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Accumulation of hydroxylated polychlorinated biphenyls (OH-PCBs) and implications for PCBs metabolic capacities in three porpoise species

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HIGHLIGHTS

- Accumulation patterns and metabolic capacities among three Phocoenidae cetaceans.
- Three porpoise species had variations in OH-PCBs accumulation features.
- Porpoises have the lowest PCBs metabolic capacities compared with any other animals.

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ABSTRACT

The present study investigated polychlorinated biphenyls (PCBs) and hydroxylated metabolites of PCBs (OH-PCBs) in blood from three porpoise species: finless porpoises (*Neophocaena phocaenoides*), harbor porpoises (*Phocoena phocoena*), and Dall's porpoises (*Phocoenoides dalli*). The porpoises were found stranded or were bycaught along the Japanese coast. Concentrations of OH-PCB were the highest in Dall's porpoises (58 pg g^{-1} wet wt), second highest in finless porpoises (20 pg g^{-1} wet wt), and lowest in harbor porpoises (8.3 pg g^{-1} wet wt). The concentrations in Dall's porpoises were significantly higher than the concentrations in finless porpoises and harbor porpoises ($p < 0.05$ and $p < 0.01$, respectively). There was a positive correlation between PCB and OH-PCB concentrations ($r = 0.67$, $p < 0.001$), suggesting the possible concentration-dependent induction of CYP enzymes. The three porpoise species may have exceptionally low metabolic capacities compared with other marine and terrestrial mammals, because low OH-PCB/PCB concentration ratios were found, which were 0.0016 for Dall's porpoises, 0.0013 for harbor porpoises, and 0.00058 for finless porpoises. Distinct differences in the OH-PCB congener patterns were observed for the three species, even though they are taxonomically closely related.

1. Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous environmental pollutants that have been detected in humans, various wildlife species and the environment (WHO, 2002). PCBs were used in industrial applications, such as in electrical transformers and as heat insulators, because of their high chemical stability, but their production was banned in most industrialized countries in the 1970s. Worldwide regulation of the production and use of PCBs was achieved by the Stockholm Convention on persistent organic pollutants (POPs) in 2001 (Bilcke, 2002).

Recent studies have shown that the toxicities of PCBs are caused not only by PCBs but also by hydroxylated metabolites of PCBs (OH-PCBs). PCBs are biotransformed into the polar metabolites OH-PCBs, methylsulfonyl-PCBs ($MeSO_2$-PCBs), and $(OH)_2$-PCBs via cytochrome P450 monooxygenase enzymes (CYPs) in the liver (Bergman et al., 1994; Letcher et al., 2000). Some OH-PCB congeners have chemical structures similar to the thyroid hormones, thyroxine (T_4) and triiodothyronine (T_3) (Brouwer et al., 1998; Cheek et al., 1999). T_4-like OH-PCB congeners compete with T_4 to bind with the thyroid hormone transport protein transthyretin (TTR), and therefore persist in blood. Several OH-PCB congeners have stronger binding affinities to TTR than T_4 (Van den Berg et al., 1991; Lans et al., 1993; Ucan-Marin et al., 2009). OH-PCBs circulate in the blood and potentially disturb thyroid hormone homeostasis and the central nervous system (Meerts et al., 2002; Purkey et al.,

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2004; Kimura-Kuroda et al., 2007). *In vitro* studies have shown that some OH-PCB congeners exert neurotoxic effects during development. In rats, prenatal exposure to 4OH-CB107 led to locomotor defects, learning and memory disorders, and auditory loss (Meerts et al., 2004). Furthermore, it has been reported in a study using reporter gene assays that extremely low doses of OH-PCBs (10^{-10} M) suppress the T_3-induced transcriptional activation of TTR (Iwasaki et al., 2002). Although numerous studies of OH-PCBs in humans and laboratory animals have been conducted, information on these contaminants in cetaceans is limited.

Coastal cetacean species are thought to be exposed to higher levels of anthropogenic contaminants than offshore species. Kajiwara et al. (2006) reported that POPs concentrations were higher in finless porpoises, which inhabit the semi-enclosed, near-shore environment along the industrial coasts of Japan, than in offshore species such as Pacific white-sided dolphins (*Lagenorhynchus obliquidens*), Dall's porpoises, and melon-headed whales (*Peponocephala electra*). Previous studies have suggested that differences in habitat and prey preference account for the variation in PCB concentrations in cetacean blood (McKinney et al., 2006; Houde et al., 2006; Moon et al., 2010; Nomiyama et al., 2010a,b). A study by McKinney et al. (2006) has indicated that populations of beluga whales (*Delphinapterus leucas*) with different exposure levels exhibited different CYP enzyme activities and that the populations with higher PCB residue levels had elevated levels of OH-PCBs.

In this study, we focused on three porpoise species that are closely related but inhabit different geographical ranges (Rosel et al., 1995). Around the Japanese coast, finless porpoises form five near-shore populations in the warm to temperate waters along the Pacific coast (Yoshida et al., 2001; Shirakihara et al., 2007), harbor porpoises inhabit the cool temperate coastal waters around Hokkaido (Gaskin et al., 1993), and Dall's porpoises are migratory and widely distributed in coastal and offshore waters in the Pacific and other seas around Japan (Miyashita and Kasuya, 1988). In this study we investigated the concentrations of PCBs and OH-PCBs in blood from specimens of these three porpoise species that were found stranded or were bycaught along the Japanese coast. Accumulation features and the metabolic capacities of the three porpoise species were compared using the PCB and OH-PCB concentrations.

2. Materials and methods

2.1. Sample collections

Blood samples from the three small cetacean species from the family Phocoenidae (19 finless porpoises, 13 harbor porpoises, and 9 Dall's porpoises) were collected from the hearts or the blood vessels of stranded or bycaught animals along the Japanese coast between 2005 and 2010 (Table S1). Six Dall's porpoises caught in the Northwest Pacific Ocean and the Bering Sea in the 1980s (Table S1) were also analyzed to assess intraspecies variation in accumulation patterns and metabolic capacities for the contaminants. For Dall's porpoise, samples from the 2000s are called "coastal" and samples from the 1980s are called "offshore." Unless otherwise noted, most of the analyses are based on data obtained from Dall's porpoise samples from the 2000s. The samples were stored in the Environmental Specimen Bank (*es*-BANK) at Ehime University, Japan, at −25 °C until analysis.

2.2. Sample preparation and chemical analysis

The extraction and clean-up methods for PCBs and OH-PCBs have been described elsewhere (Nomiyama et al., 2010a), and a detailed description of the experimental protocol as well as quality assurance and quality control can be found in the supplementary material. The PCB congeners were determined using a gas chromatograph/mass spectrometer (GC 7890A/MS 5975C; Agilent Technologies Inc., Santa Clara, CA, USA), and the OH-PCBs were determined as methyl derivatives (MeO-PCBs) using an HP-6890 gas chromatograph (Agilent Technologies Inc.) coupled with an MS-800D high-resolution mass spectrometer (JEOL, Tokyo, Japan). A total of 62 PCBs and 52 OH-PCBs as MeO-derivatives were targeted, as described by Nomiyama et al. (2010a).

2.3. Statistical analysis

All statistical analyses were carried out using StatView J 5.0 (SAS Institute Inc., Cary, NC, USA) and SigmaPlot 11.0. (Systat Software Inc., Chicago, IL). The Mann–Whitney *U*-test was used to test significant concentration differences between groups. Spearman's rank correlation coefficients were used to compare the concentrations of PCBs and OH-PCBs in each sample. A p-value < 0.05 was considered to indicate statistical significance.

3. Results and discussion

3.1. Contamination status

PCBs are neutral lipophilic compounds that strongly partition into lipids. However, OH-PCBs circulate in blood by binding strongly to thyroid hormone transport proteins (Hamers et al., 2008; Ucan-Marin et al., 2009). PCB and OH-PCB concentrations in blood are expressed as pg g^{-1} whole blood wet weight in this study so that the PCB and OH-PCB concentrations can be compared.

PCBs were detected in all of the samples analyzed. Comparing the three porpoise species, the coastal population of Dall's porpoises (samples collected in the 2000s) had the highest median PCB concentrations (37 000 pg g^{-1} wet wt), followed by that of finless porpoises (34 000 pg g^{-1} wet wt), and then that of harbor porpoises (6200 pg g^{-1} wet wt) (Table 1, Fig. S1). The harbor porpoises had significantly lower PCB concentrations than the coastal Dall's porpoises and the finless porpoises ($p < 0.001$ and $p < 0.01$, respectively). This probably reflects variations in the contaminant levels in Japanese coastal waters. Harbor porpoises inhabit the coastal waters around Hokkaido, which has the lowest human population density of the Japanese prefectures (70.2 people/km^2, national census 2010), and the low level of human activity here may explain the lower PCB concentrations found in the harbor porpoises. In contrast, finless porpoises reside in shallow waters along the industrialized coasts, and are more likely to be exposed to anthropogenic chemicals than harbor porpoises. This is also supported by the previous study by Kajiwara et al. (2006), which showed that POP contamination was higher in finless porpoises than in offshore species such as Pacific white-sided dolphins and melon-headed whales. Considering the migratory and pelagic-associated nature of Dall's porpoises, it is surprising that they have higher PCB concentrations than the coastal species. The coastal Dall's porpoise specimens used in this study were considered to be of the *dalli*-type morphotype, which is known to migrate through the Sea of Japan (Miyashita and Kasuya, 1988; Amano and Hayano, 2007), a semi-enclosed sea surrounded by industrial areas in Japan and other countries. As shown in Table 1, comparing coastal (2000s) and offshore (1980s) Dall's porpoise groups, the coastal population had significantly higher PCB concentrations (37 000 pg g^{-1} wet wt) than the offshore population (13 000 pg g^{-1} wet wt) ($p < 0.01$). Although we might have assumed that the samples from the 2000s should have had lower PCB concentrations because of increased PCB regulations and reduced use, it turned out that they