POLYBROMINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS (PBDDs/DFs) RELEASED FROM THE PRODUCTION AND RELATED FACILITIES OF BROMINATED FLAME RETARDANTS

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Introduction

Studies on polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDDs/DFs) which are unintentionally produced and released into the environment are limited. To share knowledge on PBDDs/DFs sources and their estimated emission inventory will be important in international community, as the basis of considering the total reduction of PBDDs/DFs. In Japan, national surveys on PBDDs/DFs sources have been conducted since 2002, in order to make a clear outline of the national emissions.

In this paper, we report the research results of PBDDs/DFs released and detected in the environment media around the sources. Furthermore, we compared such data with the background concentrations which were investigated in the areas considered to be less influenced by possible sources.

Materials and Methods

Facilities selected in the national surveys

World Health Organization (WHO) has published Environmental Health Criteria on PBDDs/DFs and reported possible sources [1]. Among the candidates, facilities producing or using several brominated flame retardants were selected. Table 1 summarizes the facilities during the period of 2002 to 2006.

Sampling and analysis

In ambient air, 1 – 2 sampling points were set in the vicinity of each facility, considering the wind directions. Approximately more than 1,000m^3 of ambient air was sampled continuously during more than 7 days. The particles on quartz-fiber filters and polyurethane foam plugs (PUFP) were extracted with toluene and acetone in a soxhlet extractor.

In air deposition, one sampling point at each facility was set. Air deposition was collected during about one month.

In ambient water (river or sea), two sampling points around the sewage outfall at each facility were basically set. Ambient water was sampled and filtered. The filtrates and residues were extracted with dichloromethane and with toluene, respectively, in a soxhlet extractor.

Each extract was cleaned up for the determination of PBDDs/DFs, by using multilayer silica gel column and active carbon-impregnated silica gel column. HRGC/HRMS system was used to quantify PBDDs/DFs in the extracts.

12 unlabeled (2,3,7,8-TeBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8-HxBDD, 1,2,3,6,7,8-HxBDD, 1,2,3,7,8,9-HxBDD, OBDD, 2,3,7,8-TeBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF and OBDF) and 10 $^{13}C_{12}$-labeled (2,3,7,8-TeBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8-HxBDD, 1,2,3,6,7,8-HxBDD, OBDD, 2,3,7,8-TeBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF and 1,2,3,4,6,7,8-HpBDF) congeners (Cambridge Isotope Laboratories) were used for the determination of each conger.

Monitored ion's peaks were confirmed by comparison with standard peaks, on the basis of the given isotope ratios and adopted only if the estimated allowances were within ± 15 % (± 25 % for the concentrations which were not more than 3-fold of the minimum limits of detection).

Results and discussion:

Survey results

Figure 1-3 show the survey results of the ambient air, air deposition and ambient water carried out in 2002-2006. Maximum, minimum and mean values are shown with respect to each facility's category of the year.
Background data reported by other studies[2] are also shown in Fig. 1-3. In the background data, only the values measured in mountain areas and downtown/residential areas during the same period are included. The data measured in the vicinity of waste incinerators and in industrialized areas are excluded.

As shown in Fig. 1 - 3, PBDDs/DFs were detected at $10-10^3$ pg/m^3 orders in ambient air, at 10^2-10^5 pg/m^2/day orders in air deposition and at ND-10^4 pg/L orders in ambient water.
In ambient air and air deposition, maximum and mean values for the corresponding facilities were associated well. In ambient water, the detection range was broader than in the other media. In the cases of flame retardants production facilities (2003), flame-retarded textile manufacturing facilities (2003) and flame retardants processing facilities (2006), the detected values in the same category were comparatively at the similar levels.

In ambient air around flame-retarded plastics production facilities (2002) and flame retardants processing facilities (2006), it is clear that the concentrations of PBDDs/DFs were higher compared to the background data. The values are estimated to be approximately 10 – 100 times higher than the concentrations in background areas.
In air deposition, it is more obvious that there was a big difference between the data around the estimated sources and those in the background areas. The detected levels of PBDDs/DFs near the sources were 100 times higher at least than the values in the backgrounds.
In ambient water, the data measured around flame-retarded textile manufacturing facilities (2003) were extremely high. The values detected around flame-retardants production facilities (2003) and flame retardants processing facilities (2006) are estimated to be approximately 100 times higher than those in background areas.

Brominated flame retardants produced or used in the facilities

It can be assumed that the high concentrations of PBDDs/DFs detected around the facilities originated mainly from brominated flame retardants.
The brominated flame retardants and related materials which were produced or used in the facilities are as follows.

2002: Home electric appliances recycling facilities (TVs)
Flame-retarded plastics production facilities (PS polymers, ABS polymers or epoxy polymers)
2003: Flame retardants production facilities (tetrabromobisphenol A (TBBPA))
Flame-retarded textile manufacturing facilities
(decabromodiphenyl ether (DeBDE) and/or hexabromocyclododecane (HBCD))
2004: Flame-retarded plastics molding facilities (DeBDE)
Sewerage facilities (located in industrialized urban areas)
2005: Flame retardants processing facilities (2,4,6-tribromophenol (2,4,6-TBP))
2006: Flame retardants processing facilities (DeBDE)

In our studies, PBDDs/DFs were detected in DeBDE (high concentrations) and HBCD (low concentrations) used for the textile manufacturing as impurities.
Meanwhile, the reason for such high concentrations of PBDDs/DFs in ambient water around the flame-retarded textile manufacturing facilities has not fully been explained.
In addition, PBDDs/DFs concentrations reduction after effluent treatment was also confirmed in the flame-retarded textile manufacturing facilities.

Conclusions

It was confirmed that comparatively high concentrations of PBDDs/PBDFs were detected in the environment around the production and related facilities of brominated flame retardants.

In the future, international consensus on toxicity of PBDDs/DFs and global reductions of unintentionally produced PBDDs/DFs will be focused.
Provisional emission inventory of DeBDE in Japan has been reported, but those of PBDDs/PBDFs are not prepared[3]. The possible sources using brominated flame retardants other than DeBDE have not sufficiently been investigated.
It is necessary to continue further researches on the emission sources and the reduction measures of PBDDs/DFs.

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References
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2. Ministry of the Environment (Environmental Health Department), Research results on brominated dioxins (2001-2005) (in Japanese), http://www.env.go.jp/chemi/dioxin/chosa/shuki.html
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Table 1. Facilities and environmental media surveyed in 2002-2006

2002	2003	2004	2005	2006
Home electric appliances (TVs) recycling facilities (7 facilities) Ambient air (5-40m apart), air deposition & ambient water	Flame retardants production facilities (2 facilities) Ambient air (25-1000m apart), air deposition & ambient water	Flame-retarded plastics molding facilities (6 facilities) Ambient air (20-300m apart), air deposition & ambient water	Flame retardants Processing facilities (3 facilities) Ambient air, (20-100m apart), air deposition & ambient water	Flame retardants processing facilities (2 facilities) Ambient air (5-1000m apart), air deposition & ambient water
Flame-retarded plastics production facilities (9 facilities) Ambient air (5-70 m apart), air deposition & ambient water	Flame-retarded textile manufacturing facilities (2 facilities) Ambient air (10-12m apart), air deposition & ambient water	Sewerage facilities (3 facilities) Ambient air (10-70m apart) air deposition & ambient water		

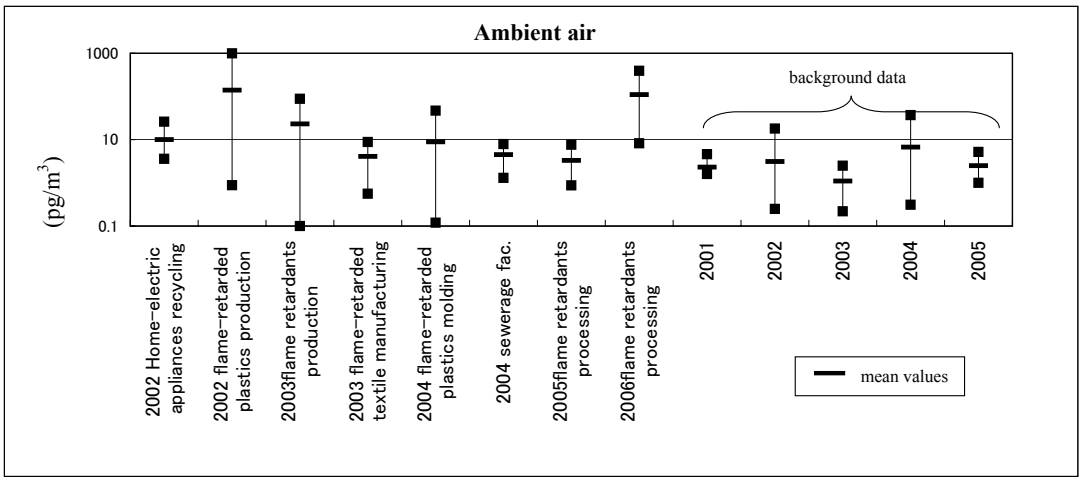

Figure 1. PBDDs/DFs detected in ambient air

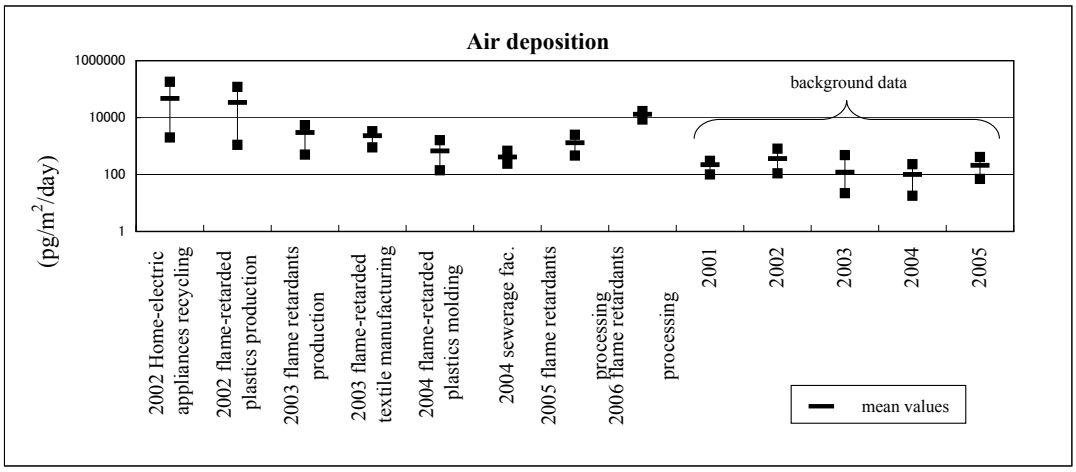

Figure 2. PBDDs/DFs detected in air deposition

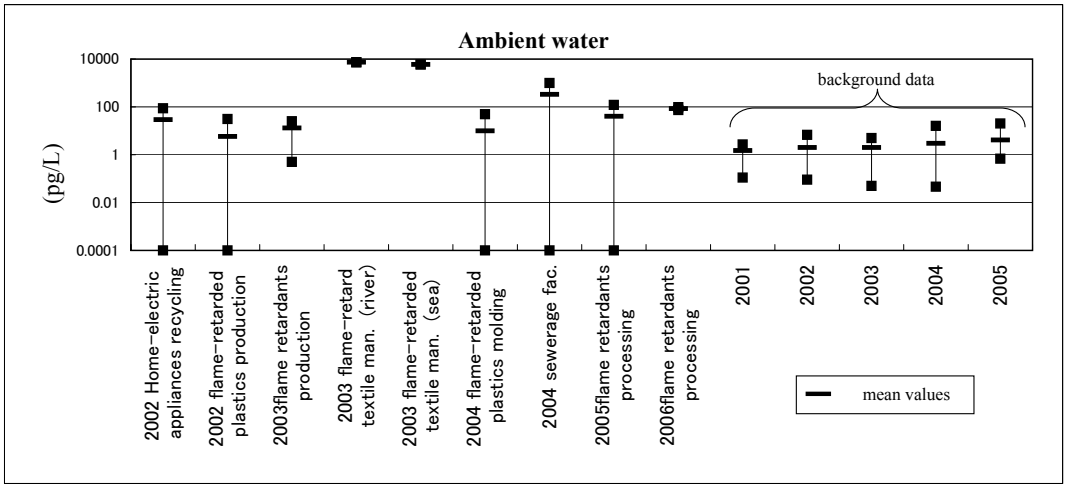

Figure 3. PBDDs/DFs detected in ambient water