doi.org/10.26434/chemrxiv.7326716.v1

Global Transport of Perfluoroalkyl Acids via Sea Spray Aerosol

Jana Johansson, Matthew Salter, Juan Acosta Navarro, Caroline Leck, E. Douglas Nilsson, Ian T. Cousins

Submitted date: 12/11/2018 • Posted date: 13/11/2018

Citation information: Johansson, Jana; Salter, Matthew; Acosta Navarro, Juan; Leck, Caroline; Nilsson, E. Douglas; Cousins, Ian T. (2018): Global Transport of Perfluoroalkyl Acids via Sea Spray Aerosol. ChemRxiv. Preprint.

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GLOBAL TRANSPORT OF PERFLUOROALKYL ACIDS VIA SEA SPRAY AEROSOL

A PREPRINT

J. H. Johansson,[*a‡] **M. E. Salter,**[ab‡] **J-C. A. Navarro,**[ab] **C. Leck,**[cb] **E. D. Nilsson,**[ab] **and I. T. Cousins**[a]

November 12, 2018

ABSTRACT

Perfluoroalkyl acids (PFAAs) are persistent organic pollutants found throughout the world's oceans. Previous research suggests that long-range atmospheric transport of these substances may be substantial. However, it remains unclear what the main sources of PFAAs to the atmosphere are. We have used a laboratory sea spray chamber to study water-to-air transfer of 11 PFAAs via sea spray aerosol (SSA). We observed significant enrichment of all PFAAs relative to sodium in the SSA generated. The highest enrichment was observed in aerosols with aerodynamic diameter $< 1.6\,\mu$m, which had aerosol PFAA concentrations up to ~ 62000 times higher than the PFAA water concentrations in the chamber. In surface microlayer samples collected from the sea spray chamber, the enrichment of the substances investigated was orders of magnitude smaller than the enrichment observed in the aerosols. In experiments with mixtures of structural isomers, a lower contribution of branched PFAA isomers was observed in the SML in relation to the bulk water. However, no clear trend was observed for the comparison of structural isomers in SSA and bulk water. Using the measured enrichment factors of perfluoroctanoic acid and perfluorooctance sulfonic acid versus sodium we have estimated global annual emissions of these substances to the atmosphere via SSA as well as their global annual deposition to land areas. Our experiments suggest that SSA may currently be an important source of these substances to the atmosphere and, over certain areas where SSA deposition is important, a significant source to terrestrial environments.

Introduction

Perfluoroalkyl acids (PFAAs) are a class of anthropogenic surfactants which have been manufactured since the 1950s[1;2;3]. These substances are made up of a fully fluorinated carbon chain linked to an acid group[2]. The perfluorinated carbon chain provides oleophobic and hydrophobic properties, as well as high stability[4]. These properties make PFAAs valuable performance chemicals on which many industry sectors rely. Examples of their applications include use as surfactants in firefighting foams[5;3;1] and as processing aids in the production of fluoropolymers[1]. Recent estimates of the cumulative global emissions of PFAAs are at least 46000 tonnes with a large fraction of this release directly to environmental waters[5;1]. As a result, PFAAs are present in rivers downstream of manufacturing facilities[6] and throughout the world's oceans[7;8;9;10;11;12;13].

PFAAs have been observed in both humans and biota worldwide[14;15;16;17]. Particular concern has been raised regarding perfluoroalkane sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs), as these substance classes include compounds identified as persistent[18], bioaccumulative[19] and toxic[20]. A number of PFAAs are subject to regulation under REACH[21] and perfluorooctance sulfonic acid (PFOS) is listed under the Stockholm Convention[22].

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[a] *Department of Environmental Science and Analytical Chemistry, Stockholm University, 11418 Stockholm, Sweden; E-mail: jana.johansson@aces.su.se*

[b] *Bolin Centre for Climate Research, 11418 Stockholm, Sweden*

[c] *Department of Meteorology, Stockholm University, 11418 Stockholm, Sweden*

‡ These authors contributed equally to this work.

Observations of PFAAs in air[23;24;25;26;27] and precipitation[23;28;29;30;31;32], as well as remote inland environments[33;34;35;36], suggest that long-range atmospheric transport may be substantial. Several pathways have been proposed to explain the origin of PFAAs observed in air and precipitation, including direct releases of PFAAs to air from manufacturing sources[37;38] and atmospheric formation of PFAAs through the degradation of volatile precursor substances[39;40;41;42;43]. Although water-to-air transfer of PFAAs from the global oceans via sea spray aerosols (SSA) has previously been discussed in the scientific literature[44;45;46], the magnitude of this pathway at the global scale has not been properly quantified. Further, since PFAAs are predominantly present in the oceans in their involatile and highly water soluble anionic form[47;48;49;50], efficient transport of these substances to the atmosphere via volatilization is considered unlikely. As such, it is assumed that PFAAs that enter the global surface oceans will remain there until they are ultimately transported into the deep oceans.[51;52;53].

Sea spray aerosols are droplets of seawater that are ejected into the atmosphere when bubbles burst on the ocean surface. The bubbles responsible are mainly formed when air is entrained into the ocean by breaking waves which result from the interaction of wind with the ocean surface. As such, the key meteorological factor governing the production of SSA is the wind speed[54;55]. The formation of SSA by bubble bursting is thought to take place via two different mechanisms. First, the film cap of each bubble fragments into numerous so-called film droplets. This type of droplet is thought to make up the majority of SSA smaller than 1 μm in diameter[56;57]. The cavity created as the film cap bursts then collapses, forming a jet of water. This water jet subsequently disintegrates into a small number of so-called jet droplets[58;59] which are large in comparison to the film droplets and are thought to comprise the majority of SSA larger than 1 μm diameter[57].

Sea spray aerosols consist of a complex mixture of sea salt and organic matter[60;61;62;63]. Bubbles are thought to scavenge surface-active organic matter as they travel through the bulk ocean[64] and the air-sea interface[65]. Previous studies have consistently shown that the organic mass fraction of SSA increases with decreasing particle size[66;67;68;69;63;70;71]. Critically, formation of both smaller film droplets and larger jet droplets is known to be sensitive to bubble size[72]. As such, it is an essential requirement of any laboratory system that is designed to produce nascent SSA with relevant physical and chemical characteristics that it reproduces the numbers and sizes of bubbles entrained by breaking waves in the open ocean[73].

Previous studies have demonstrated strong enrichment of PFAAs in laboratory generated aerosols relative to their bulk water concentration[45;44;74] using a number of different methods to produce bubbles. McMurdo *et al.*[45] utilised a piezoelectric crystal ultrasonic aerosol generating device to generate aerosols much larger ($\sim 50\,\mu$m) than those typically produced over the ocean ($< 10\,\mu$m). Although, the underlying mechanism of droplet formation by ultrasonic nebulisation is not fully understood[75], it is clear that this process is very different to the process of air entrainment in the open ocean and any bubbles present will be very different in size to those found under oceanic breaking waves. A further limitation of the McMurdo *et al.*[45] study is that aerosol enrichment factors were only derived for one PFAA, namely perfluorooctanoic acid (PFOA). Reth *et al.*[44] investigated aerosols produced via bubble bursting following air entrainment using a plunging jet, a technique that is considered more reflective of the process of nascent SSA generation[76] and extended the target substances to a range of PFCAs and PFSAs. Unfortunately, although these experiments were useful in revealing that PFAA-enrichment on aerosols is dependent on the perfluoroalkyl chain length, they were performed using tap water, which is likely to produce bubble-bursting aerosols that are very different, both in size and chemical composition, to aerosols produced by bubbles bursting in seawater. Furthermore, the production of SSA is strongly influenced by seawater salinity[77;78;79;80]. Ebersbach *et al.*[74] generated aerosols from wastewater by entraining air using a diffuser/frit. Experiments using such an approach are non-ideal in that the bubble sizes generated depend on the exact frit used and do not reproduce the bubble size distributions found under oceanic breaking waves. In summary, none of the previous studies produced data that enabled quantification of the environmental relevance of the water to air transport pathway of PFAAs via SSA at the global scale - that is size-resolved aerosol enrichment factors relative to a SSA tracer compound included in global circulation models such as sodium (Na^+).

Our study improves upon these initial laboratory experiments by using artificial seawater in a sea spray simulation chamber which produces a bubble size distribution similar to that found in breaking waves[81]. Size-resolved samples of the produced aerosols are obtained through the use of a low pressure impactor (LPI) connected downstream of the sea spray chamber. Sampling the aerosols in this way enabled us to determine i) whether PFAAs are enriched in SSA under conditions which accurately reflect the process of SSA formation; ii) whether PFAAs aerosolized as SSA have a size that facilitates long-range atmospheric transport. Another important advance over previous studies is the coincident measurement of Na^+, an important tracer of SSA, which enabled the generation of aerosol enrichment factors and subsequent estimation of the magnitude of SSA-mediated ocean-to-atmosphere transfer of PFAAs using a global circulation model. Due to a lack field data for model parameterization, model output is only generated for the two most well-studied substances, PFOA and perfluorooctane sulfonic acid (PFOS). Further experiments were performed to study the enrichment of structural PFAA isomers, as patterns of these are interesting for source elucidation of PFAAs in the atmosphere.

Materials and methods

In the following, the methods are described in brief. Full details of the sampling, extraction and instrumental analysis can be found in the Electronic Supplementary Material (ESI).

Sea spray simulation chamber

All experiments were performed using a sea spray generator developed by Salter *et al.*[81]. Here, nascent SSA was generated in the laboratory using a plunging jet (Fig. S1). Using this setup, artificial seawater was circulated continuously at 1.7 $\mathrm{L\,min^{-1}}$ from the bottom of a chamber, 47 cm in diameter and 100 cm high, through a stainless steel nozzle with an inner diameter of 4.3 mm held in a vertical position 30 cm above the air-water interface. Within this chamber the seawater was filled to a depth of 60 cm leaving a headspace of 40 cm (100 L seawater). Dry particle-free sweep-air entered the chamber at 32 $\mathrm{L\,min^{-1}}$ after passing through an ultrafilter (Type H cartridge, MSA) and an activated carbon filter (Ultrafilter, AG-AK).

Experiments

Two experiments were conducted using artificial seawater solution spiked with native target compounds. Experiment A was performed with a mix of linear compounds: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTriDA), perfluorotetradecanoic acid (PFTeDA), perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), PFOS and perfluorodecane sulfonic acid (PFDS). For experiment B the seawater was spiked with technical standards of PFOA, PFHxS and PFOS (TPFOA, brPFHxS and TPFOS). The technical standards are characterized mixtures of branched and linear isomers. The nominal concentration of each substance was approximately 10 $\mathrm{ng\,l^{-1}}$ in experiment A. In experiment B the bulk water was spiked to 52, 45 and 49 $\mathrm{ng\,l^{-1}}$ with TPFOA, brPFHxS and TPFOS respectively. The experiments were intitiated following 1 hour of system equilibration with the plunging jet switched on. Aerosol was then sampled for approximately 6 hours. Each experiment was replicated three times. The seawater was not changed between each replicate run but the concentration of PFAAs in the seawater was monitored over the period of the three replicates.

Aerosol sampling

To determine the mass of $\mathrm{Na^+}$ and PFCAs and PFSAs in particles generated using the sea spray chamber we used a 13-stage (30 $\mathrm{L\,min^{-1}}$) low pressure impactor (LPI, Dekati). Immediately upstream of the impactor the relative humidity (RH) was measured using a Vaisala model HMT333 probe. During all measurements, the sample flow to the LPI as well as the LPI itself were heated by placing a heating jacket around the sample line and the LPI. This ensured that the relative humidity at the inlet of the LPI was always below $\sim 40\,\%$ (see Tab. S1). The LPI had 50 % cut-off diameters of: 0.029, 0.060, 0.104, 0.165, 0.253, 0.391, 0.634, 0.990, 1.60, 2.45, 3.96, 6.57, and 10.16 μm aerodynamic diameter. No back-up filter was used to sample particles smaller than 0.029 μm aerodynamic diameter. Polycarbonate collection foils (Whatman Nuclepore Track-Etch Membrane; 800203) were used as the collection substrate. The outlet pressure on the LPI was continuously monitored using an analog pressure sensor (see Fig. S1).

Following removal from the impactor, LPI substrates were placed in a polypropylene centrifuge tube with 10 mL of low-organic-carbon standard deionized water (MilliQ, $> 18.2\,\mathrm{M\Omega cm}$), hereafter referred to as deionized water (DIW), and extracted in an ultrasonic bath for 60 min. LPI substrates from stages 1 to 7 were pooled, in order to achieve quantifiable concentrations in the final extracts, while substrates from stages 8 to 13 were extracted individually. All handling of filter substrates was performed inside a glove box.

Four dynamic handling blanks were prepared during the experimental period to account for potential contamination of the LPI filter substrates during handling and transport to and from the sea spray chamber. For each dynamic handling blank, the impactor was loaded with substrates and transported to the sea spray chamber where it was left for 60 min. The impactor was returned to the laboratory and the filters were handled and analysed in the same manner as the samples.

Bulk water sampling

For each experiment, bulk water was sampled in triplicate through a tap located on the side of the chamber approximately halfway between the water surface and the bottom of the chamber. Bulk water samples were collected in 50 mL polypropylene centrifuge tubes.

Surface microlayer sampling

Samples of the surface microlayer (SML) within the sea spray simulation chamber were collected in triplicate following cessation of the final aerosol sampling period for each experiment. SML samples were collected using a glass plate as per the methods of Harvey[82]. Here, a clean hydrophilic glass plate (rinsed with ethanol and DIW) was immersed into the seawater sample and withdrawn at a controlled rate so that the thin surface layer of the seawater is retained.

Determination of Na^+ and PFAAs

Aliquots (1 mL) of all aerosol samples were subsampled to determine the concentration of Na^+ by chemically suppressed ion chromatography (IC; Dionex ICS-2000) using CG16/CS16 columns.

Bulk seawater (50 mL) and SML (15 mL) samples, as well as the remaining aliquots of the aerosol samples (9 mL) were spiked with isotope-labeled internal standard and concentrated on Oasis Weak-anion exchange (WAX) solid phase extraction (SPE) cartridges ($6\,\mathrm{cm}^{-3}$, 150 mg, 30 μm) using a previously published method[83].

The final extracts were analyzed for PFAA content using ultra performance liquid chromatography coupled to tandem mass spectrometry, as further described in the SI.

Linear analytes were quantified using the internal standard method. All analytes had authentic stable isotope-labeled internal standard except PFBS, PFDS, PFTriDA and PFTeDA, for which quantification was performed using $^{18}O_2$-PFHxS, $^{13}C_4$-PFOS and $^{13}C_4$-PFOA respectively. The distribution between the linear and the sum of branched isomers was determined by comparing their respective peak areas in the precursor/product ion transitions 413/369, 399/80 and 499/80 for PFOA, PFHxS and PFOS respectively. To investigate fractionation of structural isomers, the intensity of isomer-specific product ions was monitored, according to a strategy previously described by Benskin *et al.*[84].

Quality assurance

In addition to dynamic handling blanks, each batch of samples was extracted along with a blank prepared from a non-used polycarbonate membrane and 10 mL DIW. All blank samples contained high background contamination of PFBA. As such, this analyte was omitted from the study. Apart from PFBA, no other analyte was observed above its respective instrumental quantification limit in the blank samples and so no subtraction of these concentrations from the measured values in the samples was conducted. To test the accuracy and precision of the method unused membranes were spiked with 8 ng of each linear target analyte and extracted in DIW according to the procedure descibed above. Poor accuracy and high RSDs were observed for PFDS, PFTriDA and PFTeDA (Tab. S2). This was likely due to their high surface activity, causing losses during sampling and storage. In addition, the quantification of these substances was not performed relative to an identical isotope-labelled internal standard and should therefore only be viewed as semi-quantitative. For these reasons enrichment factors of PFDS, PFTriDA and PFTeDA are not reported herein. To test the performance of the isomer analysis, unused membranes were spiked with 20, 25 and 20 ng of TPFOA, brPFHxS and TPFOS, respectively. Good precision (1.0-12%) and accuracy (93-118%) was observed for the sum of branched isomers as well as ratios of indiviual structural isomers. The mean recoveries of the internal standards relative to $^{13}C_8$-PFOA are given in Tab. S3.

Calculation of enrichment factors

The measured data was used to determine enrichment factors of each of the PFAAs in the aerosol (aerosol EFs), relative to their bulk water concentrations, as a function of particle size. This was calculated using a classical approach where the aerosol EF is defined as the ratio of the concentration of substance X in the particle to that in the bulk seawater and the concentration of substance X is normalized to the concentration of one of the major constituents of seawater, generally Na^+[85]:

$$\text{Aerosol EF}(X) = \frac{\big([X]\,/\,[\mathrm{Na}^+]\big)_{\text{particle}}}{\big([X]\,/\,[\mathrm{Na}^+]\big)_{\text{seawater}}}. \tag{1}$$

The reported aerosol EFs were calculated from the average concentration of substance X in triplicate LPI samples representing a specific aerosol size range and the average concentration of the same substance in the bulk water during the course of the complete experiment (n=6). Such enrichment factors are used under the assumption that the mass fraction of Na^+ is the same in both the seawater and the nascent aerosol produced from it.

Global Modelling

The Norwegian Earth System Model (NorESM)[86;87] was used to determine the magnitude of the transport of PFOA and PFOS to the atmosphere via SSA as well as the magnitude of the deposition of these substances to terrestrial environments via SSA transport. To estimate SSA emissions, NorESM uses the inorganic SSA source function developed by Salter *et al.*[88]. This source function simulates the number of SSAs produced from a unit area of ocean in a unit of time as a function of particle size. The source function consists of three log-normal modes (modal diameters: 0.095 μm, 0.6 μm and 1.5 μm) and depends on the two environmental parameters thought to be most important for SSA generation, wind speed and seawater temperature. Importantly, the source function was developed using the same sea spray simulation chamber utilized in the current study and when compared to a wide range of SSA source functions in the literature, it estimates an annual global flux of inorganic SSA close to the median value[88].

Annual average PFOA and PFOS emissions via SSA were modeled by rearranging Eq. 1 using the mass emissions of Na^+ via SSA in NorESM, relevant seawater PFOA and PFOS concentrations and the measured PFOA and PFOS aerosol enrichment factors presented in Fig. 2. The relevant mean enrichment factor for both PFOA and PFOS was selected for each of the modes in the source function (0.095 μm: stages 1-7 of the LPI, 0.6 μm: stages 1-7 of the LPI, 1.5 μm: stage 8 of the LPI). With regards relevant seawater concentrations of PFOA and PFOS, a series of studies[9;89;10;12;90;11;91;8;92] have measured the open ocean surface water concentrations of these substances and box and whisker diagrams summarising these measurements are presented in Figs. S2c and S2d. For these calculations we have used the median value of reported open ocean PFOA and PFOS concentrations, 34 $\mathrm{pg\,l^{-1}}$ and 20 $\mathrm{pg\,l^{-1}}$, respectively. Box and whisker diagrams summarising field measurements of PFAA open ocean surface water concentrations reported in in a series of studies[9;89;10;12;90;11;91;8;92] are presented in Figs. S2c and S2d.

Since our approach to calculating PFOA and PFOS emissions (rearranging Eq. 1) assumes that the absolute magnitude of these emissions scales linearly with the relevant enrichment factor and the seawater concentration of the substance, as well as the mass of Na^+ emitted as SSA, it is also possible to use ranges of each of these parameters to determine a best estimate of global annual PFOA and PFOS emissions along with upper and lower bounds. We have utilised the standard deviations of the calculated enrichment factors presented as error bars in Fig. 2 for the lower and upper bounds of the enrichment factors along with the mean values as a best estimate. To generate a best estimate and upper and lower bounds of PFOA and PFOS seawater concentrations we have used the median and 25th and 75th percentiles of the data presented in Figs. S2c and S2d. We have also included the uncertainty in SSA emissions by utilising a review of SSA emissions computed by 12 chemical transport and general circulation models participating in the AeroCom aerosol model intercomparison[93;94]. A summary of these 12 estimates is presented in Fig. S2b and we have used the median and 25th and 75th percentiles for our best estimate and lower and upper bounds, respectively. For these calculations we assume that the mass of sea salt in the best estimate and upper and lower bounds is distributed across particle size in the same manner as in the parameterisation of Salter *et al.*[88] so that we can apply appropriate enrichment factors. We also assume that the fraction of sea salt deposited to terrestrial regions is the same for these estimates as is calculated by NorESM (total deposition).

Results and Discussion

Laboratory experiments

The relative standard deviation (RSD) of the triplicate bulk seawater samples taken at the start and end of each aerosol sampling period was below 10 % for all substances (Fig. S3). The concentrations of the least surface active substances were stable over the course of the experiment, while a 40 % decrease in concentration was observed for PFDoDA between the start of experiment A1 and the termination of experiment A3 (Fig. S3). Clear discrepancies existed between the target concentrations and the measured seawater concentrations. Notably, this discrepancy increased with increasing PFAA chain length, which is a proxy for the surface activity of the substance[95;96;97]. Agreement between target and measured concentrations in seawater was within 20 % for some short-chain homologues, namely perfluorobutane sulfonic acid (PFBS), perfluoropentanoic acid (PFPeA) and perfluorohexanoic acid (PFHxA), whereas a 69 % discrepancy was observed for perfluorododecanoic acid (PFDoDA), the most surface active substance. Similar behavior was observed by Reth *et al.*[44], who suggested it was the result of sorptive losses to the chamber walls and partitioning to the air-water interface. Observation of concentrations above the spiked target can be attributed to background levels of PFAAs in the tap water used to prepare artificial seawater for the experiments. In Experiment B, the target concentration of the individual PFAAs studied were approximately 5 times higher than their corresponding target concentrations in Experiment A. At the higher spike level, the discrepancy between target and measured concentrations was 53, 29 and 48 % for PFHxS, PFOA and PFOS, respectively (sum of branched and linear isomers). At the lower spike level, the discrepancy was 11, 8 and 23 % for PFHxS, PFOA and PFOS, respectively (only linear isomers). The

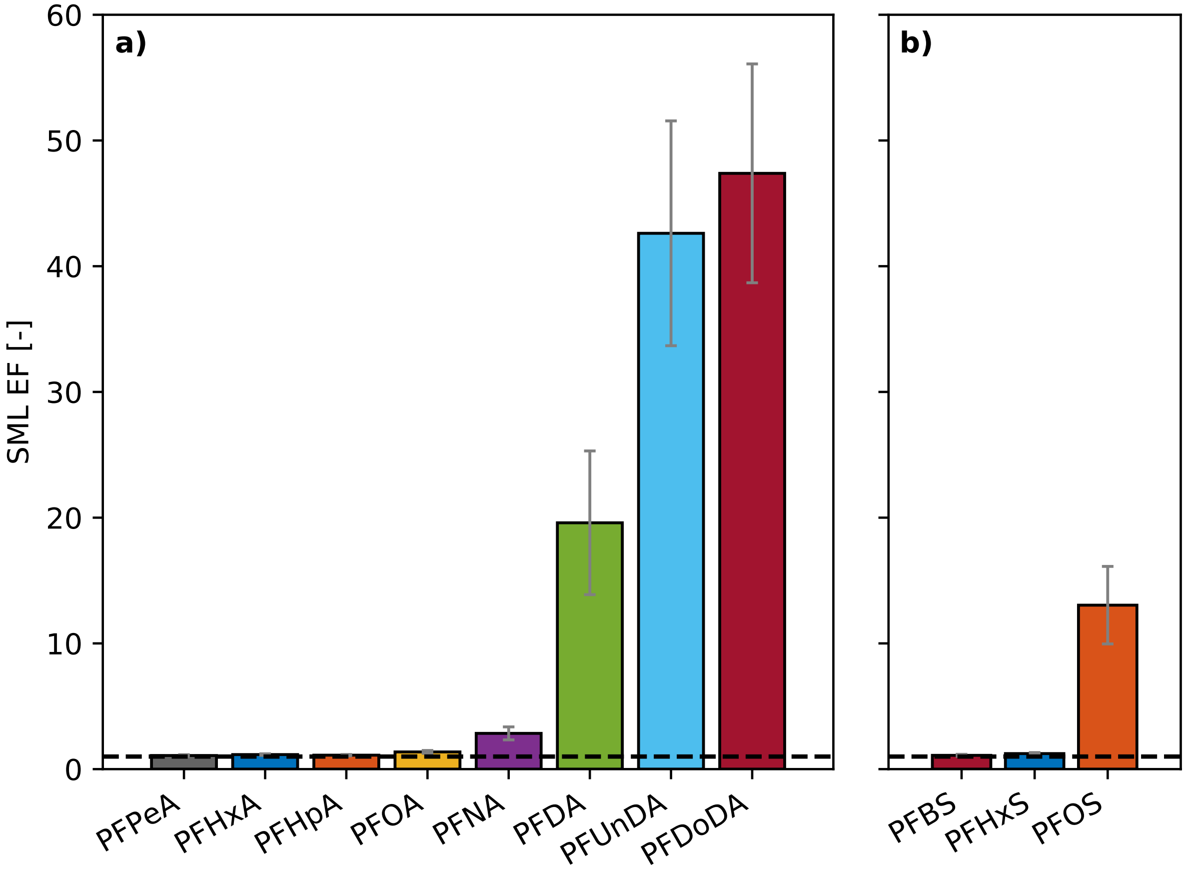

Figure 1: The SML enrichment of **a)** Perfluoroalkyl carboxylic acids (PFCAs) and **b)** Perfluoroalkane sulfonic acids (PFSAs) in Experiment A. Here error bars represent 1 standard deviation and the dashed line represents an enrichment factor of 1.

larger discrepancy observed in experiment B might be explained by a lower influence of background PFAA levels in the artifical seawater.

Moderate surface microlayer enrichment factors (SML EFs; defined as the ratio of the concentration in the SML to the concentration in the bulk seawater) were observed for PFCAs with up to 9 carbon chain lengths (SML EF: 1.1-2.9) and PFSAs with up to 6 carbon chain lengths (SML EF: 1.1, 1.2), while more substantial enrichment was observed for longer chain substances (SML EF: 13-47) (Fig. 1). Notably, SML EFs increased with increasing homologue chain length (Fig. 1). The SML EFs observed in experiments A and B agreed well for PFOA (1.4 and 2.1, respectively) and PFHxS (1.2 and 1.6, respectively). However, the SML EFs for PFOS were more than three times higher in experiment B (43) than in experiment A (13).

With the exception of PFPeA in the two smallest stages of the LPI (i.e. in aerosols $< 1.60\,\mu$m), quantifiable masses of the spiked PFAAs were present across all stages of the LPI (Fig. S4 and Fig. S5). Similar to the trend observed in the SML EFs (Fig. 1), the aerosol EFs increased with homologue chain length (Fig. 2). This suggests similar processes are enriching PFAAs in the aerosols and the sea surface microlayer. The observed aerosol enrichment factors increased with decreasing particle size and exhibited maximas in the two lowest LPI stages. In experiment A, PFOA and PFOS aerosol enrichment factors increased from $\sim$ 1800 to $\sim$ 17100 and $\sim$ 200 to $\sim$ 62100, respectively between the largest aerosol particles ($> 10.16\,\mu$m) and the smallest aerosol particles (0.029 - 0.99 μm). The aerosol EFs observed in experiments A and B were generally within 15 % agreement, although differences between 19 and 35 % were observed for five aerosol EFs. Notably, the aerosol EFs were orders of magnitude larger than the corresponding SML EFs for each substance.

To investigate the enrichment behaviour of isomeric PFAA mixtures, we analysed the distribution between linear and the sum of branched isomers in the different sample types (Fig. S9), as well as the relationship between individual branched isomers (Tab. S4). For all isomeric mixtures studied, a lower contribution of branched isomers was observed in the SML in relation to the bulk water. PFOS displayed the largest difference in contribution of branched isomers between bulk water (28 %) and SML (18 %). The contribution of branched PFOS isomers was elevated in aerosols (24-28 %) in relation to the SML, but no clear trend was observed in the comparison of different aerosol size ranges. Small aerosols ($< 1.60\,\mu$m) displayed contribution of branched PFOA isomers closer to that of the SML (14 %), while larger aerosols ($> 1.60\,\mu$m) were closer to the observation for bulk water (18 %). A similar trend was observed for the individual branched PFOA isomers (Tab. S4). For PFHxS, only slight differences were observed between bulk water, SML and aerosols.

Branching of the chain of a fluorinated surfactant is expected to lead to a reduction in surface activity of the chemical due to less efficient molecular packing[98]. However, measurements comparing the surface activity of branched and linear PFAA isomers are scarce. Shinoda *et al.*[99] reported a CMC of 8.5 mmol/L for 6-PFOA. The same author has also reported CMC values for linear PFOA of 8.0 and 9.1 mmol/L in previous studies[100]. McMurdo *et al.*[45] hypothesised that the SML as well as SSA will be more enriched in linear PFOA than in branched PFOA isomers and therefore the processes of aerosol production would act as "a very effective filtering system for the branched isomers". A number of previous studies have used the PFOA isomer pattern as a tool for source elucidation in environmental samples[31;101;6;102]. If SSA acts as a filter for branched PFOA isomers, as suggested by McMurdo *et al.*[45], use of this approach may be compromised, especially for study of atmospheric samples[31;101]. Our data suggests that the surface activity of branched and linear PFAA isomers differ to some extent. However, SSA is not an efficient filter for branched PFOA isomers. As such, the distribution of branched PFAA isomers in SSA will likely be more influenced by spatial differences in isomer pattern occurence in seawater[102] than by fractionation in the formation of SSA.

		Lower estimate	Best estimate	Upper estimate
Inorganic sea spray	Global emission (Pg yr^{-1})	3.64	6.24	9.68
	Deposition to land (Pg yr^{-1})	0.09	0.16	0.24
PFOA	Seawater concentration (pg l^{-1})	15	34	72
	Enrichment factor (-)	Mode 1,2: 13000 Mode 3: 15000	Mode 1,2: 17000 Mode 3: 21000	Mode 1,2: 22000 Mode 3: 26000
	Global emission (tonnes yr^{-1})	23	122	506
	Deposition to land (tonnes yr^{-1})	1	3	13
PFOS	Seawater concentration (pg l^{-1})	11	20	44
	Enrichment factor (-)	Mode 1,2: 38000 Mode 3: 36000	Mode 1,2: 62000 Mode 3: 50000	Mode 1,2: 86000 Mode 3: 64000
	Global emission (tonnes yr^{-1})	42	183	810
	Deposition to land (tonnes yr^{-1})	1	5	20

Table 1: Estimated annual global PFOA and PFOS emissions and deposition to land via SSA.

Comparison to previous studies

Two previous studies have attempted to determine whether PFAAs are likely to be efficiently transferred from the ocean to the atmosphere[45;44]. Both of these studies clearly highlighted the potential for SSA to act as an efficient vector for their transport. However, direct comparison to their results is impossible since (i) Reth *et al.*[44] did not use seawater and (ii) since McMurdo *et al.*[45] used an aerosol generation mechanism very different from that which generates natural SSA, a highly unconventional aerosol sampling approach (as discussed in Mader *et al.*[103]). Further, neither of the studies presented aerosol EFs normalised to Na^+.

The SML EFs determined in our study are within a factor of two of those reported by Reth *et al.*[44] for all tested substances except PFUnDA. For this substance Reth *et al.*[44] report an enrichment factor exceeding ours by a factor 4. Furthermore, the SML EF for PFOS observed in experiment B exceeded that reported by Reth *et al.*[44] by a factor of 3. Although they used a technique to obtain SML samples similar to that used in our study, a major difference in their experiment was the use of tap water rather than artificial seawater. Our measured SML enrichment factors also agree well with the SML enrichment factors measured in natural seawater samples by Ju *et al.*[104]. These authors reported PFOA SML enrichment factors that were stable over periods of days across a variety of sampling sites (PFOA EFs: 1.2-1.8). However, their reported SML enrichment factors for PFOS across the same sites and time period varied significantly (2.0-109).

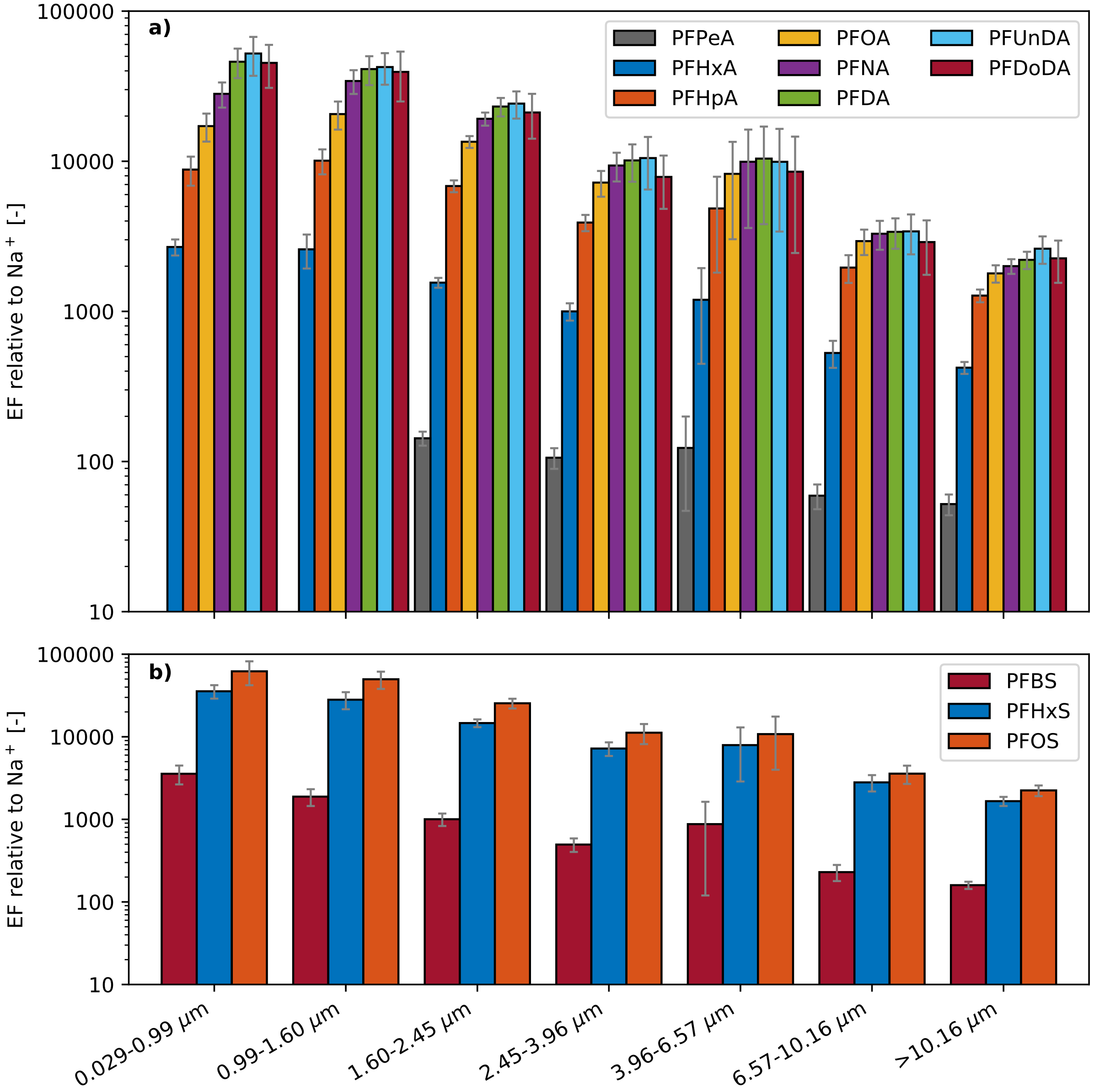

Figure 2: Enrichment factor, EF(X), relative to Na$^+$ of **a)** Perfluoroalkyl carboxylic acids (PFCAs) and **b)** Perfluoroalkane sulfonic acids (PFSAs) as a function of particle aerodynamic diameter (Experiment A). Note that PFPeA was not detectable in the two lowest stages of the impactor so no EF could be calculated. Here error bars represent 1 standard deviation following propagation of the standard deviation of the Na$^+$ and PFAA concentrations measured in the seawater and aerosol samples.

The observation that PFAAs are predominantly enriched in submicron aerosols agrees with observations on the enrichment of organic carbon in SSAs[66;68;69;63;70] and recent measurements of other carboxylic acids[105]. However, Cochran *et al.*[105] observed submicron aerosol EFs of up to about ~ 1000 for non-fluorinated carboxylic acids (sum of three test substances), some two orders of magnitude lower than the highest EFs observed in the current study for the corresponding aerosol size range. This difference likely results from the much higher surface activity of PFAAs relative to non-fluorinated carboxylic acids. The increasing enrichment with chain length was also previously observed by Cochran *et al.*[105] and suggests that the surface activity of PFAAs is a key driver of their enrichment in SSAs.

Modeling the transport of PFAAs via sea spray aerosol

The spatial distribution of the modeled PFOA emissions by SSA (Fig. 3a) and deposition to land areas by the same pathway (Fig. 3b) directly reflects the SSA production flux described previously by Salter *et al.*[88]. The emission of SSA, in turn, reflects the distribution of storms worldwide, since near surface wind speed is the dominant factor controlling SSA emissions. From Fig. 3b, it is clear that coastal regions are most impacted by transport and deposition of PFAAs following emission with SSA. However, large parts of inland Europe, Alaska and Central America are also affected. Figure S6 presents similar maps for PFOS with the only difference being the magnitude of the emission and deposition in each grid cell which results from differences in the seawater concentration and the EF.

We estimate that between 23 and 506 tonnes year^{-1} of PFOA and between 42 and 810 tonnes year^{-1} of PFOS are emitted to the atmosphere by SSA with a best estimate of 122 tonnes year^{-1} and 183 tonnes year^{-1} of PFOA and PFOS, respectively (Tab. 1). Subsequently, between 1 and 13 tonnes year^{-1} of PFOA and between 1 and 20 tonnes year^{-1} of PFOS are deposited to the terrestrial environment with a best estimate of 3 tonnes year^{-1} and 5 tonnes year^{-1} of PFOA and PFOS, respectively. In other words, only about 3 % of the PFOA and PFOS aerosolised as SSA is transported and deposited to land areas.

The total annual flux of PFOA to the atmosphere via SSA estimated in this study (Tab. 1) is comparable with PFOA emission estimates reported by Wang *et al.*[1]. These authors report total emissions (including direct releases and precursor transformation) of 14-74 tonnes for PFOA in 2012[1]. Current annual emissions of PFOS to air from industrial sources in China are estimated to be 1-1.4 tonnes[106]. Current industrial emissions of PFOS outside of China are likely minor[107]. Wang *et al.*[107] estimated that between 2003 and 2015 less than 2.8 tonnes of PFOS was formed from precursors in the environment each year. Consequently, the lower estimate of SSA-borne releases of PFOS to the global atmosphere exceed emission estimates for other potential sources of PFOS to air by one order of magnitude.

Comparison of our model results to existing inventories suggests that SSA may currently be an important source of PFAAs to the atmosphere. However, the large uncertainties in our modeling approach (revealed in Tab. 1) warrant discussion. The sea salt emissions that our estimates are based upon are uncertain by factors of between 2 and 10[94]. Further, most of the PFAA mass will be associated with SSA particles with diameters larger than 1 μm which have concentrations that are even more uncertain. It is also important to note that our estimates of PFAA emissions via SSA do not include coastal wave-breaking (which are not directly wind-driven). Here, sea spray emissions are likely to be significantly greater and much closer to coastal regions where deposition may be important. It should also be noted that the lifetime of aerosols once airborne is highly uncertain, which contributes to the uncertainty in our estimates of deposition rate and extent[108].

Further uncertainty is associated with the oceanic concentrations of PFAAs, which also vary over several orders of magnitude (Fig. S2). As is shown in our review of published seawater data (Fig. S2), median concentrations of the studied PFAAs are all in the range 6-34 pg l^{-1}. This homologue pattern is not in line with previous emission estimates, which state that the cumulative historical emissions of PFOA were between one and four orders of magnitude higher than those for other PFCA homologues[1]. This suggests that the published data on occurrence of PFAAs in seawater may not accurately reflect the true environmental conditions. We therefore chose to perform model predictions for PFOA and PFOS only. These are the two most well-studied PFAAs and therefore analytical methods are often tailored to perform well for these substances.

Due to a lack of open ocean monitoring data in the published literature, it was not possible to account for the spatial distribution of PFAAs in the global oceans. The use of seawater concentrations of PFOA and PFOS that do not vary spatially expectedly adds further uncertainty to our estimates. The data used as model input (Fig. S2) does not display any clear trends in the comparison between Northern and Southern hemisphere PFAA concentrations. For PFOA the median concentrations were 55 pg l^{-1} and 13 pg l^{-1} in the Northern and the Southern hemispheres, respectively, while for PFOS the corresponding concentrations were 24 pg l^{-1} and 30 pg l^{-1}, respectively. However, seawater concentrations of these compounds are often greater in coastal waters which are closer to anthropogenic PFAA sources[11;109]. This, when combined with coastal wave-breaking, further increases the likelihood of transport to terrestrial coastal environments.

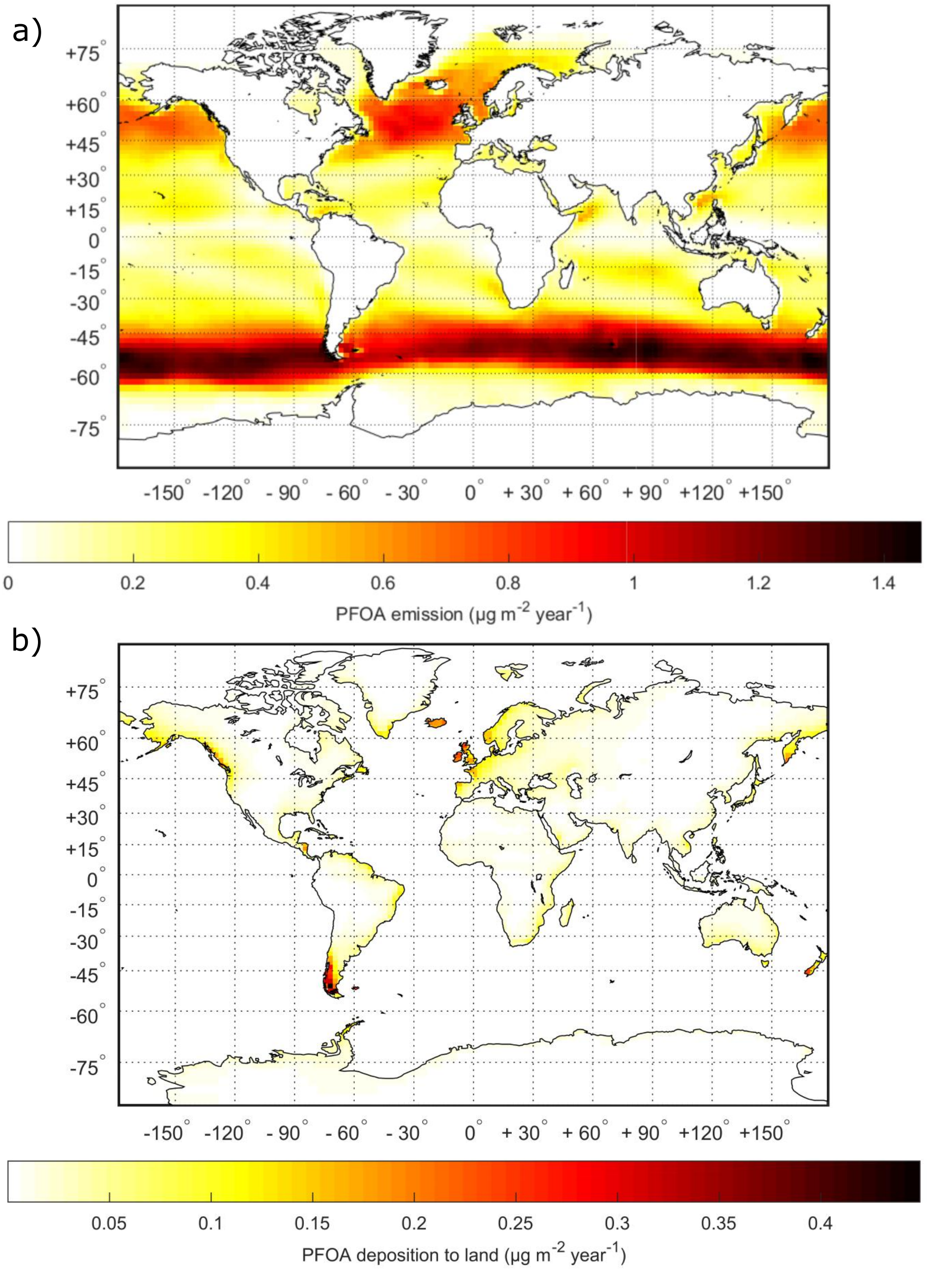

Figure 3: Global maps of **(a)** total yearly emissions of PFOA via SSA and **(b)** total yearly deposition of PFOA transported to terrestrial environments by SSA.

Another source of uncertainty stems from the aerosol EFs. We have used error propagation of the standard deviation of the Na^+ and PFAA concentrations measured in the seawater and aerosol samples to obtain the error estimates included in Fig. 2 and these error estimates are included in our emission and deposition estimates (Tab. 1). The estimated standard deviation of the aerosol EFs all fall within a single order of magnitude. Despite, the relatively low uncertainty in these values, when compared to SSA emissions and seawater PFAA concentrations, we do not include the effects of natural surface-active organic matter on the enrichment of these substances in our experiments, nor indeed potential interactions with other surface-active pollutants.

A number of studies have attempted to model the transport of PFAAs to the atmosphere via SSA[110;51;111]. These studies either assumed that PFAAs were not enriched in the seawater droplets emitted as SSA[110] or that the enrichment of PFAAs in SSA was similar to the enrichment found in SML samples[51;111]. Based upon the significant difference between the observed aerosol and SML EFs in the current study, this suggests that the approaches used by Qureshi *et al.*[110], Armitage *et al.*[51] and Webster *et al.*[111] underestimated the potential emission of PFAAs to the atmosphere via SSA dramatically.

The results of the current study highlight the potential for SSA to act as a vector for the transport of PFAAs from the oceans to the atmosphere. The approaches used have allowed us to determine the potential magnitude of this transport pathway, so that it can be placed in the context of other sources.

The only way to rigorously test our modeling approach is through comparison to atmospheric aerosol samples collected within the marine boundary layer from which both the Na^+ and PFAA concentrations have been determined. Unfortunately, such field data are currently not available in the scientific literature. Deposition of PFAAs to terrestrial areas was modeled to generate an estimate of the proportion of SSA-borne PFAAs that deposit on land and to illustrate the regions predominantly influenced by this deposition. Published deposition fluxes span over orders of magnitude[35;28;32;29;30;112;36]. This is likely related both to analytical issues and to large variation in the factors that affect atmospheric deposition of aerosols. Most field studies only report data for one or a few measurements from the same sampling site. Such data may not be suited for extrapolation to an average annual deposition flux, which is required in the comparison to our modeled data. Use of such field data to evaluate our model results is further complicated by the fact that deposition samples can be influenced by different sources of PFAAs, each of which may dominate under different sets of conditions.

Conclusions

Oceans are by far the largest environmental “reservoir” of historically-released PFAAs. As PFAAs do not degrade under environmental conditions and most PFAAs are not buried in sediments to a substantial degree, the substances are expected to persist in the global oceans indefinitely[113;114]. Our results indicate that SSAs have the capacity to circulate significant amounts of PFAAs between the oceans and the atmosphere. A portion of the mass emitted from the oceans will deposit on land, thus re-entering the terrestrial system. This suggests that human exposure to PFAAs will continue even if strict global emission controls are implemented. To determine whether the observations of water-to-air transport of PFAAs in our laboratory experiments are valid, field measurements of PFAAs in aerosols at remote locations affected by SSA using adequate aerosol sampling approaches are required. Ideally, these measurements should be conducted with high time-resolution (days rather than weeks) so that statistical trajectory analysis techniques can be applied to determine the sources of PFAAs in the samples. Critically, the mass of a reference element present in bulk seawater, such as Na^+, should be used to normalize PFAA measurements and calculate enrichment, as conducted in this study. Moreover, our results highlight the need for further study of the importance of SSA for the global transport of other persistent, water soluble and surface active substances.

Acknowledgements

The authors greatly thank Agneta Öhström for her assistance with the ion chromatography analysis, finacially supported by the Swedish Research Council (Vetenskapsrådet, project number 2016-03518) J. H. J. was funded by the Swedish Research Council FORMAS (project number 2011-1345). M. E. S was financed by Vetenskapsrådet (project number 2016-05100). The sea spray simulation chamber was previously financed by Vetenskapsrådet projects MASC (2010-3821) and CESSA (2014-5354).

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Electronic supplementary information for manuscript ”Global transport of perfluoroalkyl acids via sea spray aerosol” by Johansson *et al.*, 2018.

Sea spray simulation chamber

All experiments were performed using a sea spray generator developed by Salter *et al.*[1] (Fig. S1). The air-flow rate was maintained and quantified using a mass flow controller (Brooks, 5851S). The slight positive pressure maintained by keeping the sweep-air flow 2 L min^{-1} higher than the sampling rate prevented contamination by the room air and excess air was vented through a flutter valve on the lid of the tank. The flow through the flutter valve was determined at the start and end of each experiment using an air flow calibrator (Gilian Gilibrator-2, Sensidyne Inc.).

In order to check for contamination within the sea spray chamber, a check for sources of particles additional to bubble bursting was conducted prior to each LPI sampling period. This involved running the sweep flow at 6 L min^{-1} with the plunging jet switched off. We then checked the number of particles larger than $\sim$ 10 nm detected using a condensation particle counter (TSI, CPC 3772) during 10 min (i.e. we operated the instrument in cumulative counting mode). Using this approach we confirmed that the particle concentration was well below 1 particle per cm^3 within the chamber (with the jet turned off) prior to each experiment.

Prior to all experiments all internal polytetrafluoroethylene-coated surfaces were rinsed thoroughly with reagent grade ethanol followed by DIW.

Chemicals, standards and solvents

All standard compounds were purchased from Wellington Laboratories dissolved in methanol. Characterized isomeric mixtures of PFOA, PFHxS and PFOS (TPFOA, brPFHxS and TPFOS) were purchased as 50 $\mu\text{g mL}^{-1}$ solutions. Stable isotope-labeled and native linear PFAA standards were purchased in 2 $\mu\text{g mL}^{-1}$ solution mixtures (MPFAC-MXA and MPFAC-MXB respectively). The following isotope-labeled PFAAs were used as internal standards (IS): $^{13}C_4$-PFBA, $^{13}C_5$-PFPeA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFHpA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA, $^{13}C_2$-PFDoDA, $^{18}O_2$-PFHxS and $^{13}C_4$-PFOS. $^{13}C_8$-PFOA was used as volumetric standard in the calculation of total method recovery of the internal standard. The isotope-labelled standards were certified to contain $< 0.5\,\%$ of their native analogues.

All experiments were conducted using artificial seawater (ASW; Sigma Aldrich, S9883; manufacturer mass fraction: 55 % chloride (Cl^-), 31 % Na^+, 8 % sulfate (SO_4^{2-}), 4 % Mg^{2+}, 1 % K^+, 1 % Ca^{2+}, < 1 % other; rehydrated to an absolute salinity of 35 g kg^{-1} using DIW).

Methanol (MeOH, LiChrosolv grade), ammonium acetate (ProAnalysis) and formic acid (98 % ACS, Reag. Ph Eur) were supplied by Merck. Ammonium formiate (>99 %, for HPLC) was purchased from Fluka. A 25 % ammonium hydroxide solution was purchased from Sigma-Aldrich.

Determination of Na^+

The concentration of Na^+ in samples was determined by chemically suppressed ion chromatography (IC; Dionex ICS-2000) using CG16/CS16 columns. A Dionex ATC-1 column was used before the injection valve to trap carbonates and other ionic contaminants. The injection volume was 25 μL. The IC-analyses were quality checked using both internal and external reference samples[2]. Systematic errors were less than 2 %. The analytical detection limit for Na^+, defined as twice the level of peak-to-peak instrument noise, was 0.02 $\mu\text{Eq l}^{-1}$ and the overall analytical accuracy was better than 5 %. Aliquots (1 mL) of aerosol samples were diluted 1 to 32 with DIW to bring them into the range of analysis. Bulk seawater samples were diluted 1 to 1000 with DIW into the same analytical range as the aerosol extracts. The mean Na^+ concentration measured on each stage of the LPI for the three dynamic handling blanks was subtracted from the relevant Na^+ concentration measured in the aerosol samples.

Determination of PFCAs and PFSAs

All samples were concentrated on Oasis Weak-anion exchange (WAX) solid phase extraction (SPE) cartridges (6 cm^{-3}, 150 mg, 30 μm) using a previously published method[3]. Briefly, the cartridges were preconditioned with 4.5 mL 0.3 % NH_4OH in MeOH and activated with 4.5 mL 0.1 M formic acid in DIW. After sample loading, the cartridges were washed with 5 mL 20 % MeOH in 0.1 M formic acid followed by 2 mL 0.3 % NH_4OH in DIW, before eluting the samples with 3 mL 0.3 % NH_4OH in MeOH. After the first extraction with DIW the collection foils were extracted in 2 mL MeOH in an ultrasonic bath for 15 minutes. This extract was combined with the SPE eluent and reduced to 80 μL under a gentle flow of nitrogen at 40 °C. It was then spiked with 400 pg recovery standard and diluted with 4 mM

NH_4OAc to a final volume of 200 μL. Before analysis, the extracts were filtered using centrifugal filters (modified nylon 0.2 μm, 500 μL) purchased from VWR.

The final extracts corresponding to experiment A were analyzed on an Acquity ultra-performance liquid chromatography system coupled to a Xevo TQ-S tandem mass spectrometer (UPLC/MS/MS; Waters Corp.) according to a previously published method[4]. Briefly, the analytes were separated on a BEH C18 (50×2.1 mm, 1.7 μm particle size; Waters Corp.) analytical column using a flow rate of 0.4 mL min^{-1} and a binary gradient of mobile phase (A) 90 % water and 10 % methanol and (B) methanol, both containing 2 mM ammonium acetate. The column was heated to 40 °C. The injection volume was 5 μL. A "PFC isolator column" obtained from Waters ("PFC kit") was inserted prior to the injector to trap and delay contamination originating from the UPLC instrument and mobile phases. The mass spectrometer was operated in negative electrospray ionization mode.

The final extracts corresponding to experiment B were analyzed on an The final extracts were analyzed on a Thermo Scientific Dionex UltiMate 3000 UHPLC coupled to a ThermoScientific TSQ Quantiva mass spectrometer, according to a previously published method[5]. Analytes were separated on an Ascentis Express F5 PFP Column (2.7 μm, 10 cm $\times$ 2.1 mm, Sigma-Aldrich) equipped with an Ascentis Express F5 PFP guard column (2.7 μm, 5.0 mm $\times$ 2.1 mm), both maintained at 30°C. An Accucore C18 (2.6 μm, 50 mm $\times$ 2.1 mm, Thermo Scientific) was placed upstream of the injector to separate PFAS originating from the LC pump from those injected onto the analytical column. The mobile phases consisted of A) 20 mM ammonium formate and 20 mM formic acid in DIW and B) MeOH. The flow was set to 0.3 mL min^{-1}. The injection volume was 25 μL. The mass spectrometer was operated in negative electrospray ionization mode. Solvent blank injections were performed to monitor sample carry over. Instrumental drift was monitored by injecting a calibration standard after every 10 injections.

PFOS was quantified using the transition to m/z 99. A linear relationship ($R^2 > 0.99$) between signal and concentration was observed for all homologues in a nine point external standard calibration curve (1/X weighted linear regression) with concentrations ranging from 0.03 to 300 pg μl^{-1}. The instrumental quantification limits (QLs) were defined as the lowest mass of injected standard which gave rise to a signal-to-noise ratio above 10. For PFPeA the quantification limit was defined as the lowest sample concentration which gave rise to a signal-to-noise ratio above 10. These are given in Tab. S5.

To test whether the relative response of branched and linear isomers was influenced by the mass of analyte on column, injections of TPFOA, brPFHxS and TPFOS were made in the ranges 30-7000, 28-2942 and 45-2854 respectively. The relative standard deviations observed in these tests were used to assign uncertainty to the reported percentages of branched isomers in samples (Tab. S4), as this analytical measurement error was greater than the standard deviation observed the triplicate experiments.

For individual PFOA and PFOS isomers we use the nomenclature suggested by Benskin *et al.*[5]: linear perfluorooctanoic acid (n-PFOA), perfluoro-4-methylheptanoic acid (4-PFOA), perfluoro-5-methylheptanoic acid (5-PFOA), perfluoro-6-methylheptanoic acid (6-PFOA), linear perfluorooctane sulfonic acid (n-PFOS), perfluoro-1-methylheptane sulfonic acid (1-PFOS), perfluoro-2-methylheptane sulfonic acid (2-PFOS), perfluoro-3-methylheptane sulfonic acid (3-PFOS), perfluoro-4-methylheptane sulfonic acid (4-PFOS), perfluoro-5-methylheptane sulfonic acid (5-PFOS), perfluoro-6-methylheptane sulfonic acid (6-PFOS). Perfluoro-3-methylheptanoic acid (3-PFOA) is not reported in this study, as this substance could only be detected in injections of TPFOA above 2200 pg on column. Furthermore, dimethyl-isomers of PFOA and PFOS were not included in the study as these contributed with <0.2% to ECF PFOA and PFOS.

Additional tables

Table S1: The mean, maximum and minimum relative humidities and temperatures measured at the entrance to the LPI during each of the 6 experiments.

	Experiment A						Experiment B					
	1st replicate		2nd replicate		3rd replicate		1st replicate		2nd replicate		3rd replicate	
	RH (%)	T (°C)	RH (%)	T (°C)	RH (%)	T (°C)	RH (%)	T (°C)	RH (%)	T (°C)	RH (%)	T (°C)
Mean:	31.0	34.9	30.5	35.1	29.2	35.5	26.3	38.0	29.2	35.9	29.5	35.5
Max:	37.5	36.5	41.7	36.6	38.4	36.1	31.0	38.6	31.9	36.5	31.0	36.2
Min:	27.7	33.8	27.7	28.7	28.1	31.5	25.4	34.3	28.0	33.6	28.6	34.4

Table S2: The average accuracy (%) and relative standard deviation (RSD, %) in spike-recovery tests with linear native substances (8 ng).

	Accuracy of spiked native substances (%)	
Substance	Accuracy	RSD
PFPeA	72	1
PFHxA	79	6
PFHpA	71	1
PFOA	84	3
PFNA	81	0.4
PFDA	77	6
PFUnDA	80	4
PFDoDA	76	3
PFTriDA	40	32
PFTeDA	37	32
PFBS	105	2
PFHxS	81	2
PFOS	78	8
PFDS	17	37

Table S3: The average recovery (%) of the internal standards relative to $^{13}C_8$-PFOA.

	Recovery of internal standard (%)			
	Seawater samples		Aerosol samples	
Substance	Average	RSD	Average	RSD
MPFPeA	109	8	106	14
MPFHxA	102	8	94	15
MPFHpA	121	7	103	13
MPFOA	95	5	90	11
MPFNA	101	11	86	14
MPFDA	88	16	80	22
MPFUnDA	63	22	65	35
MPFDoDA	60	29	68	45
MPFHxS	114	6	99	16
MPFOS	88	14	84	21

Table S4: Average ratios (and standard deviation) of individual branched isomers to corresponding linear isomer in bulk water (n=18), surface microlayer (SML, n=3) and aerosol (n=3) in Experiment B. The ratios are based on chromatographic peak areas.

	4-PFOA	5-PFOA	6-PFOA	1-PFOS	34-PFOS	5-PFOS	6-PFOS
Bulk water	0.03 (0.001)	0.11 (0.006)	0.14 (0.005)	0.13 (0.027)	0.16 (0.030)	0.19 (0.031)	0.32 (0.061)
SML	0.02 (0.004)	0.07 (0.008)	0.09 (0.012)	0.09 (0.016)	0.08 (0.013)	0.08 (0.010)	0.2 (0.038)
0.029-0.99 μm	0.02 (0.003)	0.07 (0.006)	0.10 (0.006)	0.11 (0.016)	0.15 (0.023)	0.15 (0.023)	0.27 (0.028)
0.99-1.6 μm	0.02 (0.001)	0.07 (0.005)	0.10 (0.004)	0.12 (0.013)	0.16 (0.012)	0.16 (0.036)	0.30 (0.020)
1.6-2.45 μm	0.03 (0.001)	0.09 (0.002)	0.11 (0.003)	0.14 (0.016)	0.15 (0.009)	0.13 (0.024)	0.29 (0.029)
2.45-3.96 μm	0.03 (0.000)	0.10 (0.000)	0.13 (0.004)	0.15 (0.006)	0.17 (0.006)	0.15 (0.020)	0.33 (0.021)
3.96-6.57 μm	0.03 (0.001)	0.10 (0.004)	0.13 (0.007)	0.14 (0.013)	0.17 (0.011)	0.14 (0.020)	0.33 (0.024)
6.57-10.16 μm	0.03 (0.002)	0.10 (0.007)	0.13 (0.001)	0.14 (0.011)	0.16 (0.017)	0.14 (0.026)	0.34 (0.059)
>10.16 μm	0.02 (0.000)	0.09 (0.001)	0.10 (0.000)	0.11 (0.002)	0.12 (0.007)	0.14 (0.005)	0.35 (0.030)

Table S5: Instrumental quantification limits of PFAAs defined as the lowest injected standard concentration which gave rise to a signal-to-noise ratio above 10.

	Instrumental quantification limit (pg sample^{-1})	
Substance	Experiment A	Experiment B
PFPeA	3.7	
PFHxA	16	
PFHpA	3.7	
PFOA	16	6
PFNA	3.7	
PFDA	3.7	
PFUnDA	3.7	
PFDoDA	3.7	
PFTriDA	3.	
PFTeDA	3.7	
PFBS	3.3	
PFHxS	3.5	58
PFOS	3.4	58
PFDS	3.6	

Additional figures

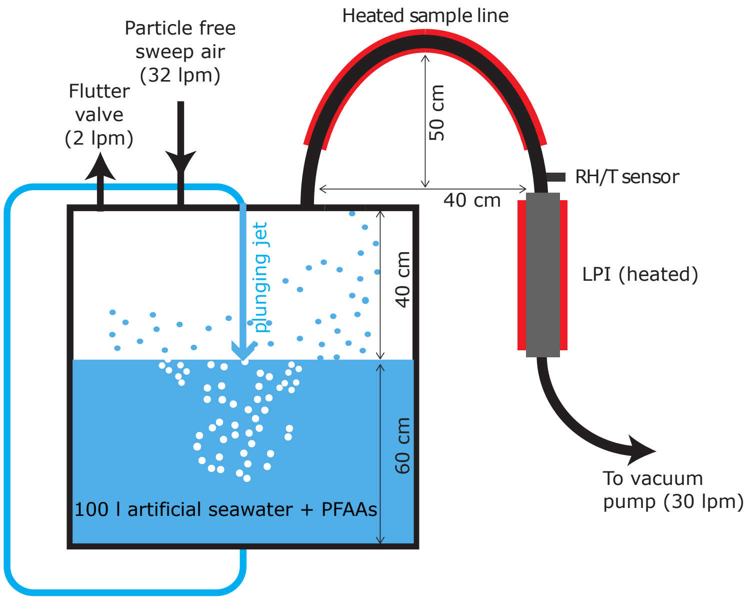

Figure S1: Schematic of the sea spray chamber used to generate nascent SSA from artifical seawater containing PFAAs. The air flow rates entering and exiting the sea spray chamber are provided in brackets.

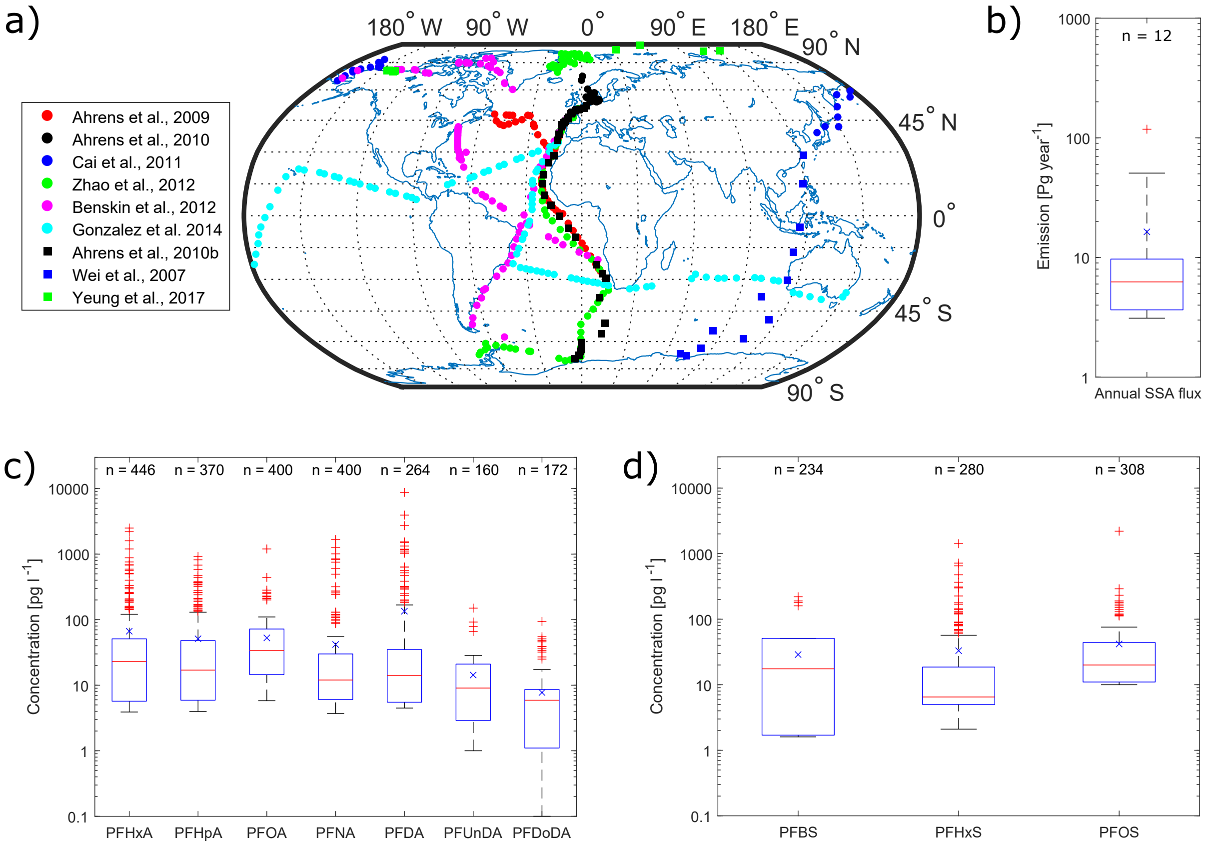

Figure S2: **(a)** The position of seawater samples collected during a series of research cruises conducted to determine PFAAs concentrations in seawater[6;7;8;9;10;11;12;13;14]. **(b)** A box and whisker plot of the global dry SSA mass emission as computed by 12 chemical transport and general circulation models participating in the AeroCom aerosol model intercomparison[15;16]. Here, the red line represents the median, the lower and upper blue boxes represent the 25th and 75th percentiles, respectively, and the whiskers represent the 10th and 90th percentiles. The blue cross represents the mean. **(c)** and **(d)** summarise the PFCA and PFSA seawater concentrations measured in the samples shown in panel a. Here, the red line represents the median, the lower and upper blue boxes represent the 25th and 75th percentiles, respectively, and the whiskers represent the 10th and 90th percentiles. The blux cross represents the mean.

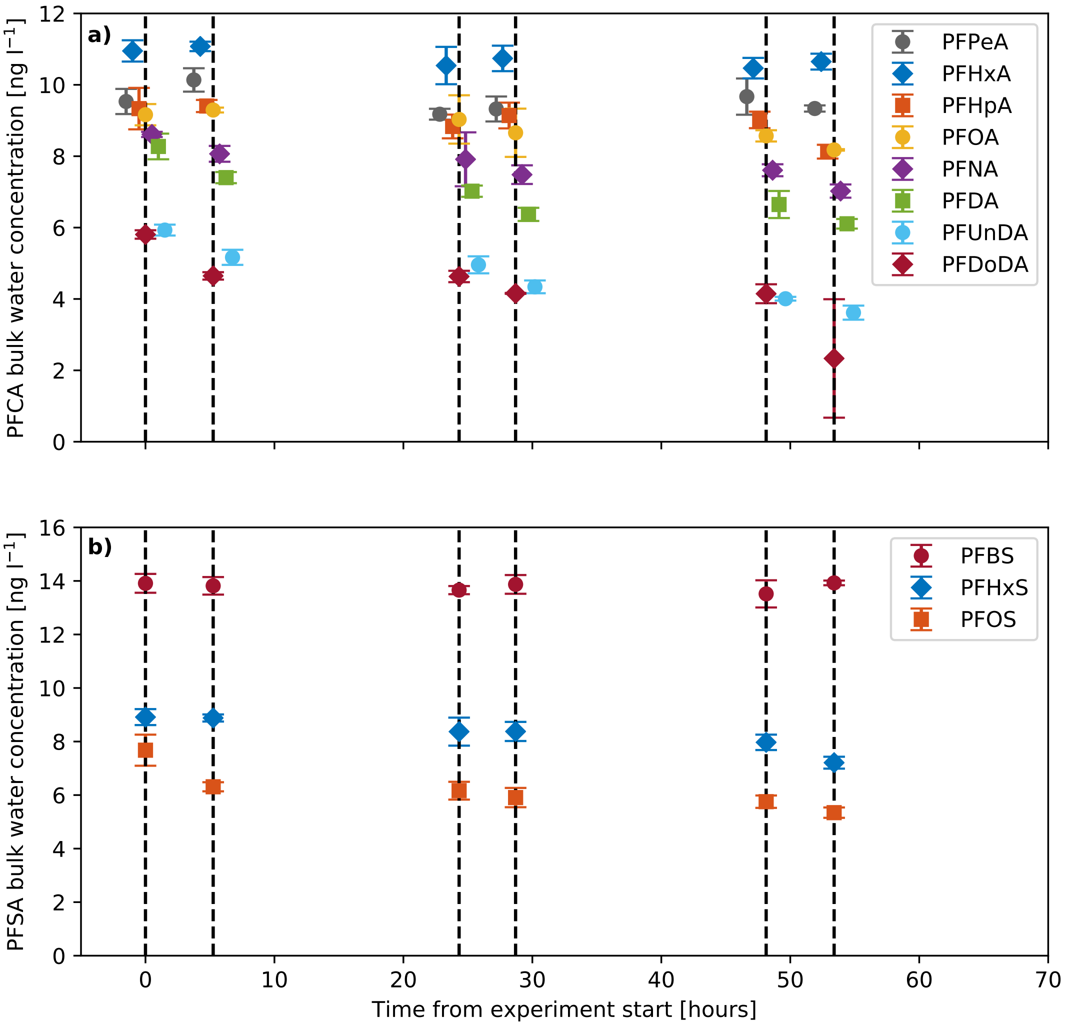

Figure S3: The temporal evolution of the bulk water concentration of **a)** perfluoroalkane carboxylic acids and **b)** perfluoroalkane sulfonic acids during the three replicate experiments. In **a)** the datapoints have been offset to increase visibility. The dashed lines represent the time of sample collection.

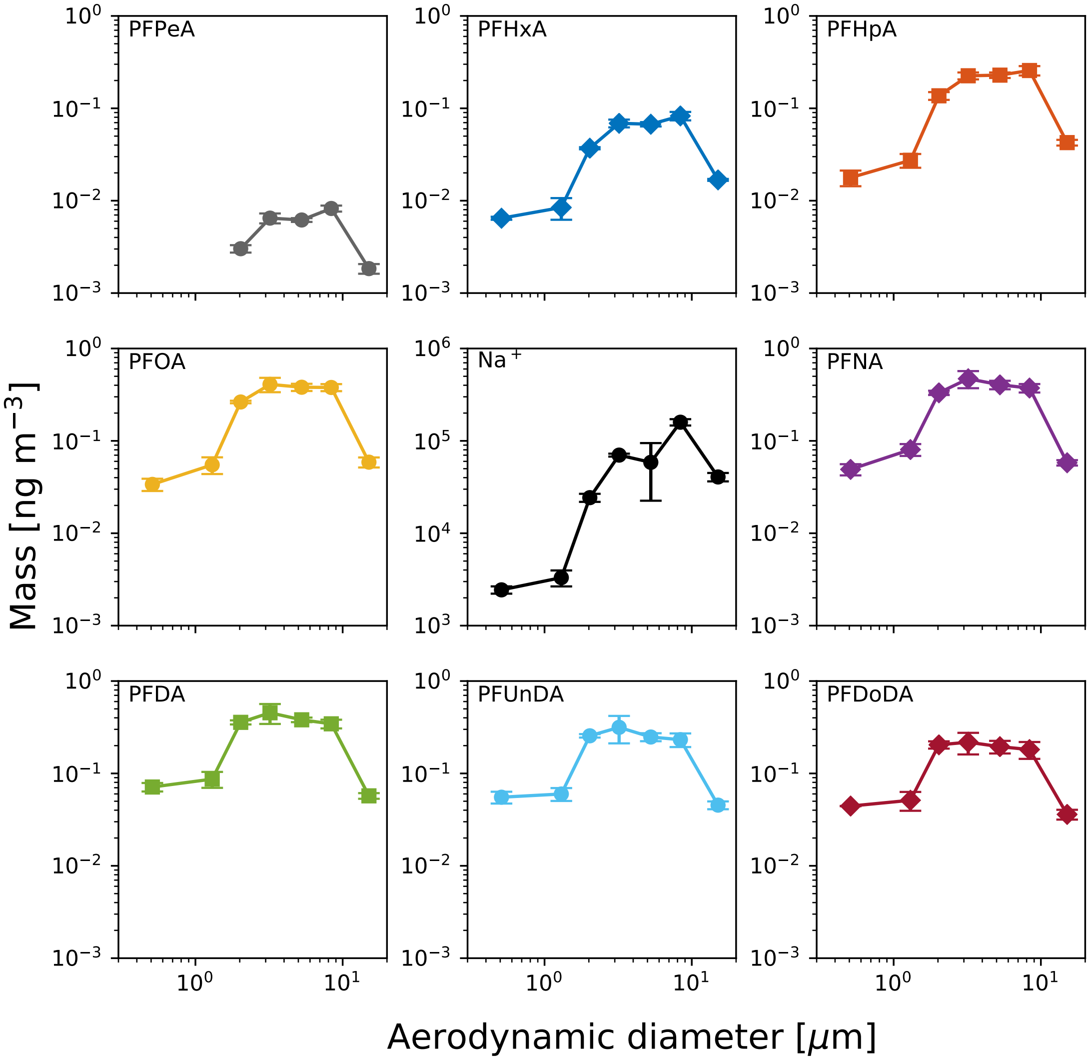

Figure S4: The aerosol mass size distribution of the measured PFCAs and Na$^+$ versus middle aerodynamic diameter. PFPeA was not detectable in the two lowest stages of the impactor and was below the quantification limit (14 pg sample^{-1}) in stage 13.

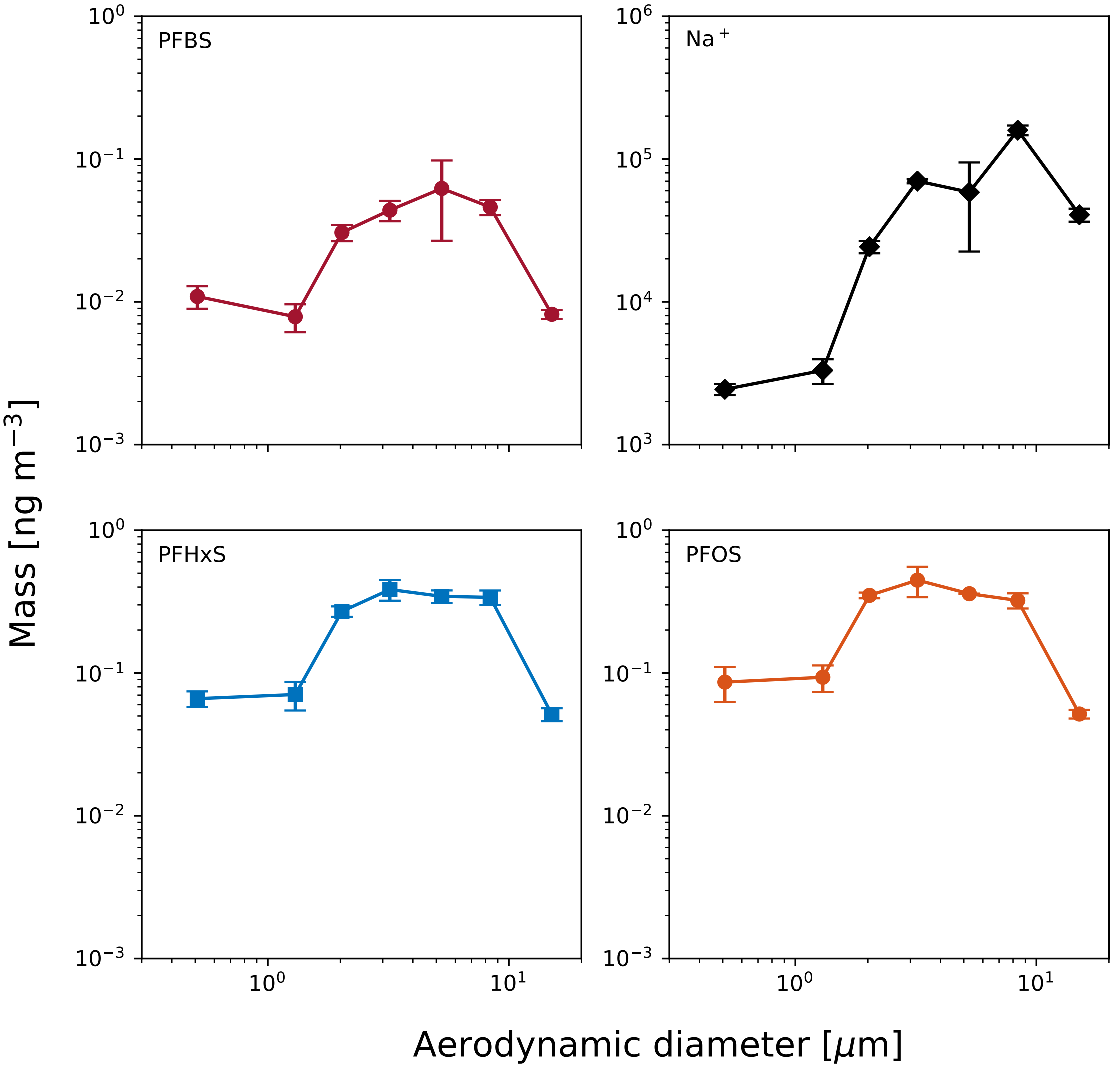

Figure S5: The aerosol mass size distribution of the measured PFSAs and Na$^+$ versus middle aerodynamic diameter.

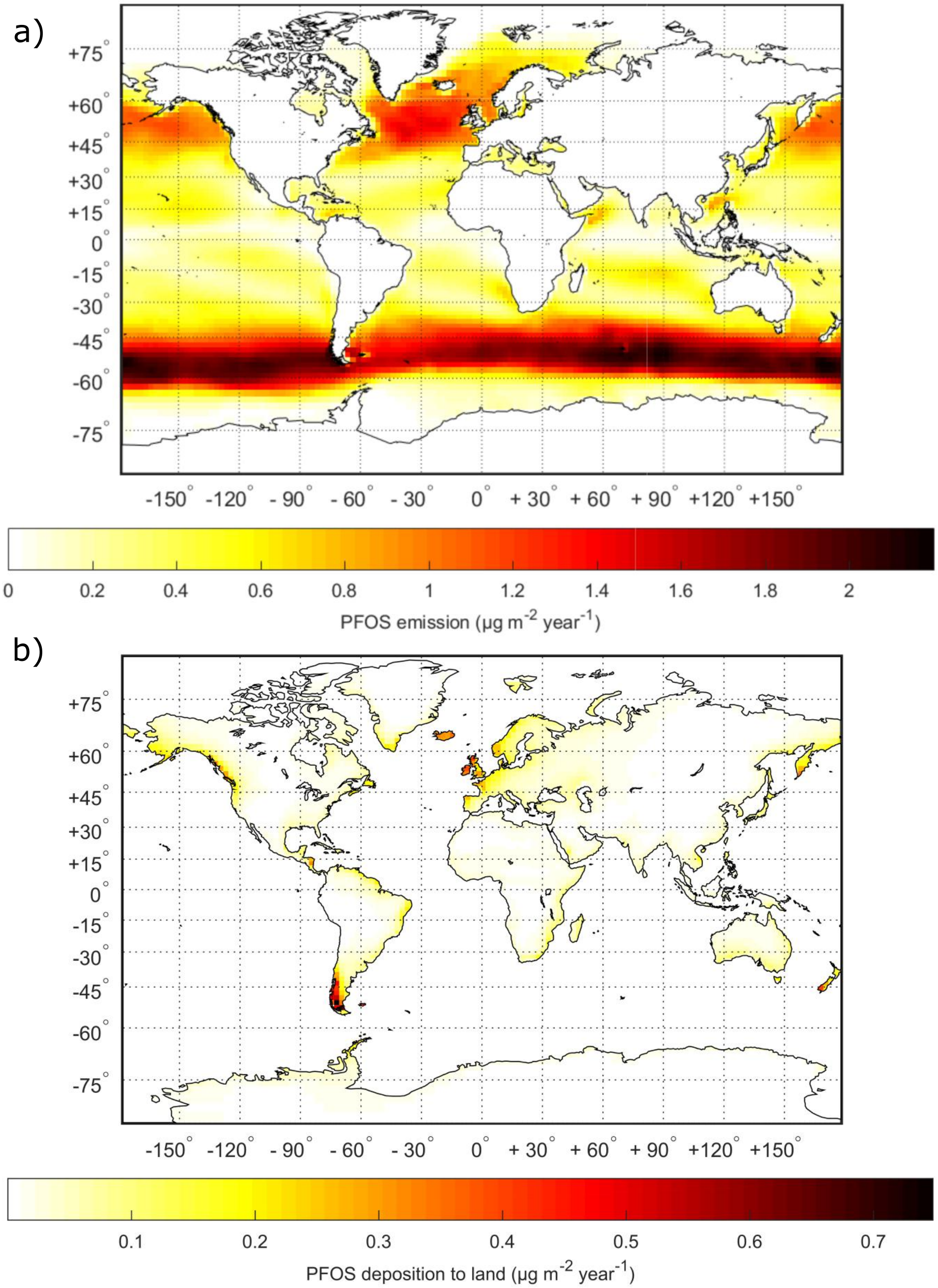

Figure S6: Global maps of **(a)** total yearly emissions of PFOS via SSA and **(b)** total yearly deposition of PFOS transported to terrestrial environments by SSA.

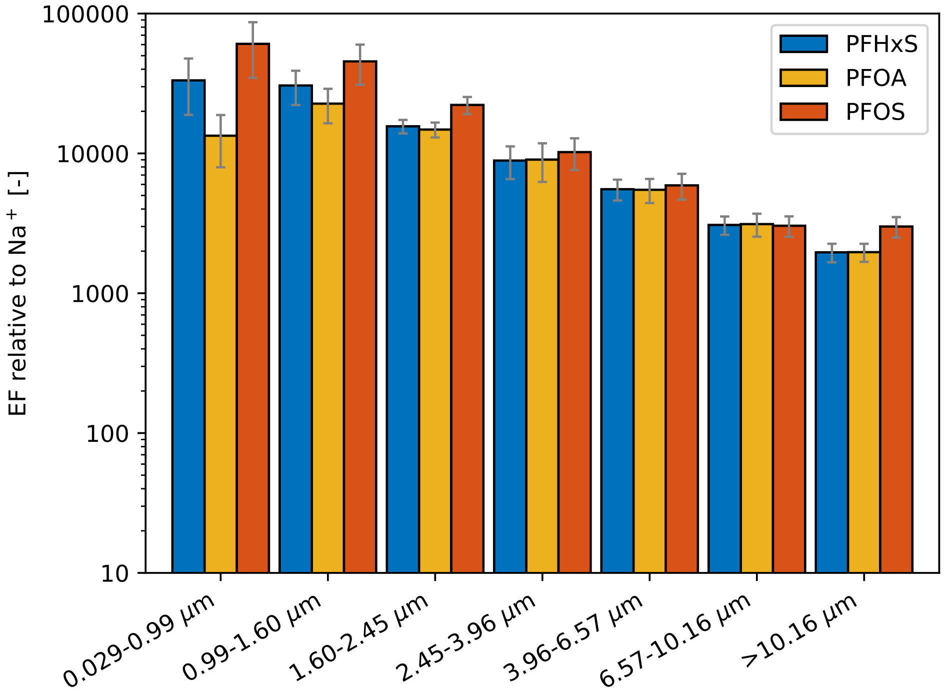

Figure S7: Aerosol enrichment factors in Experiment B (only linear homologues reported)

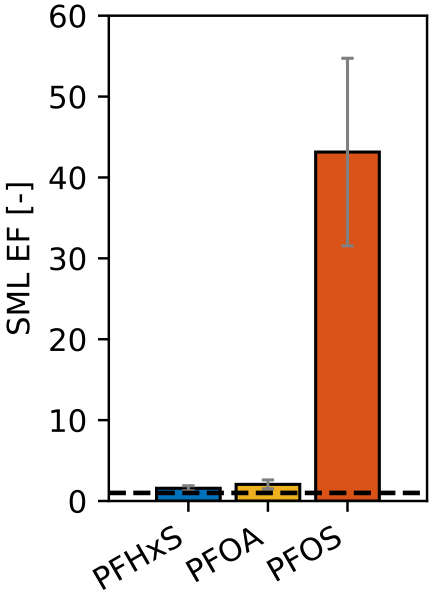

Figure S8: SML EFs in Experiment B (only linear isomers reported)

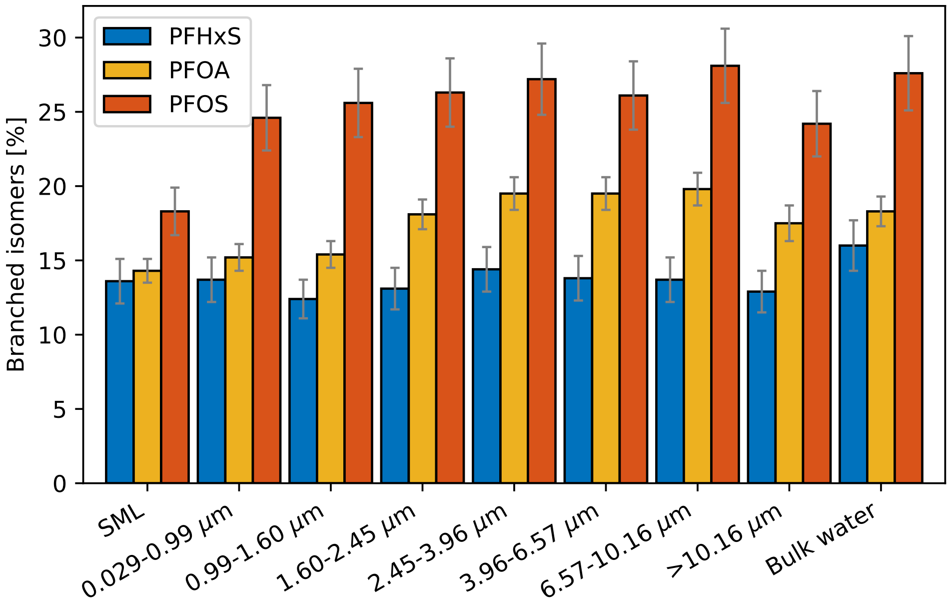

Figure S9: Contribution of the sum of branched isomers (%) to the overall concentration of PFOA, PFHxS and PFOS in Experiment B. The error bars represent the analytical measurement error, as this was greater than the standard deviation from the triplicate experiments.

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