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Measuring emissions of organophosphate flame retardants using a passive flux sampler

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Abstract

Flame retardants are used in polymers to reduce the flammability of building materials, electric appliances, fabric and papers. In recent years, organophosphate flame retardants have been used as substitutes for polybrominated flame retardants (BFRs). In Japan, the amount of organophosphate flame retardants used in 2001 was about five times more than in 2000. Recently, several studies have shown the health concerns for some organophosphate flame retardants. Little research has been performed on the emission of organophosphate flame retardants, especially the relationship between content and emissions. In this study, a new type of passive sampler was developed to measure emissions of organophosphate flame retardants from plastic materials. With this sampler, emissions from polyvinyl chloride wallpaper samples with different content of tris(2-chloroisopropyl)phosphate (TCPP) at different temperatures were examined. The observed maximum emissions of TCPP from 1, 3, 5, 10 and 20 w/w% content wallpaper materials were 262.3, 452.6, 644.8, 1119.1 and 2166.8 $\mu g\,m^{-2}\,h^{-1}$, respectively. Emissions from 5% TCPP content materials at 40 and 60 °C were 1135.7 and 2841.2 $\mu g\,m^{-2}\,h^{-1}$, respectively. A significantly positive correlation between the flux of TCPP and the TCPP content of the wallpaper samples was observed. A linear relationship was found between the inverse of temperature and the logarithm of TCPP emission. The results imply that the use of materials with a high organophosphate flame retardant content can lead to high emission rates in high-temperature indoor environments.

Keywords: Organophosphate flame retardants; Passive flux sampler; Wallpaper; TCPP

1. Introduction

In 2000, worldwide usage of flame retardants was estimated at 1.08 million tons of which 23% were organophosphate flame retardants (Nishizawa, 2003). Polybrominated diphenyl ether (PBDE) and polybrominated biphenyls (PBB) are the most frequently used types of polybrominated flame retardants (BFRs) and will be regulated by the executive branch of EU in 2006 (Directive 2002/95/EC, 2003). In recent years, organophosphate flame retardants were used as substitutes for BFRs. In Japan, the consumption of organophosphate flame retardants in 2001 was 22,000 tons, about five times that of 2000 (Japan Chemical Daily, 2002). Organophosphate flame retardants are additives to polymeric materials that typically constitute 1–30% of the composition with an average of 5–15% (Hartmann et al., 2004). Reducing the risk of fire is the main advantage of using organophosphate flame retardants. However, there are possible health risks from the toxicity of organophosphate flame retardants. Tris(2-chloroethyl)phosphate

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(TCEP) and tris(1,3-dichloro-2-propyl) phosphate (TDCPP) are carcinogenic for animals, and tris(2-chloroisopropyl)phosphate (TCPP) and tris(2-butoxyethyl) phosphate (TBEP) are possible carcinogens (WHO, 1998). Triphenyl phosphate (TPP) and trisbutyl phosphate (TBP) are associated with delayed neurotoxicity (WHO, 1991a, b).

Many organophosphate flame retardants have been detected in indoor air (Carlsson et al., 2000; Saito et al., 2001; Hartmann et al., 2004) and house dust (Marklund and Andersson, 2003; Kawahara and Yanagisawa, 2003). TCPP is also found in surface water (Andresen et al., 2004). TCPP and TCEP were the most predominantly detected organophosphate flame retardants in indoor air in Japan, the observed maximum indoor concentration of TCPP was higher than 10 $\mu g\,m^{-3}$ in Tokyo residence (Saito et al., 2001). Few studies have been performed on the emission of organophosphate flame retardants, especially the relationship between organophosphate flame retardant content and emission. In this study, a passive flux sampler was developed to determine the emission sources and evaluate the amounts of emission directly from the sources. Furthermore, the sampler was applied to establish the relationship between TCPP content and emission rate from wallpaper samples. Diffusion length dependence and temperature dependence of TCPP from the wallpaper samples were also evaluated.

2. Methods and materials

2.1. Design of the passive flux sampler

A passive sampler for organophosphate flame retardants (PFS-OFR) was developed in this study. The structure of the passive sampler is shown in Fig. 1. The PFS-OFR consisted of a circular glass plate (internal ∅47 mm, height 5 mm) and an Empore C18FF adsorbent disk (∅47 mm, thickness 0.5 mm; 3M Inc., USA).

The principle of the passive flux sampler has been described in Kumagai et al. (2002), Shinohara et al. (2003) and Fujii et al. (2003). Assuming the organophosphate flame retardant diffuses only by molecular diffusion, the flux of organophosphate flame retardants from plastic material surface can be determined by Fick's law

$$J = D\frac{C_1 - C_2}{L}, \quad (1)$$

where J ($kg\,m^{-2}\,s^{-1}$) is the flux of the target organophosphate flame retardant; D ($m^{-2}\,s^{-1}$) is the diffusion coefficient in the air; C_1 ($kg\,m^{-3}$) and C_2 ($kg\,m^{-3}$) are the surface gas phase concentrations at the emission source and adsorbent, respectively; and L (m) is the diffusion length of the sampler. In this study, the diffusion length was set at 4.5 mm. The maximum emission rates from plastics materials were determined.

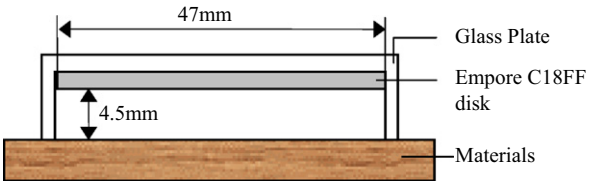

Fig. 1. Structure of PFS-OFR.

2.2. Analysis

The organophosphate flame retardants adsorbed by the Empore C18FF disk were ultrasonically extracted (W-113 MK-2, Honda Electronics Co. Ltd., Japan) for 30 min in 3 ml acetone (HPLC grade, Wako Pure Chemicals Co. Ltd., Japan). The organophosphate flame retardants were determined by a gas chromatography- flame photometric detection (GC-FPD, HP6890, Hewlett-Packard, USA) equipped with an HP-1 column (30 m × 0.25 mm i.d., 0.32 μm film thickness). The column was maintained at 70 °C for 2.0 min and then increased at 8.5 °C min^{-1} to 290 °C where it was maintained for 3 min. The injection temperature was maintained at 250 °C. An autosampler HP-7683 was used for sample injection. The injection volume was 3.0 μl and the pulsed-splitless injection mode was used. Helium was used as the carrier gas (20 ml min^{-1}, constant flow mode). The hydrogen and air flow were 90 and 100 ml min^{-1}, respectively. The 10 organophosphate flame retardant compounds studied—(trimethyl phosphate (TMP), triethylphosphate (TEP), TCEP, tris(2-ethylhexyl) phosphate (TEHP), TDCPP, tricresyl phosphate (TCP), TCPP, TBP, TBEP and TPP)—were purchased from Wako Pure Chemicals Inc.

2.3. Sample materials

The wallpaper samples with different TCPP content (1%, 3%, 5%, 10%, 20%, by weight) were donated by Kanto Leather Ltd., Japan. The main components of the wallpaper sample were polyvinyl chloride (PVC) and $CaCO_3$, 40% and 28%,