

# Transport of volatile organic compounds through PVC and LLDPE geomembranes from both aqueous and vapour phases

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**ABSTRACT:** The diffusive migration in the aqueous and vapour phases of four volatile organic compounds (VOCs: benzene, toluene, ethylbenzene and xylenes) through samples of 0.76 mm (30 mil) thick flexible poly-vinyl chloride (PVC) and 0.76 mm (30 mil) linear low-density polyethylene (LLDPE) geomembranes are compared based on both sorption and diffusion tests. Diffusion coefficients for the PVC geomembrane were in the range of  $5.0\text{--}10 \times 10^{-13} \text{ m}^2/\text{s}$  for diffusion from both the aqueous and vapour states. The range for LLDPE was  $2.5\text{--}5.0 \times 10^{-13} \text{ m}^2/\text{s}$ . Diffusive transport of VOC contaminants through geomembranes in a simulated landfill environment (i.e. in the presence of water vapour) is identical despite the phase they originated from, simplifying the analysis of contaminant transport. The partitioning (sorption) coefficients for PVC were in the range 100–1075 with respect to aqueous phase concentrations. The corresponding values with respect to vapour phase concentrations were 22–290. LLDPE partitioning (sorption) coefficients were 200–475 with respect to aqueous phase concentrations and 44–123 with respect to vapour phase concentrations.

**KEYWORDS:** Geosynthetics, Diffusion, Partitioning, Permeation, Aqueous, Vapour, Volatile organic compounds, PVC, LLDPE, Geomembranes, Landfills

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## 1. INTRODUCTION

The performance of geomembranes in the base liner system has been the primary focus of research into the performance of geomembranes and composite liners used in municipal solid waste (MSW) landfills (Koerner and Koerner 2006; Thusyanthan *et al.* 2007; Brachman and Gudina 2008a, b; El-Zein and Rowe 2008; Saidi *et al.* 2008; Rowe *et al.* 2009). However, the migration of volatile organic compounds (VOCs) from the vapour phase through the landfill cover and around the barrier system on side slopes can also contribute to both atmospheric and groundwater contamination in the vicinity of a landfill. With the advent of modern barrier systems, diffusion of VOCs through the base liner and migration in landfill gas are being recognized as primary sources of VOC contamination in groundwater (Challa *et al.* 1997; Kraemer *et al.* 1998; Eiswirth 1999). VOCs have been

detected beneath liners and in monitoring wells adjacent to landfills (Edil 2003). Field studies have investigated whether aqueous phase (in leachate) or vapour phase (in landfill gas) migration dominates the contaminant pathway (Kraemer *et al.* 1998). From MSW landfill site investigations, Challa *et al.* (1997) reported that the type of VOCs found in groundwater correlated better with VOCs present in landfill gas than VOCs existing in leachate. More research is necessary regarding vapour phase transport and the performance of geomembranes as vapour barriers in either the landfill base liner, especially on side slopes, or the final cover system.

Specifically, research into the migration of VOCs through final landfill cover materials is an essential component of developing a better understanding of landfill gas migration and the design of improved barrier systems. Depending on the local regulations, landfill covers may include a geomembrane, geosynthetic clay

liner (GCL) or compacted clay liner (or some combination of these as a composite liner) as the primary barrier to the infiltration of water into the landfill and the escape of landfill gas from the landfill. Poly-vinyl chloride (PVC) and linear low-density polyethylene (LLDPE) geomembranes are commonly used in the final cover system of landfills. The objective of this study was to assess the diffusion characteristics of PVC geomembranes with respect to VOCs dissolved in water and VOCs in the vapour phase and to compare them to the diffusion characteristics of LLDPE geomembranes.

## 2. BACKGROUND

### 2.1. Landfill gas

Landfill gas is generated by the biochemical degradation of solid waste, typically by anaerobic bacteria. Methane comprises 45 to 60% of the landfill gas volume whereas carbon dioxide is 40 to 60%, both being of concern as greenhouse gases. Non-methane organic compounds (NMOCs) including VOCs contribute only a fraction to the MSW landfill gas composition; on average 0.01 to 0.6% (USEPA 1995, 2005). Typical concentrations of these trace VOC compounds commonly found in landfill gas are listed in Table 1. The values were compiled from ten different landfill sites, including minimum and maximum concentrations levels reported and are similar to typical results published by the United States Environmental Protection Agency (USEPA 2005).

Although VOCs exist in very low concentrations (often parts per million); trace amounts can still pose significant human health and safety risks. The United States Environmental Protection Agency has classified thirty toxic organic landfill gas constituents as Hazardous Air Pollutants (HAP) under the Clean Air Act (USEPA 2003). Common aromatic and chlorinated VOCs, volatilize quickly, but resist degradation in the environment. In the province of Ontario, Canada, concentrations of organic

contaminants in landfill gas often exceed the Ambient Air Quality Guidelines set by the Ontario Ministry of the Environment in Regulation 346, Schedule 2 (MOE 2004). These toxic constituents are consistently monitored in landfills. It is apparent that final cover systems play a significant role in limiting their release to the surrounding environment. Thus, it is critical to understand the extent of potential transport of these VOCs from the gas and through the liners in these barrier systems.

### 2.2. Mechanisms of landfill gas migration

As solid waste decomposes, gas is generated, increasing the pressure inside the landfill. This pressure gradient causes convective gas flow through cracks or holes in the geomembrane (Stark and Choi 2005) or composite liner (Bouazza and Vangpaisal 2006; Bouazza *et al.* 2008). Even if the geomembrane is free from defects, gas can still migrate through the non-porous membrane by molecular diffusion due to a concentration gradient (Haxo 1990). Diffusion through the geomembrane will almost always occur over time (Rowe 2005). Therefore, the rate of diffusive transport through the geomembrane and thus, its ability to control the release of contaminants needs to be studied.

Gas that escapes below the landfill before moving towards the atmosphere can contaminate groundwater if it reaches the capillary zone and is absorbed. There are reports of landfill gas travelling 500 m through the subsoil before releasing to the groundwater (USEPA 2005). The mechanism for groundwater contamination may involve transport in the vapour phase followed by direct contact between groundwater and landfill gas where the VOCs in the vapour partition into the groundwater.

Another process involves migration of landfill gas from the warmer enclosed landfill environment to the cooler cover system. As waste decomposes, heat is generated inside the landfill and typical landfill gas temperatures range from 27 to 49°C (Prosser and Waiteo 1999). At the landfill cover and outside the landfill, the temperature

Table 1. Typical concentrations of volatile organic compounds found in landfill gas<sup>a</sup>

Compounds	Average concentration (ppmv)	Minimum concentration (ppmv)	Maximum concentration (ppmv)
Benzene	2.34	0.002	52.2
Chlorobenzene	0.34	0.002	7.6
1,2-Dichlorobenzene	0.82	0.002	1.6
1,1-Dichloroethane	1.95	0.002	19.5
1,2-Dichloroethane (EDC)	0.84	0.001	30.1
1,2-Dichloroethene	1.90	0.003	84.7
Dichloromethane (DCM)	13.33	0.003	620.0
Ethylbenzene	14.52	0.001	428.0
Styrenes	1.50	0.002	87.0
Tetrachloroethene (PCE)	4.07	0.002	180.0
Toluene	44.66	0.005	758.0
Trichloroethene (TCE)	3.16	0.003	34.0
Vinyl chloride	4.52	0.051	48.1
Xylenes	12.4	0.002	664.0

<sup>a</sup>Compiled from reported data from different landfill sites: Challa *et al.* (1997); USEPA (2005); Hodgson (1992); Lee and Jones-Lee (1994); Soltani-Ahmadi (2000); Tchobanoglous *et al.* (1993).

may be 10 to 20°C lower than in the body of the landfill and hence water condensation forms on the geomembrane in the cover. The VOCs in the vapour phase then partition into the aqueous phase (Prosser and Janecek 1995) and migrate through the geomembrane.

Research has established that air pockets or wrinkles can form in some geomembrane liners during construction (Take *et al.* 2007). Even after waste placement, wrinkles may still be present and form significant interconnected networks of flow paths for leachate and landfill gases to travel laterally through the landfill (USEPA 2005; Brachman and Guidina 2008a). It is also hypothesized that these gases travel through the side slopes between the primary and secondary leachate collection systems (Edil 2003). The diffusive transport characteristics for these cases are discussed in the subsequent sections.

### 2.3. Aqueous phase diffusive transport

For a well constructed geomembrane with minimal holes, diffusion is the dominant mode of transport for organic contaminants (Rowe *et al.* 1995, 2004; Rowe 1998, 2005; Edil 2003). Three key parameters are used to characterize the potential for diffusive migration of each compound through a geomembrane: diffusion, partitioning and permeation coefficients (Sangam and Rowe 2001). These parameters are indicative of the polymer's performance as a permeation barrier. Polyethylene, being a non-polar polymer material, is a good barrier to water, but is more permeable to non-polar hydrocarbons. Hydrocarbons are absorbed but the polymer remains resistant to chemical attack (Feldman 2002). PVC is a polar polymer, therefore, perhaps not as resistant a barrier to water or water vapour, however, being polar, it has been suggested that it should be a good barrier to non-polar solvents (Ortego *et al.* 1995).

Aqueous phase diffusion through geomembranes occurs in three steps: adsorption, diffusion and desorption. Initially, the contaminant partitions between the source medium and adjacent surface of the geomembrane. Then the compound diffuses through the geomembrane driven by chemical potential. Finally, the compound partitions between the outer geomembrane surface and the receiving medium (Sangam and Rowe 2001). After a period of time, equilibrium is reached between the concentration in the geomembrane and the concentration in either the source or receptor media (Rowe 1998). The equilibrium between geomembrane and the source medium can be related by Henry's law:

$$c_g = S_{gf} c_f \quad (1)$$

where  $c_g$  is the concentration in the geomembrane ( $M/L^3$ ),  $c_f$  is the concentration in the source fluid (either gas or liquid) ( $M/L^3$ ), and  $S_{gf}$  is the partitioning coefficient (-).

In the second step, the diffusion of the contaminant through the geomembrane is described by Fick's first law:

$$f = -D_g \frac{dc_g}{dz}, \quad (2)$$

where  $f$  is the mass flux ( $M/L^2$  per T). The diffusion coefficient,  $D_g$  ( $L^2/T$ ) is specific to the geomembrane and

contaminant of interest. Parameter  $c_g$  is the concentration of the compound in the geomembrane ( $M/L^3$ ) and  $z$  represents the distance parallel to the direction of transport. When the diffusion coefficient is constant, the change in contaminant concentration in the geomembrane with time  $t$ , is expressed by Fick's second law:

$$\frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial z^2} \quad (3)$$

The final step is also described by Henry's law:

$$c'_g = S'_{gf} c_f, \quad (4)$$

When the source and receptor fluid are the same, the partitioning coefficient into the geomembrane can be assumed to be equal to the partitioning coefficient out of the geomembrane ( $S_{gf} = S'_{gf}$ ) (Sangam 2001).

The concentration of contaminant inside the geomembrane is very difficult to measure; therefore, the change in concentration in the fluid on either side of geomembrane is measured and parameters are deduced based on measured mass transport from the source to the receptor. The mass flux from the fluid on one side to that on the other side of the geomembrane when the source and receptor fluids are alike is given by rearranging Equations 1 and 2:

$$f = -D_g \frac{dc_g}{dz} = -S_{gf} D_g \frac{dc_f}{dz} = -P_g \frac{dc_f}{dz} \quad (5)$$

where the permeation coefficient,  $P_g$  ( $L^2/T$ ) represents the mass transfer across the geomembrane (Sangam and Rowe 2001) and is given by:

$$P_g = S_{gf} D_g \quad (6)$$

Several studies have examined the diffusive migration of dilute organic contaminants in aqueous solutions through high-density polyethylene (HDPE) geomembranes both unaged (Park and Nibras 1993; Mueller *et al.* 1998; Sangam and Rowe 2001, 2005; Rowe *et al.* 2004) and aged (Islam and Rowe 2009). Xiao *et al.* (1997a) compared the sorption and permeation of some organic contaminants through HDPE, PVC and LLDPE geomembranes; Aminabhavi and Naik (1998) performed immersion tests to obtain diffusion coefficients of various organic contaminants through HDPE and LLDPE; and Nefso and Burns (2007) compared the sorption coefficients of five different organic contaminants and HDPE and PVC geomembranes. However, gaps in the research are prevalent, leaving an incomplete database of diffusive parameters and these parameters are often not relevant to landfill conditions.

### 2.4. Vapour phase diffusive migration

Permeation through a geomembrane is dependant upon diffusion (affected by the molecular size and shape of the contaminant) as well as solubility (based on the polarity of both the contaminant and the polymer barrier). This is true for contaminants in either the aqueous or vapour phase. In general, permeation is the result of diffusion and solubility (hence interaction with the polymer) of the contaminant molecule (Salame and Steingiser 1977). Partitioning of the compounds from the aqueous phase into the geomembrane

can be correlated by Henry's law, as shown previously in Equation 1. In contrast, partitioning of compounds into the geomembrane from the vapour phase is different than the aqueous phase as the equilibrium concentration of contaminant molecules in the geomembrane is directly proportional to the partial pressure of the contaminant vapour outside the geomembrane.

Simple gases such as oxygen or carbon dioxide have smaller molecular sizes than the typical monomer unit of a polymer and therefore can readily diffuse through the membrane (Fujita 1968). In the case of simple gases, behaviour is ideal; Fickian characteristics and Henry's law are obeyed and diffusion, solubility and permeation coefficients are independent of concentration. This arises because of the low solubility of gases and lack of interaction between the contaminant and the polymer (Stannett 1968; Chainey 1990).

Organic vapours have a larger molecule size than the simple gases and may be expected to be slower to diffuse through the polymer barrier. The molecular movement through a geomembrane includes both diffusion of the contaminant molecule and a micro-Brownian motion where the polymer's monomer units rearrange. This allows the larger organic molecules to pass through (Fujita 1968). Solubility of the compound is directly related to the polarity and ease of condensation of the vapour (Chainey 1990). In this study, the solubility of the vapours can be expected to follow Henry's law since the concentrations and partial pressure of the vapours remain relatively low.

Simplification of the transport mechanisms of simple gases through polymer membranes was first discussed by Graham in 1866, where it was thought that gases condensed at the outer surface of the polymer, diffused through the polymer and evaporated at the outer surface to a gas state (Stannett 1968). In accordance with this theory, at least three scenarios can be envisioned for diffusive migration of vapour phase contaminants through geomembrane liners.

First, if there are air voids between the foundation layer and the dry bottom of the geomembrane (e.g. if there is a wrinkle) or the soil below the geomembrane is dry or has a very low degree of saturation, then contaminants in the gas can partition from the vapour phase to the geomembrane and diffuse through the geomembrane. Then they partition out of the geomembrane into the media above (either gas or liquid). Second, with the same wrinkle, if water vapour condenses as a thin film on the underside of the geomembrane (as is likely in a landfill where the relative humidity is very high and where the geomembrane temperature is likely lower than the gas temperature as discussed earlier), the vapour phase VOCs will partition to the water film (Henry's law) and then partition from the water to the geomembrane, diffuse through the GM and finally partition out into the media above the geomembrane.

A third scenario exists when the geomembrane rests directly on an underlying layer in which the degree of saturation is high enough that the air voids in the soil are not continuous. VOCs in the landfill gas will dissolve in the pore water of the foundation layer and diffuse upward

to the overlying geomembrane. They will diffuse through the geomembrane and any surface film of moisture above the geomembrane or the pore fluid of soil above the geomembrane until it encounters a continuous air phase at which point the VOCs will exsolve and be released to the atmosphere.

These three scenarios involve either (a) vapour phase contaminants in contact with the geomembrane so that the key parameter is the partitioning coefficient between the vapour and geomembrane; or (b) partitioning between gas and water (Henry's law) and then partitioning between the aqueous phase and geomembrane. The situation in which the geomembrane rests on an unsaturated soil with some continuous gas-filled pores and some water-filled pores will be bracketed by the two cases discussed above.

Several researchers (Pierson and Barroso 2002; Stark and Choi 2005) have reported that vapour phase transport through non-porous geomembranes can also be estimated by the three-step mechanism used for aqueous phase diffusion.

It may be hypothesized that once the contaminant has partitioned to the geomembrane, diffusion through the geomembrane will be controlled by the geomembrane properties (i.e. the diffusion coefficient,  $D_g$ ) and that this parameter will be independent of the phase of the contaminant outside the geomembrane. Therefore, it is expected that diffusion coefficients through the geomembrane will be identical for the aqueous and vapour phase.

The diffusive transport of contaminants from both the aqueous or vapour phase is highly dependent on temperature as shown in Equation 7 (Barrer 1937). The Arrhenius relationship is used to show the temperature dependence on the sorption, diffusion and permeation coefficients over small temperature ranges, as shown below in Equations 7, 8 and 9:

$$D_g = D_{g0} \exp\left(\frac{-E_d}{RT}\right) \quad (7)$$

$$S_{gf} = S_{gf0} \exp\left(\frac{-\Delta H_s}{RT}\right) \quad (8)$$

$$P_g = P_{g0} \exp\left(\frac{-E_p}{RT}\right) \quad (9)$$

where  $E_d$  is the activation energy of diffusion,  $E_p$  the activation of permeation and  $\Delta H_s$  the heat of solution of the contaminant inside the polymer (Naylor 1989; Chainey 1990). This paper focuses on the transport of VOC contaminants in dilute aqueous concentrations through PVC and LLDPE geomembranes exposed to water above and below the liner and compares the diffusive properties to the geomembranes in direct contact with contaminants from the vapour phase.

### 3. EXPERIMENTAL INVESTIGATIONS

#### 3.1. Material and methods

The study examined a 0.76 mm (30 mil) thick flexible polyvinyl chloride (PVC) geomembrane supplied by Canadian General-Tower Limited, Cambridge, Ontario, Canada

**Table 2. Properties<sup>a</sup> of PVC geomembrane examined**

Properties	Methods (ASTM)	Units	Values
Thickness	D5199	mm (min)	0.76 ± 0.04
Tensile strength at break	D882	kN/m (min)	12.8
Elongation at break	D882	% (min)	500
Tear resistance	D1004	N (min)	27
Dimensional stability	D1204	% (max)	5.0
Water extraction	D1239	% (max)	0.25
Volatile loss	D1203	% (max)	1.0

<sup>a</sup>Canadian General-Tower Limited**Table 3. Properties<sup>a</sup> of 2000B LLDPE geomembrane examined**

Properties	Methods (ASTM)	Units	Values
Thickness	D5199	mm (min)	0.76 ± 0.02
Tensile strength at break	D638	kN/m (min)	24
Elongation at break	D6693	% (min)	875
Tear resistance	D1004	(N)	98
Puncture resistance	D4833	(N)	270
Dimensional stability	D1204	% (max)	2.0
Volatile loss	D1203	% (max)	1.0
Standard oxidative-induction time (OIT)	D3895	min	180

<sup>a</sup>Raven Industries

(Table 2) and a 0.76 mm (30 mil) LLDPE geomembrane supplied by Raven Industries, Engineered Films Division, Sioux Falls, South Dakota, USA (Table 3). Benzene, toluene, ethylbenzene and xylenes (BTEX) are four aromatic hydrocarbons commonly found in landfill leachate and landfill gas (USEPA 2003). They were the VOCs examined in this study. Significant properties of these laboratory grade chemicals (purchased from Sigma-Aldrich, Mississauga, Ontario, Canada and Chromatographic Specialties Inc, Brockville, Ontario, Canada) are presented in Table 4.

All sorption and diffusion tests used purchased BTEX standards prepared in diluted methanol by the manufacturer. The methanol could conceivably have some effect on the partitioning from the source fluid at the surface of the geomembrane in the aqueous phase tests but is unlikely to have any significant impact on the partitioning within the geomembrane itself. It is unlikely to have any effect for the vapour phase tests. Both polymers, PVC and polyethylene,

have shown good resistance to chemical degradation by methanol (Schnabel 1981). Concentrations of BTEX were reflective of typical levels of VOCs found in landfill gas. Care was taken to ensure that VOCs from the testing environment did not contaminate the water source.

### 3.2. Analytical methods

Samples were analysed by Purge and Trap gas chromatography/mass spectrometer (P&T)-GC/MS. The procedure used a Hewlett Packard 5890 GC with a P&T unit and 5972 mass selective detector (MS). VOCs purged from the samples for 11 min with helium carrier gas at a flow rate of 0.9 m/min. The temperature was then raised to 225°C for the baking step. VOCs were desorbed off the VOCARB trap inside the Purge and Trap apparatus for 4 min. Desorbed compounds travel to the VOCOL column (60 m × 0.32 mm × 2.0 μl) in the GC. Chromatographs were quantified using selective ion monitoring (SIM). This method is based on EPA method 8240 (USEPA 1996).

**Table 4. Selected properties<sup>a</sup> of organic contaminants tested**

Chemicals	Molar weight (g/mole)	Density (g/cm <sup>3</sup> )	Aqueous solubility <sup>b</sup> (mg/l)	Log <i>K</i> <sub>ow</sub>	Coefficient of diffusion in water <sup>c</sup> (m <sup>2</sup> /s)	Coefficient of diffusion in air <sup>c</sup> (m <sup>2</sup> /s)	Henry's constant <sup>c</sup> <i>k</i> (l water/l air)
Benzene	78.11	0.8765	1780	2.13	11. × 10 <sup>-10</sup>	9.6 × 10 <sup>-6</sup>	0.218
Toluene	92.14	0.8669	515	2.79	9.4 × 10 <sup>-10</sup>	8.5 × 10 <sup>-6</sup>	0.258
Ethylbenzene	106.17	0.8670	152	3.13	8.5 × 10 <sup>-10</sup>	7.7 × 10 <sup>-6</sup>	0.305
<i>m</i> -Xylene	106.17	0.8642	162	3.20	8.5 × 10 <sup>-10</sup>	7.7 × 10 <sup>-6</sup>	0.290
<i>p</i> -Xylene	106.17	0.8811	156	3.13	8.5 × 10 <sup>-10</sup>	7.7 × 10 <sup>-6</sup>	0.290
<i>o</i> -Xylene	106.17	0.8802	152	3.18	8.5 × 10 <sup>-10</sup>	7.6 × 10 <sup>-6</sup>	0.201

<sup>a</sup>From Montgomery and Welkom (1990).<sup>b</sup>At 20°C.<sup>c</sup>From Tucker and Nelken (1982), at 24°C.

In both aqueous and vapour sorption tests, 10  $\mu\text{l}$  liquid samples were taken using gas tight syringes and directly injected into the 5 ml Purge and Trap syringe filled with distilled deionized (DD) water. In the aqueous diffusion tests, 10  $\mu\text{l}$  liquid samples were taken as per the sorption tests. For the vapour diffusion tests, 100  $\mu\text{l}$  samples were taken from the aqueous phase in the cells and directly injected into the 5 ml P&T syringe. In vapour tests, compounds were measured by taking liquid samples and correlating the vapour concentrations in the cells by Henry's law. Temperature was monitored electronically for each cell to maintain a constant temperature of  $24 \pm 1^\circ\text{C}$ . For all tests, 10  $\mu\text{l}$  of 2  $\mu\text{g}/\text{ml}$  surrogates fluorobenzene and 1,4-dichlorobenzene were added as internal standards for quality control.

At regular intervals throughout the testing, a certified BTEX reference standard of known concentration was analysed. Samples from the testing cells were quantified based on this standard's area. The efficiency was calculated by using the recovery of the surrogate. Samples were rejected if the efficiency was outside the 80–120% range. The efficiency was predominantly between 95–100% throughout the testing period. Concentrations were corrected for the recovery of the surrogate. Duplicate and triplicate samples from the cells were often analysed. Blanks, spikes and quality control samples were run at a frequency of approximately 10%. Quality control samples were prepared from a separate BTEX standard source. The GC/MS had a detection limit of 1  $\mu\text{g}/\text{l}$ , established prior to testing.

### 3.3. Procedures

#### 3.3.1. Control tests

Control tests were performed to establish the mass losses of contaminants due to sampling procedures, leaks in the cells, or sorption to the cell materials: stainless steel, PTFE septums, viton o-rings. Control tests were performed in both the single and double compartment stainless steel cells for both the aqueous and vapour phase apparatus (Figures 1 and 2, respectively). In the aqueous tests, the source and receptor compartments were completely filled with DD water and sealed. In the vapour phase

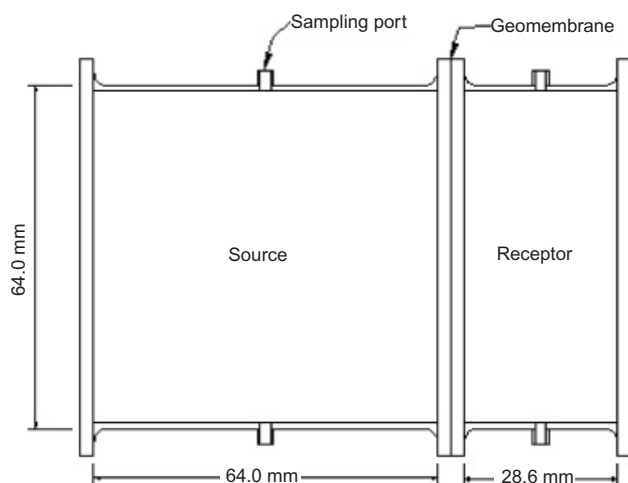


Figure 1. Schematic of an aqueous-aqueous diffusion cell

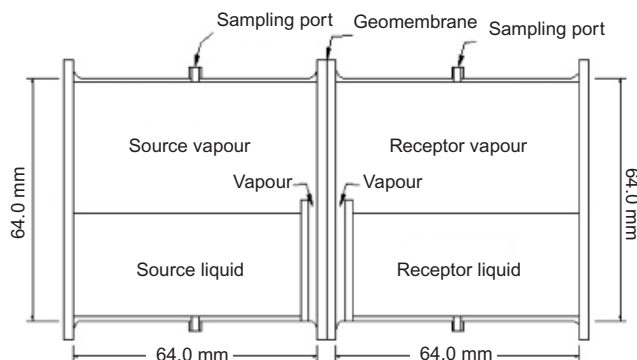


Figure 2. Schematic of a vapour-aqueous/vapour-aqueous diffusion cell

tests, the source and receptor compartments were partially filled with DD water.

For the control tests, the cells did not contain geomembrane samples. However, the viton o-rings and septums were used to mimic normal testing conditions. Samples were taken from the source and receptor at regular intervals during the diffusion cell testing period. Sampling ports were tightly sealed to prevent mass loss through the septum.

#### 3.3.2. Sorption tests

For sorption tests, after recording the initial masses of geomembrane samples, they were placed in a diffusion cell filled completely with DD water for the aqueous sorption tests. For the vapour sorption tests, geomembrane samples were suspended in the vapour space of the diffusion cell above an aqueous phase. Identical concentrations of BTEX were injected into the aqueous phase of all sorption tests as per the control cells. Samples were agitated on magnetic stirring plates and maintained at room temperature of  $24 \pm 1^\circ\text{C}$ . Contaminant concentrations were evaluated over time until equilibrium was reached.

For the aqueous sorption tests, the partitioning coefficient for each compound was calculated based on contaminant mass balance at equilibrium:

$$M_{s0} = M_{sF} + M_{gF} \quad (10)$$

where  $M_{s0}$  is the initial mass of the contaminant in solution (M);  $M_{sF}$  is the final mass of the contaminant in aqueous solution (M) and  $M_{gF}$  is the mass contained in the geomembrane (M). When Equation 10 is rearranged in terms of concentrations and volumes, it becomes:

$$c_{f0} V_{f0} = c_{fF} V_{fF} + \frac{M_g}{\rho_g} c_{gF} \quad (11)$$

where  $c_{f0}$  is the initial contaminant concentration in aqueous solution ( $\text{M}/\text{L}^3$ );  $V_{f0}$  is the initial solution volume ( $\text{L}^3$ );  $c_{fF}$  is the final contaminant concentration in solution ( $\text{M}/\text{L}^3$ );  $V_{fF}$  is the final solution volume ( $\text{L}^3$ );  $M_g$  is the initial mass of the geomembrane sample (M);  $\rho_g$  is the geomembrane density ( $\text{M}/\text{L}^3$ ) and  $c_{gF}$  is the final concentration of the contaminant in the geomembrane at equilibrium ( $\text{M}/\text{L}^3$ ). The partitioning equation can be expressed by substituting Equation 11 into Equation 1 to give:

$$S_{gf} = \frac{[c_{f0}V_{f0} - c_{fF}V_{fF}]\rho_g}{M_g c_{fF}} \quad (12)$$

For vapour sorption tests, a similar approach as in the aqueous tests was used. The partitioning coefficient for each compound was calculated based on contaminant mass balance at equilibrium for both the aqueous and vapour phases:

$$M_{s0} = M_{sF} + M_{sF}^* + M_{gF} \quad (13)$$

where  $M_{s0}$  is the initial mass of the contaminant in solution (M);  $M_{sF}$  is the final mass of the contaminant in aqueous solution (M);  $M_{sF}^*$  is the final mass of the contaminant in vapour phase (M) and  $M_{gF}$  is the mass contained in the geomembrane (M).

The partitioning coefficients for the aqueous phase can be calculated similarly to the aqueous sorption tests since the aqueous and vapour phase partitioning coefficients are related by Henry's law:

$$S_{gf}^* = kS_{gf} \quad (14)$$

where  $S_{gf}^*$  is the partitioning coefficient relative to the concentration in the vapour phase (-) and  $k$  is the Henry's law coefficient specific to each contaminant and temperature (-).

### 3.3.3. Aqueous diffusion tests

In the aqueous diffusion tests, a stainless steel double compartment cell (source and receptor) were divided by a geomembrane sample (Figure 1). The receptor cell was filled with DD water. The source cell was filled with a dilute aqueous chemical solution at concentrations levels similar to contaminant concentrations in landfill leachate. The aqueous phase was sampled to measure the initial concentration in the source. Diffusion cells were maintained at a constant temperature of  $24 \pm 1^\circ\text{C}$ . Samples were taken from the source and receptor at regular time intervals. The concentrations in the source and receptor were plotted as normalized concentrations relative to the initial concentration in the source.

### 3.3.4. Vapour diffusion tests

In the vapour diffusion tests, a modified stainless steel double compartment cell (source and receptor) was used (Figure 2). In both the source and receptor there was an aqueous phase and a vapour phase. A geomembrane sample was secured between the source and the receptor compartments. It was kept entirely in the vapour phase by a steel barrier keeping the liquid separate from the geomembrane. This set-up of the cell ensured that the geomembrane was only exposed to contaminants in the vapour phase. The receptor liquid was DD water. The source liquid was a dilute aqueous chemical solution at similar concentrations levels to the control and sorption tests. The chemicals were allowed to equilibrate between the aqueous and vapour phase of the source compartment. The source aqueous phase was sampled to measure the initial aqueous source concentration and the vapour phase concentrations were then calculated from this using

Henry's law. Diffusion cells were maintained at a constant temperature of  $24 \pm 1^\circ\text{C}$ . Samples were taken from the source and receptor liquids at regular time intervals. The concentrations in the source and receptor were plotted as normalized concentrations relative to the initial concentration in the source.

### 3.3.5. Modelling diffusion parameters

The experiments used concepts and theory of diffusion through polymers originally developed by Crank and Park (1968). The experimental procedure and concepts for modelling of permeation parameters were developed by Rowe *et al.* (1988) for clayey soils and by Rowe *et al.* (1995, 1996, 2004) for geomembranes. Sangam and Rowe (2001, 2005) reported diffusion and partition coefficients for dilute VOCs in the aqueous phase through HDPE geomembranes using this approach.

In this closed system, a finite mass boundary exists. Therefore, the mass of contaminants in the source at a given time is equal to the initial mass minus the mass diffused through the geomembrane. The equation for the concentration in the source at time  $t$  is written as:

$$c_{ss}(t) = c_{s0} - \frac{1}{H_{ss}} \int_0^t f_{ss}(\tau) d\tau \quad (13)$$

where the integral gives to total mass that has diffused from the source fluid into the geomembrane per unit area up to some time  $t$ ,  $c_{ss}(t)$  is the contaminant concentration in the source at time  $t$  ( $\text{M/L}^3$ );  $c_{s0}$  is the initial contaminant concentration in the source ( $\text{M/L}^3$ );  $H_{ss}$  is the reference height of the source reservoir (L) and  $f_{ss}(\tau)$  is the mass flux of contaminant into the geomembrane with time  $\tau$  ( $\text{M/L}^2$  per T). The decrease in contaminant concentrations in the source are modelled using Equation 13. To model the increase in concentrations in the receptor as contaminants partition out of the geomembrane, a similar equation is used:

$$c_{rs}(t) = c_{r0} + \frac{1}{H_{rs}} \int_0^t f_{rs}(\tau) d\tau \quad (14)$$

where the integral gives to total mass that has diffused out of the geomembrane into the receptor fluid per unit area up to some time  $t$ ,  $c_{rs}(t)$  is the contaminant concentration in the receptor at time  $t$  ( $\text{M/L}^3$ );  $c_{r0}$  is the initial contaminant concentration in the receptor ( $\text{M/L}^3$ );  $H_{rs}$  is the reference height of the receptor solution (L) and  $f_{rs}(\tau)$  is the mass flux of contaminant out of the geomembrane with time  $\tau$  ( $\text{M/L}^2$  per T).

Both the decrease in contaminant concentrations in the source and the increase in concentrations in the receptor as contaminants partition out of the geomembrane are modelled using finite boundary equations that measure the mass flux into or out of the geomembrane with time. The diffusion ( $D_g$ ), partition ( $S_{gf}$ ) and permeation ( $P_g$ ) coefficients of contaminants through PVC and LLDPE geomembranes in the aqueous phase were inferred by fitting theoretical results of these diffusion equations to the source and receptor concentration data from diffusion tests. The boundary conditions given by Equations 13 and 14 were used. Analysis of experimental data follows the

procedure outlined by Rowe *et al.* (1995) using the finite layer analysis program POLLUTE<sup>®</sup> v.7 (Rowe and Booker 2004). The partition ( $S_{gf}^*$ ) and permeation ( $P_g^*$ ) coefficients of contaminants through PVC and LLDPE geomembranes in the vapour phase were related to those in the aqueous phase by Henry's law (e.g. Equation 14) and were checked through similar modelling of theoretical curves as in the aqueous tests.

## 4. RESULTS AND DISCUSSION

### 4.1. Control tests

Multiple control tests were performed in the sorption, aqueous diffusion and vapour diffusion tests to account for mass loss in the stainless steel cells. Overall, benzene did not experience significant mass loss as the average concentration only decreased by less than 5% from the initial concentration. The average decrease in concentration of toluene, ethylbenzene, *m&p*-xylenes and *o*-xylenes from the initial concentration were 8, 12, 13 and 11%, respectively. The decrease in concentration may be attributed to their sorption onto the walls of the stainless steel cells. Since there was no significant change in the concentration of benzene with time, losses associated with sampling events can be considered negligible. Therefore, the dominant form of mass loss of the other contaminants is sorption to the testing material. In the following analysis of the sorption and diffusion tests using the geomembrane, the mass loss of contaminants due to sorption onto the testing material is considered based on these control tests.

### 4.2. Sorption tests

Figure 3 shows the decrease in contaminant concentrations in the solution during one of the numerous aqueous sorption tests using PVC geomembrane samples. The changes in concentration are plotted as normalized concentrations relative to the initial concentration. The equilibrium concentration was reached after 2 days. Benzene concentrations decreased by 79% of the initial concentration. The decrease in initial contaminant concentration was much higher for the other contaminants. Ethylbenzene and xylenes showed the greatest decrease of 97%, while toluene had a concentration decrease of 91%.

For the aqueous sorption tests, the partitioning coeffi-

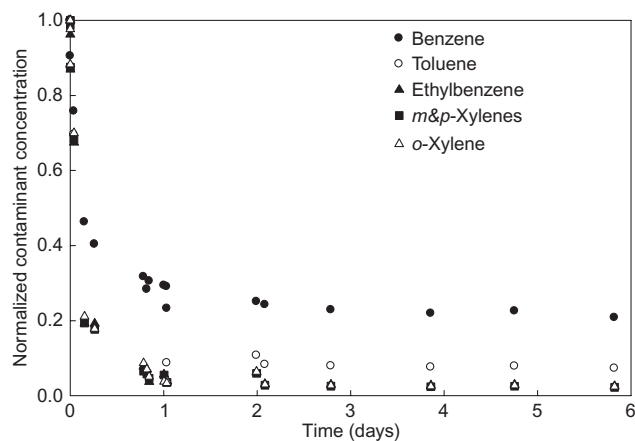


Figure 3. Measured concentrations of contaminants during sorption test with (30 mil) PVC geomembrane

icients  $S_{gf}$ , for the geomembrane were calculated in two ways as described below and these two values of  $S_{gf}$  are shown in Table 5. A non-corrected  $S_{gf}$  was calculated assuming that there was no significant mass loss of contaminants. This case assumes that the sorption of contaminants to the testing material is negligible in comparison to their attraction to the geomembrane and gives the higher value of  $S_{gf}$  in each pair of results shown in Table 5. The corrected  $S_{gf}$  took into consideration the mass loss of contaminants in the control tests; this gives the lower value of  $S_{gf}$  in each pair of results. The difference between the two calculated values shows the uncertainty and the actual partitioning coefficients are expected to lie between the uncorrected and corrected values since it is expected that with the presence of the geomembrane there will be less sorption to the test container materials than in the control tests. The highest corrected  $S_{gf} = 1085$  for the geomembrane was *m&p*-xylenes, followed by *o*-xylene ( $S_{gf} = 932$ ), ethylbenzene ( $S_{gf} = 977$ ), toluene ( $S_{gf} = 385$ ) and benzene ( $S_{gf} = 134$ ). This sorption coefficient for benzene at 24°C correlates with test results from Nefso and Burns (2007) who obtained  $S_{gf} = 106$  as the sorption coefficient of benzene through a 0.752 mm PVC geomembrane for sorption tests performed at 20°C. Vapour phase sorption tests were also performed using the stainless steel one compartment cell and are presented in Table 5. To allow a direct comparison

Table 5. Estimated partitioning coefficients of PVC and LLDPE geomembranes from sorption tests. For vapour phase tests,  $S_{gf}$  is calculated related to the concentration in the aqueous phase to allow for direct comparison with the aqueous phase test results.  $S_{gf}^*$  is the partitioning coefficient relative to the concentration in the vapour phase in these tests (the two are related by the Henry's coefficient,  $k$ , given in Table 4 with  $S_{gf}^* = kS_{gf}$ )

Contaminant	PVC aqueous phase $S_{gf}$ (-)	PVC vapour phase $S_{gf}$ (-)	PVC vapour phase $S_{gf}^*$ (-)	LLDPE aqueous Phase $S_{gf}$ (-)	LLDPE vapour phase $S_{gf}$ (-)	LLDPE vapour phase $S_{gf}^*$ (-)
Benzene	130–134	110–115	24–25	177–200	175–200	38–44
Toluene	381–385	318–325	82–84	390–400	285–300	75–77
Ethylbenzene	975–977	865–890	263–270	440–450	400–418	122–128
<i>m&amp;p</i> -Xylenes	1080–1085	950–975	275–283	470–475	425–440	123–128
<i>o</i> -Xylenes	930–932	855–904	172–182	435–440	397–400	79–80

regarding whether being in the aqueous or vapour phase directly adjacent to the geomembrane had a substantive effect on overall partitioning, values of  $S_{gf}$  from the vapour tests were first calculated based on the concentration in the aqueous phase of each tests. The results for the partitioning coefficient followed a similar trend as aqueous tests, however with somewhat less mass sorbing to the geomembrane and hence lower partitioning coefficients than in the aqueous phase tests (Table 5). The highest corrected  $S_{gf}$  for *m&p*-xylenes was 975; for *o*-xylene, 904; ethylbenzene, 890; toluene, 325; and benzene, 115. The values of  $S_{gf}^*$  relevant to partitioning between the vapour phase and the geomembrane are also given in Table 5.

Partitioning coefficients for the LLDPE geomembrane were also measured in the aqueous and vapour phases and corrected for mass loss and presented in the same manner as for PVC in Table 5. In general the sorption to LLDPE was quite different to PVC with some contaminants being similar (e.g. toluene) and others being very different (e.g. xylenes and ethylbenzene). As was the case for PVC there were slightly lower partitioning coefficients than in the aqueous phase tests.

#### 4.3. Aqueous diffusion tests

Throughout diffusion tests, contaminant concentrations in the source and receptor were monitored with time until equilibrium was reached. In repeated tests, equilibrium was reached after 7–8 days. The normalized concentrations in the source and receptor are presented in Figures 4 and 5, respectively. Both of these values were normalized relative to the initial concentration of contaminants in the source reservoir.

Concentrations in the source decreased with time as the contaminants diffused through the geomembrane. In the testing of both PVC and LLDPE geomembranes, concentrations for *m&p*-xylenes in the source decreased the greatest. The partitioning coefficient controls the decrease in source concentration; therefore the higher values of  $S_{gf}$  for *m&p*-xylenes would predict this trend. For the PVC

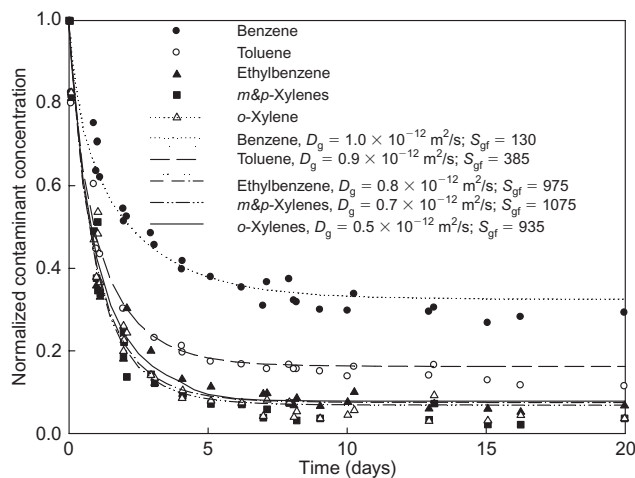


Figure 4. Contaminant concentration changes in the source with time during aqueous diffusion tests for a 0.76 mm (30 mil) PVC geomembrane

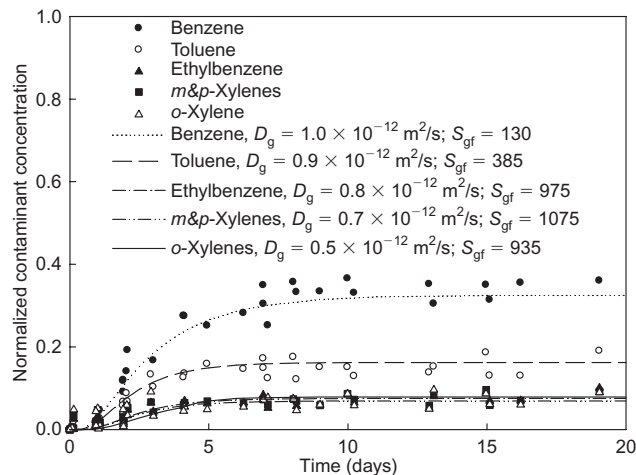


Figure 5. Contaminant concentration changes in the receptor with time during aqueous diffusion tests for a 0.76 mm (30 mil) PVC geomembrane

geomembrane, following *m&p*-xylenes, *o*-xylene concentrations decreased the greatest in the source, followed by ethylbenzene, toluene and benzene. In the case of the LLDPE geomembrane, the concentration decreases from greatest to least were *m&p*-xylenes, ethylbenzene, *o*-xylene, toluene, benzene. In both cases, benzene had the fastest increase in the receptor, followed by toluene. Ethylbenzene, *m&p*-xylenes and *o*-xylene increased at slower rates. The increase in contaminant concentration in the receptor is controlled by the permeation coefficient.

The diffusion process is dependent on the molecular size of the penetrate molecules and the pore sizes of the polymer material. Therefore, the diffusion coefficient decreases and the activation energy of the process increases as the penetrate increases in size. This was shown in these tests where benzene, with the simplest structure in comparison to the other contaminants, migrates through the polymer matrix more quickly and with less sorption than molecules with more complex structures, such as ethylbenzene and xylenes, which are more prone to being trapped in the polymer matrix.

Theoretical curves obtained with POLLUTEv7 are shown in Figures 4 and 5. An initial  $S_{gf}$  value was used from the sorption tests and adjusted to fit with the diffusion tests. The permeation coefficient for each contaminant was calculated from these curves. All three diffusive migration parameters:  $D_g$ ,  $S_{gf}$  and  $P_g$  are presented in Table 6 for the PVC geomembrane and in Table 7 for LLDPE. Benzene had the highest diffusion coefficient,  $D_g = 10 \times 10^{-13} \text{ m}^2/\text{s}$  through the PVC geomembrane and a range of  $D_g = 3.0\text{--}5.0 \times 10^{-13} \text{ m}^2/\text{s}$  for LLDPE. As a reference point it is noted that typical BTEX diffusion coefficients for intact clay liners are  $1.5\text{--}5 \times 10^{-10} \text{ m}^2/\text{s}$  (Rowe *et al.* 2004).

In previous work, Park *et al.* (1995; 1996) used a similar double compartment cell to establish partition and diffusion coefficients through HDPE, very low density polyethylene (VLDPE) and PVC geomembranes. Diffusion coefficients of  $5.4 \times 10^{-13} \text{ m}^2/\text{s}$  for toluene and  $16.1 \times 10^{-13} \text{ m}^2/\text{s}$  for *m*-xylene through 0.76 mm PVC

**Table 6. Inferred partitioning, diffusion and permeation coefficients of (30 mil) PVC geomembranes from diffusion tests in the aqueous and vapour phase. For vapour phase tests,  $S_{gf}$  and  $P_g$  are calculated related to the concentration in the aqueous phase for direct comparison with the aqueous phase test results.  $S_{gf}^*$  and  $P_g^*$  are relative to the concentration in the vapour phase in these tests (the two are related by the Henry's coefficient given in Table 4 with  $S_{gf}^* = kS_{gf}$ )**

Contaminant	PVC (30 mil) aqueous results			PVC (30 mil) vapour results				
	$D_g \times 10^{13}$ (m <sup>2</sup> /s)	$S_{gf}$ (-)	$P_g \times 10^{10}$ (m <sup>2</sup> /s)	$D_g \times 10^{13}$ (m <sup>2</sup> /s)	$S_{gf}$ (-)	$P_g \times 10^{10}$ (m <sup>2</sup> /s)	$S_{gf}^*$ (-)	$P_g^* \times 10^{10}$ (m <sup>2</sup> /s)
Benzene	10.0	130	1.3	9.0	100	0.9	22	0.2
Toluene	9.3	385	3.6	9.0	325	2.9	84	0.8
Ethylbenzene	8.0	975	7.8	8.0	850–890	6.8	260–270	2.1
<i>m&amp;p</i> -Xylenes	7.0	1075	7.5	7.0	1000	7.0	290	2.0
<i>o</i> -Xylenes	5.0	935	4.7	5.0	900	4.5	180	0.9

**Table 7. Inferred partitioning, diffusion and permeation coefficients of 30 mil LLDPE geomembranes from diffusion tests in the aqueous and vapour phase. Crystallinity 38.79%. For vapour phase tests,  $S_{gf}$  and  $P_g$  are calculated related to the concentration in the aqueous phase for direct comparison with the aqueous phase test results.  $S_{gf}^*$  and  $P_g^*$  are relative to the concentration in the vapour phase in these tests (the two are related by the Henry's coefficient given in Table 4 with  $S_{gf}^* = kS_{gf}$ )**

Contaminant	LLDPE (30 mil) aqueous results			LLDPE (30 mil) vapour results				
	$D_g \times 10^{13}$ (m <sup>2</sup> /s)	$S_{gf}$ (-)	$P_g \times 10^{10}$ (m <sup>2</sup> /s)	$D_g \times 10^{13}$ (m <sup>2</sup> /s)	$S_{gf}$ (-)	$P_g \times 10^{10}$ (m <sup>2</sup> /s)	$S_{gf}^*$ (-)	$P_g^* \times 10^{10}$ (m <sup>2</sup> /s)
Benzene	3.0–5.0	200	0.6–1.0	5.0	200	1.0	44	0.2
Toluene	4.0–5.0	400	1.6–2.0	5.0	300	1.5	77	0.4
Ethylbenzene	3.5	450	1.6	3.5	400	1.4	122	0.4
<i>m&amp;p</i> -Xylenes	3.0	475	1.4	3.5	425	1.5	123	0.4
<i>o</i> -Xylenes	2.5	440	1.1	3.0	400	1.2	80	0.2

are similar to results presented in this study. In contrast, the sorption values of 1160 for toluene and 39 for *m*-xylene through PVC, obtained by Park *et al.* (1995), varied greatly from this study's results. Park *et al.* (1995) state that the constant values for partition and diffusion coefficients are not adequate to model the transport process as theoretical curves did not always fit their experimental data.

Xiao *et al.* (1997b) also investigated diffusion and permeation through a 1.0 mm thick PVC geomembrane. The tests were run at a higher temperature (30°C) and higher initial concentration, to decrease the testing period, using a gravitational method and an open loop system where constant inert gas flow is permeated through a double compartment cell directly to a gas chromatographer for analysis of contaminant concentrations downstream of the geomembrane. This method is not as representative of landfill conditions in that the gas flow creates a pressure driven system for contaminant migration.

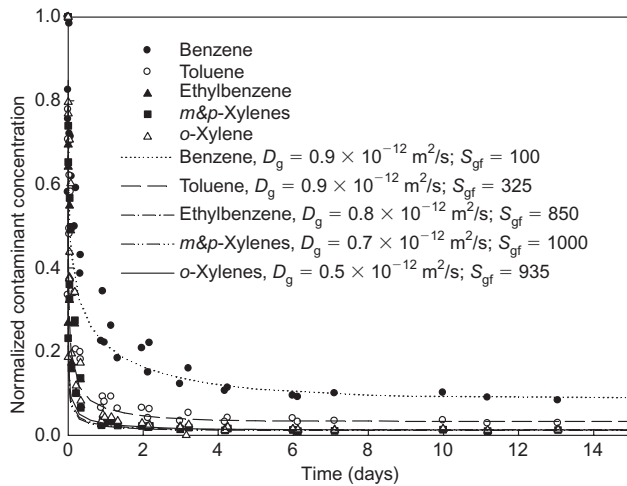
Aminabhavi and Naik (1998, 1999) investigated diffusion through a 1.06 mm thick LLDPE geomembrane using immersion sorption test, which physically measured the weight gain of contaminants into the geomembrane until equilibrium was reached, and immersion swelling tests measuring the change in volume of geomembranes until equilibrium. Diffusion and permeation coefficients were

calculated by fitting theoretical curves to the experimental data from sorption tests. This is not an accurate method of establishing diffusion and permeation coefficients as results are solely based on partitioning. In addition, the immersion sorption and swelling methods, where contaminants penetrate on both sides of the geomembrane, do not reflect actual landfill conditions where leachate and landfill gas penetrate only one side of the geomembrane and then diffuse through.

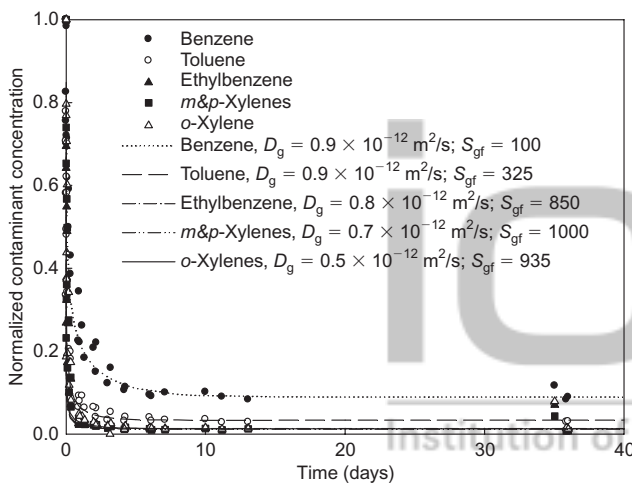
#### 4.4. Vapour diffusion tests

Vapour diffusion tests showed similar results to the aqueous tests. Equilibrium in the source was reached after 6–7 days. In Figure 6, theoretical curves are plotted with experimental data of the normalized concentrations in the source. Vapour diffusion tests require rigorous monitoring for leaks as gas can escape easily if the septum becomes punctured over time after repeated samplings. Therefore, some tests were continued beyond the established equilibrium to monitor the cells for leaks. Figure 7 shows the vapour concentrations decreased in the source and maintained equilibrium for the duration of the 36-day sampling period.

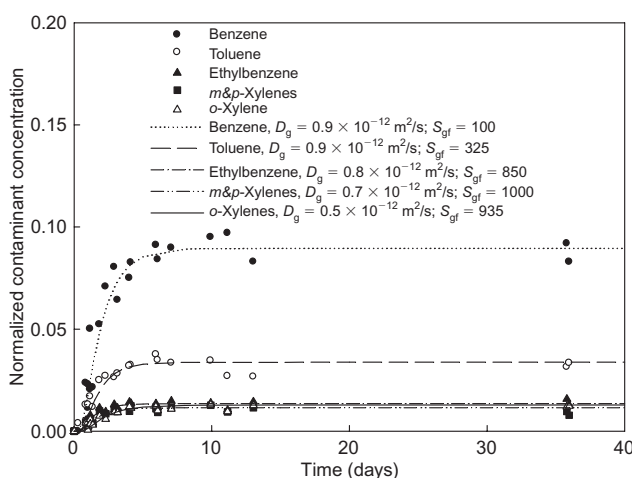
Vapour diffusion tests followed a similar trend as the aqueous tests. Concentrations for *m&p*-xylenes decreased the greatest, followed by *o*-xylene, ethylbenzene, toluene and benzene. Benzene increased in the receptor to 9% of



**Figure 6. Contaminant concentration changes in the source with time during vapour diffusion tests for a 0.76 mm (30 mil) PVC geomembrane**



**Figure 7. Contaminant concentration changes in the source with time during vapour diffusion tests for a 0.76 mm (30 mil) PVC geomembrane**



**Figure 8. Contaminant concentration changes in the receptor with time during vapour diffusion tests for a 0.76 mm (30 mil) PVC geomembrane**

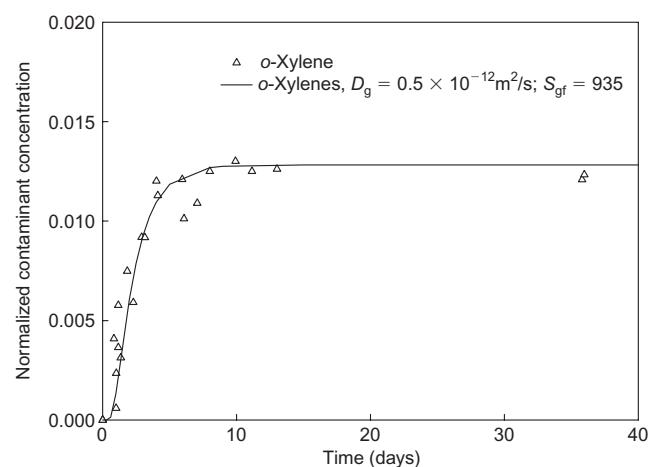
the original concentration. Figure 8 shows the normalized concentrations of contaminants in the receptor cell. The concentrations of *o*-xylene, *m&p*-xylenes and ethylbenzene in the receptor cell are low in comparison with benzene and toluene. These three contaminants have similar diffusion profiles and Figure 9 shows a detailed profile of the contaminant *o*-xylene in the receptor cell.

Theoretical curves obtained with POLLUTEv7 are plotted on Figures 6–9 and correlate well with the experimental data. The partitioning and permeation coefficients for contaminants in the vapour tests were calculated from these curves with respect to the concentrations in the aqueous phase. They allow direct comparison with the aqueous phase diffusion tests and were then converted to those with respect to the vapour phase. Thus for the vapour phase diffusion tests, Table 6 shows the diffusion coefficient for PVC as well the partitioning and permeation coefficients ( $S_{gf}$  and  $P_g$ ) with respect to the aqueous phase concentrations and the partitioning and permeation coefficients ( $S_{gf}^*$  and  $P_g^*$ ) with respect to the vapour phase concentrations.

Results for the vapour diffusion through the LLDPE geomembrane were closely related to the aqueous phase diffusion profile. The results of both phases are presented in Table 7.

#### 4.5. Comparing aqueous and vapour diffusion tests

Diffusion coefficients obtained from the vapour and aqueous phase diffusion tests were essentially identical. This supports the original hypothesis that once the chemical compound is in the polymer matrix, the source or receiving medium has no bearing on its transport. Relative to the concentration in the aqueous phase, there is a small variation in the partitioning parameters,  $S_{gf}$ , for contaminants in the vapour phase versus the aqueous phase. Values of  $S_{gf}$  from the vapour phase tests were slightly lower than those from the aqueous phase tests but generally very similar. This result may also be related to the presence of water vapour which adheres to the geomembrane in the vapour phase experiments. It is possible that in the absence of water vapour there would



**Figure 9. Concentration changes of *o*-xylene in the receptor with time during vapour diffusion tests for a 0.76 mm (30 mil) PVC geomembrane**

be a more significant difference between partitioning in vapour and aqueous phase tests, however these tests are considered to represent the situation likely in a landfill where the gas will have a high water vapour content.

## 5. CONCLUSIONS

The effectiveness of PVC and LLDPE geomembranes as barriers to the diffusion of VOC contaminants has been examined for 0.76 mm thick geomembranes. If identical material is used for geomembranes of different thickness then the same diffusion coefficients could be used irrespective of thickness. The different thickness would be considered in modelling diffusive flux of contaminant through the geomembrane and, other things being equal, the mass flux will be less the thicker the geomembrane. However, even if the same resin is used, differential cooling of geomembranes of different thicknesses could result in some difference in the crystallinity of LLDPE and this could have some effect on the diffusion coefficient.

The diffusion coefficients were found to be effectively identical for the aqueous and vapour phase tests and ranged between  $5.0 \times 10^{-13}$  and  $10 \times 10^{-13}$  m<sup>2</sup>/s for PVC and between  $2.5 \times 10^{-13}$  and  $5.0 \times 10^{-13}$  m<sup>2</sup>/s for LLDPE. These diffusion coefficients are two to three orders of magnitude lower than for typical clay liners (but so too is the thickness). The partitioning coefficients,  $S_{gf}$ , were ascertained from laboratory sorption tests. It was found that  $S_{gf}$  was higher for xylenes and ethylbenzene than toluene and benzene. Results from this study can be used to predict the rates of diffusion of liquid and vapour phase VOC contaminants through these geomembranes employed in barrier systems or final covers in landfill designs and hence will allow a quantitative comparison of the performance of different barrier systems in controlling VOC migration. Since there is a paucity of data in literature for similar vapour-phase migration of BTEX through PVC or LLDPE geomembranes, the results from this study are thought to be useful for building a database of diffusion parameters through geomembranes specific to landfill gas migration.

## NOTATIONS

Basic SI units are given in parentheses.

$c_g$	contaminant concentration in the geomembrane (kg/m <sup>3</sup> )	$c_{rs}(t)$	contaminant concentration in the receptor at time $t$ (kg/m <sup>3</sup> )
$c'_g$	contaminant concentration in the geomembrane (kg/m <sup>3</sup> )	$c_{r0}$	initial contaminant concentration in the receptor (kg/m <sup>3</sup> )
$c_{gF}$	final concentration of the contaminant in the geomembrane at equilibrium (kg/m <sup>3</sup> )	$c_{ss}(t)$	contaminant concentration in the source at time $t$ (kg/m <sup>3</sup> )
$c_f$	concentration in the source solution (either gas or liquid) (kg/m <sup>3</sup> )	$c_{s0}$	initial contaminant concentration in the source (kg/m <sup>3</sup> )
$c_{f0}$	initial contaminant concentration in solution (kg/m <sup>3</sup> )	$D_g$	diffusion coefficient (m <sup>2</sup> /s)
$c_{fF}$	final contaminant concentration in solution (kg/m <sup>3</sup> )	$D_{g0}$	diffusion coefficient constant (m <sup>2</sup> /s)
		$E_d$	activation energy of diffusion (J)
		$E_p$	activation energy of permeation (J)
		$f$	mass flux (kg/m <sup>2</sup> per t)
		$f_{rs}(\tau)$	mass flux of contaminant kg/m <sup>2</sup> per t out of the geomembrane with time $\tau$ (kg/m <sup>2</sup> per t)
		$f_{ss}(\tau)$	mass flux of contaminant into the geomembrane with time $\tau$ (kg/m <sup>2</sup> per t)
		$H_{rs}$	reference height of the receptor solution reservoir (m)
		$H_{ss}$	reference height of the source solution reservoir (m)
		$k$	Henry's law constant (dimensionless)
		$K_{ow}$	octanol-water partitioning coefficient (dimensionless)
		$M_{s0}$	initial mass of the contaminant in solution (kg)
		$M_{sF}$	final mass of the contaminant in solution (kg)
		$M_{sF}^*$	final mass of the contaminant in vapour phase (kg)
		$M_g$	initial mass of the geomembrane sample (kg)
		$M_{gF}$	mass contained in the geomembrane (kg)
		$P_g$	permeation coefficient relative to the aqueous phase (m <sup>2</sup> /s)
		$P_g^*$	permeation coefficient relative to the vapour phase (m <sup>2</sup> /s)
		$P_{g0}$	permeation coefficient constant (m <sup>2</sup> /s)
		$R$	gas constant (J/kmol per K)
		$S_{gf}$	partitioning coefficient into geomembrane relative to concentrations in aqueous phase (dimensionless)
		$S_{gf}^*$	partitioning coefficient into geomembrane relative to concentrations in vapour phase (dimensionless)
		$S_{gf0}$	partitioning coefficient constant (dimensionless)
		$S'_{gf}$	partitioning coefficient out of geomembrane into receiving medium (dimensionless)
		$t$	time (s)
		$T$	time (s)
		$V_{f0}$	initial solution volume (m <sup>3</sup> )
		$V_{fF}$	final solution volume (m <sup>3</sup> )
		$z$	represents the distance parallel to the direction of transport (m)
		$\rho_g$	geomembrane density (kg/m <sup>3</sup> )
		$\Delta H_s$	heat of solution of the contaminant inside the polymer (kJmol <sup>-1</sup> )
		$\tau$	time (s).

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