

LYSIMETER STUDY OF ANION TRANSPORT DURING STEADY FLOW THROUGH LAYERED COARSE-TEXTURED SOIL PROFILES

OLE H. JACOBSEN,¹ FEIKE J. LEIJ,² AND MARTINUS TH. VAN GENUCHTEN²

Transport of Cl and NO₃ was studied during steady-state unsaturated water flow in several lysimeters filled with a coarse sand or sandy loam. Breakthrough curves were obtained with suction cups at six different depths. The transport parameters were determined by fitting the classical convection-dispersion equation to the data assuming a homogeneous or a two-layer soil profile. As expected, the two-layer solution described the data better than the solution assuming a homogeneous soil, especially for the sand where the fitted pore-water velocities were about 60% higher in the subsoil compared with the topsoil. The average dispersivity for the sandy loam was 1.9 cm for the topsoil and 1.3 cm for the subsoil, whereas a value of 0.58 cm could be used for the entire profile for the coarse sand. Solute outflow from the lysimeters was reasonably well predicted using the transport parameters estimated from breakthrough curves obtained with the suction cups. The dispersion coefficients estimated from the effluent concentrations were generally somewhat larger than those derived from suction cup data. The total concentration had little effect on the dispersion coefficient and the pore-water velocity. No significant differences were found between NO₃ and Cl, although dispersivities for Cl were always slightly higher than those for NO₃.

Because of excess rainfall or irrigation, surface-applied fertilizers and pesticides will eventually move beyond the root zone. This process has long been of interest to agronomists since it determines the effectiveness of the applied chemicals. Solute leaching has received close scrutiny during the last few decades because of

¹ The Danish Institute for Plant and Soil Science, Flensborgvej 22, Store Jyndevad, DK-6360 Tinglev, Denmark.

² U.S. Salinity Laboratory, USDA, ARS, 4500 Glennwood Drive, Riverside, CA 92501.

Received Sept. 6, 1991; accepted Jan. 30, 1992.

growing concerns that agricultural chemicals adversely affect the quality of underlying ground water systems.

Several modeling approaches have been suggested for describing solute transport quantitatively (Addiscott and Wagenet 1985; Nielsen et al. 1986). Solute transport is commonly described with the convection-dispersion equation (CDE). For one-dimensional steady flow in a homogeneous soil the CDE can be written as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \quad (1)$$

where C is the solute concentration (ML⁻³), z is the distance from the surface (L), t is time (T), D is a dispersion coefficient reflecting the combined effects of molecular or ionic diffusion and hydrodynamic dispersion (L²T⁻¹), and v is the pore-water velocity given by q/θ in which q is the Darcian flux density (LT⁻¹) and θ is the volumetric water content (L³L⁻³). Equation (1) assumes that the solute behaves as a perfect tracer for water. Interaction of the solute with the solid phase requires the use of a retardation factor (Nielsen et al. 1986). Here we assume that D and v are effective parameters which implicitly account for possible linear sorption or anion exclusion processes. The dispersion coefficient varies approximately linearly with the apparent water velocity as long as the water content does not vary significantly (Biggar and Nielsen 1976; van Genuchten and Wierenga 1977; Yule and Gardner 1978; Nkedi-Kizza et al. 1983). The ratio D/v is often referred to as the dispersivity, λ (L).

Application of a solute pulse to an initially solute-free semi-infinite soil profile can be described with the initial and boundary conditions:

$$C(z,0) = 0 \quad z > 0 \quad (2a)$$

$$\left(vC - D \frac{\partial C}{\partial z} \right) \Big|_{z=0^+} = \begin{cases} vC_0 & 0 < t \leq t_0 \\ 0 & t > t_0 \end{cases} \quad (2b)$$

$$\frac{\partial C}{\partial z} \Big|_{z \rightarrow \infty} = 0 \quad t > 0 \quad (2c)$$

where C_0 is the solute concentration of the ap-

plied pulse (ML^{-3}) of duration t_o (T), and $z \rightarrow 0^+$ implies that the input boundary $z = 0$ is approached from within the soil profile. The solution to (1) subject to (2) was given by Lindstrom et al. (1967) as

$$C(z,t) = \begin{cases} C_o A_1(z,t) & 0 < t \leq t_o \\ C_o A_1(z,t) - C_o A_1(z,t-t_o) & t > t_o \end{cases} \quad (3)$$

with

$$A_1(z,t) = \frac{1}{2} \operatorname{erfc} \left[\frac{z - \nu t}{(4Dt)^{1/2}} \right] + \left(\frac{\nu^2 t}{\pi D} \right)^{1/2} \cdot \exp \left[-\frac{(z - \nu t)^2}{4Dt} \right] - \frac{1}{2} \left(1 + \frac{\nu z}{D} + \frac{\nu^2 t}{D} \right) \cdot \exp \left(\frac{\nu z}{D} \right) \operatorname{erfc} \left[\frac{z + \nu t}{(4Dt)^{1/2}} \right].$$

The CDE model has not always been successful in accurately quantifying transport under field conditions because of the problems of soil heterogeneity (including soil layering), preferential flow, chemical nonequilibrium, improper description of the boundary conditions, and a lack of well-defined model parameters (Butters and Jury 1989). Jury and Roth (1990) point out that validation of the CDE requires concentration measurements for different combinations of depth, time, and water flow velocities. Previous work on solute transport often focused on alternative mathematical descriptions of breakthrough curves at the column outlet in terms of the CDE or more sophisticated models. One objective of this study was to investigate if the CDE can also provide a good description of breakthrough curves (BTC's) at different depths.

Layered Soils

Natural field soils in humid climates often exhibit layering. Typically, such soils contain an A horizon with relatively high amounts of organic matter as compared to underlying B and C horizons. This situation may result in higher water retention and different hydraulic conductivity values for the upper layer, thus invalidating the homogeneity assumption. Leij et al. (1991) gave several analytical solutions of the one-dimensional CDE for a two-layer medium. One of the solutions is based on the assumption that the layers are in effect semi-infinite and that third- or flux-type conditions can be imposed at both the inlet boundary and the inter-

face of the two layers. The interface condition is expressed as

$$\left(\theta_1 \nu_1 C_1 - \theta_1 D_1 \frac{\partial C_1}{\partial z} \right) \Big|_{z=L^-} = \left(\theta_2 \nu_2 C_2 - \theta_2 D_2 \frac{\partial C_2}{\partial z} \right) \Big|_{z=L^+} \quad (4)$$

where the subscripts 1 and 2 denote the topsoil and subsoil, respectively, and L (L) is the depth of layer 1. The other conditions are the same as those given by Eq. (2). We note that Eqs. (1) and (2c) were applied to describe the transport problem for both the topsoil and the subsoil, using the subscript notation for C , D , and ν to distinguish between the two layers (Leij et al. 1991).

Because the first layer is considered to be an effectively semi-infinite profile, Eq. (3) holds immediately for the concentration distribution in the top layer (Barry and Parker 1987; Leij et al. 1991). This assumption implies that transport in the upper layer is not affected by transport in the second layer. The procedure appears justified because of the passive nature of the hydrodynamic dispersion process, assuming that diffusion is relatively small as compared to dispersion. While boundary condition (4) leads to a continuous solute flux across the interface, the concentration itself may be macroscopically discontinuous at the interface. As is true for the inlet condition (Eq. (2b)), such a discontinuity likely does not occur at the microscopic level because of diffusion (Parker and van Genuchten 1984a).

Application of Eqs. (2) and (4) to the two-layer problem leads to the following solution of the CDE for the concentration in the second layer (Leij et al. 1991):

$$C_2(z,t) = \begin{cases} C_o A_2(z,t) & 0 < t \leq t_o \\ C_o A_2(z,t) - C_o A_2(z,t-t_o) & t > t_o \end{cases} \quad (5)$$

with

$$A_2(z,t) = \frac{\nu_2}{(4D_2)^{1/2}} \int_0^t \left\{ \operatorname{erfc} \left[\frac{L - \nu_1 \tau}{(4D_1 \tau)^{1/2}} \right] + \exp \left(\frac{\nu_1 L}{D_1} \right) \operatorname{erfc} \left[\frac{L + \nu_1 \tau}{(4D_1 \tau)^{1/2}} \right] \right\} \times \left\{ [\pi(t-\tau)]^{-1/2} \exp \left[-\frac{[z-L-\nu_2(t-\tau)]^2}{4D_2(t-\tau)} \right] \right\}$$

$$-\frac{v_2}{(4D_2)^{1/2}} \exp\left(\frac{v_2(z-L)}{D_2}\right) \cdot \operatorname{erfc}\left[\frac{z-L+v_2(t-\tau)}{[4D_2(t-\tau)]^{1/2}}\right] d\tau$$

where τ is a dummy integration variable. Notice that C_2 depends on the transport parameters of both layers.

Experimental

Suction cups are often used for measuring in-situ concentrations in solute transport experiments. There has been a considerable amount of discussion in the literature on whether samples obtained with suction cups represent actual soil solution concentrations (Addiscott 1990). Van Genuchten and Wierenga (1986) pointed out that it is difficult to reason whether suction cups yield flux- or volume-averaged concentrations, or a combination of both. Fortunately, for the relatively high Peclet numbers often seen during transport in sandy soils, no significant differences are expected between the two concentration modes (Parker and van Genuchten 1984a). This conclusion is consistent with findings for a comparable coarse-textured soil by Hansen (1991) and Djurhuus (1990) that concentrations from suction cup samples were similar to those derived from effluent samples or soil cores. Suction cups often provide the only practical means for monitoring solute concentrations in the root zone. In this study a comparison will be made between observed effluent BTC's at the lysimeter outlet and predicted effluent BTC's using CDE parameters derived from suction cup data.

The total electrolyte level determines the thickness of the electric double layer. Especially for soils high in clay and ionizable organic matter, anion movement may be influenced by the applied solute concentration (James and Rubin 1986). Lower anion concentrations lead to a thicker electric double layer since a greater fraction of the anions is being expelled from soil particle surfaces toward the center of liquid-filled pores (Krupp et al. 1972). Because this part of the liquid phase is more mobile, the displacement process may be less dispersive at lower total solute concentrations. Different values for C_0 will be used in this study to investigate the effect of solute concentration on field transport. We also investigated the similarity in phys-

ical behavior of Cl and NO_3 . The movement of these two tracers in soils is expected to be quite similar (Biggar and Nielsen 1976), except that Cl is not subject to microbial transformation or assimilation processes.

In summary, the objectives of this study are to (i) evaluate the applicability of the CDE to transport in homogeneous and two-layer soil profiles using data obtained for different pore-water velocities, (ii) compare measured lysimeter effluent BTC's with those predicted using model parameters derived from suction cup data, (iii) conduct displacement experiments at different electrolyte concentration levels, and (iv) compare the transport of Cl and NO_3 .

MATERIALS AND METHODS

Table 1 provides an outline of the experiments involving two soil types and three different solute concentrations. Solute pulses were applied during steady water flow to 1.6-m deep lysimeters of 1 m². Suction cups were used to sample the solute at six different depths in 18 lysimeters, whereas for all 30 lysimeters the effluent was obtained at the bottom. Twenty-two lysimeters were uniformly packed with a Jyndevad coarse sand (Orthic Haplohumod) and eight with a Rønhave sandy loam (Typic Agrudalf). Care was taken to pack the lysimeters to the same densities as those of the fields where the soils were sampled; in both cases the boundary between the upper and lower horizon was located at $L = 0.35$ m. Table 2 provides the bulk density, clay and organic matter contents, cation exchange capacity, and the range of water contents during the experiments as measured with a neutron probe for the two layers of both soils. A thin layer of gravel was placed at the bottom of the lysimeter; the soil was presumably satu-

TABLE 1
Number of lysimeter experiments for each application rate

	C_0 (mol/L)		
	0.18	0.36	0.71
<i>Jyndevad Coarse Sand</i>			
Suction cups	1	2	2
No suction cups	2	2	2*
<i>Rønhave Sandy Loam</i>			
Suction cups	0	2	2

* 0.355 mol/L Cl and 0.355 mol/L NO_3 .

TABLE 2
Selected properties of the two layers of Jyndevad Coarse Sand and Rønhave Sandy Loam

Soil	Layer	Bulk density g/cm ³	Clay %	Organic matter %	CEC meq/100 g	θ Range cm ³ /cm ³
Jyndevad Coarse Sand	1	1.40	4	2.3	7	0.18–0.21
	2	1.50	3	0.4	2	0.13–0.16
Rønhave Sandy Loam	1	1.45	14	1.9	16	0.30–0.34
	2	1.65	21	0.5	12	0.30–0.33

rated just above the gravel layer during gravity drainage.

Six different flow rates were applied to the coarse sand and five to the sandy loam. The steady water flux was applied with a rail-driven field sprayer using irrigation water extracted from a well (35 ppm Cl, 15 ppm NO₃, EC_e ≈ 42 mmho/m, 7.0 < pH < 7.5). The low background Cl and NO₃ concentrations were subtracted from the measured concentrations prior to data analysis. The sprayer automatically irrigated the two rows of lysimeters at uniform preselected time intervals between 5 and 20 minutes and at different intensities obtained by varying the nozzle size. The lysimeter setup was covered with a roof to eliminate rainfall, whereas a wind shelter was placed on one side of the lysimeters to minimize evaporation.

The steady flow conditions were checked by daily measurements of the amount of drainage water from each lysimeter. Different evaporation conditions during the experiment and occasional brief electrical interruptions caused the outflow to vary slightly. For the parameter estimation process we therefore used an adjusted time, t_a , according to

$$t_a = \frac{Q(t)}{q_m(t)} \quad (6)$$

where $Q(t)$ is the cumulative drainage flux (L) at time t , and $q_m(t)$ is the mean drainage flux (LT⁻¹) averaged over the time interval of interest during the experiment. This adjustment is equivalent to the use of cumulative net applied water fluxes as implemented by Butters and Jury (1989). The adjustment provides a good approximation when the water flux fluctuates only slightly because of the assumption that θ and $\lambda = D/\nu$ are constant for different water fluxes. Neutron access tubes were installed in four lysimeters representing two flow rates and two soil types. Water contents measured with the neutron probe varied little among the dif-

ferent flow rates; the results can be found in Table 2.

After ensuring steady flow, a CaCl₂ or a mixed CaCl₂/Ca(NO₃)₂ pulse was applied slowly and uniformly to the soil surface at flow rates between 0.2 cm/day and 2 cm/day (Table 3). Application of 5 L of a 0.18-M pulse to the lysimeter is equivalent to supplying 125 kg nitrate-N/ha. In each row of lysimeters, suction cups were installed horizontally through the walls in five lysimeters containing coarse sand and four containing sandy loam at depths of 30, 50, 70, 90, 110, and 130 cm. Solution samples were obtained using the falling head method; a suction of 800 cm was imposed on the 4.5-cm long and 1-cm diameter ceramic suction cups yielding a sample of at most 20 ml. Chloride concentrations were determined by potentiometric titration with AgNO₃ using a Mettler Titrator, whereas spectrophotometry was used to determine NO₃ concentrations (Best 1976) with a Technicon Autoanalyzer.

The concentration data were analyzed with the nonlinear least-squares inversion program CXTFIT (Parker and van Genuchten 1984b). The program was adapted to include the two-layer solution (Eq. 5). A copy of the modified program is available from the authors.

RESULTS AND DISCUSSION

Figure 1 shows typical examples of Cl BTC's at various depths for the coarse sand (Fig. 1a) and the sandy loam (Fig. 1b). Numbers denote data points at consecutive depth locations in the lysimeters, while the solid lines were calculated with Eq. (3). Although only a few data points were measured at each depth during passage of the solute pulse, the fitted CDE curves for a homogeneous soil profile appear to give a reasonable description of the data, especially for the sandy loam.

Values for D , ν , and t_a were fitted to Eq. (3). Small errors in the mass balance were observed

TABLE 3

Values of the measured water flux, q , and the total solute concentration, C_o ; and the parameters ν , D , t_o , and the correlation coefficient, r^2 , obtained by fitting the one-layer CDE solution to observed suction cup data

Lysimeter number	q cm/d	C_o mol/L	ν cm/d	D cm ² /d	t_o d	r^2
<i>Jyndevad coarse sand</i>						
17	0.227	0.18	1.80	3.73	2.10	0.616
10	0.221	0.36	1.96	2.00	2.55	0.784
15	0.231	0.71	1.96	2.90	2.67	0.550
18	0.277	0.71	1.96	3.34	2.25	0.577
3	0.445	0.18	3.67	1.62	0.87	0.788
4	0.453	0.36	3.39	2.71	1.11	0.668
5	0.476	0.36	3.49	3.64	1.06	0.768
2	0.459	0.71	4.23	5.64	1.09	0.882
8	0.426	0.71	3.53	3.32	1.04	0.699
18	0.704	0.18	5.22	3.43	0.73	0.641
10	0.551	0.36	4.61	3.86	1.01	0.777
17	0.617	0.36	4.54	3.29	0.76	0.768
15	0.563	0.71	4.47	4.77	0.98	0.659
14	0.734	0.71	4.75	3.49	0.72	0.546
4	1.058	0.18	6.83	7.88	0.50	0.700
8	0.951	0.36	7.11	3.75	0.53	0.885
3	0.996	0.36	7.02	3.11	0.40	0.700
2	1.025	0.71	7.89	7.89	0.55	0.870
5	1.109	0.71	7.31	3.92	0.40	0.929
17	1.321	0.18	7.61	15.18	0.37	0.379
18	1.389	0.36	7.28	9.44	0.43	0.532
14	1.506	0.36	8.20	7.45	0.48	0.654
15	1.289	0.71	8.44	7.68	0.64	0.742
10	1.294	0.71	8.04	10.19	0.51	0.515
2	2.063	0.18	14.36	14.22	0.30	0.844
8	1.979	0.36	12.79	21.44	0.29	0.444
4	2.160	0.36	14.20	20.38	0.34	0.679
5	2.088	0.71	11.76	20.44	0.38	0.555
3	2.144	0.71	10.88	29.37	0.33	0.399
<i>Rønhave sandy loam</i>						
12	0.168	0.36	0.80	1.28	3.72	0.960
11	0.188	0.36	0.78	1.05	3.58	0.940
13	0.143	0.71	0.74	1.77	3.04	0.871
16	0.197	0.71	0.74	1.31	3.14	0.903
7	0.397	0.36	1.90	6.20	1.48	0.729
1	0.412	0.36	1.63	1.65	1.28	0.206
9	0.408	0.71	1.64	2.66	1.49	0.763
6	0.410	0.71	1.82	3.54	1.35	0.790
12	0.496	0.36	2.08	2.43	0.94	0.889
11	0.543	0.71	2.40	3.33	1.13	0.933
16	0.586	0.71	2.23	3.71	0.87	0.847
9	0.918	0.36	3.73	6.06	0.55	0.697
7	0.938	0.36	3.85	5.71	0.50	0.870
6	0.938	0.71	3.64	5.22	0.47	0.821
1	1.000	0.71	3.92	3.48	0.49	0.958
12	1.263	0.36	4.48	14.19	0.58	0.830
11	1.272	0.36	4.57	12.58	0.55	0.929
13	1.227	0.71	4.15	14.04	0.58	0.840
16	1.311	0.71	4.50	18.97	0.48	0.727

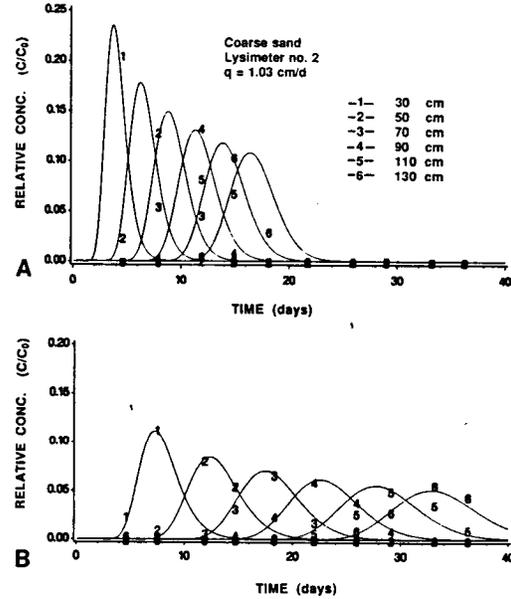


FIG. 1. Observed and fitted BTC's for Cl at six depths: (a) coarse sand and (b) sandy loam. Numbers indicate measured values, while solid lines represent solutions of the homogeneous CDE fitted to the pooled observations from six depths.

for some of the lysimeters. These errors could be due to uneven application of the solute or inadequate sampling with the suction cups. To obtain a better description of the data we therefore decided to also fit the pulse time, t_o . For each experiment, BTC's at all depths were considered simultaneously in the parameter optimization process.

The results for the homogeneous (one-layer) CDE are summarized in Table 3, which is grouped based on the gravimetrically determined average water flux (q). A few of the leaching experiments were not analyzed because of experimental problems due to freezing, ponding at the soil surface, or other technical problems. An analysis of variance showed that D/ν and $\log(D/\nu)$ did not depend significantly on the various treatments (flow rate, C_o , lysimeter). Furthermore, the normality test by Shapiro and Wilk (1965) revealed that $\lambda = D/\nu$ was better described with a lognormal than a normal distribution. This is in accordance with the studies of Biggar and Nielsen (1976) and van de Pol et al. (1977) who showed that D and ν are lognormally distributed.

The correlation coefficients for the coarse

sand (Table 3) are quite low, indicating that Eq. (3) did not accurately describe the observed data for sandy soils with relatively high organic matter content in the upper layer. This high organic matter content resulted in higher water contents and, hence, lower pore-water velocities in the upper part of the soil profile, thus delaying the movement of Cl through this layer as compared to the remainder of the soil profile. Figure 1a shows the measured pulse to be behind the calculated pulse at 30 cm (i.e., the top part of the lysimeter) and to be ahead of the calculated curve at 130 cm.

Because the soil profiles were made up of two distinct horizons, the concentrations were also fitted to the solution of the two-layer system, i.e., Eq. (3) for the topsoil and Eq. (5) for the subsoil. The introduction of two additional fitting parameters should result in higher correlations. On the other hand, too many parameters can also lead to uniqueness problems. To improve the stability of the parameter estimation process for the coarse sand, we assumed a certain degree of similarity of the transport processes in the two layers. Similarity was invoked by assuming that the same dispersivity could be used for both layers (i.e., $\lambda_1 = \lambda_2$) and that this dispersivity would be the same for all lysimeter leaching experiments. Note that, especially for the coarse sand, relatively few data points were available at times when the pulse was passing. This lack of data mandated simplifying assumptions to improve the data analysis. The constant dispersivity ($\lambda = 0.58$ cm) used in the subsequent estimation was calculated from the geometric means of λ_1 and λ_2 initially found for each experiment in the sandy soil lysimeters. The geometric means of λ_1 and λ_2 for the individual lysimeter experiments were 0.54 cm and 0.63 cm, respectively. A Student's t test of $\log(\lambda_1) - \log(\lambda_2)$ for each replicate showed that the mean of this difference was not significantly different from zero.

The fitted values for ν and t_0 are listed in Table 4 for the coarse sand, whereas Table 5 contains the fitted ν and D values for the sandy loam. Even with the restriction of having only one constant dispersivity value for both layers of the coarse sand, the results in Table 4 indicate that the correlations are improved considerably for the two-layer analysis compared with the one-layer case (Table 3). Figure 2 shows the fitted curves (solid lines) for the two-layer sys-

TABLE 4

Values of the parameters ν_1 , ν_2 , t_0 , and the correlation coefficient, r^2 , for Jyndevad Coarse Sand, obtained by fitting the two-layer CDE solution to observed suction cup data assuming $\lambda_1 = D/\nu = \lambda_2 = 0.58$ cm

Lysimeter number	ν_1 cm/d	ν_2 cm/d	t_0 d	r^2
17	1.38	2.51	1.61	0.695
10	1.77	2.20	2.21	0.811
15	1.55	2.63	2.54	0.803
18	1.71	2.45	1.66	0.645
3	3.44	3.93	0.93	0.803
4	3.10	3.86	1.03	0.708
5	2.93	4.09	1.00	0.942
2	3.70	4.72	0.82	0.814
8	2.97	4.23	1.00	0.878
18	3.09	7.84	0.72	0.847
10	3.41	5.83	0.98	0.907
17	3.38	5.72	0.76	0.946
15	3.47	5.44	0.96	0.836
14	3.87	6.67	0.69	0.775
4	5.56	7.65	0.48	0.742
8	6.13	7.85	0.54	0.910
5	6.26	8.58	0.42	0.970
3	7.38	6.86	0.46	0.704
2	6.32	9.62	0.46	0.978
17	5.77	10.85	0.34	0.754
18	5.97	10.00	0.40	0.817
14	6.80	11.17	0.43	0.887
15	6.97	11.09	0.59	0.938
10	6.59	11.02	0.44	0.722
2	13.99	15.06	0.26	0.845
8	8.95	19.21	0.26	0.826
4	11.21	17.47	0.26	0.744
5	8.69	17.21	0.32	0.879
3	7.46	19.22	0.26	0.780

tem using the data as in Fig. 1. A comparison of Figs. 1a and 2a suggests that the two-layer model gives a better description of the data. On average, ν_2 was found to be 57% higher than ν_1 for the coarse sand, indicating that the "effective" water content of layer 1 (A horizon) was 57% higher than in layer 2. This is in line with the measured θ for the two layers, although the latter showed a somewhat smaller difference, presumably due to the effect of differences in dry bulk density on the neutron probe readings. For the sandy loam, however, ν_1 and ν_2 were nearly identical. The higher clay content and the higher dry bulk density in the subsoil apparently must have compensated for the higher organic matter content in the topsoil and resulted in nearly identical water contents in the two layers. The geo-

TABLE 5

Values of the parameters ν_1 , D_1 , ν_2 , D_2 , t_0 , and the correlation coefficient, r^2 , for Rønhave sandy loam, obtained by fitting the two-layer CDE solution to observed suction cup data

Lysimeter number	ν_1 cm/d	D_1 cm ² /d	ν_2 cm/d	D_2 cm ² /d	t_0 d	r^2
12	0.84	1.34	0.75	1.06	3.72	0.973
11	0.79	1.05	0.76	1.11	3.58	0.945
13	0.69	1.76	0.81	0.95	3.04	0.907
16	0.70	1.23	0.81	1.17	3.14	0.927
7	2.17	9.82	1.64	2.70	1.48	0.813
1	1.67	2.10	1.58	1.13	1.28	0.263
9	2.03	3.11	1.34	1.28	1.49	0.930
6	1.95	4.52	1.64	1.88	1.35	0.825
12	1.99	1.98	2.26	3.12	0.94	0.916
11	2.54	3.74	2.21	2.48	1.13	0.952
16	2.09	3.70	2.42	2.89	0.87	0.864
9	4.62	3.56	3.05	3.55	0.55	0.874
7	4.09	6.76	3.60	3.42	0.50	0.894
6	3.81	5.62	3.48	4.19	0.47	0.830
1	4.26	3.63	3.69	3.51	0.49	0.973
12	3.92	13.19	5.08	9.30	0.58	0.887
11	4.47	14.53	4.59	8.66	0.55	0.938
13	3.55	13.57	4.75	7.52	0.58	0.917
16	3.53	14.13	5.86	8.10	0.48	0.871

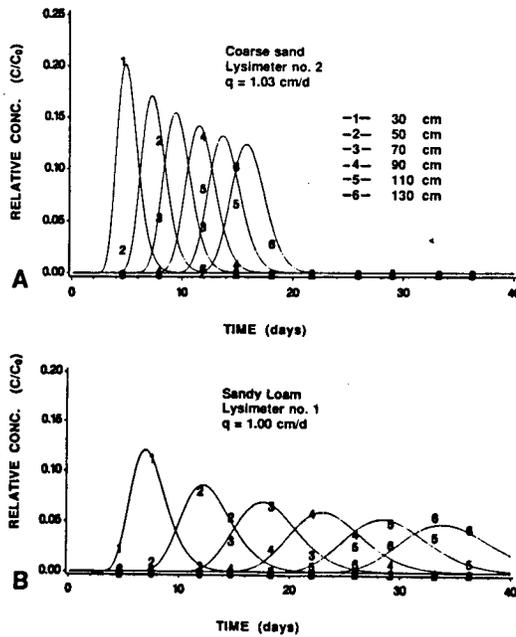


FIG. 2. Observed and fitted BTC's for Cl at six depths: (a) coarse sand and (b) sandy loam. Numbers indicate measured values, while solid lines represent solutions of the two-layer CDE fitted to the pooled observations from six depths.

metric means were 1.86 for λ_1 and 1.26 for λ_2 for the sandy loam.

Figure 3 shows the relation between the dispersion coefficient and the pore-water velocity obtained from the two-layer analysis of the sandy loam data. The geometric means of the dispersivities as shown in Fig. 3 indicate that the relationships $\log(\nu_1) - \log(D_1)$ and $\log(\nu_2) - \log(D_2)$ were reasonably well described by assuming a constant dispersivity.

Figures 4a and 4b show some typical examples of measured effluent BTC's for the coarse sand and the loamy sand, respectively. The solid lines present the BTC's predicted with Eq. (5) using parameters derived from the suction cup data. The mean travel times of the solute were well predicted for both soil types. However, D values derived from the outflow data were significantly higher than those based on suction cup data. This effect, which is especially pronounced for the coarse sand, may be explained by additional mixing at the outlet boundary. Because of the

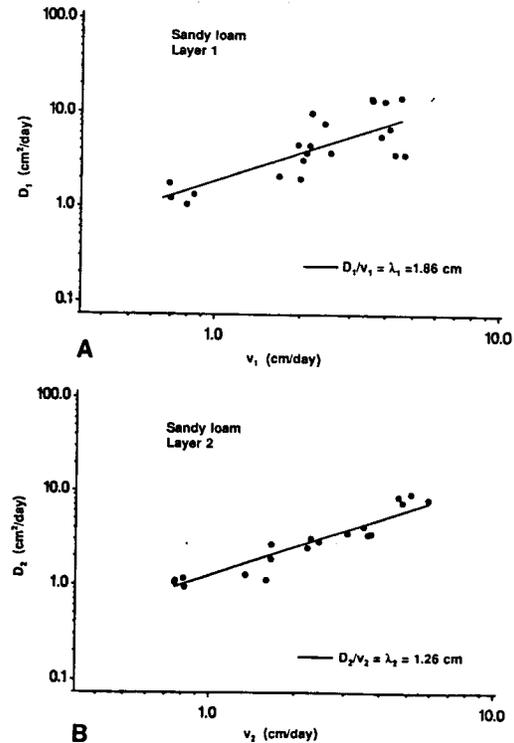


FIG. 3. The relationship between $\log D$ and $\log \nu$ for the sandy loam experiments fitted to the solution of the CDE for a two-layer profile: (a) topsoil and (b) subsoil.

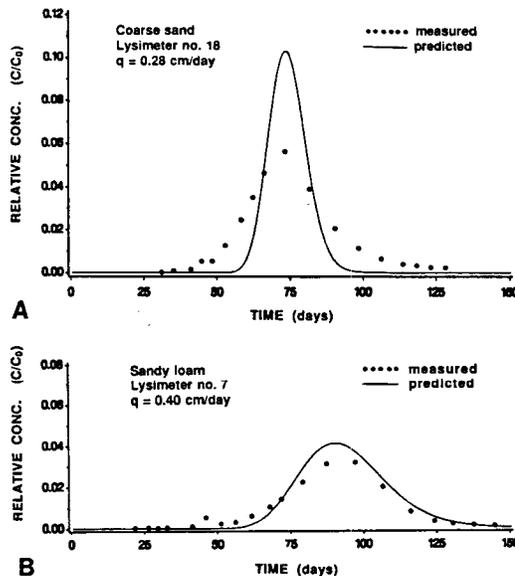


FIG. 4. Observed and predicted BTC's for Cl at the lysimeter outlet at 1.60 m: (a) coarse sand and (b) sandy loam. The solid lines show BTC's predicted with the two-layer solution using parameters obtained by fitting the two-layer model to suction cup data.

absence of pressure head control at the lower boundary, the soil becomes locally saturated, thus promoting increased longitudinal and lateral mixing. These observations are similar to those by Wierenga and van Genuchten (1989) for a large 6-m-deep repacked sandy lysimeter. Discrepancies in D between effluent and suction cup BTC's could also be caused by differences in sampling. The lysimeter can be viewed as an assembly of many parallel stream tubes with different flow rates. Suction cups probably sample only a limited number of stream tubes. This could explain the lower values for D as compared to the effluent BTC since the latter reflects contributions of all stream tubes. Note that concentrations measured on outflow samples are typically flux concentrations (Parker and van Genuchten 1984a), while only resident concentrations were considered in this analysis. However, the relative high Peclet number ($P = \nu z/D > 200$) at this depth indicates only minor differences between resident and flux concentrations. Hence, discrepancies such as those shown in Fig. 4 could not be attributed to the use of different concentration modes.

The average mass recovery, obtained by inte-

grating the measured effluent BTC, was 97% of the initially applied chloride for the sandy loam, with a coefficient of variation (CV) of 4%. The mass recovery for the coarse sand amounted to 91% with a CV of 12%. We consider these errors relatively small in view of the limited number of data points available to reliably integrate the effluent curves. The mass recoveries obtained with the two-layer CDE analysis using the suction cup data, as percentages of the initially applied chloride, were 100% (CV = 22%) for the coarse sand and 121% (CV = 10%) for the sandy loam. The excellent mass recovery for the coarse sand was probably accidental since individual lysimeters showed relatively large variations. The mass recovery for the sandy loam was quite high. An explanation for this excess recovery could be disproportionate sampling of the mobile region and the occurrence of anion exclusion.

An analysis of variance suggested that no significant differences existed in ν and D between experiments conducted at different input concentrations, C_0 . Krupp et al. (1972) observed relatively small changes in exclusion volume when C_0 changed by two orders of magnitude. The maximum value for C_0 in our experiments was only four times the minimum value. Considering the relatively poor resolution of our data, the absence of a clear concentration effect should probably have been expected in retrospect. Since fertilizer applications generally involve smaller ranges in C_0 values, our results suggest that concentration effects will not significantly affect NO_3 transport under field conditions.

The input pulse solution for eight of the lysimeter experiments contained a mixture of equivalent amounts of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$ rather than only CaCl_2 . Results for one of these experiments are shown in Fig. 5. The BTC's for the two anions look quite similar with recovery rates of 90% for NO_3 and 96% for Cl. Microbial activity was presumably minor because of the relatively low temperature at which the experiments were conducted. The breakthrough for Cl occurred slightly ahead of NO_3 in all eight experiments. The confidence limits calculated by CXTFIT indicate no significant differences in either D or ν between Cl and NO_3 . This is in agreement with previous findings by Biggar and Nielsen (1976).

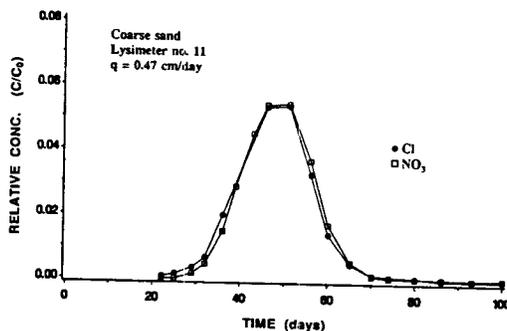


FIG. 5. Observed BTC's for Cl and NO_3 at the lysimeter outlet at 1.60 m for a coarse sand.

CONCLUSIONS

A comparison of the solutions of the CDE showed that the two-layer analysis gave a better description of Cl breakthrough curves for the sandy loam, and especially for the coarse sand, compared with the homogeneous analysis. These results reflect the presence of different water retention properties of the two soil layers.

Despite the variation of the experimental data, a fairly linear relationship between $\log \nu$ and $\log D$ emerged. For the coarse sand we made the somewhat convenient assumption of a constant value of 0.58 cm for the dispersivity, λ ; this assumption did not reduce the accuracy of the analysis. For the sandy loam, the average λ was 1.86 cm for the topsoil and 1.26 cm for the subsoil.

The analytical solution of the CDE for a two-layer soil profile, using model parameters obtained by fitting suction cup data, predicted the location of effluent BTC's very well. Hence, suction cups are useful for monitoring solute movement in field soils. However, the D values determined from effluent BTC's were in most cases greater than those derived from suction cup data. Also mass recovery based on suction cup BTC's exceeded 100% for the sandy loam soils.

The estimated values for D and ν were not affected by the input concentration, C_0 . We also found no significant differences between the behavior of Cl and NO_3 , although λ for Cl was found to be slightly higher than for NO_3 in all cases.

ACKNOWLEDGMENTS

This study was funded in part by the Danish Agricultural and Veterinary Research Council,

and the Danish Research Academy. We wish to thank Senior Scientist P. Schjønning of the Danish Institute of Plant and Soil Science, Store Jyndevad, and Professor H. E. Jensen of the Royal Veterinary and Agricultural University, Copenhagen, for their many helpful suggestions and comments.

REFERENCES

- Addiscott, T. M. 1990. Measurement of nitrate leaching: A review of methods. *In* Nitrates, agriculture, eau. R. Calvet (ed.). Institute National Agronomique, Paris-Grignon, pp. 157-168.
- Addiscott, T. M., and R. J. Wagenet. 1985. Concepts of solute leaching in soils: A review of modelling approaches. *J. Soil Sci.* 36:411-424.
- Barry, D. A., and J. C. Parker. 1987. Approximations for solute transport through porous media with flow transverse to layering. *Transp. Porous Media* 2:65-82.
- Best, E. K. 1976. An automated method for determining nitrate-nitrogen in soil extracts. *Queensl. J. Agric. Anim. Sci.* 33:161-166.
- Biggar, J. W., and D. R. Nielsen. 1976. Spatial variability of the leaching characteristics of field soil. *Water Resour. Res.* 12:78-84.
- Butters, G. L., and W. A. Jury. 1989. Field scale transport of bromide in an unsaturated soil: 2. Dispersion modeling. *Water Resour. Res.* 25:1582-1588.
- Djurhuus, J. 1990. A comparison of soil water nitrate determined by coring and solution extraction techniques. *Tidsskr. Planteavl.* 94:487-495 (in Danish with English summary).
- Hansen, E. M. 1991. Comparison of porous ceramic cups and drainage lysimeters for sampling soil water NO_3 -N-concentration. *Tidsskr. Planteavl.* 95:51-63 (in Danish with English Summary).
- James, R. V., and J. Rubin. 1986. Transport of chloride ion in a water-unsaturated soil exhibiting anion exclusion. *Soil Sci. Soc. Am. J.* 50:1142-1149.
- Jury, W. A., and K. Roth. 1990. Transfer functions and solute movement through soil: Theory and applications. Birkhäuser Verlag, Basel.
- Krupp, H. K., J. W. Biggar, and D. R. Nielsen. 1972. Relative flow rates of salt and water in soil. *Soil Sci. Soc. Am. J.* 36:412-417.
- Leij, F. J., J. H. Dane, and M. Th. van Genuchten. 1991. A mathematical analysis of one-dimensional solute transport in a layered soil profile. *Soil Sci. Soc. Am. J.* 55:944-953.
- Lindstrom, F. T., R. Haque, V. H. Freed, and L. Boersma. 1967. Theory on the movement of some herbicides in soils: Linear diffusion and convection of chemicals in soils. *J. Environ. Sci. Technol.* 1:561-565.
- Nielsen, D. R., M. Th. van Genuchten, and J. W. Biggar. 1986. Water flow and solute transport processes in the unsaturated zone. *Water Resour. Res.* 22:89S-108S.
- Nkedi-Kizza, P., J. W. Biggar, M. Th. van Genuchten, P. J. Wierenga, H. M. Selim, J. M. Davidson, and

- D. R. Nielsen. 1983. Modeling tritium and chloride 36 transport through an aggregated oxisol. *Water Resour. Res.* 19:691-700.
- Parker, J. C., and M. Th. van Genuchten. 1984a. Flux-averaged and volume-averaged concentrations in continuum approaches to solute transport. *Water Resour. Res.* 20:866-872.
- Parker, J. C., and M. Th. van Genuchten. 1984b. Determining transport parameters from laboratory and field tracer experiments. *Virginia Agric. Exper. Sta. Bull.* 84-3.
- Shapiro, S. S., and M. B. Wilk. 1965. An analysis of variance test for normality (complete samples). *Biometrika* 52:591-611.
- van de Pol, R. M., P. J. Wierenga, and D. R. Nielsen. 1977. Solute movement in a field soil. *Soil Sci. Soc. Am. J.* 41:10-13.
- van Genuchten, M. Th., and P. J. Wierenga. 1977. Mass transfer studies in sorbing porous media: II. Experimental evaluation with tritium ($^3\text{H}_2\text{O}$). *Soil Sci. Soc. Am. J.* 41:272-278.
- van Genuchten, M. Th., and P. J. Wierenga. 1986. Solute dispersion coefficients and retardation factors. *In Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods. Agronomy Monograph* 9:1025-1053.
- Wierenga, P. J., and M. Th. van Genuchten. 1989. Solute transport through small and large unsaturated soil columns. *Ground Water* 27:35-42.
- Yule, D. F., and W. R. Gardner. 1978. Longitudinal and transverse dispersion coefficients in unsaturated Plainfield sand. *Water Resour. Res.* 14:582-588.