An Experimental Study of Solute Transport in a Stony Field Soil

RAINER SCHULIN, MARTINUS TH. VAN GENCHTEN, HANNES FLÖHLER, AND PETER FERLIN

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 54-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 40 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 (CD equation) and with a regional stochastic model that assumes lognormal distributions of the pore water velocity and the dispersion coefficients 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. Poor 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 150% of the applied tracers were recovered in 1982. The effects of sampling size (0.3 vs. 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 [Roth 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 [Dhima, 1981; White, 1985]. While laboratory tracer experiments provide unique opportunities for studying conceptual mechanisms affecting solute transport [e.g., Nieuwenhuis and Biggar, 1961; Rao et al., 1980; Nieder-Kitzza 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 der 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 [Polonész et al., 1982; Flöhler, 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-teaching 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 [Parkar and van Genuchten, 1984] that assumes a lognormal distribution of the pore water velocity across the field.

EXPERIMENTAL FIELD STUDY

The tracer experiments were carried out at Creaux de Chippes 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 (calcic regosol), ex- hibits distinct layers of parent rock material of markedly dif- ferent composition. The parent material originated from col- luluvium but also contains some glicélofluvial deposits. Earlier soil formations buried under overcast material are relatively

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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 "non-stony" 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 non-stony 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 prewetted to prevent runoff from the sometimes quite hydrophobic soil surface. On April 14, 1982, a 31,450 ppm Br⁻ solution (approximately 400 ppmBr⁻) 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 mg Br⁻, 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 m⁻² 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 weighted 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 dm²) were taken in 10-cm depth intervals at five locations along the transect (+ = 1.1, 4.0, 8.0, 11.0, and 13.3 m). Unless stated otherwise, only data derived from these larger samplings have been used in subsequent calculations regarding water and stone contents.

After the first sampling was completed, the trench walls

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**TABLE 1. Physical and Chemical Properties of the Non-stony (< 1 mm) Soil at the Study Site**

<table>
<thead>
<tr>
<th>Depth, m</th>
<th>Texture*</th>
<th>Organic Carbon</th>
<th>pH</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0-0.1</td>
<td>0.8</td>
<td>0.00</td>
<td>0.75</td>
<td>37.9</td>
<td>1.4</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>0.2-0.3</td>
<td>4.7</td>
<td>21.1</td>
<td>7.4</td>
<td>39.4</td>
<td>1.4</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>0.4-0.5</td>
<td>1.1</td>
<td>10.5</td>
<td>7.4</td>
<td>41.7</td>
<td>1.3</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>0.7-0.8</td>
<td>2.0</td>
<td>20.0</td>
<td>7.4</td>
<td>43.0</td>
<td>1.0</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>1.0-1.1</td>
<td>0.1</td>
<td>3.9</td>
<td>7.6</td>
<td>42.7</td>
<td>1.0</td>
<td>0.6</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*Dry weight percentages of non-stony soil mineral phase.

†Weight percentage.
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 z = 1.5, 3.5, 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_x(t), micromoles 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_x, of the nonstony soil matrix. The standard error in w_x was about 16% of the average at the soil surface and less than 10% at all other depths. Because w_x 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 Flieder, 1984] showed that w_x displayed most of its horizontal variations as horizontal translation, rather than detectable long-range trends. Thus we assume that similar horizontal variations as in w_x 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. Instead, estimates of w_x of the bulk soil (including the stones) were obtained from the larger sampling data using the expression

$$w_x = \frac{1}{\rho_x \rho_f} \left( \frac{1}{1 - \epsilon_f} \right) \left( \frac{1 - \epsilon_s}{1 - \epsilon_f} \right)^{-1}$$

where $\rho_x$ and $\rho_f$ are the average particle densities for stony and nonstony soil fractions, respectively; $\rho_f$ is the density of water; $f$ is the gravimetric fraction of the soil; and $\epsilon_f$ is porosity of the nonstony soil matrix. Equation (1) is easily derived from gravimetric and volumetric mass balances of the soil matrix. Values for $\rho_x$ and $\rho_f$ were assumed to be 1.80 for the humic top horizon and 2.65 for the remainder of the profile, while $\epsilon_s$ was guessed to be about 0.6 and 0.5 for the surface and subsurface layers, respectively. The cross-section of the 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

$$\frac{dc}{dt} = D \frac{d^2c}{dz^2} - v \frac{dc}{dz}$$

where $c$ is the volume-averaged resident solution concentration, $D$ is the dispersion coefficient, $v \equiv qh$ 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 Amoozgar-Ford et al. [1982]. The RSM assumes that the entire field (referred to as the "global" scale) is composed of
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 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]

\[
\rho(x) = \frac{1}{\sqrt{2\pi} \sigma_n} \exp \left( -\frac{(\ln \nu - \mu_n)^2}{2\sigma_n^2} \right)
\]

where \(\mu_n\) and \(\sigma_n\) are the mean and standard deviation of \(\ln \nu\), respectively. The dispersion coefficient is assumed to be linearly related to the pore water velocity:

\[
D = \lambda \nu
\]

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

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 \(\alpha\), \(D\), and \(m_s\), where \(\alpha\) is an equivalent pulse duration. The CXTFIT analysis was done 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:

\[
M_0 = c_f \rho h m_a
\]

where \(c_f\) is the input concentration, \(\rho h m_a\) is the "local" solute load relative to the liquid-filled porosity of the soil, and the water content again assumed to be constant. While the tracers in activity were applied by means of nearly infinitesimal pulse 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 \(c_f\), 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 processes 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 \(\nu\), the Dispersion Coefficient \(D\), and the Solute Load \(m_s\)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Tracer</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Standard Error</th>
<th>Skewness</th>
<th>Kurtosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu), cm/d</td>
<td>Br(^-)</td>
<td>0.392</td>
<td>0.078</td>
<td>0.010</td>
<td>0.064</td>
<td>2.61</td>
</tr>
<tr>
<td>C(^-)</td>
<td>0.528</td>
<td>0.135</td>
<td>0.017</td>
<td>0.169</td>
<td>1.98</td>
<td></td>
</tr>
<tr>
<td>ln (\nu)</td>
<td>Br(^-)</td>
<td>-0.657</td>
<td>0.206</td>
<td>0.027</td>
<td>-0.458</td>
<td>2.99</td>
</tr>
<tr>
<td>C(^-)</td>
<td>-0.633</td>
<td>0.264</td>
<td>0.034</td>
<td>-0.183</td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td>(D), cm/d</td>
<td>Br(^-)</td>
<td>1.45</td>
<td>1.30</td>
<td>0.173</td>
<td>2.31</td>
<td>9.18</td>
</tr>
<tr>
<td>C(^-)</td>
<td>1.13</td>
<td>0.423</td>
<td>0.105</td>
<td>2.72</td>
<td>13.8</td>
<td></td>
</tr>
<tr>
<td>ln (D)</td>
<td>Br(^-)</td>
<td>0.079</td>
<td>0.770</td>
<td>0.102</td>
<td>0.055</td>
<td>3.19</td>
</tr>
<tr>
<td>C(^-)</td>
<td>-0.067</td>
<td>0.607</td>
<td>0.078</td>
<td>0.250</td>
<td>2.93</td>
<td></td>
</tr>
<tr>
<td>(m_s), cm</td>
<td>Br(^-)</td>
<td>0.835</td>
<td>0.501</td>
<td>0.066</td>
<td>0.639</td>
<td>2.65</td>
</tr>
<tr>
<td>C(^-)</td>
<td>0.261</td>
<td>0.099</td>
<td>0.013</td>
<td>0.647</td>
<td>2.82</td>
<td></td>
</tr>
<tr>
<td>ln (m_s)</td>
<td>Br(^-)</td>
<td>-0.390</td>
<td>0.704</td>
<td>0.093</td>
<td>-0.580</td>
<td>2.60</td>
</tr>
<tr>
<td>C(^-)</td>
<td>-1.42</td>
<td>0.404</td>
<td>0.052</td>
<td>-0.767</td>
<td>5.38</td>
<td></td>
</tr>
</tbody>
</table>

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 samplings 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 profiles.

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 [see Geschner and Cleary, 1979; Whitic, 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 CI 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 CI. 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 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 velocity closely fitted the normal distribution for Br and behaved intermediate between normal and lognormal for CI. 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 Bippes 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 Amoros-Ford et al. [1982] and
Fig. 6. Distributions (solid lines) along the transect of (a) the pore water velocity \( \nu \), (b) the dispersion coefficient \( D \), and (c) the solute load \( m_s \) 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 \( \nu \) 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 load \( m_s \). This is shown in Figures 5c and 6e for the bromide and chloride, 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 Geelhoed et al. [1985], may have created a favorable condition for horizontal flow.

We finally note that the frequency distributions of calculated \( m_s \) values were found to be intermediate between lognormal and normal for both tracers (Table 2). Correlations between \( m_s \) and \( \nu \) or \( D \) were found to be insignificant, except for a relatively weak one between \( m_s \) and \( D (\nu = 0.398) \) 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

<table>
<thead>
<tr>
<th>Model</th>
<th>May 18, 1983, Small Samples</th>
<th>May 18, 1983, Large Samples</th>
<th>Oct. 16, 1984, Large Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bromide, $n = 57$</td>
<td>Chlordie, $n = 61$</td>
<td>Bromide, $n = 5$</td>
</tr>
<tr>
<td>Average of local values</td>
<td>0.392</td>
<td>0.528</td>
<td>0.375</td>
</tr>
<tr>
<td>Global fit</td>
<td>0.381</td>
<td>0.402</td>
<td>0.305</td>
</tr>
<tr>
<td>RSM</td>
<td>0.381</td>
<td>0.557</td>
<td>0.394</td>
</tr>
<tr>
<td>Dispersivity, $L_w$</td>
<td></td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>Soil Load, $m_s$, cm</td>
<td>3.70</td>
<td>2.12</td>
<td>4.57</td>
</tr>
<tr>
<td>Global fit</td>
<td>6.85</td>
<td>8.38</td>
<td>12.06</td>
</tr>
<tr>
<td>RSM</td>
<td>6.87</td>
<td>2.17</td>
<td>12.08</td>
</tr>
<tr>
<td>Standard Deviation of $v$</td>
<td>0.206</td>
<td>0.264</td>
<td>0.360</td>
</tr>
<tr>
<td>RSM</td>
<td>0.0004</td>
<td>0.313</td>
<td>0.006</td>
</tr>
</tbody>
</table>

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.

### Table 4: Percent Recoveries of the Applied Bromide and Chloride Tracers

<table>
<thead>
<tr>
<th>Model</th>
<th>May 18, 1982, Small Samples</th>
<th>May 18, 1982, Large Samples</th>
<th>Oct. 16, 1984, Large Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bromide, $n = 61$</td>
<td>Chlordie, $n = 61$</td>
<td>Bromide, $n = 5$</td>
</tr>
<tr>
<td>Average of local values</td>
<td>72.8</td>
<td>130.4</td>
<td>72.8</td>
</tr>
<tr>
<td>Global fit</td>
<td>74.2</td>
<td>115.9</td>
<td>65.6</td>
</tr>
<tr>
<td>RSM</td>
<td>81.4</td>
<td>125.6</td>
<td>79.9</td>
</tr>
</tbody>
</table>

Data are estimated directly from the measured concentration and water content data and from optimized values of the field-averaged soil load $m_s$ 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 dimen-
sions 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 $a$) and global effects associ-
ated with velocity fluctuations (determining the value of $a_n$). The RSM estimate for $a_n$ 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 ef-
ffectively reducing the RSM to the global CDE model. This is manifest by near equality in estimated Br $a$ 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 distri-
bution of $s$ [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 $a$ becomes about the same as the average of the local fit CDE values (Table 3). The two esti-
mates of $a_n(x)$ for the small-sample chloride data (Table 3) agree reasonably well. In comparison to the log variance pa-
rameters inferred by Jury [1985, Tables 2-5] from various field experiments, the estimated $a_n$ 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. [1986, Table 3.1] range from as low as 0.01 cm to as high as 70 cm. Disregarding the two extreme values from their study, 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) sam-
ples, Table 3 also showed 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 distribu-
tions in Figures 2 and 3. The lesser agreement for the dis-
ersivity and the standard deviation of $a$ in a between the two samplings is most likely due to the significant horizontal redis-
tribution of the tracers and the associated short-range vari-
ations 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 agree-
ment with the expected mass balance is coincidental. The pre-
cision in measuring solute concentration profiles was not sig-
ificantly different between the large and small sample sizes
because of the high degree of spatial autocorrelation of con-
centrations over short ranges [Schulin and Flisher, 1984]. Thus differences in estimated solute loads between the two samplings should be almost entirely a result of different sam-
pling 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 distri-
bution, and likely also in the mass balance.

**EXTRAPOLATION TO TIME**

Equal performance of the CDE model and RSM in describ-
ing momentary concentration profiles versus depth can be ex-
pected, 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 Symons, 1985]. This is illustrated in Figures 7b and 8b, where calculated average concentration profiles are com-
pared with the October 1984 field-averaged sampling data. The "predicted" curves were computed with the global fit pa-
rameter 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 bro-
mine were essentially identical, as were their best fit curves for the 1983 profile because of the nearly normal distribution of $a$. 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 depth 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 bi-modal shaped concentration distributions that were ob-
erved at two of the four sampling locations in 1984. For clari-
ty 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 Flisher, 1984]. Table 3 indicates that the averaged 1984 local fit pore water velocity was less than half of the 1983 value, thus reflect-
ing the lack of downward displacement between the 1983 and 1984 samplings. The dispersivity was found to be of approxi-
mately the same magnitude as in 1983.
CONCLUSIONS

The results reported here show significant differences between
the two-dimensional spatial distributions of the bro-
mide 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: bro-
mide was applied half a year earlier than chloride and had
travelled for a full year when the first sampling took place in
May 1983. The chloride at this time had only travelled for one
winter season and thus mixed 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 trans-
port behavior of the two tracers. Increased soil water extract-
ation 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 in-
creased lateral redistribution, more mixing between otherwise
independent vertical flow paths should be expected, thus de-
coupling the relationship between average vertical travel ve-
locity and local soil properties such as the hydraulic conduc-
tivity. 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 tran-
sect, 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 conse-
quences for sampling strategies. Soluble 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
transient 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 vari-
ations in rainfall and evapotranspiration rates cannot be ig-
nored. Preliminary analysis of the data using a numerical
model that couples transient unsaturated water flow and a
soilute 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 momen-
tary, field-averaged (global) as well as local concentration dis-
tributions 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 trans-
port process. Use of a deterministic numerical model to de-
scribe 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, $\mu g/cm^3$ bulk soil.
$c_y$ gravimetric solute concentration of the nonstony soil
matrix, $\mu g/g$.
$c_i$ input concentration, $\mu g/cm^3$.
$f$ solute dispersion coefficient, $cm^2/d$.
$g$ gravimetric stone content ($>1$ mm), $g/g$.
$m_s$ solute load, cm.
$M$ applied areal solute dose, $\mu g$.
$n$ number of observed local concentration profiles.
$q$ average pore water velocity, cm/d.
$s_y$ gravimetric water content of the nonstony soil matrix,
$g/E$.
$x$ distance along transect, m.
$z$ soil depth, cm.
$z_y$ porosity of the nonstony soil matrix, $cm^3/cm^3$.
$v$ volumetric soil water content, $cm^3/cm^3$.
$D$ dispersivity, cm.
$\mu_s$ global mean of ln $v$.
$\phi(v)$ probability density function of $v$.
$\psi_a$ particle density of the nonstony ($<1$ mm solid phase,
$g/cm^3$.
$\rho_a$ particle density of the stones ($>1$ mm), $g/cm^3$.
$\phi(v)$ fluid density, $g/cm^3$.
$\sigma_a$ global standard deviation of ln $v$.

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