Modeling of PBDEs in Landfills and Other Systems

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Abstract

A mass-balance model is being developed to predict the environmental fate of polybrominated diphenyl ethers (PBDEs) in landfills and other systems where they occur. The model considers changes over time for different congeners and includes inputs (e.g. due to e-wastes and polyurethane foam), transfers between the wastes and soil, water and air, reactions that may alter the relative composition of different congeners, and accumulation over time. Specification of various terms in the model will require experimental measurements, now in progress. The model will produce a set of differential equations to be integrated simultaneously by conventional methods. The model may be extended later, with appropriate inputs, to apply to larger systems such as regions[1].

Introduction

Research on brominated flame retardants has largely been focused on concentrations in the environment and their adverse effects on human health. It is essential that research be also focussed on how these compounds reach the environment, how they are transferred from waste streams to air, water and soil, and how they are transported to distant locations, such as the far north. We have undertaken a systematic approach in which we consider mass balances for PBDEs to provide unsteady state models which can be used to characterize and predict the accumulation and movement of these compounds in the environment. This paper describes the approach, application of the model to a landfill site, the importance of obtaining experimental data which can be used to set key terms in the model, and possible extension of the model to more comprehensive systems.

Electronic waste (E-waste)

Two distinct problems exist with regards to electric and electronic equipment: the volume of computers and related electronic waste (e-waste) that are improperly disposed of in landfills, and the toxicity of both the computer chip manufacturing process and the computer itself as a waste product. E-waste has become a major environmental concern. Increasing amounts of e-waste are entering the final disposal stream as faster computer equipment replaces older or obsolete devices, with an average lifespan of only 2-4 years.

Although there are three commercial PBDE products, each of these is composed of congener mixtures. For example, the commercial Penta-BDE product is a combination predominantly of congeners BDE-47, BDE-99 and BDE-100. The commercial Octa-BDE product is composed predominantly of BDE-153 and BDE-183. The Deca-BDE is almost exclusively comprised of the BDE-209 congener. Another commercial product, not as popular as the previous three, but used nonetheless, is Tetra-BDE. It also is a combination of congeners BDE-47 and BDE-99, but contains a higher proportion of BDE-47 and a lower proportion of BDE-99 than the Penta-BDE product.

BFRs may be present in leachate from landfills, but few studies on the fate of these compounds in any waste disposal streams (landfills, sewage treatment plants, incinerators) have been reported. It is thought that some sources of BFRs and subsequently PBDEs in the environment originate from BFR-flame-retarded polymers and plastic products (electronic equipment, electronic and electrical applications, wire and cable insulation, printed circuit boards and connectors)[2]. PBDEs, TBBA and HBCDD are used as additive or reactive components in various polymers, such as high impact polystyrene (HIPS), epoxy resins and polystyrene foams[3]. Deca-BDE is typically used as an additive flame retardant in electric and electronic equipment[4]. So far, there is little data regarding the mobility versus covalent bonding of BFRs to electronic equipment. The proposed PBDE model is considered comprehensive and complex. By using another BFR in this model, the effect of leaching out from the polymer may be determined and a comparison can be made. As well, the model will attempt to address which environmental processes influence the mobility of

PBDEs through different matrixes, such as water, soil, air. A study by Gouin & Harner (2003)[5] discusses the possibility of PBDE degradation in these matrixes by microbial degradation by partitioning to soil and other environmental compartments.

Personal computers (PCs) contain approximately 1.7 kg of flame retardant, of which an estimated 70% (1.19 kg) is in the cabinet and the remaining 30% (0.51 kg) in the printed circuit board[6,7]. From a study conducted in the US, the proportion by weight of plastic estimated to be contained in PCs and monitors is approximately 23% of the overall computer materials[8,9,10].

We will develop preliminary degradation rates of commercial PBDE products: penta-BDE, octa-BDE, deca-BDE and tetra-BDE. The experimental work will provide data on background concentrations and parameter values. There is little information known about the burden of BFR in landfills. A bench scale study will address some of these data gaps. Specific objectives of the bench scale experiment include a) Obtain PBDE decay rates (penta, octa, deca-BDE) from e-waste leaching out in landfills, b) Quantify the input, transfer and accumulation terms so that material balances may be written, c) Investigate conditions with potential to significantly affect PBDE concentration from e-waste in a landfill (i.e. temperature, pH, source material and agitation rate, time of exposure), and d) Obtain rate expressions and PBDE concentration coefficients that will be used in the material balance model. The experimental model will account for PBDE and other BFR use from the mid 1980s to present day via concentration profile data obtained in the experiment. However, it may be modified to use any BFR, when describing the overall system definition for the model.

The Approach

Mass and energy balances are of fundamental importance in chemical engineering. The basis is to choose a control volume encompassing the system of interest and then to apply an equation of the form[11]:

Input - Output + Generation = Accumulation (1)

The generation term includes chemical decomposition or destruction, either of which will make this term negative. The equation may be applied on an overall basis to the entire flows and contents, or be restricted to a given species or component or subset of components. For example, mass balances could be applied to all PBDEs entering a given landfill or to given congeners or “lumps” of congeners. The latter is adopted here, identifying four “lumps”:

A: Deca-BDEs: concentration = C_A (units kg/m^3);

B: Octa-BDEs: concentration = C_B (units kg/m^3);

C: Penta-BDEs: concentration = C_C (units kg/m^3);

D: Tetra-BDEs: concentration = C_D (units kg/m^3).

The boundary of the landfill site is drawn to enclose the entire site, as illustrated in Figure 1, including several sub-systems[12]:

Subsystem 1: Solid wastes, in particular e-waste and other PBDE-containing wastes;

Subsystem 2: Air over the landfill site;

Subsystem 3: Water contained on the site and in the soil;

Subsystem 4: Soil underlying the site.

These subsystems are denoted by superscripts in the variables below. For example, $C_A^{(3)}$ designates the concentration of deca-BDE in the water within the landfill boundary. For simplicity at this stage, we consider only a height of air above the landfill up to 500 m and a depth of soil of 1 m. Moreover, we consider each of the compartments to be "well-mixed", i.e. to have a homogeneous composition within the boundaries. This assumption will later be removed, at least for the soil compartment.

Of considerable importance in the model is to consider transfer of species from compartment to compartment. In each case the transfer of species A (in units of kg/s) between compartments i and j will be assumed to be given by an equation of the form[13]:

$$N_A = k_A^{ij} A_{ij} (C_A^i - C_A^j) \quad (2)$$

where k_A^{ij} is the mass transfer coefficient for A transferring between subsystems i and j with units of m/s, whereas A_{ij} is the area of contact between sub-systems i and j with units of m^2. Clearly similar equations can be written for each of the other "lumps" (B, C and D). Note that the interfacial area A_{ij} is zero for $i = j$.

A key challenge in the model will be to estimate the mass transfer coefficients. Some of these (e.g. those between air and water) may be estimated in the first instance from data in the literature. Others will require experimental measurements, which are being undertaken at the University of British Columbia.

If we consider a single subsystem (i) and a single lump of species, A, equation (1) can be rewritten in the form[13]:

$$Q_{in}^i C_{Ain}^i - Q_{out}^i C_A^i - \sum_{j=1}^{4} k_A^{ij} A_{ij} \left(C_A^i - C_A^j\right) + V^i \sum_{\alpha=1}^{n_c} \nu_{A\alpha} r_\alpha = \frac{d\left[V^i C_A^i\right]}{dt} \quad (3)$$

where Q_{in}^i is the total volumetric inflow of material entering subsystem i, C_{Ain}^i the mass concentration of A contained in this flow, Q_{out}^i is the corresponding total outflow of material from subsystem i, V^i is the volume of subsystem i, n_c is the number of chemical reactions, n_{Aa} is the stoichiometric constant of species A in reaction a, and r_a is the rate of reaction a.

With four "lumps" and four subsystems, there are 16 such ordinary differential equations in all. Each requires an initial condition, which may either be provided by considering some earlier point in time when there were no PBDEs on the site or estimated at the current time, with time t then being 0 at the present time. The set of ordinary differential equations can be integrated using the Runge-Kutta algorithm in standard software packages such as Polymath and Matlab.

Reaction terms, r_a, n_c and n_{Aa} are extremely difficult to estimate at this stage and will be based initially on whatever information is available in the literature.

Predictions of the model will be compared with results from a major urban landfill site. Parameters in the model may then require adjustment at that stage. If the model can be validated for a landfill site, we will then consider expanding it to apply to larger and more complex systems such as an entire region.

Conclusions

A comprehensive approach for modeling PBDEs (deca-BDE, octa-BDE, penta-BDE, tetra-BDE) in a real system (e.g.landfill) is proposed. A complete set of design equations have been developed based on mass balances for the four subsystems (e-waste, air, water, soil) identified in the landfill. The resulting set of ordinary differential equations and corresponding initial conditions will be integrated numerically using standard methods. It is hoped that this model will be realistic and generic in scope so that it can be used by others investigating the degradation of PBDEs from polymers in e-waste at landfill sites and later be applied to other systems.

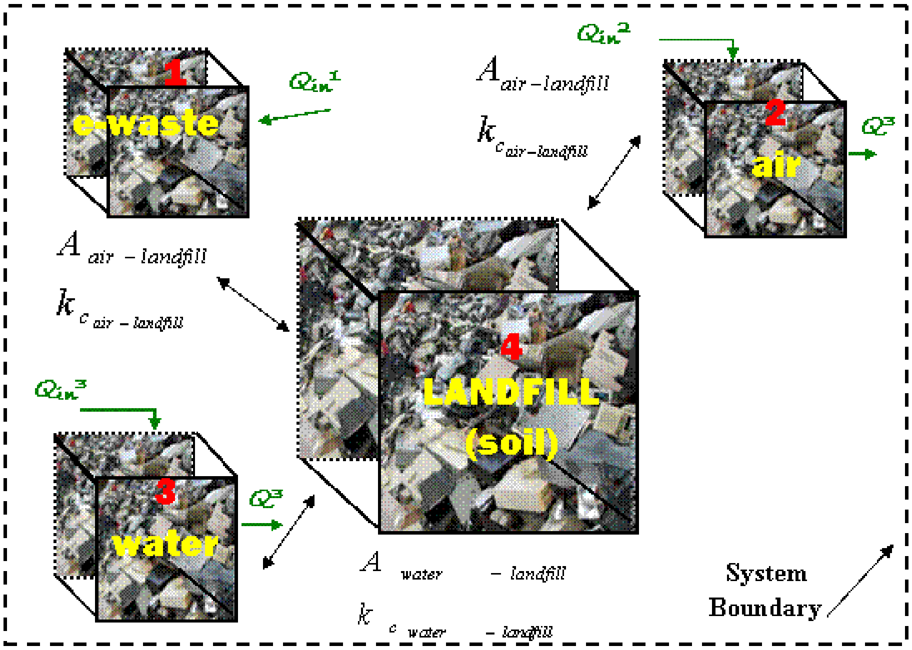

Figure 1. Overall System

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