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Partitioning and diffusion of PBDEs through an HDPE geomembrane

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ABSTRACT

Polybrominated diphenyl ether (PBDE) has been measured in MSW landfill leachate and its migration through a modern landfill liner has not been investigated previously. To assure environmental protection, it is important to evaluate the efficacy of landfill liners for controlling the release of PBDE to the environment to a negligible level. The partitioning and diffusion of a commercial mixture of PBDEs (DE-71: predominantly containing six congeners) with respect to a high-density polyethylene (HDPE) geomembrane is examined. The results show that the partitioning coefficients of the six congeners in this mixture range from 700,000 to 7,500,000 and the diffusion coefficients range from 1.3 to 6.0 $\times 10^{-15}$ m^2/s depending on the congener. This combination of very high partitioning coefficients and very low diffusion coefficients suggest that a well constructed HDPE geomembrane liner will be an extremely effective barrier for PBDEs with respect to diffusion from a municipal solid waste landfill, as illustrated by an example. The results for pure diffusion scenario showed that the congeners investigated meet the guidelines by at least a factor of three for an effective geomembrane liner where diffusion is the controlling transport mechanism.

1. Introduction

Many modern engineered landfills have a composite liner as part of a barrier system to contain contaminants and prevent their migration to the surrounding environment at a concentration that could have health or environmental impacts. High density polyethylene (HDPE) geomembranes have been commonly used in composite liners at the bottom of modern municipal solid waste (MSW) landfills and they have shown excellent performance in containing a broad range of chemicals (Rowe et al., 2004).

Polybrominated diphenyl ethers (PBDEs) are organobromine compounds ($C_{12}H_{(10-x)}Br_xO$ (x = 1, 2, …, 10) (Fig. 1a). Homolog groups (mono through deca) refer to the number of bromine atoms (represented by 'x' in the formula) replacing hydrogen on the diphenyl structure. There are 209 PBDE congeners depending on the number and location of bromines. Table 1 summarizes the PBDEs examined in this study. PBDEs have been widely used as flame retardants in products that are prone to ignition in fire situations (e.g., furniture) or items in which a fire can start (e.g., electrical devices). PBDEs allow more time either to extinguish the fire and/or to escape by slowing down ignition and fire growth (U.S. EPA, 2006). The release of PBDEs to the environment can arise from (i) the manufacturing of PBDEs, (ii) the manufacture, aging and wear of products containing PBDEs like sofas and electronics, and (iii) the recycling and disposal of such products at the end of their lives (U.S. EPA, 2006). One common source of PBDEs is household dust which has been reported to have an average PBDE concentration of more than 4600 parts per billion (ppb) (UNEP, 2004).

PBDEs can enter the human body through high fat foods such as fatty fish (Szlinder-Richert et al., 2010), supermarket food (U.S. EPA, 2006) and breast milk (U.S. EPA, 2006), or by inhalation of PBDEs in household dust (UNEP, 2004; Sjödin et al., 2008). PBDEs have been shown to bioaccumulate in fat tissues, blood, and breast milk. Since commercial production of PBDE started the 1970s, the concentration of PBDEs in human blood and tissue has doubled every five years (UNEP, 2010). Studies have shown that PBDEs are endocrine disrupters which mimic the behavior of natural hormones in human body and disrupt the chemical signaling system and hence development of brain and reproductive systems (UNEP, 2010).

Many wastes containing PBDEs find their way into landfills (e.g., household dust, old furniture, appliances, mobile phones, etc.). PBDEs have been detected in landfill leachate (Table 2) in different parts of the world (Osako et al., 2004; Danon-Schaffer et al., 2006; Haarstad and Borch, 2008; Odusanya et al., 2009) and in Canada at total concentrations up to 2.5 μg/L (personal communication with Environment Canada, 2009). Given their presence in MSW landfill

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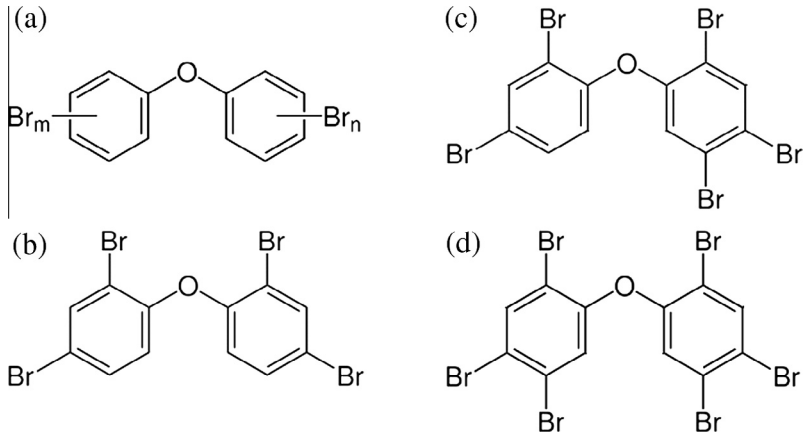

Fig. 1. Structural formula of PBDEs: (a) generic (m + n = 1, 2, . . ., 10), (b) congener 47 (tetraBDE), (c) congener 99 (pentaBDE), and (d) congener 153 (hexaBDE).

Table 1
Molecular descriptors of main congeners in DE-71 used in this study in the order of molecular volume (adapted from Li et al., 2008).

Congener (No. of Br)	Percent composition (%)	LogK_{ow}	Molecular weight (g/mole)	Molecular volume (Å^3)	Molecular polarizability (Å^3)	q^+_H	$q_{\bar{C}}$	$q_{\bar{O}}$	q^+_{Br}
						(atomic charge unit)			
47 (4)	32.4	6.81	486	806.53	31.23	0.141	−0.162	−0.092	0.060
85 (5)	2.42	7.37	565	850.05	33.86	0.140	−0.162	−0.093	0.094
99 (5)	43.9	7.32	565	854.17	33.86	0.144	−0.160	−0.090	0.064
100 (5)	8.93	7.24	565	858.55	33.86	0.143	−0.160	−0.089	0.066
154 (6)	3.30	7.82	644	893.00	36.49	0.147	−0.182	−0.076	0.067
153 (6)	3.84	7.90	644	903.68	36.49	0.144	−0.166	−0.094	0.065

q^+_H, the most positive atomic net charges on a hydrogen atom.
$q_{\bar{C}}$, the most negative atomic net charges on a carbon atom.
$q_{\bar{O}}$, the atomic net charges on the oxygen atom.
q^+_{Br}, the most positive atomic net charges on a bromine atom.

Table 2
Total PBDE concentrations reported in landfill leachate.

Reference	Location	Number of landfills	Total PBDE (ng/L)[b]
Osako et al. (2004)	Japan	7	0.096–18.17
Danon-Schaffer et al. (2006)	BC, Canada	–	1470
Haarstad and Borch (2008)	Norway	3	0.02–11.1
Odusanya et al. (2009)	South Africa	5	8.4–54.7
Environment Canada (2009)[a]	Canada	10	7.6–2476

[a] Personal communication.
[b] 1 ppb = 1000 ng/L.

leachate and the fact that most landfill regulations were developed before the potential health issues associated with PBDEs were recognized, it is important to investigate whether and, if so, under what circumstances, modern landfill liners can contain PBDEs sufficiently to prevent unacceptable impact.

There have been many studies of the diffusion of various organic compounds in landfill leachate through different types of geomembranes including diffusion of a number of organic chemicals through HDPE geomembranes (Park and Nibras, 1993; Sangam and Rowe, 2001; Joo et al., 2005; Chao et al., 2007; Islam and Rowe, 2009), PVC and LLDPE (McWatters and Rowe, 2009) and coextruded geomembranes (McWatters and Rowe, 2010). Preliminary work from the present study was reported by Taghizadeh-Saheli et al. (2011), however, the diffusion of PBDE through an HDPE geomembrane has not been reported in the archival literature.

The objective of this paper is to: (i) quantify partitioning of several common PBDE congeners to an HDPE geomembrane, (ii) evaluate the diffusion coefficient of several PBDE congeners in an HDPE geomembrane, (iii) compare the partitioning and diffusion coefficients of the different PBDE congeners, (iv) use the parameters derived from the experimental work to calculate the transport of PBDE through a typical MSW landfill barrier system.

2. Background

2.1. Regulation of polybrominated diphenyl ether (PBDE) production

With research showing the potential adverse effects of PBDEs on the human health and the environment, the European Parliament banned marketing and use of two out of three commercial mixtures of PBDE in the European Union (EU) in 2004 (U.S. EPA, 2006). The Bromine Science and Environmental Forum (BSEF) member companies, in cooperation with US EPA, voluntarily stopped the production and use of decaBDE for the US market by the end of 2012 (www.bsef.com). The Canadian Environmental Protection Act (CEPA 1999) prohibited the production of congener groups of tetraBDE and higher BDEs in 2008 and also bans the use, sale, offer for sale and import of tetraBDEs, pentaBDEs and hexaBDEs (Environment Canada, 2008). In 2009, the Stockholm Convention added two out of three commercial mixtures of PBDE