Modeling Volatile Organic Compound Transport in Composite Liners

Min-Gyun Park¹; Tuncer B. Edil, F.ASCE²; and Craig H. Benson, F.ASCE³

Abstract: Data from bench-scale composite liner experiments were compared with predictions made with two models, a finite-difference model and a semianalytical model, used to predict volatile organic compound (VOC) transport through composite liners. Transport parameters for the geomembrane and clay for five common VOCs were measured independently and used as input. Predictions from both models for all five VOCs were essentially identical. Excellent agreement was obtained between the predicted and measured concentrations for all five VOCs without model calibration. However, inherent variability in measured transport parameters has a significant effect on predictions. Volatile organic compound concentrations in the clay liner near the geomembrane-clay interface depend primarily on transport parameters for the geomembrane. However, this becomes less significant as the distance from the geomembrane-clay interface increases. DOI: 10.1061/(ASCE)GT.1943-5606.0000630. © 2012 American Society of Civil Engineers.

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Introduction

Composite liners consisting of a geomembrane overlying a clay liner are often required as bottom liners for waste containment systems. Field data indicate that composite liners are excellent hydraulic barriers (Bonaparte et al. 2002). However, theoretical studies and field data suggest that volatile organic compound (VOC) transport in composite liners can be significant (Edil 2003; Klett et al. 2005). Thus, being able to predict VOC transport in composite liners is essential when evaluating how a waste containment system may affect groundwater.

Volatile organic compound transport through compacted clay liners is well understood and VOC transport models for clay liners have been developed and validated (Barone et al. 1992; Edil et al. 1994, 1995; Kim et al. 2001; Rowe et al. 2004). In contrast, models for VOC transport through composite liners have received limited validation (Sangam and Rowe 2001b; Foose et al. 2002). Two models for composite liners were evaluated in this study: a finite-difference model by Foose et al. (2002) and a semianalytical model by Rowe et al. (2004). Both models are on the basis of the same transport theory and have been verified (Foose et al. 2002; Rowe et al. 1983). However, neither model has received extensive independent validation with experimental data. Model validation is defined in this paper as the process of demonstrating that a model is capable of making predictions consistent with measurements from a physical model or actual system (Oreskes et al. 1994; Refsgaard 1997). Cleall and Li (2011) developed an analytical solution for diffusion of VOCs through composite liners. The analytical solution yielded essentially the same predictions with the finite-difference model developed by Foose et al. (2002). Thus, their solution was not evaluated in this study.

In this study, predictions from both models were compared with data from bench-scale experiments simulating a composite liner consisting of a high-density polyethylene (HDPE) geomembrane overlying a compacted clay layer. A solution containing five common VOCs ranging in hydrophobicity was used as the source of VOCs. Transport parameters for the VOCs in the geomembrane and compacted clay were obtained from independent tests and used as input to the models. The effect of uncertainty in inputs and the effect of each transport parameter on the concentration profile were analyzed.

Background

Transport Theory

Modeling studies have shown that the total mass flux of VOCs from a well-constructed composite liner can be four to six orders of magnitude greater than the advective flux associated with flow through defects in the geomembrane (Foose et al. 2002). This difference between total and advective fluxes is because of diffusion and indicates that diffusive transport is the dominant mode of contaminant transport in composite liners (Park et al. 1996; Foose et al. 2002). Diffusion of VOCs occurs over the entire surface of a composite liner. Thus, mass transport generally is assumed to be one dimensional.

One-dimensional transport of VOCs through an intact composite liner can be described by a four-step process (Fig. 1): (1) partitioning between the leachate and geomembrane, (2) diffusion through the geomembrane, (3) partitioning between the geomembrane and the soil pore water at the down gradient surface of
the geomembrane, and (4) diffusion through the soil liner (Park and Nibras 1993; Park et al. 1996; Müller et al. 1998; Foose et al. 2001).

At the relatively low VOC concentrations encountered in modern landfill leachates, sorption in geomembranes and clays follows a linear isotherm and can be assumed to be instantaneous and reversible (Park and Nibras 1993; Joo et al. 2004; Nefso and Burns 2007; Park et al. 2012). The partition coefficient between the organic compound dissolved in water and the geomembrane, $K_g$, is defined as (Leo et al. 1971)

$$K_g = \frac{C_g}{C_w} \left(1 + \frac{1}{K_g}\right)$$

where $C_g$ = equilibrium concentration of organic compound in HDPE geomembrane ($M/L^3$); $C_w$ = equilibrium concentration of organic compound in water ($M/L^3$); and $K_g$ = dimensionless geomembrane-water partition coefficient of the organic compound.

The organic compound sorbed at the surface diffuses through the geomembrane in accordance with Fick's law (Park and Nibras 1993; Park et al. 1996; Sangam and Rowe 2001b; Joo et al. 2004, 2005). For a spatially and temporally invariant diffusion coefficient, the governing equation for one-dimensional diffusion within a geomembrane is

$$\frac{\partial C_g}{\partial t} = D_g \frac{\partial^2 C_g}{\partial z^2} , \quad -L_g < z < 0$$

where $t$ = elapsed time ($T$); $D_g$ = diffusion coefficient of the organic compound in the geomembrane ($L^2/T$); $z$ = distance along the direction of diffusion ($L$); and $L_g$ = thickness of the geomembrane ($L$) (Park and Nibras 1993; Park et al. 1996; Sangam and Rowe 2001b; Joo et al. 2004, 2005). In Eq. (2), the interface between the geomembrane and the clay liner is at $z = 0$, where $z$ is positive in the primary direction of contaminant transport.

Continuity of concentration at the interface between the geomembrane and the soil liner is described by Foose et al. (2002):

$$\frac{C_g}{K_g} \bigg|_{z=0^-} = C_s \bigg|_{z=0^+} , \quad z = 0$$

where $C_s$ = concentration of the organic compound in the pore water of the soil liner ($M/L^3$). Conservation of contaminant mass is described using Fick's first law (Foose et al. 2002):

$$J_d = -D_g \frac{\partial C_g}{\partial z} \bigg|_{z=0^-} = -nD_s \frac{\partial C_s}{\partial z} \bigg|_{z=0^+} , \quad z = 0$$

where $J_d$ = mass flux via diffusion ($M/L^2 T$); $n$ = total porosity of the soil liner; and $D_s$ = the effective diffusion coefficient in the clay liner ($L^2/T$), which is defined as

$$D_s = D_0 \tau_a$$

In Eq. (5), $D_0$ = molecular diffusion coefficient in free solution ($L^2/T$); and $\tau_a$ = apparent tortuosity (Gillham et al. 1984; Shackelford and Daniel 1991).

The VOC then diffuses downward through the clay liner in accordance with the following one-dimensional diffusion equation (Hashimoto et al. 1964; Freeze and Cherry 1979):

$$\frac{\partial C_s}{\partial t} = \frac{D^*}{R} \frac{\partial^2 C_s}{\partial z^2} , \quad 0 < z < L_s$$

In Eq. (6), $L_s$ = thickness of the clay liner ($L$); and $R$ = the retardation factor (dimensionless)
\[ R = 1 + \left( \frac{\rho_d K_d}{n} \right) \]  

(7)

where \( \rho_d \) = dry density of the soil \((M/L^3)\); and \( K_d \) = solid-water partition coefficient \((L^3/M)\)

\[ K_d = \frac{C_s}{C_j} \]  

(8)

In Eq. (8), \( C_s \) = equilibrium concentration in the liquid phase \((M/L^3)\); and \( C_{js} \) = concentration sorbed to the solid \((M/M)\). Eqs. (2) and (6) implicitly assume that the solute is not decaying or degrading during diffusion. In addition, sorption in the clay liner is assumed to be linear, instantaneous, and reversible.

Previous Composite Liner Experiments

Sangam and Rowe (2001b) investigated the relative importance of sorption and diffusion processes in the geomembrane and clay components by conducting bench-scale tests on a compacted clay barrier (30-mm thick) and a composite barrier (2.0-mm HDPE geomembrane overlying 30 mm of compacted clay) using methylene chloride (MC) and trichloroethylene (TCE) for solutes. Tests were conducted in columns 70 mm in diameter. The VOC concentration in the influent reservoir decreased at a faster rate for the composite liner than for the compacted clay liner alone, but the concentration in the effluent reservoir of the composite liner test increased at a much slower rate than in the clay liner test. Sangam and Rowe (2001b) attributed this difference to VOC sorption in the geomembrane. Presence of the HDPE geomembrane reduced the mass flux of methylene chloride by a factor of 5 and the mass flux of TCE to undetectable levels throughout the 150-day test period.

Transport Models

Eqs. (1)–(8) have been incorporated into three models used to simulate VOC transport through composite liners: the finite-difference model developed by Foose et al. (2002), the semianalytical model originally developed by Rowe et al. (1983), and the analytical model by Cleall and Li (2011). The models by Foose et al. (2002) and Rowe et al. (1983) were used in this study.

The finite-difference model developed by Foose et al. (2002) is a one-dimensional model for analyzing transport of VOCs through intact composite liners consisting of contiguous layers of finite thickness. This finite-difference model was implemented in a
Organic matter content (%) ASTM D2974 (2007e) 2.33

Water content (%)

Reduced proctor optimum (

ties of Kamm clay are summarized in Table 1. Kamm clay classifies as CL in the Unified Soil Classification System (ASTM 2011). X-ray diffraction (ASTM 2008a) indicated that Kamm clay is composed of 52% quartz, 16% plagioclase, 15% smectite, 7% potassium feldspar, and 6% illite and mica (Table 1).

Kamm clay has an organic carbon content of 0.46%, as determined by dry combustion using a Leco CNS-2000 analyzer (Nelson and Sommers 1996), and an organic matter content of 2.33%, as determined by loss on ignition (ASTM 2007e). The saturated hydraulic conductivity of Kamm clay is \( 5.5 \times 10^{-9} \) cm/s at optimum water content for standard Proctor compaction and \( 1.7 \times 10^{-8} \) cm/s at optimum water content for reduced Proctor compaction, as determined by ASTM D5856 (ASTM 2007d; Park 2010).

The clay was crushed and ground past the number four sieve (mesh opening 4.75 mm) and thoroughly mixed with tap water to achieve a water content of 22%, which is 2% wet of optimum for reduced Proctor compaction effort. A reduced compaction effort was used because of the very low hydraulic conductivity obtained for standard Proctor compaction. Higher hydraulic conductivity was preferable to ensure saturation could be obtained within a reasonable time before diffusion testing. The hydrated clay was placed in a sealed plastic bag and allowed to equilibrate for 24 h before compaction. The moist clay was compacted in three equal layers. Each layer was compacted uniformly by applying 35 blows using the standard Proctor hammer (dry density = 1.7 Mg/m³).

After the clay was placed, the clay was overlain by a glass fiber filter and a layer of lead beads 15-mm thick. The beads applied a stress of 0.6 kPa to reduce swelling. The specimen was then saturated by permeation using a 0.05% sodium azide solution. Permeation continued until the hydraulic conductivity was steady and the ratio of outflow to inflow was between 0.75 and 1.25. Sodium azide solution was used for permeation to reduce microbial activity in the clay.

### Geomembrane

After saturation was completed, water in the upper reservoir was drained, the lead beads and glass fiber filter on top of the soil were removed, and a geomembrane chamber was installed (Fig. 2). Smooth geomembrane was used for the lip and side wall of the chamber for more effective sealing. Textured geomembrane was used for the bottom of the chamber that is in contact with the clay.

The textured geomembrane was 1.5-mm-thick black high-density polyethylene geomembrane (textured HDPE geomembrane 1.50 mm, Polyflex, Inc., Grand Prairie, TX). Properties of the geomembrane are presented in Table 2. This geomembrane meets the geomembrane requirements in Wisconsin for municipal solid waste disposal.

### Table 1. Properties of Kamm Clay

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>Kamm clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>ASTM D854 (2010f)</td>
<td>2.72</td>
</tr>
<tr>
<td>Liquid limit</td>
<td>ASTM D4318 (2010c)</td>
<td>48</td>
</tr>
<tr>
<td>Plasticity index</td>
<td>ASTM D4318 (2010c)</td>
<td>27</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>ASTM D422 (2007g)</td>
<td>96</td>
</tr>
<tr>
<td>Percent finer (0.075 mm) (%)</td>
<td>ASTM D934 (2008a)</td>
<td>41</td>
</tr>
<tr>
<td>Soil classification</td>
<td>ASTM D2487 (2011)</td>
<td>CL</td>
</tr>
<tr>
<td>Mineralogy (%)</td>
<td>ASTM D934 (2008a)</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td></td>
<td>51.6</td>
</tr>
<tr>
<td>Plagioclase</td>
<td></td>
<td>15.5</td>
</tr>
<tr>
<td>Smectite</td>
<td></td>
<td>15.4</td>
</tr>
<tr>
<td>K-feldspar</td>
<td></td>
<td>7.3</td>
</tr>
<tr>
<td>Illite and mica</td>
<td></td>
<td>5.8</td>
</tr>
<tr>
<td>Dolomite</td>
<td></td>
<td>2.6</td>
</tr>
<tr>
<td>Kaolinite</td>
<td></td>
<td>1.6</td>
</tr>
<tr>
<td>Chlorite</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>Organic carbon content (%)</td>
<td>Dry combustion(^a)</td>
<td>0.46</td>
</tr>
<tr>
<td>Organic matter content (%)</td>
<td>ASTM D2974 (2007e)</td>
<td>2.33</td>
</tr>
<tr>
<td>Standard proctor maximum dry unit weight (kN/m(^3))</td>
<td>ASTM D698 (2007c)</td>
<td>17.4</td>
</tr>
<tr>
<td>Standard proctor optimum water content (%)</td>
<td>ASTM D698 (2007c)</td>
<td>18.3</td>
</tr>
<tr>
<td>Reduced proctor maximum dry unit weight (kN/m(^3))</td>
<td>-</td>
<td>16.7</td>
</tr>
<tr>
<td>Reduced proctor optimum water content (%)</td>
<td>-</td>
<td>20.0</td>
</tr>
</tbody>
</table>

\(^a\)Nelson and Sommers (1996).

### Table 2. Properties of HDPE Geomembrane

<table>
<thead>
<tr>
<th>Property</th>
<th>Test method</th>
<th>Unit</th>
<th>Test result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum thickness</td>
<td>ASTM D5994 (2010c)</td>
<td>mm</td>
<td>1.425</td>
</tr>
<tr>
<td>Asperity height</td>
<td>ASTM D7466 (2010d)</td>
<td>mm</td>
<td>0.250</td>
</tr>
<tr>
<td>Sheet density</td>
<td>ASTM D1505 (2010a); D792 (2008b)</td>
<td>g/mL</td>
<td>0.940</td>
</tr>
<tr>
<td>Tensile properties</td>
<td>ASTM D6693 (2010b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yield stress</td>
<td>kN/m</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Break stress</td>
<td>kN/m</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Yield strain</td>
<td>percent</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Break strain</td>
<td>percent</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>Tear resistance</td>
<td>ASTM D1004 (2009a)</td>
<td>N</td>
<td>187</td>
</tr>
<tr>
<td>Puncture resistance</td>
<td>ASTM D4833 (2007b)</td>
<td>N</td>
<td>400</td>
</tr>
<tr>
<td>Stress crack resistance</td>
<td>ASTM D 5397 (2007a)</td>
<td>h</td>
<td>300</td>
</tr>
<tr>
<td>Carbon black content</td>
<td>ASTM D1603 (2006)</td>
<td>percent</td>
<td>2–3</td>
</tr>
<tr>
<td>Carbon black distribution</td>
<td>ASTM D5596 (2009b)</td>
<td>Category</td>
<td>1–2</td>
</tr>
<tr>
<td>Oxidation induction time</td>
<td>ASTM D3895 (2007f)</td>
<td>min</td>
<td>&gt; 100</td>
</tr>
</tbody>
</table>
landfills (Dept. of Natural Resources 2007) and can be considered a typical HDPE geomembrane used for landfill liners in North America.

Each geomembrane chamber was custom manufactured to fit tightly in the test cell. All geomembrane chambers were leak tested with deionized (DI) water before use and washed with DI water before installation. Lead beads were placed in the geomembrane chamber to maintain good contact between the geomembrane and the clay.

**Sampling Ports**

Sampling ports were installed in the test cell as shown in Fig. 2. The lower sampling port in the clay barrier was installed after compacting the first layer of the clay. The upper sampling port in the clay was installed after compacting the second layer. Moist clay was carefully placed around the sampling port to prevent any gaps between the sampling port and clay liner.

The ports were designed to collect liquid from the central axis of the clay barrier. A glass fiber filter was packed inside the sampling port to filter soil particles. Two septa were used to eliminate leakage during sampling. Analyses conducted with the variably saturated flow and transport code HYDRUS (Hydrus-2D 2.0) showed that flow and transport within the clay would be minimally disrupted by biweekly sampling if the sample volume was less than 50 μL (Park 2010). Functionality of the sampling ports was verified by conducting preliminary tests using sodium chloride and a saturated sandy soil. Breakthrough of the salt occurred as anticipated on the basis of theory, and no leakage was detected at the sampling port (Park 2010).

**VOC Solution**

A solution composed of MC, methyl tertiary butyl ether (MTBE), trichloroethylene (TCE), toluene (TOL), and chlorobenzene (CB) was used. These VOCs represent five major classes, alkanes, ethers, alkenes, aromatic hydrocarbons, and halogenated aromatic hydrocarbons, and are among 31 VOCs that were frequently detected in alkenes, aromatic hydrocarbons, and halogenated aromatic hydrocarbons. VOCs represent five major classes, alkanes, ethers, alkenes, aromatic hydrocarbons, and halogenated aromatic hydrocarbons, and are among 31 VOCs that were frequently detected in alkenes, aromatic hydrocarbons, and halogenated aromatic hydrocarbons.

Among the detected VOCs, methylene chloride had the largest percentage (85%) of samples exceeding Wisconsin groundwater enforcement standards (ESs). Toluene had 5.2% of the samples exceeding the ES and MTBE had 3.6%. Despite frequent detection, chlorobenzene did not have any samples exceeding the ES.

Properties of the selected compounds are listed in Table 3. These compounds represent a wide range of aqueous solubility, vapor pressure (volatility), and density, including densities smaller and larger than water (Howard et al. 1991; Yaws 1995). Methylene chloride, TCE, and toluene were also used in transport studies reported by Park and Nibras (1993); Edil et al. (1995); Park et al. (1996); Kim et al. (2001); Sangam and Rowe (2001a); and Joo et al. (2004, 2005). Methylene chloride, TCE, toluene, and chlorobenzene were obtained from Sigma-Aldrich (Milwaukee, WI) and had purity ≥ 99.5%. Methyl tertiary butyl ether was obtained from Acros Organics (Morris Plains, NJ) and had a purity of 99%

**Table 4. Transport Parameters Measured for HDPE Geomembrane**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Partition coefficient ($K_p$ $m^2$/s)</th>
<th>Diffusion coefficient ($D_p$ $× 10^{13}$) $m^2$/s$^2$</th>
<th>Permeation coefficient ($P_p = K_pD_p$) $m^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>2.13 ± 0.59</td>
<td>8.86 ± 2.66</td>
<td>1.89 $× 10^{-12}$</td>
</tr>
<tr>
<td>MTBE</td>
<td>0.57 ± 0.16</td>
<td>7.74 ± 2.36</td>
<td>4.41 $× 10^{-13}$</td>
</tr>
<tr>
<td>TCE</td>
<td>63.24 ± 16.48</td>
<td>5.45 ± 1.52</td>
<td>3.45 $× 10^{-11}$</td>
</tr>
<tr>
<td>Toluene</td>
<td>86.74 ± 22.68</td>
<td>3.77 ± 1.06</td>
<td>3.27 $× 10^{-11}$</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>108.94 ± 25.80</td>
<td>3.96 ± 0.99</td>
<td>4.31 $× 10^{-11}$</td>
</tr>
</tbody>
</table>

*Note: MC: Methylene chloride, MTBE: Methyl Tertiary Butyl Ether, TCE: Trichloroethylene, TOL: Toluene, CB: Chlorobenzene.

aVerschueren (1977).

bOctanol-water partition coefficient.

bVerschueren (1977).
Volatile organic compound solutions were prepared by filling a 1-L flask with distilled and deionized (DDI) water spiked with sodium azide (0.05%) to prevent microbial activity. Once filled, the desired concentration of VOC was prepared on the basis of weight-volume calculations. A 100-μL gas tight syringe was used to introduce liquid VOC into the water. When using multiple solutes, the compounds were injected in order of decreasing density, i.e., TCE, methylene chloride, chlorobenzene, MTBE, and toluene; however, MTBE was injected before toluene because MTBE dissolves quickly in water because of its extremely high solubility. The flask was completely filled to minimize loss of VOCs in the headspace. The flasks were immediately covered with a glass stopper, sealed with Teflon tape, and placed on a magnetic stir plate for 24 h before use. For all the bench-scale composite liner experiments, the initial concentration for all five VOCs was 100 mg/L.

The VOC solution was introduced into the upper reservoir through a Teflon influent bag. Once the upper reservoir was filled, the valve connected to the influent bag was closed. The upper reservoir was flushed periodically with fresh VOC solution to maintain a relatively constant VOC concentration in the liquid above the geomembrane. The valve connected to the effluent bag was opened during sampling to equilibrate the pressure in the column. Samples (50 μL) were collected weekly from the influent reservoir and biweekly from the sampling ports in the soil using 100-μL microsyringes.

Fig. 4. Sorption isotherm of VOCs to Kamm clay: (a) methylene chloride; (b) MTBE; (c) TCE; (d) toluene; (e) chlorobenzene
Table 5. Solid-Water Partition Coefficients for Kamm Clay

<table>
<thead>
<tr>
<th>Compound</th>
<th>Soil solid-water partition coefficient (L/kg)</th>
<th>P-value (ANCOVA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{d,single}$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>0.075 ± 0.024</td>
<td>0.58</td>
</tr>
<tr>
<td>MTBE</td>
<td>0.053 ± 0.015</td>
<td>0.64</td>
</tr>
<tr>
<td>TCE</td>
<td>0.175 ± 0.062</td>
<td>0.90</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.136 ± 0.038</td>
<td>0.94</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.192 ± 0.049</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Note: ANCOVA = analysis of covariance.

Average ± standard deviation.

Fig. 5. Concentration versus time at sampling port (depth = 60 mm) for compacted clay liner diffusion tests: (a) methylene chloride; (b) MTBE; (c) TCE; (d) toluene; (e) chlorobenzene; smooth curve represents least-squares fit to Eq. (6).


**VOC Analytical Methods**

Volatile organic compound concentrations were measured using a Shimadzu GC-2010 gas chromatograph (GC) equipped with an autosampler, flame ionization detector (FID), and Restek RTX-624 column (length = 30 m, inner diameter = 0.32 mm, and film thickness = 1.80 μm). Temperatures of the injection port and the FID were set at 280°C. Aqueous samples were injected through the injection port. The sample split ratio was 3.0, and the injection volume was 0.5 μL. The column had an initial column temperature of 35°C and held time of 5 min. The column was then heated to 100°C at a rate of 10°C/min, held at 100°C for 3 min, heated to 220°C at a rate of 40°C/min, and held at 220°C. The total run time for each injection was 20 min. The detection limit was 0.20 mg/L for methylene chloride, 0.47 mg/L for MTBE, 0.13 mg/L for TCE, 0.12 mg/L for toluene, and 0.09 mg/L for chlorobenzene.

**Validation Approach**

**Model Setup**

Both models were used to simulate the composite liner used in the composite liner experiments (Fig. 2): a 1.5-mm-thick geomembrane on top of a 120-mm-thick compacted clay barrier. For the finite-difference model, the time step was set at 0.5 h, and the nodal spacing was set at 0.15 mm for the geomembrane and 2.0 mm for the clay liner. The Darcy velocity was set at 0 to simulate an intact geomembrane. The dry density (1.7 Mg/m³) and porosity (0.38) of the clay liner were computed using weight-volume relationships and data from Table 1.

The top boundary was set as a constant concentration boundary using the average upper reservoir concentration as input or a time variable concentration boundary in which the measured concentrations in the upper reservoir were used as input. The bottom boundary was set as a no flux boundary. The initial condition was zero concentration throughout the profile. Predicted concentrations from model simulations using constant and temporally variable concentration at the top boundary differed by less than 0.1%. Thus, predictions obtained using the constant concentration boundary are presented henceforth.

**Model Input Parameters**

**Partition and Diffusion Coefficients for Geomembrane**

Partition coefficients and diffusion coefficients used as inputs to the models for the geomembrane were measured independently using kinetic batch tests. Comparative analyses described in Park et al. (2012) show that the kinetic batch test is a reliable and expedient method to measure the partition coefficient and diffusion coefficient for VOCs in geomembranes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Effective diffusion coefficient ($D' \times 10^{10}$) (m²/s)</th>
<th>Apparent tortuosity ($\tau_a$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene chloride</td>
<td>1.53 ± 0.13</td>
<td>0.13 ± 0.01</td>
</tr>
<tr>
<td>MTBE</td>
<td>1.18 ± 0.05</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td>TCE</td>
<td>1.39 ± 0.13</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.17 ± 0.12</td>
<td>0.13 ± 0.01</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>1.29 ± 0.12</td>
<td>0.16 ± 0.01</td>
</tr>
</tbody>
</table>

*Average ± standard deviation.

Specimens of geomembrane were cut into strips (17 × 80 mm) from a large HDPE geomembrane sheet, washed with DDI water, and placed in a desiccator for 48 h before use in the experiments. A single strip of geomembrane (2.2 g) was placed in an amber glass vial (40 mL) and solution was added to fill the vial. The vial was then sealed with a screw cap and Teflon-coated septum. A solution concentration of 100 mg/L was used for each solute.

Mixtures of methylene chloride, MTBE, TCE, toluene, and chlorobenzene prepared using the methods described previously were used for all tests. Solution was transferred from 1-L flasks to each vial using a peristaltic pump with Teflon tubes and a short section of Viton tube was used for the roller area. After adding the solution, the vials were placed in a rotator at 30 rpm. Multiple replicate vials were made with controls. The liquid was sampled periodically by decommissioning vials at various times and transferred to autosampler vials using disposable glass pipettes. Solution concentrations were analyzed by GC using the methods described previously.

The data were analyzed assuming that a planar sheet of geomembrane is suspended in a well-stirred solution of limited volume. The analytical solution for this system is given by Crank (1975) as

![Graphical representation of measured concentrations versus time at sampling ports for bench-scale composite liner experiment (a) depth = 60 mm; (b) depth = 90 mm; error bars represent RRMS](image-url)
Fig. 7. Predicted and measured concentration versus time at sampling ports (depth = 60 and 90 mm): (a) methylene chloride; (b) MTBE; (c) TCE; (d) toluene; (e) chlorobenzene; data are for three replicate composite liner experiments; smooth lines are model predictions using independently measured transport parameters as input; dashed lines (POLLUTE) are obscured by solid lines [Foose et al. (2002) model]
\[
\frac{C_t}{C_o} = \exp \left[ \frac{D_g t \left( K_g \right)^2}{A^2} \right] \text{erfc} \left[ \frac{D_g t \left( K_g \right)^2}{A^2} \right] \tag{9}
\]

where \( C_t \) = concentration of the VOC in the solution at time \( t \) \((M/L^3)\); \( C_o \) = initial concentration of the organic compound in the solution \((M/L^3)\); \( D_g \) = geomembrane diffusion coefficient \((L^2/T)\); \( t \) = elapsed time \((T)\); \( K_g \) = geomembrane partition coefficient (dimensionless); and \( 2A \) = the average thickness of the solution in contact with both sides of geomembrane \((L)\), which is calculated by dividing the volume of the solution by the area of the geomembrane. Partition coefficients and diffusion coefficients were determined simultaneously by fitting Eq. (9) to the concentration data using nonlinear least-squares regression. A typical record of VOC concentration in the solution over time from a kinetic batch test is shown in Fig. 3 along with a fit of Eq. (9). The partition, diffusion, and permeation coefficients \((P_g = K_g D_g)\) are summarized in Table 4. The coefficients of variation (COV) fall in a narrow range for all five VOCs \((0.23–0.27)\), indicating that a similar level of uncertainty was achieved for the partition coefficients for all five VOCs.

**Partition Coefficients for Clay**

Equilibrium batch isotherm tests were conducted to determine the partition coefficients for the VOCs and Kamm clay for input to the models. The method described by Kim et al. (2001) was used for the batch tests. Soil was crushed and ground past a number four sieve (mesh opening ≈ 4.75 mm) and then air dried and stored in a desiccator at room temperature before testing. The soil \((25 \text{ g})\) was then placed in a 40-mL amber glass vial, solution was added to fill the vial \((\text{soil-liquid ratio is approximately } 1 \text{ k g/L})\), and the vial was sealed using a screw cap with a Teflon-coated septum. The largest achievable soil-liquid ratio \((1 \text{,000 g/L})\) was used for the batch tests to closely simulate conditions in the bench-scale liner, as recommended by Kim et al. (2003).

Solutions having initial concentrations of 20, 40, 60, 80, and 100 mg/L of each VOC were used for tests conducted with single solutes and multisolute mixtures. These concentrations were used to bracket the concentrations in the composite liner experiments. Solutions were prepared using the methods described previously and transferred to each vial from 1-L flasks using a peristaltic pump. The filled vials were tumbled in a rotator at 30 rpm for 7 days at 23 ± 2°C. Preliminary tests showed that
equilibrium was established in 3–4 days (Park 2010); the 7-day period was used to avoid any concern about equilibrium not being established because of the high solid-liquid ratio. After tumbling, the vials were centrifuged at 2,000 rpm (429 g) for 15 min. The supernatant was transferred to autosampler vials using disposable glass pipettes and analyzed by GC using the methods described previously.

Three replicates were prepared for single-solute tests, and two replicates were prepared for multisolute tests. For each concentration, two controls without solids were also prepared to check for losses. Losses in the controls were less than 3%. Concentrations were adjusted for losses using the loss data from the controls.

Sorption isotherms for the single-solute and multisolute tests are shown in Fig. 4. Partition coefficients were computed by fitting the linear isotherm [Eq. (8)] to the sorption data using least-square regression. The measured partition coefficients are summarized in Table 5. The isotherms are approximately linear, which is consistent with previous studies on VOC sorption to clay barrier soils (Edil et al. 1995; Kile et al. 1995; Headly et al. 2001; Lake and Rowe 2005). The partition coefficients for Kamm clay are lower than those reported in previous studies for other clay liner soils (Edil et al. 1995; Kile et al. 1995; Headly et al. 2001; Lake and Rowe 2005). The partition coefficients for Kamml clay are lower than those reported in previous studies for other clay liner soils (Edil et al. 1994, 1995; Kim et al. 2001) because of the lower organic carbon content and higher soil-liquid ratio used in the batch test.

The error bars in Fig. 6(a) represent the root residual mean square.
deviation (RRMS) from the mean concentration of replicates for each point. Concentration data for Replicates 1 and 3 at the lower (depth = 90 mm) sampling port are not available after day 50 because the lower sampling ports malfunctioned and samples could not be collected. Thus, no error bars are shown in Fig. 6(b).

The RRMS was 2.3 m g/L for methylene chloride, 0.7 m g/L for MTBE, 2.1 m g/L for TCE, 1.6 m g/L for toluene, and 1.1 m g/L for chlorobenzene.

The VOCs diffuse from the upper reservoir through the geomembrane and the clay liner consecutively. Thus, the concentrations measured at the upper port are higher than those from the lower port as shown in Fig. 6. Both the upper and lower port concentrations of methylene chloride, TCE, toluene, and chlorobenzene are similar to one other, despite their differences in hydrophobicity, i.e., as indicated by solubility and/or log Kow in Table 3. In contrast, concentrations for the less hydrophobic MTBE are markedly lower compared with other VOCs. This behavior reflects the relative rates of transport of these VOCs in the geomembrane and the clay.

Permeation coefficients for chlorobenzene, TCE, and toluene are similar (Table 4), whereas the permeation coefficient of methylene chloride is approximately one order of magnitude smaller, and that of MTBE is two orders of magnitude smaller. As a result, methylene chloride and MTBE migrate more slowly through the geomembrane, resulting in lower concentrations beneath the geomembrane. These differences become less significant deeper in the clay, in which transport parameters for the clay have greater influence.

For all five VOCs, Replicate 1 typically showed the highest measured concentrations and Replicate 3 typically showed the lowest measured concentrations. This systematic difference represents an unknown bias, which is likely because of experimental factors, e.g., variations in the geomembrane and/or clay liner properties between the replicate experiments.

Comparison of Figs. 5 and 6 shows that concentrations in the composite liner are lower than those in the clay liner. For example, on day 160, the concentration of methylene chloride at 60-mm depth is 64% lower in the composite liner than in the clay liner. The concentration is 92% lower for MTBE, 25% lower for TCE, 29% lower for toluene, and 31% lower for chlorobenzene. This indicates that the geomembrane reduces transient VOC transport, as reported by Sangam and Rowe (2001b).

**Comparison of Predicted and Measured Concentrations**

Concentrations predicted by both models are shown along with the measured concentrations in Fig. 7. These predictions were made for all five VOCs using the average partition and diffusion coefficients for the geomembrane and clay liner as input (Tables 4–6). Predicted concentrations from both models are nearly identical for all five VOCs, i.e., concentrations differ less than 0.01% throughout the 400-day simulation period. Thus, only predictions made with POLLUTE are shown henceforth.

Measured and predicted concentrations at the upper and lower sampling ports for each VOC are compared in terms of root-mean-square error (RMSE) and the percent bias (PBIAS) (Gupta et al. 1999) in Table 7. To normalize the RMSE, the COVs of the residuals were computed as the ratio of the RMSE to the average predicted concentration (Table 7). Larger RMSE indicates greater scatter between measured and predicted concentrations, and the COV normalizes the scatter relative to the magnitude of VOC concentration. Positive PBIAS indicates the model overestimates concentrations, whereas negative PBIAS indicates the model underestimates concentrations. Because predicted concentrations
Fig. 10. Upper and lower bound predicted concentrations versus time at sampling ports (depth = 60 and 90 mm): (a) methylene chloride; (b) MTBE; (c) TCE; (d) toluene; (e) chlorobenzene; bounds defined using parameter sets (±1 standard deviation) yield highest and lowest concentrations.
from both models were essentially the same, the RMSE, PBIAS, and COV were computed using the predictions from POLLUTE and are reported in Table 7 for each VOC.

For all five VOCs, the average RMSE ranges from 0.76 to 3.70 mg/L (upper port) or from 0.36 to 1.23 mg/L (lower port). Similarly, the COV ranges from 17 to 47% in the upper port, and 22 to 34% in the lower port. The average PBIAS ranged from 3 to 23% (upper port) and −3 to 17% (lower port), indicating a slight underprediction by the model.

Both PBIAS and COV increase with the volatility of the VOC, as shown in Fig. 8 in terms of vapor pressure. This suggests that the misfit between model and data is controlled more by experimental variability than a systematic issue in the model, i.e., variability and losses are more prevalent with more volatile compounds. The contribution of experimental variability to the apparent misfit is also shown in Fig. 9, which shows RMSE (apparent model uncertainty) versus RRMS (variability in triplicate experiments). The RMSE climbs proportionally with RRMS, indicating that the model uncertainty is controlled primarily by experimental reproducibility. In fact, the RRMS constitutes 62–87% of the RMSE.

**Effect of Transport Parameter Uncertainty**

Effect of uncertainty in the partition and diffusion coefficients for the geomembrane and clay liner on the model predictions are shown in Fig. 10. The upper and lower bounds in Fig. 10 correspond to the highest and lowest predicted concentrations when the measured transport parameters were varied by ±1 standard deviation from the mean (see Tables 4–6). The upper and lower bounds correspond to combinations of transport parameters that yield the largest variation in predicted concentration.

The range of the upper and lower bound predictions is larger than the experimental variability in concentrations from the bench-scale experiments. For each of the VOCs except methylene chloride, more than 90% of the concentration data from the three replicate experiments fall between the upper and lower bounds (80% for methylene chloride). Thus, most of the deviations between predicted and measured concentrations can be attributed to uncertainty in the transport parameters used as input to the model.

**Concentration-Depth Profiles**

Concentration-depth profiles predicted with the average transport parameters are shown in Fig. 11 for elapsed times of 52, 107,
163, 263, and 369 days along with concentrations measured in the upper and lower sampling ports of Replicate 2. Data for Replicate 2 are shown because data are available for both sampling ports throughout the duration of the experiment. For all five VOCs, the predicted concentration profiles agree well with the measured concentrations, with the RMSE less than 1.3 mg/L on average.

For TCE, toluene, and chlorobenzene, the concentration is much higher at the geomembrane-clay interface (clay liner depth = 0 mm) and varies more rapidly near the surface of the clay compared with methylene chloride and MTBE. The interface concentration reflects the relative magnitudes of the permeation coefficient of the geomembrane, which is higher for TCE, toluene, and chlorobenzene, and lower for methylene chloride and MTBE (Table 4), and the rate of concentration change in the clay reflects the relative magnitude of the VOC transport parameters in the clay liner, i.e., on $D^*$ and $R$.

**Conclusions**

Predictions of VOC transport in composite liners were compared with data from bench-scale composite liner experiments conducted with five common VOCs ranging in hydrophobicity and volatility. The predictions were made with two models: a finite-difference model by Foose et al. (2002) and a semianalytical model by Rowe et al. (2004). Input to the models consisted of independently...
measured VOC transport parameters for the geomembrane and the clay components of the composite liner.

The following observations and conclusions are drawn from this study:

• Concentrations predicted with both models were essentially identical (concentration difference ≤ 0.01%) throughout the simulation period of 400 days for all five VOCs.

• Predictions made with average transport parameters for the geomembrane and the clay as input were in good agreement with concentrations measured in the composite liner experiments. Concentrations were predicted with the RMSE less than 3.7 mg/L, and percent bias less than 23% for all five VOCs.

• Concentrations near the geomembrane-clay interface depend primarily on the VOC transport parameters for the geomembrane, and rates of concentration change in the clay liner depend on the VOC transport parameters for the clay.

• The favorable comparison between VOC concentrations measured in the bench-scale composite liner experiments and concentrations predicted by both models indicate that these models can be used in conjunction with carefully measured material properties and appropriate boundary conditions to predict VOC concentrations in composite liners.

• Uncertainty in predictions because of inherent variability in the transport parameters was as large as or larger than the variability in the concentration data from the bench-scale experiments. Thus, predictions of VOC transport are influenced significantly by variability in transport parameters for the geomembrane and clay. Accurate determination of these parameters is essential for reliable predictions.

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