Occurrence and Control of Brominated Flame Retardants in a Laundry Factory for Home and Office Cleaning Utensils

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Introduction

Brominated flame retardants (BFRs) in indoor dust is an indicator of contamination caused by flame retarded products and interior settings (Frederiksen et al., 2009). Home and office cleaning textile utensils such as floor mops, door mats and clean cloths are generally used to remove contamination like dust, sand and mud from the surface. Consequently, these utensils could collect and accumulate BFRs through their use, which reflects actual situation of BFR contamination in the home and office environment. In this study, we investigated a laundry factory for the above cleaning utensils in Japan. In the plant, air monitoring for BFRs and polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/DFs) was conducted in the two working places and the results were compared to those obtained in other indoor environment. We also focused on the laundry wastewater treatment process to know the treatability of BFRs and PBDD/DFs and their distribution behavior between water and sludge during the treatment. In addition, through the analysis of floor dust and wastewater sludge in the factory, we attempt to feature general BFR levels and patterns in house and office dust in Japan.

Materials and Methods

Description of the factory

At the investigated plant, approximately 17,000 door mats, 14,000 dust mops, 4,800 clean cloths and 1,000 air cleaner filters were laundered in a day on an average, which were calculated from annual number of the treated products. The laundered utensils are resupplied to the customers. The plant had two sections for the treatment of cleaning utensils, i.e., a storage (stockpile) area for unwashed and washed utensils (storage area) and an area for laundry machines (laundry area). Laundry wastewater (average flow rate: 430 m^3/day) was treated in a thickener tank after passing through a screen. In the tank, conventional flocculation was conducted using ferrous chloride and polyacrylamide as flocculating agents. Average sludge generation rate was 1,800 kg/day. The thickener filtrate was discharged into the sewage system of the municipality.

Sampling

Sampling was conducted in November 2006. Stationary air sampling (350 m^3) was conducted for six hours by a middle-volume air sampling equipment made from glass fiber filter and polyurethane foam plugs. Floor dust sample (10 g) was collected by a vacuum cleaner in the stockpile space for unwashed utensils, differently from a stationary air sampling period. Wastewater (influent and effluent, 40-50 L each) and sludge samples (2 kg) were taken by composite sampling at regular intervals over a period of 6 hours. The outside air (1,000 m^3) at the boundary of the factory site was also sampled as a reference by a high-volume air sampler for one week.

Analysis

The target substances were extracted in a soxhlet extractor (solids) and by liquid-liquid extraction in a separation funnel (liquids). The crude extracts were cleaned up by using multilayer silica gel column chromatography for the analysis of polybrominated dipheniylethers (PBDEs), followed by additional activated carbon chromatography for the analysis of PBDD/DF, polychlorinated

dibenzo-*p*-dioxins/dibenzofurans (PCDD/DFs) and dioxin-like polychlorinated biphenyls (dl-PCBs). For analyzing tetrabromobisphenol-A (TBBP-A) and tribromophenols (TBPhs), the crude extracts were derivatized (ethylated) and cleaned up by florisil column chromatography, while only florisil column chromatography was needed for the analysis of hexabromocyclododecanes (HBCDs). The final extracts were concentrated and analyzed by GC/HRMS for PBDEs, PBDD/DFs, TBBP-A and TBPhs, and by LC/MS for HBCDs.

Results and Discussion

BFRs and PBDD/DFs in work place air

The concentrations of BFRs and PBDD/DFs in the air of two working places and outside boundary are presented in Fig. 1. PBDEs were identified at 1,200 and 730 pg/m^3, respectively, in the storage and laundry areas. PBDE concentrations are one to two orders of magnitude lower than those in the dismantling hall of the E-waste recycling facilities (Sjödin et al., 2001; Takigami et al., 2006), however, higher than indoor air in Japanese residential houses by one to two orders of magnitude (Takigami et al., 2009). DecaBDE dominated the pattern of PBDEs, while concentrations of lower brominated diphenylethers (i.e., mono- to tetraBDEs) are also remarkable, especially in the gaseous phase. Such "two-peak" patterns are peculiar to this laundry factory and two locations in the factory are similar in patterns of PBDEs. Based on the identified PBDD/DF isomer concentrations, the "TEQs" for PBDD/DFs were tentatively calculated on trial by employing WHO-TEFs (van den Berg et al., 2006) of their chlorinated counterparts.

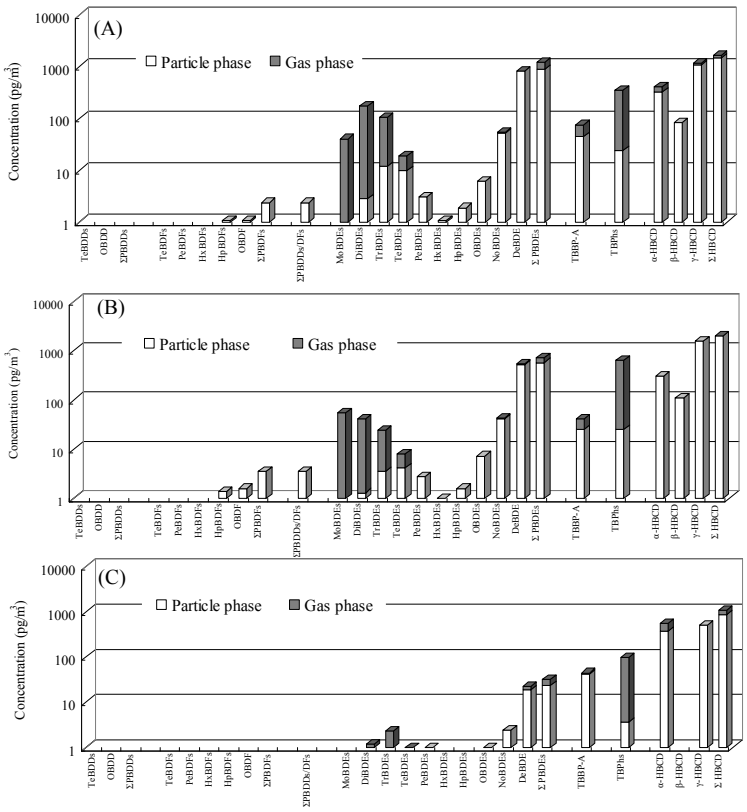

Fig.1 Air concentrations of BFRs and PBDD/DFs in the storage area for unwashed utensils (A), the vicinity of laundry machines (B) and outside boundary of the factory site (C). No bars are shown for

The PBDD/DF-TEQs in the storage area and laundry area are 0.62 and 0.61 pg/m^3, which are ten times higher than TEQs (0.052 and 0.062 pg/m^3, respectively) for PCDD/DFs and dl-PCBs. HBCD concentrations (1,700 – 2,000 pg/m^3) are also as high as PBDEs in the two work places, though those seems to be influenced by outside air.

Behavior of BFRs and PBDD/DFs during wastewater treatment

As for laundry wastewater, each of the sum of PBDEs, HBCDs and PBDD/DFs, and TBBP-A in the influent became at least one order of magnitude lower during the treatment, which indicates apparent (liquid-phase) removal of those compounds (Fig. 2). Here also TEQs for PBDD/DFs were calculated and a marked decrease from 7.1 to 0 pg/L was confirmed (in the case of congener concentration below the quantification limit, TEQ was calculated as zero). On the other hand, removal efficiency of TBPhs were quite low, for which could be partially accounted by water-soluble property of TBPhs. In order to complete the mass balance for BFRs and PBDD/DFs, concentrations detected in influent, effluent and sludge were multiplied by the corresponding average flow rates. As a result, higher brominated diphenylethers (tetra- to decaBDE) and PBDD/DFs were clearly transferred to sludge without degradations, while mono- to diBDEs showed remarkable loss from the liquid and sludge phases, suggesting vaporization or degradation.

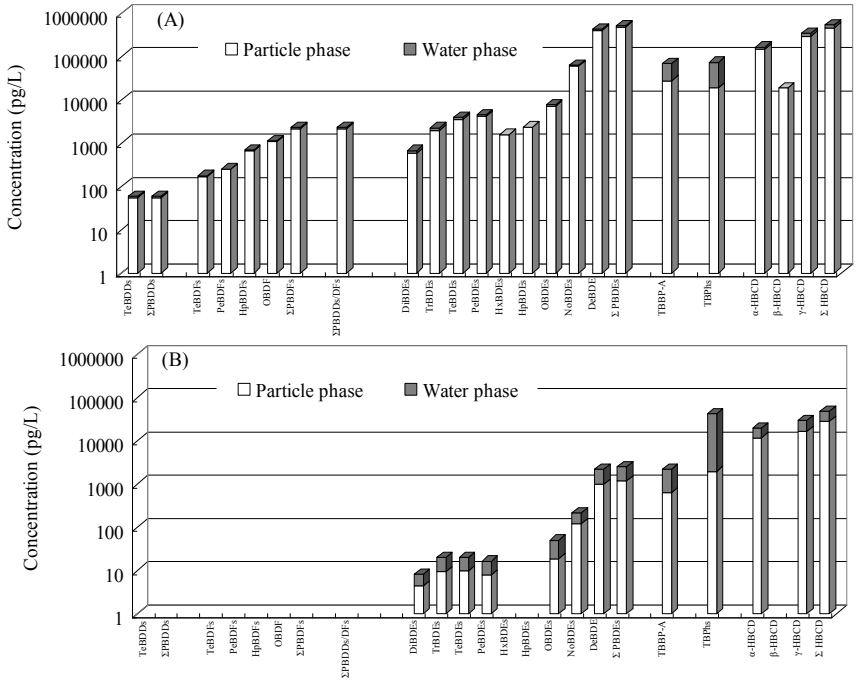

Fig. 2 The concentrations of BFRs and PBDD/DFs in the influent (A) and effluent (B) of a wastewater treatment plant. No bars are shown for homologues below detection limits.

BFR and PBDD/DF profiles in floor dust and sludge

Fig. 3 shows the concentration patterns of BFRs and PBDD/DFs in floor dust collected from the storage area and wastewater treatment sludge. The two samples showed similar patterns and the concentrations in the sludge were lower. This could be due to “dilution” of the dust with flocculants. When compared to the reported data for TV interior dust (as a “source” dust) and house dust (Takigami et al., 2006, 2008), BFR and PBDD/DF concentrations in the floor dust were in the middle

level between the two dust samples. Generally, office dust showed higher BFR and PBDD/DF level than house dust in Japan (Suzuki et al., 2006) and the floor dust would be mixtures of office and house dust, which is in accordance with the result in this study. Regarding PBDEs, the floor dust were dominated by decaBDE, and tetra- and pentaBDE concentrations were relatively high, which shows typical feature of Japanese indoor dust samples.

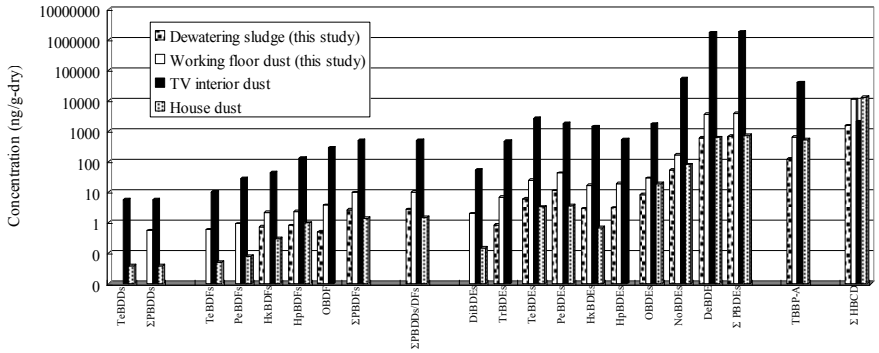

Fig. 3 The concentration patterns of BFRs and PBDD/DFs for the sludge and dust samples. No bars are shown for homologues below detection limits. Data for TV interior dust and house dust were quoted from the papers by Takigami et al. (2006, 2008)

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