Comparison of Volatile Organic Compound Transport in Composite Liners with HDPE and Ethylene-Vinyl Alcohol Co-Extruded Geomembranes

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Abstract: This study evaluated migration of five common volatile organic compounds (VOCs) through simulated composite landfill liners that employ a co-extruded geomembrane (GM) with an interior layer of ethylene-vinyl alcohol (EVOH). A series of column tests was conducted with composite liner configurations employing 1.5-mm- and 1.0-mm-co-extruded EVOH GMs with outer layers of high-density polyethylene (HDPE) or linear low-density polyethylene (LLDPE) and 1.5-mm HDPE GMs. A simulated compacted clay liner (CCL) or a geosynthetic clay liner (GCL) was placed under the GM in each test. VOC breakthrough in composite liners employing HDPE GMs (approximately 30 days) occurred approximately four times faster than for co-extruded EVOH GMs with a HDPE outer layer (approximately 130 days) and with significantly higher VOC concentrations. Co-extruded EVOH GMs with LLDPE and HDPE as an outer layer have diffusion coefficients (0.11–0.58 × 10⁻¹³ m²/s) more than 20 times lower than those for conventional HDPE GM (2.86–11.05 × 10⁻¹³ m²/s). Numerical modeling of toluene migration through a composite liner with a 0.6-m-thick CCL and a co-extruded EVOH GM indicates that numerical concentrations are approximately 42% lower at one hundred years compared with a similar composite liner with a HDPE GM. DOI: 10.1061/(ASCE)GT.1943-5606.0001484. © 2017 American Society of Civil Engineers.

Author keywords: Ethylene-vinyl alcohol (EVOH); Co-extruded geomembrane; Compacted clay liner (CCL); Geosynthetic clay liner (GCL); Composite liner; Diffusion; Volatile organic compounds (VOCs).

Introduction

Composite liners—for example, a geomembrane overlying a compacted clay liner (CCL) or a geosynthetic clay liner (GCL)—are effective in controlling leakage from landfills because the geomembrane (GM) component prevents flow over the vast majority of the surface area and the underlying soil liner limits flow through defects in the GM (Giroud and Bonaparte 1989). However, transport of nonpolar organic contaminants in composite liners via diffusion through the GM, especially volatile organic compounds (VOCs), can be appreciable even if the rate of leakage is low (Park and Niburs 1993; Edil et al. 1995; Park et al. 1996, 2012b; Rowe et al. 1996; Sangam and Rowe 2001a, 2001b; Foose et al. 2001, 2002; Edil 2007; Nefso and Burns 2007).

Co-extruded geomembranes with an ethylene-vinyl alcohol (EVOH) core can reduce diffusion of nonpolar VOCs. EVOH is a random copolymer of ethylene and vinyl alcohol including polar hydroxyl (–OH) groups that has lower diffusion coefficients than other polymers used for GMs. EVOH copolymers with lower ethylene content grades have lower diffusion coefficients for nonpolar organic contaminants; higher ethylene-content grades have more flexibility and are easier to extrude (Lagarón et al. 2001; Armstrong 2011). Eq. (1) is the chemical formula of EVOH:

\[(CH_2 – CH_2)_m(CH_2 – CH)_n OH\] (1)

Co-extruded EVOH GMs have much lower diffusion coefficients than linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and polyvinyl chloride (PVC) GMs (McWatters and Rowe 2010, 2011, 2015; Armstrong 2011). However, data describing the relative rates of VOC transport in composite liners with co-extruded EVOH GMs relative to other GMs are limited.

Migration of five common VOCs in composite liners with co-extruded EVOH GMs or a conventional HDPE GM was evaluated in this study using column tests. Tests were conducted using 1.5-mm- and 1.0-mm-co-extruded EVOH GMs with outer layers of HDPE or LLDPE overlying a CCL or GCL. Comparative tests were conducted with an HDPE GM over a CCL or GCL. Diffusion coefficients for the co-extruded EVOH GMs were back-calculated from the column test data and compared with diffusion coefficients for HDPE GMs. Numerical analysis was also conducted for typical configurations of composite liners with EVOH or HDPE GMs to illustrate how breakthrough times increase and concentrations decrease when EVOH GMs are employed in composite liners.
Materials

Organic Compounds

Five VOCs were used as organic contaminants: methylene chloride (MC), methyl tertiary butyl ether (MTBE), trichloroethylene (TCE), toluene (TOL), and chlorobenzene (CB). These VOCs are representative of the 31 VOCs (i.e., alkanes, ethers, alkenes, aromatic hydrocarbons, and halogenated aromatic hydrocarbons) observed by Klett et al. (2005) in lysimeters from 34 landfill sites in Wisconsin. Toluene was detected in 49 of 54 cells, MC in 34 cells, TCE in 15 cells, MTBE in 17 cells, and CB in 9 cells. Among the detected VOCs, MC had the largest percentage (85%) of samples exceeding Wisconsin groundwater enforcement standards (ESs); TCE represented 41% of the samples exceeding the ES; TOL, 5.2%; and MTBE, 3.6%. Despite frequent detection, no CB samples exceeded the ESs (Klett et al. 2005). General properties of these VOCs are described in Table 1 (Schwarzenbach et al. 2003; Lake and Rowe 2005; Klett et al. 2005; Park et al. 2012b).

VOC solutions were prepared by filling a 1-L flask with distilled and deionized (DDI) water and adding an appropriate amount of liquid VOCs to achieve the desired concentration (Park et al. 2012a, b; Eun 2014; Eun et al. 2014). Liquid VOC was injected into the water using a 100-μL gas-tight syringe with the tip under the water surface. When using multiple solutes, the compounds were injected in order of decreasing density. The flask was filled completely and capped to minimize VOC loss to the headspace. Sodium azide (0.05%) was added to prevent microbial activity.

Geomembranes

Two co-extruded EVOH GMs with a 0.05-mm-thick EVOH core were used. The EVOH GMs had an outer layer of LLDPE (1.0-mm thick) or HDPE (1.5-mm thick); they are referred to henceforth as the 1.0-mm EVOH GM and the 1.5-mm EVOH GM (Fig. 1). A 1.5-mm-thick smooth HDPE GM was used for comparative tests. The geomembranes were cut with a milling machine to ensure a precise fit (±0.05 mm) in the columns.

Compacted Clay Liner

Kamm clay, used as the CCL for the column tests, has been extensively characterized in previous VOC transport studies (Park et al. 2012b; Eun 2014). Kamm clay is a moderately plastic clay classifying as CL in the unified soil classification system (USCS). Kamm clay, used as the CCL for the column tests, has been extensively characterized in previous VOC transport studies (Park et al. 2012b; Eun 2014). Kamm clay is a moderately plastic clay classifying as CL in the unified soil classification system (USCS) (Lake and Rowe 2005; Klett et al. 2005; Park et al. 2012b). Kamm clay is used for constructing liners at the Dane County Landfill, a municipal solid waste (MSW) landfill in Madison, Wisconsin. The clay was compacted at a water content of 21% with a dry unit weight of 17.3 kN/m³, which yielded a saturated hydraulic conductivity of 3.5 × 10⁻⁹ m/s (Park et al. 2012b).

Geosynthetic Clay Liner

A needlepunched GCL (Bentomat ST, CETCO, Hoffman Estates, Illinois) consisting of a layer of sodium bentonite between a woven and a nonwoven geotextile was installed beneath the GM in the column tests for this study. Properties of the GCL are shown in Table 2.

Attenuation Layer

Ottawa sand was used as an attenuation layer beneath the GCL. Ottawa sand is comprised of rounded medium-size particles (<2.0 and >0.425 mm) and classifies as a poorly graded sand (SP) according to the USCS (ASTM D2487 (ASTM 2011a)). The sand is 99.3% silica (SiO₂) and contains 0.1% Fe₂O₃.

Methods

Column Tests

The column tests consisted of a GM (1.5-mm co-extruded EVOH GM, 1.0-mm co-extruded EVOH GM, or 1.5-mm HDPE GM) over a CCL or a GCL with a sand attenuation layer. The matrix of setups is shown in Fig. 2. Tests with EVOH GMs were replicated. A control test was conducted using an aluminum sheet instead of a GM to assess and account for losses.

A schematic of the column is shown in Fig. 3(a). The column (200-mm height, 155-mm diameter) was constructed of aluminum and divided into upper and lower compartments with the GM at the joint between the compartments. Two polytetrafluoroethylene (PTFE) rectangular gaskets were installed above and below the GM to minimize loss of VOC solution through the joint [Fig. 3(b)]. Rectangular PTFE gaskets were also used between the column and end plates. Two magnetic stirrers were located on the bottom surface of the top plate inside the upper reservoir.

Three sampling ports were installed in the column to monitor concentration at depths of 20, 40, and 80 mm below the GM.

Table 1. Properties of VOCs Used in Column Experiments (Data from Schwarzenbach et al. 2003; Lake and Rowe 2005; Klett et al. 2005; Park et al. 2012b)

<table>
<thead>
<tr>
<th>Compound</th>
<th>MC</th>
<th>MTBE</th>
<th>TCE</th>
<th>TOL</th>
<th>CB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>CH₂Cl₂</td>
<td>CH₃—O—C(CH₃)₃</td>
<td>CHCl = CCl₂</td>
<td>C₄H₆—CH₃</td>
<td>C₆H₅Cl</td>
</tr>
<tr>
<td>Type of compound</td>
<td>Alkane</td>
<td>Ether</td>
<td>Alkene</td>
<td>Arene</td>
<td>Arene</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>84.93</td>
<td>88.15</td>
<td>131.39</td>
<td>92.14</td>
<td>112.56</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>1.33</td>
<td>0.740</td>
<td>1.46</td>
<td>0.867</td>
<td>1.11</td>
</tr>
<tr>
<td>log Kₐq</td>
<td>1.31</td>
<td>0.94</td>
<td>2.42</td>
<td>2.69</td>
<td>2.78</td>
</tr>
<tr>
<td>Solubility (mg/L)</td>
<td>20,000</td>
<td>48,000</td>
<td>1,100</td>
<td>515</td>
<td>500</td>
</tr>
<tr>
<td>Average concentration (μg/L)</td>
<td>38.2</td>
<td>14.9</td>
<td>8.7</td>
<td>83.5</td>
<td>4.1</td>
</tr>
<tr>
<td>Vapor pressure (kPa)</td>
<td>57.5</td>
<td>32.4</td>
<td>10.0</td>
<td>3.72</td>
<td>1.59</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>8.9</td>
<td>4.5</td>
<td>3.4</td>
<td>2.4</td>
<td>2.7</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>−97.2</td>
<td>−108.6</td>
<td>−84.7</td>
<td>−94.95</td>
<td>−45.31</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>40</td>
<td>55</td>
<td>87.21</td>
<td>110.63</td>
<td>131.72</td>
</tr>
</tbody>
</table>

Note: CB = chlorobenzene; Kₐq = partition coefficient between octanol and water; MC = methylene chloride; MTBE = methyl tertiary butyl ether; TCE = trichloroethylene; TOL = toluene. Average concentration of each VOC in leachate from Klett et al. (2005).

The sampling ports included a brass connector and cap with two septa to extract samples with minimal loss of VOC during sampling. The end of the port was packed with glass-fiber filter (<0.7 μm) to prevent migration of soil solids into the sample.

Specimens of the clay were saturated by permeation in the column without the GM in place until the ratio of inflow and outflow was between 0.9 and 1.1 and the hydraulic conductivity was steady. Upward flow was employed, and a 0.05% solution of sodium azide in DDI water was used as the permeant liquid to eliminate microbial activity. After saturation, clay that swelled above the interface between the upper reservoir and lower chamber was removed and the GM was placed. Stainless steel beads were placed on the GM (1.0-kPa confining pressure) to ensure good contact between the GM and the CCL.

Similar procedures were employed for the tests with a GCL. Upward and downward flow was used to ensure that the attenuation layer was saturated. Hydraulic conductivity of the saturated GCL stabilized at $5 \times 10^{-11}$ m/s in 7 days. Bentonite paste was applied around the circumference of the GCL with a spatula to prevent sidewall leakage. After saturation, the GM was placed on the GCL and stainless steel beads were placed on the GM (1.0-kPa confining pressure) to ensure good contact.

Table 2. Engineering Properties of GCL Used in Study (Data from CETCO 2014)

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>Bentomat ST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite swell index (mL/2 g)</td>
<td>ASTM D5890 (ASTM 2011b)</td>
<td>&gt;24</td>
</tr>
<tr>
<td>Bentonite fluid loss (mL)</td>
<td>ASTM D5891 (ASTM 1995)</td>
<td>&lt;18</td>
</tr>
<tr>
<td>Bentonite mass (g/m²)</td>
<td>ASTM D5993 (ASTM 2014)</td>
<td>&gt;4,600</td>
</tr>
<tr>
<td>Grab strength (N)</td>
<td>ASTM D5993 (ASTM 2014)</td>
<td>&gt;600</td>
</tr>
<tr>
<td>Peel strength (N)</td>
<td>ASTM D4632 (ASTM 2015)</td>
<td>&gt;65</td>
</tr>
<tr>
<td>Permeability, $D = 100$ mm (m/s)</td>
<td>ASTM D5887 (ASTM 2008)</td>
<td>$5 \times 10^{-11}$</td>
</tr>
<tr>
<td>Woven geotextile mass (g/m²)</td>
<td>ASTM D5261 (ASTM 2010)</td>
<td>&gt;105</td>
</tr>
<tr>
<td>Nonwoven geotextile mass (g/m²)</td>
<td>ASTM D5261 (ASTM 2010)</td>
<td>&gt;200</td>
</tr>
<tr>
<td>Hydrated internal shear strength (kPa)</td>
<td>ASTM D5321 (ASTM 2012)</td>
<td>&gt;24</td>
</tr>
</tbody>
</table>

The sampling ports included a brass connector and cap with two septa to extract samples with minimal loss of VOC during sampling. The end of the port was packed with glass-fiber filter (<0.7 μm) to prevent migration of soil solids into the sample.

Specimens of the clay were saturated by permeation in the column without the GM in place until the ratio of inflow and outflow was between 0.9 and 1.1 and the hydraulic conductivity was steady. Upward flow was employed, and a 0.05% solution of sodium azide in DDI water was used as the permeant liquid to eliminate microbial activity. After saturation, clay that swelled above the interface between the upper reservoir and lower chamber was removed and the GM was placed. Stainless steel beads were placed on the GM (1.0-kPa confining pressure) to ensure good contact between the GM and the CCL.

Similar procedures were employed for the tests with a GCL. Upward and downward flow was used to ensure that the attenuation layer was saturated. Hydraulic conductivity of the saturated GCL stabilized at $5 \times 10^{-12}$ m/s in 7 days. Bentonite paste was applied around the circumference of the GCL with a spatula to prevent sidewall leakage. After saturation, the GM was placed on the GCL and stainless steel beads were placed on the GM (1.0-kPa confining pressure) to ensure good contact.


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The initial concentration for each VOC was 100 mg/L, which is higher than the average VOC concentrations (<100 μg/L) found in landfill leachate (Klett et al. 2005), but Kamm clay was necessary to ensure that concentrations below the GM could be measured in a reasonable time. The initial concentration was well below the solubility limit of each VOC (Table 1) and within the upper bound for which the sorption isotherm is linear and calculation of the partition coefficient is valid (Park et al. 2012a, b). VOC concentrations in the upper reservoir were measured periodically, and concentrated VOC solution was injected through the sampling port in the top plate as necessary to maintain a constant VOC concentration in the upper reservoir.

Fig. 4 shows an example of TCE concentrations recorded at the 20-mm sampling depth, middle (40-mm depth), and lower (80-mm depth) sampling ports for duplicate tests of a composite liner employing the 1.5-mm EVOH GM over a CCL. The tests are repeatable with $R^2 = 0.98$.

Transport Modeling

A one-dimensional (1D) transport model was used to back-calculate diffusion coefficients for the GMs and to make predictions regarding the relative rates of transport in an actual composite liner with a co-extruded EVOH GM or a HDPE GM. One-dimensional mass transport of a nondeaying VOC through a composite liner can be described by a four-step process: (1) partitioning between the leachate and GM; (2) diffusion through the GM; (3) partitioning out of the GM and into the pore water in the CCL or GCL; and (4) diffusion through the CCL or GCL (Foose et al. 2001). Partitioning into the soil solids or organic matter may occur during diffusion through the CCL or GCL.

Partitioning of VOC between the leachate and GM can be defined as (Leo et al. 1971; Foose et al. 2001):

$$K_g = \frac{C_g}{C_w}$$

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

Partitioning out of the GM and into the pore water of the CCL or GCL follows the same process.

Diffusion of the VOC through the GM occurs in accordance with Fick’s second law:

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

where $D_g$ = diffusion coefficient of the organic compound in the GM (L$^2$/T); $z$ = distance along the direction of diffusion (L) with the origin at the surface of the CCL or GCL; and $L_g$ = thickness of the GM (L).

Eq. (3) is valid if the diffusion coefficient in the GM is temporally and spatially invariant (Foose et al. 2001, 2002). Diffusion through a CCL and GCL also follows Fick’s second law:

$$\frac{\partial C_s}{\partial t} = D^s \frac{\partial^2 C_s}{\partial z^2}, \quad z > 0$$
where $C_s$ = concentration of the organic compound in the pore water of the soil liner (M/L3); $z$ = distance along the direction of mass transport (L); $t$ = elapsed time (T); $D^*$ = effective diffusion coefficient (L²/T); and $R$ = retardation factor.

\[
R = 1 + \left( \frac{\rho_d K_d}{n} \right)
\]

where $\rho_d$ = dry density of the soil (M/L³); $n$ = porosity of the soil; and $K_d$ = solid-water partition coefficient (L³/M).

Partitioning of VOCs between solid (mineral or organic matter) and solution is quantified by the soil partition coefficient ($K_d$): \n
\[
K_d = \frac{C_s}{C_w}
\]

where $C_s$ = concentration in the solid-phase (M/M).

Eqs. (2)–(6) were solved using the Crank-Nicolson finite-difference method in Microsoft Excel spreadsheets (Foose 2002; Foose et al. 2001, 2002; Park et al. 2012b; Eun et al. 2014). Best-fit diffusion coefficients were obtained by varying the diffusion coefficient to obtain the minimum mean square error between the measured and predicted concentrations (Fig. 5). Partition and diffusion coefficients for the soil or GCL and partition coefficients for the EVOH and HDPE GMs, obtained from independent diffusion tests and equilibrium batch tests described by Eun (2014), were used as fixed input parameters when obtaining the best-fit diffusion coefficients, as recommended by Kim et al. (2001) and Park et al. (2012a). Estimated diffusion coefficients of VOCs for the HDPE GM are compared with diffusion coefficients reported in the literature (Fig. 6). A paired F-test ($p > 0.05$) indicated that the diffusion coefficients for the HDPE GM measured in this study are not statistically different from those reported in the literature, confirming that the column test method provides reliable data.

**Fig. 5.** Predicted (smooth lines) and measured concentrations of TCE at 20, 40, and 80-mm sampling ports in CCL beneath 1.5-mm HDPE GM

**Diffusive Transport through Composite Liners**

**Transport through Composite Liners with 1.5-mm EVOH and HDPE GMs**

Concentrations of the five VOCs (MC, MTBE, TCE, TOL, and CB) at the 20-mm sampling port are shown as a function of time in Fig. 7 for column tests conducted with the 1.5-mm EVOH GM or the 1.5-mm HDPE GM over a CCL. VOC breakthrough in the composite liner employing the HDPE GM occurred more than four times faster than in the composite liner employing the 1.5-mm EVOH GM. Concentrations of VOCs higher than the detection limits (DLs: 0.22–0.82 mg/L) at the 20-mm sampling port in the column with the HDPE GM were recorded at 30 days, whereas concentrations above DLs were recorded significantly later (130 days) for the EVOH GM. After breakthrough, VOC concentrations beneath the HDPE GM increased more rapidly in comparison with the EVOH GM. For example, at 300 days the concentration of MC at the 20-mm port was 62.3 mg/L in the composite liner employing the HDPE GM, approximately 8 times higher than the concentration at 20 mm for the column with the EVOH GM (7.6 mg/L).

Concentrations for the composite liner employing a GCL and attenuation layer at the 20-mm port are shown in Fig. 8. Similar to columns with a CCL, more rapid breakthrough and higher VOC concentrations were obtained with the HDPE GM compared with the EVOH GM. Concentrations higher than DLs at the 20-mm port were recorded at 40 days with the HDPE GM and at 160 days with the EVOH GM. Breakthrough for the composite liners with a GCL was delayed approximately 30 days compared with the same configuration with a CCL (Fig. 7), most likely to the lower diffusion coefficient of the GCL compared with the CCL (Table 3). However, with increasing time, the concentration of VOCs in the sand attenuation layer increased quickly compared with those in the CCL because of the higher diffusion coefficient for the sand (Table 3). For example, at 300 days the concentration of TOL at the 20-mm port in the composite liner with GCL was 82.2 mg/L compared with 68.1 mg/L for the CCL at the same time.

After breakthrough, VOC concentrations beneath the composite liners with a HDPE GM and GCL were significantly higher.

**Fig. 6.** Comparison of VOC diffusion coefficients ($D_g$) for 1.5-mm HDPE GM obtained in this study and by Park et al. (2012a)
compared with those for the EVOH GM and GCL. For example, at 300 days, the MC concentration at the 20-mm port depth reached 72.9 mg/L in the composite liner employing HDPE GM, or 8.6 times the concentration beneath the composite liner with the 1.5-mm EVOH GM (8.5 mg/L).

**Effect of Hydrophobicity on Breakthrough Time**

Fig. 9 shows the breakthrough time of VOCs at the 20-mm port for composite liners with CCLs and GCLs versus aqueous solubility, which represents the affinity of VOC for water. The VOCs with higher aqueous solubility tend to be more polar and are therefore less hydrophobic.

Breakthrough time of VOCs at the 20-mm port with 1.5-mm EVOH decreased with increasing aqueous solubility of the VOC, whereas breakthrough for the composite liners with the HDPE GM increased with aqueous solubility. For example, breakthrough of the highly nonpolar TOL and CB occurred after 150 days when the composite liner had a 1.5-mm EVOH GM, whereas breakthrough for the more polar MTBE and MC occurred earlier (<130 days). In contrast, when the composite liner had a 1.5-mm HDPE GM, breakthrough of TOL and CB occurred much earlier than the more polar MC and MTBE. For all VOCs, however, breakthrough for the composite liners with 1.5-mm EVOH GM occurred much later (125–155 days) compared with composite liners with the 1.5-mm HDPE GM (12 to 30 days). Similar trends were obtained for the composite liners with GCLs [Fig. 9(b)], except breakthrough time occurred later because the GCL has a lower diffusion coefficient than the CCL (Table 3).

**Effect of Hydrophobicity on Concentrations at Longer Times**

VOC concentrations at the 20-mm port at 300 days are shown in Fig. 10 versus aqueous solubility for the composite liners employing a CCL or GCL.
time, VOC concentrations at 300 days decrease with increasing aqueous solubility (decreasing hydrophobicity) of the VOC for the composite liners with the EVOH and HDPE GMS. For example, TCE, TOL, and CB reached approximately 70 mg/L at 300 days in the composite liner employing a HDPE GM over a CCL, whereas concentrations in the composite liner employing the EVOH GM over a CCL were less than 10 mg/L (approximately 7 times lower).

The decrease in VOC concentration at 300 days with increasing aqueous solubility for both GMS reflects the impact of greater partitioning to the outer polyethylene surface of both GMS as the hydrophobicity of the VOC increases (aqueous solubility decreases) (Park et al. 2012b). For example, the more polar MTBE (low hydrophobicity) partitions less effectively to polyethylene than the nonpolar and hydrophobic CB or TOL (Park et al. 2012b), resulting in lower concentration at the upper surface of the GM and therefore a lower concentration beneath the composite liner. MTBE has a partition coefficient for polyethylene ($K_p = 0.8$ L/kg) that is two orders of magnitude lower than the other nonpolar VOCs tested ($K_p = 69–112$ L/kg).

For all cases, concentrations beneath the composite liners with the HDPE GM liner are much higher than those beneath the EVOH
GM liner because of the lower diffusion coefficient of the EVOH core in the co-extruded EVOH GM. VOC concentrations at the 20-mm port at 300 days in the composite liners with the GCL are slightly higher than those for the CCL for both EVOH and HDPE GMs because of the higher VOC diffusion coefficients for the attenuation layer compared with the compacted clay (Table 3). Greater sorption in the compacted clay relative to the sand in the attenuation layer also contributes to the lower concentrations at 300 days for the composite liners with a CCL (Table 4).

**Effect of Thickness and Composition of Outer Layer**

VOC concentrations at the 20-mm port for the composite liner employing 1.0-mm EVOH GM having an LLDPE outer layer are compared in Fig. 11 with those for the composite liner with a 1.5-mm EVOH GM having an HDPE outer layer. VOC concentrations higher than DLs were measured at 70 days for the composite liner with 1.0-mm EVOH GM, whereas 130 days elapsed to achieve concentrations higher than DLs for the 1.5-mm EVOH GM. VOC concentrations also increased faster for the composite liner with the 1.0-mm EVOH GM compared with those for the 1.5-mm EVOH GM. At 200 days, concentration at the 20-mm port for the composite liner with the 1.0-mm EVOH GM was approximately three times higher than for the composite liner with the 1.5-mm EVOH GM. For example, TCE was 4.2 mg/L for the 1.5-mm EVOH GM and 14.2 mg/L for the 1.0-mm EVOH GM.

Thickness and material type in the outer layer of the co-extruded EVOH GM affect the VOC concentrations shown in Fig. 11. To evaluate the impacts of thickness and material type independently, simulations were conducted with the finite-difference model for co-extruded EVOH GMs with outer layers of LLDPE or HDPE that were 1.0- and 1.5-mm thick. Diffusion and partition coefficients in Tables 3 and 4 were used as input. Concentrations predicted at the 20-mm port are shown in Fig. 12 versus time. Concentrations at the 20-mm port for the co-extruded EVOH GMs decrease with increasing thickness of the outer layer and are lower for an HDPE outer layer compared with a LLDPE outer layer. For example, the TOL concentration for a 1.0-mm EVOH GM with an LLDPE outer layer is 15.2 mg/L at 350 days; however, if the outer layer is 1.0-mm HDPE, the TOL concentration is 11.5 mg/L (24% lower).

These differences are attributed to greater partitioning of VOCs to the LLDPE layer compared with HDPE, and a higher diffusion coefficient for the LLDPE layer. The diffusion coefficient of LLDPE (7.1 × 10^{-13} m^2/s) is 120% higher than that of HDPE (3.24 × 10^{-13} m^2/s), and the partition coefficient of LLDPE (195.8 L/kg) is 110% higher than that of HDPE (84.3 L/kg) (Park et al. 1996; Eun 2014). Use of LLDPE relative to HDPE results in approximately 25% higher concentration at 300 days in the test. However, a 50% increase in thickness (1.0–1.5 mm) reduces the TOL concentration by approximately 44%. This analysis indicates that thickness of the outer layer has a more significant effect on VOC transport than polyethylene type. By Fick’s second law, rate of change in concentration is affected in the first order by equivalent diffusion coefficient of the co-extruded GM and in the second order by thickness.

**Comparison of Diffusion Coefficients of Co-Extruded EVOH GM and HDPE GM**

Diffusion coefficients for co-extruded EVOH GM and the HDPE GM were obtained by fitting the temporal concentration data simultaneously from 20-, 40-, and 80-mm sampling ports using...
the finite-difference model, as described previously. Diffusion coefficients of the VOCs for the 1.5-mm EVOH GM, 1.0-mm EVOH GM, and HDPE GM are summarized in Table 5 and compared in Fig. 13. A paired F-test showed that the GM diffusion coefficients obtained from composite liner tests employing a CCL and a GCL are not statistically different, indicating that this fitting method used to estimate the diffusion coefficient is reliable.

Co-extruded EVOH GMs with LLDPE and HDPE as the outer layer had diffusion coefficients more than 20 times lower than those for a conventional HDPE GM (0.11–0.58 × 10⁻¹³ m²/s versus 2.86–11.05 × 10⁻¹³ m²/s). Diffusion coefficients for the 1.0-mm EVOH GM are slightly lower than those for the 1.5-mm EVOH GM because the EVOH core (0.04-mm-thick film) in the 1.0-mm EVOH GM occupies a larger portion of the entire thickness of the GM compared with the 1.5-mm EVOH GM, and has significantly lower diffusion coefficient than the HDPE or LLDPE outer layer.

Table 4. Partition Coefficients for Soils and Geomembranes (Data from Eun 2014)

<table>
<thead>
<tr>
<th>Type</th>
<th>Unit</th>
<th>MC</th>
<th>R²</th>
<th>MTBE</th>
<th>R²</th>
<th>TCE</th>
<th>R²</th>
<th>TOL</th>
<th>R²</th>
<th>CB</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kamm clay</td>
<td>L/kg</td>
<td>0.097</td>
<td>0.93</td>
<td>0.092</td>
<td>0.86</td>
<td>0.178</td>
<td>0.96</td>
<td>0.192</td>
<td>0.96</td>
<td>0.217</td>
<td>0.95</td>
</tr>
<tr>
<td>Bentonite (Bentomat ST)</td>
<td></td>
<td>0.040</td>
<td>0.87</td>
<td>0.045</td>
<td>0.79</td>
<td>0.108</td>
<td>0.94</td>
<td>0.120</td>
<td>0.92</td>
<td>0.117</td>
<td>0.93</td>
</tr>
<tr>
<td>Ottawa sand</td>
<td></td>
<td>0.015</td>
<td>0.87</td>
<td>0.017</td>
<td>0.91</td>
<td>0.026</td>
<td>0.97</td>
<td>0.026</td>
<td>0.95</td>
<td>0.027</td>
<td>0.92</td>
</tr>
<tr>
<td>1.0-mm EVOH GM</td>
<td>L/kg</td>
<td>5.8</td>
<td>0.96</td>
<td>1.9</td>
<td>0.92</td>
<td>157.9</td>
<td>0.93</td>
<td>195.8</td>
<td>0.95</td>
<td>171.1</td>
<td>0.96</td>
</tr>
<tr>
<td>1.5-mm HDPE GM</td>
<td></td>
<td>3.4</td>
<td>0.96</td>
<td>0.86</td>
<td>0.96</td>
<td>69.0</td>
<td>0.96</td>
<td>88.6</td>
<td>0.94</td>
<td>112.0</td>
<td>0.84</td>
</tr>
<tr>
<td>1.5-mm EVOH GM</td>
<td></td>
<td>3.1</td>
<td>0.97</td>
<td>0.7</td>
<td>0.91</td>
<td>62.1</td>
<td>0.87</td>
<td>84.3</td>
<td>0.94</td>
<td>107.1</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table 5. Diffusion Coefficients (Dg) for Geomembranes (×10⁻¹³ m²/s) Obtained by Back-Analysis of Column Data

<table>
<thead>
<tr>
<th>Type</th>
<th>MC</th>
<th>MTBE</th>
<th>TCE</th>
<th>TOL</th>
<th>CB</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0-mm EVOH GM with CCL</td>
<td>0.49</td>
<td>0.51</td>
<td>0.15</td>
<td>0.11</td>
<td>0.12</td>
<td>0.45</td>
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<tr>
<td>1.0-mm EVOH GM with GCL</td>
<td>0.53</td>
<td>0.57</td>
<td>0.18</td>
<td>0.13</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>1.5-mm HDPE GM with CCL</td>
<td>10.0</td>
<td>11.05</td>
<td>5.17</td>
<td>4.06</td>
<td>2.86</td>
<td>0.19</td>
</tr>
<tr>
<td>1.5-mm HDPE GM (Park et al. 2012a)</td>
<td>8.86</td>
<td>7.74</td>
<td>5.45</td>
<td>3.77</td>
<td>3.96</td>
<td></td>
</tr>
<tr>
<td>1.5-mm EVOH GM with CCL</td>
<td>0.53</td>
<td>0.55</td>
<td>0.17</td>
<td>0.14</td>
<td>0.15</td>
<td>0.42</td>
</tr>
<tr>
<td>1.5-mm EVOH GM with GCL</td>
<td>0.58</td>
<td>0.61</td>
<td>0.19</td>
<td>0.15</td>
<td>0.16</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 11. MC and TCE concentrations as a function of time at 20-mm port beneath composite liners with 1.5-mm EVOH GM containing a HDPE outer layer and 1.0-mm EVOH GM containing a LLDPE outer layer: (a) MC; (b) TCE

Fig. 12. Concentration of TOL at 20-mm port beneath co-extruded EVOH GM and CCL; EVOH GM simulated with LLDPE and HDPE outer layers 1.0- and 1.5-mm thick

Fig. 13. Comparison of diffusion coefficients (Dg) for 1.5-mm HDPE GM (from Park et al. 2012a and this study) and 1.5- and 1.0-mm EVOH GM (this study)
layer (Eun 2014). The nonpolar VOCs (TOL and CB) have lower diffusion coefficients than the more polar VOCs (MC and MTBE) because migration of the nonpolar VOCs is more constrained by the more polar EVOH film (Eun 2014).

Practical Implications

Simulations were conducted with the finite-difference model to investigate the relative migration of VOCs with EVOH GMs for composite liners having thickness comparable with those found in MSW landfills. Liner configurations stipulated in Subtitle D of the Resource Conservation and Recovery Act (RCRA 2002) (GM over 0.6 m of compacted clay) and the Wisconsin Administrative Code (2015) (GM over 1.2 m of compacted clay) were investigated, using the co-extruded EVOH GM reduces contaminant breakthrough, VOC concentrations beneath the composite liner and the subgrade was assumed to be negligible.

**Table 6. Transport Parameters for Simulations of Transport of Toluene in Composite Liners for Landfills**

<table>
<thead>
<tr>
<th>Type</th>
<th>Partition coefficient (Eun et al. 2014)</th>
<th>Diffusion coefficient (\times 10^{-13} \text{ m}^2/\text{s})</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>0.19</td>
<td>1,460(^a)</td>
<td>0.375</td>
</tr>
<tr>
<td>Subgrade</td>
<td>0.01</td>
<td>0.57(^a)</td>
<td>0.30</td>
</tr>
<tr>
<td>1.5-mm HDPE GM</td>
<td>88.6</td>
<td>4.06</td>
<td>—</td>
</tr>
<tr>
<td>1.5-mm EVOH GM</td>
<td>84.3</td>
<td>0.14</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\)Effective diffusion coefficient.

**Fig. 14. Concentration of TOL at base of composite liner predicted with finite-difference model:** (a) RCRA Subtitle D composite liner; (b) Wisconsin Code composite liner

Simulated. Subgrade beneath the compacted clay liner was assumed to consist of 5 m of fine-grained soil. Diffusion and partition coefficients for the subgrade were obtained from Foose et al. (2002) and Eun (2014). Transport parameters used in the modeling are summarized in Table 6. The leachate was assumed to be TOL [the most abundant VOC in Wisconsin landfills (Klett et al. 2005)] with a constant concentration of 100 \(\mu\text{g}/\text{L}\), which is slightly higher than the geometric mean TOL concentration reported by Klett et al. (2005) for leachate in Wisconsin landfills (83.5 \(\mu\text{g}/\text{L}\)). The lower boundary condition was set at a concentration of 0 and was assumed to be time invariant. Biodegradation of the VOCs in the liner and the subgrade was assumed to be negligible.

TOC concentrations predicted at the base of the liner are shown in Fig. 14. Lower TOC concentrations are predicted for the RCRA Subtitle D and Wisconsin composite liners with a co-extruded EVOH GM relative to the composite liners with the HDPE GM. The difference is more significant for the thinner Subtitle D composite liner because the GM component has a larger impact on diffusion in a thinner composite liner. For the conditions examined, using the co-extruded EVOH GM reduces contaminant concentrations by approximately 45% compared with a HDPE GM at 100 years.

Conclusions

Transport of common VOCs through composite landfill liners with a co-extruded EVOH geomembrane (GM) were compared experimentally with those from a composite liner with a conventional HDPE GM using column tests. Tests were conducted for composite liners with a GM over a compacted clay liner (CCL) or a GM over a geosynthetic clay liner (GCL) and a sand attenuation layer. Impact of GM type was similar for the CCL and GCL configurations.

VOC breakthrough in composite liners employing HDPE GMs occurred approximately 4 times faster than for composite liners employing 1.5-mm EVOH GMs with a HDPE outer layer. After breakthrough, VOC concentrations beneath the composite liner with a HDPE GM were significantly higher compared with concentrations beneath composite liners with a co-extruded EVOH GM.

VOC transport is lower with a co-extruded EVOH GM because the EVOH core has a lower diffusion coefficient and partition coefficient for most VOCs. Co-extruded-EVOH GMs have equivalent diffusion coefficients that are more than 20 times lower than diffusion coefficients for HDPE GMs \((0.11–0.58 \times 10^{-13} \text{ m}^2/\text{s} \text{ versus} \ 2.86–11.05 \times 10^{-13} \text{ m}^2/\text{s})\). Co-extruded GMs with a thicker outer layer also transmit VOCs at a lower rate.

Modeling of toluene transport in composite liners with thickness typically found in the field indicates that concentrations at the base of the liner are as much as 45% lower over 100 years when a co-extruded EVOH GM is used in lieu of a HDPE GM of comparable thickness. The impact of the co-extruded EVOH GM on concentration is more significant for composite liners with a thinner soil barrier.

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References


