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

3

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14 Key points:

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

21 **Abstract**

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

40

41 Index terms: Biogeochemical cycles, processes, and modeling

42 1. Introduction

43 Perfluorooctane sulfonate (PFOS) is an aliphatic organofluorine molecule containing
44 eight carbon atoms, a highly fluorinated “tail” and a hydrophilic sulfonate “head” group. It has
45 been transported in wastewater and rivers to the global oceans as a terminal sink after use in
46 furniture and carpet coatings, food packaging, non-stick cookware, outdoor clothing/gear, and
47 industrial applications since the 1950s [Wang *et al.*, 2017]. Biomonitoring studies have revealed
48 high PFOS concentrations in many marine food webs and exposures pose risks to both human
49 and ecological health [Tomy *et al.*, 2004; Dassuncao *et al.*, 2017]. PFOS does not appreciably
50 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
51 partitioning to particles than other hydrophobic organic pollutants such as polychlorinated
52 biphenyls (PCBs) [Muir and Lohmann, 2013; Zareitalabad *et al.*, 2013; Rayne *et al.*, 2009].
53 Thus, Yamashita *et al.* [2008] proposed it as a novel tracer for ocean circulation. However, little
54 is known about the distribution and accumulation of PFOS in the global oceans. Here we
55 investigate processes driving the lifetime and accumulation of PFOS in the North Atlantic Ocean
56 and its transport to vulnerable Arctic regions by developing a new simulation within a 3-D ocean
57 circulation model (MITgcm).
58

59 Globally, chemical manufacturing by the 3M Company in Decatur, Alabama, USA
60 accounted for most (~80%) of the 66,000 tonnes of PFOS produced between 1958-2000
61 [Armitage *et al.*, 2009a]. 3M voluntarily discontinued manufacturing of the PFOS parent
62 chemical between 2000-2002, amid concerns about human and ecological health impacts [Land
63 *et al.*, 2015]. Some PFOS has been produced in Asia after 2000 but most chemical
64 manufacturing has shifted to other fluorinated compounds with different carbon chain lengths

65 and head groups in the larger family of poly- and perfluoroalkyl substances (PFASs) [*Wang et*
66 *al.*, 2017]. The phase out in North American PFOS production adds to its potential utility as a
67 tracer for ocean water mass ages and circulation.

68 On the continental scale, wastewater is thought to account for the majority of PFOS
69 releases (~85%) to the environment [*Buser and Morf*, 2009; *Earnshaw et al.*, 2014].
70 Atmospheric emissions of unstable PFOS precursors can also occur during chemical
71 manufacturing but are estimated to account for only 1% of total inputs to the ocean [*Armitage et*
72 *al.*, 2009a]. How changes in PFOS production have affected continental discharges and
73 subsequent accumulation in the ocean is poorly understood. Prior work suggests vertical
74 diffusion and sorption to settling particles are important for oceanic transport of PFASs
75 [*Lohmann et al.*, 2013; *Sanchez-Vidal et al.*, 2015]. Seawater PFOS measurements are limited
76 and modeling studies have not previously resolved basin-scale inputs and circulation [*Armitage*
77 *et al.*, 2009a; *Schenker et al.*, 2008]. The only prior ocean model for PFOS contained 18°
78 latitudinal bands for the globe and did not distinguish the Atlantic and Pacific basins [*Armitage*
79 *et al.*, 2009a]. Previous modeling studies for other PFASs similarly do not consider spatial
80 variability in oceanic concentrations and transport or lack detailed release estimates for
81 continental discharges [*Armitage et al.*, 2009b; *Wania et al.*, 2007; *Stemmler and Lammel*, 2010].

82 The main objectives of this work are to: 1) quantify the magnitude and spatial distribution
83 of continental PFOS discharges to the North Atlantic Ocean, and 2) better characterize the roles
84 of lateral and vertical transport processes for the distribution and lifetime of PFOS in the marine
85 water column. We develop an inventory of cumulative continental PFOS releases from
86 wastewater and rivers in North America and Europe between 1958-2010 and use it to force a
87 new 3-D simulation for the North Atlantic Ocean within the MITgcm [*Marshall et al.*, 1997]. We

88 evaluate the model using available seawater PFOS measurements and apply it to investigate how
89 changing releases have affected spatial and temporal variability in concentrations and inputs to
90 the Arctic Ocean. This information is needed to further assess the potential viability of PFOS as
91 a tracer for oceanic transport processes as well as its significance as a toxicant in marine food
92 webs since biological exposures are driven by seawater concentrations.

93 **2. Model description**

94 The MITgcm is an ocean general circulation model (<http://mitgcm.org>) that contains a
95 biogeochemical and ecological model for cycling of carbon, nitrogen, silica, phosphorus and iron
96 through inorganic, living plankton (phyto and zoo), and dead organic matter [*Dutkiewicz et al.*,
97 2012]. It has a horizontal resolution of $1^\circ \times 1^\circ$ and includes 23 vertical levels. Ocean state
98 estimates are based on the Estimating Circulation and Climate of the Ocean (ECCO-GODAE)
99 data product [*Marshall et al.*, 1997; *Wunsch and Heimbach*, 2007]. We added tracers for the
100 dissolved and particle-bound forms of PFOS that are transported laterally and vertically by
101 oceanic circulation, mixing and particle settling.

102 PFOS has a pK_a of negative three and is extremely stable in solution [*Campbell et al.*,
103 2009; *Cheng et al.*, 2009; *Vecitis et al.*, 2008]. Partitioning between the aqueous phase and
104 suspended particles is simulated using an empirically derived organic carbon normalized
105 partition coefficient ($\log K_{OC} = 2.6$) [*Higgins and Luthy*, 2006]. Particle concentrations,
106 composition and export fluxes are based on the ecology simulation embedded in the MITgcm
107 [*Dutkiewicz et al.*, 2012] and used to simulate vertical PFOS transport associated with settling
108 particles.

109 The model is initialized by assuming zero oceanic PFOS concentrations before 1958, the
110 onset of chemical production. For the years 1958 to 2010, the model is forced with $1^\circ \times 1^\circ$

111 gridded inputs to the North Atlantic Ocean between 20°N and 60°N from rivers and wastewater
112 treatment plants in North America and Europe using the inventory developed here. The
113 simulation is continued with zero inputs between 2010-2038 to capture the phase-out in PFOS
114 production. We divide annual inputs equally over each 3-hour time step in the model simulation
115 because available monitoring data do not show significant seasonal differences (Supporting
116 Information (SI), Table S1 [*Boulanger et al.*, 2005; *Schultz et al.*, 2006; *Loganathan, et al.*,
117 2007; *Plumlee et al.*, 2008; *Erickson*, 2009; *Furl et al.*, 2011; *Furdui et al.*, 2008; *D'eon et al.*,
118 2009; *Guerra et al.*, 2014]).

119 3. Continental PFOS release inventory (1958-2010)

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

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

$$128 \quad E_R = 9.6 \times 10^{-9} P_B^{1.0115} \quad (\text{Equation 3})$$

129 To estimate temporal changes in loading, we scaled per-capita releases calculated from gridded
130 European population data [*CIESIN*, 2005] by relative changes in annual production of the parent
131 chemical to PFOS (perfluorooctane sulfonyl fluoride: POSF) for all years between 1958 and
132 2010 [*Armitage et al.*, 2009a; *Paul et al.*, 2009; *Zhang et al.*, 2012].

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

$$138 \quad E_w = \beta P_w^\alpha \quad (\text{Equation 4})$$

139 where, β represents the baseline per-capita PFOS discharge rate, which is equal to 0.21 for
140 Canada and 0.47 for the U.S. (Figure S3). The parameter α is a scaling factor representing a non-
141 linear increase in PFOS releases with population served, equal to 1.24 ± 0.09 for Canada and
142 1.21 ± 0.10 for the U.S (Figure S3).

143 Only 9.9% of the municipalities in Canada [Environment Canada, 2009] and 1.8% of
144 wastewater treatment plants in the U.S. [U.S. EPA, 2008] discharge directly into the North
145 Atlantic (Figure S4, Table S2). To calculate wastewater PFOS inputs to river basins that enter
146 the North Atlantic Ocean (Figure S5, Table S3), we summed PFOS discharges derived from the
147 total populations served by wastewater treatment facilities within each catchment using ArcGIS
148 [Environment Canada, 2009; Global Runoff Data Centre, 2007; U.S. EPA, 2008]. We also
149 included direct releases (360 Mg during 1958-2002) from the 3M Decatur (Alabama) facility to
150 the Mississippi watershed that accounted for a large fraction of global production in 2002
151 [Armitage *et al.*, 2009a; Filipovic *et al.*, 2013; Scott *et al.*, 2009; 3M, 2000]. We neglected other
152 environmental release pathways such as leaching from landfills because they comprise <10% of
153 total releases on the continental scale, even though they can be important for inland rivers and
154 streams [*e.g.*, Zhang *et al.*, 2016]. We derived basin wide releases ($\mu\text{g person}^{-1} \text{ a}^{-1}$) based on
155 wastewater treatment plants within each catchment area [CIESN, 2005]. Temporal changes in

156 global historical inventories [Armitage *et al.*, 2014a; Wang *et al.*, 2014a] were used to scale
157 population-based releases over the full history of production.

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

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

171 *3.1 Uncertainty in release estimates*

172 We estimate a 5-fold uncertainty in continental PFOS discharges presented here based on
173 the 95% confidence intervals of regression relationships for the U.S. and Canada (Figure S3).
174 We propagate this uncertainty for evaluation of model results and use available measurements to
175 constrain inputs. Uncertainty estimated here is slightly lower than the approximately one order of
176 magnitude uncertainty for other PFAS inventories. In prior work, uncertainty estimates reflected
177 limited information on the magnitude of PFASs emissions from products containing these
178 compounds, assumptions about yields of atmospheric precursors, and ranges in industrial release

179 estimates [*Prevedorous et al.*, 2006, *Paul et al.*, 2009, *Armitage et al.*, 2009a; 2009b; *Wang et*
180 *al.*, 2014a; 2014b].

181 **4. Model evaluation**

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

189 Direct release values from two previous PFOS inventories based on chemical production
190 and product use are comparable to the low and median bounds for this work. *Armitage et al.*
191 [2009a] suggested cumulative direct global releases to the ocean of 2.8×10^2 to 2.3×10^3 Mg
192 between the years 1957-2002. Most releases were concentrated in North America and Europe
193 between 36-54°N [*Armitage et al.*, 2009]. *Paul et al.* [2009] similarly estimated total global
194 historical PFOS emissions to air and water to be 4.5×10^2 to 2.7×10^3 Mg between 1970-2002.
195 Indirect (atmospheric) PFOS inputs to the global oceans are thought to be smaller (5-230 Mg)
196 based on work by *Armitage et al.* [2009a]. We find the high estimate of PFOS releases derived
197 here is implausible based on these global production constraints [*Armitage et al.*, 2009; *Paul et*
198 *al.*, 2009].

199 Figure 2a compares modeled surface seawater (10 m) concentrations for the year 2010
200 based on the median scenario for PFOS releases (Figure 1) with observed surface seawater
201 concentrations between 2009 and 2011. Relatively high concentrations are apparent next to

202 continental source regions in eastern North America and the North Sea and relatively lower
203 levels are observed in the eastern subtropical region (Sargasso Sea). We divided the North
204 Atlantic Ocean into the biogeographical provinces characterized by *Longhurst* [2007] to assess
205 performance of the model in different regions. We do not consider coastal monitoring data
206 because the model is not intended to capture the fine-scale circulation and dynamics of inland
207 seas and estuaries.

208 Modeled seawater concentrations capture most of the variability in the observed data (R^2
209 = 0.90, $p=0.01$) across biogeographical provinces (Figure 2b). The grey dashed line in Figure 2b
210 indicates perfect agreement between measured and modeled results and the regression
211 relationship indicates the model has a high mean bias of 75% relative to observations for all
212 regions. Measured PFOS concentrations are lower in the western portion of the North Atlantic
213 Subtropical Gyral Province (NASW) in the Sargasso Sea, and the southern North Atlantic
214 Tropical Gyral Province (NATR), than those in the eastern North Atlantic Subtropical Gyral
215 Province (NASE). The model successfully captures these differences. Only two surface water
216 measurements ranging from <10 pg L to 59 pg L⁻¹ are available for the Gulf Stream Province
217 (GFST) [*Ahrens et al.*, 2010a; *Benskin et al.* 2012]. The model shows large ranges in PFOS
218 concentrations in the Gulf Stream due to a plume of PFOS enriched seawater transported
219 offshore (Figure 2a). Modeled seawater PFOS concentrations are elevated (>50 pg L⁻¹) in the
220 North Atlantic Drift Province (NADR) and the subarctic regions below Greenland. Surface
221 observations near the European shelf appear to support this spatial pattern (Figure 2).

222 *Yamashita et al.* [2008] collected five vertical profiles from the Labrador Sea and mid-
223 Atlantic Ocean in 2004, which we compare to modeled seawater PFOS concentrations from the
224 same regions and year. The median PFOS release scenario (solid red line in Figure 3) reasonably

225 captures observed surface enrichment at stations AO2, AO4 and AO5 and depletion at depth
226 (Figure 3). However, the median emissions scenario overestimates PFOS concentrations
227 throughout the vertical profiles (Figure 3), which is consistent with model bias identified for
228 surface water concentrations (Figure 2b). The model does not capture some of the fine scale
229 vertical variability at stations AO3-5 due to its coarse resolution ($1^\circ \times 1^\circ$). The low release
230 scenario from Figure 1 (dashed red line in Figure 3) better matches the observed magnitude of
231 seawater PFOS concentrations in the Labrador Sea but underestimates those in the mid-Atlantic.

232 This analysis suggests a mean model bias correction of 75% based on Figure 2b is
233 appropriate for all results. Therefore, cumulative PFOS inputs to the North Atlantic Ocean of
234 2.4×10^3 Mg are most consistent with available observational constraints from seawater
235 measurements. Releases of this magnitude produce mean modeled surface water (10 m)
236 concentrations of 39 ± 14 pg L⁻¹ in 2010 compared to an observed value across all offshore
237 sampling locations of 43 ± 21 pg L⁻¹ between 2009 and 2011. Hereon, this bias corrected release
238 scenario is used for all modeling and mass budget calculations.

239 **5. Model uncertainty and sensitivity analysis**

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

248 We consider uncertainty in the empirically measured partition coefficient for PFOS using
249 sensitivity analysis on the upper and lower bounds reported in the literature ($\log K_{oc} = 2.4$ to 3.8)
250 [Ahrens *et al.*, 2011; Ferrey *et al.*, 2012]. Results of our simulation suggest the mass of vertically
251 transported PFOS in the ocean associated with settling particles is negligible compared to that
252 from lateral and vertical ocean circulation (Figure S8). Modeled concentrations of PFOS bound
253 to particles (Figure S8) are consistent with limited measurements that were all $<10 \text{ pg L}^{-1}$
254 [Ahrens *et al.*, 2009a]. We examined the sensitivity of this finding to the range in partition
255 coefficients reported in the literature. The maximum $\log K_{oc}$ value reported in prior work is 3.8
256 [Ahrens *et al.*, 2011], compared to the value of 2.6 [Higgins and Luthy, 2007] specified in our
257 base simulation. This does not change our initial finding as the fraction of particle bound PFOS
258 in seawater is negligible across expected ranges of K_{oc} and potential POC concentrations in
259 seawater (Figure S9). Previous studies that considered PFOS fluxes associated with settling of
260 suspended particles in isolation suggest this may be a substantial oceanic transport process
261 [Sanchez-Vidal *et al.*, 2015]. Our model results indicate this is not the case for the North
262 Atlantic.

263 **6. Spatial distribution of PFOS in seawater**

264 The major surface currents in the Atlantic Ocean result in predominantly eastern and
265 northern transport of coastal PFOS pollution sources toward the Subarctic (Figure 4). Surface
266 water PFOS concentrations in 1980 and 2000 varied by more than an order of magnitude in
267 PFOS enriched seawater plumes from the St. Lawrence River, Florida Current, and North Sea
268 (Figure 4a). The Gulf Stream transports PFOS entrained in the Florida Current into the central
269 and eastern Atlantic Ocean, where it merges with the North Atlantic Current (NAC) and diverges
270 both north and east [Pickard and Emery, 1990]. This is visible in Figure 4a/b by offshore dilution

271 and diffusion north and east of elevated PFOS concentrations in the Gulf Stream. These results
272 help to explain the relatively lower PFOS concentrations measured in seawater from the western
273 part of the North Atlantic Subtropical Gyral Province (NASW, Figure 2).

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

283 Similarly, surface waters entrained in the Labrador Current that captures PFOS
284 discharges from the Hudson Bay sink in “convective chimneys” from the center of the Labrador
285 Gyre [Clarke and Gascard, 1983] and are transported south in NADW primarily in the western
286 Atlantic in the Deep Western Boundary Current (DWBC) [Rhein *et al.*, 2010]. Apparent ages of
287 NADW determined from tracers around 55°N are generally less than a decade, even at depths
288 greater than 3500 m [Doney and Bullister, 1992; Rhein *et al.*, 2010]. This explains the
289 penetration of PFOS to the ocean floor in this region (mean: 12 pg L⁻¹ below 1000 m) based on
290 the vertical profiles measured by Yamashita *et al.* [2008] in the Labrador Sea in 2004 (Figure 3).
291 For vertical profiles collected by Yamashita *et al.* [2008] between 25°N and 30°N (Figure 3),
292 seawater below 1000 m also contained detectable but lower levels of PFOS (generally <5 pg L⁻¹,
293 Figure 3). These water depths primarily contain NADW transported south and may have some

294 influence from Mediterranean outflow [*Pickard and Emery, 1990*]. *Rhein et al.* [2015] reported
295 the western Atlantic portion of NADW around these latitudes (in the Sargasso Sea) has an
296 apparent age of around 30 years, which suggests an influence from surface inputs of PFOS in the
297 early-mid 1970s.

298 **7. Temporal changes in PFOS concentrations and mass budgets for the North Atlantic**

299 Figure 5 shows the temporal evolution of PFOS concentrations in seawater from the
300 surface mixed layer (0-10 m), subsurface (360-510 m), and near the permanent thermocline
301 (985-1335 m). Concentrations between 0-10 m depth peak in 2001 (basin-wide median: 66 pg L⁻¹)
302 ¹), one year after maximum releases from rivers and wastewater. Spatial heterogeneity in surface
303 water concentrations is reflected by the wide variability in 95th percentile confidence intervals
304 (CI) shown in Figure 5 (2001: 9-633 pg L⁻¹) that become more homogeneous over time (2015:
305 22-53 pg L⁻¹).

306 PFOS concentrations in subsurface seawater (365-510 m) are lower and less variable than
307 surface waters due to dilution with lower concentration subsurface seawater (Figure 5). The lag
308 time between peak releases (ca. 2000) and peak subsurface concentrations (ca. 2005, 41 pg L⁻¹,
309 95th CI: 27-66) at these depths is 2-3 years. This likely reflects strong winter convection in the
310 subpolar North Atlantic, which results in mixing with subsurface waters up to ~600 m depth
311 [*McCartney and Talley, 1982*]. By 2015, median modeled concentrations declined to 37 pg L⁻¹
312 and variability in ocean concentrations is much smaller than earlier years (95th CI: 30-47, Figure
313 5).

314 A longer lag after peak releases is observed for peak PFOS concentrations in deeper
315 waters around the permanent thermocline (985-1335 m) (Figure 5). Modeled concentrations
316 plateau in 2040 around a median of 26 pg L⁻¹. The effects of water mass circulation in different

317 regions are evident in Figure 5, where the 95th percentile concentrations, representing more
318 recently ventilated water masses, peaked in 2009 at 47 pg L⁻¹ (a 9-year lag) and have declined
319 since this time. By contrast, the 5th percentile of PFOS concentrations in the North Atlantic are
320 continuing to slowly increase and are expected to reach 9 pg L⁻¹ in 2040 (lag time more than
321 three decades). Similar patterns have been reported for other pollutants in the North Atlantic
322 such as lead (Pb), due to time required for subduction and ventilation of surface seawater into the
323 thermocline [Wu and Boyle, 1997].

324 Cumulative PFOS inputs to the North Atlantic between 1958 and 2015 estimated in this
325 study are 2.4×10³ Mg. The North Atlantic PFOS reservoir in 2015 was equivalent to
326 approximately 60% of inputs in 2015 (1.4×10³ Mg, Figure 6), with the remaining fractions lost
327 to the Arctic Ocean (30%), tropical Atlantic and other regions (10%). Over time, the mass
328 distribution of PFOS has shifted toward deeper waters from >80% in the upper ocean (top 1000
329 m) in 2000 to approximately 50% in 2015, consistent with Figure 5. This has important
330 implications for reducing biological exposures as most marine life is found in the upper 1000 m
331 of the ocean [Ryther, 1969].

332 Lifetimes of PFOS against losses (reservoir/gross losses) from this work range from 1-3
333 years (half-life: $t_{1/2} = 1-2$ years) in the surface mixed layer of the North Atlantic to one to two
334 decades in the deep ocean (Table 1). Loss processes are mainly internal circulation and outflow
335 to the Arctic (>60°N), Mediterranean Sea, and the tropical Atlantic Ocean (<20°N) (Figure 6). By
336 2015, 85% of total losses from the Atlantic Ocean had been transported into the Arctic, with
337 smaller outflow to other regions. Basin-wide lifetimes are shorter in 2000 than 2015, reflecting
338 the entrainment of PFOS source regions in energetic currents in the ocean such as the Gulf
339 Stream (Figure 4). Gonzalez-Gaya et al. [2014] estimated a 5.8 year half-life in the North

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

343 Variable lag-times and vertical differences in seawater concentrations (Table 1, Figure 5)
344 help to explain mixed temporal trends in biological PFOS concentrations measured in the North
345 Atlantic and Subarctic [Bossi *et al.*, 2005; Butt *et al.*, 2010; Dassuncao *et al.*, 2017; Houde *et al.*,
346 2014]. Our results imply declining PFOS exposures for fish and marine mammals that
347 predominantly forage in the ocean surface mixed layer since 2001. Temporal changes are
348 expected to be more variable for complex food-webs with mixed prey items and biota that forage
349 from deeper seawater such as North Atlantic pilot whales [*Globicephala melas*] that mainly
350 consume squid between 400-700 m depth [Hoydal *et al.*, 1993; Li *et al.*, 2014]. A reported
351 increase in PFOS concentrations in pilot whale muscle between 1987 to present is consistent
352 with trends in mid-depth to thermocline waters shown in Figure 5 [Dassuncao *et al.*, 2017].

353 **9. Implications for PFOS inputs to the Arctic Ocean**

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

360 Circulation of PFOS transported beyond 60°N that returns south in deep water inflows
361 (>1000 m depth, blue colors in Figure 7) cumulatively totaled 4.1×10^2 Mg between 1958 and
362 2015 (Figure 7). NADW formation in the Labrador and Greenland Seas (44-65°W, 50-65°N)

363 between 1958 and 2015 resulted in 4.8×10^2 Mg PFOS transported below 1000 m. We find 25%
364 of this flux sinks below 1000 m south of 60°N , resulting in a total removal of 5.3×10^2 Mg PFOS
365 associated with Atlantic meridional overturning circulation (AMOC). The annual downward flux
366 from the surface (100 m) of the Labrador Sea in 2004 was 4.1×10^2 kg, which is in the same
367 range as previously estimated (620 kg) based on measurements [Yamashita *et al.*, 2008]. AMOC
368 has thus dramatically reduced the amount of PFOS entering the high Arctic. Weakened
369 convection in the Labrador Sea Region and AMOC due to warming polar temperatures and
370 melting of the Greenland ice sheet has been widely reported [Fisher *et al.*, 2010; Rahmstorf *et*
371 *al.*, 2015; Rhein *et al.*, 2015; Yashayaev, 2007]. These climate-driven changes thus have the
372 potential to greatly increase the magnitude of bioaccumulative pollutants entering ecologically
373 sensitive Arctic regions.

374 **10. Summary and Conclusions**

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

386 deleterious compound [*Dassuncao et al.*, 2017; *Routti et al.*, 2016; *Houde et al.*, 2011; *Tomy et*
387 *al.*, 2004].

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

399

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410

411 12. References

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628

629 **Tables**630 **Table 1.** PFOS reservoirs (Mg) in surface, mid-depth and deep waters of the North Atlantic631 Ocean (20°N-60°N) in 2000 and 2015 and lifetimes against losses (τ , a⁻¹).

	2000	2015
<i>Reservoirs (Mg)</i>		
Surface Mixed Layer	380	95
Mid-depth (100-1000 m)	630	650
Deep (1000 m to bottom)	240	650
Full Basin (20°N-60°N)	1250	1390
<i>Lifetimes (a⁻¹)</i>		
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 (20°N-60°N)	10.8	14.1

632

633 **Figure Captions**

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

638 **Figure 2.** Modeled and observed surface seawater PFOS concentrations (pg L^{-1}) in the North
639 Atlantic Ocean. Panel (A) shows modeled surface (10 m) seawater concentrations for 2010
640 compared to observations for 2009-2011. Panel (B) shows modeled and observed PFOS
641 concentrations grouped by Longhurst Biogeographical Provinces [*Longhurst, 2007*], where error
642 bars indicate standard error around the mean for both the model and observations. Grey dashed
643 line indicates 1:1 fit between modeled and observed surface water concentrations. Regression
644 slope indicates the median release scenario (Figure 1) results in a model bias relative to surface
645 water PFOS observations of 75%. Modeled surface water concentrations capture 90% of the
646 observed variability across biogeographical provinces [*Longhurst, 2007*]. *NADR* = North
647 Atlantic Drift Province [*Ahrens et al., 2009a; 2010b; Ben, GFST* = Gulf Stream Province, *NASW*
648 = North Atlantic Subtropical Province - West, *NASE* = North Atlantic Subtropical Province -
649 East, *NATR* = North Atlantic Tropical Gyral Province. Surface PFOS measurements are from:
650 *Ahrens et al.* [2009a; 2009b; 2010b]; *Benskin et al.* [2012]; *Gonzalez-Gaya et al.* [2014]; *Zhao et*
651 *al.* [2012].

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

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

661 **Figure 5.** Modeled PFOS concentrations in North Atlantic Seawater (pg L^{-1}) between 20°N and
662 60°N at different seawater depths based on the median PFOS release scenarios shown in Figure
663 1, adjusted for mean bias (75%). Shading indicates distributions of concentrations in different
664 ocean regions with the median across the whole basin indicated as a solid line. Darker shading
665 indicates 25th and 75th percentile modeled concentrations and 95th percentiles are shown as the
666 lightest blue bounds.

667 **Figure 6.** Mass flows of PFOS in the North Atlantic (Mg a^{-1}) between 20°N and 60°N for the
668 years 2000 (peak inputs) and 2015. Results are from the median release scenario (Figure 1) and
669 adjusted for mean bias (75%).

670 **Figure 7.** Modeled circulation of PFOS above and below 60°N at different seawater depths
671 between 1958-2040. Deeper waters are indicated by blue and surface waters are shown in shades
672 of red, orange and yellow. Solid black line indicates net flow, where positive numbers indicate
673 flow above 60°N (into the Arctic region) and negative numbers indicate flow below 60°N (into
674 the North Atlantic).