

Historical Developments of BFR Research

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Introduction

Flame retardants are very important products protecting the public from accidental fires, by reducing the flammability of combustible materials such as plastics and synthetic polymers. WHO (1997) published Environmental Health Criteria 192 on flame retardants. Brominated flame retardants (BFRs) contain a diversity of chemicals; however, some BFRs such as polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), and hexabromocyclododecane (HBCDs) have been attracting social concern regarding environmental pollution and human exposure for the last three decades. (WHO, 1994a, WHO, 1995, Bergman et al, 2001, de Wit, 2002, Watanabe et al, 2003). In addition, their thermal and photochemical breakdown products i.e., polybrominated and mixed brominated/chlorinated dibenzo-*p*-dioxins and dibenzofurans (PBDDs/DFs and mixed-PXDDs/DFs) are also of social concern because their toxicities are similar to those of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/DFs) (WHO, 1998)

The aim of this presentation is to review and discuss the research on the historical development of BFRs including their toxic breakdown products from the 1980s to the present, especially in Japan.

Annual consumption of BFRs in Japan

The annual consumption of BFRs in Japan, from 1986 to 2008, is shown in Table 1. BFR consumption increased markedly year by year though there was a slight decrease in the recent past 2-3

Table 1. Trends in the annual consumption of flame retardants in Japan*

Types	Compound	Amounts (tons)												
		1986	1988	1990	1992	1994	1996	1998	2000	2002	2004	2006	2008	
Brominated	TBBPA	12,000	18,000	23,000	23,000	24,000	29,000	29,500	32,300	31,000	35,000	29,000	22,500	
	PBDEs	DecaBDE	3,000	5,000	10,000	6,300	5,500	4,200	4,000	2,800	2,200	2,000	1,700	1,600
		OctaBDE	500	1,100	1,100	1,100	500	280	75	-	-	-	-	-
		TetraBDE(PentaBDE)	1,000	1,000	1,000	-	-	-	-	-	-	-	-	-
		HBCDs	600	700	700	1,400	1,600	2,000	1,850	2,000	2,400	2,600	2,600	3,000
	Bis(tetrabromophthalimido)ethane	-	600	1,000	1,300	2,500	2,500	2,000	2,000	1,500	1,500	1,500	1,300	
	Tribromophenol	100	450	450	2,000	3,500	4,100	4,300	4,300	3,800	4,150	4,000	3,150	
	Bis(tribromophenoxy)ethane	400	400	400	1,000	900	500	100	-	-	-	-	-	
	TBBPA polycarbonate oligomer	-	-	-	2,500	2,500	3,000	3,000	2,900	2,500	3,000	3,000	3,000	
	Brominated polystyrene	-	-	-	1,300	1,300	1,600	2,000	3,300	2,800	5,100	7,500	7,000	
	TBBPA epoxy oligomer	-	-	3,000	6,000	7,000	9,000	8,500	8,500	8,500	12,000	12,000	9,000	
	Bis(pentabromophenyl)ethane	-	-	-	-	1,600	3,000	4,600	5,000	5,000	5,000	6,000	5,500	
	TBBPA-bis(dibromopropylether)	-	-	-	-	-	-	1,750	2,000	1,350	1,000	800	700	
	Poly(dibromophenylene oxide)	100	200	-	-	200	400	800	-	-	-	-	-	
	Hexabromobenzene	-	-	-	-	350	350	350	350	350	350	350	350	
	Others	2,300	160	-	-	-	-	-	1,800	1,900	2,200	3,200	3,400	
	Sub-total	20,000	27,610	40,650	45,900	51,450	59,930	62,825	67,250	63,300	73,900	71,650	60,500	
	Chlorinated	4,850	5,350	5,200	5,400	5,200	5,260	5,200	5,200	5,200	4,900	4,900	4,900	
	Phosphoric	8750	8950	9150	9310	10810	9100	28000	28500	26500	30500	31000	28500	
	Inorganic	63500	56340	61400	69500	68000	70000	69000	68500	69000	79000	77000	71500	
Total	97,100	98,250	116,400	130,110	135,460	144,290	165,025	169,450	164,000	188,300	184,550	165,400		

* based on the investigation made by Kagaku Kogyo Nippo Co. Ltd.(Japan) (1987-2009)

years. However, considerable changes in the types and the consumption rates of the BFRs occurred throughout this period. For example, the consumption of PBDEs increased rapidly up to 1990, and then decreased drastically. On the other hand, use of HBCDs has slightly increased year after year. Consumption of the newly developed BFRs, as alternatives to PBDEs, such as TBBPA polycarbonate oligomer, TBBPA epoxy oligomer, and brominated polystyrene, also showed increasing trends.

Development of analytical methods for BFRs and bromine-containing dioxins

The development of the BFR research greatly depends on the improvement of analytical methods. In the 1980s, BFR product themselves were used as the standards. Determination of BFRs was mainly carried out in a gas chromatograph (GC) with a packed column, or at times fitted with a capillary column, and equipped with an electron capture detector (ECD) or coupled with mass spectrometer (MS). TBBPA and TBP were determined after ethylation of the sample extract. Recently, analytical standards for BFRs including internal isotope labeled chemicals have been developed. Therefore, current BFR determination basically uses the isotope dilution method. Determination of BFRs is usually conducted using a capillary column-GC coupled with high resolution mass spectrometer (HRGC/HRMS). Recently, HBCDs are determined using a liquid chromatograph-mass spectrometer (LC/MS or LC/MS/MS) in which their congener specific determination is also possible.

On the other hand, analysis for bromine-containing dioxins followed basically the methods for PCDDs/DFs. However, in the 1990s, there were some problems in bromine-containing dioxin analysis such as, (1) non-availability of standards of some 2,3,7,8-substituted PBDDs/DFs congeners including internal isotope labeled compounds and a large number of mixed-PXDDs/DFs congeners, (2) photochemical instability of the chemicals during the analysis, (3) interference of PBDEs in HRMS/HRMS determination, (4) thermal decomposition at the injection port and in the capillary column in GC, and (5) imperfect peak of hepta- and octa-congeners of PBDDs/DFs, etc. Recently, some PBDDs/DFs congener standards together with internal isotope labeled standards have been developed. In addition, use of thin film coatings and short capillary column minimized thermal decomposition and enabled perfect peaks of higher brominated dioxins. An intercalibration study on bromine-containing dioxins and PBDEs using 'Mixed Standard Solution' and 'Air-dried Sediment' as samples was conducted and improved the methodologies and curtailed the problems in their analysis (Takahashi et al. 2006). The Ministry of the Environmental of Japan (2008) published a manual titled "Tentative investigation methods on polybrominated dibenzo-*p*-dioxin and polybromodibenzofuran" by consolidating the latest findings.

Development of brominated flame retardants research

The first ever BFR that came under social concern was PBBs. In 1973, FireMaster[®] BP-6 (dominant: 2,2',4,4',5,5'-hexabromobiphenyl) used as flame retardant was inadvertently added to animal feed in Michigan state, USA, and caused serious contamination of farm animals and human (WHO, 1994b).

There are other BFRs that became the matter of concern because of their possible environmental pollution caused by their chemical structure and physico-chemical properties similar to PBBs. In the 1980s, PBDEs (Te- and PeBDE) were found in the fish in Sweden (Anderson et al, 1981), especially high levels of them in the fish from the Baltic (Jansson et al, 1987). In addition, PBDEs (Te-~HxBDE, DeBDE) (Watanabe et al, 1987a), TBBPA including dimethyl ether derivative of TBBPA (Watanabe et

al, 1983), HBCDs (The Japanese Ministry of the Environment, 2005), hexabromobenzene (HxBBz) (Watanabe et al, 1986), TBP including methyl ether derivative (Watanabe et al, 1985) were also found in the Japanese environment though their levels were found to be lower than those of PCBs. These BFRs were confirmed to be environmental pollutants through the results obtained in Sweden and Japan.

The preliminary environmental behavior of BFRs was evaluated based on the studies in the 1980s in Japan. A schematic representing the environmental behavior of BFRs is given in Figure 1. Briefly, almost all BFRs used are the higher brominated compounds. The higher brominated compounds are less mobile in the environment, possibly because of their low volatility, water solubility, bioaccumulation, and strong adsorption on sediments. The higher brominated compounds therefore tend to end up in sediments, at high residue levels, near their emission sources, rather than in marine organisms or humans. On the other hand, the lower brominated compounds, including environmental decomposition products of BFRs, are predicted to be more volatile, water soluble, and bioaccumulative than the higher brominated compounds. The environmental behavior and fate of lower brominated compounds are thus thought to be similar to those of chlorinated pollutants, such as polychlorinated biphenyls (PCBs) and PCDDs/DFs (Watanabe et al, 1990).

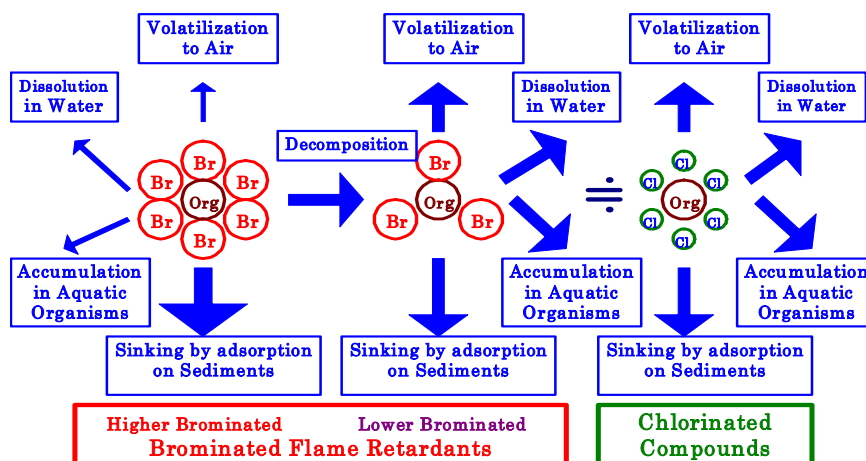


Fig.1 Schematic representation of environmental behavior of brominated flame retardants

As a result of such increasing social concern on BFRs including toxic breakdown products, the first workshop on BFRs was held in Sweden in 1989 (Swedish National Chemicals Inspectorate, 1990).

Social concern on BFRs in the 1990s was mostly on bromine-containing dioxins, the breakdown products of BFRs. However, since the marked increase in PBDE levels in Swedish human milk in the 1990s was reported by Norén et al (2000), environmental problems relating to BFR themselves have become a matter of more urgent and greater concern than ever before. In particular, PBDE levels in human milk in North America were reported to be two orders of magnitude higher than those in Sweden and Japan (Betts, 2002). In addition, toxicological data demonstrating the serious health effects of BFRs, such as thyroidogenic, estrogenic, and dioxin-like activities were reviewed by Bergman et al. (2001). Under such a situation, the Organization for Economic Cooperation and Development (OECD) held a workshop on BFRs in Switzerland in 1993 for risk alleviation activities

for selected BFRs (PBBs, PBDEs and TBBPA), and published a Risk Reduction Monograph on Selected BFRs (OECD, 1994). Many researches on BFRs, especially on the analytical methods, sources, environmental levels and behavior, routes of human exposure and human levels, temporal trends, indoor pollution, toxicology, risk assessment etc. have been conducted in the 2000s in the world. Research reports over three hundreds have been published during the symposia, BFR2001, BFR2004 and BFR2007.

In Japan, PBDE levels in human milk has increased from the 1970s and a level-off tendency was noticed in the 2000s, as also seen in Sweden (Akutsu et al. 2003). The temporal trends of PCBs, PBDEs(Mo- to NoBDE), DeBDE and HBCDs using a sediment core from Tokyo Bay has shown decreased levels of PCBs during the last few decades, while PBDEs (Mo- to NoBDE) had shown increased levels until around 1990 and then became constant. However, DeBDE and HBCD levels have been drastically increasing during the last decade (Minh et al. 2007).

Ehime University group has obtained interesting results regarding the spatial and temporal trends of BFRs in the Asia-Pacific region using archived samples in their Environmental Specimen Bank. In Japan, PBDEs levels showed increasing trend until the early/mid-1990s and then decreased. On the other hand, HBCD levels are still increasing. However, PBDE levels in China increased significantly even up to 10 times during the last decade. Therefore, they have concluded that spatial and temporal trends of BFRs contamination are different in the developed and developing countries; some BFRs like HBCDs may increase in the Asia-Pacific environment and biota in future.(Tanabe, 2008). They have also noticed high levels of PBDEs in the soil samples from the backyard e-waste recycling sites in the Asia-Pacific region (Ramu et al . 2008).

Development of BFR breakdown products research

In the later half of the 1980s, a large amount of the formation of PBDDs/DFs was noticed in the laboratory thermolysis of BFRs (Buser, 1986) , Thoma et al. 1987b) and photolysis of DeBDE (Watanabe et al. 1987b). In addition, the emission of PBDFs from a TV set to indoor air was confirmed (Bruckman et al. 1990). The German government adopted in 1994 a second modification of the Chemicals Prohibition Ordinance which imposes limits on PCDDs/DFs, as well as on eight 2,3,7,8-substituted PBDDs/DFs congeners. Therefore, bromine-containing dioxins became the chemicals of greater concern than BFRs. In the 1990s, a large number of research works on the breakdown products of BFRs were conducted (WHO,1998).

During the investigation at the metal reclamation factories from e-waste (electronic and electrical waste), located in southern Taiwan, PBDFs (TrBDF to HxBDF) together with one order magnitude higher levels of PBDEs (TrBDE to HxBDE) were found in the air at the factories. In addition, a large number of mixed-PXDFs in addition to PBDFs and PCDFs were found in the soil containing a large amount of e-waste ash at the open-air burning site (See Figure 2 below, Watanabe et al, 1993).

In the general environment in Japan, PBDDs/DFs(tri- to hexa-, dominant: PBDFs) and mixed -PXDDs/DFs as well as PCDDs/DFs were also found, though their levels were about one~two order of magnitude lower than those of PCDDs/DFs (Watanabe et al, 1995).

The data on PBDDs/DFs and mixed-PXDDs/DFs in the environment and human were limited in the published literature during the1990s; Japanese Government promulgated the Law Concerning Special Measure against Dioxin with the supplementary provisions on promotion of research and study on bromine-based dioxin in 1999. Therefore, a number of studies have been carried-out on

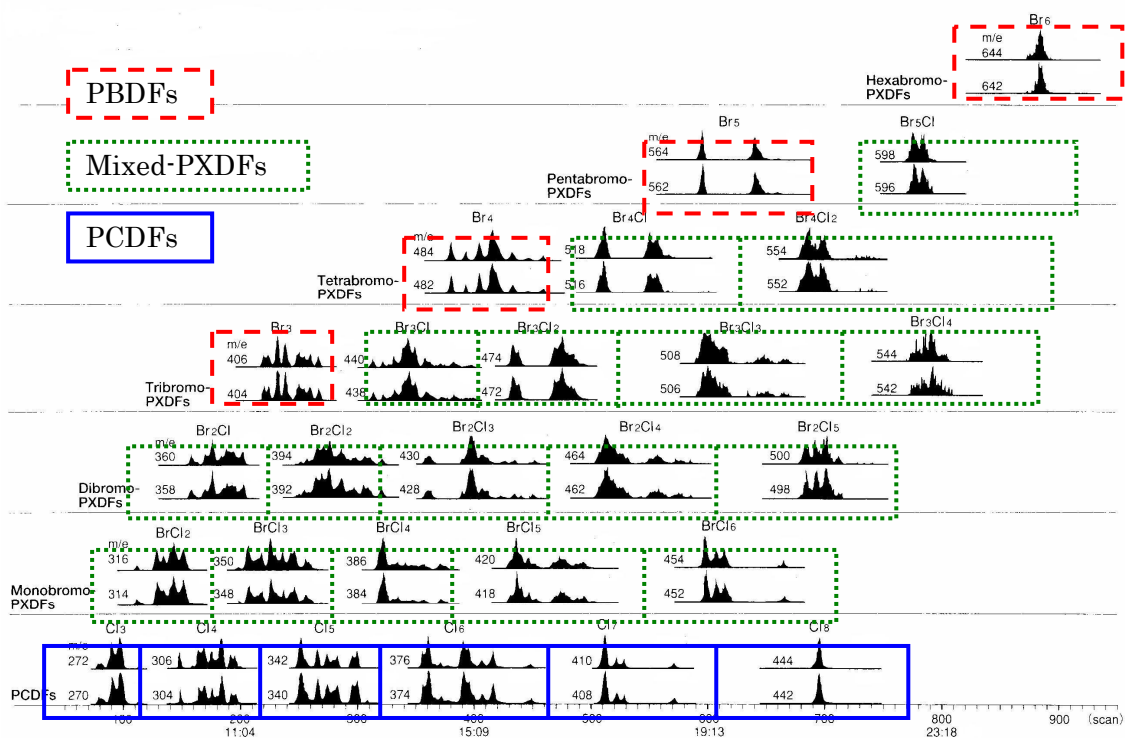


Fig.2 Mass chromatograms of PBDFs, mixed-PXDFs and PCDFs found in the soil containing a large amount of e-waste ash at the open-air burning site in Taiwan

bromine-containing dioxins along with some BFRs by the government, universities and private institutions in Japan.

The Japanese Ministry of Health and Welfare (2001) conducted an emission survey of PBDDs/DFs and mixed-PXDDs/DFs in addition to PCDDs/DFs from incineration plants in Japan in 2000. PBDDs/DFs and mixed-PXDDs/DFs were found in the samples collected at incineration plants (PCDDs/DFs \gg mixed PXDDs/DFs \gg PBDDs/DFs). The Japan Waste Research Foundation conducted an investigation on the behavior and control of dioxin-like compounds during e-waste management and recycle process. They confirmed that junk TV back covers which were manufactured in the 1980s and the 1990s contained high levels of PBDDs/DFs along with extremely high levels of PBDEs and TBBPA (Tamade et al. 2002). In incineration experiments with waste television sets containing large amount of BFRs and PBDDs/DFs in full-scale incineration facilities, Sakai et al. (2001) found that the amounts of PBDDs/DFs emitted after incineration were significantly lower than the amounts that were present before incineration. They found that the highly efficient flue-gas purification system resulted in approximately 90% decomposition of PBDDs/DFs and BFRs.

The Japanese Ministry of the Environment has been investigating on the actual exhaust conditions of bromine-containing dioxin at the sources from 2002. This investigation has been conducted at the BFR production and processing factories, recycling factories of e-waste and BFR treated textile products, etc. PBDDs/DFs, mixed-PXDDs/DFs along with PCDDs/DFs and some BFRs were determined in the samples of indoor air, effluent gas and water in such factories in addition to air, bulk

deposition, river water and sediment around the factories. In the investigation of BFR producing and processing textile factories in fiscal 2003, PBDDs/DFs (dominant: PBDFs) were found at same or higher levels than those of PCDDs/DFs in the samples such as river or estuary water near effluent outlet, even though mixed PXDDs/DFs levels were extremely lower than those of PCDDs. In addition, high levels of PBDEs and HBCDs were also found in the samples from the textile factories (The Japanese Ministry of the Environment. 2005).

The Japanese Ministry of Environment has also been investigating bromine-containing dioxins in the general environmental samples from 2001. In the investigation of fiscal 2005, PBDDs/DFs (tetra- to octa-, dominant: PBDFs) levels in all the samples except house dust were generally lower than those of PCDDs/DFs; in addition mixed PXDDs/DFs levels were extremely lower. However, in house dust samples, PBDDs/DFs exist at ng/g level (tetra- to octa-, dominant: PBDFs) and PBDEs were at µg/g level (dominant: DeBDE) (The Japanese Ministry of the Environment. 2006).

Therefore, pollution by bromine-containing dioxins as the breakdown products of BFRs are higher at or around the sources and in houses or offices having consumer products containing BFRs, though their pollution in general environment is not so serious.

Recently, occurrence of coplanar-polychlorinated/brominated biphenyls (Co-PXBs) in the human milk in Japan was found by Ohta et al.(2008). Though it is not clear whether Co-PXBs are the breakdown products of BFRs or not, their environmental and human contamination should be clarified more in detail.

Discussion and further research

In Japan, DeBDE was specified as a Type 2 Chemical Monitoring Substance of the Chemical Substances Control Law on September, 2000. In addition, HBCDs were also specified as Type 1 Chemical Monitoring Substances of the Law on September, 2004. Some BFRs such as PBDEs and HBCDs have been confirmed to be global environmental pollutants by a number of research works done until present in the world including Japan. However, there are some unclear points on the environmental pollution by BFRs, especially on sources, environmental levels, fate in the environment, exposure route to human, effects on human, etc. Further research should be performed to reduce their pollution in future.

In addition, pollution by BFRs is more serious at and around the sources than in general environment. The sources of BFRs seem to be more or less similar to those of bromine-containing dioxins. The most important sources of them should be BFR production and processing factories, incineration plants for wastes containing BFRs, recycling of e-waste and e-waste dumping sites, etc. Therefore, investigation on the reduction in the release of BFRs and their breakdown products into the environment from their sources should be made. Especially, the recycling sites of e-waste in developing countries should be paid attention. The electronic products produced 5~20years before possibly contain large amount of PBDEs and bromine-containing dioxins and hence new techniques should be developed for treatment of such wastes.

Further epidemiological studies are necessary on workers at such source areas to elucidate the exposure status and human health effects by BFRs and their break down products.

Then, inventory of the amount of the exhaust of BFRs and bromine-containing dioxin also need to be made in each country as early as possible for understanding the current and future environmental pollution by them.

High levels of BFRs and bromine-containing dioxin in house dust may be one of the important routes to human. Therefore, investigation on human effect of indoor pollution in the houses and offices which have the consumer products containing BFRs should be made.

Investigation in the environment and human on alternative chemicals of PBDEs and Co-PXB exposure should also be performed.

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