SURVEY OF CURRENT STATUS ON BROMINATED DIOXINS EMISSIONS IN JAPAN

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Introduction

Most of the compounds currently designated as POPs in Stockholm Convention are chlorinated organic compounds. However, concerns are also arising with respect to the adverse human health effects of brominated organic compounds, another group of halogenated compounds. Reports on the effects of brominated organic compounds on the environment and human health began to emerge in the mid-1980s.
It was discovered that brominated dioxins and furans (PBDDs/DFs) were generated as by products during the combustion of brominated flame retardants (BFRs).

At the COP4 of the Stockholm Convention in 2009, some types of BFRs were designated as Annex A of the Convention, and their production and use are prohibited except for limited purposes. BFRs have in itself certain toxicities, but at the same time, their potentials of generating PBDDs/DFs are feared.

PBDDs/DFs is a collective term used to denote a family of chemicals comprised of polybrominated dibenzo- *p* – dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs). Like the chlorinated dioxins (PCDDs/PCDFs), PBDDs theoretically occur in 75 isomeric forms and PBDFs in 135 forms.
Toxic equivalency factors (TEFs) of the brominated dioxins have not yet been established, contrary to PCDDs/PCDFs. However, the toxicity of 2,3,7,8 - TeBDDs/TeBDFs is expected to be equal to or even higher than that of 2,3,7,8 - TeCDDs/TeCDFs by many studies about various aspects of their toxicities, such as reproductive effects, development toxicity, and immunotoxic potential, etc..

Since FY2001, the Japanese government has started measurements of PBDDs / PBDFs and mixed brominated / chlorinated dioxins (PXDDs / DFs) where X = Cl, Br) in accordance with a requirement under Article 2 of the supplementary provision of the Act on Special Measures against Dioxins to survey the status of PBDDs / PBDFs emission from various industrial facilities.

We investigated potential emission facilities such as home electric appliances, recycling facilities, flame resisting plastics fabrication facilities, cement production facilities, in accordance with the advices of experts.
We report here on the results of this survey, the current status of brominated dioxins emissions in Japan, to promote further discussion on PBDDs / PBDFs .

Materials and methods

Certain physical properties of PBDDs/DFs have already been described, including higher molecular weights, higher melting points, and lower vapor pressures compared to PCDDs / PCDFs. However, experimental data is scarce, and little information is available regarding their actual behavior in the environment.
Given such limited knowledge, the initial version of the measurement method was created in 1998 based on the extant literature and various manuals published on PCDD / PCDFs.

Based on initial planning, field measurements assessed the presence of the 2,3,7,8-substituted isomers of PBDDs / PBDFs in gas emissions, water (effluents, environmental waters), environmental air, soil, and benthic and aquatic organisms. Additionally, cross-check studies were performed using standard solutions and fly-ash extracts (standard addition method) at five domestic institutions and three foreign institutions. Results were evaluated after accounting for within- and between-laboratory precision (%CV).
Based on the results, a standard method (draft version) for PBDDs/DFs measurement was then produced.

In 2000, gas emissions and atmospheric content were measured in a validation assessing the measurement methods (draft version). A method for measuring PBDDs / PBDFs in flame retardants and plastic waste was

established in 2001, followed in 2002 by the draft of a Provisional Survey Method for Polybrominated Dibenzo-p-Dioxins and Polybrominated dibenzofurans (hereafter referred to as the Provisional Survey Method). However, note that in contrast to PCDDs/DFs, few standard materials exist for PBDDs / PBDFs, such as 2,3,7,8-substituted isomers. Standard materials for higher substitution compounds are especially hard to obtain.

The Provisional Survey Method was revised in 2007 in response to revisions to manuals on dioxins and furans and to permit the inclusion of an analysis method for higher substitution compounds of PBDDs/DFs in the Provisional Survey Method.
Although no manual currently exists on testing for levels of BFRs, we established a method based on existing manuals and the literature on dioxins and furans.

At the survey, samples are collected for each target medium. Following the addition of an labeled 13C internal standard for cleanup spike and extraction of PBDDs/DFs by organic solvents, they are cleaned by sulfuric acid treatment and column chromatographic techniques. A labeled 13C internal standard for injection is added to the samples and identification and quantification performed by high-resolution gas chromatography-mass spectrometry (HR-GC/MS). Quantification by HR-GC/MS is performed by the electron impact ionization method at mass resolutions > 10,000.

BFRs are measured based on virtually identical sample preparation procedures and quantified by HR-GC/MS. For HBCD, measurements are performed by liquid chromatography-mass spectrometry (LC / MS), aiming at isomer separation.

Since PBDDs/DFs and brominated flame retardants are susceptible to photolysis and thermal decomposition, care must be taken to incorporate the strongest light-shielding measures possible from sample collection to the pretreatment process and to prevent thermal decomposition during measurement.

Results and discussion
Studies were performed in Japan to assess the current status of brominated dioxins emissions, with a special focus on PBDDs/DFs, in processes ranging from manufacturing to the disposal and recycling of flame retardants and plastics.The results for detected PBDDs/DFs at the facilities targeted by the surveys on current emissions are shown for emissions gas (Fig 1) and for effluents (Fig. 2).
No toxicity equivalency factor (TEF) is currently recognized internationally for PBDDs/DFs.

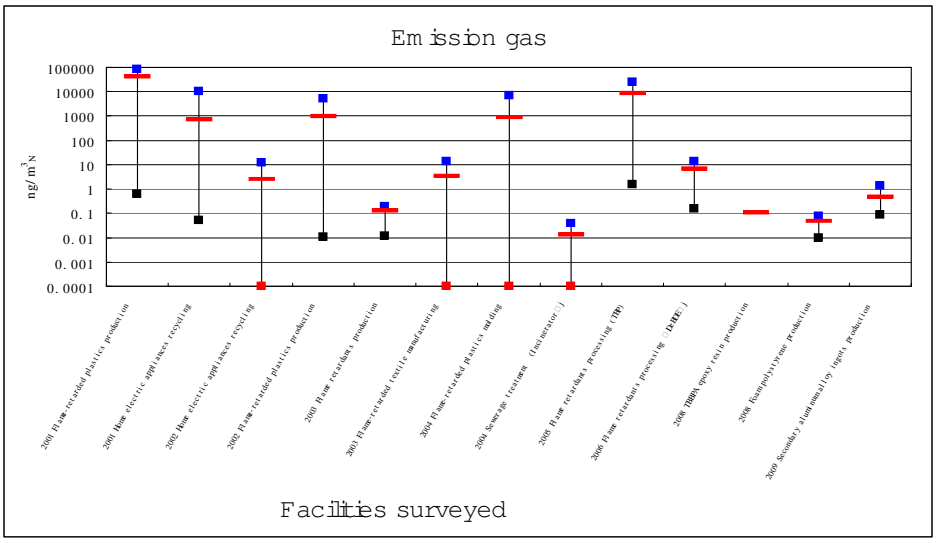

Fig . 1

To allow for an adequate margin of error, we assumed the toxicity of PBDDs/DFs to be equivalent to chlorinated dioxins. In our evaluations, we used the TEF values of chlorinated dioxins as toxic equivalent values. The toxic equivalent value is the product of actual measured concentrations and the WHO-TEF of PCDDs/DFs (1998).

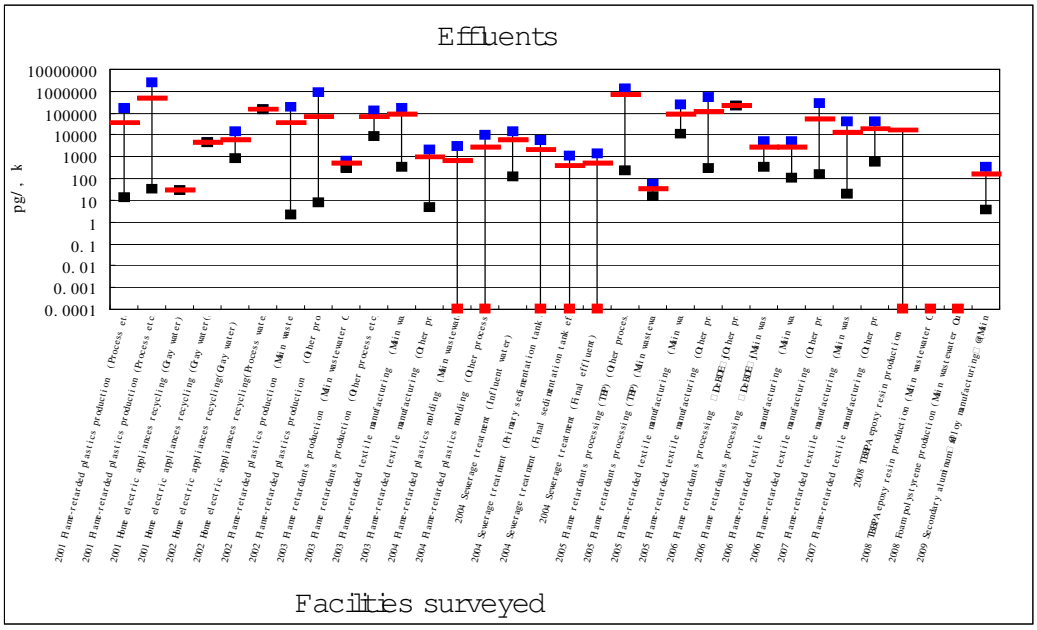

Fig. 2

PBDDs / PBDFs was detected in high concentration in flame-retarded plastics production facilities and flame retardant handling (2,4,6-TBP) facilities, home electric appliances recycling facilities, flame resisting plastics fabrication facilities in emissions gas by our investigation.
PBDDs / PBDFs has the example of detecting the measurement density comparatively in a high density in manufacturing reagent using material facilities, plastic manufacturing facility, and reagent handling (2,4,6-TBP) facilities from the result of the survey in exhaust gas. Moreover, both differences between facilities were the very large one though in the toxicity equiponderance equivalent value, there was a high example in the consumer electronic recycling facilities and plastic molding processing facilities.

In addition, in the excretion water, it was detected in high concentration in flame resisting plastics facilities, and flame resisting fiber specification facilities. Excretion of bromine flame retardant affects it in facilities detected by these high concentrations greatly. This points out to a strong association between PBDD / PBDF emissions and the discharge of bromine flame retardants.
Discussions and estimations are now underway based on the results of these current status surveys, with the goal of preparing a provisional emissions inventory. A systematic emission inventory of PBDDs / PBDFs would mark an unprecedented achievement worldwide. We will continue the efforts in long-term surveys and additional data collection will eventually lead to more effective emissions reduction measures.

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References
1. Ministry of the Environment of Japan (2002-2010), 'The survey on the status of poly-brominated dibenzo-p-dioxins and furans emissions'