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Can the use of deactivated glass fibre filters eliminate sorption artefacts associated with active air sampling of perfluorooctanoic acid?☆

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ABSTRACT

Experimental work was undertaken to test whether gaseous perfluorooctanoic acid (PFOA) sorbs to glass fibre filters (GFFs) during air sampling, causing an incorrect measure of the gas-particle equilibrium distribution. Furthermore, tests were performed to investigate whether deactivation by siliconisation prevents sorption of gaseous PFOA to filter materials. An apparatus was constructed to closely simulate a high-volume air sampler, although with additional features allowing introduction of gaseous test compounds into an air stream stripped from particles. The set-up enabled investigation of the sorption of gaseous test compounds to filter media, eliminating any contribution from particles. Experiments were performed under ambient outdoor air conditions at environmentally relevant analyte concentrations. The results demonstrate that gaseous PFOA sorbs to GFFs, but that breakthrough of gaseous PFOA on the GFFs occurs at trace-level loadings. This indicates that during high volume air sampling, filters do not quantitatively capture all the PFOA in the sampled air. Experiments with siliconised GFFs showed that this filter pre-treatment reduced the sorption of gaseous PFOA, but that sorption still occurred at environmentally relevant air concentrations. We conclude that deactivation of GFFs does not allow for the separation of gaseous and particle bound perfluorinated carboxylic acids (PFCAs) during active air sampling. Consequently, the well-recognised theory that PFCAs do not prevail as gaseous species in the atmosphere may be based on biased measurements. Caution should be taken to ensure that this artefact will not bias the conclusions of future field studies.

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1. Introduction

Perfluoroalkyl carboxylic acids (PFCAs) are anthropogenic chemicals that have been used in a range of industrial and commercial products since the 1950s (Wang et al., 2014a, b; Buck et al., 2011; Prevedouros et al., 2006) and have become commercially important due to their unique physical and chemical properties, such as combined water and oil repellency, thermal stability and strong surfactant properties (Kissa, 2001). C₈, C₉ and C₁₁–C₁₄ PFCAs have been identified as vPvB chemicals (very persistent and very bioaccumulative) and added to the Candidate List of Substances of Very High Concern for Authorisation under the European Chemical

Regulation (REACH) (ECHA, 2013). Although there has been much recent research focused on PFCAs, many questions remain concerning the mechanism of their long-range transport in the environment. The main body of literature regarding PFCA acid dissociation constants (pK_a) suggests that these substances will be dissociated at all environmentally relevant pH values (Cheng et al., 2009; Goss, 2008; Lopez-Fontan et al., 2005; Vierke et al., 2013; Wang et al., 2011). Because PFCAs are present in the environment predominantly in their anionic form, long-range riverine and oceanic transport has been suggested as an important transport pathway from sources to remote regions (Armitage et al., 2009). However, long-range aquatic transport cannot explain findings of PFCAs in remote inland environments far from point sources (Benskin et al., 2011; Guo et al., 2015; Kirchgeorg et al., 2013; Kwok et al., 2013; Müller et al., 2011; Sinclair et al., 2006; Wang et al., 2014c; Young et al., 2007), nor the fact that PFCAs have been widely detected in precipitation in ng/L concentrations (Dreyer

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et al., 2010; Filipovic et al., 2015; Kwok et al., 2010; Scott et al., 2006; Taniyasu et al., 2013). Without better determination of the environmental cycling behaviour of these compounds, our understanding of their fate, transport, bioaccumulation and risks will remain hindered.

A key property for understanding the long-range atmospheric transport potential of PFCAs is their gas-particle partitioning. Accurate field data on the distribution of PFCAs between gaseous and particulate forms would also provide clues regarding their sources to air, which are currently not well constrained. Atmospheric releases of PFCAs on sea spray aerosols (McMurdo et al., 2008; Reth et al., 2011) and from fluoropolymer manufacturing (Barton et al., 2006), are expected to generate particulate PFCAs. Atmospheric transformation of precursors is thought to occur predominantly in the gas phase (Wallington et al., 2006). PFCAs originating from this source will likely remain in the gas phase for an unknown time, before they are ultimately scavenged and “dissolved” in the aqueous fraction of aerosols. Detection of gaseous PFCAs in environmental air could therefore indicate that the substances were formed in the atmosphere, i.e. that they stem from precursor degradation.

In most of the published datasets, atmospheric PFCA concentrations have been determined using active high-volume sampling and reported for the particle-phase (i.e. the fraction bound to a glass or quartz fibre filter (G/QFF)) only. The concentration in the gas-phase (sorbed to sorbent such as polyurethane foam, XAD or combinations thereof) was either not measured (Barber et al., 2007; Müller et al., 2012; Sasaki et al., 2003; Stock et al., 2007), assuming that any gaseous concentrations are negligible, or was reported as below the detection limit (Barton et al., 2006; Boulanger et al., 2005). Occurrence of environmental gas-phase PFCAs has been reported in several passive air sampling studies (Chaemfa et al., 2010; Genualdi et al., 2010; Goosey and Harrad, 2012; Shoeib et al., 2011), two studies using conventional active air sampling (Ahrens et al., 2011; Kim and Kannan, 2007) and one study using an annular diffusion denuder (Ahrens et al., 2011). These observations of gas-phase PFCAs raise the question of whether the sampling techniques were associated with artefacts that affected the apparent distribution between the gas phase and particulates. Some studies have suggested that unintentional sampling of ultrafine particles could be the origin of artefacts either through: i) their uptake on gas-phase sample media in passive samplers, which are generally considered to sample the inhalable dust fraction in addition to gaseous substances (Klánová et al., 2007; Vierke et al., 2011), ii) their uptake on gas-phase sample media in denuders (Ahrens et al., 2012) or iii) their uptake on gas-phase sample media in high-volume samplers after passing through the filter (John and Reischl, 1978).

Another cause of sampling artefacts is that gaseous PFCAs may bind to GFFs, which would cause an overestimation of the particulate-associated fraction in the gas-particle distribution derived from conventional high-volume air sampling. This phenomenon has previously been investigated in four lab studies (Arp and Goss, 2008; Barton et al., 2006; Kaiser et al., 2005a; Miller et al., 2007), but has not been studied under realistic conditions. Arp and Goss stated that when sampling environmental concentrations (typically $<10 \text{ pg/m}^3$ (Barber et al., 2007; Dreyer and Ebinghaus, 2009; Dreyer et al., 2009; Jahnke et al., 2007; Müller et al., 2012; Shoeib et al., 2011)), very large volumes of air ($>72 \text{ 000 m}^3$) have to be pumped through the filters in order to reach equilibrium between air and filter in order to reach filter saturation (at $43 \text{ } \mu\text{g/g}_{\text{QFF}}$), so that gaseous analytes can cross the filters and reach the downstream sorbents. Therefore, it is not clear whether the concentrations reported on filters in high-volume air sampling studies (typically $500\text{--}1500 \text{ m}^3$ air sampled) represent only particle-bound

PFCAs or a combination of gaseous and particle-bound PFAAs. Furthermore, studies have found PFCAs on sorbents downstream from QFFs at low air concentrations ($\ll 43 \text{ } \mu\text{g/g}_{\text{QFF}}$), indicating that not all gas-phase chemicals are retained by the QFF (Ahrens et al., 2011; Kim and Kannan, 2007; Vierke et al., 2011).

Arp and Goss (2008) found that using a silylated polytetrafluoroethylene-coated GFF removed the effect that exposure to PFCAs had on the sorption of the test compounds to filters in an inverse gas chromatography system. They therefore suggested that with silylated GFFs and QFFs it should be possible to determine the gas-particle partitioning of PFCAs in the field, but stressed that the approach should first be validated by measuring the equilibrium sorption coefficients ($K_{\text{filt}/\text{air}}$) of the filters used. Although this approach has not been validated for air sampling it has already been used in at least one field study (Ahrens et al., 2011).

In this present paper, we test whether the observations made by Arp and Goss (2008) using inverse gas chromatography at very high filter loadings can also be made under ambient outdoor-air sampling conditions at environmentally relevant analyte concentrations. We also test whether silylation or siliconisation is efficient at reducing the sorption of gaseous PFCAs to filters. For these experiments we used a novel apparatus designed and constructed to closely simulate a high-volume air sampler. Gaseous PFOA is introduced into an air stream stripped from particles and delivered into the sampling device. The set-up enables investigation of the sorption of gaseous test compounds to deactivated GFFs, eliminating any contribution from particulates. Similar set-ups have been used to study other environmental pollutants in the past (Cotham and Bidleman, 1992; Falconer et al., 1995; Foreman and Bidleman, 1987; Mader and Pankow, 2003). The filter sorption experiments were carried out with PFOA, because this substance has received the most attention in the scientific literature on the atmospheric fate of PFCAs and because it is expected to be fairly representative of the sorption behaviour of other important PFCA homologues (i.e. at least for $\text{C}_6\text{--}\text{C}_{10}$ PFCAs).

2. Experimental

2.1. Chemicals and materials

Isotope labelled standard compounds were purchased from Wellington Laboratories in $2 \text{ } \mu\text{g mL}^{-1}$ solution mixtures. The internal standard was $^{13}\text{C}_4\text{-PFOA}$. $^{13}\text{C}_8\text{-PFOA}$ was used as a volumetric standard in the calculation of total method recovery of the internal standard. The isotope labelled standards were certified to contain $<0.5\%$ of their native analogues. Native PFOA (technical mixture) was supplied by DuPont. Hexamethyldisilazane (HMDS) and Sigmacote were purchased from Sigma-Aldrich. Sigmacote is a siliconizing reagent solution in heptane, which forms a covalent film on glass.

Methanol (LiChrosolv grade) was supplied by Merck. Acetonitrile (Chromasolv grade) was purchased from Riedel-de Haën. Toluene (Analytical grade) was purchased from Scharlau. The water used in the method was generated in a Milli-Q integral water purification system (Millipore). GFFs (142 mm diameter, binder-free MG160, penetration of $0.3 \text{ } \mu\text{m}$ aerosols $<0.002\%$) were purchased from Munktell. Centrifugal filters (modified nylon $0.2 \text{ } \mu\text{m}$, $500 \text{ } \mu\text{L}$) were purchased from VWR. All GFFs were pre-baked at $450 \text{ } ^\circ\text{C}$ for 48 h and wrapped in aluminium foil until use.

2.2. Silylation/siliconisation of GFFs

Preparation of silylated/siliconised filters was undertaken directly before the start of an experiment. Silylation was carried out by soaking pre-baked GFFs in 30 mL HMDS solution (0.12 g/

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