils. The pore size distribution is presumably fairly uniform and no significant *fingering* or hydraulic instability likely occurred.

A better fit of the data was obtained in all cases with the nonequilibrium model II (Table 3, Fig. 2). Again, the improvement is most noticeable for experiments showing *tailing* (columns 1, 2, and 4). Note that the fitted R for model II has increased as compared to the use of model I, the geometric means for Cl being 0.88 and 0.96 for model I and II, respectively, while the corresponding values for ³H₂O were 1.01 and 1.07. The geometric mean of the Peclet numbers (P_m) in model II was 104, which is considerably greater than the value of 49 for the Peclet numbers (P) in model I. This increase of the Peclet number (or decrease in D) is caused by the implicit incorporation of solute spreading due to nonequilibrium into the Peclet number for model I. In fact, the nonequilibrium could be accounted for in model I by artificially adjusting the dispersion coefficient. An effective Peclet number (P_{eff}) for use in model I in terms of model II parameters, can be obtained by equating the theoretical second moments in Table 1 for the two models (Valocchi 1985; Schulin *et al.* 1987)

$$\frac{1}{P_{eff}} = \frac{1}{P_m} + \frac{(1-\beta)^2}{\omega} \tag{11}$$

Notice that the difference between P_{eff} and P_m decreases when β ($0 \leq \beta \leq 1$) and ω increase. We note that the use of model I with an approximate P_{eff} is only valid for relatively large P -values (Valocchi 1985).

Differences between Peclet numbers for different soil columns were found to be greater than the differences in Peclet numbers between Cl and $^3\text{H}_2\text{O}$ in a particular column. This shows that the Peclet number is more a characteristic of the porous medium than of the solute. The differences in Peclet number among soil columns can not be explained with variations in ν .

The mobile water fraction, β , was found to vary from 0.73 to 0.94, β is generally higher for the symmetrical BTC's. However, we did not find a clear trend for the mass transfer coefficient, ω . Consider column 3, which has a relatively high β value (0.94) with an average θ of $0.145 \text{ m}^3/\text{m}^3$, resulting in a θ_{im} of less than 0.01. The mass transfer coefficient is also quite high in comparison with the other experiments. Both conditions favour the appearance of a relatively symmetrical BTC typical of model I. A complete nonequilibrium description is clearly not needed for this column.

The R -value for Cl was 6 to 19 % less than for $^3\text{H}_2\text{O}$. This difference is presumably caused by anion exclusion. The anions are only excluded from a region corresponding to a volumetric water content of 0.01 and 0.03. In general R is less than 1 for Cl and slightly greater than 1 for $^3\text{H}_2\text{O}$ (Tables 3 and 4). It can be argued that R for $^3\text{H}_2\text{O}$ should be set to 1 since tritium is considered a good tracer for water movement. The observed increase in R can be explained by errors in θ and q caused by, for example, evaporation during slicing, but also by some isotopic exchange/sorption of $^3\text{H}_2\text{O}$ with the solid phase (*cf.* Heemstra *et al.* 1961). Hydrogen sorption by charged surfaces is likely to be minor in this study because of the relative high calcium concentrations.

Time moments for the BTC's as calculated with Eq. (9) are shown in Table 4. The calculated m_o can be compared to the initially applied mass, m_a , to give the relative mass recovery. The discrepancy between applied and recovered solute for Cl was at most 7 %, while 15 to 28 % of the applied $^3\text{H}_2\text{O}$ did not appear in the effluent. The recovery of $^3\text{H}_2\text{O}$ was reported to be excellent for short-duration experiments (Bond *et al.* 1982), whereas for long-duration experiments Nielsen and Jackson (1968) and van de Pol *et al.* (1977) found that a significant part of the applied $^3\text{H}_2\text{O}$ could not be recovered. The disappearance cannot be explained by radioactive decay, but rather, results from exchange of molecules between the liquid and the vapour phase and subsequent self-diffusion to the environment (Wierenga 1991:pers. com.).

The mean travel times, μ_1 , for Cl and $^3\text{H}_2\text{O}$ was significantly different within one experiment (Table 4) with differences from 5 to 20 % on a pore volume basis. The relatively low Cl concentration in the effluent of column 3 gave the largest differences in travel times. This difference probably resulted from the fact that lower ambient concentrations generally increase the relative anion exclusion volume (Krupp *et al.* 1972). An average difference between the travel times for Cl and $^3\text{H}_2\text{O}$ of 10 % on a pore volume basis, may not be significant for field-scale studies. The second central moment (μ_2), which reflects the variance of the BTC, was

Table 4 – Experimental moments and estimates of parameters obtained with moment analysis according to model I and model II.

column	tracer	m_0/m_a	Experimental moments					Model I	Model II	
			μ_1'	μ_2	μ_3	S	R	P	β	ω
1	Cl	0.96	0.96	0.113	0.054	1.4	0.92	15	0.67	1.87
	$^3\text{H}_2\text{O}$	0.72	1.04	0.091	0.031	1.1	1.01	22	0.68	2.80
2	Cl	1.03	1.01	0.118	0.097	2.4	0.97	16	0.81	0.64
	$^3\text{H}_2\text{O}$	0.75	1.06	0.065	0.034	2.1	1.02	33	0.87	0.65
3	Cl	0.97	0.91	0.037	0.006	0.8	0.88	32	0.94	0.61
	$^3\text{H}_2\text{O}$	0.83	1.11	0.062	0.017	1.1	1.07	22	0.90	0.82
4	Cl	0.94	1.02	0.052	0.017	1.5	0.96	36	0.84	1.14
	$^3\text{H}_2\text{O}$	0.85	1.14	0.067	0.023	1.3	1.08	36	0.83	1.34
5	Cl	0.93	1.02	0.065	0.015	0.9	0.96	29	0.86	1.38
	$^3\text{H}_2\text{O}$	0.79	1.15	0.066	0.011	0.7	1.09	37	0.88	2.35

highest for columns 1 and 2, whereas the skewness was greatest for columns 1, 2, and 4.

Table 4 also lists the parameters for models I and II obtained with the method of moments. The values for R , determined with μ_1' , were very similar to those determined with CXTFIT for model II whereas the agreement was somewhat less for model I parameters. Peclet numbers obtained with the method of moments were generally lower than those obtained with CXTFIT for model I. The geometric mean of p decreased from 47 to 24 for Cl, and from 51 to 29 for $^3\text{H}_2\text{O}$ (Table 4).

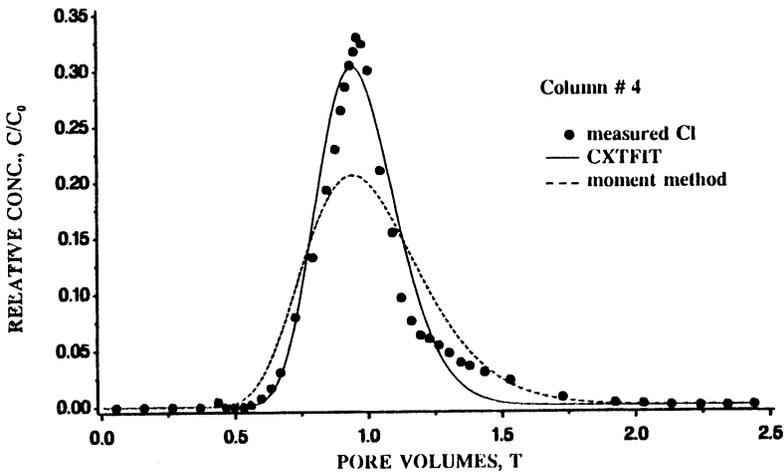


Fig. 3. Observed and fitted Cl distribution for column 4. The solid and the dashed lines represent the BTC predicted with parameters from CXTFIT and the method of moments, respectively, according to model I.

Fig. 3 shows an example of the BTC's predicted according to model I, using parameters obtained with both CXTFIT and the method of moments. The results indicate a poorer description of the data using parameters generated with the method of moments. Moments characterize unique features of the BTC, *i.e.*, mean, variance, *etc.*, in terms of the adopted transport model. If the model does not describe the data well, these unique values will also describe the data poorly. This contrasts with CXTFIT which has the flexibility to adjust parameter values for a certain model. A good example of this feature is provided by R as obtained with CXTFIT using models I and II (Table 3). At least theoretically, R should be independent of the degree of nonequilibrium (Table 1). In reality, CXTFIT produces a better fit for model II by subjectively increasing R . Hence, despite its limitations to accurately reproduce BTC's, the moment method is attractive for correctly quantifying the extent of anion exclusion since it yields the precise experimental mean travel time. Note that the parameters can also be determined from moments using a simultaneous least-squares fit as outlined by Jury and Sposito (1985). This last procedure gives additional flexibility to describe the BTC.

Values for β derived from time moments were generally a few per cent smaller than those determined with CXTFIT. Mass transfer coefficient determined with moments were in most cases higher than those obtained with CXTFIT. Note that β and ω exhibited an inverse relationship, *i.e.*, smaller values for β can be compensated for by an increase in ω without significantly altering the BTC.

Conclusions

The five undisturbed large soil columns used in this study showed significant variations in transport properties for similar experiments. A much better fit of the experimental data for columns 1, 2, and 4 was obtained with CXTFIT if the four-parameter nonequilibrium model (model II) was employed rather than the two-parameter equilibrium model (model I). However, model II described the BTC's for column 3 and 5 only slightly better. Still, even for these sandy soils, physical nonequilibrium could generally not be neglected, since an average immobile water fraction of 0.14 was found. The retardation factor R of Cl was about 10 % less than that of $^3\text{H}_2\text{O}$, indicating some anion exclusion. The Peclet numbers for model II varied between 50 and 200. Estimated model parameters deviated generally more extensively between columns than between tracers in a particular column.

Time moment analysis is a useful tool for quantifying mean travel time (μ_1), spreading (μ_2) and asymmetry (S) of BTC's. Parameter estimation by the moment method gives retardation factors equal to the experimental mean travel time. The unique solution for each parameter can adversely affect the estimation of the remaining parameters if the experimental data are poorly described with a theoretical model.

Notation

c_{im}	concentration in immobile region (ML^{-3})
c_m	concentration in mobile region (ML^{-3})
c_o	input pulse concentration (ML^{-3})
\bar{c}_k	mean concentration in the k^{th} pore volume interval (ML^{-3})
C	dimensionless concentration (normalized to c_o)
C_{im}	dimensionless concentration in immobile region (normalized to c_o)
C_m	dimensionless concentration in mobile region (normalized to c_o)
D	hydrodynamic dispersion coefficient (L^2T^{-1})
D_m	hydrodynamic dispersion coefficient for mobile zone (L^2T^{-1})
L	column length (L)
m_a	initially applied mass (M)
m_n	absolute n^{th} time moment (M)
N	total number of sampling times for each column
P	column Peclet number ($= vL/D$)
P_m	column Peclet number for mobile region ($= v_mL/D_m$)
P_{eff}	effective column Peclet number
q	Darcian water flux (LT^{-1})
R	retardation factor
S	skewness
t	time (T)
t_o	input pulse time (T)
T	pore volume equal to vt/L
T_o	dimensionless input pulse time equal to vt_o/L
\bar{T}_k	midpoint in k^{th} pore volume interval
ΔT_k	k^{th} pore volume interval
v	average pore-water velocity ($= q/\theta$) (LT^{-1})
v_m	pore-water velocity ($= q/\theta_m$) (LT^{-1})
v_1	normalized first absolute time moment of input pulse
Z	dimensionless distance in the direction of flow normalized to L
α	first order mass transfer coefficient (T^{-1})
β	dimensionless partition variable ($= \theta_m/\theta$)
θ	volumetric water content ($= \theta_{im} + \theta_m$) (L^3L^{-3})
θ_{im}	volumetric water content of immobile region (L^3L^{-3})
θ_m	volumetric water content of mobile region (L^3L^{-3})
μ_n	n^{th} central time moment
μ_n^f	n^{th} central time moment for a general input pulse
μ_n^δ	n^{th} central time moment for a Dirac input pulse
μ_n'	normalized n^{th} time moment
$\mu_n'^f$	normalized n^{th} time moment for a general input pulse
$\mu_n'^\delta$	normalized n^{th} time moment for a Dirac input pulse
ν_n	n^{th} central time moment of input pulse
ω	dimensionless mass transfer coefficient ($= \alpha L/q$).

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