Mass Balance Evaluation of Polybrominated Diphenyl Ethers (PBDEs) in Canada: System Models and Upstream Source Characterization

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Abstract
A mass balance model is developed to predict the environmental fate of Polybrominated Diphenyl Ethers (PBDEs) by identifying upstream sources of PBDEs throughout the electronic waste stream (personal computers, printers, hard drives, circuit boards, keyboards, mice). These sources have not been previously quantified. The first phase of the experiment will be based on leachate analysis from the largest landfill in Vancouver, British Columbia. Based on this initial data, mass balance models will be developed on other system specific operations, at a local, regional and national level. The target is to attempt to shed light on the concentrations of PBDEs found as far away as the Canadian Arctic. The next phases of the experiment will involve PBDE quantification in landfill sediments, leading to mass balance including all inputs and outputs to the largest sewage treatment plant in the Lower Mainland of British Columbia.

Introduction
We need to develop mass balances for these compounds because there is no quantification or characterization of the upstream sources from which these brominated flame retardants (BFRs) are originating. By attempting to obtain mass balances for different systems to determine inputs and outputs, waste streams, environmental occurrence, fate and transport and ultimate accumulation in the Arctic from a closed-loop system (landfill or sewage treatment plant), to a large scale (grid across the country), we hope to model the fate of these ubiquitous substances in order to motivate policy changes that could help deter use of these compounds and reduce their spread throughout the environment.

Objectives
- To identify and compile industrial production (sources) and waste volumes in Western Canada of Penta-, Octa-, Deca-BDE to prepare mass balance models;
- To quantify, to the extent possible, the transfer, source and accumulation terms so that mass balances may be written for PBDEs at local, regional and possibly national levels;
- To provide data and recommendations that can inform and motivate policy changes with respect to PBDEs so that environmental problems are reduced.

Research Scope and Approach
The BFRs to be studied will be congeners BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-209 of the 3 commercial PBDE products. We chose the computer waste stream for experimentation because it has historically used a high percentage of PBDEs. More

recently, BFRs in the computer stream have changed. However, many obsolete computers ending up in the landfill nowadays potentially contain elevated levels of PBDEs.

The systems of potential focus for mass balance models include relatively restricted systems (landfill, sewage treatment plant, incinerator), local (Georgia Basin), regional (Western Canada), national (imports and exports of the material) in Canada, ultimately attempting to find the dissipation rate to the Canadian Arctic.

Experiments will begin at the bench scale level testing various plastics used in the information technology (IT) sector. Computer plastics (e-waste) from the IT sector will undergo a low-level leachate test with glacial acetic acid, prior to running the same tests with landfill leachate. Once these steps are complete, the e-waste will be subjected to landfill leachate in columns. To improve statistical significance, there will be at least 6 pieces of equipment from each e-waste stream in each column.

Electronic Waste (E-Waste)

Discarded electronic equipment is a growing problem in every Canadian jurisdiction, as well as in other countries due to short useful life and obsolescence. Recycling operations are increasing and helping to divert some e-waste. Still, the amount of e-waste is growing exponentially, with much of it entering landfills and/or to incineration for final disposal. An Environment Canada[1] study predicted the amount of e-waste in Canada from 1999 and 2005 with a Waste Flow Tool (Table 1).

TABLE 1. Estimated e-waste disposal categories in Canada, 1999 and 2005[1]

Waste management method	E-waste Equipment (metric tonnes)				
	1999	%	2005	%	% increase 1999-2005
Disposed	33,972	42.35	67,324	39.48	98.17
Recycled	15,592	19.44	43,428	25.47	178.52
Reuse	24,507	30.55	47,791	28.03	95.00
Storage	6,128	7.64	11,948	7.00	94.97
TOTAL	**80,199**	**100.00**	**170,491**	**100.00**	

The amount of plastic estimated to be contained in personal computers and monitors is approximately 23% (SVTC, 2000). An estimated 9,222 tonnes of plastic were contained in obsolete computers and monitors in Canada in 1999, and approximately 4,948 tonnes of plastic from computers and monitors were disposed of in Canada in 1999[1]. The estimates for 2005 in Canada that will be disposed are 19,833 tonnes of plastics in obsolete PCs and monitors, and approximately 10,994 tonnes of plastics in computers and PCs[1].

Mass Balance Models

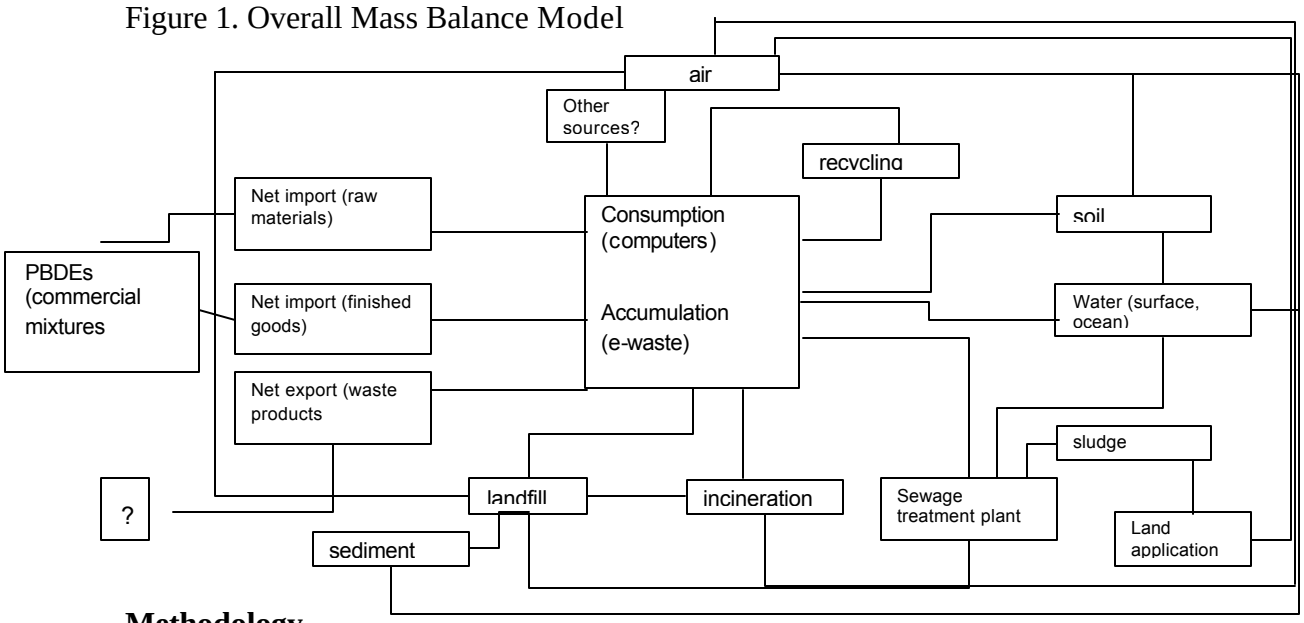
A mass balance accounts for the conservation of mass of a substance within a control volume by equating the rate of accumulation to the difference between its rates of entering and leaving the volume plus the net rate of generation within the volumes. The basic mass balance equation can be expressed as: *Flow in – flow out + generation – consumption = accumulation*. Each of these terms will differ, depending on the model. We will develop non-steady-state, multi-compartmental mass balance models of the environmental fate of PBDEs in a variety of defined systems: restricted (landfill; sewage treatment plant), local

(Georgia Basin in British Columbia), regional (Western Canada), national (imports and exports to the country, or estimate on a grid basis).

Some assumptions will be made as some data and information on PBDEs in the environment is unknown. With the use of e-waste as an upstream waste track for PBDEs, the 'accumulation' term becomes critical, as large amounts of e-waste are already stored and stockpiled and this number will increase over the years (Table 2).

An example of the overall mass balance system (i.e. national model) to be developed is shown in Figure 1.

Figure 1. Overall Mass Balance Model



Methodology

The raw material source for the experiments is electronic waste (e-waste) provided by Genesis Recycling, the only national computer waste recycling facility in Canada to recycle 100% of all computer components domestically. The number of computer units to be dismantled will include at least 6 from each manufacturer per category. The common denominator is to use source material from manufacturers in business since at least the late-1980s in an effort to establish historical time trends. This will contribute to an understanding of how e-waste is potentially leaching from landfills over time.

A risk assessment tool for analysing PBDE compounds will be used to compare the total concentration (mg/kg) to a risk-based leaching level[2]. The equation to determine leaching levels[3] is: $C_t = C_w \times \{K_{oc} f_{oc} + (?_w + ?_a * H'/?_b)\}$

where

C_t screening level in soil (mg/kg)
C_w target leachate concentration (mg/L) ($C_{standard}$ x dilution factor)
$C_{standard}$ risk-based groundwater guidance concentration or regulation
f_{oc} organic carbon content of soil (kg/kg)
H' Henry's law constant (dimensionless)

K_{oc} soil organic carbon-water partition coefficient (L/kg)
$?_w$ water-filled soil porosity (l_{water}/l_{soil})
$?_a$ air-filled soil porosity (l_{air}/l_{soil})
$?_b$ dry soil bulk density (kg/L)

Experiment Set-up and Procedure

Each piece of electronic equipment will be individually weighed prior to dismantling[4]. This weight will be recorded together with a description of the unit, model, make and year. The units will then be cut into pieces less than 50 mm in diameter[5]. The categories are: monitor casings, hard-drive casings, printers, keyboards, mice and circuit boards. The units will be disassembled, and only the casings will be cut. The units will be reweighed once they are dismantled. The leftover components of each unit will be returned to Genesis Recycling where they will be reincorporated into their recycle operation. Once the quantity of PBDE is determined analytically in the experiment, we will calculate the percentage of PBDE in the plastic per unit per cluster year by weight differential.

The plastic pieces will be pre-sorted by unit type, labelled, sealed, and placed in individual Ziploc bags, in black garbage cans, identified by code letter for each manufacturer. A field log-book will record each step to ensure proper documentation and proper protocol for experimental operating procedures. Subsequently, the plastic pieces will be placed in 2500 mL amber glass jars fitted with a Teflon cap, (previously sterilized to EPA Level I cleaning standards), to determine leachability. The cut pieces of plastic will be packed in the jars. A pre-determined ratio of glacial acetic acid (pH ranging from ~5.5 to 7) to solids will be used to simulate landfill leachate conditions.

To ensure that the samples are representative of computer plastics composition of a certain time period (to be determined as the raw material is classified), the quantities and concentrations of the sample will be manipulated to generate a final bulk concentration similar to what would be produced if all of the hard drives were manufactured with the same plastic composition.

Part I – Glacial acetic acid will be used as the extraction fluid with different pHs to determine potential leachability, starting with pH 5.5 and increasing by 0.5 steps to 7.0. The different pHs will simulate seasonal variations due to heavy precipitation events or other climactic changes that could occur at the landfill. At predetermined intervals, e.g. every two weeks, the samples will be collected in duplicate. The concentrations of congeners BDE-47, -99, -100, -153, -154, and -209 will be determined based on duplicate analysis and a GC/MS. A coefficient of variation for each set of analysis will be provided. The initial experiments will be at room temperature, which will be monitored. Later tests will be carried out at higher and lower temperatures.

Part II – Leachate from the landfill will be studied, repeating procedures from Part I of the experiment as well as landfill sediment sampling and STP inputs/outputs (sludges) will be quantified. Incinerator sampling will also be made if possible to try and close the loop on upstream sources.

Part III –Pilot scale testing will be carried out with columns 0.3 m diameter and height approximately 1 m. E-waste will be prepared as per Part I of the experiment. Sand will

be used as a filter at each end of the column, and the pore volume of the packed materials will be determined by comparing the weights of the packed column before and after saturation[6]. Each column will treat wastes from one computer manufacturer. The number of columns to be employed will depend on how the composition of the plastic changes with time.

Results/Discussion

This experiment commenced in April 2004. Results are pending.

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