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

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Abstract

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

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

Regulatory actions targeting legacy PFAS such as PFOS have led to shifts chemical production toward PFAS with shorter carbon chains and polyfluoroalkyl compounds. PFOS and its precursors were voluntarily phased out by the main global manufacturer between 2000-2002 and the stewardship program by the US Environmental Protection Agency (US EPA) for perfluorooctanoic acid (PFOA) has been very successful at reducing chemical production and environmental releases. However, many PFAS are not known to degrade and the ocean is thought to be the terminal sink following riverine transport through terrestrial ecosystems. Understanding the persistence of historical PFAS releases to the marine environment is thus important for characterizing exposure risks for wildlife and seafood consumers.

Prior modeling work has aimed to better understand PFAS transport and accumulation over large spatial and temporal scales. Given a lack of observational constraints,
most modeling simulations have assumed transport of PFAS from terrestrial ecosystems to the ocean generally occurs within a year (Table S5)\textsuperscript{23} or that mixing with seawater occurs instantaneously following continental releases.\textsuperscript{26,27} This assumption limits the potential lag time between phase out of contamination sources and changes in inputs to marine regions. However, ongoing releases from historical stockpiles and PFAS contaminated groundwater, widely discussed in the context of drinking water, may result in delayed transport to ocean margins through rivers and submarine groundwater discharges.\textsuperscript{28,29} Atmospheric transport of precursor compounds that degrade into more stable end products is thought to be an important transport mechanism for some coastal regions.\textsuperscript{12,30,31} Contemporary measurements of PFOS concentrations and composition in coastal and offshore regions are needed to provide insight into such sources.

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

The main objective of this work is to better understand factors affecting the distribution and abundance of PFAS in seawater and marine plankton from the ocean margin. We present new data on a suite of PFAS measured in samples collected from coastal/shelf and slope regions
of the Northwestern Atlantic Ocean. We use these data to better understand: (1) the significance
of continental discharges of freshwater as an ongoing source of legacy and new PFAS to the
marine environment, (2) processes affecting the vertical distribution of PFAS in the marine water
column, and (3) accumulation of PFAS at the base of the marine food web.

Methods

Sample collection

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

Sample bottles (1L high-density polyethylene) were rinsed three times with methanol, air
dried in a clean laboratory, and rinsed three times with seawater in the field before sampling.
Salinity, temperature and chlorophyll a were also measured at each station using a CTD device
on board (Table S1). Plankton were collected at selected stations by dragging a net (1 m²
opening, 335 μm mesh) at 1 m below the ocean surface for approximately 5 minutes (stations 1,
Samples were washed off the net with seawater into an HDPE jar (1 L). All samples were stored at -20°C onboard and in the laboratory before analysis in 2016.

**PFAS Extraction and Analysis**

Seawater samples were extracted following the method by Taniyasu et. al. Before extraction, each sample was thawed to room temperature, spiked with 50 μL of 0.02 ng μL⁻¹ mass labeled PFAS mixture (Wellington; Guelph, Canada) as internal standards and equilibrated overnight. Weak ion exchange SPE cartridges (Waters Oasis Wax, 6 mL, 150 mg sorbent) conditioned by sequentially eluting with 5 mL, 0.1% NH₄OH in methanol, 5 mL methanol, and 5 mL milli-Q water were used to extract and concentrate PFAS in 1-litre bulk seawater. Samples were shaken vigorously for homogenization and loaded onto the SPE cartridges with a flow rate of 2 drops per second. After sample loading, each bottle was rinsed with 20 mL milli-Q water and loaded to the SPE cartridge. The SPE cartridges were then washed with 5 mL 25 mM sodium acetate buffer before being eluted with 5 mL methanol and 5 mL of 0.1% NH₄OH in methanol to a 15 mL polypropylene centrifuge tube (Corning). The extracts were concentrated to 0.5 mL using a ZIPVAP nitrogen evaporator, transferred to 1.5 mL polypropylene autosampler vials, and mixed with 0.5 mL milli-Q water before instrumental analysis.

Plankton samples were first separated from the liquid phase via centrifugation. Each unfiltered sample was transferred to a 50 mL polypropylene centrifuge tube and centrifuged at 6000 rpm for 10 min. The supernatant liquid was removed and the procedure repeated until all plankton were separated. Wet weights (ww) and dry weights after freeze drying overnight were recorded. For each plankton sample, approximately 2 g ww equivalent was placed in a 15 polypropylene centrifuge tube and spiked with 50 μL of 0.02 ng μL⁻¹ mass labeled PFAS mixture
as internal standards (Wellington; Guelph, Canada, Table S2). Each sample was extracted twice by mixing with 4 mL 0.25 M sodium carbonate, 0.5 mL 0.5 M tetra-bultyl ammonium solution (pH =10) and 5 mL methyl-tert-butly ether (MBTE) on a horizontal mixer at 250 rpm for 30 min. The MBTE supernatants (10 mL) from the two extractions were combined and the solvent was further reduced to 0.5 mL methanol using a ZIPVAP nitrogen evaporator. The extract was transferred to a 1.5 mL polypropylene autosampler vial and mixed with 0.5 mL milli-Q water before instrumental analysis.

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

At the LC-MS interface, the capillary voltage was set at -3.8 kV and nitrogen nebulizer gas was set at 45 psi and 13 L min⁻¹. Analytes were introduced to the tandem mass spectrometer after being ionized with an electrospray ionization source operated in negative ion mode at 300 °C. The dynamic multiple reaction monitoring mode (5.0 grade N₂ as the collision gas) was used for data acquisition. To eliminate any potential carry-over, methanol was injected and passed through the system after every sample (or calibration standard).
Branched isomers for PFOA and PFOS were quantified using calibration standards for
the linear isomers, assuming the same instrumental response factor. For PFAS with detection
frequencies of greater than 70% (Table S3), we include non-detects in statistical analyses using
the Robust Regression on Order Statistics approach for censored log-normally distributed
environmental data, as described by Helsel. Individual sample concentrations reported here
represent direct measurements. Other PFAS with lower than 70% detection frequencies were not
considered in statistical data interpretations.

Quality Assurance

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

Results and Discussion
**PFAS detection, and concentrations in seawater**

Eight of the targeted 21 PFAS (PFBS, PFHxS, PFOS, PFHxA, PFHpA, PFOA, PFNA and PFDA) were detected in over 70% of the surface seawater samples (Table S3). The remaining 13 PFAS were detected in less than 40% of all the samples. Summed concentrations of the eight frequently detected PFAS ($\Sigma_8$PFAS) were $<660$-$4070$ pg L$^{-1}$ in surface seawater samples and $<470$-$3970$ pg L$^{-1}$ in subsurface samples. The most abundant PFAS in surface and subsurface seawater were PFOS (linear + branched: $<110$-$910$ pg L$^{-1}$), PFHxA ($<155$-$1000$ pg L$^{-1}$) and PFOA (linear + branched: $<93$-$900$ pg L$^{-1}$) (Figure 2, Table S3). In all the 20 surface seawater samples collected in this study, PFOS (linear + branched) exceeded the European environmental quality standard (130 pg L$^{-1}$, based on annual average exposure).$^{40}$

The highest concentration of $\Sigma_8$PFAS in both surface and subsurface seawater was found at Station 11 near Delaware Bay (Figure 1). Surface seawater from Station 11 had the highest concentrations of PFOS (830 pg L$^{-1}$), and PFCAs (PFHxS: 1000, PFHpA: 330, PFOA: 940, PFNA: 550, PFDA: 120 pg L$^{-1}$). The highest surface seawater concentrations of PFBS (180 pg L$^{-1}$) and PFHxS (240 pg L$^{-1}$) were found Station 7, near New Jersey (Figure 1). Both of the high concentration sites are adjacent to highly populated coastal watersheds that host diverse consumer and industrial PFAS uses.$^{23}$

Coastal/shelf stations (1-15) had significantly higher ($p<0.05$) PFAS concentrations than slope stations (16-21) based on a one-tailed t-test for log-transformed concentrations of each detected PFAS in surface and subsurface seawater (Figure 2, Table S4). At the coastal/shelf stations, surface concentrations of PFBS (geometric mean: 45 pg L$^{-1}$), PFHxS (130 pg L$^{-1}$), and PFOA (370 pg L$^{-1}$) were significantly higher than subsurface samples (PFBS: 35, PFHxS: 95, PFOA: 180 pg L$^{-1}$, Figure 2). For slope stations, surface samples (1-5 m) were significantly
higher than subsurface samples (10-240 m) for PFHxS (65 vs. 34 pg L\(^{-1}\)), PFOS (190 vs. 110 pg L\(^{-1}\)), PFHxA (200 vs. 120 pg L\(^{-1}\)), PFHpA (44 vs. 19 pg L\(^{-1}\)), PFOA (120 vs. 54 pg L\(^{-1}\)), and PFNA (45 vs. 17 pg L\(^{-1}\)). Differences between surface and subsurface samples for a greater number of PFAS at the slope compared to the coast likely reflects the deeper sampling depths at slope stations and less turbulent mixing of PFAS from surface water to depth compared to shallower waters.

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

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

Consistent with results from the PCA, there was a strong inverse linear relationship between declining seawater salinity and concentrations of all eight frequently detected PFAS among coastal/shelf stations (1-15, \(r_s = -0.6\) to -0.8, \(p < 0.001\), Figure 3, Figure S1, Table S5). Significantly lower salinity at the surface of coastal/shelf stations (paired t-test, \(p < 0.001\)) reinforces that this enrichment reflects ongoing inputs from rivers. The intercepts of the regressions between individual PFAS in coastal/shelf seawater and salinity (Table S5) provide an indication of PFAS concentrations in continental releases entering the marine environment via
riverine discharge. These values ranged from 510 pg L\(^{-1}\) for PFDA to 6750 pg L\(^{-1}\) for PFOS and fall within the range of PFAS concentrations we measured in inland and estuarine surface water from the same region in the same year (Table S5).\(^{22}\)

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

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

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


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

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

Figure S3 compares seawater PFAS concentrations measured in this study (August 2014) to those measured in four samples surface seawater of the same region in July 2009.$^{46}$ Maximum concentrations of PFOS in 2014 were one third of peak values measured in 2009 but average PFOS concentrations were not significantly different between 2009 and 2014. For PFOA, maximum concentrations concentration were 20% lower in 2014 but not statistically different than average concentrations reported in 2009. These statistical comparisons are limited by scarce sample numbers, reinforcing the need for additional seawater monitoring data to infer temporal trends in response to regulatory measures.

New data collected in this study suggest rivers are still a source of inputs of legacy PFAS (PFOS, PFOA, PFNA) and that concentrations in the marine environment reflect a combination of new and historic inputs. While there is some evidence for a decline in peak concentrations,
data are currently insufficient to interpret temporal trends. Prior emission inventories\textsuperscript{1,2} and modeling studies\textsuperscript{1,23} have assumed that environmental releases of legacy PFAS such as PFOS would end in less than a decade. These estimates were based on shifts in chemical production, the expected lifetimes of products containing these chemicals, and assumed declines in inputs to the marine environment and concentrations in rivers that parallel production trends. Such assumptions imply that concentrations in U.S. rivers entering the marine environment should be below detection by 2014 for legacy compounds like PFOS and PFOA that have been largely phased out of production. However, coastal/shelf measurements together with our previously reported inland surface water data\textsuperscript{22} suggest ongoing releases both within the watershed and to the marine environment. This observed lag time between source regulation and loadings to ocean margins may be explained by the significance of groundwater contamination with legacy PFAS in the Northeastern U.S.,\textsuperscript{29,48} and groundwater-surface water exchanges. Groundwater requires much longer to be transported to the marine environment (decades to centuries)\textsuperscript{49} compared to surface water inputs.\textsuperscript{23}

\textbf{Detection and accumulation of PFAS in plankton}

Tables S5 and S6 show concentrations of PFAS measured in marine plankton and their bioaccumulation factors (BAF = $C_{\text{plankton}}/C_{\text{water}}$). BAFs for marine plankton (<334 μm) were highest for PFPeA and PFHxA (log BAF = 2.9-3.4) and linear PFOS (log BAF = 2.6-4.3) and lowest for PFOA (log BAF = 1.7-2.6) and branched PFOS (log BAF = 1.7-2.8) (Figure 4).

Lower BAFs for branched compounds may reflect steric effects that inhibit uptake and accumulation.\textsuperscript{8,50} Previous studies of marine and freshwater plankton have reported ranges for PFOS (log BAF = 2.6-4.3) and PFOA (log BAF = 1.7-2.6) that agree well with our study.\textsuperscript{8,51-55}
We found that BAFs for C7-C11 PFCAs increased linearly with carbon chain length but were higher than expected for the C5 and C6 carboxylates (Figure 4A-B). Station 1 consistently had the highest BAFs for all compounds and the lowest values were observed at Station 6. The differences in BAF between Station 1 and 6 can be attributed to variability in dominant plankton communities. Different size distributions and over two orders of magnitude spatial variability in the abundance of different types of plankton species within the region have been shown by previous studies. Slopes of the increase in BAF between C7 and C11 PFCAs were not significantly different across sampling locations (Tukey multiple comparison, $p > 0.371$), suggesting similar processes governing food web uptake across these compounds (Figure 4B).

The average increase in BAF per CF2 group increase was $0.76 \pm 0.06$ log units. Based on the systematic variability across stations, we hypothesize that this reflects differences in plankton community composition that affect uptake of PFAS such as cell surface area available for sorption. The similarity in slopes for BAF increases from C7-11 PFCAs across sites suggests hydrophobic interactions introduced by the CF moiety rather than the charged polar carboxylate group drive interactions between PFAS and plankton.

We found higher concentrations of the C-5 (PFPeA) and C-6 (PFHxA) carboxylates in plankton than expected based on simple partitioning (Figure 4, log BAF = 2.9-3.4). We hypothesize that this may reflect additional uptake of precursors from seawater such as 6:2 FtS that are subsequently transformed in C-5 and C-6 carboxylates. Casal et al. also frequently detected PFPeA in marine plankton but did not report a BAF because concentrations in seawater were below their limit of quantification (LOQ). Using their LOQ of 0.6 pg L$^{-1}$ PFPeA in seawater as the maximum possible concentrations, we estimate log BAFs between 2.1 to >3.3, which is similar to results reported here.
Similar to our results for plankton, Joerss et al. found C4-C6 PFCAs had higher than expected sediment-organic carbon partition coefficients ($K_{oc}$) based on the relationship with carbon chain length generally observed for other PFCAs. BAFs for plankton are generally 1-2 orders of magnitude higher than sediment/water partition coefficients ($K_d$) reported in the literature. This may reflect higher affinity of living cells for PFAS uptake into structurally similar phospholipid bilayers compared to organic matter complexation.

We consistently detected several precursor compounds such as 6:2 fluorotelomer sulfonate (6:2FtS), perfluorooctane sulfonamide (FOSA) and N-ethyl perfluorooctane sulfonamide acetic acid (EtFOSAA) in plankton samples collected in this study (Table S6). Seawater concentrations were frequently below detection so we estimated the lower bound for BAFs using the LOD for seawater (Table S7). We estimate based on this calculation that log BAFs must be greater than 3.7 for FOSA, greater than 3.1 for EtFOSAA, and greater than 3.0 for 6:2 FtS. At Station 15, we estimated the log BAF for 6:2 FtS was greater than 1.7, which is likely an outlier. Together, these results suggest commonly detected precursor compounds in the marine environment have similar or higher BAFs than most legacy PFAS. Higher BAF values for linear PFOS than expected based on carbon chain length thus also likely reflects additional inputs to plankton from precursors such as FOSA and EtFOSAA that degrade into PFOS. We previously documented the significance of precursors for bioaccumulation of PFAS in a North Atlantic pilot whale food web, where FOSA represented the major fraction of the exposure of pilot whales prior to the phase out in production of the parent chemical between 2000-2002.

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

Vertical settling of marine particles (the biological pump) is an important contributor to the removal of many persistent organic pollutants (POPs) such as polychlorinated biphenyls.
(PCBs) from ocean surface waters. Many PFAS exist as stable ions in solution and thus have less propensity for particle-associated transport than hydrophobic POPs like PCBs. However, several studies have suggested the biological pump is an important mechanism for vertical PFAS transport in the water column.8,70

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

We compared the estimated magnitudes of vertical PFAS fluxes due to particle sinking and advective transport in seawater using vertical transport fields for the study region (42°N, 71°W – 36°N, 76°W) from the Estimating Circulation and Climate of the Ocean (ECCO-GODAE) data product71,72 (Tables S9-S10, Equations S1-S5 and related text in the SI). For most compounds, the vertical flux out of the surface (0-10 m) associated with settling particles was smaller than that associated with advective transport (Table S11). For example, we estimate that fluxes below 10 m depth associated with settling particles account for up to 18% of the vertical PFOS, less than 7% of the C5-C9 PFCAs, and up to 31% of PFDA. Exceptions to this pattern occur at coastal sites with relatively high productivity and high concentrations of PFOS precursors (e.g., site 10, Chl a = 1.7 mg m⁻³ EtFOSAA: 19 ng g⁻¹ ww) where the settling particles
can account for up to 86% of the EtFOSAA vertical transport below 10 m depth. Overall, these results suggest particle associated transport does not strongly affect the vertical distribution of PFCAs and PFSAs with less than 8 carbons but can be important for long-chain PFCAs and some PFAS precursors.

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

Supporting Information

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

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References


21. Wang, Z.; Cousins, I. T.; Scheringer, M., Comment on "The environmental photolysis of perfluorooctanesulfonate, perfluorooctanoate, and related fluorochemicals". *Chemosphere*** **2014**.


**Figure 1.** Locations of sampling stations for seawater and plankton (denoted by *) for analysis of poly- and perfluoroalkyl substances (PFAS). Stations were occupied as part of the ENV545 cruise on the R/V Endeavor between August 23-28, 2014. Blue arrows indicate predominant directions of ocean currents in the region.
Figure 2. Concentrations of the eight frequently detected PFAS in seawater from the Northwestern Atlantic Ocean margin. Panel (A) shows coastal/shelf sites and Panel (B) shows slope sites. The Limit of Detection (LOD, Table S3) for each PFAS is indicated by the dotted line. Surface samples are denoted by light green/orange colors and subsurface samples are colored dark green/orange. Significantly different concentrations based on paired one-tailed t-tests for log-transformed concentrations at \( p < 0.05 \) is denoted by * and by ** for \( p \)-values <0.01.
Figure 3. Relationship between concentrations of PFAS in seawater and salinity. Numbers on the plot correspond to sampling stations shown in Figure 1. Surface and subsurface sites are indicated by light and dark colors. Coastal/shelf stations are green and slope stations are orange. Panels (A) and (B) show scores and loadings of principal component analysis (PCA) on log-transformed and unit variance scaled PFAS concentrations. Panel (C) shows the correlation between PC1 scores and salinity \( (r_s = 0.88, p<0.001) \). Panels (D–F) show linear relationships between PFOS, PFOA and PFBS in seawater from coastal/shelf stations. Figure S1 and Table S5 show relationships for other PFAS.
**Figure 4.** Empirically derived bioaccumulation factors (BAFs) for marine plankton (L kg\(^{-1}\) wet weight) for linear perfluorocarboxylic acids (PFCAs, panel A and B) and linear (n-) and branched (br-) perfluorooctane sulfonate (PFOS, panel C) as a function of their carbon chain lengths. The regression line based on all data for the C7 to C11 PFCAs is shown by the black line of panel (B) and the grey shaded region represents the 95% confidence interval of predictions. Colored lines in panel (B) indicate regressions across individual sampling stations. Symbols indicate individual measurements.
**Figure 5.** Vertical profiles of PFAS, chlorophyll a (mg L$^{-1}$, green dot line), salinity (PSU, purple dash-dot line) and temperature (°C, orange dash line). Concentrations of PFOS and PFOA include both linear and branched isomers. Data for all the other sites are presented in Figure S4.