Passive sampling of perfluorinated chemicals in water: In-situ calibration

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ABSTRACT

Perfluorinated chemicals (PFCs) have been recognised as environmental pollutants that require monitoring. A modified polar organic chemical integrative sampler (POCIS) is able to quantify aqueous PFCs. However, with varying external water velocity, PFC sampling rates (R_s) may change, affecting accuracy of derived water concentrations. To facilitate field deployment of this sampler, two methods of in-situ calibration were investigated: performance reference compounds (PRCs) and passive flow monitors (PFMs). Increased R_s's (by factors of 1.2–1.9) with PFM loss rate (g d^{-1}) were observed for some PFCs. Results indicate PFMs can be used to correct PFC specific R_s's for more reliable estimates of environmental concentrations with a precision of about 0.01 L d^{-1}. Empirical models presented provide an improved means for aquatic monitoring of PFCs. The PRC approach was unsuccessful, confirming concern as to its applicability with such samplers.

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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 widespread distribution in the environment along with their persistence and the toxic properties of some members. Consequently, regulation of some PFCs such as perfluorooctanesulfonate (PFOS) has begun (European Commission, 2012; Houde et al., 2011; Labadie and Chevreuil, 2011; Stockholm Convention, 2010). The requirement for environmental monitoring of these chemicals is expected to increase. Muir and Lohmann (2013) recently observed that with the addition of compounds such as PFOS to the Stockholm Convention, the chemicals addressed no longer comprise just hydrophobic organics. PFOS is the anionic conjugate base of perfluorooctanesulfonic acid, and other perfluorinated sulfonic and carboxylic acids (PFSAs and PFCAs) are also typically present in natural waters as anions with moderate aqueous solubility (Kaserzon et al., 2013).

Passive sampling technologies have been successfully used for the past four decades as useful monitoring tools for a range of environmental pollutants in water (Alvarez et al., 2004b; Booij et al., 2007; Huckins et al., 1999). In more recent years a range of polymeric sorbents, traditionally used for solid phase extraction, have been employed as passive sampling receiving phases due to their high recoveries of analytes, ease of handling and effectiveness with a wider range of polar organic chemical pollutants. In particular, the polar organic chemical integrative sampler (POCIS) configuration involving sorbents including Oasis HLB, Oasis MAX and Oasis MCX has been used for emerging pharmaceuticals and personal care products, pesticides and herbicides (Alvarez et al., 2004a; Li et al., 2011; Mazzella et al., 2008; Vermeirssen et al., 2008). The latter ion exchange sorbents (OASIS MAX and MCX) have been used for chemical species that are ionised in aqueous matrices.

Recently, a modified POCIS comprising a weak anion exchange sorbent phase (Strata™ XAW) was successfully developed for quantifying perfluorinated chemicals in water (Kaserzon et al., 2012, 2013). When the effect of water flow rate (between 0.02 and 0.34 m s^{-1}) on PFC sampling rates (R_s) was examined, an increase in R_s's with increasing water flow rate for PFCs up to

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perfluorononanoate (PFNA, MW = 463) was observed. The effect of in-situ water flow rate should therefore be accounted for when deploying these modified POCIS in the field, to improve water concentration estimates for PFCs (Kaserzon et al., 2013). In this previous study, sampling rates were determined daily using hand held flow meters, but under environmental conditions this may not be practical.

The importance of in-situ calibration methods in order to adjust chemical sampling rates obtained in laboratory calibrations has been widely acknowledged (Huckins et al., 2002a). Without them, derived results of time weighted average aqueous concentrations are at best semi-quantitative (Harman et al., 2012). In the environment, conditions during sampler deployment may affect uptake behaviour of chemicals into passive samplers (PSs). In particular, deployment-specific water flow rates can affect the sampling behaviour of analytes by influencing mass transfer between the external water and the surface of the sampler (Booij et al., 2007). The effect is particularly pronounced with partition based passive samplers such as the semipermeable membrane device (SPMD) designed for monitoring hydrophobic compounds (Vrana et al., 2005). In the case of PSs designed for more polar compounds such as the POCIS, limited studies on the effects of water flow rate on sampling behaviour suggest the influence is less pronounced and may be compound specific (Kaserzon et al., 2013; Li et al., 2010; Vermeirssen et al., 2008).

The range of environmental conditions encountered by passive samplers (e.g. water flow rate, temperature, salinity) cannot always be accommodated in laboratory calibration studies due to time and resource restrictions. Methods of in-situ calibration during field deployments such as the co-deployment of data loggers and meters at multiple sites may also be costly and in many cases, multiple visits to sites for manual measurements may be similarly restrictive (O'Brien et al., 2009). An in-situ calibration method for flow rate effects on sampling rates is the co-deployment of passive flow monitors (PFMs) (O'Brien et al., 2009). In this method, the mass loss from a calcium sulphate dihydrate (gypsum) cast is used to estimate water flow rates to which the PFM is exposed. PFMs have been successfully used to calibrate the uptake rates of chemical analytes including phosphate and some polar and nonpolar herbicides and pesticides using PSs such as the phosphate sampler, Chemcatcher™, PDMS and SPMD (O'Brien et al., 2011a; O'Brien et al., 2009; O'Brien et al., 2012). The calibrations provide chemical- and sampler-specific empirical equations that can be used to account for the change in R_s with water velocity and ionic strength resulting in more accurate estimates of time-weighted average chemical concentrations. While PFMs have been suggested as a possible external correction method for POCIS (Harman et al., 2012), no studies to date have examined this.

Performance reference compounds (PRCs) have been successfully used with partitioning type samplers (e.g. SPMDs) as a means of determining the effect of environmental conditions on sampler behaviour (Booij et al., 2002; Huckins et al., 2002a). In-situ R_s values are derived from the loss rate constants of PRCs that are spiked into samplers before exposure to the aquatic environment. The application of the PRC method to passive samplers whose mode of action is not partition-based is uncertain (Alvarez et al., 2007; Shaw et al., 2009; Vallejo et al., 2013). Recent studies with Oasis HLB and Oasis MAX have suggested that desisopropylatrazine-d_5 (DIA-d_5) could be a suitable PRC for anionic analytes with POCIS containing an anion-exchange sorbent (Fauvelle et al., 2012; Mazzella et al., 2007, 2010). However, investigation of its applicability as a PRC under varying environmental conditions such as flow rate has been advocated (Mazzella et al., 2010). In addition, other compounds such as isoproturon and metolachlor have shown desorption (≤40%) from Oasis HLB under turbulent conditions (Mazzella et al.,

2010) and may also be suitable as PRCs. We therefore examine the applicability of these compounds as PRCs with the Strata™ XAW equipped PFC sampler presented here.

Overall in this current study, we evaluate the use of PRCs as well as PFMs as in-situ correction methods for PFCs with the modified POCIS. The effects of flow rate (0.02, 0.06, 0.16, 0.34 m s^{-1}) in a flow-through channel system on PFM mass loss rates and the loss kinetics of DIA-d_5, isoproturon-d_6 and metolachlor-d_6 are investigated. PRC kinetic data and PFM mass loss rates are then related to PFC sampling rates so that these methods can be assessed for their ability to provide in-situ flow rate calibration.

2. Materials and methods

2.1. Perfluorinated chemicals

PFCAs investigated in this work were perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA) and perfluoroundecanoate (PFUnDA). The PFSAs were perfluorohexanesulfonate (PFHxS) and perfluorooctanesulfonate (PFOS). R_s data for PFCs discussed in this study were taken from Kaserzon et al. (2013).

2.2. Calibration study design

A flow-through channel system at Eawag, Dübendorf, Switzerland (Vermeirssen et al., 2008) was used for the modified POCIS calibration study. The configuration of the channel system and methodology used have been described in Kaserzon et al. (2013). Flow velocities in the channel systems were 0.02, 0.06, 0.16 and 0.34 m s^{-1}. The water depth in each channel was 0.1 m. Flow rate, temperature and pH were measured daily at several points along each of the four channels (Table S2). Flow rate was measured using a flow meter (MiniAir2, Schiltknecht, Gossau, Switzerland), and also by measuring the time to fill a bucket of known dimensions (Table 1). PFMs were deployed downstream from POCIS and, similar to the POCIS, parallel to the flow in the middle of each channel from day 0–15. Preparation, extraction and analysis of modified POCIS samplers are described in Kaserzon et al. (2013).

2.3. PRC preparation and analysis

Performance reference compounds (DIA-d_5, isoproturon-d_6, metolachlor-d_6) were purchased from Novachem (Victoria, Australia). The spiking of PRCs was performed according to Mazzella et al. (2010). DIA-d_5, isoproturon-d_6 and metolachlor-d_6 (20 µg each) were dissolved in 25 mL of methanol. The solution was added to Strata™ XAW bulk sorbent and the mixture sonicated for 5 min followed by rotary evaporation. The sorbent was then dried at 60 °C for 1 h. The final bulk sorbent (28 g) contained 0.7 µg g^{-1} of each PRC. This bulk sorbent was used to prepare all deployed POCIS and blanks ($n = 2$) (600 mg per POCIS).

PRC spiked POCIS ($n = 2$) were used to determine the initial spike concentrations of each PRC. PRC analyses were conducted by Queensland Health Forensic and Scientific Services (QHFSS) using HPLC–MS/MS. An AB/Sciex API 300 mass spectrometer (Applied Biosystems, Concord, Ontario, Canada) equipped with an electrospray ionisation interface was coupled to a Shimadzu SCL-10Avp HPLC system (Shimadzu Corp., Kyoto, Japan). The analytical column used was a 5 µm Aquastar C18 column (150 × 3 mm) (Thermo Electron Corp., Bellefonte, PA). The temperature was 35 °C and flow rate of the mobile phase (A and B mobile phases 10% and 90% methanol/

Table 1
PFM mass loss rate (r_{PFM}, g d^{-1}), flow rate measured with a flow rate meter and volumetrically in the flow-through channel system together with flow rate predicted from r_{PFM} using Eq. (1).

PFM mass loss rate, r_{PFM}	Flow meter flow rate[b]	PFM predicted flow rate	Volumetric measurement of flow rate[c]
(g d^{-1})	(m s^{-1})	(m s^{-1})	(m s^{-1})
0.66[a]	0.02 ± 0.01[a]	0.004[a]	
1.04	0.02 ± 0.01	0.036	0.03
1.14	0.06 ± 0.02	0.044	0.06
2.99	0.16 ± 0.01	0.198	0.17
4.13	0.34 ± 0.05	0.293	0.35

[a] Flow rate in the holding tank from which water was distributed into the channels.
[b] 3% instrumental measurement error.
[c] Calculated from the volumetric flow rate (L min^{-1}) and the cross sectional area of the channels.