

# Aerosol Enrichment of the Surfactant PFO and Mediation of the Water–Air Transport of Gaseous PFOA

COLIN J. MCMURDO,<sup>†,‡</sup>  
DAVID A. ELLIS,<sup>\*,†,‡</sup> EVA WEBSTER,<sup>‡</sup>  
JESSICA BUTLER,<sup>†</sup>  
REBECCA D. CHRISTENSEN,<sup>‡,§</sup> AND  
LIISA K. REID<sup>‡</sup>

Department of Chemistry, Canadian Environmental Modelling Centre, and Department of Mathematics, Trent University, 1600 West Bank Drive, Peterborough, Ontario, K9J 7B8 Canada

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Aerosol-mediated transport of perfluorooctanoate (PFO) from a water body to the atmosphere and the subsequent emission of gas-phase perfluorooctanoic acid (PFOA) was investigated. The potential for this process to facilitate long-range transport of PFOA/PFO was assessed. In a laboratory experiment, aerosols were generated and collected from deionized, fresh, and ocean waters spiked with PFO and analyzed by LC-MS/MS. Gas-phase samples were also collected from the system and analyzed for PFOA. Aerosols were found to have significantly higher concentrations of PFO than the parent water body ( $\leq 80$  times for ocean waters). The PFOA, at equilibrium with the PFO in the aqueous aerosol, partitioned rapidly ( $t_{1/2} = 7.2$  s) out of the aerosol droplet. This suggests that rainout rates are likely to be longer than previously hypothesized. These results imply that water bodies are not a permanent sink for atmospheric PFOA as previous studies have suggested. The occurrence of contamination in remote regions may not depend solely on the previously hypothesized indirect sources but also on the long-range transport, via the gas phase, of direct releases of PFOA to both the aquatic and atmospheric environments.

## Introduction

Perfluorooctanoate (PFO) belongs to a class of chemicals known as perfluorinated carboxylates (PFCs). PFCs have widespread use in the manufacture of a variety of industrial and commercial products, including fluoropolymers, fire-fighting foams, and water- and oil-proof fabrics (1). In aqueous systems, PFOA is at equilibrium with its conjugate base, PFO, perfluorooctanoate. Here we use the acronym PFO(A) to refer to the conjugate pair or in cases where it may be either.

PFO is resilient to metabolic degradation (2, 3), has been identified globally as a ubiquitous contaminant of human blood (4), and has been observed in wildlife across the

northern hemisphere, including remote regions such as the Arctic (5–7). PFO is found in atmospheric particulate (8, 9), rainwater (10), fresh water (11), ocean water (12), and sediments (13) from a variety of geographical locations. It has been hypothesized that the parent carboxylate cannot be responsible for this observed widespread dissemination due to its inherent physical properties (14). This has led researchers to investigate indirect atmospheric precursor sources such as fluorotelomer alcohols which have the potential for tropospheric long-range transport and subsequent degradation to gaseous PFOA (15–17). Direct emissions of PFOA occur as a result of fluoropolymer manufacturing. When the total contributions of indirect and direct sources of PFO were evaluated, it was found that the vast majority of known historical PFO emissions have occurred via direct sources (18–20). As indirect sources account for only a fraction of the emissions of PFO to the environment it seems unlikely that indirect sources alone could account for the entire mass of PFO observed in arctic fauna as hypothesized (20, 21).

It is important to highlight the often overlooked distinction between the acid, PFOA, and its conjugate base, PFO. Historically, analysis of PFOA in environmental samples has been limited to its dissociated conjugate base PFO, and often incorrectly described as PFOA. If the acid and its conjugate base had similar physical and chemical properties this would be of little importance. However, that is not the case. The most significant differences in the physical properties of PFOA and PFO are a result of the influence of the carboxylic acid and carboxylate functional groups. The aqueous solubility of the carboxylate functional group renders PFO reasonably water soluble ( $\sim 3.4$  g/L (3)) while the carboxylic acid functional group results in a water solubility for PFOA 5 orders of magnitude lower,  $\sim 26$   $\mu$ g/L. PFO is considered to have a negligible vapor pressure,  $V_p$ , and air–water partition coefficient,  $K_{AW}$ , while PFOA has a  $V_p$  of 2.2 Pa (22) and an appreciable  $K_{AW}$  of  $\geq 1.02 \times 10^{-3}$  (23). The hydrophobic and hydrophilic nature of the PFO anion constituents results in amphiphilic properties, imparting high surface activity (1). PFO is an excellent surfactant capable of lowering the surface tension of water to 15–20 mN m<sup>-1</sup> which is far below values achievable with analogous hydrocarbon surfactants (24). Thus, when scavenged by water bodies, PFO will preferentially adsorb to the water surface. In contrast, PFOA is not a surfactant as in the neutral form the acid functional group and the perfluorinated tail are both hydrophobic.

It has been suggested that atmospherically derived gas-phase PFOA will be rapidly rained out (25) with bodies of water acting as a permanent sink for PFO (14). However, using a calculated Henry's Law Constant,  $K_{th}$ , of 6.5 Pa m<sup>3</sup> mol<sup>-1</sup> (26), similar to the measured value of 2.5 Pa m (33) mol<sup>-1</sup> (23), Hurley et al. hypothesize that the rainout rate might be on the order of centuries, with wet and dry deposition being predominantly particle-mediated (26). Barton et al. hypothesize a much faster rainout rate (27). The potential for the direct transport of PFO in the environment by transport by surface waters and ocean currents has been investigated (18, 19, 28). Atmospheric transport of gaseous PFOA has been almost entirely ignored, although it has been recently suggested that direct transport of gas-phase PFOA warrants further examination (18) due to the observation of PFOA adsorbed to atmospheric particles (8, 9). The potential for atmospheric transport of PFO via marine aerosols was considered but discounted (17, 18).

The differences in composition of marine aerosols and ocean water are well documented. Marine aerosol droplets

\* Corresponding author e-mail: davidellis@trentu.ca; tel: (705) 748 1011; fax: (705) 748 1625.

<sup>†</sup> Department of Chemistry.

<sup>‡</sup> Canadian Environmental Modelling Centre.

<sup>§</sup> Department of Mathematics.

are enriched with inorganic and organic material (29, 30), particulate organic matter (31), bacteria (32), and an array of organic pollutants (33–36) especially surfactants (37) and “surfactant organic matter” (38). It has been suggested that a “surface wave concentration effect” is responsible for concentrating surfactants at the surface (38). Adsorption of surfactants at the air–water interface increases during rough conditions when wave action generates aerosols and serves as a “surfactant pumping system” (38). Rough sea conditions can increase surface concentrations of surfactants by orders of magnitude, and these surface concentrations are orders of magnitude greater than the concentrations at depth (38).

Since PFO is a surfactant, enrichment in aerosols was expected in the investigation of their formation from deionized (DI), fresh, and ocean water. Furthermore, post-aerosol generation experimental design allowed the examination of the air–water droplet partitioning typical of a cloud prior to a rainout event. Experimental observations are explained within the context of conclusions drawn from previous studies, and some important implications toward environmental dissemination mechanisms and the long-range transport (LRT) potential of PFOA are discussed.

## Experimental Section

**Standards, Reagents, and Samples.** Perfluorooctanoic acid (96%), ammonium acetate (>98%), and potassium hydroxide (>85%) were purchased from Sigma-Aldrich (Oakville, ON, Canada). HPLC-grade methanol and acetonitrile were purchased from Fisher Scientific (Ottawa, ON). All reagents and solvents were used as received without further purification. Milli-Q water was used for all analytical applications. Sample location and storage details for the river, lake, and ocean waters are given in the Supporting Information.

**Apparatus.** A bulk chamber was assembled using an 18 L polycarbonate container with an air inlet and outlet in the top of the chamber. The bulk chamber contained 6 L of water spiked with PFO(A) and stirred continuously. A piezoelectric crystal ultrasonic aerosol generating device (Manchester Products, Cambridge, ON) operating at ~50 KHz was used to generate fine aerosol droplets (~50  $\mu\text{m}$ ) as in previous reports (39, 40). The aerosol generator was centrally suspended in the bulk chamber below the water surface. A collection vessel and aerosol breakthrough vessel were connected in series to the bulk chamber, as shown in Figure S1 of the Supporting Information, using vacuum tubing with a vacuum flow rate of 50–100 mL/min. The vessels were cooled in ice baths to condense the aerosols from the air stream.

The pHs of the bulk waters were recorded at the beginning and end of each experiment. Samples of the initial and final bulk water were taken in triplicate, and the bulk water was sampled throughout each experiment. The bulk water temperature, air temperature, and relative humidity were recorded. The condensed aerosols were collected over a 1-h period except where noted.

**Detection.** Three separate methods were used to detect the presence of gas-phase PFOA. Gas-phase PFOA was trapped and collected using KOH solutions and XAD resin tubes using three techniques. In the first two techniques aqueous alkaline and XAD resin traps were placed in-line after the aerosol collection vessel and after the aerosol breakthrough vessel. The third method employed a water condenser to ensure the condensation of all aerosols back to the bulk solution. Two aerosol breakthrough collection vessels were connected in series following the condenser, and subsequent to these a series of inline XAD tubes were connected. Details of the methods used can be found in the Supporting Information.

Liquid chromatography–mass spectrometric analyses were conducted using a Micromass Quattro triple quadrupole

**TABLE 1. Enrichment of PFO in Condensed Aerosols**

water type	initial spiked [PFO] (ppb)	initial pH	final pH	mean aerosol enrichment factor
DI water	255	5.72	5.71	5.6
lake water	797	8.22	8.45	8.1
river water	447	8.42	8.31	11.5
filtered river water	387	6.19	6.28	4.4
ocean water	205	7.48	7.86	55.7

mass spectrometer (Micromass; Manchester, UK) using conditions similar to those of Moody et al. (41).

**Experimental Scenarios.** For each scenario, the bulk water was spiked with PFO(A). Since some depletion of PFO from the bulk water was expected even in the absence of aerosol generation, a control experiment using DI and no aerosol generation was performed to provide a baseline to investigate the effect of aerosol generation. The bulk solution was stirred and samples of the bulk water were collected every hour for 12 h.

The effect of removal of the aerosols from the system on the concentration of PFO in the bulk DI water was examined in a second control experiment with the system completely sealed and no removal of aerosol.

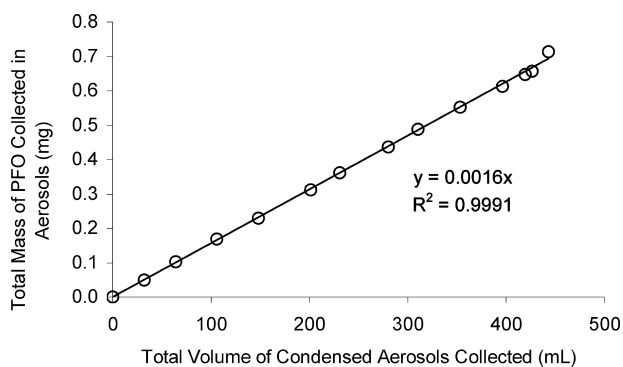
To investigate the behavior of PFO in the aerosol droplets, rather than removing the aerosols continuously as they were generated, aerosols were allowed to collect and remain in the headspace for various periods of time. The effect of these residence times on the PFO concentration in the aerosol droplets was examined.

## Results and Discussion

**Aerosol Enrichment.** It was hypothesized that aerosol droplets generated from a water body containing PFO would be enriched with the surfactant. Over 14 h of aerosol generation from DI water spiked with PFO to an initial concentration of  $255 \pm 4.45 \mu\text{g/L}$  the mean concentration of PFO in the aerosol was  $1540 \pm 112.49 \mu\text{g/L}$ , i.e., an average enrichment factor of  $5.6 \pm 0.64$ . The average rate of loss of PFO from the bulk water was 1.1% per hour during the first 14 h of aerosol generation. The corresponding rate of accumulation of PFO in the condensed aerosol was 0.5% per hour. Identical 14 h experiments with river, lake, and ocean waters showed significant enrichment in PFO for all water types as summarized in Table 1. The volume of water in the system remained constant, ruling out enhancement due to droplet evaporation. The experiment conducted with DI water was repeated at a concentration of 20 ppb and showed a similar enrichment ratio. This suggests that at environmentally relevant concentrations similar relative concentrations would be expected.

Control experiments tested the effects of atmospheric temperature (18.7–22.6 °C), water temperature (20–30 °C), relative humidity (83.3–99.9%), and aerosol generation efficiency. These factors had no significant effect on PFO enrichment in the aerosols.

The concentration of PFO in each bulk water sample and in the aerosol was effectively constant over the 14 h duration of each experiment (Figure 1). Figure 1 factors out changes in aerosol volume production efficiency with time to show the total mass collected as a function of total volume of aerosols collected. Clearly the enrichment in the aerosols remained constant over time. After 14 h the concentration in the bulk had depleted sufficiently such that it could no longer support this constant enrichment. (Figure S2 in the Supporting Information shows the relative concentrations of PFO in condensed aerosols and bulk water for DI and river waters).



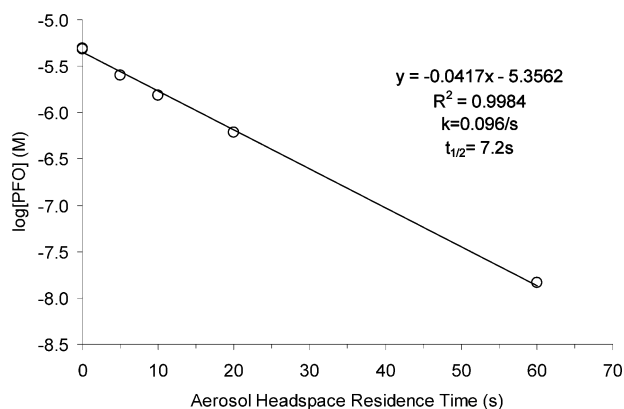
**FIGURE 1.** Plot of the total mass of PFO collected in aerosols as a function of the total volume of condensed aerosols collected for the initial 13 h of the experiment.

The volume of the bulk water was so much greater than the volume of condensed aerosol collected that, although the concentration in the aerosols was much higher, the amount of PFO in the aerosols had a negligible effect on the concentration in the bulk water. Therefore, these experiments can be translated to realistic environmental conditions where the bulk water may be considered infinitely large (e.g., oceans, waterfalls, weirs) and hence, aqueous field measurements of PFO in bulk water would not show a significant decrease due to aerosol formation despite a net flux to the air.

The aerosol surface-area-to-volume ratio is hypothesized to have a controlling influence on the degree of enrichment. The higher enrichment seen in the river and lake water may be due to the presence of particulate matter and dissolved organic carbon. This would be consistent with, for example, the observations of Higgins et al. (42) and Alzaga et al. (43). The higher enrichment in the ocean water is hypothesized to be due to the salt content of the water. The higher ionic strength of ocean water is expected to cause an increase in the hydrophobicity of the hydrophobic moiety of the PFO anion thus enriching the surface microlayer. Metal counterions may also have an effect.

**Aerosol-Catalyzed Formation of Gas-Phase PFOA.** Aerosol generation was not the only mechanism for PFO loss from the bulk water. When aerosols were not generated in the system PFO was lost from the bulk water at a rate of 0.4% per hour. A similar observation was reported by Kaiser et al. (44) who hypothesized that undissociated acid was being lost to the air in the container headspace. This loss may also be to the container walls. When aerosols were generated and allowed to recondense to the bulk (i.e., not removed from the headspace) PFO was lost from the bulk water at a rate of 0.8% per hour of aerosol generation; twice the rate of the no-generation experiment and despite the high humidity (~92%) in the chamber headspace. These experiments suggest that aerosol generation causes loss of PFO from the bulk aqueous phase by a secondary process that pertains to the aerosol. This could be indicative of the formation of gas-phase PFOA from the aerosol. Gas-phase PFOA was indeed detected by all techniques employed. The absence of water from aerosol breakthrough traps indicated the effective collection of gas-phase material. A quantitative determination of gas-phase PFOA would not have been meaningful as PFOA was adsorbed to all surfaces between generation and collection vessels. Qualitatively, these experiments support the hypothesis that aerosol generation acts as a catalyst, or intermediary, for the production of gas-phase PFOA.

To assess the residence time of PFO in the aerosol droplets in this process, aerosols were produced from filtered river water and allowed to remain in the bulk chamber headspace for various periods of time prior to collection. Figure 2 shows the concentration of PFO in samples of condensed aerosol



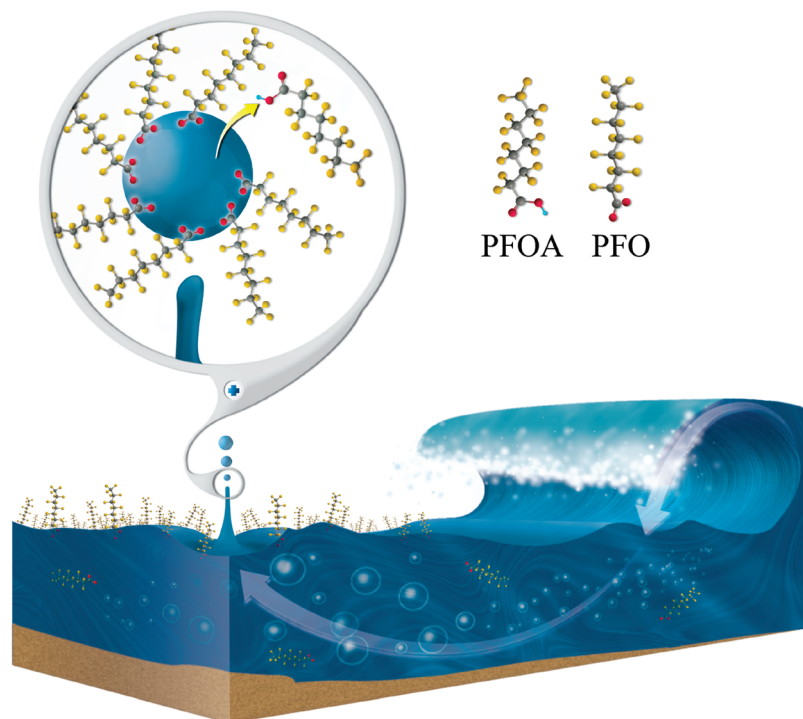
**FIGURE 2.** There is a strong exponential correlation between the concentration of PFO in the water droplets and the residence time ( $R^2 = 0.9984$ ), with a pseudo-first-order rate constant of 0.096/s and intermediary (aerosol-gas-phase) transport half-life of PFO of 7.2 s.

as a function of aerosol residence time in the headspace. A pseudo-first-order rate constant of 0.096/s (half-life 7.2 s) was determined, indicating that aerosol generation is a very efficient mechanism by which PFO present in a water body can be transferred to the atmosphere as gas-phase PFOA. The exponential form of the relationship suggests a net transfer of PFO out of the water droplets until an equilibrium condition is reached at some time greater than 60 s. Clearly, since PFO would not be present in significant quantities in air, the water droplets are acting as a net source of PFOA to the air and are not efficiently scavenging PFOA back from the air, as had been previously postulated (25).

The scavenging efficiency of water droplets in the experimental system was examined using a mathematical model (described in the Supporting Information). In this model the half-life of PFO in the bulk water was calculated as a function of the rates of aerosol generation, aerosol condensation, and net loss of PFO from the aerosol, and included the loss from the bulk water in the absence of aerosol production. By using a net loss value from the aerosol, any repartitioning back to the aerosol was included, thus effectively mimicking rainout potential within a cloud. The closed experimental system in which the parameters were identical to those in the model resulted in a measured half-life of PFO of  $60 \pm 13$  h while the model gave a value of 52 h. These results strongly suggest that there is a net flux of PFOA from water to air due to the formation of aerosols. They also suggest that a direct emission of gas-phase PFOA from the water due to bubble formation, a process that occurs in the formation of aerosols (Figure 3), is minimal. In the environment the atmospheric PFOA may partition to particulate matter, and not be efficiently scavenged directly by rain events except as sorbed to particles. Indeed, recent monitoring data have also led to the conclusion that there is a net flux of PFOA from bodies of water (45). Worthy of note is the fact that in a recent paper, Goss suggested that the  $pK_a$  of PFOA is  $-0.5$  (46). This experimental measurement of gas-phase PFOA being produced from a body of water indicates that this suggested value is most likely erroneous.

**Aerosol Enrichment in the Environment.** Enrichment of the sea-surface microlayer and atmospheric aerosols in surfactant materials has been well characterized (47–49). Preferential adsorption of surfactants at the air–water interface occurs as a result of the amphiphilic properties of the chemical, with the water-soluble moiety submerged in the water and the hydrophobic component suspended in the air (47–49). As PFO is an efficient surfactant species (1), it is logical to assume that it would behave similarly to other surfactant species in the environment. Indeed, Kaiser et al.





**FIGURE 3.** The action of a wave breaking causes air bubbles to be formed under the water surface. The bubbles burst and eject aerosol droplets with surface-concentrated PFO into the atmosphere. On the droplet surface PFO becomes protonated to form PFOA which is then released to the atmosphere as indicated by the yellow arrow. There is a net flux of PFOA to the air from a body of water due to this process.

observed that surface foam created by bubbling air through an aqueous solution was enriched in PFO by up to 3.2 times (44).

In the environment the mechanism of aerosol production occurs in two stages: the action of breaking waves produces air bubbles beneath the water's surface, and then, at the surface the trapped air bubbles burst and eject aerosol droplets into the atmosphere (38, 49) (Figure 3). Since these droplets are formed from the surface and immediate subsurface water layers that are enriched in surfactant species, PFO, the aerosols emitted to the atmosphere are also enriched with PFO. Based on the known action of surfactants the highest concentration of PFO would be expected on the surface of the aerosol droplet with the water soluble moiety adsorbed to the surface of the water droplet and the hydrophobic component protruding into the atmosphere. The magnitude of enrichment observed should therefore be dependent upon the surface-area-to-volume ratio of the droplet.

**Environmental Implications and Supporting Observations.** Atmospheric aerosols of 0.05–2  $\mu\text{m}$  with residence times on the order of 10 days are known to be transported over hundreds or even thousands of kilometers by atmospheric processes (50), thus the mechanism of aerosol enrichment alone presents significant potential for long-range transport (LRT) of PFO to remote locations. However, the very short observed aerosol-to-gas phase transfer half-life of  $\sim 7$  s suggests that the PFO will not be transported directly by the water droplets. The evolution of gas-phase PFOA from the aerosol-bound PFO significantly increases the potential for LRT, and hence it is the neutral acid in the gas phase that might be expected to be transported over long distances.

In a recent study, PFO was identified in snow from a high Arctic ice cap, indicating an atmospheric source of the chemical. Due to inconsistencies in sodium and PFO correlations, the contribution of PFO from marine aerosols was discounted (17). With three modes of transport of PFOA

to the Arctic, i.e., gas phase, aerosols, and indirect input, contributing to Arctic concentrations, the absence of a correlation between sodium and PFO would be expected. Hence, a contribution to the overall burden in the arctic due to aerosols, in addition to other sources, cannot be ruled out.

While it has been commonly accepted that ocean waters and sediments are a primary sink for PFOA (2, 3, 14, 18, 25, 51), the observed potential for re-emission indicates that the world's oceans and other water bodies may serve as a source of PFOA to the atmosphere and, furthermore, direct wet deposition rates previously used (25) to estimate the PFOA potential for atmospheric LRT may require reconsideration. The ng/L concentration of PFO measured in North American precipitation (10) is proposed to be most likely due to adsorption to particulate matter (25, 26) as has been observed in the marine atmosphere (9), Canadian Arctic air (16), ambient air near a fluoropolymer manufacturing facility (8), and indoor dust (52, 53) followed by indirect rainout events as suggested by Hurley et al. (26).

PFO is found in the environment both as its predominant linear isomer and as branched isomers (15, 54, 55). The linear and branched isomers have differing physical and partitioning properties, as evidenced in the fact that their derivatives can be separated using gas chromatography (GC) (15, 54, 55). Furthermore, branching the chain of a fluorinated surfactant leads to a change in the surface activity of the chemical due to differential molecular packing and carbon chain adlineation (56). Due to this difference, the ratio of linear isomer to branched would be greater in environmental surface microlayers; a difference that is expected to be mirrored in the resultant aerosol droplets and the bulk water from which they originate. Upon partitioning from aerosol droplets to the gas phase as PFOA, isomeric separation will occur again based on the differing Henry's Law constant ( $K_h$ ) and the  $pK_a$  of the isomers. Hence, there should be a strong difference in the transfer of the isomers to the atmospheric gas phase from an aerosol droplet. The branched isomers will tend to

partition less to the gas phase than the linear giving them a greater potential to return with the aerosol to the bulk water. Thus the processes of aerosol production and subsequent partitioning of PFOA to the gas phase act as a very effective filtering system for the branched isomers.

One industrial process for the production of PFOA that is partially responsible for the observed environmental contamination is electrochemical fluorination. This process yields ratios of ~78:22 linear to branched isomers (54). Aerosol-mediated atmospheric transport is expected to result in a greater linear/branched ratio. This trend should also be observed as a function of distance from the major sources of direct emission, the Eastern seaboard of the United States (18), i.e., remote regions should have a lower concentration of branched isomers. The relative ratio of linear to branched isomer has been observed to be 95:5 in Greenland polar bears and exclusively linear isomers in Canadian Arctic polar bears (54). While it is recognized that there is likely an important toxicokinetic component to the observed discrimination of the isomers the difference between geographically varied polar bears sampled also suggests an additional physical discrimination factor within the input of the PFOA. Based on prevailing wind patterns and the relative distance from sources, these results are expected.

In summary, it appears that aqueous media are not a permanent sink for PFO and may, in fact, act as an atmospheric source of gas-phase PFOA via aerosol formation. Furthermore, it appears from this study that wet deposition does not occur with the efficiency previously predicted, and hence PFOA may indeed have the potential to undergo LRT. A more complete re-evaluation of the potential for LRT using the measured physical properties of PFOA is warranted, although it is currently outside the scope of this publication. There is sufficient evidence to indicate that neutral PFOA is, at least in part, responsible for the burden of PFO and PFOA in remote regions.

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## Supporting Information Available

Experimental details, aerosol-mediated removal model, and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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