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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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Abstract

Here we estimate the importance of vertical eddy diffusion in removing perfluorooctanoic acid (PFOA) from the surface Ocean and assess its importance as a global sink. Measured water column profiles of PFOA were reproduced by assuming that vertical eddy diffusion in a 3-layer ocean model is the sole cause for the transport of PFOA to depth waters. The global oceanic sink due to eddy diffusion for PFOA is high, with accumulated removal fluxes over the last 40 years of 664 t, with the Atlantic Ocean accounting for 70% of the global oceanic sink. The global oceans have removed 13% of all PFOA produced to a depth greater than 100 m via vertical eddy diffusion; an additional 4 % has been removed...
via deep water formation. The top 100 m of the surface oceans store another 21% of all PFOA produced (~1100 t).

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

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

### 1. Introduction

Perfluoralkyl carboxylic acids (PFCAs) have been used by industry since the 1960s, mostly as a processing aid in the manufacture of fluoropolymers, such as during conversion of tetrafluoroethylene into polytetrafluoroethylene (PTFE) (Prevedouros et al., 2006). In the oceans, perfluorooctanoic acid (PFOA) is the most frequently detected PFCA, and often detected at greatest concentrations (Yamashita et al., 2005; Yamashita et al., 2008). Per- and polyfluoroalkyl substances compounds are transported away from their production and use locations by a combination of transport with ocean currents (Armitage et al., 2006), atmospheric transport and oxidation of fluorotelomer alcohols (Ellis et al., 2003), and transport with sea-salt aerosols (McMurdo et al., 2008; Webster and Ellis, 2008). Perfluorinated compounds have been detected in biota, including humans world-wide (Giesy and Kannan, 2002; Houde et al., 2006); PFOA and perfluorooctane sulfonate (PFOS) are the most commonly detected perfluorinated chemicals in the environment. PFOS (but not PFOA) has been included in the Stockholm
treaty on 'Persistent Organic Pollutants' (POPs) due to its persistence, bioaccumulation potential and toxicity (UNEP, 2009).

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

The biological pump removes POPs from the surface ocean through a series of partitioning steps involving dry and wet deposition, phytoplankton uptake and removal from the surface mixed layer by the organic carbon settling flux (Dachs et al., 1999; Dachs et al., 2002; Jurado et al., 2004; Jurado et al., 2005; Galban-Malagon et al., 2012). The physical pump is especially important in the North Atlantic (Norwegian and Labrador Seas) and the Southern Ocean (Weddell and Ross Seas), where both dissolved and particle-bound POPs are removed from the surface ocean through deep water formation (Broecker, 1974). For hydrophobic POPs, the physical pump is less important globally than the biological pump (Lohmann et al., 2006b), but it might be more important for hydrophilic chemicals. The magnitude and mechanisms of the oceanic sink are poorly constrained for ionic and amphiphilic organic compounds which do not sorb strongly to sinking organic matter.

The objective of this work is to estimate - for the first time - the importance of vertical (eddy) diffusion as a major removal process of persistent compounds from the surface ocean. We focus on PFOA, which in seawater exists primarily as the anion (PFO$^-$), no
matter whether its exact pKa value is around 3.7 (Burns et al., 2008) or -0.5 (Goss, 2008). The anion has a very low sorption coefficient, a negligible vapor pressure and does not degrade (Barton et al., 2007). Thus, PFOA has recently been proposed as a novel chemical tracer of ocean circulation (Yamashita et al., 2008). SF₆ has also been extensively used as a passive tracer to quantify vertical eddy diffusion coefficients but, because it is biologically available to flora and fauna, SF₆ displays a stronger seasonal variability than PFOA. Due to its low reactivity and, relative to other POPs, reduced affinity for organic carbon, PFOA should be an excellent tracer of past and current emissions, and its transport to the deep ocean will be due to subduction of water masses and vertical eddy diffusion solely.

As the ocean is generally vertically stratified, there are large concentration gradients with depth, so turbulent vertical eddy diffusion becomes a key process in removing compounds from the surface layer. In analogy with Fick's First Law, the vertical flux of compounds in the water due to vertical eddy diffusion, \( F_{\text{eddy-diff}} \) (ng m\(^{-2}\) s\(^{-1}\)), is:

\[
F_{\text{eddy-diff}} = -E \frac{\partial C}{\partial z},
\]

(1)

where \( E \) is the vertical eddy diffusion coefficient (m\(^2\) s\(^{-1}\)), \( C \) is the concentration of PFOA (ng m\(^{-3}\)) and \( z \) (m) is the vertical coordinate (positive upwards with \( z = 0 \) indicating the ocean surface). Vertical eddy diffusivities are highly variable both in time and space, ranging from \( 10^{-5} \) to \( 10^{0} \) m\(^2\) s\(^{-1}\) in the upper mixed layer of the ocean to \( 10^{-7} \) to \( 10^{-3} \) m\(^2\) s\(^{-1}\) in the open deep ocean (Gregg, 1987; Jurado et al., 2012a; Jurado et al., 2012b). A common approach for modelling purposes is to consider the stratified ocean as a three-layer water column with constant values of \( E \) in each layer: the highest values of \( E \) in the surface mixed layer,
reduced E values for the seasonal thermocline, and slightly increased E values below the
seasonal thermocline (Woods and Onken, 1982; Huisman and Sommeijer, 2002).

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

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

2. Materials and Methods

2.1. Vertical water column concentrations of PFOA

PFOA concentrations for the top 3,000 m of the water column were taken from
Yamashita et al. (2008). To date, Yamashita et al. (2008) is the only study that has
reported vertical ocean profiles of perfluoroalkyl compounds. The depth profiles from the
Japan Sea (JS2) and Mid-Atlantic Bight (AO4) were chosen as no deep water formation
occurs at these locations and data are available at a sufficiently high vertical resolution to
compare to model results. In the Japan Sea, concentrations of PFOA decreased from 50 ng m\(^{-3}\) at the surface to < 10 ng m\(^{-3}\) at 3,000 m depth. In the Mid-Atlantic Bight, concentrations dropped from ≤ 150 ng m\(^{-3}\) at the surface to ≤ 50 ng m\(^{-3}\) at 3,000 m.

2.2. Model description

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

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

\[
\frac{\partial C}{\partial t} = -\frac{\partial}{\partial z} F_{\text{eddy-diff}} = \frac{\partial}{\partial z} \left[ E \frac{\partial C}{\partial z} \right],
\]

(2)

where \(z\) is the depth and \(t\) accounts for time. To solve equation (2), we partition the domain in space using water layers ranging from \(k=0\) to \(k=N\), where \(k=0\) is the bottom layer at 3,000 m depth and \(k=N\) is the surface layer at 0 m depth, and with a uniform vertical depth increase of \(\Delta z = 1\) m. We also partition the domain in time using time steps ranging from \(n=1\) to \(n=M\), where \(n=1\) is the initial time at 1970 and \(n=M\) is the final time, and with a uniform time step increase of \(\Delta t = 0.5\) years.
As initial conditions, we assume that at the initial time step (i.e., 1970) the seawater concentration of PFOA was zero ($C = 0$) at the surface and any depth. As boundary conditions, we assume that contaminants enter the water column from the ocean surface and we assume no flux of contaminants at the bottom of the domain:

$$\frac{d C}{d z}_{z=0} = C_s$$  \hspace{1cm} (3a) \\
$$\frac{\partial C}{\partial z}_{z=H} = 0$$  \hspace{1cm} (3b)

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

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

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

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

This integration method is stable over the transition zones between the three layers, but this estimates the concentration field but not the eddy diffusivity fluxes. The vertical net eddy diffusion flux of compounds at a certain water layer $k$ and a time step $n$, $F_{\text{eddy-diff, } k}^n$ (ng m$^{-2}$ s$^{-1}$) is computed as:
where $F_{\text{eddy-diff, } k-1}$ is the net flux of compounds at the layer below $k$ due to vertical eddy diffusion. The cumulative eddy diffusion flux since 1970 ($i=0$) to 2009 ($i=n$), at a certain depth $k$, is given by, $F_{\text{cum, } k}^n$:

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

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

2.4. Forcing of the historical surface water concentration

The industrial production of PFOA started around 1950 but initially the production volume was small, so we assumed that significant loading to the ocean started in 1970 (Paul et al., 2009). Therefore, the surface water (representing the surface mixed layer) concentration was forced to follow published trends starting in 1970. In 1970, the water below the surface (i.e., below the mixed layer depth) was assumed to contain no PFOA. For PFOA, surface water concentrations were scaled on the predicted concentration trend for European seawater by van Zelm et al. (2008), with a zero concentration in 1970 and
then a linear increase from 1975 to 2009. We hence used the historical trend to estimate past surface water concentrations. This approach assumes a direct link between emission and resulting environmental concentrations, which has been observed for many other POPs (Schwarzenbach et al., 2003).

2.5. Global ocean surface water concentrations of PFOA

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

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

Values of the vertical eddy diffusion coefficient, E, are scarce in the open ocean. We represent the variation of E with depth as a three-layer structure, with a constant but different E value in each water layer. The lower boundary of the first layer (\(z = -H_1\)) is taken as the diurnal mean mixed layer depth; the second layer (with lower boundary \(z = -H_2\)) goes from the base of the diurnal mean mixed layer depth to the base of the seasonal thermocline; the third layer goes from the base of the seasonal thermocline to the bottom
of the studied domain ($z = - H_3 = -3,000 \text{ m}$). Furthermore, at the boundary of each water
layers, we assume a gradual change of $E$, with a constant gradient within 20 m at each
side of the boundary (or within 5 m if the water layer is very shallow).

To compute global ocean vertical eddy diffusion fluxes, we use $E$ values from various
microprofiler survey campaigns in the Atlantic and Pacific Oceans (Gregg, 1987;
Ruddick et al., 1997; Jurado et al., 2012a; Jurado et al., 2012b) and common reported $H$
values in the global oceans. For the diurnal mean mixed layer, we use an average $E_1$ of
$10^{-2} \text{ m}^2 \text{s}^{-1}$, ranging from $10^{-5}$ to $10^{0} \text{ m}^2 \text{s}^{-1}$, and an average depth of $H_1=60$. For the
seasonal thermocline, we use an average $E_2$ of $10^{-5} \text{ m}^2 \text{s}^{-1}$, ranging from $10^{-7}$ to $10^{-3} \text{ m}^2 \text{s}^{-1}$,
and an average depth $H_2=600 \text{ m}$. Below the seasonal thermocline, we used an average $E_3$
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 $H_3=3,000 \text{ m}$. Note the large
variability of the vertical eddy diffusion coefficients values, which can be up to 5 orders
of magnitude, but this variability is usually observed when measuring turbulence with
microprofilers (Jurado et al., 2012a; Jurado et al., 2012b). $H_1$ and $H_2$ are also subject to
seasonal and spatial changes, which are not considered here.

3. Results and Discussion

3.1. Model results and comparison with measured distribution

First, we aimed to reproduce the measured PFOA profile (Yamashita et al., 2008) for the
top 3,000 m of the Japan Sea (Figure 1a). Using three values for the vertical eddy
diffusion coefficient $E$ ($E_1 = 5 \times 10^{-3} \text{ m}^2 \text{s}^{-1}$ in the mixed layer [-10 m, 0 m], $E_2 = 8 \times 10^{-4}$
$\text{ m}^2 \text{s}^{-1}$ in the seasonal thermocline [-300 m, -10 m], and $E_3 = 2.5 \times 10^{-3} \text{ m}^2 \text{s}^{-1}$ below the
base of the seasonal thermocline [-3,000 m, -300 m]), constant in time and with a gradual
change within layers, results in an excellent agreement between modeled and measured PFOA concentrations (Yamashita et al., 2008) for profile JS2 in the Japan Sea (Figure 1a). The depth of the surface mixed layer \((z = - H_1 = -10 \text{ m})\) and the depth base of the seasonal thermocline \((z = - H_2 = -300 \text{ m})\) are consistent with measured temperature and salinity profiles in Yamashita et al. (2008). Measured PFOA concentrations at all depths were within a factor of 2 for the Japan Sea, or less (upper water column) of the model predictions. In general, our simple vertical eddy diffusion model can reproduce the observed profile for PFOA for the top of the water column extremely well, suggesting that vertical eddy diffusion has been solely responsible for the transport of PFOA to deeper waters. However, the \(E\) values needed to fit the field measurements of PFOA are close to the upper range of the \(E\) values measured in the field, and such efficient transport of PFOAs to deep waters may not be a generalized process in all the oceans.

While Yamashita et al. (2008) have measured other vertical profiles, PFOA was not detected in their South Pacific Ocean samples. The vertical profiles reported in the North Atlantic Ocean were taken in the region of deep water formation and hence the model here cannot be applied. Lastly, their profiles for the Mid-Atlantic Ocean display an unusually deep seasonal thermocline, but one of these profiles (AO4) appears consistent with transport solely due to vertical eddy diffusion. In this case, the mixed layer depth is around 100 m, and the base of the seasonal thermocline at 800 m, resulting in higher \(E\) values \((E_1 = 5 \times 10^{-3} \text{ m}^2 \text{ s}^{-1} \text{ (0-100 m)}, E_2 = 3.5 \times 10^{-3} \text{ m}^2 \text{ s}^{-1} \text{ (100-800 m)}\) and \(E_3 = 4 \times 10^{-3} \text{ m}^2 \text{ s}^{-1} \text{ (800-3,000 m)}\) for the cast AO4 (see Figure 1b). Model predictions were within 20% of the measured values.
Our derived E values are at the upper end of the E reported elsewhere, which can vary by more than 5 orders of magnitude. The large E values may be affected by the particular conditions of the sampling sites, such as additional horizontal advection driving turbulence transport of these compounds by deeper currents. Further vertical profiles of PFOA are needed to verify its potential as a diffusion tracer, but to date only Yamashita et al. provided depth profiles. The vertical dependence of E, with large values in the surface layer, depleted values in the seasonal thermocline and somewhat increased values below the seasonal thermocline, is in agreement with the E distribution reported elsewhere (Gregg, 1987; Ruddick et al., 1997; Jurado et al., 2012a). We conclude that the assumption that PFOA move to depth solely via vertical turbulent diffusion is consistent with available observations.

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

We estimated fluxes of PFOA due to vertical diffusion at 100 m depth across the major ocean basins using equation (5) with the set of E values and depths of the bottom of the diurnal mean mixed layer and seasonal thermoclines determined for the global oceans. In the Atlantic Ocean, vertical diffusive fluxes of PFOA were based on PFOA concentrations in surface waters measured in 2007 and 2009 by Benskin et al. (2012), scaled back to zero in 1970 based on the trend reported by van Zelm et al. (2008). For the Pacific Ocean, we used the range of concentrations reported in Yamashita et al. (2008) and Wei et al. (2007). For the Indian Ocean, we used the range of concentrations reported in Wei et al. (2007).
Figures 2 and 3 show the change in time and depth of the modeled PFOA concentration and fluxes. The concentrations in surface waters increase from 1970 to 2009, with a continuous decrease in concentrations and fluxes with depth. Right panels in figure 2 show the 2009 profiles using the average, lower limit and upper limit E values. We chose station 25 in the 2009 *Endeavor* Cruise in Benskin et al. (2012) as a typical example of open ocean measurements in the North Atlantic. The derived historical profiles of the concentration and vertical eddy diffusive flux for PFOA over the last four decades, assuming increasing surface concentrations, are displayed in Figure 3. Due to vertical eddy diffusion, PFOA concentrations in the water column increase, and PFOA reaches deeper waters due to eddy diffusivity.

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

The historical cumulative flux at 100 m depth from 1975 to 2007 were highest (-15x10^3 to -8.6 x10^3 ng m^-2) in the North Atlantic. Fluxes decreased towards -3.8 x10^3 to -2.4 x10^3 -ng m^-2 near the Equator, and were even lower in the South Atlantic (Table 1).
The lowest cumulative PFOA fluxes were estimated for the Pacific and Indian Ocean, \(-1.6 \times 10^3\) ng m\(^{-2}\) and \(-310\) ng m\(^{-2}\), respectively.

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

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

Due to the high variability in reported E values, using the upper and lower limit of the used E values resulted in estimations of eddy diffusivity fluxes that also varied by several orders of magnitude (Table 1). While the instantaneous turbulent fluxes may be highly variable, it is unlikely that a certain region constantly displays values of E close to the upper limit or lower limit. Therefore, the predictions obtained using the average E values seem appropriate to evaluate the mid-long-term fate of PFOA, even though the upper and
lower limits provide extreme estimates of the range of the potential importance of this
mechanism of transport (Tables 1 and 2).

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

To put the vertical diffusive flux values in the global oceans in perspective, we estimated
the flux of PFOA entering the deep Ocean via deep water formation. Deep water
formation fluxes were as in (Lohmann et al., 2006b), with the Norwegian and Labrador
Sea having areas of 4.0 and 2.7x10^12 m^2, and average deep water formation fluxes of 10
and 5 Sv (10^6 m^3 s^-1). PFOA surface water concentrations of 20 - 50 ng m^-3 were
measured in the Labrador Sea water column by Yamashita et al. (2008), while Ahrens et
al. (2010) reported 10 ng m^-3 for the Norwegian Sea. We note that for a given region in
the Atlantic Ocean, PFOA concentrations by Yamashita et al. (2008) seem higher by a
factor of around 2 than those reported by Ahrens et al. (2009). A similar discrepancy was
obtained for PFOA concentrations in seawater in a recent inter-laboratory comparison
between Japan’s National Institute of Advanced Industrial Science and Technology (factor of 2 higher) and the Canadian Centre for Inland Waters (Environment Canada),
implying a systematic error, most likely by the Japanese group (Benskin et al., 2012).

Estimated fluxes of PFOA are 3 - 16 and 2 - 8 tons yr^-1 in the Norwegian and Labrador
Sea for surface concentrations of 10 - 50 ng m^-3. PFOA was not detected in the other two
deep water formation regions, the Ross and Weddell Seas (Yamashita et al., 2008). The
maximum contribution of these Southern Seas in transporting PFOA to deep water can be estimated by assuming ½ detection limit by Yamashita et al. (2008) (of 6 ng m\(^{-3}\)) as PFOA concentrations. This would give rather insignificant fluxes of at most 1 ton yr\(^{-1}\) for each Sea. The deep water formation fluxes are similar in importance to the estimated inflow of PFOA into the Arctic Sea of 2-12 t yr\(^{-1}\) (Prevedouros et al., 2006) or 8-23 t yr\(^{-1}\) (Stemmler and Lammel, 2010). Assuming that the increase of PFOA in the North Atlantic mirrored the PFOA emissions, we can extrapolate the total amount of PFOA moved to deep waters since their industrial production started in 1970. Total amounts moved by deep water formation are estimated to be 50 - 250 tons in the Norwegian Sea and 30 - 130 tons of PFOA in the Labrador Sea over the last 40 years. Thus, vertical eddy diffusion accounts for losses of PFOA to depth on the order of 660 t (range from 1 to 4800 t), while 80 – 360 tons have been lost from the surface oceans via deep water formation. Based on measured surface concentrations, we extrapolated the amount of PFOA residing in the top 100 m of the water column (Table 2). At most, there is a 10% decline of surface water concentrations to 100 m depth, no matter which E values we chose. This equates to approximately another 1100 tons PFOA stored in the upper 100m of the world’s Oceans: mostly in the North Atlantic and Pacific Ocean (around 600 and 300 t respectively), another 170 t in the South Atlantic), and 19 t in the Indian Ocean. Prevedouros et al. (2006) reported a total historical industrial production of PFOA of 3,200 – 7,300 tons. Here we assume the average of the reported range (i.e., 5,250 tons) as the most likely production volume. Our results imply that the global Oceans have removed around 13% of the PFOA produced to depth greater than 100 m via vertical diffusion, but with a large range due to uncertainty of eddy diffusivity measurements.
(range between 0.03 and 91% of global production). An additional 4% (1.5-6.8%) will have been removed via deep water formation. Lastly, the top 100 m of the surface oceans store another 21% of all PFOA produced (1120 t, Table 2).

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

4. Implications

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

Curiously, transport due to vertical eddy diffusion has never been considered before as a significant sink of POPs, probably due to the fact that most POPs are hydrophobic and their settling associated to organic carbon is faster. In any case, vertical diffusion is a
slow but persistent and ubiquitous sink that could also be important for other POPs, and it will be the main sink for the “swimmer” type of pollutants.

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

Acknowledgements

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References


Armitage, J.M., MacLeod, M., Cousins, I.T., 2009a. Comparative Assessment of the Global Fate and Transport Pathways of Long-Chain Perfluorocarboxylic Acids (PFCAs) and Perfluorocarboxylates (PFCs) Emitted from Direct Sources. Environmental Science & Technology 43, 5830-5836.

Armitage, J.M., MacLeod, M., Cousins, I.T., 2009b. Modeling the Global Fate and Transport of Perfluorooctanoic Acid (PFOA) and Perfluorooctanoate (PFO) Emitted from Direct Sources Using a Multispecies Mass Balance Model. Environmental Science & Technology 43, 1134-1140.


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.

<table>
<thead>
<tr>
<th>Ocean region</th>
<th>[PFOA] (pg/L)</th>
<th>$F_{ave,100}$ [ng m$^{-2}$ s$^{-1}$]</th>
<th>$F_{cum,100}$ [ng m$^2$]</th>
<th>$F_{ave,100}$ [ng m$^{-2}$ s$^{-1}$]</th>
<th>$F_{cum,100}$ [ng m$^2$]</th>
<th>$F_{ave,100}$ [ng m$^{-2}$ s$^{-1}$]</th>
<th>$F_{cum,100}$ [ng m$^2$]</th>
<th>$F_{ave,100}$ [ng m$^{-2}$ s$^{-1}$]</th>
<th>$F_{cum,100}$ [ng m$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-Atlantic, (45-60 °N)</td>
<td>260$^a$</td>
<td>-2.4$\times$10$^{-5}$</td>
<td>-1.5$\times$10$^4$</td>
<td>-1.6$\times$10$^4$</td>
<td>-11$\times$10$^4$</td>
<td>-1.4$\times$10$^{-7}$</td>
<td>-34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Atlantic, (30-45 °N)</td>
<td>21-250$^a$</td>
<td>-2.1$\times$10$^{-5}$</td>
<td>-1.4$\times$10$^4$</td>
<td>-1.4$\times$10$^4$</td>
<td>-10$\times$10$^4$</td>
<td>-1.3$\times$10$^{-7}$</td>
<td>-31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Atlantic, (15-30 °N)</td>
<td>24-210$^a$</td>
<td>-1.3$\times$10$^{-5}$</td>
<td>-8,600</td>
<td>-8.6$\times$10$^5$</td>
<td>-6.3$\times$10$^4$</td>
<td>-7.8$\times$10$^{-8}$</td>
<td>-19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Atlantic, (0-15 °N)</td>
<td>18-41$^a$</td>
<td>-5.2$\times$10$^{-6}$</td>
<td>-3,800</td>
<td>-3.4$\times$10$^5$</td>
<td>-2.7$\times$10$^4$</td>
<td>-3.1$\times$10$^{-8}$</td>
<td>-8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-Atlantic, (0-15 °S)</td>
<td>10-32$^a$</td>
<td>-3.9$\times$10$^{-6}$</td>
<td>-2,400</td>
<td>-2.5$\times$10$^5$</td>
<td>-1.7$\times$10$^4$</td>
<td>-2.3$\times$10$^{-8}$</td>
<td>-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-Atlantic, (15-30 °S)</td>
<td>5-27$^a$</td>
<td>-3.1$\times$10$^{-6}$</td>
<td>-2,000</td>
<td>-2.0$\times$10$^5$</td>
<td>-1.5$\times$10$^4$</td>
<td>-1.9$\times$10$^{-8}$</td>
<td>-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-Atlantic, (30-45 °S)</td>
<td>3-110$^b$</td>
<td>-4.3$\times$10$^{-6}$</td>
<td>-2,800</td>
<td>-2.8$\times$10$^5$</td>
<td>-2.0$\times$10$^4$</td>
<td>-2.5$\times$10$^{-8}$</td>
<td>-6</td>
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<td></td>
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<tr>
<td>S-Atlantic, (45-60 °S)</td>
<td>5-8$^a$</td>
<td>-5.6$\times$10$^{-7}$</td>
<td>-360</td>
<td>-3.6$\times$10$^6$</td>
<td>-2,600</td>
<td>-3.2$\times$10$^{-9}$</td>
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<tr>
<td>Pacific, (30 °S–60 °N)</td>
<td>5-50$^{bc}$</td>
<td>-2.4$\times$10$^{-6}$</td>
<td>-1,600</td>
<td>-1.6$\times$10$^5$</td>
<td>-1.1$\times$10$^4$</td>
<td>-1.4$\times$10$^{-8}$</td>
<td>-3</td>
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<tr>
<td>Indian, (30 °S–30 °N)</td>
<td>1-10$^c$</td>
<td>-4.8$\times$10$^{-7}$</td>
<td>-310</td>
<td>-3.1$\times$10$^5$</td>
<td>-2,300</td>
<td>-2.8$\times$10$^{-9}$</td>
<td>-1</td>
<td></td>
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</tr>
</tbody>
</table>

$^a$ (Benskin et al., 2012); $^b$ (Yamashita et al., 2008); $^c$ (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

<table>
<thead>
<tr>
<th>Ocean basins</th>
<th>Surface area ($10^6$ km$^2$)</th>
<th>Amount PFOA removed by turbulence from top 100 m (tons)</th>
<th>deep water formation (tons)</th>
<th>Amount of PFOA stored in the top 100 m (tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>average E values</td>
<td>lower range E values</td>
<td>upper range E values</td>
</tr>
<tr>
<td>Norwegian Sea</td>
<td>4.0</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Labrador Sea</td>
<td>2.7</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>N-Atlantic, 45 N – 60 N</td>
<td>8</td>
<td>124</td>
<td>0.3</td>
<td>904</td>
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<tr>
<td>N-Atlantic, 30 N – 45 N</td>
<td>10</td>
<td>139</td>
<td>0.3</td>
<td>1006</td>
</tr>
<tr>
<td>N-Atlantic, 15 N – 30 N</td>
<td>11</td>
<td>95</td>
<td>0.2</td>
<td>690</td>
</tr>
<tr>
<td>N-Atlantic, 0 N - 15 N</td>
<td>9</td>
<td>34</td>
<td>0.1</td>
<td>247</td>
</tr>
<tr>
<td>S-Atlantic, 0 N - 15 S</td>
<td>9</td>
<td>21</td>
<td>0.0</td>
<td>154</td>
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<tr>
<td>S-Atlantic, 15 S - 30 S</td>
<td>11</td>
<td>22</td>
<td>0.0</td>
<td>163</td>
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<tr>
<td>S-Atlantic, 30 S - 45 S</td>
<td>10</td>
<td>28</td>
<td>0.1</td>
<td>202</td>
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<tr>
<td>S-Atlantic, 45 S - 60 S</td>
<td>8</td>
<td>3</td>
<td>0.0</td>
<td>21</td>
</tr>
<tr>
<td>Pacific, 30 S - 60 N</td>
<td>120</td>
<td>186</td>
<td>0.4</td>
<td>1352</td>
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<tr>
<td>Indian, 30 S – 30 N</td>
<td>35</td>
<td>11</td>
<td>0.0</td>
<td>79</td>
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<tr>
<td><strong>Total</strong> (range)</td>
<td></td>
<td><strong>664</strong></td>
<td><strong>1.5</strong></td>
<td><strong>4818</strong></td>
</tr>
</tbody>
</table>
Figure captions

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

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).