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Migration of dilute aqueous organic pollutants through HDPE geomembranes[☆]

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Abstract

The migration of the dilute aqueous organic contaminants through HDPE geomembranes is examined. Semi-empirical methods to estimate partition and diffusion coefficients for organic contaminants in dilute aqueous solutions with respect to high-density polyethylene (HDPE) geomembranes are proposed. These methods were evaluated by performing sorption and diffusion tests on a 2.0 mm thick HDPE geomembrane using three chlorinated hydrocarbons (dichloromethane, 1,2-dichloroethane and trichloroethylene) and four aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes). The results show that the partition coefficient (S_{gr}) can be fairly well estimated using the method based *n*-octanol/water coefficient of the contaminant and even better by that based on the chemical molecular weight. This suggests that these methods may be used as starting point to estimate the migration of organic contaminants through HDPE geomembranes. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Partitioning; Diffusion; Permeation; Organic chemicals; HDPE geomembranes

1. Introduction

Most regulations for modern landfills recommend a composite liner together with an attenuation layer as a barrier system against contaminant migration. These composite liners typically include a geomembrane liner (GM) and either a compacted clay liner (CCL) or geosynthetic clay liner (GCL). The intended function

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of the geomembrane is to impede advective contaminant migration via the reduction of water flow and to provide a diffusive barrier to inorganic contaminants (Rowe, 2001). The assessment of the effectiveness of the geomembrane liner during the design process requires the estimation of the parameters controlling the diffusive migration, especially the partitioning, diffusion and permeation coefficients. These parameters are often obtained by performing sorption and/or diffusion tests. However, no simple methods have previously been available for estimating these parameters.

This paper discusses the migration of organic contaminants through a geomembrane, the factors that affect the process and the laboratory methods used to deduce the different parameters. The paper also proposes some semi-empirical methods for estimating the partition, diffusion and permeation coefficients.

2. Background and theoretical considerations

2.1. Migration of contaminant through geomembrane

The migration of contaminants through an intact geomembrane is a molecule activated process (diffusion) that can be envisioned to occur by steps or jumps over a series of potential barriers, following the path of least resistance. For dilute aqueous solutions, the process involves three key steps (Park and Nibras, 1993; Prasad et al., 1994; Haxo and Lahey, 1988): (i) partition of the contaminant between inner surface of the geomembrane and the medium containing the contaminant (adsorption); (ii) diffusion of the permeant through the geomembrane and, (iii) partition between the outer surface of the geomembrane and the outer medium (desorption). It is important to recognize that the extent of each phase depends on various parameters among which the most important are permeant/geomembrane system and temperature.

In the initiation of the migration process, the adsorption consists of the penetrant molecule removal from the fluid and its dispersion on or into the polymer (Rogers, 1985 and Naylor, 1989). This process can be described as the distribution of the permeant between two or more phases. It may involve absorption and incorporation in microvoids, cluster formation, solvation-shell formation and other modes of mixing. The distribution of the permeant between different sorption modes may change with concentration, temperature, time and swelling of the matrix due to the interaction between the polymer and the chemical. Thus, the extent to which permeant molecules are sorbed and their mode of sorption in a polymer depend upon the activity of the permeant within the polymer at equilibrium (Müller et al., 1998).

If a geomembrane in contact with a fluid reaches equilibrium, there will be a relationship between the final equilibrium concentration in the geomembrane, c_g [ML^{-3}], and the equilibrium concentration in the fluid, c_f , [ML^{-3}]. For the simplest case where the permeant does not interact with the polymer (e.g. as is the case for a HDPE geomembrane) or at low concentrations (Rogers, 1985) as in landfill leachates, the relationship between the concentration in the fluid and the

geomembrane is given by (Henry's law):

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

where S_{gf} is called a partitioning coefficient [–] and in principle is a constant for the given molecule, fluid, geomembrane and temperature of interest.

At the second stage of the migration, the sorbed penetrant at the surface will diffuse within the material. The diffusion of contaminant in a geomembrane can be expressed by Fick's first law:

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

where, f is the mass flux or rate of transfer per unit area of section [$ML^{-2}T^{-1}$], D_g is the diffusion coefficient in the geomembrane [L^2T^{-1}], c_g is the concentration of diffusing substance and z is the direction parallel to the direction of diffusion. In transient state, the governing differential equation is (Fick's second law):

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

which must be solved for the appropriate boundary and initial conditions.

The last stage in the migration process is of the permeant desorption from the geomembrane to the outer solution. This stage is similar to the first with an inverted process and the contaminant concentration in the adjacent fluid can be expressed as:

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

where S'_{gf} is the contaminant partitioning coefficient between the outside fluid and the geomembrane. In the simplest case where the two solutions are water or water-based solutions, these two partitioning coefficients may be assumed to be the same ($S_{gf} = S'_{gf}$).

When performing a diffusion test it is much more difficult to measure the concentration change in the geomembrane than analyzing the concentration in the solution. Thus, it is useful to express the diffusion equations in terms of the concentration in adjacent solutions. If one substitutes Eq. 1 into Eq. 3, the flux from a fluid on one side of the geomembrane to a similar fluid on the other side is given by:

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

where P_g given by

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

is referred to in the polymer literature as permeability or permeation coefficient. In reality, P_g is a mass transfer coefficient that takes into account the partitioning and diffusion processes.

2.2. Factors affecting contaminant migration through geomembrane

Although the well-known principle of solubility discussed in terms of polarity: “like dissolves like” generally holds for polymers as well, its application to the diffusion and permeation parameters is more complex due to the kinetic nature of the transport process. However, 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 Taztky, 1984; Rowe et al., 1995, 1996). Strongly polar penetrant molecules have very low transport rates through polyethylene, which is very non-polar. In general, the permeation affinity has the following order: alcohols < acids < nitroderivatives < aldehydes < ketones < esters < ethers < aromatic hydrocarbons < halogenated hydrocarbons (August and Taztky, 1984). This has been confirmed by Rowe et al. (1996) who have studied diffusion of organic pollutants through HDPE geomembranes and observed that some organic compounds (methyl ethyl ketone, acetic acid) have migrated at much slower rates than the chlorinated solvents examined (dichloromethane, 1,1-dichloroethane, and 1,2-dichloroethane). Only negligible penetration of the heavy metal ions (Zn^{2+} , Ni^{2+} , Mn^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+}) from concentrated acid solutions was found (Holzlöhner and August, 1995) after 4 years of testing, so that HDPE geomembranes may be seen as virtually ideal barriers for heavy metals.

The concentration dependence of the diffusion coefficient D_g arises from the presence of permeant molecules within the polymer that weaken the interactions between adjacent polymer chains, which in turn leads to the commonly observed effects of plasticization. From immersion and permeation tests conducted on different geomembranes using neat (pure) and dilute solutions, Müller et al. (1998) found that the diffusion coefficient was considerably smaller for contaminants at low concentrations in aqueous solutions than for pure chemicals. The reported D_g values are approximately one order of magnitude lower for an aqueous solution than for a pure chemical.

The diffusion coefficient decreases with increasing permeant weight, size (molecular volume) and cross sectional area of the penetrant (Berens and Hopfenberg, 1982; Saleem et al., 1989; Aminabhavi and Naik, 1998). For example, Saleem et al. (1989) reported a decrease of D_g with the increase of molar volume for some aliphatic aromatic and chlorinated permeants through low-density polyethylene (LDPE). However, the magnitude of the decrease is higher for chlorinated chemicals than methyl substituted benzenes due to the bulky chlorine atom, which markedly reduces their mobility. The shape of the permeant has been reported to have a profound effect on diffusion (Berens and Hopfenberg, 1982; Saleem et al., 1989). Permeant with linear, flexible and symmetrical molecules have higher mobility than rigid molecules. For instance, Saleem et al. (1989) showed that the diffusion coefficient for *o*-xylene is lower than for *p*-xylene. This is attributed to the symmetrical structure of *p*-xylene compared to the distorted shape of *o*-xylene with its two adjacent methyl groups. Berens and Hopfenberg (1982) have shown that the diffusion of *n*-alkane and other elongated or flattened molecules are higher, by a factor of 10^3 , than the diffusion of spherical molecules with similar molecular weight.

In regard to polymer properties, the diffusion of a contaminant is expected to decrease with density, chain rigidity and degree of cross-linking. In the case of HDPE geomembranes (semi-crystalline polymers), the crystalline zones act as impermeable barriers to permeating molecules in two ways (Naylor, 1989). First, crystalline regions act as excluded volumes for the sorption process and as impermeable barriers for diffusion. Secondly, they act as giant cross-linking regions with respect to those chains, which enter and leave those regions from the surrounding non-crystalline matrix in which sorption and diffusion take place. The restraints of cross-linking on the segmental mobility of the polymer make the diffusion process more dependent on size, shape and concentration of the permeant molecule (Naylor, 1989; Rogers, 1985).

Temperature is an important factor that influences the overall migration process. Energy is required to achieve this activated process. Thus, the permeation process may be highly temperature dependent. It has been well established (Naylor, 1989; Chainey, 1990) that over small ranges, temperature dependence of the diffusion, solubility and permeability coefficients can be described by the Arrhenius relationship:

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

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

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

where E_d and E_p are the activation energies of diffusion and permeation, respectively, ΔH_s is the heat of solution of the penetrant in the polymer, and D_{g0} , S_{gf0} and P_{g0} are constants. It is expected that for many polymer–penetrant systems, plots of $\log D_g$ vs. the reciprocal of the absolute temperature are linear over a limited temperature range (Saleem et al., 1989; Aminabhavi and Naik, 1998).

3. Evaluation of migration parameters

3.1. Laboratory methods

The methods used to evaluate diffusion, solubility and partitioning coefficients can be classified in two categories: immersion/sorption methods and permeation/diffusion methods. The main difference between the two groups resides in the way the material is in contact with the permeant during these two tests.

In immersion/sorption tests, the geomembrane is immersed in a container filled with the permeant of interest such that both faces of the material are in contact with the permeant. Thus, the chemical permeates from both sides and then migrates within the material. As a consequence, equilibrium is reached faster than in permeation/diffusion tests. The different parameters are inferred using different

techniques as summarized in Table 1. Although these methods have been developed for pure chemicals, they have been successfully used with dilute solutions.

In permeation/diffusion methods the geomembrane divides the cell in two compartments, namely source and receptor. The source is filled with the permeant (or solution examined) while the reservoir is filled with a reference fluid of known composition. Thus, only one face of the geomembrane is in contact with the chemical or solution containing the contaminant such that the permeation takes place from the reservoir to the receptor. In this respect, these methods simulate more closely the transport process that is expected in a landfill application. The techniques used for evaluating different parameters are outlined in Table 1.

3.2. Estimation methods

Based on a number of theories of diffusion (e.g. free volume theory and molecular theory), several models have been proposed by various macromolecular researchers to predict the transport of molecules through polymer membranes. These methods have been reviewed in detail by Aminabhavi et al. (1988a, b). In general, these methods provide a good basis for understanding the diffusion process, which takes place within the geomembrane. However, due to their complexity, they are limited to macromolecular physics and chemistry and cannot be used easily and efficiently by geoenvironmental engineers. Therefore, empirical and semi-empirical models are needed to help geoenvironmental engineers select and evaluate geomembrane liners. One of the objectives of this paper is to propose several methods based on the permeant and/or geomembrane properties as summarized in Table 2 and discussed in the following paragraphs. The methods were derived based on D_g , S_{gf} , and P_g values available in the literature for the permeation of dilute organic contaminants through HDPE geomembranes.

3.2.1. Estimation based on *n*-octanol/water coefficient (k_{ow})

The *n*-octanol/water coefficient (k_{ow}) is a specific property of chemicals used to define their ability to partition between water and *n*-octanol (i.e. organic matter) when they are in solution. It may be seen as the measure of contaminant polarity and it reflects its lipophilicity. The higher the numerical value, which is usually expressed as a logarithm, the stronger the tendency of the chemical to accumulate in organic matter. Since a HDPE geomembrane is an organic material, one may anticipate a relationship between *n*-octanol/water coefficient and the permeation parameters (diffusion, partition, and solubility).

Many researchers have attempted to correlate partition S_{gf} to K_{ow} . For instance, Prasad et al. (1994), have shown that, for a limited number of chemicals, $\log S_{gf}$ is linearly related to $\log K_{ow}$. In contrast, Park and Nibras (1993) reported that for a broad range of pure organic solvents there is a second order polynomial relationship between $\log S_{gf}$ and $\log K_{ow}$. In order to extend these previous findings, an attempt is made in this paper to correlate S_{gf} values reported for HDPE geomembranes in the literature with K_{ow} . Fig. 1 shows a plot of $\log S_{gf}$ vs. $\log K_{ow}$. The excellent correlation ($r^2 = 0.97$) obtained between $\log S_{gf}$ and $\log K_{ow}$, regardless of the

Table 1

Techniques for measuring partitioning and diffusion coefficients (modified from Rowe, 1998)

Technique	Method	Comments/notes
Weight gain (sorption, immersion)	<p>Monitor increase in mass of geomembrane immersed in fluid of interest from initial value m_0 until equilibrium at m_{∞}. Plot $(m_t - m_0)/(m_{\infty} - m_0)$ vs. \sqrt{t} (or $\sqrt{t/l}$) $S_{gf} = (\rho_g/C_{TF})(m_{\infty}/m_0) - 1$ and $D_g = 0.0492 \left(t_g^2/t_{0.5} \right)$ or $D_g = \pi(a t_g/4m_{\infty})^2$</p>	<p>Faster than alternative tests but each chemical must be examined separately. Suitable for pure solvent. For aqueous solutions, weight gain must be corrected for sorbed water. Prone to error due to mass loss when weighting (especially for VOCs) S_{gf} = partitioning coefficient (aqueous solution), c_{TF} = Final equilibrium fluid concentration ρ_g = geomembrane density $t_{0.5}$ = time to get $(m_t - m_0)/(m_{\infty} - m_0) = 0.5$ t_g = geomembrane thickness a = slope of initial linear portion of sorption curve.</p>
Time lag	<p>Monitor mass movement through geomembrane with time for test where C_{F1} = constant and $C_{F2} = 0$. Plot cumulative mass, F, through geomembrane against time and extrapolate steady state value to $F = 0$ to obtain the time lag τ. Slope of the steady state line gives the permeability coefficient P_g $D_g = (t_g^2/6\tau)$ and $S_{gf} = (P_g/D_g)$</p>	<p>Possibility of errors due to maintenance of C_{F1} = constant and $C_{F2} = 0$.</p>
Diffusion/permeation	<p>Diffusion from solution on one side of geomembrane to solution on other side. Change in source and receptor solution monitored with time. At equilibrium: $S_{gf} = \left([c_{F0}V_{s0} - c_{TF}(V_{sF} + V_{rF}) - \sum V_i c_i] / (At_g c_{TF}) \right)$ D_g inferred from variation in source and receptor concentration with time.</p>	<p>Suitable for aqueous solutions (or leachate). May be used in conjunction with weight gain method to allow evaluation of parameters prior to equilibrium in the diffusion test. c_{F0} = Initial concentration in the source, c_{TF} = Final equilibrium concentration in source and receptor V_{s0} = Initial volume of source reservoirs V_{sF}, V_{rF} = Final volume of source and receptor reservoirs. $\sum V_i c_i$ = Mass removed by sampling events (V_i and c_i volume and concentration at each event). a, t_g, ρ_g = Geomembrane area and thickness and density respectively.</p>

Table 2
Summary of proposed prediction methods

Method	Parameter	Eq.#	Relationship	r^2
<i>n</i> -Octanol/ water	S_{gf}	R1	$\log S_{gf} = -1.1523 + 1.2355 \log K_{ow}$	0.97
	D_g	R2	$\log D_g = -12.3624 + 0.9205 \log K_{ow} - 0.3424 (\log K_{ow})^2$	0.72
	P_g	R3	$\log P_g = -13.4476 + 2.2437 \log K_{ow} - 0.3910 (\log K_{ow})^2$	0.84
Molar weight	S_{gf}	R4a	Oxygenated: $\log S_{gf} = -3.8883 + 0.0363 M_w$	0.81
		R4b	Chlorinated: $\log S_{gf} = -2.0467 + 0.0305 M_w$	0.94
		R4c	Aromatic: $\log S_{gf} = -0.0776 + 0.0322 M_w$	0.95
		R4d	Aliphatic: $\log S_{gf} = -0.1107 + 0.0442 M_w$	0.91
	P_g	R5	$\log P_g = -25.6933 + 0.2633 M_w - 1.099 \times 10^{-3} (M_w)^2$	0.81

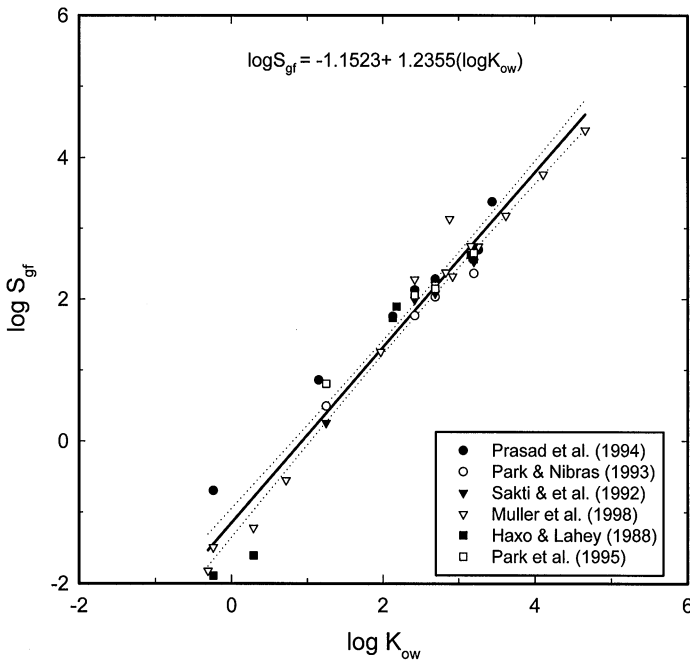


Fig. 1. Relationship between $\log K_{ow}$ and $\log S_{gf}$ for HDPE geomembranes.

properties of the geomembrane or test conditions, substantiates the fact that the partition coefficient is mainly controlled by contaminant characteristics as stated by Müller et al. (1998). As anticipated, as $\log K_{ow}$ increases, the chemical hydrophobia increases and hence the contaminant has a high attraction to the geomembrane.

The plot of $\log D_g$ against $\log K_{ow}$ shows more scatter in the data (Fig. 2) than was the case for S_{gf} (Fig. 1). It may be hypothesized that this scatter is due to a difference

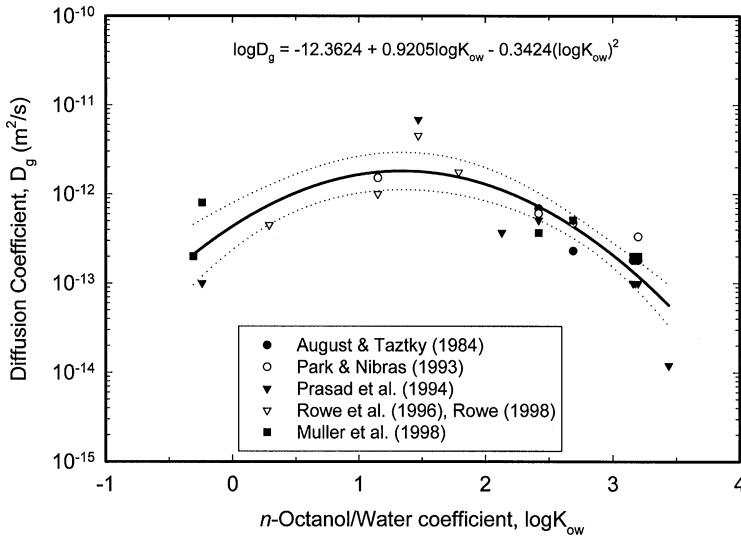


Fig. 2. Variation of diffusion coefficient D_g with n -octanol/water coefficient for aqueous organic contaminants.

in the geomembrane properties and that this difference in geomembrane properties (e.g. crystallinity) may have significant effect on the diffusion process. The plot also shows a decrease in D_g at high $\log K_{ow}$ values. This is likely due to the fact that chemicals with high $\log K_{ow}$ are mostly relatively large molecules (see Table 4) such that the diffusion is highly dependent on the molecule size. As mentioned in Section 2.1, molecular diffusion is an activated process that is completed by successive jumps. Thus, when permeant size increases, higher activation energy is required for diffusion to be completed. Similarly, the permeability (P_g) shows a relatively poor correlation with $\log K_{ow}$ (Fig. 3) but it is still better than that for diffusion because P_g is influenced by both the partitioning and diffusion coefficients.

3.2.2. Estimation based on chemical molecular weight (M_w)

In general, the sorption (and hence the partitioning coefficient) increases with the contaminant molecular weight. To better describe this variation, the chemicals were grouped in four main categories according to their molecule structures: aliphatic, aromatic, chlorinated and oxygenated. Fig. 4 shows the plot of $\log S_{gf}$ as a function of M_w and it can be seen that partitioning coefficient is dependent upon the chemical structure. This is attributed to the fact that the chemical structure affects their solubility in water and hence $\log K_{ow}$, and molecular weight. Consequently, aliphatic hydrocarbons with $\log K_{ow} \geq 3.5$ have high partitioning coefficients followed by aromatic ($2 \leq \log K_{ow} \leq 3.5$), chlorinated or halogenated ($1 \leq \log K_{ow} \leq 3$) and finally oxygenated hydrocarbons which are highly soluble in water ($\log K_{ow} \leq 0.5$). The equations associated with the inferred relations are summarized in Table 2.

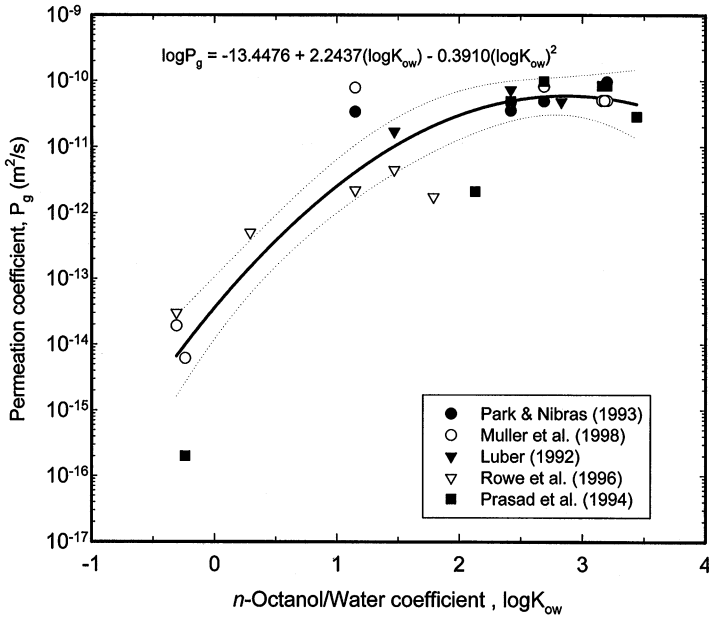


Fig. 3. Variation of permeation coefficient with *n*-octanol/water coefficient for aqueous organic solutions.

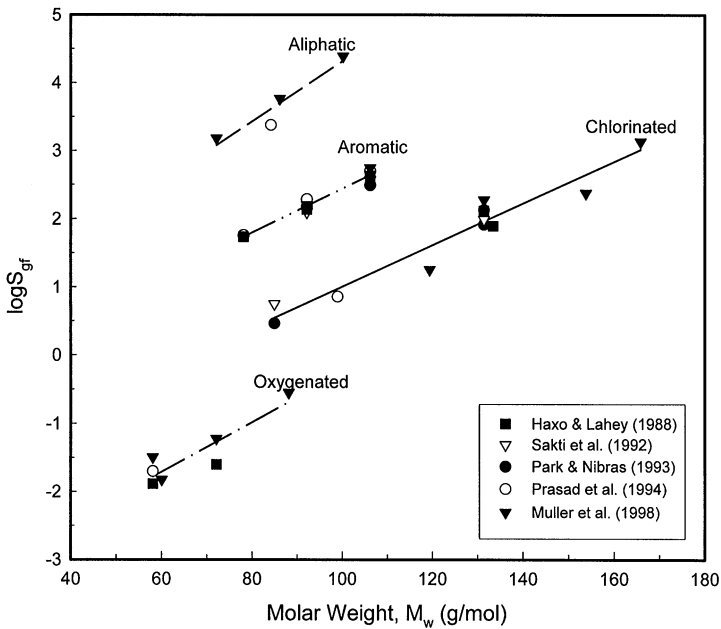


Fig. 4. Variation of partitioning coefficient (S_{gr}) with molar weight of organic compounds.

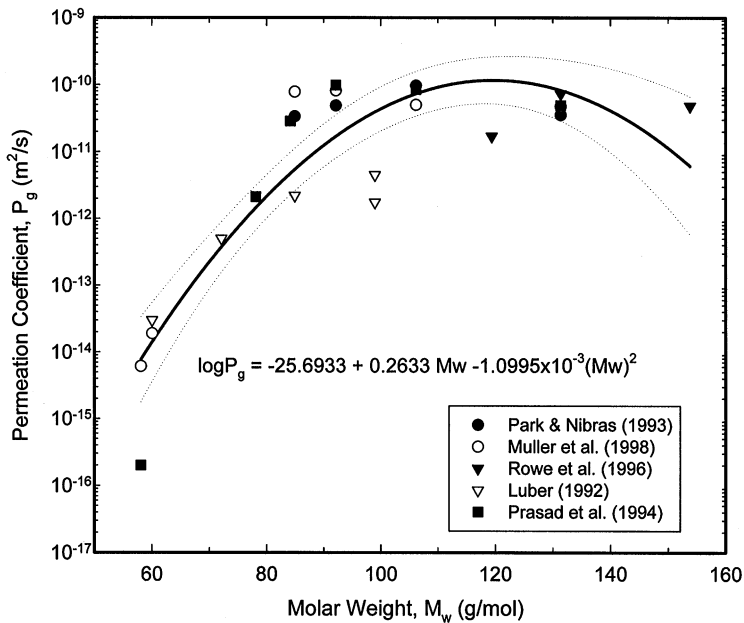


Fig. 5. Permeation coefficient variation with contaminant molar weight for organic aqueous solutions.

Correlating $\log D_g$ with M_w was unsuccessful due to the high degree of scatter in the data as found for $\log K_{ow}$. However, correlating P_g with M_w exhibited a fairly good trend as shown in Fig. 5 and the derived equation is presented in Table 2. As previously mentioned, the scatter observed for D_g is compensated by the relatively good data reported for S_{gr} making P_g less scattered.

4. Experimental investigations

4.1. Material and methods

The study was conducted using a 2.0 mm thick high-density polyethylene (HDPE) geomembrane provided by GSE Linings Inc. (Texas). Its relevant properties are presented in Table 3. Seven organic chemicals representative of chlorinated hydrocarbons (dichloromethane, 1,2-dichloroethane, and trichloroethylene) and aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes) were examined. These chemicals are commonly found in municipal solid waste leachate (Rowe, 1995). The key properties of these laboratory grade (99%+ purity) chemicals (purchased from Sigma-Aldrich, Mississauga, Ontario, Canada) are presented in Table 4.

Tests were conducted using dilute aqueous solutions prepared from high concentration mixed-stock solutions. The dilute solution concentrations ranged

Table 3
Properties of HDPE geomembrane used

Properties	Methods (ASTM)	Units	Test results
Thickness	D5199	mm	2.0
Density	D792	g/cc	0.940
Carbon black content	D1603	%	2.54
Carbon black dispersion	D3015		A1-A2
Oxidative induction time	D3895	min	133
Crystallinity	E794	%	47
Melt flow index	D1238	g/10 min	0.42
Puncture resistance	D4833	N	736
Stress cracking resistance	D5397	h	210
Initial tear resistance	D1004	N	354
Tensile properties	D638		
Strength		kN/m	
@ Yield			35
@ Break			77
Strain		%	
@ Yield			15.0
@ Break			863

Table 4
Selected properties^a of organic contaminants tested

Chemicals	Molar weight (g/mole)	Density (g/cm ³)	Molar volume ^b (cm ³)	Aqueous solubility ^c (mg/l)	Log K_{ow}	Boiling Temp. (°C)	Dipole moment (debye)
<i>Chlorinated hydrocarbons</i>							
Dichloromethane	84.93	1.3266	64.02	20000	1.25	40.2	1.60
1,2-Dichloroethane	98.96	1.2530	78.98	8690	1.45	83.5	1.44
Trichloroethylene	131.39	1.4642	89.74	1100	2.53	87.2	0.77
<i>Aromatic hydrocarbons</i>							
Benzene	78.11	0.8765	89.11	1780	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

^a From Montgomery and Welkom (1990).

^b Calculated based on chemical density and molar weight.

^c At 20°C.

from 2 to 5 mg/l. These concentrations are similar or exceed the level observed in typical landfill leachate as reported by Rowe (1995). During the test, chemical concentrations from both source and receptor were monitored with time. In order to minimize the effect of samplings on the total volume of reservoirs while providing the 0.8 ml required for gas chromatography analyses, small volumes were collected from

reservoirs and were diluted in 1% methanol/water solution. For diffusion tests, approximately 50 µl and 100 µl were collected from the source and the receptor respectively using airtight 0.5 ml syringes. For the control test, sorption samples were diluted in 4.0 ml nominal size glass vials sealed with open top cap equipped Teflon lined septa while samples from the receptor were mixed in 2 ml vials. In both cases, the vials were pre-filled with the stabilizing solution and then spiked with a designated amount of chloroform (yielding 25 µg/l) used as an internal standard in analytical quantification procedures. The dilute solutions formed were then allowed to mix at room temperature for 10–12 h. Tests were run at a laboratory temperature of 22 ± 2°C using glass cells having characteristics summarized in Table 5 and shown schematically in Fig. 6.

4.2. Analytical methods

Samples were analyzed using a Varian Gas Chromatography/Mass Spectrometer (GC/MS) consisting of a Saturn 2000 MS and a 3800 GC equipped with a 8200 CX

Table 5
Characteristics of test cells

Parameter	Units	Control cell	Sorption/ immersion cell	Diffusion cell	
				Source	Receptor
Height	cm	10.0 ± 0.5	10.0 ± 0.5	10.0 ± 0.5	3.0 ± 0.2
Diameter	cm	7.0 ± 0.2	7.0 ± 0.2	7.0 ± 0.2	7.0 ± 0.2
Volume	cm ³	385	385	385	115
Container Surface Area	cm ²	297	297	258	104
RWS ^a	cm ⁻¹	0.77	0.77	0.67	0.90

^aRWS = (Wall Surface Area/Volume)

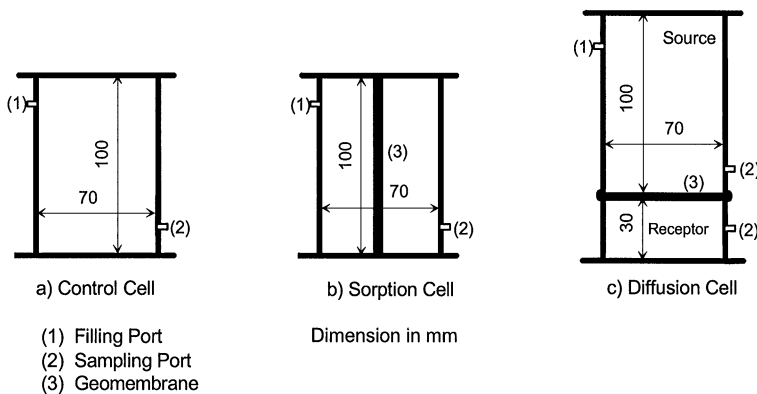


Fig. 6. Schematic of test cells used.

autosampler used in solid phase micro-extraction (SPME) and headspace modes. The chemical separations were done on a 30 m × 0.25 mm ID fused silica capillary column coated with a 0.25 µm DB-5 film using He 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 units range.

The injection system consisted of a 8200 CX Varian autosampler equipped with a 100 µm poly-dimethylsiloxane (PDMS) solid phase micro extraction (SPME) fiber (Supelco Bellfonte, PA, USA). The sampling extraction was performed in headspace 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 Star Chromatography software (Version 5.05).

Contaminant concentrations were quantified based on calibration curves obtained through the analysis of standards of known concentrations that were regularly prepared during the tests. The standard stock cocktail was prepared by spiking a 50 ml glass serum bottle filled with methanol with each of the pure chemicals to achieve concentrations of about 1000 mg/l for the chlorinated hydrocarbons and 500 mg/l for aromatic hydrocarbons. This stock was further diluted in methanol to approximately 1 and 0.5 mg/l for chlorinated and aromatic compounds respectively. This dilute stock was used to prepare the standards used for GC calibration. Standards with concentrations varying from 2–100 µg/l were prepared with the internal chloroform concentrations the same as that used for the “unknown” samples collected for the test cells.

4.3. Procedures

4.3.1. Control cell

To evaluate losses that may be occurring during the test due either to the sampling events or due to chemical/cell material interaction, control tests were conducted in a cell identical to those used for the sorption test and the source compartment in diffusion tests (Fig. 6a). The cell was sealed and then filled with chemical solution at concentration levels of about 5 mg/l levels, similar to those used for the source solution in the diffusion and sorption tests. During the test, contaminant concentrations in solution were monitored by collecting and analyzing samples following the methodology presented in Section 4.2. The measured contaminant concentrations were then plotted as normalized concentrations relative to initial concentration.

4.3.2. Sorption test

In sorption/immersion tests, geomembrane samples with known masses were immersed in a cell filled with mixed dilute solution of contaminants (Fig. 6b). In contrast with the weight gain method where the geomembrane sample weight is monitored, in the present experiment, solution samples were collected through a

sample port and analyzed by GC/MS using the procedure described in Section 4.2. Contaminant concentrations were monitored with time until equilibrium (no significant concentration change for successive samples) is reached. At the end of the test, the cell was dismantled and the geomembrane was quickly and gently wiped with a tissue and its mass measured. This final mass was then used to ascertain the total mass gained due to sorption and was compared to mass inferred from equilibrium concentration in the solution.

If M_{s0} is the initial mass of contaminant in the solution $[M]$, contaminant mass balance at equilibrium can be written as follows:

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

where M_{sF} is the final mass of contaminant in the solution $[M]$; M_{gF} the mass uptake by the geomembrane $[M]$ and M_R the mass removed by sampling events. If one expresses the masses in terms of their respective concentrations and volumes, Eq. 10 becomes:

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

with c_{f0} = initial solution concentration $[\text{ML}^{-3}]$, c_{fF} = final equilibrium solution concentration $[\text{ML}^{-3}]$, V_{f0} = initial solution volume $[\text{L}^3]$; V_{fF} = final solution volume $[\text{L}^3]$; M_g = initial mass of geomembrane $[M]$, ρ_g = geomembrane density $[\text{ML}^{-3}]$, c_{gF} = final equilibrium concentration in geomembrane $[\text{ML}^{-3}]$ and $\sum V_i c_i$ = mass removed by sampling events $[M]$ (V_i and c_i are volume and concentration at each event). The partitioning coefficient can then be obtained by substituting Eq. 11 in Eq. (1) as follows:

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

4.3.3. Diffusion test

Diffusion tests were performed in double compartment cells similar to those used by August and Taztky (1984), Haxo and Lahey (1988) and Rowe et al. (1995, 1996). According to August and Taztky (1984), this type of assembly is better suited for studying the diffusive properties of geomembranes in a landfill environment than other methods (gravimetric or immersion tests). The test apparatus shown in Fig. 6 consist of a closed system with a source and receptor reservoirs separated by the geomembrane examined. Cell characteristics are presented in Table 5. The two contaminant-free compartments and the geomembrane are sealed together using two-part epoxy adhesive type 2216 B/A (3 M St. Paul, Minnesota, USA) and cured for 7 days. Then, geomembrane-cell outside joints were covered by a thick silicone sealant. Once the silicone seal had hardened, the receptor was filled with contaminant-free megapure water (distilled deionized). Afterwards, the source reservoir was filled with a mixed dilute solution of dissolved chemicals. This filling process took approximately 5 min. The source solution was then quickly sampled for analysis. The measured initial chemical concentrations ranged from 2–5 mg/l. Each

compartment was equipped with a sampling port that allowed collection of samples for gas chromatography analyses. During the test, the concentrations in both source and receptor reservoirs were monitored with time and the results were plotted as normalized concentration relative to the initial source chemical concentrations.

The test approach was based on concepts and theory proposed by Rowe et al. (1988) for clayey soils and subsequently extended to geomembranes by Rowe et al. (1995, 1996). For these closed systems, at any time t , the mass of contaminant in the source solution is equal to the initial mass minus the mass that diffused through the geomembrane up to that time and can be written as:

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

where $c_{ss}(t)$ = concentration of contaminants in the source solution at time t [ML^{-3}]; c_{s0} = initial concentration in the source solution [ML^{-3}]; H_{ss} = reference height of source solution (volume of source fluid per unit area) [L]; $f_{ss}(\tau)$ = mass flux of contaminant into the geomembrane at time τ [$\text{ML}^{-2} \text{T}^{-1}$].

Similarly, the increase in contaminant concentrations in the receptor (due to their migration through the geomembrane) can be modeled by the following:

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

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

Diffusion (D_g) and partition (S_{gr}) coefficients were inferred by fitting a theoretical solution of the diffusion equation to the data measured using boundary conditions presented in Eqs. 12 and 13. S_{gr} values obtained from sorption tests were used as a starting point. Tests data were analyzed following the procedure described in detail elsewhere by Rowe et al. (1995) using the finite layer analysis program POLLUTE[©] v6.3.6 (Rowe and Booker, 1998) that specifically allows the modeling of the phase change and hence the partition coefficient.

5. Results and discussions

5.1. Control cell

Figs. 7 and 8 show the variation in chemical concentration as measured during the test period for chlorinated and aromatic hydrocarbons respectively. It is evident that most of the concentrations changed somewhat with time. The magnitude of the decrease was dependent on the chemical tested. For instance, among the chlorinated organic contaminants examined, only TCE experienced significant decrease in concentration (by about 25% of the initial concentration). The other compounds (DCM and 1,2-DCA) did not show any significant and measurable change

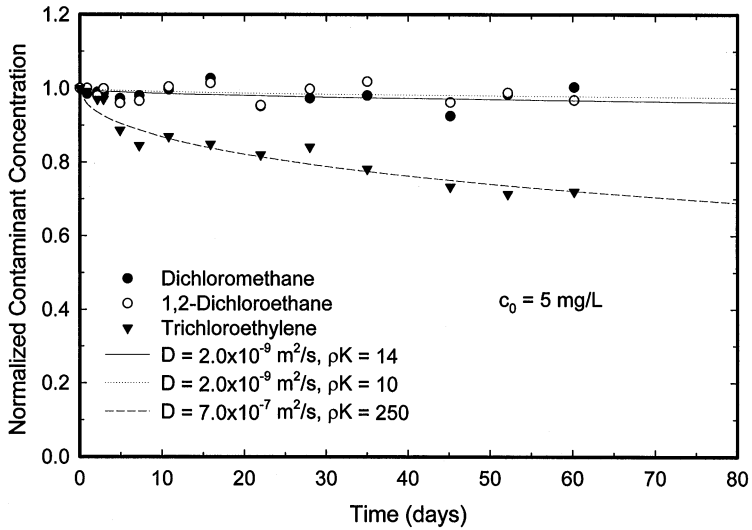


Fig. 7. Observed concentrations of chlorinated hydrocarbons in control cells.

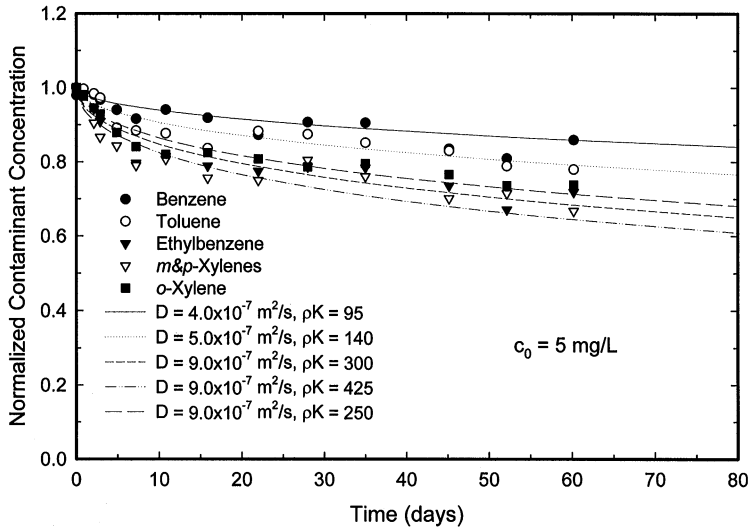


Fig. 8. Observed concentrations of aromatic hydrocarbons in control cells.

suggesting that these compounds were relatively stable in glass cells over the testing period. Similar observations have been reported by Rowe et al. (1995) for DCM solution placed in glass serum bottles and blank glass cells and monitored for up to 405 days. In contrast, concentrations of all aromatic hydrocarbons decreased during the testing period with a maximum decrease of 25% observed for *m* and *p*-xylenes

over the 60 day testing period. The decrease for other aromatic hydrocarbons is about 10, 17, 22 and 23% for benzene, toluene, *o*-xylene and ethylbenzene respectively.

The decline observed for aromatics and TCE may be attributed to their sorption into cell material (here glass) and other losses associated with sampling events and process. However, the negligible decrease in DCM and 1,2-DCA concentrations in the same control cells suggests that sorption onto cell glass may be dominant. These observations highlight the importance of the stability of compounds with respect to test cell materials. Therefore, in the immersion test, the mass of contaminant removed from the solution due to the sorption onto the cell must be considered when calculating different parameters. This also applies to diffusion tests with finite mass source for which the available diffusive mass may be reduced due to sorption onto the glass cell wall.

To account for these losses in diffusion tests with finite masses in the source reservoir, the control cells were modeled using an approach developed by Krol (2000). In this method, a fictitious layer is used as a means of removing mass from the system due to sorption onto the glass. To achieve this, the layer was modeled on top of the cell assuming a zero flux boundary condition above this fictitious layer. In the present case, a 5 mm thick layer was assumed and the theoretical curves were generated using POLLUTE[®] v6.3.6 (Rowe and Booker, 1998) as shown in Figs. 7 and 8. The inferred parameters (shown in legend) were subsequently used when modeling the diffusion tests performed in this study.

5.2. Sorption tests

The changes in contaminant concentrations monitored during the sorption tests plotted as normalized concentrations relative to the initial concentrations are shown in Figs. 9 and 10 for chlorinated and aromatic hydrocarbons respectively. Among the chlorinated, trichloroethylene (TCE) concentration decreased the most with the equilibrium concentration being 30% of the initial, followed by 1,2-dichloroethane (1,2-DCA) and dichloromethane (DCM) although they are very close with respective values of 75% and 95% of the initial concentrations. The equilibrium concentration for TCE is achieved in about 8 days whereas for DCM and 1,2-DCA it took up to 12 days before equilibrium was observed.

Among the aromatic hydrocarbons, ethylbenzene and xylenes showed the greatest decrease of about 90% of the initial concentration followed by toluene with a decrease of 80% and benzene with a concentration reduction of 60%. For compounds with high decrease (xylenes and ethylbenzene), the equilibrium concentration seems to be reached much faster. For instance, the equilibrium for *o*-xylene was reached after the first 5 days of the test while for benzene, the reduction extended such that the equilibrium was reached in up to 10 days.

Using Eq. 12, two sets of partitioning coefficients were calculated: non-corrected and corrected coefficients. For non-corrected S_{gf} , no consideration was given to the losses (this would correspond to the case where the presence of geomembrane samples, which have high affinity to the chemicals in the solution, would reduce their

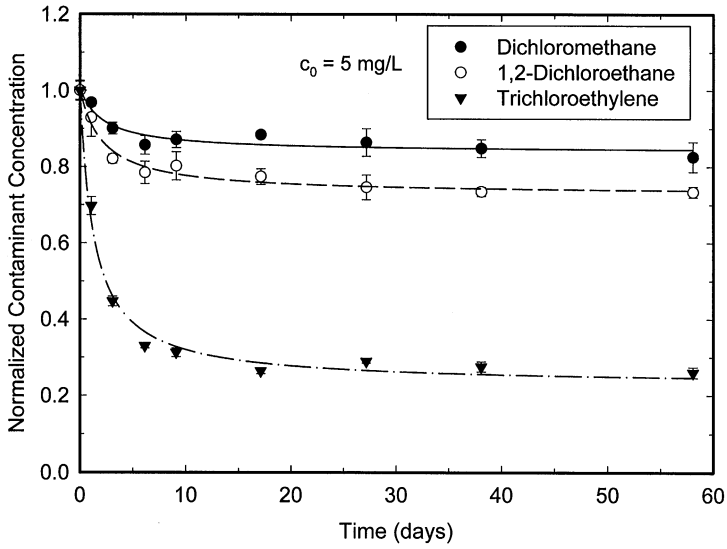


Fig. 9. Measured chlorinated hydrocarbons concentration during sorption tests.

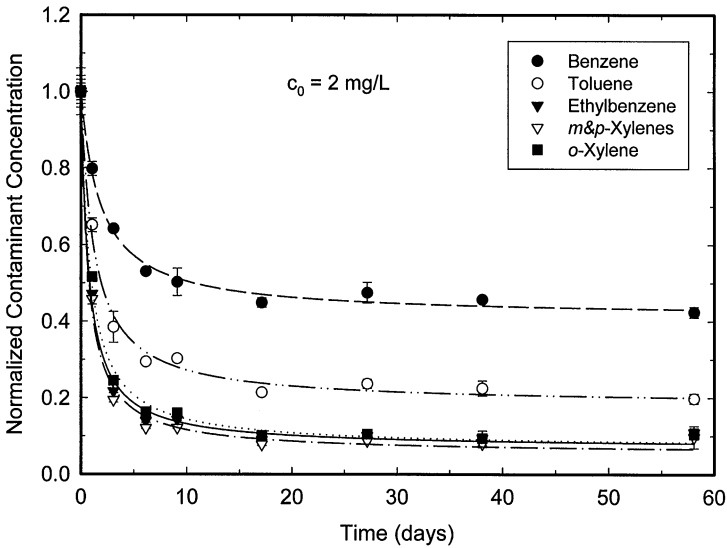


Fig. 10. Measured aromatic hydrocarbons concentration during sorption tests.

attraction to glass surface to negligible levels). The corrected values were calculated assuming that the mass loss to glass would occur even in the presence of geomembrane sample. In this case, the mass adsorbed onto the cell glass. This

Table 6
Estimated partitioning coefficient from sorption test

Chemicals	log K_{ow} **	Sorption test S_{gf}		Literature			
		Uncorrected	Corrected	a	b	c	d
<i>Chlorinated hydrocarbons</i>							
Dichloromethane	1.25	6.1	6.1	2.9			
1,2-Dichloroethane	1.45	9.4	9.4		7.2	10	
Trichloroethylene	2.53	87	59	82	135		131
<i>Aromatic hydrocarbons</i>							
Benzene	2.13	31	25				54
Toluene	2.79	120	95	150	192	160	137
Ethylbenzene	3.13	315	237				
<i>m</i> & <i>p</i> -Xylenes	3.19	408	300	310	498	556	376
<i>o</i> -Xylene	3.13	285	193				422

^aPark and Nibras (1993); ^bPrasad et al. (1994); ^cMüller et al. (1998); ^dHaxo and Lahey, 1988;
** *n*-octanol/water partition coefficient.

mass lost by sorption was estimated based on monitored chemical final concentration in control cells at the end of the test. It is expected that the real case lies between these two limiting cases.

The calculated partition coefficients are presented in Table 6. For non-corrected values for chlorinated hydrocarbons, TCE has the highest $S_{gf} = 87$ followed by the 1,2-DCA and DCM with $S_{gf} = 9.4$ and 6.1 respectively. When corrected, the calculated S_{gf} values are about 59 for TCE while for 1,2-DCA and DCM, S_{gf} values remain unchanged due to the fact no significant losses were observed in the control cells. The highest non-corrected $S_{gf} = 408$ was observed for *m* and *p*-xylenes, followed by ethylbenzene ($S_{gf} = 315$), *o*-xylene ($S_{gf} = 237$), toluene ($S_{gf} = 120$). Benzene has the lowest $S_{gf} = 31$.

These values should be considered as upper and lower bound values for corrected and non-corrected partitioning coefficients. Indeed, it may be expected that when the geomembrane samples are immersed in the solution the sorption onto the cell wall will be substantially reduced because of the higher geomembrane affinity to organic contaminants examined.

Based on these results, it appears that the partitioning coefficient increases with the increases in *n*-octanol/water coefficient (log K_{ow}). This is to be expected (as noted earlier) since an increase in log K_{ow} represents an increase of the hydrophobicity, and hence the ability of the chemical to partition with organic material. It is also evident that, for the chemicals examined, aromatic hydrocarbons have higher partitioning coefficients because of the relatively high log K_{ow} (2.13–3.20) compared to chlorinated hydrocarbons with log K_{ow} varying from 1.25 to 2.53.

5.3. Diffusion tests

Duplicate tests were performed. Contaminant concentrations measured in the source and the receptor over the 75 day testing period are shown in Figs. 11 and 12

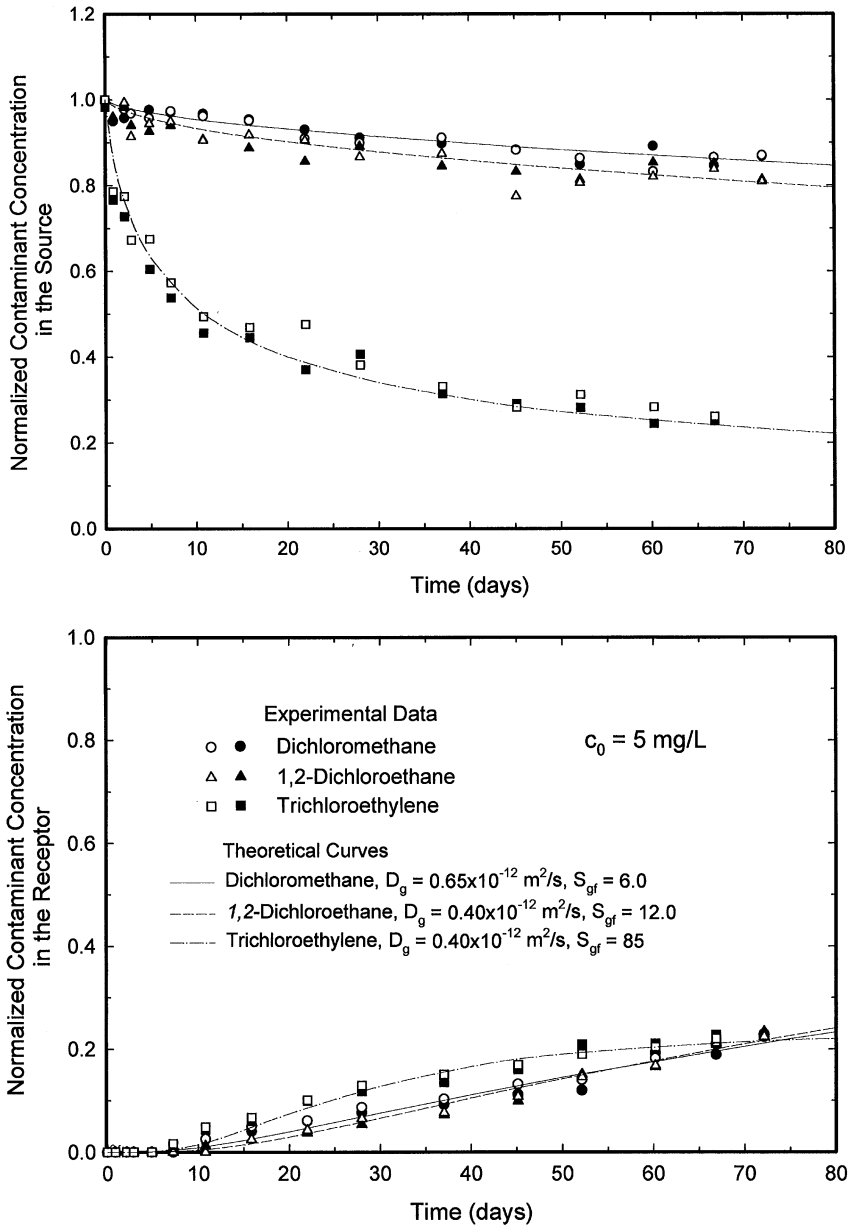


Fig. 11. Chlorinated hydrocarbons concentration change with time during the diffusion test.

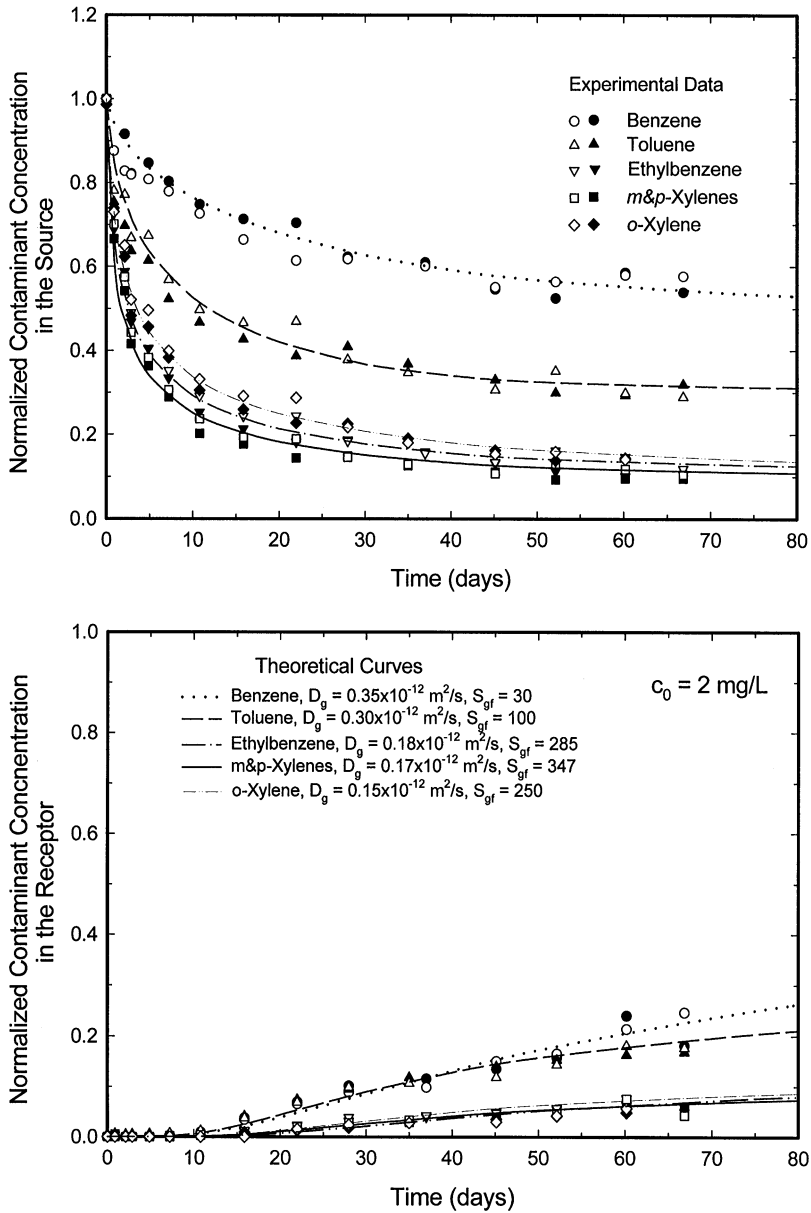


Fig. 12. Aromatic hydrocarbons concentration change with time during the diffusion test.

for chlorinated and aromatic hydrocarbons respectively. Concentrations are plotted as normalized concentration relative to the initial concentration and each data point represents the average of triplicate values quantified with GC analyses. Despite some scatter of the data, it can be seen that the source concentrations decrease with time

while the receptor concentrations increase with time as the chemicals diffuse through the geomembrane. In general, the decrease in the source concentration is controlled by the partitioning parameter while the increase in the receptor concentration is dominated by the permeation coefficient. The variations in the source and receptor are different for each contaminant indicating that the migration of the organic contaminants through a HDPE geomembrane is contaminant dependent.

Among the chlorinated compounds (Fig. 11), the greatest decrease was observed for trichloroethylene with concentration dropping to about 25% of the initial concentration. Dichloromethane (DCM) and 1,2-dichloroethane (1,2-DCA) experienced a much smaller decrease with the later having lower concentration of $0.8c_0$ and the former $0.85c_0$. Although all the chemicals breakthrough to the receptor at approximately the same time, the TCE concentration increased faster than the other two chlorinated hydrocarbons. The observations suggest that the migration properties of the DCM and 1,2-DCA are similar and that they permeate at slower rates than TCE.

The theoretical curves generated for chlorinated compounds by solving the diffusion equation with the appropriate boundary conditions (Eqs. 13 and 14) are also shown in Fig. 11 (lines). The inferred S_{gf} and D_g , and calculated P_g are summarized in Table 7. S_{gf} , D_g and P_g for DCM are respectively 6, $0.65 \times 10^{-12} \text{ m}^2/\text{s}$, and $3.9 \times 10^{-12} \text{ m}^2/\text{s}$ while for 1,2-DCA, the values are 12, $0.40 \times 10^{-12} \text{ m}^2/\text{s}$ and $4.8 \times 10^{-12} \text{ m}^2/\text{s}$. TCE parameters are 85, $0.4 \times 10^{-12} \text{ m}^2/\text{s}$ and $34.0 \times 10^{-12} \text{ m}^2/\text{s}$. The values reported for DCM is at the upper end of the range of $1\text{--}3.0 \times 10^{-12} \text{ m}^2/\text{s}$ reported by Rowe et al. (1996) for a 2 mm HDPE geomembrane using the same procedure. The 1,2 DCA permeation coefficient is similar to that reported by Rowe et al. (1996) with a value of $4.8 \times 10^{-12} \text{ m}^2/\text{s}$ that is within the reported range of $3\text{--}6 \times 10^{-12} \text{ m}^2/\text{s}$.

It appears that, under the experimental conditions used in this study, TCE permeates approximately 10 times faster than the other two chlorinated

Table 7
Inferred partitioning, diffusion and calculated permeation coefficients from diffusion tests

Contaminants	$\log K_{ow}^a$	S_{gf} (–)	D_g ($\times 10^{12} \text{ m}^2/\text{s}$)	P_g ($\times 10^{12} \text{ m}^2/\text{s}$)
<i>Chlorinated hydrocarbons</i>				
Dichloromethane	1.25	6	0.65	3.9
1,2-Dichloroethane	1.45	12	0.40	4.8
Trichloroethylene	2.53	85	0.40	34.0
<i>Aromatic hydrocarbons</i>				
Benzene	2.13	30	0.35	10.5
Toluene	2.79	100	0.30	30.0
Ethylbenzene	3.13	285	0.18	51.3
<i>m</i> and <i>p</i> -Xylene	3.19	347	0.17	59.0
<i>o</i> -Xylene	3.13	240	0.15	36.0

^a *n*-octanol/water partition coefficient.

hydrocarbons examined. The permeation rate follows TCE > 1,2-DCA > DCM. This order may be explained in terms of the affinity between the different contaminants and the HDPE geomembrane as evident from Table 4. Of the three chlorinated contaminants, TCE is the less polar (0.77 debye) followed by 1,2-DCA (1.44 debye) and DCM (1.69 debye).

For all aromatic hydrocarbons, the source concentrations decreased significantly during the diffusing test (Fig. 12). The smallest decrease in the concentration to about 60% of the initial concentration was observed for benzene while the xylenes (*m* and *p*-xylenes and *o*-xylene) and ethylbenzene have the greatest decrease with concentrations dropping to about 20% of the initial concentration. The benzene and toluene concentrations increased the most in the receptor during the testing period. Ethylbenzene and xylenes increased the least.

Fig. 12 also shows the theoretical curves (lines) generated for these diffusion tests and the estimated parameters are presented in Table 7. The permeation coefficients have the following order: *m* and *p*-xylene > ethylbenzene > *o*-xylene > toluene > benzene. This order can be related to their affinity to the HDPE geomembrane examined and the hydrophobicity of the various chemicals. In general, the more hydrophobic the chemical (i.e. the greater is the *n*-octanol/water coefficient, $\log K_{ow}$), the more the organic compound partitions to the geomembrane. For the compounds examined, *m* and *p*-xylenes have the highest $\log K_{ow} = 3.19$ (average), followed by ethylbenzene and *o*-xylene with $\log K_{ow} = 3.13$; toluene $\log K_{ow} = 2.79$ and benzene $\log K_{ow} = 2.13$.

Two key observations can be made from the results reported herein. First, it can be seen from Fig. 12 that, although their permeation rates are greater, the concentrations of ethylbenzene and xylenes in the receptor are lower than benzene and toluene. As indicated in Eq. 5, it is the flux into the receptor that controls the concentration of the contaminants and this is both a function of P_g and the concentration gradient across the geomembrane implying that any decrease in one of these two parameters will result in smaller concentration in the receptor. It can be seen from the receptor profile that for these contaminants, the concentration decreases rapidly and significantly during the first days of testing reducing the concentration gradient. The concentration will continue to decrease because the total mass of chemical is limited in the source. Thus, the concentration in the receptor will be less than for chemicals with low partitioning coefficients.

The second observation is that all S_{gf} values reported in Table 7 lie between the two values (corrected and uncorrected) previously reported from the sorption test. This substantiates the statement made earlier that these two values should be considered as the upper and lower bound for the S_{gf} .

6. Comparison between measured and estimated parameters

To evaluate the effectiveness of the proposed estimation methods, the measured values are compared to the predicted values. Fig. 13a presents the plot of measured S_{gf} (from diffusion and sorption) relative to predicted S_{gf} based molecular weight

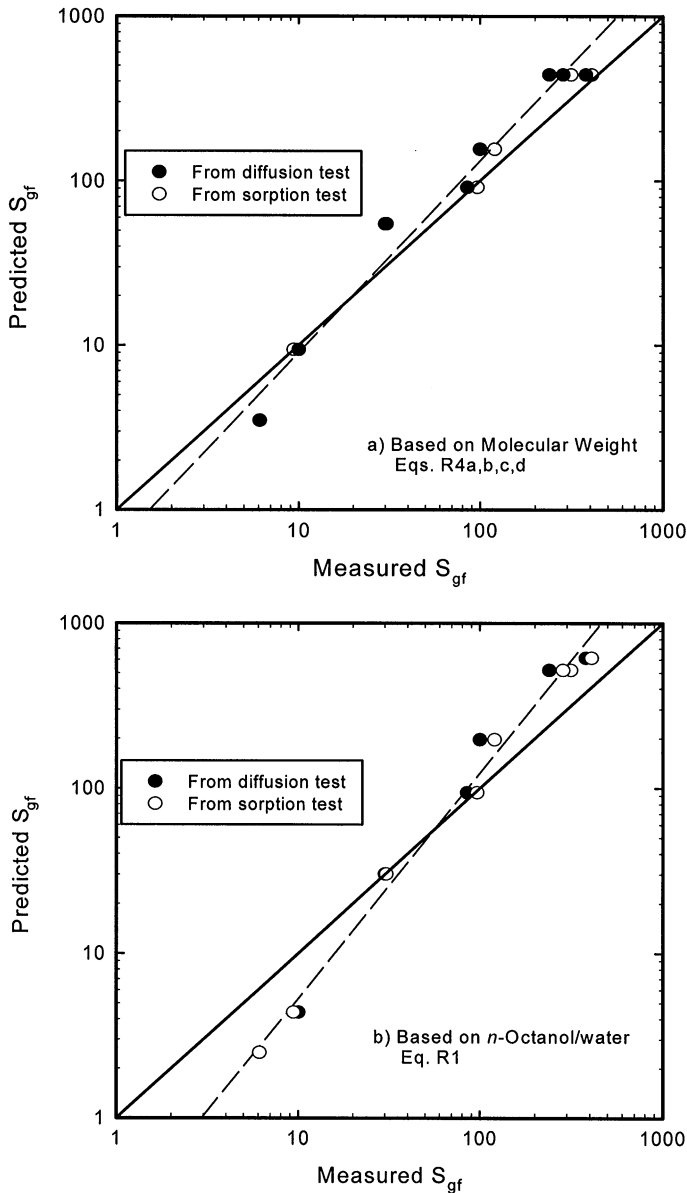


Fig. 13. Predicted and measured partitioning coefficient using different proposed relations.

relationships (Eqs. R4,a,b,c,d). The figure shows that the results are very close to 1 : 1 suggesting an excellent prediction. The predicted S_{gf} using *n*-octanol/water relation as a function of measured S_{gf} is shown in Fig. 13b. It can be seen that the $\log K_{ow}$ relationship underestimates S_{gf} for chemical, with low $\log K_{ow}$ and overestimates S_{gf} for high $\log K_{ow}$.

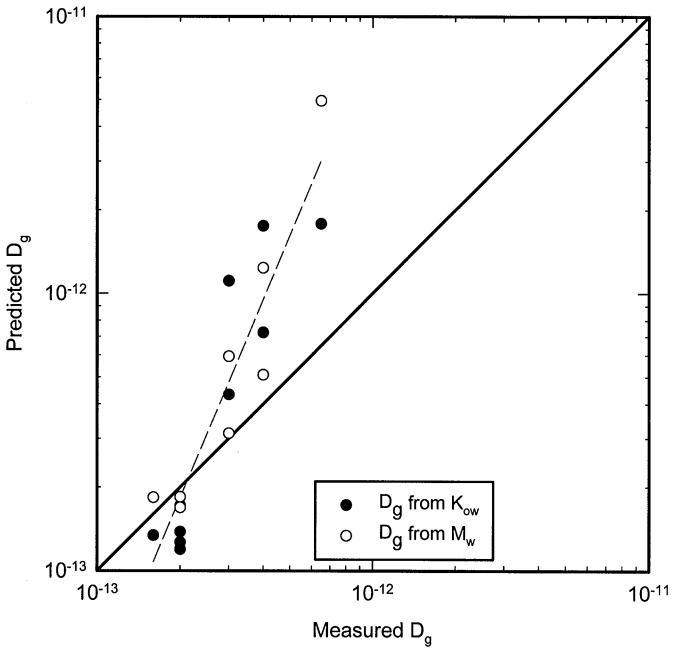


Fig. 14. Predicted and measured D_g using different proposed relations.

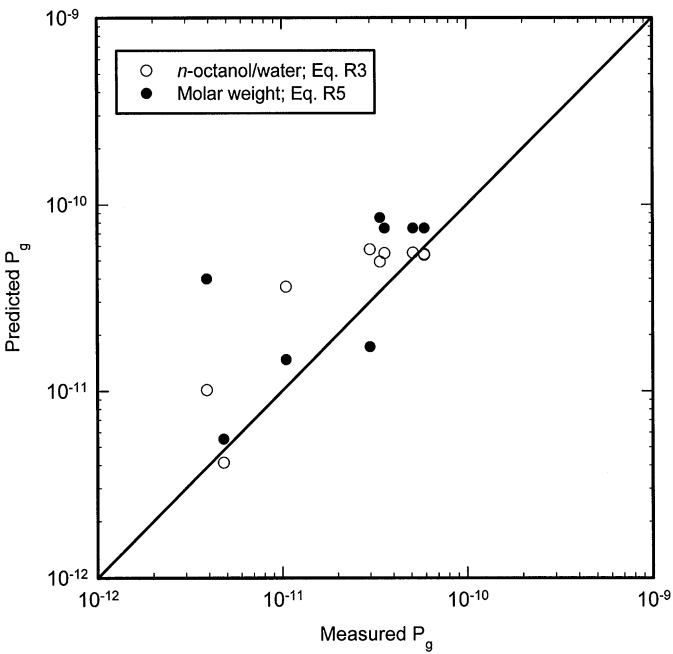


Fig. 15. Predicted and measured P_g using different proposed relations.

The Fig. 14 shows the plot of the diffusion coefficient D_g predicted against the measured D_g . It can be seen that there is a gap between the data and the 1 : 1 line plot that indicates a perfect prediction. This is because the relationship derived either based on $\log K_{ow}$ or M_w is only related to the properties of the chemical. But it is known that the properties (ie crystallinity, branching, cross-linking etc.) of the geomembrane greatly affect the diffusion coefficient. This seems to indicate that a more sophisticated model that can incorporate both the chemical (e.g. size, hydrophobicity) and geomembrane properties (e.g. crystallinity, branching) is needed.

Fig. 15 presents the variation of the predicted P_g with the measured P_g for diffusion tests. The plot shows that P_g values are significantly overestimated probably due to the over prediction observed for D_g . However, the discrepancy with the 1:1 line is less because of the good relationship provided with S_{gr} . This substantiates the fact that overall permeation is governed by the properties of both the geomembrane and chemicals.

7. Summary and conclusions

The partition and diffusion coefficients required to assess the effectiveness of a HDPE geomembrane as a diffusive barrier to organic contaminants have been presented and discussed. Based on the data presented, it appears that, for many organic contaminants, the diffusion coefficient typically lies in the range of 10^{-12} – 10^{-13} m²/s. It was found that partition coefficients show a very high variation depending on the chemical. This suggests that particular caution should be taken when choosing the partition coefficient. Various semi-empirical and empirical methods based on chemical molecular weight and the *n*-octanol/water coefficient ($\log K_{ow}$) have been proposed to estimate the diffusion, and partition coefficients. Laboratory sorption tests and diffusion tests conducted on a 2.0 mm HDPE geomembrane using three chlorinated hydrocarbons and four aromatic hydrocarbons demonstrated that S_{gr} could be estimated from the above methods.

8. For further reading

The following references are also of interest to the reader: Luber, 1992; Park et al., 1995; Sakti et al., 1992.

Acknowledgements

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