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Mass balance evaluation of polybrominated diphenyl ethers in landfill leachate and potential for transfer from e-waste

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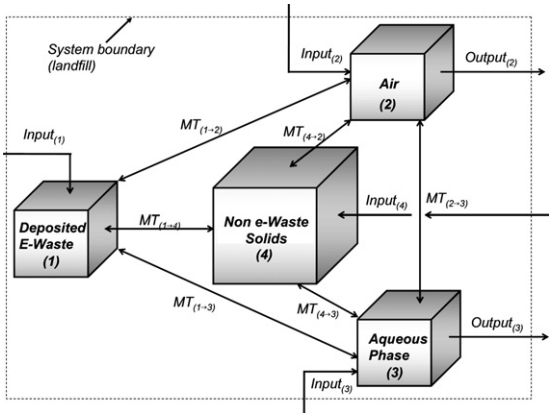
HIGHLIGHTS

- A comprehensive mass balance model is developed to track polybrominated diphenyl ethers (PBDEs).
- Landfill samples and laboratory results are used to estimate the model parameters.
- An urban landfill system is simulated, for past and future scenarios.
- Mass transfer is not rate-limiting. Chemical reaction/degradation rates are found to be rate-limiting.
- The model provides qualitative understanding of the influence of key variables.

GRAPHICAL ABSTRACT

Schematic of the various mass transfer (MT) and input/output steps for sub-systems in the landfill model. NeWS is defined as non-electronic waste solids, including sand and soil added as cover materials.



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ABSTRACT

Previous research on brominated flame retardants (BFRs), including polybrominated diphenyl ethers (PBDEs) has largely focussed on their concentrations in the environment and their adverse effects on human health. This paper explores their transfer from waste streams to water and soil. A comprehensive mass balance model is developed to track polybrominated diphenyl ethers (PBDEs), originating from e-waste and non-e-waste solids leaching from a landfill. Stepwise debromination is assumed to occur in three sub-systems (e-waste, aqueous leachate phase, and non-e-waste solids). Analysis of landfill samples and laboratory results from a solid-liquid contacting chamber are used to estimate model parameters to simulate an urban landfill system, for past and future scenarios. Sensitivity tests to key model parameters were conducted. Lower BDEs require more time to disappear than high-molecular weight PBDEs, since debromination takes place in a stepwise manner, according to the simplified reaction scheme. Interphase mass transfer causes the decay pattern to be similar in all three sub-systems. The aqueous phase is predicted to be the first sub-system to eliminate PBDEs if their input to the landfill were to be stopped. The non-e-waste solids would be next, followed by the e-waste sub-system. The model shows that mass transfer is not rate-limiting, but the evolution over time depends on the kinetic degradation parameters. Experimental scatter makes model testing difficult. Nevertheless, the model provides qualitative understanding of the influence of key variables.

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1. Introduction

1.1. Polybrominated diphenyl ethers (PBDEs)

Polybrominated diphenyl ethers (PBDEs) are stable brominated flame retardants (BFRs), commonly employed in a wide variety of products such as plastic components of computers and televisions, circuit boards, seats of cars and buses, and textiles (de Boer et al., 1997). PBDEs are believed to be released slowly over the life of the plastics in which they reside, and they can find their way into the food chain and humans (McDonald, 2002), where they are potential endocrine disruptors with the potential to surpass PCB concentrations in the environment (Rayne and Ikonomou, 2002).

Due to their physicochemical properties including hydrophobia, lipophilicity, long-range transport and tendency to bioaccumulate, PBDEs pass through wastewater treatment plants and adsorb on sediment and soil. They are also found in biosolids, causing concern due to the widespread application of biosolids on agricultural fields. Ikonomou et al. (2002) provide evidence of long-range transport to remote areas.

1.2. Environmental modelling

Material and energy balances are frequently written to account for the conservation of substances within a designated control volume, equating the rate of accumulation to the difference between rates of entry and leaving the volume plus the net rate of generation within the control volume. This approach has become a common basis for environmental modelling (Diamond et al., 1992; Mackay and Wania, 1995; Mackay, 2005). Simplifying assumptions are needed to apply this approach to PBDE modelling because information on PBDE behaviour, fate and transport in the environment is lacking.

A typical modern solid waste landfill receives municipal solid waste, construction and demolition debris, industrial waste, hazardous wastes and compost. They normally have leachate collection and removal systems, geo-membrane layers, and groundwater monitoring. For the purposes of this research, a typical landfill system is illustrated in the graphical abstract.

Although, mass balance models have had considerable success in accounting for the spread of air pollutants, we are not aware of attempts to determine the decay of PBDE concentrations from plastics in electronic waste via mass balance models (e.g. from landfills). A landfill model is proposed here to track PBDEs originating from e-waste and non-e-waste solids (abbreviated NeWS hereafter). Inputs to the model are based, whenever possible, on real data (data analysis provided by: Vista Analytical Laboratory and the Department of Ecology from the State of Washington).

2. Mass balance model

The mass balance landfill model is intended to predict the environmental fate of polybrominated diphenyl ethers (PBDEs) in landfills, with possible extension to other systems. For modelling purposes, the landfill is divided into four compartments (or sub-systems), in contact with each other as portrayed in the graphical abstract. These four sub-systems represent: (a) electronic waste (e-waste) originating from personal computers, photocopiers, printers, hard drives, circuit boards, keyboards and mice, (b) air immediately above the landfill, (c) aqueous phase consisting of leachate and gathered rainwater associated with the landfill, and (d) non-e-waste solids (NeWS) in the landfill. This refuse category also includes soil and sand, used as landfill cover. Whilst the air sub-system is formally included, it is largely excluded from subsequent consideration in this paper due to lack of experimental data. Excluding the air sub-system shows a negligible difference because the estimated mass transfer to and from air is relatively small as compared to other sources. Mass balances are applied to the three remaining sub-systems and to eight different homologue groups.

The composition of the NeWS stream is based on data from an urban landfill system (whose identity must remain confidential), the reference site for this paper. Supplementary information about this landfill is provided by Danon-Schaffer (2010). Landfill addition rates by category over many years obtained from field measurements and from landfill operators were utilized as input for the model. Contaminated disposed goods undergo several simultaneous processes that affect the surrounding region. There are multiple reactions, with species debrominating over time, thereby generating new chemical species. These species may also transfer to or from adjacent sub-systems.

To account for all possible chemical species, but not to have to deal with all 209 individual congeners, eight PBDE homologue groups are followed — deca-, nona-, octa-, hepta-, hexa-, penta-, tetra- and low-BDE brominated congeners. The low — includes tri-, di- and mono-BDE, as measured values for di- and mono-BDE in all experimental data tend to be very low relative to the higher-brominated groups. Each homologue group represents all species in the group. Key mass transfer parameters are estimated from experiments conducted in a solid–liquid contactor where particles derived from crushed electronic equipment were exposed to landfill leachate and water, as described in Danon-Schaffer (2010) and Danon-Schaffer et al. (2013).

The current model utilizes tools commonly encountered in chemical engineering to simulate complex mass transfer-reaction problems. The mass balance simulations described herein provide predictions and sensitivity analyses of the model for the evolution of PBDE concentrations at a landfill site corresponding to two scenarios: *Scenario 1*: past three decades; and *Scenario 2*: future after PBDE bans.

2.1. Conservation equations

As an initial approximation, each sub-system is treated as an isothermal lumped (well-mixed) compartment, so that the concentration of each species is assumed to be uniform throughout the sub-system and equal to the exit concentration from that sub-system. There are two mechanisms for exchange of species between sub-systems, one based on a concentration gradient (diffusion) and the other on a deposition flux (convective transport). The general mass balance for the ith species in sub-system φ can then be written:

$$\underbrace{\left[v_{f\varphi}C_{if_\varphi}\right]}_{\text{Input}} - \underbrace{\left[v_\varphi . C_{i_\varphi}\right]}_{\text{Output}} + \underbrace{\left[V_\varphi . \sum_{j=1}^{N_R} \upsilon_{ij} . r_{j_\varphi}\right]}_{\text{Generation}} + \underbrace{\left[V_\varphi . \sum_{n\neq\varphi}^{N_\varphi} a_{I_{(n\to\varphi)}} . k_{ci_{(n\to\varphi)}} \cdot \left(C_{i_n} - C_{i_\varphi}\right)\right]}_{\text{Mass transfer exchange input}} + \underbrace{\left[\sum_{n\neq\varphi}^{N_\varphi} A_{(n\to\varphi)} \cdot \left[DF_{i(n\to\varphi)} - E_{i(n\to\varphi)}\right]\right]}_{\text{Deposition minus entrainment flux input}} = \underbrace{\left[\frac{d}{dt}\left(V_\varphi . C_{i_\varphi}\right)\right]}_{\text{Accumulation}} \quad (1)$$

$i = 1,2,\ldots N_C$; $\varphi = 1,2,\ldots N_\varphi$.

Here $v_{f\phi}$ is the total volumetric flow of feed stream into sub-system φ, C_{if_ϕ} the corresponding concentration of component i in that feed stream, v_ϕ the volumetric flow rate out of sub-system φ, C_{i_ϕ} the instantaneous concentration of species i in sub-system φ, V_ϕ the total volume of sub-system φ, υ_{ij} the stoichiometric coefficient of species i in reaction j (positive when i is a product, negative if i is a reactant), r_{j_φ} the rate of reaction j per unit volume, $a_{I_{(n\to\varphi)}}$ the interphase transfer area per unit volume between sub-systems φ and n, k_{ci} the interphase mass transfer coefficient, and C_{i_n} the concentration of species i in an adjacent sub-system n in contact with sub-system φ, $A_{(n\to\phi)}$ the contact surface area between sub-systems n and φ, and $DF_{i_{(n\to\phi)}}$ the deposition flux of species i from sub-system n to sub-system φ. $E_{i_{(n\to\phi)}}$ is the entrainment flux of species i from sub-system n to sub-system φ. N_C is the number of chemical species and N_φ the number of sub-systems.