WATER RESEARCH 47 (2013) 2851–2862

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Calibration and field test of the Polar Organic Chemical Integrative Samplers for the determination of 15 endocrine disrupting compounds in wastewater and river water with special focus on performance reference compounds (PRC)

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ARTICLE INFO

Article history:
Received 24 November 2012
Received in revised form
21 February 2013
Accepted 23 February 2013
Available online 5 March 2013

Keywords:
POCIS
EDCs
PRC
Wastewater
River water

ABSTRACT

In this work, home-made Polar Organic Chemical Integrative Samplers (POCIS) were studied for passive sampling of 15 endocrine disrupting compounds (4 alkylphenols and steroid hormones) in influent and effluent samples of wastewater treatment plants (WWTPs) as well as up- and downstream of the receiving river water.

POCIS calibration at laboratory conditions was carried out using a continuous-flow calibration system. The influence of the exposure position of the POCIS within the calibration device, horizontal or vertical, to the water flow direction was evaluated. While the sampling rates of most of the target substances were not affected by the sampler position, for cis-ADT, E1, E2 and E3, the vertical position provided the highest analyte accumulation. Hence, the POCIS samplers were preferably exposed vertical to the water flow in overall experiments. Using the continuous-flow calibration device, lab-based sampling rates were determined for all the target compounds ($R_{SBPA} = 0.0326$ L/d; $R_{ScisADT} = 0.0800$ L/d, $R_{SE1} = 0.0398$ L/d, $R_{SEQ} = 0.0516$ L/d, $R_{STT} = 0.0745$ L/d, $R_{SE2} = 0.0585$ L/d, $R_{SEE2} = 0.0406$ L/d, $R_{SNT} = 0.0846$ L/d, $R_{SPG} = 0.0478$ L/d and $R_{SE3} = 0.1468$ L/d), except for DES, MeEE2, 4tOP, 4OP, 4NPs, where the uptake after 14 days POCIS exposure was found to be insignificant or indicated a no linear behaviour. Recoveries from POCIS extractions were in the range between 71 and 152% for most of the target analytes except for DES and E3 with around 59%. Good precision of the sampling procedure up till 20% was observed and limits of detection were at ng/L level. Two deuterated compounds ([$^2H_3$]-E2 and [$^2H_4$]-EQ) were successfully tested as performance reference compounds (PRC, $k_{e[^2H_3]-E2} = 0.0507$ L/d and $k_{e[^2H_4]-EQ} = 0.0543$ L/d)).

Finally, the POCIS samplers were tested for monitoring EDCs at two wastewater treatment plants, in Halle and Leipzig (Germany). BPA, E1, EQ, E2, MeEE2, NT, EE2, PG and E3 were quantified and their time-weighted average concentrations calculated on the basis of the lab-derived sampling rates were compared with the results based on conventional grab

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http://dx.doi.org/10.1016/j.watres.2013.02.049

samples. While the influent concentration of BPA, cisADT, E1, TT, PG, EE2 reached the μg/L level, the rest of the target analytes were determined at ng/L. The analyte concentrations in the effluent never exceed ng/L level except for BPA. The concentration determined by spot sampling was partially lower (BPA, E1, TT) or comparable (EQ, E2, EE2, PG, E3) to the concentration obtained by POCIS using performance reference compounds (PRC).

1. Introduction

In the last decade, the interest in endocrine disrupting compounds (EDCs) has increased due to their adverse health effects in organisms, or its progeny, altering reproductive processes (Van den Belt et al., 2004; Flores-Valverde et al., 2010; Van den Belt et al., 2003). Some EDCs, such as alkylphenols (APs), bisphenol-A (BPA) or oestrogens, have been included in the Water Framework Directive (WFD) as priority hazardous substances or emerging pollutants (Directive, 2000/60/EC) and, recently, the U.S. Environmental Protection Agency published the EPA 539 method for measuring 7 hormones in drinking water (Richardson, 2011).

An important source of APs is the degradation of alkylphenol polyethoxylates, used as surfactants, while BPA is released, for instance, from epoxy resins found in numerous industrial and household applications (Soares et al., 2008). Other oestrogens are emitted from the manufacture of polymers or from human excretion and farming waste (Lintelmann et al., 2003). Commonly, these compounds reach the environment through wastewater treatment plants (WWTPs) where they are not completely removed. Racz and Goel (2010) described the different removal techniques for the oestrogens in the WWTPs and the need to monitor these analytes in effluents. Although EDCs enter the environment at ng/L level, their concentration are high enough to disrupt the endocrine processes of several organisms (Zhao et al., 2009; Michael and Kai, 2005; Quednow and Püttmann, 2008). In this sense, the control of the concentration of such compounds in both WWTP influents and effluents has become an important topic of water monitoring and analysis (Richardson and Ternes, 2011; Petrovic et al., 2003).

Commonly, spot samples are taken to determine organic micropollutants in the different water bodies but this method provides only punctual information on water contamination and fluctuations of the concentrations are not detected. A chance of overcoming this problem is to shorten the sampling intervals (towards continuous sampling), but the time consumed and the efforts are quite tedious. An alternative to obtain a representative field concentration of organic micropollutants is the use of passive sampling devices. This sampling approach gives a time-weighted average (TWA) concentration of the analyte over the field deployment period of the sampler and, thus, a more realistic picture on environmental concentration levels is formed (Vrana et al., 2005; Greenwood et al., 2007; Kot-Wasik et al., 2007). Different types of passive sampling devices such as the Semi-Permeable Membrane Device (SPMD) (Huckins et al., 2002), the Chemcatcher® (Vrana et al., 2006a; Vermeirssen et al., 2009), the Membrane-Enclosed Silicone Collector (MESCO) (Vrana et al., 2006b), silicone rod (SR) (Paschke et al., 2007) and the Polar Organic Chemical Integrative Sampler (POCIS) (Miege et al., 2012) can be used in water sampling depending on the nature and physicochemical properties of the analytes. In the case of polar compounds, POCIS is mostly used (Zhang et al., 2008; Alvarez et al., 2005; Arditsoglou and Voutsa, 2008; Alvarez et al., 2004; Mazzella et al., 2010; Allan et al., 2010; Harman et al., 2009; Alvarez et al., 2007). In this approach, a polymeric sorbent is retained between two polar membranes and held with two stainless steel rings. This sampling device acts as an infinite sink for contaminants and analyte uptake is linear. In these conditions, an estimation of the TWA concentration (c_w^{TWA}, ng/L) of contaminants during a specific exposure period (t, days) can be calculated according to equation (1) (Alvarez et al., 2004),

$$c_w^{TWA} = \frac{m_s}{R_s\, t} \tag{1}$$

where m_s (ng) corresponds to the amount of analyte in the sorbent, and R_s (L/d) to the sampling rate.

R_s is typically estimated using uptake experiments in the laboratory. However, the laboratory and environmental conditions are not exactly the same for instance concerning water flow rates and biofouling and therefore, performance reference compounds (PRC) have been proposed in order to correct these differences (Mazzella et al., 2010; Huckins et al., 2002). PRCs can be deuterated compounds added to the sampler during the preparation and previous to the deployment that exchange isotopically with the analyte uptake. Thus, PRC dissipation and analyte uptake are theoretically equally affected by exposure conditions (Mazzella et al., 2010). PRCs have been widely used in the sampling of hydrophobic compounds (Allan et al., 2010; Harman et al., 2009). Nevertheless, their use in the determination of hydrophilic analytes using POCIS is under investigation, due to the fact that the exchange does not occur with all the PRCs (Mazzella et al., 2010; Alvarez et al., 2007). Thus, recently, Harman et al. (2011) suggested that POCIS were a useful screening tool but not useful to calculate the concentration of polar compounds in the environment, even using PRCs. However, this suggestion must be carefully researched in order to obtain proper conclusions.

Different R_s values have been calculated for APs and oestrogens by *in situ* calibration (Rujiralai et al., 2011) in WWTP effluent or by laboratory calibration (Li et al., 2010a) for their determination in natural waters using POCIS. However, PRCs have not been used in those studies.

Therefore, in this work, POCIS have been studied for the sampling of three APs, 4*t*OP, 4OP and 4NPs, eleven oestrogens