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Polybrominated diphenyl ethers in various atmospheric environments of Taiwan: Their levels, source identification and influence of combustion sources

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ABSTRACT

In this study, ambient air samples from different atmospheric environments were examined for both PBDE and PCDD/F characteristics to verify that combustion is a significant PBDE emission source. The mean ± SD atmospheric PBDE concentrations were 165 ± 65.0 pg Nm^{-3} in the heavy steel complex area and 93.9 ± 24.5 pg Nm^{-3} in the metals complex areas, 4.7 and 2.7 times higher than that (35.3 ± 15.5 pg Nm^{-3}) in the urban areas, respectively. The statistically high correlation ($r = 0.871$, $p < 0.001$) found between the atmospheric PBDE and PCDD/F concentrations reveals that the combustion sources are the most likely PBDE emission sources. Correspondence analysis shows the atmospheric PBDEs of the heavy steel and metals complex areas are associated with BDE-209, -203, -207, -208, indicative of combustion source contributions. Furthermore, the PBDEs in urban ambient air experience the influence of the evaporative releases of the commercial penta- and octa-BDE mixtures, as well as combustion source emissions. By comparing the PBDE homologues of indoor air, urban ambient air, and stack flue gases of combustion sources, we found that the lighter brominated PBDEs in urban ambient air were contributed by the indoor air, while their highly brominated ones were from the combustion sources, such as vehicles. The developed source identification measure can be used to clarify possible PBDE sources not only for Taiwanese atmosphere but also for other environmental media in other countries associated with various emission sources in the future.

1. Introduction

Polybrominated diphenyl ethers (PBDEs), structurally similar to polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs), have been extensively used as brominated flame retardants (BFRs) in a large variety of consumer products. However, concern has risen because animal and epidemiological studies show PBDEs exposure can cause liver toxicity, developmental neurotoxicity, and may relate to metabolic obesity (Chao et al., 2007; Herbstman et al., 2007; Main et al., 2007; EPA, 2009). Total PBDEs in breast milk were found associated positively with the serum of luteinizing hormone (Main et al., 2007). Prenatal PBDE exposures were significantly related to decreased total and free thyroxine levels (Herbstman et al., 2007). Our previous study also showed that increased PBDEs in breast milk was related with decreased birth weight and length (Chao et al., 2007). The commercial penta-BDE, octa-BDE and deca-BDE mixtures have been banned within the European Union (European Court of Justice, 2008). No new manufacturing or importing of commercial penta-BDE and octa-BDE mixtures has been allowed in the US (2009). Nevertheless, the use of PBDEs is still not restricted in Taiwan.

Many studies have reported that environmentally ubiquitous PBDEs are mainly the result of using PBDE-containing products indoors (Prevedouros et al., 2004; Harrad and Hunter, 2006; Sakai et al., 2006). Schenker et al. (2008) calculated global PBDE discharges from production, use and waste-management, and found that they underestimated global PBDE emissions. Their model's prediction was close to field data from environmental measurements only on simulating a "worst case" by using emission factors based on vapor pressure, high values for PBDE production, and PBDE containing waste partially burnt in open fire. It needs to be noted that PBDE emission estimation from the vapor pressures of PBDE congeners could be two orders higher than that evaluated from their K_{OA} (Prevedouros et al., 2004).

PBDE emissions from stationary and mobile combustion sources to the atmosphere were not included in the mentioned

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estimation, maybe because these emissions used to be believed to be much smaller than the evaporative releases from PBDE-containing products (Prevedouros et al., 2004; Sakai et al., 2006). However, recently the importance of stationary and mobile combustion sources with regard to atmospheric PBDEs has been uncovered (Wang et al., 2010b, 2010c). The occurrence of PBDEs in the flue gases of power plants and vehicles, as well as their PBDE concentrations highly correlated with those of combustion-originated PCDD/Fs, reveal that PBDEs are likely to be the products of combustion (Wang et al., 2010b). Our previous study (Wang et al., 2010b) also found out that in the US combustion sources are larger PBDE emitters to the atmosphere (1260 kg year^{-1}) than houses and garages (722 kg year^{-1}) Batterman et al., 2009.

Higher atmospheric PBDE concentrations in industrial sites than those in urban and residential areas have been reported (Cetin and Odabasi, 2008; Choi et al., 2008). But only ambient air sampling campaigns without measuring the highly brominated PBDE congeners, especially for BDE-209, and without fully characterizing PBDE emissions from combustion sources, the obtained conclusion that metallurgical processes are the source of PBDE emissions, and their proposed causes (Cetin and Odabasi, 2008; Choi et al., 2008) are still not convincing.

This study is a sequel to our previous research (Wang et al., 2010b) which focused on the PBDE emission characteristics of the combustion sources and estimation of their PBDE emission quantities. In the present study, ambient air samples from metals complex and urban areas were examined for both PBDE and PCDD/F characteristics to explore the relationships between these two pollutants. Furthermore, PBDE homologue profiles of the ambient air samples were compared to those of indoor air, the commercial PBDE mixtures and combustion sources to support the contention that combustion is an important PBDE emission source.

2. Materials and methods

2.1. Areas of atmospheric samplings

Ambient air samples were collected from three types of locations in Taiwan, namely heavy steel complex, metals complex, and urban areas during March–April, 2009. Each area included 5–14 atmosphere sampling sites to obtain good representative samples. The sampling locations of the three categories of atmospheric environments are depicted in Fig. S1 of Supplementary material. The sampling locations in the heavy steel complex areas (HI1–HI11) are situated in the Lin-hai industrial park in the Siaogan district (3800 population km^{-2}) of Kaohsiung city, Taiwan's largest metallurgical industrial complex with a large steel production. The region chosen to represent the heavy steel complex area is clustered with sinter plants and electric arc furnaces (EAFs). Some secondary aluminum smelters (secondary ALSs) and secondary copper smelters, and several incinerators, including one large scale municipal solid waste incinerator (MSWI), one medical waste incinerator, and some industrial waste incinerators, are also located in this region (Lee et al., 2004; Kao et al., 2007; Wang et al., 2008). The sampling sites (I1–I9) for metals complex areas are in the Gangshan (2000 population km^{-2}) and Renwu (1800 population km^{-2}) townships of Kaohsiung county, with some metallurgical facilities, two MSWIs and one power plant in or close to these areas. The sampling sites (U1–U14) for urban areas were in the Neihu (8380 population km^{-2}) and Wenshan (8300 population km^{-2}) districts of Taipei city. Except for the two MSWIs, there are no major PCDD/F and PBDE stationary sources in the urban areas. To our best knowledge, there are no other important sources or activities of outdoor PBDE emissions in these areas, such as electronics recycling facility (Cahill et al., 2007), automotive shredding facility (Cahill et al., 2007) and open burning of residential waste dumps (Gullett et al., 2010).

The meteorological data were obtained from the local air quality monitoring stations. The sampling information is detailed in Table S1 of Supplementary material, which shows that the atmospheric temperature and pressure during sampling periods ranged from 21 °C to 25 °C and 758 to 763 mm Hg. Mean wind speeds at 10 m height in each sampling area were between 1.8 and 2.1 m s^{-1}. The meteorological data shows that the weather conditions during these sampling periods did not change too much.

2.2. Sampling procedures

All the atmospheric samplings and chemical analyses in this study were carried out by our accredited laboratory, which specializes in PCDD/F samplings and analyses in Taiwan. Each ambient air sample was collected for 72 h at ~0.225 m^3 min^{-1} with PS-1 sampler (Graseby Andersen, GA) following US EPA Reference Method TO9A. A quartz fiber filter followed by PUF captured particle and gas phase PCDD/Fs and PBDEs. Concentrations are reported with respect to standard conditions of 760 mm Hg and 298 K and denoted as Nm^3.

2.3. Analytical procedures

The quartz fiber filter and PUF of each sampling site were combined for analysis to represent a whole ambient air sample. Samples were analyzed for thirty PBDE and seventeen 2,3,7,8-substituted PCDD/F congeners. PBDE analyses were performed following US EPA Method 1614, while PCDD/F analyses followed US EPA Method TO9A. PBDE and PCDD/F internal standards were spiked to the samples before Soxhlet extraction with toluene, and were used to monitor the extraction and cleanup procedures. After extraction, the extracted solution was divided into two equal aliquots. One aliquot was used to measure PBDEs and PCDD/Fs, while the other was stored for possible use. The detailed analytical procedures for PBDEs and PCDD/Fs are given in our previous works (Wang et al., 2003a; Wang et al., 2010c) and described in Supplementary material. In brief, the concentrated extract was treated with concentrated sulfuric acid, and this was followed by a series of sample cleanup and fractionation procedures, including a multi-layered silica column, alumina column and activated carbon column. The activated carbon column was used for well separating PBDEs and PCDD/Fs due to differences in planarity and absorption properties, as is the case with separations of mono-ortho PCBs from PCDD/Fs (Choi et al., 2003). The column was sequentially eluted with 25 mL dichloromethane/hexane (40/60, v/v) for PBDEs, followed by 35 mL of toluene for PCDD/Fs. The eluate was concentrated to approximately 1 mL and transferred to a vial. The concentrate was further concentrated to near dryness, using a stream of nitrogen. Immediately prior to analysis, 10 μL of the standard solution for recovery checking was added to the sample extract immediately prior to injection to minimize the possibility of loss.

2.4. Instrumental analysis

A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used for PBDE and PCDD/F analyses. For PBDEs, the HRGC (Hewlett–Packard 6970 Series gas chromatograph, CA) was equipped with a DB-5HT capillary column (L = 15 m, i.d. = 0.25 mm, film thickness = 0.1 μm) (J&W Scientific, CA). For PCDD/Fs, the HRGC was equipped with a DB-5MS fused silica capillary column (L = 60 m, i.d. = 0.25 mm, film thickness = 0.25 μm) (J&W Scientific, CA). The HRMS (Micromass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI+) source. The analyzer mode of the selected