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# Vertical Eddy Diffusion as a Key Mechanism for Removing Perfluorooctanoic Acid (PFOA) from the Global Surface Oceans

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1 **VERTICAL EDDY DIFFUSION AS A KEY MECHANISM FOR REMOVING**  
2 **PERFLUOROOCCTANOIC ACID (PFOA) FROM THE GLOBAL SURFACE**  
3 **OCEANS**

4  
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14  
15 **Abstract**

16  
17 Here we estimate the importance of vertical eddy diffusion in removing perfluorooctanoic  
18 acid (PFOA) from the surface Ocean and assess its importance as a global sink. Measured  
19 water column profiles of PFOA were reproduced by assuming that vertical eddy diffusion  
20 in a 3-layer ocean model is the sole cause for the transport of PFOA to depth waters. The  
21 global oceanic sink due to eddy diffusion for PFOA is high, with accumulated removal  
22 fluxes over the last 40 years of 664 t, with the Atlantic Ocean accounting for 70% of the  
23 global oceanic sink. The global oceans have removed 13% of all PFOA produced to a  
24 depth greater than 100 m via vertical eddy diffusion; an additional 4 % has been removed

25 via deep water formation. The top 100 m of the surface oceans store another 21% of all  
26 PFOA produced (~1100 t).

27

28 **Keywords:** *PFOA, global sink, diffusion, oceans, organic pollutants*

29

30 **Capsule:** *Vertical eddy diffusion is an important removal process for hydrophilic organic*  
31 *pollutants such as PFOA from the surface ocean.*

32

### 33 **1. Introduction**

34 Perfluoralkyl carboxylic acids (PFCAs) have been used by industry since the 1960s,  
35 mostly as a processing aid in the manufacture of fluoropolymers, such as during  
36 conversion of tetrafluoroethylene into polytetrafluoroethylene (PTFE) (Prevedouros et al.,  
37 2006). In the oceans, perfluorooctanoic acid (PFOA) is the most frequently detected  
38 PFCA, and often detected at greatest concentrations (Yamashita et al., 2005; Yamashita et  
39 al., 2008). Per- and polyfluoroalkyl substances compounds are transported away from  
40 their production and use locations by a combination of transport with ocean currents  
41 (Armitage et al., 2006), atmospheric transport and oxidation of fluorotelomer alcohols  
42 (Ellis et al., 2003), and transport with sea-salt aerosols (McMurdo et al., 2008; Webster  
43 and Ellis, 2008). Perfluorinated compounds have been detected in biota, including  
44 humans world-wide (Giesy and Kannan, 2002; Houde et al., 2006); PFOA and  
45 perfluorooctane sulfonate (PFOS) are the most commonly detected perfluorinated  
46 chemicals in the environment. PFOS (but not PFOA) has been included in the Stockholm

47 treaty on 'Persistent Organic Pollutants' (POPs) due to its persistence, bioaccumulation  
48 potential and toxicity (UNEP, 2009).

49 In general, the terrestrial environment and potentially the shelf sediments are considered  
50 the main reservoir of POPs (Jonsson et al., 2003; Meijer et al., 2003). Atmosphere and  
51 oceans can become important sinks for certain groups of POPs, such as dioxins and  
52 furans (Lohmann et al., 2006a). In previous work we have presented a framework to  
53 estimate the oceanic sink of POPs associated with settling particles ('biological pump')  
54 (Dachs et al., 2002) and deep water formation ('physical pump') (Lohmann et al., 2006b).

55 The biological pump removes POPs from the surface ocean through a series of  
56 partitioning steps involving dry and wet deposition, phytoplankton uptake and removal  
57 from the surface mixed layer by the organic carbon settling flux (Dachs et al., 1999;  
58 Dachs et al., 2002; Jurado et al., 2004; Jurado et al., 2005; Galban-Malagon et al., 2012).

59 The physical pump is especially important in the North Atlantic (Norwegian and  
60 Labrador Seas) and the Southern Ocean (Weddell and Ross Seas), where both dissolved  
61 and particle-bound POPs are removed from the surface ocean through deep water  
62 formation (Broecker, 1974). For hydrophobic POPs, the physical pump is less important  
63 globally than the biological pump (Lohmann et al., 2006b), but it might be more  
64 important for hydrophilic chemicals. The magnitude and mechanisms of the oceanic sink  
65 are poorly constrained for ionic and amphiphilic organic compounds which do not sorb  
66 strongly to sinking organic matter.

67 The objective of this work is to estimate - for the first time - the importance of vertical  
68 (eddy) diffusion as a major removal process of persistent compounds from the surface  
69 ocean. We focus on PFOA, which in seawater exists primarily as the anion (PFO<sup>-</sup>), no

70 matter whether its exact pKa value is around 3.7 (Burns et al., 2008) or -0.5 (Goss, 2008).  
71 The anion has a very low sorption coefficient, a negligible vapor pressure and does not  
72 degrade (Barton et al., 2007). Thus, PFOA has recently been proposed as a novel  
73 chemical tracer of ocean circulation (Yamashita et al., 2008). SF<sub>6</sub> has also been  
74 extensively used as a passive tracer to quantify vertical eddy diffusion coefficients but,  
75 because it is biologically available to flora and fauna, SF<sub>6</sub> displays a stronger seasonal  
76 variability than PFOA. Due to its low reactivity and, relative to other POPs, reduced  
77 affinity for organic carbon, PFOA should be an excellent tracer of past and current  
78 emissions, and its transport to the deep ocean will be due to subduction of water masses  
79 and vertical eddy diffusion solely.

80 As the ocean is generally vertically stratified, there are large concentration gradients with  
81 depth, so turbulent vertical eddy diffusion becomes a key process in removing  
82 compounds from the surface layer. In analogy with Fick's First Law, the vertical flux of  
83 compounds in the water due to vertical eddy diffusion, F<sub>eddy-diff</sub> (ng m<sup>-2</sup> s<sup>-1</sup>), is:

$$84 \quad F_{\text{eddy-diff}} = -E \frac{\partial C}{\partial z}, \quad (1)$$

85 where E is the vertical eddy diffusion coefficient (m<sup>2</sup> s<sup>-1</sup>), C is the concentration of PFOA  
86 (ng m<sup>-3</sup>) and z (m) is the vertical coordinate (positive upwards with z = 0 indicating the  
87 ocean surface).

88 Vertical eddy diffusivities are highly variable both in time and space, ranging from 10<sup>-5</sup> -  
89 10<sup>0</sup> m<sup>2</sup> s<sup>-1</sup> in the upper mixed layer of the ocean to 10<sup>-7</sup> to 10<sup>-3</sup> m<sup>2</sup> s<sup>-1</sup> in the open deep  
90 ocean (Gregg, 1987; Jurado et al., 2012a; Jurado et al., 2012b). A common approach for  
91 modelling purposes is to consider the stratified ocean as a three-layer water column with  
92 constant values of E in each layer: the highest values of E in the surface mixed layer,

93 reduced E values for the seasonal thermocline, and slightly increased E values below the  
94 seasonal thermocline (Woods and Onken, 1982; Huisman and Sommeijer, 2002).

95 In this study, we use such a three-layer vertical eddy diffusion turbulence model to study  
96 the removal of PFOA from the upper ocean. We investigate whether eddy diffusivity  
97 fluxes can explain the reported vertical profiles of PFOA. Then, best-fit values of E are  
98 obtained by reviewing the measured vertical profiles of PFOA from the few reports  
99 published. These literature derived E values are then used to obtain global vertical  
100 turbulent eddy diffusive fluxes of PFOA.

101 Therefore, the objectives of this study are (i) explain observed vertical PFOA profiles in  
102 the Japan Sea and Mid-Atlantic Bight (Yamashita et al., 2008) solely based on transport  
103 through vertical eddy diffusion, (ii) derive the eddy diffusion flux of PFOA at 100 m  
104 depth from measured global surface ocean concentrations of PFOA, (iii) estimate  
105 historical cumulative eddy diffusion fluxes of PFOA for the different oceanic regions, and  
106 (iv) compare the importance of deep water formation and vertical eddy diffusion in  
107 removing PFOA from the surface water to the mesopelagic and deep ocean.

108

## 109 **2. Materials and Methods**

### 110 ***2.1. Vertical water column concentrations of PFOA***

111 PFOA concentrations for the top 3,000 m of the water column were taken from  
112 Yamashita et al. (2008). To date, Yamashita et al. (2008) is the only study that has  
113 reported vertical ocean profiles of perfluoroalkyl compounds. The depth profiles from the  
114 Japan Sea (JS2) and Mid-Atlantic Bight (AO4) were chosen as no deep water formation  
115 occurs at these locations and data are available at a sufficiently high vertical resolution to

116 compare to model results. In the Japan Sea, concentrations of PFOA decreased from 50  
117  $\text{ng m}^{-3}$  at the surface to  $< 10 \text{ ng m}^{-3}$  at 3,000 m depth. In the Mid-Atlantic Bight,  
118 concentrations dropped from  $\leq 150 \text{ ng m}^{-3}$  at the surface to  $\leq 50 \text{ ng m}^{-3}$  at 3,000 m.

119

## 120 **2.2. Model description**

121 PFOA reaches oceanic surface waters by atmospheric inputs and oceanic circulation  
122 (Ellis et al., 2003; Armitage et al., 2006) and we presuppose that it moves to depth via  
123 vertical eddy diffusion only. The physical process of vertical eddy diffusion, i.e., vertical  
124 turbulent mixing, tends to dominate other processes in most of the open ocean, which is  
125 vertically stratified. Chemical processes for PFOA, such as microbial or photolytic  
126 degradation and sorption to sinking particles are neglected in this work, since PFOA is a  
127 persistent chemical with low hydrophobicity (Prevedouros et al., 2006; Taniyasu et al.,  
128 2013).

129 The combination of equation (1) with a mass balance approach leads to Fick's Second  
130 Law, which models the change in time and space of the concentration field  $C(z,t)$ :

$$131 \quad \frac{\partial C}{\partial t} = -\frac{\partial}{\partial z} F_{\text{eddy-diff}} = \frac{\partial}{\partial z} \left( E \left( \frac{\partial C}{\partial z} \right) \right), \quad (2)$$

132 where  $z$  is the depth and  $t$  accounts for time. To solve equation (2), we partition the  
133 domain in space using water layers ranging from  $k=0$  to  $k=N$ , where  $k=0$  is the bottom  
134 layer at 3,000 m depth and  $k=N$  is the surface layer at 0 m depth, and with a uniform  
135 vertical depth increase of  $\Delta z = 1 \text{ m}$ . We also partition the domain in time using time steps  
136 ranging from  $n=1$  to  $n=M$ , where  $n=1$  is the initial time at 1970 and  $n=M$  is the final time,  
137 and with a uniform time step increase of  $\Delta t = 0.5 \text{ years}$ .



138 As initial conditions, we assume that at the initial time step (i.e., 1970) the seawater  
 139 concentration of PFOA was zero ( $C = 0$ ) at the surface and any depth. As boundary  
 140 conditions, we assume that contaminants enter the water column from the ocean surface  
 141 and we assume no flux of contaminants at the bottom of the domain:

$$142 \quad C|_{z=0} = C_S \quad (3a)$$

$$143 \quad \left. \frac{\partial C}{\partial z} \right|_{z=H} = 0 \quad (3b)$$

144 where  $C_S$  are the measured water surface PFOA concentration, scaled on the predicted  
 145 concentration trend for European seawater by van Zelm et al. (2008) (see below), and  $H$   
 146 is the depth of the bottom of the domain, i.e. 3,000 m.

147 To solve (2) with (3), we use an implicit method for discretization, the Crank-Nicholson  
 148 method, which uses a backward difference at time, and it is based on the central  
 149 difference in space and the trapezoidal rule in time:

$$150 \quad \frac{C_k^{n+1} - C_k^n}{\Delta t} = \frac{1}{2} \frac{1}{\Delta z} \left( E_{k+1} \frac{C_{k+1} - C_k}{\Delta z} - E_{k-1} \frac{C_k - C_{k-1}}{\Delta z} \right)^{n+1} + \frac{1}{2} \frac{1}{\Delta z} \left( E_{k+1} \frac{C_{k+1} - C_k}{\Delta z} - E_{k-1} \frac{C_k - C_{k-1}}{\Delta z} \right)^n \quad (4)$$

151 where  $k$  indicates the water layer, and  $n$  indicates the time step.  $E_{k+1}$  represents the  
 152 vertical eddy diffusion coefficient at the mid-depth of the water layer above  $k$ , and  $E_{k-1}$   
 153 represents the vertical eddy diffusion coefficient at the mid-depth of the water layer  
 154 below  $k$ .

155 This integration method is stable over the transition zones between the three layers, but  
 156 this estimates the concentration field but not the eddy diffusivity fluxes. The vertical net  
 157 eddy diffusion flux of compounds at a certain water layer  $k$  and a time step  $n$ ,  $F_{\text{eddy-diff}, k}^n$   
 158 ( $\text{ng m}^{-2} \text{s}^{-1}$ ) is computed as:

159 
$$-F_{\text{eddy-diff},k}^n = -F_{\text{eddy-diff},k-1}^n + \frac{C_k^{n+1} - C_k^n}{\Delta t} \Delta z$$
 (5)

160

161 where  $F_{\text{eddy-diff},k-1}$  is the net flux of compounds at the layer below  $k$  due to vertical eddy  
 162 diffusion. The cumulative eddy diffusion flux since 1970 ( $i=0$ ) to 2009 ( $i=n$ ), at a certain  
 163 depth  $k$ , is given by,  $F_{\text{cum},k}^n$ :

164 
$$F_{\text{cum},k}^n = \sum_{i=0}^{i=n} F_{\text{eddy-diff},k}^i$$
 (6)

165

166 The model used to estimate the transport by eddy diffusion holds the mass balance at each  
 167 depth (from equation [5]). In addition, we calculated the cumulative flux at 100 m depth,  
 168 which is the amount of PFOA leaving the top 100 m water layer from 1970 to 2009, and  
 169 compared it to the reservoir of PFOA at waters below 100 m depth for the last time period  
 170 considered (2009), and mass balance was achieved.

171

172 ***2.4. Forcing of the historical surface water concentration***

173 The industrial production of PFOA started around 1950 but initially the production  
 174 volume was small, so we assumed that significant loading to the ocean started in 1970  
 175 (Paul et al., 2009). Therefore, the surface water (representing the surface mixed layer)  
 176 concentration was forced to follow published trends starting in 1970. In 1970, the water  
 177 below the surface (i.e., below the mixed layer depth) was assumed to contain no PFOA.  
 178 For PFOA, surface water concentrations were scaled on the predicted concentration trend  
 179 for European seawater by van Zelm et al. (2008), with a zero concentration in 1970 and

180 then a linear increase from 1975 to 2009. We hence used the historical trend to estimate  
181 past surface water concentrations. This approach assumes a direct link between emission  
182 and resulting environmental concentrations, which has been observed for many other  
183 POPs (Schwarzenbach et al., 2003).

184

## 185 ***2.5. Global ocean surface water concentrations of PFOA***

186 For the Atlantic Ocean, PFOA surface concentrations reported by Benskin et al. (2012)  
187 and ranging from 3 ng m<sup>-3</sup> (½ of detection limit) to 260 ng m<sup>-3</sup>, have provided the best  
188 spatial coverage to date. There are fewer reported PFOA concentrations for the Pacific  
189 and Indian Ocean. In the Pacific Ocean, concentrations range from below detection limit  
190 to 50 ng m<sup>-3</sup> (Wei et al., 2007; Yamashita et al., 2008); we used a range of 5 – 50 ng m<sup>-3</sup>.  
191 In the Indian Ocean, reported concentrations are up to 10 ng m<sup>-3</sup> (Wei et al., 2007); we  
192 assumed a range of 1 – 10 ng m<sup>-3</sup>. We defined the southern boundary for these ocean  
193 basins as the southernmost latitude where PFOA was still consistently reported above the  
194 detection limit.

195

## 196 **2.6. E values and extent of each water layer for the global oceans**

197 Values of the vertical eddy diffusion coefficient, E, are scarce in the open ocean. We  
198 represent the variation of E with depth as a three-layer structure, with a constant but  
199 different E value in each water layer. The lower boundary of the first layer ( $z = -H_1$ ) is  
200 taken as the diurnal mean mixed layer depth; the second layer (with lower boundary  $z = -$   
201  $H_2$ ) goes from the base of the diurnal mean mixed layer depth to the base of the seasonal  
202 thermocline; the third layer goes from the base of the seasonal thermocline to the bottom

203 of the studied domain ( $z = -H_3 = -3,000$  m). Furthermore, at the boundary of each water  
204 layers, we assume a gradual change of  $E$ , with a constant gradient within 20 m at each  
205 side of the boundary (or within 5 m if the water layer is very shallow).  
206 To compute global ocean vertical eddy diffusion fluxes, we use  $E$  values from various  
207 microprofiler survey campaigns in the Atlantic and Pacific Oceans (Gregg, 1987;  
208 Ruddick et al., 1997; Jurado et al., 2012a; Jurado et al., 2012b) and common reported  $H$   
209 values in the global oceans. For the diurnal mean mixed layer, we use an average  $E_1$  of  
210  $10^{-2} \text{ m}^2 \text{ s}^{-1}$ , ranging from  $10^{-5}$  to  $10^0 \text{ m}^2 \text{ s}^{-1}$ , and an average depth of  $H_1=60$ . For the  
211 seasonal thermocline, we use an average  $E_2$  of  $10^{-5} \text{ m}^2 \text{ s}^{-1}$ , ranging from  $10^{-7}$  to  $10^{-3} \text{ m}^2 \text{ s}^{-1}$ ,  
212 and an average depth  $H_2=600$  m. Below the seasonal thermocline, we used an average  $E_3$   
213 of  $10^{-4} \text{ m}^2 \text{ s}^{-1}$ , ranging from  $10^{-6}$  to  $5 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$ , and  $H_3=3,000$  m. Note the large  
214 variability of the vertical eddy diffusion coefficients values, which can be up to 5 orders  
215 of magnitude, but this variability is usually observed when measuring turbulence with  
216 microprofilers (Jurado et al., 2012a; Jurado et al., 2012b).  $H_1$  and  $H_2$  are also subject to  
217 seasonal and spatial changes, which are not considered here.

218  
219

## 220 **3. Results and Discussion**

### 221 ***3.1. Model results and comparison with measured distribution***

222 First, we aimed to reproduce the measured PFOA profile (Yamashita et al., 2008) for the  
223 top 3,000 m of the Japan Sea (Figure 1a). Using three values for the vertical eddy  
224 diffusion coefficient  $E$  ( $E_1 = 5 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  in the mixed layer  $[-10 \text{ m}, 0 \text{ m}]$ ,  $E_2 = 8 \times 10^{-4}$   
225  $\text{m}^2 \text{ s}^{-1}$  in the seasonal thermocline  $[-300 \text{ m}, -10 \text{ m}]$ , and  $E_3 = 2.5 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  below the  
226 base of the seasonal thermocline  $[-3,000 \text{ m}, -300 \text{ m}]$ ), constant in time and with a gradual

227 change within layers, results in an excellent agreement between modeled and measured  
228 PFOA concentrations (Yamashita et al., 2008) for profile JS2 in the Japan Sea (Figure  
229 1a). The depth of the surface mixed layer ( $z = -H_1 = -10$  m) and the depth base of the  
230 seasonal thermocline ( $z = -H_2 = -300$  m) are consistent with measured temperature and  
231 salinity profiles in Yamashita et al. (2008). Measured PFOA concentrations at all depths  
232 were within a factor of 2 for the Japan Sea, or less (upper water column) of the model  
233 predictions. In general, our simple vertical eddy diffusion model can reproduce the  
234 observed profile for PFOA for the top of the water column extremely well, suggesting  
235 that vertical eddy diffusion has been solely responsible for the transport of PFOA to  
236 deeper waters. However, the E values needed to fit the field measurements of PFOA are  
237 close to the upper range of the E values measured in the field, and such efficient transport  
238 of PFOAs to deep waters may not be a generalized process in all the oceans.

239 While Yamashita et al. (2008) have measured other vertical profiles, PFOA was not  
240 detected in their South Pacific Ocean samples. The vertical profiles reported in the North  
241 Atlantic Ocean were taken in the region of deep water formation and hence the model  
242 here cannot be applied. Lastly, their profiles for the Mid-Atlantic Ocean display an  
243 unusually deep seasonal thermocline, but one of these profiles (AO4) appears consistent  
244 with transport solely due to vertical eddy diffusion. In this case, the mixed layer depth is  
245 around 100 m, and the base of the seasonal thermocline at 800 m, resulting in higher E  
246 values ( $E_1 = 5 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  (0-100 m),  $E_2 = 3.5 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  (100-800 m) and  $E_3 = 4 \times 10^{-3}$   
247  $\text{m}^2 \text{ s}^{-1}$  (800-3,000 m) for the cast AO4 (see Figure 1b). Model predictions were within  
248 20% of the measured values.

249 Our derived E values are at the upper end of the E reported elsewhere, which can vary by  
250 more than 5 orders of magnitude. The large E values may be affected by the particular  
251 conditions of the sampling sites, such as additional horizontal advection driving  
252 turbulence transport of these compounds by deeper currents. Further vertical profiles of  
253 PFOA are needed to verify its potential as a diffusion tracer, but to date only Yamashita  
254 et al.<sup>17</sup> provided depth profiles. The vertical dependence of E, with large values in the  
255 surface layer, depleted values in the seasonal thermocline and somewhat increased values  
256 below the seasonal thermocline, is in agreement with the E distribution reported  
257 elsewhere (Gregg, 1987; Ruddick et al., 1997; Jurado et al., 2012a). We conclude that the  
258 assumption that PFOA move to depth solely via vertical turbulent diffusion is consistent  
259 with available observations.

260

### 261 ***3.2. The removal flux of PFOA at 100 m depth across the global oceans***

262 We estimated fluxes of PFOA due to vertical diffusion at 100 m depth across the major  
263 ocean basins using equation (5) with the set of E values and depths of the bottom of the  
264 diurnal mean mixed layer and seasonal thermoclines determined for the global oceans. In  
265 the Atlantic Ocean, vertical diffusive fluxes of PFOA were based on PFOA  
266 concentrations in surface waters measured in 2007 and 2009 by Benskin et al. (2012),  
267 scaled back to zero in 1970 based on the trend reported by van Zelm et al. (2008). For the  
268 Pacific Ocean, we used the range of concentrations reported in Yamashita et al. (2008)  
269 and Wei et al. (2007). For the Indian Ocean, we used the range of concentrations reported  
270 in Wei et al. (2007).

271 Figures 2 and 3 show the change in time and depth of the modeled PFOA concentration  
272 and fluxes. The concentrations in surface waters increase from 1970 to 2009, with a  
273 continuous decrease in concentrations and fluxes with depth. Right panels in figure 2  
274 show the 2009 profiles using the average, lower limit and upper limit E values. We chose  
275 station 25 in the 2009 *Endeavor* Cruise in Benskin et al. (2012) as a typical example of  
276 open ocean measurements in the North Atlantic. The derived historical profiles of the  
277 concentration and vertical eddy diffusive flux for PFOA over the last four decades,  
278 assuming increasing surface concentrations, are displayed in Figure 3. Due to vertical  
279 eddy diffusion, PFOA concentrations in the water column increase, and PFOA reaches  
280 deeper waters due to eddy diffusivity.

281 We estimated whether volatilization of PFOA could be another important loss process of  
282 PFOA from surface waters relative to vertical diffusion. Even assuming its  $pK_a = 3.7$   
283 (Burns et al. 2008), the concentrations of the non-ionic (acid) form of PFOA will be very  
284 low, and estimations of gross volatilization fluxes using the standard two-film models for  
285 diffusive air-water exchange points out that it would be at most 10% of its transfer to  
286 depth due to eddy diffusivity. Assuming a  $pK_a = -0.5$  (Goss et al. 2008), these  
287 volatilization fluxes are more than five orders of magnitude lower than eddy diffusivity  
288 fluxes. Thus, we consider PFOA to be a persistent, water-borne tracer that will only be  
289 removed from surface waters to depth.

290 The historical cumulative flux at 100 m depth from 1975 to 2007 were highest (-  
291  $15 \times 10^3$  to  $-8,6 \times 10^3$   $\text{ng m}^{-2}$ ) in the North Atlantic. Fluxes decreased towards  $-3,8 \times 10^3$  to -  
292  $2,4 \times 10^3$   $\text{-ng m}^{-2}$  near the Equator, and were even lower in the South Atlantic (Table 1).

293 The lowest cumulative PFOA fluxes were estimated for the Pacific and Indian Ocean, -  
294  $1,6 \times 10^3 \text{ ng m}^{-2}$  and  $-310 \text{ ng m}^{-2}$ , respectively.

295

### 296 **3.3. Comparison between removal fluxes of PFOA from the global Oceans due to** 297 **vertical eddy diffusion and deep water formation**

298 Previous results highlight that East-West gradients of PFOA in surface waters of the  
299 North Atlantic are rather small. For example, PFOA varies by less than a factor of two on  
300 a transect between  $45^{\circ}\text{N}$  and  $60^{\circ}\text{N}$  (Yamashita et al., 2008). Similarly, the Yamashita et  
301 al. (2008) transect at  $15^{\circ}\text{N}$  showed little variability in PFOA, except for one elevated  
302 sample, which was probably influenced by the Amazon River plume. This suggests that  
303 atmospheric deposition fluxes were either fairly constant longitudinally across the  
304 Atlantic and/or presumably accounted for a small fraction of the overall inputs of PFOA  
305 in most oceanic regions, as was reported for the Arctic Ocean (Armitage et al., 2009b;  
306 Stemmler and Lammel, 2010); the major uncertainty would remain with the vertical eddy  
307 diffusion coefficients. We therefore estimated the importance of the global Oceans in  
308 removing PFOA from the surface Ocean due to vertical diffusion by extrapolating our  
309 flux estimates across a given region (Table 1 and 2).

310 Due to the high variability in reported E values, using the upper and lower limit of the  
311 used E values resulted in estimations of eddy diffusivity fluxes that also varied by several  
312 orders of magnitude (Table 1). While the instantaneous turbulent fluxes may be highly  
313 variable, it is unlikely that a certain region constantly displays values of E close to the  
314 upper limit or lower limit. Therefore, the predictions obtained using the average E values  
315 seem appropriate to evaluate the mid- long-term fate of PFOA, even though the upper and



316 lower limits provide extreme estimates of the range of the potential importance of this  
317 mechanism of transport (Tables 1 and 2).

318 The North Atlantic emerged as the main sink for PFOA, with cumulative removal fluxes  
319 below 100 m depth over the last 40 years of ca. 470 t, with the South Atlantic  
320 contributing another ~ 74 t. The Pacific Ocean is estimated to have around 190 t PFOA  
321 below a depth of 100 m, while the Indian Ocean contributed only 11 t in total. The global  
322 oceanic sink of PFOAs due to eddy diffusivity is in the order of 660 t (Table 2).

323 To put the vertical diffusive flux values in the global oceans in perspective, we estimated  
324 the flux of PFOA entering the deep Ocean via deep water formation. Deep water  
325 formation fluxes were as in (Lohmann et al., 2006b), with the Norwegian and Labrador  
326 Sea having areas of 4.0 and  $2.7 \times 10^{12} \text{ m}^2$ , and average deep water formation fluxes of 10  
327 and 5 Sv ( $10^6 \text{ m}^3 \text{ s}^{-1}$ ). PFOA surface water concentrations of 20 - 50  $\text{ng m}^{-3}$  were  
328 measured in the Labrador Sea water column by Yamashita et al. (2008), while Ahrens et  
329 al. (2010) reported 10  $\text{ng m}^{-3}$  for the Norwegian Sea. We note that for a given region in  
330 the Atlantic Ocean, PFOA concentrations by Yamashita et al. (2008) seem higher by a  
331 factor of around 2 than those reported by Ahrens et al. (2009). A similar discrepancy was  
332 obtained for PFOA concentrations in seawater in a recent inter-laboratory comparison  
333 between Japan's National Institute of Advanced Industrial Science and Technology (a  
334 factor of 2 higher) and the Canadian Centre for Inland Waters (Environment Canada),  
335 implying a systematic error, most likely by the Japanese group (Benskin et al., 2012).

336 Estimated fluxes of PFOA are 3 - 16 and 2 - 8  $\text{tons yr}^{-1}$  in the Norwegian and Labrador  
337 Sea for surface concentrations of 10 - 50  $\text{ng m}^{-3}$ . PFOA was not detected in the other two  
338 deep water formation regions, the Ross and Weddell Seas (Yamashita et al., 2008). The

339 maximum contribution of these Southern Seas in transporting PFOA to deep water can be  
340 estimated by assuming  $\frac{1}{2}$  detection limit by Yamashita et al. (2008) (of  $6 \text{ ng m}^{-3}$ ) as  
341 PFOA concentrations. This would give rather insignificant fluxes of at most  $1 \text{ ton yr}^{-1}$  for  
342 each Sea. The deep water formation fluxes are similar in importance to the estimated  
343 inflow of PFOA into the Arctic Sea of  $2\text{-}12 \text{ t yr}^{-1}$  (Prevedouros et al., 2006) or  $8\text{-}23 \text{ t yr}^{-1}$   
344 (Stemmler and Lammel, 2010). Assuming that the increase of PFOA in the North Atlantic  
345 mirrored the PFOA emissions, we can extrapolate the total amount of PFOA moved to  
346 deep waters since their industrial production started in 1970. Total amounts moved by  
347 deep water formation are estimated to be 50 - 250 tons in the Norwegian Sea and 30 - 130  
348 tons of PFOA in the Labrador Sea over the last 40 years. Thus, vertical eddy diffusion  
349 accounts for losses of PFOA to depth on the order of 660 t (range from 1 to 4800 t), while  
350 80 – 360 tons have been lost from the surface oceans via deep water formation.

351 Based on measured surface concentrations, we extrapolated the amount of PFOA residing  
352 in the top 100 m of the water column (Table 2). At most, there is a 10% decline of surface  
353 water concentrations to 100 m depth, no matter which E values we chose. This equates to  
354 approximately another 1100 tons PFOA stored in the upper 100m of the world's Oceans:  
355 mostly in the North Atlantic and Pacific Ocean (around 600 and 300 t respectively),  
356 another 170 t in the South Atlantic), and 19 t in the Indian Ocean.

357 Prevedouros et al. (2006) reported a total historical industrial production of PFOA of  
358 3,200 – 7,300 tons. Here we assume the average of the reported range (i.e., 5,250 tons) as  
359 the most likely production volume. Our results imply that the global Oceans have  
360 removed around 13% of the PFOA produced to depth greater than 100 m via vertical  
361 diffusion, but with a large range due to uncertainty of eddy diffusivity measurements

362 (range between 0.03 and 91% of global production). An additional 4% (1.5- 6.8%) will  
363 have been removed via deep water formation. Lastly, the top 100 m of the surface oceans  
364 store another 21% of all PFOA produced (1120 t, Table 2).

365 As not all produced PFOA is expected to have escaped its intended use (Prevedouros et  
366 al., 2006), our calculations suggest that the majority of PFOA has reached the deeper  
367 ocean via vertical diffusion. To the best of our knowledge, this work suggests that vertical  
368 diffusion to the deep ocean is the main known sink of PFOA from the environment, even  
369 though this process has not been considered in current models of PFOA transport and fate  
370 in regional and global models (Armitage et al., 2009a). We note that coastal oceans, such  
371 as the Japan Sea, will likely exhibit markedly higher fluxes to depth, due to a combination  
372 of more efficient vertical mixing and greater surface concentrations of PFOA.

373

#### 374 **4. Implications**

375 Our results suggest that a simple eddy-diffusion model can explain the vertical profile of  
376 persistent organic compounds, that are neither prone to air-water exchange nor to  
377 degradation reactions, such as PFOA, in the surface ocean. We show here that vertical  
378 eddy diffusion fluxes are significantly higher than those due to deep water formation, thus  
379 being the main environmental known sink for PFOA. Over time, it seems likely that  
380 perfluorinated compounds will accumulate in larger concentrations in the open ocean,  
381 increasing the role of vertical eddy diffusion as a sink process even more.

382 Curiously, transport due to vertical eddy diffusion has never been considered before as a  
383 significant sink of POPs, probably due to the fact that most POPs are hydrophobic and  
384 their settling associated to organic carbon is faster. In any case, vertical diffusion is a

385 slow but persistent and ubiquitous sink that could also be important for other POPs, and it  
386 will be the main sink for the “swimmer” type of pollutants.  
387 Once emissions are abated, surface concentrations will decrease fast initially, but will  
388 slow down as eddy diffusion reduces the concentration gradient in the water column. Our  
389 results could also explain observations noticing a very slow response of global oceans  
390 with respect to decreasing concentrations of other POPs. It seems likely that after an  
391 initial fast decline as a response to decreasing inputs, ocean surface waters could enter a  
392 phase during which concentrations decrease only slowly, making these difficult to detect  
393 with the current analytical precision. For “swimmer” type compounds, such as PFOA,  
394 this lack of clear temporal trends will be due to the fact that vertical diffusion is the main  
395 sink process. For single-hoppers and multiple-hoppers, such as legacy POPs, in the large  
396 oligotrophic areas of the oceans, the biological pump is not an efficient removal process  
397 (Jurado and Dachs, 2008). It is possible that vertical diffusion has been the main sink, and  
398 nowadays, after a reduction of atmospheric inputs, the concentration gradients have  
399 decreased, or inverted, such that there is an upper direction flux of legacy POPs so the  
400 oceans are acting as a source to the atmosphere (Nizzetto et al., 2010; Zhang and  
401 Lohmann, 2010; Lohmann et al., 2012) .

402

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539

**Table 1: Ocean regions, selected range of PFOA concentrations, average of calculated turbulent fluxes at 100 m depth ( $F_{ave, 100}$ ) and the historically cumulative turbulent fluxes (1970-2009) at 100 m depth ( $F_{cum, 100}$ ). Computations made with average and range E values reported for the global oceans.**

Ocean region	[PFOA] (pg/L)	Average E values for the global oceans ( $E_1=10^{-2}$ , $E_2=10^{-5}$ , $E_3=10^{-4}$ m <sup>2</sup> s <sup>-1</sup> )		Upper range E values for the global oceans ( $E_1=10^{-1}$ , $E_2=10^{-3}$ , $E_3=5*10^{-3}$ m <sup>2</sup> s <sup>-1</sup> )		Lower range E values for the global oceans ( $E_1=10^{-5}$ , $E_2=10^{-7}$ , $E_3=10^{-6}$ m <sup>2</sup> s <sup>-1</sup> )	
		$F_{ave, 100}$ [ng m <sup>-2</sup> s <sup>-1</sup> ]	$F_{cum, 100}$ [ng m <sup>-2</sup> ]	$F_{ave, 100}$ [ng m <sup>-2</sup> s <sup>-1</sup> ]	$F_{cum, 100}$ [ng m <sup>-2</sup> ]	$F_{ave, 100}$ [ng m <sup>-2</sup> s <sup>-1</sup> ]	$F_{cum, 100}$ [ng m <sup>-2</sup> ]
N-Atlantic, (45-60 °N)	260 <sup>a</sup>	-2.4*10 <sup>-5</sup>	-1.5*10 <sup>4</sup>	-1.6*10 <sup>-4</sup>	-11*10 <sup>4</sup>	-1.4*10 <sup>-7</sup>	-34
N-Atlantic, (30-45 °N)	21-250 <sup>a</sup>	-2.1*10 <sup>-5</sup>	-1.4*10 <sup>4</sup>	-1.4*10 <sup>-4</sup>	-10*10 <sup>4</sup>	-1.3*10 <sup>-7</sup>	-31
N-Atlantic, (15-30 °N)	24-210 <sup>a</sup>	-1.3*10 <sup>-5</sup>	-8,600	-8.6*10 <sup>-5</sup>	-6.3*10 <sup>4</sup>	-7.8*10 <sup>-8</sup>	-19
N-Atlantic, (0-15 °N)	18-41 <sup>a</sup>	-5.2*10 <sup>-6</sup>	-3,800	-3.4*10 <sup>-5</sup>	-2.7*10 <sup>4</sup>	-3.1*10 <sup>-8</sup>	-8
S-Atlantic (0-15 °S)	10-32 <sup>a</sup>	-3.9*10 <sup>-6</sup>	-2,400	-2.5*10 <sup>-5</sup>	-1.7*10 <sup>4</sup>	-2.3*10 <sup>-8</sup>	-5
S-Atlantic (15-30 °S)	5-27 <sup>a</sup>	-3.1*10 <sup>-6</sup>	-2,000	-2.0*10 <sup>-5</sup>	-1.5*10 <sup>4</sup>	-1.9*10 <sup>-8</sup>	-5
S-Atlantic (30-45 °S)	3-110 <sup>a</sup>	-4.3*10 <sup>-6</sup>	-2,800	-2.8*10 <sup>-5</sup>	-2.0*10 <sup>4</sup>	-2.5*10 <sup>-8</sup>	-6
S-Atlantic (45-60 °S)	5-8 <sup>a</sup>	-5.6*10 <sup>-7</sup>	-360	-3.6*10 <sup>-6</sup>	-2,600	-3.2*10 <sup>-9</sup>	-1
Pacific (30 °S–60 °N)	5-50 <sup>b,c</sup>	-2.4*10 <sup>-6</sup>	-1,600	-1.6*10 <sup>-5</sup>	-1.1*10 <sup>4</sup>	-1.4*10 <sup>-8</sup>	-3
Indian (30 °S–30 °N)	1-10 <sup>c</sup>	-4.8*10 <sup>-7</sup>	-310	-3.1*10 <sup>-5</sup>	-2,300	-2.8*10 <sup>-9</sup>	-1

<sup>a</sup> (Benskin et al., 2012); <sup>b</sup> (Yamashita et al., 2008); <sup>c</sup> (Wei et al., 2007)



**Table 2: Ocean basins, their surface areas, calculated amount of PFOA removed from the top 100 m due to turbulence ( $F_{cum, 100}$  \* surface area, from 1970-2009) versus PFOA fluxes due to deep water formation and amount of PFOA stored in the top 100 m surface oceans**

Ocean basins	Surface area (10 <sup>6</sup> km <sup>2</sup> )	Amount PFOA removed by turbulence from top 100 m (tons)			deep water formation (tons)	Amount of PFOA top 100 m (tons)
		average E values	lower range E values	upper range E values		
Norwegian Sea	4.0	n/a	n/a	n/a	50-250	
Labrador Sea	2.7	n/a	n/a	n/a	30-130	
N-Atlantic, 45 N – 60 N	8	124	0.3	904	n/a	205 (153 - 209)
N-Atlantic, 30 N – 45 N	10	139	0.3	1006	n/a	232 (174 - 237)
N-Atlantic, 15 N – 30 N	11	95	0.2	690	n/a	159 (119 - 162)
N-Atlantic, 0 N - 15 N	9	34	0.1	247	n/a	51 (39 - 52)
S-Atlantic, 0 N - 15 S	9	21	0.0	154	n/a	39 (29 - 39)
S-Atlantic, 15 S - 30 S	11	22	0.0	163	n/a	39 (29 - 39)
S-Atlantic, 30 S - 45 S	10	28	0.1	202	n/a	46 (34 - 47)
S-Atlantic, 45 S - 60 S	8	3	0.0	21	n/a	5 (4 - 5 )
Pacific, 30 S - 60 N	120	186	0.4	1352	n/a	326 (245 - 332)
Indian, 30 S – 30 N	35	11	0.0	79	n/a	19 (14 - 19)
<b>Total</b> (range)		<b>664</b>	<b>1.5</b>	<b>4818</b>	<b>220</b> (80 – 360)	<b>1120</b> <b>(839 - 1142)</b>

## Figure captions

Figure 1: Modeled versus measured concentration of PFOA in (a) the Japan Sea (cast JS2, May 2005 Yamashita et al. [2008]) using  $E_1=5 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  [0 , -10 m],  $E_2=8 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  [-10 , -300 m], and  $E_3=2.5 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  [-300, -3,000 m], and (b) in the Mid-Atlantic Bight (cast A04, March 2004, Yamashita et al. [2008]) using  $E_1= 5 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  [0, 100 m],  $E_2= 3.5 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  [-100, -800 m], and  $E_3= 4 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  [-800, -3,000 m].

Figure 2: (a,b) Modeled concentration of PFOA and (c,d) modeled removal flux of PFOA due to vertical eddy diffusion in the station 25 in the *R/V Endeavor* Cruise at Benskin et al. [2012]. Panel (a) and (c) show modeled concentration and flux from 1970 until 2009, obtained from the average vertical eddy diffusivity,  $E$ , values for the global oceans:  $E_1 = 10^{-2} \text{ m}^2 \text{ s}^{-1}$  in the surface mixed layer (0-60 m),  $E_2 = 10^{-5} \text{ m}^2 \text{ s}^{-1}$  in the seasonal thermocline (60-600m), and  $E_3 = 10^{-4} \text{ m}^2 \text{ s}^{-1}$  below the seasonal thermocline (600-3,000m). Panel (b) and (d) show vertical profiles for the year 2009, using the average  $E$  values (solid line), upper range of the  $E$  values (dashed line):  $E_1 = 10^0 \text{ m}^2 \text{ s}^{-1}$ ,  $E_2 = 10^{-3} \text{ m}^2 \text{ s}^{-1}$ ,  $E_3 = 5 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$ , and lower range of the  $E$  values (dotted line):  $E_1 = 10^{-5} \text{ m}^2 \text{ s}^{-1}$ ,  $E_2 = 10^{-7} \text{ m}^2 \text{ s}^{-1}$ ,  $E_3 = 10^{-6} \text{ m}^2 \text{ s}^{-1}$ .

Figure 3: Historical profiles (0 – 3,000 m) of (a) the modeled PFOA concentration, and (b) the modeled removal flux of PFOA due to vertical eddy diffusion in the station 25 in the 2009 *R/V Endeavor* cruise at Benskin et al. [2012]. Concentrations and fluxes are given for the years 1970 (just before PFOA large scale production), 1980, 1990, 2000 and 2009. Concentrations and fluxes have been predicted using representative vertical eddy diffusivity,  $E$ , values for the global oceans:  $E_1 = 10^{-2} \text{ m}^2 \text{ s}^{-1}$  in the surface mixed layer (0-60 m),  $E_2 = 10^{-5} \text{ m}^2 \text{ s}^{-1}$  in the seasonal thermocline (60 - 600 m), and  $E_3 = 10^{-4} \text{ m}^2 \text{ s}^{-1}$  (600 - 3,000 m).