PERFLUORINATED COMPOUNDS IN CETACEANS FROM KOREAN COASTAL WATERS

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Abstract

Information on the occurrence and accumulation of perfluorinated compounds (PFCs) in marine mammals from Korean coastal waters is not available. In this study, we present data on the concentrations and accumulation features of 10 PFCs in the livers of minke whale and common dolphin collected from Korean coastal waters. PFOS and PFUnDA were detected in all of the liver samples from two cetacean species, indicating the widespread distribution of these contaminants in Korea. The overall concentrations of PFOS and PFUnDA were 3−20 times higher than those of other PFCs. Concentrations of PFOS measured in the livers of cetaceans from Korean coastal waters were lower than those reported for the cetacean from several other locations worldwide. Concentrations of PFOS, PFOSA and PFNA in common dolphin were significantly greater than in minke whale. Only PFOS and PFDoDA in minke whale showed a significant gender-specific difference in concentrations. Predominant PFCs were PFUnDA and PFOA, which accounted for over 70% of the total PFCs for both cetacean species. These accumulation profiles of PFCs in Korean cetaceans were different from those reported for other countries, suggesting a specific source of PFCs in Korea.

Introduction

Perfluorinated compounds (PFCs) have been used in a variety of industrial and commercial products, such as polymers, stain repellents, lubricants, paper coatings, and cosmetics since the mid-1940s[1,2]. Global monitoring of PFCs in wildlife showed widespread distribution of perfluorooctanesulfonate (PFOS) and related compounds, their environmental persistentence, and bioaccumulation potential[1,2,3]. PFOS and perflurooctaonic acid (PFOA) can adversely affect intercellular communication, membrane transport, developmental and neuroendocrine anomalies in exposed laboratory animals[4,5,6,7]. Marine mammals such as cetaceans are at the higher trophic level in the food chain and have relatively low metabolic capacity, thus these species can accumulate elevated concentrations of PFCs[3,8,9,10,11]. Total worldwide production of perfluorooctane sulfonyl fluoride (POSF) was estimated to be 96000 tons during 1970–2002 and current inventory of PFOS in ocean surface waters was estimated to be 235–1770 tons[12]. However, only limited information is available on contamination of PFCs in Korean coastal waters[13,14]. The objective of this study was to elucidate the contamination status of PFCs in the livers of two cetacean species collected from Korean coastal waters and to investigate accumulation features of these contaminants according to species and gender.

Materials and Methods

Liver samples were collected from 66 minke whales and 47 common dolphins caught incidentally in fishing nets along the Korean coasts in 2006. After biometric measurement for collected cetaceans, the specimens were dissected and immediately transported to the laboratory. Concentrations of 10 perfluorochemicals, such as PFOS, perfluorohexanesulfonate (PFHS), perfluorodecanesulfonate (PFDS), perfluorooctane sulfonamide (PFOSA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), and perfluorododecanoic acid (PFDoDA) were determined in the liver samples of two cetacean species. PFCs in livers were analyzed following the method described elsewhere[8,15]. In brief, the liver samples (~ 1 g) were homogenized with Milli-Q water. Five nanograms of internal standards ($^{13}C_4$-PFOS, $^{13}C_4$-PFOA, $^{13}C_2$-PFNA, and $^{13}C_2$-PFDA), 1 mL of 0.5 M tetrabutylammonium hydrogen sulfate solution, and 0.25 M sodium carbonate buffer were added to a PP tube. The samples were extracted twice with MTBE by shaking vigorously and evaporated to near-dryness under a gentle stream of nitrogen. The sample volume was adjusted to 1 mL of methanol, vortexed and finally filtered through a 0.2 µm nylon filter. Analyses of PFCs were performed using an Agilent 1100 series high-performance liquid chromatography (HPLC)

coupled with an Applied Biosystems API 2000 electrospray triple-quadruple mass spectrometer (ESI-MS/MS). Samples were injected twice onto a Keystone Betasil C_8 column, and sulfonates and carboxylates were analyzed separately. The quantification of individual PFC compounds in liver samples was performed using quadratic regression fit analysis weighted by 1/*x* of the extracted calibration curve. Average recoveries of $^{13}C_4$-PFOS, $^{13}C_4$-PFOA, $^{13}C_2$-PFNA, and $^{13}C_2$-PFDA were 102%, 101%, 126% and 112%, respectively. Matrix spiked recoveries ranged from 82% to 124% for all of the PFCs, except for 135% for PFDA and 143% PFUnDA. The limit of quantification (LOQ) was determined as the lowest acceptable standard in the calibration curve that is defined to be within ± 30% of the theoretical value and that has a peak area twice as great as the analyte peak are in blanks. LOQs of individual chemicals of PFCs ranged from 0.5 to 2 ng/g wet wt.

Results and Discussion

Concentrations of PFCs in cetaceans

PFOS was detected in all of the liver samples from two cetaceans species collected from Korean coastal waters. Concentrations of PFOS in the livers of minke whales and common dolphins ranged from 2.8 to 162 ng/g wet wt and from 18 to 152 ng/g wet wt, respectively. PFUnDA was found to be dominant PFC in the livers of cetaceans at concentrations ranging from 2.6 to 129 ng/g wet wt in minke whales and from 17 to 193 ng/g wet wt in common dolphins. The overall concentrations of PFOS and PFUnDA were about 3–20 times higher than the concentrations of other PFCs. The hepatic concentrations of PFOSA showed relatively higher concentration compared to other PFCs, except for PFOS and PFUnDA. The concentrations of PFDA, PFDoDA and PFOSA were similar to each other and they were found in almost all of the liver samples from both cetacean species. PFOA was measurable in 1.5% of minke whale livers and in 23% of common dolphin livers. PFHS and PFDS were measured in only a few samples and their frequencies of detection were less than 5% for both cetacean species. PFHpA was not detected in any of the samples.

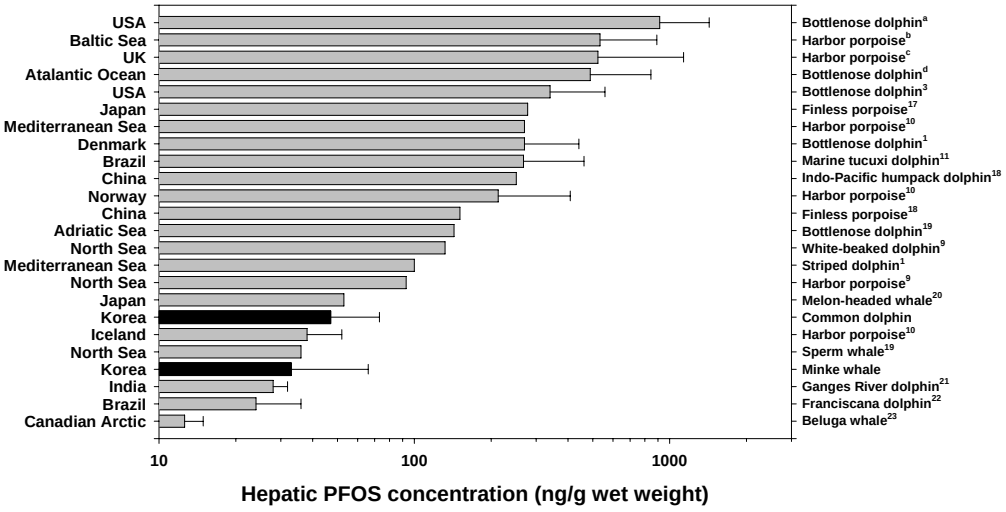

Figure 1. Comparison of average PFOS concentrations (ng/g wet wt) in livers of minke whale and common dolphin from Korean coastal waters with those reported for cetaceans from several other countries or locations. Whiskers on the bars represent the standard deviation of PFOS concentration. The black boxes indicate the PFOS concentrations measured in the livers of cetaceans in the present study.

Global comparison of PFCs in cetaceans

Concentrations of PFOS measured in the livers of cetaceans from Korean coastal waters were compared with those reported for a number of cetacean species from several other locations worldwide (Figure 1). PFOS was detectable in all of the cetacean species including the Arctic[23], indicating the ubiquitous contamination of this chemical in the marine ecosystem. The highest concentration of PFOS was found in bottlenose dolphin from South Carolina, USA[3]. Harbor porpoise from the Baltic Sea[10] and the UK[16] showed higher concentrations of PFOS, compared to cetaceans from other locations. The PFOS concentrations in most of the cetacean samples worldwide showed higher than those in two cetacean

species collected from Korean coastal waters. The PFOS concentrations in melon-headed whale from Japan[20], harbor porpoise from Iceland[10] and sperm whale from the North Sea[19] were similar to those measured in the present study. Cetaceans collected from India[21], Brazil[22] and the Canadian Arctic[23] showed lower levels thann those measured in the present study.

Species and gender differences

The total concentrations of PFOS, PFOSA, PFNA, PFUnDA and PFDoDA in the livers of common dolphin (average ± standard deviation; 140 ± 70 ng/g wet wt) were higher than those in measured in the livers of minke whale (100 ± 60 ng/g wet wt). PFOS, PFOSA and PFNA were significantly greater than in the dolphin liver samples compared to those of minke whale (Figure 2). This can be explained by the differences habitat and diet. The common dolphin is a near-shore species feeding in coastal waters, whereas minke whale migrates both through the near-shore and the off-shore waters. The major diet of common dolphin is long-lived and larger predatory fish such as herring and mackerel. Minke whale consumes small marine organisms such as shrimp and anchovy in Korean coastal waters. PFDA, PFUnDA and PFDoDA were not significantly different between the two cetacean species.

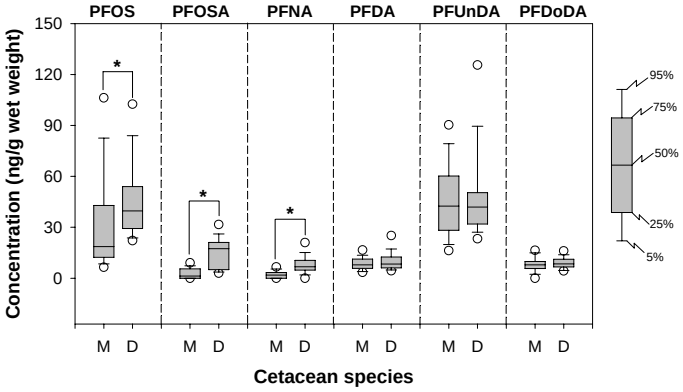

Figure 2. Comparison of PFC concentrations in the livers of minke whales and common dolphins collected from Korean coastal waters. M represents minke whale and D represents common dolphin. The symbol (*) indicates the significance at the level of $p < 0.05$ by Student *t*-test.

The gender difference in PFCs for the two cetacean species was investigated (Figure 3). Although the average concentrations of PFCs in male samples were higher than those in female samples, only PFOS and PFDoDA in minke whale showed significant gender differences. For common dolphins, no gender specific difference in PFCs concentrations was found. Previous studies have reported no gender difference in PFC concentrations in marine mammals[19,21].

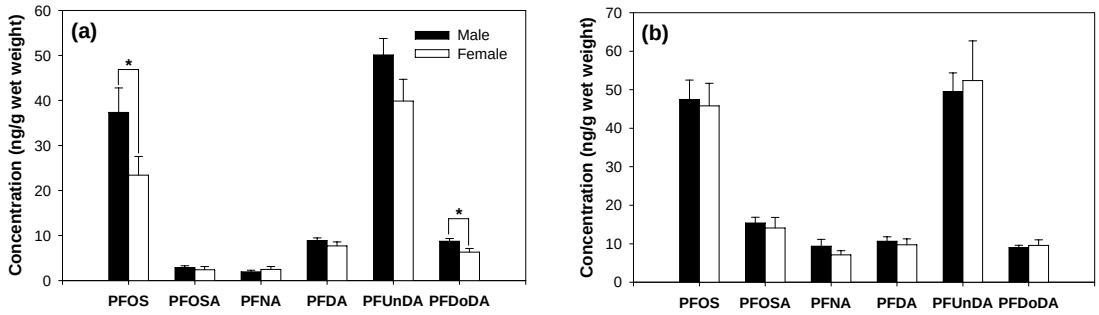

Figure 3. Comparison of PFC concentrations in the livers of male and female of (a) minke whale and (b) common dolphin collected from Korean coastal waters. Whiskers on the bars represent the standard error of individual PFC. The symbol (*) indicates the significance at the level of $p < 0.05$ by Student *t*-test.

Profiles of PFCs in cetaceans

Profiles of relative contribution of individual PFCs to the total concentrations of PFCs in both cetacean

species were compared (Figure 4). PFUnDA was the predominant compound in both cetaceans, which accounted for 49 ± 11% in minke whale and 35 ± 8% in dolphin to the total concentrations of PFCs. The second major compound to total PFCs was PFOS, accounting for 29 ± 13% in minke whale and 33 ± 8% in common dolphin. The accumulation profiles of PFCs in cetaceans in the present study were different from what have been reported in other studies. Almost all of the previous studies showed that the PFOS was the predominant PFC in cetaceans[18]. Other studies have reported PFNA to be the second most prevalent PFC after PFOS in marine mammals[17,24]. However, the contribution of PFNA was low in the present study. Some studies have reported relatively high contribution of PFUnDA to the total PFCs in the livers of cetaceans from Asian coastal waters[21]. Therefore, the predominance of PFUnDA seems to be associated with a specific source for PFC contamination in coastal waters of Korea. The contamination and accumulation of PFCs in abiotic (seawater and sediments) and biotic samples in Korean environment require further study.

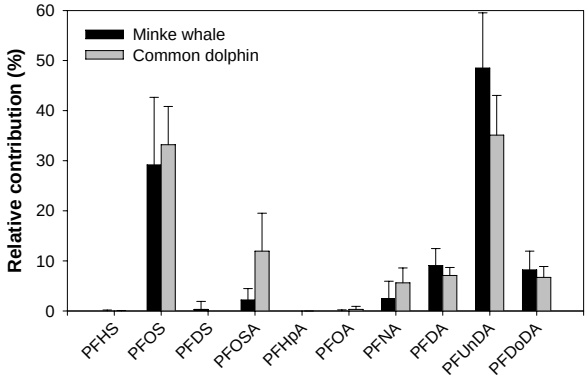

Figure 4. Relative contribution of individual PFC to the total PFC concentrations in the livers of minke whale and common dolphin collected from Korean coastal waters. Whiskers on the bars represent the standard deviation for individual contribution of PFC.

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