

VALIDATION OF TRANSPORT OF VOCs FROM COMPOSITE LINERS

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Validation of Transport of VOCs from Composite Liners

by

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REPORT SUMMARY

Composite liners consisting of a geomembrane overlying a clay liner are often required as bottom liners for waste containment systems. Composite liners are effective because the geomembrane component restricts the cross-sectional area over which advection occurs and the soil beneath the geomembrane is designed to have low hydraulic conductivity, which limits advection through defects in the geomembrane. Therefore, diffusive transport becomes the dominant mode of contaminant transport in well-constructed composite liners.

Volatile organic compound (VOC) transport through geomembranes and compacted clay liners individually are well understood, and VOC transport models have been developed and verified. In contrast, VOC transport through composite liners is not completely understood, and models for VOC transport through composite liners have received little verification. Moreover, recent research has raised significant questions regarding the effectiveness of composite liners to mitigate VOC transport. Being able to predict VOC transport is essential when evaluating potential impacts on groundwater.

A two-stage study was undertaken to conduct experiments, analyses, and assessment. The first stage consists of bench-scale laboratory tests simulating intact composite liners to verify existing transport models for composite liners. Transport parameters for the materials used in the bench-scale tests were obtained by separate experiments. In the second stage, sensitivity analyses were performed to assess the effects of diffusion coefficients, partition

coefficients, hydraulic conductivity, and porosity on model simulations. The parameters related to geomembrane showed little effect on breakthrough concentrations and the transport parameters related to the clay liner dominantly affect the breakthrough concentration. Even if all the properties are independently measured, measurement error changes the breakthrough concentration up to 2 orders of magnitude.

Field data was adopted from Klett (2006) to evaluate the contaminant model simulations for toluene using widely accepted published transport parameters for clay and composite liners in Wisconsin. The simulation results show that predicting relative concentrations with widely accepted transport parameters is difficult because relative concentration is very sensitive to the properties of the clay liner. Thus, the most conservative case must be considered in landfill designs.

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SECTION 1 INTRODUCTION

1.1 Introduction

Composite liners consisting of a geomembrane overlying a clay liner are often required as bottom liners for waste containment systems. Composite liners are effective because the geomembrane component restricts the cross-sectional area over which advection occurs and the soil beneath the geomembrane is designed to have low hydraulic conductivity, which limits advection through defects in the geomembrane (Giroud and Bonaparte 1989). Giroud et al. (1997) show that for typical design condition, advection occurs over only a very small fraction of the composite liner. The soil liner also reduces diffusion of volatile organic compounds (VOCs), which can diffuse through intact composite liners in significant quantities (Park et al. 1996; Foose et al. 1999).

Field data collected on the performance of composite landfill liners demonstrate that composite liners have low leakage rates (e.g., Othman et al. 1997). Although the leakage rates can be indicative of contaminant transport through composite liners, contaminants can also diffuse through composite liners without defects. Park et al. (1996) and Foose et al. (2002) demonstrate that for well-constructed composite liner having few defects, the mass flux of volatile organic compounds through intact portions of a composite liner can be four to six orders of magnitude greater than that through defects. Thus, diffusive transport can be the dominant mode of contaminant transport in composite liners.

Geomembranes are often perceived as being impervious. However, studies have shown that organic compounds can readily penetrate through geomembranes in a short period or time (Britton et al. 1989; Park and Bontoux 1991; Park and Nibras 1993; Buss et al. 1995; Park et al. 1996; Rowe 1998; Aminabhavi and Naik 1999; Xiao et al. 1999; Sangam and Rowe 2001; Joo et al. 2004, 2005). Defects in geomembranes are also inevitable, permitting leakage. Consequently, understanding transport through geomembranes is important when evaluating the effectiveness of a composite liner.

Analyses have also shown that transport of volatile organic compounds (VOCs) generally is more critical than transport of inorganic compounds (e.g., toxic heavy metals), even though VOCs are often found at lower concentrations in leachate (Rowe 1998; Edil 2003). VOCs are more critical for two reasons. First, water quality criteria for VOCs are generally lower than those of many inorganic compounds. Second, geomembranes do little to inhibit the transport of VOCs, because VOCs diffuse readily through geomembrane polymers (Park and Nibras 1993; Park et al. 1996; Foose et al. 2001).

VOC transport through compacted clay liners is well understood, and VOC transport models for clay liners have been developed and verified (Edil et al. 1994, 1995, Kim et al. 2001). In contrast, VOC transport through composite liners is not completely understood, and models for VOC transport through composite liners have received little verification (Sangam and Rowe 2001, Foose et al. 2002). Field data do indicate that composite liners are excellent hydraulic barriers, but recent research has raised significant questions regarding the effectiveness of composite liners to mitigate VOC

transport (Klett 2006). Being able to predict VOC transport is essential when evaluating potential impacts to groundwater.

The primary hypothesis of this study is that VOC transport through intact composite liners can be predicted by existing transport models using independently measured transport parameters. This hypothesis will be evaluated in four stages. First, VOC transport parameters of Kamm clay, a clay used for composite liners, will be measured. Second, VOC transport parameters for a HDPE geomembrane will be measured. Third, transport of VOCs will be measured from bench-scale composite liner tests. Finally, VOC transport measured from bench-scale composite liner tests will be compared with predicted VOC transport by numerical code using individually measured transport parameters, and the models will be adapted if necessary.

The verified transport model will be used to assess long-term impacts of VOCs on groundwater for typical site conditions and existing lining technologies. Changes to landfill design practices may be recommended based on the findings of this assessment.

SECTION 2 BACKGROUND

2.1 Contaminant Transport in Composite Liners

Composite liners consisting of a geomembrane overlying a clay liner are often required as bottom liners for waste containment systems. Geomembranes are impervious to diffusion of inorganic solutes compared to organic solutes (Rowe et al. 1995). Thus, the pathway for inorganic solutes through a composite liner is through defects in the geomembrane and subsequently through the soil liner via advection and diffusion. However, organic solutes can also diffuse through intact geomembranes at appreciable rates (Park and Nibras 1993). Therefore, solute transport has two pathways through composite liners: (1) advection and diffusion of inorganic and organic solutes through defects in the geomembrane and subsequently through the soil liner and (2) diffusion of organic solutes through the intact geomembrane and subsequently through the soil liner (Foose et al. 2002) (Fig. 2.1).

In composite liners, the geomembrane component restricts the cross-sectional area over which advection occurs and the soil beneath the geomembrane is designed to have low hydraulic conductivity, which limits advection through defects in the geomembrane (Giroud and Bonaparte 1989). Advection occurs over only a very small fraction of the composite liner under typical design conditions (Giroud et al. 1997). The soil liner also reduces diffusion of organic solutes, which can diffuse through intact composite liners in significant quantities (Park et al. 1996; Foose et al. 1999).

Field data collected on the performance of composite landfill liners demonstrate that composite liners have low leakage rates (e.g., Othman et al.

1997). Although the leakage rates can be indicative of contaminant transport through composite liners, contaminants can also diffuse through composite liners without defects. Park et al. (1996) and Foose et al. (2002) demonstrate that for well-constructed composite liner having few defects, the mass flux of volatile organic compounds (VOCs) through intact portions of a composite liner can be four to six orders of magnitude greater than that through defects. Thus, diffusive transport can be the dominant mode of contaminant transport in composite liners. Therefore, the remainder of this study will focus on diffusive transport of VOCs through intact composite liners and transport through defects will not be considered further.

2.1.1 VOC Transport in Geomembranes

Movement of organic contaminants from an aqueous medium through intact geomembranes consists of three steps: (1) partitioning of the contaminant between the geomembrane surface and the aqueous solution, (2) diffusion of the contaminant through the geomembrane, and (3) partition from the outer edge of the geomembrane into the receiving medium (Haxo and Lahey 1988; Park and Nibras 1993; Prasad et al. 1994; Park et al. 1996; Sangam and Rowe 2001; Joo et al. 2004; Nefso and Burns 2007). Partition-diffusion transport models have been used to describe these processes and to predict transport in geomembranes (Haxo and Lahey 1988; Park and Nibras 1993; Prasad et al. 1994; Buss et al. 1995; Park et al. 1996; Sangam and Rowe 2001; Joo et al. 2005).

Park and Nibras (1993) used a gravimetric method to measure partition coefficients and diffusion coefficients of 10 pure organic compounds and 4 aqueous phase organic compounds to polyethylene geomembranes. They also examined the effects of competitive sorption. Low density polyethylene (LDPE) geomembranes had ten times higher diffusion coefficients for pure organic compounds than HDPE geomembranes. The partition coefficients and diffusion coefficients for pure organic compounds were related to solubility, polarity, and the number of chlorine atoms.

The partition coefficient and diffusion coefficient of each organic compound present in organic chemical mixtures could be predicted as the product of the partition coefficient or diffusion coefficient and the mole fraction of the organic compound of interest. Partition coefficient and diffusion coefficient of pure organic compounds obtained from batch immersion tests were used with a mathematical model to successfully predict the mass flux of organic compounds mixed with gasoline through geomembranes. In aqueous solutions, partition coefficients remain relatively constant for concentration up to 90 % of aqueous solubility, but the diffusion coefficient increased with an increase in concentration. Competitive sorption was not evaluated with aqueous organic compounds.

Park et al. (1996) developed a double-compartment apparatus to determine the diffusion coefficient and partition coefficient for geomembranes. A mathematical model was developed to analyze the tests data. Diffusion coefficients were found to increase exponentially with aqueous concentration and decrease exponentially with geomembrane thickness, whereas partition

coefficients remained constant. Diffusion coefficients and partition coefficients increased when geomembranes were stretched.

Sangam and Rowe (2001) proposed semi-empirical relationships to predict the partition coefficient of organic compounds for HDPE geomembranes as a function of the octanol-water partition coefficient (K_{ow}) and the chemical molecular weight. These semi-empirical relationships were verified by measuring partition coefficients and diffusion coefficients for 3 chlorinated and 4 aromatic hydrocarbons to a 2.0-mm-thick HDPE geomembrane. Diffusion coefficients were overestimated by a factor of 5 on average, but partition coefficients were estimated within a factor of 2 with the proposed semi-empirical relationships.

Joo et al. (2004) measured partition coefficients of HDPE for benzene and trichloroethylene (TCE) using batch tests, and estimated diffusion coefficients from the batch test data using an analytical solution presented by Crank (1975). A linear isotherm was found suitable for aqueous organic compound solutions. Effects of other organic compounds, pH, ionic strength, and aging of HDPE geomembranes on the partition and diffusion coefficients were found to be insignificant; however, temperature was found to have significant effect on the diffusion coefficient.

Joo et al. (2005) developed a one-dimensional partition-diffusion model to predict the mass transport of organic compounds through geomembranes. Partition coefficients and diffusion coefficients were measured using a modified double-compartment apparatus (MDCA) test. Effects of aging and tension on HDPE geomembranes on the mass transport parameters were investigated

and compared to the mass transport parameters estimated from MDCA test with those from batch immersion test. For geomembranes which were 5-year aged and 8 % stretched, Partition coefficients increased by 5.1 ~ 57.6 % and diffusion coefficients increased by 10.2 ~ 86.0 %. Changes in partition and diffusion coefficients of non-stretched 5-year aged geomembranes were insignificant. However, changes in partition and diffusion coefficients of non-aged 8 % stretched geomembranes were similar to the change in those of 5-year aged 8 % stretched geomembranes. Therefore, external tension should be considered for landfill liner applications. Diffusion coefficients from MDCA tests were similar to those from batch tests; however, partition coefficients from MDCA tests were greater than those from batch tests by a factor of 2 on average due to organic compound loss and mass removal by frequent sampling.

The results suggested that tension affected the mass flux more than aging did, and MDCA tests should be used with batch tests to evaluate mass transport parameters prior to equilibrium.

Nefso and Burns (2007) measured sorption of 5 organic compounds to three polymeric geomembranes: HDPE, PP, and PVC. Concentrations of organic chemicals in the aqueous phase were measured using ^{14}C -radioactivity with a liquid scintillation counter. In general, PVC had the highest partition coefficients especially for benzene and trinitrotoluene, while HDPE had the lowest sorption coefficients. Thickness and texture of the HDPE geomembranes did not have a significant effect on the partition coefficients, as was found by Park and Nibras (1993). Aqueous solubility could be used as an

indicator of sorption to geomembranes except for trinitrotoluene with HDPE and PP. Due to inherent differences between the interaction of each compound and different polymers, the sorptive capacity of different geomembranes could not be predicted.

2.1.2 VOC Transport in Soil Liners

Edil et al. (1995) measured partition coefficients for compacted clay liners for 3 organic compounds using large-scale prototype experiments. Partition coefficients were also measured independently using batch sorption tests and estimated using empirical equations. They found that partition coefficients for VOCs in compacted clay liners can be estimated within a factor of 1.4 by simple batch tests. Similarly, partition coefficients estimated using empirical equations relating the partition coefficient to aqueous solubility and octanol-water partition coefficient and the organic carbon content of the clay were within a factor of 3 of the partition coefficient in prototype compacted clay liners.

Kim et al. (2001) measured partition coefficients and diffusion coefficients of 7 organic compounds on compacted clay using laboratory-scale column and tank tests. A one-dimensional finite-difference model was also developed to compute diffusion coefficients from the column and tank data. Partition coefficients measured by batch sorption tests were within a factor of 2 greater than those measured directly on samples collected on termination of the column and tank tests. According to a t-test with a confidence level of 95 %, partition coefficients were not significantly affected by the presence of other organic compounds. The apparent tortuosity of the organic compounds ranged

from 0.13 to 0.75 except for chlorobenzene (0.92) and 1,1,1-trichloroethane (2.92), where apparent tortuosity should be less than 1 and the typical apparent tortuosity of saturated soil ranges from 0.01 to 0.84 (Shackelford and Daniel 1990). The apparent tortuosity of the organic compounds decreased with the aqueous solubility.

Headley et al. (2001) measured partition coefficients of 3 organic compounds on 3 soils (organophilic clay, sand, and bentonite) and diffusion coefficients on 2 soils (natural clay and organophilic clay-sand-bentonite mixture) to determine contaminant transport through barriers for containment of petroleum products. The partition coefficient was found to be affected by organic matter content, soil-liquid ratio, and the hydrophobicity of the organic compound. Diffusion coefficients of 3 organic compounds were in similar magnitude in the organophilic soil mixture and natural clay, where diffusion coefficients in the organophilic soil mixture were lower than diffusion coefficients in natural clay with low organic matter content.

Kim et al. (2003) investigated the effect of soil-liquid ratio in batch tests on partition coefficients of organic compounds in landfill liner soils and the results were compared with partition coefficients measured from column tests. Batch tests were conducted to measure partition coefficients of 3 landfill liner soils using 6 organic compounds. As the soil-liquid ratio increased the partition coefficient decreased, and became stable after the soil-liquid ratio exceeded 100 g/L. According to a t-test at a 90 % confidence level, the partition coefficients measured from batch tests over 50 g/L soil-liquid ratio were statistically the same as those from the column tests. Below 50 g/L soil-liquid

ratio, the partition coefficients measured from batch tests were up to an order of magnitude greater than those measured from column tests. Therefore, using a sufficiently high soil-liquid ratio of at least 100 g/L in batch test was suggested to properly replicate conditions characteristic of compacted clay.

2.1.3 VOC Transport in Composite Liners

Foose et al. (1999) developed a numerical model and simulated diffusive transport of toluene through Subtitle D (composite liner) and composite geosynthetic clay liners (GCL). They found that the mass flux of toluene through a GCL composite liner is two orders of magnitude greater than the mass flux through a Subtitle D liner. The mass flux of the GCL composite liner was found to be higher because the GCL composite liner is thinner than the Subtitle D liner and the concentration gradient in the liner is greater than that of the Subtitle D liner. The performance of GCL composite liner could be improved by adding an additional sandy soil liner which reduces the mass flux by decreasing the concentration gradient across the liner. The thickness of the additional soil layer will vary with the diffusion coefficient, retardation factor, and porosity of the soil. They recommended a GCL composite liner with an additional soil layer beneath the GCL for an alternative liner when sufficient clay is not available.

Foose et al. (2001) compared toluene transport through three composite liners based on leakage rate, mass flux, and sorptive capacity. One composite liner consisted of a geomembrane and a GCL, and the other two a geomembrane and a soil layer (61 or 122 cm). A numerical model for

composite liners was used for simulations, which was developed by using MT3D (Zheng 1992) and MODFLOW (McDonald and Harbaugh 1988). GCL composite liner had the lowest leakage rate. However, composite liners having thicker soil barriers were found to have lower mass flux and greater sorptive capacity than the GCL composite liner. They found that the analysis must consider not only leakage rate but also diffusive transport not to mislead the conclusion.

Foose (2002) developed a transit-time design model to determine the design thickness for composite liners consisting of a geomembrane overlaying a compacted clay liner or GCL. Analytical solutions were used to develop graphical solution charts that can be used for composite liner design based on effluent concentration and mass flux. The method can be used for preliminary design of composite liners, evaluating experimental results, and verifying numerical models.

Sangam and Rowe (2001) investigated the role of HDPE geomembrane improving the effectiveness of a composite liner as a barrier of organic contaminants. They conducted laboratory diffusion tests on compacted clay (30 mm thick) and composite liner consisting of a 2.0 mm HDPE geomembrane overlaying the same compacted clay using methylene chloride and TCE for solutes. For both solutes, although the concentration in the influent reservoir decreased faster for the composite liner than for the compacted clay liner alone, and the concentration in the effluent reservoir increased at a much slower rate. The results suggested that the solute was removed from the influent reservoir and retained by sorption in the liner system, and the

composite liner has a larger sorptive capacity than the compacted clay liner alone. Presence of the HDPE geomembrane made the mass flux of methylene chloride reduce by a factor of 5, and the mass flux of TCE reduce to an undetectable level throughout the test period of 150 days. The solute transport was found to depend on the chemical partition coefficient and diffusion coefficient on the geomembrane, since they used the same clay for both liners. They recommended that the test results may be useful for modeling the implications of different design options in the preliminary design of landfill barrier systems.

2.2 Process of VOC Diffusion through Composite liner

Diffusion of VOCs can occur over the entire surface of the geomembrane of a composite liner. Thus, mass transport can be one-dimensional. Transport of VOCs through an intact composite liner can be described by a four-step process: (1) partitioning between the leachate and geomembrane, (2) diffusion through the geomembrane, (3) partitioning between the geomembrane and the soil pore water at the down gradient surface of the geomembrane, and (4) diffusion through the soil liner (Park and Nibras 1993; Park et al. 1996; Mueller et al. 1998; and Foose et al. 2001) (Fig. 2.2).

2.2.1 VOC Diffusion through Geomembrane

Transport of VOC through geomembrane is a molecule activated process called diffusion (Nefso and Burns 2007). Mass transport of organic

contaminant from an aqueous medium through geomembranes consists of three steps. (1) partition of the contaminant between the geomembrane surface and the leachate, (2) diffusion of the contaminant through the geomembrane, and (3) partition from the outer edge of the geomembrane into the receiving medium (Park and Nibras 1993; Park et al. 1996; Sangam and Rowe 2001; and Joo et al. 2004).

In the first step of mass transport process, the adsorption consists of the organic molecule removal from the fluid and its diffusion on or into the polymer which can be described as a distribution of organic compound between different phases (Sangam and Rowe 2001). The distribution of the organic compound between different phases may change with concentration, temperature, time and swelling of the matrix due to the interaction between the polymer and the chemical. Thus, sorption in a polymer depends on the activity of the organic compound within the polymer at equilibrium (Müller et al. 1998).

For the simplest case where the organic compound does not interact with the polymer or at relatively low concentrations as in landfill leachates, the partition coefficient between an organic compound dissolved in water and HDPE geomembrane, $K_{\text{HDPE-W}}$, is defined as follows:

$$K_{\text{HDPE-w}}' = \frac{C_g}{C_{w,\text{eq}}} \quad (2.1)$$

where C_g = equilibrium concentration of organic compound in HDPE geomembrane [M/ L³]; $C_{w,\text{eq}}$ = equilibrium concentration of organic compound in water [M/L³]; and $K_{\text{HDPE-w}}'$ = dimensionless HDPE-water partition coefficient of organic compound which is defined as

$$K'_{\text{HDPE-w}} = K_{\text{HDPE-w}} \times \rho_{\text{HDPE}} \quad (2.2)$$

where $K_{\text{HDPE-w}}$ = HDPE-water partition coefficient [L^3/M]; and ρ_{HDPE} = density of the geomembrane [M/L^3].

At the second step of mass transport, the sorbed organic compound at the surface will diffuse within the geomembrane. For a constant diffusion coefficient, the governing equation for the organic compound movement within a geomembrane is as follows (Crank 1975):

$$\frac{\partial C_g}{\partial t} = D_g \frac{\partial^2 C_g}{\partial z^2}, \quad -L_g < z < 0 \quad (2.3)$$

where C_g = concentration of the organic compound in the geomembrane [M/L^3]; t = elapsed time [T]; D_g = diffusion coefficient of the organic compound in the geomembrane [L^2/T]; z = distance along the direction of diffusion [L]; and L_g = thickness of the geomembrane [L]. The interface between the geomembrane and soil liner is at $z = 0$, where z is positive in the primary direction of contaminant transport.

The last step in the mass transport process is the organic compound desorption from the geomembrane to the outer solution or medium, which is an inverted process to the first step (Fig. 2.2).

2.2.2 VOC Diffusion at the Interface between Geomembrane and Soil Liner

At the interface between the geomembrane and soil liner, continuity of contaminant mass can be described using Fick's first law (Foose 2002; Foose et al. 2002):

$$J_d = -D_g \frac{\partial C_g}{\partial z} \Big|_{z=0^-} = -nD^* \frac{\partial C_s}{\partial z} \Big|_{z=0^+}, \quad z = 0 \quad (2.4)$$

where J_d = mass flux via diffusion [M/L^2T] and n = total porosity of the soil liner. Continuity of concentration at the interface between the geomembrane and soil liner is described by (Foose 2002):

$$\frac{C_g}{K'_{HDPE-W}} \Big|_{z=0^-} = C_s \Big|_{z=0^+}, \quad z = 0 \quad (2.5)$$

where K'_{HDPE-W} = dimensionless HDPE-water partition coefficient.

2.2.3 VOC Diffusion through Soil Liner

Mass transfer of VOC diffusion in pore water is caused by random molecular motions of the solutes (Edil et al. 1995). In a one-dimensional saturated porous medium, diffusion mass transport of a non-decaying solute can be expressed by (Hashimoto et al. 1964; Freeze and Cherry 1979):

$$\frac{\partial C_s}{\partial t} = \frac{D^*}{R} \frac{\partial^2 C_s}{\partial z^2}, \quad z > 0 \quad (2.6)$$

where C_s = concentration of the organic compound in the pore water of the soil liner [M/L^3]; z = distance along the direction of mass transport [L]; t = elapsed time [T]; R = retardation factor; and, D^* = the effective diffusion coefficient [L^2/T] which is defined as

$$D^* = D_0 \tau_a \quad (2.7)$$

where D_0 = molecular diffusion coefficient in free solution [L^2/T]; and τ_a = apparent tortuosity. The apparent tortuosity is not a directly measurable term, but rather serves as a correction factor to account for the tortuous flow path in

the pore space (Grathwohl 1998). Typically τ_a ranges between 0.01 and 0.5 for clay (Shackelford and Daniel 1990), but τ_a as low as 0.003 have been reported for montmorillonite clays (Satwasky et al. 1997). Kim et al. (2001) reported apparent tortuosities of 0.13 to 0.75 for a range of organic compounds in a clay liner.

The retardation factor is defined as

$$R = 1 + \left(\frac{\rho_d K_d}{n} \right) \quad (2.8)$$

where n = total porosity of the porous medium; ρ_d = dry density of the soil [M/L^3]; and K_d = soil-water partition coefficient [L^3/M].

The retardation factor of a solute shown is defined in terms of a soil-water partition coefficient. Partitioning of organic compounds between solids and solution can be quantified by the partition coefficient (K_d) as follows

$$K_d = \frac{C_s}{C_w} \quad (2.9)$$

where C_w = equilibrium concentration in solution [M/M], and C_s = concentration adsorbed to the solid [M/L^3].

Sorption is the key process in attenuation of contaminants in porous media, and the fate of VOCs highly depends on their sorptive behavior due to limited solubility, non-polarity and affinity for the solid phase (Edil et al. 1995).

Several variables can affect the values of experimentally determined partition and diffusion coefficient. Partition coefficients determined in batch tests have been found to depend on physical and mineralogical parameters of the solid, the concentration and characteristics of the contaminant, and the solid liquid ratio (Mackay et al. 1985; Voice and Weber 1985; and Kim et al.

2003). The sorption capacity is also found to strongly depend on the amount and type of organic matter present in the soil (Cohen et al. 1991; Headley et al. 2001).

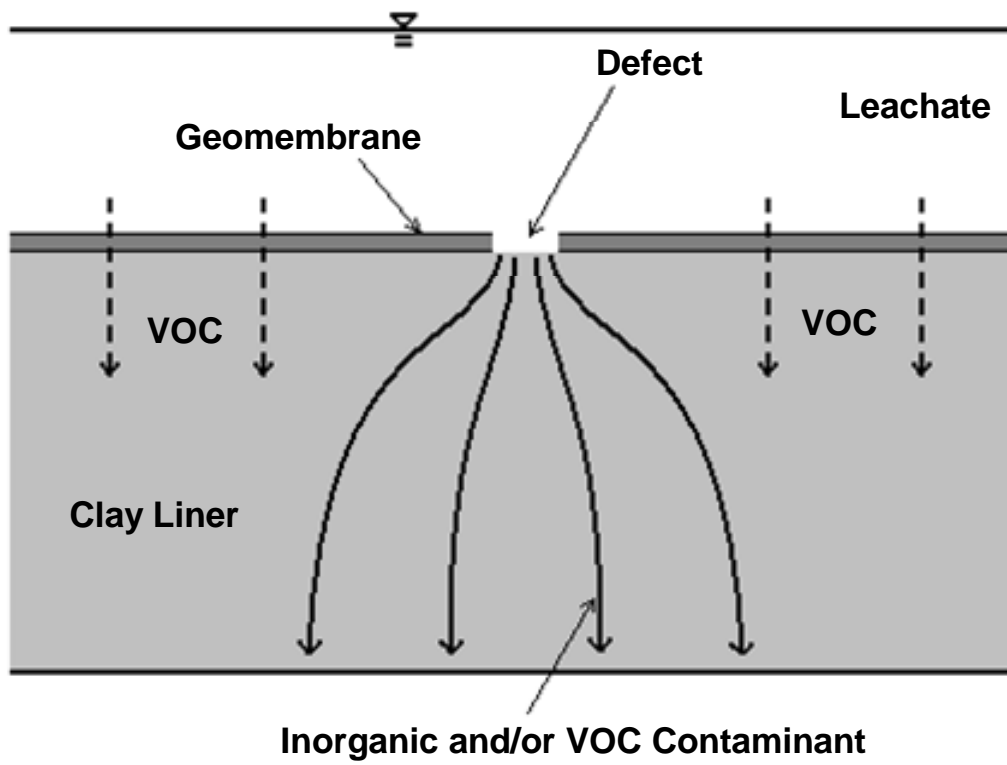
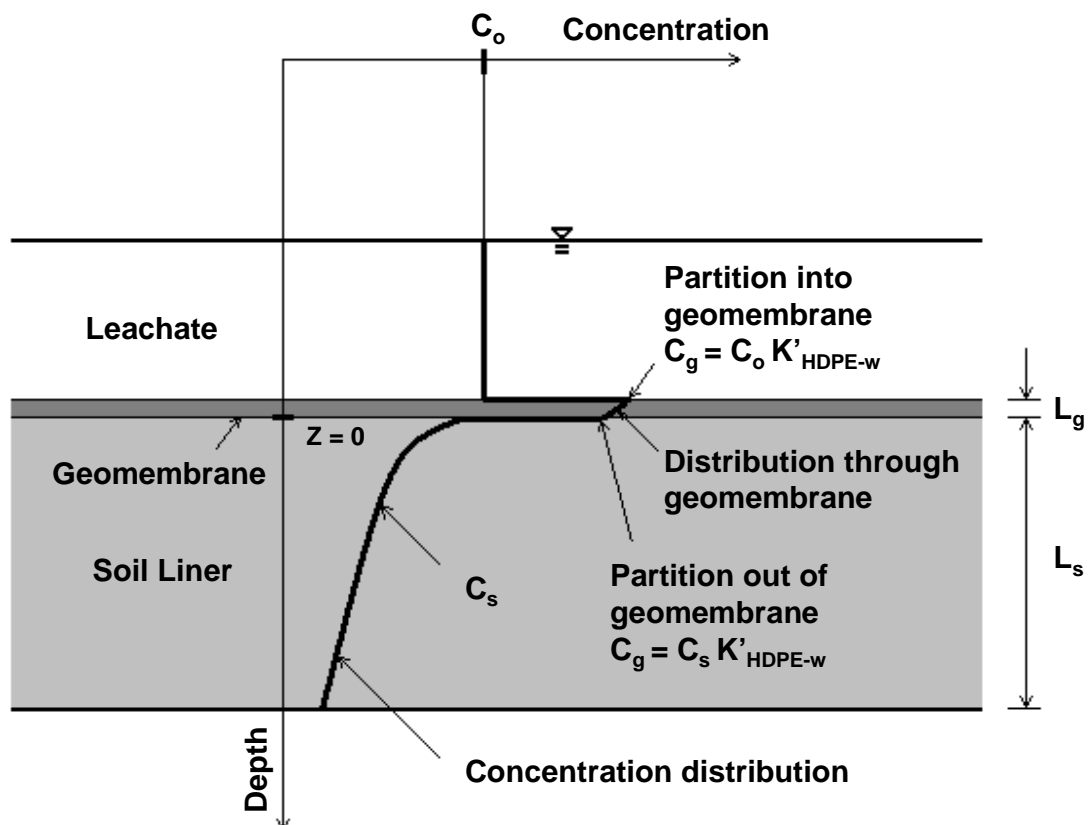


Fig. 2.1. Pathways of contaminant transport in composite liners



C_o = Leachate Concentration

C_g = VOC Concentration in Geomembrane

C_s = VOC Concentration in Soil Pore Water

K'_{HDPE-w} = Partition Coefficient of Geomembrane

L_g = Thickness of Geomembrane

L_s = Thickness of Soil Liner

Fig. 2.2. Schematic diagram of diffusion through composite liners

SECTION 3 MATERIALS AND METHODS

3.1 Materials

3.1.1 Liner Soil

The soil used in this study (Kamm clay) is used as a landfill liner material at Dane County Landfill No. 2 in Madison, Wisconsin. Kamm clay has a specific gravity of solids of 2.72, a liquid limit of 48, and a plasticity index of 27. The organic carbon content is 0.46% as determined by dry combustion using a Leco CNS-2000 analyzer (Nelson and Sommers 1996), and the organic matter content was 2.33% as determined by loss on ignition. The standard Proctor maximum dry unit weight (ASTM D-698) was 17.4 kN/m^3 at an optimum water content of 18.3. Reduced Proctor maximum dry unit weight is 16.7 kN/m^3 at an optimum water content of 20.0% (Table 3.1). The saturated hydraulic conductivity is $5.5 \times 10^{-9} \text{ cm/s}$ at optimum water content and maximum dry unit weight for standard Proctor compaction and $1.7 \times 10^{-8} \text{ cm/s}$ for reduced Proctor compaction.

3.1.2 Geomembrane

Black textured high-density polyethylene geomembrane was used for this study. The geomembrane is 1.5 mm thick and was obtained from Poly-flex[®], Inc. of Grand Prairie, Texas. Specimens of geomembrane were cut from a large HDPE geomembrane sheet, washed with distilled water, and placed in a desiccator for 48 h before use. Properties of the geomembrane are presented in Table 3.2.

3.1.3 Organic Compounds

Methylene chloride (MC), methyl tertiary butyl ether (MTBE), trichloroethylene (TCE), toluene (TOL), and chlorobenzene (CB) were selected for testing. These volatile organic compounds were selected among frequently detected VOCs in 34 engineered landfills in Wisconsin (Table A.1) (Klett 2006). Properties of selected compounds are listed in Table 3.3. The selected compounds represent a wide range of aqueous solubility and density which includes species lighter and heavier than water. The selection of these compounds were made after careful considerations of several factors. The selection process is described in Appendix A.

3.2 Methods

3.2.1 Preparation of VOC Solutions

VOC solutions for batch sorption tests and diffusion tests were prepared by filling a 1000 mL flask with distilled and deionized water. Sodium azide (0.05 g/L) was used to prevent microbial activity. The flask was completely filled to minimize loss of VOCs in the headspace. Once filled, the desired concentration of VOC was prepared based on weight-volume calculations. A 100 μ L gas tight syringe was used to introduce liquid VOCs into the water. When using multiple solutes, the compounds were injected in the order of decreasing density (trichloroethylene, methylene chloride, chlorobenzene, methyl tertiary butyl ether, and toluene); however, MTBE was injected prior to toluene because MTBE dissolves quickly into water because of its extremely high solubility. The flasks were immediately covered with a glass stopper and sealed with Teflon[®]

tape. The sealed flasks were placed on a magnetic stir plate for 24 h before use.

VOC solutions for column tests were prepared in Teflon[®] bags equipped with a stainless steel fitting. A magnetic stir bar was planted inside the bag, and the procedure was the same as preparing VOC solutions in flasks.

3.2.2 Kamm Clay Batch Sorption Test

Batch isotherm tests were determined to estimate the soil-water partition coefficients for the VOCs. Soil was crushed and ground past a No. 4 sieve (4.75 mm mesh opening), and then air dried and stored in a desiccator at room temperature before testing. Amber glass vials (40 mL) with screw caps and Teflon[®]-coated septa were used for the batch isotherm test.

Pretreated soil (25 g) was placed in a vial and 25 mL of solution was added to fill the vial (soil-liquid ratio ≈ 1). The head space was kept as small as possible to prevent volatilization. The soil-liquid ratio was as large as possible to minimize measurement noise and to simulate the condition in soil. Kim et al. (2003) found that if the soil-liquid ratio is not higher than a certain value (e.g., 100g/L) in a batch sorption test, the measured partition coefficient will not properly simulate the field situation, and retardation factors will be overestimated.

Solutions having concentrations of 20, 40, 60, 80, and 100 mg/L were used for the tests with individual VOCs and with a mixture of all five VOCs. The solutions were prepared in flasks (1 L) and stirred with magnetic stirrers for 24 h. The solutions were transferred to each vial using a pump with Teflon[®] tubes.

The solutions were extremely volatile; therefore, two control tubes were used for each concentration before and after transferring the solution from the flask to vials to determine the organic compound loss during transfer.

After adding the solution, the vials were placed in a rotator at 30 RPM for 7 d to ensure sorption equilibrium, where the time taken to attain sorption equilibrium was about 3 d. Subsequently, the vials were centrifuged at 2000 RPM for 15 m at room temperature ($23 \pm 2^\circ\text{C}$). The supernatant was transferred to auto-sampler vials using disposable glass pipettes. The samples were analyzed by the gas chromatograph.

3.2.3 HDPE Geomembrane Batch Sorption Test

Geomembrane samples were cut into strips (5×50 mm) for batch tests. Approximately 3.5 g of geomembrane (4 strips) was placed in an amber glass vial (40 mL) with screw cap and Teflon-coated septum, and 38 mL of solution was added to fill the vial (HDPE-liquid ratio ≈ 0.08). This solid-liquid ratio was approximately the same as the solid-liquid ratio in the upper reservoir of the bench-scale composite liner tests (described subsequently).

Solutions having concentrations of 20, 40, 60, 80, and 100 mg/L were used for the test with methylene chloride, MTBE, TCE, toluene, and chlorobenzene individually and all mixed. The solutions were made in flasks (1 L) and stirred with magnetic stirrers for 24 h. The solutions were transferred to each vial using a pump with Teflon tubes. After adding the solution, the vials were placed in a rotator for 7 d, where the equilibrium time was about 4 d. The

liquid was sampled and transferred to auto-sampler vials using disposable glass pipettes. The samples were analyzed by the gas chromatograph.

3.2.4 Geomembrane Diffusion Test

Geomembrane diffusion tests were conducted using a confined double-compartment apparatus to measure the diffusion coefficient of the geomembrane, following the method used by Park and Nibras (1996). The apparatus consists of two aluminum columns separated by a sheet of geomembrane (Fig. 3.1). Both compartments have the same inner diameter of 140 mm. The height of the top column is 171.6 mm and that of the bottom column is 50.4 mm to obtain and detect higher penetrant concentrations and achieve overall equilibrium faster. Nitrile gaskets were used.

The effluent compartment was initially filled with deionized (DI) water containing no organic chemicals. The geomembrane was placed on top of the water such that no air bubbles were trapped. The influent compartment was then placed on the geomembrane and clamped tightly with eight nuts and bolts evenly distributed along the flange. The influent compartment was filled with an aqueous VOC solution prepared using the method described in section 3.2.1. During the test, the solution in the effluent compartment was stirred continuously with a magnetic stirrer to obtain a well-mixed solution. Samples were taken periodically from sampling ports to monitor concentrations of the influent and effluent reservoir.

3.2.5 Compacted Clay Liner and Composite Liner Diffusion Test

In this study, the single reservoir diffusion test method described by Shackelford (1991) was adopted. A schematic of the compacted clay liner test set up is shown in Fig. 3.2, and the composite liner diffusion test set up in Fig. 3.3. All parts used were made of stainless steel or brass. All tubing and bags were made of Teflon[®].

Soil used for the clay liner was crushed and ground past a No. 4 sieve. The soil was hydrated manually to a water content of 22% which is 2% wet of optimum of reduced Proctor compaction. Hydration was achieved by spraying tap water onto the ground soil and then mixing the soil and water with a trowel. Water was sprayed in stages to prevent the soil from producing large clods. The hydrated soil was then wrapped in plastic bags and allowed to equilibrate for 24 h prior to compaction. Compaction was performed in 3 layers, and 40 blows were applied to each layer with a standard Proctor hammer.

After compaction, a glass fiber filter was placed on top of the soil for compacted clay liner test, and a geomembrane chamber for composite liner test. Lead beads were placed on top of the glass fiber filter to reduce swelling. The specimen was saturated by permeating until the hydraulic conductivity became steady and the ratio of outflow to inflow was between 0.75 and 1.25. A 0.05% sodium azide solution was used for permeation during the final 20 days to reduce microbial activity in the clay. Water in the upper reservoir was drained before introducing VOC solution.

For composite liner diffusion test, the glass fiber filter on top of the soil was replaced with a geomembrane chamber (Fig. 3.4). Geomembrane

chamber was built to eliminate advection and simulate pure diffusion. Smooth surface geomembrane was used for the lip and side wall of the chamber, and textured geomembrane was used for the bottom of the chamber. Geomembrane parts were cut precisely to fit tightly in the column and welded both inside and outside by a solder gun using the same geomembrane material as a welding rod. Geomembrane chambers were tested for leakage by filling the chamber with DI water. Leaking areas were re-welded until the chamber held water without leakage. Geomembrane chambers were washed with DI water and wiped before installation.

VOC solution was introduced into the upper reservoir via an influent bag. Once the upper reservoir was filled, the influent bag was disconnected. Influent reservoir was flushed periodically with fresh VOC solution to enhance the movement of VOC and shorten the running time of the test. The effluent bag was attended during sampling to equilibrate the pressure in the column. During the test, concentrations were monitored by samples taken from the influent reservoir and sampling ports in the soil.

Sampling ports were designed as shown in Fig. 3.5. Sampling ports were designed to extract samples with micro-syringes to minimize sampling effect. As shown in Fig. 3.5, glass fiber filter was slightly compacted inside the sampling port to filter soil particles, and 2 septa were used to eliminate leakage even while sampling. Sampling port functioning was verified by diffusing sodium chloride into saturated sandy soil and measuring the electrical conductivity of periodically taken samples. The electrical conductivity increased with time and became stable. Also no leakage was detected at the sampling

port. Thus this sampling port design was used for compacted clay liner and composite liner diffusion tests.

3.2.6 VOC Analytical Method

VOC concentrations were measured using a SHIMADZU GC-2010 gas chromatograph equipped with an auto sampler, a flame ionization detector (FID) and a Restek RTX-624 column (length 30 m, inner diameter 0.32 mm, and film thickness 1.80 μm). Temperatures of the injection port and the FID were set to 280 $^{\circ}\text{C}$. The sample split ratio was 3.0, and the injection volume was 0.5 μL . The column had an initial column temperature of 35 $^{\circ}\text{C}$ and hold time of 5 min. The column was then heated to 100 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ and held at 100 $^{\circ}\text{C}$ for 3 min. Next, the column was heated to 220 $^{\circ}\text{C}$ at a rate of 40 $^{\circ}\text{C}/\text{min}$ and held at 220 $^{\circ}\text{C}$. The total run time for each injection was 20 min.

For auto sampler vials, amber glass vials (2.0 mL) with screw caps and Teflon[®]-coated septa were used. For samples from the column tests, 50 μL glass vial inserts were used to reduce sampling volume.

3.2.7 Data Analysis

3.2.7.1 Batch Tests

HDPE-water partition coefficients were obtained by monitoring the concentration decrease of an organic compound in the aqueous phase, as shown as follows:

$$K_{\text{HDPE-w}} = \frac{(C_{w,i} - C_{w,eq}) \times V_w}{M_{\text{HDPE}} \times C_{w,eq}} \quad (3.1)$$

where $K_{\text{HDPE-w}}$ = HDPE-water partition coefficient of the organic compound [L^3/M]; $C_{w,i}$ = initial concentration of the organic compound in water [M/L^3]; $C_{w,eq}$ = equilibrium concentration of the organic compound in water [M/L^3]; V_w = volume of the water applied [L^3]; and M_{HDPE} = mass of the HDPE geomembrane [M].

The dimensionless HDPE-partition coefficient ($K'_{\text{HDPE-w}}$) can be defined as

$$K'_{\text{HDPE-w}} = K_{\text{HDPE-w}} \times \rho_{\text{HDPE}} \quad (3.2)$$

where ρ_{HDPE} = density of the geomembrane [M/L^3].

Soil-water partition coefficient (K_d) can be quantified as follows;

$$K_d = \frac{(C_{w,i} - C_{w,eq}) \times V_w}{M_s \times C_{w,eq}} \quad (3.3)$$

where; $C_{w,i}$ = initial concentration in solution [M/L^3]; $C_{w,eq}$ = equilibrium concentration in solution [M/L^3]; V_w = volume of the water applied [L^3]; and M_s = mass of soil.

For each data set, linear sorption isotherms were fit to the data to determine the partition coefficient of each compound, as in previous studies (Park and Nibras 1993; Edil et al. 1995; Kile et al. 1995; Headly et al. 2001; Sangam and Rowe 2001; Joo et al. 2004; Lake and Rowe 2005; and Nefso and Burns 2006). As linear sorption isotherm is used in this study, partition coefficients are assumed to be constant.

3.2.7.2 Column Tests

For geomembrane diffusion tests and compacted clay liner diffusion tests, experimental data from the reservoir and sampling ports will be plotted as concentration vs. time. Diffusion coefficients will be obtained by fitting the concentration vs. time curve with a theoretical curve using a one-dimensional advection diffusion transport equation in the form of a computer program, POLLUTE[®]. To best fit the concentration vs. time curve, diffusion coefficient will be changed systematically, and partition coefficients from the batch test will be used for input values. For compacted clay liners, total porosity is used rather than effective porosity since Kim et al. (1997) found that the two are nearly the same for the soil liner tested, and saturated condition is assumed which is reasonable because compacted soil liners should be constructed such that the degree of saturation is over 85 % (Benson et al. 1999).

Finally, VOC transport measured from bench-scale composite liner tests will be compared with predicted VOC transport by existing models (Foose et al. 2001; Rowe and Booker 2004) using individually measured transport parameters.

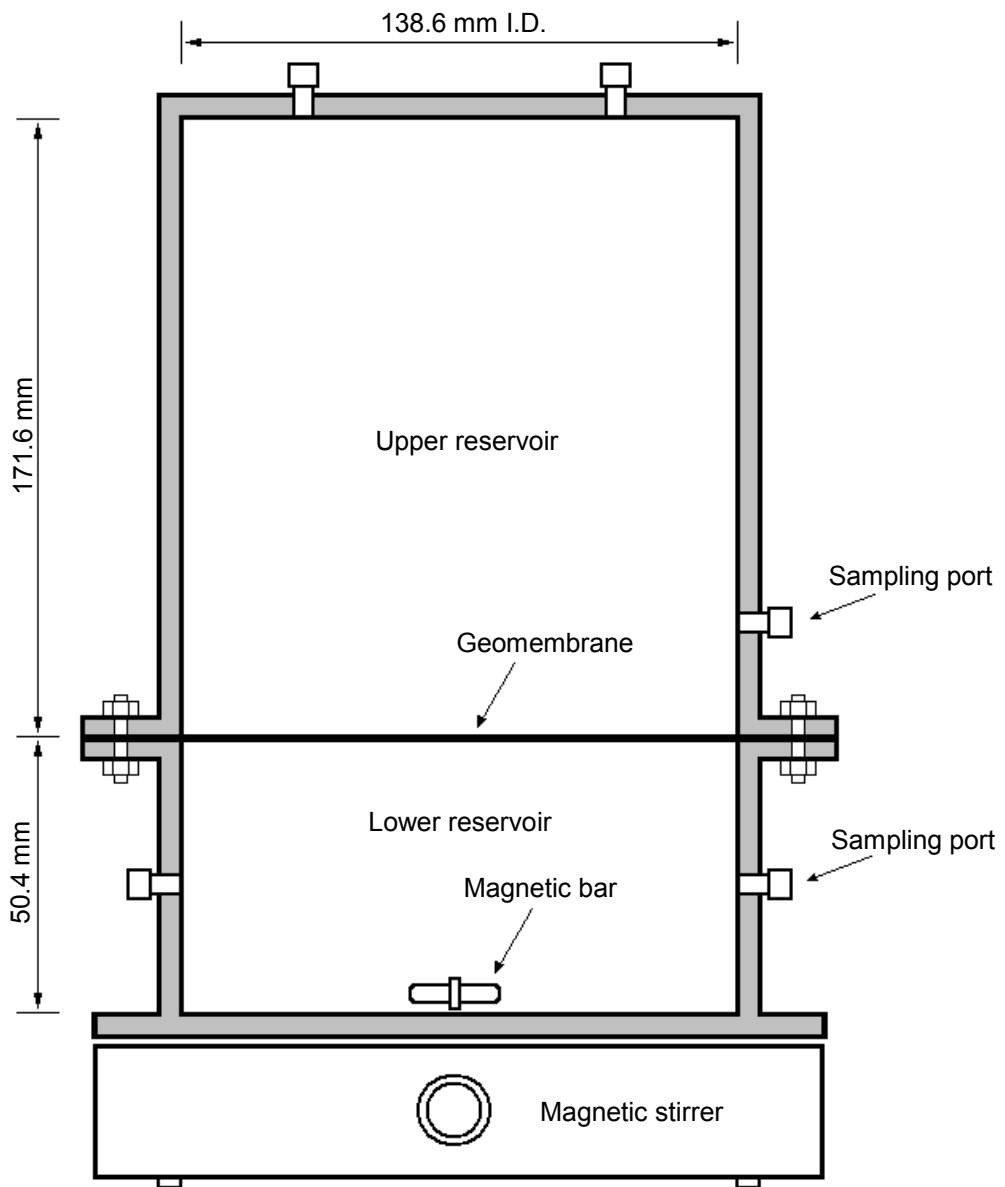


Fig. 3.1. Diffusion test set-up for geomembrane

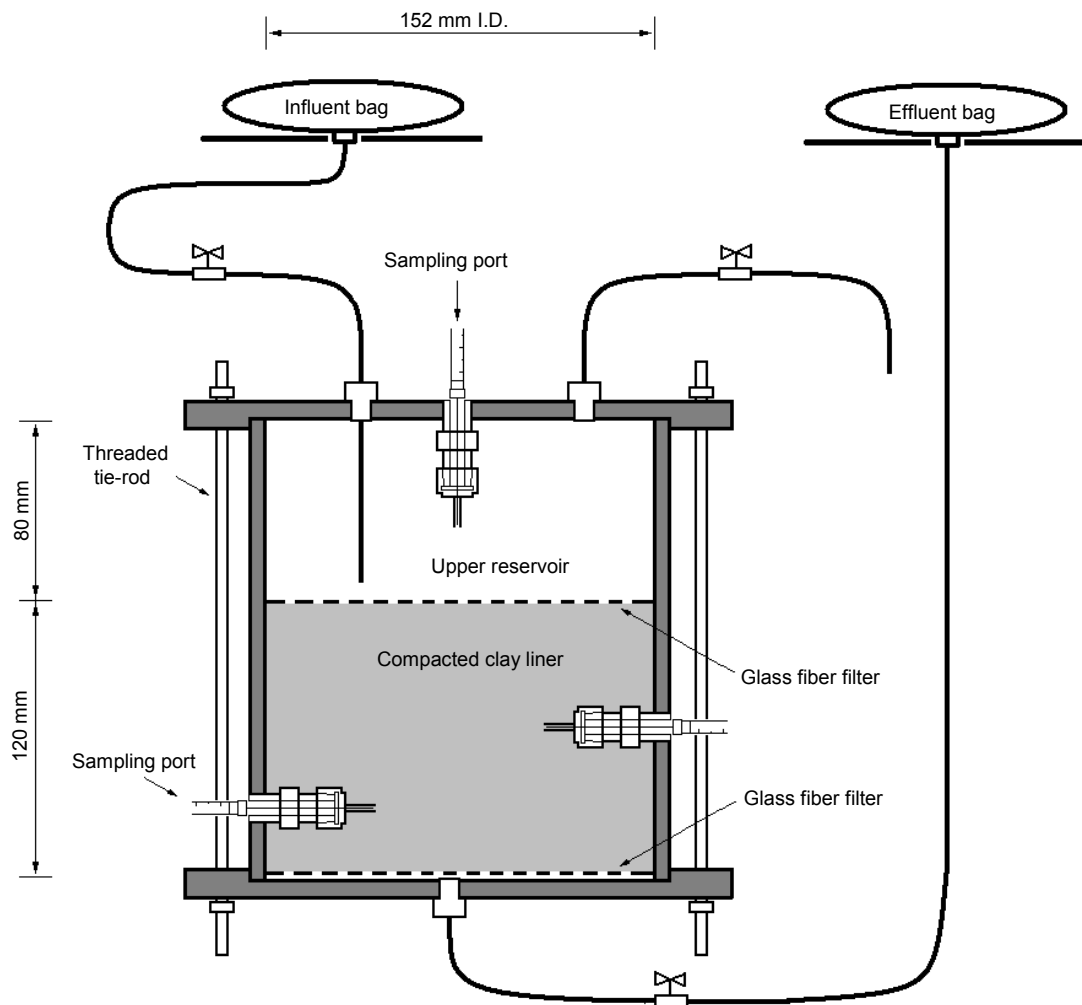


Fig. 3.2. Diffusion test set-up for compacted clay liner

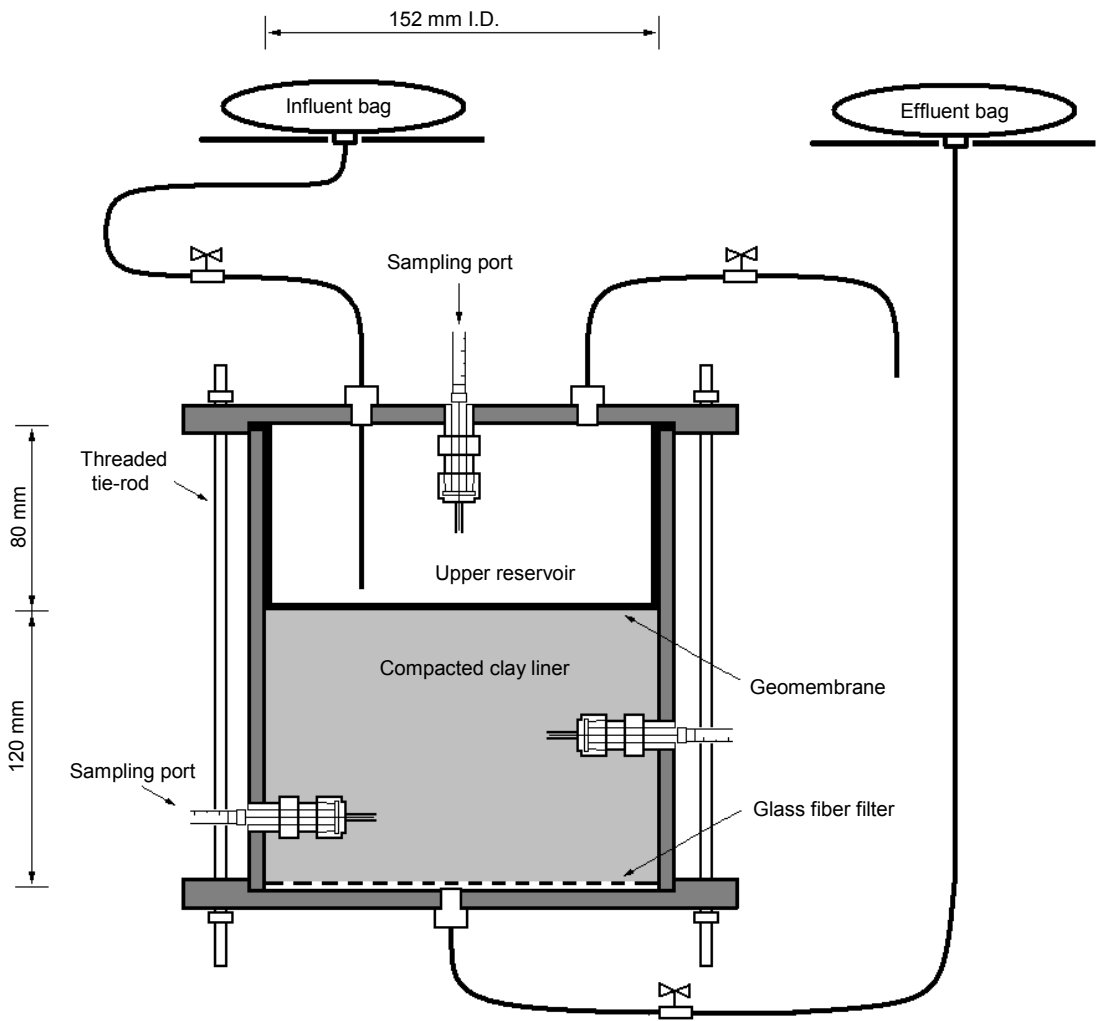


Fig. 3.3. Diffusion test set-up for composite liner



Fig. 3.4. Geomembrane chamber

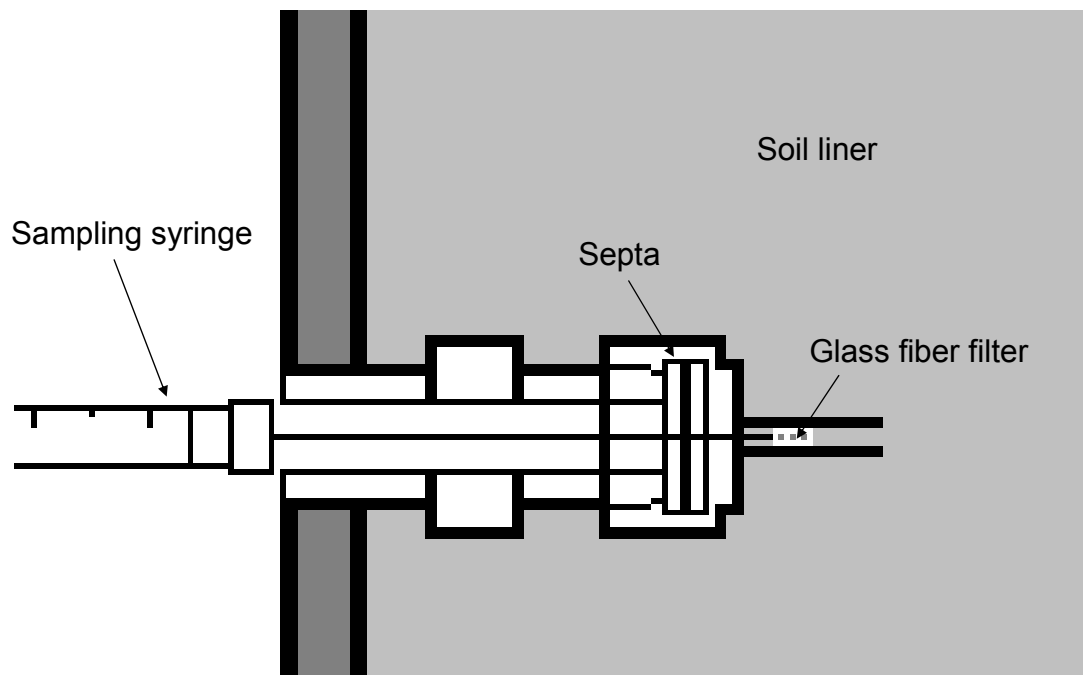


Fig. 3.5. Sampling port

Table 3.1. Characteristics of Kamm clay

Property	Kamm Clay
Specific gravity	2.72
Liquid limit	48
Plasticity index	27
Organic carbon content (%)	0.46
Organic matter content (%)	2.33
Standard Proctor maximum dry unit weight (kN/m ³)	17.4
Standard Proctor optimum water content (%)	18.3
Reduced Proctor maximum dry unit weight (kN/m ³)	16.7
Reduced Proctor optimum water content (%)	20.0

Table 3.2. Properties of the geomembrane

Property	Test method	Unit	Test result
<i>Thickness</i>	ASTM D 5994		
minimum average		microns	1,425
lowest individual of 8 of 10 readings		microns	1,350
lowest individual of 10 readings		microns	1,275
Asperity height	GRI GM12	microns	250
Sheet density	ASTM D 1505 / D 792	g/cc	0.940
<i>Tensile properties</i>	ASTM D 6693		
Yeild stress		kN/m	22
Break stress		kN/m	40
Yeild strain		%	12
Break strain		%	700
Tear resistance	ASTM D 1004	N	187
Puncture resistance	ASTM D 4833	N	400
Stress crack resistance	ASTM D 5397	hours	300
Carbon black content	ASTM D 1603	%	2-3
Carbon black distribution	ASTM D 5596		Cat. 1-2
Oxidative induction time	ASTM D 3895	minutes	100

Table 3.3. Properties of volatile organic compounds

Compound	MC	MTBE	TCE	TOL	CB
Chemical Formula	CH ₂ Cl ₂	CH ₃ -O- C(CH ₃) ₃	CHCl=C Cl ₂	C ₆ H ₅ - CH ₃	C ₆ H ₅ Cl
Molecular weight (g/mol) ¹	84.93	88.15	131.39	92.14	112.56
Density (g/cm ³) ^a	1.33	0.740	1.46	0.867	1.11
Molecular Diameter (nm) ^b	0.474	0.584	0.530	0.561	0.553
Melting Point (°C) ^a	-97.2	-108.6	-84.7	-94.95	-45.31
Boiling Point (°C) ^a	40.0	55.0	87.21	110.63	131.72
log K _{ow} ^c	1.31	0.94	2.42	2.69	2.78
K _{oc} ^d	47.9	12.3	100	37~178	126
Solubility (mg/L) ^a	20000	48000	1100	515	500

MC : Methylene chloride, MTBE : Methyl Tertiary Butyl Ether, TCE : Trichloroethylene,
TOL : Toluene, CB : Chlorobenzene

^a Verschueren, K. (1997)

^b Berens and Hopfenberg (1982)

^c octanol-water partition coefficient, Schwarzenbach et al. (2003)

^d U.S. EPA

SECTION 4 RESULTS

4.1 Batch Sorption Test

4.1.1 VOC Sorption on Geomembrane

VOC batch sorption tests were performed with geomembrane to measure the HDPE-water partition coefficients for methylene chloride, MTBE, TCE, toluene, and chlorobenzene. Fig. 4.1 to Fig. 4.5 shows sorption isotherms of single-solute and multi-solute condition. At low concentrations as in landfill leachates, where the organic compounds do not interact with the polymer, a linear sorption model is obeyed (Joo et al. 2004). Park and Nibras (1993) found that sorption and desorption of organic compounds into geomembrane are approximately linear for aqueous concentration less than 100 mg/L. HDPE-water partition coefficients were calculated by linear relationship between the equilibrium concentration in geomembrane (C_S) and the equilibrium concentration in water (C_W) by linear regression with zero intercept. The results were consistent with previous studies (Park and Nibras 1993; Sangam and Rowe 2001; Joo et al. 2004; and Nefso and Burns 2006).

Fig. 4.6 shows a logarithmic linear relationship between HDPE-water partition coefficients (K_{HDPE-w}) and octanol-water partition coefficients (K_{ow}), which was similar to the relationship found by Sangam and Rowe (2001). HDPE-water partition coefficient increases as octanol-water partition coefficient increases, which suggests HDPE-partition coefficient is related to properties of organic compounds (Joo et al. 2004). Thus, HDPE-partition coefficient can be estimated from the linear logarithmic relationship with octanol-water partition coefficient.

The presence of other organic compounds may affect the sorption of a given organic compound into HDPE geomembranes (Joo et al. 2004). Park and Nibras (1993) found that the decrease of HDPE-water partition coefficients and HDPE diffusion coefficients of individual organic compounds in a mixture could be predicted with their mole fractions, where the activities of each compound affect each other.

An analysis of covariance (ANCOVA) was conducted to assess whether the partition coefficients in the single-solute and multi-solute tests were significantly different from each other. The null hypothesis of ANCOVA is that the slopes of separate data sets are equal, thus the factor distinguishing the data sets is insignificant. P-values smaller than 0.05 result in rejection of null hypothesis with 95% of confidence. HDPE-water partition coefficients and p-values of ANCOVA tests are summarized in Table 4.1.

As shown in Table 4.1, HDPE-water partition coefficients of single-solute and multi-solute condition were statistically the same for methylene chloride, MTBE, and toluene. However, TCE and chlorobenzene had statistically different HDPE-water partition coefficient between single-solute and multi-solute conditions. HDPE-water partition coefficients in multi-solute conditions tends to decrease in compounds which have high HDPE-water partition coefficients, which suggests a possibility of competition or change in activity of compounds which have high affinity to HDPE geomembranes.

4.1.2 VOC Sorption on Kamm Clay

VOC batch sorption tests were conducted with Kamm clay to measure soil-water partition coefficients for methylene chloride, MTBE, TCE, toluene, and chlorobenzene. Fig. 4.7 to Fig. 4.11 shows sorption isotherms of single-solute and multi-solute condition. Linear isotherms were fit to the data to determine the soil-water partition coefficient, which is consistent with previous studies (Edil et al. 1995; Kile et al. 1995; Headly et al. 2001; Lake and Rowe 2005).

The presence of other organic compounds may affect the sorption of a given organic compound due to the potential competition or change in activity of the organic compound (Kim et al. 2001). ANCOVA was conducted to assess the effect of competition between each compound in multi-solute conditions. Soil-water partition coefficients and p-values of ANCOVA test are presented in Table 4.2. As is shown in Table 4.2, all p-values were larger than 0.05, which suggests soil-water partition coefficients of single-solute and multi-solute condition are not statistically different within the concentration ranges that were used. A similar conclusion was reached by Kim et al. (2001).

Soil-water partition coefficients measured in this study are lower than those of previous studies (Edil et al. 1994; Edil et al. 1995; and Kim et al. 2001) due to low organic carbon content of Kamm clay and high soil-liquid ratio used for the batch test. Kim et al. (2003) observed that soil-water partition coefficients of organic compounds measured by batch tests were significantly influenced by soil-liquid ratio, where soil-water partition coefficient strongly decreased as soil-liquid ratio increased.

Fig. 4.12 shows the relationship between soil-water partition coefficients (K_d) and octanol-water partition coefficients (K_{ow}). Soil-water partition coefficient increases as octanol-water partition coefficient increases, where only toluene was off the trend. According to a study by Kile et al. (1995), the formation conditions and origins of soil can cause differences in the sorption capacities of organic compounds between different soils. Thus, the soil-water partition coefficient for organic compounds estimated by soil organic matter or organic carbon content might be significantly different from measured values. This tendency was also observed by Kim et al. (2003), where significantly different soil-water partition coefficients were obtained from different soils which had similar organic contents.

Kile et al. (1995) also found that sorption of relatively nonpolar solutes to soil organic matter depends on soil organic matter composition and its polarity. Among the solutes used in this study, toluene is the most nonpolar compound where the sorption capacity can be relatively sensitive than polar compounds. Thus, the broad range of the organic carbon normalized soil-water partition coefficient (K_{oc}) of toluene also can be explained.

4.2 Diffusion Test

4.2.1 Compacted Clay Liner Diffusion Test

Diffusion tests on the compacted clay were performed to measure the effective diffusion coefficients for methylene chloride, MTBE, TCE, toluene, and chlorobenzene through the compacted clay. To determine the effective diffusion coefficient, POLLUTE (Rowe et al. 2004) was used to fit the data. POLLUTE is

a software package for analyzing contaminant transport which is widely used in landfill design and remediation.

A one-dimensional model was used to simulate the column test on a 120 mm-thick compacted clay specimen. The dry density of the clay was set at 1.7 g/cm³ and the porosity of the clay liner was set at 0.375 (Kamm clay with reduced Proctor compaction). Batch sorption test results were used for the soil-water partition coefficient of each compound (Table 4.2). The top boundary was set as constant concentration boundary (100 ppm), and the bottom boundary was set as no flux boundary. The effective diffusion coefficient was changed to fit the model prediction of the concentration-time data as measured at one of the sampling ports (see Section 3.2.5).

Measured concentrations at sampling port 1 and a fitted curve of each VOC are shown in Fig. 4.13 to Fig. 4.17. Clay liner 1 and 2 are replicates. Concentrations at sampling port 2 were too low to be analyzed.

The effective diffusion coefficient and the apparent tortuosity in the compacted clay liner of each compound are summarized in Table 4.3. Effective diffusion coefficients ranged from 1.1×10^{-6} cm²/s to 2.0×10^{-6} cm²/s which was within a factor of 2. Apparent tortuosities ranged from 0.11 to 0.14 which were close to the lower end of apparent tortuosity measured by Kim et al. (2001) (0.13 ~ 0.75).

According to breakthrough concentrations, methylene chloride had the highest mobility and chlorobenzene had the lowest mobility. Although TCE had greater effective diffusion coefficient than MTBE, MTBE broke through faster than TCE because of its low soil-water partition coefficient. Therefore, not only

the effective diffusion coefficient but also the partition coefficient affects the mobility of the compound.

4.2.2 Composite Liner Diffusion Test

Composite liner diffusion tests were conducted to compare the results with the predicted VOC transport simulation using POLLUTE. Measured concentrations at sampling port 1 are shown in Fig. 4.18 to Fig. 4.22.

For the simulation using POLLUTE, a 1.5 mm geomembrane was added on top of the compacted clay liner model (see Section 4.2.1). Darcy's velocity and outflow was set at 0, and all the other input parameters were the same as the compacted clay liner model. Since only the diffusion coefficients in the geomembrane were unknown, the diffusion coefficients were manually adjusted to produce best fit curves (Fig. 4.18 to Fig. 4.22). Also diffusion coefficients in the geomembrane were estimated using empirical relationships suggested by Joo et al. (2005) and Sangam and Rowe (2001).

Joo et al. (2005) proposed an empirical relationship relating the molecular diameter to the diffusion coefficient as follows:

$$\log D_g = -5.368 - 5.534d_m$$

where D_g = diffusion coefficient of the organic compound in the geomembrane (cm^2/s) and d_m = molecular diameter the organic compound (nm).

Simulations using diffusion coefficients in the geomembrane estimated by Joo et al. (2005) and Sangam and Rowe (2001) are plotted with the breakthrough curves (Fig. 4.18 to Fig. 4.22). Simulations using the maximum

and minimum published diffusion coefficients in the geomembrane were also plotted for methylene chloride, TCE and toluene.

For TCE and toluene, the simulations using the maximum and minimum published diffusion coefficients were in the data range, and both estimation methods predicted the breakthrough concentration within 6 % comparing to the POLLUTE best fit curve. Both estimation methods also predicted chlorobenzene breakthrough concentration within 10 % comparing to the POLLUTE best fit curve.

For MTBE, the simulation using the method of Joo et al. (2005) underestimated the breakthrough concentration by a factor of 4 and the simulation using the method of Sangam and Rowe (2001) overestimated the breakthrough concentration by 40 % comparing to the POLLUTE best fit curve.

For methylene chloride, the simulation using Joo et al. (2005) underestimated the breakthrough concentration by 27 % and the simulation using Sangam and Rowe (2001) method overestimated the breakthrough concentration within 9 % comparing to the POLLUTE best fit curve. POLLUTE best fit curve was close to the simulation using the maximum diffusion coefficient in the geomembrane, and the simulation using the minimum diffusion coefficient in the geomembrane was out of the data range and underestimated the breakthrough concentration by a factor of 3.5.

Simulations using the method of Sangam and Rowe (2001) estimated the breakthrough concentration within 10 % comparing to the POLLUTE best fit curve for all the compounds except for MTBE. However, simulations using both

estimation methods were all in the data range except for the method of Joo et al. (2005) with MTBE.

Measured diffusion coefficients from previous studies and the diffusion coefficients obtained by POLLUTE best fit curves are summarized in Fig. 4.23 along with the empirical relationship (Park and Nibras 1993; Park et al. 1996; Sangam and Rowe 2001; Joo et al. 2004; and Joo et al. 2005). The empirical relationship is within the range of published values. The diffusion coefficients of TCE and toluene obtained by POLLUTE best fit curves are also within the range of published values, and that of methylene chloride is close to the highest published value. The estimated diffusion coefficients of TCE, toluene and chlorobenzene are within a factor of 2 comparing to the diffusion coefficients obtained by POLLUTE best fit curves. However, the diffusion coefficient of MTBE is underestimated by a factor of 4, and the diffusion coefficient of methylene chloride is underestimated by a factor of 2.5 (Table 4.4).

Sangam and Rowe (2001) proposed an empirical relationship relating the octanol-water partition coefficient to the diffusion coefficient as follows:

$$\log D_g = -8.3624 + 0.9205 \log K_{ow} - 0.3424 (\log K_{ow})^2$$

where, D_g = diffusion coefficient of the organic compound in the geomembrane (cm^2/s) and K_{ow} = octanol-water partition coefficient. The empirical relationship is plotted in Fig. 4.24 with published values and diffusion coefficients obtained from POLLUTE best fit curves. The empirical relationship is in the range of published values, and the empirical relationship estimated the diffusion

coefficients within a factor of 2 compared to the diffusion coefficients obtained from the POLLUTE best fit curves for all five compounds (Table 4.4).

4.2.3 Sensitivity Analysis

Despite having all the transport properties measured, measurement error will exist in those measured properties, because volatile organic compounds are very hard to control in experiments. Therefore, the measurement error might mislead the contaminant transport simulation for landfill design.

A sensitivity analysis was performed to assess the effects of diffusion coefficients, partition coefficients, hydraulic conductivity, and porosity on model simulations. Toluene was selected for the sensitivity analysis because of the availability of data from previous studies.

A one-dimensional model was used to simulate the field condition of a composite liner system with a 2 mm thick geomembrane, 1.22 m (4 ft) clay liner, 3.05 m (10 ft) attenuation layer, and a 1 m thick aquifer. An intact composite liner with no defects in the geomembrane was assumed. The dry density of the clay liner and the attenuation layer was set at 1.7 g/cm^3 . The porosity of the attenuation layer was set at 0.29 and the porosity of the aquifer was set at 0.4. The top boundary was set as constant concentration boundary (1 mg/L), and the bottom boundary was set as no flux boundary. The hydraulic head of the leachate above the geomembrane was set at 0.3 m. Elapsed time was set at 30 years (2 times the maximum projected operating life of landfill in Wisconsin according to NR 504.05) and relative concentration (concentration at the bottom of the liner over source concentration, C/C_0) was used for the results.

This sensitivity analysis is intended to assess the measurement error on composite liner model simulations. The average coefficient of variation from previous studies was used to estimate a reasonable measurement error range for each parameter. Published measured data used in sensitivity analysis are summarized in Table 4.5.

The average coefficient of variation for the diffusion coefficient in the geomembrane was 23.4 % (Park and Nibras 1993; Park et al. 1996; Joo et al. 2004; and Joo et al. 2005), the HDPE-water partition coefficient 14.1 % (Park and Nibras 1993; Park et al. 1996; Joo et al. 2004; and Joo et al. 2005), hydraulic conductivity of the clay liner 23.9 % (Kim et al. 1997), effective diffusion coefficient of the clay liner (tortuosity) 47.0 %, soil-water partition coefficient of the clay 57.6 % (Edil et al. 1995; Kim et al. 2001; and Kim et al. 2003), porosity of the clay liner 2.94 % (Kim et al. 1997). The average case was set to the parameters used for the POLLUTE best fit line and the maximum and minimum of each parameter are summarized in Table 4.6.

Fig. 4.25 shows the result of the composite liner sensitivity analysis. Differences in relative concentration due to measurement error of the diffusion coefficient in the geomembrane, HDPE-water partition coefficient, and porosity of the clay liner were less than 7 % and the hydraulic conductivity had no effect on relative concentration. Measurement error of the soil-water partition coefficient of the clay liner can change the relative concentration by a factor of 3, and that of the effective diffusion coefficient of the clay liner can change the relative concentration an order of magnitude higher and 2 orders of magnitude lower. Therefore, the accuracy of the soil-water partition coefficient and the

effective diffusion coefficient of the clay liner is critical for an accurate contaminant transport simulation through composite liners. As shown in Fig. 4.26 for effective diffusion coefficient and Fig. 4.27 for soil-water partition coefficient, the difference of relative concentration due to measurement error is larger in the early stage and decreases with time.

Additional sensitivity analyses were performed to assess the effect of each parameter varying within a typical range on model simulations. Range of each parameter was estimated by widely accepted published values.

According to the previous studies, diffusion coefficient of toluene through the geomembrane varied from 2.3×10^{-9} to 5.5×10^{-9} cm²/s, HDPE-water partition coefficient from 57 to 151 (Park and Nibras 1993; Park et al. 1996; Sangam and Rowe 2001; and Joo et al. 2004, 2005), apparent tortuosity for organic compounds in compacted clay from 0.13 to 0.75 (Kim et al. 2001), and the average of each parameter was selected by the median between the maximum and minimum. Porosity of compacted clay range from 0.17 to 0.35 with an average of 0.29 (Kim et al. 1997). From Benson et al. (1999), hydraulic conductivity of compacted clay liners vary from 2.0×10^{-9} to 8.0×10^{-7} cm/s and the average is 4.4×10^{-8} cm/s. However, 1.0×10^{-7} cm/s was selected for the maximum hydraulic conductivity because of the regulation (NR 504.06). The range of soil-water partition coefficient of the clay liner was determined by multiplying the average organic carbon normalized soil-water partition coefficient (K_{oc}) to the weight fraction of organic carbon (f_{oc}). The organic carbon fraction varied between 0.1 to 6 % and the average was 1.9 % in liner

clays (Kim et al. 2001). Parameters used in this analysis are summarized in Table 4.7

Fig. 4.28 shows the result of composite liner sensitivity analysis. Changes in relative concentration due to the diffusion coefficient in the geomembrane and HDPE-water partition coefficient were less than 12 % and the hydraulic conductivity had no effect on relative concentration. The relative concentration varied more than 13 orders of magnitude due to the soil-water partition coefficient, 11 orders of magnitude due to the effective diffusion coefficient, and 4 orders of magnitude due to porosity of the clay liner. The parameters related to geomembrane have little effect on breakthrough concentrations and the transport parameters related to the clay liner dominantly affect the breakthrough concentration. Since this is a pure diffusion simulation, hydraulic conductivity of the clay liner did not affect the breakthrough concentration. The results were consistent with Foose (2002), who found that the concentration at the bottom of the composite liner is sensitive to the properties of the clay liner and has little to do with the transport properties of the geomembrane.

Fig. 4.29 shows the result of compacted clay liner sensitivity analysis. The relative concentration varied more than 13 orders of magnitude due to the soil-water partition coefficient, 6 orders of magnitude due to hydraulic conductivity, 5 orders of magnitude due to the effective diffusion coefficient, and 3 orders of magnitude due to porosity of the clay liner. The soil-water partition coefficient affected the breakthrough concentration the most. However, hydraulic conductivity, effective diffusion coefficient, and porosity can significantly change the breakthrough concentration.

The results show that predicting the breakthrough concentration is difficult only using widely accepted transport parameters instead of actually measuring the transport properties of liner components. Although all the properties are known, measurement error should be considered in predicting contaminant transport and landfill design.

4.2.4 Field Data Analysis

Field data was adopted from Klett (2006) to evaluate the contaminant model simulations using widely accepted published transport parameters. Fig. 4.30 shows relative concentrations of toluene from clay and composite lined landfills with contaminant transport simulations. The same model and properties used in sensitivity analysis was used (Table 4.7). The average cases combine all the average parameters and the conservative cases combine the maximum diffusion coefficient in the geomembrane, HDPE-water partition coefficient, effective diffusion coefficient in the clay, hydraulic conductivity, and porosity of the clay with the minimum soil-water partition coefficient.

Both of the average cases of the composite liner and the clay liner under-predicted the relative concentration by more than 6 orders of magnitude. Using the minimum soil-water partition coefficient, the most affecting parameter, increased the relative concentration close to the conservative case but still under-predicted some data points.

Even the conservative cases for the composite liner and clay liner did not compose the upper boundary and some data points were still above the conservative case curve. When soil-water partition coefficient was set at 0 with

the conservative case, the relative concentration curve was able to compose the upper boundary except for few data points where some of these relative concentrations were even larger than 1.

According to the simulations in Fig. 4.30, composite liner is more effective than clay liners in limiting organic contaminant transport.

The simulation results show that predicting relative concentrations with widely accepted transport parameters is difficult because relative concentration is very sensitive to the properties of the clay liner. Thus, the most conservative case must be considered in landfill designs.

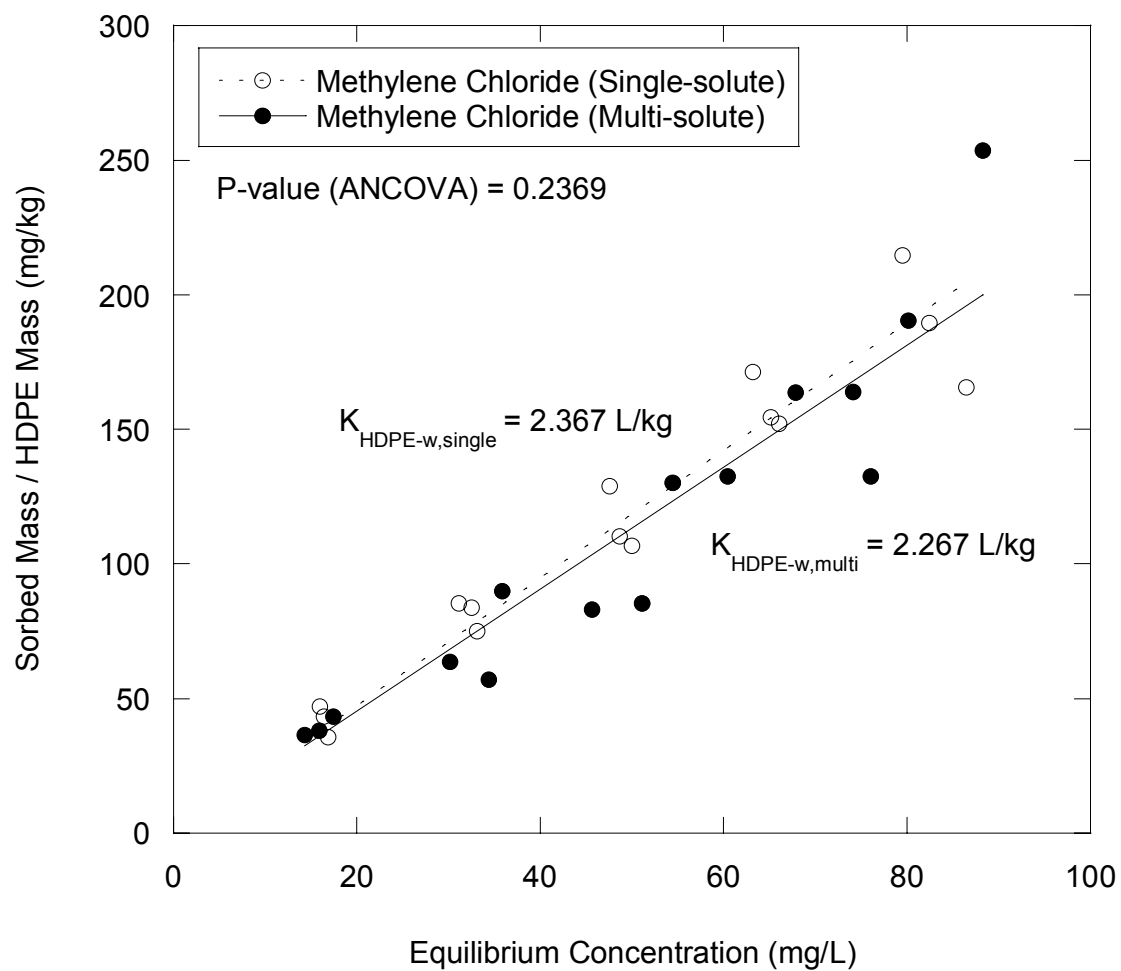


Fig. 4.1. Sorption isotherm of methylene chloride to HDPE geomembrane

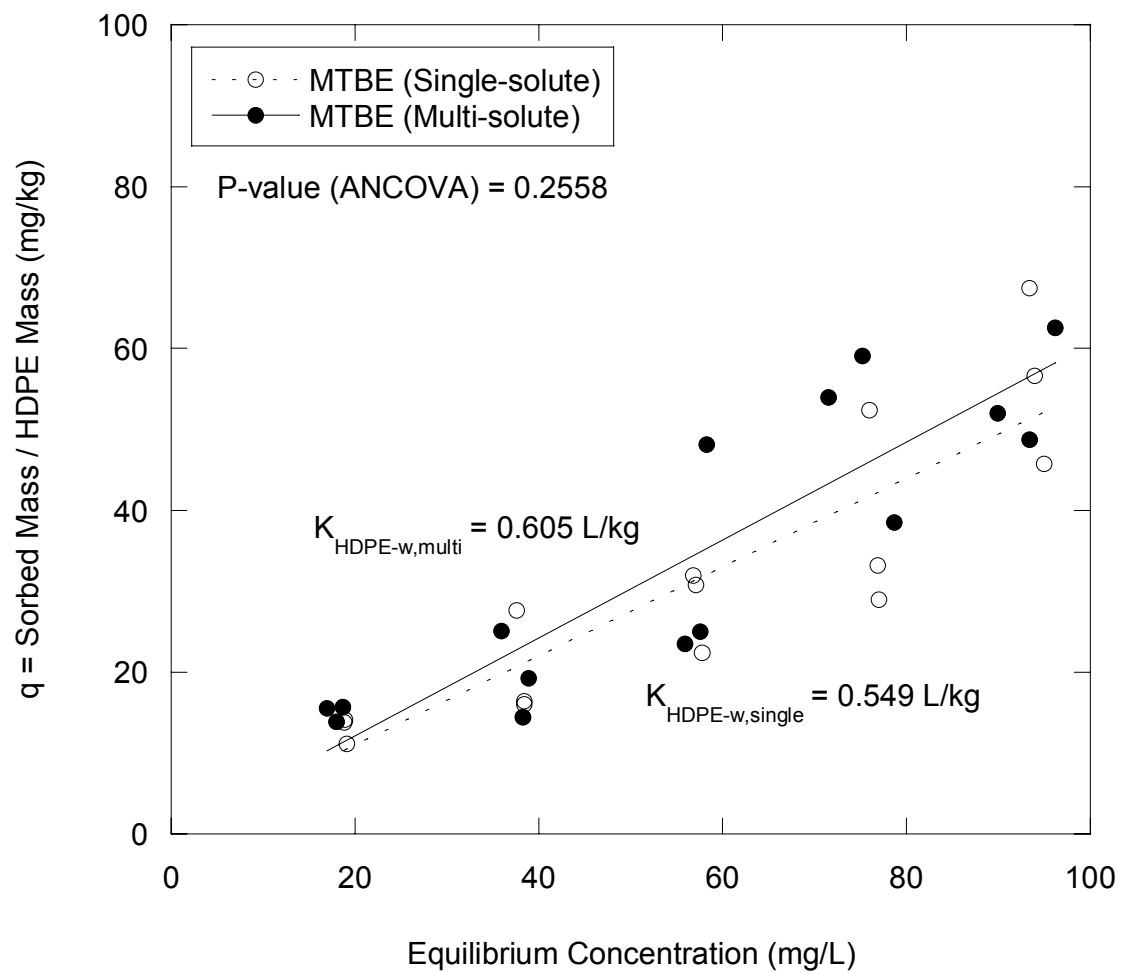


Fig. 4.2. Sorption isotherm of MTBE to HDPE geomembrane

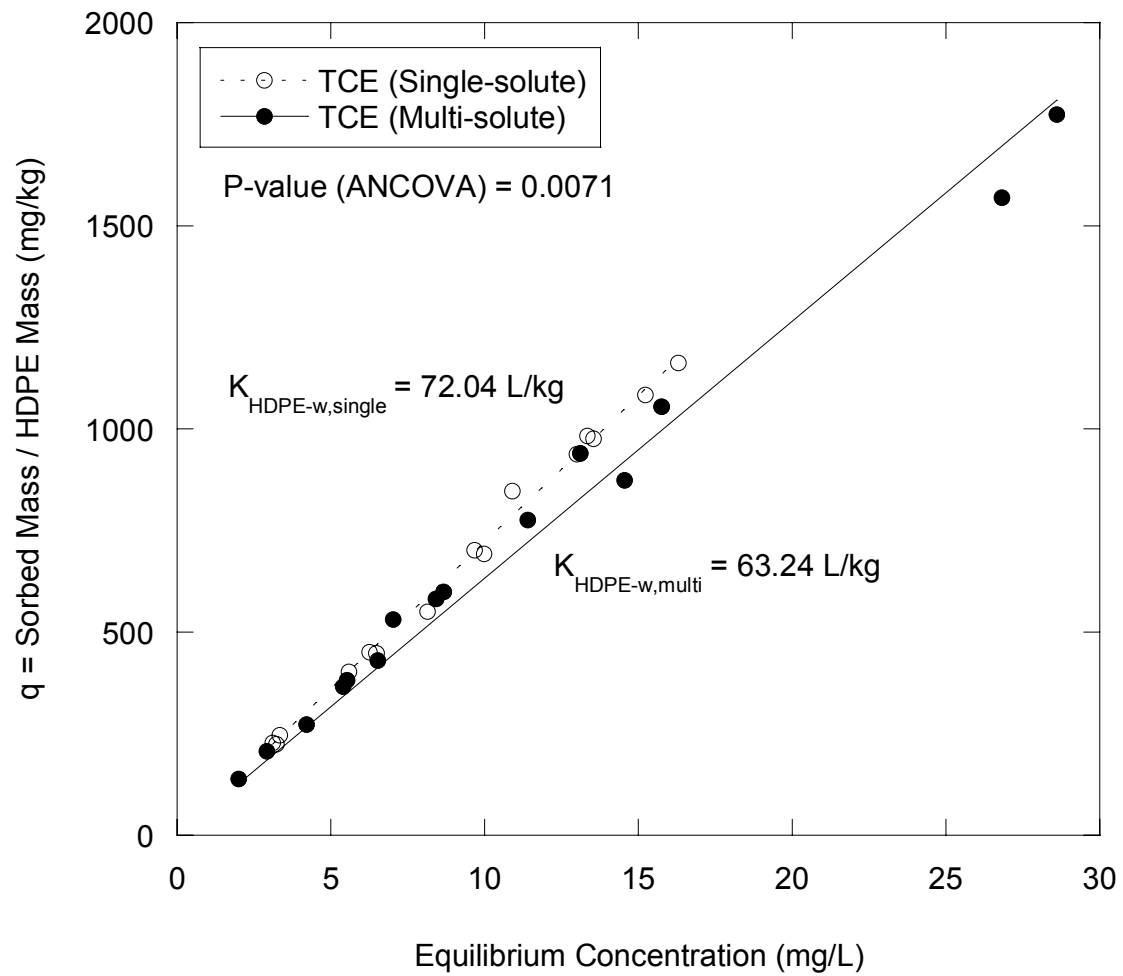


Fig. 4.3. Sorption isotherm of TCE to HDPE geomembrane

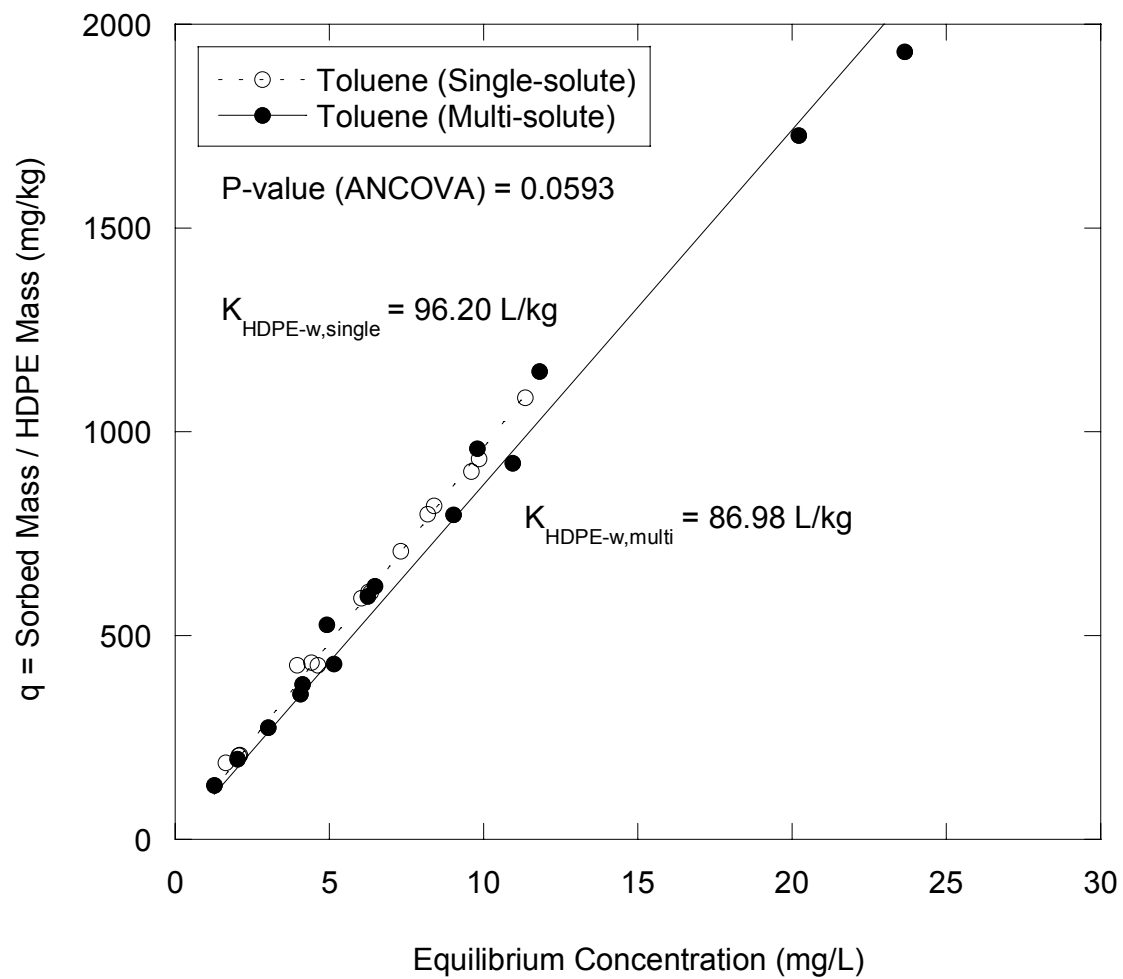


Fig. 4.4. Sorption isotherm of toluene to HDPE geomembrane

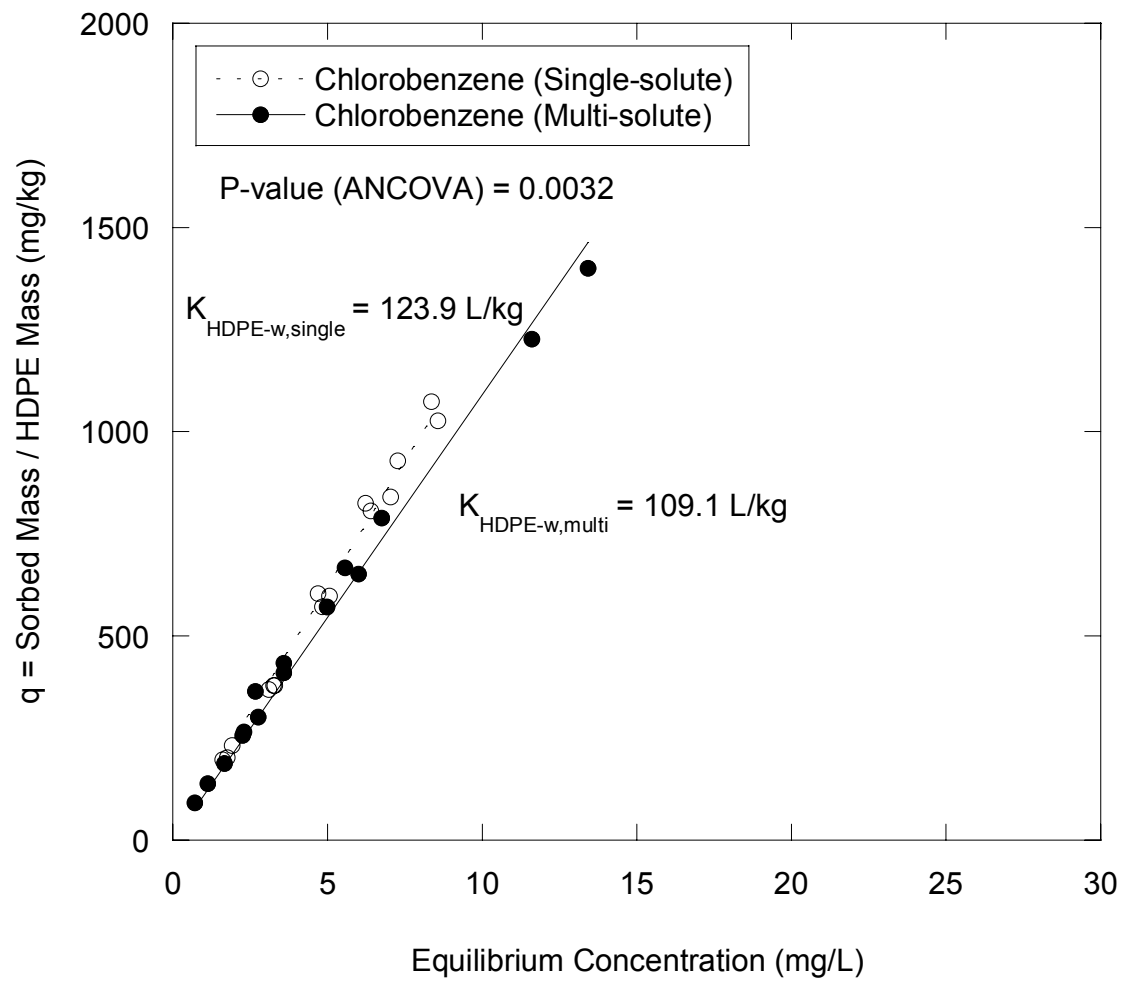


Fig. 4.5. Sorption isotherm of chlorobenzene to HDPE geomembrane

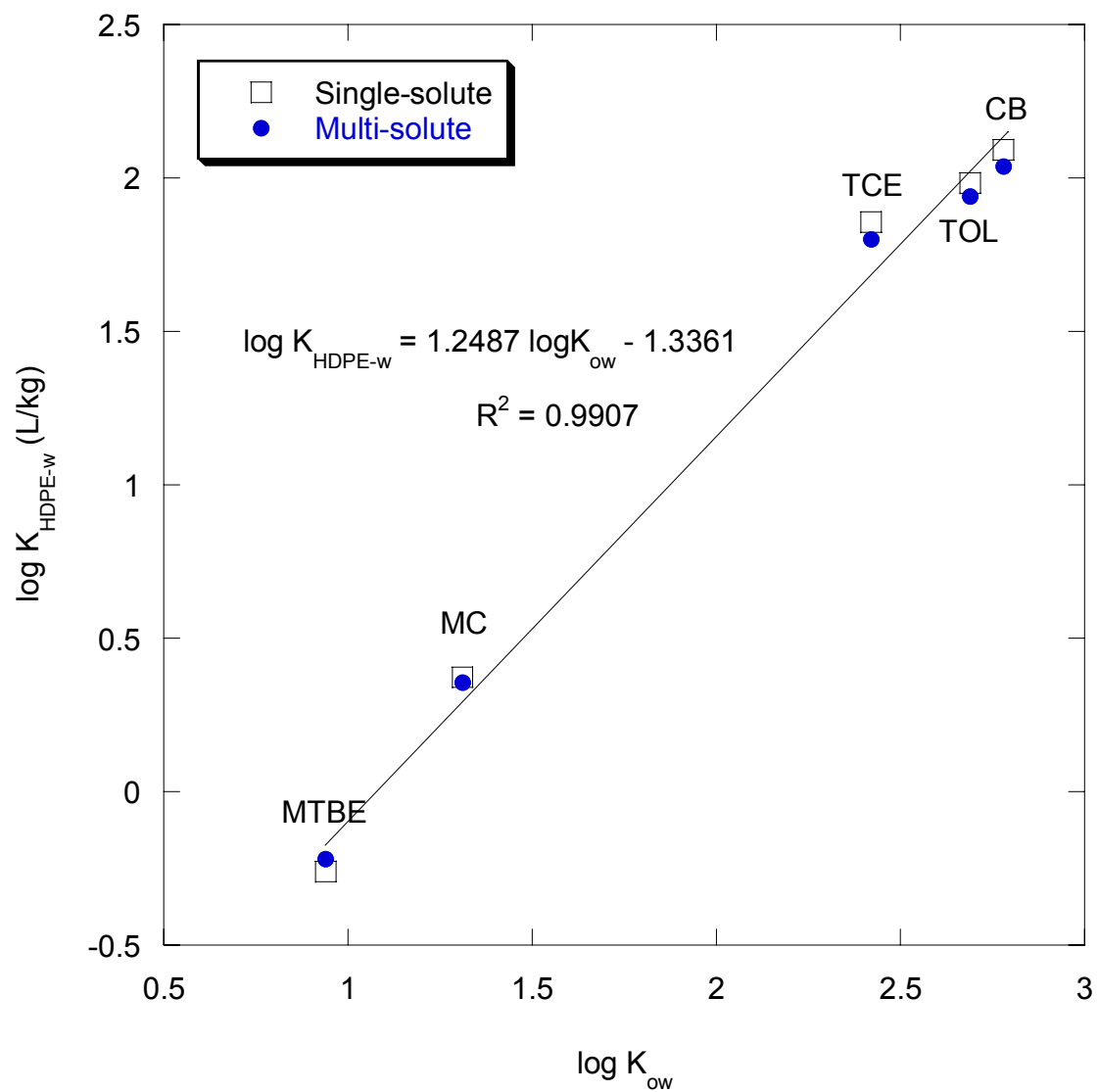


Fig. 4.6. Relationship between HDPE-water partition coefficients (K_{HDPE-w}) and octanol-water partition coefficients (K_{ow}) of VOCs tested

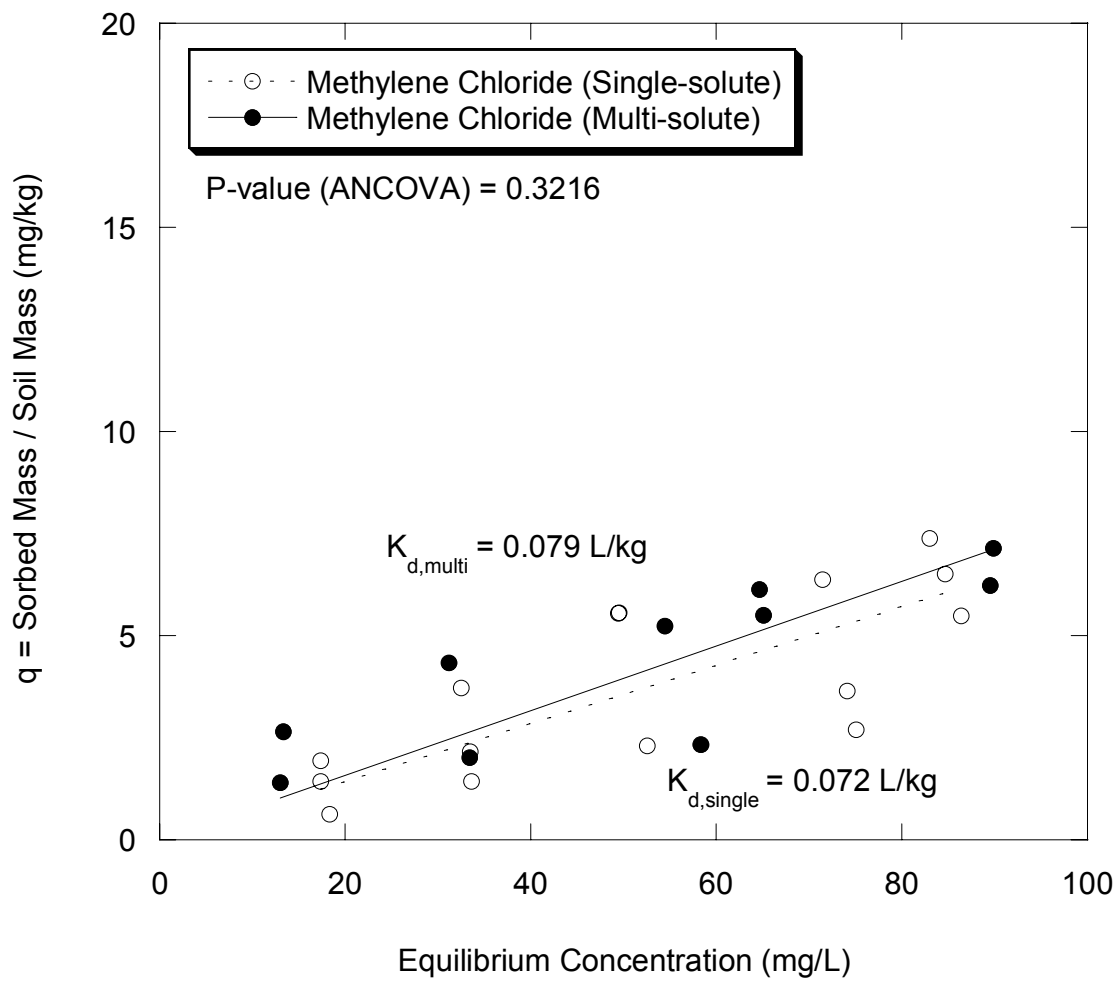


Fig. 4.7. Sorption isotherm of methylene chloride to Kamm clay

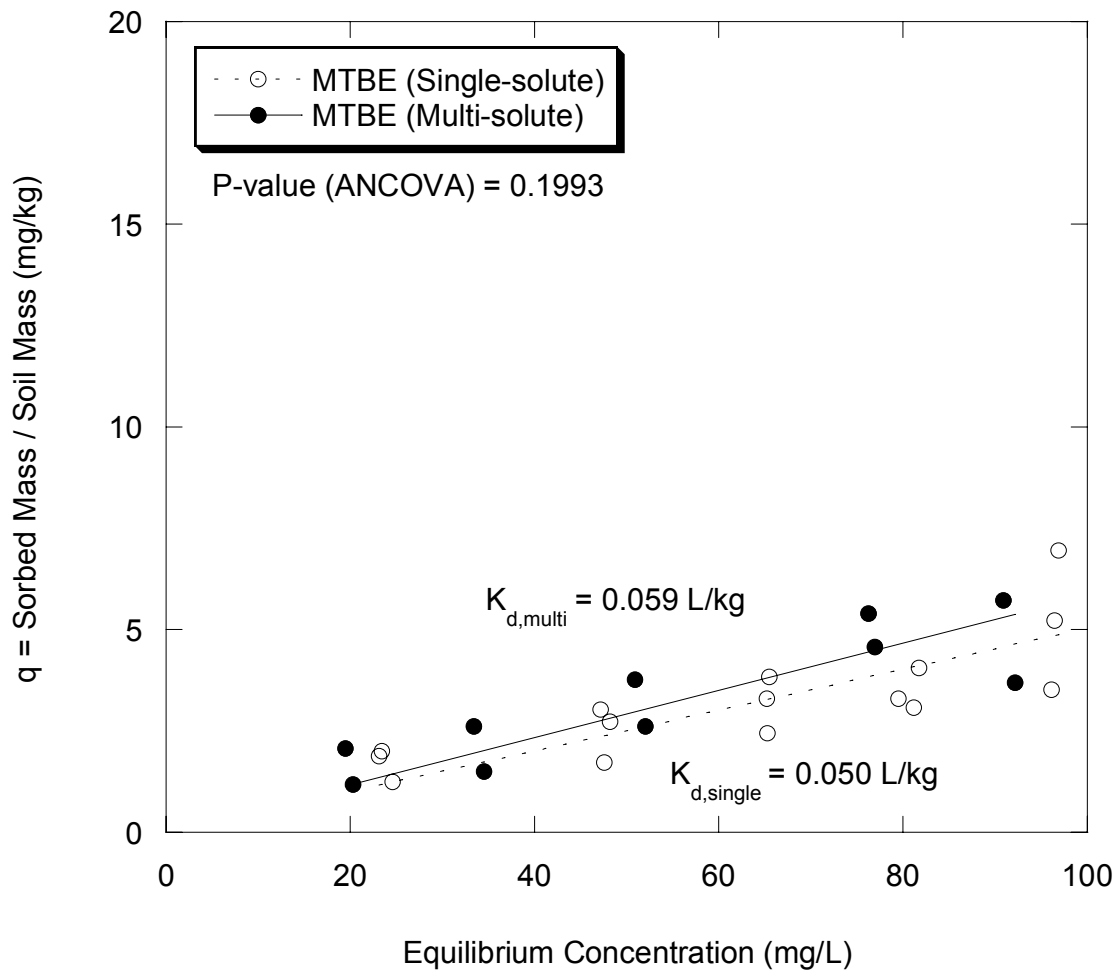


Fig. 4.8. Sorption isotherm of MTBE to Kamm clay

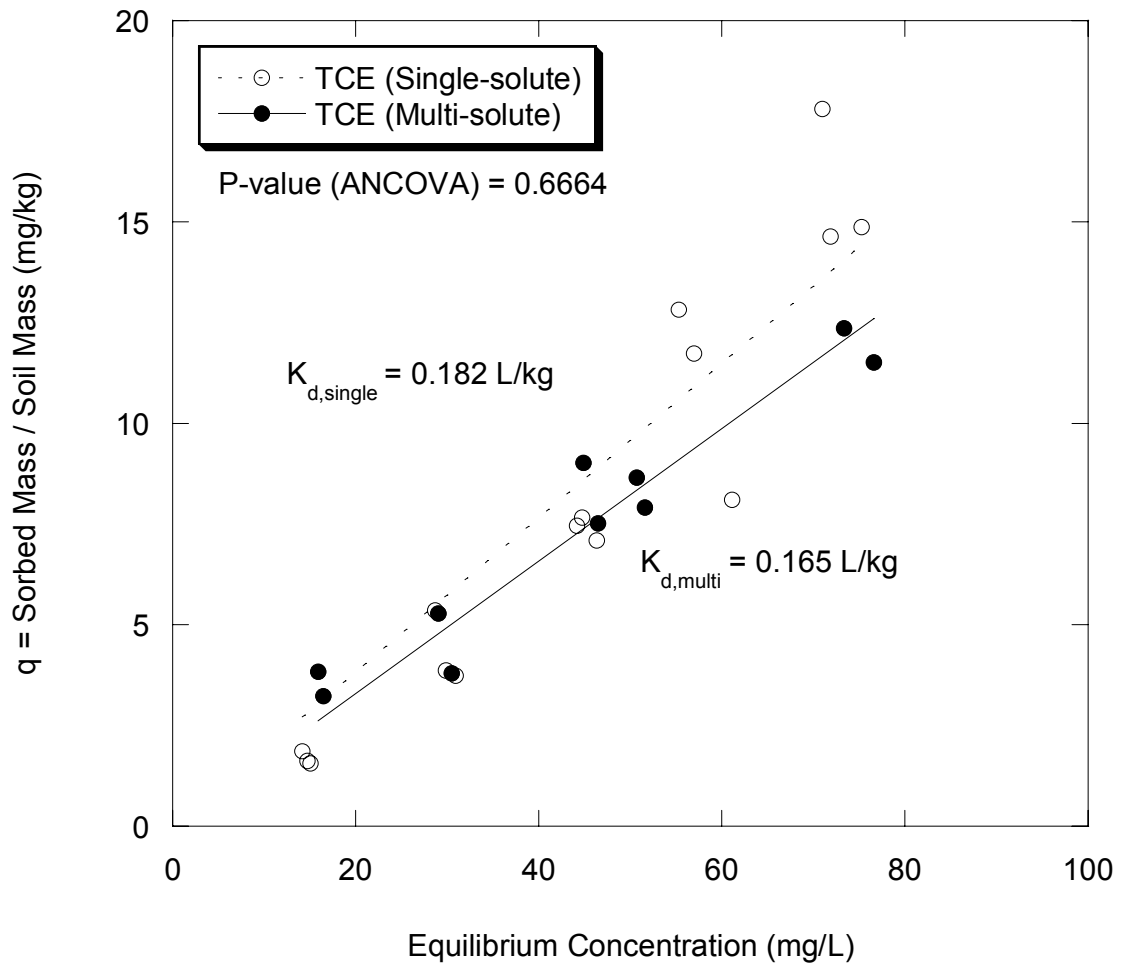


Fig. 4.9. Sorption isotherm of TCE to Kamm clay

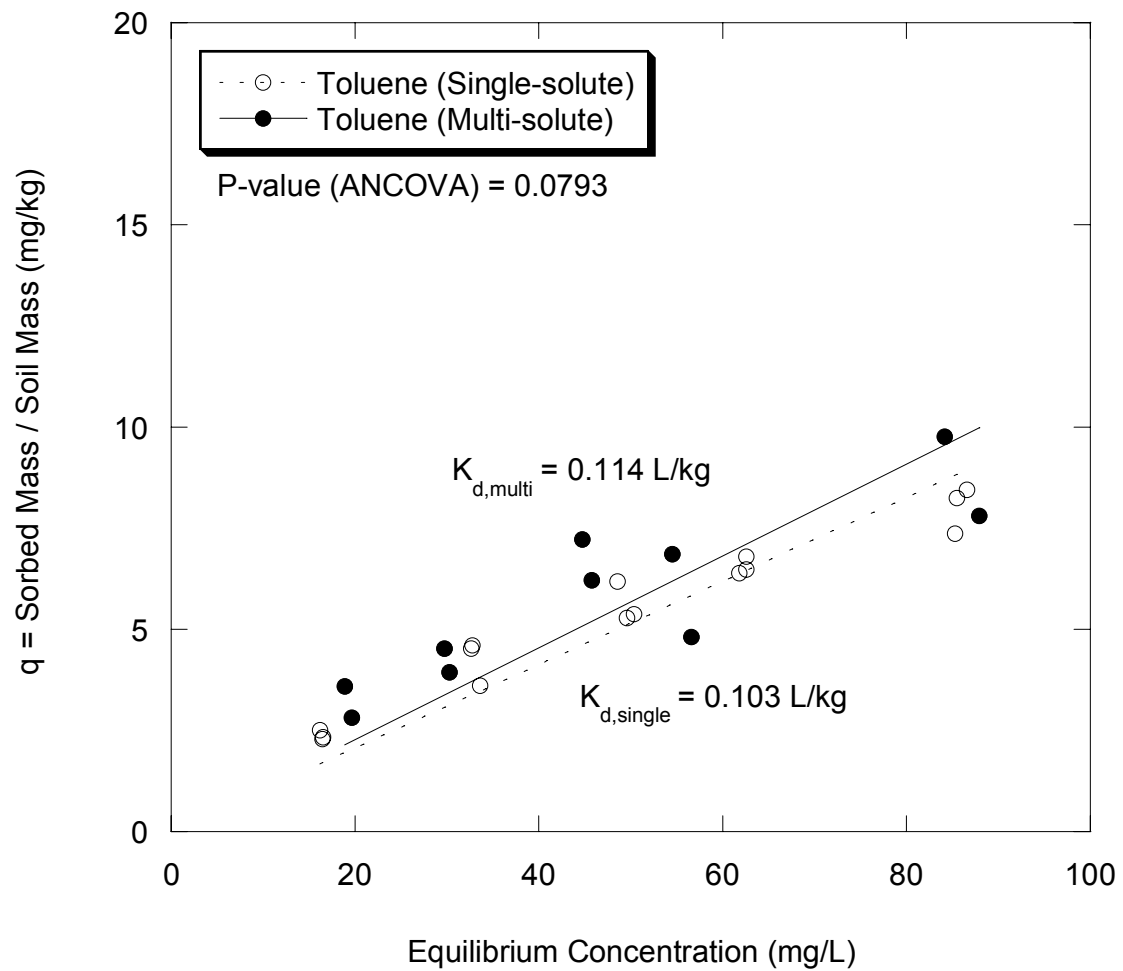


Fig. 4.10. Sorption isotherm of toluene to Kamm clay

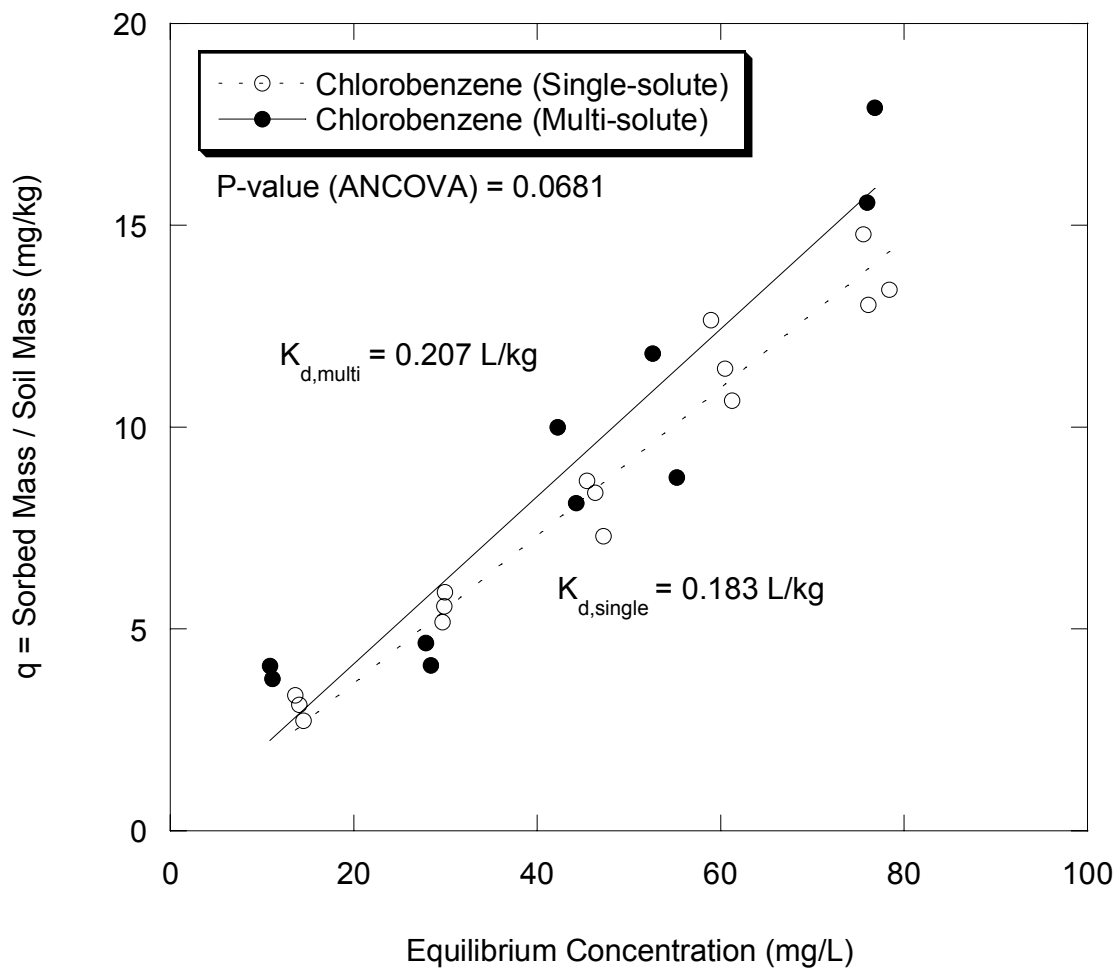


Fig. 4.11. Sorption isotherm of chlorobenzene to Kamm clay

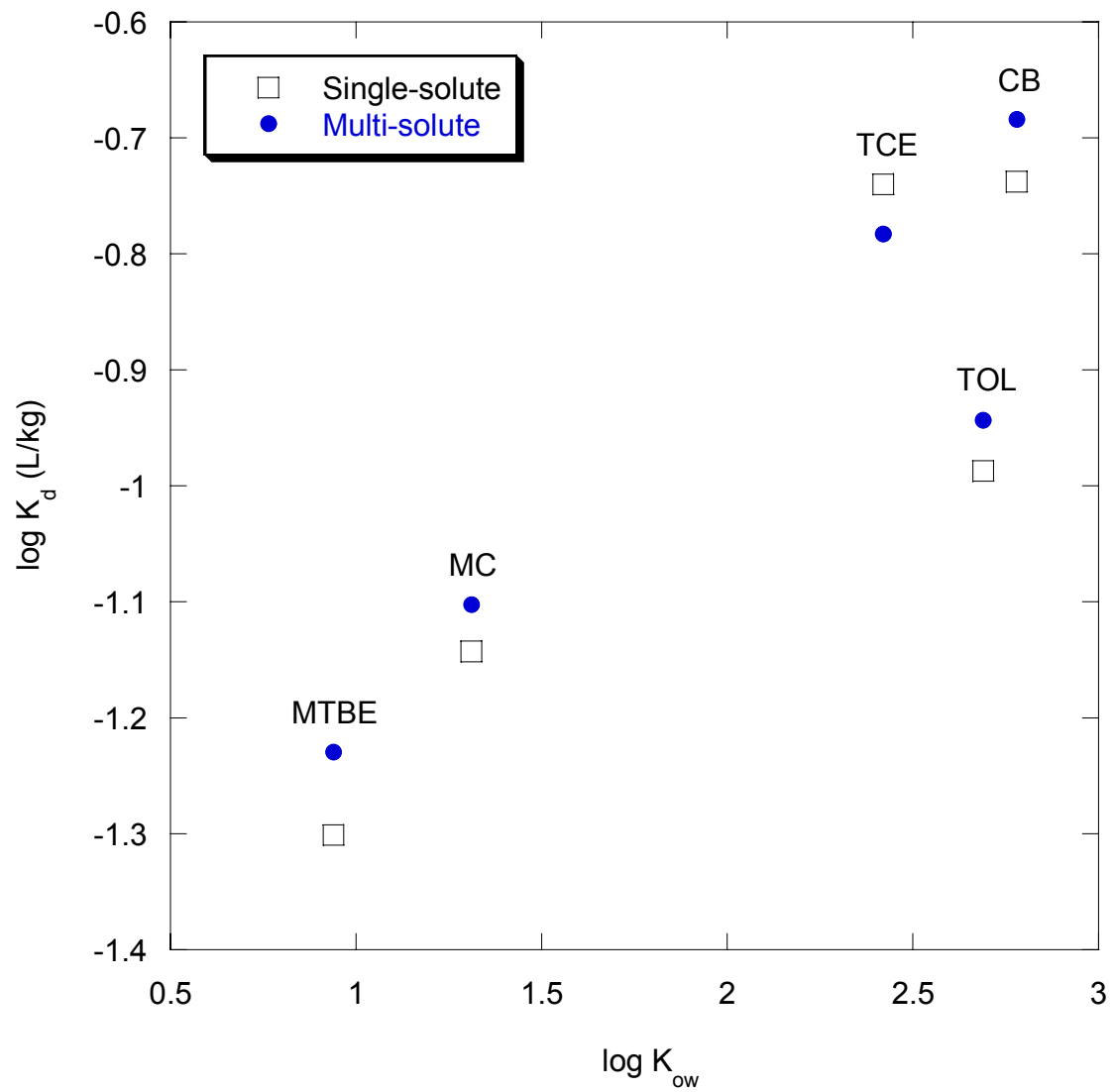


Fig. 4.12. Relationship between soil-water partition coefficients (K_d) and octanol-water partition coefficients (K_{ow}) of VOCs tested

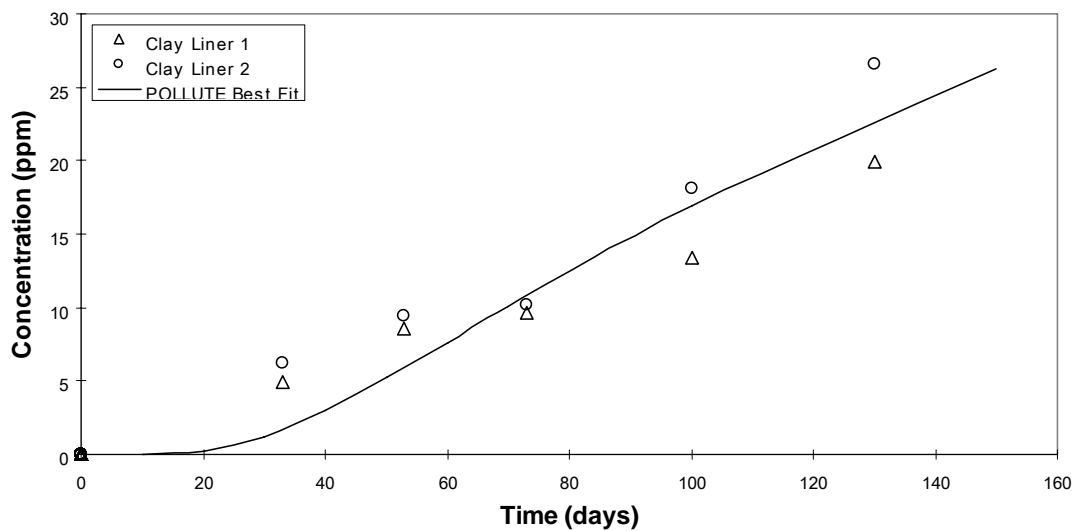


Fig. 4.13. Methylene chloride breakthrough concentration at sampling port 1 in compacted clay liner diffusion test

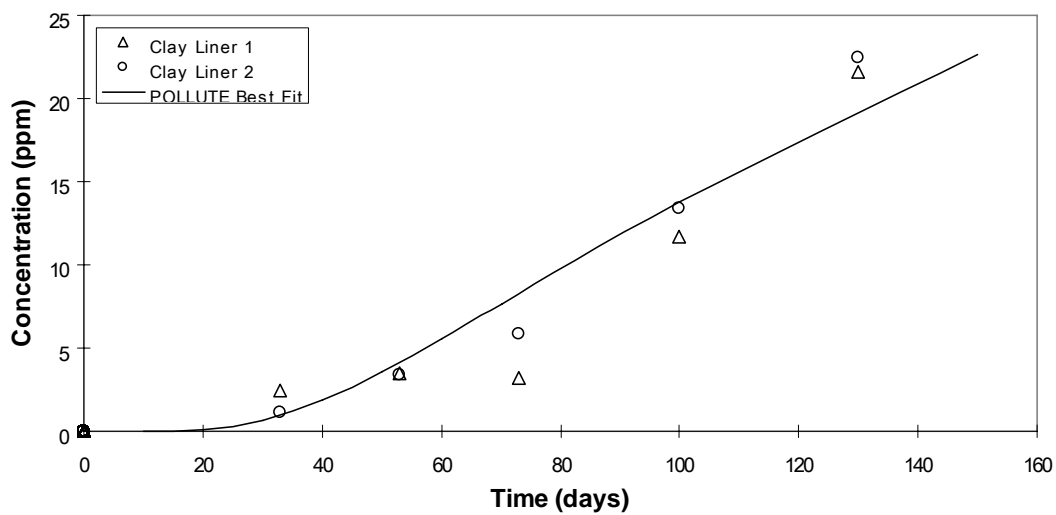


Fig. 4.14. MTBE breakthrough concentration at sampling port 1 in compacted clay liner diffusion test

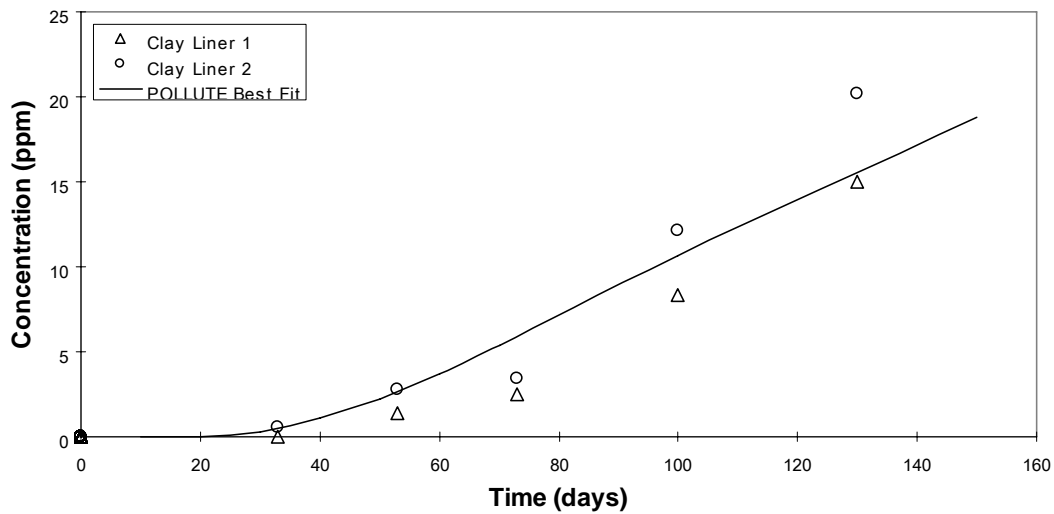


Fig. 4.15. TCE breakthrough concentration at sampling port 1 in compacted clay liner diffusion test

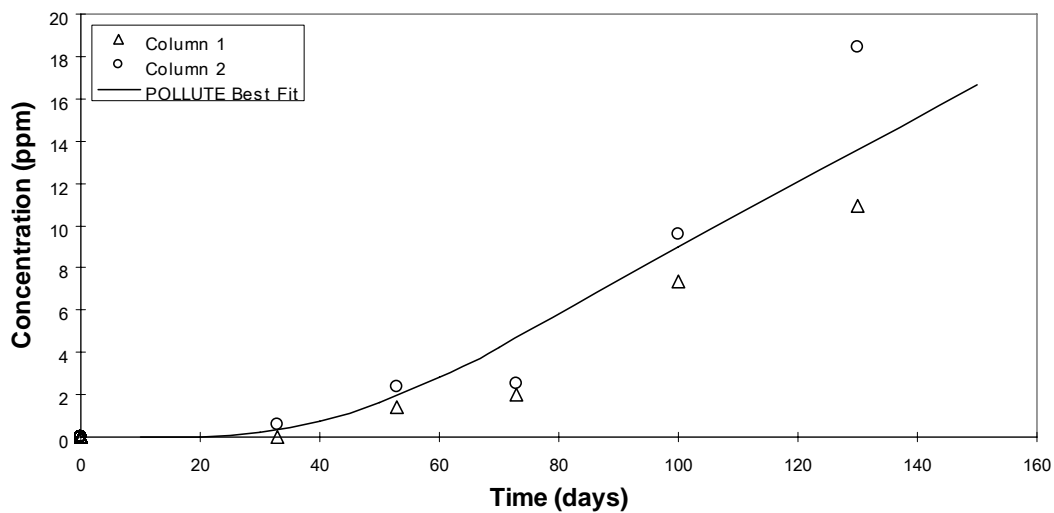


Fig. 4.16. Toluene breakthrough concentration at sampling port 1 in compacted clay liner diffusion test

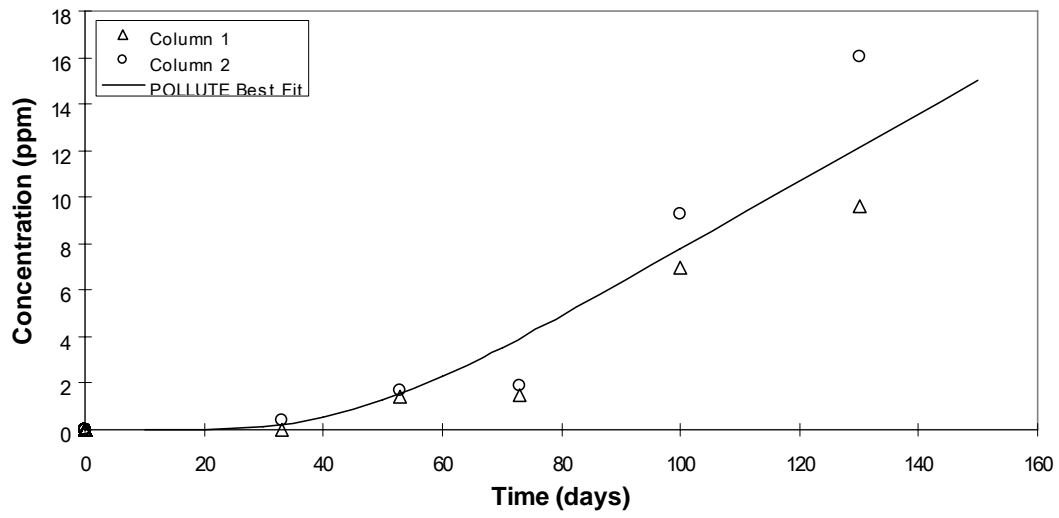


Fig. 4.17. Chlorobenzene breakthrough concentration at sampling port 1 in compacted clay liner diffusion test

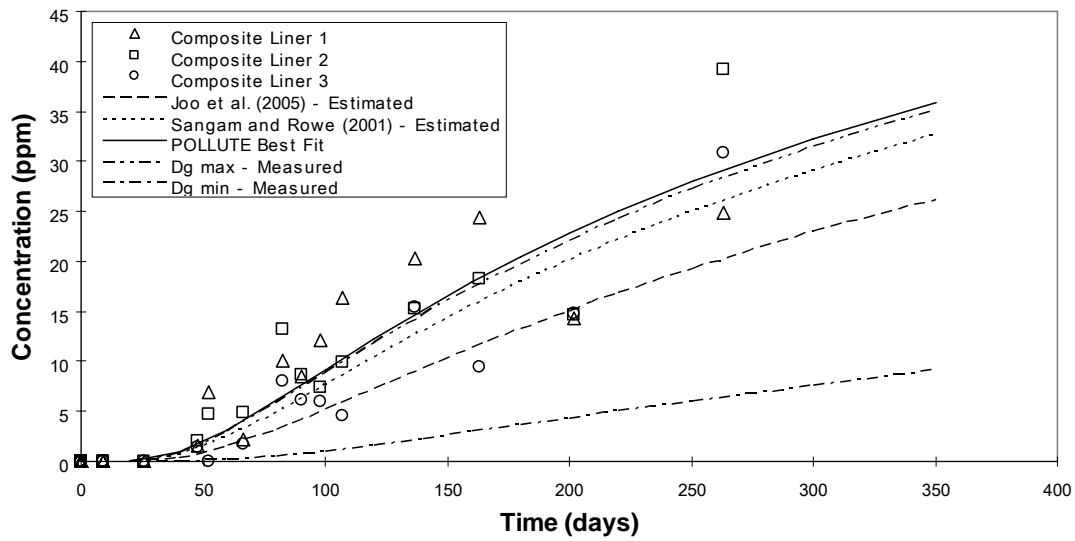


Fig. 4.18. Methylene chloride breakthrough concentration at sampling port 1 in composite liner diffusion test

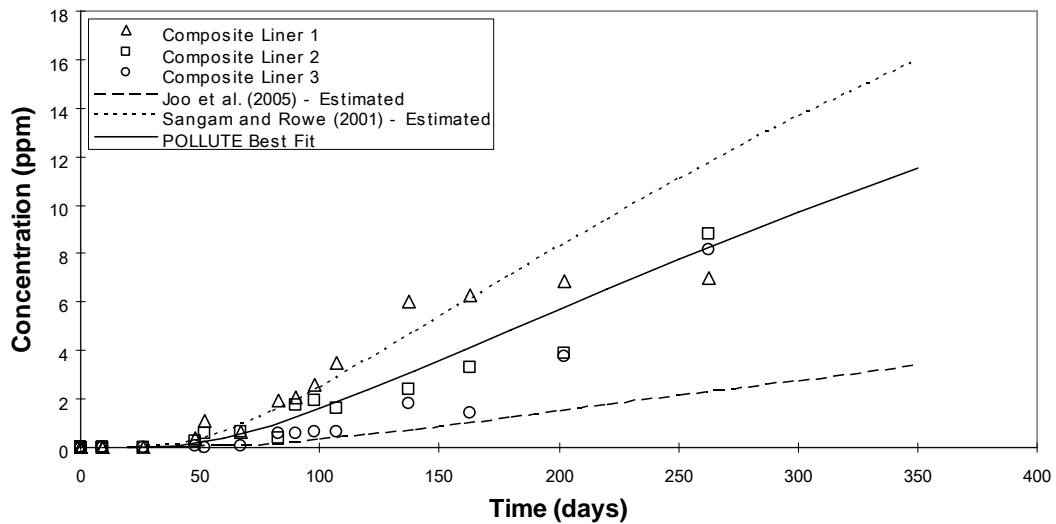


Fig. 4.19. MTBE breakthrough concentration at sampling port 1 in composite liner diffusion test

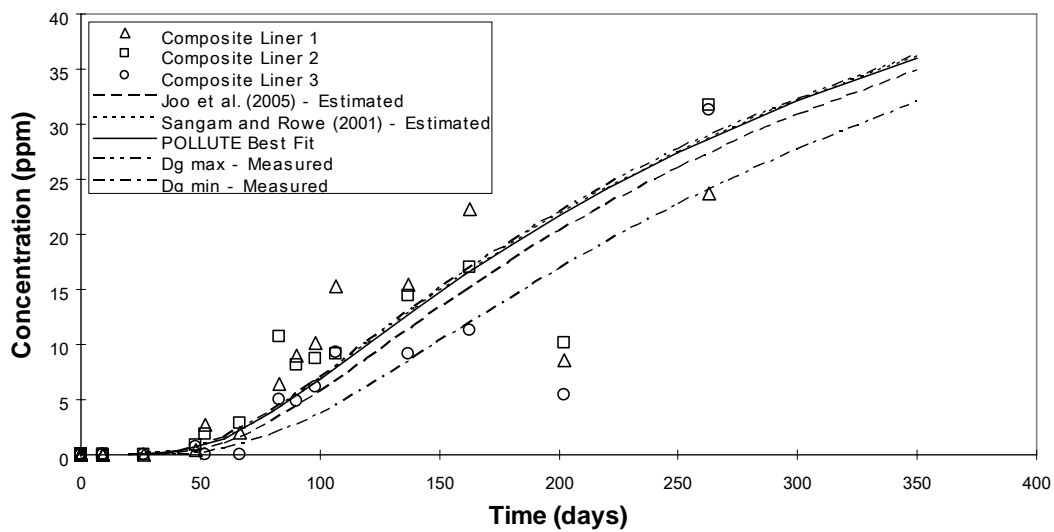


Fig. 4.20. TCE breakthrough concentration at sampling port 1 in composite liner diffusion test

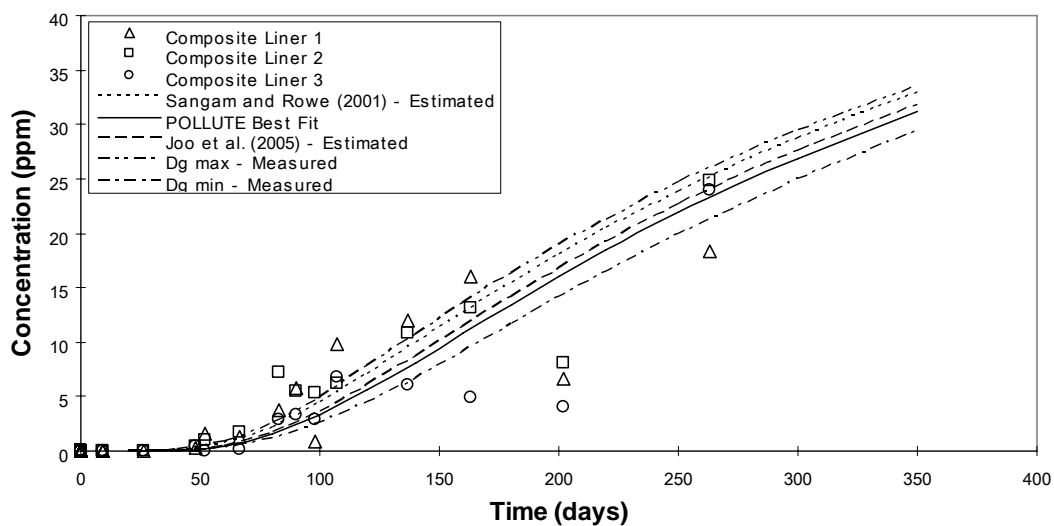


Fig. 4.21. Toluene breakthrough concentration at sampling port 1 in composite liner diffusion test

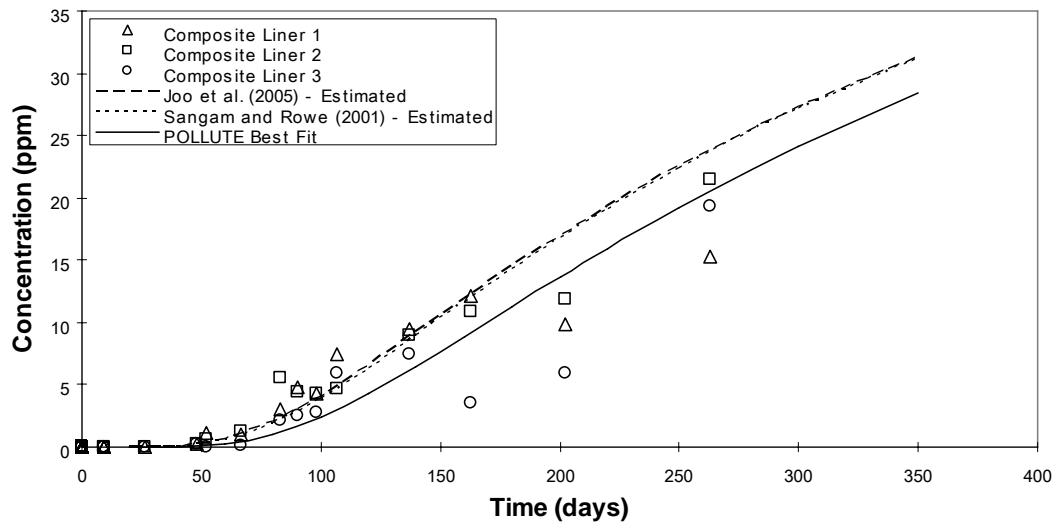


Fig. 4.22. Chlorobenzene breakthrough concentration at sampling port 1 in composite liner diffusion test

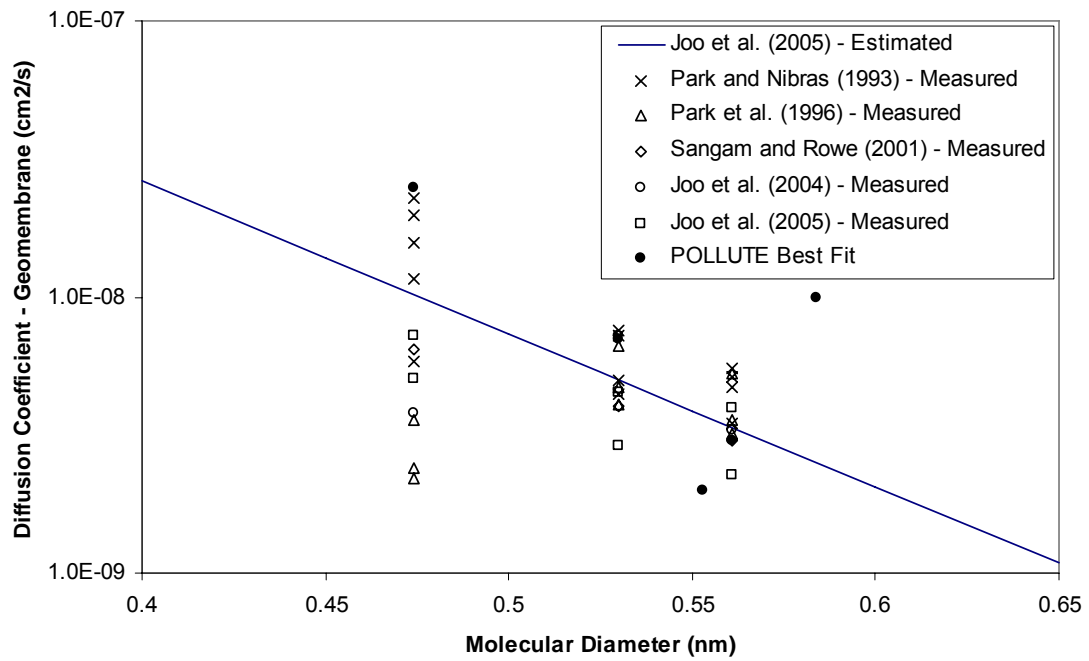


Fig. 4.23. Relationship between diffusion coefficient (D_g) and molecular diameter (d_m) proposed by Joo et al. (2005)

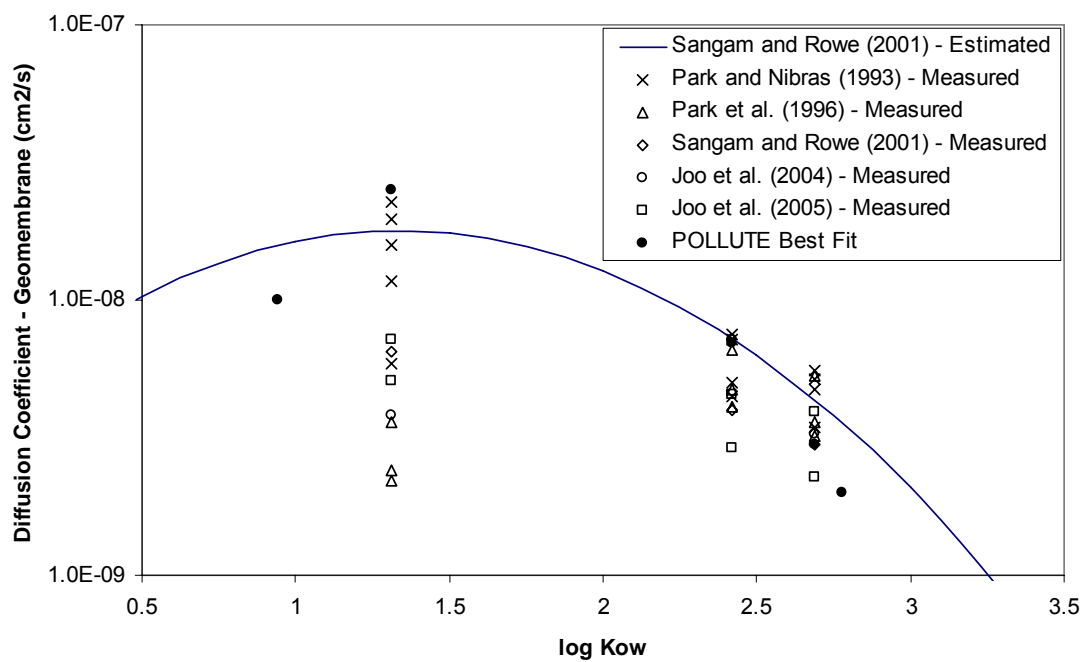


Fig. 4.24. Relationship between diffusion coefficient (D_g) and octanol-water partition coefficient (K_{ow}) proposed by Sangam and Rowe (2001)

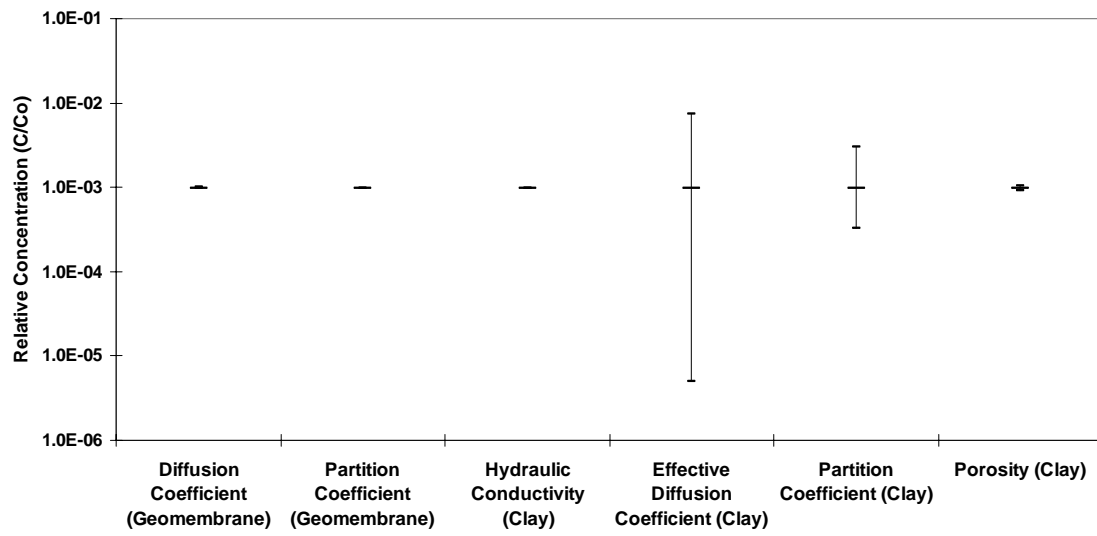


Fig. 4.25. Composite liner sensitivity analysis (measurement error)

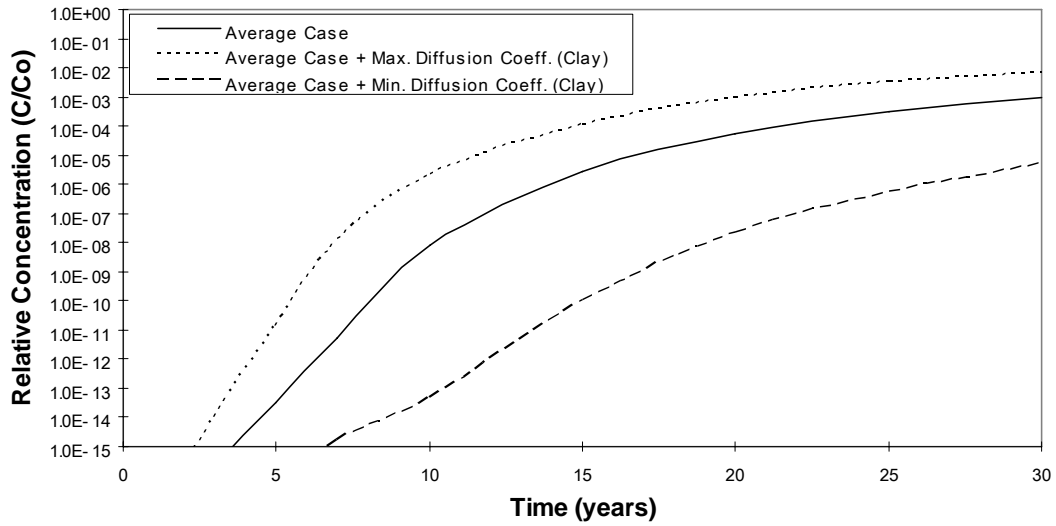


Fig. 4.26. Relative concentration of toluene at the bottom of a composite liner with measurement error of effective diffusion coefficient in the clay liner

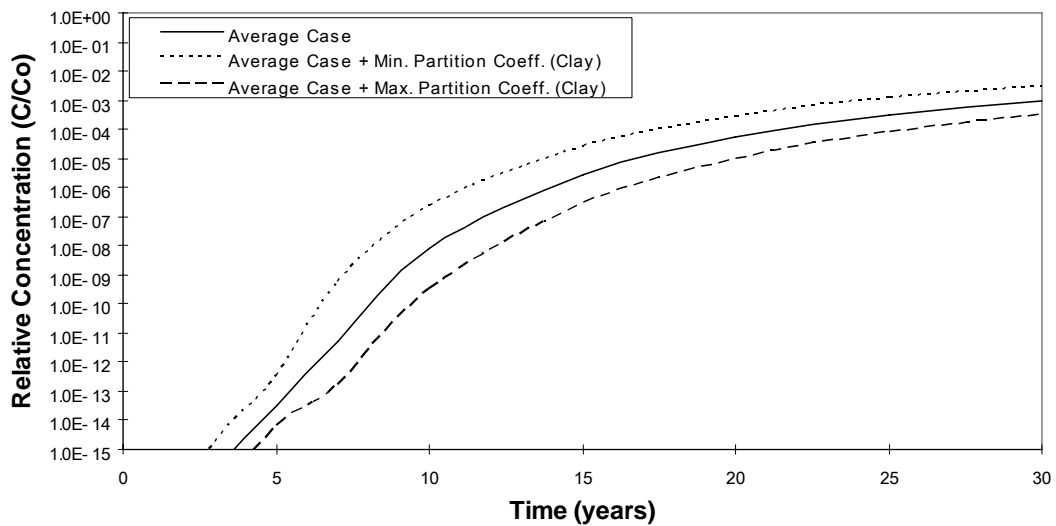


Fig. 4.27. Relative concentration of toluene at the bottom of a composite liner with measurement error of soil-water partition coefficient of the clay

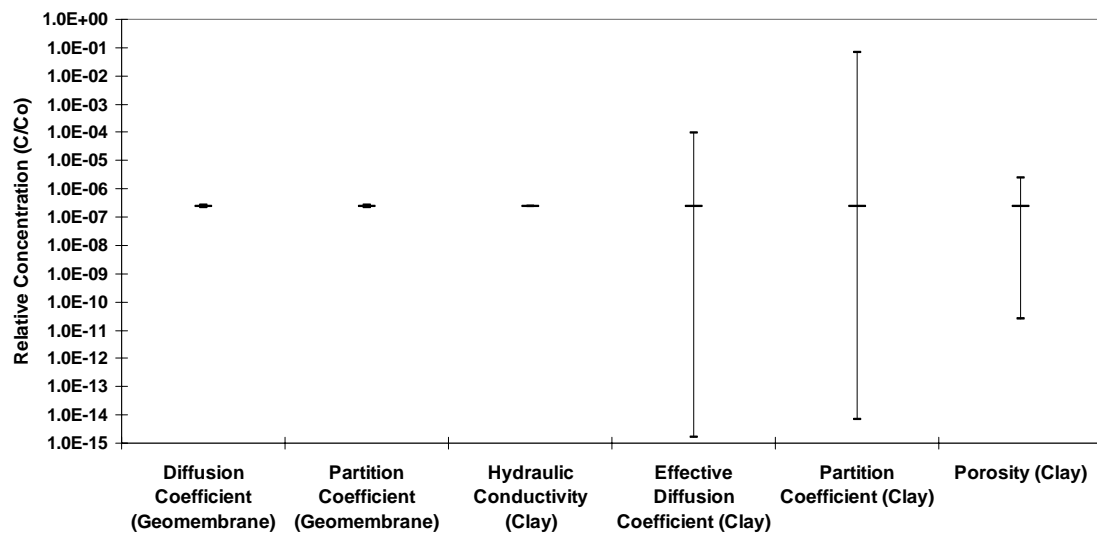


Fig. 4.28. Composite liner sensitivity analysis (published values)

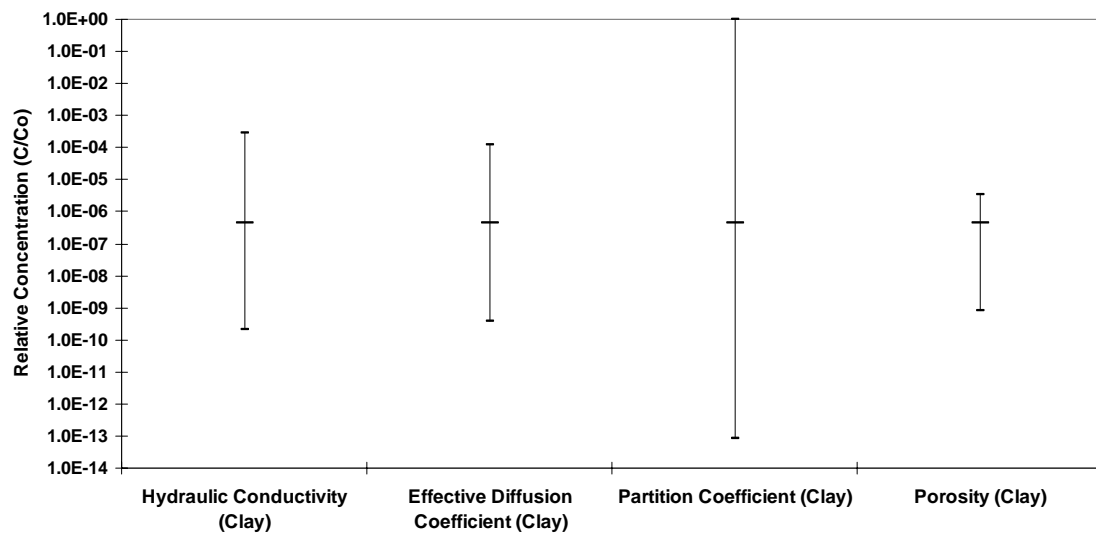


Fig. 4.29. Compacted clay liner sensitivity analysis (published values)

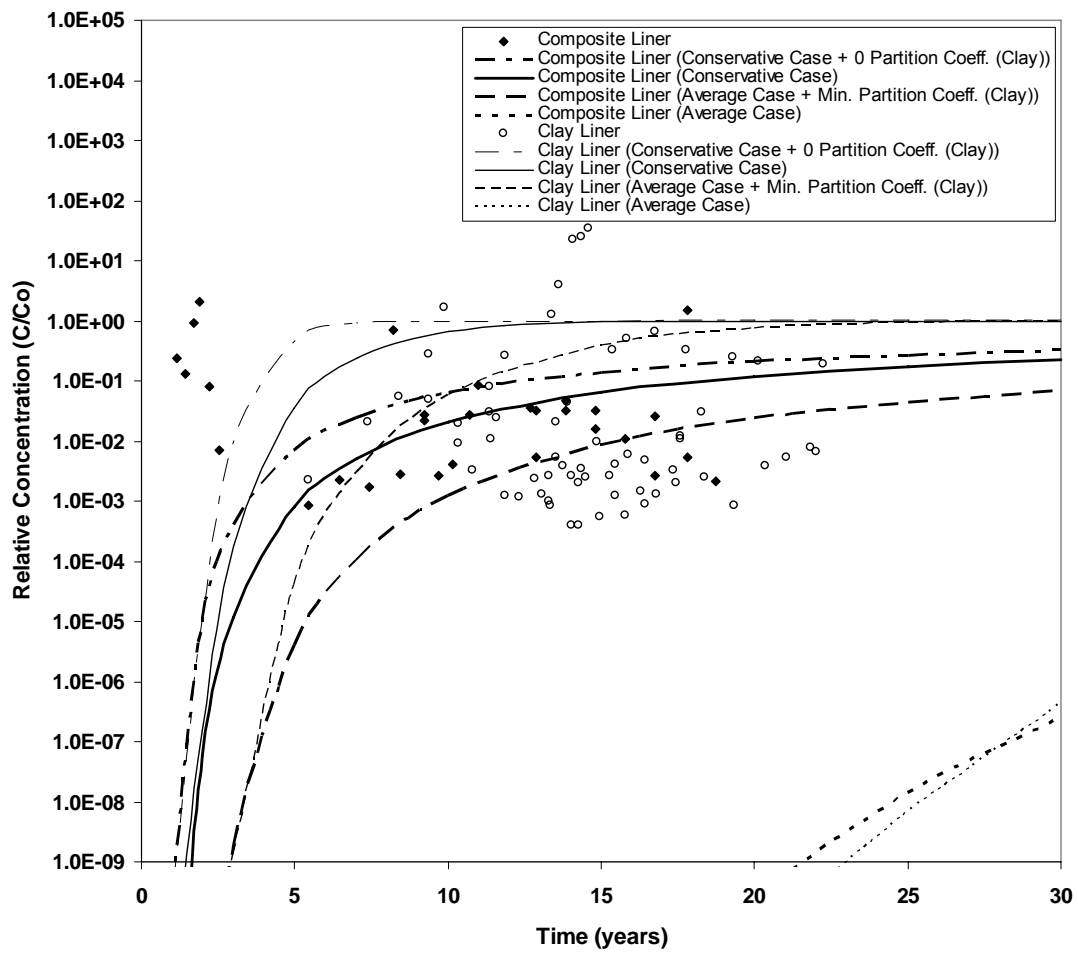


Fig. 4.30. Relative concentrations of toluene from clay and composite lined landfills with contaminant transport simulations

Table 4.1. HDPE-water partition coefficients of geomembrane

Compound	HDPE-water partition coefficient (L/kg)				P-value (ANCOVA)
	$K_{\text{HDPE-W, single}}$	R^2	$K_{\text{HDPE-W, multi}}$	R^2	
Methylene Chloride	2.367	0.920	2.267	0.882	0.2369
MTBE	0.549	0.782	0.605	0.781	0.2558
TCE	72.04	0.995	63.24	0.983	0.0071
Toluene	96.20	0.996	86.98	0.985	0.0593
Chlorobenzene	123.9	0.991	109.1	0.990	0.0032

Table 4.2. Soil-water partition coefficients of Kamm clay

Compound	Soil-water partition coefficient (L/kg)				P-value (ANCOVA)
	$K_{\text{d, single}}$	R^2	$K_{\text{d, multi}}$	R^2	
Methylene Chloride	0.072	0.615	0.079	0.573	0.3216
MTBE	0.050	0.720	0.059	0.630	0.1993
TCE	0.182	0.910	0.165	0.916	0.6664
Toluene	0.103	0.855	0.114	0.592	0.0793
Chlorobenzene	0.183	0.958	0.207	0.891	0.0681

Table 4.3. Effective diffusion coefficients and apparent tortuosities in compacted clay liner

Compound	Effective diffusion coefficient (cm ² /s)	Apparent tortuosity
Methylene Chloride	1.5×10^{-6}	0.12
MTBE	1.2×10^{-6}	0.14
TCE	1.4×10^{-6}	0.14
Toluene	1.1×10^{-6}	0.11
Chlorobenzene	1.3×10^{-6}	0.14

Table 4.4. Estimated diffusion coefficient in geomembrane

Compound	Diffusion coefficient in geomembrane (cm ² /s)		
	POLLUTE best fit	Joo et al. (2005)	Sangam and Rowe (2001)
Methylene Chloride	2.50×10^{-8}	1.02×10^{-8}	1.80×10^{-8}
MTBE	1.00×10^{-8}	2.51×10^{-9}	1.58×10^{-8}
TCE	7.00×10^{-9}	5.00×10^{-9}	7.22×10^{-9}
Toluene	3.00×10^{-9}	3.37×10^{-9}	4.31×10^{-9}
Chlorobenzene	2.00×10^{-9}	3.73×10^{-9}	3.54×10^{-9}

Table 4.5 Measured properties of composite liner components (toluene)

Component	Property	Measurement	Method	Reference	
Geomembrane	Diffusion coefficient ($\times 10^{-9}$ cm ² /s)	4.72 \pm 0.90	Batch test	Park and Nibras (1993)	
		4.03 \pm 1.12	Column test	Park et al. (1996)	
		3.27 \pm 0.30	Batch test	Joo et al. (2004)	
		3.11 \pm 1.17	Column test	Joo et al. (2005)	
	Partition coefficient	63.45 \pm 14.90	Batch test	Park and Nibras (1993)	
		86.27 \pm 20.50			
		83.92 \pm 2.76			
		151.03 \pm 10.80	Column test		
		140 \pm 5			Park et al. (1996)
		57.32 \pm 17.47			Joo et al. (2004)
119.58 \pm 9.52	Column test	Joo et al. (2005)			
Clay	Hydraulic conductivity ($\times 10^{-8}$ cm/s)	2.63 \pm 0.28	Column test	Park et al. (1997)	
		2.02 \pm 0.21			
		3.87 \pm 0.40			
		1.57 \pm 0.13			
		2.62 \pm 0.31			
		2.86 \pm 0.27			
		3.68 \pm 1.54			Tank test
		1.28 \pm 0.69			
		4.06 \pm 1.41			
		1.43 \pm 0.54			
	1.70 \pm 0.58				
	1.78 \pm 0.43				
	Tortuosity	0.253 \pm 0.119	Column test	Kim et al. (2001)	
	Partition coefficient (L/kg)	0.93 \pm 0.49	Batch test	Edil et al. (1995)	
		0.80 \pm 0.48	Batch test	Kim et al. (2001)	
1.08 \pm 0.67		Batch test	Kim et al. (2003)		
1.02 \pm 0.53					
Porosity	0.314 \pm 0.031	Column test	Kim et al. (1997)		
	0.357 \pm 0.028	Tank test			

Table 4.6. Parameters for sensitivity analysis (measurement error)

Parameter		Average	Maximum	Minimum
Geomembrane	Diffusion coefficient (cm ² /s)	3.00x10 ⁻⁹	3.70x10 ⁻⁹	2.30x10 ⁻⁹
	Partition coefficient	81.76	93.29	70.23
Clay liner	Hydraulic conductivity (cm/s)	1.70x10 ⁻⁸	2.11x10 ⁻⁸	1.29x10 ⁻⁸
	Diffusion coefficient (cm ² /s)	1.10x10 ⁻⁶	1.62x10 ⁻⁶	5.83x10 ⁻⁷
	Partition coefficient (L/kg)	0.114	0.180	0.048
	Porosity	0.375	0.386	0.364

Table 4.7. Parameters for sensitivity analysis (published values)

Parameter		Average	Maximum	Minimum
Geomembrane	Diffusion coefficient (cm ² /s)	3.90x10 ⁻⁹	5.50x10 ⁻⁹	2.30x10 ⁻⁹
	Partition coefficient	104	151	57
Clay liner	Hydraulic conductivity (cm/s)	4.4x10 ⁻⁸	1.0x10 ⁻⁷	2.0x10 ⁻⁹
	Diffusion coefficient (cm ² /s)	3.74x10 ⁻⁶	6.38x10 ⁻⁶	1.11x10 ⁻⁶
	Partition coefficient (L/kg)	2.03	6.45	0.11
	Porosity	0.29	0.35	0.17

SECTION 5 SUMMARY

5.1 Summary

A previous study by Klett (2006) compared lysimeter VOC concentration data from Wisconsin landfills with an existing analytical solution for transport through the liner using widely accepted parameters. The analytical solution under-predicted the concentrations determined from field data for all of the compounds examined in the study, thus parameters and the model used are re-considered in this study.

In this study, batch tests and column tests were employed to measure VOC transport parameters for use in a numerical transport model for composite liners given by Rowe and Booker (2004).

VOC batch sorption tests were conducted using methylene chloride, MTBE, TCE, toluene, and chlorobenzene with HDPE geomembrane and Kamm clay, a landfill liner material used at Dane County Landfill No. 2 in Madison, Wisconsin. Batch tests were performed in single-solute and multi-solute conditions.

For HDPE geomembrane, the results were consistent with previous studies, and linear sorption isotherm could be fitted to batch test data. HDPE-water partition coefficient increased as octanol-water partition coefficient of the VOC increased. The result of ANCOVA test between single-solute and multi-solute conditions suggests a possibility of competition or change in activity of compounds which have high affinity to HDPE geomembranes.

Also linear sorption isotherm could be fitted to Kamm clay batch test data. ANOVA test suggests soil-water partitions of single-solute and multi-solute

conditions are not statistically different which was consistent with Kim et al. (2001). Soil-water partition coefficient increased as octanol-water partition coefficient of the VOC increased except for toluene. Kile et al. (1995) found that sorption of relatively nonpolar solutes to soil organic matter depends on soil organic matter composition and its polarity, and toluene was the most nonpolar compound used in this study. Thus sorption capacity of toluene can be relatively sensitive than polar compounds.

Compacted clay liner diffusion tests were performed to measure the effective diffusion coefficient of Kamm clay. Breakthrough concentration data were manually fitted with POLLUTE to determine the effective diffusion coefficient of each compound. POLLUTE is a software package for analyzing contaminant transport which is widely used in landfill design and remediation.

Diffusion coefficient of organic compounds in geomembrane was estimated using empirical relationships proposed by Joo et al. (2005) and Sangam and Rowe (2001).

Composite liner diffusion tests were conducted and the results were compared with POLLUTE contaminant transport simulations using individually measured and estimated (i.e., diffusion coefficient of organic compounds in geomembrane) transport parameters. Simulations predicted the breakthrough concentrations of TCE, toluene, and chlorobenzene within 10 % of difference. The breakthrough concentration of methylene chloride could be predicted within a factor of 2 and that of MTBE within a factor of 4.

Sensitivity analyses were performed to assess the effects of diffusion coefficients, partition coefficients, hydraulic conductivity, and porosity on model

simulations. The parameters related to geomembrane have little effect on breakthrough concentrations and the transport parameters related to the clay liner affect the breakthrough concentration significantly.

The sensitivity analysis showed that breakthrough concentration is very sensitive to the properties of the clay liner and predicting the breakthrough concentration is difficult only using widely accepted transport parameters instead of actually measuring the transport properties of liner components. Even if all the properties are independently measured, measurement error changes the breakthrough concentration up to 2 orders of magnitude.

Field data were adopted from Klett (2006) to evaluate the contaminant model simulations for toluene using widely accepted published transport parameters for clay and composite liners in Wisconsin. The simulation results show that predicting relative concentrations with widely accepted transport parameters is difficult because relative concentration is very sensitive to the properties of the clay liner. Thus, the most conservative case must be considered in landfill designs.

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APPENDIX A

Procedure of Volatile Organic Compound Selection

Dichloromethane (methylene chloride), trichloroethylene (TCE), chlorobenzene, toluene, and methyl tertiary butyl ether (MTBE) were selected for testing based on relatively high detection frequency in leachate as well as their broad range of solubilities and molecular diameters. The selection procedure is as follows.

Table A.1 shows the frequently detected VOCs in Wisconsin landfills (Klett 2006). Only the compounds which were liquid phase in room temperature were selected for the convenience of making accurate concentration solutions. This eliminates chloromethane, dichlorodifluoromethane, chloroethane, vinyl chloride, p-dichloro-benzene, and naphthalene.

Four properties (solubility, octanol-water partition coefficient, molecular diameter, and molecular diffusion coefficient) were left to consider, and a simplification was required to consider all these properties; therefore, finding relationships between each property were attempted.

Error! Reference source not found. shows the relationship between octanol-water partition coefficients and solubilities in logarithmic scale. As is shown, these two properties have a strong relationship.

Fig. A.2 shows the relationship between molecular diffusion coefficients in free solution and molecular diameters, and these two properties show a strong relationship as well. Molecular diameters were calculated using Berens' formula (Berens 1985).

Only the aqueous solubility and the molecular diameter can be considered, because the octanol-water partition coefficient depends on

aqueous solubility, and the molecular diffusion coefficient in free solution depends on molecular diameter.

Xylenes, ethylbenzene, tetrachloroethylene, and p-dichlorobenzene were excluded for low aqueous solubilities, and acetone, methyl ethyl ketone were excluded for short half lives. Tetrahydrofuran was excluded because it is non-carcinogenic itself and less harmful in low concentrations than other VOCs.

To narrow the choice and help the decision, VOCs far from the trend line in

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Fig. A.2 were excluded; 1,1,1-trichloroethane and cis-1,2-dichloroethane were excluded by **Error! Reference source not found.**, and Benzene was

excluded by

Fig. A.2 (Acetone and ethylbenzene were already excluded). 1,2-dichloroethane was excluded because it was not detected in lysimeters but only in leachates (Klett, 2006).

Table A.2 shows the selected VOCs. 1,2-dichloropropane was excluded because it was relatively rare in landfills than dichloromethane, and 1,1-dichloroethane was excluded because of the low flash point. Now 5 compounds are left with 1 chlorinated alkanes, 1 chlorinated alkene, 2 arenes (1 arene and 1 chlorinated arene), and 1 ether.

Methylene chloride, TCE, toluene, chlorobenzene, and MTBE can make a good contrast of solubility (**Error! Reference source not found.**) and molecular diameter (**Error! Reference source not found.**). MTBE is a compound with high aqueous solubility and large molecular diameter; therefore, it can compare the effectiveness of each property.

Methylene chloride, TCE and toluene were studied by Edil et al. (1994) and Kim et al. (2001) with compacted clay liners, and by Joo et al. (2005) and Park and Nibras (1993) with HDPE geomembrane. Park and Nibras (1993) also included chlorobenzene in their study. MTBE and TCE were studied by Nefso and Burns (2007) with HDPE geomembranes.

The retention time of each compounds using RTX-624 capillary column with the GC are dichloromethane, 5.2 min; MTBE, 5.6 min; TCE, 9.9 min; toluene, 11.9 min; and chlorobenzene, 14.9 min. The smallest retention time interval is 0.4 min, and this time is sufficient to identify each compound.

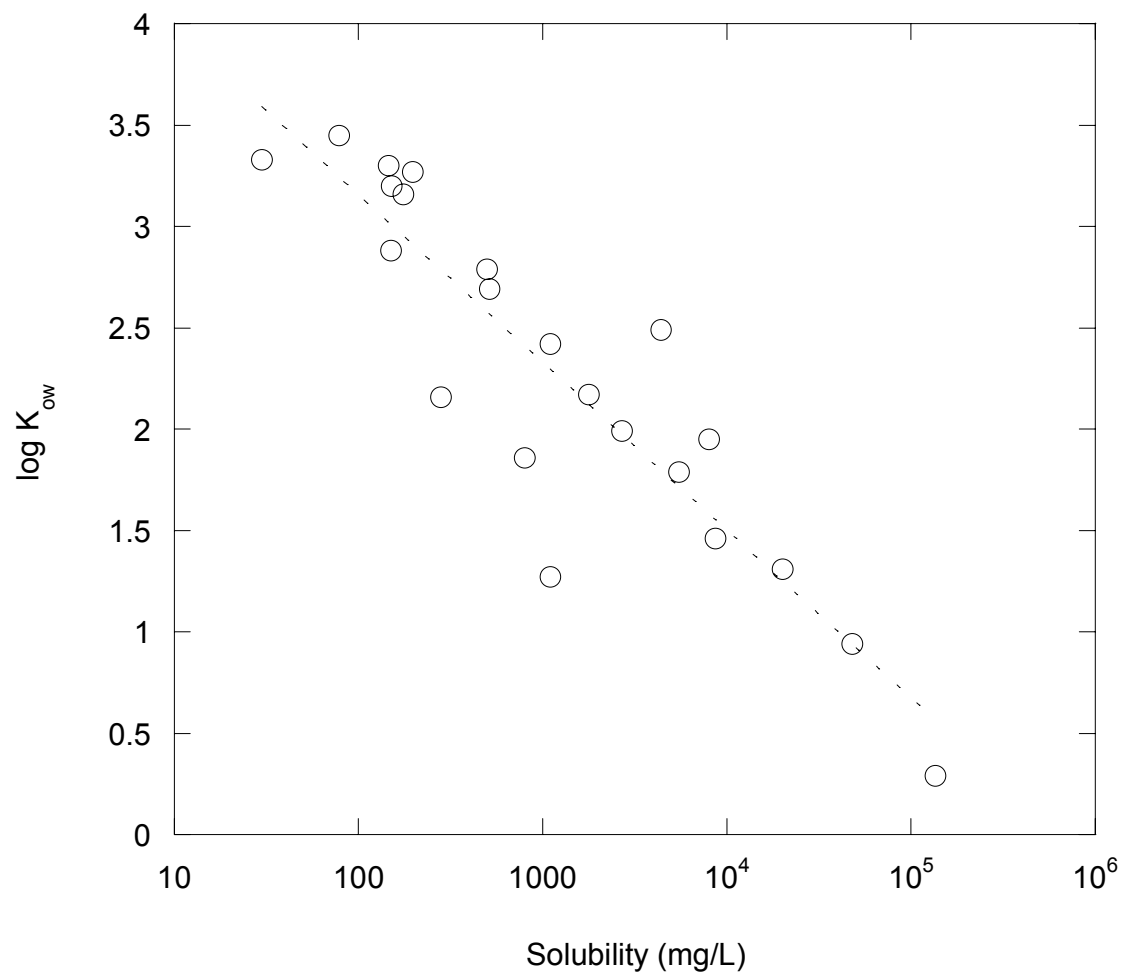


Fig. A.1. Relationship between octanol-water partition coefficient and solubility of frequently detected VOCs in Wisconsin landfills

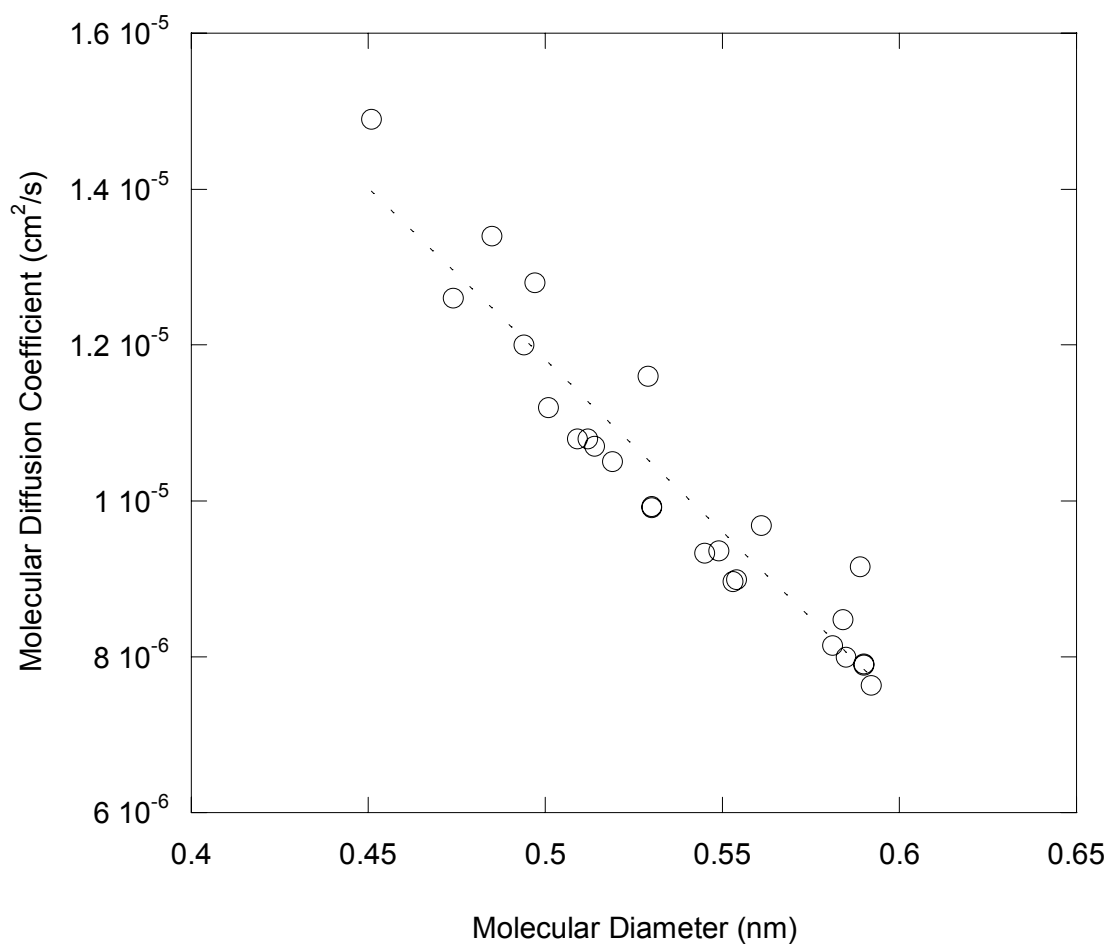


Fig. A.2. Relationship between molecular diffusion coefficient and molecular diameter of frequently detected VOCs in Wisconsin landfills

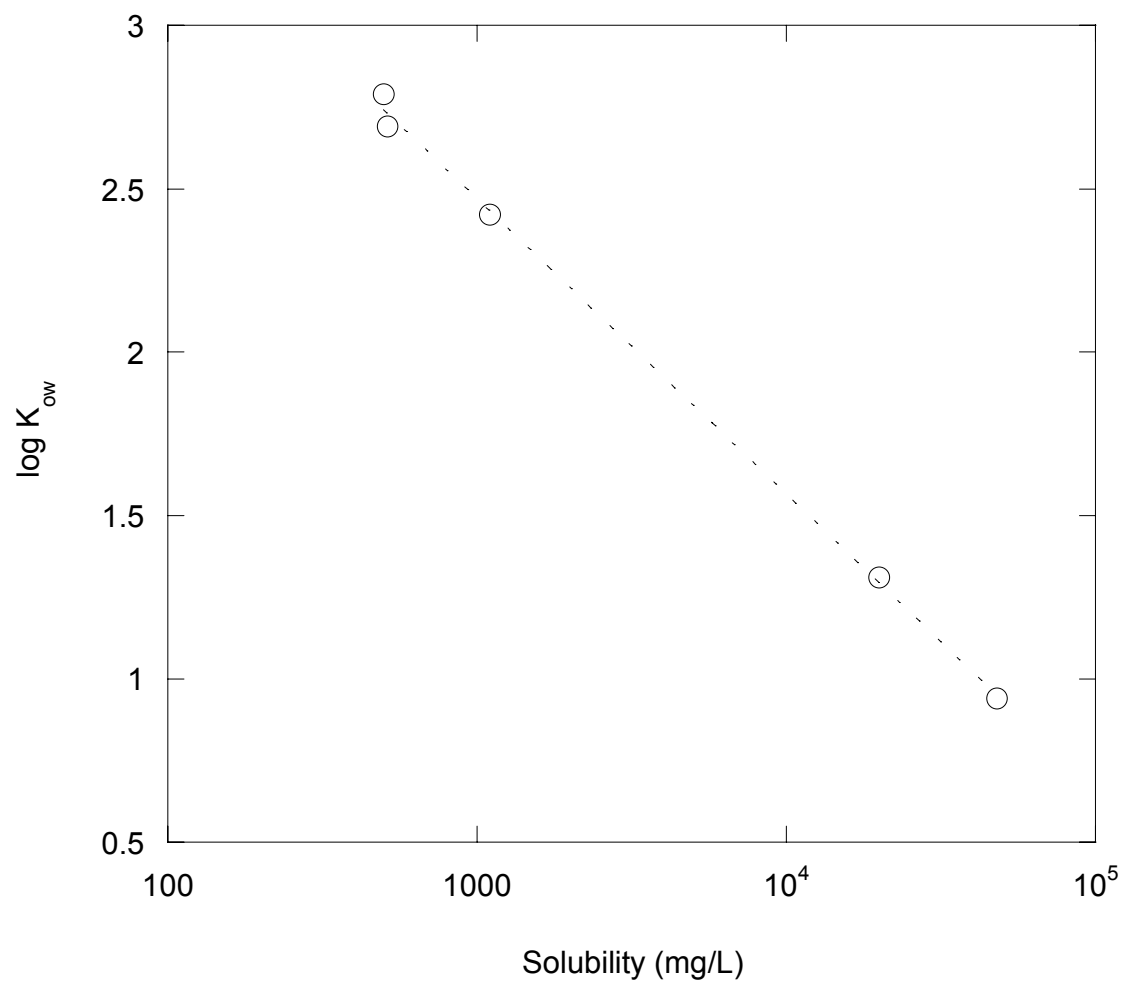


Fig. A.3. Relationship between octanol-water partition coefficient and solubility of VOCs selected for this study

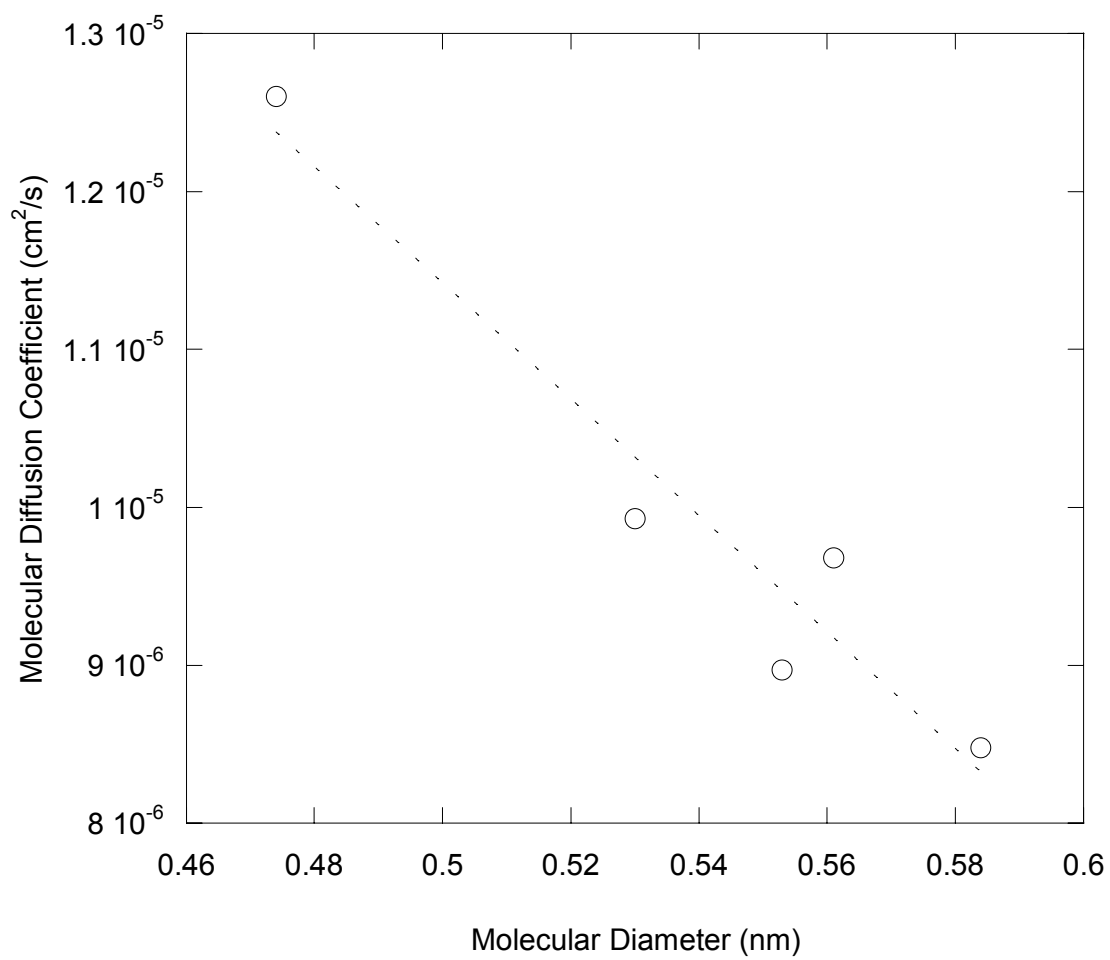


Fig. A.4. Relationship between molecular diffusion coefficient and molecular diameter of VOCs selected for this study

Table A.1. Frequently detected VOCs in Wisconsin landfills

Compounds	Chemical Formula	M.P.(°C) ^a	B.P.(°C) ^a	Half lifes (days) ^b
Alkanes				
Chloromethane (Methylchloride)	CH ₃ Cl	-97.7	-24.09	28~112
Dichloromethane (Methylenechloride)	CH ₂ Cl ₂	-97.2	40	28~112
Trichloromethane (Chloroform)	CHCl ₃	-63.41	61.17	7~28
Dichlorodifluoromethane	CCl ₂ F ₂	-158	-29.8	112~672
Chloroethane (Ethylchloride)	CH ₂ Cl-CH ₃	-138.4	12.3	28~112
1,1-Dichloroethane	CHCl ₂ -CH ₃	-96.9	57.3	128~616
1,2-Dichloroethane	CH ₂ Cl-CH ₂ Cl	-35.7	83.5	400~720
1,1,1-Trichloroethane	CCl ₃ -CH ₃	-30.01	74.09	560~1092
1,2-Dichloropropane	CH ₂ Cl-CHCl-CH ₃	-100.53	96.4	668~5156
Alkenes				
Vinyl Chloride (Chloroethene)	CHCl=CH ₂	-153.84	-13.8	112~720
Cis-1,2-Dichloroethene	CHCl=CHCl	-80.0	60.1	112~720
Trichloroethylene (TCE)	CHCl=CCl ₂	-84.7	87.21	38~1653
Tetrachloroethylene (PCE)	CCl ₂ =CCl ₂	-22.3	121.3	38~1653
Arenes (Aromatic hydrocarbons)				
Benzene	C ₆ H ₆	5.49	80.09	28~112
Chlorobenzene	C ₆ H ₅ Cl	-45.31	131.72	272~600
p-Dichlorobenzene	C ₆ H ₄ Cl ₂	53.09	174	112~720
Toluene	C ₆ H ₅ -CH ₃	-94.95	110.63	51~210
Ethylbenzene	C ₆ H ₅ -CH ₂ -CH ₃	-94.96	136.19	176~228
Xylene O-	CH ₃ -C ₆ H ₄ -CH ₃	-25.2	144.5	180~360
Xylene M-	CH ₃ -C ₆ H ₄ -CH ₃	-47.8	139.12	28~529
Xylene P-	CH ₃ -C ₆ H ₄ -CH ₃	13.25	138.37	28~112
Naphthalene	C ₁₀ H ₈	80.26	217.9	25~258
Ketones				
Acetone (2-propanone)	CH ₃ -CO-CH ₃	-94.7	56.05	4~28
Methyl Ethyl Ketone (2-Butanone)	CH ₃ -CO-CH ₂ -CH ₃	-86.4	79.6	4~28
Ethers				
Methyl Tertiary Butyl Ether (MTBE)	CH ₃ -O-C(CH ₃) ₃	-108.6	55.0	112~720
Furans				
Tetrahydrofuran	C ₄ H ₈ O	-108.44	65	N/A

^a Verschueren (1977), ^b anaerobic condition in soil, Howard et al. (1991)

(Continued)

Compounds	Solubility (mg/L) ^a	log K _{ow} ^b	Molecular diameter(nm) ^c	Molecular diffusion coefficient (cm ² /s) ^d
Alkanes				
Chloromethane (Methylchloride)	4000cm ³ /L	0.91	0.451	1.49
Dichloromethane (Methylenechloride)	20000	1.31	0.474	1.26
Trichloromethane (Chloroform)	8000	1.95	0.512	1.08
Dichlorodifluoromethane	280	2.16	N/A	1.11
Chloroethane (Ethylchloride)	5740	N/A	0.494	1.2
1,1-Dichloroethane	5500	1.79	0.519	1.05
1,2-Dichloroethane	8690	1.46	0.509	1.08
1,1,1-Trichloroethane	4400	2.49	0.549	9.36
1,2-Dichloropropane	2700	1.99	0.545	9.33
Alkenes				
Vinyl Chloride (Chloroethene)	1100	1.27	0.485	1.34
Cis-1,2-Dichloroethene	800	1.86	0.501	1.12
Trichloroethylene (TCE)	1100	2.42	0.530	9.93
Tetrachloroethylene (PCE)	150	2.88	0.554	8.99
Arenes (Aromatic hydrocarbons)				
Benzene	1780	2.17	0.529	1.16
Chlorobenzene	500	2.79	0.553	8.97
p-Dichlorobenzene	79	3.45	0.581	8.15
Toluene	515	2.69	0.561	9.68
Ethylbenzene	152	3.2	0.589	9.16
Xylene O-	175	3.16	0.585	8
Xylene M-	146	3.3	0.590	7.91
Xylene P-	198	3.27	0.590	7.89
Naphthalene	30	3.33	0.592	7.63
Ketones				
Acetone (2-propanone)	miscible	-0.24	0.497	1.28
Methyl Ethyl Ketone (2-Butanone)	136000	0.29	0.530	9.91
Ethers				
Methyl Tertiary Butyl Ether (MTBE)	48000	0.94	0.584	8.48
Furans				
Tetrahydrofuran	miscible	N/A	0.514	1.07

^a Verschueren (1977), ^b Schwarzenbach et al. (2003), ^c Berens and Hopfenberg (1982), ^d Yaws (1995)

Table A.2. VOCs selected for this study

Compounds	Chemical Formula	Solubility (mg/l)	Molecular Diameter (nm)
Methyl Tertiary Butyl Ether (MTBE)	$\text{CH}_3\text{-O-C}(\text{CH}_3)_3$	48000	0.584
Dichloromethane (Methylenechloride)	CH_2Cl_2	20000	0.474
Trichloroethylene (TCE)	$\text{CHCl}=\text{CCl}_2$	1100	0.530
Toluene	$\text{C}_6\text{H}_5\text{-CH}_3$	515	0.561
Chlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	500	0.553

APPENDIX B

Sampling Effect Evaluation Using HYDRUS-2D

Sampling of pore water from the clay liner may affect VOC transport and change the concentration profile. To evaluate this issue, computer simulations were performed with HYDRUS-2D (Simunek et al. 1999) to evaluate how sampling might affect VOC transport. HYDRUS-2D is a software package for simulating water, heat, and solute movement in a two-dimensional variably saturated media.

An axisymmetrical rectangular geometry (75 mm (H) x 121.5 mm (V), 76 vertical columns and 121 horizontal columns) was used to simulate the column test with a 1.5 mm geomembrane overlaying a 120 mm clay liner. Saturated hydraulic conductivity of the clay was set at 5.6×10^{-9} cm/s and the dry density was set at 1.7 g/cm^3 . The van Genuchten parameter α was set to 0.55 m^{-1} and n was set to 1.11 using the pedotransfer functions in Timjum et al. (1997) and the index properties of Kamm clay. The geomembrane was simulated using a layer of very low hydraulic conductivity (5.6×10^{-13} cm/s) at the surface of the domain. For numerical stability, graduated hydraulic conductivity was applied in three layers (each 1.5 mm thick), hydraulic conductivities (from top to bottom) were set at 5.6×10^{-12} cm/s, 5.6×10^{-11} cm/s, and 5.6×10^{-10} cm/s. The top and bottom horizontal boundaries were set as constant pressure head boundaries, and the vertical sides were set as no flow boundaries (Fig. B.1). Pressure heads were set at 600 mm for the top boundary and 721.5 mm for the bottom boundary to avoid advection (the same total head at top and bottom boundary). Sampling ports were located in the clay liner at a depth of 60 mm and 90 mm on the same side of the vertical boundary. Periodic sampling was simulated as a variable flux boundary, where 50 μL of sample was extracted every two

weeks at a rate of 1 $\mu\text{L/s}$. A linear distribution of pressure head (600 mm at the top and 721.5 mm at the bottom) was used as the initial condition throughout the composite liner (i.e., no gradient in total head). For solute transport, the top boundary was set as a constant concentration boundary (100 ppm), and the bottom boundary was set as a mass conservative flux boundary at an initial concentration of 0 ppm. The solute transport initial condition was set as no solute (0 ppm) throughout the domain.

Of the VOCs used in the experiment at program, methylene chloride is the most mobile and chlorobenzene is the least mobile. Thus, simulations were conducted using transport properties for these VOCs (Table 4.2).

The Crank-Nicholson scheme was used for temporal derivatives and the Galerkin finite element was used for the spatial derivatives. The initial time step was set at 1 s, the minimum time step was set at 0.01 s, and the maximum time step was set at 10 s. Concentrations at both sampling ports with and without sampling are shown in Fig. B.2 for methylene chloride and Fig. B.3 for chlorobenzene. Concentrations with and without sampling appear the same in both sampling ports for both compounds shown in this analysis. The percent change in concentration caused by sampling is less than 1 % over an entire year in all cases.

Based on this analysis, a 50 μL was extracted on a biweekly basis. This sampling plan is expected to have negligible impact on VOC concentrations within the column.

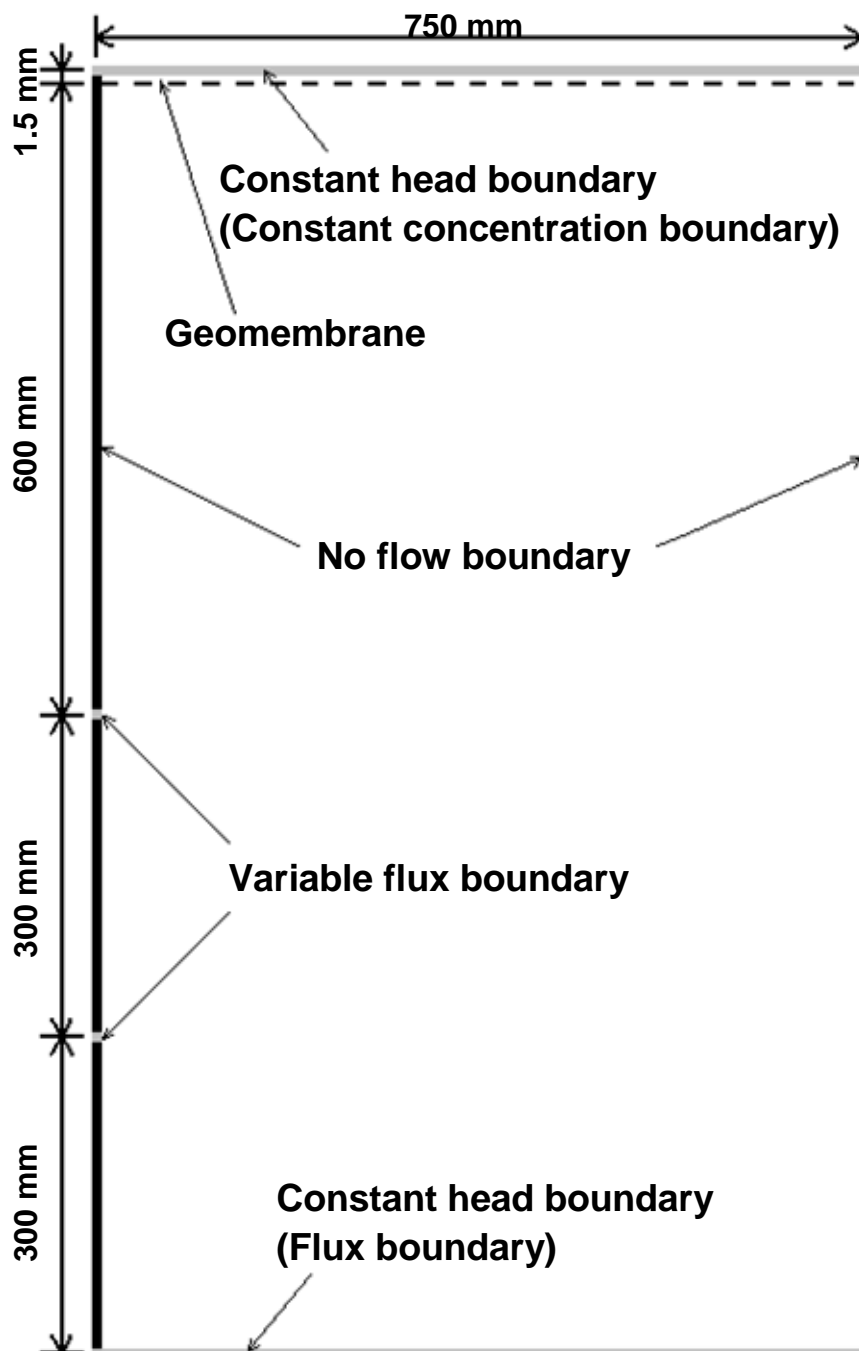


Fig. B.1. Boundary conditions applied for simulations of column experiments to evaluate impacts of pore water sampling

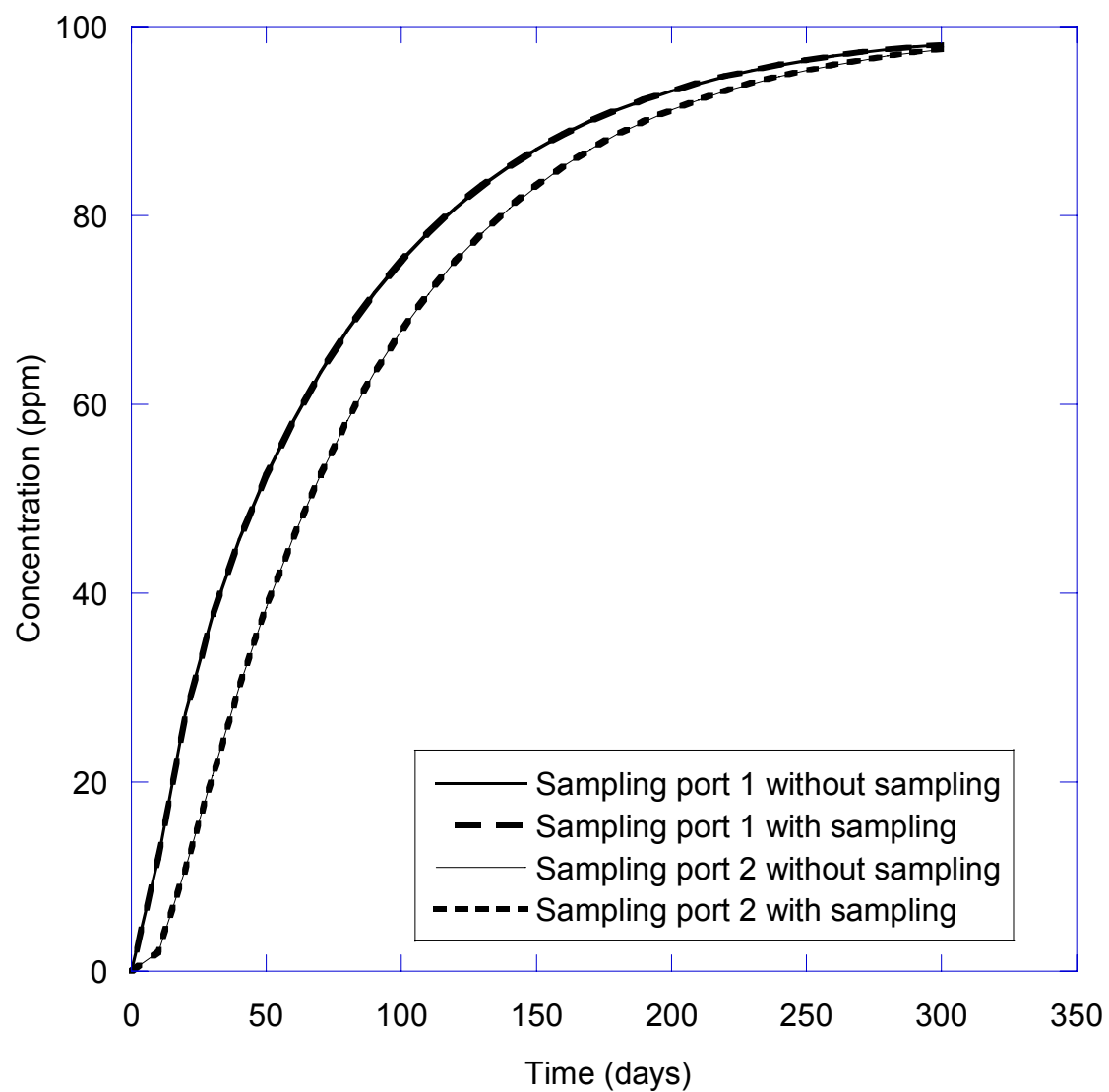


Fig. B.2. Sampling port concentration vs. time for methylene chloride

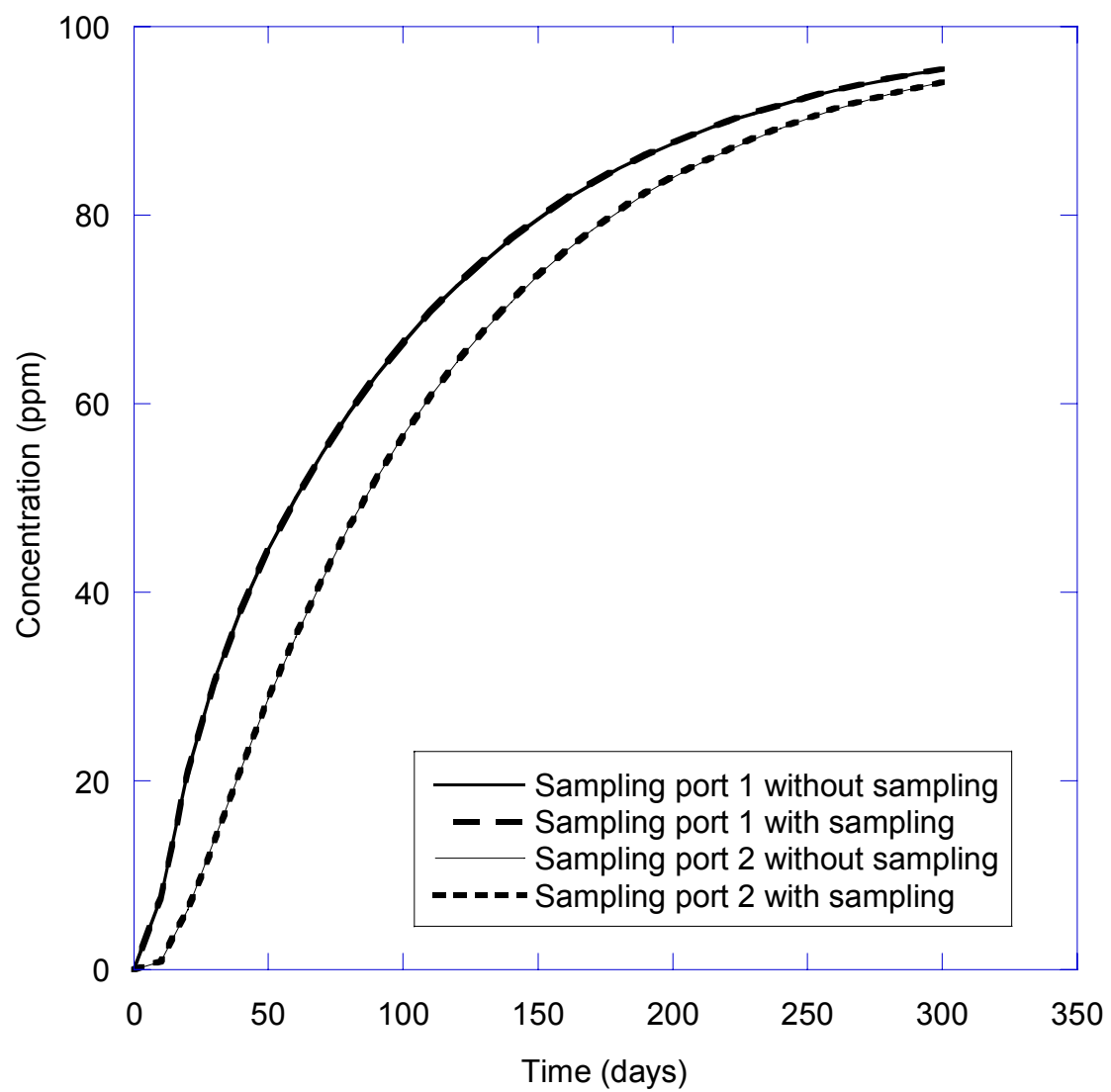


Fig. B.3. Sampling port concentration vs. time for chlorobenzene

APPENDIX C

Bacterial Viability Analysis of Flushed Influent Reservoir Solutions

Bacterial viability analysis was conducted to examine the possibility of biodegradation of organic solutes in the influent reservoir of the column tests. DAPI (4',6-diamidino-2-phenylindole) and a LIVE/DEAD[®] BacLight[™] bacterial viability kit were used for staining samples. Stained images were compared with light microscopic images.

Influent samples were collected by filtering 100 mL of flushed influent reservoir solution through a 0.2- μ m polycarbonate membrane. Flushed influent solutions were collected from composite liner diffusion columns and clay liner diffusion columns. Samples retained on the filter were transferred onto gelatin-coated slides by gently pressing the filter (retained sample side down) onto the wetted slide using 20 μ L of distilled deionized water. Slides with the filters were air dried in a dessicator, and then the filters were peeled away from the slide. Black teflon[®]-coated slides with 7-mm wells were used to produce 4 wells for replicate analysis.

For DAPI (blue-fluorescent nucleic acid stain) staining, samples were stained by adding 40 μ L of 1 ppm DAPI solution to each well and incubating the slides in the dark. Excess DAPI was washed away with distilled deionized water after 5 min. For staining using the LIVE/DEAD[®] BacLight[™] bacterial viability kit, samples were stained by adding 20 μ L of staining solution to each well and incubating in the dark. Excess staining solution was washed away with distilled deionized water after 15 min. The staining solution was made by combining equal volume of 3.34 mM SYTO[®] 9 (green-fluorescent nucleic acid stain) and 20 mM propidium iodide (red-fluorescent nucleic acid stain), and diluting the dye mixture to 0.30 %. SYTO[®] 9 and propidium iodide differ both in

their spectral characteristics and in their ability to penetrate healthy bacterial cells. SYTO[®] 9, when used alone, labels all bacteria with intact and damaged membranes. In contrast, propidium iodide penetrates only bacteria with damaged membranes, causing a reduction in SYTO[®] 9 stain fluorescence when both dyes are present. Thus, with an appropriate mixture of SYTO[®] 9 and propidium iodide stains, bacteria with intact cell membranes (considered alive) stain fluorescent green, whereas bacteria with damaged membranes (considered dead) stain fluorescent red.

Stained samples were viewed on a Zeiss Axioplan 2 epifluorescence microscope, which can also function as a light microscope. The excitation/emission maxima for the dyes were 360/400 nm for DAPI stain, 480/500 nm for SYTO[®] 9 stain, and 490/635 nm for propidium iodide stain. Chroma standard filter sets from Chroma Technology Corp. of Rockingham, Vermont (31000v2 for DAPI, 31001 for SYTO[®] 9, and 31002 for propidium iodide) were used for visualizing stained samples. A phase-contrast microscope was used for light microscopic images to enhance the boundary of each object. Images were captured with an Olympus DP70 microscope digital camera.

DAPI staining images are shown in Fig. C.1. Blue stains were rarely found. Moreover, when blue stains were present in the blue-fluorescent microscopic image, objects were not found in the same location on the light microscopic image. The results were inconclusive; thus LIVE/DEAD[®] staining was conducted.

LIVE/DEAD[®] staining images are shown in Fig. C.2. The population of green stains was small, but various sizes of organisms were found. However, all the organisms were scored dead (all green stains were also stained red). Therefore, the bacterial viability analysis indicated no live bacteria were present, suggesting that biodegradation of organic compounds is not occurring in the influent.

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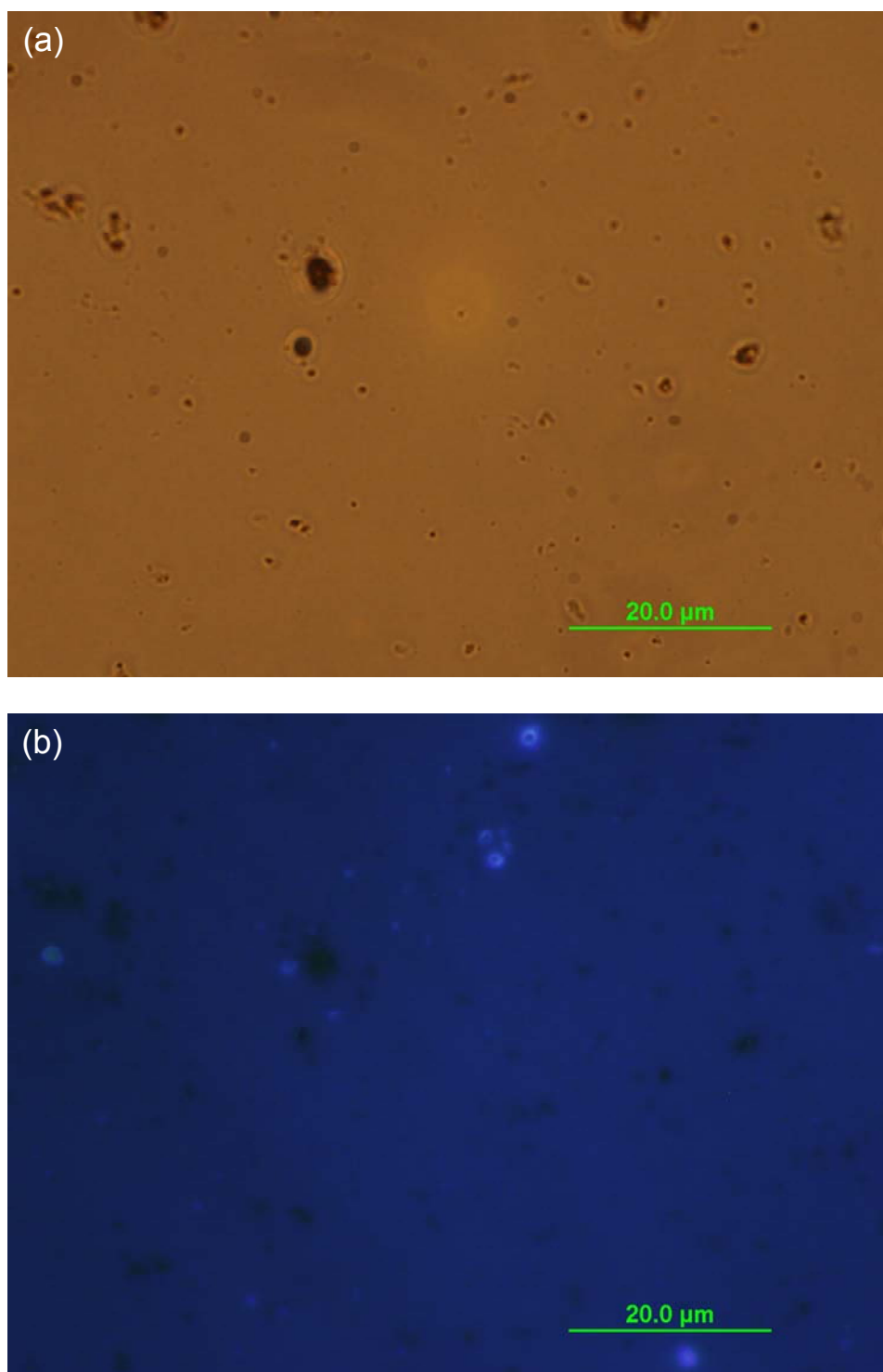


Fig. C.1. DAPI staining (a) light microscopic image, (b) blue-fluorescent microscopic image

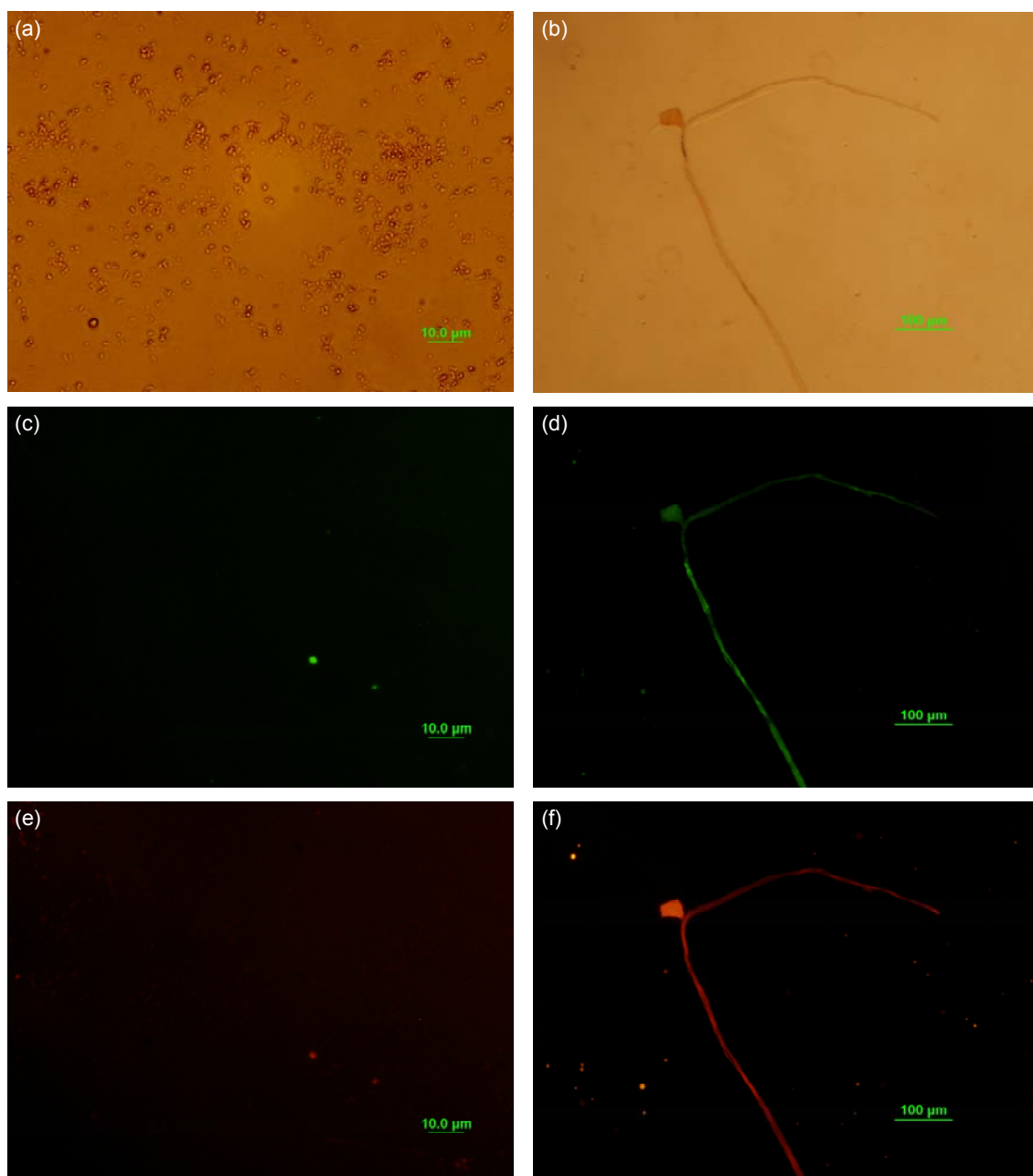


Fig. C.2. LIVE/DEAD staining (a) (b) light microscopic image, (c) (d) green-fluorescent microscopic image, and (e) (f) red-fluorescent microscopic image