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In situ air–water and particle–water partitioning of perfluorocarboxylic acids, perfluorosulfonic acids and perfluorooctyl sulfonamide at a wastewater treatment plant

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HIGHLIGHTS

- PFCAs, PFSAs and HFOSA were measured in different phases at a WWTP.
- Particle-dissolved (R_d) and air–water (Q_{AW}) concentration ratios were determined.
- R_d values agreed well with equilibrium partition coefficients from the literature.
- Q_{AW} values derived for PFOA agreed well with K_{AW} values reported in the literature.
- Uncertainties in Q_{AW} values are attributed to the wide range of pK_a values reported.

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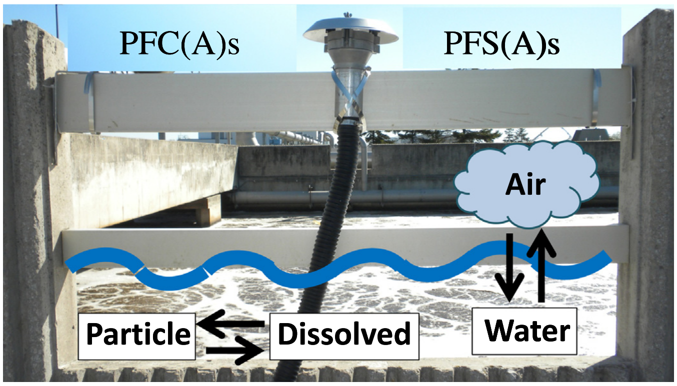
GRAPHICAL ABSTRACT



ABSTRACT

In situ measurements of air and water phases at a wastewater treatment plant (WWTP) were used to investigate the partitioning behavior of perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs) and perfluorooctyl sulfonamide (HFOSA) and their conjugate bases (PFC$^-$s, PFS$^-$s, and FOSA$^-$, respectively). Particle-dissolved (R_d) and air–water (Q_{AW}) concentration ratios were determined at different tanks of a WWTP. Sum of concentrations of $C_{4-12,14}$ PFC(A)s, $C_{4,6,8,10}$ PFS(A)s and (H)FOSA were as high as 50 pg m^{-3} (atmospheric gas phase), 2300 ng L^{-1} (aqueous dissolved phase) and 2500 ng L^{-1} (aqueous particle phase). Particle-dissolved concentration ratios of total species, log R_d, ranged from −2.9 to 1.3 for PFS(A)s, from −1.9 to 1.1 for PFC(A)s and was 0.71 for (H)FOSA. These field-based values agree well with equilibrium partitioning data reported in the literature, suggesting that any *in situ* generation from precursors, if they are present in this system, occurs at a slower rate than the rate of approach to equilibrium. Acid Q_{AW} were also estimated. Good agreement between the Q_{AW} and the air–water equilibrium partition coefficient for C_8PFCA suggests that the air above the WWTP tanks is at or near equilibrium with the water. Uncertainties in these Q_{AW} values are attributed mainly to variability in pK_a values reported in

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the literature. The WWTP provides a unique environment for investigating environmental fate processes of the PFCAs and PFSAs under 'real' conditions in order to better understand and predict their fate in the environment.

1. Introduction

Perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs) and perfluorooctyl sulfonamide (HFOSA) and their conjugate bases (PFC^-s, PFS^-s, and $FOSA^-$, respectively) have been produced since 1950 (Prevedouros et al., 2006). Today, these anthropogenic compounds are ubiquitous in the environment and wastewater treatment plants (WWTPs) are known to be one source for per- and polyfluorinated compounds into the environment (Houde et al., 2006; Ahrens, 2011).

To better understand and to be able to model the fate of PFC(A)s, PFS(A)s and (H)FOSA, knowledge of their partitioning between different environmental phases (e.g. between water and particles or between air and water) is crucial. Several studies have investigated the particle-dissolved partitioning under controlled conditions (Ochoa-Herrera and Sierra-Alvarez, 2008; Pan et al., 2009; Enevoldsen and Juhler, 2010) as well as in the field (Ahrens et al., 2010; Kwadijk et al., 2010; Labadie and Chevreuile, 2011; Li et al., 2011); whereas limited data are available for air–water partitioning of these compounds (Li et al., 2007; Kutsuna and Hori, 2008). Absence of such data can be attributed to the challenges associated with the design of reliable laboratory experiments. For example the surface active behavior of $PFCs^-$ and $PFSs^-$ might bias the results (Li et al., 2007). The present study combines new water-side measurements at different tanks of a WWTP with previously reported air-side results (Vierke et al., 2011) to investigate the particle-dissolved partitioning behavior in water and air–water partitioning behavior of PFC(A)s, PFS(A)s and (H)FOSA.

The overall process of wastewater treatment is dynamic. Chemicals within the wastewater are partitioning between the freely dissolved phase and particles present in the wastewater. At the same time, chemicals present in the dissolved phase, surface water are subject to exchange with the overlying atmosphere. It is possible that sub-processes such as particle–water and air–water partitioning are able to approach equilibrium. This would require that the rate of approach to equilibrium is much faster than, for example, any rate of formation associated with precursor degradation.

The aim of the present study is to derive *in situ* particle-dissolved (R_d) and air–water (Q_{AW}) concentration ratios for PFC(A)s, PFS(A)s and (H)FOSA for a WWTP, while taking into account the ionizability of these compounds. The derived values are then compared to reported thermodynamic equilibrium partition coefficients. Uncertainties associated with both the *in situ* values and the reported values are discussed in light of improvements that can be made to future investigations. To our knowledge, this is the first field-based study investigating air–water partitioning of PFCAs, PFSAs and HFOSA.

2. Methods and materials

2.1. Terminology

In the aqueous environment, acids are in equilibrium with their conjugate bases. The acid–base equilibrium depends on the pH of the medium and the pK_a of the acids. As suggested in the literature (Buck et al., 2011) we refer to the PFCA acids by adding an "A" to the acronym (Table 1). This system was also applied to PFSAs (Table 1). To facilitate the readers' understanding of acronyms the conjugate bases are indicated with a minus symbol. It is in line with this definition to name the perfluoroctanesulfonic acid as PFOSA, which in other studies was used for the HFOSA. Here, HFOSA represents the acid and $FOSA^-$ represents the conjugate base. For both species parenthesis are used, i.e. PFS(A), PFC(A) and (H)FOSA.

2.2. Chemicals

The present study focuses on $C_{4-12,14}$ PFC(A)s (Perfluorobutanoate PFB^-, Perfluoropentanoate PFP^-, Perfluorohexanoate $PFHx^-$, Perfluorohepantoate $PFHp^-$, Perfluorooctanoate PFO^-, Perfluorononanoate PFN^-, Perfluorodecanoate PFD^-, Perfluoroundecanoate $PFUnD^-$, Perfluorododecanoate $PFDoD^-$, Perfuorotetradecanoate $PFTD^-$ and the respective acids), $C_{4,6,8,10}$ PFS(A)s (Perfluorobutane sulfonate $PFBS^-$, Perfluorohexane sulfonate $PFHxS^-$, Perfluorooctane sufonate $PFOS^-$, Perfluorodecanesulfonate $PFDS^-$ and the respective acids) and (H)FOSA. Detailed information on analytes, mass-labeled internal standards and other chemicals used are provided in Tables SM1 and SM2.

2.3. Sampling

Sampling was conducted on a WWTP in Ontario, Canada with all samples being collected between 15th and 28th of April 2010. Air and water sampling were carried out at an aeration tank and at a secondary clarifier. Water samples were also collected from a primary clarifier. Results for the gas-phase concentrations of PFCAs, PFSAs and HFOSA were previously reported (Vierke et al., 2011) and are summarized briefly below. In that study active and passive air sampling was performed. The comparison of the results obtained from active and passive air sampling was used to produce reliable results for PFCAs, PFSAs and HFOSA in the gas phase.

For air sampling, as part of the previously reported study (Vierke et al., 2011), one high volume air sampler was installed at each sampling site at the rail of the tanks (approximately 2 m above the water surface) and samples were collected once a week over 24 h, resulting in an average air volume of 140 m^3. The particulate phase was collected on glass fiber filters (GFFs) (Pall, Quebec, Canada, Type A/E Glass 102 mm diameter, baked at 250 °C before sampling) and the gas phase was collected on PUF/XAD/PUF cartridges (precleaned large PUF plug, Supelco, Oakville, ON, Canada, 7.6 cm length, 6 cm diameter, 15 g of XAD-2 (SupelcoTM-2), Supelco) (Vierke et al., 2011). At the end of the 24 h air sampling period, water samples were collected from the corresponding tanks (note: the water component of this study was not part of the previous publication). Approximately 1 L water was collected in a brown glass bottle. The bottles and a bucket, by which the water was carried, were rinsed several times with the corresponding water from the tank. Surface water temperatures were not measured as they were expected to be in a similar range as the air temperatures recorded above the tanks, given the time of the year. Average temperatures for each 24 h sampling period ranged from 7 to 12 °C.

2.4. Extraction and instrumental analysis

Extraction and instrumental analysis are described elsewhere (Ahrens et al., 2010; Vierke et al., 2011) and in Table SM 3 and in Chapter 2 in the SM.