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Atmospheric concentrations and gas/particle partitioning of neutral poly- and perfluoroalkyl substances in northern German coast

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HIGHLIGHTS

- Most of PFASs species exist in the gas phase.
- Atmospheric PFASs in Büsum were from the long range atmospheric transport.
- Gas/particle partitioning of neutral PFASs agreed with the $\log K_{SP}-\log p^{\circ}_{L}$ relation.

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ABSTRACT

Total 58 high volume air samples were collected in Büsum, Germany, from August 2011 to October 2012 to investigate air concentrations of 12 per- and polyfluoroalkyl substances (PFASs) and their gas/particle partitioning. The total concentration (vapor plus particle phases) of the 12 PFASs (ΣPFASs) ranged from 8.6 to 155 pg/m^3 (mean: 41 pg/m^3) while fluorotelomer alcohols 8:2 (8:2 FTOH) dominated all samples accounting for 61.9% of ΣPFASs and the next most species were 10:2 FTOH (12.7%). Air mass back trajectory analysis showed that atmospheric PFASs in most samples were from long range atmospheric transport processes and had higher ratios of 8:2 to 6:2 FTOH compared to the data obtained from urban/industrial sources. Small portion of particle PFASs in the atmosphere was observed and the average percent to ΣPFASs was 2.0%. The particle-associated fractions of different PFASs decreased from perfluorooctane sulfonamidoethanols (FOSEs) (15.5%) to fluorotelomer acrylates (FTAs) (7.6%) to perfluorooctane sulfonamides (FOSAs) (3.1%) and FTOHs (1.8%), indicating the functional group obviously influenced their gas/particle partitioning. For neutral compounds with acid dissociation constant (pK_a) > 7.0 (i.e., FTOHs, FOSEs and FOSAs), a significant log-linear relationship was observed between their gas/particle partition coefficients (K_{SP}) and vapor pressures (p°_{L}), suggesting the gas/particle partitioning of neutral PFASs agreed with the classical $\log K_{SP}-\log p^{\circ}_{L}$ relation. Due to the pK_a values of 6:2 and 8:2 FTA below the typical environmental pH conditions, they mainly exist as ionic form in aerosols, and the corrected $\log K_{SP}$ (neutral form) were considerably lower than those of FTOHs, FOSEs and FOSAs with similar vapor pressures. Considering the strong partitioning potential to aqueous phases for ionic PFASs at higher pH values, a need exists to develop a model taking account of the ad/absorption mechanism to the condensed phase of aerosols for ionizable PFASs (e.g., FTAs).

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) have been widely produced and used in high volume for several decades in a variety of consumer and industrial products (Paul et al., 2009). They have attracted scientific and regulatory scrutiny due to their potential for environmental persistence, bioaccumulation and possible adverse effects on humans and wildlife (Gewurtz et al., 2012). PFASs comprise a wide range of chemicals with different fluorocarbon chains ($CF_3[CF_2]_n$-). Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are the most well-known PFASs because of their presence in global environments and adverse effects (Lindstrom et al., 2011a,b).

Ellis et al. (2004) pointed out one of important sources of PFOS and PFOA in the environment is the degradation of neutral

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precursors, such as fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAs), perfluorooctane sulfonamides (FOSAs) and perfluorooctane sulfonamidoethanols (FOSEs). These precursors are more volatile than PFOA and PFOS, and are believed to be more importantly by diffuse sources during their manufacture, use and disposal (Paul et al., 2009). Therefore, they are more likely to release into the atmosphere and undergo long range atmospheric transport (LRAT). During the LRAT, they can be degraded to, for example PFOA and PFOS, by •OH radicals initiated oxidation (Ellis et al., 2004; Martin et al., 2006). These precursors have been detected in many field studies in the atmosphere of the North America, Europe, Asia, and the Polar areas (Butt et al., 2010; Ahrens et al., 2011b; Li et al., 2011; Ahrens et al., 2012; Vento et al., 2012).

Previous studies showed that the reaction rates with •OH radicals are quite low for these neutral PFASs, and the atmospheric residence time of FTOHs would be more than 50 d (Piekarz et al., 2007). These provide the possibility of regional and global atmospheric transport of PFASs. Recent finding supports the oxidation of volatile precursors in the atmosphere as a major source of PFOA and PFOS (Young et al., 2007). Thus, the atmospheric partitioning of these precursors between the gas and particle phases plays a key role on their abilities to undergo the LRAT and global distribution.

Previous studies indicated that sampling artifacts for PFASs would occur using conventional high volume active air sampler (Arp and Goss, 2008; Ahrens et al., 2011a). During sampling, vapor phase PFASs can adsorb to filter (blow-on sampling artifact) and compounds adsorbed on particulate matter can volatilize after collection on filter (blow-on sampling artifact). However, both effects are expected to occur simultaneously. Ahrens et al. (2011a) investigated the influences of sampling artifacts and found a negligible influence on the gas/particle partitioning of the FTOHs, FTAs, FOSAs and FOSEs. Arp and co-workers (Arp et al., 2008a,b; Arp and Goss, 2009a,b) discussed the gas/particle partitioning behavior of apolar, polar and ionizable organic compounds including perfluorocarboxylic acids and developed a model taking into account the ambient relative humidity (RH) and acid dissociation constant (pK_a). PFASs are occurring generally in their neutral form in air, however, they would change into ionic forms under the specific pH condition when they partition to the particle, especially on the wet particles (aqueous aerosols). Thus, the dissociation and partitioning extent of PFASs to the atmospheric particles rely on the pK_a and the pH condition. Arp and Goss (2009b) pointed out that the gas/particle partition coefficient (K_{SP}) can be estimated by their molecular structure descriptors. Pankow (2003) proposed a unified modeling framework for gas/particle partitioning of neutral and ionizing compounds to single and multi-phase aerosol particles, which involved the vapor pressure of compound as a pure liquid (subcooled if necessary) at the temperature of interest ($p^o{}_L$). The K_{SP} and $p^o{}_L$ do agree with the classical Junge–Pankow model for nonpolar, nonionizable semi-volatile organic compounds (SVOCs) (Wang et al., 2013). For PFASs, previous studies indicated that the variation of the particle phase percentages for different species was likely owing to the changes of vapor pressure with different chain length for the neutral forms (Vierke et al., 2011; Ahrens et al., 2011c, 2012). However, few data are available for atmospheric PFASs, in particular for data on their gas/particle partitioning. Therefore, robust data sets of polar/ionizable compounds (e.g., PFASs) were needed to verify and improve the existing gas/particle partitioning models, which will promote the understanding of the LRAT, deposition, and overall fates of PFASs in the atmospheric environment.

In the present study, the gas and particle phase samples were collected simultaneously for one year at the weather station in Büsum, a seaside village in northern Germany. The concentrations of four PFAS classes (i.e., FTOHs, FTAs, FOSAs and FOSEs) were determined separately for gas and particle phase. Their gas/particle partitioning behavior and the relation to their $p^o{}_L$ were investigated and discussed. This will contribute new information to help address the partitioning of PFASs to particle and yield new insights into their environmental fates.

2. Materials and methods

2.1. Air sampling

Sampling campaign was conducted from August 3, 2011 to October 2, 2012 at the seaside village Büsum (54.13°N, 8.88°E), Germany (Fig. 1), and a total of 58 samples were collected. Air sample (about 2800 m^3 over 7 day periods) was collected using a high-volume air sampler. A glass fiber filter (GFF, pore size: 0.7 μm) and a self-packed polyurethane foam (PUF)/XAD-2 cartridge (PUF: φ5.0 cm × 2.5 cm; 35 g XAD-2, particle size: 0.3–1.0 mm) were simultaneously employed to collect particle and gas phase separately. Field blanks of GFFs and PUF/XAD-2 cartridge were collected by exposure them for 1 min at the sampling site and treated in the same way as real samples. Both PUF/XAD-2 cartridge and filters were stored until analysis at −20 °C. Detailed information on the sampling dates, air volume, total suspended particulate (TSP) and the average temperature for each sample are listed in Table S1.

2.2. Sample preparation and analysis

Prior to extraction, PUF/XAD-2 cartridge and GFFs were spiked with 2.5 ng of mass-labeled surrogate standards (FTOH (M+5) 6:2, 8:2 and 10:2, MeFOSA D3, EtFOSA D5, MeFOSE D7 and EtFOSE D9). PUF/XAD-2 and GFF were extracted with the modified Soxhlet apparatus (MX extractor, specially designed for the self-packed PUF/XAD-2 cartridge) for 16 h using dichloromethane (DCM) separately. Extracts were concentrated to approximately 2 mL using hexane as keeper and passed over 3 g Na_2SO_4 to remove residual water. Samples were further evaporated to 200 μL and spiked with 10 μL of 100 pg/μL 9:1 FTOH as internal standard.

The instrumental analysis was described in detail elsewhere (Dreyer et al., 2008). Briefly, analysis was performed using an Agilent 6890 gas chromatograph coupled with an Agilent 5973 mass spectrometer in selective ion monitoring (SIM) mode with positive chemical ionization (PCI) mode with methane as reagent gas. Analytes were separated on 60 m SUPELCO WAX® 10 column (60 m × 0.25 mm × 1.0 μm). Helium was used as carrier gas at a flow rate of 1.3 mL/min and the injection volume was 2.0 μL in the pulse splitless mode. The temperature program was as follows: initial temperature 50 °C hold for 2 min, increased to 70 °C at a rate of 3 °C/min, then increased at a rate of 10 °C/min to 130 °C, 20 °C/min to 220 °C and 120 °C/min to 275 °C, then held for 5 min. Finally, the temperature changed to 270 °C at the rate of 10 °C/min and held for 10 min. The full names, abbreviations and their other detailed information of the 12 compounds determined in this study are summarized in Table 1. The response factors were calculated from the calibration curves based on the ratio between the target compound and the corresponding surrogate.

2.3. Quality assurance and control

All PUF and XAD-2 were pre-cleaned with solvents and GFFs were baked at 450 °C for 12 h prior to their usage. The cartridges were protected against UV-sunlight during sampling using aluminum foil in order to avoid the degradation of the target compounds. Details of the breakthrough tests were given elsewhere (Xie et al., 2013). Method detection limits (MDLs) were derived from mean blank values plus three times the standard deviation (Table 1).