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DETERMINATION OF THE LONG-RANGE ATMOSPHERIC TRANSPORT POTENTIAL OF PERFLUOROALKYL ACIDS ASSOCIATED WITH SEA SPRAY AEROSOLS

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Introduction

Perfluoroalkane sulfonic acids and perfluoroalkyl carboxylic acids consist of fully fluorinated carbon chains (C3-C16) linked to a sulfonic or carboxylic acid group (1). These substances belong to the family of perfluoroalkyl acids (PFAAs), which are persistent anthropogenic chemicals ubiquitous in environments and biota all over the world (2-4). Findings suggest that long-range atmospheric transport may be substantial (5-7), but it is currently not known what the main sources of atmospheric PFAAs are or how the compounds are transported in the atmosphere.

PFAAs are present throughout the world's oceans (8), which are currently assumed to be final sink of PFAAs in the environment (9, 10). Sea spray aerosols (i.e. small droplets ejected from the ocean into the atmosphere) have been suggested as a potential source of PFAAs to the atmosphere (11, 12). The major source of sea spray aerosols is bubble bursting at the ocean surface (13). Air is entrained into the water mainly through the action of breaking waves caused by wind-drag on the ocean surface (14). While air bubbles are rising to the surface, organic material in the bulk water of biogenic (15-17) and anthropogenic origin (18) associates itself with the walls of the bubbles. Once the bubbles reach the ocean surface and burst, the organic material concentrated on the bubble walls is injected with the aerosol into the atmosphere.

Strong enrichment of PFAAs in laboratory generated bubble-bursting aerosols (relative to their bulk water concentration) has been shown previously (11, 12). However, although these studies showed that transport of PFAAs on aerosols generated by bubble bursting is possible, they did not quantify the environmental importance of this process. Our study repeats these initial laboratory studies at more environmentally realistic experimental conditions. Specifically, we have used artificial seawater in these experiments rather than the tap water that was used in previous work (12). Furthermore, the target concentration of PFAAs in our experiments was 1 ng/L. This concentration represents the upper bound of environmental sea water concentrations reported for the open oceans (8), but is an order of magnitude lower than that used in previous experiments (12).

The apparatus in Fig. 1 has been augmented with a low pressure impactor (LPI) to allow the separation of aerosols into different size fractions. This enables the determination of the size fraction of aerosols that the PFAA's are predominantly enriched in. Such information is key to predicting the atmospheric long-range transport potential of pollutants attached to sea spray aerosols. Specifically, our experiments allow us to test the hypotheses: (i) that PFAAs that are transported from seawater to air are associated with those sea spray aerosols that have a size that facilitates long-range atmospheric transport, and (ii) that the global cycling of PFAAs is currently largely misinterpreted due to the omission of sea spray aerosol transport processes in global transport models.

Materials and Methods

We have used a sea spray chamber developed by Salter et al. (19) (Fig. 1). The sea spray chamber is a closed system that can be used for controlled experiments in the laboratory. It has been shown that the system can produce a bubble size distribution very similar to that found in breaking waves (19). In order to generate aerosols, water was pumped through the lid creating a water jet which impinged on the water surface, forming bubbles of different diameter and ultimately water spray aerosols. Also shown in Fig. 1 is the 13-stage (30 L min-1) LPI (Dekati) that was used to determine the bulk chemical composition of the sea spray particles generated in the chamber as a function of particle size.

The chamber was filled with 100 L artificial sea water (absolute salinity 35 g/kg). The water was then spiked with 250 µL of a 400 pg/µL PFAA mix (MPFAC-MXB from Wellington Laboratories). The sea

spray generator was operated for approximately 12 h while the generated aerosols were continuously sampled. The experiment was repeated four times with the same spiked seawater sample. Before and after each repetition bulk water was sampled through a tap located on the side of the chamber approximately halfway between the water surface and the bottom of the chamber.

Polycarbonate collection foils (Whatman, Nuclepore Track-Etch Membrane) were used to collect the aerosols in the impactor. Following removal from the impactor these were spiked with isotope-labeled internal standard, placed in a polypropylene tube with 10 mL of MilliQ water and extracted in an ultrasonic bath during 60 minutes. The collection foils from impactor stages 9 to 13 were extracted individually while those collection foils from stages 1 to 8 were pooled in order to achieve quantifiable concentrations in the final extracts. 8 mL of the extracts were cleaned up on Oasis WAX solid phase extraction cartridges using a previously published method (20). The final extracts were analysed on an Acquity ultra-performance liquid chromatography system coupled to a Xevo TQ-S tandem mass spectrometer (UPLC/MS/MS) according to a previously published method (21). The target analytes were perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorohexane sulfonic acid (PFHxS) and perfluorooctane sulfonic acid (PFOS).

A 2 mL aliquot of the extracts was taken out for quantification of the major ionic constituents which was conducted by chemically suppressed ion chromatography (IC; Dionex ICS-2000). Further details on this method was described by Leck et al. (22).

Results and discussion

The total transfer from bulk water to aerosols increased linearly with homologue chain length and ranged from 0.20% for PFHxA to 1.8% for PFDA. The percent transfer from the bulk seawater to aerosols of different diameters is displayed in Fig. 2. All substances displayed a similar pattern, reflecting the mass size distribution of the sea spray aerosol generated in the chamber.

Future analysis of the inorganic ions in the extracts from each impactor stage of each experiment will allow derivation of enrichment factors for the PFAA's in the aerosol. Classically, the enrichment factor, EF, is defined as the ratio of the concentration of the substance X to the concentration of one of the major constituents of seawater in the particle such as sodium ($Na+$) to the same ratio for bulk seawater.

We hypothesise that the smallest aerosols were the most highly enriched in PFAAs in accordance with recent measurements of other carboxylic acids (23). Preliminary calculations based on the data from Table 1 suggest that the enrichment factors span from 2000 (PFHxA) to 10000 (PFOS) for aerosols <1.6 μm. In the absence of precipitation, particles in this size range may have a residence time in the atmosphere of several days to a month (24) meaning that they may be transported thousands of kilometers in the atmosphere. Aerosols with a diameter larger than ~3μm have atmospheric lifetimes of less than a day and are unlikely to be of importance for long-range atmospheric transport (24). For smaller aerosols (aerosol diameters <1.6 μm), the efficiency of transfer to the aerosol from the seawater increased as the PFAA chain length increased and was more efficient for perfluoroalkane sulfonic acids than for perfluoroalkyl carboxylic acids. The transfer was 0.09% and 0.2% for PFOA and PFOS respectively.

These experimental results support previous studies in suggesting that the oceans can act as a potentially significant source of PFAAs to the atmosphere. In addition to this our results show that PFAAs are associated with those smaller sea spray aerosols that can be transported with air masses over long distances. Future work in our group will evaluate the magnitude of sea spray aerosol-mediated transport based on typical atmospheric residence times of the different aerosol size fractions. This will enable a comparison of the importance of this pathway in relation to other sources of PFAAs to the atmosphere.

References

1. Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, de Voogt P, et al. (2011) Integrated Environmental Assessment and Management. 7(4):513-41.
2. Giesy JP, Kannan K. (2001) Environmental Science & Technology. 35(7):1339-42.

3. Houde M, Martin JW, Letcher RJ, Solomon KR, Muir DCG. (2006) Environmental Science & Technology. 40(11):3463-73.
4. Lau C, Anitole K, Hodes C, Lai D, Pfahles-Hutchens A, Seed J. (2007) Toxicological Sciences.99(2):366-94.
5. Wang X, Halsall C, Codling G, Xie Z, Xu B, Zhao Z, et al. (2013) Environmental science & technology. 48(1):173-81.
6. Young CJ, Furdui VI, Franklin J, Koerner RM, Muir DCG, Mabury SA. (2007) Environmental Science & Technology. 41(10):3455-61.
7. Benskin JP, Phillips V, St. Louis VL, Martin JW. (2011) Environmental Science & Technology. 45(17):7188-94.
8. Yamashita N, Kannan K, Taniyasu S, Horii Y, Petrick G, Gamo T. (2005) Marine pollution bulletin. 51(8):658-68.
9. Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH. (2006) Environmental Science & Technology. 40(1):32-44.
10. Armitage JM, Schenker U, Scheringer M, Martin JW, MacLeod M, Cousins IT. (2009) Environmental Science & Technology. 43(24):9274-80.
11. McMurdo CJ, Ellis DA, Webster E, Butler J, Christensen RD, Reid LK. (2008) Environmental Science & Technology. 42(11):3969-74.
12. Reth M, Berger U, Broman D, Cousins IT, Nilsson ED, McLachlan MS. (2011) Environmental Chemistry. 8(4):381-8.
13. Blanchard DC. (1983) Springer. p. 407-54.
14. Woodcock A, Kientzler C, Arons A, Blanchard D. 1953.
15. Mochida M, Kitamori Y, Kawamura K, Nojiri Y, Suzuki K. (2002) Journal of Geophysical Research. 107(D17).
16. O'Dowd CD, Facchini MC, Cavalli F, Ceburnis D, Mircea M, Decesari S, et al. (2004) Nature. 431(7009):676-80.
17. Facchini MC, Rinaldi M, Decesari S, Carbone C, Finessi E, Mircea M, et al. (2008) Geophysical Research Letters. 35(17).
18. Cincinelli A, Stortini A, Perugini M, Checchini L, Lepri L. (2001) Marine Chemistry. 76(1):77-98.
19. Salter ME, Nilsson ED, Butcher A, Bilde M. (2014) Journal of Geophysical Research. 119(14):9052-72.
20. Löfstedt Gilljam J, Leonel J, Cousins IT, Benskin JP. (2015) Environmental science & technology.
21. Vestergren R, Ullah S, Cousins IT, Berger U. (2012) Journal of Chromatography A.
22. Leck C, Svensson E. (2015) Atmospheric Chemistry and Physics. 15(5):2545-68.
23. Cochran RE, Jayarathne T, Stone EA, Grassian VH. (2016) The journal of physical chemistry letters.
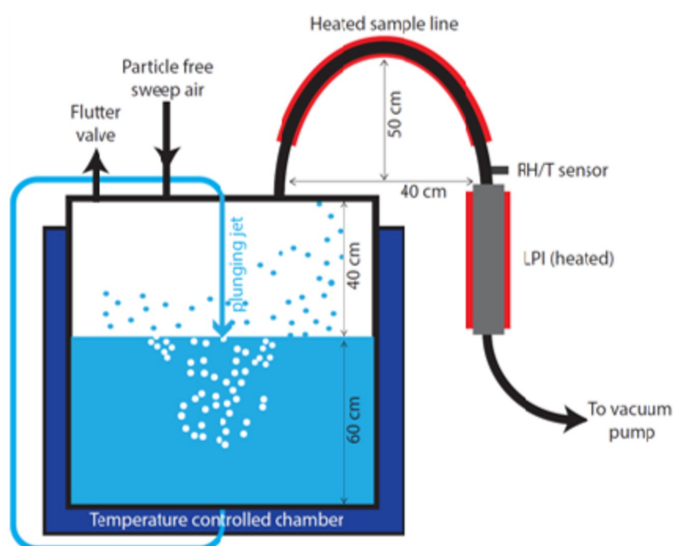24. Slinn S, Slinn W. (1967) Atmospheric Environment. 1980;14(9):1013-6.

Fig. 1. Schematic drawing of the sea spray chamber and aerosol sampling used in the experiments.
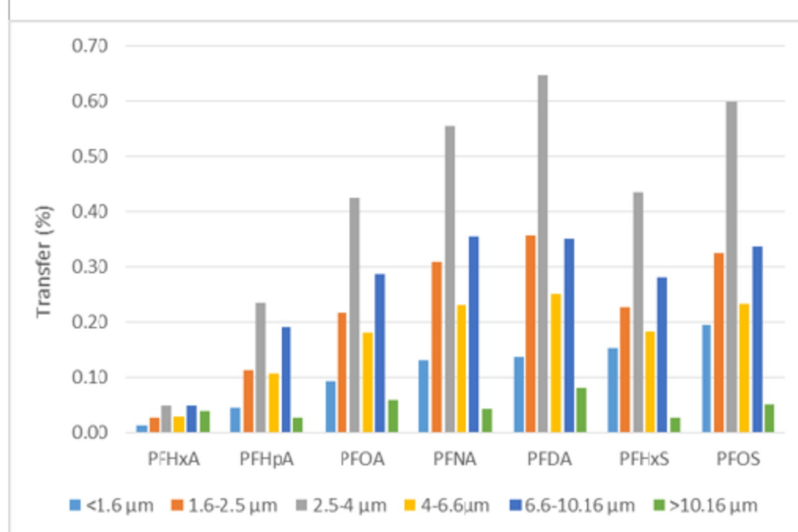

Fig. 2. Percent transfer from bulk water to impactor stages representing different aerosol diameters.