Temporal Trends of Brominated Flame Retardants and Other Emerging POPs in Waters around East Asia: Retrospective Studies Using Archived Samples from es-Bank, Ehime University, Japan

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Introduction

Brominated flame retardants (BFRs) are a group of compounds that are added to a wide range of products, such as printed circuit boards, computer cases, electronic appliances, automobiles and construction materials to prevent the outbreak of fire. Among them, additive flame retardants like polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) are the focus of current concerns due to their persistence, bioaccumulative nature, and possible adverse effects on humans and wildlife. Although the potential risk of these BFRs in wildlife is not clear, experimental studies using PBDEs and HBCDs have shown various effects including immunological and neurotoxic effects and propensity to disrupt thyroid hormone homeostasis (de Wit, 2002; Darnerud et al., 2001, Reistad et al., 2006).

Consequently, since May, 2009, certain lower brominated PBDE congeners, i.e., major components of Penta- and Octa-BDE mixtures, have been listed to eliminate as persistent organic pollutants (POPs) under the Stockholm Convention. However, usage of other BFRs including Deca-BDE and HBCD mixtures are still continuing, and environmental release of BFRs may be continued or increase in future by disposal of used materials and/or their reuse/recycling. In addition to BFRs, certain groups of perfluorochemicals (PFCs) such as perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), which have been used widely as surfactants and surface protectors in number of domestic consumers and industrial applications, have been recently concerned as ‘emerging POPs’ and included in the list of restriction by the Stockholm Convention.

Monitoring studies over a period of time can provide information regarding contaminant variability and trends in exposure. Although several monitoring studies have shown increasing BFR levels in various environmental matrices and human tissues from North American and European countries, informations on emerging POPs in the environment of East Asia are still limited, particularly in remote regions and offshore waters. Asia is currently a major global industrial center with some of the fastest economic growth rates in the world. Urbanization and onset of industrialization have resulted in increased production and usage of new chemicals and their subsequent release into the environment in this region. The present paper summarizes recent studies conducted at Global COE project, Ehime University, Japan on temporal trends of emerging POPs such as BFRs and PFCs in waters around East Asia and Lake Baikal, Russia.

Materials and Methods

Fat or liver tissue samples of aquatic mammals archived in Environmental Specimen Bank (es-BANK) of Ehime University were used to evaluate temporal trends of BFRs (PBDEs and HBCDs) and PFCs in the
environment of Japan, South China and Lake Baikal. Archived fat or liver tissue of four aquatic mammal species, including adult male melon-headed whales (*Peponocephala electra*) mass stranded along Japanese coast in 1982, 2001 and 2006, adult male striped dolphins (*Stenella coeruleoalba*) dead along Japanese coast during 1978-2003, adult male finless porpoises (*Neophocaena phocaenoides*) collected from coastal waters of South China Sea in 1990, 2000 and 2001, and juvenile male Baikal seals collected in 1992, 1995, 1998, and 2005, were employed for chemical analysis. All the samples were collected under the stranding network of Japan or academic volunteers with official permissions from local governments, and stored in our es-BANK at –25°C until chemical analysis. Some details of samples and analytical methods can be found in our original papers (Ramu et al., 2006; Isobe et al., 2007; 2009a, 2009b; Tanabe, 2008; Hart et al., 2008).

**Results and Discussion**

In marine mammals from Japan, PBDE levels significantly increased during the last several decades and were 1 to 2 orders of magnitude higher in recent years than in the 1970s and 1980s (Fig. 1). Striped dolphins showed increase in mean concentrations of PBDEs from 13 ng/g lipid wt. in 1978 to 640 ng/g lipid wt. in 2003 (Isobe et al. 2009a). Similarly, melon-headed whales showed 10 times increase in PBDE levels from 1982 to 2006 (Tanabe, 2008). On the other hand, there were indications that PBDE concentrations are leveling off in recent years. Our previous study on northern fur seals from Sanriku coast, Japan reported that PBDE levels peaked in the early 1990s and since then appear to decline (Kajiwara et al. 2004).

Likewise to PBDEs, HBCD concentrations in marine mammals from Japan have risen significantly during the last decades. HBCD levels in melon-headed whales in 2006 were significantly higher than in 1982, showing about fifty-fold increase (Tanabe, 2008). Continuous increasing trend was also noticed for HBCD concentrations in striped dolphins, from 12 ng/g lipid wt. in 1978 to 710 ng/g lipid wt. in 2003 (Isobe et al., 2009a) (Fig. 1). In recent years, HBCD concentrations in marine mammals appear to exceed PBDEs, presumably reflecting increasing usage of HBCDs over PBDEs in Japan.

![Fig. 1. Temporal trends in PBDE and HBCD concentrations in marine mammals from Japan. Data cited from Kajiwara et al. (2004), Isobe et al. (2007, 2009a), and Tanabe (2008).](image-url)
In addition to BFRs, melon-headed whales showed 10 times increase in total PFC levels from 20.3 ng/g wet wt. in 1982 to 215 ng/g wet wt. in 2006 (Hart et al., 2008). Contribution of perfluorocarboxylates, particularly longer chained isomers, to total PFC concentrations increased from 1982 to 2006 (Fig. 2). This may reflect PFC production shifted from PFOS to longer chain perfluorocarboxylates in Eastern Asian countries. Considering less information and remarkable increase in PFC concentrations, more studies on the temporal trends and potential sources of PFCs are warranted.

Increasing environmental contamination by PBDEs and HBCDs was also noticed in finless porpoises from Chinese coastal waters. Mean concentrations of total PBDEs in finless porpoises from the South China Sea increased significantly (six fold) from 113 ng/g lipid wt. in 1990 to 714 ng/g lipid wt. in 2001 (Ramu et al. 2006). The significant increase of PBDE levels in finless porpoises suggests that PBDEs have been used more extensively in recent years in China. Although HBCDs were detected in all the finless porpoises from South China Sea, unlike cetaceans from Japan, the levels in 2000/01 were still approximately twenty times lower than those of PBDEs (Isobe et al., 2007) (Fig. 3). These results may indicate that demand for HBCDs has increased only moderately in this region.

Fig. 2. Temporal variations of PFC composition in melon-headed whales from Japan. Data cited from Hart et al. (2009).

Fig. 3. Temporal variations of organohalogen compounds in finless porpoises from the South China Sea ($p<0.001$, $U$-test). Data cited from Ramu et al. (2006) and Isobe et al (2007).
BFRs were detected in the blubber of Baikal seals collected in 1992, 1995, 1998, and 2005 (Isobe at al. 2009b). No obvious trend was observed for PBDEs, whereas HBCDs showed a significant increasing trend during this period. This suggests that contamination by BFRs, particularly HBCDs, is ongoing. Difference in the temporal trends of BFRs observed between aquatic mammal species may reflect their long range transport to remote areas as well as their regional usage.

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