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

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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 projected to continue increasing to 2038.

TOC art
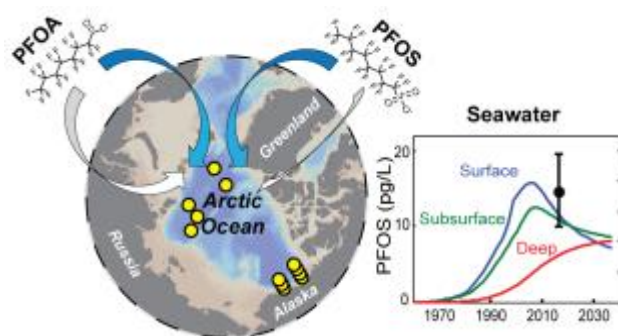
Introduction

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) - perfluorooctane sulfonate (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

64 varied across different locations, likely due to their complex sources and transport pathways

65 in the Arctic.[19]

66   Compared to the major ocean basins, the Arctic Ocean is smaller and has a much

67 greater continental shelf area (70%) and freshwater inputs.[23] It provides an oceanic pathway

68 between the Pacific and the Atlantic basins and plays an important role in the global

69 thermohaline circulation through its role in the Atlantic Meridional Overturning Circulation.[23]

70 Water of Atlantic origin enters the Arctic through the east side of the Fram Strait into the

71 Eurasian Basin or the Barents Sea (Figure 1). Water flows in a counter-clockwise direction in

72 the Nansen basin and then either to the Amundsen basin, or to the Makarov or Canada basins.

73 A minor influx of Pacific water enters the Canada Basin through the Bering Strait (Figure 1).

74 Seasonally varying fresh water input also contributes to Arctic surface waters and are thought

75 to be important for inputs of other contaminants.[24–26] The outflows of the Arctic Ocean are all

76 to the Atlantic through either the western side of the Fram Strait[24] or the complex channels of

77 the Canadian Archipelago.[27]

78   The entire Arctic Ocean is seasonally covered by ice.[28] Both the formation (reduced

79 wind-mixing) and melting of sea-ice (fresher surface layer) contribute towards ocean

80 stratification. Complex surface and subsurface dynamics of the Arctic water column mean

81 surface water PFAS measurements are not sufficient for understanding spatial and temporal

82 variability and mass accumulation. In addition, biological exposures extend beyond the

83 surface mixed layer for benthic and demersal food webs.

84   While information on PFASs in the Arctic is limited to surface waters, several studies

85 show the penetration of other organic contaminants to deeper waters. Sobek and Gustafsson[29]

86 demonstrated that concentrations of polychlorinated biphenyls (PCBs) were greatest in the

87 intermediate and deep water in samples collected in the early 2000s. A similar enrichment in

88 deeper waters was also confirmed for polybrominated diphenylethers (PBDEs) in the central

89 Arctic Ocean.[30] Previous work had already shown that the presence of

90 hexachlorocyclohexanes (HCHs) in deeper waters caused their export from the Arctic

91 Ocean.[31] Additional vertical profiles were reported for PCBs and PBDEs for the North

92 Atlantic, confirming their penetration to below 2000 m.[32] Yamashita et al.[22] also showed

93 detectable concentrations of several PFASs in the Subarctic Labrador Sea region at depths

94 greater than 3500 m in vertical profiles from 2004. For these profiles, surface water PFAS

95 concentrations were enriched relative to subsurface waters. The available evidence for these

96 organic contaminants implies that persistent compounds are present in deep waters at

97 concentrations that may exceed those measured in the surface water. A recent study has

98 shown accumulation of PCBs and PBDEs in deep-sea organisms.[33]

99   In the present investigation, water samples were collected and analyzed from different

100 depths of the water column at eight locations in the central Arctic (seawater, snow and

101 meltpond water), and seven stations on the Arctic shelf (Figure 1). The aims of this study

102 were to: (i) understand the spatial and vertical patterns of PFASs in Arctic Ocean seawater;

103 (ii) assess the roles of atmospheric and oceanic transport of PFASs into the Arctic Ocean; and

104 (iii) reconcile measured PFAS data with modeled results for different Arctic ocean water

105 masses based on a geochemical Arctic Ocean box model.

106

107 **Materials and Method**

108   Details of analytical standards and reagents used in the present study are given in the

109 Supporting Information (SI).

110   *Sample collection.* Sampling locations are shown in Figure 1. Coordinates and further

111 details of sample collection, including temperature and salinity data for all cruises are

112 provided in SI Tables S1 and Figure S1.

113   Water samples (1L/layer of water/location) were collected on two separate cruises in 2012

114   as follows: (1) four locations during expedition ARK-XXII/3 in the Central Arctic from

115   surface to bottom (up to 4220 m) by the research icebreaker *Polarstern* between August and

116   September 2012 (SI Tables S1i); and (2) seven locations on the Beaufort Chuckchi shelf from

117   surface to bottom (up to 385 m) by the United States Coast Guard icebreaker *Healy* in

118   October 2012 (SI Tables S1i). Snow and melt pond water samples were also collected in four

119   ice stations during the expedition ARK-XXII/3 (SI Table S1i). Details of the cruise reports

120   can be found elsewhere.[34,35]

121   *Analytical standards and reagents.* Potassium salts of perfluorobutane sulfonate (PFBS),

122   PFOS and $^{13}C_4$ PFOS; sodium salts of perfluorodecane sulfonate (PFDS), perfluorohexane

123   sulfonate (PFHxS) and $^{18}O_2$PFHxS, perfluorooctanesulfonamido acetate (FOSAA; *N*-methyl

124   and *N*-ethyl substituted: MeFOSAA, EtFOSAA), d_3MeFOSAA, d_5EtFOSAA,

125   perfluorooctanesulfonamide (FOSA), $^{13}C_8$ FOSA, perfluorohexanoate (PFHxA), $^{13}C_2$PFHxA,

126   perfluoroheptanoate (PFHpA), PFOA, $^{13}C_4$PFOA, perfluorononanoate (PFNA), $^{13}C_5$PFNA,

127   perfluorodecanoate (PFDA), $^{13}C_2$PFDA, perfluoroundecanoate (PFUnDA), $^{13}C_2$PFUnDA,

128   were obtained from the Wellington Laboratories (Guelph, ON).

129   *Chemical and Instrumental analyses.* Samples (seawater: 400 mL (duplicate), snow and

130   meltpond water: 200mL (single)) were extracted using a solid phase extraction (SPE)

131   cartridge (Strata-X-AW cartridge, Phenomenex, Torrence, CA) following the ISO 25101

132   method.[36] Details of the method are provided in the SI. Separation and quantification of

133   PFASs in seawater, snow and melt pond water samples were performed using an Acquity

134   ultra performance liquid chromatograph (UPLC) and a Xevo TQ-S tandem mass

135   spectrometer (MS/MS - Waters Corporation) operated in negative ionization mode with an

136   atmospheric electrospray interface. An Acquity BEH C18 column (2.1 × 75 mm, 1.7 μm, 100

137   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-labelled standards was used to quantify PFASs with

mass-labelled standards (SI Table S2). Internal calibration curves were constructed at 5, 10,

50, 100, 200, 500, 1000, 5000, and 10000 pg/mL with the addition of an internal mass-

labelled standard with the final concentration of 100 pg/mL. In the current investigation,

target PFASs included C_4-C_{10} PFSAs, C_5-C_{14} 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 pipette, pipette tips and falcon tubes) were tested for the presence of target PFASs

(<0.1pg/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, Torrence, 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) were 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 non-spike samples before extraction; mass-labelled standards were spiked into the LC vials before instrumental analysis. The recoveries were calculated by the difference between the measured valued in the spike and non-spike samples divided by the theoretical values X 100%; most of the target PFASs had the recoveries ranged from 85-106%, except 60% for FOSA (SI Table S3). The recoveries of the mass-labelled standards in the real samples (*n*=69) based on external calibration curve were 78-121%, except 65% for FOSA (SI Tables S4-5). 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 ± 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

188 PFOS, the model is forced by inputs from the Atlantic Ocean between 1958-2038 based on

189 the 3-D ocean circulation model developed by Zhang et al.[39] PFOS mass inflow is stratified

190 by depth based on seawater inflow for the surface, subsurface and deep Arctic seawater. We

191 do not include PFAS inputs from the Pacific Ocean since inflow of seawater is small relative

192 to the Atlantic Ocean and no data are available on temporal changes in PFAS inputs for the

193 Pacific. Atmospheric deposition is based on ice-core data from Young et al.[16] We present

194 model simulations forced by both the median (cumulatively: 2410 Mg) and low (842 Mg)

195 emissions scenarios for continental PFOS discharges to the North Atlantic from North

196 American and European wastewater and rivers reported by Zhang and co-workers[39] between

197 1958 and 2038.

198   For PFOA, we do not have a comparable 3-D simulation to resolve oceanic inflow at the

199 surface, subsurface and in deep waters. We therefore estimate only the contribution of

200 atmospheric deposition to surface water (PML) concentrations based on deposition rates

201 measured in the Devon Ice Cap from the Canadian High Arctic between 1993 and 2007.[15]

202 Deposition prior to 1993 was fixed at the lowest recorded value (7 ng/m^2/year). For recent

203 years we assumed two scenarios representing deposition that continues from 2007 values and

204 complete elimination. This allows us to estimate the relative contribution of atmospheric

205 inputs compared to oceanic inflow.

206

207 **Results and Discussion**

208   *PFAS concentrations and profiles.* In total, 69 samples were analyzed for 39 PFASs in

209 seawater, snow and melt pond water. Only thirteen PFASs (C6-C12 PFCAs; C6, 8, 10 PFSAs;

210 MeFOSAA and EtFOSAA, and FOSA) showed detectable concentrations (individual

211 compound range: <5 – 343 pg/L) (SI Table S7). Therefore, the following discussion will only

212 focus on these thirteen PFASs. Figure 2 and SI Tables S7a-d show that the detection of

213 PFASs in the four depth profiles was limited to the PML and halocline (150 m below the

214 surface), except for the North Barents Sea (PS80/227) where PFOS was detected down to 250

215 m below surface. The detection frequency and range (%, pg/L) of the 13 detectable PFASs are

216 provided in SI Table S8.

217   *PFASs in the Central Arctic Surface water.* Surface water concentrations of total PFASs

218 in the Central Arctic Ocean ranged from 11 – 174 pg/L. Previous investigations reported total

219 PFAS concentrations of 45-280 pg/L in surface water from the Greenland Sea[21] and the

220 average concentrations of PFOA and FOSA combined were 112 pg/L in the East Greenland

221 Arctic Ocean.[18] Average total PFAS concentrations were reported as 500±170 pg/L in surface

222 water of the Arctic Ocean[19] and 40-250 pg/L in the Canadian Arctic.[17] Results from this study

223 (average total PFAS: 98±73pg/L) were approximately 5-fold lower than previous

224 measurements of PFAS concentrations in Arctic Ocean surface waters.

225   *PFASs in the Arctic Ocean water column.* In the four vertical water column profiles, the

226 detection of PFAS was limited to the PML and halocline (150 m below the surface), except

227 for the North Barents Sea (PS80/227) where PFOS was detected down to 250 m below

228 surface. Among the four vertical profiles, maximum individual PFAS concentrations (pg/L)

229 were as follows: 50 (PFOA), 47 (PFOS), 40 (PFBS), 39 (PFNA), 37 (PFHxA), 35 (PFHpA),

230 27 (PFDS), 22 (PFHxS), and 17 (PFUnDA). The composition of PFASs varied with location

231 and depth, highlighting the combination of different sources (rivers, atmosphere, ocean

232 currents) and circulation of the Arctic. Similar composition profiles were only observed in

233 some layers of water columns (50 and 75 m below surface near the Pole – PS80/364 and 10

234 and 50 m below surface at the Amundsen basin - East of Gakkel Ridge – PS80/254). To better

235 understand the interplay between PFASs sources and mixing in the Arctic Ocean, we need to

236 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 run-off, 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

262   Amundsen Basin - East Gakkel Ridge (PS80/275). The presence of PFASs in the Atlantic

263   layer most likely reflects long-range oceanic transport, since pronounced vertical settling

264   would result in penetration to greater depths, as was previously demonstrated for PCBs.[29]

265   Prior work shows particle settling in the North Atlantic is negligible as a transport pathway

266   for PFASs compared to lateral ocean circulation.[32,39]

267   Yamashita et al. reported surface water concentrations of 160-338 pg/L for PFOA, 15-36

268   pg/L for PFNA, and 8.6-36 pg/L for PFOS in 2003.[20] In the Labrador Sea and North Atlantic

269   Ocean, they also detected PFOA at ~ 50 and 20 pg/L down to 3000 m. In the Atlantic layer in

270   the Arctic Ocean sampled here, though, only PFOS (11- 37 pg/L) and PFNA (13 pg/L) were

271   detected in the North Barents Sea (PS80/227). Unexpectedly PFOA, typically a major PFASs,

272   was not detected in this study above LOQ the (5 pg/L) in the waters deeper than 75 m. At the

273   locations further away from the Atlantic Ocean, such as Nansen Basin - West Gakkel Ridge

274   (PS80/254), Amundsen Basin - East Gakkel Ridge (PS80/275), and near the Pole (PS80/364),

275   no detectable PFASs were observed in the Atlantic layer. In summary, few PFASs were

276   detected (at low concentrations, < 50 pg/L, see Figure 2) in the Arctic Ocean water below the

277   PML and halocline, implying a combination of dilution and delayed transport into the deeper

278   Arctic water.

279   *Concentrations of PFASs in the water column along the Arctic shelf.* Concentrations of

280   PFASs in water samples collected along the Chuckchi Sea shelf at different depths from

281   nearshore to offshore are shown in Figure 3 and SI Tables 7e-k. PFOA was the dominant

282   PFAS in almost all samples (detection frequency: 100%; mean 44 ng/L, median 42 ng/L),

283   followed by PFOS (91%; mean 14 ng/L, median 10 ng/L) and PFNA (88%; mean and median

284   of 14 ng/L). Concentrations were in general comparable to those measured in the Central

285   Arctic Ocean. Different PFAS composition profiles were observed between the samples

286   collected along the Arctic shelf and the Arctic Ocean. One of the reasons might be the

287 complexity in water sources. The water sources of the Arctic Ocean are mainly Atlantic water

288 and sea ice melt, whereas the Arctic shelf represents a combination of Atlantic water, Pacific

289 water, sea ice melt and river run-off.[28] Several observations stand out: First, the ratios of

290 PFOA/PFNA in two different sampling routes from nearshore to offshore increased (Stations

291 HLY1203/70 and 71: 1.6, Station HLY1203/66: 4.9, Station HLY1203/62: 7.9; and Station

292 HLY1203/72: 1.9, Station HLY1203/76: 3.6, Station HLY1203/78: 5.3). Second, PFDA was

293 only detected in samples collected from nearshore stations (HLY1203/70 and 71). The

294 decreasing contribution of PFNA to PFOA from nearshore to offshore areas and detection of

295 PFDA limited to nearshore area suggested these sources might come from river run-off to the

296 nearshore area, and then diluted when getting into offshore area. Seasonally varying fresh

297 water inputs are thought to be important sources of other contaminants to the Arctic surface

298 waters.[24–26] Third, MeFOSAA was detected in water sample from the Arctic shelf. MeFOSAA

299 is an oxidation product of MeFOSE, which was primarily incorporated into polymeric

300 materials as a surface treatment for products like carpets and textiles.[45,46] It is also believed to

301 be a PFOS precursor. In contrast to the anionic nature and persistence of PFCAs and PFSAs,

302 MeFOSE is a neutral and volatile compound; it is expected to present in the atmosphere and

303 will ultimately degrade to PFOS under environmental or biological condition.[45] An earlier

304 study also showed the detection of MeFOSE in the Arctic atmosphere.[47] Fourth, the PFAS

305 composition profiles were quite different at the water layers between 50 m (PFOA: 69%,

306 PFBS: 10%, PFHxS: 10%; PFOS: 12%) and 76 m (PFOA: 78%; PFNA: 22%) depth at

307 Station HLY1203/62. Different composition profiles of PFAS between the nearshore and

308 offshore samples may be explained by different sources (river run-off at the near shore) and

309 the dilution effect by ocean water. The different PFAS compositions between the surface and

310 bottom waters may be explained partly by the contribution of ice melt in the surface (changes

311 in salinity from the surface to the bottom).

312   *Concentrations of PFASs in melt pond water and snow.* Samples were collected from

313   mostly first year ice, integrating PFAS deposition from up to one year.[48] More PFASs

314   (PFUnDA, FOSA, and EtFOSAA) were detected in melt pond water and snow samples

315   compared to seawater from the Arctic shelf and central basin (SI Table S7l). Snow samples

316   showed detectable concentrations of PFCAs (C6-C12), PFSAs (C8 and C10), MeFOSAA,

317   EtFOSAA and FOSA (Figure 4). Various PFCAs were detected at concentrations greater than

318   100 pg/L, including PFHxA, PFOA, PFNA, PFDA, PFOS and FOSA. Total PFAS

319   concentrations (403 ±405pg/L) in the present investigation were much lower than the snow

320   samples collected from Japan and the U.S. (concentrations in the ng/L range),[49] and similar or

321   greater to previously reported for the Devon ice cap[15,16] and surface snow from glacier in

322   Svalbard, Norway.[50] Relatively high total PFASs were observed at Station 5 - PS80/323

323   (1600 pg/L; Station 1: 298 pg/L and Station 8: 368 pg/L), which was at similar to

324   concentrations in snow samples collected downstream of Svalbard, Norway (1470 pg/L).[50]

325   Spatial trends might imply that proximity to Eurasian continental atmospheric emissions were

326   a main source of elevated PFASs in snow (see SI Table S9).

327   Snow has been suggested to be an effective scavenger of PFAS in the atmosphere;

328   enhanced PFAS concentrations in snow are interpreted as evidence for a primary source of

329   PFAA to the Arctic via atmospheric oxidation of volatile precursors.[16] Atmospheric oxidation

330   of volatile FTOHs under low NOx conditions may form PFCAs of different chain lengths,[13,51]

331   whereas atmospheric oxidation of volatile perfluorooctane sulfonamidoethanols (e.g., FOSE)

332   may result in different perfluorooctane sulfonamido derivatives as well as PFOS.[52,53]

333   Intermediate compounds such as saturated and unsaturated fluorotelomer acids

334   (FTCAA/FTUCAs: 6:2, 8:2, and 10:2) were suggested to be the connection between the

335   volatile fluorotelomer precursors and PFCAs; they were below their respective detection

336   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 imply 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 11-36 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

362 modeled value (range: 5-15 pg/L) is slightly higher than observations (<5 pg/L), suggesting

363 the lower emissions scenario is more consistent with observed concentrations. Despite

364 relatively low concentrations in deep Arctic waters due to dilution and mixing, the majority of

365 the PFOS mass (74%, Figure 5 top panel) is still expected in this region of water column.

366 Only 4% of the modeled PFOS mass is found in the PML and 22% in the mid-depth/halocline

367 waters according to this model calculation. Although PFOS concentrations in surface and

368 mid-depth waters peaked in the early 2000s, concentrations in deeper waters are still

369 increasing based on model simulations and thus may be detectable in future ocean campaigns.

370   For PFOA, modeled mean concentrations in the PML from atmospheric deposition are

371 estimated to be between 11 and 19 pg/L, depending on assumptions related to recent PFOA

372 inputs (Figure 5 bottom panel), compared to the mean observed concentration in surface

373 waters of 32 ± 15 pg/L. While the PFOS burden in Arctic seawater is accounted for mainly by

374 North Atlantic inputs, modeling results for PFOA suggest approximately 34-59% of surface

375 water concentrations are from atmospheric inputs. These results are consistent with a variety

376 of studies that show atmospheric transport and degradation of PFOA precursors is a more

377 important source to the global ocean than for PFOS where direct discharges are estimated to

378 comprise more than 95% of total inputs.[57–59]

379   *Mass budget of PFASs in the Arctic Ocean.* We derived mass budgets for PFASs in

380 sampling regions of the Arctic basin, including the central Arctic Ocean, the

381 Beaufort/Chuckhi Sea and the ice layer (Table 1). Combining volumes and measured PFAS

382 concentrations resulted in the following PFAS budgets (in Mg) for the surface Central Arctic

383 Ocean: PFOA 8.6 ± 6.8; PFOS 4.8 ± 4.4; PFNA 4.2 ± 3.4; PFHpA 3.9 ± 3.8; PFHxA $3.6 \pm$

384 3.8; PFBS 3.6 ± 2.4, and PFHxS 2.3 ± 2.1 Mg. In total, there are 31 ± 26 Mg of PFASs present

385 in the upper Arctic Ocean water (Table 1). We note that the amount of PFOA and PFOS at ½

386 LOQ (2.5 pg/L) in the Atlantic water layer down to 1000 m would add ~10 Mg per congener.

387   For the Beaufort and Chuckhi Seas, the total PFAS budget amounted to 4.9 Mg,

388 dominated by PFOA (almost 3 Mg), with 900 kg from PFNA and almost 1 Mg from PFOS

389 (Table 1). In August 2012, a total of 4.1×10^6 km^2 were covered by ice, most of which was thin

390 first year ice.[60] Assuming a 1m thickness (a rough estimation) across the Arctic, and average

391 PFAS concentrations derived from snow and meltwater resulted in a stock of around 1.8 Mg

392 of total PFASs in ice, dominated by > 400 kg each from PFNA, PFOA and PFOS.

393   Overall, the PFAS budgets in the Arctic Ocean derived here are lower than modeled

394 masses for PFOS shown in Figure 5 due to different regions of the Arctic considered, and in

395 comparison to mass budgets present in the North Atlantic (200 Mg in surface layer).[61]

396 Overall, we find the PML and halocline in the Arctic Ocean already contain more PFASs than

397 PCBs (2 Mg), due to the much greater dissolved PFAS concentrations. Comparably greater

398 proportions of PCB inputs have reached the deeper water masses, where an estimated 35 Mg

399 are contained.[29]

400   *Environmental Implications.* Both atmospheric and oceanic transport of PFASs have

401 been proposed as important long-range transport mechanisms.[12,14] Detection of PFAS in snow

402 samples in this study suggests the ongoing importance of atmospheric deposition for some

403 PFCAs, which may come from atmospheric oxidation of volatile precursor compounds or

404 particles. We report low concentrations of PFASs in the Atlantic water layer of the Arctic

405 Ocean, which is consistent with mixing and dilution of inputs from the Atlantic Ocean. Yet

406 PFAS concentrations in deeper water masses are predicted to increase over time (Figure 5). A

407 recent investigation calculated vertical transport of PFASs based on an estimate of the settling

408 of organic matter and measured concentrations of PFASs bound to particles. The authors

409 suggesting the biological pump a sink of some PFASs.[62] Our observations of limited

410 penetration of PFASs at depth suggests this flux must be minimal for most areas of the Arctic.

411 Results for PFASs contrast vertical profiles of PCBs and PBDEs in the Arctic[29,30] indicating

412 vertical transport processes are weaker and potentially irrelevant for PFASs, as suggested by

413 some modeling work.[39]

414   With the implementation of Stockholm Convention and PFOA Stewardship program,

415 the emission of PFOS-based and PFOA and higher-chain length PFCAs should be greatly

416 reduced and the inputs of these PFASs are expected to decrease. By contrast, short-chain

417 PFASs have been introduced into market as replacement and their environmental levels are

418 expected to increase. A recent study showed increased contribution of PFBS to PFOS in

419 marine mammals during the period 2002 to 2012 in South China.[63] Although analytical

420 methods are available for measuring some short-chain PFASs (C4-C7 PFAAs), more sensitive

421 chromatographic techniques should be developed to measure low levels in the samples for

422 some 'ultra-short'-chain PFAAs (e.g., C2 and C3). Long term PFAS monitoring in snow

423 samples from different ice stations may be useful to determine the input of PFAS via

424 atmospheric deposition to the Arctic.

425

426 **Supporting Information.** Details on the sampling, locations and auxiliary measurements,

427 PFASs' chemical analysis, concentrations and QA/QC measures. This material is available free

428 of charge via the Internet at http://pubs.acs.org.

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Table 1: Average concentrations (pg/L), volumes (km³) for the surface water of the Central Arctic and Beaufort/Chuckchi Seas and corresponding mass budgets (kg) for PFASs

Central Arctic		PFHxA	PFHpA	PFOA	PFNA	PFBS	PFHxS	PFOS	sum PFASs
Volume of surface ocean (km³)	Average conc[a]	11	12	25	13	11	7	14	
337000	S.D.	11	11	20	10	7	6	13	
	mass (kg)	**3590**	**3940**	**8550**	**4230**	**3590**	**2330**	**4850**	**31100**
	S.D.	3790	3760	6810	3380	2430	2190	4470	26800
Beaufort/ Chukchi	Average conc[b]			42	13			14	79
Volume (km³)	S.D.			19	7			9	32
71700	**mass (kg)**			**3030**	**899**			**982**	**4910**
	S.D.			1329	476			671	2480
Snow/meltpond water	Average conc	69	31	115	107		6	99	
Volume (km³)	S.D.	58	13	101	86		7	136	
4100	**mass (kg)**	**283**	**127**	**472**	**439**		**25**	**406**	**1750**
	S.D.	**238**	**53**	414	353		29	558	1640

[a]Average concentrations of locations PS80/275, PS80/254, PS80/364 and PS80/227 up to the depth of 75m from surface; [b]Average 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; S.D. denotes standard deviation of the average values.

Figure 1. Map of stations occupied for this study. Sea-ice and melt-ponds 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*. (*Red and black lines indicate circulation of respective intermediate and deep waters of Atlantic origin; green lines indicate major freshwater input by rives; yellow lines indicate the Pacific water flux through Bering Strait. The map was obtained from Ocean Data View*)
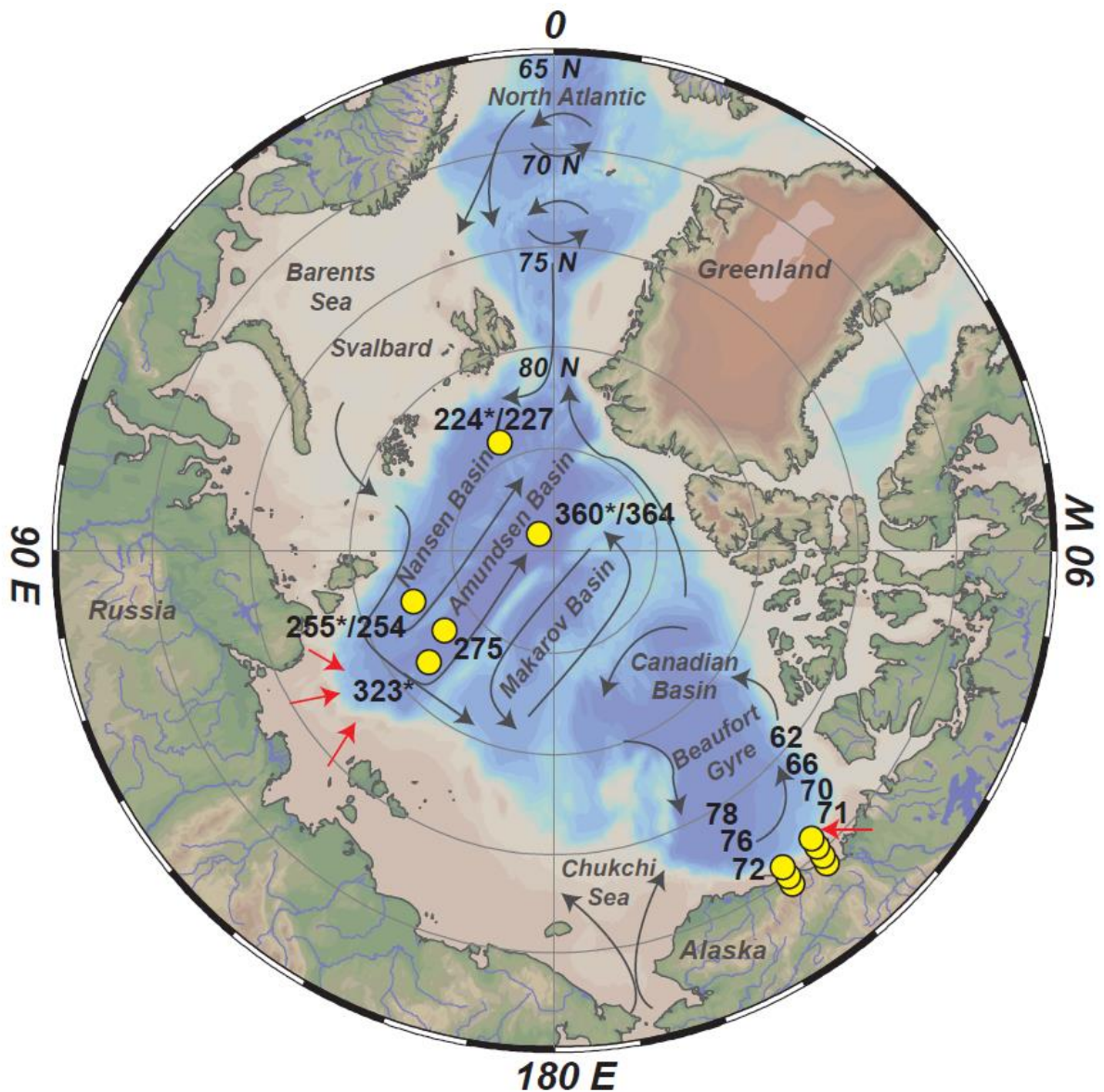
Figure 2. Total PFAS concentration (pg/L), composition (%) and temperature (T, in °C; show in black dots and trends in black line) in water samples from the Arctic Ocean. (Total PFAS concentration is the sum of detectable PFASs; open circle indicates sample below LOQ; zero was assigned for calculating total PFAS when the samples were found below LOQ).
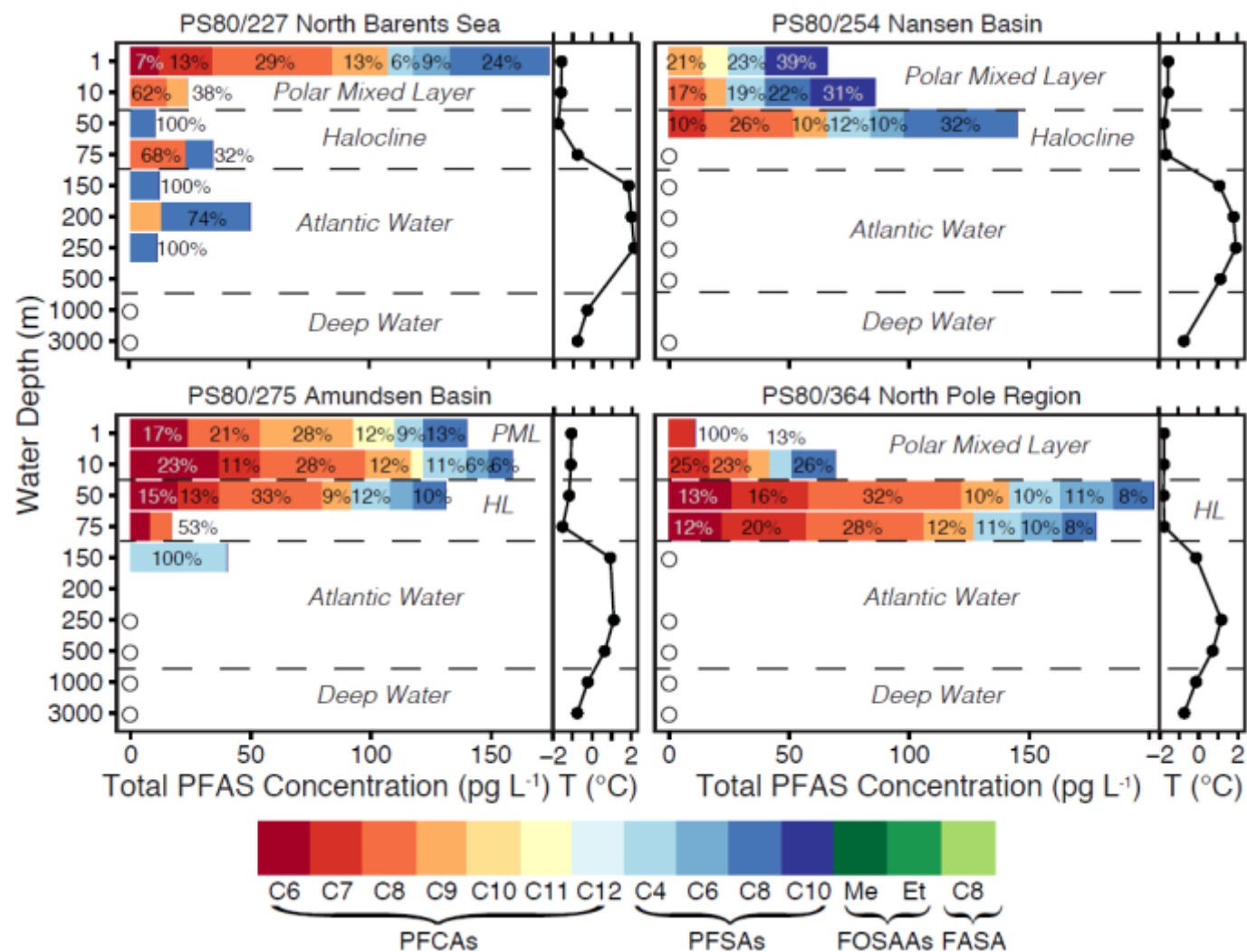
Figure 3. Total PFAS concentration (pg/L) and composition in water samples from the Arctic shelf: (A) transect at 144 °W longitude; (b) transect at 139 °W longitude (see Figure 1). (Total PFAS concentration is the sum of detectable PFASs; zero was assigned for calculating total PFAS when the samples were found below LOQ)
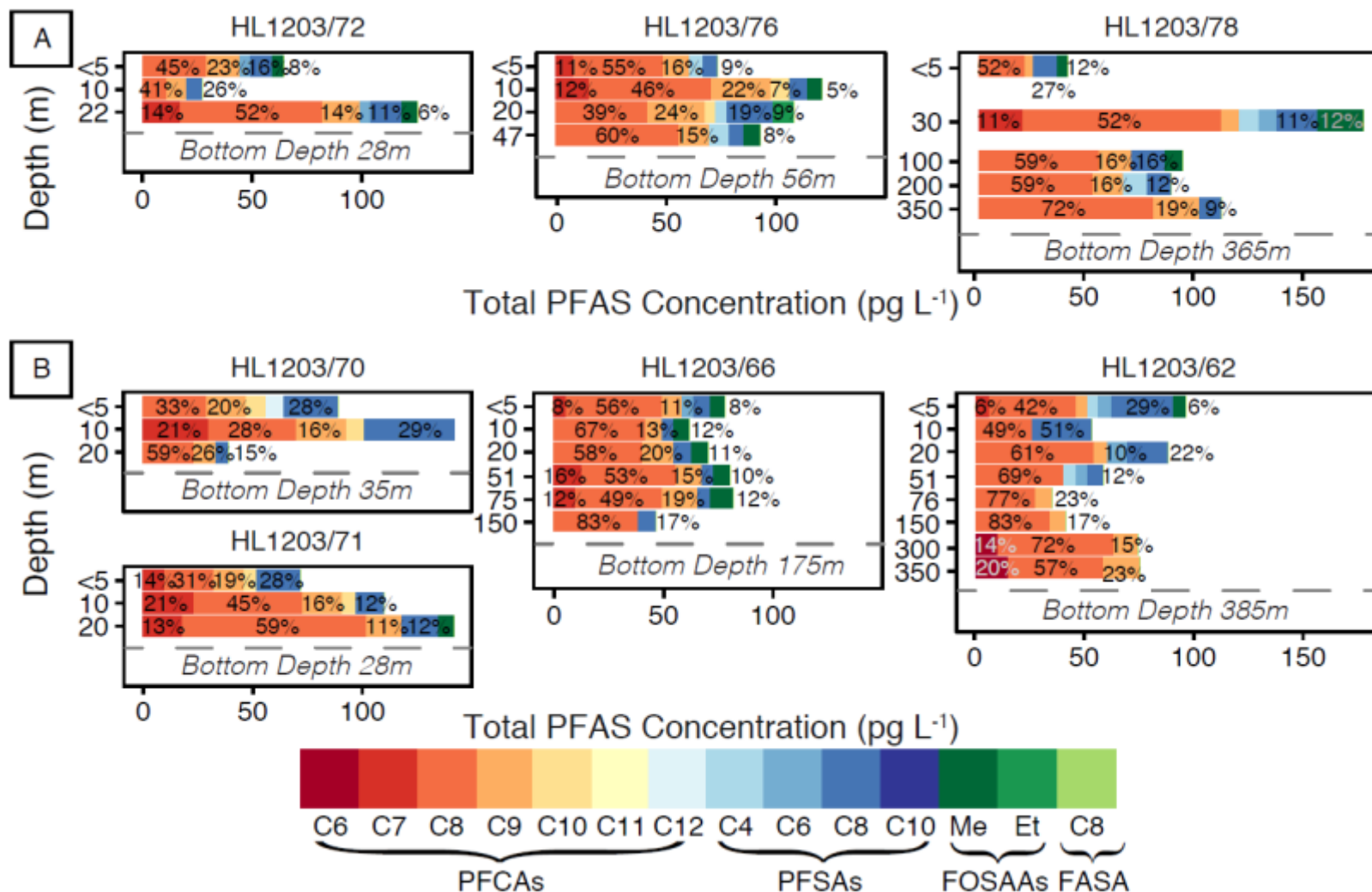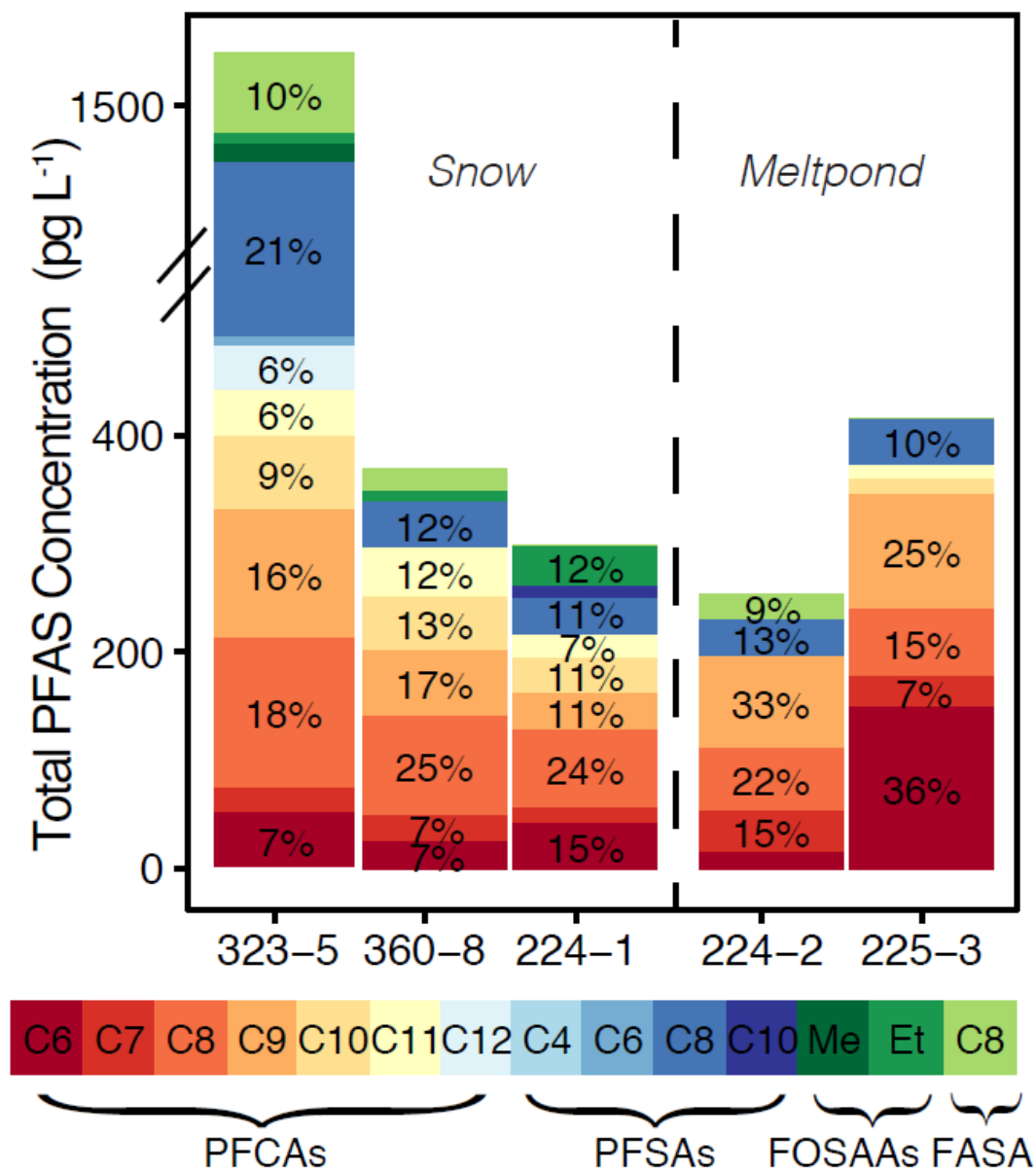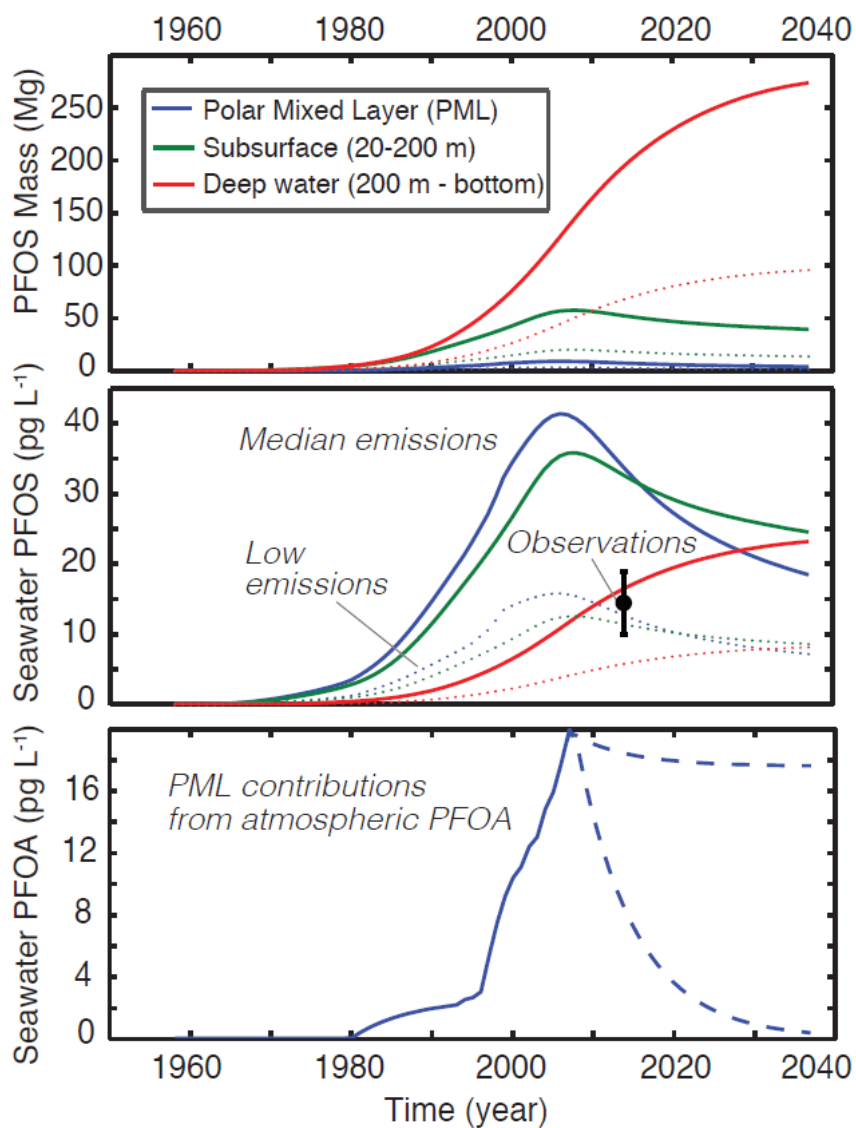
Figure 4. Concentrations and composition of PFAS in snow and meltpond water samples collected from the ice station in the Arctic (see Figure 1 for locations)

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

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