A Review of Recent Studies on Brominated Flame Retardants in the Asia-Pacific Region

Shin Takahashi¹, Tomohiko Isobe¹, Annamalai Subramanian¹, Takumi Takasuga¹, Shin-ichi Sakai², Shinsuke Tanabe¹

¹ Center for Marine Environmental Studies, Ehime University, Matsuyama 790-8577, Japan
² Environment Preservation Center, Kyoto University, Japan

Introduction
Recently, environmental issues relating to brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) have become a matter of great concern due to their persistent and bioaccumulative properties and potential toxic risk to humans. Growth in interest on PBDEs has been exponential as their apparent increase in the environment over the last few decades in Europe and North America. However, there is still little information on contamination of BFRs in the Asia-Pacific region (Watanabe and Sakai, 2003). Significant contamination by BFRs may arise from rapid industrialization in some Asian countries. Therefore, we have started monitoring studies on the contamination status of BFRs as well as legacy POPs in the Asia-Pacific region. In this presentation, we review our recent studies on BFRs including PBDEs and HBCDs in mussels, skipjack tunas, marine mammals, human breast milk, house and office dusts, sediment cores and terrestrial environments such as waste dumping sites to delineate their present status of contamination, global distribution, human exposure, potential sources and temporal trends.

Materials and Methods
The mussel and tuna samples archived in our specimen bank (es-BANK) were used as sentinel species to elucidate the pollution status and distribution of PBDEs and HBCDs in the Asia-Pacific region (Ueno et al. 2004, 2006; Ramu et al. 2005, 2007). The blubber of cetaceans stranded along the coasts of Japan, Hong Kong, the Philippines and India were also employed for chemical analysis (Kajiwara et al. 2006a). To examine the temporal trends, the archived fat tissue samples of northern fur seals from the Pacific coast of northern Japan and finless porpoises from Hong Kong coasts were analyzed for PBDEs and HBCDs (Kajiwara et al. 2004, 2006b). The sediment core samples from Tokyo Bay were also analyzed for BFRs as well as PCBs (Isobe et al. 2007). Human breast milk was collected from various Asian countries to understand human exposure to PBDEs (Sudaryanto et al. 2005, 2007). The soil samples were collected from open waste dumping sites in India, Vietnam and Cambodia to elucidate contamination of BFRs and brominated dioxins due to waste disposal as potential source in terrestrial environments (Takahashi et al 2006). House and office dust samples were collected from Tsukuba and Matsuyama, Japan (Suzuki et al. 2006). Analysis of PBDEs and HBCDs was described in elsewhere (Kajiwara et al. 2006a, Isobe et al. 2007). A resent result on the determination of several organobromine compounds including decabromodiphenylethane in finless porpoise was also reviewed (Takasuga et al. 2006)

Results and Discussion
Contamination Status and Global Distribution
In our latest results of Asia-Pacific Mussel Watch Project, widespread contamination by PBDEs in the coastal waters of Asia became apparent with higher concentrations in mussels from Hong Kong and Korea (Ramu et al. 2005, 2007) (Figure 1). Another study focused on cetaceans also showed the highest PBDEs concentrations in samples from Hong Kong (Kajiwara et al. 2006a). As a further finding of spatial distribution, relatively high concentrations of PBDEs were detected in skipjack tunas
collected from off-Taiwan and the East and South China Seas (Ueno et al. 2004). These results suggest the existence of significant pollution sources of PBDEs even in some Asian developing nations. The highest concentrations of PBDEs found in mussels and cetaceans from coastal waters in Hong Kong and Korea seems to be comparable to those in European and/or North American countries.

HBCDs were also detected in skipjack tunas and mussels from some Asian countries (Ueno et al. 2006; Ramu et al. 2007). Elevated concentrations of HBCDs were found in skipjack tunas from areas around Japan, implicating major sources of HBCDs in this region. In addition, high atmospheric transportability of α-HBCD isomer was suggested from the result of tunas from various latitudes of the Asia-Pacific region.

Human Exposure and Potential Sources
PBDEs were detected in all the milk samples from Japan, China, the Philippines, Malaysia, Korea, Indonesia, Cambodia, Vietnam and India (Sudaryanto et al. 2005, 2007). This result indicates that human exposure to PBDEs occurs in Asian developing countries as well as other developed nations. Nevertheless, the concentrations of PBDEs in human milk were much lower than those of PCBs and DDTs. The extent of contamination by PBDEs in human milk from Asian countries seems to be comparable to those reported from Europe, but one or two order of magnitude lower than levels found in North America. Among the Asian countries studied, relatively high concentrations of PBDEs were found in milk samples from China, Japan, Korea and Indonesia. However, except for North America, difference in PBDE levels between the countries was relatively small compared with those found in marine organisms. In addition, composition profiles of PBDEs in the human milk were rather different among the countries and even among individual samples, suggesting various sources and routes of human exposure to PBDEs. In fact, we found PBDEs in house and office dusts collected from Japan at comparable levels to European countries (Suzuki et al. 2006).

Figure 1. Distribution of PBDEs in mussels from coastal waters of various Asian countries.
In our recent study on contamination of PBDEs around open dumping sites in India, Cambodia and Vietnam, significantly higher concentrations of PBDEs were found in soils from areas within/nearby dumping sites than reference locations (Takahashi et al. 2006). This result indicates that waste dumping sites play a role as a potential source for PBDEs. Dioxin-related compounds such as polybrominated dibenzo-\(p\)-dioxins and dibenzofurans were also detected in some of the soil samples from dumping sites.

**Temporal Trends**

Analytical results of the archived samples of northern fur seals from the Pacific coast of northern Japan indicated; the lowest PBDE level was detected in 1972 and the peak concentration around 1991-1994, and slightly decreased in the late 1990s (Kajiwara et al. 2004) (Figure 2). This pattern is apparently different from the temporal trends of PCBs and DDTs, for which maximum levels were around 1970s. The chronology of PBDE contamination of fur seals from northern Japan is different from that in the Great Lakes and the Canadian Arctic, and rather similar to that in Europe where an earlier regulation on the commercial production of Penta-BDE was implemented. Noteworthy, a significant increasing trend in the concentrations of HBCDs was found in fur seals collected in 1990s (Kajiwara et al. 2006b) (Figure 2). Furthermore, the concentrations of HBCDs were almost close to those of PBDE in fur seals collected during the late 1990s despite apparently higher levels of PBDEs than HBCDs in fur seals collected before 1991. Increasing trends of PBDEs and HBCDs during the last few decades were also found in our recent studies on small cetaceans stranded along the coasts of Japan and China and in sediment cores from Tokyo Bay (Isobe et al. 2007).

Some other organobromine compounds including decabromodiphenylethane, one of alternatives for PBDEs, were also detected in a blubber sample of finless porpoise from Japanese coasts at significant levels (Takasuga et al. 2006). Further studies on such emerging compounds are required to clarify their contamination status and temporal trend.

**Future Subjects**

Our recent investigations clearly indicate the widespread contamination of PBDEs in the Asia-Pacific region. Consumption of brominated flame retardants in future may increase due to rapid industrialization in Asian developing countries like China.

**Figure 2.** Temporal trends in the concentrations of PBDEs and HBCD in northern fur seals from the Pacific coast of northern Japan and annual consumption of commercial PBDEs and HBCD products in Japan.
Waste dumping and unsuitable material recycling (e.g., ‘e-waste’ problem) may cause serious environmental contamination. A series of our findings underlines the need for long-term monitoring of pollution by PBDEs as well as other potential persistent contaminants such as HBCD and decabromodiphenylethane in the Asia-Pacific region. It is also imperative to find out potential sources of these compounds and to evaluate their toxic risk for wildlife, ecosystems and humans.

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