AIR-WATER PARTITIONING OF PERFLUORINATED CARBOXYLIC AND SULFONIC ACIDS AT A WASTEWATER TREATMENT PLANT

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Introduction

Perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs) belong to the group of per- and polyfluorinated chemicals (PFCs). Due to their unique properties they are used in various industrial and consumer products. At the same time they are persistent, bioaccumulative and toxic and are detected in various environmental media. The most widely investigated compounds in these classes are perfluorooctane carboxylic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). Implementation of regulatory measures and/or voluntarily phase outs of PFOA and PFOS have resulted in a reduction of their production and replacement by other PFCAs and PFSAs. Furthermore, precursors, which may degrade to PFOA, PFOS and other PFCAs and PFSAs, are still in use.

The detection of PFCAs and PFSAs in remote regions such as the Arctic has raised questions about their transport pathways and sources. The relative importance of oceanic transport of the conjugate bases of PFCAs and PFSAs versus atmospheric transport of volatile precursors like fluorotelomer alcohols is discussed in the literature[1, 2]. The atmospheric transport of the neutral PFCAs has also been demonstrated[3, 4]. In order to better understand the relevance of the different transport pathways, greater knowledge of the partitioning behavior between air and water is crucial. However, so far only laboratory-scale and modeling studies are available and field studies investigating these processes at the point of emission are rare. One study investigated the air-water partitioning behavior in rain[5] and another study calculated fluxes from water to air[6]. A wastewater treatment plant (WWTP) was shown to be a source for PFCs into the atmosphere[7].

The objective of this study was to investigate the air-water transfer and partitioning behavior of PFCAs and PFSAs at an aeration tank and secondary clarifier at a WWTP by collecting coupled air and water samples. The air-water partitioning coefficient (Q_{AW}) of PFCAs and PFSAs was calculated and interpreted based on measured and estimated pK_a values that are published in the literature. The pK_a plays a key role in the air-water exchange process for ionizable chemicals.

Materials and methods

This study focused on the C_4–C_{12} and C_{14} PFCAs and C_4, C_6, C_8, C_{10} PFSAs present in the gas-phase and aqueous dissolved phase. Air and water sampling was conducted concurrently at an aeration tank and a secondary clarifier at a WWTP in Ontario, Canada, in April 2010. In total, six water samples were collected (three from each tank, 1 L grab samples) using a precleaned bucket attached to a pole. Furthermore 24 air samples were collected (12 from each site, as part of a longer term air study)[8], although for the purpose of comparing with water concentrations, only three air sampling periods will be used that coincide with the timing of the water sampling. Air samples (24h, ~140 m^3) were collected using high volume samplers positioned at the perimeter of the aeration and secondary clarifier tanks, approximately 2-3 m above the water surface. The air sampling train comprised a glass fibre filter (GFF) for capturing the particulate phase and a PUF/XAD/PUF cartridge for the gas-phase.

Extraction of the PUF/XAD/PUF cartridges was done by Soxhlet using petroleum ether followed by methanol; the petroleum ether fraction was not analysed for the present study. GFF extracts were also not analysed. Filtered water samples (using glass microfiber filters (Whatman, 4.7 cm diameter)) were extracted on WAX-cartridges (OASIS WAX 6 cc 150 mg 30 μm)[9]. Extracts were concentrated by rotary evaporation and nitrogen blow down. For final cleaning of air sample extracts, acetic acid and EnviCarb (100-400 mesh, Supelco) was used.

Instrumental analysis was performed using high pressure liquid chromatography tandem mass spectrometry (HPLC-MS/MS) in the electrospray negative ionisation mode. For quantification and quality control, all samples were fortified with mass-labeled internal standards prior to extraction.

Blanks for air (n=5)[8] were collected by inserting the sampling media in the sampler for 1 min. Blanks were processed as real samples and all air sampling data were blank-corrected prior to reporting. Water blanks based on HPLC-grade water are currently being analysed and blank correction for water concentrations will follow. The sensitivity of the analysis approach was assessed by performing an IDL-type calculation on blank extracts. In the case of water, extracted tap water was used for the determination of IDLs. The instrument response in air blank samples and tap water was extrapolated to a concentration that would give a S/N value of three. IDL values were then converted to concentrations by dividing by average air and water sample volumes.

Results and discussion

The IDL values were 0.01 to 0.5 ng L^{-1} in the dissolved phase. Blank concentrations and IDLs for air are reported elsewhere[8] and ranged from not detected to 7 pg m^{-3} and from 0.005 to 0.1 pg m^{-3}, respectively.

Air and water concentrations (gas-phase and dissolved phase, respectively)

Results for air have been reported previously[8]. Briefly, mean gas-phase concentrations for the sum of PFCAs and PFSAs was 69 pg m^{-3} at the aeration tank and 34 pg m^{-3} at the secondary clarifier (n=12 from each site). The highest concentrations at the aeration tank (> 10 pg m^{-3}) were found for C_4, C_6 and C_8 PFCAs followed by C_5, C_7 PFCA and C_8 PFSA (> 5 pg m^{-3}). In water, PFOS showed the highest mean concentrations with 1800 ng L^{-1} at the aeration tank and 700 ng L^{-1} at the secondary clarifier (n=3, respectively). The mean of the sum of all other PFCs in the dissolved phase was 140 ng L^{-1} at the aeration tank and 130 ng L^{-1} at the secondary clarifier (n=3, respectively).

Calculation of air-water partitioning quotients.

In the dissolved phase, neutral (HA) and ionic (A^-) species of PFCAs and PFSAs are in equilibrium. Therefore the measured concentration (c(total)) in the dissolved phase is the concentration of HA (c(HA)) and A^- (c(A^-)). The water concentration of the neutral species can be calculated using the following equation:

Equation (1) $c(HA) = (c(total))/(1+10\text{^}(pH-pK_a))$

The air-water partitioning coefficient, K_{AW}, calculated as the ratio of concentration in air (gas phase) and in water (dissolved phase) applies to the neutral acids, PFCAs and PFSAs. This is because the ionized form of the PFCAs and PFSAs are not expected to be present in the atmospheric gas-phase due to their low vapor pressures[5]. Thus, if PFCAs or PFSAs are detected in the gas phase of the atmosphere it is assumed to be the neutral acids. For the purposes of this study we use an air-water partitioning quotient (Q_{AW}) in lieu of K_{AW} due to uncertainty of whether or not the air-water system is in equilibrium. In the case of the aeration tank, we expect near-equilibrium between air and water given the rapid mass-transfer (water-to-air transfer) associated with the aeration process; whereas the calm conditions at the secondary clarifier are likely to result in a situation where there is substantial departure from equilibrium reflected by lower air concentrations relative to concentrations in water.

For the current study, the pH of the wastewater was ~7.5 in both tanks. The literature values of pK_a for PFCAs and PFSAs are quite variable and based on either experimental data[10] (mostly for PFOA [11, 12, 13]) or estimated [14, 15, 16, 17]. For PFSAs, the pK_a values ranged from –5.5 to 0.14 and for PFCAs, pK_a values ranged from –0.21 (C_{14} PFCA) to 3.8 (PFOA). For PFDoDA only one pK_a value is reported in the literature and for PFHpA and PFNA all reported values are negative. The lowest and highest of these reported pK_a values were used to calculate a range of neutral species water concentrations using Eq. 1. The resulting concentrations of neutral species and Q_{AW} values ranged up to five orders of magnitude.

Preliminary results for mean Q_{AW} values are shown in Table 1. Results are not reported for PFBS, PFDS and PFTDA that were not detected in air samples. These data will be adjusted when blank results for HPLC-grade water become available. This will likely result in lower blank-corrected water concentrations and higher values of Q_{AW}.

Table 1: Mean Q_{AW} values for PFCAs and PFSAs at the aeration tank (n = 3). For each sample, concentrations of neutral species in the dissolved aqueous phase were calculated using Eq. 1 with a minimum and maximum reported pK_a which resulted in two Q_{AW} values for each compound ([a] mean from two samples only, n = 2, because analytes were not detected in air or were below blank levels in air).

	Aeration Tank	
	Q_{AW} (min pK_a)	Q_{AW} (max pK_a)
PFHxS	6.5×10^5	1.5
PFOS	2.1×10^4	4.8×10^{-2}
PFBA	$3.3E\times10^1$	7.9
PFPA[a]	2.4×10^1	4.4
PFHxA	5.7×10^1	5.0
PFHpA	9.1×10^1	8.3×10^1
PFOA	4.6×10^1	4.6×10^{-3}
PFNA	3.1×10^1	2.9×10^1
PFDA	1.2×10^1	1.1×10^{-2}
PFUnDA[a]	6.4	5.2×10^{-3}
PFDoDA[a]	3.0	3.0

Discussion of air-water partitioning

The Q_{AW} values show that WWTPs can be a source for PFCs to the atmosphere, because a transfer from the water to the air occurs. The extent of water-air transfer depends strongly on pH of the wastewater and the pK_a value for the compound as only neutral species will be available for water-air gas-exchange.

For the PFCs investigated here, a comparison of the field-derived Q_{AW} at the aeration tank to a laboratory-derived K_{AW} can only be done for PFOA as K_{AW} values are not yet available for other PFCs. For PFOA, a measured K_{AW} of 0.001 is reported in the literature[18]. This compares well with the Q_{AW} value of 0.0046 (Table 1) based on the maximum pK_a (3.8[19]) value. When the minimum pKa value is used (Eq. 1) the resulting Q_{AW} for PFOA (46) is orders of magnitude higher than the measured K_{AW}. It will be interesting to pursue this comparison further as additional measured K_{AW} values become available for the PFCs.

Estimated K_{AW} values are available in the literature and show an increasing trend with increasing chain length for PFCAs [20, 21, 22, 23]. However, this trend is not observed in the Q_{AW} values derived in this study (Table 1).

In conclusion, this study presents the first field-based data for air-water partitioning of PFCAs and PFSAs. The location of the study at the WWTP is unique and provided relatively high concentrations which facilitated the analysis. However, the applicability of the results to other air-water systems (e.g. lakes, oceans) needs to be investigated further. Finally, uncertainties in pK_a values have a high influence on calculated Q_{AW} and these uncertainties need to be addressed in future studies.

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