Accessory publication

Water-to-air transfer of perfluorinated carboxylates and sulfonates in a sea spray simulator

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Aerosol size distribution

In Fig. A1, the median aerosol volume size distribution from the sea spray simulator is shown in order to visualise the approximate size distribution of aerosol mass. The aerosol size distribution created was measured with a DMPS (Differential Mobility Particle Sizer) and an OPC (Optical Particle Counter) (Grimm GmbH, model 7.309), together covering the range between 0.02 μm up to 2.2 μm D_p. The custom-made DMPS system consisted of a CPC Condensation Particle Counter (Model TSI 3010, TSI Inc.) together with a differential mobility analyser operated with closed loop sheath air,[1] delivering aerosol size distribution between 0.02 and 0.25 μm in 15 bins. The OPC (Grimm GmbH, model 7.309) measured the aerosol size distribution in 12 channels between 0.26 and 2.2 μm. The size distribution was compensated for loss of small particles due to Brownian motion and for sedimentation of large particles due to the long, horizontal, sampling line needed (3 m). The spectrum in Fig. A1 was measured in North Atlantic seawater.[2] In this case, the set-up involved a continuous water flow out of the tank as in Fig. 1a in the main manuscript. The flow of water used to create the aerosol was high, 20 L min^{-1}, resulting in a high average aerosol flux of 5.6×10^6 particles m^{-2} s^{-1}. It can be seen that the aerosol volume (and hence mass) is dominated by particles >0.2-μm diameter. In addition, a substantial amount of aerosol mass was likely above the upper range of the OPC. Traditionally, super-micrometre particles have been attributed to jet drops, and sub-micrometre to film drops.

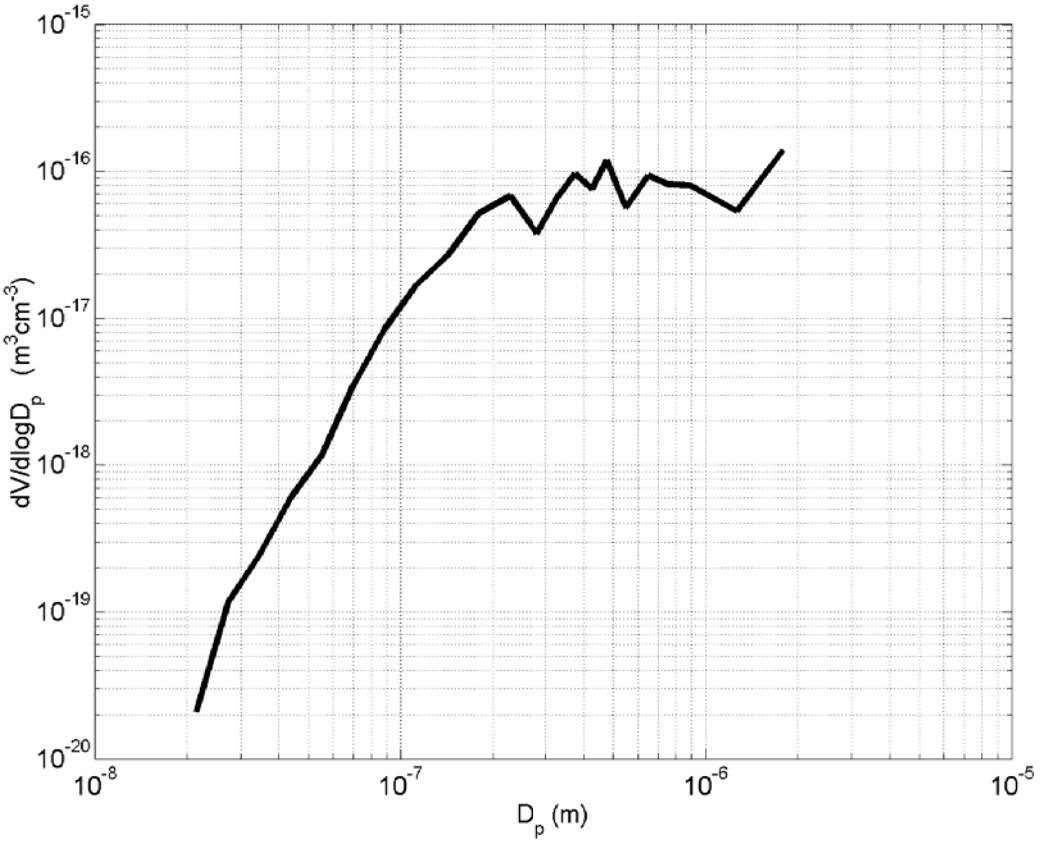

Fig. A1. Aerosol volume size distribution produced in the sea spray generation apparatus using North Atlantic seawater.[2] D_p is the dry aerosol diameter.

Analytical methods

Standards and solvents

The native analytical reference standards and recovery standards (RSTDs) including their abbreviations are listed in Table A1. They were purchased through Sigma-Aldrich (Sweden), Fluka (Switzerland), ABCR (Germany) or Interchim (France) respectively. The mass-labelled internal standards (ISTDs) are also listed in Table A1. $^{13}C_4$–PFOA and $^{13}C_2$–PFDA were obtained from Wellington Laboratories (Canada) and $^{18}O_2$–PFOS was kindly provided by the 3M company. Methanol Mulitsolvent was obtained from Scharlau (Spain). Formic acid p.a. and ammonium acetate p.a. were purchased from Merck (Germany). Water was obtained from a Milli-Q water purification unit (Millipore AB, Sweden).

Table A1. Target analytes with abbreviations, monitored transitions as well as collision energies and sample cone voltages

Compound	Obtained as	Abbreviation	Precursor ion (m/z)	Product ion (m/z)	Collision energy (eV)	Cone voltage (V)
Perfluorohexanoate	Acid	PFHxA	312.9	268.9	9	20
Perfluoroheptanoate	Acid	PFHpA	362.9	318.9	9	23
Perfluorooctanoate	Acid	PFOA	412.9	368.9	10	25
Perfluorononanoate	Acid	PFNA	462.9	418.9	12	25
Perfluorodecanoate	Acid	PFDA	512.9	468.9	13	25
Perfluoroundecanoate	Acid	PFUnA	562.9	518.9	15	25
Perfluorododecanoate	Acid	PFDoA	612.9	568.9	13	25
Perfluorotetradecanoate	Acid	PFTeDA	712.9	668.9	13	25
Perfluorohexane sulfonate	Potassium salt	PFHxS	398.9	80.0	64	55
Perfluorooctane sulfonate	Potassium salt	PFOS	498.9	80.0	77	57
Perfluorodecane sulfonate	Ammonium salt	PFDS	598.9	80.0	80	67
Internal standards (ISTDs)						
$^{13}C_4$–Perfluorooctanoate	Acid	$^{13}C_4$–PFOA	416.9	371.9	10	25
$^{13}C_2$–Perfluorodecanoate	Acid	$^{13}C_2$–PFDA	514.9	469.9	13	25
$^{18}O_2$–Perfluorooctane sulfonate	Ammonium salt	$^{18}O_2$–PFOS	502.9	84.0	77	57
Recovery standards (RSTDs)						
3,5-Bis(trifluoro-methyl)phenyl acetate	Acid	3,5-BTPA	270.9	226.9	10	30
7H-Perfluoroheptanoate	Acid	7H-PFHpA	344.9	280.9	9	23

Water analysis

Water samples were directly analysed by HPLC/ESI-MS/MS after large volume injection and on-line pre-concentration using a column switching system described in Holm et al.[3] The samples were prepared as follows. A volume of 40 mL of water was filtrated through a syringe filter (GHP Acrodisc Minispike, 0.45 µm, 13 mm, PP, Waters, USA) and spiked with 400 pg of each ISTD. Ammonium acetate (320 mM in 0.5 mL Milli-Q water) was added before the sample was split into two 20-mL aliquots, one for the analysis of C6 to C8 PFAAs and one for the analysis of C9 to C14 PFAAs. For the analysis of C6 to C8 PFAAs the pH was adjusted to 2–3 by adding 200 µL of formic acid.

Manual injections of 20 mL sample were performed. An HP Series 1050 pump (Agilent, USA) was used for sample loading (enrichment of the PFAAs) on a Chromolith trapping column (RP-18e, 4.5 × 10 mm, Merck, Germany). Milli-Q-water buffered with 4-mM ammonium acetate was used to load C6 to C8 PFAAs, whereas for C_9 to C_{14} compounds a methanol–water mixture (40 + 60) with 4-mM ammonium acetate was employed. The flow rate was 4.5 mL min^{-1}. After complete sample loading the columns were switched and an Alliance 2695 pump (Waters, USA) was used to deliver the mobile phase (binary gradient of water and methanol with 4-mM ammonium acetate) for back-flushing of the trapping column and PFAA separation on the analytical column (ACE 3 C18, 2.1 × 150 mm, 3 µm particles, ACT, UK). The flow rate was set to 0.15 mL min^{-1}. A Quattro II mass spectrometer (Micromass, UK) in the multiple

reaction monitoring mode was used for detection and quantification of the analytes. Monitored transitions as well as collision energy and sample cone voltages are summarised in Table A1. Further details of the HPLC/ESI-MS/MS method are given in McLachlan et al.[4]

Filter and PUF extraction

The GF/F filter (carefully folded) was placed in a 50-mL PP tube. After addition of the ISTDs (3 ng $^{13}C_4$–PFOA, 3 ng $^{18}O_2$–PFOS, and 2 ng $^{13}C_2$–PFDA) the filter was covered with methanol (~25 mL) and extracted in an ultrasonic bath for 40 min. The extract was transferred into a new PP tube and the extraction was repeated twice with 15 and 10 mL of methanol respectively. The volume of the combined extracts was reduced to 250 µL under nitrogen. Ammonium acetate (250 µL of a 4–mM aqueous solution) and the RSTDs (2.5 ng 7H-PFHpA and 2.5 ng 3,5-BTPA) were added. The extract was filtrated through a 0.45-µm GHP filter (see 'Water analysis' above) before instrumental analysis. PUF plugs were extracted analogously with the following changes. The volume of methanol in the first extraction step was 15 mL. PUFs were repeatedly centrifuged to retrieve all extraction solvent. The final filtration step was not necessary for the PUF extracts. Filter and PUF extracts were analysed on the same HPLC/ESI-MS/MS system as the water samples, but without the column switching system. Aliquots of 50 µL were injected automatically at a flow rate of 0.18 mL min^{-1}. For further details see Table A1 and McLachlan et al.[4]

Quality control

Procedural blank extractions were performed with each batch of samples for all matrices. Procedural blank contamination was not observed for any of the target analytes except for PFHxA, PFHpA and PFOA. The method limits of detection (MLDs) for these three compounds were defined as average concentration plus three times the standard deviation in the procedural blank extractions. The MLDs for all other compounds were defined using three times the baseline noise measured in procedural blank chromatograms. Method limits of quantification (defined as three times MLD) for the different target analytes were in the range 0.4–2.0 ng L^{-1} of water, 0.04–0.20 ng of filter and 0.03–0.15 ng or PUF. Recoveries of all target compounds including the ISTDs were determined by spiking experiments. They ranged between 61–113 %, 66–94 % and 84–107 % for the water, GF/F and PUF extraction method respectively.

Critical micelle concentrations

Table A2. Critical micelle concentrations (CMCs) for PFAAs reported in the literature

The medians were used for preparing Fig. 2 in the main manuscript

Compound	Number of perfluorinated carbons	Literature CMC data (M)	Median CMC
PFBA	3	0.74[5]	0.725
		0.75[6]	
		0.42[7]	
		0.71[7]	
PFPA	4	0.53[8]	0.53
PFHxA	5	0.082[7]	0.082
		0.051[7]	
		0.09[8]	
PFHpA	6	0.032[9]	0.03
		0.03[8]	
		0.025[10]	
		0.029[10]	
		0.031[10]	
PFOA	7	0.00305[9]	0.00885
		0.0091[5]	
		0.009[7]	
		0.0087[7]	
		0.0055[7]A	
		0.0055[7]A	
		0.009[11]	
		0.0087[6]	
		0.0091[12]	
		0.012[8]	
PFNA	8	0.0056[8]	0.00305
		0.00305[9]	
		0.0008[13]	
PFDA	9	0.00078[5]	0.00085
		0.00089[7]	
		0.00085[5]	
PFUnA	10	0.00048[8]	0.00048
PFOS	8	0.0060[9]	0.0031
		0.000203[14]	

[A]Although these values are identical and measured in the same study they were individual measurements conducted at two temperatures (288 and 303 K respectively).

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