

DIFFUSIVE TRANSPORT OF BISPHENOL-A THROUGH AN HDPE GEOMEMBRANE

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ABSTRACT

Bisphenol A (BPA) is used as a monomer in the production of polycarbonate plastics and epoxy resins which are used in many consumer products. Concentration of BPA in landfill leachate is reported to be up to 17,200 µg/L with an average of 1,330 µg/L. In this study the diffusion of BPA through 0.5 mm high-density polyethylene (HDPE) geomembrane is discussed. The partitioning coefficients for BPA and an HDPE geomembrane is presented based on a sorption tests that is described.

RÉSUMÉ

Le Bisphénol A (BPA) est utilisé comme monomère dans la production des plastiques polycarbonates et des résines époxy qui sont utilisées dans beaucoup de produits de consommation. La concentration de BPA dans les lixiviats de décharge est signalée d'être au maximum 17.200 ug/L avec une moyenne de 1.330 ug/L. Dans cette étude, la diffusion de BPA à travers d'une géomembrane de polyéthylène haute densité (HDPE) de 0.5 mm d'épaisseur est examinée. Les coefficients de pénétration de la géomembrane sont estimés en conformité avec les résultats de ces tests.

1 INTRODUCTION

High density polyethylene (HDPE) geomembranes have been widely used as a key component of composite liners on the base of landfills because of their excellent resistance to a wide range of chemicals (Rowe et al. 2004). Diffusive properties of various aromatic and chlorinated organic constituents of landfill leachate for HDPE geomembranes have been studied (Park and Nibras 1993, Aminabhavi and Naik 1999, Sangam and Rowe 2001, Rowe et al. 2004, Joo et al. 2005, Islam and Rowe 2009). However there is no data in the literature for diffusion of contaminants of emerging concerns, such as BPA, which is found in landfill leachate in different parts of the world (Yashuhara et al. 1997; Yashuhara et al. 1999; Yamamoto et al. 2001; Schwarzbauer et al. 2002; Urase and Miyashita 2003; Asakura et al. 2004; Lyko et al. 2004; Li et al. 2006; Kurata et al. 2008; Tueten et al. 2009).

Bisphenol A (BPA) is a chemical produced in large quantities for use primarily in the production of polycarbonate (PC) plastics and epoxy resins.

Polycarbonate (PC) is widely used in food contact materials, such as infant feeding bottles, microwave ovenware, food containers and water bottles (FAO/WHO 2010). Polycarbonate is typically clear and hard and marked with the recycle symbol "7" or may contain the letters "PC" near the recycle symbol (NTP 2008).

Epoxy resins are used as protective linings for a variety of canned foods and beverages and as a coating on metal lids for glass jars and bottles (FAO/WHO 2010).

Most of BPA uses result in the exposure of consumers, including infants, to BPA through their diet (FAO/WHO 2010). Other sources of human exposure have also been proposed, for example some polymers used in dental sealants or composites contain bisphenol A-derived materials (NTP 2008) or BPA in air and dust (FAO/WHO 2010).

In 2004, the estimated production of bisphenol A in the United States was approximately 2.3 billion pounds, most of which was used in polycarbonate plastics and resins (NTP 2008). The NTP has some concern for effects on the brain, behaviour, and prostate gland in fetuses, infants, and children at current human exposures to bisphenol A (NTP 2008).

The objective of this paper is to discuss techniques that are proposed for assessing the diffusion characteristics of HDPE geomembranes with respect to BPA dissolved in water.

2 MATERIAL AND METHODS

2.1 HDPE geomembrane

In this study 0.5 mm high density polyethylene (HDPE) geomembrane (manufactured by Solmax International Inc., Quebec) is examined.

2.2 Bisphenol-A (BPA)

The 99% pure bisphenol-A in the form of crystals purchased from Sigma-Aldrich. The chemical structure of BPA is shown in Figure 1. To make standard solutions, 50 mg of BPA is solved in 50mL methylene chloride (DCM) to get a 1000ppm standard. The same solution is made in methanol to be used as spike. These standards are diluted to 2000 ppb, 1000 ppb, 500 ppb, 200 ppb, to get a standard calibration curve.

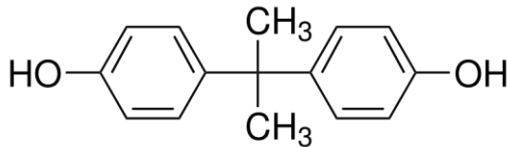


Figure 1. Chemical structure of Bisphenol A (C₁₅H₁₆O₂) (NTP 2008)

BPA is reported to have moderate water solubility at room temperature. The reported solubility of BPA in water from different references range from 120 to 380 ppm (Staples et al. 1998; Li et al. 2007)

3 BPA IN LANDFILL LEACHATE

Data from nearly one hundred municipal solid waste sites in different parts of the world is reviewed and concentrations of BPA have been reported ranging from 0.01 ppb (Kurata et al. 2008) to 8400 ppb (Urase and Miyashita 2003). The concentration in BPA in a hazardous waste landfill has been reported up to 17200 ppb (Yamamoto et al. 2001). A summary of BPA concentrations observed in landfill leachate is presented in Table 1.

4 EXTRACTION AND ANALYSIS

The extraction method for BPA is adopted from Yamamoto and Yasuhara (1999), Li et al. (2001) and Badham et al. (2010). The procedure is as follows:

- Add 50 mL water and 5 g sodium chloride to separatory funnel
- Acidify with hydrochloric acid (pH<2)
- Add 1 mL sample from the test cell
- Add 25 mL of DCM, shake separatory funnel for 5 min, drain DCM to a round-bottom flask through anhydrous sodium sulphate and filter paper
- Rinse sodium sulphate with DCM
- Extract with 25 ml DCM 2 more times and rinse sodium sulphate with DCM after each extraction
- Concentrate extract to 10 mL with rotary evaporator
- Sample 100 uL of the 10 mL sample and bring it to dryness under a stream of nitrogen gas
- Add 100 uL hexane to the residue
- Derivatize the sample with 100 uL Tri-Sil reagent

- Analyse the sample by GC-MS (GC, Varian 4000 MS/MS detector and Varian MS workstation V.6.6 software)

Table 1. BPA concentration in landfill leachate (ug/L)

Reference	Location	Min ppb	Max ppb
Yashuhara et al. (1997)	Japan	0.15	12.3
Yashuhara et al.(1999)	Japan	6.32	2980
Yamamoto et al.(2001)	Japan	1.3	17200
Urase and Miyashita(2003)	Japan	26	8400
Asakura et al.(2004)	Japan	0.07	228
Lyko et al. (2004)	Germany	800	5800
Li et al. (2006)	China	13	2923
Kurata et al. (2008)	Japan	0.01	3600
Tueten et al.(2009)	India, Japan, SE Asia	0.18	4300
Environment Canada (personal contact, 2009)	Canada	0.2	1940

5 SORPTION TEST

Sorption tests are performed in duplicate or triplicate with two control cells. They involve:

- recording the initial masses of the approximately 1 cm x 8 cm geomembrane samples (the average of five weighings),
- adding 40 mL Distilled Deionized (DD) water to a 40 mL glass vial and spiking with 200 uL of 1000 ppm BPA in methanol,
- tumbling the bottles end over end for 10 min, then adding the pre-weighed geomembrane to the bottle which was then placed back into the tumbler,
- removing GMB and analyzing a 1 mL sample from the bottle contents after the determined test duration, and
- repeating the test for different time durations to establish the time when equilibrium is achieved (i.e., when there is no significant change in concentration with longer immersion time).

For the sorption tests, the partitioning coefficient was calculated based on contaminant mass balance at equilibrium using the approach described by McWatters and Rowe (2009) as repeated below:

$$M_{s0} = M_{sF} + M_{gF}, \quad [1]$$

where M_{s0} is the initial mass of the contaminant in solution [M]; M_{sF} is the final mass of the contaminant in aqueous

solution [M] and M_{gF} is the mass contained in the geomembrane [M]. When Equation 1 is rearranged in terms of concentrations and volumes, it becomes:

$$c_{f0}V_{f0} = c_{fF}V_{fF} + \frac{M_g}{\rho_g}c_{gF} \quad [2]$$

where c_{f0} is the initial contaminant concentration in solution [ML^{-3}]; V_{f0} is the initial solution volume [L^3]; c_{fF} is the final contaminant concentration in solution [ML^{-3}]; V_{fF} is the final solution volume [L^3]; M_g is the initial mass of the geomembrane sample [M]; ρ_g is the geomembrane density [ML^{-3}] and c_{gF} is the final concentration of the contaminant in the geomembrane at equilibrium [ML^{-3}]. The concentration of contaminant in the GM and solution at equilibrium can be written as follows:

$$c_{gF} = S_{gf}c_{fF} \quad [3]$$

where S_{gf} is the partitioning coefficient.

The partitioning coefficient can be calculated by substituting Equation 2 into Equation 3 to give:

$$S_{gf} = \frac{[c_{f0}V_{f0} - c_{fF}V_{fF}]\rho_g}{M_g c_{fF}} \quad [4]$$

6 DIFFUSION TEST

The diffusion tests are conducted in duplicate with a blank and a control cells using a stainless steel double compartment cell (source and receptor) separated by a geomembrane sample (Figure 2). The receptor cell is filled with Distilled Deionized (DD) water. The source cell is filled with a dilute aqueous chemical solution at concentrations low enough to be less than the solubility limit and high enough to be detectable in the typical sample volume (4 mL of 1000 ppm BPA in methanol in 475 mL DD water which is equal to 8.4 ppm). The source is sampled 10 minutes after spiking to measure the real initial concentration in the source and to compare it with calculated initial concentration. Samples are taken from the source and receptor at regular time intervals. The concentrations in the source and receptor will be plotted as normalized concentrations relative to the initial concentration in the source.

Aqueous phase transport through geomembranes occurs in three steps (Sangam and Rowe 2001): adsorption, diffusion and desorption. Initially, the contaminant partitions between the source medium and adjacent surface of the geomembrane. Then the compound diffuses through the geomembrane driven by chemical potential. Finally, the compound partitions between the outer geomembrane surface and the

receiving medium. After a period of time, equilibrium is reached between the concentration in the geomembrane and the concentration in either the source or receptor media. The equilibrium between geomembrane and the source medium can be related by an analogy (Equation 3) to Henry's law.

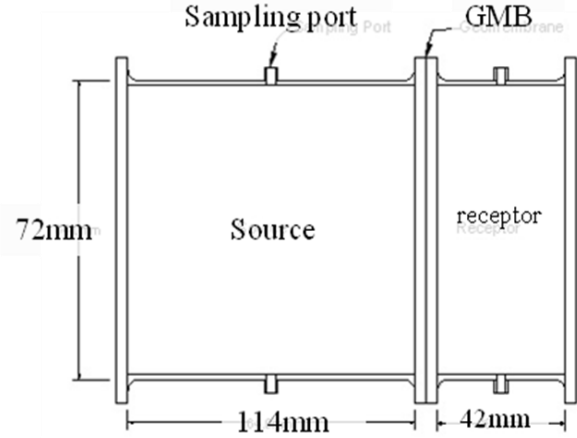


Figure 2. Schematic of a diffusion cell (after McWatters and Rowe 2009)

In the second step, the diffusion of the contaminant through the geomembrane is described by Fick's first law:

$$f = -D_g \frac{dc_g}{dz} \quad [5]$$

where f is the mass flux [$ML^{-2}T^{-1}$]. The diffusion coefficient, D_g [L^2T^{-1}] is specific to the geomembrane and contaminant of interest. c_g is the concentration of the compound in the geomembrane [ML^{-3}] and z represents the distance parallel to the direction of transport. When the diffusion coefficient is constant, the change in contaminant concentration in the GM with time t , is expressed by Fick's second law:

$$\frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial z^2} \quad [6]$$

The final step is also described by Henry's law:

$$c'_{gF} = S'_{gf}c_{fF} \quad [7]$$

When the source and receptor fluid/solvent are essentially the same, the partitioning coefficient into the geomembrane can be assumed to be equal to the

partitioning coefficient out of the geomembrane ($S_{gf}=S_{gf}$) (Sangam 2001).

The concentration of contaminant inside the geomembrane is very difficult to measure; therefore, the change in concentration in the fluid on either side of geomembrane is measured and parameters are deduced based on measured mass transport from the source to the receptor. The mass flux from the fluid on one side to that on the other side of the geomembrane when the source and receptor fluids are alike is given by rearranging Equations 1 and 5:

$$f = -D_g \frac{dc_g}{dz} = -S_{gf} D_g \frac{dc_f}{dz} = -P_g \frac{dc_f}{dz} \quad [8]$$

Where the permeation coefficient, P_g [L^2T^{-1}] represents the mass transfer across the geomembrane (Sangam and Rowe 2001) and is given by:

$$P_g = S_{gf} D_g \quad [9]$$

7 MODELING DIFUSSION PARAMETERS

The diffusion experiment is a closed system, in which there is a finite mass boundary condition describing the source. The mass of contaminants in the source at a given time is equal to the initial mass minus the mass that has partitioned/diffused into the geomembrane. The equation for the concentration in the source at time t is written as:

$$c_{ss}(t) = c_{s0} - \frac{1}{H_{ss}} \int_0^t f_{ss}(\tau) d\tau \quad [10]$$

where the integral gives to total mass that has diffused from the source fluid into the geomembrane per unit area up to some time t , $c_{ss}(t)$ is the contaminant concentration in the source at time t [ML^{-3}]; c_{s0} is the initial contaminant concentration in the source [ML^{-3}]; H_{ss} is the reference height of the source reservoir [L] and $f_{ss}(\tau)$ is the mass flux of contaminant into the geomembrane with time τ [$ML^{-2}T^{-1}$]. The decrease in contaminant concentrations in the source are modeled using Equation 10. To model the increase in concentrations in the receptor as contaminants partitions out of the geomembrane, a similar equation is used:

$$c_{rs}(t) = c_{r0} + \frac{1}{H_{rs}} \int_0^t f_{rs}(\tau) d\tau \quad [11]$$

where the integral gives to total mass that has diffused out of the geomembrane into the receptor fluid per unit area up to some time t , $c_{rs}(t)$ is the contaminant concentration in the receptor at time t [ML^{-3}]; c_{r0} is the initial contaminant concentration in the receptor [ML^{-3}]; H_{rs} is the reference height of the receptor solution [L] and $f_{rs}(\tau)$ is the mass flux of contaminant out of the geomembrane with time τ [$ML^{-2}T^{-1}$].

Both the decrease in contaminant concentrations in the source and the increase in concentrations in the receptor as contaminants partition out of the geomembrane are modeled using finite boundary equations that account for the mass flux into or out of the geomembrane with time. The diffusion (D_g), partition (S_{gf}) and permeation (P_g) coefficients of contaminants through HDPE geomembranes in the aqueous phase were inferred by fitting theoretical results of these diffusion equations to the source and receptor concentration data from diffusion tests. The boundary conditions given by Equations 10 and 11 were used. Analysis of experimental data was conducted using the finite layer analysis program POLLUTE[®] v.7 (Rowe and Booker 2004).

8 RESULTS AND DISCUSSIONS

24-hour sorption test were performed in triplicate and it showed no sorption of BPA to geomembrane after 24hr. Longer sorption tests are being performed.

For diffusion test, four cells (two diffusion cells, one blank cell and one control cell) are set up. They were sampled 10 minutes after spiking and also after 24 hours and 48 hours. The analyses of the samples still have not shown any decrease in the source concentration or increase in the receptor concentration. The sampling will be continued until equilibrium is reached between the source and the receptor. The final results will be presented in the oral presentation...

9 DISCUSSIONS AND CONCLUSIONS

The effectiveness of HDPE geomembranes as barriers to the diffusion of BPA will be studied.

The partitioning and diffusion coefficients for an HDPE geomembrane and BPA will be estimated for the first time using the techniques described in this paper. Additional testing will be conducted to improve the methods and obtain more data. The results from this study can be used to predict the rates of diffusion of BPA through HDPE geomembranes and base on them propose recommendations to improve barrier system design (as needed) for BPA.

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