Science of the Total Environment 616–617 (2018) 554–563

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Tissue-specific bioaccumulation of long-chain perfluorinated carboxylic acids and halogenated methylbipyrroles in Dall's porpoises (*Phocoenoides dalli*) and harbor porpoises (*Phocoena phocoena*) stranded in northern Japan

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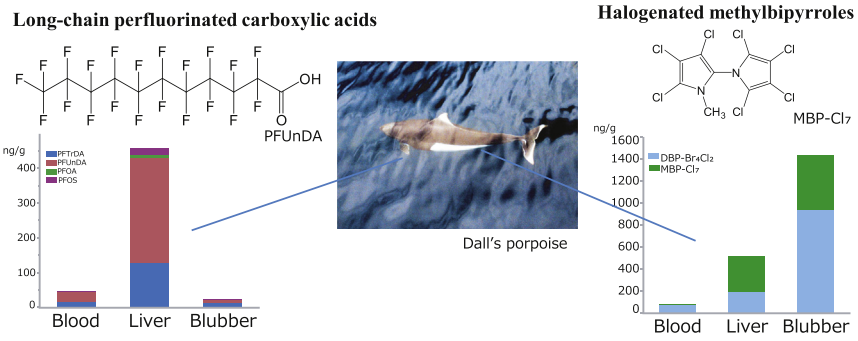
HIGHLIGHTS

- Perfluoroalkyl substances (PFASs) and natural halogenated compounds (NHCs) were analyzed in Dall's and harbor porpoises.
- PFAS profile was dominated by perfluoroundecanoic and perfluorotridecanoic acids.
- Halogenated bipyrroles and methoxylated bromodiphenyl ethers accumulated in porpoises.
- PFASs accumulated in liver, whereas NHCs accumulated in blubber of both species.
- No correlation was observed between PFASs and NHCs in any of the tissues.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 July 2017
Received in revised form 4 October 2017
Accepted 4 October 2017
Available online xxxx

Editor: Adrian Covaci

Keywords:
Perfluoroalkyl substances
Halogenated methylbipyrrole
Bioaccumulation
Dall's porpoise

ABSTRACT

This study investigated accumulation of perfluoroalkyl substances (PFASs), persistent organochlorines (OCs), and naturally produced halogenated compounds (NHCs), including brominated methylbipyrroles and methoxylated bromodiphenyl ethers, in liver, blood, and blubber from Dall's porpoises (*Phocoenoides dalli*) and harbor porpoises (*Phocoena phocoena*) stranded in Hokkaido, northern Japan. Profiles of the PFASs were dominated by perfluoroundecanoic acid and perfluorotridecanoic acid, both of which accounted for 70% of the total measured PFAS concentrations in both porpoise species. The mean concentrations of the $\sum$PFCA were 573 ng/g wet weight (ng/g-wet) in liver, 62 ng/g-wet in whole blood, and 28 ng/g-wet in blubber from the Dall's porpoises, and were significantly higher ($p < 0.05$) than those in the harbor porpoises. The hepatic concentrations of perfluorooctane sulfonate (PFOS) were <14 ng/g-wet, and accounted for only 3% of the total measured PFASs. The profiles of PFASs in the porpoises resembled those in fish species in this area, implying a common source of exposure to PFASs in East Asia. On the other hand, in the blubber of Dall's porpoises, NHCs were dominated by 2,3,3′,4,4′,5,5′-heptachloro-1′-methyl-1,2′-bipyrrole (867 ng/g-wet), 5,5′-dichloro-1,1′-dimethyl-3,3′,4,4′-tetrabromo-2,2′-bipyrrole (481 ng/g-wet), and 6-methoxy-2,2′,4,4′-tetrabromodiphenyl ether (30 ng/g-wet),

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http://dx.doi.org/10.1016/j.scitotenv.2017.10.033

Harbor porpoise
Japan

which were present at higher concentrations than in harbor porpoises. Factor analysis with varimax rotation revealed that factor 1 had higher eigenvectors (element in eigenvalues) for long-chain PFCAs and PFOS, which was found in the highest concentrations in the liver, whereas factor 2 was mainly associated with lipid soluble NHCs and OCs in both species. No correlations were observed between long-chain PFCAs and NHCs in the porpoises, probably because of the different sources and accumulation kinetics. Future research should assess the temporal trends and long-term effects of PFASs and NHCs in the tissues of mammals from the Asia-Pacific region.

1. Introduction

Perfluoroalkyl substances (PFASs) such as perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) have been used as surface tension depressants in the manufacturing industry. In recent years, studies in many geographical locations have investigated the global distribution of PFASs in aquatic organisms (Houde et al., 2011). PFASs have been identified in liver, blood, and kidney tissues from biota, with some of the highest concentrations of PFASs being measured in marine mammals from the Arctic (Reiner et al., 2011). Consumption of fish products is the largest contributor to dietary intake of PFOS and perfluoroalkyl calboxylic acids (PFCAs) with carbon chains longer than eight atoms (> C8) (Fujii et al., 2015b; Vestergren et al., 2012). A previous study revealed that PFASs are not biomagnified at low trophic levels, such as in aquatic organisms in the marine food web, but are greatly biomagnified at high trophic levels, such as in seals, whales, and polar bears (Kelly et al., 2009).

Restriction of the use of PFOS by the Stockholm Convention in 2009 may result in a decrease in the PFOS concentrations in marine biota (Hart et al., 2008a; Sedlak et al., 2017). However, the concentrations of PFOA have remained stable, and those of long chain PFCAs (perfluorononanoic acid (PFNA) to perfluorotetradecanoic acid (PFTeDA)) have increased over time in marine wildlife and human (Hart et al., 2008b; Glynn et al., 2012). Therefore, replacements of PFASs, such as the C4 sulfonate and the C6 acid have been used, due to their different pharmacokinetics (shorter half-lives) and lower toxicity than PFOA and PFOS (Gebbink et al., 2016; Lam et al., 2016). The bioaccumulation potentials of these chemicals vary depending on the tissue (Labadie and Chevreuil, 2011). Thus, empirical measurements of the partitioning behavior of PFCAs and PFOS in different tissues are required to understand the toxicokinetics of PFASs in dolphins and porpoises (Fujii et al., 2015a; Kato et al., 2016).

Naturally occurring halogenated compounds (NHCs) are also of concern because of their persistence, bioaccumulation potential, and global distribution, particularly in aquatic biological samples. Two kinds of bipyrroles, chlorinated 1′-methyl-1,2'-bipyrroles (MBP-Cl_7) and halogenated 1,1′-dimethyl-2,2′-bipyrroles (DBP-Br_4Cl_2), and methoxylated polybrominated diphenyl ethers (MeO-BDEs) have been found in fish and mammals from Japanese coastal waters (Haraguchi et al., 2006, 2009a, 2009b; Marsh et al., 2005). The bipyrroles are thought to originate from marine bacteria (*Pseudoalteromonas*) (Pangallo et al., 2012), whereas MeO-BDEs are produced by marine sponges, algae, or bacteria (Haraguchi et al., 2010; Malmvärn et al., 2008). These NHCs have similar lipophilicity to legacy persistent organic pollutants (POPs) and can biomagnify at high trophic levels via the food chain (Weijs et al., 2009), and accumulate in mammal blubber (Alonso et al., 2017; Haraguchi et al., 2006, 2009a; Marsh et al., 2005; Mwevura et al., 2010; Shaul et al., 2015; Tittlemier et al., 2002; Vetter et al., 2001). However, few studies have measured PFASs and NHCs in mammals from the northwest Pacific Ocean. Evaluation of pollutants in animals from this region provides a unique opportunity to access the influences of Asian and Russian production of PFASs and POPs to this area.

Dall's porpoises (*Phocoenoides dalli*) of the dalli-type population in the northwestern Pacific Ocean (Hayano et al., 2003) are often distributed in the pelagic zone over the continental shelf adjacent to the slopes of the Bering Sea and oceanic waters near Japan (Suzuki et al., 2016). They prefer to inhabit cold waters deeper than 180 m, and their primary prey are mesopelagic squids and fish (Ohizumi et al., 2000). Harbor porpoises (*Phocoena phocoena*) are bottom-feeding small cetaceans that inhabit bays, estuaries, and harbors, and migrate to the coast of Honshu (Japanese mainland) in the winter, and move north in the summer in the North Pacific Ocean (Taguchi et al., 2010). They feed on small schooling fish such as herring and anchovies. Marine top predators, such as dolphins and porpoises, can accumulate pollutants such as POPs in their fat.

The aims of the present study were to assess the profiles and concentrations of PFASs, NHCs, and selected organochlorines (OCs) in liver, blood, and blubber from Dall's and harbor porpoises stranded on the coast of Hokkaido, northern Japan, and to clarify the difference in the tissue distributions of PFASs, NHCs, and legacy POPs using principle component analysis (PCA) and factor analysis. The profiles of long-chain PFCAs were compared with those in local fish, human serum, and human diet, which were measured in previous studies, to evaluate potential sources and trends.

2. Materials and methods

2.1. Sample collection

Dall's porpoise (*Phocoenoides dalli*) ($n = 10$) and harbor porpoise (*Phocoena phocoena*) ($n = 6$) samples were obtained from stranding on the coast near Rausu in Hokkaido, Japan between 2010 and 2013 (Fig. S1). All the porpoises were captured by accident in fixed fishing nets in the same location, and were dead by the time researchers reached the location (Table S1). The samples were collected by Stranding Network Hokkaido using a standard protocol (Matsuishi, 2011). Liver, whole blood, and blubber samples were collected from both species, and were stored at −20 °C until required for analysis.

2.2. Chemicals, sample preparation and instrumental analysis

The chemicals used are detailed in the Supplementary Material. The clean-up methods for PFCAs are described elsewhere (Fujii et al., 2012a, 2015b). Briefly, each sample (0.1–1 g) of liver, blood, or blubber was spiked with internal standard mixture of 1 ng each of $^{13}C_4$-labeled PFOA, $^{13}C_5$-labeled PFNA, $^{13}C_2$-labeled perfluorodecanoic acid (PFDA), $^{13}C_2$-labeled perfluoroundecanoic acid (PFUnDA), $^{13}C_2$-labeled perfluorododecanoic acid (PFDoDA), and 3 ng of $^{13}C_8$-labeled PFOS. Each sample was homogenized and extracted with methanol and 0.5 M tetrabutylammonium hydrogen sulfate/0.25 M sodium carbonate buffer (pH 10) and methyl *tert*-butyl ether (1 mL). The samples were mixed by vortex for 3 h and centrifuged at 13,420 ×*g* for 5 min, and then the organic layer was removed. The residue was derivatized at 60 °C for 1 h using a 0.1 M benzyl bromide/methyl *tert*-butyl ether solution (100 μL). The derivatized PFCAs were analyzed by GC/MS with electron capture negative ionization (GC/ECNI/MS 6890GC, 5973 inert MSD, Agilent Technologies, Santa Clara, CA) in selected ion monitoring mode. The GC/MS conditions and target ions are described in the Supplementary Material (Table S2).

After measurement of the PFCAs, the residue was redissolved in 200 μL of acetonitrile and analyzed for PFOS and the other sulfonates