

BTEX Diffusion and Sorption for a Geosynthetic Clay Liner at Two Temperatures

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Abstract: The diffusion and sorption characteristics of a geosynthetic clay liner (GCL) are examined for a group of volatile aromatic hydrocarbons: benzene, toluene, ethylbenzene, *m&p*-xylene, and *o*-xylene (BTEX) at two different temperatures. It is shown that geotextile component of a GCL contributes to the sorption of hydrocarbons by the GCL. While the partitioning coefficients of the BTEX compounds have the order *m&p*-xylene \approx ethylbenzene $>$ *o*-xylene $>$ toluene $>$ benzene, the diffusion coefficients have the order benzene $>$ toluene $>$ ethylbenzene $>$ *m&p*-xylene \approx *o*-xylene. The reduction in diffusion and sorption coefficients with decreasing temperature have opposite effects in terms of the rate of contaminant movement through a GCL. However, it is shown that the decrease in transport due to a reduced diffusion coefficient dominates and mass transport is reduced at lower temperature.

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Introduction

Geosynthetic clay liners (GCLs) are used in various barrier systems to provide containment of contaminated soil and water. A GCL provides both a hydraulic and diffusion barrier to the transport of contaminants. Many investigators have examined the hydraulic conductivity of GCLs with respect to water, leachates, and some organic and saline permeants (see Bouazza 2002 for a review). However while there is literature dealing with diffusion and sorption of volatile organic compounds (VOCs) for various soils (e.g., Barone et al. 1992; Headley et al. 2001) including sand-bentonite mixtures (e.g., Gullick 1998; Khandelwal et al. 1998; Krol and Rowe 2004), there is paucity of archival literature dealing with the diffusion of the VOCs through a GCL. Lake and Rowe (2004) examined diffusion of dichloromethane (DCM), dichloromethane (DCA), trichloroethylene (TCE), benzene, and toluene through a GCL at room temperature. They concluded that the order of the rate of mass transport through the GCL was DCM \approx 1, 2 DCA $>$ benzene $>$ TCE $>$ toluene and diffusion coefficients at room temperature and confining pressures lower than approximately 10 kPa ranging from approximately 2×10^{-10} to

3×10^{-10} m²/s. All these previous studies have been at room temperature.

Spills and leaks of hydrocarbons have caused contamination at a number of Arctic Distant Early Warning Line (DEW line) sites in northern Canada over 40 years of operation. The Canadian Department of National Defense has initiated the cleanup of these sites and in the summer of 2001 a subsurface composite geosynthetic barrier [consisting of an high density polyethylene (HDPE) geomembrane and a GCL] was installed to provide short term control of the migration of hydrocarbons at one of these sites (Li et al. 2002). While the advective movement of contaminants is controlled by the geomembrane, the primary transport mechanism through the barrier system is diffusion. Since the site is located in the Arctic, the ground is frozen for most of the year. Thus the potential for contaminant migration is largely restricted to the summer months, when the average temperature is about 5–7°C. Thus, the diffusion and sorption of hydrophobic compounds through the GCL at 5–7°C are of particular interest.

The objective of this paper is to examine the diffusion and sorption characteristics of the benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds which represent the lighter hydrocarbons and more mobile components of Arctic diesel (jet fuel A-1), for the GCL used as part of the barrier wall described by Li et al. (2002). A particular focus of this paper is on the effect of temperature on diffusion and sorption at two temperatures, namely, the typical laboratory temperature of 22°C and the average summer temperature at the Arctic site of 5–7°C. The relative sorption of the geosynthetic (e.g., cover and carrier geotextiles) and bentonite components of the GCL as observed in batch tests will be examined. Finally the diffusion coefficients and the partitioning coefficients for the entire GCL are discussed and a sensitivity analysis is used to illustrate the effect of temperature on diffusion and sorption of the BTEX compounds as they migrate through the GCL.

Materials

The basic properties of the BTEX compounds examined are given in Table 1. The needle-punched reinforced GCL was composed of

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Table 1. Selected Properties^a of Organic Contaminants Tested

Chemicals	Molar weight (g/mol)	Density (g/cm ³)	Molar volume ^b (cm ³)	Aqueous solubility ^c (mg/L)	Henry's law constant ^d (kPa m ³ /mol)	log <i>k</i> _{ow} (-)	Diffusion coefficients in free solution ^c (×10 ⁹ m ² /s)	Diffusion coefficients in air ^c (×10 ⁵ m ² /s)	Boiling temperature (°C)
Benzene	78.11	0.88	89.11	1,780	0.55	2.13	1.16	0.93	80.1
Toluene	92.14	0.87	106.28	515	0.67	2.79	0.97	0.84	110.6
Ethylbenzene	106.17	0.87	122.46	152	0.80	3.13	0.92	0.75	136.2
<i>m</i> -Xylene	106.17	0.86	122.85	162	0.50–0.78	3.20	0.79	0.68	138.0
<i>p</i> -Xylene	106.17	0.87	122.47	156	0.51–0.88	3.18	0.79	0.67	138.3
<i>o</i> -Xylene	106.17	0.88	120.62	152	0.50	3.13	0.80	0.73	144.0

^aFrom Montogomery and Welkom, (1990) and Rowe (2001) except where otherwise noted.

^bAt 20°C.

^cAt 25°C from Yaws (1995).

^dAt 20°C from Schnoor (1996).

a uniform layer of granular sodium bentonite encapsulated between a scrim reinforced nonwoven polypropylene carrier and a staple fiber nonwoven polypropylene cover geotextile. The average mass per unit area of the cover and carrier geotextiles, geotextile fibers in the bentonite layer, and bentonite were 250, 270, 26, and 3,800 g/m², respectively.

Test Methods

Diffusion Tests

Stainless steel, which has been used by several investigators to examine the sorption of BTEX compounds (Morrissey and Grismer 1999; Headley et al. 2001; and Sleep and McClure 2001), was used to manufacture the diffusion cells (Fig. 1). Three stainless steel springs were used to apply a confining stress of 9.5 kPa to the GCL during hydration and diffusion testing; this corresponded to the typical confining stress anticipated for the field application being examined. For other applications, different pressures can be applied to the GCL by using springs of different stiffness. Two 1.25 mm thick perforated stainless steel plates (porosity, *n*=0.4) were used to support the GCL sample and allow the application of a uniform confining pressure (Fig. 1).

For this particular field application, some groundwater was retrieved and it was analyzed. The groundwater had insufficient ions (the predominant cations were Na⁺, K⁺, Mg²⁺, and Ca²⁺: at concentrations of only 6.9, 6.5, 4.9, and 3.2 mg/L, respectively) to affect the swelling property of sodium bentonite, hence de-ionized distilled water (DDW) was used to hydrate the GCL sample (from the bottom up) under a hydraulic gradient of 15–20. Following hydration, solutions containing BTEX each at a concentration of about 2,500 μg/L were placed into the source reservoir and sampled immediately to obtain the initial concentrations. Subsequently, 50 μL samples were taken from the source and receptor reservoirs until the test termination. Magnetic stirrers were used to ensure a uniform contaminant concentration in both reservoirs during the test.

Sorption/Immersion Tests

Sorption/immersion tests were performed to define the partitioning coefficients of the BTEX compounds for the both cover and carrier geotextiles at 22 and 5°C. Test solutions with concentrations of 625, 1,250, and 2,500 μg/L were prepared by injecting designated amounts of BTEX–methanol stock into capped 250 mL glass serum bottles filled with DDW. Geotextile samples with the same mass and dimensions as in the GCL used for the diffu-

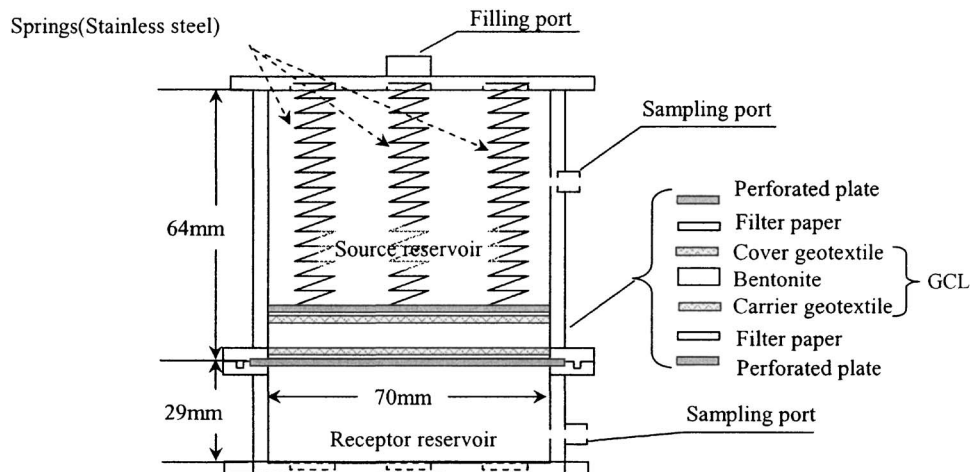


Fig. 1. Schematic of diffusion cell

sion tests (i.e., diameter of 70 mm and mass of about 1.0 g) were placed in a 40 mL glass vial with sufficient BTEX solution to give a solid:solution ratio of 1:40. The first sample was collected immediately to establish the initial concentration. The contaminant concentrations were monitored with time until equilibrium was reached.

Batch Sorption Tests

The batch sorption tests for the bentonite were performed based on *ASTM E1195-01*. The glass tubes were filled with bentonite and the working solution (the same as used for the geotextile sorption/immersion tests) at a soil:solution ratio of 1:10. The tubes were, shaken for 48+1 h, left for 18–24 h to equilibrate, centrifuged at 2,000–3,000 rpm for 180 min, and then left 24 h before 50 μL aliquots were taken from the supernatant, using a gas tight syringe, to obtain the aqueous concentration. The temperature of the centrifuged apparatus used could not be varied and so the bentonite batch sorption tests were performed only at 22°C.

Analytical Methodology

The BTEX samples obtained from the diffusion and the batch sorption tests vials were analyzed using a Varian Gas Chromatograph/Mass Spectrometer (Saturn 2000 MS and a 3800 GC). The chemical separations were done on a 30 m \times 0.25 μm inner diameter (i.d.) fused silica capillary column coated with a 0.25 μm DB-5 film using helium carrier gas at flow rate of 1.3 mL/min. The column temperature was programmed to hold the initial temperature of 35°C for 0.5 min, followed by two ramps of 10°C/min to 100°C, and 50°C/min to 200°C with a final hold of 3 min. The scan for chemical identification was performed in 35–200 mass unit ranges. The injection system consisted of a 8200 CX Varian autosampler equipped with a 100 μm polydimethylsiloxane solid phase microextraction fiber (Supelco Bellfonte, Pa.). The sampling extraction was performed in head-space mode for 10 min from 2 mL vials, and then the fiber is desorbed in the injector port for 2 min. Chemical spectra were identified using the NIST spectra library, and calibrated and quantified using *Varian Saturn 2000 Chromatography* software (Version 5.05). Reliable detection limits of gas chromatography/mass spectrometry (GC/MS) (calculated at the 95% confidence interval) ranged between 2 and 5 $\mu\text{g/L}$ for the various VOCs tested in this study.

The contaminant concentrations were quantified based on calibration curves obtained through the analysis of standards of known concentrations. The standard stock cocktail was prepared by spiking a 250 mL glass serum bottle filled with methanol with each of the pure chemicals to achieve concentrations of about 1 g/L. This stock was further diluted to prepare the standards, with concentrations varying from 2 to 100 $\mu\text{g/L}$ being used for GC calibration. Quality control procedures involved the use of duplicates, a lab blank, and a standard sample with a known concentration of 50 $\mu\text{g/L}$ which was used to compare with the concentration obtained from the GC/MS. The variation of data was within about 5%.

Modeling Methods

Contaminant Transport and Boundary Conditions

One-dimensional contaminant transport of a single reactive solute through a homogeneous, saturated porous media, with linear reversible sorption and instantaneous equilibrium is described by

$$n \frac{\partial c}{\partial t} = n D_e \frac{\partial^2 c}{\partial z^2} - \rho_d K_d \frac{\partial c}{\partial t} \quad (1)$$

where c =concentration at depth z and time t [ML^{-3}]; n =porosity [-]; D_e =effective diffusion coefficient [$\text{L}^2 \text{T}^{-1}$]; ρ_d =dry density [ML^{-3}]; and K_d =partitioning coefficient [$\text{L}^3 \text{M}^{-1}$]. Based on consideration of mass balance, the mass of contaminant in the source solution at time, t , is equal to the initial mass minus the mass that diffused through the GCL up to that time

$$c_s(t) = c_0 - \frac{1}{H_s} \int_0^t f_i(\tau) d\tau \quad (2)$$

where c_0 =initial concentration in the source compartment [ML^{-3}]; H_s =height of source fluid (volume of source fluid per unit area) [L]; and $f_i(\tau)$ =mass flux of contaminant into the soil at any time τ [$\text{ML}^{-2} \text{T}^{-1}$]. Similarly, the concentration in the receptor compartment at any time, $c_b(t)$, is given by

$$c_b(t) = c_{b0} + \frac{1}{H_{br}} \int_0^t f_b(\tau) d\tau \quad (3)$$

where c_{b0} =initial concentration in the receptor compartment [ML^{-3}]; H_{br} =height of the fluid in the receptor compartment (volume of receptor fluid per unit area) [L]; and $f_b(\tau)$ =mass flux of contaminant into the receptor at any time τ [$\text{ML}^{-2} \text{T}^{-1}$]. In this study, the computer program *POLLUTE* v6.3 (Rowe and Booker 1998), was used to solve Eq. (1) subject to the boundary conditions defined by Eqs. (2) and (3).

Modeling Temperature Dependent of Sorption and Diffusion

Sorption and diffusion may both be expected to be influenced by temperature. The simplest description of kinetic effects is provided by the Arrhenius equation (Clark 1996; Schnoor 1996; and Kellner et al. 1998)

$$R_k = A \exp\left(-\frac{X}{RT}\right) \quad (4)$$

where R_k =reaction rate; A =constant; X =activation energy [J mol^{-1}] for diffusion or heat of solution for sorption; T =absolute temperature (K); and R =universal gas constant [$=8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$]. Several investigators (Rogers 1965; Aminabhavi et al. 1996; Aminabhavi and Naik 1999) have shown that for polymers, the temperature dependence of the diffusion (permeability) and sorption coefficients over small ranges of temperature can be represented by an Arrhenius type relationship. Altshuler and Belfort (1983) showed that for dilute aqueous solutions, the effect of temperature on the partitioning coefficient for activated carbon is described by Arrhenius equation. Chiou (1987) showed that the effect of temperature on sorption could be described by the Clausius–Clapeyron equation which has the same general form as the Arrhenius equation.

Based on Eq. (4), the ratio of the reaction rate at two different temperatures T_1 and T_2 can be written as follows:

$$\frac{R_{kT_1}}{R_{kT_2}} = \exp\left[\left(-\frac{X}{R}\right) \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \quad (5)$$

In this study, R_k is taken to represent the partitioning coefficient, K_d .

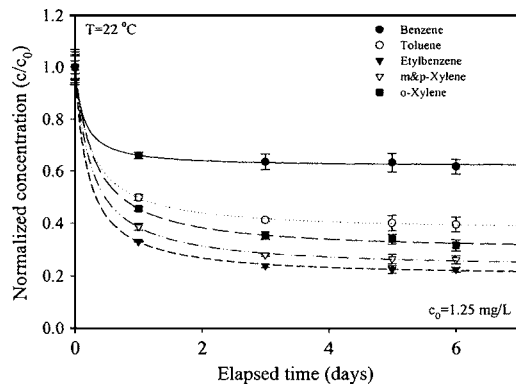


Fig. 2. Observed concentration of benzene, toluene, ethylbenzene, *m&p*-xylene, and *o*-xylene compounds at 22°C (cover geotextile)

The diffusion coefficient in water depends on both the temperature and water viscosity at that temperature (Reid et al. 1987). The ratio of the diffusion coefficients in free solution at two temperatures is given by

$$\frac{D_{Ti}}{D_T} = \left(\frac{273 + Ti}{273 + T} \right) \cdot \frac{\eta_T}{\eta_{Ti}} \quad (6)$$

where D_T and D_{Ti} =diffusion coefficients at the temperatures T and Ti °C, and η_T and η_{Ti} =viscosity of water at T and Ti °C.

Results and Discussion

Partitioning Coefficients for Geotextiles

Fig. 2 shows the change in contaminant concentration (normalized with respect to the initial concentration) with elapsed time for a sorption/immersion tests at 22°C. Each data point represents the average of multiple evaluations of the concentration by the GC/MS; the bars shown represent the standard deviation. Similar results were obtained at 5°C except that it took longer for the contaminant concentration to reach equilibrium at 5°C rather than at 22°C. Fig. 3 shows the equilibrium concentrations and sorption isotherms of benzene compound for both the cover and carrier geotextiles at 22 and 5°C. A least-squares fit to the data typically had correlation coefficients greater than 90%. Table 2 summarizes the partitioning coefficients estimated from the sorption/immersion tests.

The needle-punched components of both the cover and carrier geotextiles comprise polypropylene fibers manufactured from a 10 melt polymer. However, only the carrier geotextile has a woven scrim with yarns manufactured from a 4 melt polymer produced by a different supplier. Thus it is not surprising that the partitioning coefficients for the cover geotextile are consistently different from those for the carrier geotextile, with the difference being attributed to the presence of the scrim.

Partitioning Coefficients for Bentonite Layer

Fig. 4 shows the equilibrium concentrations and sorption isotherms of each BTEX compound for the bentonite alone at 22°C. The least-squares fit to the experimental data typically have correlation coefficients greater than 96% and gave the values of K_{db} indicated in Table 3. These values are very similar to those reported by Lake and Rowe (2004) for bentonite from a similar

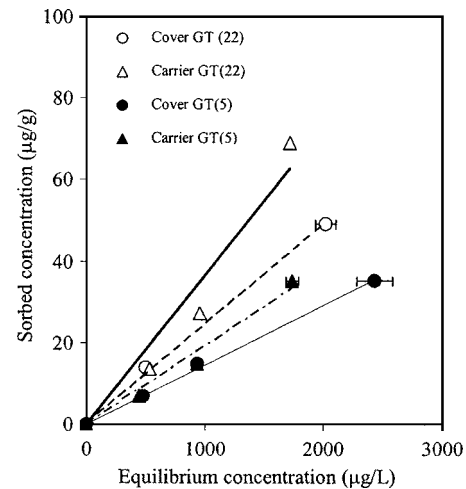


Fig. 3. Sorption of benzene compounds onto geotextiles

GCL (viz: 0.4 mL/g for benzene and 1.2 mL/g for toluene) and this provides some confirmation of the present results.

The bentonite layer in the GCL includes some geotextile fibers due to needle-punching. Although the mass of geotextile fiber in the bentonite layer is small, the partitioning coefficients for the geotextile are much larger than for bentonite alone (see Tables 2 and 3). Thus it is appropriate to consider sorption onto the geotextile fibers in the bentonite layer when assessing the equivalent partitioning coefficients $K_{d\text{beq}}$ for the bentonite layer. For a given mass per unit area of fiber and bentonite, the value of $K_{d\text{beq}}$ can be obtained from the measured partitioning coefficients of the geotextile and bentonite, viz:

$$K_{d\text{beq}} = \frac{(m_{db} \cdot K_{db} + m_{db\text{GT}i} \cdot K_{d\text{GT}i})}{m_{ab} + m_{db\text{GT}i}} \quad (7)$$

where m_{db} and $m_{db\text{GT}i}$, respectively, represent a dry mass of bentonite and a geotextile fiber per unit area in the bentonite layer, and K_{db} and $K_{d\text{GT}i}$ =partitioning coefficients for bentonite and cover geotextile, respectively. The fiber mass, $m_{db\text{GT}i}$, was measured five times and the average value was used in Eq. (7) to obtain the values given for bentonite and fiber in Table 3. Consideration of the presence of these fibers increased the partitioning coefficients by about 25%. For ethylbenzene, *m&p*-xylene, and *o*-xylene, this corresponded to an increase in K_d by about 1 mL/g relative to bentonite alone. However, the sorption parameters for the bentonite with fibers are still quite low. Inference of the partitioning coefficients at different temperatures is based on the Arrhenius's equation

Since the temperature in the diffusion cell was 7°C, the partitioning coefficients used for modeling the diffusion tests were obtained using the Arrhenius's equation [Eq. (5)] and the data at 22 and 5°C to deduce partitioning coefficient at 7°C. Thus, rewriting the Arrhenius's equation in terms of K_d rather than R_k allows the partitioning coefficient K_d to be estimated at any temperature from

$$\frac{K_{dT_1}}{K_{dT_2}} = \theta^{(T_1 - T_2)} \quad (8)$$

where

Table 2. Hydrocarbon-Geotextile Partitioning Coefficients at 22 and 5°C Deduced from Batch Tests: K_d (mL/g)

Chemicals	Temperature 22°C				Temperature 5°C			
	Cover geotextile (K_{dGT1}):mg/L	R^2	Carrier geotextile (K_{dGT2}):mg/L	R^2	Cover geotextile (K_{dGT1}):mg/L	R^2	Carrier geotextile (K_{dGT2}):mg/L	R^2
Benzene	25.8(±1.3)	0.86	32.2(±4.4)	0.95	15.3(±0.7)	1.00	21.0(±1.9)	0.98
Toluene	86.7(±1.5)	0.98	97.4(±7.3)	0.99	55.1(±0.0)	0.99	74.4(±0.0)	0.99
Ethylbenzene	228.8(±0.0)	0.99	247.7(±34.0)	0.93	107.1(±0.0)	0.99	144.4(±0.0)	1.00
<i>m&p</i> -Xylene	263.3(±3.9)	0.97	297.8(±5.3)	0.91	134.1(±0.0)	0.99	167.7(±5.4)	0.99
<i>o</i> -Xylene	163.3(±27.0)	0.94	192.1(±25.0)	0.88	81.8(±2.5)	0.88	108.3(±8.4)	0.94

$$\theta = \frac{X}{RT_1 T_2} \quad (9)$$

In general, the θ lies between 1.0 and 1.1 (Schnoor, 1996). Based on the ratio of partitioning coefficient of each compound at 5°C to that at 22°C (Table 2), the best fit to the data was obtained for θ between about 1.03 and 1.04.

Evaluation of Mass Losses during Diffusion Test

Blank tests were conducted using the diffusion apparatus without any GCL present to allow an assessment of mass loss due to sorption onto the Teflon coated stirrers or cell. The concentration of benzene decreased by about 10% at 22°C and by 3% at 7°C. Modeling was conducted to assess the effect of these mass losses on the interpretation of the diffusion test results for each contaminant as discussed below.

Diffusion Coefficients for Each Layer

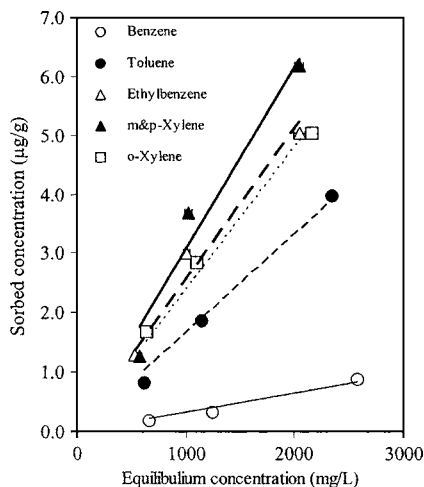
Diffusion was modeled for a layered system comprised of: (1) the upper perforated plate; (2) the cover geotextile; (3) the bentonite layer with the geotextile fibers; (4) the carrier geotextile; and (5) the lower perforated plate (Fig. 1). The physical properties of these layers are given in Table 4. For modeling diffusion at 22°C, the partitioning coefficients of the BTEX compounds were based on the results from the batch immersion/sorption tests (Tables 2 and 3).

The perforated plate (with 291, 2.5 mm diameter holes) was highly porous and did not have any significant tortuosity. No ben-

tonite was observed in the holes after the tests and so the effective diffusion coefficient for the plate was taken to be that in free solution, D_0 .

Although there was relatively little bentonite in the cover and carrier geotextile before hydration, some bentonite did swell into these geotextiles during hydration. Thus the effective diffusion coefficient of the BTEX compounds through the geotextile pores was considered to be bracketed by two limiting cases: (1) assuming negligible bentonite in the geotextile, the diffusion coefficient was taken to be that in free solution D_0 , and (2) assuming the bentonite was uniformly distributed throughout the entire thickness of the GCL at the same void ratio, the diffusion coefficient in the geotextile layer was taken to be the same as in the bentonite layer. Case (1) is discussed in this section; case (2) is discussed in the following section. The diffusion coefficients in free solution at 22 and 7°C were estimated from Eq. (6) ($\eta_{22}=0.94, \eta_7=1.41$ Pa s) using the published diffusion coefficient in free solution at 25°C (Table 1; $\eta_{25}=0.89$ Pa s). The diffusion coefficient for the bentonite layer was obtained by the iterative solution of Eq. (1), until a statistically based best-fit curve was obtained corresponding to the minimum summation of square error (SSE).

Fig. 5 shows the observed variations of the BTEX concentration (normalized with respect to the initial concentrations) in the source and receptor compartments at 22°C. Each data point represents the average of multiple evaluations of the concentration by GC/MS and the bars show the standard deviation. The best-fit theoretical curves generated by solving the diffusion equation with the appropriate boundary conditions are also shown in Fig. 5 (for the case with mass loss). The estimated diffusion coefficients for the benzene, toluene, ethylbenzene, *m&p*-xylene, and *o*-xylene at 22°C are given in Table 5 together with the SSE for the best-fit parameters. Although consideration (or not) of mass loss made a small difference to the SSE, at 22°C this did not have any effect on the estimated diffusion coefficients which were insensitive to the small amount of mass loss for these tests (see Table 5). The best fit diffusion coefficients in the bentonite layer

**Fig. 4.** Sorption of benzene, toluene, ethylbenzene, *m&p*-xylene, and *o*-xylene compounds onto bentonite at 22°C**Table 3.** Partitioning Coefficients for Hydrocarbons with Respect to Bentonite and Bentonite with Geotextile Fibers Deduced from Batch Tests at Temperature of 22°C

Chemicals	K_d for bentonite at 22°C		R^2	K_d for bentonite with GT fibers at 22°C	
	(mg/L)			(mg/L)	
Benzene	0.3–0.4 (0.97)	0.97		0.4–0.5	
Toluene	1.7–1.8 (0.99)	0.99		2.1–2.2	
Ethylbenzene	2.5–2.6 (0.96)	0.96		3.5–3.8	
<i>m&p</i> -Xylene	3.1–3.2 (0.96)	0.96		4.2–4.3	
<i>o</i> -Xylene	2.4–2.5 (0.99)	0.99		2.9–3.3	

Table 4. Physical Properties of Geosynthetic Clay Liner Used For Modeling

	Thickness (mm)	n	ρ_d (kg/m ³)
Perforated plate	1.25	0.4	3,720
Cover geotextile	1.1	0.75	230
Bentonite layer	7.5–8.1	0.8	450–500
Carrier geotextile	0.8	0.64	330

were benzene: 3.2×10^{-10} , toluene: 2.7×10^{-10} , ethylbenzene: 2.5×10^{-10} , *m&p* and *o*-xylene: 2.2×10^{-10} m²/s.

Fig. 6 shows the experimental data and theoretical predictions for 7°C. The theoretical predictions were obtained using sorption and diffusion parameters (Tables 6 and 7, respectively) estimated from Eqs. (6) and (8) ($\theta=1.03$) and the corresponding parameters at 22°C. Visual inspection indicates that these predictions [based on Eqs. (6) and (8) and data at 22°C] are quite good. Alternate diffusion parameters could be obtained by minimizing the SSE to get the best fit to the data at 7°C. The best-fit curve resulted in a slightly better visual fit to the data (not shown) and corresponded to a slightly lower SSE (SSE=0.016 versus 0.023) and diffusion coefficient (1.9×10^{-10} m²/s as compared to 2.1×10^{-10} m²/s). However while the best-fit curves are marginally better than those based on the predicted parameters [based on Eqs. (6) and (8) and

Table 5. Diffusion Coefficients for Each Modeled Layer at 22°C

Chemicals	$D_{GT}=D_0^a$	Effective diffusion coefficients $\times 10^{10}$ (m ² /s)	
		D_b	D_b
		Zero mass loss	Considering mass loss
Benzene	10.9	3.2–3.5 ^b SSE=0.014	3.2–3.5 SSE=0.035
Toluene	9.1	2.7–2.9 SSE=0.051	2.7–2.9 SSE=0.029
Ethylbenzene	8.5	2.5–2.8 SSE=0.084	2.5–2.8 SSE=0.054
<i>m&p</i> -Xylene	7.2	2.2–2.4 SSE=0.014	2.2–2.4 SSE=0.014
<i>o</i> -Xylene	7.3	2.2–2.4 SSE=0.016	2.2–2.4 SSE=0.022

^a D_0 =diffusion coefficient in free solution and D_{GT} : for geotextile.

^bSSE=summation square errors. This error was the same for the D values in the range quoted and hence all are equally valid from a statistical perspective. Visual inspection would suggest that the lower values generally give the best fit.

the data at 22°C], it is concluded that the predicted values are adequate for practical purposes and there would really be no need to perform the tests at 7°C to obtain diffusion and sorption parameters. Based on the data at 7°C and minimizing the SSE, the estimated diffusion coefficient for the BTEX compounds are 1.9

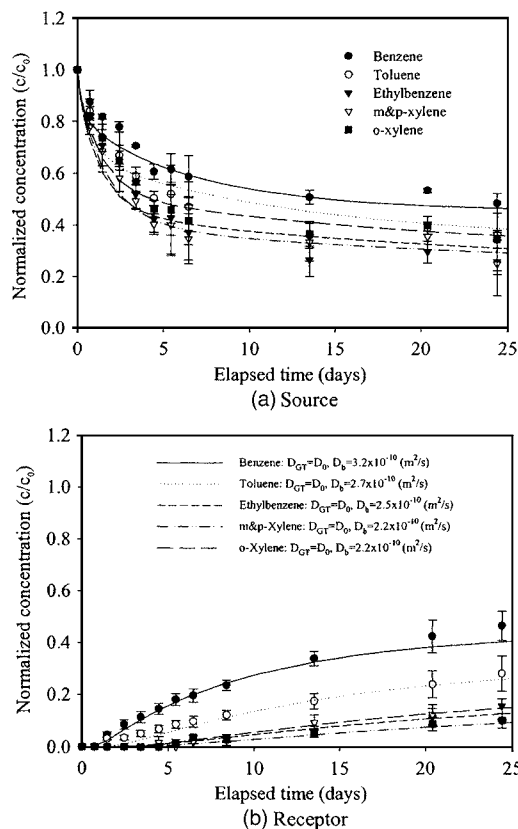


Fig. 5. Predicted and observed change of benzene, toluene, ethylbenzene, *m&p*-xylene, and *o*-xylene concentration with time during diffusion tests at 22°C ($D_{GT}=D_0$, mass loss considered)

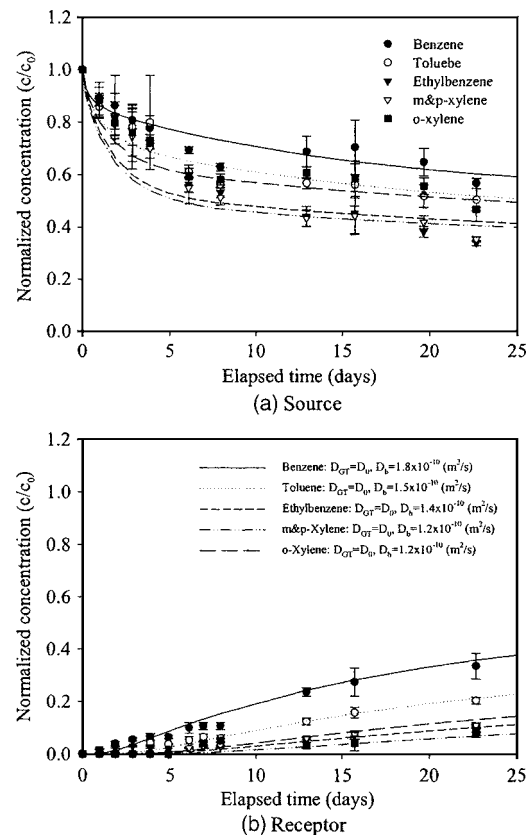


Fig. 6. Predicted and observed change of benzene, toluene, ethylbenzene, *m&p*-xylene, and *o*-xylene concentration with time during diffusion tests at 7°C ($D_{GT}=D_0$, mass loss considered)

Table 6. Predicted Partitioning Coefficients for Benzene, Toluene, Ethylbenzene, *m&p*-Xylene, and *o*-Xylene Compounds at 7°C: (mL/g)

Chemicals	Cover geotextile: K_{dGT1}	Bentonite layer with fibers: K_{dbeq}	Carrier geotextile: K_{dGT2}
Benzene	16.6	0.4	20.7
Toluene	55.6	1.5	62.5
Ethylbenzene	146.9	2.5	159.0
<i>m&p</i> -Xylene	167.4	3.0	191.1
<i>o</i> -Xylene	87.5	2.0	107.3

$\times 10^{-10}$, 1.6×10^{-10} , 1.5×10^{-10} , and 1.3×10^{-10} m²/s, respectively. These and the predicted values (shown in brackets) are given in Table 7.

Geotextile Layer Contaminated by Bentonite

The theoretical results presented in the previous section were based on the limiting case assuming negligible bentonite in the carrier and cover geotextiles. This section examines the second limiting case where it is assumed that bentonite is uniformly distributed in both the bentonite and geotextile layer (with dry density, porosity and partitioning coefficients as shown in Tables 8 and 9 for 22 and 7°C, respectively). This assumption implies that the effective diffusion coefficient for both geotextiles (D_{GT}) is the same as the D_b of bentonite. The actual situation is expected to lie between the two limiting cases that are considered herein.

Figs. 7 and 8 show the observed concentration and predicted curves (considering mass loss) for the BTEX compounds at 22 and 7°C. The diffusion coefficients (Table 10) are slightly larger values than the values estimated in the previous section due to decrease of D_{GT} in both geotextile layers. The difference represent a 10–15% variation (e.g., best estimates ranging between 3.2 and 3.7×10^{-10} m²/s for benzene and 2.2 – 2.6×10^{-10} m²/s for xylenes—compare Tables 5 and 10); this would not significantly affect the predicted performance of a GCL as a barrier. The use of the higher value would be conservative.

Table 7. Diffusion Coefficients of Each Modeled Layer at 7°C

Chemicals	Effective diffusion coefficients $\times 10^{10}$ (m ² /s)		
	$D_{GT}=D_0^a$	D_b Zero mass loss	D_b Considering mass loss
Benzene	7.0	1.9 ^b (2.1–2.3) ^c SSE=0.016 ^d	1.8 (2.1–2.3) SSE=0.013
Toluene	5.8	1.6 (1.7–1.9) SSE=0.015	1.5 (1.7–1.9) SSE=0.016
Ethylbenzene	5.5	1.5 (1.6–1.8) SSE=0.057	1.4 (1.6–1.8) SSE=0.094
<i>m&p</i> -Xylene	4.8	1.3 (1.4–1.5) SSE=0.037	1.2 (1.4–1.5) SSE=0.102
<i>o</i> -Xylene	4.9	1.3 (1.4–1.6) SSE=0.027	1.2 (1.4–1.6) SSE=0.043

^a D_0 =diffusion coefficient in free solution and D_{GT} : for geotextile.

^bDiffusion coefficient estimated by minimum SSE.

^cDiffusion coefficient calculated based on Eq. (6) and data at 22°C.

^dSSE=summation square errors for diffusion coefficient^b estimated by minimum SSE.

Table 8. Physical Properties and Equivalent Partitioning Coefficients of Each Layer of Geosynthetic Clay Liner at 22°C

	Cover geotextile layer	Bentonite layer with fibers	Carrier geotextile layer
Dry density (kg/m ³)	586.0	359.0	696.0
Porosity	0.63	0.88	0.51
Equivalent partitioning coefficients (mL/g)	—	—	—
Benzene	10.3	0.6	15.6
Toluene	35.0	2.6	47.6
Ethylbenzene	90.9	4.8	120.0
<i>m&p</i> -Xylene	104.8	5.7	144.3
<i>o</i> -xylene	65.3	4.1	93.3

Equivalent Parameters for the Entire Geosynthetic Clay Liner

To identify the factors contributing to sorption in the GCL, the analysis performed in the previous section separately examined the diffusion and sorption in the cover geotextile, bentonite, and carrier geotextile. However, in practice one would like to be able to use a single set of parameters for the entire GCL. In this section, the individual diffusion and sorption parameters are combined to give equivalent parameters for the entire GCL. The equivalent partitioning coefficients, K_{deq} , can be obtained, assuming complete mixing of the bentonite and geotextile, by combining the contributions of the partitioning coefficients for the bentonite and fiber, the cover, and the carrier geotextiles, viz

$$K_{deq} = \frac{(m_{db} \cdot K_{db} + m_{dbGT1} \cdot K_{dGT1} + m_{dGT1} \cdot K_{dGT1} + m_{dGT2} \cdot K_{dGT2})}{m_{ab} + m_{dbGT1} + m_{dGT1} + m_{dGT2}} \quad (10)$$

where the partitioning coefficients K_{db} , K_{dGT1} , and K_{dGT2} , at each temperature, are obtained from Tables 2, 3, and 6.

The estimated values of D_{GCL} and K_{deq} at 22 and 7°C are given in Table 11. Figs. 9 and 10 show the observed and calculated variation in concentrations of benzene at 22 and 7°C. In this mod-

Table 9. Physical Properties and Equivalent Partitioning Coefficients of each Layer of Geosynthetic Clay Liner at 7°C

	Cover geotextile layer	Bentonite layer with fibers	Carrier geotextile layer
Dry density (kg/m ³)	633.0	409.0	743.0
Porosity	0.61	0.86	0.49
Equivalent partitioning coefficients (mL/g)	—	—	—
Benzene	6.3	0.5	9.5
Toluene	21.1	2.0	28.9
Ethylbenzene	54.7	3.7	72.7
<i>m&p</i> -Xylene	62.5	4.4	87.3
<i>o</i> -Xylene	32.9	2.7	49.2

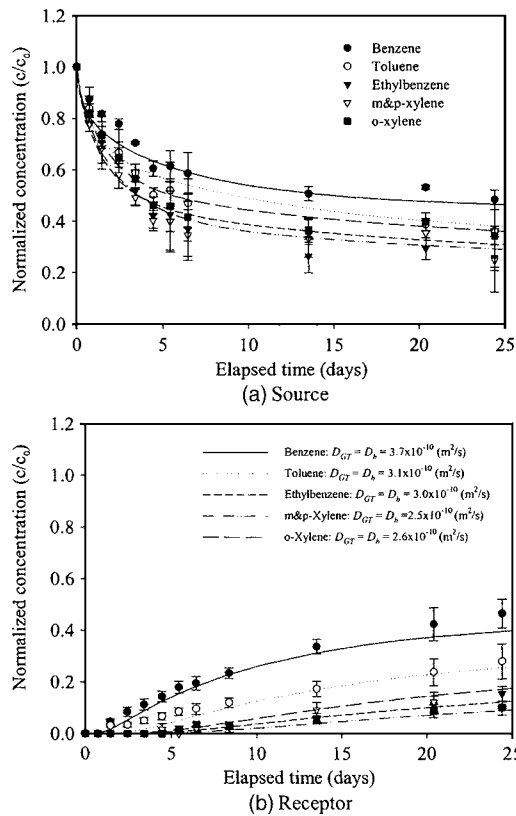


Fig. 7. Predicted and observed change of benzene, toluene, ethylbenzene, *m&p*-Xylene, and *o*-xylene concentration with time during diffusion tests at 22°C ($D_{GT}=D_b$, loss considered)

eling, the calculated K_{deq} was fixed at the value calculated as described above and the diffusion coefficients were estimated by obtaining a best fit between the observed and predicted response (with the minimum SSE for the best fit being given in Table 11). Given the scatter in test results, the diffusion coefficient for benzene could range between 3.7×10^{-10} and 4.0×10^{-10} m²/s and still give a reasonable fit to the data with the best fit (the lowest SSE) being obtained for $D_{GCL}=3.7 \times 10^{-10}$ m²/s. This value is larger than for bentonite layer alone (Table 7) because the less tortuous geotextile layers have been combined with the bentonite layer to obtain bulk parameters for the GCL.

The results presented in this section for toluene, ethylbenzene, and xylenes were obtained assuming that the ratio of diffusion coefficient for the different contaminants to that for benzene was the same as for the free solution. The fact that these parameters give values that give good visual fits and low SSE values indicates that the diffusion coefficient measured for one BTEX compound can be used to predict that of the others (assuming the same ratio as in free solution at 25°C) and that Eqs. (6) and (8) are effective for estimating the diffusion coefficients and the partitioning coefficients at different temperatures.

Effect of Temperature

Fig. 11 shows the observed benzene concentrations in the source and receptor compartments at 22 and 7°C and it can be seen that mass transport to the receptor is slower at 7°C than at 22°C. This is despite the partially compensating effects of a decrease in diffusion D_e and sorption K_d parameters as illustrated in Fig. 12 which shows the effect of different combinations of the param-

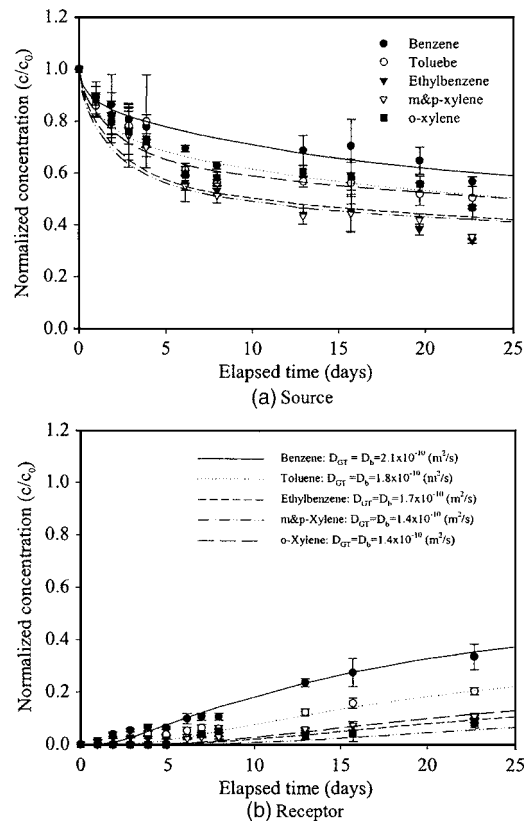


Fig. 8. Predicted and observed change of benzene, toluene, ethylbenzene, *m&p*-Xylene, and *o*-xylene concentration with time during diffusion tests at 7°C ($D_{GT}=D_b$, loss considered)

eters for benzene estimated at 22°C (D_{22}, K_{d22}) and 7°C (D_7, K_{d7}). While it is recognized that in practice one would never get combinations of parameters such as for curves (b) (D_7, K_{d22}) and (d) (D_{22}, K_{d7}), a theoretical examination of these cases does show the effect of changes in D_e and K_d (due to temperature) on mass transport. Thus comparing curves (a) and (d) (Fig. 12) it can be seen that the reduction in K_d alone (due to a drop in temperature) gives rise to an increase in mass transport to the receptor. In

Table 10. Diffusion Coefficients ($D_{GT}=D_b$) of Benzene, Toluene, Ethylbenzene, *m&p*-Xylene, and *o*-Xylene Compounds

Chemicals	Effective diffusion coefficients $\times 10^{10}$ (m ² /s)	
	$D_{GT}=D_b$ at 22°C	$D_{GT}=D_b$ at 7°C
Benzene	3.7–4.0 SSE=0.031 ^a	2.1 (2.4–2.6) ^b SSE=0.01
Toluene	3.1–3.3 SSE=0.026	1.8 (2.0–2.2) SSE=0.072
Ethylbenzene	2.9–3.2 SSE=0.033	1.7 (1.9–2.0) SSE=0.052
<i>m&p</i> -Xylene	2.5–2.7 SSE=0.010	1.4 (1.6–1.8) SSE=0.061
<i>o</i> -Xylene	2.6–2.8 SSE=0.015	1.4 (1.6–1.8) SSE=0.019

^aSSE=summation square errors. This error was the same for the D values in the range quoted and hence all are equally valid from a statistical perspective. Visual inspection would suggest that the lower values generally give the best fit.

^bDiffusion coefficient calculated based on Eq. (6) and data at 22°C.

Table 11. Diffusion Coefficients (D_{GCL}) of Benzene, Toluene, Ethylbenzene, *m&p*-Xylene, and *o*-Xylene Compounds for Entire Geosynthetic Clay Liner

Chemicals	Effective diffusion coefficients $\times 10^{10}(\text{m}^2/\text{s})$		Equivalent partitioning coefficients (mL/g)	
	D_{GCL} at 22°C	D_{GCL} at 7°C	K_{deq} at 22°C	K_{deq} at 7°C
Benzene	3.7–4.0 ^a SSE=0.029	2.2 ^b (2.4–2.6) ^c SSE=0.012	4.4	2.6
Toluene	3.1–3.3 SSE=0.031	1.8 (2.0–2.2) SSE=0.007	14.5	8.7
Ethylbenzene	2.9–3.2 SSE=0.041	1.7 (1.9–2.0) SSE=0.028	36.0	21.6
<i>m&p</i> -Xylene	2.5–2.7 SSE=0.039	1.5 (1.6–1.8) SSE=0.044	42.4	25.4
<i>o</i> -Xylene	2.6–2.8 SSE=0.028	1.5 (1.6–1.8) SSE=0.01	27.1	14.1

^aSSE=Summation square errors.^bDiffusion coefficient estimated by minimum SSE.^cDiffusion coefficient calculated based on Eq. (6) and data at 22°C.

contrast, when D_e alone changes [compare curve (a) with (b)] there is large decrease in mass transport through the GCL. The combined effect of reducing both D_e and K_d due to a decrease in temperature [compare curves (a) and (c) in Fig. 12] results in a decrease in mass transport through the GCL to the receptor, demonstrating that the change in diffusion coefficient due to a change in temperature dominates over the effect of the change in partitioning coefficient.

Conclusions

Tests were performed to evaluate the diffusion and sorption parameters for the BTEX compounds (benzene, toluene, ethylbenzene, *m&p*-Xylene, and *o*-xylene) and a GCL at the low confining pressure expected in shallow barrier applications. Particular emphasis was placed on the effect of temperature on both diffusion and sorption and the appropriateness of equations that could be

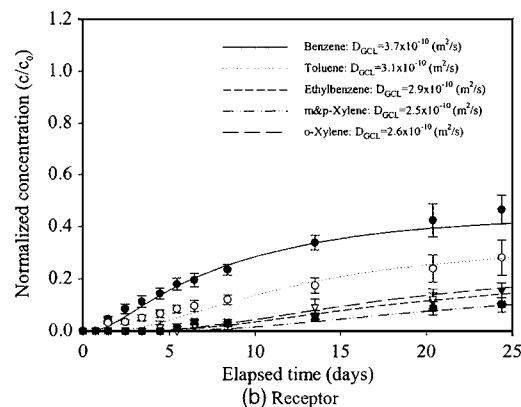
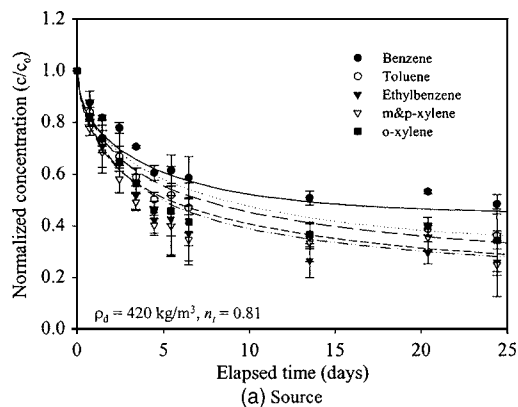


Fig. 9. Predicted and observed change in benzene, toluene, ethylbenzene, *m&p*-Xylene, and *o*-xylene concentrations with time during diffusion tests at 22°C using bulk geosynthetic clay liner parameters

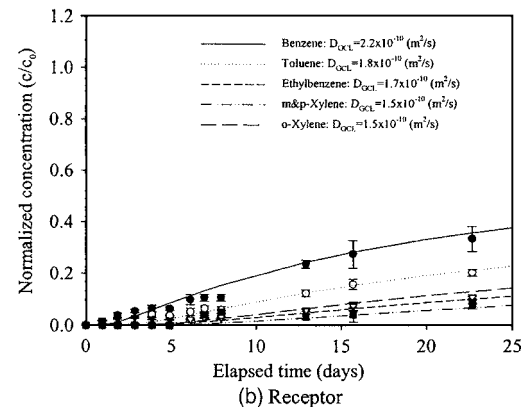
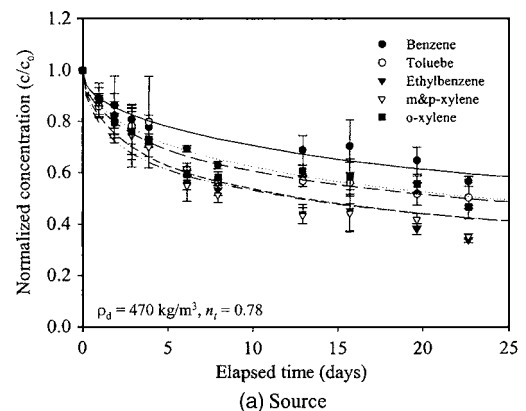


Fig. 10. Predicted and observed change in benzene, toluene, ethylbenzene, *m&p*-Xylene, and *o*-xylene concentrations with time during diffusion tests at 7°C using bulk geosynthetic clay liner parameters

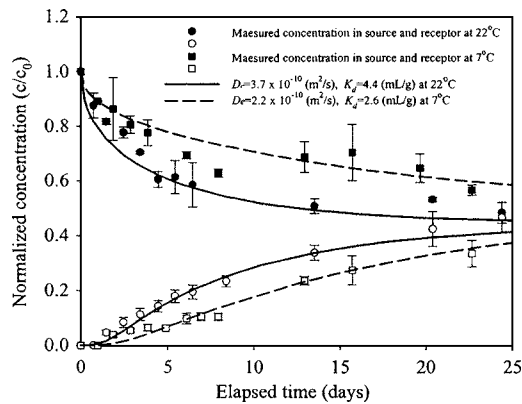


Fig. 11. Comparison of benzene concentration at 22 and 7°C

used to predict parameters at one temperature based on values obtained at another (room) temperature.

The sorption/immersion tests indicated that the partitioning coefficients for the carrier geotextile were greater than those for the cover and that the sorption onto the geotextile component of the GCL dominated over sorption by the bentonite component. Thus, sorption by a GCL will be greater than for a similar amount of bentonite alone. These results also suggest that sorption will be product specific and may change from one product to another (even for the same manufacturer) depending on the type and amount of geotextile used. The following conclusions can be drawn from this work:

1. Both diffusion and sorption depend on temperature and both parameters were lower at 7°C than at 22°C. The effect of a lower diffusion coefficient dominated over the effect of a lower sorption coefficient and resulted in lower mass transport across the GCL at 7°C rather than at 22°C.
2. The use of Eqs. (6) and (8) to predict diffusion and sorption parameters at 7°C based on parameters obtained at 22°C, resulted in a good fit to the experimental data (a sum of least squares error of less than 0.1) at 7°C.
3. The diffusion coefficients (at 22°C, 7°C) for the BTEX compounds through the GCL followed the order benzene(3.7×10^{-10} , 2.2×10^{-10} m²/s) > toluene(3.1×10^{-10} , 1.8×10^{-10} m²/s) > ethylbenzene(2.9×10^{-10} , 1.7×10^{-10} m²/s) > m&p-xylene(2.5×10^{-10} , 1.5×10^{-10} m²/s) \approx o-xylene(2.6×10^{-10} ,

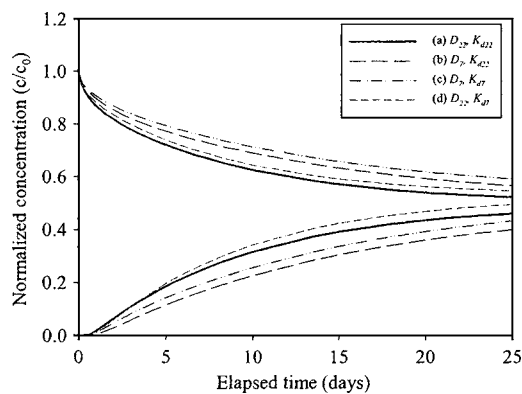


Fig. 12. Theoretical curves obtained from four combinations of D_e and K_d (benzene)

1.5×10^{-10} m²/s); and corresponded to the order of the diffusion coefficients in free water.

4. The BTEX partitioning coefficients (at 22°C, 7°C) for the entire GCL followed the order; m&p-xylene(42, 25 mL/g) > ethylbenzene(36, 22 mL/g) > o-xylene(27, 14 mL/g) > toluene(15, 8.7 mL/g) > benzene(4.4, 2.6 mL/g).

The diffusion coefficients of the BTEX compounds reported herein were obtained under the low confining pressure (9.5 kPa). Hence, the diffusion coefficients reported in this study are expected to be near the upper and end of the range of the diffusion coefficients for BTEX compounds likely to be experienced in practical application involving the use of GCLs as barrier.

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References

- Altshuler, G., and Belfort, G. (1983). "Selective adsorption of organic homologues onto activated carbon from dilute aqueous solutions." Treatment of water by granular activated carbon, Advances in Chemistry Series 202, Proc. Symposium Sponsored by the Division of Environmental Chemistry at the 181st Meeting of the American Chemical Society, Atlanta, M. J. McGuire, and I. H. Suffet, eds., American Chemical Society, Washington, D.C., 29–61.
- American Society for Testing and Materials, (ASTM). (2005). "Standard test method for determining a sorption constant (K_{oc}) for an organic chemical in soil and sediments." E1195-01, Vol. 11.05, Philadelphia.
- Aminabhavi, T. M., Harlapur, S. F., Balundgi, R. H., and Ortego, J. D. (1996). "Sorption kinetics and diffusion of alkanes into tetrafluoroethylene/propylene copolymer membrane." *J. Appl. Polym. Sci.*, 59, 1857–1870.
- Aminabhavi, T. M., and Naik, H. G. (1999). "Sorption/desorption studies on polypropylene geomembrane in the presence of hazardous organic liquids." *J. Appl. Polym. Sci.*, 72, 1291–1298.
- Barone, F. S., Rowe, R. K., and Quigley, R. M. (1992). "A laboratory estimation of diffusion and adsorption coefficients for several volatile organics in a natural clayey soil." *J. Contam. Hydrol.*, 10, 225–250.
- Bouazza, A. (2002). "Geosynthetic clay liners." *Geotext. Geomembr.*, 20, 3–17.
- Chiou, C. T. (1987). "Theoretical considerations of the partition uptake of nonionic organic compounds by soil organic matter." *Reactions and movement of organic chemicals in soils*, B. L. Sawhney, and K. Brown, eds., SSSA Special Publication Number 22, 1–30.
- Clark, M. M. (1996). *Transport modeling for environmental engineers and scientist*, Wiley, New York.
- Gullick, R. W. (1998). "Effects of sorbent addition on the transport of inorganic and organic chemicals in soil-bentonite cutoff wall containment barriers." PhD thesis, The Univ. of Michigan, Ann Arbor, Mich.
- Headley, V. J., Boldt-Leppoin, E. J. B., Haug, D. M., and Peng, J. (2001). "Determination of diffusion and adsorption coefficients for volatile organics in an organophilic clay-sand-bentonite liner." *Can. Geotech. J.*, 38, 809–817.
- Kellner, R., Mermet J. M., Otto, M., and Widmer, H. M. (1998). *Analytical chemistry*, Wiley, New York.

- Khandelwal, A., Rabideau, A. J., and Shen, P. (1998). "Analysis of diffusion and sorption of organic solutes in soil-bentonite barrier materials." *Environ. Sci. Technol.*, 32, 1333–1339.
- Krol, M. M., and Rowe, R. K. (2004). "Diffusion of TCE through soil-bentonite slurry walls." *Soil Sediment Contamination*, 13(1), 81–101.
- Lake, C. B., and Rowe, R. K. (2004). "Volatile organic compound diffusion and sorption coefficients for a needle-punched GCL." *Geosynthet. Int.*, 11(4), 257–272.
- Li, H. M., Bathurst, R. J., and Rowe, R. K. (2002). "Use of GCLs to control migration of hydrocarbons in severe environmental conditions." *Proc. International Symp. on Geosynthetic Clay Barriers*, Nuremberg, Germany, 187–198.
- Montgomery, J. H., and Welkom, L. M. (1990). *Groundwater chemicals desk reference*, Lewis, Chelsea, Mich.
- Morrissey, A. F., and Grismer, E. M. (1999). "Kinetics of volatile organic compound sorption/desorption on clay minerals." *J. Contam. Hydrol.*, 36, 291–312.
- Reid, C. R., Pausnitz, M. J., and Poling, E. B. (1987). *The properties of gases & liquids*, 4th Ed., McGraw-Hill, New York.
- Rogers, C. E. (1965). "Solubility and diffusivity." *Physics and chemistry of the organic solid state*, F. David, M. M. Labes, and A. Weissberger, eds., Wiley Interscience, New York, 509–635.
- Rowe, R. K. (2001). "Barrier systems." *Geotechnical and geoenvironmental engineering handbook*, Chap. 25, Kluwer Academic, Norwell, Mass., 739–788.
- Rowe, R. K., and Booker, J. R. (1998). "POLLUTE v6.3." GAEA Technologies Ltd., Whitby, Ontario, <www.gaea.ca.>
- Schnoor, L. J. (1996). *Environmental modeling—Fate and transport of pollutants in water, air, and soil*, Wiley, New York.
- Sleep, B. E., and McClure, D. P. (2001). "The effect of temperature on adsorption of organic compounds to soils." *Can. Geotech. J.*, 38, 46–52.
- Yaws, C. L. (1995). *Handbook of transport property data*, Gulf, Houston.