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Polyfluorinated compounds in the atmosphere along a cruise pathway from the Japan Sea to the Arctic Ocean

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ABSTRACT

Neutral polyfluorinated alkyl substances (PFASs) were measured in high-volume air samples collected on board the research vessel *Snow Dragon* during the 4th Chinese National Arctic Expedition from the Japan Sea to the Arctic Ocean in 2010. Four volatile and semi-volatile PFASs (fluorotelomer alcohols (FTOHs), fluorotelomer acids (FTAs), perfluoroalkyl sulfonamides (FASAs), and sulfonamidoethanols (FASEs)) were analyzed respectively in the gas and particle phases. FTOHs were the dominant PFASs in the gas phase (61–358 pg m^{-3}), followed by FTAs (5.2–47.9 pg m^{-3}), FASEs (1.9–15.0 pg m^{-3}), and FASAs (0.5–2.1 pg m^{-3}). In the particle phase, the dominant PFAS class was FTOHs (1.0–9.9 pg m^{-3}). The particle-associated fraction followed the general trend of FASEs > FASAs > FTOHs. Compared with other atmospheric PFAS measurements, the ranges of concentrations of $\sum$FTOH in this study were similar to those reported from Toronto, north America (urban), the northeast Atlantic Ocean, and northern Germany. Significant correlations between FASEs in the gas phase and ambient air temperature indicate that cold surfaces such as sea-ice, snowpack, and surface seawater influence atmospheric FASEs.

1. Introduction

In recent years, ionic per- or polyfluorinated alkyl substances (PFASs) have been detected globally (Giesy and Kannan, 2001). Among these ubiquitous compounds have been found perfluorooctane sulfonate (PFOS) and perfluorocarboxylates (PFCAs) such as perfluorooctanoate (PFOA), which are widespread and persistent environmental contaminants that have been detected in polar bears from the Canadian and European Arctic (Smithwick et al., 2005a,b), dolphins in the Atlantic Ocean (Houde et al., 2005), seawater from the Pacific, Atlantic, and Arctic Oceans (Yamashita et al., 2005; Wei et al., 2007; Ahrens et al., 2009, 2010), and fur seal pups and penguin eggs in Antarctica (Schiavone et al., 2009).

The stability of PFOS and PFCAs precludes degradation or metabolism, which contributes to their global dispersion, persistence, and bioaccumulation. High water solubility and a low Henry's law constant render PFOS and PFCAs susceptible to wet deposition, making it unlikely that they are transported long distances atmospherically in the vapor phase (Loewen et al., 2008). It has been hypothesized that these chemicals are transported atmospherically as volatile precursors to remote areas where their degradation products are then deposited (Renner, 2001). Alternatively, long-range transport of PFCAs and PFOS to remote areas by ocean currents has also been hypothesized (Prevedouros et al., 2006).

Atmospheric transport with subsequent degradation of volatile and semi-volatile precursor compounds (e.g., fluorotelomer alcohols (FTOHs), perfluoroalkyl sulfonamides (FASAs), and perfluoroalkyl sulfonamidoethanols (FASEs)) to persistent PFCAs and PFOS has been hypothesized as a main transport mechanism (Ellis et al., 2004; Sulbaek Andersen et al., 2005; D'Eon et al., 2006; Martin et al., 2006). Because of their slow reaction with hydroxyl radicals, atmospheric lifetimes of more than 10–20 d for FTOHs and more than 20–50 d for FASAs have been estimated in smog chamber studies (Ellis et al., 2003; Martin et al., 2006). Field studies have indicated an atmospheric residence time of more than 50 d for FTOHs (Piekarz et al., 2007). These data indicate the possibility of regional and long-range atmospheric transport of FTOHs and FASAs. PFCAs and perfluoroalkyl sulfonates (PFSAs) have also been detected in snow samples from the high Arctic, where contamination is solely from atmospheric sources. This finding confirms the indirect precursor-based atmospheric transport and deposition of these compounds (Young et al., 2007).

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Several datasets are available for ambient air as well as for indoor air samples. 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, *N*-ethyl fluorooctane sulfonamide (EtFOSA), *N*-methyl fluorooctane sulfonamidoethanol (MeFOSE), and *N*-ethyl fluorooctane sulfonamidoethanol (EtFOSE) were found to be widely distributed in the atmosphere of north America, Europe, and over an Atlantic transect (Martin et al., 2002; Shoeib et al., 2004; Stock et al., 2004b; Boulanger et al., 2005; Shoeib et al., 2005; Dreyer and Ebinghaus, 2009; Dreyer et al., 2009a,b). PFASs are manufactured by two main synthesis routes. Generally, the production of FASAs/FASEs is associated with the electrochemical fluorination (ECF) process, which has been in use since the 1950s. FASAs/FASEs are predominantly used as paper protectors, as water- and dirt-proofing in carpets/leathers/textiles, as performance chemicals (e.g., in aqueous film-forming fire-fighting foams, AFFFs) (De Voogt and Saez, 2006), and as an insecticide (Sulfluramid). The second manufacturing process, telomerization, has been in use since the 1970s to produce exclusively linear compounds, including FTOHs. The production of FTOHs has continued to increase, particularly for use as precursors in the production of fluorinated polymers used in paper and carpet treatments, as well as in the production of paints, coatings, and adhesives (Dinglasan et al., 2006).

The aim of this study was to investigate the inter-hemispherical gradient of neutral (volatile and semi-volatile) precursors of PFOS and PFCAs in ambient air, starting from the Japan Sea, adjacent to urbanized regions, and then on a transect towards the Arctic Ocean. Data presented in this study yield new information on the spatial atmospheric distribution of PFASs on a regional scale, as well as the identification of their source regions in the northern Hemisphere. The airborne PFAS data are compared with the results of previous studies. This study provides the first evidence of the occurrence of airborne PFASs in ambient air samples from the Japan Sea to the Arctic Ocean.

2. Materials and methods

2.1. Chemicals and standards

All solvents (methanol, acetone, dichloromethane, and *n*-hexane) were residue-grade and additionally distilled in a full glass unit prior to use. Details of the analytical standards of FTOHs (FTOH 6:2, 8:2, 10:2, and 12:2), fluorotelomer acrylates (FTA 6:2, 8:2, and 10:2), Me- and EtFOSA, Me- and EtFOSE, and mass-labeled internal standards are summarized in Table S2 (Supplementary Materials).

2.2. Sampling cruise

Air samples were taken onboard the Arctic expedition of the *R/V Snow Dragon* from the Japan Sea to the high Arctic (33.2–84.5°N) during June–September 2010 (see Fig. 1). Air samples ($\sim$500 m^3/sample, $\sim$48 h) were taken using a high-volume air sampler placed in front of the ship's upper deck (20 m above sea level), with a glass fiber filter ([GFF], GF/F, pore size: 0.7 μm) to trap airborne particles, and a self-packed PUF/XAD-2 glass column (PUF: Ø 5.0 cm × 2.5 cm; 35 g XAD-2, particle size: 0.3–1.0 mm) for the gaseous phase. Both air column and filters were stored at −20 °C until analysis. Sampling parameters, including date, position, temperature, and wind speed, are listed in Table S1 in the Supplementary Materials.

2.3. Sample preparation and instrumental analysis

Extraction and clean-up of the samples was done in a clean laboratory (class 10000). All solvents were residue-analysis grade and were distilled prior to use. Samples were spiked with 2500 pg of mass labeled internal standards (Wellington Laboratories) prior to extraction. Air columns were extracted in a modified Soxhlet apparatus for 16 h using dichloromethane/hexane (1/1), and air filter samples were Soxhlet extracted using dichloromethane for 16 h, respectively. Extracts were evaporated to 1–2 mL with rotary evaporator and then passed a glass column (i.d. 1 cm, length: 15 cm) packed with 3 g Na_2SO_4 to remove residual water. The extracts were further concentrated down to 150 μL and spiked with 1000 pg ^{13}C–HCB as injection standard.

Detailed analysis methods have been described elsewhere (Dreyer et al., 2008). In brief, analysis was performed using gas chromatography–mass spectrometry (GC–MS) using an Agilent 6890 gas chromatograph and an Agilent 5973 mass spectrometer, Agilent Technologies) in selective ion monitoring (SIM) mode with positive chemical ionization (PCI). The ion masses are summarized in Table S2 in the Supplementary Materials. The response factors were derived from the calibration curves (6-points) made for response ratio between targets compounds (0–250 ng mL^{-1}) and mass labeled internal standards (12.5 ng mL^{-1}).

2.4. Quality assurance and control

All air columns were pre-cleaned with organic solvents (methanol, acetone, and hexane/acetone in turn for 96 h) and GFFs were heated at 450 °C for 12 h prior to use. Na_2SO_4 was cleaned with dichloromethane for 12 h and heated at 450 °C for 12 h prior to use. To avoid degradation of the target compounds, air columns were protected against UV–sunlight during sampling using aluminum foil. Breakthrough of the target analytes using these sampling methods has been checked previously on board the German icebreaker *R/V Polarstern*. Three field blanks were run for each sample type, with blanks showing very low values ranging from 0.01 to 0.2 pg m^{-3} (12:2 FTOH). Method detection limits (MDLs) were derived from mean blank values plus three times the standard deviation (σ) (for compounds showing no blanks, a peak area of 100 was adopted as background response), which ranged from 0.1 to 0.3 pg m^{-3} for both gas and particle phases.

2.5. Air mass back-trajectories

Air mass origins of the individual air samples collected during the cruise segments were calculated using NOAA's HYSPLIT model. Air mass back-trajectories (BTs) were calculated in 6-h steps tracing back the air masses for 5 d using the sampling height as arrival height.

3. Results and discussion

3.1. Concentrations of airborne PFASs

Total air concentrations of target compounds at various points sampled along the cruise route are presented in Fig. 1 and summarized in Table 1 (for details, see Table S3, Supplementary Materials). PFASs were detected in all air samples, with FTOHs/FTAs and FASAs/FASEs ubiquitous at the sites sampled, except for MeFOSA, which was not detected at sample site A6.

3.1.1. FTOHs, FTAs, FASEs, and FASAs in the gas phase

The PFAS concentrations in the gas phase ranged from 77.9 to 416 pg m^{-3}, and the highest gas-phase total concentrations of PFASs (416 pg m^{-3}) were measured in sample A2 in the Okhotsk Sea, followed by sample A1 (346 pg m^{-3}) in the Sea of Japan. The lowest total PFAS concentrations were found in samples A4 (78 pg m^{-3}) in the Bering Sea and A9 (118 pg m^{-3}) in the Beaufort Sea.