

An Experimental Study of Solute Transport in a Stony Field Soil

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The transport of two conservative tracers, bromide and chloride, was studied in a stony field soil under natural soil, vegetative, and climatic conditions. Small tracer pulses were applied evenly over the 94-m² plot area in April 1982 (bromide) and October 1982 (chloride). A 15-m-long, 3-m-deep transect through the plot area was extensively sampled in May 1983, approximately 400 days after the bromide and 200 days after the chloride was applied. Tracer concentrations were obtained from 842 samples taken at 61 locations along the transect. Two-dimensional contour plots of the data showed a relatively uniform displacement in the vertical direction, as well as a significant horizontal redistribution during the study period. The data were analyzed with the classical convection-dispersion equation (CDE) and with a regional stochastic model that assumes logarithmic distributions of the pore water velocity and the dispersion coefficient across the field. Both models successfully described momentary field-averaged concentration distributions but failed to predict observed concentration data in October 1984 when another, less intensive sampling was carried out. Pore water velocities could be estimated reasonably well with as few as five vertical sampling lines, whereas dispersion coefficients and solute loads required numerous additional samplings. A field scale dispersivity of about 8 cm was obtained for the CDE model. Between 75 and 130% of the applied tracers were recovered in 1982. The effects of sampling size (0.3 versus 3 kg dry soil weight) were found to be relatively small.

INTRODUCTION

Recent concern about soil and groundwater pollution has spurred numerous experimental and theoretical studies of chemical transport in the unsaturated (vadose) zone. Theoretical models for predicting solute transport in the unsaturated zone are usually based on classical Fickian-type convection-dispersion equations. Predictions obtained with these models have generally been reasonably accurate for miscible displacement experiments involving repacked laboratory soil columns, especially when inert tracers are used. Unfortunately, recent studies suggest that laboratory experiments may not reflect actual transport conditions in the field and hence that laboratory-verified models cannot be safely used to predict field-scale solute transport (see *Sposito et al.* [1986] for a review). A major reason for this inability to extrapolate laboratory experiments to field conditions is thought to be the natural heterogeneity of field soils.

Field heterogeneity can affect transport on both a regional and a local scale. Regional heterogeneity is manifested by spatial variabilities in transport properties across the field, notably in the pore water velocity and the dispersivity [*Biggar and Nielsen*, 1976]. Local effects are attributed to preferential transport through large continuous macropores and may lead to non-Fickian vertical displacement at any location in the field [*Bouma*, 1981; *White*, 1985]. While laboratory tracer experiments provide unique opportunities for studying conceptual mechanisms affecting solute transport [e.g., *Nielsen and Biggar*, 1961; *Rao et al.*, 1980; *Nkedi-Kizza et al.*, 1984], they should always be augmented with field studies if the ultimate purpose is to predict actual transport in the field. Thus focus is increasingly shifting from laboratory to field scale

tracer studies [*Biggar and Nielsen*, 1976; *van de Pol et al.*, 1977; *Jury et al.*, 1982; etc.].

In this paper we present the results of a field tracer experiment involving two nonadsorbing and conservative anions, bromide and chloride. The study was initially motivated by concerns about the long-term behavior of airborne and subsequently deposited fluoride in stony field soils along the Rhone river in southern Switzerland [*Polomski et al.*, 1982; *Flühler*, 1983]. The fluoride-contaminated study site is characterized by heterogeneous and very stony soils that are exposed to summer droughts as well as to extreme infiltration events due to snow melts and intense thunderstorms. Because of this and the remote location of the site, no reliable measurements of the water regime and the soil hydraulic properties (unsaturated hydraulic conductivity and soil water retention curves) could be obtained by conventional methods. To still trace the movement of the soil solution in and below the root zone of the site under natural soil, climatic, and vegetative conditions, a field-leaching experiment with bromide and chloride was carried out. Observed tracer distributions after two travel time intervals are described in terms of the classical convection-dispersion equation, as well as with a regional stochastic model [*Parker and van Genuchten*, 1984] that assumes a log-normal distribution of the pore water velocity across the field.

EXPERIMENTAL FIELD STUDY

The tracer experiments were carried out at Creux de Chippis near the town of Sierre on a north-facing field with 10% slope, close to the valley bottom of the Rhone river. Elevation of the study site is approximately 650 m above sea level, with alpine mountains on both sides of the valley rising to about 3000 m. Climate in the valley is comparatively mild and dry, with an average annual temperature of 9°C and an annual precipitation of 580 mm. Potential evapotranspiration averaged about 900 mm/yr during the study period. The soil at the site, classified as a Udipsamment (calcaric regosol), exhibits distinct layers of parent rock material of markedly different composition. The parent material originated from colluvium but also contains some glaciofluvial deposits. Earlier soil formations buried under overcast material are relatively

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Paper number 6W4580.
0043-1397/87/006W-4580\$05.00

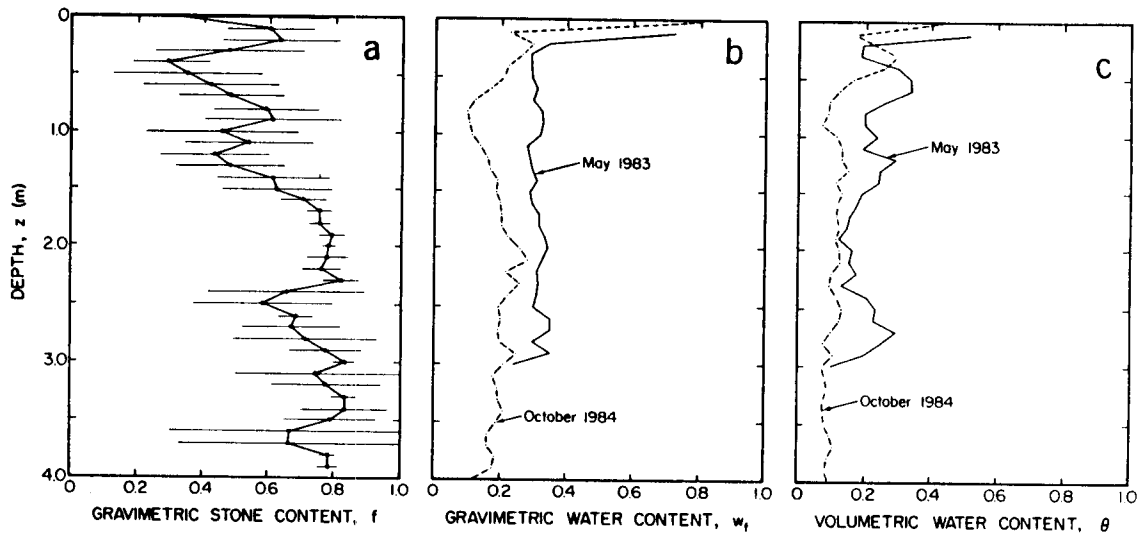


Fig. 1. Distributions of (a) measured gravimetric stone content f , (b) measured gravimetric water content w_f of the nonstony soil matrix, and (c) volumetric water content θ of the bulk soil including stones as calculated with (1).

well developed at depths between 40 and 60 cm and between 100 and 120 cm.

Figure 1a shows the (dry) weight fraction of the soil consisting of particles exceeding 1 mm in diameter (error bars indicate 95% confidence intervals based on Student's t distribution). We will refer to this fraction of the solid phase as the "stony" fraction and to the remainder as the "nonstony" fraction. Up to 85% by weight of the soil below 1.5 m is due to stones, some of which had diameters of more than 20 cm. As shown in Table 1, the nonstony soil mineral fraction consisted primarily of sand, some silt, and generally less than 2% clay, while the upper 5 to 10 cm of topsoil contained about 16% organic carbon. Because of the mainly calcareous parent material, with visible amounts of precipitated gypsum present at depths below 40–50 cm, calcium was the predominant cation in the ammonium acetate extracts (Table 1). Except for the slightly acidic humic top horizon, the pH of the soil varied little, increasing from 7.2 to 7.6 with depth.

A 94-m² plot area, covered mainly by grass and only two small shrubs, was selected for the leaching experiment. The area was first pretreated to prevent runoff from the sometimes quite hydrophobic soil surface. On April 14, 1982, a 31,450-ppm Br⁻ solution (approximately 400 meq/L) was distributed evenly over the plot area. The cationic composition (Ca²⁺ : Mg²⁺ : K⁺ : Na⁺ = 10.3:2.7:5.1:6.8, all in milliequivalents per 100 g) was chosen to match the composition of soil solution samples taken at depths of 10–20 cm prior to the tracer

application. The bromide solution was manually applied onto the soil surface by distributing 25-mL aliquots through the mesh openings of a 10 by 10 cm cord grid in a 1 by 1 m wooden frame. This procedure was repeated until the entire plot area was treated, requiring a total of 9400 aliquots. The total solute dose was 980 meq/m², which is equivalent to about 78.6 g bromide per square meter of soil surface. On October 28, 1982, a chloride solution was sprayed in aliquots of 0.5 L/m² on the same area. The solution concentration was 142 g Cl⁻ per liter, resulting in a total dose of 71 g per square meter of surface area.

On May 18, 1983, a trench was dug along a 15-m transect downslope through the plot area. A total of 842 soil samples were collected from the profile wall on a 20 by 20 cm grid scheme down to depths between 190 and 310 cm. The samples were taken from the bottom to the top of the trench wall along 75 vertical sampling lines, the uppermost sampling in each case being 10 cm below the soil surface. The samples weighed between 0.3 and 0.5 kg after oven drying. To obtain more representative values of both water content and stone content, also "large" samples of 2–5 kg weight (approximately 1.5–3 dm³) were taken in 10-cm depth intervals at five locations along the transect ($x = 1.1, 4.0, 8.0, 11.0, \text{ and } 13.3$ m). Unless stated otherwise, only data derived from these larger samplings have been used in subsequent calculations requiring water and stone contents.

After the first sampling was completed, the trench walls

TABLE 1. Physical and Chemical Properties of the Nonstony (< 1 mm) Soil at the Study Site

Depth, m	Texture*			Organic Carbon†	pH	Ionic Composition, meq per 100 g			
	Clay	Silt	Sand			Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
0.0–0.1	0.8	29.0	70.2	16.3	6.1	37.9	5.3	0.6	0.6
0.2–0.3	4.7	21.1	74.2	3.2	7.2	39.4	1.4	0.6	0.2
0.4–0.5	1.1	10.5	88.4	2.2	7.4	41.7	1.1	0.6	0.2
0.7–0.8	2.0	20.0	88.0	2.0	7.4	45.0	1.0	0.5	0.2
1.0–1.1	0.1	3.9	96.0	1.4	7.6	42.7	1.0	0.6	0.1

*Dry weight percentages of nonstony soil mineral phase.

†Weight percentage.

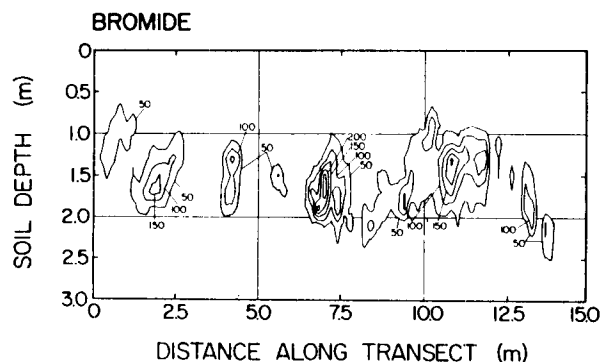


Fig. 2. Observed distributions of the gravimetric bromide concentration c_f of the nonstony soil matrix on May 18, 1983 (399 days after Br was applied).

were covered with polyvinyl chloride plastic to shield the walls from evaporation and rainfall. Another set of 165 large samples along four vertical lines, again in 10-cm depth increments, was taken on October 16, 1984. The four sampling locations this time were at positions $x = 1.5, 2.5, 12.0,$ and 13.0 m along a transect that ran parallel to but 1.5 m apart from the first one.

All samples were first oven dried at 105°C for at least 48 hours and then passed through a standard 1-mm mesh sieve to remove the stones. Stone and water contents were determined for all samples. Bromide and chloride were extracted from the sieved, nonstony soil by shaking for 48 hours, centrifuging, and filtering suspensions made up of 25 g nonstony soil in 50-mL aliquots of distilled water. Concentrations in the extract were determined using a Wescan ion chromatograph. To reduce interference with sulfate peaks due to gypsum dissolution, some extracts had to be diluted tenfold prior to the chromatographic analysis. The tracer distributions along five vertical sampling lines ($x = 12.0, 12.2, 12.4, 12.8,$ and 14.0 m) could not be analyzed because the entire samples were needed for fluoride extraction.

Contour plots of the observed gravimetric bromide and chloride concentrations, c_f (micrograms per gram of dry soil), of the nonstony soil matrix for the 1983 sampling are shown in Figures 2 and 3, respectively. Volumetric concentrations of the soil solution were calculated from the gravimetric values shown in Figure 1b by dividing by the measured gravimetric water content, or wetness w_f , of the nonstony soil matrix. The

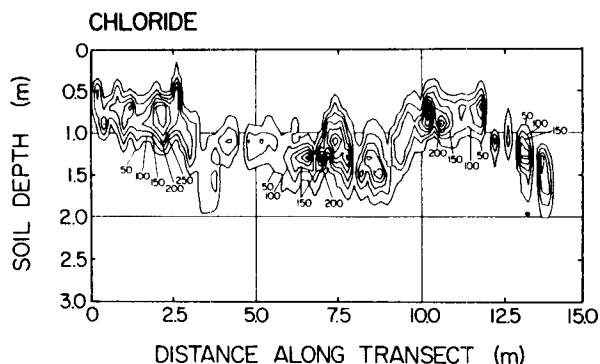


Fig. 3. Observed distributions of the gravimetric chloride concentration c_f of the nonstony soil matrix on May 18, 1983 (202 days after Cl was applied).

standard error in w_f was about 16% of the average at the soil surface and less than 10% at all other depths. Because w_f changed little with depth, except for the surface horizon (see Figure 1b), the volumetric concentrations exhibited essentially the same spatial distribution as the gravimetric data in Figures 2 and 3 (results not shown here). Global, field-averaged concentration profiles were calculated by taking arithmetic averages of all 61 local (vertical) concentration distributions along the transect (small sample data).

The gravimetric water content and the fraction of stones were not found to be correlated with the measured solute concentrations. Preliminary geostatistical analysis [Schulin and Flühler, 1984] showed that w_f displayed most of its horizontal variations as short-range fluctuations (< 1 m), with no detectable long-range drifts. Thus we assume that similar horizontal variations as in w_f also occurred in the volumetric water content. The high stone content made it very difficult to take volumetric samples and thus precluded the direct measurement of volumetric water contents θ . Instead, estimates of θ of the bulk soil (including the stones) were obtained from the larger sampling data using the expression

$$\theta = w_f \rho_f \left\{ \rho_w \left[\frac{1}{1 - \epsilon_f} + \frac{f \rho_f}{(1 - f) \rho_s} \right] \right\}^{-1} \quad (1)$$

where ρ_s and ρ_f are the average particle densities for stony and nonstony soil fractions, respectively; ρ_w is the density of water; f is the gravimetric stone content of the soil; and ϵ_f is porosity of the nonstony soil matrix. Equation (1) is easily derived from gravimetric and volumetric mass balances of the soil matrix. Values for ρ_f and ρ_s were assumed to be 1.80 for the humic top horizon and 2.65 for the remainder of the profile, while ϵ_f was guessed to be about 0.6 and 0.5 for the surface and subsurface layers, respectively. Average volumetric water content distributions thus calculated are shown in Figure 1c. Standard errors of the horizontal averages varied between 5 and 33% of the mean values shown in that figure.

DATA ANALYSIS

The field data were analyzed in terms of two conceptually different one-dimensional transport models: the classical convection-dispersion equation (CDE) and a regional stochastic model (RSM) discussed by Parker and van Genuchten [1984]. Assuming constant liquid flow in a homogeneous soil profile without sources or sinks of water and solutes, the CDE model for an inert tracer is given by

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

where c is the volume-averaged resident solution concentration, D is the dispersion coefficient, $v = q/\theta$ is the average pore water velocity with q representing the Darcian flux density, t is time, and z is vertical distance from the soil surface.

The regional stochastic model of Parker and van Genuchten [1984] is based on frequent observations that infiltration rates, hydraulic conductivities, and pore water velocities are lognormally distributed across a field [Nielsen et al., 1983]. The formulation is very similar to the one-dimensional stochastic transport models of Bresler and Dagan [1981] and Amoozegar-Fard et al. [1982]. The RSM assumes that the entire field (referred to as the "global" scale) is composed of

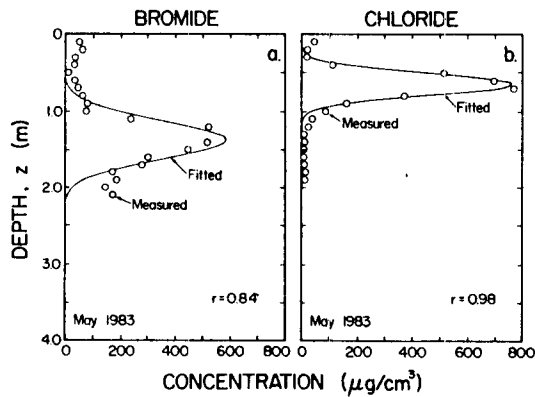


Fig. 4. Typical observed and fitted local concentration profiles for (a) bromide ($t = 399$ days after application) and (b) chloride ($t = 202$ days) on May 18, 1983.

numerous independent one-dimensional soil columns, with transport in each individual column (referred to as the "local" scale) being described by the CDE (equation (2)). No convective transport or transverse dispersion of solute between two neighboring columns is allowed. The pore water velocity, although taken to be constant with time and depth in each column, is assumed to vary lognormally among the vertical columns along the transect according to the probability density function [Parker and van Genuchten, 1984]

$$\rho(v) = \frac{1}{v\sigma_{\ln}(2\pi)^{1/2}} \exp\left[-\frac{(\ln v - \mu_{\ln})^2}{2\sigma_{\ln}^2}\right] \quad (3)$$

where μ_{\ln} and σ_{\ln} are the mean and standard deviation of $\ln v$, respectively. The dispersion coefficient is assumed to be linearly related to the pore water velocity:

$$D = \lambda|v| \quad (4)$$

where the dispersivity λ is a deterministic parameter, taken to be constant over the field. This assumption defines $\rho(D)$ completely in terms of $\rho(v)$ and λ .

The analytical solution of (2) for a semi-infinite profile subject to a flux- and pulse-type solute application at the soil surface was used in conjunction with the least squares fitting program CXTFIT of Parker and van Genuchten [1984] to estimate for each observed local concentration profile the

three unknowns v , D , and t_0 , where t_0 is an equivalent pulse duration. The CXTFIT code assumes steady state flow, a constant water content in the entire profile, and the absence of any sources or sinks of water and solutes. All local concentration distributions were analyzed with the CDE model, whereas the global, field-averaged concentration distributions were analyzed with both the CDE model and the RSM. For the regional stochastic model a uniform areal solute dose M_0 was selected:

$$M_0 = c_0 m_0 \quad (5)$$

where c_0 is the input concentration, $m_0 = vt_0$ is the "local" solute load relative to the liquid-filled porosity of the soil, and the water content again is assumed to be constant. While the tracers in actuality were applied by means of nearly infinitesimal pulses approximating Dirac delta functions, we decided to use a small nonzero pulse time t_0 to facilitate the immediate use of CXTFIT. Given the independently measured input concentration c_0 , use of t_0 serves only to quantify the amount of recovered solute at any location along the transect. The approximation with a nonzero, finite pulse length has little or no effect on calculated concentration distributions at depths of more than a few centimeters.

We emphasize that the objective of our analysis is not to simulate the actual three-dimensional physical transport process leading to the observed tracer distributions. Rather, the above models are merely used as analytical tools to quantitatively characterize the variability of the observed tracer distributions. Thus fitted values of the pore water velocity are a measure of the center of mass of the vertical tracer distribution at a given location along the transect. The dispersion coefficient similarly reflects the variance of the vertical displacement process. The same type of information can also be obtained by calculating zero, first, and second moments of the observed tracer distributions. The approach followed here facilitates comparison with data from other field experiments (see the introduction) that have been analyzed in a similar fashion. We also felt that moments would give too much weight to data at very low depths and hence to natural background levels in the case of chloride. In any case, our analysis in terms of the CDE model and RSM is not meant to imply that the two transport models correctly reflect the actual transport processes at the field site.

TABLE 2. Statistics of the Pore Water Velocity v , the Dispersion Coefficient D , and the Solute Load m_0

Parameter	Tracer	Mean	Standard Deviation	Standard Error	Skewness	Kurtosis
v , cm/d	Br ⁻	0.392	0.078	0.010	0.064	2.61
	Cl ⁻	0.528	0.135	0.017	0.169	1.88
$\ln v$	Br ⁻	-0.957	0.206	0.027	-0.458	2.99
	Cl ⁻	-0.673	0.264	0.034	-0.183	1.95
D , cm ² /d	Br ⁻	1.45	1.30	0.173	2.31	9.18
	Cl ⁻	1.13	0.823	0.105	2.72	13.8
$\ln D$	Br ⁻	0.079	0.770	0.102	0.035	3.19
	Cl ⁻	-0.067	0.607	0.078	0.250	2.93
m_0 , cm	Br ⁻	0.835	0.501	0.066	0.639	2.65
	Cl ⁻	0.261	0.099	0.013	0.647	2.82
$\ln m_0$	Br ⁻	-0.390	0.704	0.093	-0.580	2.69
	Cl ⁻	-1.42	0.404	0.052	-0.767	5.38

Data are derived from 57 bromide and 61 chloride local concentration distributions using the CDE model (small-sample data).

TWO-DIMENSIONAL TRACER DISTRIBUTIONS

The 1983 contour plots in Figure 2 for bromide and Figure 3 for chloride show a considerable lateral redistribution of the tracers with time but a comparatively uniform displacement in the vertical direction. As will be shown in detail below, this first impression is confirmed by considering the variation along the transect of the estimated parameters in the classical CDE model. In spite of its many underlying assumptions, the CDE provided a surprisingly good fit to most of the 61 local concentration profiles that were measured in May 1983. Only two representative examples are shown here, one for bromide in Figure 4a and one for chloride in Figure 4b. Correlation coefficients between measured and fitted curves in most cases exceeded 0.9 and were sometimes as high as 0.99. In general, fits were slightly better for chloride than for bromide. A relatively few locations showed poor fits between observed and calculated distributions; these usually occurred at locations where the observed concentrations lacked a distinct peak and exhibited a relatively strong erratic component. At four out of 61 locations, Br concentration profiles could not be analyzed accurately because of incomplete sampling at deeper depths and hence are not included in the analyzed results shown in Table 2. However, observed data at these locations were still included in the transect-averaged (global) concentration profile.

One feature in the observed data that was not accounted for in the CDE model is the slightly elevated concentrations behind the solute peak, especially close to the soil surface (Figure 4). These elevated concentrations rarely amounted to more than 1% of the applied solute mass and could have been the result of some upward flow of water and solutes due to evaporation and root water uptake at or close to the soil surface. Alternatively, they could have been caused by an asymmetric (non-Fickian) displacement process often observed in undisturbed or aggregated soils [van Genuchten and Cleary, 1979; White, 1985].

Figure 5 shows distributions along the transect of the CDE-estimated local pore water velocity, the dispersion coefficient, and the solute load for the May 1983 bromide sampling, $t = 399$ days after application of the tracer. Similar results for the 1983 chloride sampling ($t = 202$ days after Cl application) are shown in Figure 6. Relevant statistics of the parameter estimation process are given in Table 2. The plots of the pore water velocity in Figures 5a and 6a exhibit relatively narrow 95% confidence intervals, which illustrates that this parameter could be estimated rather precisely from the observed data. Changes in v are fairly smooth over short distances, with chloride showing more erratic long-range variations than bromide. The opposite is true for the dispersion coefficient, which is comparatively ill defined at many locations. The bromide plot (Figure 5b), in particular, shows strong short-range fluctuations in D . Given the great uncertainty in fitted D values, there is hardly any difference between the averages of the local fit D values for bromide and chloride in Table 2. The average value of v for Br, however, is significantly less than that for Cl. The higher pore water velocity for chloride is easily explained by noting that chloride displacement occurred primarily during the relatively wet 1982/1983 winter and spring seasons, when average precipitation and potential evapotranspiration rates were 0.133 and 0.17 cm/d, respectively. The bromide experiment, on the other hand, also included the preceding growing season, when water fluxes were much lower owing to

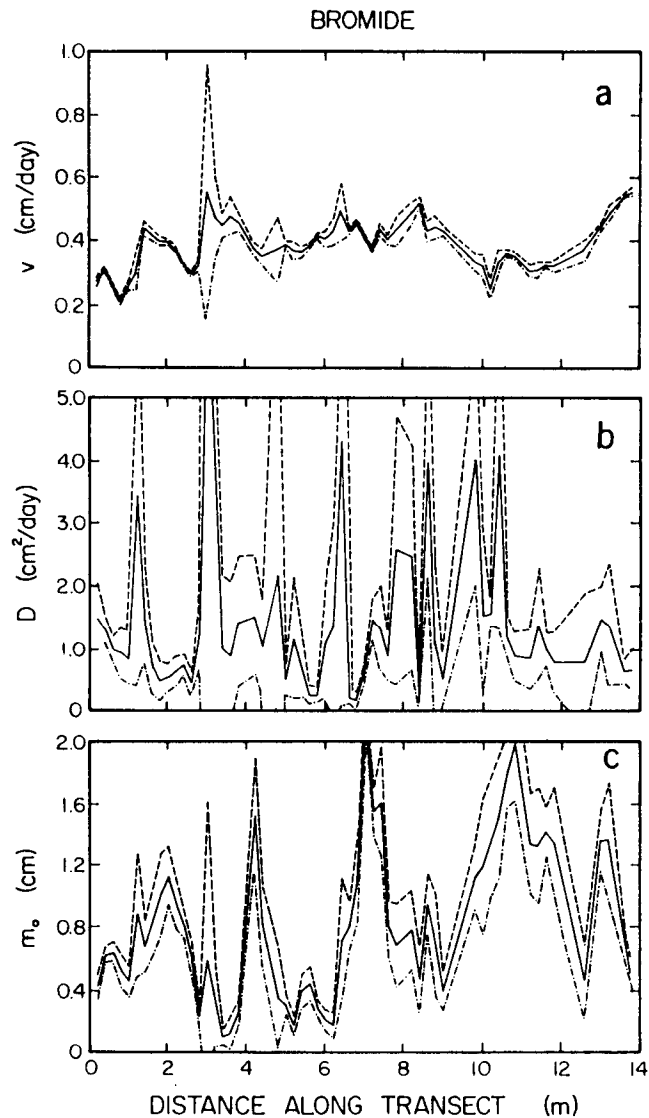


Fig. 5. Distributions (solid lines) along the transect of (a) the pore water velocity v , (b) the dispersion coefficient D , and (c) the solute load m_0 for the May 18, 1983, bromide sampling. The dashed and dashed-dotted lines represent 95% confidence limits.

lower precipitation (an average of 0.117 cm/d) and higher evapotranspiration rates (0.33 cm/d). Water flow during that time period was also much more erratic owing to occasional rainstorms and intermittent periods of high evapotranspiration.

Local fit dispersion coefficients were found to be more or less lognormally distributed for both tracers as illustrated in Table 2 by the skewness and kurtosis of the $\ln D$ values. However, pore water velocities closely fitted the normal distribution for Br and behaved intermediately between normal and lognormal for Cl. The correlation between local fit D and v parameters was found to be weak for chloride ($r = 0.432$) and negligible for bromide ($r = 0.186$). A much stronger correlation ($r = 0.795$) between D and v was observed by Biggar and Nielsen [1976] for their field tracer experiments within a 150-ha field under ponded conditions. The absence of a correlation between D and v in our experiments is contrary to the assumption of the RSM that D and v are perfectly correlated. Sensitivity analyses by Amoozegar-Fard *et al.* [1982] and

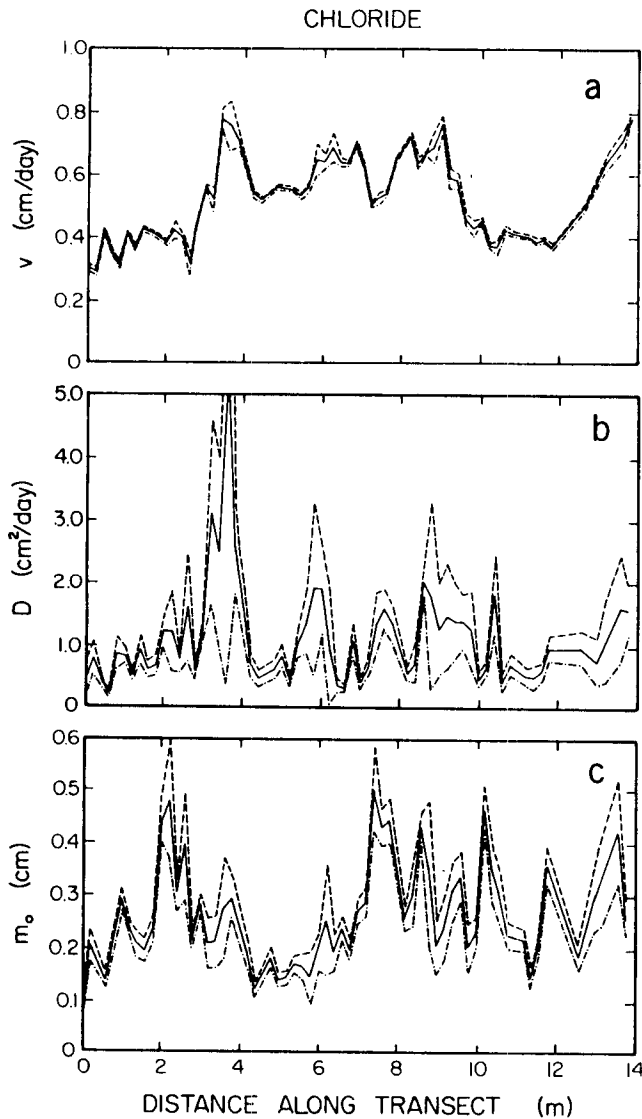


Fig. 6. Distributions (solid lines) along the transect of (a) the pore water velocity v , (b) the dispersion coefficient D , and (c) the solute load m_0 for the May 18, 1983, chloride sampling. The dashed and dashed-dotted lines represent 95% confidence limits.

others suggest that variations in D , in addition to those caused by variations in v through (4), are of minor importance in the stochastic description of average field scale solute transport.

Considerable variations along the transect also occurred in the estimated solute loads m_0 . This is shown in Figures 5c and 6c for the bromide and chloride ions, respectively. Since extreme care was taken to apply the solute evenly to the soil surface and to avoid surface runoff, the fluctuations must have been caused almost entirely by lateral redistribution within the soil profile. Maximum and minimum peak concentrations were as far as 2 m apart for the bromide, indicating significant lateral transport of the tracer. The two-dimensional Cl distribution was much smoother, showing less fluctuation along the transect as compared to the Br distribution. The significant horizontal movement of the bromide, especially, must have been caused by lateral convective transport. We speculate that horizontal water flow could have been enhanced somewhat by root water uptake during the growing season. Also, the horizontal stratification of the soil, implying anisotropy of the

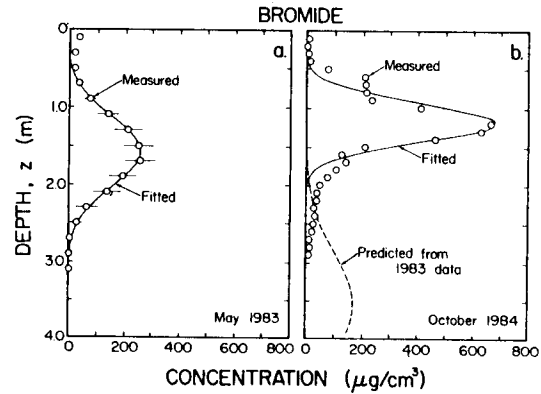


Fig. 7. (a) Measured and fitted global bromide concentration distributions on May 18, 1983. (b) Measured, fitted, and predicted distributions on October 16, 1984. Calculated curves are for both the CDE model and the RSM.

effective hydraulic conductivity tensor as pointed out by Gelhar *et al.* [1985], may have created a favorable condition for horizontal flow.

We finally note that the frequency distributions of calculated m_0 values were found to be intermediate between lognormal and normal for both tracers (Table 2). Correlations between m_0 and v or D were found to be insignificant, except for a relatively weak one between m_0 and D ($r = 0.398$) in the case of chloride.

FIELD-AVERAGED TRANSPORT

The analysis above focused on two-dimensional spatial distributions of the tracers. In practice, one is usually more interested in field-averaged one-dimensional displacement patterns. Figure 7a shows the global, field-averaged bromide concentration profile with depth for the 1983 transect data, together with the calculated 95% confidence intervals and the least squares optimized curves for the CDE model and RSM. Similar results for chloride are shown in Figure 8a. The measured global or "lumped" profiles are very smooth, as the observed scatter in the local concentration distributions has been averaged out. The goodness of fit is excellent and essentially the same for both models.

Table 3 shows that the estimated global pore water velocities, derived from the lumped concentration distributions in

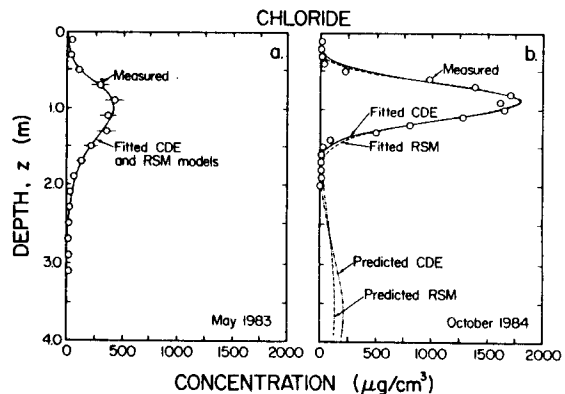


Fig. 8. (a) Measured and fitted global chloride concentration distributions on May 18, 1983. (b) Measured, fitted, and predicted distributions on October 16, 1984.

TABLE 3. Estimated Transport Parameters

Model	May 18, 1983, Small Samples		May 18, 1983, Large Samples		Oct. 16, 1984, Large Samples	
	Bromide, <i>n</i> = 57	Chloride, <i>n</i> = 61	Bromide, <i>n</i> = 5	Chloride, <i>n</i> = 5	Bromide, <i>n</i> = 4	Chloride, <i>n</i> = 4
<i>Pore Water Velocity v, cm/d</i>						
CDE model						
Average of local values	0.392	0.528	0.375	0.528	0.128	0.118
Global fit	0.381	0.492	0.395	0.514	0.127	0.121
RSM	0.381	0.557	0.394	0.512	0.128	0.125
<i>Dispersivity λ, cm</i>						
CDE model						
Average of local values	3.70	2.12	4.37	2.58	8.18	2.92
Global fit	6.85	8.38	12.06	9.55	2.80	3.39
RSM	6.87	2.17	12.08	9.72	2.84	2.06
<i>Solute Load m_0, cm</i>						
CDE model						
Average of local values	0.835	0.261	0.739	0.189	1.356	0.753
Global fit	0.917	0.283	0.899	0.204	1.359	0.756
RSM	0.918	0.302	0.899	0.205	1.366	0.758
<i>Standard Deviation of $\ln v$</i>						
CDE model						
(from local values)	0.206	0.264	0.360	0.306	0.118	0.109
RSM	0.0004	0.313	0.0006	0.002	0.0001	0.165

Data are derived from the May 1983 small- and large-sample data and the October 1984 large-sample data using both the deterministic CDE model and the RSM.

Figures 7a and 8a using both the CDE model and the RSM, agree very well with the averages of the local fit velocities. This close agreement also holds for the large-sample data but, as explained above, not for the bromide vis-à-vis the chloride tracer. Good agreement between the two models is also found for the estimated solute loads, with the average of the local fit small-sample estimates being only about 10% less than the global estimate. Converted to amounts of solute mass applied per unit soil surface area (equation (5)), the different estimates for the recovered surface load m_0 vary between 73 and 82% of the applied dose for bromide and between 116 and 134% for chloride (Table 4, small-sample data). These recovery percentages seem quite reasonable, especially in view of the significant lateral displacements of the two tracers during the study period, presumably also perpendicular to the transect, and in view of the simplifying assumptions of having constant water contents and pore water velocities with time and depth.

In contrast to v and m_0 , Table 3 shows rather large differences between the various estimates for the field-averaged dispersivity λ . For the CDE model, λ can be calculated as being either the ratio of the averaged local fit D and v values or the ratio of D and v derived from the global transect-averaged concentration distribution. Both estimates are included in Table 3. The dispersivity derived from the averaged D and v values is about half of the global value for bromide and only about a fourth of that for chloride. Larger values for the global dispersivity are to be expected, since this parameter, in addition to local dispersion effects, indirectly also accounts for fluctuations in the local pore water velocity around its mean value. The dispersivity in the RSM should be viewed as a local scale parameter, since fluctuations in v are already included in the lognormal velocity distribution. However, the small-sample data in Table 3 show that the value of λ for the RSM agrees well with the average CDE local fit dispersivity only for

TABLE 4. Percent Recoveries of the Applied Bromide and Chloride Tracers

	May 18, 1982, Small Samples		May 18, 1982, Large Samples		Oct. 16, 1984, Large Samples	
	Bromide, <i>n</i> = 61	Chloride, <i>n</i> = 61	Bromide, <i>n</i> = 5	Chloride, <i>n</i> = 5	Bromide, <i>n</i> = 4	Chloride, <i>n</i> = 4
Measured	72.8	130.4	72.8	99.3	77.4	163.5
CDE model						
Average of local values	74.2	115.9	65.6	83.9	64.5	179.2
Global fit	81.4	125.6	79.9	90.6	64.8	179.9
RSM	81.6	134.1	79.9	91.0	65.0	180.4

Data are estimated directly from the measured concentration and water content data and from optimized values of the field-averaged solute loads m_0 in Table 3.

chloride and not for bromide. The RSM yielded a dispersivity for bromide that is nearly equal to the global fit dispersivity of the CDE model. Clearly, the parameter optimization process with the RSM must have "stretched" the local scale to dimensions comparable to the global scale of the 15-m transect. The small-sample Br data in Table 3 suggest that the RSM is unable to effectively distinguish between local scale dispersion effects (determining the value of λ) and global effects associated with velocity fluctuations (determining the value of σ_{ln}). The RSM estimate for σ_{ln} was found to be nearly zero for bromide. Obviously, the effects of velocity fluctuations are in this case directly included in the fitted dispersivity, thus effectively reducing the RSM to the global CDE model. This is manifested by near equality in estimated Br λ values for the RSM and the global fit CDE model. This behavior agrees with our finding that the pore water velocity for Br exhibits a Gaussian distribution. If we interpret solute concentration profiles in terms of a probability density function of travel distances and thus of travel velocities at a given time, then the CDE model should indeed correspond to a Gaussian distribution of v [Rao et al., 1981].

In contrast to bromide, the pore water velocity distribution for the small-sample chloride data is fairly lognormal (Table 2), and the RSM-fitted λ becomes about the same as the average of the local fit CDE values (Table 3). The two estimates of $\sigma(\ln v)$ for the small-sample chloride data (Table 3) agree reasonably well. In comparison to the log variance parameters inferred by Jury [1985, Tables 2-5] from various field experiments, the estimated σ^2 values of our chloride data lie at the lower end of the range given by Jury (0.12-1.56). Similar agreement with literature data occurs for the field scale CDE dispersivity values in Table 3. Field dispersivities as compiled by Gelhar et al. [1985, Table 3-1] range from as low as 0.11 cm to as high as 70 cm. Disregarding the two extreme values from their study, λ ranged from 2.7 to 20 cm. Since most of the data in the study of Gelhar et al. were obtained from fine- to medium-textured soils, this agreement with our estimates is remarkable. It shows once again [Schulin et al., 1987] that the transport characteristics of stony soils do not differ much from those of undisturbed nonstony soils.

EFFECTS OF SAMPLING SIZE AND SAMPLING FREQUENCY

In addition to results for the small-sized (0.3-0.5 kg) samples, Table 3 also shows field-averaged parameters estimated from the larger-sample (3-5 kg) data that were collected at five locations along the May 1983 transect. Results for the two sample sizes are reasonably consistent. Pore water velocity estimates derived from the small set of larger samples agree closely with those estimated from the larger set of small-sized samples. This is not too surprising considering the relatively uniform vertical displacement of the observed tracer distributions in Figures 2 and 3. The lesser agreement for the dispersivity and the standard deviation of $\ln v$ between the two samplings is most likely due to the significant horizontal redistribution of the tracers and the associated short-range variations in parameter estimates as shown in Figures 4 and 5 for the smaller sized samples. Given that only five vertical profiles for the large-sized samples were available, it is thus unlikely that a reliable estimate for the field-averaged dispersivity was obtained. In spite of the erratic fluctuations in CDE-fitted local solute loads, surprisingly good estimates of the overall

solute load were obtained from the few large-sample locations in 1983 (Table 3). We believe that the relatively close agreement with the expected mass balance is coincidental. The precision in measuring solute concentration profiles was not significantly different between the large and small sample sizes because of the high degree of spatial autocorrelation of concentrations over short ranges [Schulin and Flühler, 1984]. Thus differences in estimated solute loads between the two samplings should be almost entirely a result of different sampling numbers and locations. We conclude from our analysis that reliable estimates of the average pore water velocity for the 15-m transect can be obtained from samples taken at as few as five locations, whereas considerable errors have to be expected in the dispersivity, in the pore water velocity distribution, and likely also in the mass balance.

EXTRAPOLATION IN TIME

Equal performance of the CDE model and RSM in describing momentary concentration profiles versus depth can be expected, as shown by Simmons [1982] through a comparative analysis of Fickian and lognormal travel time distributions. However, significant differences between the two models may emerge when "snapshots" at different times are compared [Jury and Sposito, 1985]. This is illustrated in Figures 7b and 8b, where calculated average concentration profiles are compared with the October 1984 field-averaged sampling data. The "predicted" curves were computed with the global fit parameter values obtained from the May 1983 small-sample data. Hence they represent expected distributions subject to the assumption inherent in the two models, that is, constant water flow, constant water content, and constant dispersivity with depth and time. The CDE and RSM predictions for bromide were essentially identical, as were their best fit curves for the 1983 profile because of the nearly normal distribution of v . For chloride, however, a wider spreading of the solute front and a lower peak concentration are predicted for 1984 with the RSM as compared to the CDE.

The comparisons in Figures 7b and 8b of the computed and actually measured concentration distributions show that the extrapolations in time failed completely. The measured 1984 concentration peaks were located at roughly the same depths as in 1983, or even moved slightly upward. If any downward leaching had taken place, as would have been expected during the winter of 1983/1984, it must have been counteracted by upward flow during the exceptionally dry summer of 1984. This upward movement might also explain the distinctly bimodal-shaped concentration distributions that were observed at two of the four sampling locations in 1984. For clarity of presentation we did not include the 95% confidence intervals on the measured 1984 concentration values; they were about 10 times larger than those shown for the 1983 data in Figures 7a and 8a. The optimized parameter values for the average 1984 concentration profiles are given in Table 4. The dispersivity and solute load values are not very reliable, since only four locations were sampled in 1984. Moreover, two of the sampling locations were very close together (1 m) and fell within the range of spatial dependency [Schulin and Flühler, 1984]. Table 3 indicates that the averaged 1984 local fit pore water velocity was less than half of the 1983 value, thus reflecting the lack of downward displacement between the 1983 and 1984 samplings. The dispersivity was found to be of approximately the same magnitude as in 1983.

CONCLUSIONS

The results reported here show significant differences between the two-dimensional spatial distributions of the bromide and chloride tracers for the 1983 intense (small-sized) sampling scheme. It is unlikely that these differences are due to chemical processes, as both ions are known as almost ideal tracers, especially for the type of coarse-textured soils found at our study site. The only important difference between the two tracers in this experiment was their time of application: bromide was applied half a year earlier than chloride and had traveled for a full year when the first sampling took place in May 1983. The chloride at this time had only traveled for one winter season and thus missed the effects of root water uptake by the natural grass vegetation during the previous growing season. Thus we cautiously conclude that root water uptake must have been the principal factor causing the different transport behavior of the two tracers. Increased soil water extraction during the growing season perhaps would have enhanced lateral movement of water and solutes; it certainly must have slowed down the vertical displacement. As a result of the increased lateral redistribution, more mixing between otherwise independent vertical flow paths should be expected, thus decoupling the relationship between average vertical travel velocity and local soil properties such as the hydraulic conductivity. This might be a reason why travel velocities of bromide were closer to the normal distribution than those of chloride.

Comparison of the two models shows that for the relatively short 15-m transect of this study the assumption of a random lognormal pore water velocity distribution did not offer an advantage over the classical CDE model in the data analysis. Failure of the RSM to perform better than the CDE model may in part be attributed to the short length of the transect relative to the "effective local scale" of the study site. Strong variations in the local fit dispersion coefficients along the transect, as well as the lateral redistributions of the tracers over a range of one to several meters, imply that this effective local scale, which forms the conceptual basis of the RSM, is of the order of several meters. This finding has potential consequences for sampling strategies. Solute sampling schemes that do not cover this effective transect length are unlikely to yield reliable mass balance and dispersivity estimates. On the other hand, accurate local pore water velocity estimates can possibly be obtained by sampling schemes that cover a much smaller transect or field area.

Failure of the two models to give adequate predictions of solute displacement by simple extrapolation in time using the average parameter values of the past travel history does not disprove the validity of both models. The failure only reflects the incorrect assumption that the water flow regime was at steady state during the study period. The absence of any net downward movement during the 17-month period between the first and the second sampling shows that temporal variations in rainfall and evapotranspiration rates cannot be ignored. Preliminary analysis of the data using a numerical model that couples transient unsaturated water flow and a solute transport model also indicated the need for reliable estimates of the root water extraction term. In view of the spatial and temporal nonuniformity of the transport process leading to the observed tracer distributions, the classical CDE model provided surprisingly good descriptions of the momentary, field-averaged (global) as well as local concentration distributions in spite of all the underlying CDE assumptions.

This point illustrates that a good model fit must always be interpreted cautiously, especially in case of a complex transport process. Use of a deterministic numerical model to describe field-averaged concentration distributions appears, within certain limits, to be justified by the main conclusion of this study, i.e., that the CDE model and RSM both adequately described momentary distributions of the field-averaged tracer data.

NOTATION

c	volumetric solute concentration of the nonstony soil matrix, $\mu\text{g}/\text{cm}^3$ bulk soil.
c_f	gravimetric solute concentration of the nonstony soil matrix, $\mu\text{g}/\text{g}$.
c_0	input concentration, $\mu\text{g}/\text{cm}^3$.
D	solute dispersion coefficient, cm^2/d .
f	gravimetric stone content (> 1 mm), g/g .
m_0	solute load, cm.
M_0	applied areal solute dose, μg .
n	number of observed local concentration profiles.
v	average pore water velocity, cm/d .
w_f	gravimetric water content of the nonstony soil matrix, g/g .
x	distance along transect, m.
z	soil depth, cm.
ϵ_f	porosity of the nonstony soil matrix, cm^3/cm^3 .
θ	volumetric soil water content, cm^3/cm^3 .
λ	dispersivity, cm.
μ_{\ln}	global mean of $\ln v$.
$\rho(v)$	probability density function of v .
ρ_f	particle density of the nonstony (< 1 mm) solid phase, g/cm^3 .
ρ_s	particle density of the stones (> 1 mm), g/cm^3 .
ρ_w	fluid density, g/cm^3 .
σ_{\ln}	global standard deviation of $\ln v$.

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(Received June 23, 1986;
revised May 20, 1987;
accepted May 22, 1987.)