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Characterization of Polychlorinated Biphenyls and Polybrominated Diphenyl Ethers in Sediments from Leachate and Control Wells of Benowo Dumping Site, Surabaya, Indonesia: A Preliminary Report

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Abstract—Concentrations of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) have been measured in fourteen sediment samples collected from leachate ponds, control wells, leachate treatment plants (LTPs), and a reference site of Benowo dumping site of Surabaya City, Indonesia. The PCBs and PBDEs were analyzed by gas chromatograph-mass spectrometer (GC-MS) using internal standards. Concentrations of ∑PCBs and ∑PBDEs in all samples ranged from 0.10 to 30 ng/g dw (mean = 8.8 ng/g dw) and 0.08 to 45 ng/g dw (mean = 7.8 ng/g dw), respectively. Although the profiles of PCBs and PBDEs varied between the sites, overall pattern showed domination of hexa-, penta-, tri-, tetra- and hepta-CBs, respectively for PCBs, and BDE-209, -207, -206, -99 and -47, respectively for PBDEs. The profiles indicated either Ar1260, KC600, or ClophenT64 and Deca-BDE product mixture were widely used in Surabaya City. Furthermore, decreasing levels of PCBs and PBDEs were observed along the LTPs system, indicating the capacity of this system to reduce and degrade those contaminants. To our knowledge, this is the first study on the characterization of PCBs and PBDEs in sediments from leachate pond, control wells, and LTPs system in and around dumping site.

Keywords: PCBs, PBDEs, sediments, leachate, LTPs, Benowo dumping site, Surabaya City, *es*-Bank

INTRODUCTION

Landfill leachate is the liquid material produced in the landfill system. These leachates contain high organic matter and other pollutants. Therefore, it could be a spot pollutant source and may pose potential health risk to both surrounding

Table 1. Levels of PCBs and PBDEs (ng g^{-1} dw) in leachate sediments from Benowo dumping site, Indonesia and in WWTPs sludge and several other locations worldwide.

Countries	*n*	PBDEs	PCBs	Sampling time (year)	References
Australia	16	1137	n.a.	2006	Clarke *et al.*, 2008
Palo Alto, Calf., USA	n.a.	1440	n.a.	n.a.	North, 2004
Beijing, China	8	n.a.	101	2007	Li *et al.*, 2009
Kuwait	18	191	n.a.	2005–2006	Gevao *et al.*, 2008
China	31	94	n.a.	2005	Wang *et al.*, 2007
Valenton, France	n.a.	n.a.	201	1998–1999	Blanchard *et al.*, 2001
Acheres, France	n.a.	n.a.	2720	1998–2000	Blanchard *et al.*, 2001
Spain	5	572	n.a.	2005	Eljarrat *et al.*, 2008
Surabaya, Indonesia	1	13	30	2008	This study

n.a. = not available; dw = dry weight; *n* = number of sample.

ecosystems and human (Salem *et al.*, 2008). Leachate has been of great concern (SEPA, 2003; Saruji and Mangkoedihardjo, 2007) due to possible contamination of groundwater and surface water surrounding landfill sites and ultimately a potential threat to fish, other aquatic organisms and human. As a water based solution, leachate may contain four groups of contaminants such as dissolved organic matter, inorganic macro-components (common cations and anions including SO_4^{2-}, Cl, Fe, Al, Zn and NH_3), heavy metals (Pb, Ni, Cu, Hg, etc.) and halogenated compounds such as PCBs, dioxin, etc. (Caville and Robinson, 2005).

On the other hand PCBs and PBDEs are environmental pollutants that have attracted the attention of the public and policy makers due to their potential toxic effects on human and wildlife (Wurl and Obbard, 2005). Although studies on characterization of leachate such as chemical oxygen demand (COD), biological oxygen demand (BOD), pH, temperature profiles, NH_3, etc. have been traditionally done (Osako *et al.*, 2004; Sarudji and Mangkoedihardjo, 2007), studies on PCBs and PBDEs in dumping site leachate ponds, control wells, and LTP systems are still scarce.

The present study aims to characterize PCBs and PBDEs in sediments collected from landfill leachate, LTP pond, control well, and a reference site of Benowo dumping site, Surabaya, Indonesia and to evaluate the capability of LTP systems on reducing organic pollutants such as PCBs and PBDEs. Furthermore, this study provides the preliminary information on PCBs and PBDEs contamination in sediments from dumping sites to assess their potential risk and control studies for better management of the environment.

MATERIALS AND METHODS

Sample collection and pretreatment

A total of 14 sediment samples were collected from different sites in and around Benowo dumping site and its LTP systems (control wells: *n* = 4; raw

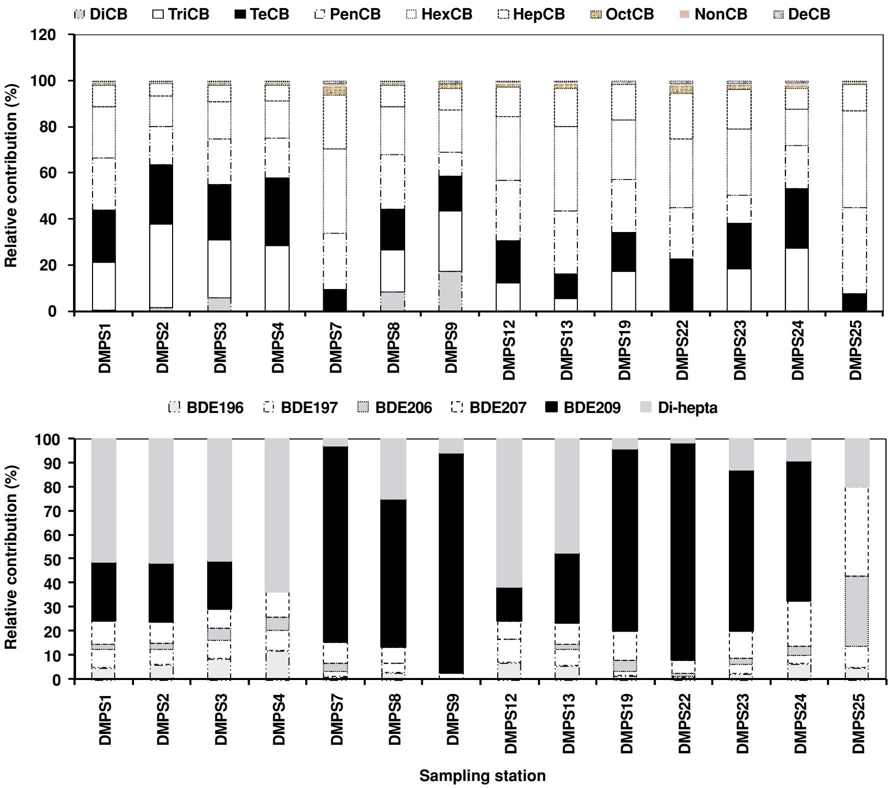

Fig. 1. Profiles of CB homologues (upper) and BDE congeners (lower) in sediments.

leachate pond: $n = 1$; LTP systems: $n = 8$; reference site: $n = 1$) of Surabaya City, Indonesia during August and September, 2008. Samples were deep frozen prior to transport and stored in Environmental Specimen Bank (*es*-Bank) of Ehime University, Japan. Sediment samples were freeze-dried for over 96h and mixed homogenously before analysis.

Extraction and clean-up

BFRs and PCBs were analyzed using the method described by Minh *et al.* (2007) and Isobe *et al.* (2007) with slight modification. Briefly, approximately 10 g of freeze dried sediment sample was spiked with $^{13}C_{12}$-BDEs ($^{13}C_{12}$-BDE-3, -15, -28, -47, -99, -153, -154, -183, -197, -207 and -209), ^{13}C-HBCD (α-, β- and γ-$^{13}C_{12}$-HBCD) and $^{13}C_{12}$-PCBs ($^{13}C_{12}$-CB-28, -52, -95, -101, -118, -105, -153, -138, -167, -156, -157, -178, -180, -170, -189, -194, -208, -206 and -209) as labeled recovery internal standards (LRIS) for measuring the extraction efficiency and losses during extraction and clean-up. The sample was extracted using a mixture of 50% of acetone/hexane (v/v), shaken vigorously for 60 minutes using

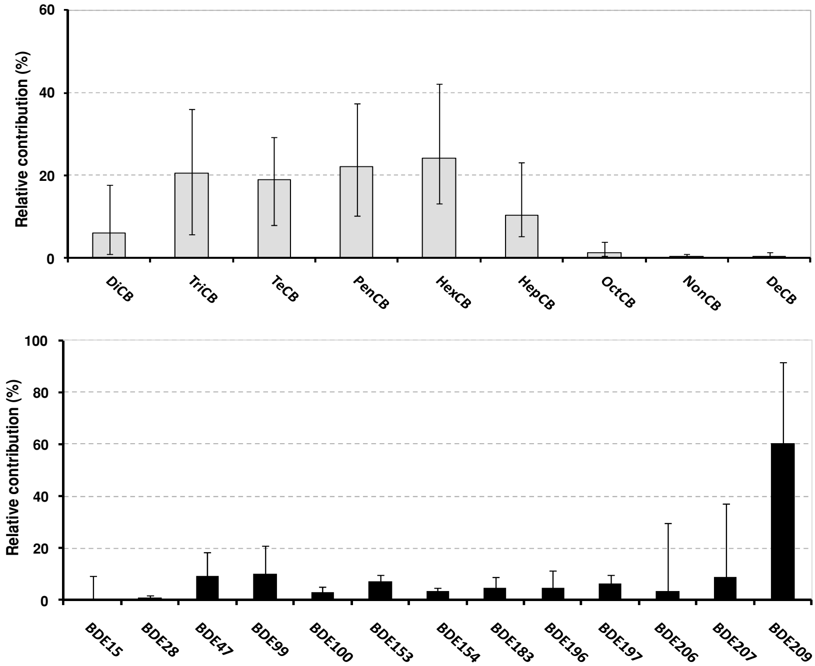

Fig. 2. Profiles of PCB (upper) and PBDE (lower) in the sediment samples.

an electric shaker and ultrasonicated for 15 minutes. Then the concentrated extract was passed through a multi layer silica gel column for clean-up. For further clean-up, the extract was treated with concentrated H_2SO_4 and subsequently cleaned up by gel permeation chromatography (GPC). The fraction containing PBDEs and PCBs was concentrated to 5 ml and treated with activated copper strings to remove sulpher. $^{13}C_{12}$-labeled BDE-139 was added as a labeled instrument performance and matrix internal standard (LIPMIS) prior to GC-MS analysis.

Instrumental analysis

Quantification of PCBs and PBDEs were carried out by GC-MS using electron ionization in selective ion monitoring (EI-SIM) mode. The instrumental condition was kept as described previously by Kajiwara *et al.* (2004). Concentrations of all target compounds are expressed as ng/g dry weight unless otherwise specified.

RESULTS AND DISCUSSION

PCBs and PBDEs were detected in the entire sediments from raw leachate pond (DMPS1), LTP systems (LTP-1: DMPS2, -3, -4, -7, -8, -9; LTP-2: DMPS12,

-13), control wells (DMPS19, -22, -23, and -24) and surrounding areas (DMPS25), ranging between 0.10 and 30 ng/g dw and from 0.08 to 45 ng/g dw, respectively, indicating a potential source of these contaminants in dumping site and their contamination in the ambient environment.

Levels of PCBs and PBDEs were found to decrease significantly after the treatment processes in LTP-1 (from 30 ng/g dw in raw leachate sediment to 0.40 ng/g dw in the final settlement (DMPS9 and DMPS13) and from 13 ng/g dw to 0.60 ng/g dw respectively, indicating the capability of LTP-1 in reducing both PCBs and PBDEs. Similarly, Blanchard *et al.* (2004) also found 76% reduction of PCB levels in WWTP systems. Furthermore, higher removal efficiency of BFRs in leachate treatment processes was also confirmed in a study from landfill system in Japan (Osako *et al.*, 2004). In the global comparison, levels of PCBs (30 ng/g dw) and PBDEs (13 ng/g dw) found in sediments from raw leachate in this study are lower than in sewage sludge of waste water treatment plant worldwide (Table 1).

The profiles of PCBs and PBDEs in the study area are shown in Fig. 1. Same PCBs profiles were observed in both control wells and raw leachate indicate possible contamination of wells by leaching/release of PCBs from leachate. However, this pattern was not observed in the case of PBDEs. Higher contribution of lower BDE-congeners observed in raw leachate than control wells could be due to their physicochemical properties (high water solubility) or debromination of BDE-209 (Tokarz *et al.*, 2008) in leachate sediment. Higher contribution of BDE-209 in the sediments of control wells may be due to the proximity of the point sources (Hale *et al.*, 2006) and the physicochemical property of this congener which has a tendency to bind to organic rich soil and sediment particles.

Overall, the PCBs profiles were found in the order of hexa- > penta- > tri- > tetra-CBs, while PBDEs were found as BDE-209 > -207 > -206 > -99 > -47 (Fig. 2). These profiles were relatively similar to Ar1260, KC600, or ClophenT64 for PCBs (Ishikawa *et al.*, 2007) and Deca-BDE formulation for PBDEs (La Guardia *et al.*, 2006), which thus could be the major products used in Surabaya, Indonesia.

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