

# Effect of Surface Fluorination on Diffusion through a High Density Polyethylene Geomembrane

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**Abstract:** The relative improvement of the diffusive barrier function of high density polyethylene (HDPE) geomembranes to volatile organic compounds (VOCs) when subjected to surface fluorination is experimentally examined. The surface fluorination consisted of applying elemental fluorine, which exchanged with hydrogen along polymer chains at the surface of a polyolefin substrate. Sorption and diffusion tests were performed on both traditional “untreated” and “fluorinated” 1.5 mm HDPE geomembranes using dilute aqueous organic contaminants commonly found in municipal solid waste leachate. The partitioning coefficient is shown to remain essential the same after the surface fluorination; however, the surface fluorination resulted in a reduction in both the diffusion and the permeation coefficients by factors ranging between 1.5 and 4.5, depending on the hydrocarbon examined. Modeling of VOC diffusion through a geomembrane/compacted clay composite liner indicated that contaminant impacts were about 1.7–2.9 times lower when a fluorinated geomembrane is used. To achieve the same level of protection as provided by the fluorinated geomembrane underlain by 0.60 m of compacted clay, one would need an additional 0.4–0.9 m of compacted clay in conjunction with a conventional (untreated) geomembrane. The importance of the thickness of the treated layer is highlighted.

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## Introduction

It is well established that intact high density polyethylene (HDPE) geomembranes used as part of a composite liner (geomembrane/compacted clay) system for municipal solid waste (MSW) landfills provide a barrier to advective migration for all contaminants and diffusive migration for inorganic contaminants. However, HDPE geomembranes have limited effectiveness with regard to controlling the diffusion of volatile organic compounds (VOCs). Several investigations (Park and Nibras 1993; Prasad et al. 1994; Rowe et al. 1995, 1996; Sangam and Rowe 2001) have shown that many organic contaminants can readily migrate through the geomembrane liner and hence could potentially pollute groundwater if there is not an adequately compacted clay liner and/or an attenuation layer below the geomembrane. Thus, there is a potential role for improved geomembranes that can be more effective as barrier to VOCs.

The migration of an organic contaminant through a geomembrane is a three-steps process (Park and Nibras 1993): (1) parti-

tion of the contaminant between inner surface of the geomembrane and the medium containing the contaminant (adsorption); (2) diffusion of the penetrant through the geomembrane; and (3) partition between the outer surface of the geomembrane and the outer medium (desorption). Several researchers (e.g., Rogers 1985; Naylor 1989; Park and Nibras 1993; Sangam and Rowe 2001, etc.) have provided detailed descriptions of the migration processes as well as a discussion of the factors that affect the overall process. These factors include the geomembrane properties (e.g., density, crystallinity, crosslinking, chain branching, etc.), chemical properties (e.g., polarity, size, etc.), and temperature. In general, the well-known principle of solubility “like dissolves like” holds, and it has been shown that in most polymer-penetrant systems, both diffusion and permeation coefficients exhibit a general increase with similarity between the components (August and Tatzky 1984; Rowe et al. 1995, 1996; Sangam and Rowe 2001).

One means of improving the effectiveness of a geomembrane with regard to the permeation of organic contaminants is to treat the material in order to reduce its affinity to these chemicals by fluorinating the surface of the geomembrane. The technique consists of applying elemental fluorine, which exchanges with hydrogen along polymer chains at the surface of a polyolefin substrate (Smart 1994). Although the method has been widely used in the packaging industry, its applicability to landfill geomembrane liners has not previously been examined.

The objective of the paper is to examine the potential improvement in the diffusive properties of HDPE geomembranes when their surfaces are fluorinated. The paper presents the sorption, diffusion, and permeation coefficients for organic contaminants for both “untreated” and “treated” geomembranes. The paper also outlines the level of barrier improvement achieved by the surface treatment and addresses the potential implications for the design of landfill barriers.

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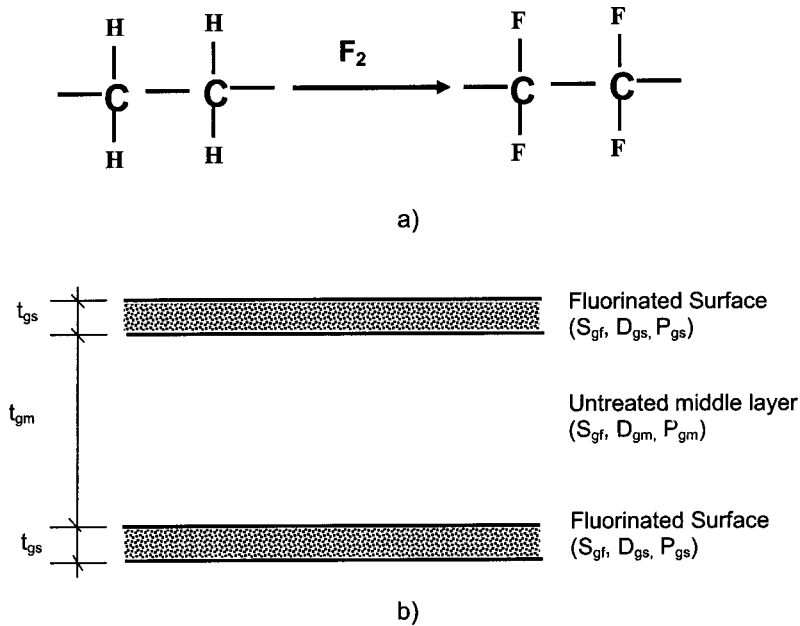


Fig. 1. Surface fluorination: (a) molecule exchange equation; and (b) idealized three-layered fluorinated geomembrane system

## Overview of Surface Fluorination

Surface fluorination is a technique that applies a controlled oxidation using elemental fluorine ( $F_2$ ) to exchange with hydrogen ( $H_2$ ) on the polymer chains at the surface of the geomembrane as illustrated in Fig. 1. The fluorination proceeds via a free radical mechanism wherein fluorine atoms exchange for hydrogen atoms. This exchange is due to the weakness of the F–F bond, the strength of the C–F bond, the stability of the HF group that is formed as a consequence of the reaction, and the extremely low activation energy for hydrogen abstraction and substitution (Anand et al. 1994). Thus, the fluorine becomes covalently (permanently) bonded in place of hydrogen at the surface, creating a barrier layer to certain hydrocarbons.

Surface fluorination of HDPE substrates are commercially available and are being routinely used in the polyolefin container industry to improve the shelf life storage of hydrocarbon fluids. The permeation resistance of HDPE to hydrocarbons is increased by a factor that may reach 2 orders of magnitude for thin HDPE substrates (Barsamyan and Sokolov 1999). However, the physical performance properties (e.g., tensile properties) of the containers remain practically unchanged, since for surface fluorination, fluorine/hydrogen exchange occurs only in a thin layer along the exposed surfaces.

The increase in the permeation resistance to hydrocarbons arises from at least three synergistic effects (Anand et al. 1994). First, the application of elemental fluorine raises the surface energy as the surface water wettability increases. As a consequence, the effective solubility parameter of the modified polymer increases (compared to the solubility parameters of organic solvents) and hence reduces the solubility (or partitioning) of the nonpolar organic liquids in the material. Second, the surface fluorination reduces the free volume of the polymer through which the chemical can permeate, leading to a reduction in the solubility or partitioning. The last cause is the crosslinking that accompanies the fluorination. The direct effect of crosslinking is the reduction of the segmental mobility of the polymer chains and hence the reduction of the diffusivity of larger penetrant mol-

ecules. The level of reduction in the permeation of hydrocarbons depends essentially on the thickness of the fluorinated surface layer, which in turn depends on the number of treatments and other factors previously cited. For example, Carstensen et al. (1999) showed that a quadruple fluorination treatment of an HDPE pipe resulted in a 80-fold improvement compared to a twofold improvement provided by a single treatment.

There are two fundamental methods of surface fluorination (Anand et al. 1994): posttreatment (postforming) and in situ treatment. The main difference between the methods resides not only in the terms of their principles of operation but also in regard to economic flexibility, applicability, and the ultimate properties of the product. In post-treatment, the polymer is exposed to fluorine after it has been formed resulting in an improvement in operational flexibility and better economics for smaller productions. In contrast, in situ treatment uses existing polymer-processing equipment to apply the desired fluorine to the polymer. Independent of the method used, the effectiveness of the treatment depends on several factors including the fluorine partial pressure and dilution, reaction time, temperature, and the presence of coreactants (Anand et al. 1994).

## Experimental Investigation

### High Density Polyethylene Geomembranes

The investigation was conducted on both untreated and fluorinated geomembranes provided by Fluoro-Seal Inc. (Texas) with

Table 1. Selected Properties of Untreated and Fluorinated High Density Polyethylene Geomembranes

Properties	ASTM	Untreated	Fluorinated
Thickness (mm)	D 5199	1.5	1.5
Density (g/cm <sup>3</sup> )	D 792	0.950	0.953
Crystallinity (%)	E 794	61.3±1.3	61.0±4.2
Oxidative induction time (min)	D 3895	120±1.5	196±2.6

**Table 2.** Selected Properties<sup>a</sup> of Organic Contaminants Examined

Chemicals	Molecular weight (g/mole)	Density $\rho$ (g/cm <sup>3</sup> )	Molar volume <sup>b</sup> (cm <sup>3</sup> )	Aqueous solubility <sup>c</sup> (mg/L)	$\log K_{ow}$ <sup>d</sup>	Boiling temperature (°C)	Dipole moment (Debye)
Dichloromethane	84.93	1.3266	64.02	20,000	1.25	40.2	1.60
1,2-Dichloroethane	98.96	1.2530	78.98	8,690	1.45	83.5	1.44
Trichloroethylene	131.39	1.4642	89.74	1,100	2.53	87.2	0.77
Benzene	78.11	0.8765	89.11	1,780	2.13	80.1	0.00
Toluene	92.14	0.8669	106.28	515	2.79	110.6	0.30
Ethylbenzene	106.17	0.8670	122.46	152	3.13	136.2	0.36
<i>m</i> -Xylene	106.17	0.8642	122.85	161.9	3.20	138.0	0.30
<i>o</i> -Xylene	106.17	0.8802	120.62	152	3.13	144.0	0.63
<i>p</i> -Xylene	106.17	0.8669	122.47	156	3.18	138.3	0.00

<sup>a</sup>From Montgomery and Welkom (1990).<sup>b</sup>Calculated based on chemical density and molar weight.<sup>c</sup>At 20°C.<sup>d</sup> $\log K_{ow}$ : octanol–water partitioning coefficient.**Table 3.** Inferred Partitioning Coefficients ( $S_{gf}$ ) from Sorption Test for Both Untreated and Fluorinated Geomembranes

Chemical	Untreated geomembrane				Fluorinated geomembrane				$S_{gf}$ <sup>a</sup>
	$c_{f0}$	SU1 $M_g=7.722$ g	SU2 $M_g=7.757$ g	Average	$c_{f0}$ <sup>b</sup>	SF1 $M_g=7.769$ g	SF2 $M_g=7.794$ g	Average	
Dichloromethane	4.6	12	14	13	4.7	13 <sup>c</sup>	12 <sup>c</sup>	13	13
1,2-Dichloroethane	4.7	14	10	12	4.8	10	13	12	12
Trichloroethylene	2.7	97	92	95	2.5	102	92	97	96
Benzene	3.6	56	58	57	3.7	51	63	57	57
Toluene	2.6	116	128	122	2.6	134	130	132	127
Ethylbenzene	1.5	260	224	242	1.4	247	240	244	243
<i>m</i> & <i>p</i> -Xylenes	1.4	274	290	282	1.3	321	274	298	290
<i>o</i> -Xylene	1.7	254	234	244	1.5	245	203	224	234

<sup>a</sup>Average of  $S_{gf}$  values for both treated and untreated geomembranes.<sup>b</sup>Initial solution concentrations (mg/L).<sup>c</sup>Equilibrium not reached.**Table 4.** Diffusion ( $D_g$ ), Partitioning ( $S_{gf}$ ), and Permeation ( $P_g$ ) Coefficients Inferred from Diffusion Tests

Contaminants	Untreated geomembrane				Fluorinated geomembrane					PR	
	$c_0$ <sup>a</sup> (mg/L)	$D_g$ ( $10^{-12}$ m <sup>2</sup> /s)	$S_{gf}$	$P_g$ ( $10^{-12}$ m <sup>2</sup> /s)	$c_0$ <sup>a</sup> mg/L	$S_{gf}$	$D_{gf}$ ( $10^{-13}$ m <sup>2</sup> /s)	$P_{gf}$ ( $10^{-12}$ m <sup>2</sup> /s)	$P_{gs}$ ( $10^{-14}$ m <sup>2</sup> /s)	Outer layer <sup>b</sup>	Average <sup>c</sup>
Dichloromethane	5.1	0.25	14	3.5	5.2	20	1.2	2.4	4.0	87	1.5
1,2-Dichloroethane	4.9	0.18	18	3.2	5.1	18	0.99	1.7	1.9	166	1.9
Trichloroethylene	2.9	0.28	120	33.6	2.4	120	0.91	10.9	8.6	391	3.1
Benzene	3.6	0.2	60	12	3.9	60	0.76	4.5	3.8	314	2.7
Toluene	2.7	0.22	140	30.8	2.3	140	0.62	8.7	6.5	477	3.5
Ethylbenzene	1.6	0.16	260	41.6	1.3	260	0.36	9.4	6.5	643	4.4
<i>m</i> & <i>p</i> -Xylenes	1.5	0.15	300	45	1.3	300	0.33	9.9	6.8	666	4.5
<i>o</i> -Xylene	1.8	0.11	250	27.5	1.6	250	0.28	7	5.0	550	3.9

<sup>a</sup>Initial solution concentrations (mg/L).<sup>b</sup>PR=permeation reduction factor= $P_g/P_{gs}$ .<sup>c</sup>PR=permeation reduction factor= $P_g/P_{gf}$ .

properties as given in Table 1. The untreated geomembrane is a 1.5 mm thick HDPE smooth geomembrane having a density of 0.95 g/cm<sup>3</sup>, a crystallinity of about 61%, and a standard oxidative induction time (OIT) of 120 min. The treated geomembrane is formed by fluorinating (post-treatment) the same geomembrane on both surfaces. To infer the thickness of fluorinated layer, both untreated and fluorinated were cross sectioned with a razor blade, given a thin, sputter-deposited gold coating (to alleviate charging problems during the ensuing examination), and then examined by scanning electron microscopy combined with energy dispersive x-ray spectroscopy. The thickness of the fluorinated layer was inferred to range from 1 to 5 μm with an average value of about 4 μm.

The difference between the two materials is apparent from the high Std-OIT of about 196 min measured on disk specimens cut across the treated geomembrane as opposed to 120 min for the untreated geomembrane. This value is 63% higher than the untreated measured OIT and is probably caused by the presence of the two layers formed by the fluorination process that reduces the diffusion of oxygen through the material during testing.

### Contaminants

The contaminants examined are VOCs including chlorinated aliphatic [dichloromethane (DCM), 1,2-dichloroethane (1,2-DCA), and trichloroethylene (TCE)] and aromatic hydrocarbons [benzene, toluene, ethylbenzene, and xylenes (BTEX)]. These contaminants are commonly found in MSW landfill leachate (Rowe et al. 1995). The tests were performed using dilute aqueous mixed solutions of laboratory grade chemicals (99% + purity) and having the properties summarized in Table 2. The initial concentrations of each contaminant in the solution ranged from 1.3 to 5.2 mg/L (Tables 3 and 4).

Samples collected during the tests were analyzed using a gas chromatography/mass spectrometer (GC/MS) equipped with an autosampler used in solid phase microextraction and headspace modes. The equipment conditions and the complete analytical procedure used were the same as described in detail by Sangam and Rowe (2001). The tests were conducted at a laboratory temperature of 23±2°C.

### Experimental Procedure

#### Sorption Test

Geomembrane coupons (both untreated or fluorinated) were immersed in a cell (70 mm diameter × 100 mm high) filled with a dilute solution of VOCs having initial concentrations in the range of 1.3–4.7 mg/L (Table 3). These concentrations are similar or exceed slightly typical concentrations expected in leachate landfill as reported by Rowe (1995). The change in contaminant concentrations in the solution was monitored with time until equilibrium (no significant concentration change for successive samples) was reached. The partitioning coefficient ( $S_{gf}$ ) is then calculated using the procedure described by Sangam and Rowe (2001) using the following expression:

$$S_{gf} = \frac{[c_{f0}V_{f0} - c_{fF}V_{fF} - \sum V_i c_i] \rho_g}{M_g c_{fF}} \quad (1)$$

with  $c_{f0}$ =initial solution concentration [ML<sup>-3</sup>],  $c_{fF}$ =final equilibrium solution concentration [ML<sup>-3</sup>],  $V_{f0}$ =initial solution volume [L<sup>3</sup>];  $V_{fF}$ =final solution volume [L<sup>3</sup>];  $M_g$ =initial mass of geomembrane [M];  $\rho_g$ =geomembrane density [ML<sup>-3</sup>]; and

$\sum V_i c_i$ =mass removed by sampling events [M] ( $V_i$  and  $c_i$  are volume and concentration at each event).

#### Diffusion Test

Diffusion tests were conducted in a double compartment cell similar to that used by Haxo and Lahey (1989) and Sangam and Rowe (2001) and consisting of a closed system with source and receptor reservoirs separated by the geomembrane examined. The receptor (70 mm diameter × 30 mm high) was initially filled with contaminant-free water (de-ionized water) while the source reservoir (70 mm diameter × 100 mm high) was filled with the mixed dilute aqueous solution of chemicals (see Sangam and Rowe 2001 for details regarding filling procedure). The initial contaminants concentration in source solution varied from 1.3 to 5.2 mg/L (Table 4). During the test, the chemical concentrations in both source and receptor solution were monitored with time as contaminants diffused through the geomembranes.

The governing differential equation for the diffusive migration of contaminants through the geomembrane as observed in these tests can be written

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

where  $D_g$ =diffusion coefficient of the geomembrane [L<sup>2</sup>T<sup>-1</sup>];  $c_g$ =concentration of diffusing substance in the geomembrane [ML<sup>-3</sup>]; and  $z$ =position through the specimen [L]. Since the concentrations ( $c_f$ ) in the reservoir are monitored, the flux  $j$  [ML<sup>-2</sup>T<sup>-1</sup>], associated with the process, can be written as (Rowe 1998; Sangam and Rowe 2001)

$$j = -S_{gf} D_g \frac{dc_f}{dz} = -P_g \frac{dc_f}{dz} \quad (3)$$

where  $P_g = S_{gf} D_g$ , referred to as the permeation coefficient, =contaminant mass transfer coefficient [L<sup>2</sup>T<sup>-1</sup>]; and  $S_{gf} = c_g / c_f$  [-]=partitioning coefficient of the contaminant between the geomembrane and the adjacent fluid and depends on chemical/geomembrane system.

$D_g$  and ( $S_{gf}$ ) were deduced following the procedure described by Sangam and Rowe (2001) using the finite layer analysis program POLLUTE© v6.3.6 (Rowe et al. 1999) that specifically allows modeling of the phase change and the boundary conditions associated with these tests.

#### Modeling Approach

First, the contaminant transport properties were established for the untreated geomembrane following the procedure outlined above and described in detail by Sangam and Rowe (2001). Then, the fluorinated geomembrane was modeled as a three-layered material consisting of two identical outer layers representing the thin fluorinated surface layers (each 4 μm thick on average) and a middle layer (not affected by the surface treatment) that was the same as the untreated geomembrane. The contaminant flux into and out of the sample is controlled by the ratio  $P_{gs}/t_{gs}$ , where  $P_{gs}$  is the permeation coefficient through the outer fluorinated layers and  $t_{gs}$  is the thickness of the surface layer. The different permeation coefficients can be interrelated using the series resistance model (Mohr et al. 1991)

$$\frac{t_g}{P_{gf}} = \frac{2(t_{gs})}{P_{gs}} + \frac{t_{gm}}{P_{gm}} \quad (4)$$

where  $t_g$ ,  $t_{gs}$ , and  $t_{gm}$ =thicknesses of the geomembrane, thin surface layer assumed to be affected by fluorination, and middle

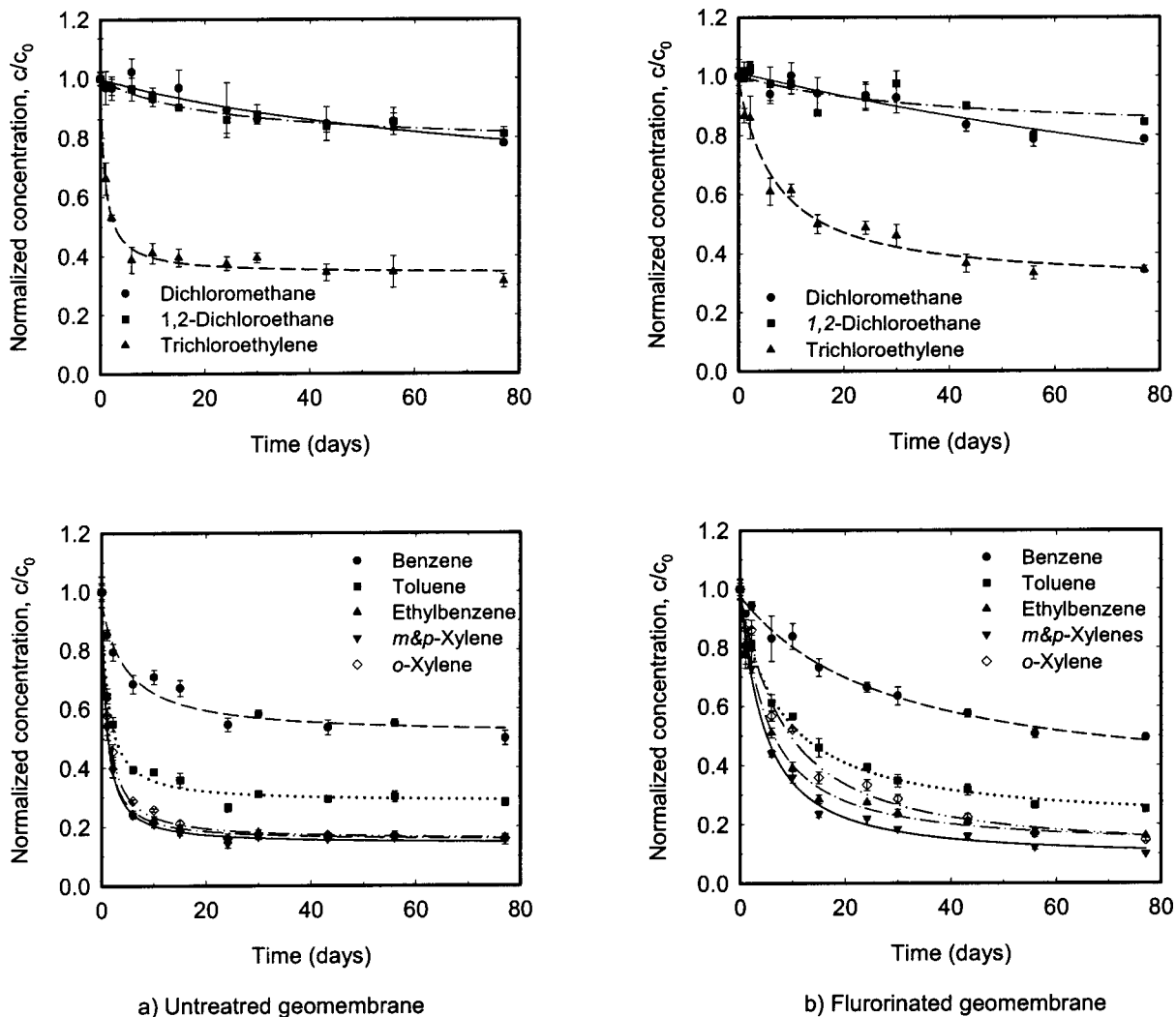


Fig. 2. Variation in contaminant concentration during sorption test SU1 (untreated) and SF1 (fluorinated)

unaffected layer, respectively; and  $P_{gf}$  and  $P_{gm}$  represent the permeation coefficient for the entire fluorinated geomembrane and middle untreated layer, respectively.

Since surface fluorination is a treatment that creates a thin barrier layer on the surface of the geomembrane, it was hypothesized that  $D_{gs}$  (diffusion coefficient through the surface layers) will be affected much more than  $S_{gf}$  as shown by the sorption test results discussed later. Thus, for the modeling,  $S_{gf}$  was not changed through the entire thickness of the geomembrane while  $D_{gf}$  through fluorinated geomembrane was varied until a good fit was obtained to the measured data. Finally,  $P_{gs}$  is computed using Eq. (4). However,  $D_{gs}$  cannot be calculated since the exact partitioning coefficients for these layers are not known.

## Results and Discussion

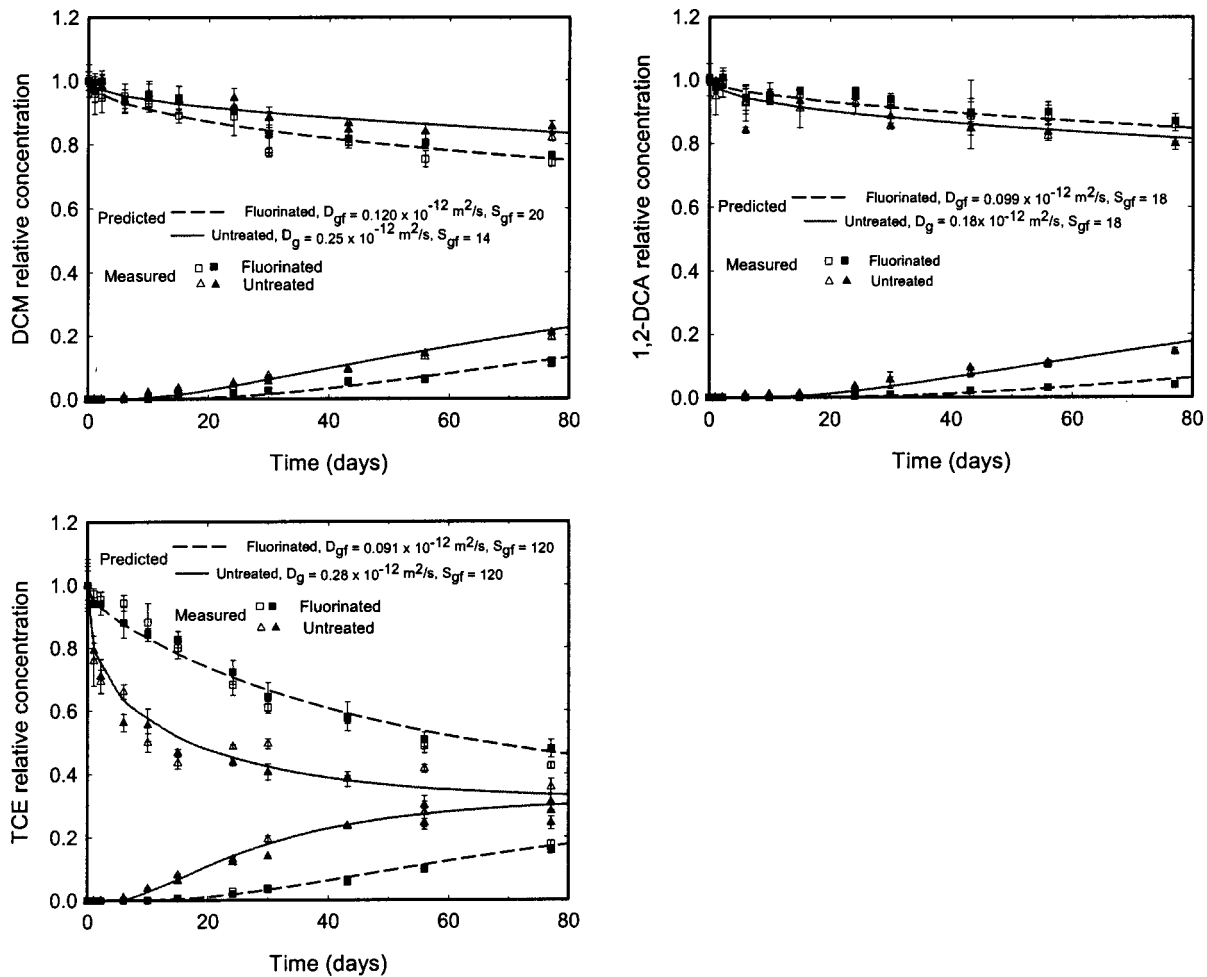
### Sorption Test

The typical changes in contaminant concentrations monitored during the sorption tests are shown in Fig. 2 for both untreated (a) and fluorinated (b) geomembranes (control tests were also conducted without a geomembrane but are not shown). These varia-

tions are plotted as normalized concentrations relative to the initial concentrations with each data point representing the average of triplicate concentration measurements and the bars representing the standard deviation. These decreases in the contaminant concentration with time are typical of this type of sorption process as previously observed by Sangam and Rowe (2001) and are mainly the consequence of chemicals removal from the solution.

For the untreated geomembrane, all chemicals reached equilibrium approximately within the first 10 days of testing, except for DCM and 1,2-DCA [Fig. 2(a)]. Dichloromethane and 1,2-DCA took almost 40 days before reaching equilibrium. Among the chlorinated contaminants, TCE concentration decreased the most with the equilibrium concentration of 60% of the initial, followed by 1,2-DCA and DCM (although DCM and 1,2-DCA were very close). Among the aromatic contaminants, ethylbenzene and xylenes showed the greatest decrease of about 82% of the initial concentration followed by toluene with a decrease of 65% and benzene with a concentration reduction of 40%.

For the fluorinated geomembrane [Fig. 2(b)], the decrease in contaminant concentrations at equilibrium is similar to that of the untreated geomembrane. However, the equilibrium is not reached as fast as for the untreated geomembrane. For aromatic hydrocar-



**Fig. 3.** Variation in chlorinated hydrocarbon concentrations with time in source and receptor during diffusion tests for untreated and fluorinated geomembranes

bons and TCE, the equilibrium is approached after 40 days, whereas for DCM the equilibrium was not reached after almost 80 days of testing.

The partitioning coefficient calculated using Eq. (1) is summarized in Table 3 and it can be seen that  $S_{gf}$  values for the untreated and fluorinated samples are similar. Among the chlorinated hydrocarbons, TCE has the highest  $S_{gf}=96$  followed by the 1,2-DCA and DCM with  $S_{gf}=12$  and 13, respectively for the untreated geomembrane. As previously mentioned, DCM did not reach equilibrium and hence the real  $S_{gf}$  value may be slightly higher than the reported value. For the aromatics, the highest  $S_{gf}=290$  was obtained for *m*&*p*-xylenes, followed by ethylbenzene ( $S_{gf}=243$ ), *o*-xylene ( $S_{gf}=234$ ), and toluene ( $S_{gf}=127$ ). Benzene has the lowest  $S_{gf}=57$ .

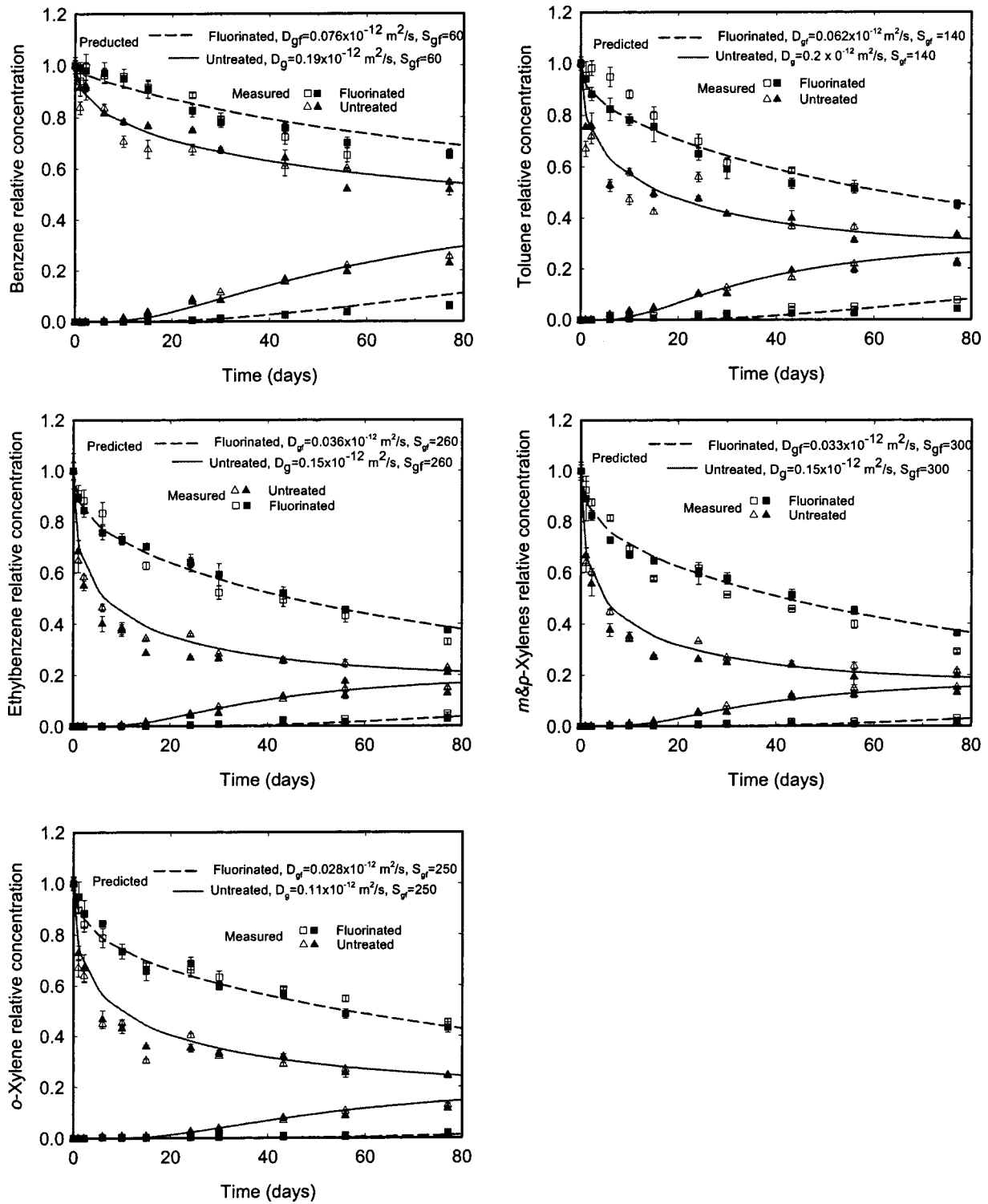
The sorption test results presented above revealed two major findings. First,  $S_{gf}$  were not significantly affected by the surface treatment. This is because only thin surface layers of about 4  $\mu\text{m}$  are fluorinated and, thus, more than 99.5% of the material remained untreated. As a consequence, the fluorinated geomembrane will sorb essentially the same mass of contaminant as the untreated geomembrane. Second, the sorption curves for the fluorinated geomembrane indicated that the equilibrium time could be four times longer than for the untreated geomembrane. This suggests that the contaminants examined diffuse into the sample at slower rates for the fluorinated geomembrane than for the untreated geomembrane. This observation is attributable to the sur-

face modifications associated with the fluorination treatment. In fact, as previously mentioned in "Overview of Surface Fluorination," the direct effects of fluorination (increase of surface polarity and additional crosslinking) reduce the segmental mobility of the polymer chains required to achieve the diffusive jumps and hence the diffusive migration of chemicals into the geomembrane.

### Diffusion Test

Duplicate diffusion tests were conducted. Figs. 3 and 4 show typical variations in the source and receptor concentrations for both the untreated (circle) and the fluorinated (square) geomembrane as measured during the diffusion test for chlorinated hydrocarbons and BTEX, respectively. The results are plotted as normalized concentrations relative to the initial concentration measured at the beginning of the test with each point representing the average of at least triplicate concentration quantified by GC/MS analyses and the bars shown on the points representing the standard deviation.

It can be seen that, for both cases, the concentration in the source decreased faster for the untreated geomembrane than for the fluorinated geomembrane. Meanwhile, the increase in the receptor as the contaminants migrate is lower for the fluorinated geomembrane compared to the original untreated geomembrane with the notable exception of DCM. In general, the change in the source concentration is predominantly controlled by  $S_{gf}$  while the



**Fig. 4.** Variation in benzene, toluene, ethylbenzene, and xylenes concentrations with time in source and receptor during diffusion tests for untreated and fluorinated geomembranes

receptor variation is controlled by  $P_g$  of the contaminant. From the data in Figs. 3 and 4, one may anticipate that either the partitioning or diffusion coefficients (or both) decreased due to the fluorination treatment, and hence the permeation coefficient also decreased. Since the fluorinated layers are very thin, it does not matter whether the change in  $P_g$  was due to a change in  $D_g$  or  $S_{gf}$  as the net effect is the same. If there is a change in  $S_{gf}$  in the

fluorinated layer, it has very little effect on the bulk sorption since the layers are so thin as confirmed by the sorption tests previously discussed.

As evident from Fig. 3, DCM exhibits a completely different pattern compared to other chemicals when the geomembrane is fluorinated. The DCM concentration in the source solution decreases more rapidly for the fluorinated geomembrane than for the

untreated material, whereas its concentration in the receptor does not increase as quickly for the fluorinated geomembrane compared to the untreated geomembrane. This pattern indicates that the large amount of chemical that is removed from the source solution is not completely transferred to the receptor, suggesting a greater sorption. Based on this, it should be expected that the partitioning coefficient is higher while the diffusion coefficient is reduced. This observation confirms the suspicion from sorption tests suggesting that the partitioning coefficient may be higher than obtained in the sorption tests because equilibrium was not reached when the test was terminated.

The best-fit theoretical curves (lines) generated by solving the diffusion equation subjected to the appropriate boundary conditions are also shown in Figs. 3 and 4. The inferred partitioning and diffusion coefficients together with the calculated permeation coefficient are presented in Table 4.  $S_{gf}$  values obtained from the diffusion tests agree well with those calculated for sorption tests. For example, for the untreated geomembrane, the toluene  $S_{gf}$  calculated from the sorption test is 122 compared to 140 from the diffusion test.

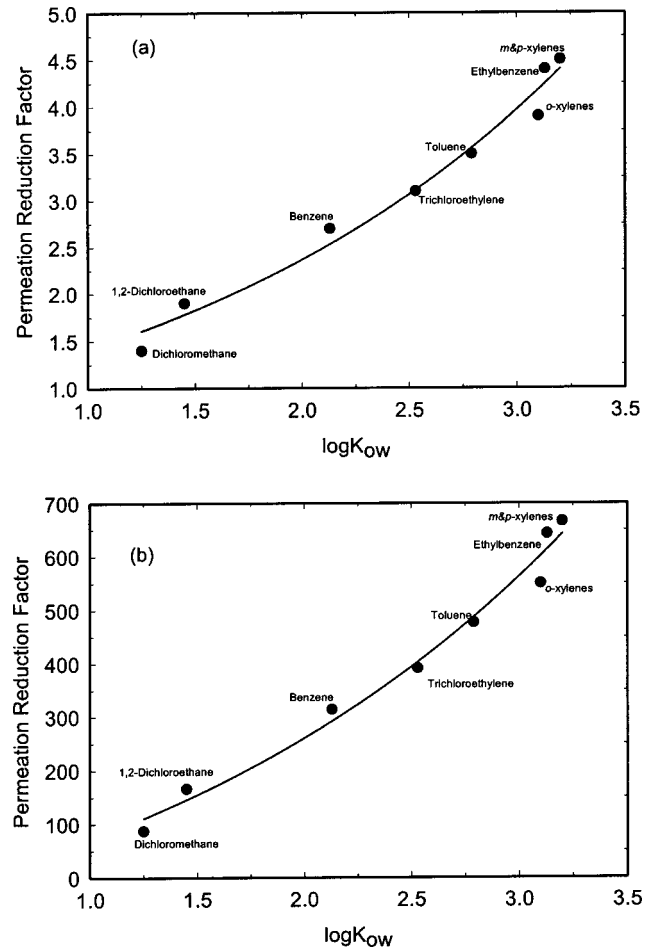
The inferred diffusion coefficients for the untreated geomembrane varied from  $0.18 \times 10^{-12}$  to  $0.28 \times 10^{-12}$  m<sup>2</sup>/s for chlorinated compounds with trichloroethylene diffusing the fastest. For aromatic chemicals,  $D_g$  values are lower and ranged between  $0.11 \times 10^{-12}$  and  $0.22 \times 10^{-12}$  m<sup>2</sup>/s. Toluene has the highest  $D_g = 0.22 \times 10^{-12}$  m<sup>2</sup>/s and *o*-xylene the lowest with  $D_g = 0.11 \times 10^{-12}$  m<sup>2</sup>/s.

In general, the diffusion and partition coefficients obtained for the untreated geomembrane are similar to values reported in the literature. For instance,  $D_g$  and  $S_{gf}$  measured for toluene for the untreated geomembrane are  $0.22 \times 10^{-12}$  m<sup>2</sup>/s and 140, respectively, compared to  $0.20 \times 10^{-12}$  m<sup>2</sup>/s and 160 reported by Müller et al. (1998), for a 1 mm thick HDPE geomembrane having a crystallinity of 59%. This suggests that the procedure adopted in this investigation is relatively reliable and accurate.

When the geomembrane is subjected to a surface fluorination,  $S_{gf}$  values were essentially the same as for the untreated geomembrane except for DCM, which had a higher  $S_{gf}$  of 20 for treated compared with 14 untreated. This may be attributed to the fact that the surface layer polarity increased due to fluorination. Among all chemicals tested, dichloromethane is the most polar (1.60 Debye) and hence it is likely to be most attracted to the surface layer. As a consequence, the partitioning between the solution and the surface layers increased. As presented in Table 4, the average diffusion coefficients ( $D_{gf}$ ) for fluorinated geomembrane vary from  $0.91 \times 10^{-13}$  to  $1.20 \times 10^{-13}$  m<sup>2</sup>/s for chlorinated compounds while for aromatics, the values range between  $0.28 \times 10^{-13}$  and  $0.76 \times 10^{-13}$  m<sup>2</sup>/s. These values are about 1–2 orders of magnitude lower than those inferred for the untreated geomembrane.

## Discussion

To assess the degree of barrier function improvement provided by fluorination, the permeation coefficient measured for the fluorinated geomembrane is compared to the original untreated geomembrane in terms of the permeation reduction (PR) factor. Two reduction factors are calculated. The first reduction factor compares the average permeation coefficient  $P_{gf}$  of the fluorinated geomembrane to the untreated permeation coefficient ( $P_g$ ). The second factor is the ratio between the untreated permeation



**Fig. 5.** Variation of permeation reduction factor due to fluorination with *n*-octanol/water partitioning coefficients for: (a) entire geomembrane; and (b) fluorinated outer layers

coefficient ( $P_g$ ) and the permeation coefficient ( $P_{gs}$ ) of the fluorinated outer layer. A summary of PR values is presented in Table 4 and represented in Fig. 5.

Fig. 5(a) shows the overall reduction in permeation coefficient for the fluorinated geomembrane. Of the chlorinated hydrocarbons, DCM has the lowest decrease with a factor of 1.4 followed by 1,2-DCA with PR=1.9. Trichloroethylene has the highest reduction in the permeation coefficient when the geomembrane is fluorinated with PR=3.1. This reduction appears to be inversely related to the hydrophobicity of the contaminant. High hydrophobicity corresponds to high log( $K_{ow}$ ) and consequently low hydrophobicity corresponds to low log( $K_{ow}$ ). Trichloroethylene, with higher hydrophobicity [ $\log(K_{ow})=2.53$ ], has the highest decrease while DCM, with the lowest log( $K_{ow}$ )=1.25 (low hydrophobicity), experienced the lowest decrease in permeation.

For the aromatic compounds, the data show that the permeation coefficient measured for the fluorinated geomembrane decreased by factors of between 2.7 and 4.5. The highest decreases were observed for *m,p*-xylenes and ethylbenzene with a ratio of 4.5 and 4.4, respectively, while benzene has the lowest decrease of about 3.5. Toluene and *o*-xylene are reduced by factors of about 3.5 and 3.9, respectively. As observed for chlorinated compounds, the reduction in the permeation coefficient increases with the increase in the hydrophobicity expressed in term of log( $K_{ow}$ ).

**Table 5.** Maximum Contaminant Concentration in Aquifer Due to Hypothetical Landfill

Contaminant	$c_0$ ( $\mu\text{g/L}$ )	Half-life (years)		CCL thickness (m)	$c_{\text{max}}$ in aquifer ( $\mu\text{g/L}$ )		
		Leachate	CCL		Fluorinated	Untreated	Reduction
Dichloromethane	3,300 <sup>a</sup>	10 <sup>a</sup>	50 <sup>b</sup>	0.6	99.0	188	1.8
				1.0	—	103	
				1.1	—	91	
1,2-Dichloroethane	1,000	10	50	0.6	27.3	46.3	1.7
				0.9	—	30.0	
				1.0	—	26.3	
Trichloroethylene	1,000	10	50	0.6	24.3	56.1	2.3
				1.0	—	31.2	
				1.2	—	24.2	
Benzene	20 <sup>a</sup>	25 <sup>a</sup>	125 <sup>b</sup>	0.6	1.0	2.0	2.0
				1.0	—	1.2	
				1.2	—	1.0	
Toluene	1,000 <sup>a</sup>	15 <sup>a</sup>	125 <sup>b</sup>	0.6	27.6	66.7	2.4
				1.2	—	32.2	
				1.4	—	26.6	
Ethylbenzene	500	15	125	0.6	8.2	22.8	2.8
				1.2	—	10.9	
				1.5	—	8.2	
<i>m</i> & <i>p</i> -Xylenes	500	15	125	0.6	7.5	20.9	2.8
				1.2	—	9.9	
				1.5	—	7.5	
<i>o</i> -Xylenes	500	15	125	0.6	6.5	18.6	2.9
				1.2	—	8.9	
				1.5	—	6.7	

<sup>a</sup>From Ontario Regulation 232/98 (1998).

<sup>b</sup>From Rowe (1998).

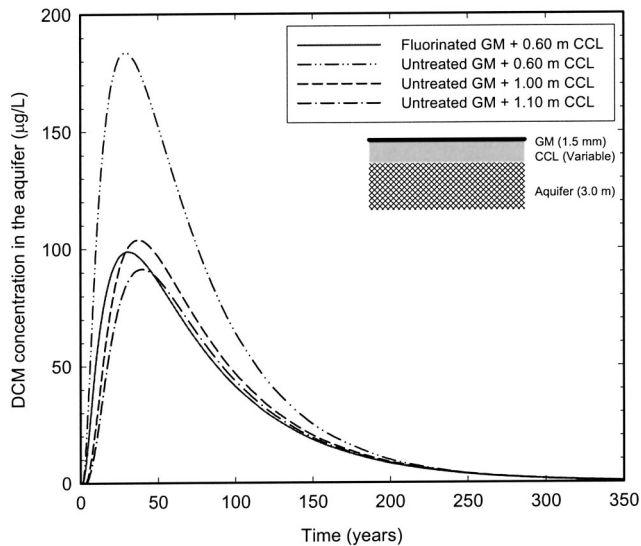
A relationship was established between the reduction factors deduced for the thin fluorinated layers and the hydrophobicity of compound tested [Fig. 5(b)]. Again, there was an increase of permeation reduction factor with  $\log(K_{ow})$ , indicating that highly hydrophobic chemical will permeate at a lower rate in the fluorinated geomembrane compared to the untreated geomembrane. This can be explained in terms of the properties of outer fluorinated layers. As previously noted in "Overview of Surface Fluorination," the surface fluorination increases the surface energy and hence increases the water wettability (Anand et al. 1994). In this context, the affinity between water and the relatively more polar geomembrane surface is enhanced and, consequently, the affinity between the geomembrane and organic chemical decreases. The second factor is that the migration becomes highly chemical size dependant because of the additional crosslinking caused by the fluorination that restricts the segmental mobility of the polymer chains (Rogers 1985; Naylor 1989). It can be seen that chemicals with high  $\log(K_{ow})$  are bigger molecules (see Table 2), indicating that they will be more affected by the fluorination.

The reduction in permeation of the hydrocarbon inferred for the fluorinated outer layers ranges between 87 and 666 and is consistent with the reduction of about 2 orders of magnitude generally reported for completely fluorinated thin films (Anand et al. 1994; Carstensen et al. 1999; Lagow and Wei 1999). It follows from this that the net effect of fluorination on the diffusive performance of a geomembrane will be highly dependant on the ratio of fluorinated layer thickness to geomembrane thickness ( $t_{gs}/t_g$ ). Carstensen et al. (1999) indicated that petrol permeation has been reduced from approximately 3.3 to 0.17 g/m<sup>2</sup>/day (19-fold) with

a fluorinated layer thickness of one fifth (20%) of the HDPE pipe thickness. In the present case, the total fluorinated layer thickness (sum of the two 4  $\mu\text{m}$  layers) is only about 8  $\mu\text{m}$  and hence only about 0.5% of the treated geomembrane. The direct consequence is that the middle untreated layer has a significant overall permeation and net effect of fluorination is less than for thin fluorinated films.

### Implications for Landfill Design

To evaluate the consequences of the reduction factors mentioned above, modeling analyses were conducted assuming a hypothetical 1,000  $\times$  1,000 m landfill having an average height of waste of 20 m with a single composite liner system. The barrier system consists of a geomembrane (GM) (untreated or fluorinated) over 0.6 m of a compacted clay liner (CCL) with a hydraulic conductivity of  $1 \times 10^{-9}$  m/s. In this case, it is assumed that there is no natural attenuation layer below the barrier, the barrier system being directly underlain by a 3 m thick aquifer. Compacted clay properties were taken directly from Rowe (1998), while geomembranes parameters were based on results obtained from the present study. The initial contaminant concentrations summarized in Table 5 are selected based on Ontario landfill regulation *O. Reg. 232/98*. The diffusion coefficients for the clay layer were taken to about  $2.5\text{--}6.3 \times 10^{-10}$  m<sup>2</sup>/s (Ontario Regulation 232/98 1998), while sorption was considered to be negligible. Since the permeation properties are of concern, it was assumed that the



**Fig. 6.** Calculated variation in dichloromethane concentration in aquifer due to hypothetical landfill

geomembrane is free of defects (holes) and therefore any contaminants collected in the aquifer have migrated essentially by diffusion.

Fig. 6 presents an example of the calculated variation in contaminant concentrations with time in the aquifer for different barrier systems in the case of dichloromethane. First, the minimum system of (GM+0.6 m CCL) is examined for both untreated and fluorinated geomembranes and the results being summarized in Table 5. It can be seen that contaminants impact is higher for the case where an untreated geomembrane is used. For example, the DCM maximum impact calculated is about 188  $\mu\text{g/L}$  for the untreated geomembrane while for a fluorinated geomembrane the impact is about 99.0  $\mu\text{g/L}$ . Similarly, the calculated *m&p*-xylene maximum concentration is 20.9  $\mu\text{g/L}$  for an untreated geomembrane compared to 7.5  $\mu\text{g/L}$  for a fluorinated geomembrane. For the conditions examined, the fluorination of the HDPE geomembrane helps reduce contaminant impacts to levels between 1.7 and 2.9 times lower than the impact given by the untreated GM.

To examine the significance of the reduction, a series of analyses was performed to estimate the compacted clay thickness that would be required for use with the untreated geomembrane to provide a composite liner that would give the same impact as a fluorinated geomembrane over 0.6 m of compacted clay (Fig. 6). The results in Table 5 indicate that about 0.4–0.9 m additional compacted clay is required to achieve the same level of protection as provided by the fluorinated geomembrane for the contaminants examined.

The fact that the fluorinated layer has a notable effect while being so thin (4  $\mu\text{m}$ ) has several important practical implications. First, the performance of the treated geomembrane could be further improved by adopting procedures that increased the thickness of the fluorinated layer. Second, care is needed if specifying the permeation characteristics required or the thickness of the fluorinated layer (since a thickness less than that of the geomembrane tested herein could result in properties that do not meet the design requirements). Third, further research is required to assess how well the fluorinated layer stands up to field use (e.g., scratching during installation). A field trial using a fluorinated geomembrane has been reported by Li et al. (2002) and this geomembrane is

presently being examined in terms of its short-term and long-term performances.

## Summary and Conclusion

An evaluation of the effectiveness of fluorination in improving the diffusive barrier properties of a 1.5 mm HDPE has been conducted. The investigation consisted of performing sorption and diffusion tests on both the original untreated geomembrane and a fluorinated treated geomembrane and comparing the respective diffusion, partitioning, and permeation coefficients for chlorinated and aromatic hydrocarbons commonly found in MSW landfill leachates.

Sorption tests indicated that the partition parameter ( $S_{gf}$ ) is not significantly affected and remains unchanged except for dichloromethane for which  $S_{gf}$  appeared to have increased. In contrast, diffusion test results showed that, for the chemical examined, the diffusion coefficient decreased and, as a consequence, the permeation coefficients decreased by a factor varying from 1.4 to 4.5 when the geomembrane is fluorinated compared to the untreated material. It was also found that the reduction factor is chemical dependant and was exponentially related to the *n*-octanol/water coefficient of the contaminant examined indicating that highly hydrophobic contaminants are greatly affected by fluorination treatment.

The impact of the examined contaminants on an aquifer due to the presence of a hypothetical landfill with a composite liner system consisting of a 1.5 mm thick HDPE geomembrane (untreated or treated) on 0.6 m of compacted clay liner was analyzed. The results showed that the use of the fluorinated geomembrane reduced the maximum contaminant concentrations by a factor of about 1.7–2.9. Furthermore, the analyses indicated that, for the conditions examined, additional 0.4–0.9 m (i.e., 1.0–1.5 m total thickness) CCL thickness, is required under the untreated geomembrane to reduce contaminants to levels achieved by the use of fluorinated geomembrane in conjunction with 0.6 m of compacted clay.

The results of this study suggest that surface fluorination treatment may improve the effectiveness of HDPE geomembranes as a barrier to organic contaminants, especially aromatic hydrocarbons. It appears that the performance of the treated geomembrane could be further improved by increasing the thickness of the fluorinated layer. It also follows that different fluorinated geomembranes may have quite different properties depending on the thickness of the fluorinated layer and this (or a surrogate of this) should be specified and monitored. Finally, research is required to assess how well the fluorinated layer stands up to scratching during installation and other environmental agents encountered in the field.

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## Notation

The following symbols are used in this paper:

- $c_{fF}$  = final equilibrium solution concentration [ ];  
 $c_{f0}$  = initial solution concentration [ $\text{ML}^{-3}$ ];  
 $c_g$  = concentration of diffusing substance in geomembrane;  
 $D_g$  = diffusion coefficient of geomembrane [ $\text{L}^2 \text{T}^{-1}$ ];  
 $D_{gf}$  = average diffusion coefficient through fluorinated geomembrane [ $\text{L}^2 \text{T}^{-1}$ ];  
 $D_{gs}$  = diffusion coefficients through surface layers [ $\text{L}^2 \text{T}^{-1}$ ];  
 $j$  = flux [ $\text{ML}^{-2} \text{T}^{-1}$ ];  
 $M_g$  = initial mass of geomembrane [M];  
 $P_g, P_{gf}, P_{gs}$  = permeation coefficients of untreated, fluorinated geomembranes, and outer fluorinated layers [ $\text{L}^2 \text{T}^{-1}$ ];  
 $S_{gf}$  = partitioning coefficient of contaminant [–];  
 $t_g, t_{gs}, t_{gm}$  = thickness of thin fluorinated surface and unaffected middle layers [L];  
 $V_{fF}$  = final solution volume [ $\text{L}^3$ ];  
 $V_{f0}$  = initial solution volume [ $\text{L}^3$ ];  
 $V_i, c_i$  = volume [ $\text{L}^3$ ] and concentration [ $\text{ML}^{-3}$ ] at sampling event  $i$ ;  
 $z$  = position in geomembrane [L]; and  
 $\rho_g$  = geomembrane density [ $\text{ML}^{-3}$ ].

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