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MEARSUREMENTS TRIAL AND CURRENT STATUS OF BROMINATED DIOXIN EMISSIONS

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Introduction

There have been growing concerns on the influence of polybrominated dibenzo-p-dioxins and furans, PBDD/DFs, related substances of polychlorinated dibenzo-p-dioxins and furans (PCDD/DFs) on the environment and human health. However, little is known about the emission pathways of these compounds. The Law Concerning Special Measures against Dioxins of Japan requires the government to promote "the research and study of PBDD/DFs with regard to the extent of their effects on human health, the process of generation, and others". Since 2002, the Ministry of the Environment of Japan (MOE) has conducted a series of field studies to survey the emissions of PBDD/DFs and related compounds from the related sources involving brominated flame retardant (BFRs). It is important for the global community to share the knowledge on PBDD/DFs sources and their estimated emission, in order to consider the way to reduce the total emission of PBDD/DFs. Here we report the survey results on the current status of PBDD/DFs emissions in Japan.

Materials and methods

Table 1 summarizes the facilities surveyed from 2002 to 2014. Sampling and analysis were conducted in accordance to the Provisional Survey Method for PBDD/DFs. Emission gases were collected with filters, absorption liquids, and adsorption columns at the emission outlets of processes in each facility, where PBDD/DFs may be produced. The samples were then extracted in toluene.

Discharged water was sampled at the drain outlets of processes where PBDD/DFs may be generated. Water sample was also collected at the main effluent after the treatment. The sample liquid was then filtered after adding of ^{13}C-labeled internal standards. The filtrates and residues were extracted by Soxhlet extractors in dichloromethane and toluene, respectively. To measure PBDD/DFs, the extract was further cleaned up by multilayer silica gel- and active carbon-impregnated silica gel-columns. We added the ^{13}C-labeled internal standards to the extracts for an injection spike. Quantitative detection of PBDD/DFs was performed by a high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS; the electron impact ionization method, mass resolutions >10,000) with ^{13}C-labeled internal standards. Since PBDD/DFs are possibly photo- and thermo-fragile, all samples were handled under dark and low temperature conditions.

Results and Discussion

The measurement data for PBDD/DFs in the emissions from the facilities are shown in Figures 1 and 2. We detected PBDD/DFs in the emission gas from all types of the measured facilities, although there is variation in the concentrations. In particular, high concentrations were observed at the facilities producing flame-retarded plastics and those handling flame retardants (Tribromophenols, TBPs). We also detected PBDD/DFs in the effluents from all types of the measured facilities. High concentrations of PBDD/DFs (10^5-10^6 pg/L, 100-1,000 pgTEQ/L orders at the highest level) were observed in the process water of the recycling plants of home electric appliances, the facilities producing flame-retarded plastics and those processing flame retardants(TBP and DeBDE). PBDD/DFs were also detected at most 10^5pg/L, 100 pgTEQ/L orders in the effluents collected at the main wastewater outlets in the facilities producing flame-retarded plastics and the processing plants for flame-retarded textiles.

MOE has tried to set up a provisional emission inventory of PBDD/DFs, based on the results of the present surveys. However, as an issue that test calculation of the provisional emission inventories, if the measured concentration of below the detection limit, and is calculated using the 1/2 of the value of the lower limit of detection, annual emissions are greatly affected by the domestic amount of activity.

The amount of emission percentage to the water system (%) becomes very big in the sewage treatment facilities survey in fiscal year 2004 in particular because it's very large in the domestic activity

quantity. At the time of the investigation of 2004, fewer standard substance of brominated dioxins had been supplied compred with chlorination dioxins, and the detection lower limit was high because the sensitivity of the measurement was low.
Under the present circumstances, it became possible to measure in high sensitivity by the improvements shown below. About the minimum limit of detection after an improvement, comparison of the minimum-limit-of-detection value of the effluents in the 2004 fiscal year in sewer processing plant, the influent water in the 2014 fiscal year, and final effluent is shown in Figure 3.
1) Additional standard (1,2,3,4,6,7,8-HpBDD, ^{13}C12-1,2,3,4,6,7,8-HpBDD, ^{13}C12-OBDF)
2) High sensitivity due to the grouping of the measurement (1 group → 3 Group)
3) Change of the final sample liquid volume 50 μL → 20 μL
4) Increase in the amount of sample (mass sample collection in the discharged water local) 40 L → 200 L
Figure 4 shows the emission rates (%) of provisional emission inventory by measurement improvements before and after improvement (water-system). There have been high emissions into water from flame retardant textile processing facilities and sewage treatment facility.

Acknowledgements
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References
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Table 1. Facilities surveyed in 2002-2014

Year of surveys	Facilities surveyed	Related BFRs	Number of facilities
2002	Home electric appliances (TVs) recycling facilities	–	7
	Flame-retarded plastics production facilities	–	8
2003	Flame retardants production facilities	TBBPA,TBBPA polycarbonate oligomer	2
	Flame-retarded textile manufacturing facilities	DeBDE, HBCD	3
2004	Flame-retarded plastics molding facilities	DeBDE	6
	Sewage treatment facilities	–	3
2005	Flame retardants processing facilities (TBP)	2,4,6-TBP	3
2006	Flame retardants processing (DeBDE)	DeBDE	2
2008	TBBPA epoxy resin production facilities	TBBPA	1
	Foam polystyrene production facilities	HBCD	1
2009	Secondary aluminum alloy ingots production facilities	–	3
2010	Cement manufacturing facilities	–	2
2011	Home electric appliances recycling facilities	–	10
2012	Waste incineration facilities	–	6
2013	Flame-retarded textile manufacturing facilities	DeBDE	4
2014	Sewage treatment facilities		5

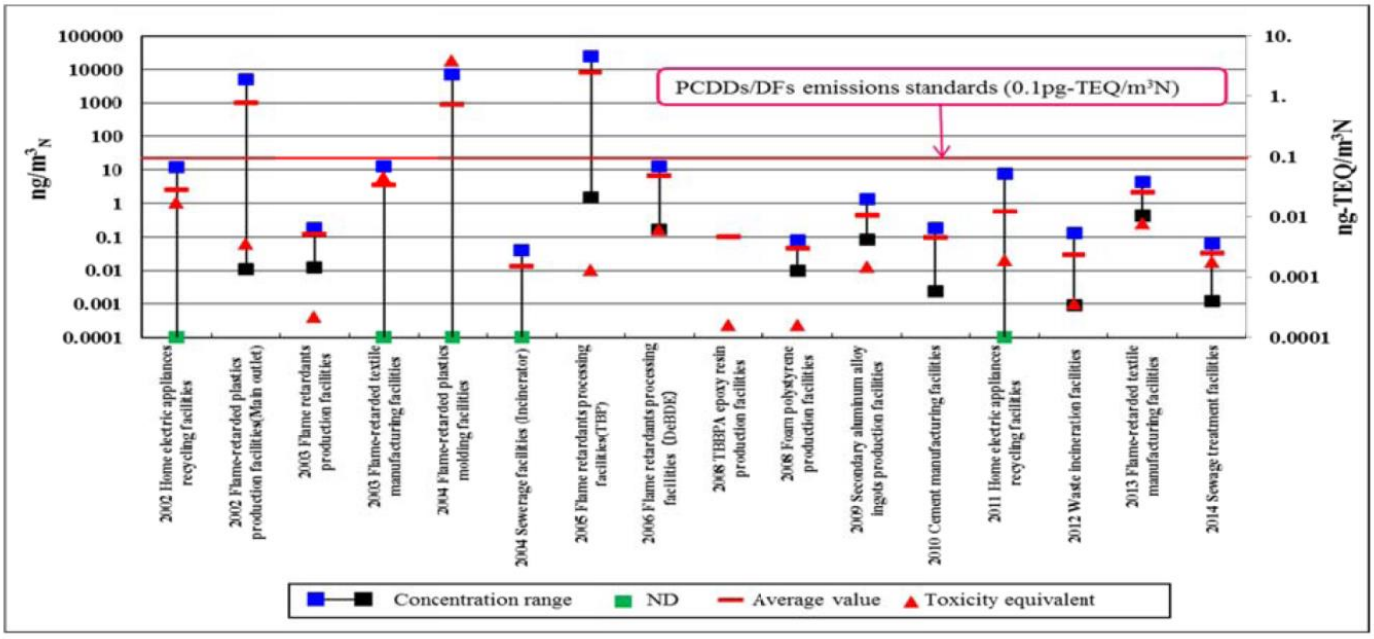


Figure 1. Levels of PBDEs/DFs in emission gas from various sources

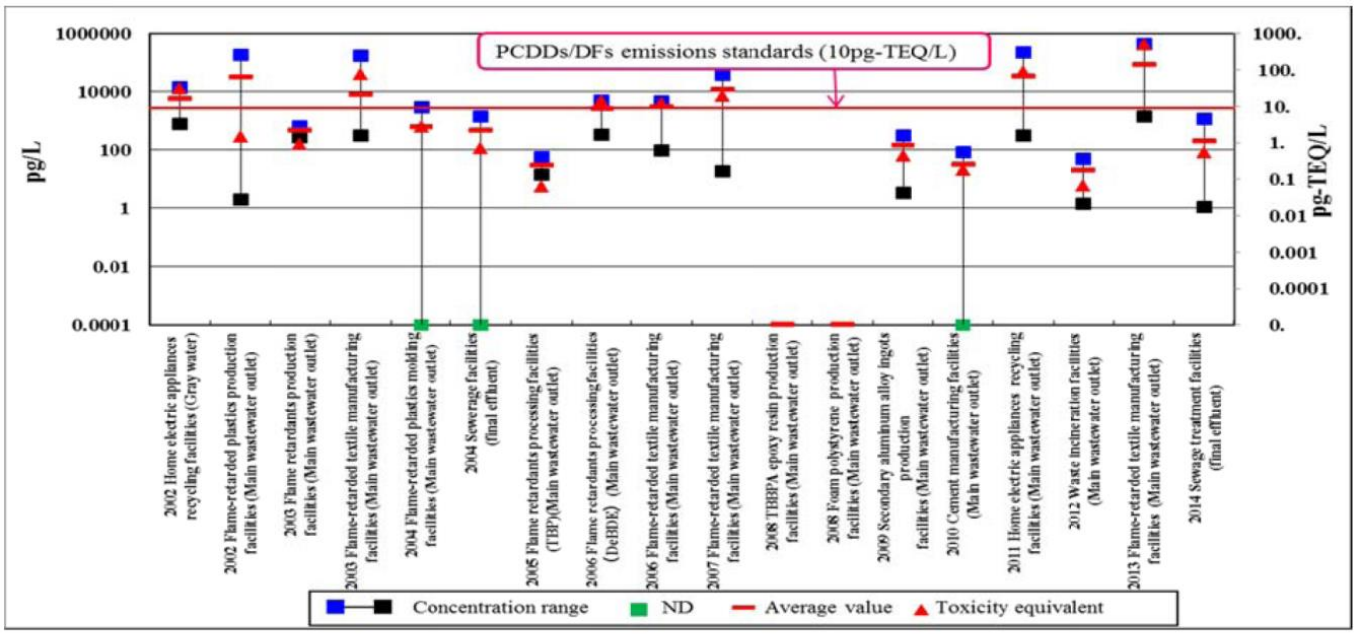
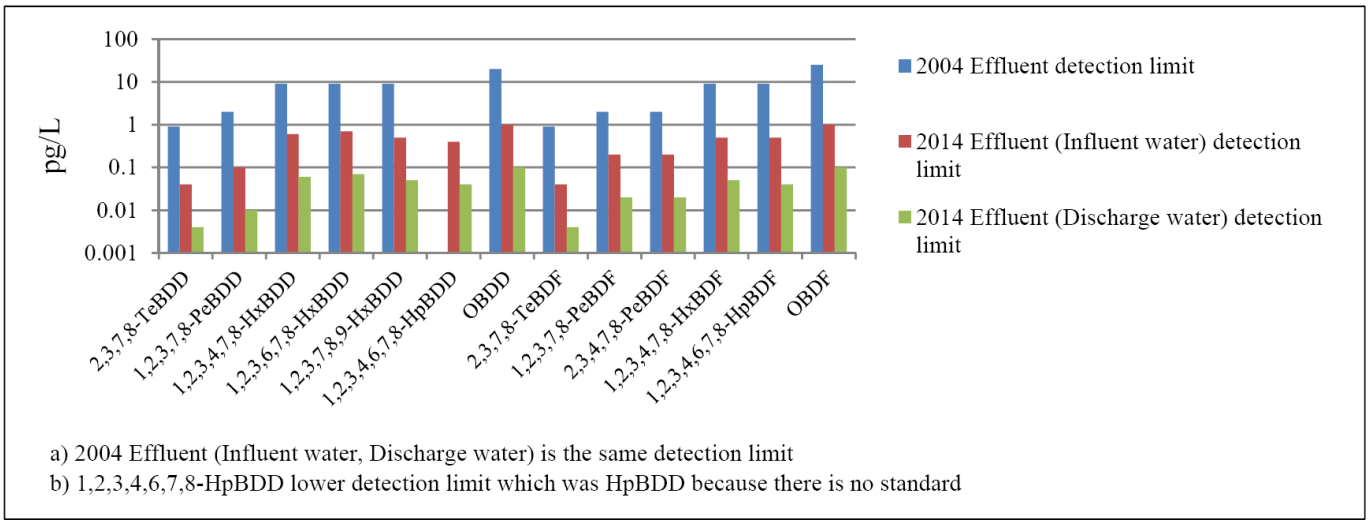
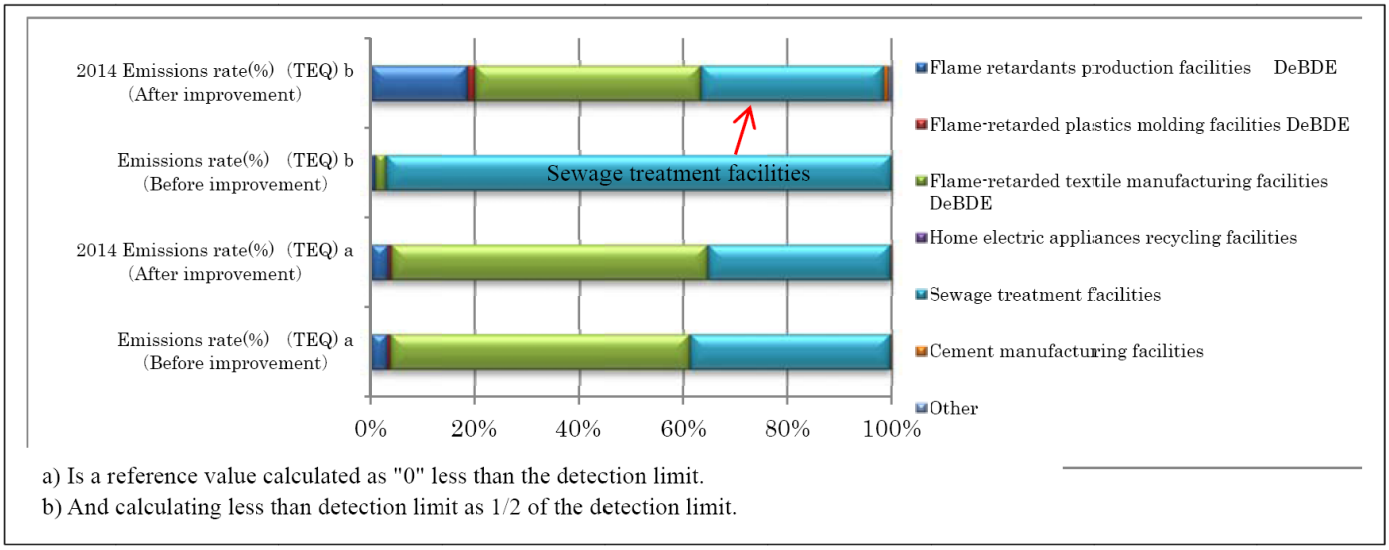


Figure 2. Levels of PBDEs/DFs in effluents from various sources



a) 2004 Effluent (Influent water, Discharge water) is the same detection limit
b) 1,2,3,4,6,7,8-HpBDD lower detection limit which was HpBDD because there is no standard

Figure 3. In 2004 and 2014 PBDDs/DFs detection limit



a) Is a reference value calculated as "0" less than the detection limit.
b) And calculating less than detection limit as 1/2 of the detection limit.

Figure 4. Annual emission ratio (%) to a water system of PBDDs/DFs before and after the method for measurement improvement