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A PASSIVE SAMPLING TOOL FOR TIME INTEGRATIVE MONITORING OF PERFLUOROALKYL SUBSTANCES IN AQUEOUS ENVIRONMENTS

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Introduction

Worldwide concern is mounting about the use of poly- and perfluoroalkyl substances (PFASs) also referred to as perfluoroalkylcarboxylates (PFCAs; CnF2n+1COO-) and sulfonates (PFSAs; CnF2n+1SO3-) and their prevalence in humans and the environment. Under particular focus are perfluorooctanesulfonate (PFOS) and Perfluoroctanoate (PFOA). PFASs are persistent in the environment and are resistant to normal environmental breakdown. Because of this, they can transport through the environment and food chain, and accumulate at levels that may cause adverse effects to human and environmental health (EPA 2015). The moderate water solubility of these compounds means they are frequently found in aquatic environments, and transport via waterways appears to be a major distribution pathway (Ahrens 2011). PFASs are not effectively removed in wastewater treatment plants (WWTPs) and in some instances are enriched in the effluent (Heidler et al. 2008). This makes WWTP outfalls potential point sources in the environment (Huset et al. 2008) and emphasises the need for ongoing identification, monitoring and management strategies.

Data on the prevalence of PFASs in aqueous media such as oceans, rivers, lakes and ground water aquifers is based on the collection of discrete (grab) samples with reported levels ranging from low ng/L to µg/L (Suja et al. 2009). The collection of representative samples is a requirement for reducing error in estimating micropollutant (PFASs) concentrations over defined time scales and for accurate assessment of environmental burden (Ort et al. 2010). For this reason, passive sampling techniques have become increasingly important complementary tools in pollution monitoring schemes worldwide and are now specified in water sampling protocols (ISO 2016). Advantage of passive sampling techniques include providing time-averaged concentrations, relatively low limits of detection, cost effectiveness where extended deployment periods are desirable as well as ease and flexibility of deployment (Harman et al. 2012).

In 2012, the first passive sampler based on the Polar Organic Chemical Integrative Sampler (POCIS) was introduced for the monitoring of a range of PFASs (Kaserzon et al. 2012). As PFASs exist in most environmental waters as anions, thus modifications to the POCIS design included the use of a weak anion-exchange (WAX) sorbent to specifically target these chemicals. Results showed that while all PFASs targeted were successfully sampled, a limitation with this design was the short period of linear uptake of PFASs ($t_{1/2}$ = 3-13 days), meaning samplers would not be effective for longer deployment periods. Furthermore, through its design (i.e. use of polyethersulfone membrane in front of the sampler receiving phase) a drawback with the POCIS and other similar samplers for polar organic contaminants, is that the membrane does not entirely control the contaminant flux in all environmental scenarios. Thus, during field deployments chemical uptake rates can vary with amount of turbulence at the water boundary layer at the surface of the sampler (Kaserzon et al. 2013). This adds complexity when trying to relate laboratory calibration data with in-situ field data to derive quantitative water concentrations, because the sampling rates determined in the laboratory are only applicable under similar exposure conditions.

The aim of this study was to investigate alternative passive sampler methods for the monitoring of PFASs in aquatic environments. Two sampler designs were investigated, one sampler configuration comprised of a 5 nm micropore ceramic tube and another comprised of a microporous polyethylene (PE) material (both containing weak anion exchange material as a receiving phase). The objectives of this sampler design were twofold: (i) increase the linear range of the sampling device for the sampling of PFASs (ii) eliminate the flow dependency of the sampler to reduce uncertainties related to quantitative water concentration estimates. We present laboratory calibration data (over 30 days) as well as in-field calibration data assessing the performance of the samplers under a real deployment scenario at a contaminated site receiving runoff from a busy airport.

Materials and methods

Perfluoroalkyl compounds investigated - PFASs investigated in this work were perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA) and perfluorodecanoate (PFDA), Perfluorohexanesulphonate (PFHxS), perfluorobutanesulfonate (PFBS) and perfluorooctanesulfonate (PFOS).

Passive sampling devices – samplers comprised of (i) pure ceramic tube (length: 7 cm, diameter: 0.7cm porosity: 5 nm; Bopp et al. 2005) and (ii) microporous polyethylene (PE) material (length: 7 cm, diameter: 0.8 cm porosity: 2.5 nm (PALL, Germany).

Laboratory calibration of passive samplers – ceramic passive samplers were deployed in a 5 L water tank fortified with PFASs (1 μg L^{-1}). Samplers were exposed in time series for 7, 14, 21, 28 and 35 days. Daily grab samples (1 mL) were collected on each day. Grab samples were analysed by direct injection by LC-MS. Passive samples were extracted and analysed by LC-MS as described in Baduel et al. (2015).

Field deployment of passive samplers - Duplicate passive samplers (ceramic and PE samplers) were deployed for 7, 14, 28, 35 and 70 days (from August to October, 2015) at a site that received runoff from an airport with a fire fighting training grounds where PFAS were used. Grab samples were collected at sampler deployment sites with each sampler deployment / retrieval. All samples were extracted and analysed as above.

Data Modelling – Accumulation of PFASs in passive samplers was analysed using a one-compartment first order kinetic model, Eq. 1, below, where C_s is the PFAS concentration in the sorbent, K_{sw} the sorbent-water sorption coefficient, C_w the concentration in water, R_s the initial sampling rate (at t ½= 0), and ms the mass of sorbent.

Results and discussion

Data processing for the studies is still underway. Therefore the below findings represent very initial results examined so far.

Laboratory calibration

Eight PFASs (PFHxA, PFHpA, PFOA, PFNA PFDA, PFHxS, PFBS and PFOS) linearly accumulated in ceramic passive sampler over 35 days in laboratory trials. Sampling rates (R_s) ranged from 10 – 40 mL d^{-1}. R^2 was > 0.9 for all analytes with the exception of PFBS ($R^2 = 0.7$). Fig 1. Shows accumulation of PFOS and PFOA in the laboratory study. Fig. 2 shows a photo of the sampling device.

Field deployment

All eight PFASs under investigation were detected in ceramic passive sampling devices deployed in the field with levels ranging between 0.03 ng $sampler^{-1}$ (PFDA) and 19 ng $sampler^{-1}$ (PFOS). PE samplers detected all PFASs except for PFDA. Levels ranged from 0.04 ng $sampler^{-1}$ (PFNA) to 12 ng $sampler^{-1}$ (PFHxS). Field derived sampling rates (R_s; mL d^{-1}) ranged from 10 to 50 (perfluorononanoic - perfluorohexanoic) with the PE samplers and from 20 to 40 (perfluorononanoic - perfluorooctanesulfonate) with ceramic samplers. Half time to equilibrium ($t_{1/2}$) with both samplers was > 1 month for most PFASs with the exception of PFNA which showed $t_{1/2}$ = ~10 days. Figure 3 shows an example of the accumulation of PFOS and PFOA over 70 days during the field trial.

This study highlights the viability of passive samplers as a monitoring tool to quantify aqueous concentrations of PFCs in the environment. Data processing in still under way and more work is in progress to assess the robustness of the sampler under various environmental conditions. Additional potential application could examine primary transport routes of PFCs and aid in informing feasible avenues of remediation, monitoring and management.

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Eq. 1 $$C_s = K_{sw}C_w\left[1-\exp\left(-\frac{R_s t}{m_s k_{sw}}\right)\right]$$

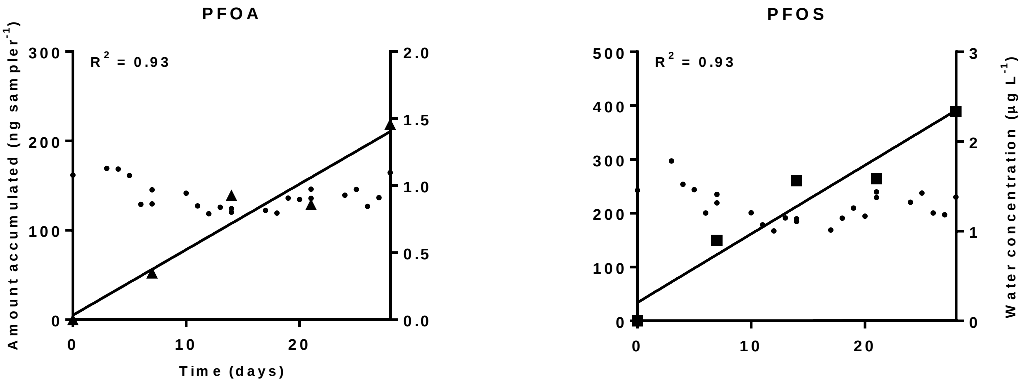

Figure 1. Accumulation of PFOA and PFOS in passive samplers (ng sampler^{-1}) during a 30 day laboratory study (black squares/triangles) and concentrations in grab samples (ng L^{-1}) over the deployment period (black dots).

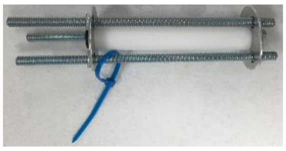

Figure 2. Photograph of the PE passive sampling device contained within metal deployment apparatus.

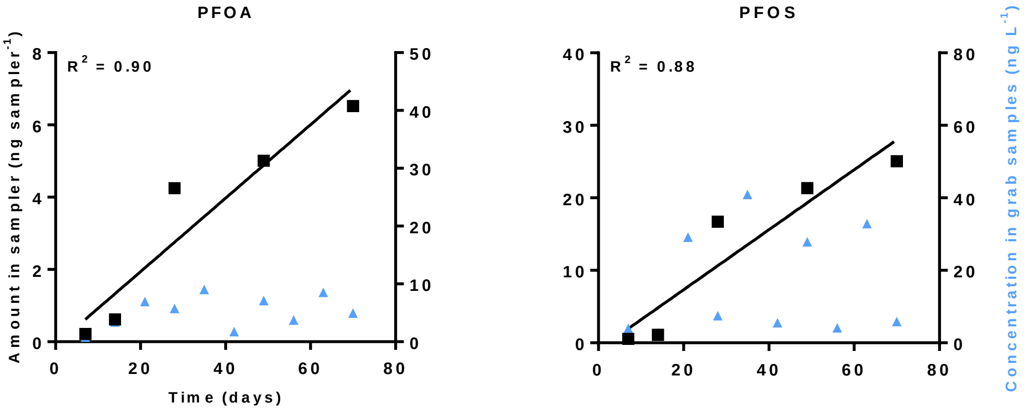

Figure 3. Accumulation of PFOA and PFOS in passive samplers (ng sampler^{-1}) during a 70 day field deployment (black squares) and concentrations in grab samples (ng L^{-1}) over the deployment period (blue triangles).