POLYBROMINATED DIPHENYL ETHERS AND DIOXIN-RELATED COMPOUNDS DETECTED IN SOIL SAMPLES FROM WASTE DUMPING SITES IN ASIAN DEVELOPING COUNTRIES

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Introduction

The production and usage of the persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) have been restricted with various efforts to reduce release of unintentionally produced POPs such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/DFs). Such restrictions were enforced in many developed countries followed by implication of the Stockholm Convention, while the regulations and banning on POPs have not yet been fully in some developing countries. It has become a matter of serious concern that remarkable economic growth in developing countries has caused increasing waste disposal and environmental problems. Our previous study indicated elevated contamination by PCDDs/DFs in waste dumping sites in some Asian developing countries because of the uncontrolled burning of solid wastes[1].

In addition, environmental issues relating to brominated flame retardants (BFRs) such as poly-brominated diphenyl ethers (PBDEs) have become a matter of great concern due to their bioaccumulative properties and potential toxic risk to humans and wildlife[2]. Even though many studies on PBDEs have been conducted in developed nations, very little information on BFRs is available in Asia-Pacific regions[3]. Recently, *e-waste* issues in Asian countries (i.e. exporting electronic wastes to developing countries and their unregulated disposal/recycling) have been documented because of potential release of hazardous materials from e-waste[4]. The uncontrolled combustion of e-waste including BFRs may cause the formation of dioxin-related compounds such as polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDDs/DFs)[2].

In this study, PBDEs and dioxin-related compounds such as PBDDs/DFs and monobromo-polychlorinated dibenzo-*p*-dioxins and dibenzofurans (MoBPCDDs/DFs) were analyzed in soil samples collected from open dumping sites and various locations in Asian developing countries, India, Vietnam and Cambodia, and the result was discussed with those reported in our previous study on PCDDs/DFs and coplanar PCBs[1].

Materials and Methods

Samples

Soil samples were collected in open dumping sites in India (Chennai and Kolkata), Cambodia (Phnom Penh) and Vietnam (Hochiminh and Can Tho) during 1999-2004. These open dumping sites are located close to human habitats, and there are people scavenging in these dumpsites for collecting recyclable wastes. Uncontrolled burning of solid wastes was often observed in the dumpsites. Soil samples were collected at each location at depths from 0 to 10 cm at five points with an area of approximately 25 m^2 and combined together and considered as a representative sample. The soils were also collected from road sides around dumping sites and an e-waste deposited site. Agricultural areas far from industrial activities, which

are hereinafter referred to as 'control sites', were also sampled. Soils were kept in clean plastic bags, maintained at 4 °C, transported to laboratory, and stored at -20 °C until chemical analysis.

Chemical Analysis

Soil sample was sieved by 2-mm mesh screen before chemical analysis. The samples for the analysis of PBDEs were not air- and freeze-dried to prevent degradation/evaporation of certain congeners during the sample drying process. Sub-samples for the analysis of dioxin-related compounds, PBDDs/DFs and MoBPCDDs/DFs, were derived from the samples analyzed in our previous study for PCDDs/DFs and coplanar PCBs[1], that were already air-dried and sieved. PBDEs and dioxin-related compounds, PBDDs/DFs and MoBPCDDs/DFs, in soil samples were analyzed following the method described elsewhere[5,6] with slight modifications.

Results and Discussion

Contamination Status of PBDEs

PBDEs were detected in all the soil samples analyzed in this study (Table 1). The highest concentration of PBDEs (500 ng/g dry wt) was observed in the sample from a dumping site in Can Tho, Vietnam. Relatively high concentrations of PBDEs were also found in the soils from an e-waste deposited site in Chennai, India. Concentrations of PBDEs in soil samples from dumping sites were higher than those from control sites in India and Vietnam. These facts suggest that municipal wastes containing various plastics and textiles and e-waste play a role as potential sources for PBDEs. Besides, relatively high concentrations of PBDEs in the soils from road sides around dumping sites in India and Cambodia may indicate their dispersion outside the dumping sites and/or occurrence of other potential sources of PBDEs.

Concentration levels of PBDEs in the soils collected in and around dumping sites in Asian developing countries were comparable to those from urban/industrialized regions and areas around waste recycling/incineration plants in Japan[7-9] and other developed countries[10,11], but were lower than those from e-waste dump sites in China[12,13]. However, available data on PBDEs in soils is still limited and the analyzed PBDE congeners were different among the studies. Further monitoring studies on PBDEs in soils are required in various regions/areas in developing as well as developed countries.

Table 1. Concentrations of PBDEs in soil samples from India, Cambodia and Vietnam

Country (City)	Sampling year	Location type [a]	*n* [b]	Sum of di- to heptaBDEs (ng/g dry wt)	Sum of di- to decaBDEs (ng/g dry wt)
India (Kolkata)	2004	CS	*2*	n.d.	0.45-0.56
		DS	*4*	0.21-11	2.1-13
India (Chennai)	2002-2004	CS	*1*	0.51	2.3
		RSDS	*1*	1.6	9.0
		DS	*2*	0.47-2.6	2.0-11
		EWDS	*3*	0.39-12	2.9-72
Cambodia (Phnom Penh)	1999-2000	RSDS	*2*	2.4-3.5	13-24
		DS	*5*	0.32-54	0.61-58
Vietnam (Can Tho)	2004	CS	*2*	n.d.	0.18-0.30
		DS	*5*	0.23-29	1.2-500

[a] CS: control site (agricultural area), DS: dumping site, RSDS: road side around dumping site, EWDS: e-waste deposited site, [b] number of sample

Except for the samples from dumping sites in Phnom Penh, Cambodia and Kolkata, India, concentrations of a decabrominated congener were the highest among the PBDE congeners in all the soil samples analyzed (Figure 1). This indicates common usage of decaBDE mixtures in these countries/areas.

On the other hand, selective adsorption and retention of a decabrominated congener on soil particles may be attributable to its higher adsorptive property than lower brominated congeners[2]. A similar trend was also observed in the soils from Japan[8,9], where decaBDE mixtures have been used as a major PBDE-based flame retardant[2]. On the other hand, higher proportions of tetra- to pentabrominated congeners were noted in the soils from dumping sites in Phnom Penh, Cambodia and Kolkata, India. This may reflect the usage of pentaBDE mixtures in these regions or thermal- and/or photo-degradation of PBDEs in dumping sites.

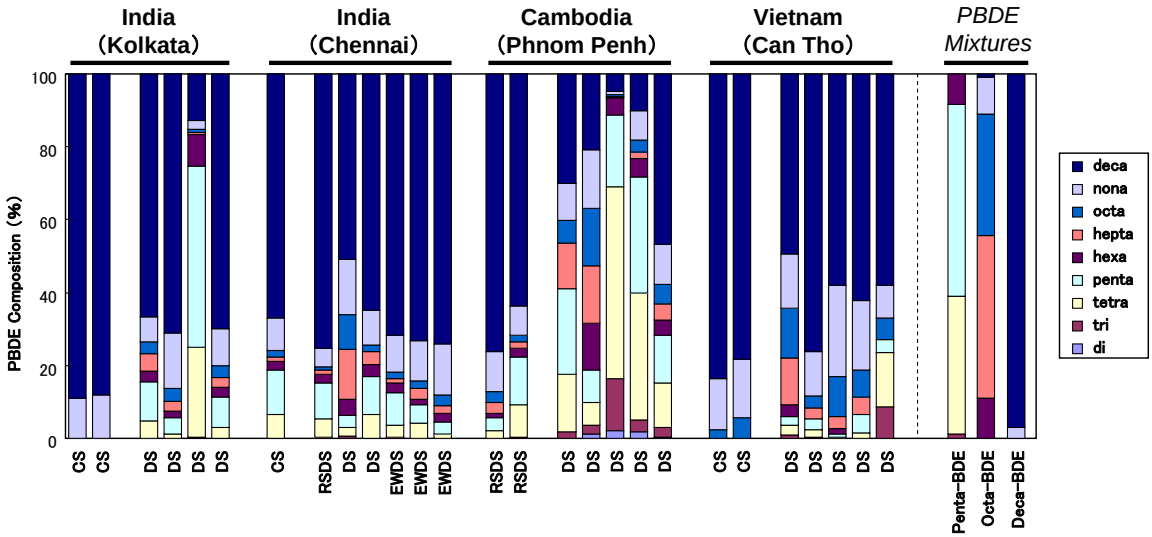

Figure 1. Composition of PBDE congeners in soil samples from India, Cambodia and Vietnam (CS: control site, DS: dumping site, RSDS: road side around dumping site, EWDS: e-waste deposited site)

Contamination Status of Dioxin-Related Compounds

Dioxin-related compounds, PBDDs/DFs and MoBPCDDs/DFs, were detected in several soil samples from India (Chennai) and Cambodia (Phnom Penh) (Table 3). To our knowledge, this is a first report on the detection of PBDDs/DFs and MoBPCDDs/DFs in dumping sites in Asian developing countries. Except for one sample from the control site in Cambodia, these dioxin-related compounds were found only in the soils from dumping sites, suggesting occurrence of their sources or formation there. PBDEs, which were analyzed for comparison with dioxin-related compounds in the same samples, were detected in all the soil samples (Table 2). Similar to the results shown above, higher concentrations of PBDEs were observed in dumping sites than in control sites.

The Spearman rank correlation coefficient test was applied for the data sets of PBDEs, PBDDs/DFs, MoBPCDDs/DFs, PCDDs/DFs and coplanar PCBs in the soils, using the integrated data obtained from both our present and previous studies[1] (concentrations below the detection limits were assumed as 'zero' in the calculation). No significant correlation was observed between the concentrations of PBDEs and all the dioxin-related compounds tested, while significant positive correlations were noted between each the concentrations of PBDDs/DFs, MoBPCDDs/DFs, PCDDs/DFs and TEQs. This result suggests different major sources and behavior in the dumping sites between PBDEs and dioxin-related compounds, i.e. PBDEs might have originated from flame retarded plastics, but dioxin-related compounds such as PBDDs/DFs, MoBPCDDs/DFs and PCDDs/DFs might have been formed in *de novo* process by the uncontrolled combustion of solid wastes, etc.

Concentration levels of PBDDs/DFs and MoBPCDDs/DFs in the soils from dumping sites in Asian developing countries were comparable to those collected around waste incineration plants in Japan[7,8].

Congener profiles of PBDDs/DFs and MoBPCDDs/DFs in the soils from Asian developing countries were similar to those reported in Japan; MoBPCDD and PBDF congeners were detected at higher concentrations than MoBPCDF and PBDD congers, respectively. Further studies on dioxin-related compounds are required to elucidate their levels, distribution, behavior and implication of toxic risk on humans living around dumping sites and in waste recycling plants.

Table 2. Concentrations of dioxin-related compounds, MoBPCDDs/DFs, PBDDs/DFs, PCDDs/DFs and coplanar PCBs, and PBDEs in soil samples from India, Cambodia and Vietnam

Country (City)	Location type [a]	*n* [b]	MoBPCDDs/DFs (pg/g dry wt) [c]	PBDDs/DFs (pg/g dry wt)[d]	PBDEs (pg/g dry wt)[e]	PCDD/DFs (pg/g dry wt)[f]	Co-PCBs (pg/g dry wt)[f]
India (Chennai)	DS	*2*	56-60	99-2000	9200-9700	5100-20000 (46-160)[g]	1300-2300 (4.7-9.9)
	CS	*1*	n.d.	n.d.	1100	19 (0.14)	12 (0.019)
Cambodia (Phnom Penh)	DS	*2*	n.d.-21000	19-87	2700-11000	490-200000 (29-170)	450-13000 (7.2-140)
	CS	*1*	n.d.	7.0	3600	40 (2.0)	490 (0.66)
Vietnam (Hochiminh)	DS	*2*	n.d.	n.d.	3000-7000	480-880 (3.6-4.4)	1000-2000 (0.64-1.0)
	CS	*1*	n.d.	n.d.	960	130 (0.36)	46 (0.027)

[a] CS: control site (agricultural area), DS: dumping site, [b] number of sample, [c] sum of tri- to heptachlorinated congeners, [d] sum of tetra- to octabrominated congeners, [e] sum of mono- to decabrominated congeners, [f] data cited from Minh et al.[1], [g] figures in parenthesis indicate TEQs based on WHO-TEFs.

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