Temperature effect on diffusive transport of volatile organic compounds through a composite liner system

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ABSTRACT: In municipal solid waste (MSW) landfills, degradation of organic wastes due to microbial activity generates heat and a subsequent increase in temperature within the landfill body, which induces critical concerns to manage the landfill. In this study, partition and diffusion coefficients for selected VOCs such as phenol, methylene chloride (MC), toluene (TOL), and TCE, which have different chemical characteristics, were measured for a high density poly-ethylene (HDPE) geomembrane (GM) using kinetic batch tests at 23 °C (room temperature), 38 °C (intermediate temperature), and 75 °C (high temperature). Diffusive transport of MC and TOL at different temperatures through RCRA (60 cm-CCL with GM) profile of the liner was investigated by using one-dimensional finite difference modeling. The effect of transient temperature in the system was considered by using a constitutive equation with variables including the chemical properties to predict transport parameters. For the conditions examined, at high temperature (75 °C), increases contaminant concentrations by approximately 75-85% compared at lower temperature (23 °C) at 100 years. Diffusive transport of TOL is less sensitive compared to that of MC because of the lower polarity and molecular activity to HDPE.

Keywords: temperature; volatile organic compound; transport parameters; composite barrier; geomembrane.

1 INTRODUCTION

In municipal solid waste (MSW) landfills, degradation of organic wastes due to aerobic and anaerobic microbial activity generates heat and a subsequent increase in temperature within the landfill body. Temperatures on the order of 50 °C are common and temperatures in excess of 100 °C have been reported (Rowe and Islam, 2009). The highest temperatures are typically in the main body of waste, gradually decreasing towards the edge and bottom of the waste mass (Rowe 2005). The aerobic or anaerobic decomposition of waste induces chemical reactions, which is a major component of solid waste (e.g., glucose) and is shown as:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 1770 \text{ kJ/mol} (aerobic)$$
 (1)

$$C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2 + 100 \text{ kJ/mol} (anaerobic)$$
 (2)

Elevated temperatures in a landfill can affect transport of organic contaminants [i.e., volatile organic compounds (VOCs)] because diffusive transport of VOCs through geomembranes (GMs) used in composite liners increases with increasing temperature due to increased molecular activity (Crank and Park, 1968; Aminabhavi and Naik, 1998; McWatters and Rowe, 2015). Sorption, diffusion, and permeation of contaminants through a GM are altered by temperature changes. For example, diffusion, permeation, and sorption coefficients increase with increasing temperature (Crank and Park, 1968; Aminabhavi and Naik, 1998; Rowe et al., 2005; McWatters and Rowe, 2015). Moreover, the transport behavior of VOCs varies with the chemical characteristics as well as increased molecular activity (Sangam and Rowe, 2001; Edil, 2007; Eun et al., 2014, 2017, 2018). The chemical characteristics such as molecular weight, solubility, and hydrophobicity might be influenced by temperature, and interrelate to the transport behavior. Howev-

er, there is limited studies to investigate the transport behavior combining chemical characteristics of VOCs with elevated temperatures.

In this study, partition and diffusion coefficients for selected VOCs such as phenol, methylene chloride (MC), toluene (TOL), and TCE, which have different chemical characteristics, were measured for a high density polyethylene (HDPE) geomembrane using kinetic batch tests at 23 °C (room temperature), 38 °C (intermediate temperature), and 75 °C (high temperature). The transport parameters obtained at different temperatures were evaluated based on several chemical characteristics of the VOCs. Numerical modeling of diffusive transport coupled with three temperatures and chemical types for selected VOCs (i.e., methylene chloride, toluene) through field profiles of a composite liner including 0.6 m-compacted clay liner (CCL) and GM was performed to compare the transport behavior and flux.

2 MATERIALS AND METHODS

2.1 Geomembranes

A black textured 1.5 mm-thick HDPE GM was used for this study (Polyflex, Inc., Grand Prairie, Texas). This geomembrane meets the geomembrane requirements in Wisconsin for municipal solid waste landfills (Department of Natural Resources, 2007) and can be considered a typical HDPE GM for landfill liners in North America. Specimens of GM were cut from a large HDPE GM sheet, washed with distilled and deionized (DDI) water, and placed in a desiccator for 48 h before use in the experiments.

2.2 Volatile organic compounds

General properties of the organic compounds used in the study are in Table 1. Methylene chloride (MC), trichloroethylene (TCE), toluene (TOL), and phenol were selected as representative compounds typically found in lysimeters beneath MSW landfills in Wisconsin (Klett et al. 2005). These VOCs have been used extensively in previous studies (Eun et al., 2014, 2017, 2018). Phenol was used due its similarity with EVOH, which might yield greater partitioning and diffusion. Phenol has a hydroxyl group (-OH) attached to an unsaturated aromatic hydrocarbon.

The VOC and phenol solutions were prepared by filling a 1-L flask with distilled and deionized (DDI) water (Eun et al., 2014, 2017, 2018). Sodium azide (0.05%) was added to prevent microbial activity. The flask was filled completely to minimize loss of VOCs in the headspace. Once filled, the desired concentration of VOC was prepared based on weight-volume calculations. Liquid VOC was injected into the water using a 100 mL gas tight syringe. When using multiple solutes, the compounds were injected in order of decreasing density. VOC concentrations were measured using a Shimadzu GC-2010 gas chromatograph (GC) equipped with an auto sampler, flame ionization detector (FID), and Restek RTX-624 column.

Compound	MC	TCE	TOL	Phenol
Chemical formula	CH_2Cl_2	CHCl=CCl ₂	C ₆ H ₅ -CH ₃	C ₆ H ₅ OH
Type of compound	Alkane	Alkene	Arene	AOC
Molecular weight (g/mol)	84.93	131.39	92.14	94.11
Density (g/mL)	1.33	1.46	0.867	1.07
log K _{ow}	1.31	2.42	2.69	1.48
Solubility (mg/L)	20000	1100	515	82800
Vapor pressure (kPa)	57.5	10.0	3.72	0.05
Dielectric constant	8.9	3.4	2.4	4.3
Melting point (°C)	-97.2	-84.7	-94.95	42.7
Boiling point (°C)	40	87.21	110.63	181.7

Table 1 Properties of VOCs used in experiments.

(K_{ow}: Partition coefficient between octanol and water, AHC: Aromatic Organic Compound)

2.3 Kinetic batch tests

Kinetic batch tests were conducted using the method in Eun et al. (2017, 2018) using samples of conventional 1.5-mm HDPE GM sheet to obtain the diffusion coefficient. Membrane samples, cut into strips (17 mm \times 80 mm) similar to those in the equilibrium batch tests, were placed in 40-mL amber glass vials. Solution with 100 mg/L each of the four compounds was added to fill the vial, which was sealed with a screw cap and PTFE-coated septum. Control tests were also conducted without GM specimens. The vials were prepared and handled using the same method employed for the batch tests. Duplicate vials were prepared (including controls) for periodic decommissioning during the experiment. Samples were decommissioned and sampled after 1, 2, 3, 5, 7, and 9 d from the start of the test. The supernatant was transferred to auto-sampler vials using a glass syringe without opening the cap of the vial and was then analyzed by GC using the aforementioned methods. Temperature was maintained using insulated vials placed on the heating plate and stirrer shown in Fig. 1. Concentrations were adjusted for losses using the loss data from the controls as done for the equilibrium batch tests. Concentration data were analyzed assuming a planar sheet of geomembrane suspended in a well-stirred solution of fixed volume. This system is described by (Crank 1975) as

$$\frac{C_t}{C_0} = \exp\left(\frac{D_g t(K_g)^2}{A^2}\right) \operatorname{erfc}\left(\frac{D_g t(K_g)^2}{A^2}\right)^{0.5}$$
(3)

where C_t is the concentration of the VOC in the solution $[M/L^3]$ at time t [T], C_0 is the initial concentration of the organic compound in the solution $[M/L^3]$, D_g is the diffusion coefficient $[L^2/T]$ in the GM, K_g is the partition coefficient (dimensionless), and A is the half thickness of the solution in contact with both sides of the GM [L], which is calculated by dividing the volume of the solution by the area of the GM. Eq. 3 was fit to the data using non-linear least-squares regression with Microsoft Excel Solver with the generalized reduced gradient algorithm.



Figure 1. Experimental setup of batch test at elevated temperatures: (a) Photo; (b) a cross-sectional schematics.

3 RESULT AND DISCUSSIONS

3.1 Results of kinetic batch test

Figure 2 shows a comparison of transport parameters (i.e., partition and diffusion coefficient) obtained from kinetic batch test at different temperatures. For all compounds, the partition and diffusion coefficients increase systematically with increasing temperature. The partition coefficients (K_g) of more polar and non-polar VOCs were ranged from 4 to 6 L/kg and 67 L/kg to 86 L/kg, respectively at room temperatures (23 °C). The partition coefficients of more polar VOCs (i.e., MC, Phenol) for HDPE GMs were 20 to 25 times lower compared to those of non-polar VOCs (i.e., TCE, TOL). Furthermore, the increment of the partition coefficients of the polar VOCs is meaningfully smaller with increasing temperature than those of the non-polar VOCs. The molecular activity of the polar VOCs is less sensitive with increasing temperature because the molecular attraction of more polar VOCs would be greater than that of non-polar VOCs due to the high polarity and dielectric constant.

The diffusion coefficients (D_g) of more polar VOCs such as MC and Phenol for HDPE GMs were 30% to 40% higher compared to those of non-polar VOCs such as TCE and TOL, which might be distributed to the higher partition coefficients of more polar VOCs. The diffusion coefficients (D_g) of more polar and non-polar VOCs were ranged from 0.7 to 1.0 cm²/s×10⁻⁸ and 0.4 to 0.5 cm²/s×10⁻⁸, respectively at room temperatures (23 °C). The diffusion coefficients for HDPE increased by average 22% by increasing the temperature from 23 °C to 35 °C and by average 53% by increasing from 23 °C to 75 °C. The increment of the diffusion coefficient of the polar VOCs is remarkably higher with increasing temperature due to the lower affinity to HDPE.



Figure 2. Comparison of partition and diffusion coefficient at 23 °C, 38 °C, and 75 °C from batch test.

3.2 Effect of temperature and chemical properties on partition coefficients

Figure 3 shows the relationship between partition coefficient and selected chemical properties such as octanol-water partition coefficient (log K_{ow}) and water solubility (S) at different temperatures described by the Arrhenius equation. The Arrhenius equation is a formula for the temperature dependence of reaction rates. The effect of temperature on a transport parameter is described by the Arrhenius equation as:

$$X = X_0 \exp\left(-\frac{E}{RT}\right) \tag{4}$$

where E is activation energy, R is university gas constant, and T is absolute temperature (K). The coefficient can be obtained from a least-squares fit of data to the Eq. (4). Fig. 3(a) shows the distribution of K_g with elevation of temperature and types of VOCs. Depending on the polarity of VOCs and increased molecular activity due to temperature, the partition coefficients varied.



Figure 3. Variation of partition coefficients with temperature and chemical properties.

By using the Arrhenius equation, the relationships between K_g and the chemical properties were normalized and presented with high R² values (> 97.3). As the octanol-water partition coefficient increased, the partition coefficients increased linearly. However, as the water solubility increased, the partition coefficients decreased linearly. The derived equations were used for numerical simulation of VOC transport through composite liner.

3.3 Effect of temperature and chemical properties on diffusion coefficients

Similar to the partition coefficient (Fig. 3), Figure 4 shows the relationship between diffusion coefficient and selected chemical properties such as octanol water partition coefficient (log K_{ow}) and molecular diameter (d_m) at different temperatures described by the Eq. (4). Depending on the polarity of VOCs, the diffusion coefficients varied. By using the Eq. (4), the relationship between D_g and chemical properties was normalized and presented with higher R² values (>87.0). As the octanol-water partition coefficient and molecular diameter increased, the diffusion coefficients decreased linearly. The derived equations were used for numerical simulation of VOC transport through composite liner.



Figure 4. Variation of diffusion coefficients with temperature and chemical properties.

3.4 Breakthrough curve of voc with temperature

A numerical simulation with finite difference method (FDM) was used to investigate the relative migration of VOCs with HDPE GMs for composite liners having thickness comparable with those found in MSW landfills and to make predictions regarding the relative rates of transport in an actual composite liner with a HDPE GM. The one-dimensional (1-D) contaminant transport of a nondecaying VOC through a composite liner can be described by a four-step process (Foose et al., 2002): (1) partitioning between the leachate and GM; (2) diffusion through the GM; (3) partitioning out of the GM and into the pore water in the CCL; and (4) diffusion through the CCL (Foose et al. 2001). Partitioning into the soil solids or organic matter may occur during diffusion through the CCL. The Crank-Nicolson interpolation was used to solve the transport equations in Microsoft Excel spreadsheets. Liner configurations stipulated in Subtitle D of the Resource Conservation and Recovery Act (RCRA 2002) (GM over 0.6 m of compacted clay) were simulated. Subgrade beneath the compacted clay liner was assumed to consist of 5 m of fine-grained soil. Temperature effects on transport parameters of HDPE GMs were considered by using the derived equations. Temperature effects on transport parameters of CCL were considered from literatures (Kim et al., 2003; Rowe et al., 2005; Eun et al., 2017).

Lower concentrations for both MC and TOL are predicted for the RCRA Subtitle D at lower temperature relative to the composite liners at high temperature. For the conditions examined, at high temperature (75 °C), increases contaminant concentrations by approximately 75-85% compared at lower temperature (23 °C) at 100 years. The difference is more significant for MC because the molecular interaction of polar VOCs would be higher than that of non-polar VOCs due to high polarity. In other words, diffusive transport of TOL is less sensitive compared to that of MC because of the lower polarity and molecular activity to HDPE.



Figure 5. Breakthrough curves of MC and TOL with different temperatures at 23 °C, 38 °C, and 75 °C: (a) MC; (b) TOL.

4 CONCLUSSIONS

In this study, diffusive transport coupled with temperature and chemical change for selected volatile organic compounds (VOCs) (i.e., methylene chloride, toluene) through field profiles of a composite liner including compacted clay liner (CCL) and geomembrane (GM) was investigated. One-dimensional finite difference modeling employing with transport parameters obtained from batch test was conducted for RCRA (60 cm-CCL with GM) profile of the liner. The effect of transient temperature in the system was considered by using a constitutive equation with variables including the chemical properties (i.e., octanolwater partition coefficient, aqueous solubility, and molecular diameter) to predict transport parameters (i.e., partition and diffusion coefficient) at 23 °C (room temperature), 35 °C (intermediate temperature), and 75 °C (high temperature). The chemical characteristics of each material in the co-extruded EVOH GM showed a strong linear relationship with the partition and diffusion coefficient on a log-log scale. The diffusion transport increased significantly as the temperature increased. However, temperature sensitivity of diffusive transport varies depending on the chemical properties. Lower concentrations for both MC and TOL are predicted for the RCRA Subtitle D at lower temperature relative to the composite liners at high temperature. For the conditions examined, at high temperature (75 °C), increases contaminant concentrations by approximately 75-85% compared at lower temperature (23 °C) at 100 years. Diffusive transport of TOL is less sensitive compared to that of MC because of the lower polarity and molecular activity to HDPE.

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