2017

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Citation/Publisher Attribution

Zhang, X., Y. Zhang, C. Dassuncao, R. Lohmann, and E. M. Sunderland, North Atlantic Deep Water formation inhibits high Arctic contamination by continental perfluorooctane sulfonate discharges, *Global Biogeochem. Cycles* 2017, 31, 1332–1343, doi:10.1002/2017GB005624
Available at: http://dx.doi.org/10.1002/2017GB005624

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This is a pre-publication author manuscript of the final, published article.

North Atlantic Deep Water Formation Inhibits High Arctic Contamination by Continental Perfluorooctane Sulfonate (PFOS) Discharges

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Key points:

- Perfluorooctane sulfonate (PFOS) shows promise as a new ocean tracer but is also a potent toxicant
- PFOS concentrations in the upper North Atlantic Ocean peaked between 2002 and 2005 but are still increasing in the deep ocean.
- Sinking, convection and southward transport of subpolar surface waters greatly reduces PFOS inputs to the high Arctic

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. The stability, low reactivity, and high water solubility of PFOS combined with the North American phase-out in production around the year 2000, make it a potentially useful new tracer for ocean circulation. Here we characterize processes affecting the lifetime and accumulation of PFOS in the North Atlantic Ocean and transport to sensitive Arctic regions by developing a 3-D simulation within the MITgcm. The model captures variability in measurements across biogeographical provinces ($R^2 = 0.90$, p=0.01). In 2015, the North Atlantic PFOS reservoir was equivalent to 60% of cumulative inputs from the North American and European continents (1400 Mg). Cumulative inputs to the Arctic accounted for 30% of continental discharges, while the remaining 10% was transported to the tropical Atlantic and other regions. PFOS concentrations declined rapidly after 2002 in the surface mixed-layer (half-life: 1-2 years) but are still increasing below 1000 m depth. During peak production years (1980-2000), plumes of PFOS enriched seawater were transported to the Subarctic in energetic surface ocean currents. However, Atlantic Meridional Overturning Circulation (AMOC) and deep ocean transport returned a substantial fraction of this northward transport (20%, 530 Mg) to southern latitudes and reduced cumulative inputs to the Arctic (730 Mg) by 70%. Weakened AMOC due to climate change is thus likely to increase the magnitude of persistent bioaccumulative pollutants entering the Arctic Ocean.

Index terms: Biogeochemical cycles, processes, and modeling

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, non-stick 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 [*Wang et al.,* 2015]. It is not volatile and has much higher water solubility and lower affinity for partitioning to particles than other hydrophobic organic pollutants such as polychlorinated biphenyls (PCBs) [*Muir and Lohmann,* 2013; *Zareitalabad et al.*, 2013; *Rayne et al.*, 2009]. Thus, *Yamashita et al.* [2008] proposed it as a novel tracer for ocean circulation. However, little is known about the distribution and accumulation of PFOS in the global oceans. Here we investigate processes driving the lifetime and accumulation of PFOS in the North Atlantic Ocean and its transport to vulnerable Arctic regions by developing a new simulation within a 3-D ocean circulation model (MITgcm).

Globally, chemical manufacturing by the 3M Company in Decatur, Alabama, USA accounted for most (~80%) of the 66,000 tonnes of PFOS produced between 1958-2000 [*Armitage et al.,* 2009a]. 3M voluntarily discontinued manufacturing of the PFOS parent chemical between 2000-2002, amid concerns about human and ecological health impacts [*Land et al., 2015*]. Some PFOS has been produced in Asia after 2000 but most chemical manufacturing has shifted to other fluorinated compounds with different carbon chain lengths and head groups in the larger family of poly- and perfluoroalkyl substances (PFASs) [*Wang et al.*, 2017]. The phase out in North American PFOS production adds to its potential utility as a tracer for ocean water mass ages and circulation.

On the continental scale, wastewater is thought to account for the majority of PFOS releases (~85%) to the environment [*Buser and Morf*, 2009; *Earnshaw et al.*, 2014]. Atmospheric emissions of unstable PFOS precursors can also occur during chemical manufacturing but are estimated to account for only 1% of total inputs to the ocean [*Armitage et al.*, 2009a]. How changes in PFOS production have affected 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 et al.*, 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 1958-2010 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 oceanic 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 (phyto and zoo), and dead organic matter [*Dutkiewicz et al.*, 2012]. It has a horizontal resolution of 1°x1° 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.*, 2012] 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°x 1°

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 2010-2038 to capture the phase-out in PFOS production. We divide annual inputs equally over each 3-hour time step in the model simulation because available monitoring data do not show significant seasonal differences (Supporting Information (SI), Table S1 [*Boulanger et al.,* 2005; *Schultz et al.,* 2006; *Loganathan, et al.,* 2007; *Plumlee et al.,* 2008; *Erickson*, 2009; *Furl et al.*, 2011; *Furdui et al.*, 2008; *D'eon et al.*, 2009; *Guerra et al.*, 2014].

3. Continental PFOS release inventory (1958-2010)

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):

$$E_R = 9.6\times10^{-9}\,P_B^{1.0115} \qquad \text{(Equation 3)}$$

To estimate temporal changes in loading, we scaled per-capita releases calculated from gridded European population data [*CIESIN,* 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, Figure S2) from 19 Canadian facilities between 2009-2010 [*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:

$$E_W = \beta P_W^{\alpha} \qquad \text{(Equation 4)}$$

where, β 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 α is a scaling factor representing a non-linear 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. EPA*, 2008] discharge directly into the North Atlantic (Figure S4, Table S2). To calculate wastewater PFOS inputs to river basins that enter the North Atlantic Ocean (Figure S5, Table S3), we summed PFOS discharges derived from the total populations served by wastewater treatment facilities within each catchment 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; 3*M*, 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.*, 2014a; *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 population-based PFOS emission factors were approximately one 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.*, 2014a; *Wang et al.*, 2014a].

We assumed all riverine PFOS will enter the ocean within one 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 1.5-2.5 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 5-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 one 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 [*Prevedorous 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 2.7×10^3 Mg PFOS has cumulatively entered the North Atlantic since 1958 (low bound: 5.3×10^2 Mg, high bound 1.3 ×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 1.5×10^3 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 2.8×10^2 to 2.3×10^3 Mg between the years 1957-2002. Most releases were concentrated in North America and Europe between 36-54°N [*Armitage et al.*, 2009]. *Paul et al.* [2009] similarly estimated total global historical PFOS emissions to air and water to be 4.5×10^2 to 2.7×10^3 Mg between 1970-2002. 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.*, 2009; *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 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 Gyral Province (NASE). The model successfully captures these differences. Only two surface water measurements ranging from <10 pg L to 59 pg L^{-1} are available for the Gulf Stream Province (GFST) [*Ahrens et al.*, 2010a; *Benskin et al.* 2012]. The model shows large ranges in PFOS concentrations in the Gulf Stream due to a plume of PFOS enriched seawater transported offshore (Figure 2a). Modeled seawater PFOS concentrations are elevated (>50 pg L^{-1}) in the North Atlantic Drift Province (NADR) and the subarctic regions below Greenland. Surface observations near the European shelf appear to support this spatial pattern (Figure 2).

Yamashita et al. [2008] collected five vertical profiles from the Labrador Sea and mid-Atlantic Ocean in 2004, which we compare to modeled seawater PFOS concentrations from the same regions and year. The median PFOS release scenario (solid red line in Figure 3) reasonably captures observed surface enrichment at stations AO2, AO4 and AO5 and depletion at depth (Figure 3). However, the median emissions scenario overestimates PFOS concentrations throughout the vertical profiles (Figure 3), which is consistent with model bias identified for surface water concentrations (Figure 2b). The model does not capture some of the fine scale vertical variability at stations AO3-5 due to its coarse resolution (1°×1°). The low release scenario from Figure 1 (dashed red line in Figure 3) better matches the observed magnitude of seawater PFOS concentrations in the Labrador Sea but underestimates those in the mid-Atlantic.

This analysis suggests a mean model bias correction of 75% based on Figure 2b is appropriate for all results. Therefore, cumulative PFOS inputs to the North Atlantic Ocean of 2.4×10^3 Mg are most consistent with available observational constraints from seawater measurements. Releases of this magnitude produce mean modeled surface water (10 m) concentrations of 39±14 pg L^{-1} in 2010 compared to an observed value across all offshore sampling locations of 43±21 pg L^{-1} between 2009 and 2011. Hereon, this bias corrected release scenario is used for all modeling and mass budget calculations.

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 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 (Figure 2b, Figure 3). Thus, we retain the base assumption that most PFOS releases in wastewater will be transported to the ocean within one 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 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*, 2007] 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 Figure 4a/b 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.*, 2010]. 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.*, 2010]. 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-mid 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 0-10 m depth peak in 2001 (basin-wide median: 66 pg L^{-1}), one 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 (ca. 2000) and peak subsurface concentrations (ca. 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 viability 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 2.4×10^3 Mg. The North Atlantic PFOS reservoir in 2015 was equivalent to approximately 60% of inputs in 2015 (1.4×10^3 Mg, Figure 6), with the remaining fractions lost to the Arctic Ocean (30%), tropical Atlantic and 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 1-3 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 (>60ºN), Mediterranean Sea, and the tropical Atlantic Ocean (<20ºN) (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 North

Atlantic based on observations for another PFAS with the same number of carbon atoms. For seawater between 100-1000 m, modeled half-lives for PFOS in this study were approximately three years.

Variable lag-times and vertical differences in seawater concentrations (Table 1, 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; Houde et al.,* 2014]. Our results imply declining PFOS exposures for fish and marine mammals that predominantly forage in the ocean surface mixed layer since 2001. 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 400-700 m depth [*Hoydal et al.,* 1993; *Li et al.,* 2014]. A reported increase in PFOS concentrations in pilot whale muscle between 1987 to present is consistent with trends in mid-depth to thermocline waters shown in Figure 5 [*Dassuncao et al.,* 2017].

9. Implications for PFOS inputs to the Arctic Ocean

Figure 7 shows gross PFOS flows at differ 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 mid-depth 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 (44-65ºW, 50-65ºN) 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 5.3×10^2 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; *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.

10. Summary and Conclusions

We developed a new 3-D simulation for the fate of cumulative PFOS inputs (2.4×10^3 Mg) to the North Atlantic Ocean between 1958 to 2015. Results suggests 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 1.4×10^3 Mg. Model results suggest 7.3×10^2 Mg PFOS has entered the Arctic Ocean from the North Atlantic, and smaller amounts (2.9×10^2 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 5.3×10^2 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.

11. Acknowledgments

Financial support for this work was provided by the U.S. National Science Foundation (PLR 1203496) and the Smith Family Foundation. X.Z. received support from a Postdoctoral Fellowship from the Natural Sciences and Engineering Research Council of Canada. We acknowledge Global Runoff Data Centre (http://www.bafg.de/) and Socioeconomic Data and Applications Center (http://sedac.ciesin.columbia.edu/) for GIS data. We thank D.C.G. Muir, S. Fraser, S.A. Smyth, P. Guerra (Environment Canada), J.M. Armitage (University of Toronto), I. Cousins (Stockholm University), A. Pistocchi and R. Loos (Joint Research Centre of the

European Commission), for valuable communications during this study. We thank Stephanie Dutkiewicz (MIT) for assistance with the MITgcm.

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Tables

Table 1. PFOS reservoirs (Mg) in surface, mid-depth and deep waters of the North Atlantic Ocean (20ºN-60ºN) in 2000 and 2015 and lifetimes against losses (τ, a^{-1}).

	2000	**2015**
Reservoirs (Mg)		
Surface Mixed Layer	380	95
Mid-depth (100-1000 m)	630	650
Deep (1000 m to bottom)	240	650
Full Basin (20ºN-60ºN)	1250	1390
Lifetimes (a^{-1})		
Surface Mixed Layer	2.6	1.6
Mid-depth (100-1000 m)	4.0	4.7
Deep (1000 m to bottom)	13.9	20.9
Full Basin (20ºN-60ºN)	10.8	14.1

Figure Captions

Figure 1. Direct continental inputs of PFOS to the North Atlantic Ocean (20ºN-60ºN) from European and North American (U.S. and Canada) wastewater and rivers between 1958 and 2010. Median estimates are shown as the solid line and shaded grey indicates 95% confidence intervals for North American releases. European inputs are based on *Pistocchi and Loos* [2009].

Figure 2. Modeled and observed surface seawater PFOS concentrations (pg L^{-1}) in the North Atlantic Ocean. Panel (A) shows modeled surface (10 m) seawater concentrations for 2010 compared to observations for 2009-2011. Panel (B) shows 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; Ben, *GFST* = Gulf Stream Province, *NASW* = North Atlantic Subtropical Province - West, *NASE* = North Atlantic Subtropical Province - East, *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]; *Zhao et al.* [2012].

Figure 3. Comparison of modeled and observed vertical profiles of PFOS measured in the Labrador Sea and Mid-Atlantic Ocean by *Yamashita et al.* [2008]. Observations are shown in black and model scenarios are in red based on the median (solid line) and low (dashed line) PFOS release estimates shown in Figure 1.

Figure 4. Modeled temporal evolution of surface water (10 m) PFOS concentrations in the North Atlantic Ocean between 1980 and 2020. The model is forced with the median release scenarios from rivers and wastewater shown in Figure 1 and zero releases between 2010-2020, adjusted by the mean model bias of 75% shown in Figure 2. Major surface currents are shown as white arrows. NAC = North Atlantic Current, LC = Labrador Current, NS = North Sea.

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%).

Figure 7. Modeled circulation of PFOS above and below 60°N at different seawater depths between 1958-2040. 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).