Measurement of effective air diffusion coefficients for trichloroethene in undisturbed soil cores

Shannon L. Bartelt-Hunt, James A. Smith*

Program of Interdisciplinary Research in Contaminant Hydrogeology, Department of Civil Engineering, PO Box 400742, University of Virginia, Charlottesville, VA 22904-4742, USA

Received 18 October 2000; received in revised form 22 June 2001; accepted 5 November 2001

Abstract

In this study, we measure effective diffusion coefficients for trichloroethene in undisturbed soil samples taken from Picatinny Arsenal, New Jersey. The measured effective diffusion coefficients ranged from 0.0053 to 0.0609 cm²/s over a range of air-filled porosity of 0.23–0.49.

The experimental data were compared to several previously published relations that predict diffusion coefficients as a function of air-filled porosity and porosity. A multiple linear regression analysis was developed to determine if a modification of the exponents in Millington’s [Science 130 (1959) 100] relation would better fit the experimental data. The literature relations appeared to generally underpredict the effective diffusion coefficient for the soil cores studied in this work. Inclusion of a particle-size distribution parameter, \(d_{10}\), did not significantly improve the fit of the linear regression equation.

The effective diffusion coefficient and porosity data were used to recalculate estimates of diffusive flux through the subsurface made in a previous study performed at the field site. It was determined that the method of calculation used in the previous study resulted in an underprediction of diffusive flux from the subsurface. We conclude that although Millington’s [Science 130 (1959) 100] relation works well to predict effective diffusion coefficients in homogeneous soils with relatively uniform particle-size distributions, it may be inaccurate for many natural soils with heterogeneous structure and/or non-uniform particle-size distributions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Diffusion; Trichloroethene; Heterogeneity; Unsaturated zone
1. Introduction

Organic vapor transport in the unsaturated zone is important in understanding the distribution of organic contaminants in the subsurface and their exchange between the subsurface environment and the atmosphere (Marshall, 1959). Many studies have shown gaseous diffusion to be an important mechanism in the transport of vapors through the subsurface (Currie, 1970; Marrin and Kerfoot, 1988; Fuentes et al., 1991; Shonnard and Bell, 1993; Smith et al., 1996). Although advection of contaminants in the vadose zone periodically occurs due to factors such as vapor extraction systems, water infiltration, barometric pressure changes, and gaseous density differences, diffusional transport is constantly occurring due to localized or regional concentration gradients (Arands et al., 1997). The relative importance of diffusion and advective fluxes out of the subsurface under natural conditions was simulated by Choi et al. (submitted for publication). It was found that under some conditions, advective flux may be significant compared to diffusive flux; however, the diffusive flux was never an insignificant component of the total flux out of the subsurface.

Industrial compounds such as trichloroethene (TCE), benzene, and carbon tetrachloride are common contaminants in the subsurface. Because of their relatively low water solubilities and high vapor pressures, these solutes have high Henry’s law constants (Marrin and Kerfoot, 1988) and are referred to as volatile organic compounds (VOCs). When VOCs contaminate shallow ground water, volatilization from ground water to soil gas followed by diffusion through the unsaturated zone soil gas to land surface may be a significant natural subsurface attenuation mechanism (Smith et al., 1996).

Because diffusion plays an important role in the transport of VOCs and other contaminants in the subsurface, it is important to understand the relation between diffusional flux and soil properties such as bulk density and water content. In general, diffusion through a porous medium is hindered by the tortuous nature of the pores, the diminished cross-sectional area available for movement, and possibly by the pore size (Grathwohl, 1998). The impedance to diffusion caused by the porous media is defined as the tortuosity ($\tau$) and relates the effective diffusion coefficient ($D^*$) to the free air diffusion coefficient ($D_{\text{air}}$) by the following relation:

$$D^* = \alpha \tau D_{\text{air}}$$

where $\alpha$ is the air-filled porosity. Occasionally, $\tau$ is defined to include the effects of air-filled porosity; however, we feel that the above equation is preferable because it distinguishes between the effects of media and water content. Buckingham (1904) measured diffusion through wet and dry sands and soils and developed an equation of the form

$$\frac{D^*}{D_{\text{air}}} = \epsilon \alpha^{2x}$$

where $D^*$, $D_{\text{air}}$ and $\alpha$ are as previously defined and $\epsilon$ is a constant. It was found that $x$ was approximately equal to 2 for the soil types used. In studying the diffusion of acetone and
carbon disulfide through two repacked soils at a variety of moisture contents, Penman (1940) found that for $0.0 < a < 0.6$, an equation of the form:

$$D^*/D_{air} = 0.66a$$

provided the best fit to the experimental data. Currie (1970), in studying oxygen and carbon dioxide diffusion in a partially saturated soil, developed an empirical relation of the form:

$$D^*/D_{air} = a^{4}/\varepsilon^{5/2}$$

where $D^*$, $D_{air}$, and $a$ are as previously defined and $\varepsilon$ is porosity. Many additional empirical relations relating tortuosity to air-filled porosity have been proposed and a summary of their development can be found in Sallam et al. (1984). A disadvantage of these studies is that the structure of the porous media used may not be indicative of porous media in the field. As a result, empirical relations developed in these studies may not be applicable to undisturbed soils containing heterogeneities or a relatively non-uniform particle-size distribution.

Previously developed theoretical relations also may not be applicable in undisturbed soils. Millington (1959) derived a theoretical expression for a wetted homogeneous porous medium:

$$D^*/D_{air} = a^{10/3}/\varepsilon^{2}$$

Extensions of this model have also been developed (Millington and Shearer, 1971; Troeh et al., 1982; Nielson et al., 1984). For example, Millington and Shearer (1971) derived the following expression for gas diffusion in partially saturated, aggregated media:

$$\frac{D}{D_o} = \frac{(1 - S_{WA})^2[A - \theta_A/A + S]^{2n}[1 - P^{2n}] \times [(P - \theta_P) - (P - \theta_P)^{2n}] + (P - \theta_P)^{2n} + (1 - S_{WP})^2(P - \theta_P)^{2n}}{(1 - S_{WA})^2[A - \theta_A/A + S]^{2n}[1 - P^{2n}] + (P - \theta_P) - (P - \theta_P)^{2n} + (1 - S_{WP})^2(P - \theta_P)^{2n}}$$

where $D=$ effective diffusion coefficient; $D_o =$ free air diffusion coefficient; $S_{WA} =$ fractional liquid saturation of the aggregate pore space; $S_{WP} =$ fractional liquid saturation of the inter-aggregate pore space; $P =$ inter-aggregate pore area (pore area within a soil particle); $\theta_A =$ volume of water per unit bed volume in the aggregate pore space; $\theta_P =$ volume of water per unit bed volume in the inter-aggregate pore space.

In general, these relations are more mathematically complex, and require data that are not readily available such as pore-size distributions.

Numerous studies have compared experimentally determined effective diffusion coefficients with Millington’s (1959) expression and other various theoretical models. Karimi et al. (1987) measured the vapor-phase diffusion of benzene through a simulated landfill cover at relatively high values of air-filled porosity and determined that diffusion could be accurately predicted using Millington’s (1959) relation, although no other
theoretical models were examined. Sallam et al. (1984) measured freon diffusion through soils at low values of air-filled porosity and also concluded that the expression developed by Millington (1959) was the best fit to the data, although a minor modification was suggested to improve the fit. Finally, Collin and Rasmuson (1988) compared experimental diffusivity data for a variety of soil types, including both disturbed and undisturbed samples. It was found that the expression developed by Millington and Shearer (1971) produced the best predictions for the effective diffusion coefficients; however, the Millington (1959) expression was not included in the comparison.

In the previously discussed works, various moisture contents were obtained by mechanical mixing of water and soil, and the resulting moisture distributions were homogeneous and potentially different from natural soils (McCarthy and Johnson, 1995). Although Millington’s (1959) equation is generally considered the best predictor of VOC diffusion in heterogeneous soils (McCarthy and Johnson, 1995), many of the previous studies performed compare the model to effective diffusion coefficient data obtained from soils that may not be indicative of natural conditions. In general, a lack of basic diffusion coefficient data for organic chemicals in soil makes diffusion measurements in undisturbed media of prime concern (Fuentes et al., 1991).

In the present study, effective diffusion coefficients were determined for TCE in undisturbed soil cores taken from Picatinny Arsenal, New Jersey. Moisture content was varied to determine the effect of air-filled porosity on the effective diffusion coefficient \(D^*\) in undisturbed soils. The theoretical relation developed by Millington (1959) was modified in an attempt to better describe diffusion through undisturbed soil. Diffusive fluxes calculated in a previous study at the field site (Smith et al., 1996) and fluxes calculated with the data generated by this study are compared.

2. Methods and materials

2.1. Description of field site and sampling techniques

The field site chosen for this research was Picatinny Arsenal located in north central New Jersey. The study area is located in a previously glaciated valley above 50–65 m of stratified and unstratified drift that overlies a weathered bedrock surface. The water table depth varies from 1 to 4 m below land surface (Imbrigiotta and Martin, 1996). Previous studies provide a more detailed geologic description of the site and information on the contamination history (Imbrigiotta and Martin, 1996, Smith et al., 1990, 1992, 1996).

Intact soil cores were taken from Picatinny Arsenal, New Jersey in August 1998, August 1999, and December 1999. Four soil depths (0–0.15, 0.53–0.69, 1.22–1.37, and 2.33–2.49 m from the surface) were sampled to measure the vertical distribution of effective diffusion coefficients in the subsurface. Soil cores were collected in brass core liners 15.24 cm in length and 5.00 cm in diameter (Ben Meadows Co.) using a stainless-steel, split-spoon sampler. Cores removed from the sampler were capped with Teflon end caps (Ben Meadows Co.).
2.2. Experimental apparatus

In the laboratory, cores were stored in the dark at 7 °C to prevent water evaporation. Before use in the experimental apparatus, cores were cut in half and the portion of the soil disturbed by this process (approximately 1–3 cm) was removed from each half of the core. A series of diffusion experiments was run on the halved cores at three different moisture contents: field, field plus a 5-ml addition of distilled, deionized (DI) water, and field plus a 10-ml addition of DI water. The moisture content was varied in each core by gradually adding water onto the top face of the core using a 1-ml autopipet.

Measurement of the effective air diffusion coefficient was made using a steady-state, one-flow technique developed by Batterman et al. (1996). The two major advantages of the one-flow method over the traditional two-flow and reservoir methods are the elimination of pressure gradients that may cause advective flow and the ability to easily manipulate the vapor concentration (Batterman et al., 1996). The high concentration side of the diffusion cell is maintained by a gas flow rate at a constant TCE concentration and the low side is kept near zero by the use of a sorbent (Fig. 1). The method is based on a Fick’s law approach to estimate the diffusive flux through the soil. By setting the Fick’s law expression for the flux equal to the equation for the steady-state mass flux through the soil, $D^*$ is calculated as

$$D^* = \frac{(C_1 - C_2) Q_2 L}{A C_2}$$

where $C_1$ is the inflow TCE concentration (μg/ml), $C_2$ is the outflow TCE concentration (μg/ml), $Q_2$ is the gas flow rate across the top of the column (ml/s), $L$ is the length of the column (cm), and $A$ is the area of the column (cm$^2$).

Fig. 1. Schematic diagram showing the laboratory apparatus. (1) Water/organic vapor trap, (2) mass flow controllers, (3) glass column filled with trichloroethylene and glass beads, (4) glass column filled with DI water and glass beads, (5) soil sample chamber designed for one-flow, sorbent-based technique, and (6) septum for measuring inflow TCE concentration. $C_1$ to $C_3$ denote concentrations and $Q_1$ and $Q_2$ denote air-flow rates. Subscripts 1 and 2 denote the high concentration side of the soil core; subscript 3 denotes the near-zero concentration side of the soil core. Schematic diagram of soil sample chamber is adapted from Batterman et al. (1996).
The soil column used in these experiments consisted of the brass core liner containing the soil sample and two aluminum end caps. The end caps had an internal diameter of 5.0 cm and an internal length of 15.0 cm. Each had three 0.635-cm-diameter Swagelok® ports on its face; two for flushing the chamber space with TCE vapor and one for monitoring the pressure drop along the column with an oil manometer. The pressure drop between the ends of the column was found to be negligible in all experiments. The end caps also had one 0.635-cm-diameter port on the side fitted with a septum. This port was used for measuring vapor concentration in the chamber headspace. Soil columns were oriented in the vertical direction during experimentation, and fine stainless-steel mesh screens were placed on each soil face to support the soil during testing. Approximately 10 g of powdered activated carbon (Aldrich Chemical Co.) was placed in the lower end cap before experimentation, and all ports on this end cap were sealed.

After the end caps were attached to the soil core liner, the soil sample chamber was tested for leaks before every experiment by testing the ability of the chamber to hold a constant pressure. The chamber was then inserted into the experimental apparatus. The entire experimental apparatus was checked for leaks periodically, both by soap bubbles and differential pressure.

TCE vapor was generated by first flowing compressed air through 0.635 cm ID Tygon tubing to a glass column (Omnifit) containing powdered activated carbon and drierite (W.A. Hammond Drierite) to remove water and organic vapors. The flow of clean, dry air was split through two Cole-Palmer 33115- and 33116-series gas mass-flow controllers. One branch of the air flow passed through another gas mass-flow controller operating at 6.4 cm³/min, through a Kontes Chromaflex glass column containing 3-mm glass beads and DI water and then through a similar column containing 3-mm glass beads and liquid TCE (99% purity, Aldrich Chemical Co.). The second branch of air flow passed through another mass-flow controller operating at 12.4 cm³/min and then flowed through a column containing 3-mm glass beads and DI water. The two gas streams were mixed, and flowed across the top of the soil chamber. A sampling port was located just upstream of the soil sample chamber to measure TCE inflow concentration. To minimize interactions between TCE and the apparatus, inert components such as glass tubing, inert plastic column fittings, and stainless-steel Swagelok® fittings (Dibert Valve and Fitting Co.) were used downstream of the TCE column. A schematic of the diffusion apparatus is shown in Fig. 1.

Samples of TCE concentration in the inflow line ($C_1$, see Fig. 1) and the top headspace of the soil sample chamber ($C_2$) were taken by inserting a 25-µl Hamilton Series 700 removable needle syringe (Fisher Scientific Inc.) into a septum port and withdrawing a 10-µl sample. Analysis was performed with a Perkin-Elmer AutoSystem XL gas chromatograph (GC). The gas chromatograph was equipped with a 0.25-ID capillary column, flame ionization detector (FID), and a 1022 integrator.

After TCE flow began across the top of the column, paired inflow and outflow samples were taken every 15 min for the first hour. Standards were run before and after each pair and a blank was run between inflow and outflow pairs. Typical $R^2$ for standard curves were above 0.90. After the first hour, samples were taken approximately once every 2 h over the course of the day. Fig. 2 shows a typical concentration profile for a diffusion
 experiment. TCE concentrations in the inflow and outflow of the column appeared to reach steady state after a few hours. Experiments were allowed to run overnight before final sampling occurred, however, to insure that the experiment had truly reached steady state. All experiments were conducted at atmospheric pressure and at a constant temperature of 22 \( ^\circ\)C. In addition, the validity of the assumption of the activated carbon acting as a perfect sorbent was examined by sampling from a syringe port located in the bottom headspace just above the activated carbon. Samples were taken from this port periodically near the end of the experiment. All samples taken from this port were at a TCE concentration below the detection limits of the GC, indicating that the assumption of a perfect sorbent was valid.

After the series of three experiments were performed on each core, the soil was extruded from the core sleeve and the volumetric moisture content was determined by weighing the soil before and after oven drying for 24 h at 110 \( ^\circ\)C. This determined the volume of water in the core during the last experiment. To determine the moisture content during the two previous experiments, the volume of water added for each experiment (5 ml) was subtracted from the total water volume. This method of back calculating the moisture content before each subsequent addition of water assumes that no water evaporated from the core between or during experiments. This was a reasonable assumption as the cores were capped and stored in the dark at 7 \( ^\circ\)C during equilibration and experiments were conducted at 100% relative humidity.

The specific gravity of each core was determined according to the American Society for Testing and Materials (1979) Standard Test Method for Specific Gravity of Soils (ASTM D854). The specific gravity was used to calculate the volume of soil, a value required for the determination of the porosity of the sample. Sieve analyses were performed to determine the particle-size distributions of the soil cores.

Fig. 2. Plot of the ratio of outflow concentration to inflow concentration over time for surface core C at 17.9% volumetric moisture content. This graph is indicative of the steady-state conditions for all other cores.
3. Results

3.1. Diffusion coefficient measurements

Experiments were performed on seven cores at three moisture contents, and on one core (core 6) at only one moisture content. The experiment performed on core 6 at the field moisture content resulted in a ratio of inflow concentration to outflow concentration of 0.93. Batterman et al. (1996) indicates that the one-flow technique used in this study is valid for an outflow/inflow \((C_2/C_1)\) ratio of 0.70–0.95. Above 0.95, the concentration difference is difficult to measure accurately. No further experiments at greater moisture contents were performed on core 6 because adding moisture to the core would only increase the outflow/inflow ratio. The core characteristics and effective diffusion coefficient measurements for the 22 experiments performed are presented in Table 1.

The moisture content of the cores ranged from 0.012 to 0.26. The measured effective diffusion coefficients ranged from 0.0053 to 0.0609 cm²/s.

Each effective diffusion coefficient reported in Table 1 was the average of three to six replicates \((N)\) taken after the system reached steady state. Effective diffusion coefficients were calculated with Eq. (7) for each paired inflow and outflow concentration. The average and standard error of the effective diffusion coefficients were then determined.

A multiple linear regression was performed to determine if a modification in the exponents of Millington’s (1959) equation would better fit the experimental data. An
equation of the form \( \log y = A \log X_1 + B \log X_2 \) was used where \( y = \) tortuosity, \( X_1 = \) air-filled porosity, and \( X_2 = \) porosity. The regression equation developed from this analysis is:

\[
D^*/D_{\text{air}} = a^{2.5}/e^{1.3}
\]

(8)

The \( R^2 \) for this equation was 0.07 \((n = 22)\). The low value of \( R^2 \) indicates that porosity and air-filled porosity are relatively poor predictors of the effective diffusion coefficient for the undisturbed soil cores.

<table>
<thead>
<tr>
<th>Core</th>
<th>Moisture content</th>
<th>All values in square centimeters per second</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Penman (1940)</td>
<td>Currie (1970)</td>
</tr>
<tr>
<td>1</td>
<td>0.186</td>
<td>0.0325</td>
</tr>
<tr>
<td></td>
<td>0.22</td>
<td>0.0325</td>
</tr>
<tr>
<td></td>
<td>0.26</td>
<td>0.0325</td>
</tr>
<tr>
<td>2</td>
<td>0.145</td>
<td>0.0312</td>
</tr>
<tr>
<td></td>
<td>0.179</td>
<td>0.0312</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>0.0312</td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>0.0203</td>
</tr>
<tr>
<td></td>
<td>0.053</td>
<td>0.0203</td>
</tr>
<tr>
<td></td>
<td>0.089</td>
<td>0.0203</td>
</tr>
<tr>
<td>4</td>
<td>0.012</td>
<td>0.0154</td>
</tr>
<tr>
<td></td>
<td>0.046</td>
<td>0.0154</td>
</tr>
<tr>
<td></td>
<td>0.081</td>
<td>0.0154</td>
</tr>
<tr>
<td>5</td>
<td>0.052</td>
<td>0.0172</td>
</tr>
<tr>
<td></td>
<td>0.075</td>
<td>0.0172</td>
</tr>
<tr>
<td></td>
<td>0.098</td>
<td>0.0172</td>
</tr>
<tr>
<td>6</td>
<td>0.043</td>
<td>0.0162</td>
</tr>
<tr>
<td>7</td>
<td>0.035</td>
<td>0.0168</td>
</tr>
<tr>
<td></td>
<td>0.075</td>
<td>0.0168</td>
</tr>
<tr>
<td></td>
<td>0.116</td>
<td>0.0168</td>
</tr>
<tr>
<td>8</td>
<td>0.019</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>0.046</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>0.072</td>
<td>0.018</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Core 1</th>
<th>Core 2</th>
<th>Core 3</th>
<th>Core 4</th>
<th>Core 5</th>
<th>Core 6</th>
<th>Core 7</th>
<th>Core 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage gravel</td>
<td>0.27</td>
<td>0.57</td>
<td>38.13</td>
<td>38.10</td>
<td>45.90</td>
<td>22.20</td>
<td>12.30</td>
</tr>
<tr>
<td>Percentage coarse to medium sand</td>
<td>48.64</td>
<td>43.29</td>
<td>33.98</td>
<td>38.26</td>
<td>43.10</td>
<td>34.80</td>
<td>57.20</td>
</tr>
<tr>
<td>Percentage fine sand</td>
<td>34.90</td>
<td>35.12</td>
<td>25.92</td>
<td>13.10</td>
<td>16.97</td>
<td>16.80</td>
<td>19.20</td>
</tr>
<tr>
<td>Percentage silt and clay</td>
<td>16.18</td>
<td>21.02</td>
<td>1.97</td>
<td>9.74</td>
<td>1.83</td>
<td>2.50</td>
<td>1.40</td>
</tr>
</tbody>
</table>
3.2. Comparison of relations predicting effective diffusion coefficients

The experimental data are compared to values of $D^*$ predicted by two empirical relations, Currie (1970) and Penman (1940), one theoretical equation, Millington (1959), and the results of the multiple linear regression analysis, as seen in Table 2.

To calculate the effective diffusion coefficient from these relations, $D_{\text{air}}$ at $22 \degree C$ was calculated to be 0.0744 cm$^2$/s, by adjusting the calculation made by Cho and Jaffé (1990) at $25 \degree C$ using $D_T(K) = D_{298}(T/298)^{1.5}$ (Bird et al., 1960).

Particle-size analyses were also performed on each core; results can be seen in Table 3. Coefficients of uniformity calculated for all cores were above 6.0, indicating that all soil samples are poorly sorted.

4. Discussion

In this study, 14 of the 22 measured diffusion coefficients were higher than values predicted by Millington’s (1959) expression. A paired $t$-test with $21 (n - 1)$ degrees of freedom was used to determine if the difference of the mean of the values predicted by Millington’s (1959) relation and the mean of the experimental data was statistically different from zero. An underlying assumption of the paired $t$-test is that the data follow a normal distribution. A Lilliefors test for normality was conducted on the difference of the means and it was determined that the data were normal at the 10% significance level. The $t$-test statistic was calculated to be 2.258. Results of the paired $t$-test indicated that the means of the values predicted by Millington’s (1959) relation were statistically different from the means of the experimental data at the 5% significance level. We attribute this difference to heterogeneities in the soil cores, the relatively non-uniform particle-size distributions of the soil cores, or a combination of both factors.

Several observations lead us to believe that heterogeneities exist in some or all of the intact soil cores. First, visual observations of each end of the soil cores showed that distinctly different particle-size distributions were present at different ends for some of our cores. For example, several cores had primarily gravel-size particles at one end and primarily sand and silt at the other end. Visual analysis of other soil cores taken from the same general location as part of another study also supports the theory that heterogeneities exist in individual cores (Olson et al., submitted for publication). Second, substantial heterogeneities exist in the unsaturated zone at the field site. For example, porosity values among the depths sampled in this study varied by a factor of 2, from 0.31 to 0.66 (Table 1). Air-filled porosity values at the field moisture content also ranged from 0.29 to 0.48 (Table 1). In addition, the data suggest that heterogeneities between core halves are significant. For the 0.53- to 0.69-m sampling depth at field moisture content, the air-filled porosity varied from 0.30 in core 4 to 0.39 in core 3. The porosities between core halves were also significantly different; 0.31 for core 4 and 0.41 for core 3. Effective diffusion coefficients measured at the field moisture content in these cores also provide further evidence that heterogeneities are present. $D^*$ in core 4 was 0.0133 cm$^2$/s, whereas $D^*$ for core 3 was 0.0609 cm$^2$/s. These data do not provide definitive evidence that the soil cores themselves were heterogeneous, but it is likely. This evidence coupled with the visual
observations of each end of the cores makes it reasonable to believe that heterogeneities exist in some or all of the individual soil cores themselves.

Heterogeneities may have multiple effects on the effective diffusion coefficient. Heterogeneities may increase the effective diffusion coefficient due to the existence of macropores caused by dessication, plant roots, or worm holes. Heterogeneities can also limit diffusion by layering. For example, a layer with a low diffusion coefficient located between two layers with high diffusion coefficients will result in a relatively low composite diffusion coefficient.

In addition, the particle-size distributions presented in Table 3 suggest that the soil cores analyzed in this study have a relatively non-uniform pore-size distribution, which may in turn affect the tortuosity. We effectively measure an average (macroscopic) tortuosity for our soil cores because we cannot quantify individual molecular path lengths of diffusing molecules. If the range of microscopic tortuosity values is increased by broadening the distribution of pore sizes in a soil core (even though the overall porosity and moisture content do not change), it is possible that the average (macroscopic) tortuosity will change. To our knowledge, this phenomenon has not been investigated previously. Although our experiments were not designed to specifically test this hypothesis, we offer this as a possible explanation as to why our effective diffusion coefficients often differ significantly from those predicted by the Millington (1959) relation.

Several experimental studies have compared measured diffusion coefficients to Millington’s (1959) relation, and for the most part, these studies have shown that the theoretical relation is a good predictor of the measured effective diffusion coefficient. However, these studies have used homogeneous soil specimens with relatively narrow particle-size distributions. For example, Karimi et al. (1987) found Millington’s (1959) relation to adequately predict effective diffusion coefficients for benzene in a landfill cover soil consisting of 54% clay and 46% silt and fine sands. The soil was sieved to a particle size of 2 mm and thoroughly mixed before use. Similarly, Sallam et al. (1984) found Millington’s (1959) expression to be a good predictor of effective diffusion coefficients in a Yolo silt loam, which was sieved to 2 mm and mixed with water to adjust the moisture content. The soil was packed uniformly into the diffusion cell before experimentation. In one study by Fuentes et al. (1991) that measured effective diffusion coefficients in undisturbed soil, differences between the measured effective diffusion coefficient and the values predicted using Millington’s (1959) relation were observed, although no conclusions were drawn to explain this result. This observation supports our assertion that heterogeneities and/or relatively non-uniform particle-size distributions can lead to significant differences between measured and predicted values.

4.1. Analysis of predictive models

Although the $R^2$ for the regression equation developed in this study was only 0.07, it is still a better fit to the data than the literature relations to which it was compared. The poor correlation for the regression equation indicates that there is no strong relation between air-filled porosity, porosity and $D^*$ for the undisturbed cores. This suggests that another factor is controlling the magnitude of the effective diffusion coefficient for these cores, perhaps one related to the soil heterogeneity or particle-size distribution.
An analysis was performed to determine if the addition of another variable, \( d_{10} \), would improve the fit of the regression equation developed in this study. This parameter is defined as the grain diameter at which 10% of the soil sample is finer by weight. It was thought that samples with a larger number of fine grains (smaller \( d_{10} \)) might have a smaller effective air diffusion coefficient, resulting in a smaller tortuosity. A plot of tortuosity versus \( d_{10} \) for all 22 data points did not show a strong relation, and a linear regression fit to the data had an \( R^2 \) of 0.0002 (\( n = 22 \)). A multiple linear regression was also performed using an equation of the same form as before: \( \log y = a \log X_1 + b \log X_2 + c \log X_3 \), with \( X_3 = d_{10} \) and the other variables as previously defined. It was found that the addition of the third parameter, \( d_{10} \), did not significantly improve the fit over the two-parameter regression model.

4.2. Calculation of diffusive fluxes at Picatinny Arsenal, New Jersey

In 1996, Smith et al. measured natural TCE vapor fluxes out of the subsurface at Picatinny Arsenal, New Jersey, using a vertical flux chamber. The diffusive flux component was then calculated by Fick’s law using TCE vapor concentration gradients measured at the site. A comparison of total flux to diffusive flux indicated that the diffusive flux alone did not account for the total TCE flux measured with the vertical flux chamber. The authors concluded that other mechanisms, such as advective transport, were contributing to TCE vapor transport from the subsurface to the atmosphere (Smith et al., 1996).

In calculating the diffusive flux, the authors made the assumption that the unsaturated zone had uniform properties. Porosity was assumed to be 0.30, and an average moisture content of 0.20 was determined from moisture content data taken at depth. From these values, an air-filled porosity of 0.10 was calculated. A single effective diffusion coefficient was calculated for the entire subsurface by substituting these values into the relation developed by Currie (1970). The diffusive flux was then determined by multiplying the effective diffusion coefficient by the concentration gradient measured in the unsaturated zone at the field site.

Based on the results of the current study, Currie’s (1970) relation may not provide the most accurate estimate for the effective diffusion coefficient at this site. To determine the effect of the relation used to predict effective diffusion coefficients on the magnitude of the diffusive flux, calculations of the diffusive flux were made as described above, only using the other relations described in this work [Millington (1959), Penman (1940), and the linear regression developed in the present work]. Results may be seen in Table 4.

This analysis indicates that the calculated diffusive fluxes are very sensitive to the relation used to estimate the diffusion coefficient. Diffusive fluxes calculated as in Smith et al. (1996) vary by more than an order of magnitude depending on the relation used. Both Currie’s (1970) and Millington’s (1959) equation predicted the lowest diffusive fluxes. The relation developed by Penman (1940) gives the highest diffusive flux of all the relations used.

The porosities measured for the cores analyzed in this study vary with depth, indicating that the assumption made by Smith et al. (1996) of a uniform porosity of 0.30 may not accurately describe the subsurface conditions at the field site. To provide a more accurate
estimate of diffusive flux at the field site, the subsurface was characterized as consisting of four layers, each having a uniform porosity. An effective diffusion coefficient was calculated for each layer using the porosity for that layer, and a moisture content of 0.20. This moisture content was chosen to be consistent with Smith et al. (1996). The effective diffusion coefficients in each layer were combined into a composite diffusion coefficient using the following equation:

$$D^*_{\text{ave}} = \frac{b}{\sum_{m=1}^{n} \frac{b_m}{D^*_m}}$$

where $D^*_{\text{ave}}$ is the composite effective diffusion coefficient (cm$^2$/s), $D^*_m$ is the effective diffusion coefficient for the $m$th layer (cm$^2$/s), $b_m$ is the thickness of the $m$th layer (m), and $b$ is the total thickness (m). This equation is analogous to the equation developed for composite vertical hydraulic conductivity in layered media (Fetter, 1994). As before, calculations of effective diffusion coefficients were made using the relations developed by Millington (1959), Currie (1970), Penman (1940), and the results of the multiple linear regression analysis from the present work. Results of this analysis can be seen in Table 5.

Analysis of these data show that the composite method for calculating a diffusion coefficient for the unsaturated zone resulted in larger diffusive fluxes than when a single value for the diffusion coefficient is used for the entire unsaturated zone. This indicates that the method of subsurface characterization used in the Smith et al. (1996) study underpredicted diffusive fluxes through the soil. The calculated diffusive fluxes were much larger when a composite diffusion coefficient was used because the measured porosity values were larger than the estimated porosity of 0.30 used by Smith et al. (1996) at most depths. A comparison between the total fluxes measured by the vertical flux chamber in the Smith et al. (1996) study and the recalculated diffusive fluxes suggests that although the diffusive fluxes
calculated in the present study may not account for the entire flux measured out of the subsurface, advective fluxes caused by atmospheric pressure gradients may be less important than previously thought. In some cases, the recalculated diffusion flux is larger than the total flux. This observation may be explained by downward TCE vapor advection during a period of increasing atmospheric pressure.

5. Conclusions

The results of this study indicate that although the commonly used literature relations do an adequate job of predicting effective diffusion coefficients through homogeneous soils or soils with a narrower particle-size distribution such as sands, they may not adequately predict effective diffusion coefficients for undisturbed soils. Millington’s (1959) equation, long accepted as the best predictor of diffusion through natural soils (McCarthy and Johnson, 1995), underpredicted the experimental data in this study by as much as 70%. The results of a linear regression model produced a weak correlation between the effective diffusion coefficient and the air-filled porosity and porosity of the soil, indicating that effective diffusion coefficients in undisturbed media may be controlled by another parameter. Unfortunately, information providing insight into the governing factor was not collected in this study leading to a need for further experimentation.

The effective diffusion coefficient and porosity data collected in this study were then used to recalculate estimates of diffusive flux made in a previous study at the field site (Smith et al., 1996). It was determined that the method used to make the calculations of diffusive flux may have resulted in an underprediction of diffusive flux from the subsurface.

Table 5
Comparison of trichloroethene diffusion fluxes from the unsaturated zone to the atmosphere at Picatinny Arsenal, USA

<table>
<thead>
<tr>
<th>Date</th>
<th>Smith et al. (1996)</th>
<th>Millington (1959)</th>
<th>Penman (1940)</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/23/93</td>
<td>2.18</td>
<td>3.38</td>
<td>22.73</td>
<td>5.78</td>
</tr>
<tr>
<td>8/24/93</td>
<td>7.89</td>
<td>12.19</td>
<td>82.07</td>
<td>20.8</td>
</tr>
<tr>
<td>10/7/93</td>
<td>2.61</td>
<td>4.03</td>
<td>27.15</td>
<td>6.9</td>
</tr>
<tr>
<td>10/8/93</td>
<td>1.7</td>
<td>2.63</td>
<td>17.68</td>
<td>4.94</td>
</tr>
<tr>
<td>4/14/94</td>
<td>0.26</td>
<td>0.41</td>
<td>2.74</td>
<td>0.69</td>
</tr>
<tr>
<td>6/9/94</td>
<td>0.22</td>
<td>0.34</td>
<td>2.27</td>
<td>0.58</td>
</tr>
<tr>
<td>6/10/94</td>
<td>0.33</td>
<td>0.52</td>
<td>3.47</td>
<td>0.88</td>
</tr>
<tr>
<td>7/21/94</td>
<td>0.97</td>
<td>1.5</td>
<td>10.1</td>
<td>2.57</td>
</tr>
</tbody>
</table>

Effective diffusion coefficients used to calculate the fluxes were determined by the indicated relation (e.g. Currie, Millington, etc.) and field data from Smith et al. (1996). The unsaturated zone was divided into four layers for this comparison.

* Uses the relation of Currie (1970) to calculate effective diffusion coefficients.
Acknowledgements

The authors acknowledge J. Dante for assisting in the collection of laboratory data. This research has been supported (in part) by a grant from the U.S. Environmental Protection Agency’s Science to Achieve Results (STAR) program. Although the research described in the article has been funded wholly or in part by the U.S. Environmental Protection Agency’s STAR program through Grant R826162, it has not been subjected to any EPA review and therefore does not necessarily reflect the views of the agency, and no official endorsement should be inferred. Additional support for S.L. Bartelt-Hunt was provided by the Department of Defense Graduate Research Fellowship program.

References


