Polybrominated Diphenyl Ethers in Soils from Various Locations in Surabaya City, Indonesia: Dumping Site and Urban Areas as Important Sources

Muhammad Ilyas[1,2], Agus Sudaryanto[1,2], Iwan Eka Setiawan[2], Adi Slamet Riady, Tomohiko Isobe[1], Shin Takahashi[1] and Shinsuke Tanabe[1]

[1] Center for Marine Environmental Studies (CMES), Ehime University, 2-5 Bunkyo-cho, Matsuyama, Japan

[2] Agency for the Assessment and Application of Technology (BPPT), Jl.M.H. Thamrin 8, Jakarta, Indonesia

Introduction

Environmental contamination by brominated flame retardants (BFRs), particularly polybrominated diphenyl ethers (PBDEs) which are used in high volumes as flame retardants of numerous types of polymers and resins in furniture and electronic components (Watanabe & Sakai, 2003), has become a global issue due to their increasing levels in the environment, wildlife and human. These compounds as those of persistent organic pollutants (POPs) have unique properties such as low volatility, persistent, chemically stable and bioaccumulative nature, and thus the bioaccumulation of these compounds to wildlife has been of concern (Xia et al., 2008; Letcher et al., 2009). PBDEs also have similar potential toxicity as legacy POPs to generate effects on thyroid hormone levels, kidney morphology, reproductive success, fetal toxicity/teratogenicity, neurodevelopment and liver ethoxy-resorufin-*O*-deethylase activity (Darnerud, 2003).

As has been shown in global cycle of POPs, soils could serve as reservoir pollutants via atmospheric deposition and/or direct applications, which the storage capacity for these contaminants is, dependent upon the types and contents of organic matter (Nam et al., 2008). Worldwide soil contamination by PBDEs (Hassanin et al., 2004; Wang et al., 2005; Leung et al., 2007; Sun et al., 2009; Eguchi et al., 2009), point to the potential human exposure to PBDEs through direct contact with soil (residences, parks, schools and playgrounds) and/or indirect such as inhalation vaporized soil contaminants and bioavailability in soil (Mueller et al., 2006). Therefore, characterization of PBDEs in soil from various locations is important to assess the fate, behavior and potential risks of these compounds to human. The present study aims at evaluating the levels, distribution and profiles of PBDEs in soil samples from several locations (representing different activities) such as urban city roads, dumping site and agricultural areas in Surabaya city, Indonesia.

Materials and Methods

Study Area and Sample Collection

Surabaya is the largest industrial city in the eastern part of Indonesia, having three industrial areas (Rungkut; the biggest industrial estate, Ngagel; built since Dutch colony and Tandes; the new center of developing industry of Surabaya city). The major industries are shipping, electronics, home appliances, textiles, cosmetics, traditional herbs, handicrafts, ceramics, and flour. This city, located between 7°12'–7°21' south latitude and between 112°36'–112° 54' east longitude is 3-6 meters above sea level (Fig.1). The city is surrounded by Madura Strait on the northern and eastern parts, Sidoarjo regency on the southern and Gresik regency on the western part with a total area and population around 33,306 km^2 and 2.7 million in 2004, respectively. Twenty-three soil samples were collected during August - September 2008 from three locations representing different activities (Fig.1), namely municipal dumping site (Benowo=DMPS; *n*=6), roads (urban/industrial/commercial road at city and rural=ROAD; *n*=14) and agricultural areas (Sukolilo=AGR; *n*=3). Samples were kept in ice boxes, transported to Japan and stored at -20˚C in the Environmental Specimen Bank (*es*-Bank) of Ehime University (Tanabe, 2006), prior to chemicals analyses.

Chemical Analysis

Extraction and Clean-up

PBDEs were analyzed using the method described by Minh et al. (2007) with slight modification.

Briefly, around 5~10 g dried samples were spiked with $^{13}C_{12}$-BDEs ($^{13}C_{12}$-BDE-3, -15, -28, -47, -99, -153, -154, -183, -197, -207, -209) as labeled recovery internal standards (LRIS) for measuring the extraction efficiency and losses during extraction and clean-up. The samples were liquid-liquid extracted using a mixture of 50% of acetone/hexane (v/v), shaken vigorously for 60 minutes using an electric shaker and ultra-sonified for 15 minutes. The extracts were then centrifuged and the supernatants collected and concentrated to about 1~2 ml in a rotary evaporator. As the first step of clean-up procedures, the concentrated supernatants were passed through a multi layer silica gel column using 25% of DCM/Hexane (v/v) as the solvent for elution. For further clean-up, the concentrated supernatants were treated with concentrated H_2SO_4 prior to gel permeation chromatography (GPC). The GPC fractions containing organohalogens were concentrated and passed through a column packed with 4 g of activated silica gel for final purification and fractionation. The fractions containing PBDEs were eluted by 80 ml of 5% dichloromethane in hexane (v/v), concentrated to 5 ml and treated with activated copper strings. $^{13}C_{12}$-labeled BDE-126 and BDE-205 were added as a labeled instrument performance and matrix internal standard prior to gas chromatography analysis.

Instrumental Analysis

Quantification of PBDEs was carried out by a gas chromatograph coupled with a mass spectrometer detector (GC-MS) using electron ionization with selective ion monitoring (EI-SIM) mode. All the congeners were quantified using the isotope dilution method to the corresponding $^{13}C_{12}$-labeled congeners. The instrumental condition was kept as described previously by Minh et al. (2007). Forty BDE congeners from mono- to deca-BDE (BDE-3, -15, -28, -49, -71, -47, -79, -66, -77, -100, -119, -99, -118, -85, -126, -155, -154, -153, -139, -140, -138, -128, -169, -184, -183, -182, -180, -171+190, -170, -201, -197+204, -203, -196, -205, -194, -207, -206, -209) were analyzed in this study. Concentrations of all the targeted BDEs congeners were summed to obtain the values of ΣPBDEs. Concentrations of PBDEs were expressed as nanogram per gram dry weight (ng g^{-1}dw) unless otherwise specified. For quality assurance (QA)/quality control (QC), procedural blanks for every 7 samples were performed to check for any contamination during samples processing. In addition, recovery check and instrument performance were done using internal standards during extraction and just prior to GC-MS analysis.

Results and Discussion

Levels and Spatial Distribution

Concentrations and spatial distribution of total PBDEs in soil samples from roads, dumping sites, and agricultural sites are shown in Fig.1. Levels of PBDEs varied according to sampling locations and suggest localized sources of these compounds in Surabaya. Concentrations of these compounds were found higher in soils from dumping site (mean: 9.7 ng g^{-1}dw; range: 0.87-24 ng g^{-1}dw) and urban roads (mean 10 ng g^{-1}dw; 0.58-22 ng g^{-1}dw) than those from agricultural site (mean 0.23 ng g^{-1}dw; 0.08-0.35 ng g^{-1}dw). These results indicate ubiquitous occurrence of these compounds in the environment, and suggest that municipal dumping site as well as main roads, particularly from urban, industrial and commercial areas (ROAD-2, -3, -6, -7, -8, -9, -12 and -14) in Surabaya could be major sources of PBDEs contamination. The role of dumping site as source of contaminants including PBDEs has also been reported in several Asian developing countries (Eguchi et al., 2009). Concentrations of PBDEs in agricultural soil were quite low and contamination in this location may be due to deposition from particulate matter through atmospheric transportation.

Compared with other studies, concentrations ranges of PBDEs in soils samples from dumping site at the present study were lower than those in Bantar Gebang dumping site, Jakarta (Indonesia; 0.11-255 ng g^{-1}dw), Phnom Phen (Cambodia; 0.55-91 ng g^{-1}dw) and Hanoi (Vietnam; 1.2-429 ng g^{-1}dw), but comparable with a study in Chennai (India; 0.82-19 ng g^{-1}dw), as reported by Eguchi et al. (2009). The levels of PBDEs in all these municipal dumping sites, were not as high as those observed from the e-waste recycling activities in China such as recycling site (0.26-824 ng g^{-1}dw) in Guiyu, Guangdong Province (Wang et al., 2005), acid leaching site (2720-4250 ng g^{-1}dw) and a printer roller dumping site (593-2890 ng g^{-1}dw) from Southeast China (Leung et al., 2007). Furthermore, levels of PBDEs in road soils from urban/industrial/commercial areas of the present study were lower compared to those in urban (0.016-211 ng g^{-1}dw) and industrial soils (6.0-144 ng g^{-1}dw) at Taiyuan, China (Li et al., 2008). However, levels of tetra- to hexa-BDEs were relatively comparable with those similar congeners in European background soils (0.06-12 ng g^{-1}dw), (Hassanin et al., 2004). Concentrations of PBDEs in agricultural soils were also comparable with similar areas in India (n.d.-0.18 ng g^{-1}dw) and Vietnam (0.02-0.42 ng g^{-1}dw) but lower than Cambodia (n.d.-182 ng g^{-1}dw) (Eguchi et al., 2009) and irrigated soils from Beijing, China (0.50-3.3 ng g^{-1}dw) (Sun et al., 2009).

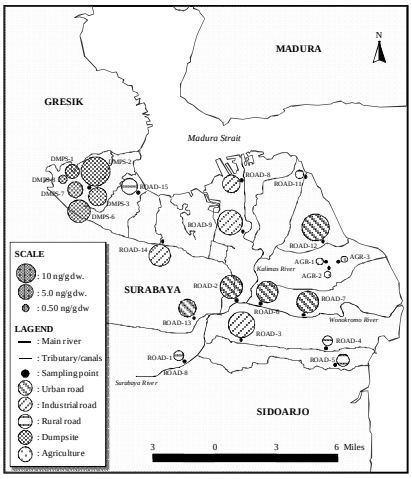

Figure 1. Levels and distribution of PBDEs in soil samples from various locations of Surabaya (DMPS= dumping site; ROAD= road and AGR= agriculture).

Profiles of PBDEs

Of the PBDE congeners analyzed, BDE-15, -47, -49, -66, -99, -100, -155, -154, -183, -196, -197, -203, -201, -208, -207, -206 and BDE-209 were detected in soils from the present study. Deca BDE homologue (BDE-209) was the predominant in all the samples and accounted for 70% in soil from roads, 64% from dumping site and 62% from agriculture; followed in the order by nona-, octa-, hepta-, penta-, tetra-, hexa-, di-, tri- and mono-BDE homologue (Fig. 2). Despite the fact that Deca-BDE commercial formulation (consisting mainly BDE-209) is the currently used major BFRs, the dominant BDE-209 in soils matrices is due to fact that this congener has a strong binding affinity to particles. Besides BDE-209, BDE-207; -206; -197 and -47 were among the dominant congeners detected in the soils of the present study. Similar profiles of PBDEs in soil samples of the present study have also been reported in other worldwide studies (Hassanin et al., 2004; Wang et al., 2005; Leung et al., 2007; Sun et al., 2009).

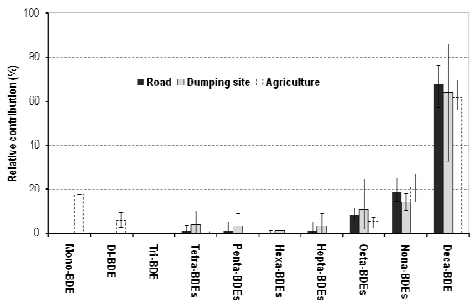

Figure 2. PBDE homologue profiles in soil samples from dumping site, road and agriculture areas of Surabaya.

The wide detection ranges of octa- to nona-BDEs (BDE-206, -207, -208, -203, -201, -197, -196, -194, -205) and other lower BDE congeners in the samples may suggest debromination from BDE-209, possibly from photolytic (Soderstrom et al., 2004) and/or bacterial debromination (Yen et al., 2008). For example, two of six soil samples from dumpsite (DMPS1 and DMPS8) were also found to contain

high contribution of lower BDE congeners (tetra- to octa-BDEs) relative to other samples, which could be additional from photolytic and/or microbially mediated reductive debromination (Soderstrom et al., 2004; Yen et al., 2008). Moreover, these two samples are associated with dumpsite leachate and thus the possibility to accumulate the lighter congeners which are more hydrophilic. On the other hand, the detection of lower congeners from mono- to hepta-BDEs could also be due to atmospheric transportation. For instance, the larger proportion of BDE-3 and BDE-15 in soils from agricultural sites (far from sources) than road and dumping site (considered as sources) may be due to deposition from atmospheric transportation of these volatile congeners. Finally, the variation of PBDE profiles (Fig.2), including the available penta-, hexa-, hepta-, octa- and nona-BDEs in soil samples of the present study may suggest that Penta- and Octa-BDE product mixtures could also be used in Surabaya.

Acknowledgements
This study was supported by Grants-in-Aid for Scientific Research(S) (No. 20221003) from Japan Society for the Promotion of Science (JSPS), Research Grants for Promoting and Developing Sound Material-cycle Societies (Nos. K2121 and K2129) from Ministry of the Environment, & Global Center of Excellence (G-COE) Program by the Ministry of Education, Culture, Sport, Science and Technology (MEXT) and JSPS.

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