

Vertical Profiles, Sources, and Transport of PFASs in the Arctic Ocean

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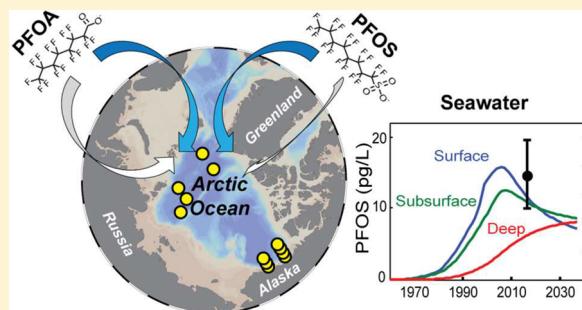
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S Supporting Information

ABSTRACT: The relative importance of atmospheric versus oceanic transport for poly- and perfluorinated alkyl substances (PFASs) reaching the Arctic Ocean is not well understood. Vertical profiles from the Central Arctic Ocean and shelf water, snow and meltwater samples were collected in 2012; 13 PFASs (C6–C12 PFCAs; C6, 8, 10 PFSAs; MeFOSAA and EtFOSAA; and FOSA) were routinely detected (range: <5–343 pg/L). PFASs were only detectable above 150 m depth in the polar mixed layer (PML) and halocline. Enhanced concentrations were observed in snow and meltpond samples, implying atmospheric deposition as an important source of PFASs. Model results suggested atmospheric inputs to account for 34–59% (~11–19 pg/L) of measured PFOA concentrations in the PML (mean 32 ± 15 pg/L). Modeled surface and halocline measurements for PFOS based on North Atlantic inflow (11–36 pg/L) agreed with measurements (mean, 17, range <5–41 pg/L). Modeled deep water concentrations below 200 m (5–15 pg/L) were slightly higher than measurements (<5 pg/L), suggesting the lower bound of PFAS emissions estimates from wastewater and rivers may provide the best estimate of inputs to the Arctic. Despite low concentrations in deep water, this reservoir is expected to contain most of the PFOS mass in the Arctic (63–180 Mg) and is projected to continue increasing to 2038.



INTRODUCTION

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are groups of anthropogenic chemicals having a perfluoroalkyl moiety ($C_nF_{2n+1}-$) with different polar heads (e.g., carboxylate, sulfonate, phosphonate).¹ Much attention has been given to two perfluoroalkyl acids (PFAAs) - perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) because of their potential toxic and bioaccumulative effects, as well as their ubiquitous occurrence in the environment including remote areas.^{2–10} In May 2009, PFOS and chemicals that can degrade to PFOS were listed in the Stockholm Convention as Persistent Organic Pollutants, and parties to the Convention must seek to eliminate the production and use of PFOS.¹¹

Since PFAAs are strong acids and highly soluble in water, oceans are believed to be the final global sink for these compounds.¹² Atmospheric transport of volatile fluorotelomer alcohols (FTOHs) and subsequent oxidative reactions of these compounds are also sources of PFAAs in remote areas like the Arctic, as evidenced by the detection of the FTOHs and their intermediates in remote areas.^{13–16} Inputs of surface waters from the North Pacific and North Atlantic and atmospheric deposition all lead to accumulation of PFASs in Arctic surface waters. The majority of seawater inflow to the Arctic occurs

from mid-depth North Atlantic seawater (20–200 m) and results in PFASs being present below the polar mixed layer (PML).^{10,12}

Several previous studies have reported PFAA concentrations in surface water in different oceans.^{3,17–21} Relatively higher concentrations were found in the Atlantic (PFOS: <5–291 pg/L; PFOA: <4–439 pg/L) compared to the Pacific (PFOS: <5–78 pg/L; PFOA: <4–142 pg/L),^{3,20} and higher concentrations were observed in coastal regions compared to off-shore areas.^{6,22} Previous PFAS measurements in Arctic seawater have been limited to surface water (<20 m depth).^{17–19,21} The composition of PFASs previously measured in surface waters varied across different locations, likely due to their complex sources and transport pathways in the Arctic.¹⁹

Compared to the major ocean basins, the Arctic Ocean is smaller and has a much greater continental shelf area (70%) and freshwater inputs.²³ It provides an oceanic pathway between the Pacific and the Atlantic basins and plays an

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important role in the global thermohaline circulation through its role in the Atlantic Meridional Overturning Circulation.²³ Water of Atlantic origin enters the Arctic through the east side of the Fram Strait into the Eurasian Basin or the Barents Sea (Figure 1). Water flows in a counterclockwise direction in the

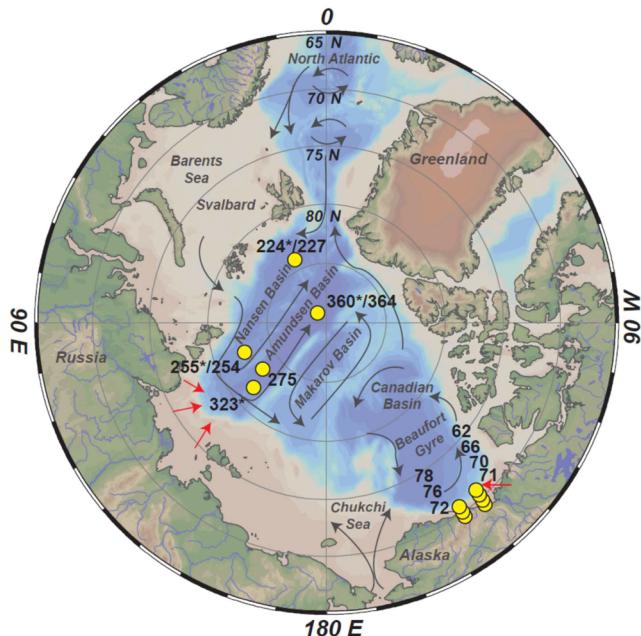


Figure 1. Map of stations occupied for this study. Sea-ice and meltponds were sampled at stations denoted “*”. Vertical profiles to a depth of >2000 m were obtained at Stations 227, 364, 254, and 275 collected in October 2012 on the research icebreaker *Polarstern*. Profiles on the shelf were <400 m (Stations 62–78) collected in August/September 2012 the United States Coast Guard icebreaker *Healy*. (Gray lines indicate circulation of intermediate and deep waters; red lines indicate major freshwater input by rivers. The map was obtained from Ocean Data View).

Nansen basin and then either to the Amundsen basin, or to the Makarov or Canada basins. A minor influx of Pacific water enters the Canada Basin through the Bering Strait (Figure 1). Seasonally varying fresh water input also contributes to Arctic surface waters and are thought to be important for inputs of other contaminants.^{24–26} The outflows of the Arctic Ocean are all to the Atlantic through either the western side of the Fram Strait²⁴ or the complex channels of the Canadian Archipelago.²⁷

The entire Arctic Ocean is seasonally covered by ice. Both the formation (reduced wind-mixing) and melting of sea-ice (fresher surface layer) contribute toward ocean stratification. Complex surface and subsurface dynamics of the Arctic water column mean surface water PFAS measurements are not sufficient for understanding spatial and temporal variability and mass accumulation. In addition, biological exposures extend beyond the surface mixed layer for benthic and demersal food webs.

While information on PFASs in the Arctic is limited to surface waters, several studies show the penetration of other organic contaminants to deeper waters. Sobek and Gustafsson²⁹ demonstrated that concentrations of polychlorinated biphenyls (PCBs) were greatest in the intermediate and deep water in samples collected in the early 2000s. A similar enrichment in deeper waters was also confirmed for polybrominated diphenylethers (PBDEs) in the central Arctic Ocean.³⁰

Previous work had already shown that the presence of hexachlorocyclohexanes (HCHs) in deeper waters caused their export from the Arctic Ocean.³¹ Additional vertical profiles were reported for PCBs and PBDEs for the North Atlantic, confirming their penetration to below 2000 m.³² Yamashita et al.²² also showed detectable concentrations of several PFASs in the Subarctic Labrador Sea region at depths greater than 3500 m in vertical profiles from 2004. For these profiles, surface water PFAS concentrations were enriched relative to subsurface waters. The available evidence for these organic contaminants implies that persistent compounds are present in deep waters at concentrations that may exceed those measured in the surface water. A recent study has also shown accumulation of PCBs and PBDEs in deep-sea organisms.³³

In the present investigation, water samples were collected and analyzed from different depths of the water column at eight locations in the central Arctic (seawater, snow, and meltpond water), and seven stations on the Arctic shelf (Figure 1). The aims of this study were to (i) understand the spatial and vertical patterns of PFASs in Arctic Ocean seawater; (ii) assess the roles of atmospheric and oceanic transport of PFASs into the Arctic Ocean; and (iii) reconcile measured PFAS data with modeled results for different Arctic ocean water masses based on a geochemical Arctic Ocean box model.

MATERIALS AND METHODS

Details of analytical standards and reagents used in the present study are given in the Supporting Information (SI).

Sample Collection. Sampling locations are shown in Figure 1. Coordinates and further details of sample collection, including temperature and salinity data for all cruises are provided in SI Tables S1 and Figure S1.

Water samples (1 L/layer of water/location) were collected on two separate cruises in 2012 as follows: (1) four locations during expedition ARK-XXII/3 in the Central Arctic from surface to bottom (up to 4220 m) by the research icebreaker *Polarstern* between August and September 2012 (SI Tables S1i); and (2) seven locations on the Beaufort Chuckchi shelf from surface to bottom (up to 385 m) by the United States Coast Guard icebreaker *Healy* in October 2012 (SI Tables S1i). Snow and melt pond water samples were also collected at four ice stations during the expedition ARK-XXII/3 (SI Table S1i). Details of the cruise reports can be found elsewhere.^{34,35}

Analytical Standards and Reagents. Potassium salts of perfluorobutanesulfonate (PFBS), PFOS, and ¹³C₄-PFOS; sodium salts of perfluorodecanesulfonate (PFDS), perfluorohexanesulfonate (PFHxS) and ¹⁸O₂-PFHxS, perfluoroctanesulfonamido acetate (FOSAA; *N*-methyl and *N*-ethyl substituted: MeFOSAA, EtFOSAA), d₃-MeFOSAA, d₅-EtFOSAA, perfluoroctanesulfonamide (FOSA), ¹³C₈-FOSA, perfluorohexanoate (PFHxA), ¹³C₂-PFHxA, perfluoroheptanoate (PFHpa), PFOA, ¹³C₄-PFOA, perfluorononanoate (PFNA), ¹³C₅-PFNA, perfluorodecanoate (PFDA), ¹³C₂-PFDA, perfluoroundecanoate (PFUnDA), ¹³C₂-PFUnDA, were obtained from Wellington Laboratories (Guelph, ON).

Chemical and Instrumental Analyses. Samples (seawater: 400 mL (duplicate), snow and meltpond water: 200 mL (single)) were extracted using a solid phase extraction (SPE) cartridge (Strata-X-AW cartridge, Phenomenex, Torrance, CA) following the ISO 25101 method.³⁶ Details of the method are provided in the SI. Separation and quantification of PFASs in seawater, snow and melt pond water samples were performed using an Acquity ultra performance liquid chromatograph

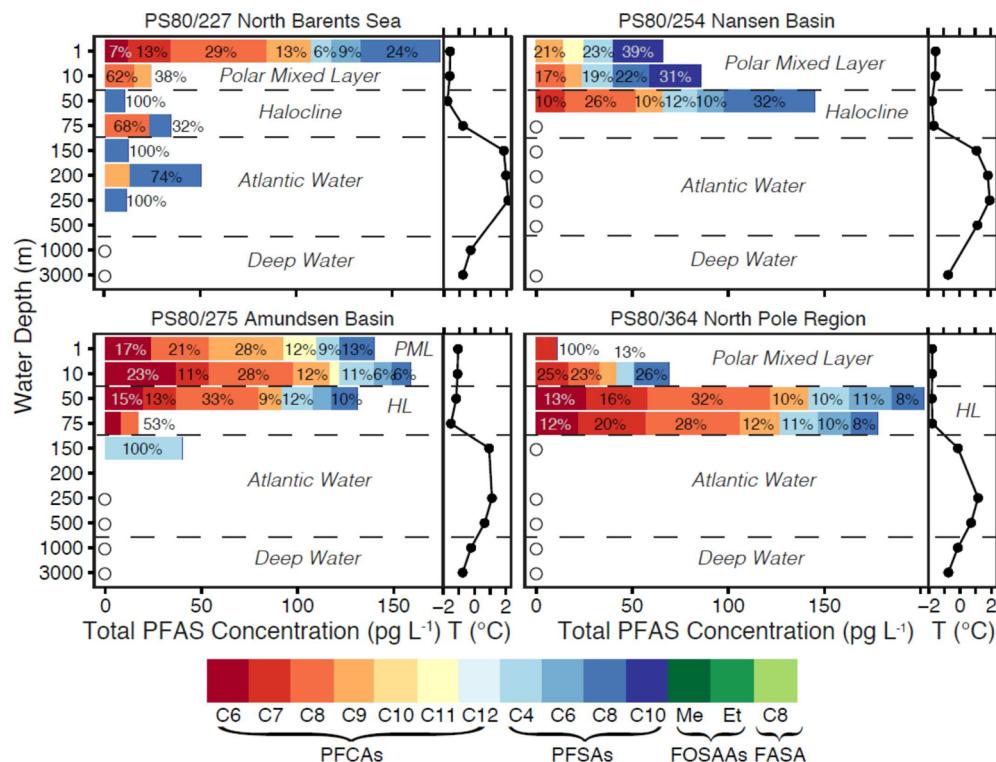


Figure 2. Total PFAS concentration (pg/L), composition (%), and temperature (T, in °C; shown in black dots and trends in black line) in water samples from the Arctic Ocean. (Total PFAS concentration is the sum of detectable PFASs; open circle indicates sample below LOQ; zero was assigned for calculating total PFAS when the samples were found below LOQ).

(UPLC) and a Xevo TQ-S tandem mass spectrometer (MS/MS - Waters Corporation) operated in negative ionization mode with an atmospheric electrospray interface. An Acquity BEH C18 column (2.1 × 75 mm, 1.7 μm, 100 Å), maintained at 40 °C was used to achieve chromatographic separation. A 4 μL extract aliquot was injected onto the column, with 2 mM ammonium acetate in Milli-Q water and MeOH used as mobile phases. Detailed MS/MS conditions, including collision energies, cone voltages, and MS/MS optimization parameters have been reported elsewhere.³⁷ Internal calibration using corresponding mass-labeled standards was used to quantify PFASs with mass-labeled standards (SI Table S2). Internal calibration curves were constructed at 5, 10, 50, 100, 200, 500, 1000, 5000, and 10 000 pg/mL with the addition of an internal mass-labeled standard with the final concentration of 100 pg/mL. In the current investigation, target PFASs included C₄–C₁₀ PFSAAs, C₅–C₁₄ PFCAs, FOSAA, MeFOSAA, EtFOSAA, and FOSA. Other PFASs including polyfluoroalkyl phosphate diesters (diPAPs: 4:2, 6:2, 6:2/8:2, 8:2/8:2, 10:2), fluorotelomer unsaturated carboxylates (FTUCAs: 6:2, 8:2, 10:2), fluorotelomer sulfonates (FTSAs: 4:2, 6:2, 8:2), perfluorinated phosphinates (PFPIAs: 6:6, 6:8, 8:8), N-methyl and N-ethyl substituted perfluorooctanesulfonamide (MeFOSA and EtFOSA) were also monitored during LC-MS/MS analysis. The standards for the congeners of PFSA, FOSA, FOSAA, and PFOA were the linear isomer, whereas the samples were composed of both branched and linear isomers; the concentrations reported for the present study included both linear and branched isomers based on the calibration curve of the linear isomer of the standard.

Quality Assurance/Quality Control. All the reagents and apparatus (sampling bottles, transfer pipet, pipet tips, and

falcon tubes) were tested for the presence of target PFASs (<0.1 pg/mL). Since Milli-Q water and Waters OASIS WAX-SPE cartridges contained trace amount PFASs, polished Milli-Q water and PFOA-free extraction cartridges (Strata-X-AW cartridge, Phenomenex, Torrance, CA) were used throughout the method development and sample extraction (see the discussion in the SI). Sample extraction was performed in the Advanced Laboratory for Fluorinated and Other New Substances in the Environment (ALFONSE), at the University of Toronto at Scarborough, a Class 100 clean laboratory. Deep layer water samples (3000 m depth from 4 different stations) served as field blanks and were found below limits of quantification (LOQs: 5–20 pg/L, SI Table S3). The definition of LOQs will be explained below. Matrix recoveries were confirmed using the deep layer (3000 m) of water samples (*n* = 4) by spiking 100 μL of the native standards (1 pg/μL) into spike samples and equal amount of MeOH into nonspike samples before extraction; mass-labeled standards were spiked into the LC vials before instrumental analysis. The recoveries were calculated by the difference between the measured values in the spike and nonspike samples divided by the theoretical values × 100%; most of the target PFASs had the recoveries ranged from 85 to 106%, except 60% for FOSA (SI Table S3). The recoveries of the mass-labeled standards in the real samples (*n* = 69) based on external calibration curve were 78–121%, except 65% for FOSA (SI Tables S4–S5). Seawater samples were extracted in duplicate and the variability of measured concentrations was found to be at most 23%; the reported values for seawater were an average of the duplicate analysis. The limits of quantification (LOQs) were defined based on several criteria, including (i) the lowest concentration of standard on the calibration curve that could be accurately

measured within $\pm 20\%$ of its theoretical value; (ii) a signal-to-noise ratio equal to or greater than 10; (iii) concentration factor; and (iv) sample volume. The LOQs of the present study were 5–10 pg/L for PFAAs and 20 pg/L for FOSA (SI Table S2b). The interlaboratory comparison between ALFONSE and MTM was limited to PFOA and PFOS, and their respective relative standard deviations for PFOA and PFOS were 27 and 15% at most (see SI for more details, including SI Table S6).

Modeled inputs of PFOS and PFOA to the Arctic Ocean. To help evaluate the contributions of atmospheric and oceanic inputs to observed PFOS and PFOA concentrations, we developed a three-compartment geochemical box model for the Arctic Ocean adapted from Soerensen et al.³⁸ representing: (1) the polar mixed layer: PML, (2) the subsurface ocean (20–200 m depth including the halocline), and (3) the deep ocean (200 m - bottom). For PFOS, the model is forced by inputs from the Atlantic Ocean between 1958 and 2038 based on the 3-D ocean circulation model developed by Zhang et al.³⁹ PFOS mass inflow is stratified by depth based on seawater inflow for the surface, subsurface and deep Arctic seawater. We do not include PFAS inputs from the Pacific Ocean since inflow of seawater is small relative to the Atlantic Ocean and no data are available on temporal changes in PFAS inputs for the Pacific. Atmospheric deposition is based on ice-core data from Young et al.¹⁶ We present model simulations forced by both the median (cumulatively: 2410 Mg) and low (842 Mg) emissions scenarios for continental PFOS discharges to the North Atlantic from North American and European wastewater and rivers reported by Zhang and co-workers³⁹ between 1958 and 2038.

For PFOA, we do not have a comparable 3-D simulation to resolve oceanic inflow at the surface, subsurface and in deep waters. We therefore estimate only the contribution of atmospheric deposition to surface water (PML) concentrations based on deposition rates measured in the Devon Ice Cap from the Canadian High Arctic between 1993 and 2007.¹⁵ Deposition prior to 1993 was fixed at the lowest recorded value (7 ng/m²/year). For recent years we assumed two scenarios representing deposition that continues from 2007 values and complete elimination. This allowed us to estimate the relative contribution of atmospheric inputs compared to oceanic inflow.

RESULTS AND DISCUSSION

PFAS Concentrations and Profiles. In total, 69 samples were analyzed for 39 PFASs in seawater, snow and melt pond water. Only 13 PFASs (C6–C12 PFCAs; C6, 8, 10 PFSAs; MeFOSAA, EtFOSAA, and FOSA) showed detectable concentrations (individual compound range: <5–343 pg/L) (SI Table S7). Therefore, the following discussion will only focus on these 13 PFASs. Figure 2 and SI Tables S7a–d show that the detection of PFASs in the four depth profiles was limited to the PML and halocline (150 m below the surface), except for the North Barents Sea (PS80/227) where PFOS was detected down to 250 m below surface. The detection frequency and range (%), pg/L) of the 13 detectable PFASs are provided in SI Table S8.

PFASs in the Central Arctic Surface Water. Surface water concentrations of total PFASs in the Central Arctic Ocean ranged from 11–174 pg/L. Previous investigations reported total PFAS concentrations of 45–280 pg/L in surface water from the Greenland Sea²¹ and the average concentrations of PFOA and FOSA combined were 112 pg/L in the East

Greenland Arctic Ocean.¹⁸ Average total PFAS concentrations were reported as 500 ± 170 pg/L in surface water of the Arctic Ocean¹⁹ and 40–250 pg/L in the Canadian Arctic.¹⁷ Results from this study (average total PFAS: 98 ± 73 pg/L) were approximately 5-fold lower than previous measurements of PFAS concentrations in Arctic Ocean surface waters.

PFASs in the Arctic Ocean water column. In the four vertical water column profiles, the detection of PFAS was limited to the PML and halocline (150 m below the surface), except for the North Barents Sea (PS80/227) where PFOS was detected down to 250 m below surface. Among the four vertical profiles, maximum individual PFAS concentrations (pg/L) were as follows: 50 (PFOA), 47 (PFOS), 40 (PFBS), 39 (PFNA), 37 (PFHxA), 35 (PFHpA), 27 (PFDS), 22 (PFHxS), and 17 (PFUnDA). The composition of PFASs varied with location and depth, highlighting the combination of different sources (rivers, atmosphere, ocean currents) and circulation of the Arctic. Similar composition profiles were only observed in some layers of water columns (50 and 75 m below surface near the Pole – PS80/364 and 10 and 50 m below surface at the Amundsen basin – East of Gakkel Ridge – PS80/254). To better understand the interplay between PFASs sources and mixing in the Arctic Ocean, we need to take a closer look at water mass circulation.

PFASs in Arctic Ocean Water Masses. The upper Arctic Ocean is strongly stratified and consists of different water masses distributed from the surface to the bottom, with different circulation patterns.⁴⁰ In summer, with the sea ice melt and river runoff, the surface water of the Arctic forms the polar mixed layer (PML), which has a lower salinity compared to the deeper water layer. In the present study, the depth of the PML ranged from 10 to 30 m from surface, where we detected C6–C9 and C11 PFCAs, C4, C6, and C8 PFSAs (SI Table S7a). The PML is mixed by waves, ice rafting, and turbulence caused by the wind stress on the surface. Below the PML is the halocline, the layer above a deeper, warmer and saltier Atlantic Layer.⁴⁰ In the current investigation, the depths of the halocline ranged from 75 to 150 m from surface, where we detected the same suite of PFASs as in the PML. Freezing seawater can change the salinity of seawater during brine formation, which might transport contaminants from the surface to the halocline layer. The different compositions of PFASs in seawater between the PML and the halocline layer (Figure 2) may be explained partly due to different mixing regimes and partly by atmospheric deposition or sea ice melt on a seasonal basis. The upward heat flux from the Atlantic layer warms the transition layer of halocline that prevents further sinking of the surface water, and thus reduces the vertical transport of contaminants to the deep and bottom water.⁴⁰ However, transport (e.g., due to sinking) of contaminants bound to organic carbon or particles may also take place,⁴¹ as a recent study has shown accumulation of PCBs and PBDEs in deep-sea organisms.³³

The ventilation age of the Atlantic layer water varies from 10–80 years, with the water masses closest to the cold halocline being youngest.⁴² The lifetime of tracers in the PML is typically <1 year, in the halocline ~10 years, in the Atlantic water ~25 years, and in Arctic Deep water ~75–300 years.^{43,44} The depths of the Atlantic layer ranged from below the halocline to 1000 m depth, where PFNA and PFOS were detected in 150–250 m below surface the North Barents Sea (PS80/227) and PFBS was detected 150 m below surface in the Amundsen Basin – East Gakkel Ridge (PS80/275). The presence of

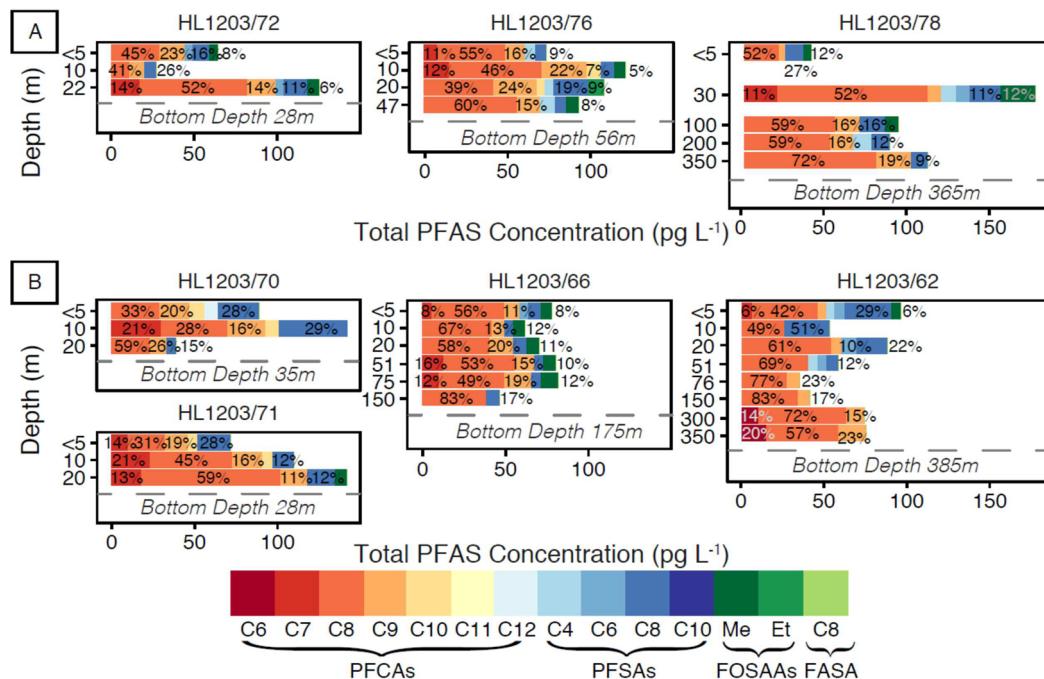


Figure 3. Total PFAS concentration (pg/L) and composition in water samples from the Arctic shelf: (A) transect at 144°W longitude; (B) transect at 139°W longitude (see Figure 1). (Total PFAS concentration is the sum of detectable PFASs; zero was assigned for calculating total PFAS when the samples were found below LOQ).

PFASs in the Atlantic layer most likely reflects long-range oceanic transport, since pronounced vertical settling would result in penetration to greater depths, as was previously demonstrated for PCBs.²⁹ Prior work shows particle settling in the North Atlantic is negligible as a transport pathway for PFOOs compared to lateral ocean circulation.^{32,39}

Yamashita et al. reported surface water concentrations of 160–338 pg/L for PFOA, 15–36 pg/L for PFNA, and 8.6–36 pg/L for PFOS in 2003.²⁰ In the Labrador Sea and North Atlantic Ocean, they also detected PFOA at ~ 50 and 20 pg/L down to 3000 m. In the Atlantic layer in the Arctic Ocean sampled here, though, only PFOS (11–37 pg/L) and PFNA (13 pg/L) were detected in the North Barents Sea (PS80/227). Unexpectedly PFOA, typically a major PFASs, was not detected in this study above LOQ (the 5 pg/L) in the waters deeper than 75 m. At the locations further away from the Atlantic Ocean, such as Nansen Basin – West Gakkel Ridge (PS80/254), Amundsen Basin – East Gakkel Ridge (PS80/275), and near the Pole (PS80/364), no detectable PFASs were observed in the Atlantic layer. In summary, few PFASs were detected (at low concentrations, $< 50 \text{ pg/L}$, see Figure 2) in the Arctic Ocean water below the PML and halocline, implying a combination of dilution and delayed transport into the deeper Arctic water.

Concentrations of PFASs in the Water Column Along the Arctic shelf. Concentrations of PFASs in water samples collected along the Chuckchi Sea shelf at different depths from nearshore to offshore are shown in Figure 3 and SI Tables 7e–k. PFOA was the dominant PFAS in almost all samples (detection frequency: 100%; mean 44 ng/L , median 42 ng/L), followed by PFOS (91%; mean 14 ng/L , median 10 ng/L) and PFNA (88%; mean and median of 14 ng/L). Concentrations were in general comparable to those measured in the Central Arctic Ocean. Different PFAS composition profiles were observed between the samples collected along the Arctic shelf

and the Arctic Ocean. One of the reasons might be the complexity in water sources. The water sources of the Arctic Ocean are mainly Atlantic water and sea ice melt, whereas the Arctic shelf represents a combination of Atlantic water, Pacific water, sea ice melt and river runoff.²⁸ Several observations stand out: First, the ratios of PFOA/PFNA in two different sampling transects from nearshore to offshore increased (Stations HLY1203/70 and 71:1.6, Station HLY1203/66:4.9, Station HLY1203/62:7.9; and Station HLY1203/72:1.9, Station HLY1203/76:3.6, Station HLY1203/78:5.3). Second, PFDA was only detected in samples collected from nearshore stations (HLY1203/70 and 71). The decreasing contribution of PFNA to PFOA from nearshore to offshore areas and detection of PFDA limited to nearshore area suggested these sources might come from river runoff to the nearshore area, and then diluted when getting into offshore area. Seasonally varying fresh water inputs are thought to be important sources of other contaminants to the Arctic surface waters.^{24–26} Third, MeFOSAA was detected in water sample from the Arctic shelf. MeFOSAA is an oxidation product of MeFOSE, which was primarily incorporated into polymeric materials as a surface treatment for products like carpets and textiles.^{45,46} It is also believed to be a PFOS precursor. In contrast to the anionic nature and persistence of PFCAs and PFSAs, MeFOSE is a neutral and volatile compound; it is expected to present in the atmosphere and will ultimately degrade to PFOS under environmental or biological condition.⁴⁵ An earlier study also showed the detection of MeFOSE in the Arctic atmosphere.⁴⁷ Fourth, the PFAS composition profiles were quite different at the water layers between 50 m (PFOA: 69%, PFBS: 10%, PFHxS: 10%; PFOS: 12%) and 76 m (PFOA: 78%; PFNA: 22%) depth at Station HLY1203/62. Different composition profiles of PFAS between the nearshore and offshore samples may be explained by different sources (river runoff at the near shore) and the dilution effect by ocean water. The different

PFAS compositions between the surface and bottom waters may be explained partly by the contribution of ice melt in the surface (changes in salinity from the surface to the bottom).

Concentrations of PFASs in Melt Pond Water and Snow. Samples were collected from mostly first year ice, integrating PFAS deposition from up to one year.⁴⁸ More PFASs (PFUnDA, FOSA, and EtFOSAA) were detected in melt pond water and snow samples compared to seawater from the Arctic shelf and central basin (SI Table S7). Snow samples showed detectable concentrations of PFCAs (C6–C12), PFSAs (C8 and C10), MeFOSAA, EtFOSAA, and FOSA (Figure 4).

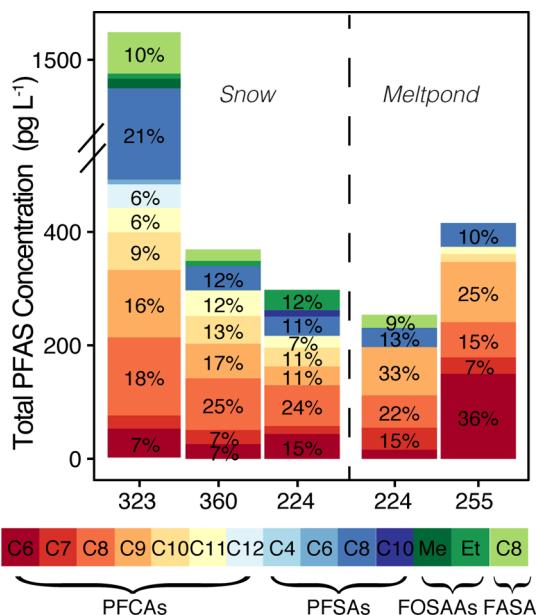


Figure 4. Concentrations and composition of PFAS in snow and meltpond water samples collected from the ice station in the Arctic (see Figure 1 for locations).

Various PFCAs were detected at concentrations greater than 100 pg/L, including PFHxA, PFOA, PFNA, PFDA, PFOS, and FOSA. Total PFAS concentrations (403 ± 405 pg/L) in the present investigation were much lower than the snow samples collected from Japan and the U.S. (concentrations in the ng/L range),⁴⁹ and similar or greater to previously reported for the Devon ice cap^{15,16} and surface snow from glacier in Svalbard, Norway.⁵⁰ Relatively high total PFASs were observed at Station 5 – PS80/323 (1600 pg/L), which was similar to concentrations in snow samples collected downstream of Svalbard, Norway (1470 pg/L).⁵⁰ Spatial trends might imply that proximity to Eurasian continental atmospheric emissions were a main source of elevated PFASs in snow (see SI Table S9).

Snow has been suggested to be an effective scavenger of PFAS in the atmosphere; enhanced PFAS concentrations in snow are interpreted as evidence for a primary source of PFAA to the Arctic via atmospheric oxidation of volatile precursors.¹⁶ Atmospheric oxidation of volatile FTOHs under low NO_x conditions may form PFCAs of different chain lengths,^{13,51} whereas atmospheric oxidation of volatile perfluorooctane sulfonamidoethanols (e.g., FOSE) may result in different perfluorooctane sulfonamido derivatives as well as PFOS.^{52,53} Intermediate compounds such as saturated and unsaturated fluorotelomer acids (FTCAs/FTUCAs: 6:2, 8:2, and 10:2) were suggested to be the connection between the volatile

fluorotelomer precursors and PFCAs; they were below their respective detection limits in this study (FTCAs: 1000 pg/L; FTUCA: 10 pg/L). In a smog chamber study, Ellis et al.¹³ observed a production of approximately 1:1 ratio of C8 and C9 PFCAs after oxidation of 8:2 FTOH using the Cl atom as surrogates to OH radicals. A recent investigation showed that heterogeneous photooxidation of 6:2 FTOH yielded C6 and C5 PFCAs in a ratio ranging from 1:1 to 6:1, depending on the surface of the substrates and the length of illuminated period.⁵⁴ Results from these studies imply that observed ratios ranging from 1:1 to 6:1 between different pairs of PFCAs support the occurrence of oxidation of fluorotelomer-based precursors (e.g., FTOH). On the other hand, the ratio between C8 and C9 PFCAs due to direct global emission was reported to be approximately 8:1;¹² and the biotransformation of 8:2 FTOH through beta oxidation preferentially yielded PFOA.⁵⁵ Based on these two results, a recent study suggested that the ratio between C8 and C9 PFCAs due to direct source and biotransformation might be greater than 8:1.⁵⁶ Although we did not detect intermediates in snow samples, the ratios between different pairs of PFCAs may be an indicator of atmospheric oxidation of volatile fluorotelomer precursors (see SI Table S10). The ratios of C8/C9 (1.2 ± 0.7) and C10/C11 (1.3 ± 0.3) PFCAs were broadly consistent with those found in high Arctic ice caps (C8/C9: 1.5 ± 0.8 and C10/C11: 0.9 ± 0.8). Although variable ratios of C6/C7 PFCAs (2.4 ± 1.8) were observed, our results were within the ratio obtained by heterogeneous photooxidation of 6:2 FTOH.

Modeled PFAS Fluxes into the Arctic Ocean. Figure 5 shows the results of geochemical box model simulations for PFOS and PFOA in the Arctic Ocean. For PFOS, modeled concentrations are highest in the PML and halocline, consistent with the observations reported in Figures 2 and 3. For 2012, the modeled PFOS concentration in the PML and subsurface waters were between 11 and 36 pg/L (low and median scenarios) and agreed well with the mean measured value of 17 pg/L in the PML (range: < 5–41). For PFOS, the modeled contribution of atmospheric deposition to surface water concentrations was minor at <3 pg/L (or up to 30% of observed concentrations; SI Figure S3). In deeper waters, the modeled value (range: 5–15 pg/L) is slightly higher than observations (<5 pg/L), suggesting the lower emissions scenario is more consistent with observed concentrations. Despite relatively low concentrations in deep Arctic waters due to dilution and mixing, the majority of the PFOS mass (74%, Figure 5 top panel) is still expected in this region of water column. Only 4% of the modeled PFOS mass is found in the PML and 22% in the mid-depth/halocline waters according to this model calculation. Although PFOS concentrations in surface and mid-depth waters peaked in the early 2000s, concentrations in deeper waters are still increasing based on model simulations and thus may be detectable in future ocean campaigns.

For PFOA, modeled mean concentrations in the PML from atmospheric deposition are estimated to be between 11 and 19 pg/L, depending on assumptions related to recent PFOA inputs (Figure 5 bottom panel), compared to the mean observed concentration in surface waters of 32 ± 15 pg/L. While the PFOS burden in Arctic seawater is accounted for mainly by North Atlantic inputs, modeling results for PFOA suggest approximately 34–59% of surface water concentrations are from atmospheric inputs. These results are consistent with a variety of studies that show atmospheric transport and

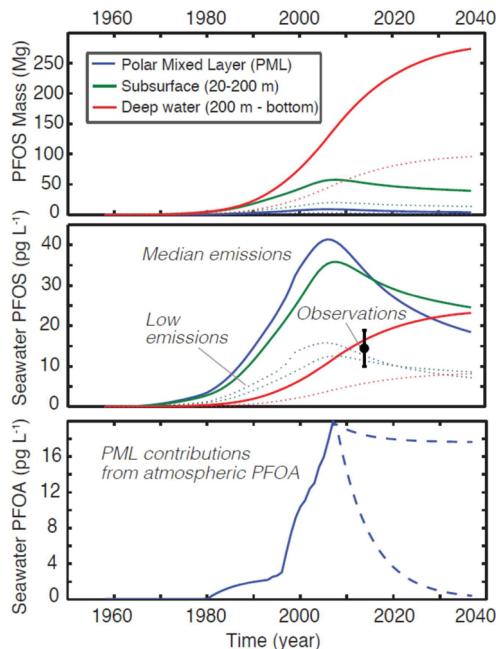


Figure 5. Modeled PFOS and PFOA concentrations in surface waters (PML, 0–20 m), subsurface (including the halocline, 20–200 m), and deep waters (200 m–bottom) of the Arctic Ocean based on the geochemical box model adapted from Soerensen et al.³⁸ For PFOS, median and low emissions scenarios represent uncertainty in the magnitude of historic discharges from North American and European wastewater and rivers into the North Atlantic Ocean, that then circulate into the Arctic based on the 3-D ocean simulation of Zhang et al.³⁹ For PFOA, resolved oceanic inputs are not available, thus we used deposition rates from the Devon ice cap in the Canadian High Arctic to estimate the contribution of atmospheric inputs to those observed in the polar mixed layer (PML) in this work (bottom panel). Dashed lines represent alternate assumptions for deposition after 2007: the top line assumes deposition values from 2007 continue, and the bottom line assumes zero deposition.

degradation of PFOA precursors is a more important source to the global ocean than for PFOS where direct discharges are estimated to comprise more than 95% of total inputs.^{57–59}

Mass Budget of PFASs in the Arctic Ocean. We derived mass budgets for PFASs in sampling regions of the Arctic basin, including the central Arctic Ocean, the Beaufort/Chukchi Sea and the ice layer (Table 1). Combining volumes and measured PFAS concentrations resulted in the following PFAS budgets (in Mg) for the surface Central Arctic Ocean: PFOA 8.6 ± 6.8 ; PFOS 4.8 ± 4.4 ; PFNA 4.2 ± 3.4 ; PFHpA 3.9 ± 3.8 ; PFHxA 3.6 ± 3.8 ; PFBS 3.6 ± 2.4 ; and PFHxS 2.3 ± 2.1 Mg. In total, there are 31 ± 26 Mg of PFASs present in the upper Arctic Ocean water (Table 1). We note that the amount of PFOA and PFOS at 1/2 LOQ (2.5 pg/L) in the Atlantic water layer down to 1000 m would add ~ 10 Mg per congener.

For the Beaufort and Chukchi Seas, the total PFAS budget amounted to 4.9 Mg, dominated by PFOA (almost 3 Mg), with 900 kg from PFNA and almost 1 Mg from PFOS (Table 1). In August 2012, a total of 4.1×10^6 km² were covered by ice, most of which was thin first year ice.⁶⁰ Assuming a 1m thickness (a rough estimation) across the Arctic, and average PFAS concentrations derived from snow and meltwater resulted in a stock of around 1.8 Mg of total PFASs in ice, dominated by >400 kg each from PFNA, PFOA, and PFOS.

Overall, the PFAS budgets in the Arctic Ocean derived here are lower than modeled masses for PFOS shown in Figure 5 due to different regions of the Arctic considered, and in comparison to mass budgets present in the North Atlantic (200 Mg in surface layer).⁶¹ Overall, we find the PML and halocline in the Arctic Ocean already contain more PFASs than PCBs (2 Mg), due to the much greater dissolved PFAS concentrations. Comparably greater proportions of PCB inputs have reached the deeper water masses, where an estimated 35 Mg are contained.²⁹

Environmental Implications. Both atmospheric and oceanic transport of PFASs have been proposed as important long-range transport mechanisms.^{12,14} Detection of PFAS in snow samples in this study suggests the ongoing importance of atmospheric deposition for some PFCAs, which may come

Table 1. Average Concentrations (pg/L), Volumes (km³) for the Surface Water of the Central Arctic and Beaufort/Chukchi Seas and Corresponding Mass Budgets (kg) for PFASs

Central Arctic		PFHxA	PFHpA	PFOA	PFNA	PFBS	PFHxS	PFOS	sum PFASs
surface ocean	average conc ^a	11	12	25	13	11	7	14	
volume (km ³)	SD	11	11	20	10	7	6	13	
337 000	mass (kg)	3590	3940	8550	4230	3590	2330	4850	31 100
	SD	3790	3760	6810	3380	2430	2190	4470	26 800
Beaufort/Chukchi	average conc ^b			42	13			14	79
volume (km ³)	SD			19	7			9	32
71 700	mass (kg)			3030	899			982	4910
	SD			1329	476			671	2480
snow/meltpond water	average conc	69	31	115	107		6	99	
volume (km ³)	SD	58	13	101	86		7	136	
4100	mass (kg)	283	127	472	439		25	406	1750
	SD.	238	53	414	353		29	558	1640

^aAverage concentrations of locations PS80/275, PS80/254, PS80/364, and PS80/227 up to the depth of 75 m from surface. ^bAverage concentrations of locations HL1203/72, HL1203/76, HL1203/78, HL1203/70, HL1203/71, HL1203/66, and HL1203/62 up to the depth of 75m from surface; Half LOQ was used for calculating the average value when the sample was below LOQ; SD denotes standard deviation of the average values.

from atmospheric oxidation of volatile precursor compounds or particles. We report low concentrations of PFASs in the Atlantic water layer of the Arctic Ocean, which is consistent with mixing and dilution of inputs from the Atlantic Ocean. Yet PFAS concentrations in deeper water masses are predicted to increase over time (Figure 5). A recent investigation calculated vertical transport of PFASs based on an estimate of the settling of organic matter and measured concentrations of PFASs bound to particles. The authors suggesting the biological pump a sink of some PFASs.⁶² Our observations of limited penetration of PFASs at depth suggests this flux must be minimal for most areas of the Arctic. Results for PFASs contrast vertical profiles of PCBs and PBDEs in the Arctic^{29,30} indicating vertical transport processes are weaker and potentially irrelevant for PFASs, as suggested by some modeling work.³⁹

With the implementation of Stockholm Convention and PFOA Stewardship program, the emission of PFOS-based and PFOA and higher-chain length PFCAs should be greatly reduced and the inputs of these PFASs are expected to decrease. By contrast, short-chain PFASs have been introduced into market as replacement and their environmental levels are expected to increase. A recent study showed increased contribution of PFBS to PFOS in marine mammals during the period 2002 to 2012 in South China.⁶³ Although analytical methods are available for measuring some short-chain PFASs (C4–C7 PFAAs), more sensitive chromatographic techniques should be developed to measure low levels in the samples for some “ultrashort”-chain PFAAs (e.g., C2 and C3). Long-term PFAS monitoring in snow samples from different ice stations may be useful to determine the input of PFAS via atmospheric deposition to the Arctic.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.7b00788](https://doi.org/10.1021/acs.est.7b00788).

Details on the sampling, locations and auxiliary measurements, PFASs' chemical analysis, concentrations and QA/QC measures ([PDF](#))

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Notes

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Supporting Information

Vertical Profiles, Sources and Transport of PFASs in the Arctic Ocean

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Total No of pages: 35

No of Figures: 3

No of Tables: 10

Table of Content

S4	Sample collection
	Analytical standards and reagents
	Extraction method
	Polished Milli-Q water
S5	Interlaboratory comparison between ALFONSE and MTM
S8	Table S1. Sample information
	i) location
S9	ii) details with water depth (m), Temperature (°C), salinity (‰) from the Central Arctic (a)-(d) and the Arctic shelf (e)-(k)
	a. PS80/364 Near the Pole
S10	b. PS80/275 Amundsen Basin - East Gakkel Ridge
S11	c. PS80/227 North Barents Sea
S12	d. PS80/254 Nansen Basin - West Gakkel Ridge
S13	e) HL1203/70
	f) HL1203/71
S14	g) HL1203/62
S15	h) HL1203/66
	i) HL1203/72
	j) HL1203/76
S16	k) HL1203/78
	Table S2. Analytical standards used in current investigation
S17	Figure S1. Temperature (°C) and salinity (‰) of the samples collected in (a) the Central Arctic and (b) the Arctic shelf
S19	Figure S2. An example showing PFOA concentration in cartridge blanks during method development stage.
S20	Table S3.
	a) Matrix recoveries (%) using the deep layer water samples ($n=4$)
S21	b) Limit of quantifications (LOQs)
S22	Table S4. A summary of mass labelled standard recoveries (%) based on external calibration curve in the samples ($n=69$)
S23	Table S5. Mass labelled standard recoveries (%) in samples collected from the Central Arctic (a)-(d), the Arctic shelf (e)-(k), and different ice stations (l) based on external calibration curve in the samples.
	a) PS80/364 Near the Pole
	b) PS80/275 Amundsen Basin - East Gakkel Ridge
	c) PS80/227 North Barents Sea
S24	d) PS80/254 Nansen Basin - West Gakkel Ridge
	e) HL1203/70
	f) HL1203/71
	g) HL1203/62
S25	h) HL1203/66
	i) HL1203/72
	j) HL1203/76
	k) HL1203/78

- I) Ice stations
- S26 Table S6a. Concentrations (pg/L) of detectable PFASs in the samples analyzed by MTM.
- Table S6b. Relative standard deviation (%) of detectable PFASs between ALFONSE and MTM in the samples.
- Table S6c. Recoveries (%) of PFOA and PFOS in the samples.
- S27 Table S7. PFAS concentrations (pg/L) in different samples collected from the Central Arctic (a)-(d), the Arctic shelf (e)-(k), and different ice stations (l)
 - a) PS80/364 Near the Pole
 - b) PS80/275 Amundsen Basin - East Gakkel Ridge
 - c) PS80/227 North Barents Sea
 - d) PS80/254 Nansen Basin - West Gakkel Ridge
 - e) HL1203/70
 - f) HL1203/71
 - g) HL1203/62
 - h) HL1203/66
 - i) HL1203/72
 - j) HL1203/76
 - k) HL1203/78
 - l) Ice station samples
- S32 Table S8. Range (pg/L) and detection frequency (%) of the thirteen detectable PFASs.
- S33 Table S9: Regression of PFAS concentrations in snow/meltwater versus latitude or longitude
- S34 Table S10. Ratios of different pair PFCAs in snow and meltpond water samples.
- S35 Figure S3. Modeled PFOS concentration in the PML due to atmospheric deposition.
- S36 Literature cited in the SI

Sample collection

Water samples at different depths were collected by a 24 CTD rosette sampler. Water samples collected from the CTD rosette sampler were stored in a 1 L PP bottle. For snow and meltpond water samples, they were first collected by a pre-cleaned stainless steel bucket, and then transferred into the 1L PP bottle. No field blank was available for meltpond and snow samples.

Chemicals

Analytical standards and reagents

Except for 4:2- and 10:2 diPAPs, all analytical and mass-labelled standards were obtained from the Wellington Laboratories (Guelph, ON); 4:2- and 10:2- diPAPs were synthesized as described elsewhere.¹ A list of PFAS monitored in the current investigation is given in Table S1. The purity of all standards was over 98%. The standards for the congeners of PFSA, FOSA, FOSAA, and PFOA were the linear isomer, whereas the samples were composed of both branched and linear isomers; the concentrations reported for the present study included both linear and branched isomers based on the linear isomer of the standard.

Ammonium acetate (>99%), and ammonia (NH₃, 30%) were obtained from Sigma-Aldrich. Methanol (MeOH, LCMS grade) was acquired from EMD Chemicals Inc. (Mississauga, ON). Solid phase extraction cartridges were purchased from cartridges from Waters for OASIS WAX-SPE cartridge (6 cc, 150 mg sorbent, 30 µm particle size) and Phenomenex (Torrence, CA) for Strata-X-AW cartridge (6 cc, 200 mg sorbent, 33 µm particle size).

Extraction method

Samples (Seawater, snow, meltpond water) were extracted using a solid phase extraction (SPE) cartridge (Strata-X-AW cartridge, Phenomenex, Torrence, CA) following the ISO 25101 method.² In brief, 1L of the seawater samples were transferred into 2 x 400 mL and 200 mL PP bottles. Methanol (3 x 2mL) was used to rinse the original bottle and collected, the 6 mL MeOH were divided and transferred to the three PP bottles. Snow and meltpond water samples did not have 1 L of volume, and the volume were measured using a graduated cylinder; MeOH (3 x 1 mL) was used to rinse the graduated cylinder and added to the snow or meltpond water samples. Samples (seawater: 400 mL, snow and meltpond water: 200mL) were first spiked with 20 pg of individual mass labelled standards before extraction. The SPE cartridge was first preconditioned by a passage of 4 mL of 0.1% NH₄OH in MeOH, 4 mL of MeOH, and 4 mL of polished Milli-Q water in sequence. After that, the 200/400 mL of samples were loaded onto the preconditioned cartridge. The flow rate was adjusted to 1-2 drops/s. After loading the samples, 4 mL of the buffer solution (25 mM ammonium acetate) was added to the cartridge. The cartridge was then centrifuge at 3500 rpm for 5 min and then dried under vacuum for 1 hr. The neutral fraction was collected by adding a 4 mL of MeOH, whereas the anionic fraction was collected by adding a 4 mL of 0.1% NH₄OH in MeOH. The 4 mL of the eluate was concentrated under a gentle stream of nitrogen in a heat block (40°C), and then reconstituted to 200 uL with MeOH. The 200 uL extract was centrifuged at 6000 rpm for 5 min before transferring to HPLC vial for instrumental analysis.

Polished Milli-Q water

Water from the Milli-Q system in the laboratory contained detectable levels of PFOS and PFNA (range: 50-200 pg/L). Therefore, for every batch of extraction, the water (1 L) was first pre-cleaned (i.e., polished Milli-Q water) by passing through a WAX SPE cartridge and collected for procedure blanks. Cartridge and procedure blanks were performed to confirm

any contamination that might be introduced from the cartridge and during extraction process, respectively. Initially, Waters OASIS WAX-SPE cartridges were used for method development and validation. However, low levels of PFOA (0.08 – 2.1 pg) were observed from the cartridges (SI Figure S2). Another cartridge (Strata-X-AW cartridge, Phenomenex, Torrence, CA) of similar retention property was found to be free of PFOA, and thus all the method development and sample extraction were done using this cartridge.

Interlaboratory comparison between ALFONSE and MTM

Four randomly selected samples (200 mL from 1 L sample) and one blank sample (200 mL of pre-cleaned water) prepared from ALFONSE were sent to Man-Technology-Environment (MTM) Research Centre, Örebro University for analysis. In brief, samples (200 mL) were spiked with 100 pg of mass-labelled standards and extracted following the ISO25101.¹ Samples were concentrated to 0.2 mL and then transferred to LC vial with the addition of a recovery standard (7H-PFH_pA) and 0.3 mL of 2 mM ammonium acetate in water before instrumental analysis. Samples were analyzed using a Acquity I-class UPLC couple to a Xevo TQ S tandem mass spectrometer. An Acquity BEH C18 column (2.1 × 100 mm, 1.7 µm, 100 Å), maintained at 60 °C was used to achieve chromatographic separation. A 10 µL extract aliquot was injected onto the column, with 2 mM ammonium acetate in Milli-Q water and MeOH (7/3: v/v) and 2 mM ammonium acetate in MeOH used as mobile phases. Detailed MS/MS conditions, including collision energies, cone voltages, and LC parameters can be found elsewhere.³

The four selected samples were PS80/227-surface, HL1203/70-4m, HL1203/66-10 m, and HL1203/78-29m, and their recoveries (%) for PFOA and PFOS were 87-97 and 93-95, respectively. Because of higher detection limit (MTM: 20 pg/L, ALFONSE: 5-20 pg/L) and smaller concentration factor (MTM: 1000x, ALFONSE: 2000x), fewer PFASs were detected in MTM. No detectable PFAS concentrations (<20 pg/L) were found in the blank sample, and detectable PFASs were C6-C9 PFCAs and PFOS (Table S6a).

Table S1. Analytical standards used in current investigation.

Class	Acronymn	Name	Mass-labelled standard used for quantification	External calibration
Perfluoroalkane sulfonate (PFSA)	PFBS	Perfluorobutane sulfonate	$^{18}\text{O}_2$ PFHxS	
	PPeS	Perfluoropentane sulfonate	$^{18}\text{O}_2$ PFHxS	
	PFHxS	Perflurohexane sulfonate	$^{18}\text{O}_2$ PFHxS	
	FFhpS	Perfluoroheptane sulfonate	$^{13}\text{C}_4$ PFOS	
	PFOS	Perfluorooctane sulfonate	$^{13}\text{C}_4$ PFOS	
	PFNS	Perfluorononane sulfonate	$^{13}\text{C}_4$ PFOS	
	PFDS	Perfluorodecane sulfonate	$^{13}\text{C}_4$ PFOS	
Perfluroinated carboxylate (PFCA)	PFHxA	Perfluorohexanoate	$^{13}\text{C}_2$ PFHxA	
	PFHpA	Perfluoroheptanoate	$^{13}\text{C}_4$ PFHpA	
	PFOA	Perfluorooctanoate	$^{13}\text{C}_4$ PFOA	
	PFNA	Perfluorononanoate	$^{13}\text{C}_5$ PFNA	
	PFDA	Perfluorodecanoate	$^{13}\text{C}_2$ PFDA	
	PFUnDA	Perfluoroundecanoate	$^{13}\text{C}_2$ PFUnDA	
	PFDoDA	Perfluorododecanoate	$^{13}\text{C}_2$ PFDoDA	
	PFTrDA	Perfluorotridecanoate	$^{13}\text{C}_2$ PFDoDA	
	PFTeDA	Perfluorotetradecanoate	$^{13}\text{C}_2$ PFTeDA	
Fluorotelomer carboxylate (FTCA)	3:3 FTCA	3:3 Fluorotelomer carboxylate	$^{13}\text{C}_2$ 6:2 FTUCA	
	5:3 FTCA	5:3 Fluorotelomer carboxylate	$^{13}\text{C}_2$ 6:2 FTUCA	
	7:3 FTCA	7:3 Fluorotelomer carboxylate	$^{13}\text{C}_2$ 6:2 FTUCA	
Fluorotelomer unsaturated carboxylate (FTUCA)	6:2 FTUCA	6:2 Fluorotelomer unsaturated carboxylate	$^{13}\text{C}_2$ 6:2 FTUCA	
	8:2 FTUCA	8:2 Fluorotelomer unsaturated carboxylate	$^{13}\text{C}_2$ 8:2 FTUCA	
	10:2 FTUCA	10:2 Fluorotelomer unsaturated carboxylate	$^{13}\text{C}_2$ 10:2 FTUCA	
Fluorotelomer sulfonate (FTSA)	4:2 FTSA	4:2 Fluorotelomer sulfonate	$^{13}\text{C}_2$ 4:2 FTSA	
	6:2 FTSA	6:2 Fluorotelomer sulfonate	$^{13}\text{C}_2$ 6:2 FTSA	
	8:2 FTSA	8:2 Fluorotelomer sulfonate	$^{13}\text{C}_2$ 8:2 FTSA	
polyfluoroalkyl phosphate diester (diPAP)	4:2 diPAP	4:2 Fluorotelomer phosphate diester	$^{13}\text{C}_4$ 6:2 diPAP	
	6:2 diPAP	6:2 Fluorotelomer phosphate diester	$^{13}\text{C}_4$ 6:2 diPAP	
	6:2/8:2 diPAP	6:2/8:2 Fluorotelomer phosphate diester	$^{13}\text{C}_4$ 6:2 diPAP	
	8:2 diPAP	8:2 Fluorotelomer phosphate diester	$^{13}\text{C}_4$ 8:2 diPAP	
Perfluorinated phosphinate (PFPiA)	10:2 diPAP	10:2 Fluorotelomer phosphate diester	$^{13}\text{C}_4$ 8:2 diPAP	
	C6/C6 PFPiA	Bis (perfluorohexyl) phosphinate		x

	C6/C8 PFPiA	Perfluoro (hexyloctyl) phosphinate		x
	C8/C8 PFPiA	Bis (perfluoroctyl) phosphinate		x
Perfluorooctane sulfonamide (FOSA)	FOSA	Perfluorooctane sulfonamide	¹³ C ₈ FOSA	
	MeFOSA	Methyl perfluorooctane sulfonamide	d ₃ MeFOSA	
	EtFOSA	Ethyl perfluorooctane sulfonamide	d ₅ EtFOSA	
Perfluorooctane sulfonamidoacetate (FOSAA)	FOSAA	Perfluorooctane sulfonamidoacetate		x
	MeFOSAA	Methyl perfluorooctane sulfonamidoacetate	d ₃ MeFOSAA	
	EtFOSAA	Ethyl perfluorooctane sulfonamidoacetate	d ₅ EtFOSAA	

Table S2. Sample information i) location and ii) details with water depth (m), Temperature (°C), salinity (‰) from the Central Arctic (a)-(d) and the Arctic shelf (e)-(k)

i)

Sampling location	Date	Start time	Latitude	Longitude	Sample type	Research vessel
PS80/364 Near the Pole	2012-09-22	17:31	88.8090	57.2545	Seawater	Polarstern
PS80/275 Amundsen Basin - East Gakkel Ridge	2012-08-25	00:43	83.3837	125.0888	Seawater	Polarstern
PS80/227 North Barents Sea	2012-08-09	19:25	84.0243	31.2277	Seawater	Polarstern
PS80/254 Nansen Basin - West Gakkel Ridge	2012-08-20	06:02	82.7087	109.1437	Seawater	Polarstern
HL1203/70	2012-10-19	08:13	69.7063	-139.3698	Seawater	Healy
HL1203/71	2012-10-19	09:06	69.6533	-139.5620	Seawater	Healy
HL1203/62	2012-10-19	00:42	70.1845	-138.7717	Seawater	Healy
HL1203/66	2012-10-19	05:17	69.8922	-139.0093	Seawater	Healy
HL1203/72	2012-10-19	17:35	70.1922	-144.6363	Seawater	Healy
HL1203/76	2012-10-19	20:52	70.5315	-144.2693	Seawater	Healy
HL1203/78	2012-10-19	22:51	70.697	-144.0855	Seawater	Healy
PS80/224 Station 1	2012-08-09	not available	84.0505	31.1138	snow, meltpond water	Polarstern
PS80/255 Station 3	2012-08-20	not available	82.6707	109.5895	meltpond water	Polarstern
PS80/323 Station 5	2012-09-05	not available	81.9255	131.1287	snow	Polarstern
PS80/360 Station 8	2012-09-22	not available	88.8277	58.8635	snow	Polarstern

ii) a. PS80/364 Near the Pole

Bottle No.	Depth water [m]	Temp [°C]	Sal [%]	Samples for PFAS analysis
1	4354.7	-0.6286	34.9440	
2	4249.8	-0.6405	34.9443	
3	4000.4	-0.6668	34.9442	
4	3500	-0.7179	34.9395	
5	2999.7	-0.7457	34.9333	x
6	2499.6	-0.7448	34.9261	
7	2000.2	-0.6666	34.9210	
8	1500.1	-0.5094	34.9133	
9	999.8	-0.1405	34.9000	x
10	799.7	0.0833	34.8912	
11	499.8	0.6959	34.8816	
12	499.8	0.7051	34.8811	x
13	300.1	1.2413	34.8663	
14	249.9	1.1546	34.8309	x
15	199.5	0.9394	34.7714	
16	149.6	-0.1360	34.4941	x
17	100.1	-1.3445	34.1227	
18	74.8	-1.7755	33.8193	x
19	49.9	-1.8048	33.6920	x
20	29.7	-1.7820	33.1713	
21	19.8	-1.7852	33.0015	
22	19.8	-1.7902	32.9391	
23	9.9	-1.7880	32.9535	x
24	1.1	-1.7873	32.9495	x

ii) b. PS80/275 Amundsen Basin - East Gakkel Ridge

Bottle No.	Depth water [m]	Temp [°C]	Sal [%]	Samples for PFAS analysis
1	4219.9	-0.6447	34.9440	
2	4119.8	-0.6555	34.9442	
3	3499.8	-0.7196	34.9420	
4	3000.1	-0.7578	34.9353	x
5	2500.3	-0.7642	34.9275	
6	2000	-0.7183	34.9209	
7	1500.4	-0.5841	34.9143	
8	1000	-0.2175	34.9042	x
9	800	-0.0108	34.8962	
10	700.1	0.1376	34.8911	
11	600.5	0.3477	34.8873	
12	500	0.6510	34.8869	x
13	400.3	0.9951	34.8860	
14	350.3	1.2686	34.8959	
15	249.8	1.1181	34.8314	x
16	199.6	1.1857	34.8342	
17	149.7	0.3732	34.6243	x
18	100.6	-1.0930	34.3030	
19	75	-1.5085	34.0751	x
20	50.4	-1.6972	33.3272	x
21	30	-1.7153	32.6602	
22	19.6	-1.5415	31.4763	
23	10.1	-1.0860	30.2386	x
24	1.3	-1.0547	30.1041	x

ii) c. PS80/227 North Barents Sea

Bottle No.	Depth water [m]	Temp [°C]	Sal [%]	Samples for PFAS analysis
1	3993.7	-0.6587	34.9437	
2	3993.7	-0.6587	34.9437	
3	3993.7	-0.6588	34.9436	
4	3500.1	-0.7120	34.9427	
5	3500.1	-0.7122	34.9427	
6	2999.9	-0.7567	34.9384	x
7	1999.7	-0.7500	34.9239	
8	1999.7	-0.7500	34.9238	
9	1500.3	-0.6268	34.9187	
10	1500.3	-0.6251	34.9187	
11	1000.2	-0.2527	34.9068	x
12	500	1.1964	34.9229	
13	500	1.2040	34.9241	
14	500	1.2075	34.9243	
15	250.5	2.1436	34.9369	
16	250.5	2.1536	34.9353	x
17	200.3	2.0113	34.8967	x
18	150	1.8652	34.8578	x
19	100.2	0.2212	34.5707	
20	75.2	-0.7544	34.3851	x
21	50.1	-1.7382	34.2058	x
22	24.7	-1.5504	34.0287	
23	8.2	-1.5947	33.0609	x
24	1.6	-1.5697	33.1511	x

ii) d. PS80/254 Nansen Basin - West Gakkel Ridge

Bottle No.	Depth water [m]	Temp [°C]	Sal [%]	Samples for PFAS analysis
1	3549	-0.6988	34.9428	
2	3448.7	-0.7085	34.9428	
3	2999.8	-0.7616	34.9373	x
4	2500.3	-0.7732	34.9294	
5	2000.3	-0.7381	34.9227	
6	1500.4	-0.6152	34.9163	
7	1001	-0.2675	34.9021	
8	800.7	0.0126	34.8930	
9	701.3	0.2827	34.8965	
10	600.1	0.6615	34.9061	
11	500	1.1034	34.9178	
12	500	1.1111	34.9181	x
13	399.6	1.5816	34.9277	
14	300.1	1.7453	34.9115	
15	249.9	1.8958	34.9101	x
16	199.7	1.7763	34.8670	x
17	147.7	1.0555	34.6883	x
18	99.7	-1.1461	34.3106	
19	74.8	-1.6903	34.1503	x
20	49.6	-1.7985	34.0350	x
21	25	-1.6711	33.9440	
22	19.8	-1.6011	33.7887	
23	9.7	-1.5884	33.0241	x
24	1.1	-1.5668	32.7281	x

ii) e. HL1203/70, Bottom depth 35 m

Bottle No.	Depth water [m]	Temp [°C]	Sal [%]	Samples for PFAS analysis
1	28.813	1.3995	27.7318	
3	20.417	1.4052	27.7127	x
4	10.081	1.3973	27.7104	x
5	3.6	1.3952	27.7108	x

ii) f. HL1203/71, Bottom depth 28 m

Bottle No.	Depth water [m]	Temp [°C]	Sal [%]	Samples for PFAS analysis
1	22.976	0.9744	27.7005	
3	19.891	1.0203	27.6959	x
4	9.934	1.0724	27.6931	x
5	2.661	1.0813	27.6932	x

ii) g. HL1203/62, Bottom depth 385 m

Bottle No.	Depth water [m]	Temp [°C]	Sal [%]	Samples for PFAS analysis
1	367.58	0.5097	34.7878	
3	348.87	0.3092	34.6882	
4	300.52	-0.1024	34.4925	x
5	251.9	-0.9271	33.9795	
6	199.24	-1.2591	33.5018	
7	175.2	-1.3848	33.0714	
8	149.74	-1.3925	32.7876	x
9	124.36	-1.3268	32.4943	
10	99.94	-1.1913	32.2183	
11	75.55	-0.907	31.8240	x
12	50.14	-0.9124	31.8251	x
14	39.9	-0.6185	31.5794	
15	29.7	-0.4883	31.0223	
16	19.31	-0.2219	30.3842	x
17	10.1	1.1034	29.0266	x
18	2.68	1.2917	28.7653	x

ii) h. HL1203/66, Bottom depth 175 m

Bottle No.	Depth water [m]	Temp [°C]	Sal [%]	Samples for PFAS analysis
1	162.52	-1.3569	33.2138	
3	151	-1.3771	33.1345	x
4	125.23	-1.405	32.9343	
5	99.7	-1.3903	32.6812	
6	74.8	-1.2485	32.2927	x
7	50.23	-0.728	31.4914	x
8	39.41	-0.401	30.9368	
9	29.16	1.3025	29.0177	
10	20.34	2.0517	27.8702	x
12	9.97	1.5895	27.6544	x
13	2.27	1.5891	27.6529	x

ii) i. HL1203/72, Bottom depth 28 m

Bottle No.	Depth water [m]	Temp [°C]	Sal [%]	Samples for PFAS analysis
1	22.21	1.3037	27.4026	x
3	10.201	1.1333	27.274	x
4	2.757	1.1469	27.2681	x

ii) j. HL1203/76, Bottom depth 53 m

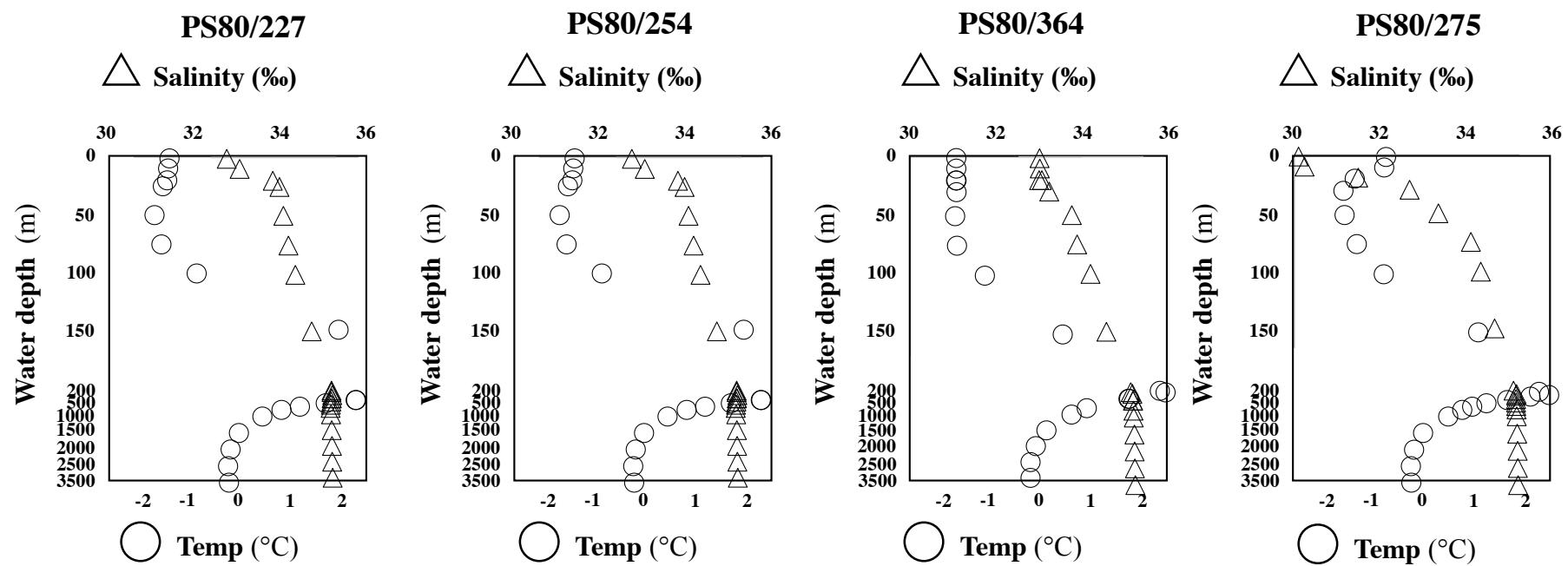
Bottle No.	Depth water [m]	Temp [°C]	Sal [%]	Samples for PFAS analysis
2	46.669	-0.3408	31.8644	x
4	40.25	-0.5319	31.6018	
6	20.146	-0.1992	30.3325	x
7	10.327	1.0149	28.9166	x
8	1.821	1.3818	27.1171	x

ii) k. HL1203/78, Bottom depth 357 m

Bottle No.	Depth water [m]	Temp [°C]	Sal [%]	Samples for PFAS analysis
1	340.46	0.4197	34.7181	x
3	300.35	0.3416	34.6846	
4	250.7	-0.0482	34.4904	
5	199.45	-0.9898	33.6443	x
6	174.58	-1.3089	33.2522	
7	149.72	-1.1807	32.9097	
8	124.15	-0.9953	32.7109	
9	100.2	0.0517	32.4492	x
11	74.29	0.0732	32.2655	
12	50.16	0.1035	31.8957	
13	39.32	0.6616	31.0666	
14	29.18	-0.0469	30.3637	
15	19.47	1.1002	29.7457	x
16	9.5	1.9112	26.6612	x
17	1.6	1.9164	26.6487	x

Figure S1. Temperature ($^{\circ}\text{C}$) and salinity (‰) of the samples collected in a) the Central Arctic and b) the Arctic shelf (see Table S2 for sample location)

(a)



(b)

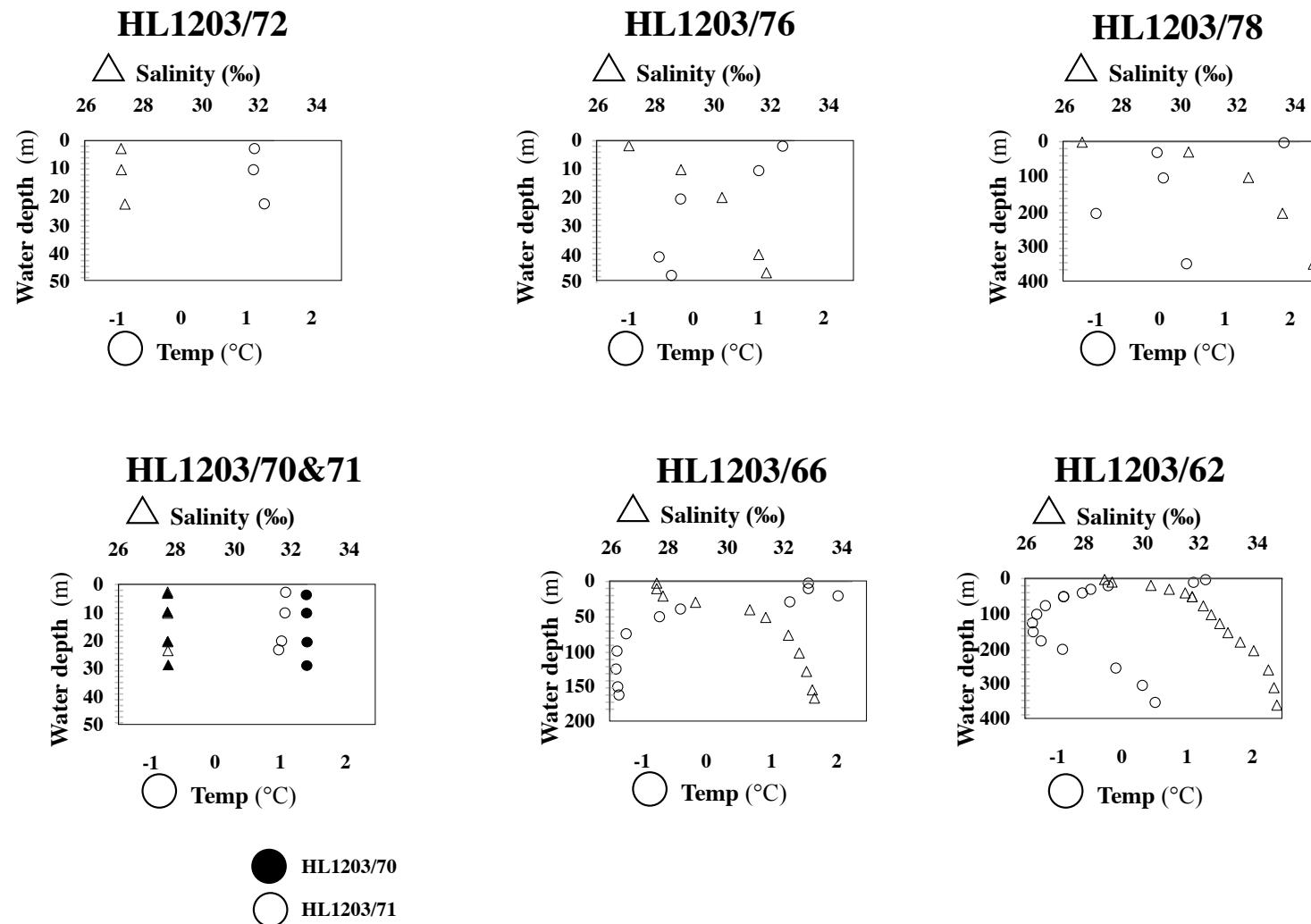


Figure S2. An example showing PFOA concentration in cartridge blanks during method development stage.

PFOA chromatograms in cartridge blanks

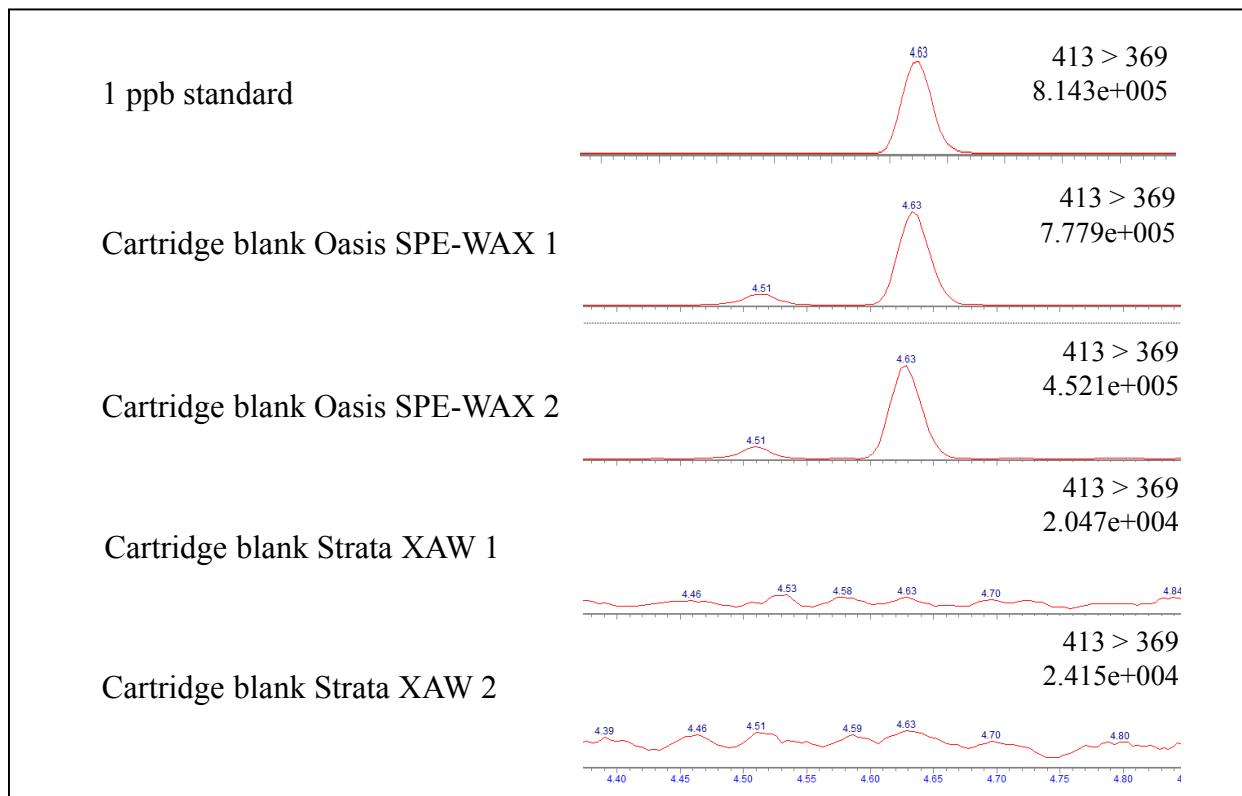


Table S3. Matrix recoveries and Limits of quantitation**a) Matrix recoveries (%) using the deep layer water samples (n=4)**

Matrix
recoveries
(n=4)

Analyte	mean	SD
PFPeA	104	10
PFHxA	104	8
PFHpA	95	9
PFOA	96	13
PFNA	88	13
PFDA	89	7
PFUnDA	87	10
PFDoDA	83	10
PFTriDA	81	9
PFTeDA	82	8
PFBS	103	5
PFHxS	105	8
PFOS	93	5
PFDS	92	5
FOSAA	75	10
MeFOSAA	85	10
EtFOSAA	91	8
FOSA	60	8
6:2 FTUCA	105	6
8:2 FTUCA	87	8
10:2 FTUCA	85	10

b) Limits of quantification (LOQs)

LOQ	
Analyte	pg/L
PFPeA	10
PFHxA	5
PFHpA	5
PFOA	5
PFNA	5
PFDA	5
PFUnDA	5
PFDoDA	10
PFTriDA	10
PFTeDA	10
 PFBS	5
PFHxS	5
PFOS	5
PFDS	10
 FOSAA	10
MeFOSAA	5
EtFOSAA	5
 FOSA	20
 6:2 FTUCA	10
8:2 FTUCA	10
10:2 FTUCA	10

LOQs of 6:2-, 8:2- and 10:2-FTCA were 1ng/L.

Table S4. A summary of mass labelled standard recoveries (%) based on external calibration curve in the samples (n=69)

Analyte	mean	SD
PFPeA	102	9
PFHxA	104	8
PFHpA	103	14
PFOA	99	9
PFNA	97	12
PFDA	97	12
PFUnDA	100	11
PFDoDA	101	9
PFHxS	109	8
PFOS	92	12
MeFOSAA	95	7
EtFOSAA	101	15
FOSA	65	4

Table S5. Mass labelled standard recoveries (%) based on external calibration curve in the samples collected at the Central Arctic (a)-(d) and the Arctic shelf (e)-(k), and different ice stations (l) (see Table S2 for sample location)

a) PS80/364

	PS80/364	¹³ C ₅ PFPeA	¹³ C ₂ PFHxA	¹³ C ₄ PFHpA	¹³ C ₄ PFOA	¹³ C ₅ PFNA	¹³ C ₂ PFDA	¹³ C ₂ PFUnDA	¹³ C ₂ PFDoDA	¹⁸ O ₂ PFHxS	¹³ C ₄ PFOS	d ₃ MeFOSAA	d ₅ EfFOSAA	C ₈ FOSA
Depth (m)	1	107	109	98	105	95	82	97	105	93	85	79	80	59
	10	91	91	107	92	93	96	98	106	81	84	88	84	65
	50	100	98	105	101	109	112	121	116	100	103	116	106	68
	75	93	92	91	106	100	108	117	119	104	105	103	101	65
	150	93	89	84	103	100	98	105	113	87	93	109	107	56
	250	102	95	95	103	109	101	109	122	100	103	105	109	63
	500	101	96	98	103	110	113	116	125	107	107	108	108	65
	1000	91	89	114	96	87	93	101	106	88	90	94	93	67

b) PS80/275

	PS80/275	¹³ C ₅ PFPeA	¹³ C ₂ PFHxA	¹³ C ₄ PFHpA	¹³ C ₄ PFOA	¹³ C ₅ PFNA	¹³ C ₂ PFDA	¹³ C ₂ PFUnDA	¹³ C ₂ PFDoDA	¹⁸ O ₂ PFHxS	¹³ C ₄ PFOS	d ₃ MeFOSAA	d ₅ EfFOSAA	C ₈ FOSA
Depth (m)	1	79	87	81	91	100	91	102	104	103	104	112	107	58
	10	78	91	91	104	103	87	102	102	106	109	97	91	55
	50	92	102	96	114	105	98	110	109	107	113	96	94	70
	75	84	91	83	99	100	89	100	103	103	111	95	90	68
	150	96	111	101	116	119	111	115	105	104	111	108	108	52
	250	95	98	88	98	114	110	110	110	103	117	97	99	65
	500	109	112	83	121	101	114	117	103	98	119	96	103	70
	1000	109	116	106	108	110	101	109	105	99	111	99	108	61

c) PS80/227

	PS80/227	¹³ C ₅ PFPeA	¹³ C ₂ PFHxA	¹³ C ₄ PFHpA	¹³ C ₄ PFOA	¹³ C ₅ PFNA	¹³ C ₂ PFDA	¹³ C ₂ PFUnDA	¹³ C ₂ PFDoDA	¹⁸ O ₂ PFHxS	¹³ C ₄ PFOS	d ₃ MeFOSAA	d ₅ EfFOSAA	C ₈ FOSA
Depth (m)	1	99	91	68	105	115	102	112	98	93	105	132	104	61
	8	101	95	90	115	108	99	98	106	99	101	120	104	60
	50	101	93	85	108	108	102	110	105	92	96	114	107	70
	75	105	95	79	102	107	116	121	114	107	110	125	113	72
	150	98	88	97	103	96	106	93	93	93	95	117	102	68
	200	83	73	68	87	81	76	90	76	85	80	89	87	76
	250	103	97	105	108	107	98	111	99	103	104	119	107	73
	1000	98	94	89	110	109	105	110	102	97	101	121	112	67

d) PS80/254

	PS80/254	¹³ C ₅ PFPeA	¹³ C ₂ PFHxA	¹³ C ₄ PFHpA	¹³ C ₄ PFOA	¹³ C ₅ PFNA	¹³ C ₂ PFDA	¹³ C ₂ PFUnDA	¹³ C ₂ PFDoDA		¹⁸ O ₂ PFHxS	¹³ C ₄ PFOS	d_3 MeFOSAA	d_5 EFOSAA	C_8 FOSA
Depth (m)	1	92	80	87	88	94	88	102	86		78	83	72	88	64
	10	93	88	96	111	117	104	118	115		78	81	78	84	60
	50	93	68	74	73	77	76	89	78		98	81	76	76	67
	75	90	70	74	71	82	75	91	84		78	73	73	81	69
	150	102	101	107	105	115	114	129	115		95	106	122	120	65
	200	103	108	92	105	115	109	132	112		56	54	62	58	61
	250	90	88	97	90	99	100	115	104		92	95	105	100	76
	500	96	98	108	109	109	107	120	110		97	95	117	113	68

e) HL1203/70

	HL1203/70	¹³ C ₅ PFPeA	¹³ C ₂ PFHxA	¹³ C ₄ PFHpA	¹³ C ₄ PFOA	¹³ C ₅ PFNA	¹³ C ₂ PFDA	¹³ C ₂ PFUnDA	¹³ C ₂ PFDoDA		¹⁸ O ₂ PFHxS	¹³ C ₄ PFOS	d_3 MeFOSAA	d_5 EFOSAA	C_8 FOSA
Depth (m)	4	89	90	86	104	85	95	111	109		117	87	85	106	71
	10	83	90	78	113	101	96	108	115		119	88	89	106	67
	20	91	90	102	106	101	102	111	106		112	110	89	112	69

f) HL1203/71

	HL1203/71	¹³ C ₅ PFPeA	¹³ C ₂ PFHxA	¹³ C ₄ PFHpA	¹³ C ₄ PFOA	¹³ C ₅ PFNA	¹³ C ₂ PFDA	¹³ C ₂ PFUnDA	¹³ C ₂ PFDoDA		¹⁸ O ₂ PFHxS	¹³ C ₄ PFOS	d_3 MeFOSAA	d_5 EFOSAA	C_8 FOSA
Depth (m)	3	94	106	103	106	101	102	110	111		113	113	95	98	61
	10	95	97	101	110	96	112	114	97		107	113	99	96	63
	20	92	101	93	100	103	116	116	112		107	111	102	101	61

g) HL1203/66

	HL1203/66	¹³ C ₅ PFPeA	¹³ C ₂ PFHxA	¹³ C ₄ PFHpA	¹³ C ₄ PFOA	¹³ C ₅ PFNA	¹³ C ₂ PFDA	¹³ C ₂ PFUnDA	¹³ C ₂ PFDoDA		¹⁸ O ₂ PFHxS	¹³ C ₄ PFOS	d_3 MeFOSAA	d_5 EFOSAA	C_8 FOSA
Depth (m)	2	105	100	106	101	94	93	95	102		89	92	86	101	61
	10	99	100	103	102	87	84	91	100		95	93	87	104	62
	20	107	107	93	92	100	103	108	100		104	107	97	93	65
	50	107	116	127	97	109	113	114	103		100	108	96	96	69
	75	102	99	105	96	112	106	93	109		117	91	87	114	67
	150	92	101	98	88	110	96	94	101		110	93	84	120	71

h) HL1203/62

	HL1203/62	¹³ C ₅ PFPeA	¹³ C ₂ PFHxA	¹³ C ₄ PFHpA	¹³ C ₄ PFOA	¹³ C ₅ PFNA	¹³ C ₂ PFDA	¹³ C ₂ PFUnDA	¹³ C ₂ PFDoDA		¹⁸ O ₂ PFHxS	¹³ C ₄ PFOS	d ₃ MeFOSAA	d ₅ EFOSAA	C ₈ FOSA
Depth (m)	3	111	115	119	100	110	94	109	109		111	104	98	100	60
	10	111	107	104	89	102	88	97	110		102	89	99	101	62
	20	115	105	115	94	104	96	105	106		103	90	95	99	62
	50	111	103	94	106	108	116	104	108		112	94	93	112	64
	75	114	108	97	103	108	116	104	103		104	102	90	108	60
	150	101	106	107	89	107	98	74	89		115	88	90	118	64
	300	95	103	108	94	109	94	97	99		115	91	91	122	62
	352	98	101	105	89	98	92	93	94		101	94	94	117	61

i) HL1203/72

	HL1203/72	¹³ C ₅ PFPeA	¹³ C ₂ PFHxA	¹³ C ₄ PFHpA	¹³ C ₄ PFOA	¹³ C ₅ PFNA	¹³ C ₂ PFDA	¹³ C ₂ PFUnDA	¹³ C ₂ PFDoDA		¹⁸ O ₂ PFHxS	¹³ C ₄ PFOS	d ₃ MeFOSAA	d ₅ EFOSAA	C ₈ FOSA
Depth (m)	3	102	100	92	100	79	81	82	82		109	80	95	95	65
	10	102	97	102	101	77	82	83	80		103	83	98	101	63
	22	96	91	94	93	86	89	93	97		109	90	101	103	68

j) HL1203/76

	HL1203/76	¹³ C ₅ PFPeA	¹³ C ₂ PFHxA	¹³ C ₄ PFHpA	¹³ C ₄ PFOA	¹³ C ₅ PFNA	¹³ C ₂ PFDA	¹³ C ₂ PFUnDA	¹³ C ₂ PFDoDA		¹⁸ O ₂ PFHxS	¹³ C ₄ PFOS	d ₃ MeFOSAA	d ₅ EFOSAA	C ₈ FOSA
Depth (m)	2	109	112	116	105	87	90	91	91		106	75	98	96	61
	10	102	105	105	104	76	78	88	92		113	74	103	99	63
	20	110	112	115	111	87	96	97	104		110	80	102	99	65
	47	107	113	92	112	84	90	90	100		124	82	103	98	67

k) HL1203/78

	HL1203/78	¹³ C ₅ PFPeA	¹³ C ₂ PFHxA	¹³ C ₄ PFHpA	¹³ C ₄ PFOA	¹³ C ₅ PFNA	¹³ C ₂ PFDA	¹³ C ₂ PFUnDA	¹³ C ₂ PFDoDA		¹⁸ O ₂ PFHxS	¹³ C ₄ PFOS	d ₃ MeFOSAA	d ₅ EFOSAA	C ₈ FOSA
Depth (m)	2	107	108	104	88	93	83	91	91		107	85	90	89	62
	29	100	105	97	87	93	98	95	97		110	81	101	96	65
	101	105	109	107	99	100	98	107	102		116	88	101	94	66
	202	90	106	100	87	93	87	104	88		109	82	99	94	68
	344	97	107	115	90	94	84	97	96		110	83	99	99	62

l) Ice station

	¹³ C ₅ PFPeA	¹³ C ₂ PFHxA	¹³ C ₄ PFHpA	¹³ C ₄ PFOA	¹³ C ₅ PFNA	¹³ C ₂ PFDA	¹³ C ₂ PFUnDA	¹³ C ₂ PFDoDA	¹⁸ O ₂ PFHxS	¹³ C ₄ PFOS	d ₅ MeFOSAA	d ₅ EFOSAA	C ₈ FOSA
PS80/224 Station 1 snow	119	101	124	112	86	98	92	91	112	115	98	89	71
PS80/224 Station 1 melt pond water	111	102	69	99	88	95	88	98	97	108	97	88	75
PS80/255 Station 3 melt pond water	115	102	81	107	96	94	108	119	110	106	97	95	67
PS80/323 Station 5 snow	110	105	98	113	99	94	106	118	105	104	95	93	68
PS80/360 Station 8 snow	112	105	122	94	92	99	96	103	105	99	93	105	70

Table S6a. Concentrations (pg/L) of detectable PFASs in the samples analyzed by MTM.

PS80/227 surface	PFHpA	PFOA	PFOS
ALFONSE	22	50	41
MTM	20	67	51
HL1203/70 - 4m	PFHpA	PFOA	PFOS
ALFONSE		29	25
MTM		43	30
HL1203/66 - 10m	PFHpA	PFOA	PFOS
ALFONSE		42	5
MTM		47	
HL1203/78 - 29m	PFHpA	PFOA	PFOS
ALFONSE	20	91	19
MTM		111	

Blank cell indicates sample below respective LOQs.

Table S6b. Relative standard deviation (%) of detectable PFASs between ALFONSE and MTM in the samples.

	PFHpA	PFOA	PFOS
PS80/227 surface	6	20	15
HL1203/70 - 4m		27	14
HL1203/66 - 10m		8	
HL1203/78 - 29m		14	

Table S6c. Recoveries (%) of PFOA and PFOS in the samples.

	PFOA	PFOS
PS80/227 surface	97	95
HL1203/70 - 4m	93	93
HL1203/66 - 10m	89	93
HL1203/78 - 29m	87	94

Recovery was calculated by comparing the peak area of the mass-labelled standards to those of the recovery standard (7H-PFH_A)

Table S7. PFAS concentrations (pg/L) in different samples collected from the Central Arctic (a)-(d), the Arctic shelf (e)-(k), and different ice stations (l) (see Table S2 for sample location) (value shown in the table were an average between duplicate extractions; blank cell indicate sample below corresponding LOQ: 5 pg/L for C6-C11 PFCAs, C4, C6, C8 PFSAs, MeFOSAA, EtFOSAA; 10pg/L for PFDoDA and PFDS; 20pg/L for FOSA)

a) PS80/364

	PS80/364	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EtFOSAA	FOSA
Depth (m)	PML	1	11						9		18				
	HL	10	17	16	9										
		50	26	32	64	20			21	22	17				
		75	22	35	49	21			20	17	14				
	AW	150													
		250													
		500													
	DW	1000													

b) PS80/275

	PS80/275	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EtFOSAA	FOSA
Depth (m)	PML	1	24		30	39		17	12		18				
	HL	10	37	17	44	19		5	18	9	10				
		50	20	17	43	12				16	10	13			
		75	8		9										
	AW	150							40						
		250													
	DW	500													
		1000													

c) PS80/227

	PS80/227	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EtFOSAA	FOSA
Depth (m)	PML	1	12	22	50	23			11	15	41				
		8			15	9									
	HL	50									10				
		75		23							11				
	AW	150									12				
		200									37				
		250									11				
		1000			13										

d) PS80/254

	PS80/254	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EfFOSAA	FOSA
Depth (m)	PML	1			14		11		15			26			
	10			15	9				16		19	27			
	50		15	37	14				18	14	47				
	75														
	150														
	200														
	250														
	500														

e) HL1203/70

	HL1203/70	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EfFOSAA	FOSA
Depth (m)	4			29	18	9		8			25				
	10		30	40	23	8					41				
	20			23	10						6				

f) HL1203/71

	HL1203/71	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EfFOSAA	FOSA
Depth (m)	3		10	22	14	6					20				
	10		23	50	18	6					13				
	20		18	84	16						17		7.2		

g) HL1203/66

	HL1203/66	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EfFOSAA	FOSA
Depth (m)	2		6	44	9				5	8		6.5			
	10			42	8					5		7.3			
	20			41	14					8		7.7			
	50		13	43	12					5		8.0			
	75		10	40	16					6		10.1			
	150			39						8					

h) HL1203/62

	HL1203/62	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA		PFBS	PFHxS	PFOS	PFDS		MeFOSAA	EfFOSAA		FOSA
Depth (m)																		
3		6	40	5						5	6	28			6.0			
10			26									27						
20			54	6							9	19						
50			40							6	5	7						
75			27	8														
150			34	7														
300	10		53	11														
352	15		43	17														

i) HL1203/72

	HL1203/72	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA		PFBS	PFHxS	PFOS	PFDS		MeFOSAA	EfFOSAA		FOSA
Depth (m)																		
3				29	15						5	10			5.0			
10				11	9							7						
22			17	65	17						5	14			7.1			

j) HL1203/76

	HL1203/76	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA		PFBS	PFHxS	PFOS	PFDS		MeFOSAA	EfFOSAA		FOSA
Depth (m)																		
2			8	41	12					6		7						
10			15	56	27	9						8			6.5			
20				42	26	5				5		21				9.7		
47				56	14					9		7			7.3			

k) HL1203/78

	HL1203/78	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA		PFBS	PFHxS	PFOS	PFDS		MeFOSAA	EfFOSAA		FOSA
Depth (m)																		
2				21	4						11				5			
29			20	91	8					9	8	19			21			
101				55	15							15			8			
202				52	14					11		11						
344				80	21							10						

1) Ice stations

	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA		PFBS	PFHxS	PFOS	PFDS		MeFOSAA	EfFOSAA		FOSA
PS80/224 Station 1 snow	44	14	72	33	33	21					34	11			36		
PS80/224 Station 1 melt pond water	16	39	57	85							34						23
PS80/255 Station 3 melt pond water	150	29	62	106	14	13					42						
PS80/323 Station 5 snow	109	49	294	253	142	92	88		18	343				36	19		156
PS80/360 Station 8 snow	26	25	91	61	49	45				43				9			20

Table S8. Range (pg/L) and detection frequency (%) of the thirteen detectable PFASs.

	PFHxS	PFOS	FOSA	EtFOSAA	MeFOSAA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
Range (pg/L)	<5-22	<5-343	<5-156	<5-36	<5-36	<5-150	<5-49	<5-294	<5-253	<5-142	<5-92	<5-88
Detection frequency (%)	12	48	4	6	25	150	49	54	49	14	6	2

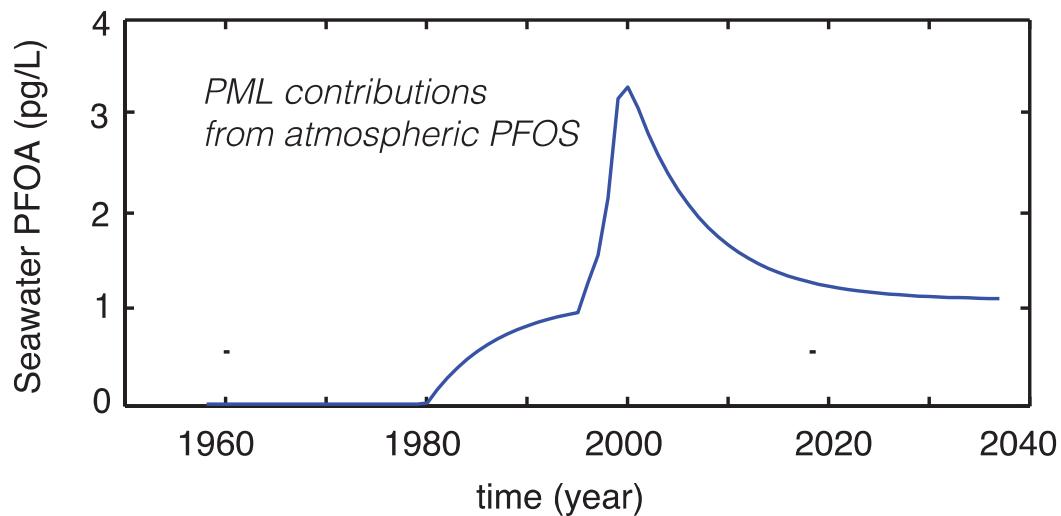
Table S9: Linear regression of PFAS concentrations in snow/meltwater versus latitude or longitude

	PFHxA 5	PFHpA 5	PFOA 5	PFNA 5	PFDA 4	PFUnDA 4	PFOS 5	EtFOSAA 3	FOSA 3
n									
R ² with latitude	0.42	0.20	0.15	0.33	0.09	0.03	0.23	0.31	0.56
R ² with longitude	0.74	0.34	0.50	0.70	0.32	0.30	0.54	0.17	0.92
Significance with longitude	0.06	0.30	0.18	0.08			0.16		

Table S10. Ratios of different pair PFCAs in snow and meltpond water samples.

	PFHxA/PFHpA	PFOA/PFNA	PFDA/PFUnDA
PS80/224 Station 1 snow	3.1	2.2	1.6
PS80/224 Station 1 melt pond water	0.4	0.7	
PS80/255 Station 3 melt pond water	5.1	0.6	1.0
PS80/323 Station 5 snow	2.2	1.2	1.5
PS80/360 Station 8 snow	1.1	1.5	1.1

Figure S3. Modeled PFOS concentration in the PML due to atmospheric deposition.



Literature cited in the SI

1. D'Eon, J. C.; Mabury, S. A. Production of perfluorinated carboxylic acids (PFCAs) from the biotransformation of polyfluoroalkyl phosphate surfactants (PAPS): exploring routes of human contamination. Environ. Sci. Technol. 2007, 41, 4799–4805.
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3. Eriksson, U.; Kärrman, A. World-Wide Indoor Exposure to Polyfluoroalkyl Phosphate Esters (PAPs) and other PFASs in Household Dust. Environ. Sci. Technol. 2015, 49, 14503–14511.