

Accumulation of Brominated Flame Retardants in Harbour and Dall's Porpoises from Hokkaido

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Abstract—In the present study, stranded or by-caught harbour porpoises (*Phocoena phocoena*) and Dall's porpoises (*Phocoenoides dalli*) were collected from Hokkaido, Japan, and brominated flame retardants (PBDEs and HBCDs) and Polychlorinated biphenyls (PCBs) concentrations in their blubber were measured. All the target compounds were detected in all the specimens. Levels of PCBs were significantly higher than those of PBDEs and HBCDs. PCBs, PBDEs and HBCDs levels in harbour porpoises of the present study were lower than those in Dall's porpoises ($p = 0.03$). This result might reflect the difference in habitat and feeding behavior between these species. Additionally, HBCDs levels in harbor porpoises and Dall's porpoises analyzed in this study were higher than finless porpoises from Seto Inland Sea, suggesting contamination by HBCDs is more serious in Hokkaido. To evaluate the temporal trends, blubber samples of adult male harbour porpoises and Dall's porpoises collected in 1985–2009 and 1980–2008 were analyzed. Concentrations of PCBs in both species did not show any trend during 1980–2009. In contrast, remarkable increasing trend of HBCDs in harbour porpoise was observed. PBDEs and HBCDs concentrations in Dall's porpoises also increased during the survey period. These results suggest growing consumption of these chemicals in Japan and surrounding countries in recent years.

Keywords: polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDs), harbour porpoise, Dall's porpoise, temporal trends

INTRODUCTION

Concern over environmental contamination by brominated flame retardants (BFRs), especially by PBDEs and hexabromocyclododecanes (HBCDs), has increased in recent years because of their similar physicochemical and toxicological characteristics to those of persistent organic pollutants (POPs). Cetaceans are considered to be particularly susceptible to the effects of contaminant exposure

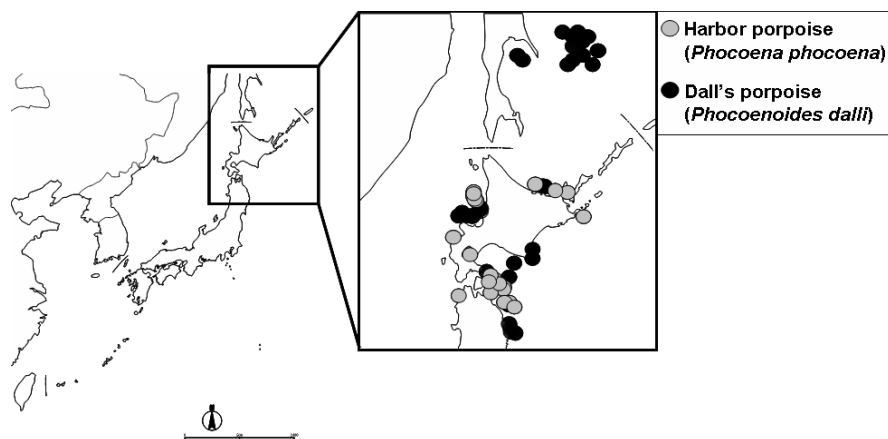


Fig. 1. Sampling locations of harbour porpoises and Dall's porpoises in the present study.

because they have long life spans and feed high in the food web. Although some reports on the status of contamination and bioaccumulation of Organochlorinated compounds (OCs) and BFRs in dolphins and porpoises have already been published (Rahman *et al.*, 2001; Ramu *et al.*, 2005, 2006; Kajiwara *et al.*, 2006a; Law *et al.*, 2006; Isobe *et al.*, 2007, 2009). However, there is still little information on specific accumulation features of PBDEs and HBCDs in small cetaceans in Japanese waters.

In the present study, stranded or by-caught harbour porpoises (*Phocoena phocoena*) and Dall's porpoises (*Phocoenoides dalli*) were collected from Hokkaido, Japan to investigate the contamination status, accumulation features and temporal trends of BFRs (PBDEs and HBCDs) and PCBs accumulated in their blubber.

MATERIALS AND METHODS

Sample collection

Harbour porpoise and Dall's porpoise samples, either stranded or by-caught, were collected from Hokkaido, Japan (Fig. 1). Blubber samples were excised from the animals, and stored at the Environmental Specimen Bank (*es*-BANK) of Ehime University at -25°C until chemical analysis.

Chemical analysis

Analysis of BFRs (PBDEs and HBCDs) and PCBs were carried out following the procedures described in previous studies (Isobe *et al.*, 2007; Kunisue *et al.*, 2008). Identification and quantification of PCBs, PBDEs and HBCDs were performed using a GC-MS and LC-MS/MS.

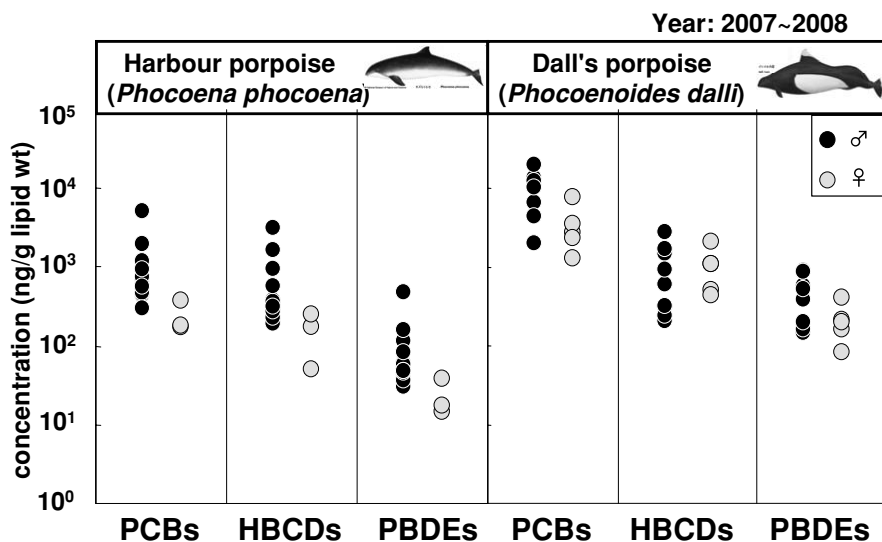


Fig. 2. Concentrations (ng/g lipid weight) of organohalogen compounds in archived blubber samples of harbour porpoises and Dall's porpoises.

RESULTS AND DISCUSSION

Present status of contamination by organohalogen compounds

Organohalogen compounds were detected in all the blubber samples of harbour and Dall's porpoises stranded along Hokkaido, Japan (Fig. 2). Among the organohalogen compounds in the specimens stranded in 2007–08, concentrations of PCBs ranked first followed by HBCDs and PBDEs. Levels of PCBs and PBDEs were in the same range as those reported for other cetaceans from Japanese and Asian coastal waters (Kajiwara *et al.*, 2006a, b; Isobe *et al.*, 2009). The extensive usage and subsequent discharge of HBCDs into the environment in Japan might have resulted in the high HBCD levels found in the present study.

BFRs and PCBs levels in Japanese phocoenoidae

Coastal and Offshore species

Levels of PCBs, PBDEs and HBCDs in Dall's porpoise were higher than those in harbour porpoise (Fig. 3). Since Dall's porpoise is an oceanic species and migrated mainly from Okhotsk to Japan Sea, this species is exposed to contaminants released from countries surrounding Sea of Japan. Considering these facts, pollution sources of PBDEs in the Asian region apart from those from Japan is suspected.

Northern Japan and Seto Inland Sea

The observed levels of PCBs and PBDEs in harbour and Dall's porpoises

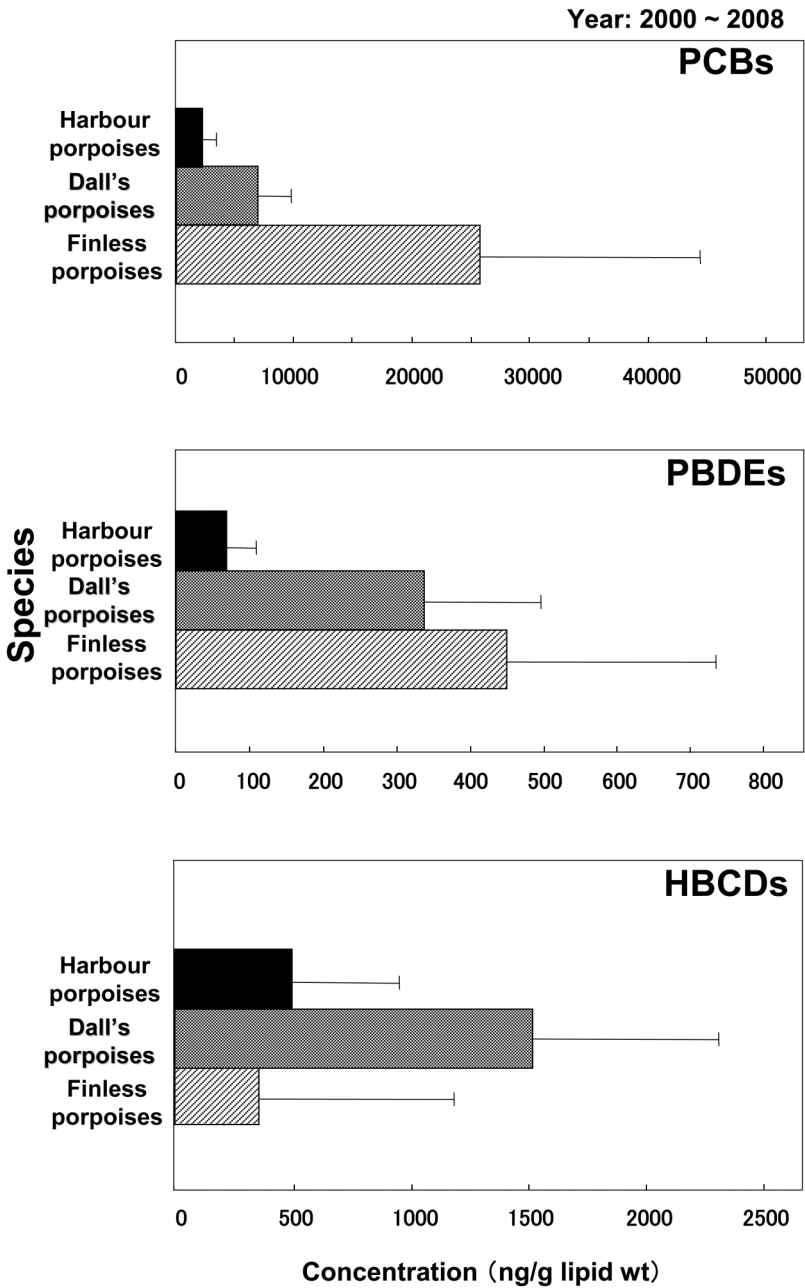


Fig. 3. Concentrations of organohalogen contaminants in harbour, Dall's and finless porpoises.

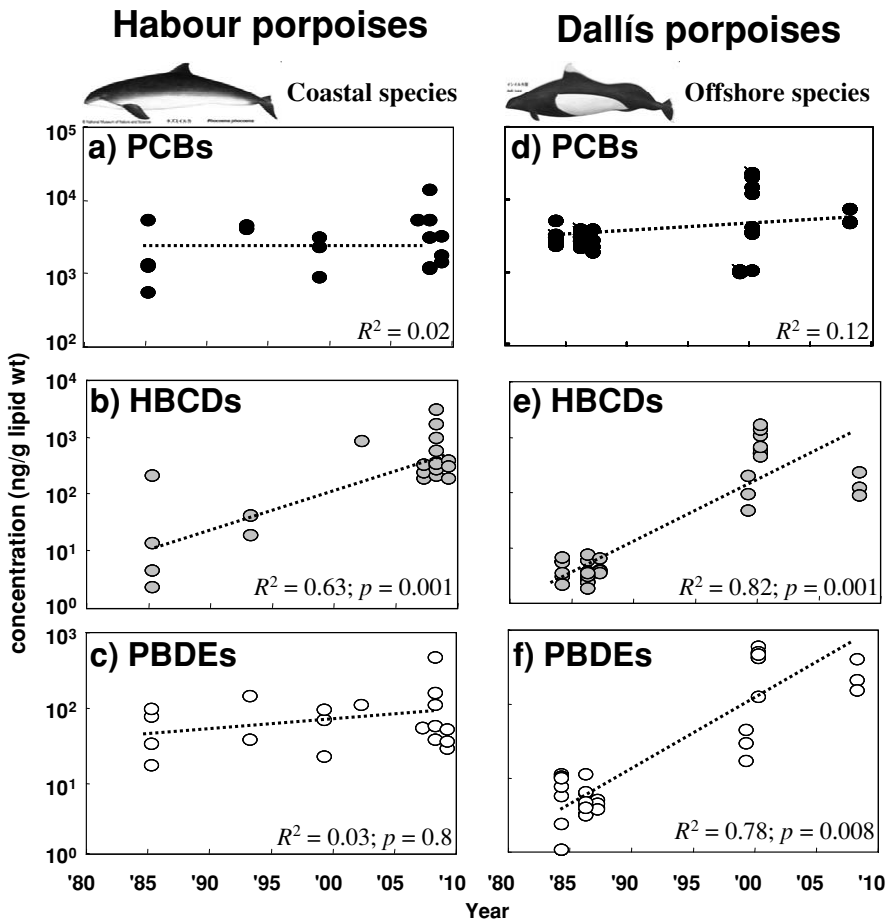


Fig. 4. Temporal trends in concentrations of PCBs, HBCDs and PBDEs in blubber of harbour porpoises (a, b, c) and Dall's porpoises (d, e, f), respectively. Spearman rank correlation was used to examine the strength of associations between parameters. Dots lines represent linear regression lines.

were lower than finless porpoise (*Neophocaena phocaenoides*) from the Seto Inland Sea (Fig. 3). Since finless porpoise usually inhabits coastal and enclosed waters close to cities and industrial areas, they might have been exposed to a variety of chemicals and accumulate lipophilic compounds. Harbour porpoise in this study, however, had lower PBDEs and PCBs levels than those in Dall's porpoise even though they stay in shallow coastal waters without long range migration. Although the reason for the low level of organohalogen contaminants in this species is still unclear, the fact that the areas where they were found stranded do not have heavy human activities may partially account for this

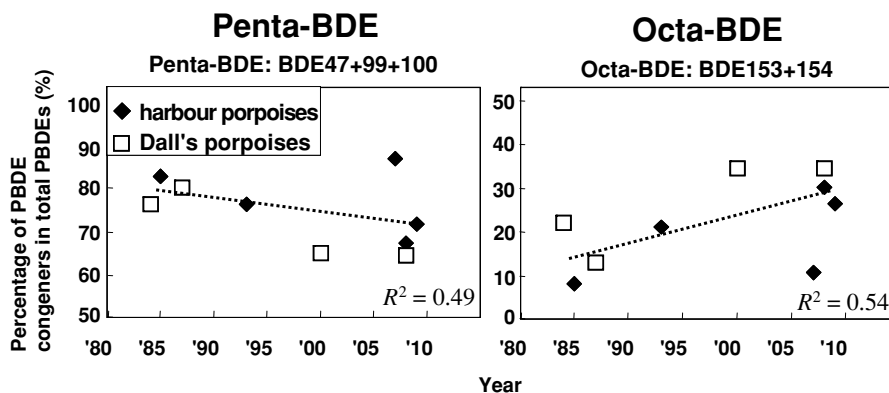


Fig. 5. Temporal trends in PBDE congener profiles in blubber of harbour porpoises and Dall's porpoises. Dots lines represent linear regression lines.

difference.

On the other hand, levels of HBCD in Dall's porpoise were significantly higher than finless porpoises from the Seto Inland Sea. Possible contamination source of HBCDs to Dall's porpoise and harbour porpoise could be located in northern Japan or surrounding countries of Japan Sea.

Temporal trends of organohalogen contaminants

To evaluate the temporal trends of contamination by PCBs and BFRs, blubber samples of Harbour and Dall's porpoises collected in 1985–2008 and archived in the *es*-BANK of Ehime University were analyzed. To avoid the effect of gender and age, only adult male specimens were selected.

PCBs

Concentrations of PCBs in both harbour and Dall's porpoises did not change significantly during this period (Fig. 4). Relatively steady levels of PCBs suggest continuous discharge of these contaminants from the stock pile of old transformers and capacitors in the surrounding countries and also possibly in Japan, although the production of PCBs was banned about 40 years ago.

HBCDs

Levels of HBCDs in harbour porpoise showed an increasing trend from 1985 to 2009, whereas a drastic increase was observed also in Dall's porpoises from Japan in the present study (Fig. 4). HBCDs have been extensively used since the mid-1980s and consumption and subsequent input into the environment is still increasing. This could be the result of differences in the habitat of these two species. Furthermore, this may indicate the high transportability of HBCDs from pollution sources to open ocean.

PBDEs

Levels of PBDEs in the harbour porpoise did not show an increasing trend, whereas apparent increasing trend was observed in Dall's porpoise (Figs. 4c and

f). The significant temporal increase of PBDE levels in the porpoises observed in the present study indicates the continuous use PBDEs in recent years. In addition, it could be seen from Fig. 4, that the harbour porpoise had higher levels of PBDEs even from the year 1985, whereas the levels were lower in Dall's porpoise specimens of the year 1987 and increased to higher levels continuously in the specimens until 2008. This result shows the time lag of pollution due to habitat difference. Differences in temporal trends of PBDE between coastal and offshore species from Japan suggest time lag of pollution.

The concentration of Octa-BDE (BDE-153+154) has increased since 1985, while some lower brominated congeners decreased (Fig. 5). This result implies an increase in demand, particularly for the highly brominated diphenyl ethers such as OctaBDE during the survey period of this study. Similar PBDE congener profile was observed in northern fur seals from Japan (Kajiwara *et al.*, 2008), and Japanese human adipose tissue (Choi *et al.*, 2003).

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