Chemosphere 200 (2018) 351–357

Contents lists available at ScienceDirect

Chemosphere

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

Investigation and application of diffusive gradients in thin-films technique for measuring endocrine disrupting chemicals in seawaters

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HIGHLIGHTS

- XDA-DGT was developed for determining EDCs in seawaters.
- XDA-DGT is suitable for a range of pH (7–9) and ionic strength (0.4–0.8 M).
- XDA-DGT showed good linear uptakes for EDCs over 15 d in artificial seawater.

ARTICLE INFO

Article history:
Received 30 December 2017
Received in revised form
12 February 2018
Accepted 16 February 2018
Available online 17 February 2018

Handling Editor: Keith Maruya

Keywords:
Diffusive gradients in thin-films
Endocrine disrupting chemicals
Seawater
Passive sampling
Water analysis

ABSTRACT

Endocrine disrupting chemicals (EDCs) can be released to coastal waters and affect the endocrine system of marine organisms. To monitor their levels in seawaters, a simple, robust passive sampling method, the diffusive gradients in thin-films (DGT) technique, was developed with XDA-1 resin as a binding agent. Six EDCs (including three estrogens, two pesticides and bisphenol A) were used to assess the performance of the DGT. The XDA-1 binding gel showed adequate ability for adsorbing EDCs in seawaters. The DGT sampler exhibited linear accumulation for the EDCs during a 15-day deployment and diffusion coefficients and sampling rates were calculated. The DGT measurement was independent of pH in the range 7.0–9.0 and ionic strength in the range 0.4–0.8 M. Field applications of this DGT in a coast of Dalian (China) showed comparable results to those from grab sampling. Five EDCs were detected with concentrations ranging from 0.7 to 19.4 ng L^{-1}. This study is a first attempt to apply DGT sampler for determining EDCs in seawaters.

1. Introduction

Endocrine disrupting chemicals (EDCs) are exogenous substances that can interfere with endocrine systems and cause adverse developmental, reproductive, neurological, and immune effects (Theo et al., 1993; Diamanti-Kandarakis et al., 2009). EDCs were listed as hazardous pollutants by both the US Environmental Protection Agency (USEPA) and the European Union (EU) (Harding et al., 2006; Legler et al., 2015). More than 1400 substances can be potential EDCs according to a list published by the Endocrine Disruption Exchange of the TEDX research institute, including (but not limited to) food additives, pesticides, plasticizers, estrogens, dyes, etc. (website, 2017). EDCs can be released to the environment via wastewater treatment plants (WWTPs) or direct discharge of household and industrial wastewaters (Laganà et al., 2004; Zhang and Zhou, 2008; Gu et al., 2017). Despite their low concentrations (from ng L^{-1} to μg L^{-1}) present in the aquatic environment (Kim et al., 2007; Kasprzyk-Hordern et al., 2008; Yoon et al., 2010), concerns about EDCs pollution have been increasing due to the fact that even a trace amount of them is adequate to exert effects (Welshons et al., 2003; Vandenberg et al., 2012).

Coastal water is an important part of ecosystems with high levels of biodiversity, and provides lots of nutrients for marine life, while it is also a major sink for most pollutants (Olsen et al.; Shahidul Islam and Tanaka, 2004; Beaumont et al., 2008). Large

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https://doi.org/10.1016/j.chemosphere.2018.02.096
0045-6535/

amounts of EDCs can be discharged into coastal waters through rivers and drain outlets, which may influence the endocrine systems of the marine organisms (Zhang et al., 2016). Thus, it is essential to investigate the environmental levels of EDCs in coastal waters for further assessing their potential risks to marine ecosystem and human health (Ismail et al., 2017).

The determination of EDCs levels in coastal waters is usually carried out by grab sampling, while grab sampling cannot represent the pollution status of the surroundings well because it may miss the discharge events or the concentration changes resulted from violent turbulences at the sampling district (Arditsoglou and Voutsa, 2012; Xu et al., 2014). Compared with the grab sampling, passive sampling is much more economic and convenient to operate, and more importantly, it can provide time-weighted average concentrations of analytes (Stuer-Lauridsen, 2005; Vrana et al., 2005; Schnoor and Gentleman, 2009). Among the current aquatic passive samplers, the technique of diffusive gradients in thin-films (DGT) can be applied without calibration rather than other samplers (such as polar organic chemical integrative sampler, POCIS) with a need of performance reference compounds (Chen et al., 2013, 2017).

DGT has been developed to measure both inorganic and organic substances since 1990s (Zhang and Davison, 1995; Cai et al., 2017). Indeed, there has been a few investigations on measuring EDCs in aquatic environment by DGT method such as measuring phenol, 4-chlorophenol, bisphenols, pesticides and estrogens in WWTPs and rivers (Dong et al., 2014a, 2014b; Fauvelle et al., 2015; Zheng et al., 2015; Guo et al., 2017b). Although some EDCs measurements with DGT have been proved to be independent of pH and ionic strength (IS), the studied pH and IS scales could not cover the conditions of seawater (pH about 8.0 and IS about 0.7 M) and these studies were all finally applied to freshwater environment. It is unclear whether DGT is suitable for measuring EDCs in seawaters.

In our previous study, a DGT sampler with a kind of Macroporous XDA resin as binding gel (named XDA-DGT) was developed for measuring antibiotics in seawaters (Xie et al., 2017). We found the XDA binding gel has high capacity for antibiotics and can adapt to the seawater conditions. In this study, six EDCs (including three estrogens, two pesticides and bisphenol A) that are widely used, frequently detected in aquatic environments were chosen as model compounds (Shi et al., 2014), and experiments were carried out to investigate whether the XDA-DGT can be applied for determining EDCs in seawaters, including evaluation of adsorption kinetics, validation of linear mass accumulation over time and investigating effects of pH and ionic strength on the measurements. The XDA-DGT sampler was also deployed in a coast, alongside grab samplings, to evaluate its application in the field. As far as we know, this is a first attempt to measure marine EDCs by the DGT technique.

2. Experimental section

2.1. Reagents and materials

EDCs standards, 17β-Estradiol (Estradiol), 17α-Ethynylestradiol (Ethynylestradiol) and Estriol were purchased from J&K Scientific Ltd. (China). Bisphenol A was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Atrazine and Acetochlor were purchased from Shandong Binnong Technology Co., Ltd (China). Internal standards, Atrazine-D_5 and Bisphenol A-D_{14} were purchased from Dr. Ehrenstorfer (Germany). Purities of all the chemicals are more than 95%. Physical-chemical properties of the target compounds are listed in Table S1 in the Supporting Information (SI).

Methanol of HPLC grade was purchased from Sigma-Aldrich (St Louis, MO, USA). Macroporous XDA-1 resin with polystyrene as functional groups was obtained from Sunresin Co., Ltd. (China). The surface area and average pore diameter of the resin are 1000–1200 m^2/g and 2.6–3.2 nm, respectively. Agarose was purchased from Solarbio Science & Technology Co., Ltd. (China). Polytetrafluoroethylene (PTFE) and polyethersulfone (PES) filter membranes were obtained from Tianjin Jinteng Experiment Equipment Co., Ltd. (China) with diameters of 25 mm and pore sizes of 0.45 μm. All the experiments except for those investigating the effect of pH and ionic strength on DGT measurement were performed in artificial seawater. The artificial seawater was prepared according to Kester' formulation (Kester et al., 1967) and all the ingredients were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (China).

2.2. XDA-DGT preparation

The XDA-DGT consists of a 0.8 mm thick agarose diffusive gel, a 0.5 mm thick XDA binding gel and acetonitrile-butadiene-styrene (ABS) base and cap. The diffusive gel and the binding gel were prepared according to a previously reported procedure (Xie et al., 2017).

2.3. Analysis of EDCs and detection limits

The analyte concentration measured by DGT, C_{DGT}, can be calculated by the following equation (Chen et al., 2012):

$$C_{DGT} = \frac{M(\Delta g + \delta)}{DAt} \quad (1)$$

where M is the measured mass of a target analyte accumulated on the binding gel, Δg is the thickness of the diffusion layer, δ is the diffusive boundary layer thickness, D is the diffusion coefficient of the analyte in the diffusive gel, t is the exposure time and A is the DGT exposure area. Under well-stirred conditions such as the turbulent seawater, δ is much smaller than Δg therefore it can be neglected (Zheng et al., 2015).

As detailed in the SI, the EDCs were quantified by a Waters Xevo TQ-S ultra-performance liquid chromatography coupled with a triple quadrupole mass detector (Table S2). The instrumental limits of quantitation (LOQ) were calculated based on the signal/noise ratios of 10. Method detection limits (MDLs) were calculated from the LOQs for a DGT deployment time of 3 days at 25 °C. Both LOQs and MDLs are listed in Table S3. No EDCs could be detected in the blank DGT units.

2.4. XDA-DGT performance in laboratory

2.4.1. Possible adsorption by DGT materials

Diffusive gels and two types of filter membranes (PES and PTFE) were exposed in 10 mL of artificial seawater containing 100 μg L^{-1} EDCs ($n = 3$). All the solutions were shaken horizontally for 12 h. Concentrations of the EDCs before and after the exposure were measured to evaluate the possible adsorption.

2.4.2. Binding gel adsorption kinetics and elution efficiencies

To investigate the uptake kinetics of EDCs to the binding gel, which is an important factor affecting performance of the DGT, XDA binding gels were immersed in 10 mL of 100 μg L^{-1} of EDCs solutions and shaken for various time from 5 min to 24 h ($n = 3$). Concentrations of the EDCs were measured before and after the adsorption, and the difference between them was regarded as the amount taken up by the binding gels.

The elution efficiencies of the EDCs were obtained by exposing binding gels to 10 mL of 100 μg L^{-1} of EDCs solutions for 12 h ($n = 5$). The binding gels were taken out and then eluted twice with