SPATIAL AND VERTICAL DISTRIBTUION OF PERFLUORINATED COMPOUNDS IN CANADIAN ARCTIC AND SUB-ARCTIC OCEAN WATER

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Introduction

Perfluoroalkyl acids (PFAs) are fully fluorinated carbon-atom chains bonded to either a sulfonate or carboxylate functional group and are used primarily as surfactant compounds in consumer based applications. Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are two PFAs that have received the most attention and much of the concern surrounds the ubiquitous presence of both compounds in the environment. PFOS and PFOA have been detected in human serum(*1*), freshwater and marine biota(*2-4*), and surface water(*5, 6*). The stability that makes fluorinated surfactants so desirable appears to preclude any degradation or metabolism, and contributes to the global bioaccumulation and persistence of PFOS and PFOA.

There is still considerable debate as to the means by which these compounds are transported to remote regions. Initially, because of the low vapour pressure and high water solubility, the prevailing view was that PFAs would likely be transported by oceanic currents (*7*) and that atmospheric transport of the acids themselves would be negligible. Atmospheric transport of volatile PFA-precursor compounds is also a plausible means of delivery of these compounds to remote regions as suggested by Ellis *et al*.(*8*). Recently, McMurdo *et al*. has shown that PFOA (and likely other PFAs) can in fact be transported in the gaseous phase *via* an initial aerosol-mediated transport step(*9*). This suggests that not only can these compounds be transported to remote regions in the gaseous phase but, more importantly, water may not be a permanent sink for these compounds.

The objective of the current study was to examine the spatial and vertical distribution of PFAs in Canadian Arctic seawater and to build on the earlier work of Yamashita *et al.* (*10, 11*). Water samples were collected off the Canadian Coast Guard icebreaker *CCGS Amundsen* in 2007. Our study sites are listed in Figure 1. Both near and offshore seawater was examined as it has been suggested that coastal waters may be contributing to the overall loadings of PFAs to offshore waters. In addition, we also present a novel approach to seawater sampling in the field using SPE cartridges.

Material and Methods

Chemicals. All native PFA standards were purchased from either Wellington Laboratories or SynQuest. Mass labelled compounds of C_4, C_6, C_8, C_{10}, C_{11}, C_{12} (PFCAs) and PFOS were provided by Wellington Laboratories. OmniSolv methanol and water were from VWR.

Preparation of SPE cartridges. Waters Oasis 150 mg WAX 6 cc cartridges were conditioned in a clean room with 4mL 1% ammonium/methanol solution, 4 mL methanol and 4 mL SPE cleaned OmniSolv water. The cartridge was then placed in a 50 mL polypropylene tube, sealed with wax film and shipped to the field.

Collection and extraction of seawater in the field. Surface water samples (4-5 m depth) were collected in poly- and perfluorinated free Niskin bottles and transferred immediately into 4 L polypropylene bottle (PPB). A Rosette sampler was used to collect seawater samples at varying depths. To minimize exposure of the samples to possible volatile PFA precursors, a tube leading directly from the Rosette and into a 4 L PPB was employed. To equalize the pressure in the PPB a second hole was placed on the lid of the bottle. Samples were taken to the lab onboard the ship for extraction. Water (1-4 L) was then pulled through the SPE cartridges using a peristaltic pump operating at a flow of 5-10 mL/min. To further minimize contamination by airborne PFA-precursors, a SPE cartridge was attached to a tube and fastened onto the second hole in the lid of the PPB. In essence, this cartridge was used as an 'air-trap' and significantly reduced the amount of airborne PFAs that could

contaminate our samples. Cartridges were then placed into the 50 mL tube and shipped back to the laboratory at Environment Canada (EC).

Elution of the SPE cartridges. Prior to elution, cartridges were centrifuged in the travel centrifuge tube for 2 min at 3000 rpm to remove residual water. Cartridges were eluted with 4 mL methanol at rate of 1 drop/sec into 15 mL polypropylene tube. PFAs were captured by further eluting the cartridges with 6 mL of 0.1% ammonium/methanol solution. Extracts were reduced in volume to 0.5ml, fortified with instrument performance internal standard ($^{13}C_9$) and 0.5 mL OmniSolv water.

LC/MS/MS analysis. An Agilent 1100 HPLC was coupled to an API 4000 triple quadrapole mass spectrometer, which was operated in the ESI –ve ion mode. Injections were made into a C_{18} guard column and separations were achieved on a C_{18} column maintained at 35^{o}C.

QA/QC. A large volume of water (9 L) was prepared by forcing OmniSolv water through an SPE cartridge. Portions of this were sent in the field as travel blanks and some remained in the laboratory at EC. This allowed us to compare possible contamination that might have occurred during shipping. The prepared water was also used as our laboratory blank. A few of the field blanks were processed on the ship to allow us to assess the efficacy of the SPE 'air-traps'; significant amounts of PFAs (sub-ng) were detected on the 'air-traps'. In general, there was good agreement between the analyte concentrations measured in the laboratory blanks processed in the clean-room at EC and the field blanks processed onboard the ship. This suggests that even though significant amounts of PFAs were present in the air in the laboratory on the ship, the SPE 'air-traps' performed well enabling extractions in the field to be conducted. Each sample extract was analyzed in duplicate with the average value being reported. The agreement between the duplicates was usually within 10%. The blank response for a chemical was subtracted from the response of that chemical in the sample.

Results and Discussion

Concentrations of PFOA and PFOS in Canadian arctic surface waters are shown in Figure 1. C6 to C11 PFCAs as well as PFBS, PFHxS and PFOS were detected in almost all samples. PFOA was the major PFCA with concentrations ranging from 7 pg/L measured at the mouth of Nachvak Fjord to 234 ng/L near the town of Kuujjuarapik on Hudson Bay. Our mean PFOA concentrations in water from the Labrador Sea at the Makkovik Margin (*n=2*, 182 pg/L) were ~ 3x greater than those measured by Yamashita *et al.(10)* for a site (AO1) in the central Labrador Sea but similar to concentrations measured further south off Newfoundland *(11)*. Concentrations of PFOS in seawater ranged from ~ 10 pg/L from McClintock Channel to 424 pg/L from Kuujjuarapik. PFOS was the dominant PFSA detected and accounted for over ~ 75% of the ΣPFSAs. Yamashita *et al. (11)* measured PFOS and PFBS concentrations in seawater from their more remote Labrador Sea site (12 pg/L and 18 pg/L, respectively) that were 6.x smaller and ~2x greater than the respective mean PFOS and PFBS measured in our study. However, the overall spatial trends observed in this study are consistent with those observed by Muir *et al*. (12) in a Canadian Arctic transect on the icebreaker Oden in 2005.

Our sampling sites also allowed us to the study movement of PFAs from coastal waters to the open ocean. For both Fjords sampled, there is an apparent decrease in PFCAs concentrations from waters within the Fjords relative to concentrations at the mouth of Fjords. For example, coastal PFOA concentrations within the Anaktalak Fjord (202 pg/L) is ~ 4x smaller than at the mouth of Fjord (66 pg/L). A similar trend is observed for the Nachvak Fjord. Taken together, these results support the hypothesis that coastal waters may be delivering PFCAs to the open ocean.

Vertical Depth Profile. Concentration profiles of PFAs were similar in Northern Baffin Bay and coastal Labrador and show a rapid decrease and a levelling out half-way down the water column (Fig. 2 and 3). In the Northwater Polyna water column PFOS concentrations decrease sharply followed by a peak in concentration at the bottom of the water column. Conversely, in the water column from the Labrador Sea, PFOS concentrations show a noticeable increase followed by a rapid decrease at the bottom of column is in general agreement with Yamashita *et al*.(*10*) and with Sturman *et al. (13)* who examined depth profiles in Anaktalak Fjord and Lancaster Sound. In addition, temperature and salinity measurements for both water columns (data not shown) suggest that the overall water mass sampled is well mixed from the surface to the depth sampled. A similar observation was made by Yamashita *et al*. (*10*).

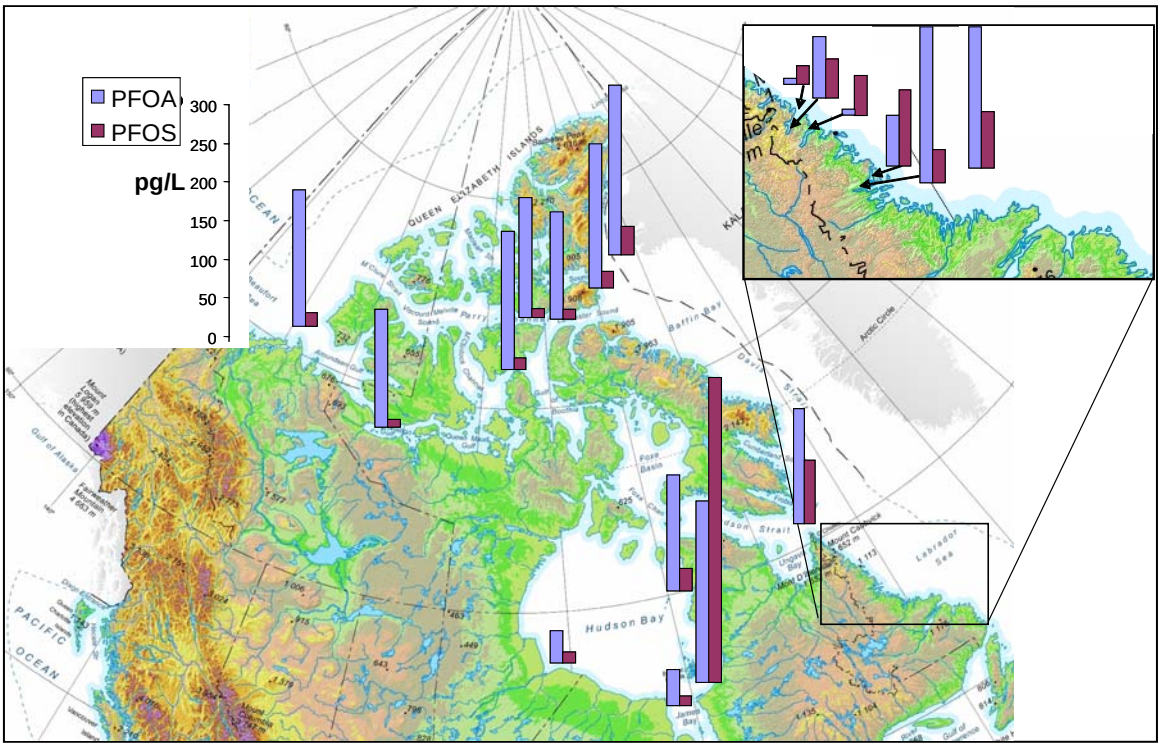

Figure 1. Spatial concentrations (pg/L) of PFOS and PFOA in Canadian Arctic and sub-Arctic seawater

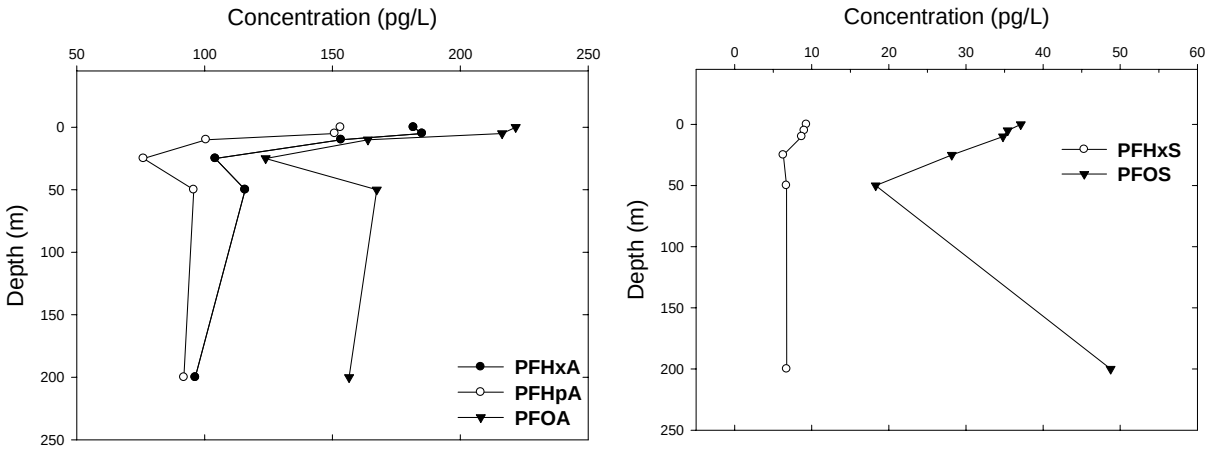

Figure 2. Vertical profiles of PFAs in an ocean water column from the NorthWater Polyna.

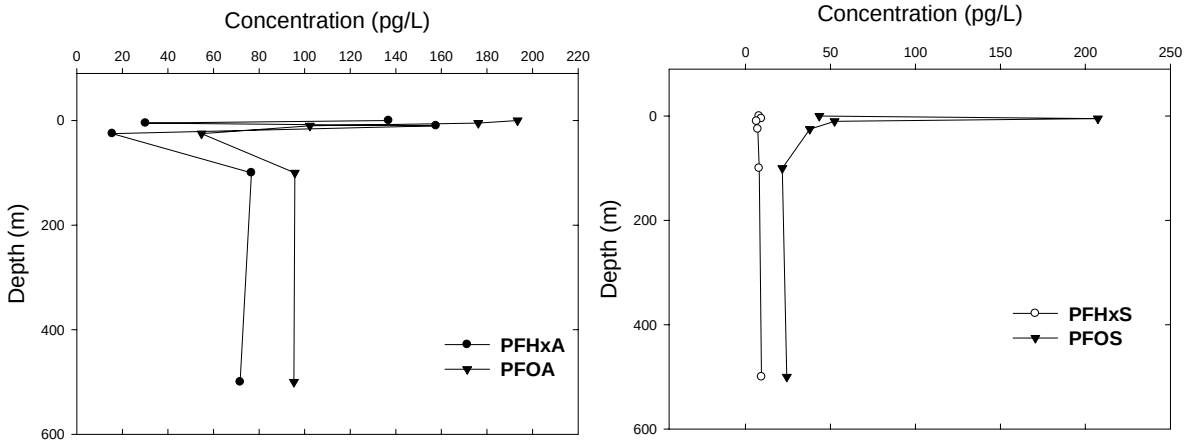

Figure 3. Vertical profiles of PFAs in an ocean water column from the Labrador Sea.

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