



## In situ measurement of perfluoroalkyl substances in aquatic systems using diffusive gradients in thin-films technique



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### ARTICLE INFO

#### Article history:

Received 9 February 2018

Received in revised form

21 June 2018

Accepted 13 July 2018

#### Keywords:

Perfluoroalkyl substances

Diffusive gradients in thin-films

Diffusion coefficients

Passive sampling

Surface waters

Wastewaters

### ABSTRACT

To better understand the environmental impact of ubiquitous perfluoroalkyl substances (PFASs) in waters, reliable and robust measurement techniques are needed. As one of the most widely used passive sampling approaches, diffusive gradients in thin-films (DGT) is not only easy to handle but also provides time-weighted analyte concentrations. Based on DGT with XAD18 as a binding agent, we developed a new methodology to measure two frequently detected PFASs in surface waters and wastewaters, i.e. perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). Their diffusion coefficients in the diffusive gel, measured using an independent diffusion cell, were  $4.37 \times 10^{-6}$  and  $5.08 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  at 25 °C, respectively. DGT had a high capacity for PFOA and PFOS at 196 and 246  $\mu\text{g}$  per gel disk, suggesting the DGT sampler was suitable for deployment of several weeks. Time-integrated concentrations of PFOA and PFOS in a natural lake and river, and a municipal wastewater treatment plant effluent using DGT samplers deployed *in situ* for 12–33 d were comparable to those measured by a solid-phase extraction method coupled with high-frequency grab sampling. This study demonstrates that DGT is an effective tool for *in situ* monitoring of PFASs in natural waters and wastewaters.

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## 1. Introduction

Emerging contaminants perfluoroalkyl substances (PFASs) have been produced and used for more than 60 years (Lindstrom et al., 2011; Wang et al., 2017). Due to their thermal stability and oxidative resistance, PFASs are widely used as surfactants and surface protectors in commercial products and industries including protective coatings and fire-fighting foams (Giesy and Kannan, 2002; Kusoglu and Weber, 2017; Renner, 2001; Wu et al., 2015). Generally, two sources account for the release of PFASs into the environment: one is direct sources such as the manufacturing of PFASs and consumption of products containing PFASs, and the other is indirect sources like reaction impurities or degradation of precursors (Zareitalabad et al., 2013). Two long-chain, fully fluorinated PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate

(PFOS), are ubiquitously present in natural waters (Boulanger et al., 2004; Lindim et al., 2016; Wang et al., 2015; Xiao et al., 2015; Zhang et al., 2016), drinking water (Hu et al., 2016; Schwanz et al., 2016; Xiao et al., 2013) and wastewater (Arvaniti and Stasinakis, 2015; Kwon et al., 2017; Pan et al., 2016; Xiao et al., 2012b) at concentrations ranging from  $\text{pg L}^{-1}$  to  $\mu\text{g L}^{-1}$  levels (Krafft and Riess, 2015a; Zareitalabad et al., 2013). Besides, it is generally accepted that they are persistent, bioaccumulative and recalcitrant to removal by drinking-water and municipal wastewater treatment (Xiao, 2017).

To reduce their emission, PFOS was listed on the Stockholm Convention as persistent organic pollutants in May 2009 whereas PFOA was proposed by European Union to be listed in the Stockholm Convention in October 2015 (Lam et al., 2017). The environmental quality standard (expressed as an annual average value) for PFOS in freshwaters corresponding to the long term exposure scenario for human consumption of freshwater fish set by European Commission is at  $0.65 \text{ ng L}^{-1}$ , whereas a provisional threshold of  $0.4 \mu\text{g L}^{-1}$  was proposed by US Environmental Protection Agency

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(USEPA) for PFOA in drinking waters (Valsecchi et al., 2017). In 2016, USEPA issued lifetime drinking water health advisory level of  $70 \text{ ng L}^{-1}$  for the combined concentration of PFOA and PFOS (Weber et al., 2017). Due to their relatively high polarity and moderate water solubility, the majority of PFASs are distributed in the liquid phase (Kaserzon et al., 2012; Li et al., 2017). As such, accurate determination of PFASs concentrations in natural waters and wastewaters is necessary to better understand their biogeochemistry and to further evaluate their potential effect on aquatic organisms and human beings.

Most strategies for PFASs measurement need to collect large-volume water samples through grab/spot sampling, which are sent back to laboratory for chemical pre-concentration before quantitative analysis using high-sensitive equipments such as liquid chromatography – negative ion electrospray tandem mass spectrometry (LC–MS/MS) (Richardson and Kimura, 2016; Yu et al., 2013). However, the methodology provides only snapshots of PFASs concentration at specific sampling time; for periodical monitoring, it can be time-consuming and costly. To screen PFASs and capture the concentration-dependent biogeochemical behavior of PFASs in environments, *in situ* analysis is preferable. However, field analysis of PFASs were not feasible due to the non-portability and non-specification of instruments (Giesy and Kannan, 2002). Therefore, *in situ* preconcentration of PFASs in passive sampling samplers followed by laboratorial analysis is an alternatively promising solution (Roll and Halden, 2016; Vrana et al., 2005). Moreover, this practice is a very common approach for many other groups of organic substances.

The advantages of passive sampling over traditional spot sampling include *in situ* time-integrating and labor-saving continuous monitoring, lower detection limits, cleaner sample matrices and easier sample storage. Based on polar organic chemical integrative sampler (POCIS), several passive samplers have been successfully used to monitor PFASs (Alvarez et al., 2007; Fedorova et al., 2013; Kaserzon et al., 2012). However, a drawback of POCIS-based samplers is the necessity of *in situ* calibration of the sampling rates caused by the different field conditions from laboratory calibrations (Kaserzon et al., 2014). Hydrodynamic conditions, such as flow rate, temperature, and turbulence, could affect sampling rates, thereby contributing to the uncertainty and variation in concentration estimates of PFASs in water (Kaserzon et al., 2013, 2014).

Passive sampling technique based on diffusive gradients in thin-films technique (DGT) is independent of water flow rate, so it has the potential to provide concentrations with improved performance compared to other passive samplers (Sigg et al., 2006). In the last >20 years, DGT has been established to measure labile inorganic species in aquatic environments, such as metals (Gu et al., 2017; Guan et al., 2016; Luo et al., 2010, 2018; Pan et al., 2015; Zhang and Davison, 1995; Zhang et al., 2017), phosphate (Guan et al., 2015; Santner et al., 2010; Zhang et al., 1998), phosphite (Han et al., 2018), nitrate (Cai et al., 2017; Huang et al., 2016), and fluoride (Zhou et al., 2016). Recently, DGT samplers based on XAD resin, activated charcoal or hydrophilic–lipophilic balance powder as the binding agent have been extended to measure trace organics in waters including antibiotics (Chen et al., 2013), bisphenols (Zheng et al., 2015), polar organic contaminants (Challis et al., 2016), household and personal care products (including preservatives, antioxidants and disinfectants) (Chen et al., 2017), illicit drugs (Guo et al., 2017), anionic pesticides (Guibal et al., 2017) and endocrine disrupting compounds (Chen et al., 2018). These pioneering studies shed light on using DGT as a fully quantitative passive sampling technique to monitor polar organics such as PFASs in aquatic systems. DGT measurement ( $C_{DGT}$ ) can provide time-averaged concentrations of organics in water using equation (1), which is derived from Fick's first law of diffusion:

$$C_{DGT} = M \times \Delta g / (D \times A \times t) \quad (1)$$

The measured mass ( $M$ , ng) of a target organic accumulated on the binding gel at a given time ( $t$ , s) can be obtained by measuring its concentration in the eluate solutions. The DGT sampling area ( $A$ ,  $\text{cm}^2$ ) and the thickness ( $\Delta g$ , cm) of the diffusion layer (diffusive gel + filter membrane) are sampler-specific and standardized for routine use. The diffusion coefficient ( $D$ ,  $\text{cm}^2 \text{ s}^{-1}$ ) of the organics in the diffusion layer is temperature-specific and can be measured by a diffusion cell or using DGT samplers (Luo et al., 2010).

Recently, XAD resins have been used as the core binding phase in passive air samplers (Loewen et al., 2008) and cartridges (Sinclair et al., 2007) for measuring PFASs. These resins are also known for effectively removing PFASs from water and wastewater (Du et al., 2015; Xiao et al., 2012a). To better understand the concentration-dependent environmental behavior and impact of PFASs in aquatic system, here, we developed a DGT sampler with a binding layer comprising XAD18 incorporated into agarose gel, and evaluated its performance characteristics to measure two typical PFASs, i.e. PFOA and PFOS. The binding kinetics, elution efficiencies by methanol, and capacities of the XAD18 binding gel were studied. The possible effects of pH, ionic strength, dissolved organic matter (DOM), deployment time, and competition between PFOA and PFOS were also investigated. The DGT samplers were deployed in natural waters and wastewaters, and the measured concentrations based on high-sensitivity LC–MS/MS were compared with those from conventional spot sampling.

## 2. Experimental section

### 2.1. Reagents, materials, and solutions

All containers and pipets were made of polypropylene (PP) plastics. PFOA (>98%) was supplied by Tokyo Chemical Industry Co, LTD. (Tokyo, Japan). PFOS (>97%, potassium salt) was purchased from Strem Chemicals (Newburyport, MA, USA) and has two isomers. Perfluoro-*n*-[1,2,3,4- $^{13}\text{C}_4$ ]octanoic acid ( $^{13}\text{C}_4$ -PFOA) and sodium perfluoro-1-[1,2,3,4- $^{13}\text{C}_4$ ]octanesulfonate ( $^{13}\text{C}_4$ -PFOS) were purchased from Cambridge Isotope Laboratories (MA, USA) and used as internal standards for instrument analysis with LC–MS/MS. Methanol (HPLC grade) was purchased from Merck (Darmstadt, Germany). Ammonium hydroxide solution (~10%, HPLC grade) was supplied by CNW technologies GmbH (Duesseldorf, Germany). Ammonium acetate (for mass spectrometry, eluent additive for LC–MS/MS) was obtained from Sigma–Aldrich chemie GmbH. Acetic acid glacial (HPLC grade,  $\geq 99.7\%$ ) was from Tedia Company, Inc (Fairfield, OH, USA). Humic material (fulvic acid  $\geq 90\%$ ) was purchased from Aladdin Industrial Corp., China. Stock solutions of PFOA and PFOS were prepared at  $5000 \text{ mg L}^{-1}$  in methanol (HPLC grade) and stored in sealed amber PP plastic bottles at  $-20^\circ\text{C}$ .

### 2.2. DGT preparation

Standard DGT piston samplers consisted of a round base, a binding gel layer using finely-ground XAD18 (particle size 25–75  $\mu\text{m}$ , Amberlite™, Rohm and Haas Company) as the binding resin, a 0.75-mm-thick diffusive gel layer, a 0.13-mm-thick, 0.45- $\mu\text{m}$  hydrophilic polyethersulfone (PES) filter membrane to prevent adherence of particles to the gels and a cap with a 2.51- $\text{cm}^2$  round window that holds all the layers tightly together (Guan et al., 2015). The resin gel acts as a sink, inducing a flux of a solute from the solution through the diffusive gel.

The diffusive gels and binding gels were prepared according to a previously published procedure (Chen et al., 2012; Guan et al.,

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