

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

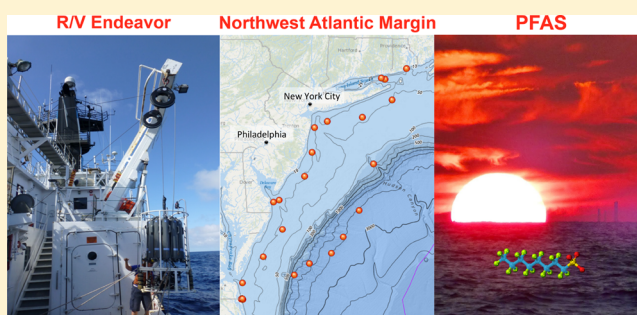
 Xianming Zhang,^{†,‡,*} Rainer Lohmann,[§] and Elsie M. Sunderland^{†,‡}
[†]Harvard John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, United States

[‡]Department of Environmental Health, Harvard T.H. Chan School of Public Health, Harvard University, Boston, Massachusetts 02115, United States

[§]Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island 02882, United States

S Supporting Information

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 that 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 that 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 = $C_{\text{plankton}}/C_{\text{water}}$) for perfluorinated carboxylic acids (PFCAs) with five and six carbons ($\log \text{BAF} = 2.9\text{--}3.4$) and linear PFOS ($\log \text{BAF} = 2.6\text{--}4.3$) in marine plankton compared to PFCAs with 7–11 carbons. We postulate that this reflects additional contributions from precursor compounds. Known precursor compounds detected here have among the highest BAFs ($\log \text{BAF} > 3.0$) for all PFAS in this study, suggesting that 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.^{1–3} Human exposure to PFAS has been associated with adverse health effects such as immune suppression and metabolic disruption.⁴ 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.^{5,6} PFAS in seawater and marine plankton drive accumulation in marine food webs.^{7,8} Prior work has examined the distribution and composition of PFAS in seawater from different regions.^{8–16} 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.^{8,17}

Regulatory actions targeting legacy PFAS such as PFOS have led to shifts in chemical production toward PFAS with shorter

carbon chains and polyfluoroalkyl compounds.¹⁸ PFOS and its precursors were voluntarily phased out by the main global manufacturer between 2000 and 2002,¹⁹ and the stewardship program by the U.S. Environmental Protection Agency (U.S. EPA) for perfluorooctanoic acid (PFOA) has been very successful at reducing chemical production and environmental releases.²⁰ However, many PFAS are known not to degrade under natural conditions,²¹ and the ocean is thought to be the terminal sink following riverine transport through terrestrial ecosystems.^{22–24} Understanding the fate of historical PFAS releases to the marine environment is thus important for characterizing exposure risks for wildlife and seafood consumers.

Received: May 30, 2019

Revised: September 18, 2019

Accepted: September 28, 2019

Published: September 29, 2019

Prior modeling work^{1,2,3,25} has aimed to better understand PFAS transport and accumulation over large spatial and temporal scales. Given the lack of observational constraints, most modeling simulations have assumed that transport of PFAS from terrestrial ecosystems to the ocean generally occurs within a year (Table S5)²³ and that mixing with seawater occurs instantaneously following continental releases.^{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 discharge.^{28,29} Atmospheric transport of precursor compounds that degrade into more stable end products is thought to be an important input source for some coastal regions.^{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.^{32–34} By contrast, many PFAS are ionized in the aqueous environment and thus are more hydrophilic and not volatile.³⁵ Prior work has suggested that settling particles may provide a significant removal pathway for PFAS in marine ecosystems.⁸ By contrast, the modeling work of Zhang et al.²³ suggested that vertical advection was the predominant pathway for PFOS entry into the deep North Atlantic Ocean, and that particle settling accounted 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 importance of freshwater continental discharges 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 and 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 and 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 (approximately 20% of the U.S. population) reside within the watersheds of these rivers. Sampling depths were selected based on in situ CTD measurements of the vertical profiles of temperature, salinity, and chlorophyll a (Chl a). Generally, we obtained one sample 2 m above the seafloor

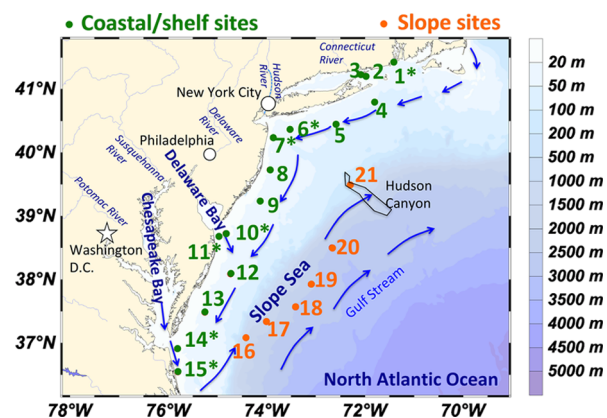


Figure 1. Locations of sampling stations for seawater and plankton (denoted by *) for analysis of poly- and perfluoroalkyl substances (PFAS). Stations were occupied as part of the ENV545 cruise on the R/V Endeavor between August 23, 2014 and August 28, 2014. Blue arrows indicate predominant directions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

and one sample at the depth where temperature, salinity, and/or Chl a showed substantial variation.

Sample bottles (1 L 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 min (stations 1, 6, 7, 10, 11, 14, and 15 in Figure 1). Samples were washed off the net with seawater into an HDPE jar (1 L). All samples were stored at –20 °C on board and in the laboratory before analysis in 2016.

PFAS Extraction and Analysis. Seawater samples were extracted following the method by Taniyasu et al.³⁶ Before extraction, each sample was thawed to room temperature and spiked with 50 μL of 0.02 ng μL⁻¹ mass-labeled PFAS mixture (Wellington, Guelph, Canada; Table S2) 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 of methanol, and 5 mL of Milli-Q water were used to extract and concentrate PFAS in 1 L of 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 of Milli-Q water and loaded to the SPE cartridge. The SPE cartridges were then washed with 5 mL of 25 mM sodium acetate buffer before being eluted with 5 mL of 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 of polypropylene autosampler vials, and mixed with 0.5 mL of 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 was 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 mL polypropylene centrifuge

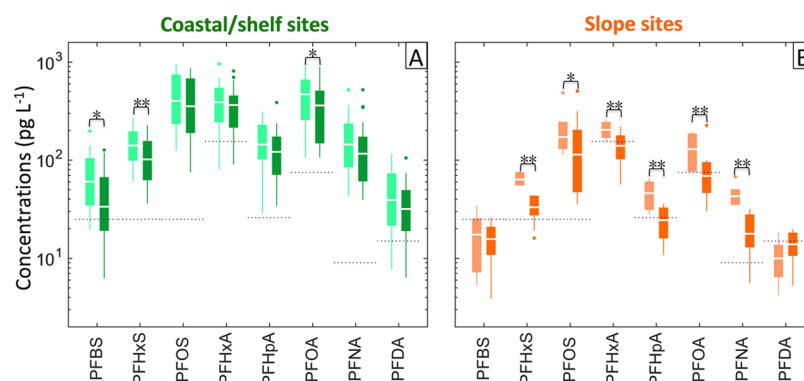


Figure 2. Concentrations of the eight frequently detected PFAS in seawater from the Northwestern Atlantic Ocean margin. (A) Coastal/shelf sites. (B) Slope sites. The limit of detection (LOD; Table S3) for each PFAS is indicated by the dotted line. Surface samples are denoted by light green/orange colors, 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 .

tube and spiked with 50 μL of 0.02 $\text{ng } \mu\text{L}^{-1}$ mass-labeled PFAS mixture as internal standards (Wellington, Guelph, Canada; Table S2). Each sample was extracted twice by mixing with 4 mL of 0.25 M sodium carbonate, 0.5 mL of 0.5 M tetrabutyl ammonium solution ($\text{pH} = 10$), and 5 mL of methyl *tert*-butyl 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 of methanol using a ZIPVAP nitrogen evaporator. The extract was transferred to a 1.5 mL polypropylene autosampler vial and mixed with 0.5 mL of 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 (4.6×12.5 mm; 5 μm) online SPE column and eluted with 0.85 mL of 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 (3.0×50 mm; 2.7 μm) reversed-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 to 60% methanol for 7 min, held for 1 min, and 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 the 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 $^{\circ}\text{C}$. The dynamic multiple reaction monitoring mode (5.0 grade N_2 as the collision gas) was used for data acquisition. To eliminate any potential carryover, 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.³⁷ Individual sample concentrations reported here represent direct measure-

ments. 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.^{22,29} A guard column was installed between the mobile phases and online SPE column to remove 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 of water) were included in each extraction batch. Whole method recoveries tested using the positive controls were 62–117%, which is comparable to the recoveries reported by previous studies.^{36,38,39} Potential analyte loss during the 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 3. 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 the duplicates was $20 \pm 15\%$. Stations with duplicate samples are reported as averaged values. Five field blanks (1 L of HPLC-grade water was 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 ($\Sigma_8\text{PFAS}$) were < 660 to 4070 pg L^{-1} in surface seawater samples and < 470 to 3970 pg L^{-1} in subsurface samples. The most abundant PFAS in surface and subsurface seawater were PFOS (linear + branched, < 110 to 910 pg L^{-1}), PFHxA (< 155 to 1000 pg L^{-1}), and PFOA (linear + branched, < 93 to 900 pg L^{-1}) (Figure 2 and 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 $\Sigma_8\text{PFAS}$ in both surface and subsurface seawater was found at station 11 near Delaware Bay (Figure 1). Surface seawater from station 11 had the highest

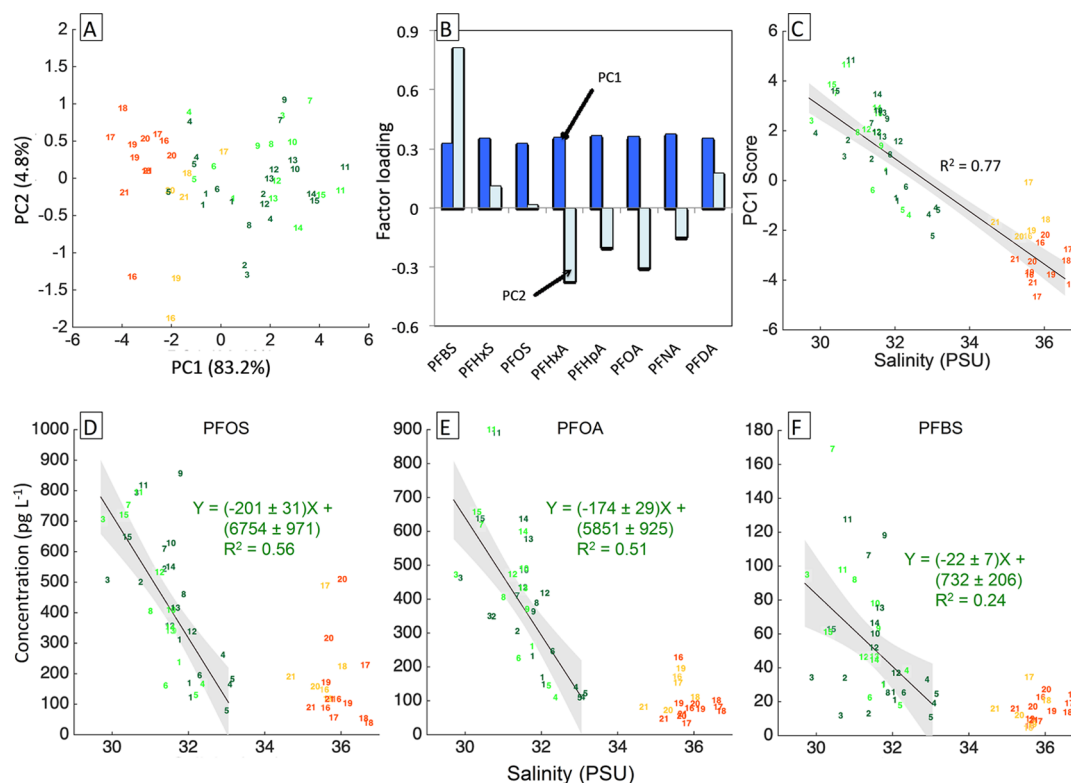


Figure 3. Relationship between PFAS concentrations in seawater and salinity. Numbers on the plot correspond to the sampling stations shown in Figure 1. Surface and subsurface sites are indicated by light and dark colors, respectively. Coastal/shelf stations are colored green, and slope stations are colored orange. (A, B) Scores and loadings of principal component analysis (PCA) on log-transformed and unit-variance-scaled PFAS concentrations. (C) Correlation between PC1 scores and salinity ($r_s = 0.88$, $p < 0.001$). (D–F) Linear relationships between PFOS, PFOA, and PFBS in seawater from coastal/shelf stations. Figure S1 and Table S5 show relationships for other PFAS.

concentrations of PFOS (830 pg L^{-1}) and PFCAs (PFHxA, 1000 pg L^{-1} ; PFHpA, 330 pg L^{-1} ; PFOA, 940 pg L^{-1} ; PFNA, 550 pg L^{-1} ; and PFDA, 120 pg L^{-1}). The highest surface seawater concentrations of PFBS (180 pg L^{-1}) and PFHxS (240 pg L^{-1}) were found in 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 and 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 those of subsurface samples (PFBS, 35 pg L^{-1} ; PFHxS, 95 pg L^{-1} ; and 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 reflect the deeper sampling depths at slope stations and less turbulent mixing of PFAS from surface water to deeper ocean.

Continental Discharges Are the Main Sources 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, respectively. 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 that 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 is a strong inverse linear relationship between 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, and Table S5). The significantly lower salinity at the surface of coastal/shelf stations (paired t test, $p < 0.001$) reinforces the fact that this enrichment reflects ongoing inputs from rivers. The intercepts of the regressions between the 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 fell 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 1 if all

PFAS in nearshore seawater originated from continental discharges. We find that the ratios for PFOS (8.9) and PFNA (6.7) are much higher than the range of 2.0–3.0 for most PFAS (Table S5). This suggests that 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 in 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 replacements for PFOS, and transformation of volatile precursors can result in deposition of PFBS to the surface ocean.^{1,44,45} The 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 S2A 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 1 (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 S2B 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 (stations 10 and 11) and Chesapeake Bay (stations 14 and 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 (Table S5).²²

Figure S3 compares seawater PFAS concentrations measured in this study (August 2014) to those measured in four samples of surface seawater of the same region in July 2009.⁴⁶ Maximum concentrations of PFOS in 2014 were one-third the peak values measured in 2009, but the average PFOS concentrations were not significantly different between 2009 and 2014. For PFOA, maximum concentrations were 20% lower in 2014 but not statistically different than the 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 that rivers are still a source of legacy PFAS (PFOS, PFOA, and PFNA) to the marine environment and that concentrations in seawater 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^{1,2} and modeling studies^{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 data²² suggest ongoing releases are occurring both within the watershed and to the marine environment. The 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 United States^{29,48} and groundwater–surface water exchanges. Groundwater requires a much longer time to be transported to the marine environment (decades to centuries)⁴⁹ compared to surface water inputs.²³

Detection and Accumulation of PFAS in Plankton. Tables S6 and S7 show concentrations of PFAS measured in marine plankton and their bioaccumulation factors (BAF = $C_{\text{plankton}}/C_{\text{water}}$). BAFs for PFPeA and PFHxA (log BAF = 2.9–3.4) were higher than that for PFOA (log BAF = 1.7–2.6). BAFs for linear PFOS (log BAF = 2.6–4.3) were higher than that for branched PFOS (log BAF = 1.7–2.8) (Figure 4).

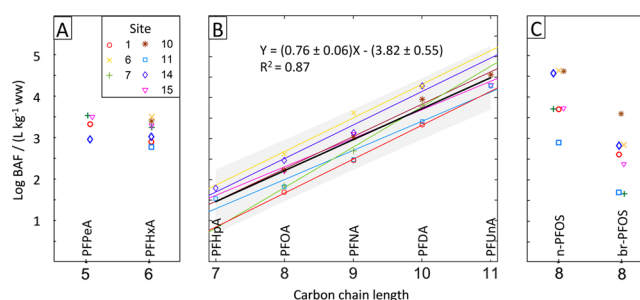


Figure 4. (A–C) Empirically derived bioaccumulation factors (BAFs) for marine plankton (L kg^{-1} wet weight) for linear perfluorocarboxylic acids (PFCAs) (A, B) and linear (n-) and branched (br-) perfluorooctane sulfonate (PFOS) (C) as a function of their carbon chain lengths. The regression line based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

Lower BAFs for branched compounds may reflect steric effects that inhibit uptake and accumulation.^{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.^{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 6 consistently had the highest BAFs for all the C7–C11 PFCAs, and the lowest values were observed at station 1. The differences in BAFs between stations 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 were shown by previous studies.^{56–59} Slopes of the increase in BAFs 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 BAFs per CF₂ group increase was 0.76 ± 0.06 log units. Based on the systematic variability across stations, we hypothesize that this reflects differences in plankton community composition^{56–59} that affect uptake of PFAS such as cell surface area available for sorption. The similarity in slopes for BAF increases from C7 to C11 PFCAs across sites suggests that 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 C5 (PFPeA) and C6 (PFHxA) carboxylates in plankton than those expected based on simple partitioning (Figure 4A, log BAF = 2.9–3.4). We hypothesize that this may reflect additional uptake of precursors from seawater such as 6:2 fluorotelomer sulfonate (6:2 FtS) that are subsequently transformed in C5 and C6 carboxylates.^{60–62} Casal et al.⁸ 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 were between 2.1 and >3.3 ,⁸ which is similar to the results reported here.

Similar to our results for plankton, Joerss et al.⁶³ found that 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.^{64–66} This may reflect higher affinity of living cells for PFAS uptake into structurally similar phospholipid bilayers compared to organic matter complexation.⁶⁷

We consistently detected several precursor compounds such as 6:2 fluorotelomer sulfonate (6:2 FtS), 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). This calculation suggests 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 that the log BAF for 6:2 FtS was greater than 1.7, which is likely an outlier. Together, these results suggest that commonly detected precursor compounds in the marine environment have similar or higher BAFs than most legacy PFAS. Higher than expected BAF values for linear PFOS based on carbon chain length thus also likely reflect 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 and 2002.⁶⁸

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.^{32–34} 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 that the biological pump is an important mechanism for vertical PFAS transport in the water column.^{8,69}

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 and

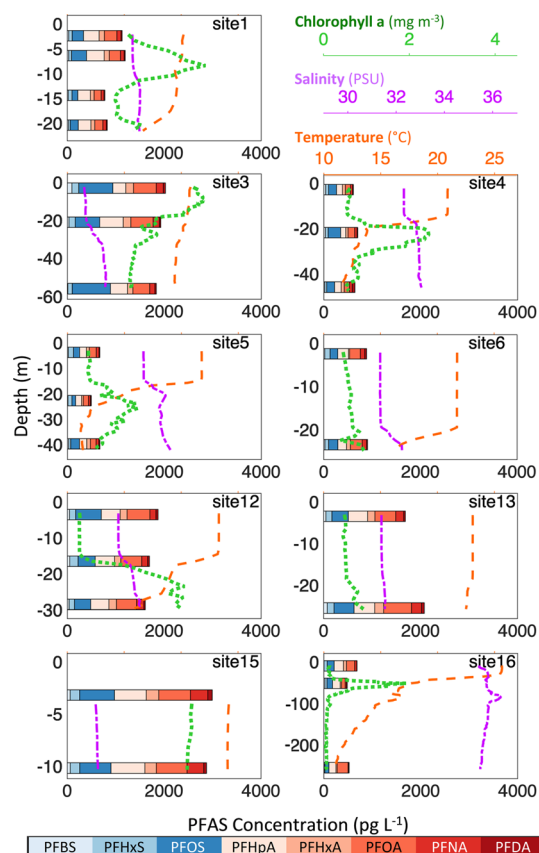


Figure 5. Vertical profiles of PFAS, chlorophyll *a* (mg L^{-1} , green dotted line), salinity (PSU, purple dash-dotted line), and temperature ($^{\circ}\text{C}$, orange dashed line). Concentrations of PFOS and PFOA include both linear and branched isomers. Data for all the other sites are presented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

Figure S4). This is not surprising based on the estimated fraction of PFAS associated with the particle phase across the 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 the linear PFOS, <0.8 to 5.2% of the branched PFOS, and <4.9 to 15.8% of the total PFOS were 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 product^{70,71} (Tables S9 and S10, eqs. S1 to S5, and related text in the

Supporting Information). 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 the 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 that particle-associated transport does not strongly affect the vertical distribution of PFCAs and PFSA with less than eight carbons but can be important for long-chain PFCAs and some PFAS precursors.

In summary, this study indicates that biological uptake of PFCA and PFSA precursors such as 6:2 FtS and EtFOSAA is important for observed concentrations of PFAS in marine food webs, suggesting that additional research is warranted. In addition to the precursor compounds measured in this study, total organofluorine mass budgets⁷² suggest that there are many potential unknown precursors to PFCAs and PFSA that may also be important for bioaccumulation of PFAS and assessment of risks to human and ecological health. Our findings suggest that contributions from precursors to bioaccumulation of degradation products such as the C5 and C6 PFCAs and PFOS should be considered in regulatory evaluations of risks associated with source releases. Data presented here indicate that inventories that only account for direct releases of PFCAs and PFSA may underestimate bioaccumulation in marine food webs.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.9b03230](https://doi.org/10.1021/acs.est.9b03230).

Seawater and plankton sampling locations, depths, and ancillary data, full names, and acronyms of PFAS measured, concentrations of frequently detected PFAS (pg L⁻¹) in seawater, comparison of concentrations of PFAS in surface and subsurface seawater at coastal/shelf sites and at slope sites, results of linear regression analysis for PFAS concentrations and salinity at coastal/shelf sites, plankton properties and concentrations (ng g⁻¹ ww) of measured PFAS in plankton, empirically derived BAF (L kg⁻¹ ww) from water and plankton PFAS measurements, fractions of PFAS bound to plankton in surface seawater, estimated flux of PFAS (ng m⁻² d⁻¹) due to the sinking of particles and advection of seawater from the surface (0–10 m) to the deeper ocean, percent contributions of biological pump to vertical transport of PFAS from a 0–10 to 10–20 m depth, variations of PFHxS, PFHpA, PFHxA, PFNA, and PFDA seawater concentrations with salinities, linear correlations between concentrations of PFOA and PFOS and PFNA measured in seawater, comparison of PFAS concentrations in seawater measured in August 2014 with those measured in July 2009, and vertical profiles of concentrations and composition of PFAS (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xianming.zhang@gmail.com. Tel: 857-600-0969.

ORCID

Xianming Zhang: 0000-0002-5301-7899

Rainer Lohmann: 0000-0001-8796-3229

Elsie M. Sunderland: 0000-0003-0386-9548

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge financial support for this study from the Smith Family Foundation, the U.S. National Science Foundation (PLR 1203496), the Rhode Island Endeavor Program (RIEP) for support of EN 545, the Harvard John A. Paulson School of Engineering and Applied Sciences TomKat fund, and the NIH Superfund Research Program (P42ES027706). X.Z. acknowledges a postdoctoral fellowship from the Natural Sciences and Engineering Research Council of Canada (NSERC). We thank Caoxin Sun (University of Rhode Island), Lynne Butler (R/V Endeavor), and the crew for assistance with field sample collection.

■ REFERENCES

- (1) Armitage, J. M.; Schenker, U.; Scheringer, M.; Martin, J. W.; MacLeod, M.; Cousins, I. T. Modeling the Global Fate and Transport of Perfluorooctane Sulfonate (PFOS) and Precursor Compounds in Relation to Temporal Trends in Wildlife Exposure. *Environ. Sci. Technol.* **2009**, *43*, 9274–9280.
- (2) Wang, Z.; Cousins, I. T.; Scheringer, M.; Buck, R. C.; Hungerbühler, K. Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. *Environ. Int.* **2014**, *62*–75.
- (3) Boucher, J. M.; Cousins, I. T.; Scheringer, M.; Hungerbühler, K.; Wang, Z. Toward a Comprehensive Global Emission Inventory of C4–C10 Perfluoroalkanesulfonic Acids (PFSA) and Related Precursors: Focus on the Life Cycle of C6- and C10-Based Products. *Environ. Sci. Technol. Letters* **2019**, *6*, 1–7.
- (4) Sunderland, E. M.; Hu, X. C.; Dassuncao, C.; Tokranov, A. K.; Wagner, C. C.; Allen, J. G. A review of the pathways of human exposure to poly- and perfluoroalkyl substances (PFASs) and present understanding of health effects. *J. Exposure Sci. Environ. Epidemiol.* **2019**, *29*, 131–147.
- (5) Hu, X. D. C.; Dassuncao, C.; Zhang, X. M.; Grandjean, P.; Weihe, P.; Webster, G. M.; Nielsen, F.; Sunderland, E. M. Can profiles of poly- and Perfluoroalkyl substances (PFASs) in human serum provide information on major exposure sources? *Environ. Health* **2018**, *17*, 11.
- (6) Knutsen, H. K.; Alexander, J.; Barregård, L.; Bignami, M.; Brüschweiler, B.; Ceccatelli, S.; Cottrill, B.; Dinovi, M.; Edler, L. Risk to human health related to the presence of perfluorooctane sulfonic acid and perfluorooctanoic acid in food. *EFSA J.* **2018**, *16*, No. e05194.
- (7) Awad, E.; Zhang, X.; Bhavsar, S. P.; Petro, S.; Crozier, P. W.; Reiner, E. J.; Fletcher, R.; Tittlemier, S. A.; Braekevelt, E. Long-Term Environmental Fate of Perfluorinated Compounds after Accidental Release at Toronto Airport. *Environ. Sci. Technol.* **2011**, *45*, 8081–8089.
- (8) Casal, P.; González-Gaya, B.; Zhang, Y.; Reardon, A. J.; Martin, J. W.; Jimenez, B.; Dachs, J. Accumulation of Perfluoroalkylated Substances in Oceanic Plankton. *Environ. Sci. Technol.* **2017**, *51*, 2766–2775.
- (9) Zhao, Z.; Xie, Z.; Tang, J.; Sturm, R.; Chen, Y.; Zhang, G.; Ebinghaus, R. Seasonal variations and spatial distributions of

perfluoroalkyl substances in the rivers Elbe and lower Weser and the North Sea. *Chemosphere* **2015**, *129*, 118–125.

(10) Kwok, K. Y.; Wang, X. H.; Ya, M.; Li, Y.; Zhang, X. H.; Yamashita, N.; Lam, J. C.; Lam, P. K. Occurrence and distribution of conventional and new classes of per- and polyfluoroalkyl substances (PFASs) in the South China Sea. *J. Hazard. Mater.* **2015**, *285*, 389–397.

(11) Gonzalez-Gaya, B.; Dachs, J.; Roscales, J. L.; Caballero, G.; Jimenez, B. Perfluoroalkylated substances in the global tropical and subtropical surface oceans. *Environ. Sci. Technol.* **2014**, *48*, 13076–13084.

(12) Yeung, L. W.; Dassuncao, C.; Mabury, S.; Sunderland, E. M.; Zhang, X.; Lohmann, R. Vertical profiles, sources, and transport of PFASs in the Arctic Ocean. *Environ. Sci. Technol.* **2017**, *51*, 6735–6744.

(13) Li, L.; Zheng, H.; Wang, T.; Cai, M.; Wang, P. Perfluoroalkyl acids in surface seawater from the North Pacific to the Arctic Ocean: Contamination, distribution and transportation. *Environ. Pollut.* **2018**, *238*, 168–176.

(14) Takemine, S.; Matsumura, C.; Yamamoto, K.; Suzuki, M.; Tsurukawa, M.; Imaishi, H.; Nakano, T.; Kondo, A. Discharge of perfluorinated compounds from rivers and their influence on the coastal seas of Hyogo prefecture, Japan. *Environ. Pollut.* **2014**, *184*, 397–404.

(15) Zhou, Y.; Wang, T.; Li, Q.; Wang, P.; Li, L.; Chen, S. Q.; Zhang, Y. Q.; Khan, K.; Meng, J. Spatial and vertical variations of perfluoroalkyl acids (PFAAs) in the Bohai and Yellow Seas: Bridging the gap between riverine sources and marine sinks. *Environ. Pollut.* **2018**, *238*, 111–120.

(16) Beskoski, V. P.; Yamamoto, K.; Yamamoto, A.; Okamura, H.; Hayashi, M.; Nakano, T.; Matsumura, C.; Fukushima, K.; Wada, S.; Inui, H. Distribution of perfluoroalkyl compounds in Osaka Bay and coastal waters of Western Japan. *Chemosphere* **2017**, *170*, 260–265.

(17) Tomy, G. T.; Budakowski, W.; Halldorson, T.; Helm, P. A.; Stern, G. A.; Friesen, K.; Pepper, K.; Tittlemier, S. A.; Fisk, A. T. Fluorinated organic compounds in an eastern Arctic marine food web. *Environ. Sci. Technol.* **2004**, *38*, 6475–6481.

(18) Wang, Z.; DeWitt, J. C.; Higgins, C. P.; Cousins, I. T. A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? *Environ. Sci. Technol.* **2017**, *51*, 2508–2518.

(19) 3M, *Sulfonated perfluorochemicals: life-cycle waste stream estimates—Final report for 3M specialty materials*. 2000, 1063–1072. <http://www.chemicalindustryarchives.org/dirtysecrets/scotchgard/pdfs/226-0681.pdf> (accessed February 2014).

(20) Zushi, Y.; Hogarth, J. N.; Masunaga, S. Progress and perspective of perfluorinated compound risk assessment and management in various countries and institutes. *Clean Technol Environ* **2012**, *14*, 9–20.

(21) Wang, Z.; Cousins, I. T.; Scheringer, M. Comment on "The environmental photolysis of perfluorooctanesulfonate, perfluorooctanoate, and related fluorochemicals". *Chemosphere* **2015**, *122*, 301.

(22) Zhang, X.; Lohmann, R.; Dassuncao, C.; Hu, X. C.; Weber, A. K.; Vecitis, C. D.; Sunderland, E. M. Source attribution of poly- and perfluoroalkyl substances (PFASs) in surface waters from Rhode Island and the New York Metropolitan Area. *Environ. Sci. Technol. Lett.* **2016**, *3*, 316–321.

(23) Zhang, X.; Zhang, Y.; Dassuncao, C.; Lohmann, R.; Sunderland, E. M. North Atlantic Deep Water formation inhibits high Arctic contamination by continental perfluorooctane sulfonate discharges. *Global Biogeochem. Cycles* **2017**, *31*, 1332–1343.

(24) Walsh, J. J. Importance of Continental Margins in the Marine Biogeochemical Cycling of Carbon and Nitrogen. *Nature* **1991**, *350*, 53–55.

(25) Armitage, J. M.; MacLeod, M.; Cousins, I. T. Modeling the Global Fate and Transport of Perfluorooctanoic Acid (PFOA) and Perfluorooctanoate (PFO) Emitted from Direct Sources Using a Multispecies Mass Balance Model. *Environ. Sci. Technol.* **2009**, *43*, 1134–1140.

(26) Wania, F. A global mass balance analysis of the source of perfluorocarboxylic acids in the Arctic Ocean. *Environ. Sci. Technol.* **2007**, *41*, 4529–4535.

(27) Armitage, J.; Cousins, I. T.; Buck, R. C.; Prevedouros, K.; Russell, M. H.; MacLeod, M.; Korzeniowski, S. H. Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources. *Environ. Sci. Technol.* **2006**, *40*, 6969–6975.

(28) Kwon, E. Y.; Kim, G.; Primeau, F.; Moore, W. S.; Cho, H. M.; DeVries, T.; Sarmiento, J. L.; Charette, M. A.; Cho, Y. K. Global estimate of submarine groundwater discharge based on an observationally constrained radium isotope model. *Geophys. Res. Lett.* **2015**, *41*, 8438–8444.

(29) Weber, A. K.; Barber, L. B.; LeBlanc, D. R.; Sunderland, E. M.; Vecitis, C. D. Geochemical and hydrologic factors controlling subsurface transport of Poly- and perfluoroalkyl substances, Cape Cod, Massachusetts. *Environ. Sci. Technol.* **2017**, *51*, 4269–4279.

(30) Pickard, H. M.; Criscitiello, A. S.; Spencer, C.; Sharp, M. J.; Muir, D. C.; Silva, A. O. D.; Young, C. J. Continuous non-marine inputs of per- and polyfluoroalkyl substances to the High Arctic: a multi-decadal temporal record. *Atmos. Chem. Phys.* **2018**, *18*, 5045–5058.

(31) Young, C. J.; Furdui, V. I.; Franklin, J.; Koerner, R. M.; Muir, D. C.; Mabury, S. A. Perfluorinated acids in arctic snow: new evidence for atmospheric formation. *Environ. Sci. Technol.* **2007**, *41*, 3455–3461.

(32) Wagner, C. C.; Amos, H. M.; Thackray, C. P.; Zhang, Y.; Lundgren, E. W.; Forget, G.; Friedman, C. L.; Selin, N. E.; Lohmann, R.; Sunderland, E. M. A global 3-D ocean model for PCBs: Benchmark compounds for understanding the impacts of global change on neutral persistent organic pollutants. *Global Biogeochem. Cycles* **2019**, 469.

(33) Nizzetto, L.; Gioia, R.; Li, J.; Borgà, K.; Pomati, F.; Bettinetti, R.; Dachs, J.; Jones, K. C. Biological pump control of the fate and distribution of hydrophobic organic pollutants in water and plankton. *Environ. Sci. Technol.* **2012**, *46*, 3204–3211.

(34) Dachs, J.; Lohmann, R.; Ockenden, W. A.; Méjanelle, L.; Eisenreich, S. J.; Jones, K. C. Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. *Environ. Sci. Technol.* **2002**, *36*, 4229–4237.

(35) Muir, D.; Lohmann, R. Water as a new matrix for global assessment of hydrophilic POPs. *TrAC, Trends Anal. Chem.* **2013**, *46*, 162–172.

(36) Taniyasu, S.; Kannan, K.; So, M. K.; Gulkowska, A.; Sinclair, E.; Okazawa, T.; Yamashita, N. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. *J. Chromatogr. A* **2005**, *1093*, 89–97.

(37) Helsel, D. R. *Nondetects and data analysis: statistics for censored environmental data*; Wiley-Interscience: Hoboken, N.J., 2005; p xv, 250 p.

(38) D'eon, J. C.; Crozier, P. W.; Furdui, V. I.; Reiner, E. J.; Libelo, E. L.; Mabury, S. A. Perfluorinated Phosphonic Acids in Canadian Surface Waters and Wastewater Treatment Plant Effluent: Discovery of a New Class of Perfluorinated Acids. *Environ. Toxicol. Chem.* **2009**, *28*, 2101–2107.

(39) Castiglioni, S.; Valsecchi, S.; Polesello, S.; Rusconi, M.; Melis, M.; Palmiotto, M.; Manenti, A.; Davoli, E.; Zuccato, E. Sources and fate of perfluorinated compounds in the aqueous environment and in drinking water of a highly urbanized and industrialized area in Italy. *J. Hazard. Mater.* **2015**, *282*, 51–60.

(40) Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Official Journal of the European Union, 2013. L226: p. 1–17.

(41) Schenker, U.; Scheringer, M.; Macleod, M.; Martin, J. W.; Cousins, I. T.; Hungerbuhler, K. Contribution of volatile precursor substances to the flux of perfluorooctanoate to the arctic. *Environ. Sci. Technol.* **2008**, *42*, 3710–3716.

- (42) Zhao, L. J.; Folsom, P. W.; Wolstenholme, B. W.; Sun, H. W.; Wang, N.; Buck, R. C. 6:2 Fluorotelomer alcohol biotransformation in an aerobic river sediment system. *Chemosphere* **2013**, *90*, 203–209.
- (43) Gustafson, C.; Key, K.; Evans, R. L. Aquifer systems extending far offshore on the U.S. Atlantic margin. *Sci. Rep.* **2019**, *9*, 8709.
- (44) Australian National Industrial Chemicals Notification and Assessment Scheme (NICNAS), Indirect precursors of perfluorobutanesulfonate (PFBS): Environment tier II assessment. <https://www.nicnas.gov.au/chemical-information/imap-assessments/imap-assessments/tier-ii-environment-assessments/indirect-precursors-of-perfluorobutanesulfonate-pfbs> - ChemicalIdentity (accessed Aug 2018). 2018.
- (45) Del Vento, S.; Halsall, C.; Gioia, R.; Jones, K.; Dachs, J. Volatile per- and polyfluoroalkyl compounds in the remote atmosphere of the western Antarctic Peninsula: an indirect source of perfluoroalkyl acids to Antarctic waters? *Atmos. Pollut. Res.* **2012**, *3*, 450–455.
- (46) Benskin, J. P.; Muir, D. C. G.; Scott, B. F.; Spencer, C.; De Silva, A. O.; Kylin, H.; Martin, J. W.; Morris, A.; Lohmann, R.; Tomy, G.; Rosenberg, B.; Taniyasu, S.; Yamashita, N. Perfluoroalkyl Acids in the Atlantic and Canadian Arctic Oceans. *Environ. Sci. Technol.* **2012**, *46*, 5815–5823.
- (47) Ahrens, L.; Barber, J. L.; Xie, Z. Y.; Ebinghaus, R. Longitudinal and Latitudinal Distribution of Perfluoroalkyl Compounds in the Surface Water of the Atlantic Ocean. *Environ. Sci. Technol.* **2009**, *43*, 3122–3127.
- (48) Bräunig, J.; Baduel, C.; Heffernan, A.; Rotander, A.; Donaldson, E.; Mueller, J. F. Fate and redistribution of perfluoroalkyl acids through AFFF-impacted groundwater. *Sci. Total Environ.* **2017**, *596*–597, 360–368.
- (49) Post, V. E.; Vandenbohede, A.; Werner, A. D.; Teubner, M. D. Groundwater ages in coastal aquifers. *Adv. Water Resour.* **2013**, *57*, 1–11.
- (50) Houde, M.; Czub, G.; Small, J. M.; Backus, S.; Wang, X.; Alae, M.; Muir, D. C. Fractionation and bioaccumulation of perfluoro-octane sulfonate (PFOS) isomers in a Lake Ontario food web. *Environ. Sci. Technol.* **2008**, *42*, 9397–9403.
- (51) Lam, N. H.; Cho, C. R.; Lee, J. S.; Soh, H. Y.; Lee, B. C.; Lee, J. A.; Tatarozako, N.; Sasaki, K.; Saito, N.; Iwabuchi, K.; Kannan, K.; Cho, H. S. Perfluorinated alkyl substances in water, sediment, plankton and fish from Korean rivers and lakes: a nationwide survey. *Sci. Total Environ.* **2014**, *491*–492, 154–62.
- (52) Loi, E. I. H.; Yeung, L. W. Y.; Taniyasu, S.; Lam, P. K. S.; Kannan, K.; Yamashita, N. Trophic Magnification of Poly- and Perfluorinated Compounds in a Subtropical Food Web. *Environ. Sci. Technol.* **2011**, *45*, 5506–5513.
- (53) Fang, S.; Chen, X.; Zhao, S.; Zhang, Y.; Jiang, W.; Yang, L.; Zhu, L. Trophic magnification and isomer fractionation of perfluoroalkyl substances in the food web of Taihu Lake, China. *Environ. Sci. Technol.* **2014**, *48*, 2173–82.
- (54) Xu, J.; Guo, C. S.; Zhang, Y.; Meng, W. Bioaccumulation and trophic transfer of perfluorinated compounds in a eutrophic freshwater food web. *Environ. Pollut.* **2014**, *184*, 254–61.
- (55) Gebbink, W. A.; Bignert, A.; Berger, U. Perfluoroalkyl Acids (PFAAs) and Selected Precursors in the Baltic Sea Environment: Do Precursors Play a Role in Food Web Accumulation of PFAAs? *Environ. Sci. Technol.* **2016**, *50*, 6354–62.
- (56) O'Reilly, J. E.; Zetlin, C. A. (1998) Seasonal, horizontal, and vertical distribution of phytoplankton chlorophyll a in the northeast US continental shelf ecosystem. *NOAA Technical Report NMFS 139* https://repository.library.noaa.gov/view/noaa/3055/noaa_3055_DS1.pdf (accessed September 2019).
- (57) Kane, J. Decadal Distribution and Abundance Trends for the Late Stage Copepodites of Pseudocalanus spp. (Copepoda: Calanoida) in the US Northeast Continental Shelf Ecosystem. *J. Northw. Atl. Fish. Sci.* **2014**, *46*, 1–13.
- (58) Friedland, K. D.; Record, N. R.; Asch, R. G.; Kristiansen, T.; Saba, V. S.; Drinkwater, K. F.; Henson, S.; Leaf, R. T.; Morse, R. E.; Johns, D. G. Seasonal phytoplankton blooms in the North Atlantic linked to the overwintering strategies of copepods. *Elem Sci Anth* **2016**, *4*.
- (59) Bi, H.; Ji, R.; Liu, H.; Jo, Y.-H.; Hare, J. A. Decadal changes in zooplankton of the Northeast U.S. continental shelf. *PLoS One* **2014**, *9*, No. e87720.
- (60) Zhang, S.; Lu, X.; Wang, N.; Buck, R. C. Biotransformation potential of 6: 2 fluorotelomer sulfonate (6: 2 FTSA) in aerobic and anaerobic sediment. *Chemosphere* **2016**, *154*, 224–230.
- (61) Houtz, E. F.; Sutton, R.; Park, J.-S.; Sedlak, M. Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. *Water Res.* **2016**, *95*, 142–149.
- (62) Wang, N.; Szostek, B.; Buck, R. C.; Folsom, P. W.; Sulecki, L. M.; Gannon, J. T. 8-2 Fluorotelomer alcohol aerobic soil biodegradation: Pathways, metabolites, and metabolite yields. *Chemosphere* **2009**, *75*, 1089–1096.
- (63) Joers, H.; Apel, C.; Ebinghaus, R. Emerging per- and polyfluoroalkyl substances (PFASs) in surface water and sediment of the North and Baltic Seas. *Sci. Total Environ.* **2019**, *686*, 360.
- (64) Higgins, C. P.; Luthy, R. G. Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* **2006**, *40*, 7251–7256.
- (65) Ahrens, L.; Yeung, L. W. Y.; Taniyasu, S.; Lam, P. K. S.; Yamashita, N. Partitioning of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonamide (PFOSA) between water and sediment. *Chemosphere* **2011**, *85*, 731–737.
- (66) Chen, H.; Zhang, C.; Yu, Y.; Han, J. Sorption of perfluorooctane sulfonate (PFOS) on marine sediments. *Mar. Pollut. Bull.* **2012**, *64*, 902–906.
- (67) Xie, W.; Bothun, G. D.; Lehmler, H.-J. Partitioning of perfluorooctanoate into phosphatidylcholine bilayers is chain length-independent. *Chem. Phys. Lipids* **2010**, *163*, 300–308.
- (68) Dassuncao, C.; Hu, X. C.; Zhang, X.; Bossi, R.; Dam, M.; Mikkelsen, B.; Sunderland, E. M. Temporal Shifts in Poly- and Perfluoroalkyl Substances (PFASs) in North Atlantic Pilot Whales Indicate Large Contribution of Atmospheric Precursors. *Environ. Sci. Technol.* **2017**, *51*, 4512–4521.
- (69) Sanchez-Vidal, A.; Llorca, M.; Farré, M.; Canals, M.; Barceló, D.; Puig, P.; Calafat, A. Delivery of unprecedented amounts of perfluoroalkyl substances towards the deep-sea. *Sci. Total Environ.* **2015**, *526*, 41–48.
- (70) Marshall, J.; Hill, C.; Perelman, L.; Adcroft, A. Hydrostatic, quasi-hydrostatic, and nonhydrostatic ocean modeling. *J. Geophys. Res.: Oceans* **1997**, *102*, 5733–5752.
- (71) Wunsch, C.; Heimbach, P. Practical global oceanic state estimation. *Phys. D* **2007**, *230*, 197–208.
- (72) Miyake, Y.; Yamashita, N.; Rostkowski, P.; So, M. K.; Taniyasu, S.; Lam, P. K.; Kannan, K. Determination of trace levels of total fluorine in water using combustion ion chromatography for fluorine: a mass balance approach to determine individual perfluorinated chemicals in water. *J. Chromatogr. A* **2007**, *1143*, 98–104.