



## Effect of Geomembrane Ageing on the Diffusion of VOCs through HDPE Geomembranes

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### ABSTRACT

This paper describes the migration of four commonly found volatile organic compounds (VOCs) in landfill leachates e.g., benzene, toluene, ethylbenzene, and xylenes through 1.5mm thick high density polyethylene (HDPE) geomembranes. Diffusion and sorption tests were conducted at room temperature (i.e., 22°C) on both unaged and 13-month aged geomembrane samples. Ageing of geomembrane was carried out at 85°C by immersing in synthetic leachate. The diffusion, partitioning, and permeation coefficients were estimated according to one dimensional diffusive flow equation based on Fick's second law using a computer program POLLUTE<sup>®</sup> v7. The results have shown that the permeation coefficients decreased by about 35-40% for aged geomembrane, which is probably due to the increase in geomembrane crystallinity of the aged sample. It is concluded that, other things being equal, ageing of HDPE geomembrane will result an improved barrier for diffusion of organic contaminants.

### 1. INTRODUCTION

Municipal solid waste landfills generate a wide variety of organic compounds mainly from incoming waste or biotic and abiotic reactions happening within the landfills (Kim et al. 1995; Rügge et al. 1995). High density polyethylene (HDPE) geomembranes have been used as part of the modern engineered landfill liner systems because of their resistance to advective transport of leachate and stress cracking, high strength, and availability of effective seaming techniques (Haxo 1990; Eith and Koerner 1997). HDPE geomembrane also serve as an excellent barrier to the diffusive migration of inorganic contaminants (e.g., toxic heavy metals) (Rowe 2005; Sangam and Rowe 2005). However, volatile organic compounds (VOCs) can readily diffuse through HDPE geomembranes at the molecular level by a process of sorption and diffusion (Park and Nibras 1993; Prasad et al. 1994; Rowe 1998, 2005; Sangam and Rowe 2001, 2005; Joo et al. 2004, 2005; Chao et al. 2006, 2007). Therefore, the diffusion of VOCs is may be a controlling factor in the design of landfill liner systems, because VOCs are more toxic at much lower concentration than many inorganic contaminants (Rowe 1998).

The transport of organic compounds through a geomembrane can be described by three key steps (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). Several factors influence the diffusive movement of organic compounds through a geomembrane, for example: (1) thickness, density, crystallinity, degree of cross-linking, and chain rigidity of the polymer; (2) polarity, shape, molecular weight, molecular volume, and initial concentration of the penetrant chemical; and (3) temperature (Rogers 1985; Naylor 1989; Sangam and Rowe 2001, 2005). Among these factors the crystallinity of the polymer is an important factor when an HDPE geomembrane is considered as a potential barrier to VOCs migration because diffusive migration occurs through the amorphous region of the semicrystalline HDPE geomembranes. Michaels and Parker (1959) and Michaels and Bixler (1961) conducted studies on the flow of gases through several unaged polyethylene sheets having different crystallinities. Their results have shown that the diffusion coefficients of gases (e.g., helium, oxygen, methane, ethane, propane, propylene etc.) decreased significantly with the increase of polymer crystallinity. For example, for methane gas the diffusion coefficients were  $5.4 \times 10^{-11}$ ,  $1.9 \times 10^{-11}$  and  $0.57 \times 10^{-11}$  m<sup>2</sup>/s, respectively when the crystallinities of the polymer were 29, 43, and 77% (Michael and Bixler 1961). The crystallinity was calculated from the percent amorphous volume of the polymer.

Joo et al. (2004) investigated the effect of ageing on the migration of organic compounds by conducting batch immersion tests on both virgin and 5-year aged HDPE geomembranes. Aged geomembrane was exhumed from a real landfill after 5 years. No significant changes in partitioning and diffusion coefficients were evident, although the diffusion coefficients were slightly lower for aged geomembrane. The crystallinity of the geomembranes was not reported in this paper. However, recent laboratory studies (Sangam 2001; Rowe et al. 2008; Rowe and Rimal 2008) have shown that the crystallinity of the HDPE geomembrane increases with the increase of ageing duration.

The objective of this study is to investigate the effect of geomembrane ageing on the migration of VOCs through HDPE geomembranes by giving special considerations to the change of geomembrane crystallinity. Partitioning and diffusion coefficients of representative VOCs were estimated for both unaged and aged HDPE geomembranes and the respective values were compared for both geomembranes.

## 2. MATERIALS AND METHODS

### 2.1 High Density Polyethylene (HDPE) Geomembrane

Experiments were conducted on both unaged and aged 1.5mm HDPE geomembranes. The HDPE geomembrane examined in this study was manufactured by GSE Lining Technology Inc., Houston, TX, USA. The oxidative induction time, OIT, (ASTM D3895) and crystallinity (ASTM E794) of the unaged geomembrane were 174min, and 38%, respectively. The crystallinity of the geomembrane increased to 46% after ageing for 13 months by immersion in synthetic leachate at 85°C. The oxidative induction time of the aged geomembrane was 0.92min and this corresponded to depletion of antioxidants in the geomembrane. Based on loss of OIT immersion of the geomembrane in leachate at different temperatures, the aging for 13 months at 85°C was estimated to correspond to about 45 years at room temperature (22°C) and 15 years at 35°C based on information provided by Rowe et al. (2008). A TA Instruments Q-100 series differential scanning calorimeter was used to measure the oxidative induction time and crystallinity of the geomembrane. The leachate was comprised of trace metals and surfactant in distilled water. Interested readers are referred to Rowe et al. (2008) for details regarding the effect of the complete composition of leachate on depletion of OIT and changes in crystallinity of geomembranes.

### 2.2 Organic Compounds

Four volatile organic compounds (VOCs) commonly found in landfill leachate (benzene, toluene, ethylbenzene, and xylenes: BTEX – see Rowe 2005) were examined. Laboratory grade BTEX standards were purchased from Sigma-Aldrich, Mississauga, ON, Canada. Table 1 presents the significant properties of these chemicals. Tests were conducted by diluting the standard solution with deionized distilled (DD) water to get a target concentration of 2.5mg/L.

Table 1. Selected properties<sup>a</sup> of organic contaminants tested.

Contaminants	Molecular weight (g/mol)	Density (g/cm <sup>3</sup> )	Molar volume (cm <sup>3</sup> )	Aqueous solubility <sup>b</sup> (mg/L)	log K <sub>ow</sub> <sup>c</sup>	Boiling temperature (°C)
Benzene	78.11	0.8765	89.11	1780	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

<sup>a</sup>Montgomery and Welkom (1990), and Sangam and Rowe (2001).

<sup>b</sup>At 20°C.

<sup>c</sup>*n*-octanol/water coefficient.

### 2.3 Analytical Methods

BTEX samples were analyzed using a Varian Gas Chromatography/Mass Spectrometer (GC/MS) equipped with a 30m × 0.25mm ID × 0.25µm DB-5 fused silica capillary column. Helium was used as carrier gas with a flow rate of 1.3mL/min. The sample was extracted in headspace mode from 2mL vials in 5minutes using a 8200 CX Varian autosampler equipped with 100µm polydimethylsiloxane solid phase micro extraction fiber. The desorption was done in 1minute. The chromatographs were quantified using Varian Saturn 2000 Chromatography software (Version 5.05). Calibration curves were produced through analysis of known standards and the BTEX concentrations were quantified based on these calibration curves. The performance of the GC was checked each time samples were tested by running a known standard sample and was found to be predominantly within the 95% of the target value.

## 2.4. Test Procedures

### 2.4.1 Sorption Test

Sorption tests were conducted at room temperature (i.e., 22°C) in 250mL glass serum bottles equipped with screw-tight Teflon lined caps. Air-dried geomembrane specimens with known masses were placed in the bottles, which were filled completely with dilute aqueous BTEX solution. The initial concentration of BTEX was in the range of 2.0 to 2.6mg/L (Table 2). The concentrations of contaminants were monitored with time until equilibrium was reached. Using the method described by Sangam and Rowe (2001), the partitioning coefficient of each contaminant was calculated according to the following. The mass balance equation at equilibrium can be expressed as:

$$M_{s0} = M_{sF} + M_{gF} + M_R \quad [1]$$

where  $M_{s0}$  and  $M_{sF}$  are respectively the initial and final mass of contaminant in the solution [M],  $M_{gF}$  is the mass of contaminant adsorbed to the geomembrane [M], and  $M_R$  is the mass of contaminant removed during sampling events. Eq.1 can be written as follows by expressing the masses in terms of their respective concentrations and volumes:

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

where  $c_{f0}$  and  $c_{fF}$  are the initial and final solution concentrations respectively [ $ML^{-3}$ ],  $V_{f0}$  and  $V_{fF}$  are respectively the initial and final volume of the solution [ $L^3$ ],  $M_g$  is the initial mass of geomembrane [M],  $\rho_g$  is the geomembrane density [ $ML^{-3}$ ],  $c_{gF}$  is the final equilibrium concentration in geomembrane [ $ML^{-3}$ ],  $V_i$  is the volume of solution taken at each sampling event [ $L^3$ ],  $c_i$  is the concentration of contaminant at each sampling event [ $ML^{-3}$ ]. At equilibrium, the concentration of contaminant in the geomembrane can be expressed as follows (Henry's law):

$$c_{gF} = S_{gf}c_{fF} \quad [3]$$

where  $S_{gf}$  is the partitioning coefficient [-], which depends on contaminant, geomembrane, fluid, and temperature of interest. Substituting Eq.3 in Eq.2, the partitioning coefficient can be expressed as follows:

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

To evaluate the loss of contaminants due to sampling and sorption on to the glass bottles and caps, control tests were conducted without placing the geomembrane in the similar glass serum bottles. The concentration of BTEX in the control test was the same as in the sorption test. The equilibrium concentration obtained from control test was used to establish  $\sum V_i c_i$  in Eq. 4 and hence obtain the corrected values of  $S_{gf}$ .

Table 2. Partitioning coefficients from sorption tests for both unaged and aged geomembranes.

Contaminants	Unaged geomembrane (crystallinity = 38%)				Aged geomembrane (crystallinity = 46%)			
	$c_0^a$ (mg/L)	$S_{gf}(-)$			$c_0^a$ (mg/L)	$S_{gf}(-)$		
		Uncorrected	Corrected	Predicted <sup>b</sup>		Uncorrected	Corrected	Predicted <sup>b</sup>
Benzene	2.58	75	54	58	2.49	64	43	44
Toluene	2.54	158	125	130	2.51	127	97	96
Ethylbenzene	2.20	395	316	340	2.24	376	288	300
<i>m&amp;p</i> -Xylenes	2.02	506	379	420	1.96	413	303	345
<i>o</i> -Xylene	2.33	357	284	305	2.23	348	275	280

<sup>a</sup> Initial solution concentration.

<sup>b</sup> Considering mass loss in modeling.

## 2.4.2 Diffusion Test

Diffusion tests were also conducted at room temperature using double compartment glass cells with the source (70mm diameter × 100mm high) and receptor (70mm diameter × 30mm high) reservoirs separated by geomembrane. Similar types of cell have been used in diffusion tests by other researchers (Haxo and Lahey 1988; Rowe et al. 1995, 1996; Sangam and Rowe 2001, 2005). The receptor compartment was filled first with DD water then the source compartment was filled with dilute aqueous BTEX solution with concentrations in the range of 2.0 – 2.5mg/L (Table 3). Samples were taken at regular time intervals and analyzed using GC/MS.

The diffusion of organic compounds through HDPE geomembrane can be modeled by Fick's first law.

$$f = -D_g \frac{dc_g}{dz} \quad [5]$$

where  $f$  is the mass flux [ $ML^{-2}T^{-1}$ ],  $D_g$  is the diffusion coefficient of the compound in the geomembrane [ $L^2T^{-1}$ ],  $c_g$  is the concentration of compound in the geomembrane [ $ML^{-3}$ ], and  $z$  is the distance along the direction of diffusion [L]. The governing differential equation for a change in contaminant concentration at any point in the geomembrane with time,  $t$  is expressed by Fick's second law:

$$\frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial z^2} \quad [6]$$

If the source and receptor fluids are similar, the flux associated with the diffusion 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  $P_g$  is the permeation coefficient or mass transfer coefficient ( $= S_{gf}D_g$ ) [ $L^2T^{-1}$ ].

By applying the appropriate boundary conditions as described by Sangam and Rowe (2001), the diffusion equations were solved using a finite layer contaminant transport model POLLUTE<sup>®</sup> 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 (without geomembrane). The loss of contaminant observed in the control cell was considered in the modeling according to the procedure described by Krol (2000).

Table 3. Partitioning ( $S_{gf}$ ), diffusion ( $D_g$ ) and permeation ( $P_g$ ) coefficients estimated from diffusion tests for both unaged and aged geomembranes.

Contaminants	Unaged geomembrane (crystallinity = 38%)				Aged geomembrane (crystallinity = 46%)				PR <sup>b</sup>
	$c_0^a$ (mg/L)	$S_{gf}$ (-)	$D_g$ ( $10^{-12}m^2/s$ )	$P_g$ ( $10^{-12}m^2/s$ )	$c_0^a$ (mg/L)	$S_{gf}$ (-)	$D_g$ ( $10^{-12}m^2/s$ )	$P_g$ ( $10^{-12}m^2/s$ )	
Benzene	2.52	55	0.24	13.2	2.45	44	0.18	7.9	0.6
Toluene	2.44	125	0.22	27.5	2.52	102	0.18	18.4	0.67
Ethylbenzene	2.17	345	0.18	62.1	2.20	300	0.14	42.0	0.68
<i>m&amp;p</i> -Xylenes	2.02	440	0.17	74.8	2.01	350	0.13	45.5	0.61
<i>o</i> -Xylene	2.32	320	0.17	54.4	2.31	290	0.12	34.8	0.64

<sup>a</sup> Initial concentration in the source.

<sup>b</sup> Permeation reduction factor, PR =  $P_g(\text{aged})/P_g(\text{unaged})$ .

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Sorption Test

Figure 1 shows the concentration of BTEX during the sorption test on both unaged and aged geomembranes. The concentrations are reported as the normalized concentrations relative to the initial concentrations measured at the start of the test. It can be seen that the concentrations of contaminants decreased with time and leveled off as the equilibrium concentrations were reached. The highest decrease was observed for *m&p*-xylenes while the lowest decrease was observed for benzene for both unaged and aged geomembranes. The equilibrium concentrations were reached faster for the unaged than for the aged geomembrane. For example, for unaged geomembrane the equilibrium concentration of toluene was reached after 20 days and for aged geomembrane it took about 35 days before reaching the equilibrium concentration.

The partitioning coefficients ( $S_{gf}$ ) calculated using Eq.4 with and without accounting for mass losses are given in Table 2. The  $S_{gf}$  values of BTEX increased with the increase of *n*-octanol/water coefficients ( $\log K_{ow}$ ) and with the decrease of aqueous solubility of the contaminants. Similar trends have been observed by other researchers (Müller et al. 1998; Sangam and Rowe 2001, 2005; Joo et al. 2004, 2005). The  $S_{gf}$  values obtained for aged geomembrane are lower than that for the unaged geomembrane. For instance, the corrected  $S_{gf}$  of ethylbenzene for unaged and aged geomembranes were 316 and 288 respectively. The lower  $S_{gf}$  values for aged geomembrane results in the lesser decrease in BTEX concentrations observed for aged geomembrane compared to unaged geomembrane. The measured concentrations were fitted with the POLLUTE<sup>®</sup> considering the loss of contaminants observed from control test and the resulting  $S_{gf}$  values from the best fit curves are also given in Table 2. The calculated  $S_{gf}$  values lie between the corrected and uncorrected values.

#### 3.2 Diffusion Test

Figure 2 shows the variations in BTEX concentrations with time in the source and receptor for both unaged and aged geomembranes. The concentrations are normalized to the initial concentration as for the sorption tests. Each data point is the average of triplicate concentrations measured by the GC/MS and the vertical bars represent the standard deviations. For both unaged and aged geomembranes, the concentrations of ethylbenzene and xylenes reached their equilibrium concentrations at earlier time than benzene and toluene. The equilibrium concentrations of contaminants in the source were found smaller for unaged geomembrane compared to the aged geomembrane. For example, the concentration of toluene dropped to about 31% of the initial concentration for unaged geomembrane compared to a drop of 38% for aged geomembrane by the end of the testing period (i.e., approximately 85 days). The predicted concentrations using the finite layer contaminant transport model POLLUTE<sup>®</sup> v7 are plotted as lines in Figure 2. The loss of contaminants observed from control test was considered in model predictions. The predicted diffusion ( $D_g$ ) and partitioning ( $S_{gf}$ ) coefficients together with the calculated permeation coefficients ( $P_g$ ) are shown in Table 3. It can be seen that the diffusion coefficients appear to decrease with increasing molecular volume (Tables 1 and 3) as has been observed by other researchers (Park and Nibras 1993; Sangam and Rowe 2001, 2005; Joo et al. 2004, 2005). The activation energy for diffusion process increases with the increase of contaminant molecular size which leads to the decrease of diffusion coefficient for larger sized molecules (Joo et al. 2004). The values of  $D_g$  and  $S_{gf}$  were found lower for the aged geomembrane compared to the unaged geomembrane. For instance,  $D_g$  and  $S_{gf}$  values for toluene were  $0.18 \times 10^{-12} \text{ m}^2/\text{s}$  and 102, respectively. For aged geomembrane and for unaged geomembrane these values were  $0.22 \times 10^{-12} \text{ m}^2/\text{s}$  and 125, respectively. Likewise, the calculated permeation coefficients were about 40% lower for aged geomembrane than for unaged geomembrane. It should be noted that, the values of partitioning coefficients ( $S_{gf}$ ) obtained from diffusion tests are comparable to those obtained from sorption tests (Tables 2 and 3).

To evaluate the effect of ageing on the barrier performance of HDPE geomembranes with respect to VOCs diffusion, a permeation reduction factor (PR) was calculated by dividing the permeation coefficient of aged geomembrane by that of the unaged geomembrane as shown in Table 3. The permeation reduction factor varied in the range of 0.6 to 0.68. The higher crystallinity in the aged geomembrane played an important role in impeding the permeation of contaminants. Because, the crystalline zones act as impermeable barrier for diffusion process also act as relatively excluded volumes for sorption process to take place (Rogers 1985; Naylor 1989).

Diffusion through HDPE geomembrane is a molecular activated process and an activation energy is required within the zone of chain segments for a successful diffusion step to occur (Michaels and Bixler 1961; Rowe 2005). The crystallites in the polymer act as crosslinking agents which reduce the mobility of amorphous chain segments and cause an increase in activation energy. The higher activation energy is responsible for lower diffusive migration of contaminants through HDPE geomembrane (Michaels and Bixler 1961; Naylor 1989; Rogers 1985). Another factor that influences the decrease in diffusive migration is the increase of tortuous flow path in the higher crystalline polymer. Michaels and Parker (1959) have shown that the tortuosity in the polymer increases with the increase in polymer crystallinity. Considering these factors it appears that the diffusive migration of contaminants will reduce with the increase of

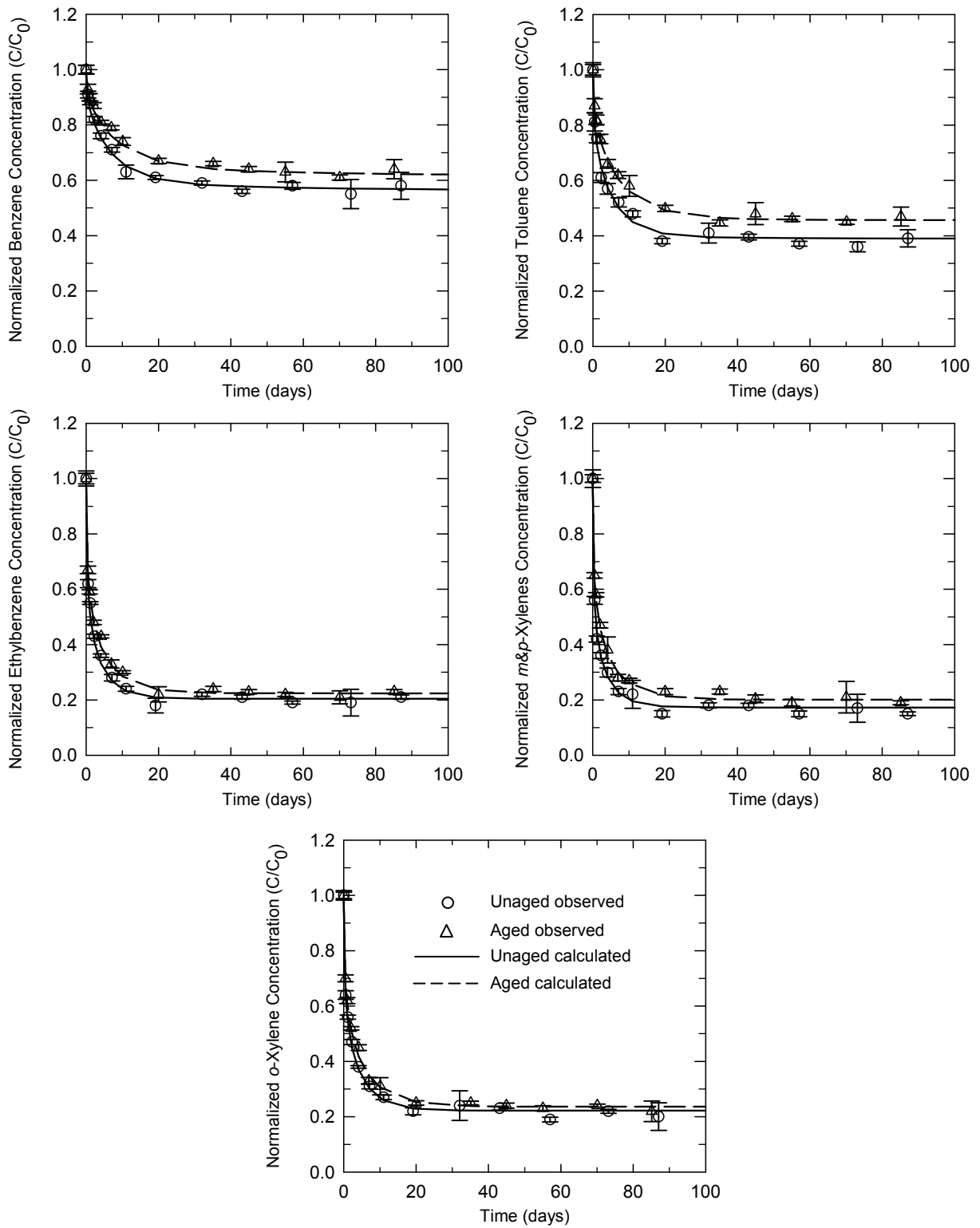


Figure 1. Variation in observed and calculated concentrations of benzene, toluene, *m&p*-xylenes, and *o*-xylene with time during sorption tests on both unaged and aged geomembranes.

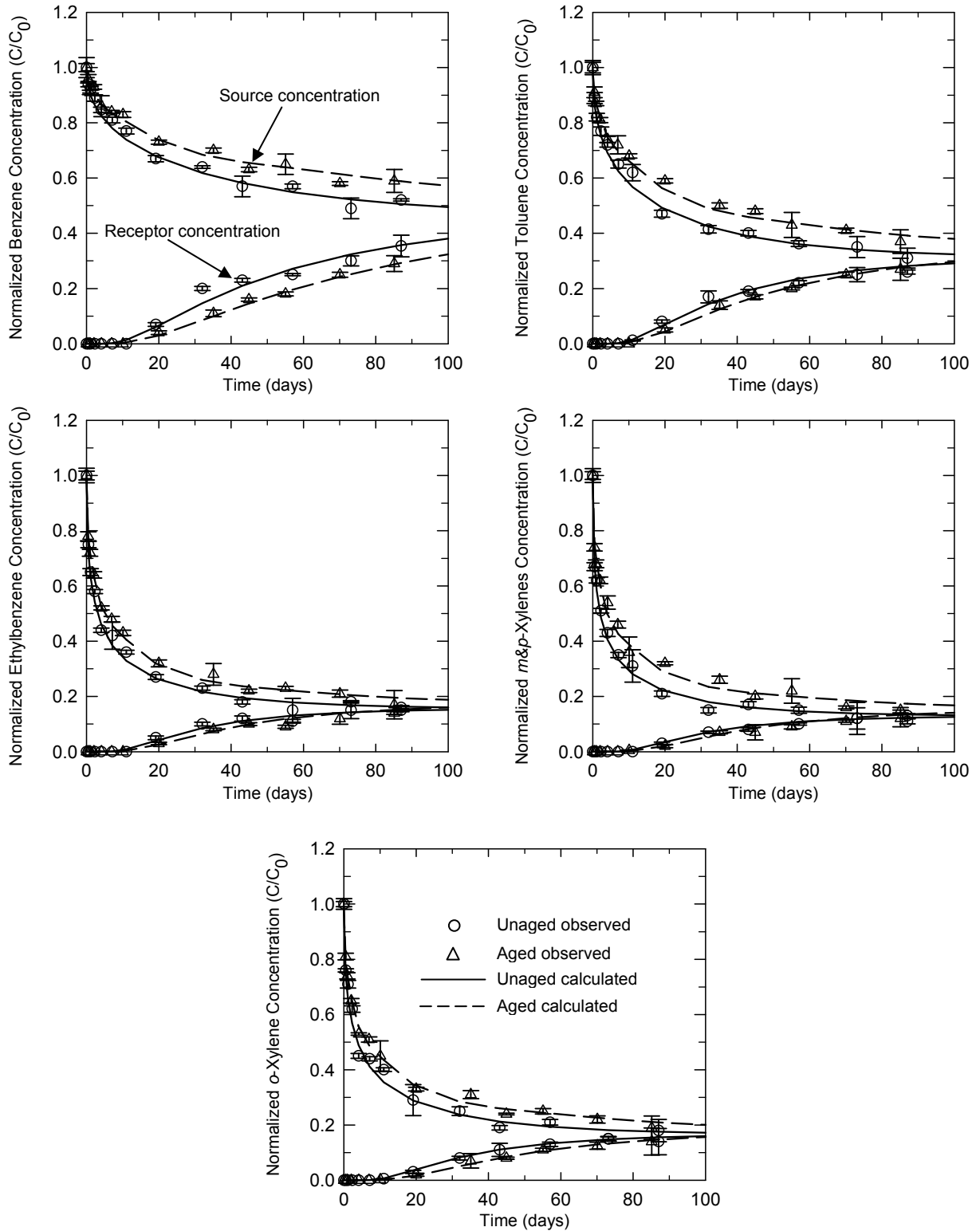


Figure 2. Variation in observed and calculated concentrations of benzene, toluene, *m*&*p*-xylenes, and *o*-xylene with time during diffusion tests on both unaged and aged geomembranes.

geomembrane crystallinity and as stated earlier that crystallinity of HDPE geomembrane increases with ageing. Therefore, it can be concluded that, other factors such as resistance to chemical degradation, resistance to possible catastrophic puncture, mechanical stability and quality of construction being equal, the diffusive migration of VOCs through HDPE geomembrane will be less for an aged geomembrane than for a virgin geomembrane. For a better understanding of diffusion process through aged geomembrane, the effect of ageing on different geomembranes at different ageing durations with different crystallinities will be addressed in a subsequent paper.

#### 4. CONCLUSIONS

Experimental results on the migration of a group of volatile organic compounds (VOCs): benzene, toluene, ethylbenzene, xylenes (BTEX) through high density polyethylene geomembrane are presented in this study. Sorption and diffusion tests were conducted at room temperature using dilute aqueous BTEX solution to investigate the effect of ageing of HDPE geomembranes. Ageing of geomembrane was conducted at 85°C by immersing in synthetic leachate for 13 months. Based on OIT depletion at different temperatures this corresponded to about 45 and 15 years of aging at temperatures of 22 and 35°C, respectively. The data from the sorption and diffusion tests were analyzed using a finite layer contaminant analysis program POLLUTE<sup>®</sup>v7 and the values of  $S_g$  and  $D_g$  were estimated for the best fit curves. Permeation coefficients were calculated for both unaged and aged geomembranes and were found to be reduced by about 35-40% for aged geomembrane. The increase in crystallinity appears to control the reduction in permeation coefficients for the aged geomembrane. Therefore, ageing of geomembrane appears to reduce the diffusive migration of organic contaminants through HDPE geomembranes (other things being equal).

#### ACKNOWLEDGEMENTS

The research presented in this paper was funded 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 Terrafix Geosynthetics Inc. The authors are grateful to their industrial partners, Solmax International, Terrafix Geosynthetics Inc, Ontario Ministry of Environment, Gartner Lee Ltd, AMEC Earth and Environmental, Golder Associates Ltd., and CTT group and especially to Terrafix Geosynthetics Inc. (Toronto, Canada) for providing the geomembrane tested.

#### REFERENCES

- ASTM D3895. Standard Test Method for Oxidative-induction Time of Polyolefins by Differential Scanning Calorimetry, *Annual Book of ASTM Standards*, Philadelphia, USA, 08.02, 539–544.
- ASTM E794. Standard Test Method for Melting and Crystallization Temperatures by Thermal Analysis, *The American Society for Testing and Materials*, 14.02, 483–486.
- 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, *Journal of Hazardous Materials*, 132 (5), 519-526.
- 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, *Journal of Environmental Engineering*, 142, 227-235.
- 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, *Geotextiles and Geomembrane*, 15(4–6), 277–287.
- Haxo, H.E., Jr. (1990). Determining the transport through geomembranes of various permeants in different applications, *Geosynthetic Testing for Waste Containment Applications*, Koerner, R.M. Ed., ASTM Special Publication 1081, Proceedings of Symposium, Las Vegas, NV, USA, January 1990, 75-94.
- Haxo H.E., Jr. and Lahey, T. (1988). Transport of dissolved organics from dilute aqueous solutions through flexible membrane liner, , 5, 275–294.
- Joo, J. C., Kim, J. Y. and Nam, K. (2004). Mass transfer of organic compounds in dilute aqueous solutions into HDPE geomembranes, *Journal of Environmental Engineering*, 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. *Journal of Environmental Engineering*, 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 cocomposting facility, *Water Environment Research*, 67(7), 1044–1051.
- Krol, M.M. (2000). Implications of Trichloroethylene Diffusion Through Soil-bentonite Slurry Walls. *MESc Thesis, Department of Civil and Environmental Engineering, The University of Western Ontario*, London, Ontario, Canada, 144p.
- Michael, A.S. and Bixler, H. J. (1961). Flow of gases through polyethylene, *Journal of Polymer Science*, L, 413-439.

- Michael, A.S. and Parker, R.B., Jr. (1959). Sorption and Flow of gases through polyethylene, *Journal of Polymer Science*, XLI, 53-71.
- 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, *Proceedings of the 6<sup>th</sup> International Conference on Geosynthetics*, Atlanta, IFAI, 239–248.
- Naylor, T. de V. (1989). *Permeation Properties*. *Comprehensive Polymer Science*, C. Booth and C. Price, eds., 2, 643-668.
- Park, J. K. and Nibras, M. (1993). Mass flux of organic chemicals through polyethylene geomembranes, *Water Environment Research*, 65, 227– 237.
- Park, J. K., Sakti, J. P. and Hoopes, J. A. (1996). Transport of organic compounds in thermoplastic geomembranes. I: Mathematical model, *Journal of Environmental Engineering*, 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 Management and Research*, 12, 61–71.
- Rogers, C. E. (1985). Permeation of gases and vapors in polymers, *Polymer Permeability*, J. Comyn, ed., Chap. 2, Elsevier, London, 11– 73.
- Rowe, R. K. (1995). Leachate characterization for MSW landfills, *Proceedings of the 5th International Landfill Symposium*, Sardinia, Italy, 2, 327–344.
- Rowe, R. K. (1998). Geosynthetics and the minimization of contaminant migration through barrier systems beneath solid waste, *Keynote Lecture, Proceedings of the 6<sup>th</sup> International Conference on Geosynthetics*, Atlanta, 27–103.
- Rowe, R. K. (2005). Long-term performance of contaminant barrier systems, *Géotechnique*, 55(9), 631–678.
- Rowe, R.K. and Booker, J.R. (1998). *POLLUTE v.7 -1D Pollutant Migration Through a Non- Homogeneous Soil*, © 1983, 1990, 1994, 1997, 1998, 2004. Distributed by GAEA Technologies Ltd., Whitby, ON, Canada.
- 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: In: De Groot, DenHoedt, Termaat (Eds.), Applications, Design and Construction*, A.A. Balkema, Rotterdam, The Netherlands, 737–742.
- Rowe, R.K., Hrapovic, L. and Korasic, N. (1995). Diffusion of chloride and dichloromethane through an HDPE geomembrane, *Geosynthetics International*, 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, *Geosynthetics International*, (In review).
- Rowe, R.K. and Rimal, S. (2008). Depletion of antioxidants from HDPE geomembrane in a composite liner, *Journal of Geotechnical and Geoenvironmental Engineering*, In press.
- 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), *Environmental Science and Technology*, 29(5), 1395–1400.
- Sangam, H. P. (2001). Performance of HDPE geomembrane liners in landfill applications, *Ph.D. Thesis, Department of Civil and Environmental Engineering, The University of Western Ontario*, Ontario, Canada, 400p.
- Sangam, H. P. and Rowe, R. K. (2001). Migration of dilute aqueous organic pollutants through HDPE geomembranes, *Geotextiles and Geomembranes*, 19(6), 329–357.
- Sangam, H. P. and Rowe, R. K. (2005). Effect of surface fluorination on diffusion through a high density geomembrane, *Journal of Geotechnical and Geoenvironmental Engineering*, 131(6), 694-704.