

Permeation of BTEX through Unaged and Aged HDPE Geomembranes

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Abstract: The effects of aging of high-density polyethylene (HDPE) geomembranes on the diffusion and partitioning of a group of volatile organic compounds (VOCs) are examined. Two different 1.5 mm thick HDPE geomembranes were aged in the laboratory at 85°C by immersing in a synthetic leachate for up to 32 months. The results of partitioning and diffusion tests performed at room temperature on both unaged and aged geomembranes using a dilute aqueous solution containing four VOCs commonly found in landfill leachates [benzene, toluene, ethylbenzene, and xylenes (BTEX)] are reported. The diffusion and partitioning coefficients decreased with increased aging. The calculated permeation coefficients decreased by 36–62% after aging the geomembrane for about 10–32 months. This decrease in diffusion, partitioning, and permeation coefficients is related to the increase in geomembrane crystallinity during aging. A relationship between partitioning, diffusion, and permeation coefficients with the geomembrane crystallinity is established and could potentially be used to evaluate the migration of VOCs through HDPE geomembranes. Aging of HDPE geomembrane did not increase diffusive transport of organic contaminants.

DOI: 10.1061/(ASCE)GT.1943-5606.0000056

CE Database subject headings: Geomembranes; Aging; Crystal growth; Volatile organic chemicals; Polyethylene.

Introduction

High-density polyethylene (HDPE) geomembranes have been widely used as a component of modern composite landfill liner systems because of their excellent resistance to the advective flow of leachate, resistance to chemical attack, and the availability of effective seaming techniques (Haxo 1990; Eith and Koerner 1997) however despite their wide use there are still a number of issues that need to be addressed concerning their use in composite landfill liners (Rowe 2005; Brachman et al. 2008a,b; Saidi et al. 2008). One of these issues relates to the potential for contaminants to diffuse through intact HDPE geomembranes. A wide range of organic and inorganic compounds are found in municipal solid waste landfill leachate (Kim et al. 1995; Rügge et al. 1995; Joo et al. 2004; Rowe et al. 2004). When used as part of a composite liner, HDPE geomembranes have been shown to be an excellent barrier to the advective-diffusive migration of inorganic and ionic contaminants (Rowe et al. 1996; Rowe 2005). However, volatile organic compounds (VOCs) have been shown to diffuse through an intact HDPE geomembrane (Park and Nibras 1993; Prasad et al. 1994; Rowe et al. 1995; Fong et al. 1998; Rowe 1998, 2005; Sangam and Rowe 2001, 2005; Joo et al. 2004, 2005; Chao et al. 2006, 2007). Thus, it is important to consider the diffusive migration of VOCs through HDPE geomembrane when designing landfill liner systems.

The mass transfer of organic contaminants through an HDPE geomembrane involves three key mechanisms (Haxo and Lahey 1988; Park and Nibras 1993; Prasad et al. 1994; Park et al. 1996; Sangam and Rowe 2001, 2005): (1) partitioning between the inner surface of the geomembrane and the medium containing the organic compound (adsorption); (2) diffusion through the geomembrane; and (3) partitioning between the outer surface of the geomembrane and the outer medium (desorption). These transport mechanisms are generally influenced by various factors, for example: (1) density, crystallinity, thickness, degree of cross-linking, and chain rigidity of the polymer; (2) molecular weight, molecular volume, shape, polarity, and initial concentration of the compound; (3) interaction between the polymer and the organic compound; and (4) temperature (Rogers 1985; Naylor 1989; Sangam and Rowe 2001, 2005; Chao et al. 2006). Among these factors the crystallinity of the polymer is considered to be an important factor, since the diffusion of organic compounds occurs through the amorphous region of the semicrystalline HDPE geomembrane. Studies conducted by Michaels and Parker (1959), Michaels and Bixler (1961), and Michaels et al. (1963) have shown that the diffusion coefficients of different gases (e.g., helium, oxygen, methane, ethane, propane, propylene etc.) decreased with the increase of polymer crystallinity. For example, for propane gas the diffusion coefficients were 3.1×10^{-11} , 1.1×10^{-11} , and 0.25×10^{-11} m²/s, respectively, when the crystallinities of the polymers were 29, 43, and 77% (Michaels and Bixler 1961).

Although a number of investigators have examined the transport of VOCs through virgin HDPE geomembranes as cited above, there is a paucity of research in the literature relating to the diffusion of VOCs through aged HDPE geomembranes. Rowe et al. (2003) examined the partitioning and diffusion of VOCs through a 1.5 mm geomembrane (GM) removed from a municipal solid waste landfill leachate lagoon after 14 years. This GM, with a crystallinity of 65–68%, had permeation coefficients at room temperature of between 1.4×10^{-12} m²/s and 1.8×10^{-11} m²/s

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Note. This manuscript was submitted on June 23, 2008; approved on December 2, 2008; published online on February 21, 2009. Discussion period open until January 1, 2010; separate discussions must be submitted for individual papers. This paper is part of the *Journal of Geotechnical and Geoenvironmental Engineering*, Vol. 135, No. 8, August 1, 2009. ©ASCE, ISSN 1090-0241/2009/8-1130–1140/\$25.00.

Table 1. Selected Properties of Geomembranes

Properties	Method	Unit	Geomembrane #1 (GM1)			Geomembrane #2 (GM2)		
			Time=0	Time =13 months ^a	Time =32 months ^a	Time=0	Time =10 months ^a	Time =25 months ^a
Thickness (nominal)	ASTM D5199	mm	1.5	1.5	1.5	1.5	1.5	1.5
Std-OIT	ASTM D3895	min	174	0.92	0.89	135	1.41	1.53
HP-OIT	ASTM D5885	min	903	67	63	244	81	79
Crystallinity	ASTM E794	%	38	46	54	48	55	61
MI	ASTM D1238 ^b	g/10 min	12.6	11.1	10.9	14.3	13.6	12.0
Density	ASTM D792	g/cc	0.946	—	—	0.947	—	—
Tensile properties	ASTM D6693	—	—	—	—	—	—	—
Strength at yield	—	kN/m	28.5	31.9	33.4	27.8	31.5	30.5
Strength at break	—	kN/m	60.8	59.0	52.9	44.8	42.5	30.0
Strain at yield	—	%	23.5	21.3	21.5	21.2	21.8	22.6
Strain at break	—	%	945	922	859	823	764	640

^aAged at 85°C.^bUsing 21.6 kg load.

for seven VOCs (dichloromethane, 1,2-dichloroethane, trichloroethylene, benzene, toluene, ethylbenzene, and xylenes). However there was no virgin material to compare with the aged GM. Joo et al. (2004) investigated the transport of VOCs in aqueous solution through both virgin and 5-year aged 2.0 mm HDPE geomembranes. The aged geomembrane was exhumed from a landfill after 5 years of service. The properties of the aged geomembrane (e.g., density, oxidative induction time, carbon black content, puncture resistance, and tensile elongation properties) were almost the same as the virgin geomembrane. The results from batch immersion tests showed no significant changes in the partitioning coefficients of the contaminants examined although the diffusion coefficients were 23% lower for aged geomembrane than the unaged geomembrane. The permeation coefficients at room temperature ranged from 6.1×10^{-12} to 7.4×10^{-11} m²/s for the VOCs examined (benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene, chloroform, methylene chloride, tetrachloroethylene, 1,1,1-trichloro-ethylene). Unfortunately, the crystallinity of the geomembrane was not reported in this paper.

It has been shown from several recent laboratory studies (Sangam 2001; Rowe et al. 2008; Rowe and Rimal 2008) that the crystallinity of the HDPE geomembrane increases with aging however until now, the effect of aging and crystallinity on diffusion has not been examined. Thus the primary objective of this study is to examine the effect of accelerated geomembrane aging on the diffusion of VOCs through HDPE geomembranes at room temperature. A secondary objective is to establish an empirical

relationship between partitioning, diffusion, and permeation coefficients with geomembrane crystallinity. The present paper substantially expands on the results reported by Islam and Rowe (2008).

Experimental Procedure

HDPE Geomembranes

Two different 1.5 mm HDPE geomembranes were examined. One geomembrane (manufactured by GSE Lining Inc., Texas) is designated as GM1 and the other geomembrane (manufactured by Solmax International, Quebec) is designated as GM2 for this paper. Tests were conducted on both unaged and aged samples at room temperature (i.e., 22°C). Aging of geomembrane was carried out at 85°C by immersing in a synthetic leachate. The leachate was comprised of trace metals and surfactant in distilled water. For geomembrane GM1, the tests were conducted on unaged, 13-, and 32-month aged samples. For geomembrane GM2, the tests were conducted on unaged, 10-, and 25-month aged specimens. Table 1 shows the key properties of the geomembranes tested. Based on considerations of the depletion of antioxidants and the change in tensile break properties at different temperatures, the equivalent aging durations at 20°C were estimated to be 65–200 years for samples aged for 10–13 months and 440–685 years for samples aged for 25–32 months at 85°C

Table 2. Selected Properties^a of Organic Contaminants Tested

Contaminants	Molecular weight (g/mol)	Density (g/cm ³)	Molar volume (cm ³)	Aqueous solubility ^b (mg/L)	log <i>K</i> _{ow} ^c	Boiling temperature (°C)
Benzene	78.11	0.8765	89.11	1,780	2.13	80.1
Toluene	92.14	0.8669	106.28	515	2.79	110.6
Ethylbenzene	106.17	0.8670	122.46	152	3.13	136.2
<i>m</i> -xylene	106.17	0.8642	122.85	162	3.20	138.0
<i>p</i> -xylene	106.17	0.8802	122.47	156	3.18	138.3
<i>o</i> -xylene	106.17	0.8811	120.62	152	3.13	144.0

^aMontgomery and Welkom (1990) and Sangam and Rowe (2001).^bAt 20°C.^c*n*-octanol/water coefficient.

Table 3. Partitioning Coefficients, S_{gf} , from Immersion Tests for Both Unaged and Aged Geomembrane GM1 (All Numbers Rounded to Nearest 5)

Contaminants	Unaged GM, time=0 month crystallinity=38%			Aged GM, time=13 months crystallinity=46%			Aged GM, time=32 months crystallinity=54%		
	$S_{gf}(-)$			$S_{gf}(-)$			$S_{gf}(-)$		
	Uncorrected	Corrected	Modeled ^a	Uncorrected	Corrected	Modeled ^a	Uncorrected	Corrected	Modeled ^a
Benzene	75	55	60	65	45	45	45	25	30
Toluene	160	125	130	125	100	100	95	70	75
Ethylbenzene	395	315	340	375	290	300	285	215	245
<i>m&p</i> -xylenes	505	380	420	415	305	345	305	220	255
<i>o</i> -xylene	360	280	305	350	275	280	265	210	235

^aConsidering mass loss in modeling.

(Islam 2009). At 35°C the equivalent aging durations were estimated to be 20–45 years for samples aged for 10–13 months and 100–145 years for samples aged for 25–32 months at 85°C (Islam 2009).

Organic Compounds

Four volatile aromatic hydrocarbons: benzene, toluene, ethylbenzene, and xylenes (BTEX) commonly found in landfill leachate (Rowe 1995; Rowe et al. 2004) were examined. Laboratory grade BTEX standards were purchased from Sigma-Aldrich, Mississauga, Ont., Canada. Table 2 shows the key properties of these chemicals. Tests were carried out by diluting the standard solution with deionized distilled water (DDW). The initial concentrations of contaminants were in the range from 2.0 to 2.6 mg/L.

Analytical Methods

A Varian gas chromatography/mass spectrometer (GC/MS) equipped with a 30 m × 0.25 mm ID × 0.25 μm DB-5 fused silica capillary column was used to analyze BTEX samples. Helium was used as carrier gas with a flow rate of 1.3 mL/min. The column temperature was programmed to 35°C initially to hold for 0.5 min then rose to 200°C at two ramps of 10°C/min to 100°C and 50°C/min to 200°C with a final hold time of 3 min. The sample was extracted in headspace mode from 2 mL vials in 5 min using a 8200 CX Varian autosampler equipped with 100 μm polydimethylsiloxane solid phase micro extraction fiber and the desorption was done in 1 min. The volume of headspace in the vial was 1.2 mL. The chromatographs were quantified using Varian Saturn 2000 chromatography software (Version 5.05). BTEX concentrations were quantified based on the calibration curves that were produced through analysis of known stan-

dards. The performance of the GC/MS was checked each time samples were tested by running duplicates, a lab blank, and a known standard sample and was found to be within the 95% of the target value.

Test Procedures

Partitioning Test

Partitioning experiments were performed at room temperature (i.e., 22 ± 1°C) in 250 mL glass serum bottles equipped with screw-tight Teflon lined caps. HDPE geomembrane specimens (approximately 15 mm × 125 mm) were washed with DDW and dried in air and their masses were recorded before placing into the glass serum bottles. The bottles were filled completely with dilute aqueous BTEX solution and sampled immediately to get the initial concentrations. The concentrations of contaminants were monitored with time until the equilibrium concentration was reached. The partitioning coefficient of each contaminant was calculated following the method described by Sangam and Rowe (2001) and briefly described as follows. When the equilibrium is reached, the mass balance equation in the geomembrane-aqueous solution system can be written as

$$M_{s0} = M_{sF} + M_{gF} + M_R \quad (1)$$

where M_{s0} and M_{sF} = initial and final mass of contaminant in the solution respectively [M]; M_{gF} = mass of contaminant uptake by geomembrane [M]; and M_R = mass of contaminant removed during sampling events [M]. By converting the masses in terms of their respective concentrations and volumes, Eq. (1) can be expressed as follows:

Table 4. Partitioning Coefficients, S_{gf} , from Immersion Tests for Both Unaged and Aged Geomembrane GM2 (All Numbers Rounded to Nearest 5)

Contaminants	Unaged GM, time=0 month crystallinity=48%			Aged GM, time=10 months crystallinity=55%			Aged GM, time=25 months crystallinity=61%		
	$S_{gf}(-)$			$S_{gf}(-)$			$S_{gf}(-)$		
	Uncorrected	Corrected	Modeled ^a	Uncorrected	Corrected	Modeled ^a	Uncorrected	Corrected	Modeled ^a
Benzene	60	40	45	45	30	35	40	25	25
Toluene	100	75	90	90	65	80	75	50	65
Ethylbenzene	345	275	305	290	220	265	265	200	240
<i>m&p</i> -xylenes	380	280	365	300	215	285	280	200	250
<i>o</i> -xylene	305	240	275	260	205	240	240	185	225

^aConsidering mass loss in modeling.

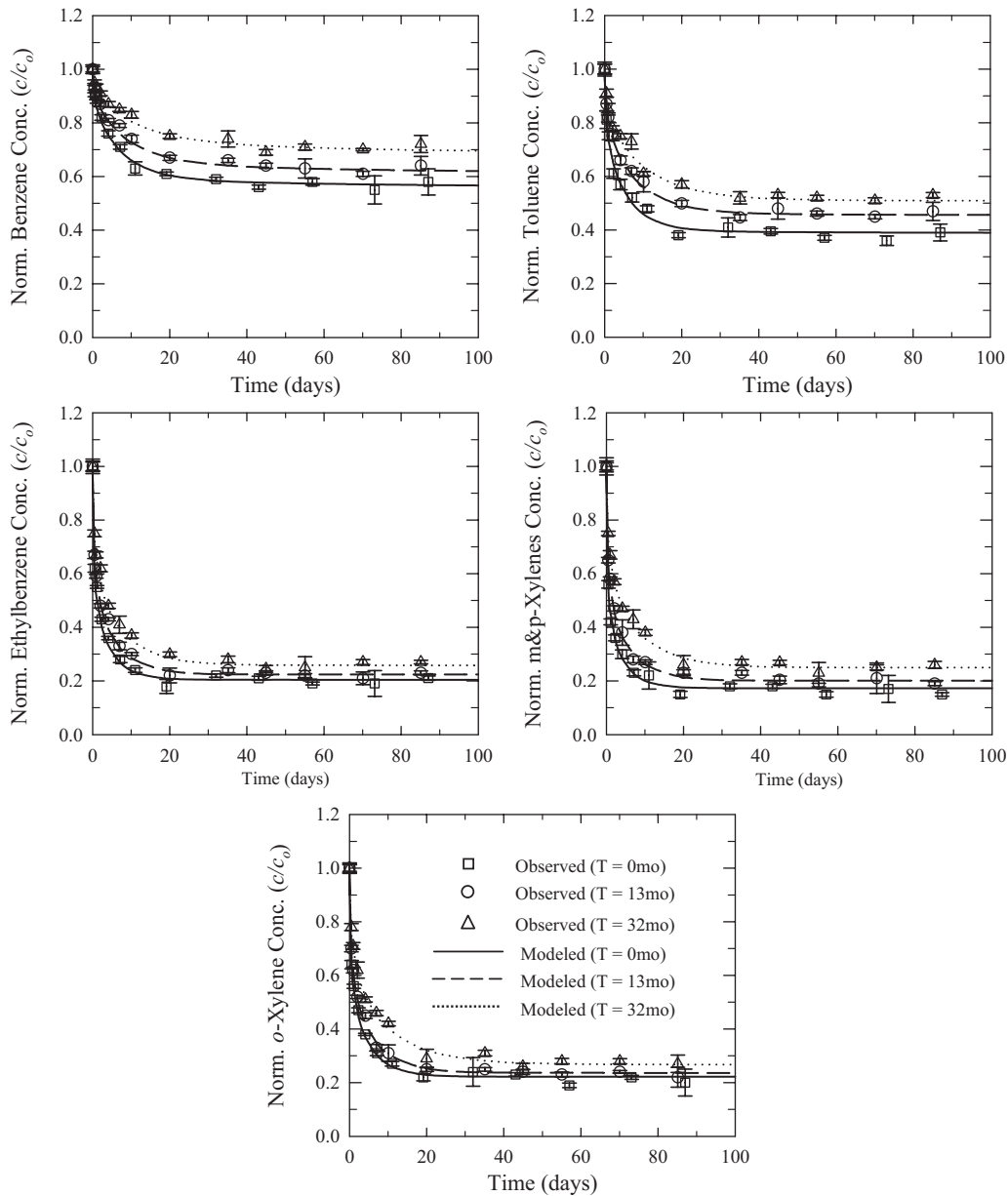


Fig. 1. GMI partitioning tests: variation in observed and modeled concentrations of benzene, toluene, *m&p*-xylenes, and *o*-xylene with time for both unaged and aged geomembranes

$$c_{f0}V_{f0} = c_{fF}V_{fF} + \frac{M_g}{\rho_g}c_{gF} + \sum V_i c_i \quad (2)$$

where c_{f0} and c_{fF} =respectively, initial and final concentrations of the solution [ML^{-3}]; V_{f0} and V_{fF} =respectively, initial and final volume of the solution [L^3]; ρ_g =geomembrane density [ML^{-3}]; M_g =initial mass of geomembrane [M]; c_{gF} =final equilibrium concentration in geomembrane [ML^{-3}]; V_i =volume of solution removed at each sampling event [L^3]; and c_i =concentration of contaminant at each sampling event [ML^{-3}]. The concentration of contaminant in the geomembrane and solution at equilibrium can be written as follows:

$$c_{gF} = S_{gf}c_{fF} \quad (3)$$

where S_{gf} =partitioning coefficient [-] and is dependent on temperature, fluid, geomembrane, and contaminant of interest. The

partitioning coefficient can be obtained by substituting Eq. (3) in Eq. (2) as shown in the following:

$$S_{gf} = \frac{[c_{f0}V_{f0} - c_{fF}V_{fF} - \sum V_i c_i] \rho_g}{M_g c_{fF}} \quad (4)$$

The uncorrected S_{gf} was calculated directly from Eq. (4) assuming no mass loss to the glass. It is expected that some contaminants will be adsorbed on to glass bottles and caps. To account for this loss of contaminant from solution, control tests were conducted using similar glass serum bottles having the same concentration of contaminants as in the partitioning test. Sampling for control tests was done at the same time as for the partitioning tests were sampled and the equilibrium concentration obtained from control test was used to calculate the corrected S_{gf} values. Since the amount of partitioning to the glass is likely to be less when there is geomembrane present than when it is not

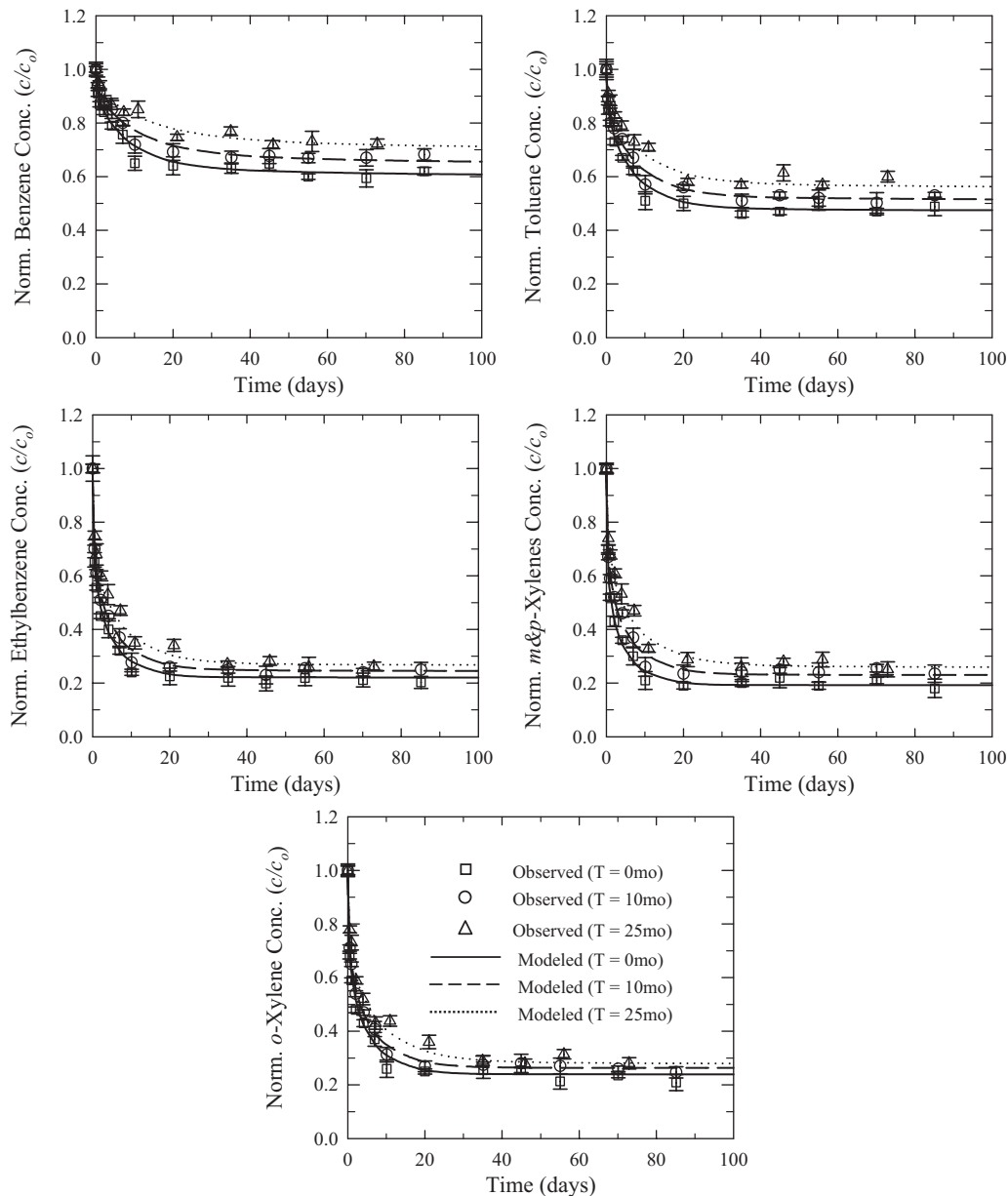


Fig. 2. GM2 partitioning tests: variation in observed and modeled concentrations of benzene, toluene, *m&p*-xylenes, and *o*-xylene with time during partitioning tests on both unaged and aged geomembranes

present (due to preferential partitioning to the GM) the actual partitioning coefficient is expected to lie between the corrected and uncorrected values given in Tables 3 and 4.

Diffusion Test

Diffusion tests were carried out at room temperature in double compartment glass cells with the source (70 mm diameter \times 100 mm high) and receptor (70 mm diameter \times 30 mm high) reservoirs separated by the geomembrane. The same types of cell have been used by other researchers (Haxo and Lahey 1988; Rowe et al. 1995, 1996; Sangam and Rowe 2001, 2005) in conducting diffusion tests. A two-part epoxy adhesive (type 2216 B/A, 3M St. Paul, Minn.) was used to seal the geomembrane with the source and receptor compartments and cured for 7 days. After curing, the outside of the geomembrane-compartment joint was covered with a thick silicone sealant and dried in air at room temperature for 7 days for hardening of the silicone. The receptor

compartment was filled first with DDW then the source compartment was filled with dilute aqueous BTEX solution and sampled immediately to obtain the initial concentrations. Liquid samples were taken from the source and receptor compartments at regular time intervals and analyzed using GC/MS.

The permeation of organic compounds through an HDPE geomembrane is primarily a diffusion mechanism and can be modeled by Fick's first law as follows:

$$f = -D_g \frac{dc_g}{dz} \quad (5)$$

where f = mass flux or permeation rate per unit area [$\text{ML}^{-2}\text{T}^{-1}$]; D_g = diffusion coefficient of organic compound in the geomembrane [L^2T^{-1}]; c_g = concentration of compound in the geomembrane [ML^{-3}]; and z = distance parallel to the direction of diffusion [L]. The change in contaminant concentration at any

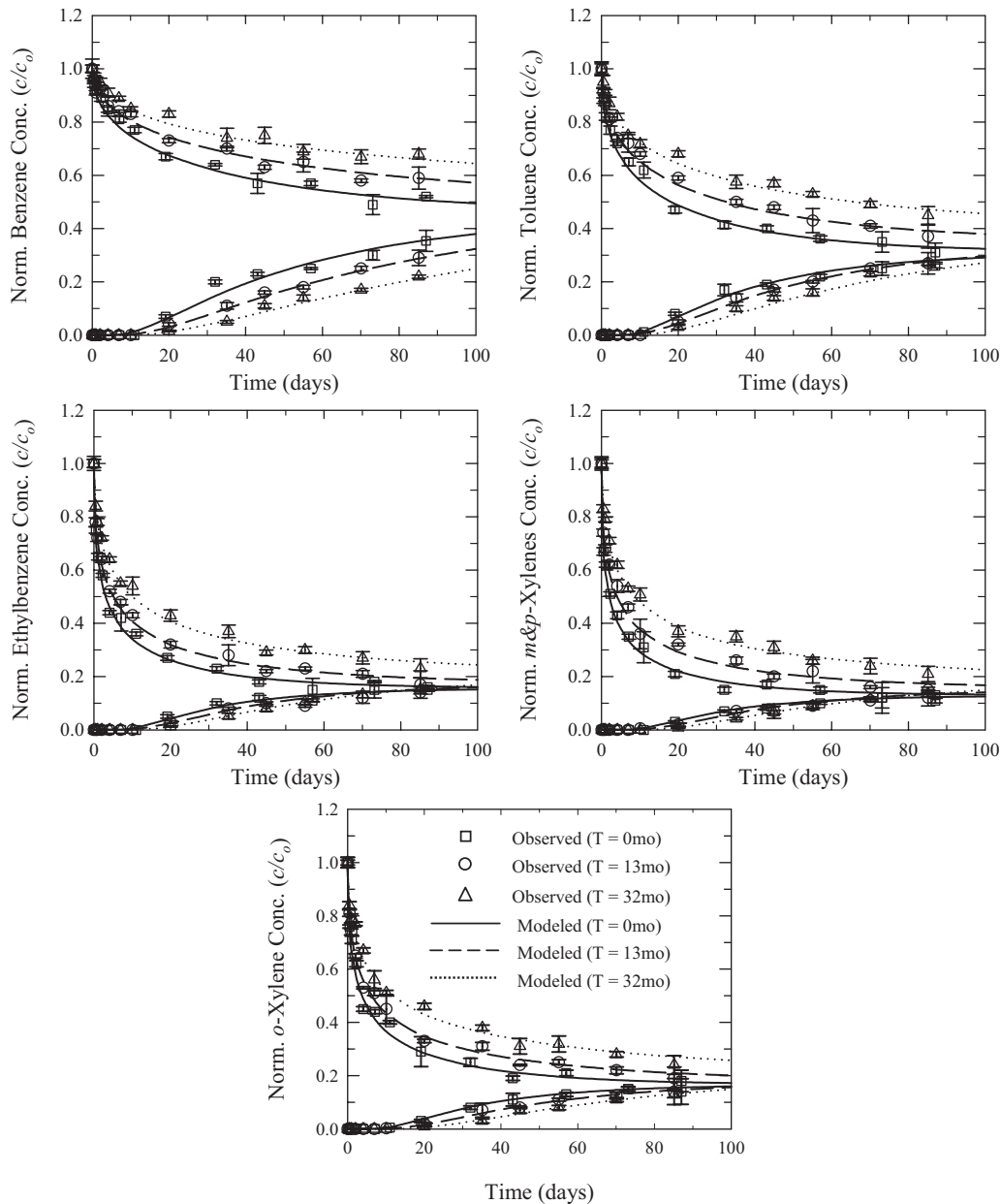


Fig. 3. Diffusion tests on GM1: variation in observed and modeled concentrations of benzene, toluene, *m&p*-xylenes, and *o*-xylene with time during diffusion tests on both unaged and aged geomembranes

point in the geomembrane with time, t is governed by the following differential equation according to Fick's second law:

$$\frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial z^2} \quad (6)$$

When the source and receptor fluids are similar, the flux involved with the migration process can be obtained by substituting Eq. (3) into Eq. (5)

$$f = -D_g \frac{dc_g}{dz} = -S_{gf} D_g \frac{dc_f}{dz} = -P_g \frac{dc_f}{dz} \quad (7)$$

where $P_g (=S_{gf} D_g)$ =permeation coefficient or mass transfer coefficient [$L^2 T^{-1}$]; and $c_f (=c_{ff})$ =equilibrium concentration in the source reservoir [ML^{-3}].

There was a finite mass boundary for both the source and receptor. Considering the mass balance in these closed systems,

the mass of contaminant in the source solution at any time t is equal to the initial mass minus the mass that diffused into the geomembrane and can be expressed as follows:

$$c_{ss}(t) = c_{s0} - \frac{1}{H_{ss}} \int_0^t f_{ss}(\tau) d\tau \quad (8)$$

where $c_{ss}(t)$ =contaminant concentration in the source solution at time t [ML^{-3}]; c_{s0} =initial concentration in the source solution [ML^{-3}]; H_{ss} =reference height of solution in the source (volume of source solution per unit area) [L]; and $f_{ss}(\tau)$ =mass flux of contaminant from the source into the geomembrane at time τ [$ML^{-2}T^{-1}$]. Similarly, the contaminant concentration in the receptor compartment at any time t can be written as follows:

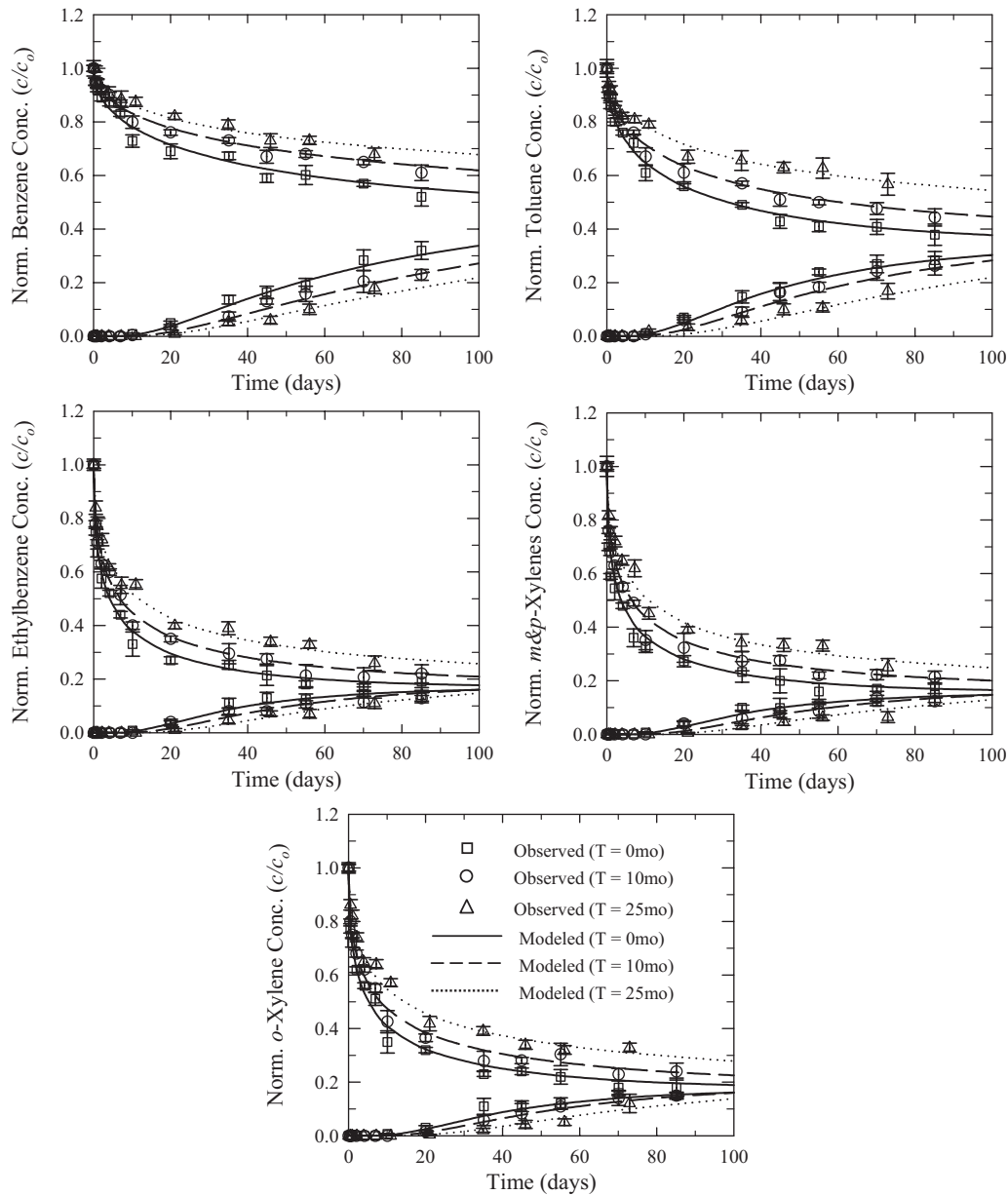


Fig. 4. Diffusion tests on GM2: variation in observed and modeled concentrations of benzene, toluene, *m&p*-xylenes, and *o*-xylene with time during diffusion tests on both unaged and aged geomembranes

$$c_{rs}(t) = c_{r0} + \frac{1}{H_{rs}} \int_0^t f_{rs}(\tau) d\tau \quad (9)$$

where $c_{rs}(t)$ = contaminant concentration in the receptor solution at time t [ML^{-3}]; c_{r0} = initial concentration in the receptor solution [ML^{-3}]; H_{rs} = reference height of solution in the receptor (volume of receptor solution per unit area) [L]; and $f_{rs}(\tau)$ = mass flux of contaminant from the geomembrane into the receptor at time τ [$\text{ML}^{-2}\text{T}^{-1}$].

The diffusion equations were solved by applying the boundary conditions provided in Eqs. (8) and (9) using a finite layer contaminant transport model POLLUTE v7 (Rowe and Booker 2004). The diffusion and partitioning coefficients were estimated by fitting the theoretical concentrations from diffusion equations to the concentrations observed in the source and receptor. Control tests were conducted, to account for the loss during diffusion tests, in the cell similar to the source compartment but with no

geomembrane as described by Krol (2000) and values deduce both with and without a correction for the mass sorbed to glass in the control experiments are reported.

Results and Discussion

Partitioning Test

The changes in BTEX concentrations during the partitioning tests are presented in Figs. 1 and 2, respectively, for the geomembranes GM1 and GM2. The concentrations are plotted as the normalized concentrations relative to the initial concentrations. Each data point represents the average of triplicate concentrations evaluated by GC/MS and the vertical bars represent the standard deviation. Other things being equal, the lower the normalized equilibrium concentration the higher the partitioning coefficient with the order

Table 5. Partitioning (S_{gf}), Diffusion (D_g), and Permeation (P_g) Coefficients from Diffusion Tests on Both Unaged and Aged Geomembrane GM1

Contaminants	Unaged GM, time=0 month crystallinity=38%			Aged GM, time=13 months crystallinity=46%			Aged GM, time=32 months crystallinity=54%			PR ₁ ^a	PR ₂ ^b
	S_{gf} (-)	D_g (10 ⁻¹² m ² /s)	P_g (10 ⁻¹² m ² /s)	S_{gf} (-)	D_g (10 ⁻¹² m ² /s)	P_g (10 ⁻¹² m ² /s)	S_{gf} (-)	D_g (10 ⁻¹² m ² /s)	P_g (10 ⁻¹² m ² /s)		
Benzene	55	0.24	13	45	0.18	7.9	35	0.14	4.9	0.60	0.37
Toluene	125	0.22	28	100	0.18	18	80	0.14	11	0.67	0.41
Ethylbenzene	345	0.18	62	300	0.14	42	230	0.11	25	0.68	0.41
<i>m&p</i> -xylenes	440	0.17	75	350	0.13	46	260	0.10	26	0.61	0.35
<i>o</i> -xylene	320	0.17	54	290	0.12	35	235	0.09	21	0.64	0.39
Average ^c =0.64											0.38

Note: S_{gf} values rounded to nearest 5, D_g , and P_g rounded to two significant digits.

^aPermeation reduction factor, $PR_1 = P_g(13\text{-month aged})/P_g(\text{unaged})$.

^bPermeation reduction factor, $PR_2 = P_g(32\text{-month aged})/P_g(\text{unaged})$.

^cAverage represents the average of PR values for benzene, toluene, ethylbenzene, *m&p*-xylenes, and *o*-xylene.

(highest to lowest S_{gf}) *m&p*-xylenes > ethylbenzene > *o*-xylene > toluene > benzene for both types of geomembrane. A similar trend was observed by Sangam and Rowe (2001, 2005).

Tables 3 and 4 show the calculated partitioning coefficients (S_{gf}) using Eq. (4) with and without considering mass losses for the geomembranes GM1 and GM2, respectively. The losses of contaminants during partitioning tests were 11, 13, 18, 21, and 16%, respectively, for benzene, toluene, ethylbenzene, *m&p*-xylenes, and *o*-xylene. The values of partitioning coefficients (S_{gf}) increased with the increase of hydrophobicity [i.e., with the increase of *n*-octanol/water coefficients ($\log K_{ow}$)] of the contaminants (Table 2). The partitioning coefficients have also shown to increase with the decrease of contaminant aqueous solubilities (Table 2). These results are in accordance with the results obtained by other researchers (Müller et al. 1998; Sangam and Rowe 2001, 2005; Joo et al. 2004, 2005). Another important observation from the results of partitioning tests is that the S_{gf} values of BTEX decreased with the increase of aging durations. For example, for the geomembrane GM1, the corrected S_{gf} values of ethylbenzene for unaged, 13- and 32-month aged GM1 specimens were 320, 290, and 215 respectively (Table 3). Similarly, for the geomembrane GM2, the corrected S_{gf} values of ethylbenzene were 275, 220, and 200, respectively, for unaged, 10- and 25-month aged specimens (Table 4).

Theoretical partitioning curves were generated (shown as lines in Figs. 1 and 2) using the contaminant transport model

POLLUTE and were fitted to the experimental concentrations. Due to the nature of the boundary conditions, both S_{gf} and D_g can uniquely be inferred from the one test (to experimental accuracy) and the value of S_{gf} can be compared with that obtained from the partitioning tests. The modeled S_{gf} values are presented in Tables 3 and 4 for the geomembranes GM1 and GM2, respectively. The modeled S_{gf} values lie between the values obtained from the partitioning tests using Eq. (4).

Diffusion Test

Figs. 3 and 4 show the variations in BTEX concentrations (normalized with respect to the initial concentrations) with time in the source and receptor compartments during diffusion tests for the geomembranes GM1 and GM2, respectively. Similar to the partitioning tests, each data point represents the average of at least triplicate concentrations measured by GC/MS and the bars represent standard deviation. The experimental concentrations were fitted using the finite layer contaminant transport model POLLUTE and are plotted as lines in Figs. 3 and 4. The best-fit curves were obtained by trial and error considering the least summation of square errors between the theoretical and experimental data points. Model predictions considered the loss of contaminants during diffusion tests. The mass losses were 9, 12, 21, 24, and 17% for benzene, toluene, ethylbenzene, *m&p*-xylenes, and *o*-xylene, respectively, during diffusion test. The concentrations

Table 6. Partitioning (S_{gf}), Diffusion (D_g), and Permeation (P_g) Coefficients from Diffusion Tests on Both Unaged and Aged Geomembrane GM2

Contaminants	Unaged GM, time=0 month crystallinity=48%			Aged GM, time=10 months crystallinity=55%			Aged GM, time=25 months crystallinity=61%			PR ₁ ^a	PR ₂ ^b
	S_{gf} (-)	D_g (10 ⁻¹² m ² /s)	P_g (10 ⁻¹² m ² /s)	S_{gf} (-)	D_g (10 ⁻¹² m ² /s)	P_g (10 ⁻¹² m ² /s)	S_{gf} (-)	D_g (10 ⁻¹² m ² /s)	P_g (10 ⁻¹² m ² /s)		
Benzene	50	0.19	9.5	40	0.15	5.7	30	0.13	3.9	0.60	0.41
Toluene	100	0.19	19	80	0.15	12	60	0.11	6.6	0.63	0.35
Ethylbenzene	310	0.16	50	270	0.12	32	230	0.09	21	0.65	0.42
<i>m&p</i> -xylenes	340	0.15	51	290	0.11	32	250	0.08	20	0.63	0.39
<i>o</i> -xylene	295	0.14	41	255	0.11	28	220	0.08	18	0.68	0.44
Average ^c =0.64											0.40

Note: S_{gf} values rounded to nearest 5, D_g and P_g rounded to two significant digits.

^aPermeation reduction factor, $PR_1 = P_g(10\text{-month aged})/P_g(\text{unaged})$.

^bPermeation reduction factor, $PR_2 = P_g(25\text{-month aged})/P_g(\text{unaged})$.

^cAverage represents the average of PR values for benzene, toluene, ethylbenzene, *m&p*-xylenes, and *o*-xylene.

of contaminants in the source decreased with time, whereas the concentrations in the receptor increased as the contaminants diffused through the geomembrane. The final equilibrium concentration is directly related to the partitioning coefficient S_{gf} . The final source concentration increased with the increase of aging duration. For example, for the geomembrane GM1, the concentrations of toluene in the source dropped to about 31, 38, and 45% of the initial concentration by the end of the testing period (i.e., after approximately 85 days) for unaged, 13- and 32-month aged specimens, respectively (Fig. 3).

The diffusion (D_g) and partitioning (S_{gf}) coefficients deduced from the best-fit curves to the diffusion data are presented in Tables 5 and 6 for geomembranes GM1 and GM2, respectively. The diffusion coefficients tend to decrease with increasing contaminant molecular volume (Tables 2, 5, and 6). A similar trend was observed by other researchers (Park and Nibras 1993; Sangam and Rowe 2001, 2005; Joo et al. 2004, 2005). The reason for the lower diffusion coefficient is the higher activation energy required for diffusion of larger molecules (Joo et al. 2004, 2005). The values of D_g decreased with the increased aging durations for both types of geomembranes. For example, the diffusion coefficients (D_g) of toluene for unaged, 13- and 32-month aged geomembrane GM1 were 0.22×10^{-12} , 0.18×10^{-12} , and 0.14×10^{-12} m²/s, respectively (Table 5). Similarly, for GM2 geomembrane the diffusion coefficients of toluene for unaged, 10- and 25-month aged geomembrane were 0.19×10^{-12} , 0.15×10^{-12} , and 0.11×10^{-12} m²/s, respectively (Table 6). Similar to the diffusion coefficients, the values of partitioning coefficients (S_{gf}) also decreased with the increase of aging durations as has been seen in partitioning tests. For example, for the geomembrane GM1, the values of toluene for unaged, 13- and 32-month aged specimens were 125, 100, and 80, respectively. Likewise, for the geomembrane GM2, the S_{gf} values of toluene for unaged, 10- and 25-month aged geomembrane were 100, 80, and 60, respectively. Furthermore, the partitioning coefficients (S_{gf}) obtained from diffusion tests fall within the range of corrected and uncorrected partitioning coefficients from partitioning tests (Tables 3–6). The permeation coefficients (P_g) for both geomembranes, calculated by multiplying respective diffusion (D_g) and partitioning (S_{gf}) coefficients, are also shown in Tables 5 and 6. The calculated permeation coefficients were also found to be lower with the increased aging durations.

It appears that the crystallinity of the geomembrane played an important role in reducing the values of D_g , S_{gf} , and P_g for both geomembranes. The values of D_g , S_{gf} , and P_g were lower for the unaged geomembrane GM2 because of the higher crystallinity of the unaged geomembrane GM2 (i.e., 48%) compared to the unaged geomembrane GM1 (i.e., 38%) (Tables 5 and 6). Fig. 5 shows the variations in D_g and S_{gf} , with geomembrane crystallinity for both geomembranes and Table 7 shows the respective equations of linear regression lines. For P_g the best fit was obtained by fitting least square quadratic lines with the experimental data. An unconstrained linear regression through the test data did not project to zero when crystallinity approached 100% (Islam 2009). However, one might expect them to approach zero when crystallinity is 100% because in the fully crystalline state there would be no amorphous region for diffusion and partitioning to occur; therefore, the regression lines shown in Fig. 5 are forced to pass through zero value when the crystallinity is 100%. Good agreement (with coefficient of determination, $R^2 > 0.95$) between the three coefficients (e.g., D_g , S_{gf} , and P_g) and geomembrane crystallinity was observed (Table 7).

The migration parameters (i.e., D_g , S_{gf} , and P_g) of BTEX

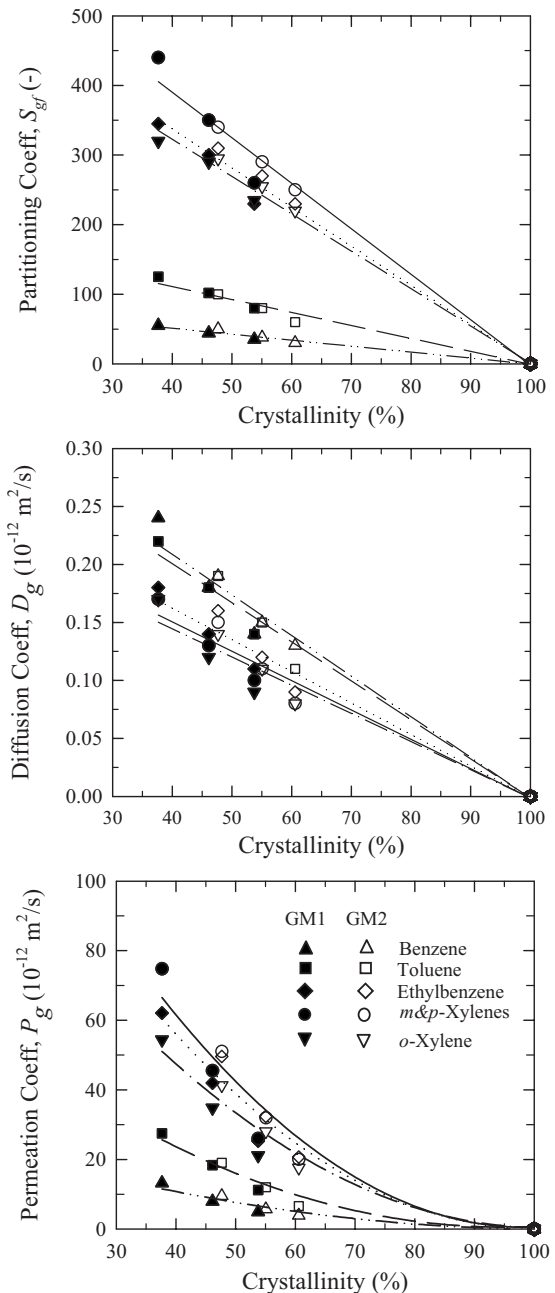


Fig. 5. Variation in partitioning (S_{gf}), diffusion (D_g), and permeation (P_g) coefficients with crystallinity for both GM1 and GM2 considering that the regression lines meet zero at 100% crystallinity

observed by Rowe et al. (2003) are in good agreement with the calculated parameters using the equations described in Table 7 for the crystallinity of the geomembrane examined. For example, for this geomembrane with crystallinity of 67.5%, the observed values of D_g , S_{gf} , and P_g for benzene are 0.12×10^{-12} m²/s, 26, and 3.1×10^{-12} m²/s, respectively, and the corresponding calculated values are 0.11×10^{-12} m²/s, 27, and 3.4×10^{-12} m²/s.

Care should be taken in using the relationships described in Table 7 because the diffusion through HDPE geomembrane depends not only on the crystallinity but also on the tortuosity of the geomembrane (Michaels and Bixler 1961) and the concentration of contaminants (Park et al. 1996). The dependence on tortuosity is discussed in the following section. Thus while Table 7 could be used to obtain preliminary estimates of parameters for an HDPE

Table 7. Relationships between Partitioning (S_{gf}), Diffusion (D_g), and Permeation (P_g) Coefficients with Geomembrane Crystallinity (C) for Regression Lines through Zero at 100% Crystallinity

Contaminants	Partitioning coefficient (S_{gf}) (-)	Diffusion coefficient (D_g) (m^2/s)	Permeation coefficient (P_g) (m^2/s)
Benzene	$S_{gf}=85-0.854C$ $R^2=0.988$	$D_g=3.49 \times 10^{-13}-3.5 \times 10^{-15}C$ $R^2=0.988$	$P_g=2.8 \times 10^{-11}-5.45 \times 10^{-13}C+2.6 \times 10^{-15}C^2$ $R^2=0.956$
Toluene	$S_{gf}=186-1.869C$ $R^2=0.989$	$D_g=3.36 \times 10^{-13}-3.4 \times 10^{-15}C$ $R^2=0.988$	$P_g=7.0 \times 10^{-11}-14.6 \times 10^{-13}C+7.7 \times 10^{-15}C^2$ $R^2=0.949$
Ethylbenzene	$S_{gf}=562-5.618C$ $R^2=0.994$	$D_g=2.71 \times 10^{-13}-2.7 \times 10^{-15}C$ $R^2=0.983$	$P_g=15.6 \times 10^{-11}-31.42 \times 10^{-13}C+15.8 \times 10^{-15}C^2$ $R^2=0.970$
<i>m&p</i> -xylenes	$S_{gf}=652-6.537C$ $R^2=0.991$	$D_g=2.52 \times 10^{-13}-2.5 \times 10^{-15}C$ $R^2=0.977$	$P_g=17.4 \times 10^{-11}-35.22 \times 10^{-13}C+17.9 \times 10^{-15}C^2$ $R^2=0.965$
<i>o</i> -xylene	$S_{gf}=537-5.364C$ $R^2=0.996$	$D_g=2.42 \times 10^{-13}-2.4 \times 10^{-15}C$ $R^2=0.972$	$P_g=12.8 \times 10^{-11}-25.2 \times 10^{-13}C+12.4 \times 10^{-15}C^2$ $R^2=0.951$

Note: Unit of crystallinity (C) is %.

GM with a given crystallinity, tests should be performed if the values are critical to the performance of the system.

Evaluation of Effects of Aging

To evaluate the effect of aging on the diffusive migration of VOCs through HDPE geomembranes, a permeation reduction (PR) factor was calculated by dividing the permeation coefficient of aged geomembrane by that of unaged geomembrane (Tables 5 and 6). The average permeation reduction factors, for the geomembrane GM1, were 0.64 and 0.38, respectively, after 13 and 32 months of aging at 85°C. Similar reduction factors were observed for the geomembrane GM2. For example, after 10 and 25 months of aging the average reduction factors were 0.64 and 0.40, respectively, for the geomembrane GM2.

The diffusive migration of VOCs through an HDPE geomembrane is considered to be a molecular activated process and sufficient activation energy must be concentrated within the zone of chain segments for a successful diffusion step to occur (Michaels and Bixler 1961). The mobility of amorphous chain segments are reduced due to the presence of crystalline zone in the geomembrane. Because of the reduction in the amorphous region, higher activation energy is required for the diffusion to take place which eventually reduces the chance of diffusive migration (Michaels and Bixler 1961; Rogers 1985; Naylor 1989). Diffusion through a polymeric material is also expected to decrease because of the irregular shape of interconnected amorphous regions surrounded by impenetrable crystallites (Michaels and Bixler 1961). The irregularities in amorphous regions or tortuosity increases as the degree of polymer crystallinity increases (Michaels and Parker 1959). Thus higher crystallinity in the aged geomembrane lowered the permeation of contaminants through HDPE geomembrane because the crystalline zones perform as an impermeable barrier for the diffusion process and reduce the volume of amorphous material where partitioning can take place (Crank and Park 1968; Rogers 1985; Naylor 1989).

Conclusions

The effects of aging on the diffusive migration of a group of VOCs: benzene, toluene, ethylbenzene, xylenes (BTEX) through high-density polyethylene geomembrane was examined. Partitioning and diffusion tests were conducted at room temperature using both unaged and aged geomembranes. The diffusion (D_g)

and partitioning (S_{gf}) coefficients were estimated from the best-fit theoretical curves using a finite layer contaminant analysis program POLLUTE v7.

Using data obtained for the two GMs at three crystallinities for each, correlations were established between the diffusion characteristics and the degree of crystallinity. These relationships could be used to obtain preliminary estimates of diffusion parameters for an HDPE GM with a given crystallinity, however if the values are critical to the performance of the system then tests should be performed for the particular material being examined. The proposed equations gave good predictions of the diffusion, partitioning, and permeation coefficients for the geomembrane aged by 14 years exposure to leachate in a lagoon prior to diffusion testing by Rowe et al. (2003).

It was shown that the diffusion, partitioning, and permeation coefficients all decreased with an increase in geomembrane aging. The permeation coefficients were reduced by approximately 36 and 62% after 13 and 32 months of aging at 85°C for geomembrane GM1. For the geomembrane GM2, the reductions were about 36 and 60%, respectively, for 10 and 25 months of aging at 85°C. The crystallinity of the geomembrane controls the reduction in permeation coefficients for aged geomembranes and a strong correlation was developed between the various diffusion parameters and crystallinity. Since an increase in polymer crystallinity causes a decrease in the mobility of amorphous chain segments there was a consequent decrease in the diffusive transport of VOCs. The results of this study suggest that while the geomembrane remains intact, the aging of the geomembrane did not cause any increase in diffusive transport but rather, when the geomembrane crystallinity increased with physical aging, there was a reduction in the diffusive migration of organic contaminants through the two different HDPE geomembranes examined.

Acknowledgments

The funding of this research was provided by the Natural Science and Engineering Research Council of Canada (NSERC), Canada Foundation for Innovation (CFI), the Ontario Innovation Trust, the Centre for Research in Earth and Environmental Technologies (an Ontario Center of Excellence), the Ontario Ministry of Environment, and Terraflux Geosynthetics Inc. The writers are grateful to their industrial partners, Solmax International, Terraflux Geosynthetics Inc., Ontario Ministry of Environment, Gartner Lee Ltd., AMEC Earth and Environmental, Golder Associates Ltd.,

and CTT group. The writers would also like to thank Solmax International and Terrafix Geosynthetics Inc. for providing the geomembranes tested.

References

- Brachman, R. W. I., and Gudina, S. (2008a). "Geomembrane strains from coarse gravel and wrinkles in a GM/GCL composite liner." *Geotext. Geomembr.*, 26(6), 488–497.
- Brachman, R. W. I., and Gudina, S. (2008b). "Gravel contacts and geomembrane strains for a GM/CCL composite liner." *Geotext. Geomembr.*, 26(6), 448–459.
- Chao, K. P., Wang, P., and Lin, C. H. (2006). "Estimation of diffusion coefficients and solubilities for organic solvents permeation through high-density polyethylene geomembrane." *J. Environ. Eng.*, 132(5), 519–526.
- Chao, K. P., Wang, P., and Wang, Y. T. (2007). "Diffusion and solubility coefficients determined by permeation and immersion experiments for organic solvents in HDPE geomembrane." *J. Hazard. Mater.*, 142(1–2), 227–235.
- Crank, J., and Park, G. S. (1968). *Diffusion in polymers*, J. Crank and G. S. Park, eds., Chap. 6, Academic, New York, 165–217.
- Eith, A. W., and Koerner, G. R. (1997). "Assessment of HDPE geomembrane performance in a municipal waste landfill double liner system after eight years of service." *Geotext. Geomembr.*, 15(4–6), 277–287.
- Fong, C. F. C. M., Moresoli, C., Xiao, S., Li, Y., Bovenkamp, J., and De Kee, D. (1998). "Modeling diffusion through geomembranes." *J. Appl. Polym. Sci.*, 67(11), 1885–1889.
- Haxo, H. E., Jr. (1990). "Determining the transport through geomembranes of various permeants in different applications." *Geosynthetic testing for waste containment applications*, R. M. Koerner, ed., ASTM Special Publication 1081, *Proc. Symp.*, Las Vegas, ASTM, Philadelphia, 75–94.
- Haxo, H. E., Jr., and Lahey, T. (1988). "Transport of dissolved organics from dilute aqueous solutions through flexible membrane liner." *Hazard. Waste Hazard. Mater.*, 5(4), 275–294.
- Islam, M. Z. (2009). "Long-term performance of HDPE geomembranes as landfill liners." Ph.D. thesis, Queens' Univ., Kingston, Ont., Canada.
- Islam, M. Z., and Rowe, R. K. (2008). "Effect of geomembrane ageing on the diffusion of VOCs through HDPE geomembranes." *Proc., GEOAMERICAS 2008*, Cancun, Mexico, Industrial Fabrics Association International, Roseville, Minn., 459–467.
- Joo, J. C., Kim, J. Y., and Nam, K. (2004). "Mass transfer of organic compounds in dilute aqueous solutions into HDPE geomembranes." *J. Environ. Eng.*, 130(2), 175–183.
- Joo, J. C., Nam, K., and Kim, J. Y. (2005). "Estimation of mass transport parameters of organic compounds through high-density polyethylene geomembranes using a modified double-compartment apparatus." *J. Environ. Eng.*, 131(5), 790–799.
- Kim, J. Y., Park, J. K., Emmons, B., and Armstrong, D. E. (1995). "Survey of volatile organic compounds at a municipal solid waste composting facility." *Water Environ. Res.*, 67(7), 1044–1051.
- Krol, M. M. (2000). "Implications of trichloroethylene diffusion through soil-bentonite slurry walls." M.E.Sc. thesis, Univ. of Western Ontario, London, Ont., Canada.
- Michaels, A. S., and Bixler, H. J. (1961). "Flow of gases through polyethylene." *J. Polym. Sci.*, 50(154), 413–439.
- Michaels, A. S., and Parker, R. B., Jr. (1959). "Sorption and Flow of gases through polyethylene." *J. Polym. Sci.*, 41(138), 53–71.
- Michaels, A. S., Vieth, W. R., and Barrie, J. A. (1963). "Diffusion of gases in polyethylene terephthalate." *J. Appl. Phys.*, 34(1), 13–20.
- Montgomery, J. H., and Welkom, L. M. (1990). *Groundwater chemicals desk reference*, Lewis, Chelsea, Mich.
- Müller, W., Jacob, L., Tatzky, G. R., and August, H. (1998). "Solubilities, diffusion and partitioning coefficients of organic pollutants in HDPE geomembranes: Experimental results and calculations." *Proc., 6th Int. Conf. on Geosynthetics*, Atlanta, IFAI, 239–248.
- Naylor, T. de V. (1989). *Permeation properties. Comprehensive polymer science*, C. Booth, and C. Price, eds., Chap. 2, 643–668.
- Park, J. K., and Nibras, M. (1993). "Mass flux of organic chemicals through polyethylene geomembranes." *Water Environ. Res.*, 65(3), 227–237.
- Park, J. K., Sakti, J. P., and Hoopes, J. A. (1996). "Transport of organic compounds in thermoplastic geomembranes. I: Mathematical model." *J. Environ. Eng.*, 122(9), 800–806.
- Prasad, T. V., Brown, K. W., and Thomas, J. C. (1994). "Diffusion coefficients of organics in high-density polyethylene (HDPE)." *Waste Manage. Res.*, 12(1), 61–71.
- Rogers, C. E. (1985). "Permeation of gases and vapors in polymers." *Polymer permeability*, J. Comyn, ed., Elsevier Applied Science, London, 11–73.
- Rowe, R. K. (1995). "Leachate characterization for MSW landfills." *Proc., 5th Int. Landfill Symp.*, Sardinia, Italy, 2, Springer, Heidelberg, Germany, 327–344.
- Rowe, R. K. (1998). "Geosynthetics and the minimization of contaminant migration through barrier systems beneath solid waste." *Keynote Lecture, Proc., 6th Int. Conf. on Geosynthetics*, Atlanta, Industrial Fabrics Association International, Roseville, Minn., 27–103.
- Rowe, R. K. (2005). "Long-term performance of contaminant barrier systems." *Geotechnique*, 55(9), 631–678.
- Rowe, R. K., and Booker, J. R. (2004). "POLLUTE v.7-1D." Pollutant migration through a non-homogeneous soil, © 1983, 1990, 1994, 1997, 1998, 2004. Distributed by GAEA Technologies Ltd., Whitby, Ont., Canada, (www.gaea.ca).
- Rowe, R. K., Hrapovic, L., and Armstrong, M. D. (1996). "Diffusion of organic pollutants through HDPE geomembranes and composite liners and its influence on groundwater quality." *Geosynthetics: Applications, design and construction*, M. B. De Groot, G. DenHoedt, and R. J. Termaat, eds., Balkema, Rotterdam, The Netherlands, 737–742.
- Rowe, R. K., Hrapovic, L., and Korasic, N. (1995). "Diffusion of chloride and dichloromethane through an HDPE geomembrane." *Geosynthet. Int.*, 2(3), 507–536.
- Rowe, R. K., Islam, M. Z., and Hsuan, Y. G. (2008). "Leachate chemical composition effects on OIT depletion in HDPE geomembranes." *Geosynthet. Int.*, 15(2), 136–151.
- Rowe, R. K., Quigley, R. M., Brachman, R. W. I., and Booker, J. R. (2004). *Barrier systems for waste disposal facilities*, 2nd Ed., E & FN Spon, London.
- Rowe, R. K., and Rimal, S. (2008). "Depletion of antioxidants from HDPE geomembrane in a composite liner." *J. Geotech. Geoenviron. Eng.*, 134(1), 68–78.
- Rowe, R. K., Sangam, H. P., and Lake, C. B. (2003). "Evaluation of an HDPE geomembrane after 14 years as a leachate lagoon liner." *Can. Geotech. J.*, 40(3), 536–550.
- Rügge, K., Bjerg, P. L., and Christensen, T. H. (1995). "Distribution of organic compounds from municipal solid waste in the groundwater downgradient of a landfill (Grindsted, Denmark)." *Environ. Sci. Technol.*, 29(5), 1395–1400.
- Saidi, F., Touze-Foltz, N., and Goblet, P. (2008). "Numerical modelling of advective flow through composite liners in case of two interacting adjacent square defects in the geomembrane." *Geotext. Geomembr.*, 26(2), 196–204.
- Sangam, H. P. (2001). "Performance of HDPE geomembrane liners in landfill applications." Ph.D. thesis, Univ. of Western Ontario, Ontario, Canada.
- Sangam, H. P., and Rowe, R. K. (2001). "Migration of dilute aqueous organic pollutants through HDPE geomembranes." *Geotext. Geomembr.*, 19(6), 329–357.
- Sangam, H. P., and Rowe, R. K. (2005). "Effect of surface fluorination on diffusion through a high-density polyethylene geomembrane." *J. Geotech. Geoenviron. Eng.*, 131(6), 694–704.