

PBDEs FATE IN THE INDOOR ENVIRONMENT- A MULTIMEDIA MODEL STUDY

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Introduction

PBDEs have been widely used as additive flame retardants in consumer products such as polyurethane foam (PUF) cushions, computers and carpets (1). In response to the concerns on PBDEs' toxic effects, Europe and North America have moved to ban production and use of the Penta and Octa formulations in new products (2). Recently, the Europe Union moved to restrict the use of Deca. However, these mitigative actions are directed to new uses and not to the existing, in-use stock of products and materials that continue to release PBDEs into the indoor environment (3,4). Knowledge of PBDE dynamics indoors is important if we are to minimize our exposure via indoor dust and via our food supply that bears the burden of PBDEs exported from indoors to outdoors.

Hazrati and Harrad (1) found PBDE air concentrations in an office decreased by ~80% after a computer was replaced with a newer model, which indicates that concentration of PBDEs indoors can be significantly affected by PBDE-containing products. Other studies have met with limited success when relating PBDE concentrations in indoor dust and/or air to the number or volume of products potentially containing PBDEs. Allen et al. (5) have improved the prediction of PBDEs in indoor dust by using XRF to measure the bromine content of products and materials suspected of containing PBDEs, but still considerable variability remains in the relationship between XRF-bromine loading and PBDE dust concentration.

PBDE concentrations indoors are not only related to emissions from sources but may also be affected by other factors and processes: the indoor environment contains a wide variety of materials that can be a sink or source for PBDEs (6,7). Materials such as PUF can act as sinks or buffers for indoor organic chemicals, prolonging their presence and hence exposure (8). In addition, indoor activities can also influence chemical concentrations indoors (5). Multimedia models have been useful tools for elucidating the behaviour of semi-volatile chemicals such as PBDEs (9). Bennett and Furtaw (10) developed and applied a fugacity-based indoor model to study the behavior of pesticides after spraying indoors. We have extended the model by adding PUF as another compartment. We applied the model in order to address the following questions: (1) what is the emission rate of PBDEs from an indoor source(s); (2) what is the fate and behaviour of PBDEs in a room; and (3) what factors influence the fate of PBDEs indoors?

Methods

We briefly describe the model in general and its application to a test system, that of the office described by Harrad and Hazrati (1). The model considers gas- and particle-phases of a chemical with inputs from outdoor air via advection (gas- and particle-phases), volatilization and resuspension of gas- and particle-phase PBDEs, respectively, from PBDE-containing sources such as PUF furniture, and a "direct" emission of gas- and particle-phases from PBDE-containing products such as electronic equipment (1,5). Losses occur through air advection, dust removal and chemical transformation. For PBDE-impregnated PUF furniture and carpets, we adopt a pseudo-state-state approach whereby we specify the fugacity of these compartments according to measured PBDE concentrations, which is analogous to the treatment of "in-place" sediment pollution in lakes (11). For modeling PUF, we assume that its porous structure is analogous to snow and as such, we adopted the method of Daly and Wania (12) for chemical exchange with respect to snow. Gas-phase diffusion, particle-phase advection (deposition and resuspension) and compressing the PUF as occurs when sitting or bouncing on furniture were considered to be the dominant processes for chemical exchange between air and PUF.

In the office (area \times height=4.84 m² \times 2.70 m), the materials likely containing PBDEs were: carpet (fully carpeted, thickness=0.005m), a computer with printer, plugs and wires (included with the computer), and 2 PUF-padded chairs (area \times thickness=1.66 m² \times 0.05 m). Two samples from the PUF chair (2.6, 2.7 g) and 2 carpet samples (19.3, 20.8 cm²) were analysed for BDE-28, 47, 66, 100, 99, 154 and 153. The carpet samples were thoroughly vacuumed to remove the dust. Each sample was Soxhlet extracted in 300 mL n-hexane at 60°C for 10 h. The procedures followed are detailed by Harrad et al. (3). The model was run for each of the 7 congeners list above. The fugacities of PUF and carpet for each congener were derived from the measured concentrations and used as input for the model. Emissions from the electronic equipment including the old and new computers were solved using the mass balance equations in which the fugacity of the air was set based on measured concentrations in the office before and after computer replacement. These emission rates are referred to as “computer” although the printer and cables likely contributed.

Results and Discussion

The total measured concentrations of PBDE were 2140 and 173 ng·g⁻¹ in the PUF and carpet, respectively (Figure 1). BDE-99 and BDE-47 were the two dominant congeners which comprised 52 and 28% in PUF, and 39 and 43% in the carpet, respectively.

Measured \sum_7 BDE air concentrations decreased by ~80% from 1.1 to 0.3 ng/m³ and emissions were estimated at 35 to 5.4 ng·h⁻¹ before and after computer replacement, respectively. The contribution to air concentrations (and the entire system) from outdoor air was minimal at 0.04 ng·h⁻¹. The estimated emission from the old computer was comprised of 72% BDE-99 followed by 10%, 9.5% and 5.6% of BDE-47, 100 and 154, respectively. Along with the magnitude of emissions, the congener profile changed with the new computer (including the same printer before and after computer replacement) to 53%, 4%, 6% and 31% of BDE-99, 47, 100 and 154, respectively (Figure 1).

The scenario after the computer replacement in the office was used to illustrate PBDEs' fate processes in the indoor environment. The main removal process was dust removal, which included X% of the PBDEs impregnated into the carpet (Figure 2). Air advection to outdoors accounted for 3 ng/h loss in this scenario, and 10.6 ng/h in the old computer scenario. summarises the magnitude of the major fate processes of the \sum_7 BDE, which are dominated by particle movement of particle-phase PBDE.

A sensitivity analysis revealed that particle-related parameters, such as particle concentration in air, and particle deposition and resuspension rates, had the greatest influence on indoor fate. Thus, although net air-carpet exchange was -0.5 ng/h, deposition and resuspension rates were 5.5 and 4.47 ng/h, respectively. In addition, temperature, air exchange rate, air-PUF and air-carpet partition coefficients were also influential parameters.

Air concentrations increase marginally as a function of air temperature, assuming a constant emission rate from the new computer (Figure 3a). Although all gross fluxes between air, PUF and carpet increase with temperature, the greatest increases are fluxes from carpet-to-air (WHY?) followed by air-to-PUF. This results in a slight increase in the net flux from air-to-PUF and a greater decrease in net air-to-carpet exchange with temperature (Figure 3b). Overall, the flux from air-to-PUF and -carpet decreases with increasing temperature.

Dust removal (vacuuming) is an important removal mechanism for PBDE indoors, although the process transfers the geographic location of PBDEs in the environment – vacuuming of course, is not an ultimate loss process. Increasing dust removal reduces air concentrations, again assuming a constant emission rate (Figure 4a). As the dust removal rate increases, PBDE air concentrations decrease. The decrease in air concentrations is due to increased fluxes from PUF-to-air and air-to-carpet as a function of dust removal rate (Figure 4b).

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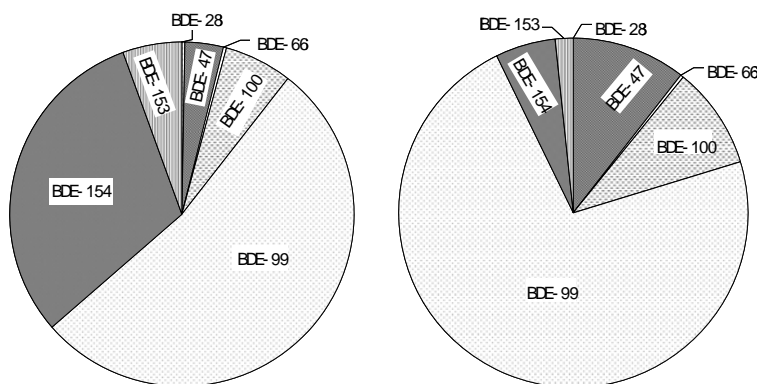


FIGURE 1. PBDE congener emission profiles before and after a computer replacement.

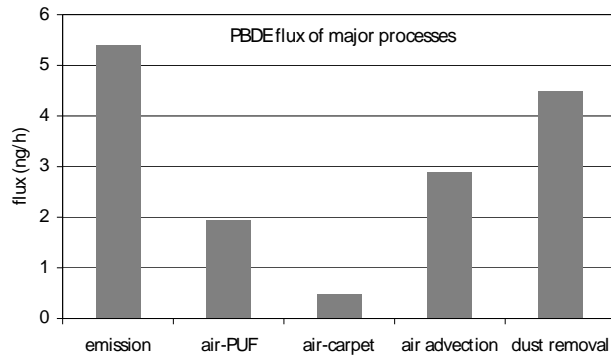


FIGURE 2. Estimated rates of movement of Σ_7 BDE in the indoor environment considering the “new” computer scenario.

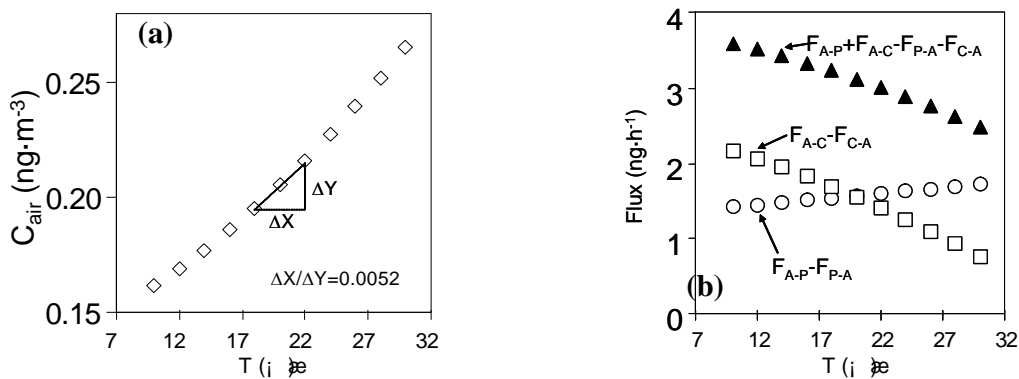


FIGURE 3. Effect of temperature on (a) bulk air concentration of Σ PBDE and (b) air-PUF and air-carpet flux of Σ PBDE . F: flux (ng/h); subscript A: air; subscript P: PUF; subscript C: carpet

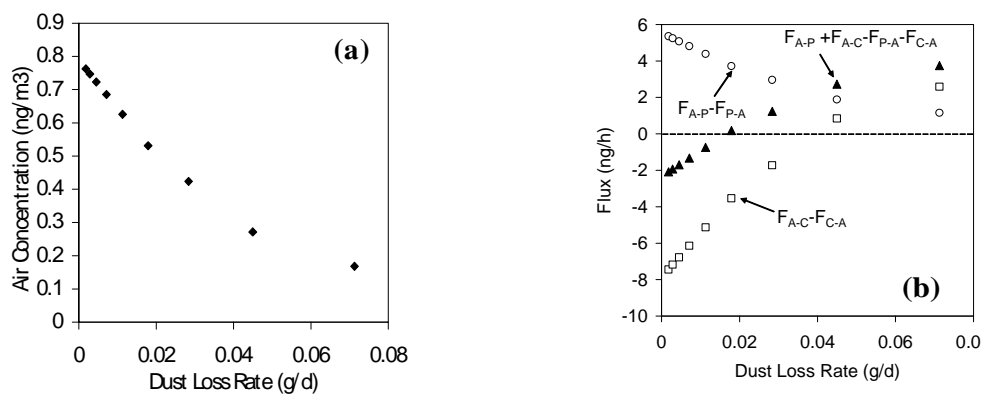


FIGURE 4. Effect of dust loss rate on (a) bulk air concentration of Σ PBDE and (b) air-PUF and air-carpet flux of Σ PBDE . F: flux (ng/h); subscript A: air; subscript P: PUF; subscript C: carpet.