Environmental Release and Behavior of Brominated Flame Retardants -An Overview

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Introduction

Some BFRs such as polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), Tetrabromobisphenol-A (TBBPA) and hexabromocyclododecane (HBCD) have attracted social concern due to their occurrence and persistence in the environment and human exposure for the last two decades[1]. Recently, the environmental occurrence of BFRs has become a matter of great concern. One of the reasons for this is due to the increasing levels of PBDEs in human milk in Sweden from 1972 to 1997[2]. Furthermore, some recent toxicological studies have demonstrated that BFRs can elicit serious health effects such as thyroidogenic, estrogenic and dioxin-like activity, as summarized by Bergman[3]. Therefore, there is an emerging question at present whether the concentrations of PBDEs and other BFRs continue to increase in the environment and cause some toxic effects on humans? Another social concern with BFRs over the past decade has been on their thermal by-products i.e., polybrominated and mixed-bromo/chlorinated dibenzo-p-dioxins and –dibenzofurans (PBDDs/DFs and PXDDs/DFs)[4].

This report addresses the annual consumption of BFRs, their occurrence in waste television sets in Japan, emission sources, environmental behavior, temporal trends of PBDEs and by-products on BFRs in Japan.

Annual consumption of brominated flame retardants in Japan

The annual consumption of BFRs has drastically increased from year to year from 1986 to 1990's and saturated recently in Japan. However, great changes in the kinds of BFRs used and their consumption amounts were recognized during this period. That is, the consumption of PBDEs had rapidly increased until 1990, and subsequently decreased thereafter. PBDEs consumption in 1990 was 12,100 tons (DecaBDE:10,000tons, OctaBDE:1,100tons, TetraBDEs: 1,000tons), while that in 2000 was 2,800 tons of DecaBDE only. As the consumption of PBDEs is decreasing, newly developed BFRs such as TBBPA, polycarbonate oligomer, TBBPA epoxy oligomer and brominated polystyrene have been used as alternatives to PBDEs.

Characterization of waste flame-retarded products in Japan

The information on present status of waste flame-retarded products and flame retardants types used in those wastes is really needed because of the fact that these waste products may be one of the main emission sources of BFRs to the environment. A survey of the waste television sets manufactured in the years 1987-1995 was conducted at bulky waste management facilities in September 2000, in Japan. It was found that the TVs manufactured 10 to 20 years ago, when PBDEs had been heavily used, are being wasted in Japan at present. The BFRs contained in the samples of waste TV sets (a mixture of 40 TV sets manufactured in 1987-1995) was analyzed[5].

The casing materials and printed circuit boards contained small amount of both PBDEs and TBBPA. Nona- to decaBDE were found in casing materials and tetra- to pentaBDEs were detected in printed circuit boards. In addition, it is also presumed that BFRs types had changed during 1990 to 1997 in Japan based on an another survey of thirteen waste TV casings[5].

Emission Sources

One of the most possible emission sources of BFRs to the environment should be effluents from the factories producing BFRs, flame-retarded polymers and plastic products such as electrical appliances. A Swedish surveillance study on BFRs in river sediments surrounding a plastic industry that uses TBBPA[7] and textile industries[8] showed higher levels of TBBPA and PBDEs in the downstream of the plants than those in the upstream. Other possible sources of BFRs may be similar to those of PBDDs/DFs and PXDDs/DFs since bromine-containing dioxins are thermal by-products of some BFRs, as described in EHC 205[4]. These include municipal or hazardous waste incinerators, recycle facilities of plastics and metals from electronic devices, disposal sites, and real fire accidents.

Environmental behavior of brominated flame retardants

The environmental behavior of BFRs has been predicted on the basis of the earlier studies in Japan and Sweden[9,10,11]. Briefly, the higher brominated compounds are less mobile in the environment, possibly due to their low volatility, low water solubility and strong adsorption to sediments. Therefore, the higher brominated compounds tend to end up in sediments at high residue levels near their emission sources but not so in marine organisms and 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 chlorinated pollutants such as PCBs and PCDDs/DFs.

Considerable amount of data is available on the levels and composition of PBDEs in the environment, biota and human, though the data on other BFRs are few. On the basis of the available data on PBDEs, the environmental behavior and fate are discussed in more details.

(1) **Air:** The major congeners detected in air were BDE-47, -99, -100, -153 and –209. Little is known regarding the occurrence of hepta- to nona-BDEs in air. BDE-209 is dominant in airborne dust. Vapor pressures of PBDEs reported to decrease linearly with increasing bromine content[12]. BDE-47 was showed to be primarily in the atmospheric vapor phase and expected to be more susceptible to long-range transport compared to the higher brominated congeners[13]. On the other hand, more than 99% of deca-BDE was found to be bound to particles in ambient air at a plant dismantling electronics[14]. Therefore, the higher brominated congeners could be less mobile in the atmosphere.

(2) **Water and Sediment:** The PBDEs congener profiles in water and sediment seem to be almost the same as those in the atmosphere[10,15], although there exists only a few data on PBDEs in water. A Swedish survey on PBDEs in sediments from European estuaries and the Baltic Sea showed large differences in their concentrations and composition between the sampling sites[15]. That is, BDE-47 and –99 were found in both European estuaries and the Baltic Sea though BDE-209 was detected with high concentration in European estuaries. Water solubility of PBDEs is reported to decrease generally with increasing bromine contents according to Tomy et al.[16]. Therefore, BDE-47 and –99 could move great distances in aqueous phase due to their higher water solubility than

BDE-209, which is less mobile in aqueous phase.

(3) **Biota:** Considerable amount of data exists on the occurrence of PBDEs in fish and mammals, although PBDEs levels in biota varied widely depending on the species and the collection sites. Nevertheless, the PBDEs congener profiles in biota seem to resemble each other, though there are a few exceptions. BDE-47 is dominant in biota, followed by BDE-99, -100, -153 and –154. The lower brominated compounds such as BDE-47 and –99 are highly bioavailable. Their bioaccumulation factors were reported to be higher than those of PCBs in blue mussels[17]. Biomagnification of tri- to hexaBDEs was also recognized to occur in food chains[18]. On the other hand, BDE-209 is rarely found in biota. Although Kierkgaard et al. found the ability of rainbow trout to accumulate BDE-209, the uptake efficiency was extremely low[19]. Therefore, BDE-209 is generally considered to be less bioaccumulative, and possibly due to its large molecular size and strong adsorption to sediment. However, a recent report showed the occurrence of BDE-209 with BDE-183 in wild falcon in Sweden[20]

(4) **Humans:** PBDEs have been found in human milk and blood of both general population and occupationally exposed workers[2,14]. The main PBDEs congeners found in humans are BDE-47 (dominant), -100, -99, 153, -154, -183 and –209. The PBDEs congener profiles in general population seem to be essentially similar to those in biota. However, PBDEs congener profiles in occupationally exposed workers at electronics dismantling facility are dominated by BDE-183 and –209, which is obviously different from those in biota and non-occupationally exposed persons[14]. It is clear that BDE-209 as well as the lower brominated congeners can be accumulated in humans. Generally, food is expected to be the main exposure routes for PBDEs to general population as in the case of PCBs and PCDDs/DFs. Lind et al. revealed that the major exposure route of PBDEs to humans was fish, which accounted for almost half of the total PBDEs intake [21]. Then, the major exposure route to workers at the facilities involved with BFRs should be air contaminated in the workplaces

Temporal trends

In Sweden, PBDEs in guillemot eggs from Baltic Sea showed an increase in concentrations since the 1970s and then declined in the 1990s[22]. PBDEs levels in human milk in stockholm showed a decreasing trend from 1998 to 2000 though an increasing trend was observed from 1972 to 1997[23]. However, in the North American environment, Alaee reported that PBDEs levels in biota and sediment cores showed a steady increasing trend, possibly due to continued usage of the pentaBDE formulation[24]. In Japan, Ohta et al. reported that PBDEs levels in Japanese sea bass collected at Osaka showed a decreasing trend after 1990[25]. Therefore, it seems that the temporal trends of PBDEs levels in the environment and humans considerably vary depending on the countries.

Brominated and mixed-bromo/chlorinated dibenzo-p-dioxins and - dibenzofurans

The bromine containing dioxins are still one of the environmental problems from the use of BFRs. Sakai et al. reported the occurrence of PBDDs/DFs at ppm levels in current waste TV casing, waste PC casing and printed circuit boards[5,6]. Japanese Ministry of Welfare conducted the emission survey of PBDDs/DFs and mixed-PXDDs/DF in addition to PCDDs/DFs from 75 incineration plants in Japan in 2000[26]. PBDDs/DFs and mixed-PXDDs/DFs as well as PCDDs/DFs were found in effluent gas at incineration plants. Average mixed-PXDDs/DFs (monobrominated congeners only) were 12% of those of PCDDs/DFs. Soderstrom and Malklund reported that

combustion of bromine and chlorine-containing waste at MSW increased the total formation of halogenated dioxins, especially mixed-PXDDs/DFs[27]. In waste incineration, all kinds of BFRs may be a source of bromine. Some mixed-PXDDs/DFs possibly convert into more stable PCDDs/DFs in the environment by photochemical debromination[28].

Further studies

To assess in detail the environmental and human exposure of PBDEs, tetra- to decaBDE including hepta- to nonaBDE should be determined. Further investigation on the environmental behavior, temporal trend, exposure routes to human and toxicity of decaBDE and other BFRs including their thermal by-products, environmental decomposition products and biological metabolites are needed.

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