North Atlantic Deep Water formation inhibits high Arctic contamination by continental perfluorooctane sulfonate discharges

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Abstract

Perfluorooctane sulfonate (PFOS) is an aliphatic fluorinated compound with eight carbon atoms that is extremely persistent in the environment and can adversely affect human and ecological health. Its production was phased out in North America in 2000, but the ocean is the terminal PFOS sink. This study develops a new model for PFOS cycling in the North Atlantic Ocean and transport to sensitive Arctic regions based on best understanding of ocean physics and ecology. Results suggest that in 2015, 60% of cumulative PFOS discharges from North America and Europe were still present in the North Atlantic and 30% had entered the Arctic Ocean. Most of the remaining fraction was transported to the South Atlantic. The lifetime of PFOS in the surface ocean is less than 5 years due to rapid penetration into deeper waters where it persists for decades or longer before being transported to other basins. During peak production years, most continental PFOS pollution was transported to the sub-Arctic but large-scale overturning of the North Atlantic Ocean reduced the total burden entering the high Arctic by 70%. Climate-driven changes in ocean circulation that are weakening this process may thus increase the vulnerability of the Arctic to continental pollution.

1. Introduction

Perfluorooctane sulfonate (PFOS) is an aliphatic organofluorine molecule containing eight carbon atoms, a highly fluorinated “tail,” and a hydrophilic sulfonate “head” group. It has been transported in wastewater and rivers to the global oceans as a terminal sink after use in furniture and carpet coatings, food packaging, nonstick cookware, outdoor clothing/gear, and industrial applications since the 1950s [Wang et al., 2017]. Biomonitoring studies have revealed high PFOS concentrations in many marine food webs and exposures pose risks to both human and ecological health [Tomy et al., 2004; Dassuncao et al., 2017]. PFOS does not appreciably degrade under environmental conditions due to the strength of carbon-fluorine bonds.
empirically derived organic carbon normalized partition coefficients can also occur during chemical manufacturing but are estimated to account for only 1% of total inputs to the ocean [Armitage et al., 2009a]. The impact of changes in PFOS production on continental discharges and subsequent accumulation in the ocean is poorly understood. Prior work suggests vertical diffusion and sorption to settling particles are important for oceanic transport of PFASs [Lohmann et al., 2013; Sanchez-Vidal et al., 2015]. Seawater PFOS measurements are limited and modeling studies have not previously resolved basin-scale inputs and circulation [Armitage et al., 2009a; Schenker et al., 2008]. The only prior ocean model for PFOS contained 18° latitudinal bands for the globe and did not distinguish the Atlantic and Pacific basins [Armitage et al., 2009a]. Previous modeling studies for other PFASs similarly do not consider spatial variability in oceanic concentrations and transport or lack detailed release estimates for continental discharges [Armitage et al., 2009b; Wania, 2007; Stemmler and Lammel, 2010].

The main objectives of this work are to (1) quantify the magnitude and spatial distribution of continental PFOS discharges to the North Atlantic Ocean and (2) better characterize the roles of lateral and vertical transport processes for the distribution and lifetime of PFOS in the marine water column. We develop an inventory of cumulative continental PFOS releases from wastewater and rivers in North America and Europe between 1958 and 2010 and use it to force a new 3-D simulation for the North Atlantic Ocean within the MITgcm [Marshall et al., 1997]. We evaluate the model using available seawater PFOS measurements and apply it to investigate how changing releases have affected spatial and temporal variability in concentrations and inputs to the Arctic Ocean. This information is needed to further assess the potential viability of PFOS as a tracer for ocean transport processes as well as its significance as a toxicant in marine food webs since biological exposures are driven by seawater concentrations.

2. Model Description

The MITgcm is an ocean general circulation model (http://mitgcm.org) that contains a biogeochemical and ecological model for cycling of carbon, nitrogen, silica, phosphorus, and iron through inorganic, living plankton (phytoplankton and zooplankton), and dead organic matter [Dutkiewicz et al., 2009]. It has a horizontal resolution of 1° × 1° and includes 23 vertical levels. Ocean state estimates are based on the Estimating Circulation and Climate of the Ocean (ECCO-GODAE) data product [Marshall et al., 1997; Wunsch and Heimbach, 2007]. We added tracers for the dissolved and particle-bound forms of PFOS that are transported laterally and vertically by oceanic circulation, mixing and particle settling.

PFOS has a $pK_a$ of negative three and is extremely stable in solution [Campbell et al., 2009; Cheng et al., 2009; Vecitis et al., 2008]. Partitioning between the aqueous phase and suspended particles is simulated using an empirically derived organic carbon normalized partition coefficient ($\log K_{OC} = 2.6$) [Higgins and Luthy, 2006]. Particle concentrations, composition, and export fluxes are based on the ecology simulation embedded in the MITgcm [Dutkiewicz et al., 2009] and used to simulate vertical PFOS transport associated with settling particles.
The model is initialized by assuming zero oceanic PFOS concentrations before 1958, the onset of chemical production. For the years 1958 to 2010, the model is forced with $1^\circ \times 1^\circ$ gridded inputs to the North Atlantic Ocean between 20°N and 60°N from rivers and wastewater treatment plants in North America and Europe using the inventory developed here. The simulation is continued with zero inputs between 2010 and 2038 to capture the phaseout in PFOS production. We divide annual inputs equally over each 3 h time step in the model simulation because available monitoring data do not show significant seasonal differences (supporting information Table S1) [Boulanger et al., 2004; Schultz et al., 2006; Loganathan et al., 2007; Plumlee et al., 2008; Erickson et al., 2009; Furl et al., 2011; Furdui et al., 2008; D'éon et al., 2009; Guerra et al., 2014].


We developed a time-dependent inventory of PFOS inputs from wastewater treatment plants and rivers to the North Atlantic between 1958 and 2010. We neglect PFOS originating from degradation of atmospheric precursors because atmospheric inputs to the ocean are thought to be small [Armitage et al., 2009a].

PFOS inputs from European rivers to the North Atlantic (Figure S1) are based on monitoring data for 2006–2007 and the relationship derived by Pistocchi and Loos [2009] between measured PFOS concentrations in river water ($E_R$, kg a$^{-1}$) and population within a watershed basin ($P_B$):

$$ E_R = 9.6 \times 10^{-9} P_B^{1.0115} \tag{1} $$

To estimate temporal changes in loading, we scaled per-capita releases calculated from gridded European population data [Center for International Earth Science Information Network, Columbia University et al., 2005] by relative changes in annual production of the parent chemical to PFOS (perfluorooctane sulfonyl fluoride: POSF) for all years between 1958 and 2010 [Armitage et al., 2009a; Paul et al., 2009; Zhang et al., 2012].

Comprehensive riverine PFOS monitoring data are not available for North America for any year. Thus, we compiled PFOS wastewater monitoring data (Table S1 and Figure S2) from 19 Canadian facilities between 2009 and 2010 [Guerra et al., 2014] and 36 U.S. facilities in 2007 [Erickson et al., 2009]. Following Pistocchi and Loos [2009], we related PFOS releases ($E_W$, µg d$^{-1}$) to population served ($P_W$) using power regression analysis:

$$ E_W = \beta P_W^a \tag{2} $$

where $\beta$ represents the baseline per-capita PFOS discharge rate, which is equal to 0.21 for Canada and 0.47 for the U.S. (Figure S3). The parameter $a$ is a scaling factor representing a nonlinear increase in PFOS releases with population served, equal to 1.24 ± 0.09 for Canada and 1.21 ± 0.10 for the U.S. (Figure S3).

Only 9.9% of the municipalities in Canada [Environment Canada, 2009] and 1.8% of wastewater treatment plants in the U.S. [U.S. Environmental Protection Agency (EPA), 2008] discharge directly into the North Atlantic (Figure S4 and Table S2). To calculate wastewater PFOS inputs to river basins that enter the North Atlantic Ocean (Figure S5 and Table S3), we summed PFOS discharges derived from the total populations served by wastewater treatment facilities within each catchment area using ArcGIS [Environment Canada, 2009; Global Runoff Data Centre, 2007; U.S. EPA, 2008]. We also included direct releases (360 Mg during 1958–2002) from the 3M Decatur (Alabama) facility to the Mississippi watershed that accounted for a large fraction of global production in 2002 [Armitage et al., 2009a; Filipovic et al., 2013; Scott et al., 2009; 3M, 2000].

We neglected other environmental release pathways such as leaching from landfills because they comprise <10% of total releases on the continental scale, even though they can be important for inland rivers and streams [e.g., Zhang et al., 2016]. We derived basin wide releases (µg person$^{-1}$ a$^{-1}$) based on wastewater treatment plants within each catchment area [CIESN, 2005]. Temporal changes in global historical inventories [Armitage et al., 2009b; Wang et al., 2014a] were used to scale population-based releases over the full history of production.

There are no data available for riverine or wastewater PFOS discharges in North Africa, Mexico, and Central America. We assumed that population-based PFOS emission factors were approximately 1 order of magnitude lower than those in Northern Europe based on wastewater monitoring data (Figure S6) from other
developing areas [Filipovic et al., 2013; Xie et al., 2013]. We scaled temporal changes in population-based inputs using global historical release inventories in the same manner as other regions [Armitage et al., 2009b; Wang et al., 2014a].

We assumed all riverine PFOS will enter the ocean within 1 year except for systems where flow is mediated by the presence of a large inland water body (i.e., the St. Lawrence River/Lake Ontario, the Nelson River/Lake Winnipeg, and the Danish Straits/Baltic Sea). We estimated transport times for these systems by calibrating the lag time in a one-box model to measured PFOS concentrations leaving these systems, given inputs estimated from this work (Table S4). Resulting lag times ranged between 1.5 and 2.5 years. We did not use the residence time for each of these water bodies because we do not expect PFOS to be well mixed.

3.1. Uncertainty in Release Estimates

We estimate a five-fold uncertainty in continental PFOS discharges presented here based on the 95% confidence intervals of regression relationships for the U.S. and Canada (Figure S3). We propagate this uncertainty for evaluation of model results and use available measurements to constrain inputs. Uncertainty estimated here is slightly lower than the approximately 1 order of magnitude uncertainty for other PFAS inventories. In prior work, uncertainty estimates reflected limited information on the magnitude of PFASs emissions from products containing these compounds, assumptions about yields of atmospheric precursors, and ranges in industrial release estimates [Prevedouros et al., 2006; Paul et al., 2009; Armitage et al., 2009a, 2009b; Wang et al., 2014a, 2014b].

4. Model Evaluation

The median discharge scenario based on wastewater and riverine monitoring data suggests that $2.7 \times 10^3$ Mg PFOS has cumulatively entered the North Atlantic since 1958 (low bound: $5.3 \times 10^2$ Mg, high bound $1.3 \times 10^4$ Mg, Figure 1). North American coastal releases accounted for 59% of total releases, and the remaining 41% was from Europe (Figure 1). Inputs to the North Atlantic peaked in the year 2000 and declined to negligible amounts by 2010 (Figure 1). For the median release scenario, an additional $1.5 \times 10^3$ Mg of PFOS flowed into the North Atlantic indirectly from the Gulf of Mexico and Mediterranean Sea.

Direct release values from two previous PFOS inventories based on chemical production and product use are comparable to the low and median bounds for this work. Armitage et al. [2009a] suggested cumulative direct global releases to the ocean of $2.8 \times 10^2$ to $2.3 \times 10^3$ Mg between the years 1957 and 2002. Most releases were concentrated in North America and Europe between 36 and 54°N [Armitage et al., 2009b]. Paul et al. [2009] similarly estimated total global historical PFOS emissions to air and water to be $4.5 \times 10^2$ to $2.7 \times 10^3$ Mg between 1970 and 2002. Indirect (atmospheric) PFOS inputs to the global oceans are thought to be smaller ($5–230$ Mg) based on work by Armitage et al. [2009a]. We find the high estimate of PFOS releases derived here is implausible based on these global production constraints [Armitage et al., 2009a; Paul et al., 2009].

Figure 2a compares modeled surface seawater (10 m) concentrations for the year 2010 based on the median scenario for PFOS releases (Figure 1) with observed surface seawater concentrations between 2009 and 2011. Relatively high concentrations are apparent next to continental source regions in eastern North America and the North Sea, and relatively lower levels are observed in the eastern subtropical region (Sargasso Sea). We divided the North Atlantic Ocean into the biogeographical provinces characterized by Longhurst [2007] to
assess performance of the model in different regions. We do not consider coastal monitoring data because the model is not intended to capture the fine-scale circulation and dynamics of inland seas and estuaries.

Modeled seawater concentrations capture most of the variability in the observed data ($R^2 = 0.90$, $p = 0.01$) across biogeographical provinces (Figure 2b). The grey dashed line in Figure 2b indicates perfect agreement between measured and modeled results, and the regression relationship indicates that the model has a high mean bias of 75% relative to observations for all regions. Measured PFOS concentrations are lower in the western portion of the North Atlantic Subtropical Gyral Province (NASW) in the Sargasso Sea, and the southern North Atlantic Tropical Gyral Province (NATR), than those in the eastern North Atlantic Subtropical Province (NASE) and the North Atlantic Drift Province (NADR) below Greenland. Surface PFOS measurements are from Ahrens et al. [2009a, 2009b, 2010b; Benskin et al., 2012; Gonzalez-Gaya et al., 2014, and Zhao et al., 2012].

Figure 2. Modeled and observed surface seawater PFOS concentrations (pg L$^{-1}$) in the North Atlantic Ocean. (a) The modeled surface (10 m) seawater concentrations for 2010 compared to observations for 2009–2011. (b) The modeled and observed PFOS concentrations grouped by Longhurst Biogeographical Provinces [Longhurst, 2007], where error bars indicate standard error around the mean for both the model and observations. Grey dashed line indicates 1:1 fit between modeled and observed surface water concentrations. Regression slope indicates the median release scenario (Figure 1) results in a model bias relative to surface water PFOS observations of 75%. Modeled surface water concentrations capture 90% of the observed variability across biogeographical provinces [Longhurst, 2007]. NADR = North Atlantic Drift Province [Ahrens et al., 2009a, 2010b; Benskin et al., 2012]; GFST = Gulf Stream Province, NASW = North Atlantic Subtropical Province (west), NASE = North Atlantic Subtropical Province (east), and NATR = North Atlantic Tropical Gyral Province. Surface PFOS measurements are from Ahrens et al. [2009a, 2009b, 2010b; Benskin et al. (2012); Gonzalez-Gaya et al., 2014, and Zhao et al. (2012).
5. Model Uncertainty and Sensitivity Analysis

For all ocean inputs, we conducted sensitivity analyses allowing for additional lag times of 2, 5, and 10 years between PFOS distribution in products and releases from watersheds to the ocean (Figure S7). Some studies have suggested that there may be a substantial lag between wastewater PFOS releases to aquatic systems and transport to marine areas due to slow transport in groundwater [Filipovic et al., 2013]. We find introducing an additional lag exacerbates overestimates for recently measured surface seawater concentrations (Figures 2b and 3). Thus, we retain the base assumption that most PFOS releases in wastewater will be transported to the ocean within 1 year.

We consider uncertainty in the empirically measured partition coefficient for PFOS using sensitivity analysis on the upper and lower bounds reported in the literature (log $K_{oc} = 2.4$ to $3.8$) [Ahrens et al., 2011; Ferrey et al., 2012]. Results of our simulation suggest that the mass of vertically transported PFOS in the ocean associated with settling particles is negligible compared to that from lateral and vertical ocean circulation (Figure S8). Modeled concentrations of PFOS bound to particles (Figure S8) are consistent with limited measurements that were all $<10$ pg L$^{-1}$ [Ahrens et al., 2009a]. We examined the sensitivity of this finding to the range in partition coefficients reported in the literature. The maximum log $K_{oc}$ value reported in prior work is 3.8 [Ahrens et al., 2011], compared to the value of 2.6 [Higgins and Luthy, 2006] specified in our base simulation. This does not change our initial finding as the fraction of particle bound PFOS in seawater is negligible across expected ranges of $K_{oc}$ and potential POC concentrations in seawater (Figure S9). Previous studies that considered PFOS fluxes associated with settling of suspended particles in isolation suggest this may be a substantial oceanic transport process [Sanchez-Vidal et al., 2015]. Our model results indicate this is not the case for the North Atlantic.

6. Spatial Distribution of PFOS in Seawater

The major surface currents in the Atlantic Ocean result in predominantly eastern and northern transport of coastal PFOS pollution sources toward the Subarctic (Figure 4). Surface water PFOS concentrations in 1980 and 2000 varied by more than an order of magnitude in PFOS enriched seawater plumes from the St. Lawrence River, Florida Current, and North Sea (Figure 4a). The Gulf Stream transports PFOS entrained in the Florida Current into the central and eastern Atlantic Ocean, where it merges with the North Atlantic Current (NAC) and diverges both north and east [Pickard and Emery, 1990]. This is visible in Figures 4a and 4b by offshore dilution and diffusion north and east of elevated PFOS concentrations in the Gulf Stream. These results help to explain the relatively lower PFOS concentrations measured in seawater from the western part of the North Atlantic Subtropical Gyral Province (NASW, Figure 2).

Transport patterns for PFOS enriched surface waters (Figure 2) imply the North Atlantic is a large source to the Arctic. North Atlantic seawater enters the Arctic at multiple depths. This circulation is critical for transfer of heat into polar regions and meridional overturning of the ocean [Askenov et al., 2010]. PFOS discharges...
from the North Sea (Figure 4) are predominantly transported north into the Norwegian and Greenland Seas [Smith et al., 2011]. Surface waters from this area enriched in PFOS become dense during winter cooling, sink, and form the lower limb of the North Atlantic Deep Water (NADW) that flows south as part of global thermohaline circulation [Pickard and Emery, 1990]. The Norwegian and Greenland Sea regions supply an estimated 80% of the NADW [Harvey and Thedorou, 1986; Pickard and Emery, 1990].

Similarly, surface waters entrained in the Labrador Current that captures PFOS discharges from the Hudson Bay sink in “convective chimneys” from the center of the Labrador Gyre [Clarke and Gascard, 1983] and are transported south in NADW primarily in the western Atlantic in the Deep Western Boundary Current (DWBC) [Rhein et al., 2015]. Apparent ages of NADW determined from tracers around 55°N are generally less than a decade, even at depths greater than 3500 m [Doney and Bullister, 1992; Rhein et al., 2015]. This explains the penetration of PFOS to the ocean floor in this region (mean: 12 pg L\(^{-1}\) below 1000 m) based on the vertical profiles measured by Yamashita et al. [2008] in the Labrador Sea in 2004 (Figure 3). For vertical profiles collected by Yamashita et al. [2008] between 25°N and 30°N (Figure 3), seawater below 1000 m also contained detectable but lower levels of PFOS (generally <5 pg L\(^{-1}\), Figure 3). These water depths primarily contain NADW transported south and may have some influence from Mediterranean outflow [Pickard and Emery, 1990]. Rhein et al. [2015] reported the western Atlantic portion of NADW around these latitudes (in the Sargasso Sea) has an apparent age of around 30 years, which suggests an influence from surface inputs of PFOS in the early to middle 1970s.

7. Temporal Changes in PFOS Concentrations and Mass Budgets for the North Atlantic

Figure 5 shows the temporal evolution of PFOS concentrations in seawater from the surface mixed layer (0–10 m), subsurface (360–510 m), and near the permanent thermocline (985–1335 m). Concentrations between 0 and 10 m depth peak in 2001 (basin-wide median: 66 pg L\(^{-1}\)), 1 year after maximum releases from rivers and wastewater. Spatial heterogeneity in surface water concentrations is reflected by the wide variability in 95th percentile confidence intervals (CI) shown in Figure 5 (2001: 9–633 pg L\(^{-1}\)) that become more homogeneous over time (2015: 22–53 pg L\(^{-1}\)).

PFOS concentrations in subsurface seawater (365–510 m) are lower and less variable than surface waters due to dilution with lower concentration subsurface seawater (Figure 5). The lag time between peak releases (circa 2000) and peak subsurface concentrations (circa 2005, 41 pg L\(^{-1}\), 95th CI: 27–66) at these depths is 2–3 years. This likely reflects strong winter convection in the subpolar North Atlantic, which results in
mixing with subsurface waters up to ~600 m depth [McCartney and Talley, 1982]. By 2015, median modeled concentrations declined to 37 pg L\(^{-1}\) and variability in ocean concentrations is much smaller than earlier years (95th CI: 30–47, Figure 5). A longer lag after peak releases is observed for peak PFOS concentrations in deeper waters around the permanent thermocline (985–1335 m) (Figure 5). Modeled concentrations plateau in 2040 around a median of 26 pg L\(^{-1}\). The effects of water mass circulation in different regions are evident in Figure 5, where the 95th percentile concentrations, representing more recently ventilated water masses, peaked in 2009 at 47 pg L\(^{-1}\) (a 9 year lag) and have declined since this time. By contrast, the 5th percentile of PFOS concentrations in the North Atlantic are continuing to slowly increase and are expected to reach 9 pg L\(^{-1}\) in 2040 (lag time more than three decades). Similar patterns have been reported for other pollutants in the North Atlantic such as lead (Pb), due to time required for subduction and ventilation of surface seawater into the thermocline [Wu and Boyle, 1997]. Cumulative PFOS inputs to the North Atlantic between 1958 and 2015 estimated in this study are \(2.4 \times 10^3\) Mg. The North Atlantic PFOS reservoir in 2015 was equivalent to approximately 60% of inputs in 2015 (\(1.4 \times 10^3\) Mg, Figure 6), with the remaining fractions lost to the Arctic Ocean (30%), tropical Atlantic plus other regions (10%). Over time, the mass distribution of PFOS has shifted toward deeper waters from >80% in the upper ocean (top 1000 m) in 2000 to approximately 50% in 2015, consistent with Figure 5. This has important implications for reducing biological exposures as most marine life is found in the upper 1000 m of the ocean [Ryther, 1969].

Lifetimes of PFOS against losses (reservoir/gross losses) from this work range from 1 to 3 years (half-life: \(t_{1/2} = 1–2\) years) in the surface mixed layer of the North Atlantic to one to two decades in the deep ocean (Table 1). Loss processes are mainly internal circulation and outflow to the Arctic (>60°N), Mediterranean Sea, and the tropical Atlantic Ocean (<20°N) (Figure 6). By 2015, 85% of total losses from the Atlantic Ocean had been transported into the Arctic, with smaller outflow to other regions. Basin-wide lifetimes are shorter in 2000 than 2015, reflecting the entrainment of PFOS source regions in energetic currents in the ocean such as the Gulf Stream (Figure 4). Gonzalez-Gaya et al. [2014] estimated a 5.8 year half-life in the

**Figure 5.** Modeled PFOS concentrations in North Atlantic Seawater (pg L\(^{-1}\)) between 20°N and 60°N at different seawater depths based on the median PFOS release scenarios shown in Figure 1, adjusted for mean bias (75%). Shading indicates distributions of concentrations in different ocean regions with the median across the whole basin indicated as a solid line. Darker shading indicates 25th and 75th percentile modeled concentrations and 95th percentiles are shown as the lightest blue bounds.

**Figure 6.** Mass flows of PFOS in the North Atlantic (Mg a\(^{-1}\)) between 20°N and 60°N for the years 2000 (peak inputs) and 2015. Results are from the median release scenario (Figure 1) and adjusted for mean bias (75%).
North Atlantic based on observations for another PFAS with the same number of carbon atoms. For seawater between 100 and 1000 m, modeled half-lives for PFOS in this study were approximately 3 years. Variable lag times and vertical differences in seawater concentrations (Table 1 and Figure 5) help to explain mixed temporal trends in biological PFOS concentrations measured in the North Atlantic and Subarctic (Bossi et al., 2005; Butt et al., 2010; Dassuncao et al., 2017). Our results imply declining PFOS exposures since 2011 for fish and marine mammals that predominantly forage in the ocean surface mixed layer. Temporal changes are expected to be more variable for complex food webs with mixed prey items and biota that forage from deeper seawater such as North Atlantic pilot whales (Globicephala melas) that mainly consume squid between 400 and 700 m depth (Hoydal and Lastein, 1993; Li et al., 2015). A reported increase in PFOS concentrations in pilot whale muscle between 1987 and the present is consistent with trends in middepth to thermocline waters shown in Figure 5 (Dassuncao et al., 2017).

8. Implications for PFOS Inputs to the Arctic Ocean

Figure 7 shows gross PFOS flows at different seawater depths into and out of the Arctic (above 60°N) from the North Atlantic between 1958 and 2040. Most inputs to the Arctic Ocean are from middepth inflow (20–1000 m), which cumulatively accounted for 1.1 × 10^3 Mg PFOS between 1958 and 2015 (surface inflow, 0–20 m = 60 Mg). Some of the North Atlantic inflow sank and mixed with deep water from the Arctic before traveling south, thereby reducing inputs to the high Arctic.

Circulation of PFOS transported beyond 60°N that returns south in deep water inflows (>1000 m depth, blue colors in Figure 7) cumulatively totaled 4.1 × 10^2 Mg between 1958 and 2015 (Figure 7). NADW formation in the Labrador and Greenland Seas (44–65°W, 50–65°N) between 1958 and 2015 resulted in 4.8 × 10^2 Mg PFOS transported below 1000 m. We find 25% of this flux sinks below 1000 m south of 60°N, resulting in a total removal of 5.3 × 10^5 Mg PFOS associated with Atlantic meridional overturning circulation (AMOC). The annual downward flux from the surface (100 m) of the Labrador Sea in 2004 was 4.1 × 10^2 kg, which is in the same range as previously estimated (620 kg) based on measurements (Yamashita et al., 2008). AMOC has thus dramatically reduced the amount of PFOS entering the high Arctic. Weakened convection in the Labrador Sea Region and AMOC due to warming polar temperatures and melting of the Greenland ice sheet has been widely reported (Fisher et al., 2010;...

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**Table 1.** PFOS Reservoirs (Mg) in Surface, Middepth, and Deep Waters of the North Atlantic Ocean (20°N–60°N) in 2000 and 2015 and Lifetimes Against Losses (τ, a−1)

<table>
<thead>
<tr>
<th>Reservoirs (Mg)</th>
<th>2000</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface mixed layer</td>
<td>380</td>
<td>95</td>
</tr>
<tr>
<td>Middepth (100–1000 m)</td>
<td>630</td>
<td>650</td>
</tr>
<tr>
<td>Deep (1000 m to bottom)</td>
<td>240</td>
<td>650</td>
</tr>
<tr>
<td>Full basin (20°N–60°N)</td>
<td>1250</td>
<td>1390</td>
</tr>
<tr>
<td>Lifetimes (a−1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface mixed layer</td>
<td>2.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Middepth (100–1000 m)</td>
<td>4.0</td>
<td>4.7</td>
</tr>
<tr>
<td>Deep (1000 m to bottom)</td>
<td>13.9</td>
<td>20.9</td>
</tr>
<tr>
<td>Full basin (20°N–60°N)</td>
<td>10.8</td>
<td>14.1</td>
</tr>
</tbody>
</table>

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**Figure 7.** Modeled circulation of PFOS above and below 60°N at different seawater depths between 1958 and 2040. Deeper waters are indicated by blue, and surface waters are shown in shades of red, orange, and yellow. Solid black line indicates net flow, where positive numbers indicate flow above 60°N (into the Arctic region) and negative numbers indicate flow below 60°N (into the North Atlantic).
Rahmstorf et al., 2015; Rhein et al., 2015; Yashayaev, 2007). These climate-driven changes thus have the potential to greatly increase the magnitude of bioaccumulative pollutants entering ecologically sensitive Arctic regions.

9. Summary and Conclusions

We developed a new 3-D simulation for the fate of cumulative PFOS inputs ($2.4 \times 10^3$ Mg) to the North Atlantic Ocean between 1958 and 2015. Results suggest concentrations in surface waters (upper 1000 m) reached maximum levels several years after peak global PFOS production (before 2005) but concentrations in the deep ocean will continue to rise until 2040. Modeled temporal changes in the North Atlantic (Figure 5) contrast previous work that suggested ocean concentrations will decline slowly in all PFOS source regions and will increase in remote regions for several decades [Armitage et al., 2009a]. The abrupt phase out of most chemical manufacturing of PFOS around the year 2000, its high stability in seawater, and limited transport associated with settling of suspended particles in the ocean water column reinforce its potential as a novel tracer of ocean circulation. Recent declines in PFOS concentrations in the upper ocean are important for protecting marine food webs known to bioaccumulate this deleterious compound [Dassuncao et al., 2017; Routti et al., 2016; Houde et al., 2011; Tomy et al., 2004].

In 2015, we estimate the North Atlantic (20–60°N) reservoir of PFOS to be $1.4 \times 10^3$ Mg. Model results suggest $7.3 \times 10^3$ Mg PFOS has entered the Arctic Ocean from the North Atlantic, and smaller amounts ($2.9 \times 10^2$ Mg, Figure 6) have been transported to the tropical and southern Atlantic Ocean and other regions. When peak discharges were occurring, surface currents in the Atlantic Ocean transported PFOS from continental source regions to the Subarctic, explaining the large Arctic inputs. However, a large fraction of the PFOS that reached high latitudes became part of the NADW and was transported south in global thermohaline circulation. We estimate AMOC has cumulatively prevented $5.3 \times 10^3$ Mg PFOS from entering the high Arctic since the onset of its production in 1958. Weakened AMOC in an era of rapidly changing climate is thus expected to increase the burden of persistent, bioaccumulative contaminants entering ecologically sensitive Arctic regions.

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