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1 **Poly- and Perfluoroalkyl Substances in Seawater and Plankton from the**
2 **Northwestern Atlantic Margin**

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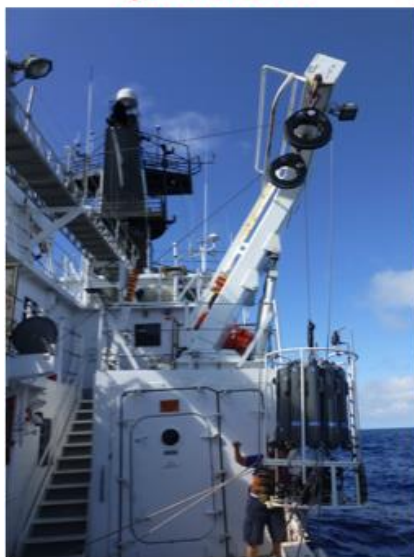
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12 TOC Art

R/V Endeavor



Northwestern Atlantic Margin



PFAS



13

14 **Abstract**

15 The ocean is thought to be the terminal sink for poly- and perfluoroalkyl substances (PFAS) that
16 have been produced and released in large quantities for more than 60 years. Regulatory actions
17 have curbed production of legacy compounds such as perfluorooctane sulfonate (PFOS) and
18 perfluorooctanoic acid (PFOA) but impacts of regulations on PFAS releases to the marine
19 environment are poorly understood. Here we report new data for 21 targeted PFAS in seawater
20 and plankton from the coast, shelf and slope of the Northwestern Atlantic Ocean. We find strong
21 inverse correlations between salinity and concentrations of most PFAS, indicating ongoing
22 continental discharges are the major source to the marine environment. For legacy PFAS such as
23 PFOS and PFOA, a comparison of inland and offshore measurements from the same year (2014)
24 suggests there are ongoing releases to the marine environment from sources such as submarine
25 groundwater discharges. Vertical transport of most PFAS associated with settling particles from
26 the surface 10 m to deeper waters is small compared to advective transport except for
27 perfluorodecanoic acid: PFDA (35% of vertical flux) and precursor compounds to PFOS (up to
28 86%). We find higher than expected bioaccumulation factors ($BAFs = C_{plankton}/C_{water}$) for
29 perfluorinated carboxylic acids (PFCAs) with five and six carbons ($\log BAFs = 2.9-3.4$) and
30 linear PFOS ($\log BAF = 2.6-4.3$) in marine plankton compared to PFCAs with 7-11 carbons. We
31 postulate that this reflects additional contributions from precursor compounds. Known precursor
32 compounds detected in this study have among the highest BAFs ($\log BAFs > 3.0$) for all PFAS
33 in this study, suggesting additional research on the bioaccumulation potential of unknown
34 organofluorine compounds is urgently needed.

35 **Introduction**

36 Poly- and perfluoroalkyl substances (PFAS) are a class of more than 4700 anthropogenic
37 chemicals that have been widely produced since the 1950s for diverse commercial and industrial
38 applications.¹⁻³ Human exposures to PFAS have been associated with adverse health effects such
39 as immune suppression and metabolic disruption.⁴ Seafood consumption is a major pathway for
40 PFAS exposure, accounting for 86% of mean chronic adult exposure to perfluorooctane
41 sulfonate (PFOS) according to the 2018 review by the European Food Safety Authority.^{5,6} PFAS
42 concentrations in seawater and marine plankton drive accumulation in marine food webs.^{7,8} Prior
43 work has examined the distribution and composition of PFAS in seawater from different
44 regions.⁸⁻¹⁶ However, there is still limited understanding of the how temporal shifts in sources
45 and biogeochemical processes affect uptake and accumulation of PFAS at the base of marine
46 food webs.^{8,17}

47 Regulatory actions targeting legacy PFAS such as PFOS have led to shifts chemical
48 production toward PFAS with shorter carbon chains and polyfluoroalkyl compounds.¹⁸ PFOS
49 and its precursors were voluntarily phased out by the main global manufacturer between 2000-
50 2002¹⁹ and the stewardship program by the US Environmental Protection Agency (US EPA) for
51 perfluorooctanoic acid (PFOA) has been very successful at reducing chemical production and
52 environmental releases.²⁰ However, many PFAS are not known to degrade²¹ and the ocean is
53 thought to be the terminal sink following riverine transport through terrestrial ecosystems.²²⁻²⁴
54 Understanding the persistence of historical PFAS releases to the marine environment is thus
55 important for characterizing exposure risks for wildlife and seafood consumers.

56 Prior modeling work^{1,23,25} has aimed to better understand PFAS transport and
57 accumulation over large spatial and temporal scales. Given a lack of observational constraints,

58 most modeling simulations have assumed transport of PFAS from terrestrial ecosystems to the
59 ocean generally occurs within a year (Table S5)²³ or that mixing with seawater occurs
60 instantaneously following continental releases.^{26,27} This assumption limits the potential lag time
61 between phase out of contamination sources and changes in inputs to marine regions. However,
62 ongoing releases from historical stockpiles and PFAS contaminated groundwater, widely
63 discussed in the context of drinking water, may result in delayed transport to ocean margins
64 through rivers and submarine groundwater discharges.^{28,29} Atmospheric transport of precursor
65 compounds that degrade into more stable end products is thought to be an important transport
66 mechanism for some coastal regions.^{12,30,31} Contemporary measurements of PFOS concentrations
67 and composition in coastal and offshore regions are needed to provide insight into such sources.

68 Most traditional persistent organic pollutants (POPs) are hydrophobic and partition
69 readily to suspended particles in aquatic ecosystems. Settling and burial of these particles
70 provides an efficient removal mechanism for such compounds.³²⁻³⁴ By contrast, many PFAS are
71 ionized in the aqueous environment and thus more hydrophilic and not volatile.³⁵ Prior work has
72 suggested that settling particles may still provide a significant removal pathway for PFAS in
73 marine ecosystems.⁸ By contrast, the modeling work of Zhang et al.²³ suggests vertical advection
74 is the predominant pathway for PFOS to reach the deep North Atlantic Ocean and particle
75 settling accounts for less than 1% of the PFOS removal from the surface ocean. Additional data
76 on concentrations of long and short chain PFAS in marine plankton are needed to support such
77 inferences.

78 The main objective of this work is to better understand factors affecting the distribution
79 and abundance of PFAS in seawater and marine plankton from the ocean margin. We present
80 new data on a suite of PFAS measured in samples collected from coastal/shelf and slope regions

81 of the Northwestern Atlantic Ocean. We use these data to better understand: (1) the significance
82 of continental discharges of freshwater as an ongoing source of legacy and new PFAS to the
83 marine environment, (2) processes affecting the vertical distribution of PFAS in the marine water
84 column, and (3) accumulation of PFAS at the base of the marine food web.

85 **Methods**

86 *Sample collection*

87 We collected surface (1-5 m depth) and subsurface (6-250 m) seawater samples from 21
88 coastal/shelf and slope stations using a CTD-Niskin bottle rosette array (SBE 911+, Sea-Bird
89 Electronics) on board the R/V Endeavor between August 23-28, 2014. Sites occupied were
90 located in the Northwestern Atlantic Ocean between Rhode Island Sound and the Eastern Shore
91 of Virginia (41.43°N, 71.42°W – 36.55°N, 75.85°W, Figure 1, Table S1). This region is part of
92 the Mid-Atlantic Basin and receives freshwater inputs from four major river systems (Hudson,
93 Delaware, Susquehanna and Potomac, Figure 1). More than 60 million people reside within the
94 watersheds of these rivers (approximately 20% of the US population). Sampling depths were
95 selected based on *in situ* CTD measurements of the vertical profiles of temperature, salinity and
96 Chl-a. Generally, we obtained one sample 2 m above the seafloor and one sample at the depth
97 where temperature, salinity and/or Chl-a showed substantial variation.

98 Sample bottles (1L high-density polyethylene) were rinsed three times with methanol, air
99 dried in a clean laboratory, and rinsed three times with seawater in the field before sampling.
100 Salinity, temperature and chlorophyll a were also measured at each station using a CTD device
101 on board (Table S1). Plankton were collected at selected stations by dragging a net (1 m²
102 opening, 335 µm mesh) at 1 m below the ocean surface for approximately 5 minutes (stations 1,

103 6, 7, 10, 11, 14, and 15 on Figure 1). Samples were washed off the net with seawater into an
104 HDPE jar (1 L). All samples were stored at -20°C onboard and in the laboratory before analysis
105 in 2016.

106 *PFAS Extraction and Analysis*

107 Seawater samples were extracted following the method by Taniyasu et. al.³⁶ Before
108 extraction, each sample was thawed to room temperature, spiked with 50 μL of $0.02 \text{ ng } \mu\text{L}^{-1}$
109 mass labeled PFAS mixture (Wellington; Guelph, Canada) as internal standards and equilibrated
110 overnight. Weak ion exchange SPE cartridges (Waters Oasis Wax, 6 mL, 150 mg sorbent)
111 conditioned by sequentially eluting with 5 mL, 0.1% NH_4OH in methanol, 5 mL methanol, and 5
112 mL milli-Q water were used to extract and concentrate PFAS in 1-litre bulk seawater. Samples
113 were shaken vigorously for homogenization and loaded onto the SPE cartridges with a flow rate
114 of 2 drops per second. After sample loading, each bottle was rinsed with 20 mL milli-Q water
115 and loaded to the SPE cartridge. The SPE cartridges were then washed with 5 mL 25 mM
116 sodium acetate buffer before being eluted with 5 mL methanol and 5 mL of 0.1% NH_4OH in
117 methanol to a 15 mL polypropylene centrifuge tube (Corning). The extracts were concentrated to
118 0.5 mL using a ZIPVAP nitrogen evaporator, transferred to 1.5 mL polypropylene autosampler
119 vials, and mixed with 0.5 mL milli-Q water before instrumental analysis.

120 Plankton samples were first separated from the liquid phase via centrifugation. Each
121 unfiltered sample was transferred to a 50 mL polypropylene centrifuge tube and centrifuged at
122 6000 rpm for 10 min. The supernatant liquid was removed and the procedure repeated until all
123 plankton were separated. Wet weights (ww) and dry weights after freeze drying overnight were
124 recorded. For each plankton sample, approximately 2 g ww equivalent was placed in a 15
125 polypropylene centrifuge tube and spiked with 50 μL of $0.02 \text{ ng } \mu\text{L}^{-1}$ mass labeled PFAS mixture

126 as internal standards (Wellington; Guelph, Canada, Table S2). Each sample was extracted twice
127 by mixing with 4 mL 0.25 M sodium carbonate, 0.5 mL 0.5 M tetra-butyl ammonium solution
128 (pH =10) and 5 mL methyl-tert-butly ether (MBTE) on a horizontal mixer at 250 rpm for 30 min.
129 The MBTE supernatants (10 mL) from the two extractions were combined and the solvent was
130 further reduced to 0.5 mL methanol using a ZIPVAP nitrogen evaporator. The extract was
131 transferred to a 1.5 mL polypropylene autosampler vial and mixed with 0.5 mL milli-Q water
132 before instrumental analysis.

133 Sample extracts were analyzed for 21 PFAS (Table S2 provides their full names and
134 abbreviations) using an Agilent 6460 LC-MS/MS system equipped with an Agilent 1290 Infinity
135 Flex Cube online-SPE. Each 300 μ L extract was loaded into an Agilent Zorbax SB-Aq
136 (4.6 \times 12.5mm; 5 μ m) online SPE column and eluted with 0.85 mL 0.1% (v:v) formic acid at a
137 flow rate of 1 mL min⁻¹. Analytes from the SPE column were loaded to an Agilent Poroshell 120
138 EC-C18 (3.0 \times 50mm; 2.7 μ m) reverse phase HPLC column using ammonium acetate (2 mM) in
139 methanol and water as the mobile phase. At a flow rate of 0.5 mL min⁻¹, the elution gradient was
140 linearly increased from 3% methanol to 60% for 7 minutes, held for 1 minute, then linearly
141 increased to 100% methanol for 3 min, which was maintained until the end of the sample run (14
142 min).

143 At the LC-MS interface, the capillary voltage was set at -3.8 kV and nitrogen nebulizer
144 gas was set at 45 psi and 13 L min⁻¹. Analytes were introduced to the tandem mass spectrometer
145 after being ionized with an electrospray ionization source operated in negative ion mode at 300
146 °C. The dynamic multiple reaction monitoring mode (5.0 grade N₂ as the collision gas) was used
147 for data acquisition. To eliminate any potential carry-over, methanol was injected and passed
148 through the system after every sample (or calibration standard).

149 Branched isomers for PFOA and PFOS were quantified using calibration standards for
150 the linear isomers, assuming the same instrumental response factor. For PFAS with detection
151 frequencies of greater than 70% (Table S3), we include non-detects in statistical analyses using
152 the Robust Regression on Order Statistics approach for censored log-normally distributed
153 environmental data, as described by Helsel.³⁷ Individual sample concentrations reported here
154 represent direct measurements. Other PFAS with lower than 70% detection frequencies were not
155 considered in statistical data interpretations.

156 *Quality Assurance*

157 To minimize blank concentrations during instrumental analysis, we replaced all Teflon
158 tubing with stainless steel, as described in previous work.^{22,29} A guard column was installed
159 between the mobile phases and online SPE column to removal potential contamination in the
160 solvent. At least one negative control (field or procedural blank) and one positive control (spiked
161 with 2 ng of the 21 PFAS in 500 mL water) were included in each extraction batch. Whole
162 method recoveries tested using the positive controls were 62-117%, which is comparable to
163 recoveries reported by previous studies.^{36,38,39} Potential analyte loss during sample preparation
164 was corrected using internal standards spiked prior to sample extraction. The limit of detection
165 (LOD, Figure 2) was defined as equivalent to the blank plus the concentration corresponding to a
166 signal-to-noise ratio of three. Duplicate samples were taken at sites 3 (20 m), 4 (21 m), 7 (2 m),
167 13 (3 m), and 21(43 m) and the relative difference between duplicates was 20±15%. Stations
168 with duplicate samples are reported as averaged values. Five field blanks (1L HPLC grade water
169 added to the CTD tube and then transferred to the sampling bottle), prepared following the same
170 sample preparation procedures as described above, were all below instrument detection limits.

171 **Results and Discussion**

172 ***PFAS detection, and concentrations in seawater***

173 Eight of the targeted 21 PFAS (PFBS, PFHxS, PFOS, PFHxA, PFHpA, PFOA, PFNA
174 and PFDA) were detected in over 70% of the surface seawater samples (Table S3). The
175 remaining 13 PFAS were detected in less than 40% of all the samples. Summed concentrations
176 of the eight frequently detected PFAS (Σ_8 PFAS) were <660-4070 pg L⁻¹ in surface seawater
177 samples and <470-3970 pg L⁻¹ in subsurface samples. The most abundant PFAS in surface and
178 subsurface seawater were PFOS (linear + branched: <110-910 pg L⁻¹), PFHxA (<155-1000 pg
179 L⁻¹) and PFOA (linear + branched: <93-900 pg L⁻¹) (Figure 2, Table S3). In all the 20 surface
180 seawater samples collected in this study, PFOS (linear + branched) exceeded the European
181 environmental quality standard (130 pg L⁻¹, based on annual average exposure).⁴⁰

182 The highest concentration of Σ_8 PFAS in both surface and subsurface seawater was found
183 at Station 11 near Delaware Bay (Figure 1). Surface seawater from Station 11 had the highest
184 concentrations of PFOS (830 pg L⁻¹), and PFCAs (PFHxA: 1000, PFHpA: 330, PFOA: 940,
185 PFNA: 550, PFDA: 120 pg L⁻¹). The highest surface seawater concentrations of PFBS (180 pg
186 L⁻¹) and PFHxS (240 pg L⁻¹) were found Station 7, near New Jersey (Figure 1). Both of the high
187 concentration sites are adjacent to highly populated coastal watersheds that host diverse
188 consumer and industrial PFAS uses.²³

189 Coastal/shelf stations (1-15) had significantly higher ($p<0.05$) PFAS concentrations than
190 slope stations (16-21) based on a one-tailed t-test for log-transformed concentrations of each
191 detected PFAS in surface and subsurface seawater (Figure 2, Table S4). At the coastal/shelf
192 stations, surface concentrations of PFBS (geometric mean: 45 pg L⁻¹), PFHxS (130 pg L⁻¹), and
193 PFOA (370 pg L⁻¹) were significantly higher than subsurface samples (PFBS: 35, PFHxS: 95,
194 PFOA: 180 pg L⁻¹, Figure 2). For slope stations, surface samples (1-5 m) were significantly

195 higher than subsurface samples (10-240 m) for PFHxS (65 vs. 34 pg L⁻¹), PFOS (190 vs. 110 pg
196 L⁻¹), PFHxA (200 vs. 120 pg L⁻¹), PFHpA (44 vs. 19 pg L⁻¹), PFOA (120 vs. 54 pg L⁻¹), and
197 PFNA (45 vs. 17 pg L⁻¹). Differences between surface and subsurface samples for a greater
198 number of PFAS at the slope compared to the coast likely reflects the deeper sampling depths at
199 slope stations and less turbulent mixing of PFAS from surface water to depth compared to
200 shallower waters.

201 *Continental discharges are the main source of PFAS to the marine environment*

202 Figure 3A shows the results of principal components analysis (PCA) on log-transformed
203 and unit variance scaled concentrations of the eight frequently detected PFAS. The first two
204 principal components (PC1 and PC2) account for 83.2% and 4.8% of the data variance. The
205 coastal/shelf sites have higher scores for PC1 than the slope sites. PC1 has positive loadings for
206 all the PFAS (Figure 3B) and is highly correlated with salinities of the seawater samples (Figure
207 3C). PFBS, PFHxS and PFDA have positive loadings for PC2. Results of the PCA suggest rivers
208 are the dominant source of all PFAS detected in seawater. We hypothesize that PFAS with
209 elevated loadings of PC2 also have additional input sources, such as atmospheric deposition and
210 degradation of precursor compounds (Figure 3B).^{1,41,42}

211 Consistent with results from the PCA, there was a strong inverse linear relationship
212 between declining seawater salinity and concentrations of all eight frequently detected PFAS
213 among coastal/shelf stations (1-15, $r_s = -0.6$ to -0.8 , $p < 0.001$, Figure 3, Figure S1, Table S5).
214 Significantly lower salinity at the surface of coastal/shelf stations (paired t-test, $p < 0.001$)
215 reinforces that this enrichment reflects ongoing inputs from rivers. The intercepts of the
216 regressions between individual PFAS in coastal/shelf seawater and salinity (Table S5) provide an
217 indication of PFAS concentrations in continental releases entering the marine environment via

218 riverine discharge. These values ranged from 510 pg L⁻¹ for PFDA to 6750 pg L⁻¹ for PFOS and
219 fall within the range of PFAS concentrations we measured in inland and estuarine surface water
220 from the same region in the same year (Table S5).²²

221 The ratios between the regression intercepts and median inland surface water
222 concentrations should be close to one if all PFAS in nearshore seawater originated from
223 continental discharges. We find the ratios for PFOS (8.9) and PFNA (6.7) are much higher than
224 the range 2.0-3.0 for most PFAS (Table S5). This suggests seawater concentrations of PFOS and
225 PFNA reflect a combination of ongoing inputs from rivers and legacy accumulation from historic
226 discharges. Submarine groundwater discharge is an important hydrological process for the
227 coastal and shelf region of this study.⁴³ In groundwater, PFAS have much longer transport times
228 from sources to marine ecosystems than surface water.^{28,29}

229 For PFBS, only 25% of the variability in measured concentrations can be explained by
230 salinity (Figure 3F) and loadings of PC2 are high (Figure 3B). PFBS and its precursors such as
231 methyl perfluorobutane sulfonamide (MeFBSA) and sulfonamidoethanol (MeFBSE) are being
232 produced as a replacement for PFOS and transformation of volatile precursors can result in
233 deposition of PFBS to the surface ocean.^{1,44,45} Highest concentrations of PFBS were detected
234 next to coastal regions with large population centers such as the mouth of the Hudson River
235 basin (Station 7) and the Connecticut River (Station 3) (Table S3). The watersheds of these rivers
236 are known to contain many industries that use and release PFAS.³ PC2 loadings in the PCA
237 (Figure 3B) and the relatively weak relationship between PFBS and salinity are suggestive of
238 other source contributions such as atmospheric deposition.^{1,44,45}

239 ***Evidence for ongoing sources of legacy PFAS to the marine environment***

240 Figure S2(A) shows a linear correlation between PFOS and PFOA across all stations (R^2
241 = 0.65, $p < 0.05$). The slope of the regression relationship is close to one (0.89 ± 0.09 , Figure S2).
242 This is consistent with primary inputs from aquatic discharges (rivers or groundwater) because
243 high atmospheric inputs from precursor degradation are generally reflected by relative
244 enrichment in PFOA.^{1,25,46,47}

245 Figure S2(B) shows a linear relationship ($R^2 = 0.90$, $p < 0.05$) between PFOA and PFNA,
246 suggesting that PFNA inputs have been changing concurrently with PFOA and PFOS. Stations
247 with the highest concentrations of PFNA (near Delaware Bay: 10, 11 and Chesapeake Bay: 14,
248 15) are outliers to this relationship. This may reflect continued inputs of PFNA adjacent to highly
249 populated watersheds. PFNA in seawater for other regions sampled appears to be dominated by
250 historical inputs, as supported by the comparison with inland measurements from the same
251 year.²²

252 Figure S3 compares seawater PFAS concentrations measured in this study (August 2014)
253 to those measured in four samples surface seawater of the same region in July 2009.⁴⁶ Maximum
254 concentrations of PFOS in 2014 were one third of peak values measured in 2009 but average
255 PFOS concentrations were not significantly different between 2009 and 2014. For PFOA,
256 maximum concentrations concentration were 20% lower in 2014 but not statistically different
257 than average concentrations reported in 2009. These statistical comparisons are limited by scarce
258 sample numbers, reinforcing the need for additional seawater monitoring data to infer temporal
259 trends in response to regulatory measures.

260 New data collected in this study suggest rivers are still a source of inputs of legacy PFAS
261 (PFOS, PFOA, PFNA) and that concentrations in the marine environment reflect a combination
262 of new and historic inputs. While there is some evidence for a decline in peak concentrations,

263 data are currently insufficient to interpret temporal trends. Prior emission inventories^{1,2} and
264 modeling studies^{1,23} have assumed that environmental releases of legacy PFAS such as PFOS
265 would end in less than a decade. These estimates were based on shifts in chemical production,
266 the expected lifetimes of products containing these chemicals, and assumed declines in inputs to
267 the marine environment and concentrations in rivers that parallel production trends. Such
268 assumptions imply that concentrations in U.S. rivers entering the marine environment should be
269 below detection by 2014 for legacy compounds like PFOS and PFOA that have been largely
270 phased out of production. However, coastal/shelf measurements together with our previously
271 reported inland surface water data²² suggest ongoing releases both within the watershed and to
272 the marine environment. This observed lag time between source regulation and loadings to ocean
273 margins may be explained by the significance of groundwater contamination with legacy PFAS
274 in the Northeastern U.S.,^{29,48} and groundwater-surface water exchanges. Groundwater requires
275 much longer to be transported to the marine environment (decades to centuries)⁴⁹ compared to
276 surface water inputs.²³

277 *Detection and accumulation of PFAS in plankton*

278 Tables S5 and S6 show concentrations of PFAS measured in marine plankton and their
279 bioaccumulation factors ($BAF = C_{\text{plankton}}/C_{\text{water}}$). BAFs for marine plankton (<334 μm) were
280 highest for PFPeA and PFHxA (log BAF = 2.9-3.4) and linear PFOS (log BAF = 2.6-4.3) and
281 lowest for PFOA (log BAF = 1.7-2.6) and branched PFOS (log BAF = 1.7-2.8) (Figure 4).
282 Lower BAFs for branched compounds may reflect steric effects that inhibit uptake and
283 accumulation.^{8,50} Previous studies of marine and freshwater plankton have reported ranges for
284 PFOS (log BAF = 2.6-4.3) and PFOA (log BAF = 1.7-2.6) that agree well with our study.^{8,51-55}

285 We found that BAFs for C7-C11 PFCAs increased linearly with carbon chain length but
286 were higher than expected for the C5 and C6 carboxylates (Figure 4A-B). Station 1 consistently
287 had the highest BAFs for all compounds and the lowest values were observed at Station 6. The
288 differences in BAF between Station 1 and 6 can be attributed to variability in dominant plankton
289 communities. Different size distributions and over two orders of magnitude spatial variability in
290 the abundance of different types of plankton species within the region have been shown by
291 previous studies.⁵⁶⁻⁵⁹ Slopes of the increase in BAF between C7 and C11 PFCAs were not
292 significantly different across sampling locations (Tukey multiple comparison, $p > 0.371$),
293 suggesting similar processes governing food web uptake across these compounds (Figure 4B).
294 The average increase in BAF per CF₂ group increase was 0.76 ± 0.06 log units. Based on the
295 systematic variability across stations, we hypothesize that this reflects differences in plankton
296 community composition⁵⁶⁻⁵⁹ that affect uptake of PFAS such as cell surface area available for
297 sorption. The similarity in slopes for BAF increases from C7-11 PFCAs across sites suggests
298 hydrophobic interactions introduced by the CF moiety rather than the charged polar carboxylate
299 group drive interactions between PFAS and plankton.

300 We found higher concentrations of the C-5 (PFPeA) and C-6 (PFHxA) carboxylates in
301 plankton than expected based on simple partitioning (Figure 4, $\log \text{BAF} = 2.9\text{-}3.4$). We
302 hypothesize that this may reflect additional uptake of precursors from seawater such as 6:2 FtS
303 that are subsequently transformed in C-5 and C-6 carboxylates.⁶⁰⁻⁶² Casal et al.⁸ also frequently
304 detected PFPeA in marine plankton but did not report a BAF because concentrations in seawater
305 were below their limit of quantification (LOQ). Using their LOQ of 0.6 pg L^{-1} PFPeA in
306 seawater as the maximum possible concentrations, we estimate $\log \text{BAFs}$ between 2.1 to >3.3 ,⁸
307 which is similar to results reported here.

308 Similar to our results for plankton, Joeress et al.⁶³ found C4-C6 PFCAs had higher than
309 expected sediment-organic carbon partition coefficients (K_{oc}) based on the relationship with
310 carbon chain length generally observed for other PFCAs. BAFs for plankton are generally 1-2
311 orders of magnitude higher than sediment/water partition coefficients (K_d) reported in the
312 literature.⁶⁴⁻⁶⁶ This may reflect higher affinity of living cells for PFAS uptake into structurally
313 similar phospholipid bilayers compared to organic matter complexation.⁶⁷

314 We consistently detected several precursor compounds such as 6:2 fluorotelomer
315 sulfonate (6:2FtS), perfluorooctane sulfonamide (FOSA) and N-ethyl perfluorooctane
316 sulfonamide acetic acid (EtFOSAA) in plankton samples collected in this study (Table S6).
317 Seawater concentrations were frequently below detection so we estimated the lower bound for
318 BAFs using the LOD for seawater (Table S7). We estimate based on this calculation that log
319 BAFs must be greater than 3.7 for FOSA, greater than 3.1 for EtFOSAA, and greater than 3.0 for
320 6:2 FtS. At Station 15, we estimated the log BAF for 6:2 FtS was greater than 1.7, which is likely
321 an outlier. Together, these results suggest commonly detected precursor compounds in the
322 marine environment have similar or higher BAFs than most legacy PFAS. Higher BAF values
323 for linear PFOS than expected based on carbon chain length thus also likely reflects additional
324 inputs to plankton from precursors such as FOSA and EtFOSAA that degrade into PFOS. We
325 previously documented the significance of precursors for bioaccumulation of PFAS in a North
326 Atlantic pilot whale food web, where FOSA represented the major fraction of the exposure of
327 pilot whales prior to the phase out in production of the parent chemical between 2000-2002.⁶⁸

328 ***Limited vertical transport of PFAS associated with particles in the marine water column***

329 Vertical settling of marine particles (the biological pump) is an important contributor to
330 the removal of many persistent organic pollutants (POPs) such as polychlorinated biphenyls

331 (PCBs) from ocean surface waters.^{33,34,69} Many PFAS exist as stable ions in solution and thus
332 have less propensity for particle-associated transport than hydrophobic POPs like PCBs.
333 However, several studies have suggested the biological pump is an important mechanism for
334 vertical PFAS transport in the water column.^{8,70}

335 In this study, the vertical distribution of PFAS measured in unfiltered seawater was not
336 correlated with primary productivity, as indicated by *Chl a* concentrations (Figure 5, Figure S4).
337 This is not surprising based on the estimated fraction of PFAS associated with the particle phase
338 across sampling stations. For the C4 and C6-PFSAs (perfluoroalkanesulfonic acids) and C5-C9
339 PFCAs, solids accounted for less than 5% of the PFAS mass in the water column (Table S8). The
340 linear isomer of PFOS has greater affinity for plankton than the shorter chain PFSAs and PFCAs,
341 as reflected by the higher BAF (Figure 4). Across sampling locations, 1.5-26% of linear PFOS,
342 <0.8-5.2% of branched PFOS and <4.9-15.8% of total PFOS was bound to plankton in surface
343 seawater (Table S8).

344 We compared the estimated magnitudes of vertical PFAS fluxes due to particle sinking
345 and advective transport in seawater using vertical transport fields for the study region (42°N,
346 71°W – 36°N, 76°W) from the Estimating Circulation and Climate of the Ocean (ECCO-
347 GODAE) data product^{71,72} (Tables S9-S10, Equations S1-S5 and related text in the SI). For most
348 compounds, the vertical flux out of the surface (0-10 m) associated with settling particles was
349 smaller than that associated with advective transport (Table S11). For example, we estimate that
350 fluxes below 10 m depth associated with settling particles account for up to 18% of the vertical
351 PFOS, less than 7% of the C5-C9 PFCAs, and up to 31% of PFDA. Exceptions to this pattern
352 occur at coastal sites with relatively high productivity and high concentrations of PFOS
353 precursors (e.g., site 10, *Chl a* = 1.7 mg m⁻³ EtFOSAA: 19 ng g⁻¹ ww) where the settling particles

354 can account for up to 86% of the EtFOSAA vertical transport below 10 m depth. Overall, these
355 results suggest particle associated transport does not strongly affect the vertical distribution of
356 PFCAs and PFSAAs with less than 8 carbons but can be important for long-chain PFCAs and
357 some PFAS precursors.

358 In summary, this study indicates biological uptake of PFCA and PFSA precursors such as
359 6:2 FtS and EtFOSAA are important for observed concentrations of PFAS in marine food webs,
360 suggesting additional research is warranted. In addition to the precursor compounds measured in
361 this study, total organofluorine mass budgets⁷³ suggest there are many potential unknown
362 precursors to PFCAs and PFSAAs that may also be important for bioaccumulation of PFAS and
363 assessment of risks to human and ecological health. Our findings suggest contributions from
364 precursors to bioaccumulation of degradation products such as the C-5 and C-6 PFCAs and
365 PFOS should be considered in regulatory evaluations of risks associated with source releases.
366 Data presented here indicate inventories that only account for direct releases of PFCAs and
367 PFSAAs may underestimate bioaccumulation in marine food webs.

368 **Supporting Information**

369 Supporting Information Available: Additional figures and tables. This material is available free
370 of charge via the Internet at <http://pubs.acs.org>.

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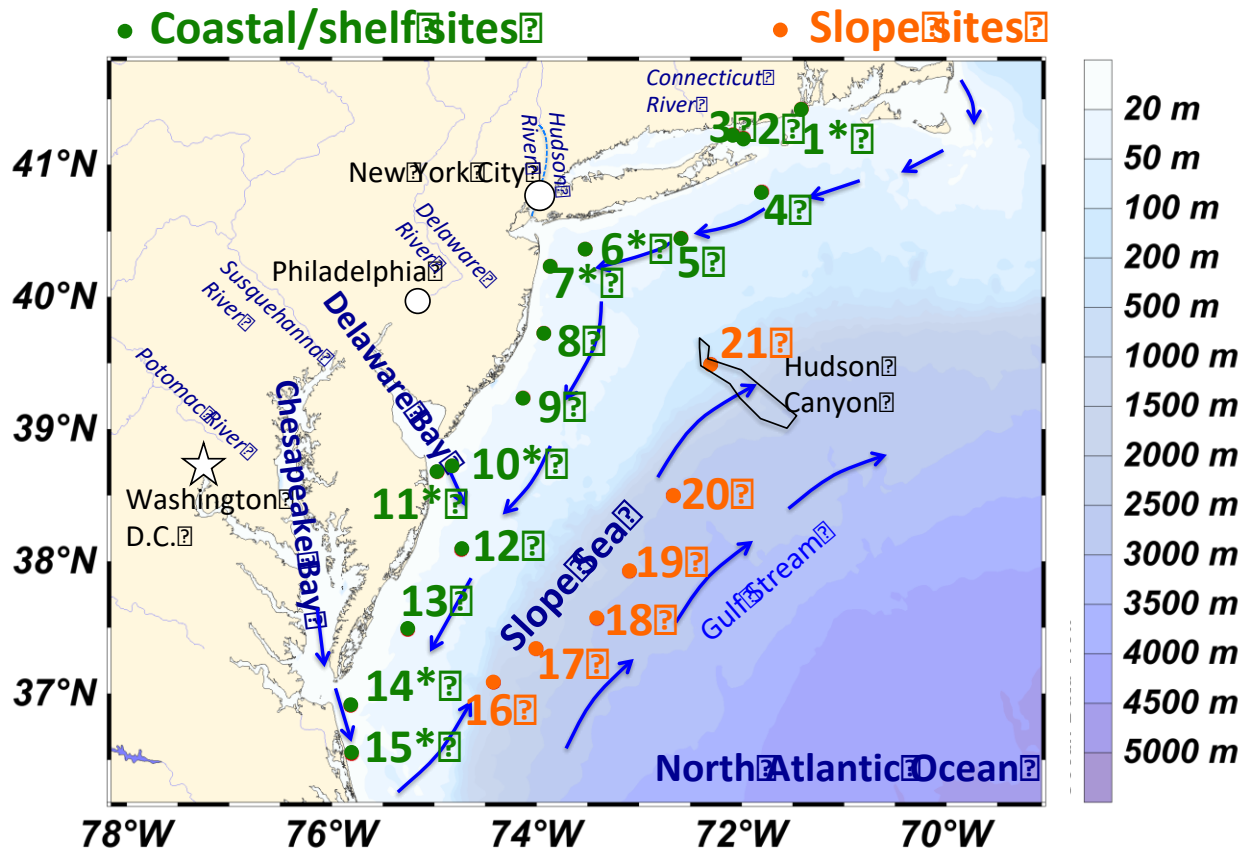
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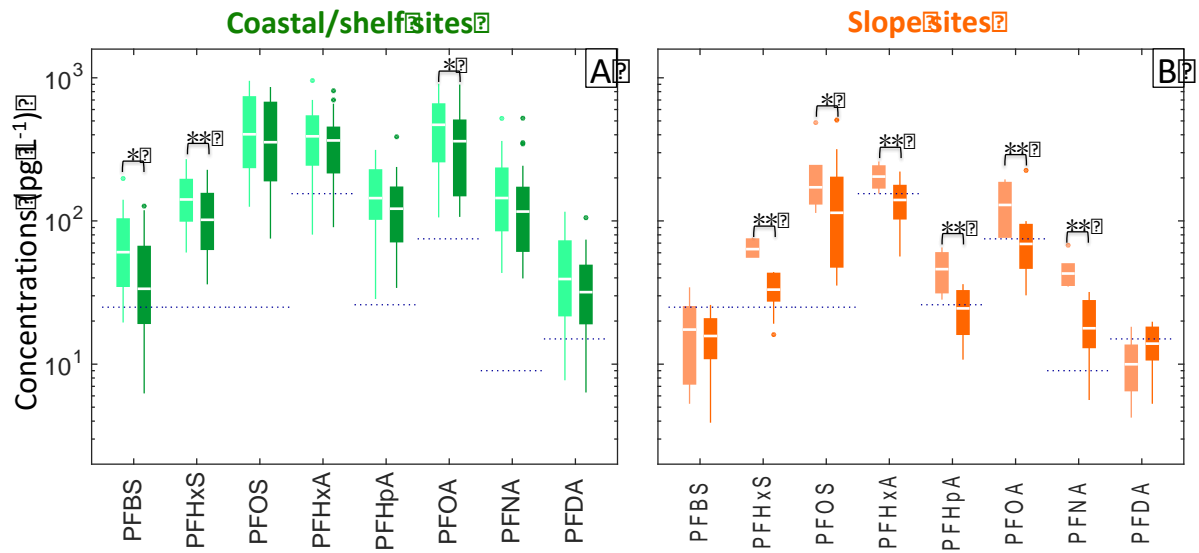
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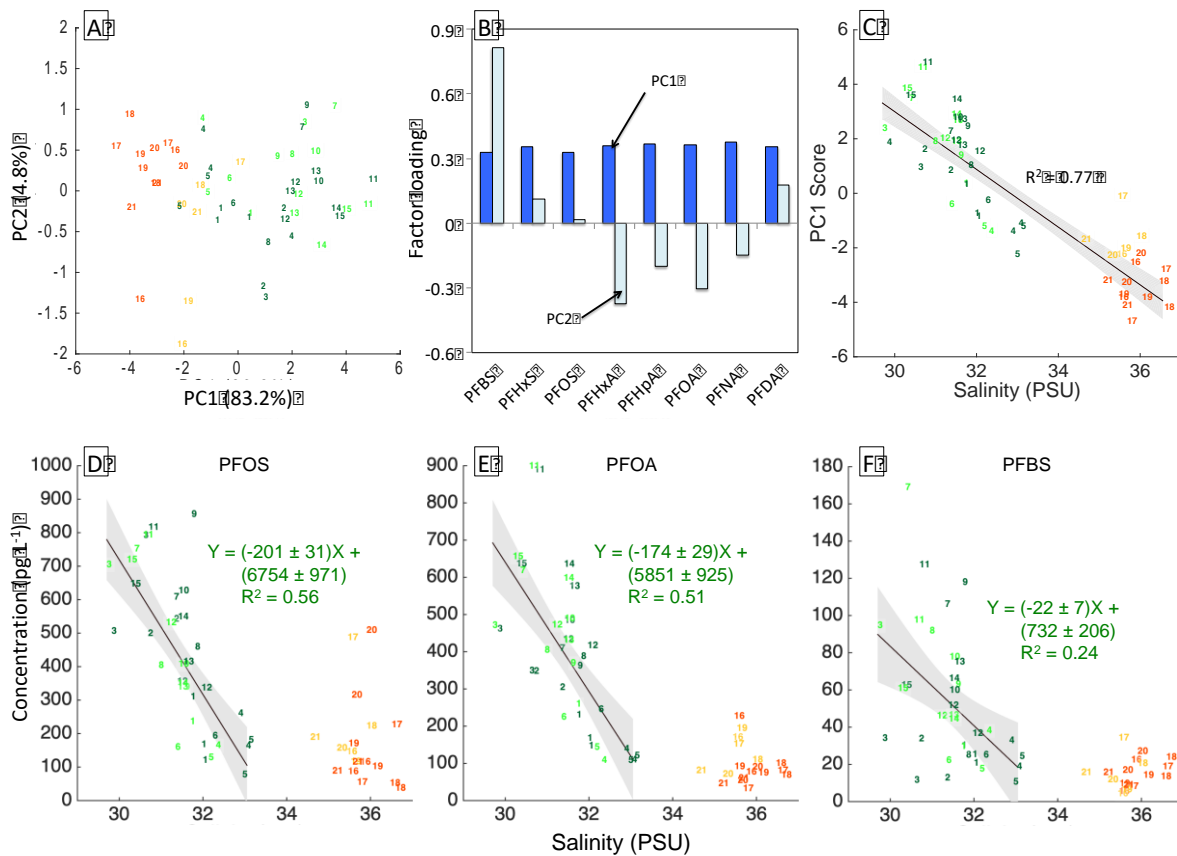
621 **Figure 1.** Locations of sampling stations for seawater and plankton (denoted by *) for analysis of
 622 poly- and perfluoroalkyl substances (PFAS). Stations were occupied as part of the ENV545
 623 cruise on the R/V Endeavor between August 23-28, 2014. Blue arrows indicate predominant
 624 directions of ocean currents in the region.

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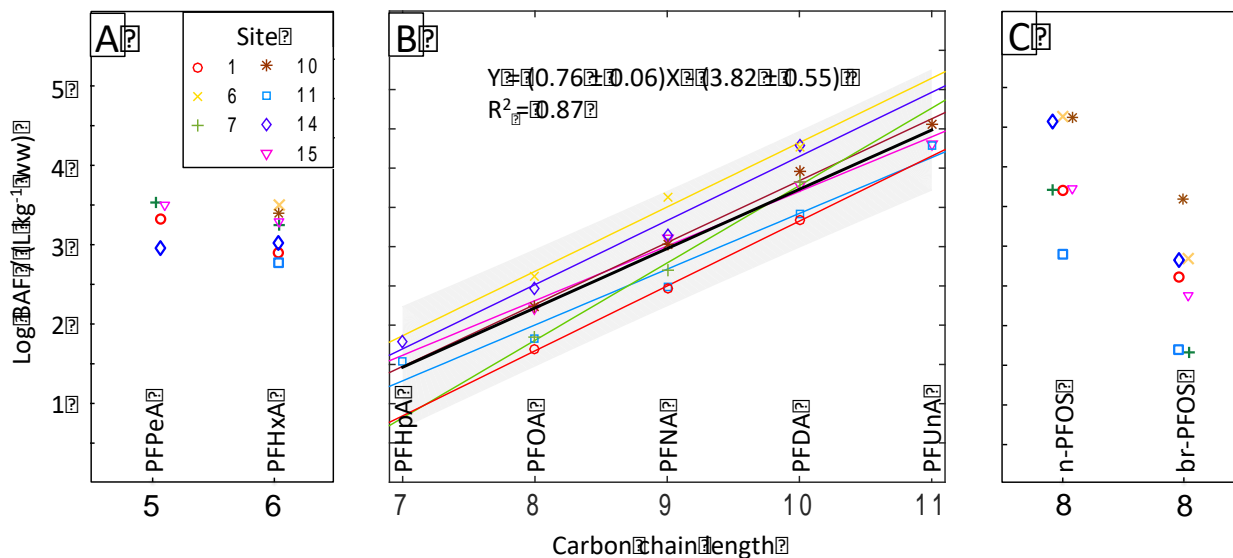
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627 **Figure 2.** Concentrations of the eight frequently detected PFAS in seawater from the
628 Northwestern Atlantic Ocean margin. Panel (A) shows coastal/shelf sites and Panel (B) shows
629 slope sites. The Limit of Detection (LOD, Table S3) for each PFAS is indicated by the dotted
630 line. Surface samples are denoted by light green/orange colors and subsurface samples are
631 colored dark green/orange. Significantly different concentrations based on paired one-tailed t-
632 tests for log-transformed concentrations at $p < 0.05$ is denoted by * and by ** for p -values < 0.01 .



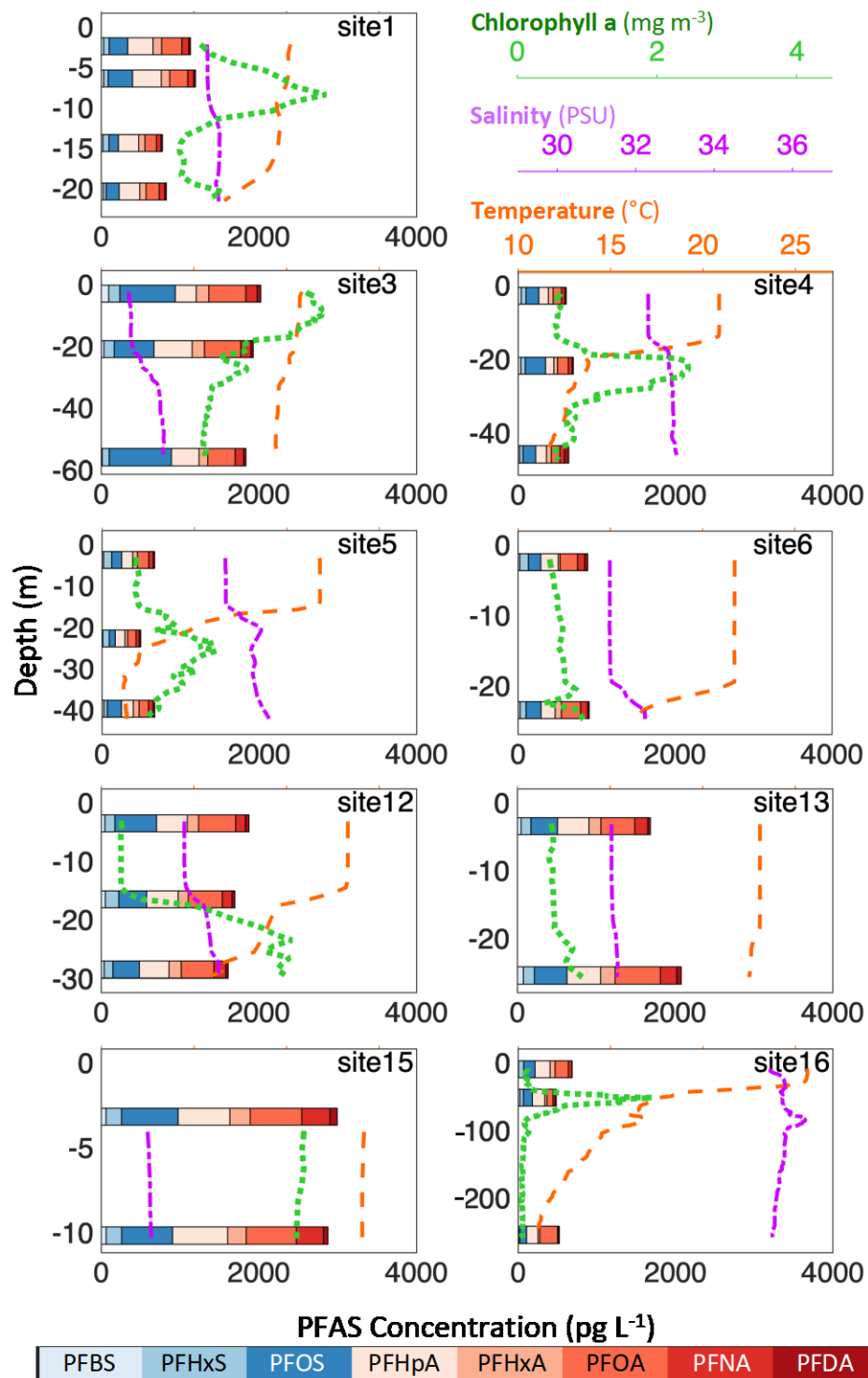
633

634 **Figure 3.** Relationship between concentrations of PFAS in seawater and salinity. Numbers on
 635 the plot correspond to sampling stations shown in Figure 1. Surface and subsurface sites are
 636 indicated by light and dark colors. Coastal/shelf stations are green and slope stations are orange.
 637 Panels (A) and (B) show scores and loadings of principal component analysis (PCA) on log-
 638 transformed and unit variance scaled PFAS concentrations. Panel (C) shows the correlation
 639 between PC1 scores and salinity ($r_s = 0.88$, $p < 0.001$). Panels (D-F) show linear relationships
 640 between PFOS, PFOA and PFBS in seawater from coastal/shelf stations. Figure S1 and Table S5
 641 show relationships for other PFAS.



642

643 **Figure 4.** Empirically derived bioaccumulation factors (BAFs) for marine plankton (L kg^{-1} wet
 644 weight) for linear perfluorocarboxylic acids (PFCAs, panel A and B) and linear (n-) and
 645 branched (br-) perfluorooctane sulfonate (PFOS, panel C) as a function of their carbon chain
 646 lengths. The regression line based on all data for the C7 to C11 PFCAs is shown by the black
 647 line of panel (B) and the grey shaded region represents the 95% confidence interval of
 648 predictions. Colored lines in panel (B) indicate regressions across individual sampling stations.
 649 Symbols indicate individual measurements.



650

651 **Figure 5.** Vertical profiles of PFAS, chlorophyll a (mg L^{-1} , green dot line), salinity (PSU, purple
 652 dash-dot line) and temperature ($^{\circ}\text{C}$, orange dash line). Concentrations of PFOS and PFOA
 653 include both linear and branched isomers. Data for all the other sites are presented in Figure S4.