Particle-size distribution of airborne poly- and perfluorinated alkyl substances

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ABSTRACT

Eleven particle-size-segregated samples were taken to investigate the particle-size distribution of perfluoroalkyl substances (PFASs) using two five stage impactors in parallel. Samples were extracted with methanol and detected by HPLC/MS–MS. Investigation yielded reproducible results for the parallel samples over the entire sampling period. Particle-size distribution varied between perfluorooctane sulfonate (PFOS) and other perfluoroalkyl sulfonates (PFSAs), perfluorooctane carboxylate (PFOA) and other perfluoroalkyl carboxylates (PFCAs) and n-methyl-perfluorooctanesulfonamido ethanol (MeFOSE). Whereas PFOA and MeFOSE were predominantly observed in smallest size fraction (<0.14 μm), maximum PFOS mass fractions were observed in the coarser size fractions between 1.38 and 3.81 μm. The reason for this different behaviour remained unclear and indicated a complex atmospheric PFAS processing and sampling which should be further investigated and optimized, respectively.

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1. Introduction

In the past, numerous studies investigated the environmental distribution and fate of poly- and perfluorinated alkyl substances (PFASs) and characterized certain PFASs as being potentially toxic, persistent, bioaccumulating and/or globally distributed. As consequence of these findings, some of these compounds have been regulated in manufacturing and use; their production was (partly voluntarily) reduced or completely ceased (European Community, 2006; US-EPA, 2006).

Modelling and measurement approaches identified the atmospheric transport as one (long-range) transport pathway enabling PFASs to reach pristine ecosystems (Cousins et al., 2011 and references therein). The occurrence of PFASs in the atmosphere was confirmed by measurement-based approaches like direct detection of PFASs in air or precipitation (Shoeib et al., 2006; Dreyer et al., 2009, 2010; Kwok et al., 2010) or indirect detection of PFASs in biota of remote lakes, peatbogs, or ice cores (Young et al., 2005; Ahrens et al., 2010; Dreyer et al., 2012; Kirchgeorg et al., 2013).

In air samples, PFASs were detected in the gas- or particle phase as far as the sampling method was capable of separating these fractions. Interestingly, the particle fraction itself was rarely further characterized although particle size is an important parameter influencing the fate of atmospherically transported compounds. Until now, only two studies investigated the particle-size distribution of airborne PFASs; both of them were source-related. Barton et al. (2006) conducted particle-size segregated sampling of perfluorooctanoate (PFOA) close to a manufacturing facility in the US and observed this compound mainly related to a particle size of <0.28 μm. Harada et al. (2006) investigated PFOA and perfluorooctane sulfonate (PFOS) in the respirable particle fractions of an urban region in Japan. They reported PFOS and PFOA mainly in the coarser fractions (>3.3 μm) and related these findings to degradation of fluorinated precursors or automobile exhausts as sources.

Information about the particle-size distribution of particle-bound PFASs is of particular interest to discuss the atmospheric transport of PFASs. Therefore, the objective of this study was to extend the knowledge about the particle-size distribution of a large spectrum of PFASs at a site without any known distinct PFAS sources. To increase the data certainty, eleven particle-size-segregated samples were taken in parallel and analysed for 25 PFASs. Results of this study may also help to further evaluate passive air sampling data since certain passive samplers (PAS), e.g. polyurethane foam (PUF) based PAS, may also sample substantial amounts of small particles.

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2. Method

2.1. Sampling

Samples were taken at the Helmholtz-Zentrum Geesthacht, Geesthacht, Germany (53° 24′ 31″ N, 10° 25′ 40″ E). The site has a semirural character and is characterized by winds coming predominantly from westerly directions. Particle-size-segregated sampling was conducted at environmental conditions and in parallel (A, B) using two cascade impactors (LPI; Berner-type, Hauke KG, Austria) (Fig. S1). The cut-off diameters to separate different particle-size classes were 11.4 μm (A4, B4), 3.81 μm (A3, B3), 1.38 μm (A2, B2), 0.46 μm (A1, B1), and 0.14 μm (back-up filter, A0, B0; Fig. S2). These cut-off diameters were chosen to still enable the detection of PFASs in particle-size-segregated samples without increasing the sampling duration too much. Back-up filters consisted of glass fibre filters (glass fibre prefilter 13440-24q, Satorius, Germany). The impaction plates (A1, B1 to A4, B4) were covered with aluminium foil (Hauke KG, Austria). Additional gels or pastes sometimes used in impactor sampling to prevent bounce-off-effects were avoided for reasons of contamination. Samples were stored at −20 °C until analysis. Impactor samples were taken continuously for periods of usually two weeks starting in December 2007 until May 2008 (Table S1). Overall, eleven parallel particle-size-segregated samples were taken.

2.2. Sample preparation

Each particle-size fraction of both samplers was extracted separately. For extraction, samples were placed into pre-cleaned 15 mL PP centrifuge tubes and spiked with 50 μL of a solution containing mass-labelled PFASs (5 ng abs.; $^{18}O_2$-PFHxS, $^{13}C_4$-PFOS, $^{13}C_4$-PFBA, $^{13}C_4$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_4$-PFNA, $^{13}C_4$-PFDA, $^{13}C_4$-PFUnDA, $^{13}C_4$-PFDoDA, $^{13}C_8$-FOSA; full names in the SI). Extraction was performed twice by ultrasonication for 15 min using 7 mL of methanol (ULTRA RESI-ANALYZED, Baker, Germany), each. After each extraction step, samples were centrifuged for 10 min at 4116 g/5000 rpm (Universal 320, Hettich, Tuttlingen, Germany). Supernatants of each sample were combined in a separate 15 mL PP centrifuge tube and evaporated to 150 μL using a gentle stream of preheated nitrogen (purity 5.5). Evaporated samples were transferred to 200 μL amber glass vials. 50 μL water:methanol 4:1 (v:v) were added for better instrumental performance.

2.3. Instrumental analysis and quantification

25 PFASs (PFBS, PFHxS, PFHpS, PFOS, PFDS, PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxDA, PFOcDA; FOSA, MeFOSA, EtFOSA, MeFOSE, EtFOSE, MeFBSA, MeFBSE; full names in the SI) were determined by high performance liquid chromatography (HPLC; HP 1100, Agilent Technologies, Waldbronn, Germany) – tandem mass spectrometry (API 3000, ABSciex, Darmstadt, Germany) using negative electrospray ionization (ESI(−)-MS/MS). Separation was conducted using a Synergi Hydro RP 80A column (Phenomenex, USA; 150 * 2 mm, 4 micron). Details on instrumental conditions are described elsewhere (Kirchgeorg et al., 2010).

Quantification was based on peak areas. Analyte concentrations were calculated with the isotope dilution method with nine point calibrations. Method quantification limits (MQL) were calculated on the basis of field blanks (2 * average blank (VDI 2464-3, 2012)) or signal to noise ratios (S/N = 10) depending on which method gave the more conservative value and were between 10 and 150 pg/sample.

2.4. Quality assurance and quality control

Gels or pastes occasionally used in impactor sampling to prevent bounce-off-effects were avoided reducing the risk of PFAS contamination. Sample preparation and extraction were conducted in a clean lab. PFAS-containing materials were avoided during sampling as well as during sample preparation, laboratory work and instrumental analysis. Glassware, non-glass items, and tables were carefully cleaned with methanol and acetone before each use. Laboratory blanks were run with each set of samples (11 blanks in total). Additionally five field blanks were taken. Mass-labelled internal standards were used to correct losses occurring during laboratory work and instrumental analyses. The standard measurement uncertainty calculated according to ISO 20988 (2007) on the basis of paired measurements ranged from 6% (FOSA) to 174% (EtFOSE). The standard uncertainty for PFOA was 41%, for PFOS 25%.

3. Results and discussion

3.1. PFAS particle phase concentrations

Eighteen of 25 PFASs were quantified at least once using impactors as sampling devices. Substances which could not be quantified were the long-chain acids PFDS, PFHxDA, and PFOcDA as well as the neutral PFASs MeFBSA, MeFBSE, MeFOSA and EtFOSA. Average concentrations (Σ particle sizes) of quantified analytes over the entire sampling period are given in Fig. 1. An average concentration of 2.8 pg m^{-3} was obtained for the total of PFASs. Among them, PFOA (0.1–4.8 pg m^{-3}; average concentration 0.7 pg m^{-3}), PFOS (0.2–3.5 pg m^{-3}; average concentration 0.65 pg m^{-3}) and MeFOSE (0.1–4.4 pg m^{-3}; average concentration 0.67 pg m^{-3}) were observed at highest concentrations. Concentrations of remaining PFASs were clearly lower and these substances were less frequently quantified (Table 1). Conventional high volume (HV-)sampling conducted at the same site (Dreyer et al., 2009) yielded slightly lower average values for most of the investigated PFASs (Fig. 1), however, concentrations were principally in the same order of magnitude. The differences most obviously affected PFOA and MeFOSE. Adsorption of certain vapour-phase PFASs to glass fiber filters was described in the past (Arp and Goss, 2008, 2009b; Barton et al., 2009). However, as glass fiber filters were used for both, HV-sampling and impactor sampling, and adsorption capacity is assumed to be higher for HV filters (larger filters) this process does not appear to be a likely explanation for the observed differences between both sampling methods. Instead, observed deviations may have been a result of different glass fibre filters used for sampling. Whereas filters used for conventional HV-sampling allow penetration of particles starting with a particle size of 0.3 μm (Macherey-Nagel, 2013) back-up filters used for impactor sampling are capable of collecting smaller particles (smallest particle size not known, Satorius, 2013). This may imply that e.g. PFOA (in contrast to PFOS) is attached to very small particles and passed the HV-filter but not the impactor filter (average PFOA concentrations: impactor stages 0–4: 0.75 pg m^{-3}; impactor stages 1 to 4 (i.e. >1.4 μm): 0.22 pg m^{-3}; high volume sampler: 0.23 pg m^{-3}). This explanation is corroborated by our particle-size distribution results (see below).

3.2. PFAS particle-size distribution

On the basis of the results presented above, we decided to discuss the particle-size distributions of the main analytes PFOA, PFOS and MeFOSE in detail. For these analytes, particle-size distributions were calculated on the basis of concentrations and are presented in Fig. 2. For the remaining PFASs, which are those PFASs occurring at