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Observation of emerging per- and polyfluoroalkyl substances (PFASs) in Greenland marine mammals

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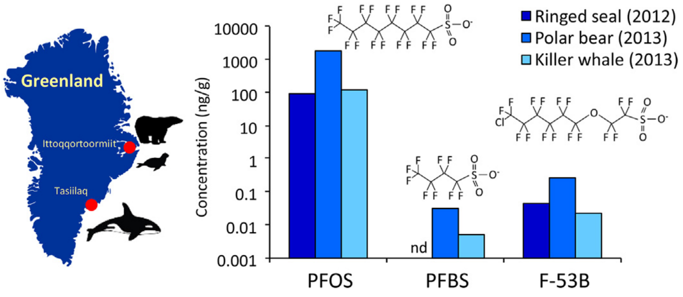
HIGHLIGHTS

- The emerging PFASs, F-53B and PFBS, were detected in East Greenland marine mammals.
- F-53B and PFBS liver concentrations were 3–4 orders of magnitude lower than PFOS.
- Killer whales were exposed to 17 PFASs but patterns differed compared to ringed seals and polar bears.

GRAPHICAL ABSTRACT



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ABSTRACT

The present pilot study examined emerging per- and polyfluoroalkyl substances (PFASs), i.e., a suite of short chain perfluoroalkyl acids (PFAAs), PFAA precursors and replacement chemicals, and legacy PFASs (long chain length PFAAs) in livers from ringed seals, polar bears and, for the first time, killer whales from East Greenland collected in 2012–2013. Among the emerging PFASs, perfluorobutanesulfonic acid (PFBS) and F-53B (a chlorinated polyfluorinated ether sulfonic acid) were detected in Arctic wildlife, albeit at concentrations approximately four orders of magnitude lower compared to perfluorooctanesulfonic acid (PFOS). PFOS was positively correlated with F-53B, but not PFBS in all three species. A total of 17 PFASs were detected in killer whales, including in a mother–fetus pair, demonstrating maternal transfer. ΣPFAS concentrations in killer whales (269 ± 90 ng/g) were comparable to concentrations found in ringed seals (138 ± 7 ng/g), however, an order of magnitude lower compared to concentrations found in polar bear livers (2336 ± 263 ng/g). Patterns of long chain PFAAs in killer whales differed from the pattern in ringed seals and polar bears. Of the monitored PFAA precursors, only perfluorooctanesulfonamide (FOSA) was detected in all three species, and FOSA/PFOS ratios and isomer patterns indicated that killer whales have a potential lower metabolic capacity to degrade FOSA compared to polar bears and ringed seals.

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) – in particular perfluoroalkyl acids (PFAAs) such as perfluoroalkylsulfonic acids (PFSAs) and perfluoroalkylcarboxylic acids (PFCAs) – are widely recognized as global environmental contaminants (Buck et al., 2011). Long chain length PFSAs (i.e. $\geq C_6$ PFSAs) and PFCAs (i.e. $\geq C_8$ PFCAs) are persistent and bioaccumulative, and have been reported at elevated concentrations in remote Arctic wildlife (Butt et al., 2010; Houde et al., 2011). Although the production of several PFASs has been phased-out recently in Europe and North America, e.g. perfluorooctanesulfonic acid (PFOS) and its precursors were phased out in 2002 by 3 M, and emissions of long chain PFCAs and their precursors are to be eliminated by 2015 (Martin et al., 2010; US EPA, 2006), manufacturing of other PFASs has gone unnoticed (De Silva et al., 2011; Wang et al., 2013a). Recent manufacturing phase-outs have also led to shifts in formulations, often to short-chain or semi-fluorinated substances (Wang et al., 2013b).

While less bioaccumulative than their longer chain homologues (Goeritz et al., 2013), short chain PFAAs such as perfluorobutanesulfonic acid (PFBS) are nevertheless persistent in the environment, and has recently been detected in Swedish herring (*Clupea harengus*) (Ullah et al., 2014). Physicochemical properties and environmental fate of several PFOS and PFOA replacement chemicals were estimated recently and found to be comparable to PFOS and PFOA itself (Gomis et al., 2015; Wang et al., 2013a). For example, the PFOS replacement chemical F-53B (a chlorinated polyfluorinated ether sulfonic acid) had comparable octanol–water (K_{ow}), air–water (K_{aw}), octanol-air partition coefficient (K_{oa}), acid-dissociation constant (pK_a), and bioconcentration and bioaccumulation factor (BCF and BAF) values as PFOS (Gomis et al., 2015; Wang et al., 2013a). F-53B has been detected in Chinese rivers (~40 ng/L) and sewage sludge (~2 ng/g) at comparable concentrations to PFOS (Ruan et al., 2015; Wang et al., 2013a). Information on the environmental fate of several PFCA precursors, e.g. fluorotelomer-based polyfluoroalkyl phosphate esters (PAPs), is limited. Despite the fact that PAPs can be degraded to PFCAs (D'Eon and Mabury, 2011), they have been detected in mussels and fish from Europe, the Great Lakes, and the Indian Ocean (Guo et al., 2012; Zabaleta et al., 2015).

Although there is ample information on PFAA exposure ($C_{6,8,10}$ PFSAs, FOSA, and C_6–C_{15} PFCAs) to Greenland ringed seals (*Pusa hispida*) and polar bears (*Ursus maritimus*) (Bossi et al., 2005; Dietz et al., 2008; Rigét et al., 2013; Rotander et al., 2012), it remains unknown whether ringed seals, polar bears or other Arctic marine mammals are exposed to other per- and polyfluoroalkyl substances, such as short chain PFAAs, alternative replacement chemicals (F-53B), or other PFOS and PFCA precursors. Based on biopsies, killer whales (*Orcinus orca*) in Alaskan and Norwegian waters have been reported to be most contaminated marine mammal with respect to persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), organochlorine pesticides and polybrominated diphenyl ethers (PBDEs) (Letcher et al., 2010), however, there are no data on legacy or emerging PFAS exposure to killer whales residing in Greenland waters or any other region. Of the emerging PFASs, the short chain PFBS has been detected in the Arctic environment (sediment and water) (Stock et al., 2007; Yamashita et al., 2008), however, reportings on F-53B and other PFAA precursors (e.g. PAPs) in the Arctic are so far non-existing.

The objective of this study was to investigate whether Arctic marine mammals (ringed seals, polar bears, and killer whales) were exposed to short chain PFAAs, the PFOS replacement F-53B, and PAPs and to determine their importance relative to legacy (longer chain) PFAAs. Additionally, killer whale exposure and maternal transfer of PFASs were investigated and concentrations and patterns (including isomers) were compared to ringed seals and polar bears.

2. Materials and methods

2.1. Chemicals and reagents

Targeted PFASs in the present study included: $C_{4,6,8,10}$ PFSAs (including a mixture of branched and linear PFOS), $C_{4\text{-}14}$ PFCAs, FOSA and its methyl and ethyl derivatives (Me- and EtFOSA), FOSAA and its methyl and ethyl derivatives (Me- and EtFOSAA), four monoPAPs (4:2, 6:2, 8:2, 10:2), 11 diPAPs (4:2/4:2, 4:2/6:2, 6:2/6:2, 6:2/8:2, 8:2/8:2, 6:2/10:2, 8:2/10:2, 6:2/12:2, 10:2/10:2, 8:2/12:2, 6:2/14:2), and 6:2 chlorinated polyfluorinated ether sulfonate (6:2 Cl-PFAES, with trade name F-53B). A total of 19 isotopically-labeled standards were included in this study and details on the isotopically-labeled and native standards can be found in Table S1 in the Supplementary material. All solvents and reagents were of the highest commercial purity and employed as received.

2.2. Sample collection and preparation

All sampling was conducted in cooperation with local Inuit subsistence hunters in Greenland in 2012 and 2013. Liver samples from ringed seals ($n = 10$) and polar bears ($n = 8$) were collected in Ittoqqortoormiit/Scoresby Sound area, while samples of killer whale livers ($n = 6$) were collected in the Tasiilaq/Ammassalik area (Fig. S1 and Table S2). The killer whale samples included liver samples from a mother–fetus pair. Samples from ringed seals and polar bears were collected <1 h post mortem while sampling of killer whales could take as long as 12 h due to transport at sea and appropriate tidal time for dissection. After sampling, liver tissues were stored at −20 °C prior to processing. The extraction and clean-up was based on published methods (Gebbink et al., 2013, 2015). Briefly, homogenized liver samples (0.5 g) were spiked with isotopically-labeled internal standards and extracted three times with acetonitrile (3 mL) by sonication. Concentrated extracts (~1 mL) were loaded on preconditioned (with methanol and water) weak anion exchange (WAX) cartridges (150 mg, 6 mL, Waters) and subsequently washed with aqueous formic acid and water. Neutral compounds were eluted with 3 mL methanol (fraction 1) and ionic compounds were eluted with 4 mL of a solution of 1% ammonium hydroxide in methanol (fraction 2). Both fractions were dried under a stream of nitrogen at 35 °C and the residuals were re-dissolved in methanol. The extracts were filtered using centrifugal filters (modified nylon 0.2 μm, 500 μl) and $^{13}C_8$-PFOA and $^{13}C_8$-PFOS were added as recovery standards prior to ultra-performance liquid chromatography-tandem mass spectrometry (UPLC/MS/MS) analysis.

2.3. Instrumental analysis and quantification

For all instrumental analyses, chromatographic separation was carried out on an Acquity UPLC system (Waters) equipped with a BEH C18 (50 × 2.1 mm, 1.7 μm particle size, Waters) analytical column. A trapping column was installed prior to the injector to delay any contamination from the UPLC system and solvents. Mobile phases, gradient programs and flow rates for the different UPLC methods can be found in Tables S3 and S4. Connected to the UPLC system was a Xevo TQ-S triple quadrupole mass spectrometer (Waters) operated in negative ion electrospray ionization (ESI−) mode. The capillary voltage was set at 2.0 kV, and the source and desolvation temperatures were set at 150 °C and 350 °C, respectively. The desolvation and cone gas flows (nitrogen) were set at 650 L/h and 150 L/h, respectively. Compound-specific optimized cone voltages and collision energies are listed in Table S1.

Quantification was performed using an isotope dilution approach. Analytes lacking an analogous labeled standard were quantified using the internal standard with the closest retention time