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Published

2013

Conference Title

SETAC Europe 23rd Annual Meeting Abstract Book

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# Passive sampling of perfluorinated chemicals in water: *in situ* correction of flow effects on chemical sampling rates

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## 1. Introduction

Perfluorinated chemicals (PFCs) are a family of anthropogenic pollutants that are the subject of increasing scrutiny and concern due to their wide-spread environmental distribution and the persistence, bioaccumulation and toxic properties of some members. Consequently regulation and monitoring of some PFCs has begun, and the requirement for monitoring of these chemicals is expected to increase.

A recently developed modified polar organic chemical integrative sampler (POCIS) provides a means for quantifying perfluorinated chemicals in water. However, changes in external flow rates may alter POCIS sampling behaviour and consequently affect estimated aqueous concentrations of PFC analytes. Therefore it is important that water flow rate over the sampler should be accounted for during field deployments.

In this study, sampling behaviour of the modified POCIS was calibrated using a previously developed<sup>[1]</sup> passive flow monitor (PFM) to measure *in-situ* water flow conditions. This cost-effective external calibration method would allow for adjustment of laboratory derived sampling rates for a more reliable estimation of environmental water concentrations.

## 2. Materials and methods

Passive samplers were constructed using a modification of the commercial polar organic chemical integrative samplers (POCIS) In this design, two 0.45  $\mu\text{m}$  membranes (47 mm diameter, PALL Australia) enclosed 600 mg of Strata X-AW sorbent (Phenomenex, Australia) giving a total exchangeable surface area of 16  $\text{cm}^2$ . The sampling and quantification of perfluoro alkyl carboxylates and sulfonates viz. perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFHxS) and perfluorooctanesulfonate (PFOS) were investigated in this work. Flow-controlled experiments were conducted with the modified POCIS deployed in a four channel system<sup>[2]</sup> through which river water fortified with PFCs (250 - 350  $\text{ng L}^{-1}$ ) flowed. Water flow rates were between 2 and 34  $\text{cm s}^{-1}$ . POCIS samplers were exposed for up to 15 d. Composite daily grab samples were also collected on each day for comparison with POCIS and water temperature, salinity and pH were recorded. Passive flow monitors were co-deployed in each channel system with POCIS for 15 days. All samples were analysed by LC-MS<sup>[3]</sup>. Water flow rates were estimated using PFMs and compared with measurements using a hand held flow monitor. Models were applied<sup>[4]</sup> using PFMs to determine site specific time-averaged water flow rate and consequently site specific POCIS sampling rates ( $R_s$ ) from the mass accumulated within the POCIS.

## 3. Results and discussion

### 3.1. Prediction of water flow rate with PFM

PFM devices are solid casts of gypsum and the basis of their operation is that they lose mass as a result of water flow over them. The daily mass loss rate of the PFM device ( $\Gamma_{\text{PFM}}$ ,  $\text{g d}^{-1}$ ) in this work corresponded well with that from a previous study<sup>[1]</sup> ( $R^2=0.95$ , Figure 1). In addition the predicted water flow rate derived from the PFM was consistent with a hand held flow monitor, within the flow rate range of 6 – 15  $\text{cm s}^{-1}$ . However, for almost stagnant (2  $\text{cm s}^{-1}$ ) and highly turbulent (34  $\text{cm s}^{-1}$ ) flow conditions, the PFM did not provide an accurate prediction (Table 1). Similar results were observed by O'Brien et al.,<sup>[4]</sup> during the calibration of PFM

loss rate at flow rates of 0 - 40  $\text{cm s}^{-1}$ . A linear increase in  $r_{\text{PFM}}$  with water flow rate allows for estimation of water flow rate from:  $v(\text{cm s}^{-1}) = (r_{\text{PFM}} - 0.4)/15.85$

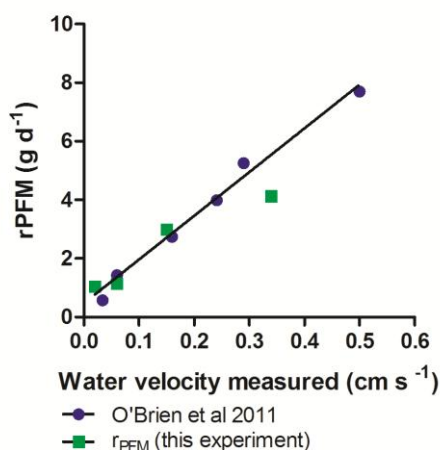


Figure 1: PFM loss rate ( $r_{\text{PFM}}$ ) versus measured water flow rate in this study (green squares) compared with O'Brien et al., 2011 (blue dots).

Table 1: Measured flow rate (using hand-held flow monitor) vs predicted (using PFM) water flow rate

Measured flow rate $\text{cm s}^{-1}$	PFM predicted flow rate $\text{cm s}^{-1}$	PFM loss rate ( $r_{\text{PFM}}$ ) $\text{g d}^{-1}$
2	5	1.0
6	6	1.1
16	18	3.0
34	26	4.1

### 3.2. Correlating POCIS $R_s$ with PFM predicted water flow

A plot of sampling rate ( $\text{L d}^{-1}$ ) for the uptake of PFCs into the POCIS versus  $r_{\text{PFM}}$  (PFM loss rate,  $\text{g d}^{-1}$ ) showed  $R_s$  to be a linear function of  $r_{\text{PFM}}$  (within the range of 1 - 4  $\text{g d}^{-1}$ ) (Figure 2). The use of the PFM can therefore allow direct estimation of  $R_s$  for the PFCs in this study within this range which corresponds to a water flow rate of 6 – 15  $\text{cm s}^{-1}$ . From  $R_s$ , as well as knowledge of the analyte amount accumulated in the sampler and the exposure time of the sampler, time-averaged aqueous PFC concentrations can be derived. At higher water velocities, where the PFM appears less sensitive, results from this study and O'Brien et al., (2011)<sup>[1]</sup> show a levelling off effect on  $R_s$  with increase in water flow rate (> 15  $\text{cm s}^{-1}$ ). This could suggest further investigation into non-linear relationships would be required at highly turbulent flow rate. Under typical field deployment conditions however, such flow rates are rare.

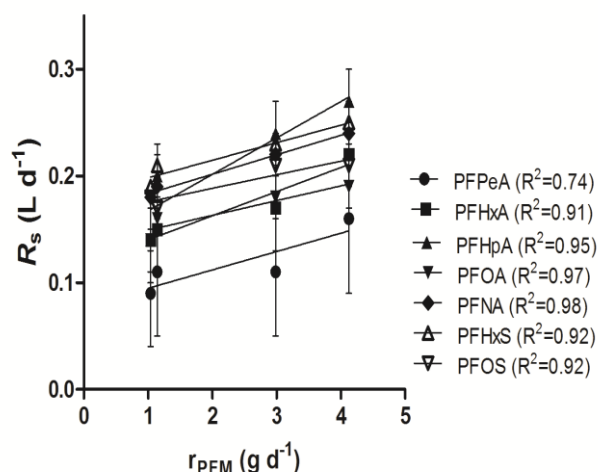


Figure 2: POCIS  $R_s$  for the uptake of PFCs relative to  $r_{PFM}$  measured using co-deployed PFMs.

## 4. Conclusions

This study represents the first calibration of the modified POCIS using a co-deployed PFM device for selected PFCs. It suggests PFMs can be an effective in-situ calibration tool to improve the estimation of POCIS-derived water concentrations. The range applicable for effective PFM deployment falls within the range of water velocities likely encountered under field conditions. At higher  $R_s$  where the PFM is less effective, a plateau of  $R_s$  for some chemicals has also been observed. However, such turbulent conditions are very rarely encountered during field deployments. Given appropriate co-calibration the PFM could have a wider application for deployment with a range of POCIS devices and chemical analytes.

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**Acknowledgement** - The authors thank Christie Bentley and Jack Thompson for laboratory and analytical support, respectively. This research was funded by the Australian Research Council's Linkage Projects scheme (LPO883675), with industry partner support of SEQWater, NMI, DW WA, EPA Victoria, EPA South Australia, Office of Environment and Heritage NSW, Brisbane City Council, GBRMPA, DERM, Queensland Health Forensic and Scientific Services (QHFSS), Griffith University and The University of Queensland. Scholarship support for Sarit Kaserzon was provided from Water Quality Research Australia (WQRA).