Thermal effects on polybrominated diphenyl ether mass transfer and emission from computer cases

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A B S T R A C T

The increase in temperature of some consumer products, especially electronic devices, results in an increase of semivolatile organic compound (SVOC) emissions. Brominated Flame Retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs), are used in many electronic casings and circuit boards to protect consumers from fires. However, the heat from the internal circuitry increases the SVOC vapor pressure and the material–air partition coefficient decreases, driving SVOC transport out of the substrate and into the indoor environment. In the case of a computer tower, the cooling fan also increases the mass transfer coefficient, further increasing emissions. Such enhanced emissions are a concern since recent studies claim adverse health effects of PBDEs on human health. In this study, a simplified heat and mass transfer model is developed to characterize the combined heat and mass transfer problem for a computer tower in an indoor space to determine the levels of PBDE that would be outgassed. As expected, higher temperatures increase the emission rate of the SVOC and explain one of the transport mechanisms for BFRs into the environment. The emission rate of PBDEs was on the order of tens of nanograms per hour. The concentration of PBDEs in the air increases 40–80% for every 5 °C increase inside the computer case, depending on the congener. If these emission rates prove to be toxicologically significant, then models such as the one proposed can be used in risk analysis modeling and to develop mitigation strategies.

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1. Introduction

In 1973, the National Commission on Fire Prevention and Control published their seminal report, America Burning [1]. This report on the fire burden in the United States led to the creation of the United States Fire Administration and focused the nation's attention on the problem of fire. This focus in turn led to a fountain of research on materials flammability and flame retardation in the 1970s and 80s that, combined with the increasing flammability of less expensive synthetic polymeric materials used in furnishings and appliances has expanded the use of flame retardants.

Halogenated flame retardants are commonly used today as a flame retardant because they are easily included as an additive [2] in many polymer products such as polyurethane foams or high impact polystyrenes and can convey enough flame retardancy to achieve desired ratings on standard regulatory flame tests like UL-94 [3–5]. Of the classes of halogenated flame retardants, brominated flame retardants (BFRs) are notable because their dissociation temperature lies in a region ideal for acting as a fire inhibitor while maintaining environmental stability [3]. Additionally, using them as an additive can slow down the initial burn rate

of a fire and delay onset of flashover long enough for occupants to escape during fire events [6]. Of the classes of BFRs, PBDEs have been widely used as a flame retardant treatment [7].

Polybrominated diphenyl ethers (PBDEs) are used widely as a BFR in products. There are 209 congeners for PBDEs [8] but the most common are pentaBDE, octaBDE, and decaBDE. These products are formulations of various PBDE congeners. PentaBDE was mostly used in polyurethane foams (mattresses, seat cushions, upholstered furniture, and rigid insulation), but also in printed circuit boards. PentaBDE was banned from sale in Europe, Japan, Canada, Australia and the US around 2004, but other countries may still use it today. OctaBDE was used in high-impact plastics (fax machines, computers, automobile trim, telephones, and kitchen appliances) but was likewise phased out of new products in the US and Europe from about 2004 forward [7]. DecaBDE is used in carpet foam pads, draperies, television sets, computers, stereos and other electronics, cable insulation, adhesives, and textile coating [9]. All uses of decaBDE in products in the US are slated to be phased out by the end of 2013 [7]. Despite these bans, some products that have a long consumer life are still a source for pentaBDE and octaBDE and there is some concern that decaBDE may break down into lower, and more harmful, congeners [10].

The aforementioned bans on many of the lower congeners arose from animal model tests that showed liver toxicity,

thyroid hormone disruption, developmental toxicity, neurodevelopment deficits, and cancer, when laboratory animals were exposed to significant levels of PBDEs [11,12]. Some findings show that certain PBDEs bioaccumulate and biomagnify [13,14], and levels in humans are higher in North Americans than Europeans [15].

Many contaminants in indoor environments are due to indoor source emissions. With the trend of tighter buildings, these emissions become a larger concern for increased exposure to contaminants in the indoor environment. Americans spend about 90% of their time indoors [16], so higher indoor concentrations coupled with longer exposure time yields a larger dose to building occupants [17]. A large source of concern then is electronics, which typically use PBDEs to offset the fire risk posed by electrical failure. A study performed by Arcadis [18] indicated that of the 1.45 million tons of plastics used in electronic and electrical plastics, 186,000 tons were flame retarded using halogenated flame retardants (FRs). There is a strong argument for such measures, as according to Ahrens [19], there was an average of 360 non-confined structure fires involving computer equipment per year for the years 1999–2003. Of these non-confined structure fires, 80 involved the "appliance housing or casing" of the computer. These housings are typically made of high impact polystyrene (HIPS) or acrylonitrile butadiene styrene (ABS) plastics [20]. There is a fair amount of research examining the effectiveness of flame retarding electronic housings or the plastics that comprise them. Hilado [21] and Morgan and Bundy [5] have found in bench scale cone calorimeter testing that HIPS and ABS plastics samples exhibit lower peak heat release rates when flame retarded though only Morgan confirms that the flame retardant used is a BFR. Dipietro and Stepniczka [4] showed with TGA testing that HIPS and ABS plastics exhibited increased limiting oxygen indexes when retarded with increasing weight percentages of bromine. Nearer to the full scale, Babrauskas [22] details the results of a NIST study in measuring HRRs of computer monitors. The data display that monitors made of HIPS plastics with higher UL-94 ratings, typically corresponding to more flame retardants, likewise exhibit lower peak Heat Release Rates (HRRs) than their less retarded counterparts.

While the flame retardant performance of PBDEs in the HIPS and ABS plastics of computer cases has been examined, there is less exploration modeling the human exposure aspects of PBDEs that might off-gas from the polymers, especially due to the elevated temperatures seen in electronic housings. Models have been developed to predict emissions of volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs), of which PBDEs are a class, from materials into indoor environments [23–31]. A model for SVOC emission rates and concentrations was developed for di-2-ethylhexyl phthalate (DEHP) emissions from vinyl flooring [31]. The authors concluded that the mechanisms for emissions of SVOCs were the external controls, such as partitioning from the material into the gas phase, the convective mass transfer coefficient, and adsorption to various sinks while for VOCs, internal controls, such as the diffusion coefficient in the material itself, was the controlling factor.

In this paper, a model is developed that couples the thermal effects of heated electronics with the mechanisms of SVOC emissions from polymeric materials. Model parameters are used from physical and chemical data collected from literature as well as from experiments. Partitioning of PBDEs from the gas phase to the particulate phase is also examined since large compounds with lower-saturation vapor pressures have similar to or larger concentrations than the gas phase concentration [32]. The airborne particles provide one exposure pathway of the compound. The increase in emissions due to increased temperature shows the need for understanding this important pathway for PBDE emission and subsequent exposure.

2. Model description

The development of the model is similar to the previous VOC and SVOC models developed in literature [23–31] with the addition of the coupled heat transfer problem, two chambers, different boundary conditions, and a few different assumptions. A schematic of the computer tower in an indoor space is given in Fig. 1.

2.1. Heat and mass transfer

The mechanisms for heat and mass transfer are shown in the schematic representation of the slab in Fig. 2. For transient heat and mass diffusion, the governing equation in the slab is

$$\frac{\partial \phi(x,t)}{\partial t} = \chi \frac{\partial^2 \phi(x,t)}{\partial x^2} \tag{1}$$

where $\chi = \alpha$, D (thermal diffusivity or the diffusion coefficient) and $\phi = T$, C_m (temperature or concentration of the SVOC in the material), t is time, and x is the distance from $x = 0$ on the left of the slab to $x = L$ on the right, where L is the thickness of the slab. The diffusion coefficient is initially assumed to be independent of concentration. This assumption will be discussed later. The initial concentration and temperature are assumed to be constant throughout the slab.

$$C_m(x,0) = C_{m0} \text{ for } 0 \leqslant x \leqslant L \tag{2}$$

$$T(x,0) = T_0 \text{ for } 0 \leqslant x \leqslant L \tag{3}$$

A few simplifications may be assumed. Examining the diffusion time scales for the temperature and the concentration, it becomes obvious that the temperature diffusion functions on a much faster time scale than the mass diffusion. The diffusion time scale is on the order of $\tau \propto x^2/\alpha$ for temperature and $\tau \propto x^2/D$ for the concentration. For typical values, the diffusion time scale for temperature is on the order of minutes and on the order of tens to hundreds of days for concentration. Therefore, a lumped circuit analysis may be used for the temperature, as shown in Fig. 2.

2.2. Temperature profile

The temperature profile may be solved using a lumped circuit analysis, shown in Fig. 2. The convective and conductive resistances are, $1/hA$ and L/kA respectively, where h is the heat transfer coefficient, A is the area, and k is the thermal conductivity of the slab. Since the ambient temperatures, $T_{\infty,1}$ and $T_{\infty,2}$, are known, the heat flux may be calculated as

$$q_x'' = \frac{T_{\infty,2} - T_{\infty,1}}{\frac{1}{h_1 A} + \frac{L}{kA} + \frac{1}{h_2 A}} \tag{4}$$
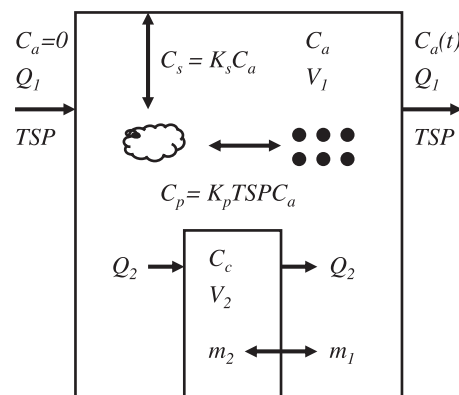

Fig. 1. Schematic of computer tower in indoor space.