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Development and application of the diffusive gradients in thin films technique for simultaneous measurement of methcathinone and ephedrine in surface river water

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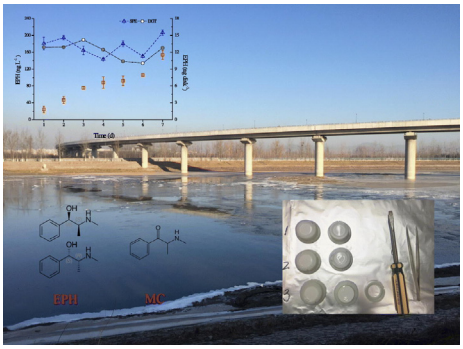
HIGHLIGHTS

- Suitable DGT configuration for EPH and MC measurement was developed.
- DGT was tested and deployed in the real water environment for its applicability.
- DGT concentrations were comparable to the solid phase extraction concentrations.
- EPH was dominant in Beijing urban rivers, while MC was below its detection limit.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a passive sampling technique, diffusive gradients in thin films (DGT) was developed to simultaneously measure two drugs, methcathinone (MC) and ephedrine (EPH) in surface water. Four types of binding gels and four types of filter membranes were tested for the optimal configuration. XAD18 agarose binding gel and agarose diffusive gel, together with polyethersulfone filter membrane were used for measuring MC and EPH in the DGT device. 5% NH_3 in acetonitrile was used as the elution solvent, with the elution efficiency for MC and EPH higher than 71%. At 25 °C, the diffusion coefficients of MC and EPH in the diffusive gel were 7.60×10^{-6} cm^2 s^{-1} and 6.62×10^{-6} cm^2 s^{-1}, respectively. The DGT was effective in a wide range of pH (4–11) and ionic strength (NaCl: 0.001–0.5 M). The DGT device was deployed in Beijing urban surface water for successive 7 days to measure the time-weighted concentrations of MC and EPH. Results showed that EPH was detected in all samples, while MC was below its detection limit. DGT concentrations were comparable to the concentrations determined by SPE. This study demonstrated that the developed DGT method was effective to monitor the two drugs in surface water *in situ*.

1. Introduction

As one kind of polar organic micro-pollutants, drugs of abuse have potent pharmacological and biological activities (Pal et al., 2013;

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Petrie et al., 2016). The worldwide consumption and limited removal in the sewage treatment plants (STPs) resulted in their occurrence of these drugs and their metabolites in the aquatic ecosystem. Due to the continuous input to the surrounding environment, these drugs are deemed as the "pseudo-persistent" substances and likely to induce DNA damage of aquatic organisms, increasing health and ecological risks (Binelli et al., 2012; Catalá et al., 2015; Liao et al., 2015; Mendoza et al., 2014; Parolini et al., 2015, 2016). To improve understanding of the occurrence, distribution and fate of these chemicals and their potential risk on aquatic and human life, it necessitates the accurate measurement of these hydrophilic compounds in the water samples.

In recent years, drugs of abuse have been detected in various water bodies, such as river, lake, coastal water, and even in drinking water and groundwater, with concentrations ranging from pg L^{-1} to ng L^{-1} (Baker and Kasprzyk-Hordern, 2013; Boleda et al., 2011; Jurado et al., 2012; Li et al., 2016). In most of these studies, active sampling technique, especially solid phase extraction (SPE), was commonly used for drugs measurement. The active sampling approach however, was time-consuming and costly (Togola and Budzinski, 2007). It gave the monitoring data at the time of sampling campaign, which was likely to neglect the information such as the change of flow rate, chemical inputs, and the effect of precipitation (Bartelt-Hunt et al., 2009). Consequently, fluctuations on weekly and seasonal concentrations were reported in different studies (Chiaia-Hernandez et al., 2011; Lai et al., 2011; Reid et al., 2011; Thomas et al., 2012; van Nuijs et al., 2011). Passive sampling, which could measure time-weighted concentration was adopted to address this concern. Of the various passive samplers, the semi-permeable membrane device (SPMD) was the most widely used, which is able to measure low concentrations of organic pollutants and mimic their bioconcentration (Zhang et al., 2008). However, SPMD was not able to detect polar organic compounds such as pharmaceuticals (Petty et al., 2004). Polar organic chemical integrative sampler (POCIS) can monitor polar organic micro-pollutants, including pharmaceutical and illicit drugs in water (Bartelt-Hunt et al., 2009; Fedorova et al., 2014; Togola and Budzinski, 2007). This method however, is semi-quantitative and requires complex pre-experiment to determine the key parameter *Rs* for the accurate calculation of the target compounds (Togola and Budzinski, 2007). In 1994, Davison and Zhang invented the diffusive gradients in thin films (DGT) to measure the speciation of heavy metals in water (Davison and Zhang, 1994), Then the DGT device was successfully developed to measure metals, nutrients and some inorganic elements in water environment and soil/sediments (Chen et al., 2012; Ding et al., 2010; Glæsner et al., 2012; Huynh et al., 2012; Xu et al., 2013). Recently, this technique was successively applied for quantifying polar organics including antibiotics and bisphenols in surface water and sewage (Chen et al., 2012, 2013a, 2013b, 2015; Zheng et al., 2014). Due to its independent of water flow, convenient operation and high stability to the outside interference, DGT was expected to be able to measure those drugs of abuse in the aquatic environment.

The objective of this study was to investigate the feasibility of DGT method to measure methcathinone (MC) and ephedrine (EPH) in the surface water. According to China Narcotic Control Bureau, MC was one kind of emerging synthetic illicit drug with large amount of production in China (China National Narcotics Control Commission, 2016). EPH was the drug therapeutically used for treating influenza, asthma or hypotension (Mendoza et al., 2014), and it was also the precursor drug for synthesis of amphetamine and methamphetamine (China National Narcotics Control Commission, 2016). To test the DGT method, in this study, the binding gel, diffusive gel and the filter membrane used in DGT for the two drugs were determined. The uptake kinetics and elution efficiency by the selected gel, the diffusion coefficient (D) of each drug, the uptake capacity of the binding gel, and the effect of water parameters such as pH and ionic strength on the drugs uptake were investigated as well. The established DGT method was deployed in Beijing urban river water, together with the active sampling method for comparison. The result from this study could examine the feasibility of DGT technique to determine the two drugs, and provide an alternative method for monitoring polar drugs of abuse in the aquatic environment.

2. Experimental section

2.1. Reagents and materials

MC, EPH and the internal standard (EPH-HCl-*d8*) were purchased from Cerilliant Corporation (Round Rock, TX). The properties of the drugs were shown in Supplementary Materials (Table S1). Stock solution at 100 mg L^{-1} of MC or EPH were prepared in methanol (HPLC grade) and stored in sealed amber glass bottles at −20 °C. Acetonitrile (ACN) and methanol (MeOH) were purchased from Fisher (Poole, UK). Milli-Q water was prepared by a Milli-Q system (Millipore, MA, US). SPE cartridges (Oasis MCX, 60 mg, 3 mL) were obtained from Waters Corporation (Milford, MA, US). Filter membranes used in this study had diameters of 25 mm and pore sizes of 0.45 μm. Nylon (NL), mixed cellulose ester (MCE), and hydrophilic polytetrafluoroethylene (PTFE) were purchased from Shanghai Anpel Scientific Instrument Co., and polyethersulfone (PES) was obtained from Pall Co., USA. Four different agarose binding gels (XAD18, HLB, MCX and activated carbon) stored in 0.01 M NaCl solution were purchased from DGT Research Ltd., UK. The standard DGT configuration which was purchased from DGT Research Ltd. included the acetonitrile-butadiene-styrene (ABS) molding, a 0.5-mm thick of binding gel (XAD18 agarose), a 0.8-mm thick of agarose diffusive gel and a PES membrane filter (0.14 mm thickness). The exposure area of the DGT plastic body was 3.1 cm^2.

2.2. Measurement of the diffusion coefficients (D)

The theory of DGT was based on Fick's first law (Chen et al., 2015). Target compounds diffuse through the diffusive layer and are quickly adsorbed by the resin in the binding gel. If the solution is well stirred, concentration could be kept constant in the solution and there exists a stable concentration gradient in the diffusive layer in the experiment. There are two methods in determining the diffusion coefficient. One is the use of diffusion cell (Zheng et al., 2014), and the other is through DGT deployment (Wang et al., 2016). In this study, the diffusion coefficient (D) values were measured in a diaphragm diffusion cell, according to the procedure by Zheng et al. (2014). The cell comprised two compartments, between which there located a 0.80-mm thick agarose diffusive gel. In the source compartment the solution contained 50 mL of 2 mg L^{-1} MC or EPH. In the receptor compartment the solution was the same except for the absence of drugs. In the two compartments the solutions were thoroughly stirred during the experiment. Samples were taken at certain time intervals from both compartments for MC or EPH analysis. The D values were calculated by plotting the measured mass of each drug diffused into the receptor compartment *vs* time, Eq. (1):

$$D = (\text{slope})\frac{\Delta g}{CA} \tag{1}$$

where, A (~2.51 cm^2) was the area of the connecting window of the diffusion cell, C was the compound concentration in the receptor compartment, and Δg (~0.089 cm) was the thickness of the diffusive gel.

When the volume of the eluent (V_e, L) was known, M could be calculated by Eq. (2):

$$M = \frac{C_e(V_e + V_{gel})}{f_e} \tag{2}$$

where C_e (μg L^{-1}) was the compound concentration in the eluent, V_{gel} (L) was the volume of the binding gel, which was 0.15 mL in this study, and f_e was the recovery rate from the elution.