Introduction

Perfluorinated compounds (PFCs) have been widely used in many applications since the 1950s. Common PFCs in the environment include perfluorinated carboxylic acids such as Perfluoroheptanoic acid (PFHpA), Perfluorohexanoic acid (PFHxA), Perfluorooctanoic acid (PFOP), Perfluorooctane sulfonylic acid (PFOS), PerfluorobutaneSulfonate (PFBS). The combined persistence, bioaccumulation and toxicity to some animals has prompted government agencies worldwide to place regulations and restrictions on specific PFCs. Perfluorooctane sulfonate and perfluorooctane sulfonamide were added to Annex B of the Stockholm Convention on Persistent Organic pollutants in May 2009.

The aim of this study was to develop and calibrate a passive sampler for monitoring these PFCs in water and apply this calibration data to determine environmental concentrations of PFCs in Sydney Harbour, Australia.

Materials and Methods

Calibration study

A tank calibration study was conducted to derive uptake and sampling rates and data was compared with those derived under field conditions (i.e. Sydney Harbour). PFC samplers were deployed in time series, over 13 d, in a 1500 L water tank (Average flow rate 0.23 m s⁻¹, temp 27 °C, salinity 0.4 g L⁻¹). PFCs of interest were spiked into the tank at nominal concentration of 250 ng L⁻¹. Daily grab samples were collected and temperature, flow, pH parameters were recorded. Uptake and sampling rates (R_u) for the PFCs were deduced from the linear uptake equation (where C_u = concentration in the sampler and C_w = concentration in the water).  

Field study

Passive samplers for PFCs were constructed using polar organic chemical integrative samplers (POCIS). In this design two 0.45 micron polyethersulfone membranes (47 mm, Pall, Australia) enclosed 600 mg of Strata X-AW sorbent (Phenomenex, Australia). Duplicate samplers were deployed, during October 2010, in a time-series for 2, 3 and 5 d at Sydney Harbour, Australia. Duplicate grab samples (1 L) were collected at 1-t intervals during each passive sampler removal. Flow rate (0.15 m s⁻¹) temperature (22 °C) and salinity (31 g L⁻¹) were recorded. The limit of detection for the analysis method (LC/MS/MS) employed was 0.1 - 5 ng mL⁻¹.

Results

Sampling rates (R_u) for PFCs in calibration study ranged from 0.116 - 0.256 L d⁻¹. Some correlation between compound size and R_u occurred but not for all compounds.

Predicted TWA concentrations of PFCs in Sydney Harbour using laboratory calibrated sampling rates (3.7 and 6.6 L d⁻¹), correlated well with concentrations in grab samples (ng L⁻¹) (MND 33%, r² = 0.96).

Nine PFCs were detected in duplicate samplers (0.2 - 15 ng sampler⁻¹) from Sydney Harbour. PFDoDA was only detected in grab sample replicates, while PFPeA was only detected in passive samplers.

Conclusions

- Uptake of PFCs of interest in laboratory and field passive samplers was linear between 3 and > 7 d when exposed to environmental concentrations (< 250 ng L⁻¹).
- Despite varied conditions between the calibration study and Sydney Harbour field study (i.e. temp and flow) laboratory derived sampling rates (R_u 0.116 - 0.256 L d⁻¹) showed good prediction of concentrations in the environment.
- Further calibration studies under various flow rates and temperatures are required as well as the use of smaller pore limiting membranes to extend the kinetic sampling stage.
- To our knowledge, this data provides the first PFC passive sampler calibration data and introduces a novel time-weighted-average concentration monitoring tool for PFCs in the aqueous environment.