

## Contamination Status of Brominated Flame Retardants (BFRs) in Baikal Seals (*Pusa sibirica*)

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(Received 28 January 2009; accepted 11 March 2009)

**Abstract**—Brominated flame retardants (BFRs) including polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) were determined in Baikal seals (*Pusa sibirica*) collected from Lake Baikal to reveal their contamination status, accumulation features and temporal trends. Organohalogen compounds analyzed were detected in all the blubber samples of Baikal seals. DDTs were the most abundant contaminants followed by PCBs, CHLs, HCHs, PBDEs, HBCDs, and HCB. BFR levels found in Baikal seals were lower than those in other marine mammals from European or American coastal waters, implying that seals in this region were less exposed to BFRs. This suggests that there is no heavy industry producing or using BFRs in the watershed of Lake Baikal and the contamination might have resulted from long-range atmospheric transport. Concentrations of PBDEs and HBCDs in the blubber of Baikal seals collected in 2005 were significantly higher in males than in females. This gender dependent difference could be due to transfer of these contaminants from mother to pup during gestation and lactation. In addition, temporal trends of organohalogen contamination in Baikal seals were investigated using the blubber of male juvenile seals collected in 1992, 1995, 1998, and 2005. No obvious trend was observed for PBDEs, whereas HBCDs showed a significant increasing trend during this period, suggesting that contamination by these organohalogen compounds, particularly HBCDs, is ongoing.

Keywords: Bikal seal, PBDEs, HBCDs

### INTRODUCTION

Many incidents of mass mortalities of marine mammals have been observed worldwide since 1980's. In Lake Baikal, a severe mass mortality of 8,000 Baikal seals (*Pusa sibirica*) was reported in 1987/88. Although morbillivirus infection

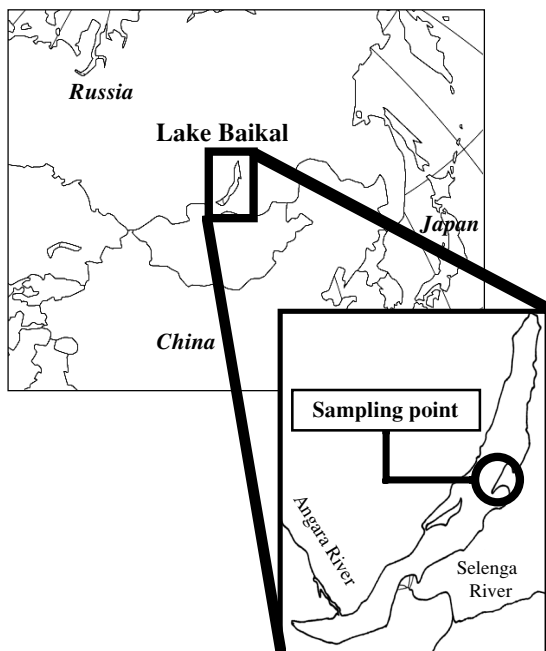


Fig. 1. Sampling location.

was found to be the primary cause of the mass mortality, xenobiotic pollutants, particularly organohalogen compounds, were suspected to be one of the contributing factors affecting health of the Baikal seals. Lake Baikal, declared as a natural world heritage by UNESCO, is the largest and deepest freshwater lake in the world, with water surface area of 31,000 km<sup>2</sup> and depth of 1,670 m. Baikal seal is an endemic species and the top predator in Lake Baikal ecosystem. In our previous study, we reported that Baikal seals accumulated organochlorine contaminants (OCs), including PCBs, DDTs and dioxin like compounds, and showed evidence of induced drug-metabolizing enzyme, i.e., cytochrome P450 (CYP), in their body (Nakata *et al.*, 1997; Tanabe *et al.*, 2003; Tsydenova *et al.*, 2004; Hirakawa *et al.*, 2007). Production and usage of PCBs and DDTs were regulated during 1990's in Russia. As a result of the declining load into the environment, a significant decrease of PCB and DDT levels in Baikal seals from 1992 to 2003 was reported (Tanabe *et al.*, 2003). In contrast, demand and consequent discharge of brominated flame retardants (BFRs) have been increasing, especially in the last two decades. Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), which are used as additive BFRs, have been detected in a wide range of environmental and biological matrices as a result of their bioaccumulative features (Law *et al.*, 2003, 2005; Covaci *et al.*, 2006), similar to persistent OCs. There is, however, no information on contamination

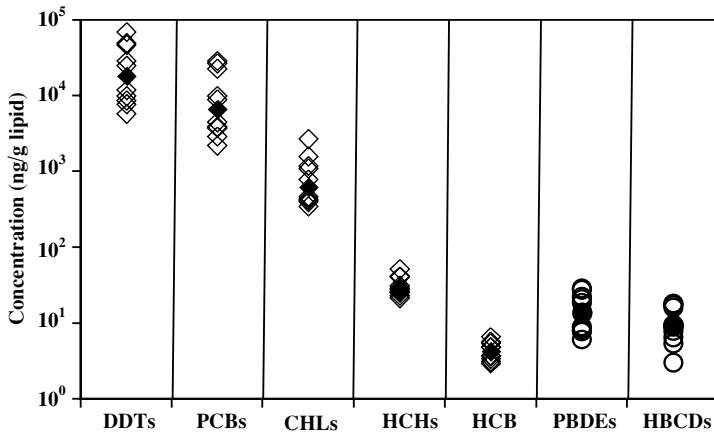


Fig. 2. Concentrations of organohalogen compounds in the blubber of Baikal seals collected from Lake Baikal in 2005 (closed and open symbols indicate median and individual concentrations, respectively).

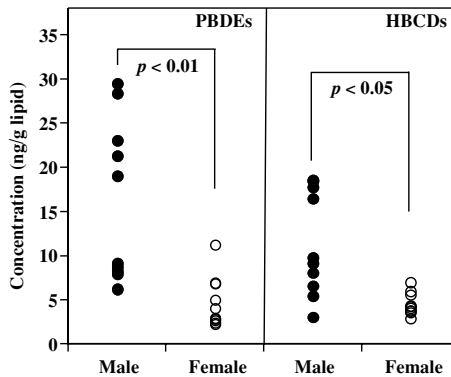


Fig. 3. Gender differences in PBDE and HBCD concentrations in blubber of Baikal seals.

status by BFRs in this region. In this study, 14 PBDE congeners and 3 HBCD isomers were determined in Baikal seals collected from Lake Baikal to reveal their contamination status, accumulation features and temporal trends.

## MATERIALS AND METHODS

### *Samples*

Blubber samples of Baikal seals (*Pusa sibirica*), including adult ( $n = 6$ ) and juvenile ( $n = 4$ ) males, and adult ( $n = 6$ ) and juvenile ( $n = 4$ ) females, were

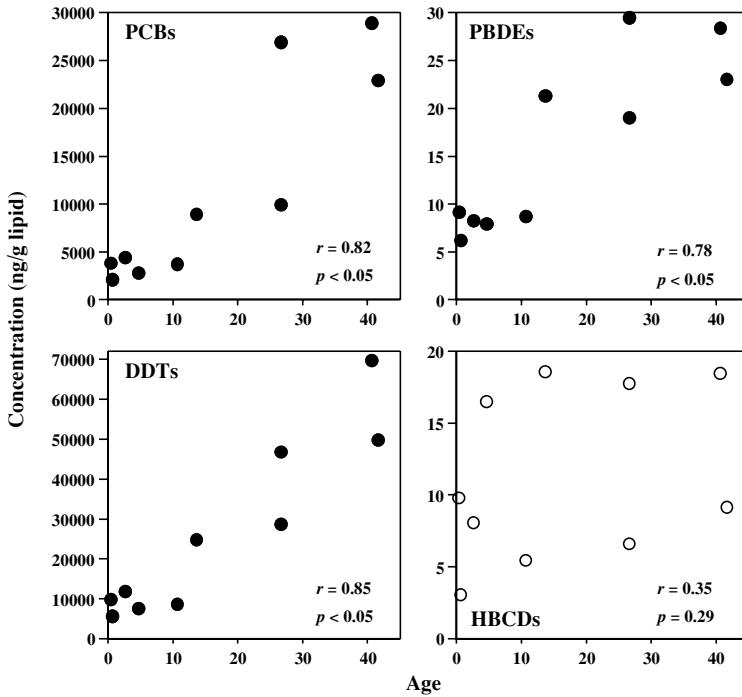


Fig. 4. Age dependent accumulation of organohalogen compounds in Baikal seals collected from Lake Baikal in 2005.

collected from Lake Baikal in 2005 (Fig. 1). To estimate the temporal trends, male juvenile blubber samples collected in 1992 ( $n = 4$ ), 1995 ( $n = 5$ ), and 1998 ( $n = 5$ ) were also analyzed. All the samples were collected under official permission from the local government. The animals were shot, dissected immediately and then stored in Environmental Specimen Bank (*es*-BANK) of Ehime University (Tanabe, 2006) at  $-25^{\circ}\text{C}$  until chemical analysis.

#### Chemical analysis

OCs (PCBs, DDTs, HCHs, CHLs and HCB) and BFRs (PBDEs and HBCDs) were analyzed following the methods described previously (Ueno *et al.*, 2004; Kunisue *et al.*, 2005; Isobe *et al.*, 2007). Blubber samples were Soxhlet extracted with diethyl ether/hexane solution. The aliquot of extract was spiked with internal standards, cleaned and fractionated using a gel permeation chromatography and an activated silica gel column. Identification and quantification of OCs, PBDEs and HBCDs were achieved using GC-ECD, GC-MS, and LC-MS-MS, respectively. Concentrations are expressed as ng/g lipid weight, unless otherwise stated.

## RESULTS AND DISCUSSION

*Contamination status*

Organohalogen compounds analyzed in the present study were detected in all the blubber samples of Baikal seals. Concentrations of organohalogen compounds in the blubber of Baikal seals collected in 2005 are shown in Fig. 2. DDTs were the most abundant contaminants followed by PCBs, CHLs, HCHs, PBDEs, HBCDs, and HCB. BFR levels found in Baikal seals were lower than those in other marine mammals from European or American coastal waters, implying that seals in this region were less exposed to BFRs, when compared to other regions. This suggests that there is no heavy industry producing or using BFRs in the watershed of Lake Baikal and the contamination might have resulted from long-range atmospheric transport.

*Accumulation features and temporal trends*

Concentrations of PBDEs and HBCDs in the blubber of Baikal seals collected in 2005 were significantly higher in males than in females (Fig. 3). The possible reason for this sex dependent difference could be due to transfer of these contaminants from mother to pup during gestation and lactation. Concentrations of PCBs, DDTs, and PBDEs in Baikal seals collected in 2005 showed statistically significant age-dependent increasing trends (Fig. 4). On the other hand, no relationship between HBCD concentrations and age was observed, suggesting rapid increase in usage and consequent load into the environment of this compound in recent days. In addition, temporal trends of organohalogen contamination in Baikal seals were investigated using the blubber of male juvenile seals collected in 1992, 1995, 1998, and 2005. No obvious trend was observed for PBDEs, whereas HBCDs showed a significant increasing trend during this period. This suggests that contamination by these organohalogen compounds, particularly HBCDs, is ongoing.

*Acknowledgments*—This study was supported by Grants-in-Aid for Scientific Research (S: 20221003, B: 18310046), and for Young Scientists (B: 19780239) from Japan Society for the Promotion of Science (JSPS), and the Global Environment Research Fund (RF-064) from the Ministry of Environment. Authors are also grateful to support from Global COE Program provided by the Ministry of Education, Culture, Sports, Science and technology and JSPS and MEXT's program "Promotion of Environmental Improvement for Independence of Young Researchers" under the Special Coordination Funds for Promoting Science and Technology.

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