Gas phase advection and dispersion in unsaturated porous media

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[1] Gas phase miscible displacement experiments were conducted to quantitatively investigate the advective and dispersive contributions to gas phase transport in unsaturated porous media over a range of soil water contents. Furthermore, the independence of measured dispersivity values was evaluated through comparison of nonreactive and reactive tracer transport. Methane was used as a nonreactive tracer, while difluoromethane (DFM) and trichloroethene (TCE) were used as reactive tracers. At soil water contents below 17%, measured dispersivity values are observed to be independent of the tracer compound and of the soil water content. Conversely, the dispersivities are tracer dependent at the highest soil water contents, wherein the values for DFM and TCE are 3 and 6 times larger than that of methane’s, respectively. The significantly larger dispersivity values obtained for DFM and TCE are most likely due to rate-limited mass transfer of these compounds between the gas phase and soil water, which is not observed for methane because of its minimal water partitioning. The dispersivity values observed here range between 0.3 and 3 cm and are similar to those reported in the literature. The results indicate that within a given “ideal transport” range, dispersivities measured at one soil water content with a given tracer may be representative of the same porous media system at other soil water contents and for other compounds.

INDEX TERMS: 1832 Hydrology: Groundwater transport; 1866 Hydrology: Soil moisture; 1875 Hydrology: Unsaturated zone; KEYWORDS: gas transport, diffusion, dispersion, advection, unsaturated, porous media

1. Introduction

[2] Enhanced understanding of solute transport in subsurface systems has enabled increasingly sophisticated and accurate predictions of contaminant transport and risk analysis. However, while much attention has been given to examination of aqueous phase transport in the vadose zone, many fundamental questions regarding the transport of contaminants in the gas phase remain unanswered. Gas phase contaminant transport is particularly important in understanding and predicting the subsurface transport of volatile organic compounds (VOCs) [Baehr et al., 1989; Brusseau, 1991; Kayano and Wilson, 1992; McCoy and Rolston, 1992; Batterman et al., 1995; Skan and Stephens, 1995; Arands et al., 1997; Poulsen et al., 1998b], naturally occurring subsurface gases (e.g., radon) [Mosley et al., 1996; van der Spoel et al., 1998, van der Spoel et al., 1999; van der Pal et al., 2001], and gaseous emissions from landfills [Metcalfe and Farquhar, 1987; Valsaraj and Thibodeaux, 1988; Cripps, 1999; Williams et al., 1999; Poulsen et al., 2001]. Many concepts developed through the examination of aqueous phase systems are readily applied to gas phase transport, such as equilibrium phase partitioning, interphase mass transfer constraints, and relationships between advective and dispersive processes. However, quantification of the relative importance of such contributions under various system conditions requires experiments and modeling focused specifically on gaseous or volatile contaminants.

[3] Advection in the gas phase is largely controlled by natural (e.g., barometric) or induced (e.g., soil vapor extraction) pressure gradients, although other variables, such as temperature, may also play a role. The average rate of advection of a compound relative to the movement of soil gas is dictated by its chemical and physical interactions with other phases in the porous media system. Such interactions include adsorption of the gas phase compound to the soil gas-soil water interface, dissolution into soil water, and sorption of dissolved solute to the solid phase. The influence of several factors on gas phase retention has been examined, including such variables as solute chemistry [Li and Voudrias, 1992; Ruiz et al., 1998], mineral composition [Rhue et al., 1988; Pennell et al., 1992; Ruiz et al., 1998], soil water content [Unger et al., 1996; Silva, 1997; Garcia-Herruzo et al., 2000], and temperature [Koo et al., 1990; Goss, 1992, 1993].

[4] Dispersion is generally represented as consisting of diffusional and mechanical mixing components. The relative contribution of mechanical mixing versus diffusional processes to dispersion has not been completely elucidated for gas phase systems, particularly for partially saturated systems. In comparison to aqueous phase transport, diffusion is likely to be more significant for gas phase transport because of the much larger diffusion coefficients associated with the gas phase relative to the aqueous phase.

[5] In general, compounds with lower molecular weights would be expected to exhibit greater diffusive flux than heavier molecular weight compounds. Conversely, the mechanical mixing contribution to dispersion is conceptualized as being dependent only on the physical properties of the porous medium and not on those of the compound. Mechanical mixing is the general term for several
specific sources of pore-scale velocity variations, including differences in pore size (e.g., larger pores promote higher velocities than smaller pores), differences in velocity along the cross section of individual pores (e.g., fluids have larger velocity in the center of the pore relative to near the pore walls), and the tortuosity of flow paths. Reported gas phase dispersivities, the primary term representing mechanical mixing, range between approximately 0.1 and 5 cm for various systems [Armstrong et al., 1994; Popovicova and Brusseau, 1997; Ruiz et al., 1999; Garcia-Herruzo et al., 2000]. However, the influence of specific system properties, such as soil water content or particle and pore size distributions on such values has yet to be examined. Furthermore, it has not been demonstrated that current means of measuring dispersivity values do indeed yield solute-independent dispersivity values. For example, and as will be discussed in detail in section 3, the incorporation of additional transport processes, such as rate-limited mass transfer, into the dispersivity term results in lumped values. Such lumped dispersivities will be larger for solutes experiencing greater nonideal transport and, as a result, will be solute dependent.

In the current study, gas phase miscible displacement experiments were conducted to investigate the advective and dispersive contributions to gas phase transport in unsaturated porous media over a range of soil water contents. Compounds that demonstrate a range of possible interactions with the porous medium were selected to assess how solute retention processes influenced the measured dispersivities. The results were analyzed to quantitatively determine the relative contributions of diffusion and mechanical mixing to dispersive transport.

2. Materials and Methods

2.1. System Overview

The experiments were conducted using a natural porous medium, Vinton fine sand. Relevant physical properties of the material are reported in Table 1. Methane was used as a non-reactive tracer gas, while difluoromethane (DFM) and trichloroethylene (TCE) were used as reversibly retained reactive tracers to examine the influence of interphase mass transfer processes on dispersion processes. DFM is a water-soluble nonsorbing compound, and its transport is therefore influenced by gas water mass transfer. TCE interacts with both solid and aqueous phases of the porous medium, and thus its transport is influenced by sorption and gas water mass transfer. Physicochemical properties of the tracers are summarized in Table 2.

A detailed diagram of the miscible displacement system is shown in Figure 1. The tracer gases were each custom mixed in a balance of nitrogen to ~100 ppmv and introduced into the system via high-pressure gas cylinders (Air Products, Long Beach, California; Spectra Gases, Branchburg, New Jersey; or Air Liquide, Houston, Texas). All gases passed through a 500 or 250 mL gas washing bottle (Pyrex, Ace Glass, Vineland, New Jersey) for humidification prior to contacting the wetted porous medium. This was done to prevent drying of the porous medium. Separate humidification bottles were used for the carrier gas (ultrahigh purity nitrogen) and the tracers to avoid cross-contamination. The temperature and relative humidity of the gases were measured by passing them through a column bypass line containing a custom-made humidity chamber into which a thermohygrometer probe was inserted (Dwyer Instruments, Michigan City, Indiana). The column bypass line also allowed for various system variables (e.g., flow rate, $C_0$ voltage) to be measured or set without precontamination of the porous medium.

A 10.5 cm (7.06 cm inner diameter) stainless steel column (MODcol, St. Louis, Missouri) was used with dispersion plates (nominal 20 $\mu$m pore size) fitted at both ends to promote an even distribution of vapor across the column cross section. Bed support frits (2–4 $\mu$m pores) were also inserted between the porous medium and the diffusion plates to prohibit the grains from clogging the dispersion plates and to minimize column dead volume. Stainless steel three-way valves (Whitey, Arizona Valve and Fittings Company, Phoenix, Arizona) were used to switch between the tracer and the carrier gas. All system components through which gases flowed were connected with 1/8 inch stainless steel tubing and 1/8 inch stainless steel Swagelok fittings (Arizona Valve and Fittings Company, Phoenix, Arizona). High-resolution metering valves (Cole Parmer, Vernon Hills, Illinois), differential pressure gauges (Dwyer Instruments, Michigan City, Indiana), and third-stage high-precision pressure regulators (model 44-4660S24,}

![Figure 1. Schematic of experiment system.](image-url)

### Table 1. Physical Properties of Porous Medium

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Texture</td>
<td></td>
</tr>
<tr>
<td>Percent Sand</td>
<td>97</td>
</tr>
<tr>
<td>Percent Silt</td>
<td>1.8</td>
</tr>
<tr>
<td>Percent Clay</td>
<td>1.2</td>
</tr>
<tr>
<td>Organic carbon content, wt/wt %</td>
<td>0.01</td>
</tr>
<tr>
<td>Particle density, g cm$^{-3}$</td>
<td>2.69</td>
</tr>
<tr>
<td>Specific surface area, m$^2$ g$^{-1}$</td>
<td>3.54</td>
</tr>
</tbody>
</table>

*Soil, Water, and Plant Analysis Laboratory, Tucson, Arizona.

*Micromeritics Instrument Co, Norcross, Georgia.

### Table 2. Physicochemical Properties of Compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Methane</th>
<th>TCE</th>
<th>DFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{b_{sat}}$, mg L$^{-1}$</td>
<td>$24^{b}$</td>
<td>$1198^{b}$</td>
<td>$4355^{b}$</td>
</tr>
<tr>
<td>$K_{sv}$, mL g$^{-1}$</td>
<td>na</td>
<td>0.014$^{d}$</td>
<td>na</td>
</tr>
<tr>
<td>$K_{i}$</td>
<td>$27^{c}$</td>
<td>$0.367^{c}$</td>
<td>$0.505^{c}$</td>
</tr>
<tr>
<td>$D_{w}$, cm$^2$ s$^{-1}$</td>
<td>$0.205^{b}$</td>
<td>$0.082^{b}$</td>
<td>$0.112^{b}$</td>
</tr>
</tbody>
</table>

$^{a}$Values given at 25°C; na, not applicable.

$^{b}$Schwarzenbach et al. [1993].

$^{c}$Deeds et al. [1999].

$^{d}$Measured [COSTANZA-ROBINSON, 2001].
2.2. Miscible Displacement Experiments

[11] The porous medium was heated overnight at 105°C to dry it and remove any volatile contamination. After allowing the porous medium to cool under vacuum in a desiccator, it was mixed with the desired amount of water and packed wet into the column. The porous medium was tamped in the column at small increments, typically 1 cm, to minimize the formation of particle-size layering in the column. Aliquots of the wet porous medium were collected prepacking and postpacking to gravimetrically determine preexperiment soil water contents. After the experiment, the column was unpacked, and a small (<20 g) aliquot was taken from near the column inlet, three points along the axis of flow, and near the column outlet for gravimetric soil water content measurement. In addition, the remainder of the porous medium in the column was used to measure a composite column-averaged soil water content. In all cases the column average soil water content measured after the experiment was close to the soil water content measured prior to the experiment, indicating there was minimal loss of water during the experiments.

[12] The experimental system, including all tubing, valves, and connectors, was initially flushed for several minutes with methanol to remove any residual machine oil or other organic contamination. Sections of the system were flushed with water for up to 25 min. The water-filled sections were then weighed, emptied, oven-dried, and weighed again to determine the dead volume contained in various portions of the system. The total system dead volume measured in this manner was 4.5 cm³, which is ~3% of the total column porosity.

[13] The nitrogen carrier gas was flushed through the system until a steady FID baseline was achieved prior to each tracer experiment. The carrier flow rate was matched to the tracer gas flow rate. Multitracer experiments could not be conducted because of the use of flow-through detection, which does not incorporate analytical separation. Therefore tracer experiments were conducted sequentially, using identical experimental conditions. Experiments were conducted at least in duplicate and often in triplicate. When the column was not in use, it was sealed to minimize drying of the system.

[14] In order to achieve a constant-concentration tracer input pulse, the water in the tracer humidification bottle had to be saturated with the compound of interest prior to introduction of the gas to the column. Saturation was achieved by passing the gas through the humidification bottle and the column bypass line until a steady FID signal was observed. The tracer pulse was introduced to the system by switching between the tracer and carrier gas line using a three-way directional switching valve. The input pulse was continued until a relative concentration of one was achieved. Relative concentration is defined as the ratio of actual concentration, C, to input concentration, C₀. Upon switching back to the carrier gas line to elute the tracers from the system, a significant pressure surge was created because of back pressure in the system. Use of a high-precision third-stage regulator minimized this surge, but it could not be completely eliminated. The surge is manifested in the breakthrough curves as a temporary increase in solute concentration above C/C₀ = 1.

[15] Experiments were conducted with an inlet pressure of 20,685 Pa (~210 cm of water) and at a nominal column flow rate of 50 cm³ min⁻¹, with 20 cm³ min⁻¹ directed to the FID and the remainder vented prior to the detector via the split vent line. The chosen flow rate falls within the wide range of velocities reported as typical for soil vapor extraction remediation systems. Total column flow rate was measured as the sum of flow at the FID outlet and the split vent. Actual column volumetric flow rates were slightly smaller owing to gas expansion associated with the postcolumn pressure drop. Gas expansion and consequent concentration gradient effects along the length of the column were not considered to be important, given that the induced pressure gradient along the column was ~3%. This is well below the 20% gradient commonly considered as the cutoff for considering gas compressibility in flow equations [Alzaydi et al., 1978; Wilson et al., 1988; Massmann, 1989; Johnson et al., 1990].

3. Data Analysis

[16] Breakthrough curves are plotted as relative concentration (C/C₀) (e.g., measured effluent concentration normalized by the input concentration) versus eluted pore volume. A single pore volume represents the gas-filled volume contained in the packed column. Breakthrough curves can be analyzed in a comparative or absolute manner. The comparative manner of analysis uses a nonreactive tracer as a reference to which to compare the retention of reactive compounds in the same system [Skopp, 1984; Jin et al., 1995]. Comparative moments analysis is useful either when the exact pore and dead volumes of the system are not known or when pressure gradients and gas expansion complicate the relationship between average linear gas velocity, time, and volumetric flux.

[17] The zeroth moment M₀ obtained from moments analysis represents the area under the breakthrough curve or the mass eluted from the system. Comparison of the zeroth moment to the known input pulse provides a check on the mass recovery for the experiment. The zeroth moment is calculated as

\[ M_0 = \frac{\sum_i^n \left( c_i + c_{i+1} \right) / 2 (t_{i+1} - t_i) }{T_0} \]

where \( c \) is the relative concentration (C/C₀) (dimensionless), \( t \) is time (min), \( T_0 \) is the solute input pulse width given in time (min), and subscripts 1 and 2 refer to two consecutive time points.

[18] Percent recovery is calculated by the following:

\[ \text{Recovery} = \frac{M_0}{T_0} \times 100. \]
Mass recoveries significantly different from 100% can indicate leaks in the system, irreversible sorption, degradation or transformation of the solute, lack of control over flow rates, or analytical problems associated with sample analysis. None of these factors are operative in this experimental system; therefore recoveries very close to 100% are expected.

For a nonreactive tracer, the mean travel time through the system corresponds to the first normalized temporal moment, pulse width corrected, and is calculated as

$$T = \sum_i \left( \frac{(w + d_i)}{2} (t_i - t_0) \right) - 0.5T_0. \quad (3)$$

The retardation factor is defined as the ratio of the mean travel time of a given compound and the mean travel time of a nonreactive tracer. Thus, by definition, the retardation factor of a nonreactive tracer is one.

The breakthrough curves were simulated using a one-dimensional advective-dispersive solute transport model. Input parameters for the model include the size of the input pulse (in pore volumes) and the retardation factor. These two parameters are obtained independently using the method of comparative moments, described above. The output of the model, used in this manner, is an optimized value for the Peclet number ($Pe$), defined here as a dimensionless number representing the ratio of advective to dispersive processes experienced by a solute. The specific formulation of the Peclet number varies as a function of the application and field of study. The formulation used herein, where $Pe$ is referenced to a macroscopic length scale (i.e., column length) and to the total dispersion coefficient, is commonly used in the fields of soil physics and hydrology. Because different formulations are used in other disciplines, such as chemical engineering, caution should be exercised in interpreting the absolute values of Peclet numbers reported herein and in comparing them to previous studies.

The Peclet number is a function of the flow rate, the diffusion coefficient of the solute, and the physical properties of the porous medium. The optimized Peclet number can be related directly to the dispersion coefficient $D$ by the following equation:

$$D = \frac{vL}{Pe}, \quad (4)$$

where $v$ is the average linear velocity of the carrier gas (cm s$^{-1}$) and $L$ is column length (cm). The dispersion coefficient can be further defined as

$$D = D_0 \tau + \alpha v, \quad (5)$$

where $D_0$ is the diffusion coefficient in air (cm s$^{-1}$), $\tau$ is the tortuosity factor defined between 0 and 1 and inversely proportional to tortuosity of the gas pathways in the porous media (dimensionless), and $\alpha$ is the dispersivity (cm). Equation (5) can be rewritten as

$$D = D_{\text{diff}} + D_{\text{mm}}, \quad (6)$$

where the subscripts diff and mm refer to diffusion and mechanical mixing processes, respectively. Values for $D$ and $D_{\text{diff}}$ will be determined from the optimized Peclet number and by independent calculation, respectively. $D_{\text{diff}}$ is calculated using diffusion coefficients reported in the literature and tortuosity estimates, as described further. Values for the mechanical mixing term $D_{\text{mm}}$ are determined as the difference between $D$ and $D_{\text{diff}}$.

The tortuosity factor used in the dispersion equations will depend on air-filled porosity in the system and thus is dependent on soil water content for partially saturated systems. Tortuosity factors predicted using a number of empirical and semiempirical models have been reported in the literature [Penman, 1940; Millington, 1959; Moldrup et al., 1996, 1997; Schaefer et al., 1997; Moldrup et al., 1998; Poulsen et al., 1998a; Moldrup et al., 2000]. The various models have been shown to be most accurate for specific soil types, in different soil water content regions, and for either packed columns or undisturbed soil cores. A modification of the composite Penman-Millington-Quirk (PMQ) model presented by Moldrup et al. [1997] was used here because this equation has been shown to most accurately predict tortuosity factors in packed columns over a range of soil water contents. The modified PMQ equation is written as

$$\tau = 0.66n \left( \frac{\theta_w}{n} \right)^2, \quad (7)$$

where $n$ is the total porosity of the porous medium (dimensionless).

As expected, a general decrease in the calculated tortuosity factor, corresponding to increased tortuosity, is obtained with increasing soil water contents. Potential uncertainty in the calculated tortuosity factors is neglected in error calculations for the various dispersion parameters, discussed in section 4.

The value of $D_{\text{diff}}$ will vary according to the diffusion coefficient of the compound in question. For example, it is expected that methane will experience more diffusional dispersion than will DFM because the diffusion coefficient for methane is almost twice as large as for DFM (see Table 2). Conversely, the dispersivity term $\alpha$ in $D_{\text{mm}}$ is considered to be a property only of the physical system and should be compound independent. Therefore the $D_{\text{mm}}$ term should remain constant for all compounds at a given velocity in the same porous medium system, while dispersivity $\alpha$ should remain constant for all compounds regardless of velocity. Thus methane’s $D_{\text{mm}}$ value should be equal to that of DFM or TCE under the same experimental conditions. If the dispersivity values are observed to be compound independent, it may be concluded that they are functions of only the porous medium, as is generally assumed. Conversely, if the calculated dispersivity values differ for methane, DFM, and TCE, it may be concluded either that the diffusion behavior was not properly accounted for or that processes other than mechanical mixing and diffusion are contributing to dispersion.

In addition to diffusion and mechanical mixing processes, potential contributions from rate-limited mass transfer effects must be considered for DFM and TCE dispersion. Partitioning between the gas phase and soil water may cause aqueous phase diffusion rate limitations to become significant if the soil water films are sufficiently thick or if gas advection is sufficiently fast. At high soil water contents, additional dispersion may be introduced by the presence of isolated or disconnected air-filled porosity. While methane would be excluded from such disconnected porosity, dissolved DFM or TCE may diffuse to and volatilize into such isolated air pockets in the porous medium. Thus the soil water may cause observable mass transfer constraints. Such mass transfer constraints are expected to be more significant at higher soil water contents. In addition, TCE is also sorbed slightly by the soil grains. Thus rate-limited sorption/desorption must also be considered as a possible source of TCE dispersion. Because these additional sources of dispersion would influence methane, DFM, and TCE...
differently, solute dependence in the dispersivity value may be an indication of such processes occurring in the system. In this case the dispersivity would represent a “lumped” parameter and no longer represent just the contribution of mechanical mixing.

4. Results and Discussion

4.1. Breakthrough Curves and Moment Analysis

[25] Miscible displacement experiments were conducted at 11 soil water contents ranging between ~2 and ~20%. TCE was not used in experiments 7 and 8, and DFM was not used in experiment 9. The measured specifications and flow conditions for each experiment are given in Table 3. Figure 2 shows the measured postexperiment average soil water contents and the soil water content profile along the length of the column. The profiles show that the soil water content within each column was very uniform, lending support both for the uniformity of the wetting and packing method as well as for the adequacy of the gas humidification method.

[26] Replicate arrival waves for methane and DFM for experiment 1 (2% $q_w$) are shown in Figure 3. The overlap of the replicates is representative of all results and demonstrates the reproducibility of the experimental conditions. For Figures 4–7, a single replicate is shown; however, the data included in the tables represent the average of all replicates. Mass recoveries calculated from the breakthrough curves and known input pulses ranged between 99 and 102% (100.5 ± 1%) and are given in Table 4.

4.2. Modeling Results and Dispersion Calculations

4.2.1. Nonreactive tracer (methane).

[27] The arrival and elution waves for methane experiments 2, 7, and 10 ($q_w$ = 2.6, 9.7, and 16.9%, respectively) and for all DFM and TCE experiments are presented in Figure 4. At low and intermediate soil water contents, breakthrough curves for methane, DFM, and TCE are symmetrical with sharp arrival and elution waves, indicating relatively ideal flow conditions. At higher soil water contents the DFM and TCE curves show significantly increased tailing for both the arrival and elution waves. Sources of dispersion will be discussed quantitatively in section 4.2. In addition to differences in spreading among the various soil water content experiments, the magnitude of DFM and TCE retention in the system is strongly dependent on soil water content (see Table 4). This is expected since DFM and TCE partition into and thus are retarded by the water phase.

### Table 3. Packed Column Specifications and Flow Conditions

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$\theta_F$</th>
<th>$\theta_W$</th>
<th>$\theta_a$</th>
<th>$\rho_w$ g cm$^{-3}$</th>
<th>PV$_s$, cm$^3$</th>
<th>$Q$, PV min$^{-1}$</th>
<th>$v$, cm min$^{-1}$</th>
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<tbody>
<tr>
<td>1</td>
<td>0.361</td>
<td>0.019</td>
<td>0.341</td>
<td>1.72</td>
<td>155.7</td>
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<td>3.2</td>
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<tr>
<td>2</td>
<td>0.366</td>
<td>0.026</td>
<td>0.330</td>
<td>1.71</td>
<td>155.0</td>
<td>3.1</td>
<td>3.3</td>
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<tr>
<td>3</td>
<td>0.358</td>
<td>0.031</td>
<td>0.327</td>
<td>1.73</td>
<td>149.1</td>
<td>3.0</td>
<td>3.4</td>
</tr>
<tr>
<td>4</td>
<td>0.374</td>
<td>0.034</td>
<td>0.340</td>
<td>1.68</td>
<td>155.1</td>
<td>3.1</td>
<td>3.2</td>
</tr>
<tr>
<td>5</td>
<td>0.374</td>
<td>0.052</td>
<td>0.323</td>
<td>1.68</td>
<td>147.1</td>
<td>2.9</td>
<td>3.4</td>
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<td>148.3</td>
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<tr>
<td>8</td>
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<tr>
<td>11</td>
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<td>0.196</td>
<td>0.197</td>
<td>1.63</td>
<td>90.0</td>
<td>1.8</td>
<td>5.6</td>
</tr>
</tbody>
</table>

*PV, column air-filled pore volume; $Q$, volumetric flow rate; $v$, average linear velocity.*

### Figure 2.
Postexperiment soil water content profile in packed columns.

### Figure 3.
Replicate arrival waves for methane and DFM from experiment 1 ($q_w = 1.9\%$).
The methane dispersion coefficient generally decreases slightly as soil water content increases, except for the highest soil water content (see Table 5). The decrease is a result of a decrease in the effective diffusion coefficient due to larger gas phase tortuosities at higher soil water contents. The decrease in diffusional contributions to $D$ offsets the slight increase in $D_{max}$ associated with the small increase in velocity that occurred with increasing soil water content.

The relative contributions of diffusion and mechanical mixing to the total dispersion coefficient are plotted in Figure 5.

Figure 4. Arrival and elution waves for (a) methane, experiments 2, 7, and 10; (b) all DFM experiments; and (c) all TCE experiments. Note that “elution pore volumes” refers to the pore volumes since the input pulse ended and elution began, allowing comparison of elution behavior for experiments with different input pulse sizes.

Figure 5. Relative contributions of diffusion and mechanical mixing to methane dispersio

Figure 6. Dispersivities calculated for methane, DFM, and TCE as a function of soil water content.
For the lowest soil water content, diffusion provides the major contribution, reflecting the lower tortuosity and resultant enhanced diffusion associated with this lowest soil water content. Conversely, mechanical mixing provides the predominant contribution for the highest soil water contents, reflecting the increased linear velocities and greater tortuosities at the highest soil water contents (see Table 3 and (5)). However, for the majority of the soil water content range, diffusion and mechanical mixing contribute roughly equally to total dispersion.

To focus specifically on mechanical mixing, it is useful to examine the dispersivity value, rather than the total $D$ term. The dispersivity coefficient calculated from the methane data remains relatively constant for all soil water contents, with the possible exception of the highest soil water content (Figure 6). This indicates that despite increasing soil water content, there is negligible increase in the degree of physical heterogeneity, such as variability in the gas-filled pore distribution, affecting nonreactive transport, except perhaps at the highest soil water content.

### 4.2.2. Reactive tracers.

The solid lines in Figures 4b and 4c represent the simulated DFM and TCE breakthrough curves, respectively. For experiments 10 and 11 the ideal transport model does not fit the data quite as well as it does for the lower soil water contents. Therefore it is instructive to closely examine the observed DFM and TCE transport behavior to determine whether nonequilibrium processes may be occurring in the 17% (10) and 20% $b_{tr}$ (11) experiments. The calculated and calibrated dispersion parameters are summarized in Table 5.

Similar to the methane results, calculated dispersion coefficients for DFM and TCE remain relatively constant at soil water contents <13.6%. At soil water contents higher than 13.6%, dispersion coefficients decrease slightly and sharply increase at the highest soil water contents. Examining the relative contributions of diffusion and mechanical mixing to total dispersion (Figure 7) reveals that in contrast to the methane results, mechanical mixing is more significant than diffusion for both DFM and TCE. This is consistent with the smaller diffusion coefficients of DFM and TCE compared to that of methane, which results in smaller $D_{diff}$ terms for the former compounds.

In contrast to the differences in magnitude of diffusion terms, the absolute magnitudes of the $D_{mom}$ (or $c$) terms determined for DFM and TCE are comparable to that of methane’s for all but the two highest soil water contents (Figure 6). This latter observation is expected if the dispersivity parameter truly represents the physical system and does not represent a lumped parameter (e.g., including diffusional and nonequilibrium effects). If other sources of dispersion were lumped into the dispersivity term, tracer-dependent dispersivities would result. Thus the independence of the calculated dispersivity values at soil water contents <17% provides support for the assumptions made above. Specifically, it appears that diffusion was appropriately accounted for literature diffusivities and tortuosity estimates and that diffusion and mechanical mixing are the only processes contributing to dispersion in this soil water content region.

A significant discrepancy is observed between the dispersivity values determined for DFM and TCE versus those determined for methane (Figure 6) at the two highest soil water contents, experiments 10 ($b_{tr} = 16.9\%$) and 11 ($b_{tr} = 19.6\%).

### Table 4. Moments Analysis Results for Methane, DFM, and TCE

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$b_{tr}$</th>
<th>Percent Recovery</th>
<th>$n$</th>
<th>Percent Recovery</th>
<th>$R'_{TOT} \pm SD$</th>
<th>$n$</th>
<th>Percent Recovery</th>
<th>$R'_{TOT} \pm SD$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.019</td>
<td>101.7</td>
<td>3</td>
<td>100.5</td>
<td>1.074 $\pm$ 0.004</td>
<td>3</td>
<td>99.7</td>
<td>1.669 $\pm$ 0.023</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>0.026</td>
<td>99.8</td>
<td>2</td>
<td>99.7</td>
<td>0.991 $\pm$ 0.004</td>
<td>2</td>
<td>99.7</td>
<td>1.372 $\pm$ 0.037</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>0.031</td>
<td>99.9</td>
<td>3</td>
<td>100.7</td>
<td>1.049 $\pm$ 0.001</td>
<td>2</td>
<td>99.4</td>
<td>1.369 $\pm$ 0.025</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>0.034</td>
<td>100.3</td>
<td>3</td>
<td>101.5</td>
<td>1.092 $\pm$ 0.016</td>
<td>2</td>
<td>99.7</td>
<td>1.248 $\pm$ 0.002</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>0.052</td>
<td>99.7</td>
<td>2</td>
<td>99.7</td>
<td>1.149 $\pm$ 0.013</td>
<td>3</td>
<td>98.6</td>
<td>1.322 $\pm$ 0.074</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>0.076</td>
<td>100.2</td>
<td>3</td>
<td>99.5</td>
<td>1.296 $\pm$ 0.013</td>
<td>2</td>
<td>100.0</td>
<td>1.486 $\pm$ 0.016</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>0.097</td>
<td>100.0</td>
<td>3</td>
<td>100.4</td>
<td>1.356 $\pm$ 0.012</td>
<td>3</td>
<td>–</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>0.136</td>
<td>99.4</td>
<td>1</td>
<td>99.7</td>
<td>1.676 $\pm$ 0.009</td>
<td>5</td>
<td>–</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>0.136</td>
<td>100.4</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>99.5</td>
<td>1.923 $\pm$ 0.020</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>0.169</td>
<td>101.8</td>
<td>4</td>
<td>101.3</td>
<td>1.754 $\pm$ 0.009</td>
<td>3</td>
<td>99.7</td>
<td>2.334 $\pm$ 0.031</td>
<td>2</td>
</tr>
<tr>
<td>11</td>
<td>0.196</td>
<td>2.2</td>
<td>4</td>
<td>101.5</td>
<td>2.204 $\pm$ 0.018</td>
<td>2</td>
<td>99.4</td>
<td>3.095 $\pm$ 0.025</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 7. Relative contributions of diffusion and mechanical mixing to (a) DFM dispersion and (b) TCE dispersion.
Acknowledgments.\] Ruiz et al.\], 29 30 Brusseau Values for Calculated and Calibrated Dispersion Variables Therefore it is likely that rate
4 0.076 0.06 0.167 9.2 0.063 0.037 0.025 0.44
5 0.097 0.06 0.144 11.7 0.054 0.031 0.021 0.34
6 0.136 0.07 0.112 15.6 0.045 0.025 0.030 0.44
7 0.136 0.07 0.112 13.1 0.054 0.025 0.017 0.26
8 0.169 0.08 0.080 21.5 0.039 0.019 0.017 0.22
9 0.097 0.06 0.144 11.7 0.054 0.031 0.021 0.34
10 0.136 0.07 0.112 13.1 0.054 0.025 0.017 0.26
11 0.196 0.09 0.054 13.6 0.077 0.014 0.055 0.59

Because DFM and TCE are influenced by retention and methane is not, it is likely that some type of rate-limited retention process is responsible for the enhanced dispersivities obtained for DFM and TCE at these two soil water contents. As noted above, inclusion of nonequilibrium effects in the mechanical mixing term produces a lumped dispersion parameter that is no longer independent.

One possible cause of the enhanced dispersivities is rate-limited sorption/desorption. However, transport of TCE in the same porous medium under water-saturated conditions was well described by a solute transport model based on instantaneous sorption/desorption [Costanza-Robinson, 2001]. Therefore it appears that sorption of TCE by the Vinton sand is not measurably rate limited. In addition, DFM is not measurably sorbed by the porous medium used herein. Another possible cause is rate-limited retention at the air-water interface. However, it has been suggested that adsorption at the air-water interface is an instantaneous process [Lorden et al., 1998]. In any event, adsorption at the air-water interface is minimal for the high soil water content experiments, as has been described elsewhere [Costanza-Robinson, 2001]. With elimination of the previous two retention processes, the only process that remains is aqueous dissolution and associated rate-limited diffusion.

Both DFM and TCE are water soluble and thus undergo mass transfer between the soil gas and soil water phases. While such transfer is usually considered to be essentially instantaneous for aqueous phase transport, it may not be for gas phase transport given the generally greater velocities associated with gas flow. In addition, to obtain an equilibrium distribution, the compound must diffuse throughout the water bodies, which are relatively thick at the highest soil water contents. This aqueous phase diffusion process has been shown to contribute to rate-limited behavior for gas phase transport [e.g., Brusseau, 1991; Gierke et al., 1992; Popovicova and Brusseau, 1998]. Thus it is likely that rate limitations associated with aqueous phase diffusion are influencing the transport of DFM and TCE for experiments 10 and 11 and are the cause of the enhanced dispersivity values. Moreover, TCE has a slightly lower aqueous phase diffusion coefficient than DFM, which would result in greater diffusion rate limitations and hence the greater dispersion experienced by TCE.

5. Conclusions

The results presented herein indicate that both mechanical mixing and diffusion contribute significantly to gas phase transport in unsaturated porous media under the conditions employed in the experiments. The relative contribution of individual dispersion processes for methane, DFM, and TCE were governed largely by the differences in their diffusion coefficients. Changes in gas phase tortuosity and linear velocity due to soil water content changes represented secondary effects.

The results indicate that soil water content alone does not dramatically influence gas phase dispersion in unsaturated porous media. However, solute reactivity, such as dissolution into the bulk water and sorption to the solid phase, coupled with high soil water contents appears to cause a significant increase in observed dispersion. At soil water contents of 17 and 20%, the highest soil water contents examined here, it is likely that rate-limited mass transfer behavior became an important factor controlling DFM and TCE transport, resulting in large discrepancies between the dispersivities obtained for the reactive versus the nonreactive compounds.

In general, the observed dispersivities fell within the range of reported experimental values and model input values. Typical gas phase dispersivity values range approximately from 0.1 to 5 cm, depending on soil type and soil column length, while those reported here range from 0.3 to 3 cm [Armstrong et al., 1994; Popovicova and Brusseau, 1997; Ruiz et al., 1999; Garcia-Herrero et al., 2000]. To the authors’ knowledge, gas phase dispersivity values have not been previously reported over a wide range of soil water contents, such as are reported here. These results indicate that within a given “ideal transport” range, dispersivities are tracer and water content independent. Thus dispersivities measured at one soil water content with a given compound may be representative of the same porous media system at other soil water contents and for other compounds.

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