

1 Diffusive gradients in thin-films (DGT) for *in situ*  
2 sampling of selected endocrine disrupting  
3 chemicals (EDCs) in waters

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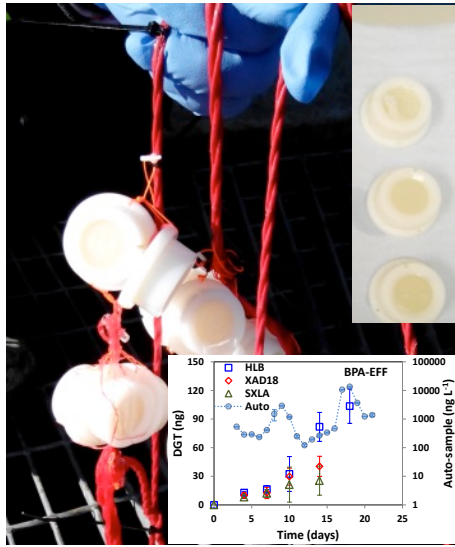
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## 20 **ABSTRACT**

21 A passive water sampler based on the diffusive gradients in thin-films (DGT) technique was developed  
22 and tested for 3 groups of endocrine disrupting chemicals (EDCs, including oestrogens, alkyl-phenols  
23 and bisphenols). Three different resins (hydrophilic-lipophilic-balanced (HLB), XAD18 and Strata-XL-  
24 A (SXLA)) were investigated for their suitability as the binding phase for DGT devices. Laboratory  
25 tests across a range of pH (3.5-9.5), ionic strength (0.001-0.5 M) and dissolved organic matter  
26 concentration (0-20 mg L<sup>-1</sup>) showed HLB and XAD18-DGT devices were more stable compared to  
27 SXLA-DGT. HLB-DGT and XAD18-DGT accumulated test chemicals with time consistent with  
28 theoretical predictions, while SXLA-DGT accumulated reduced amounts of chemical. DGT  
29 performance was also compared in field deployments up to 28 days, alongside conventional active  
30 sampling at a wastewater treatment plant. Uptake was linear to the samplers over 18 days, and then  
31 began to plateau/decline, indicating the maximum deployment time in those conditions. Concentrations  
32 provided by the DGT samplers compared well with those provided by auto-samplers. DGT integrated  
33 concentrations over the deployment period in a way that grab-sampling cannot. The advantages of the  
34 DGT sampler over active sampling include: low cost, ease of simultaneous multi-site deployment, *in*  
35 *situ* analyte pre-concentration and reduction of matrix interferences compared with conventional  
36 methods. Compared to other passive sampler designs, DGT uptake is independent of flow rate and  
37 therefore allows direct derivation of field concentrations from measured compound diffusion  
38 coefficients. This passive DGT sampler therefore constitutes a viable and attractive alternative to  
39 conventional grab and active water sampling for routine monitoring of selected EDCs.

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41 **Keywords:** Passive sampling, Diffusive gradients in thin-films (DGT), Wastewater, Water  
42 Framework Directive, Water Quality, Monitoring

## 43 1. INTRODUCTION

44 Passive sampling techniques have become popular for the monitoring of organic compounds  
45 present in aquatic systems (Chen et al. 2013, Chen et al. 2015b, Miège et al. 2015, Mills et al.  
46 2014, Mills et al. 2007, Vrana et al. 2005) since first introduced in the 1980s (Soedergren 1987).  
47 Passive sampling can provide several advantages over traditional grab sampling, namely: *in*  
48 *situ* measurement of time-weighted average (TWA) concentrations; analyte pre-concentration  
49 and reduced matrix interference; low cost; ease of deployment. Different designs of passive  
50 water sampler have been developed and are available for sampling a range of organic chemicals  
51 in water. Among the most popular are: semipermeable membrane devices (SPMDs, (Huckins  
52 et al. 1990)); the polar organic chemical integrative sampler (POCIS, with hydrophilic-  
53 lipophilic-balanced (HLB) resin as the receiving phase, (Alvarez et al. 2004)) and the  
54 Chemcatcher (Kingston et al. 2000). POCIS and Chemcatcher have been developed for  
55 monitoring many polar organic chemicals (POCs) in the aquatic environment (Miège et al.  
56 2015, Mills et al. 2014). However, these samplers can have problems: their uptake of chemical  
57 compounds is dependent on hydrodynamic conditions (water flow and turbulence), and can be  
58 affected by other environmental parameters such as pH, salinity/ionic strength (IS), dissolved  
59 organic matter (DOM) and fouling/biofouling (Harman et al. 2012, Li et al. 2011, Li et al.  
60 2010, MacLeod et al. 2007, Togola and Budzinski 2007). These can result in considerable  
61 measurement uncertainty (Harman et al. 2012, Mills et al. 2014). The approach often used to  
62 compensate for these difficulties when analysing hydrophobic chemicals is to add performance  
63 reference compounds (PRCs) to the samplers and check on the amount lost during deployment,  
64 since this is a function of flow rate and uptake rates can then be derived and measured amounts  
65 ‘corrected’ accordingly (Belles et al. 2014, Harman et al. 2012, Vallejo et al. 2013). However,  
66 this approach will not work for POCs, due to the discrepancy between factors controlling the  
67 release of PRCs and those controlling the uptake of target chemicals (Harman et al. 2012).

68 Other novel passive water sampling devices are therefore needed for environmental monitoring  
69 under conditions of changing aquatic environments, to provide more reliable data. Reliable  
70 and accurate data on environmental concentrations is crucial for risk assessment of these  
71 chemicals and studying their fate in the environment (Zhu et al. 2016). Diffusive gradients in  
72 thin-films (DGT), developed by Zhang and Davison in 1994 (Davison and Zhang 1994), has  
73 been amply demonstrated to provide quantitative *in situ* measurements of trace components in  
74 aqueous systems (Zhang and Davison 1995). Originally developed for heavy metals and  
75 nutrients, studies over the last two decades have shown that the DGT technique has the potential  
76 to be a standard sampling technique, because of its simplicity and wide applicability (Davison  
77 and Zhang 2012, Zhang and Davison 2015) for a wide range of inorganic species (Davison and  
78 Zhang 2012). DGT samplers can be directly applied in the field without *in-situ* calibration, as  
79 the transport of the analyte is solely controlled by its molecular diffusion and the thickness of  
80 the diffusion layer (Davison and Zhang 1994, Zhang and Davison 1995). Thus, this approach  
81 is insensitive to hydrodynamic conditions (Davison and Zhang 2012, Zhang and Davison  
82 1995), which is an important virtue over other passive samplers. It has been demonstrated that  
83 DGT provides accurate TWA concentrations of dissolved labile chemicals in aquatic systems.  
84 Over 700 papers have now been published using DGT, with over 300 users in more than 30  
85 countries. Building on this track record, DGT has been developed more recently to sample a  
86 range of organic chemicals, including antibiotics (Chen et al. 2015a, Chen et al. 2012, Chen et  
87 al. 2013), household and personal care products (Chen et al. 2017), polar organic contaminants  
88 (Challis et al. 2016), anionic pesticides (Guibal et al. 2017), bisphenols (Zheng et al. 2015),  
89 phenol and 4-chlorophenol (Dong et al. 2014a, Dong et al. 2014b), glyphosate and  
90 aminomethyl phosphonic acid (Fauvelle et al. 2015) and illicit drugs (Guo et al. 2017). This  
91 paper develops DGT for a very important new set of selected endocrine disrupting compounds.  
92 EDCs can be broadly defined as exogenous chemicals that can interfere with any aspect of

93 endocrine hormone action (Zoeller et al. 2012), which can pose adverse effects on reproduction  
94 and metabolism to human and animals. Oestrogens, alkyl-phenols and bisphenols are among  
95 the well-known EDCs, which have been widely-used in products for daily life. They have  
96 attracted much attention from the public and scientists (Diamanti-Kandarakis et al. 2009) and  
97 their occurrence in the environment, especially the aquatic environment has been widely  
98 reported (Arditsoglou and Voutsas 2008, Tijani et al. 2013). Their presence in freshwaters is  
99 mainly attributed to direct discharge from wastewater treatment plants (WWTPs) and indirect  
100 inputs from agricultural (animal husbandry) activities (Tijani et al. 2013, Xu et al. 2012).  
101 POCIS and Chemcatcher passive samplers have been applied to some EDCs in earlier studies  
102 (Arditsoglou and Voutsas, 2008, Vallejo et al., 2013). Considering the effect of hydrodynamics  
103 of the water on the quantification of EDCs using the above two samplers, it is crucial to develop  
104 a DGT-based sampler that is much less affected by the condition of the water. Thus, a validated  
105 DGT device for measurement of these EDCs in the aquatic environment would make a very  
106 helpful contribution to monitoring, source apportionment and fate studies.

107 In this study, a DGT sampler was therefore developed for common, major oestrogens, alkyl-  
108 phenols and bisphenols in waters. The performance of three types of DGT was systematically  
109 tested in the laboratory under a range of pH, ionic strength and dissolved organic matter. Field  
110 trials were also performed, alongside conventional sampling, in the challenging field conditions  
111 of a WWTP.

## 112 **2. MATERIALS AND METHODS**

### 113 **2.1 DGT Principle**

114 A typical DGT device is composed of a backing piston and a front cap with 2 cm diameter  
115 window (see Supplementary data (SD) **Figure SD1** for schematic diagram). Layers of resin  
116 gel, diffusive gel and a protective filter are placed successively and securely between the top

117 of the piston and the back of the cap. The principle of the DGT technique is based on Fick's  
118 first law of diffusion (Davison and Zhang 2012, Zhang and Davison 1995). The DGT measured  
119 concentration,  $C_{DGT}$ , is a TWA concentration over the period of deployment. It can be expressed  
120 using Equations (1) and (2) when the thickness of the diffusive boundary layer (DBL,  $\delta$ ) is  
121 either negligible or not negligible compared to the thickness of the diffusive layer ( $\Delta g$ ),  
122 respectively (Zhang and Davison 1995):

$$123 \quad C_{DGT} = \frac{M\Delta g}{DA t} \quad (1)$$

$$124 \quad C_{DGT} = \frac{M(\Delta g + \delta)}{DA t} \quad (2)$$

125 where  $M$  is the measured mass of test chemical accumulated in the binding gel layer,  $D$  is the  
126 diffusion coefficient of test chemical in the diffusive gel,  $t$  is the exposure time and  $A$  is the  
127 exposure window area of the cap.

## 128 **2.2 Chemical and Reagents**

129 Three groups of EDCs - oestrogens, alkyl-phenols and bisphenols, were selected for this study,  
130 as follows: diethylstilbestrol (DES), estrone (E1),  $\beta$ -estradiol (E2), estriol (E3) and  $17\alpha$ -  
131 ethinylestradiol (EE2), 4-*tert*-octylphenol(4-*t*-OP) and nonylphenol (NP), and bisphenol-A  
132 (BPA). High purity standards of these chemicals were purchased from Sigma-Aldrich (UK).  
133 Stable isotope-labelled internal standards (SIL-ISs), estrone-2,4,16,16- $d_4$  (E1- $d_4$ ),  $17\beta$ -  
134 Estradiol-2,4,16,16,17- $d_5$  (E2- $d_5$ ), estriol-2,4- $d_2$  (E3- $d_2$ ),  $17\alpha$ -ethinylestradiol-2,4,16,16- $d_4$   
135 (EE2- $d_4$ ), 4-*n*-octyl- $d_{17}$ -phenol (4-*n*-OP- $d_{17}$ ) and 4-*n*-nonylphenol-2,3,5,6- $d_4$  (4-*n*-NP- $d_4$ ) were  
136 purchased from QMX Laboratories (UK), BPA- $d_{16}$  was purchased from Sigma-Aldrich (UK).  
137 E1, E2, E3, EE2 and BPA were selected as the test chemicals for the laboratory experiments,  
138 while all eight EDCs were analysed for the field validation. Information on target EDCs and  
139 SIL-ISs is provided in **Table SD1**. The preparation of standards followed previously published

140 procedures (Chen et al. 2016). All reagents were at least analytical grade with  $\geq 99\%$  purity,  
141 organic solvents are HPLC grade. Ammonia solution ( $\text{NH}_4\text{OH}$ , 5 M) was purchased from  
142 Sigma-Aldrich (UK). Hydrochloric acid (HCl, 35.5-37.5%), methanol (MeOH), acetonitrile  
143 (ACN) and ethyl acetate (EA) were obtained from Fisher Scientific (UK). Deionised water with  
144 resistivity  $>18.2 \text{ M}\Omega \text{ cm}^{-1}$  was used in the experiments (Milli-Q water purification system  
145 (Millipore, UK).

### 146 **2.3 DGT Preparation and Procedure**

147 Three polymer-based resins were tested in this study to select the best binding gel for DGT:  
148 HLB from Waters Corporation (UK), XAD18 from Dow Chemical Company (USA) and  
149 Strata-XL-A (SXLA) from Phenomenex Inc(UK). The selection of the resins was based on  
150 their commercial availability, potential fast adsorption and large capacity for the target  
151 compounds. The resins were pre-washed with MQ water, immersed in methanol, and then  
152 washed in MQ water before use. The diffusive gels, polyacrylamide gel (PA gel, 1.0 mm),  
153 agarose gel (AG gel, 1.5 % agarose, different thicknesses), and binding gels (0.4 mm, HLB,  
154 XAD18 and SXLA resins) were prepared according to previously published procedures (Chen  
155 et al. 2017, Zhang and Davison 1999). The reagents used for gel making are described in the  
156 SD. The diffusive gels and resin gels were washed, cut and stored according to the procedure  
157 described previously (Chen et al. 2017).

### 158 **2.4 Performance Tests of DGT in Laboratory**

159 Tests were carried out to develop the DGT. These were: 1) adsorption of test chemicals to DGT  
160 holders, diffusive gels and membrane filters; 2) extraction recoveries for the three binding gels;  
161 and 3) uptake capacity and kinetics of the three binding gels. The diffusion coefficients ( $D$ ) for  
162 the selected EDCs in the diffusive gel were determined using the diffusion cell method (Zhang  
163 and Davison 1999). Details on the measurement and the calculation are given in the SD. The  
164 measured  $D$  values for test chemicals at  $25 \text{ }^\circ\text{C}$  are given in Table SD2. The  $D$  values at different



165 temperatures (1-35 °C) are estimated and given in **Table SD2**. The performance of the three  
166 types of DGT devices was subsequently tested for: 1) effects of pH, IS and DOM and 2) time  
167 and diffusion layer thickness dependence (see **SD**). The ratio of  $C_{\text{DGT}}$  to the directly measured  
168 concentration ( $C_b$ ) of EDCs in the bulk solution was used to evaluate the performance of DGT  
169 under the different conditions. A ratio of  $C_{\text{DGT}}/C_b$  from 0.9 to 1.1 was used to indicate satisfactory  
170 performance. The theoretical mass accumulated in the DGT was predicted using equation (1)  
171 and compared with the data obtained in the performance tests of different times and different  
172 diffusion layer thicknesses.

## 173 **2.5 Field Application in a WWTP**

174 DGT devices (1 mm agarose diffusive layer) with HLB, XAD18 or SXLA resins as binding  
175 gels were deployed *in situ* in the influent and effluent at a wastewater treatment plant (WWTP)  
176 in the UK simultaneously for 2 weeks (freely suspended at about 30 cm below the water  
177 surface). The WWTP employs a traditional activated sludge treatment and serves ca. 100,000  
178 inhabitants in an area of ~400 km<sup>2</sup>; the average effluent flow was ca. 45,000 m<sup>3</sup> d<sup>-1</sup> during the  
179 sampling period. The samplers were retrieved in triplicate after 4, 7, 10 and 14 days. Longer  
180 deployments were carried out only with HLB-DGT devices retrieved after 18, 21 and 28 days.  
181 A separate set of HLB-DGT devices prepared with different thicknesses of agarose diffusive  
182 gels (0.35, 0.5, 1, 1.5 and 2 mm) was deployed at the same sites for 8 days to estimate the *in*  
183 *situ* DBL thickness at t.

184 Water samples were also taken using an auto sampler and conventional grab-sample method at  
185 both influent and effluent sites for comparison with the DGT measurements. All-weather  
186 refrigerated automatic samplers were used to collect the influent and effluent in the WWTP  
187 with constant flow mode (~100 mL h<sup>-1</sup>) to provide 24-hour composite water samples. Grab  
188 samples were collected between 10 and 11 am on day 0, 7 and 14 of the DGT deployment using

189 1 L pre-cleaned amber bottles, following previously reported procedures (Chen et al. 2017).  
190 Temperature and pH in the influent and effluent were recorded daily (Table SD3).

## 191 **2.6 Chemical Analysis and Quality Assurance /Quality Control (QA/QC)**

192 All samples from the laboratory experiments were analysed on a Thermo Finnigan high  
193 performance liquid chromatography (HPLC) coupled with a photodiode array detector (DAD)  
194 for 5 test chemicals (see SD for set-up). All DGT and active samples from the field work were  
195 pre-treated according to the optimised extraction procedures, and analysed with an LC-tandem  
196 mass spectrometer (LC-MS/MS, Waters, UK) following the procedures reported by Chen et al.  
197 2016 (see also SD). Quality control procedures were included during sample preparation,  
198 collection, pre-treatment and analysis. These included: 1) parallel blank and control  
199 experiments accompanying laboratory tests; 2) DGT field blanks 3) DGT deployment carried  
200 out in at least triplicate, unless stated otherwise; 4) procedural blanks and replicate samples  
201 which were pre-treated in each set of extractions for both field DGT and wastewater samples;  
202 5) recovery tests of DGT extractions and wastewater sample SPEs, by spiking target chemicals  
203 and SIL-ISs; 6) matrix effects for the water samples were also assessed by LC-MS/MS; 7) a  
204 set of calibration standards were run before the analysis of each batch of samples; and 8) solvent  
205 blank samples and QC standard samples were injected daily to check for interference and cross  
206 contamination, and the instrument performance.

207 Detection limit (DL) is defined as the concentration that represents 3 times the signal to noise  
208 ratio (S/N). The instrument DLs (IDLs) (results given in Table SD4) of each EDC were  
209 calculated using standards with low concentrations; method DLs (MDLs) for DGT and water  
210 samples were estimated from IDLs, absolute extraction recoveries (DGT and SPE for  
211 wastewater) and the concentration factors (Chen et al. 2016). Details of calculations are given  
212 in the SD.

## 213 **2.7 Statistics**

214 All the laboratory experiment and field sampling was carried out at least in triplicate, unless  
215 stated and the results expressed as the average  $\pm$  standard deviation. The statistical analysis was  
216 conducted by IBM *SPSS* Statistics software (Version 22). Differences were statistically tested  
217 at the 5% significance level with non-parametric testing when  $n = 3$  or 4. For the extraction  
218 recovery experiments ( $n=12$ ), so differences were tested by the analysis of variance (ANOVA).

## 219 **3. RESULTS AND DISCUSSION**

### 220 **3.1 Method Detection Limits (MDLs)**

221 Field DGT blank samples did not contain detectable levels of EDCs. The DGT field MDLs  
222 were calculated for 7 and 14-day deployments at 10 °C (the average water temperature during  
223 field application). They ranged from 0.89 to 5.1 ng L<sup>-1</sup> (**Table SD4**) when deployment was for  
224 14 days.. The 14 day DGT MDLs were slightly higher than those for the SPE of large volume  
225 (500 mL) water samples, (0.33 to 1.7 ng L<sup>-1</sup>, **Table SD3**). For example, the MDL of E1 was  
226 0.89 ng L<sup>-1</sup> for 14-day DGT samples and 0.26 ng L<sup>-1</sup> for water samples - similar to data reported  
227 (0.20 ng L<sup>-1</sup>) from the literature ([Liu et al. 2011](#)). The typical concentration of E1 in freshwater  
228 is 1s-10s ng L<sup>-1</sup> ([Kolpin et al. 2002](#), [Liu et al. 2011](#)); the MDLs are therefore good enough for  
229 environmental applications. Lower MDLs for DGTs deployed in field studies could be  
230 achieved if needed, by combining replicate DGT samples, and/or further reducing the final  
231 sample volume, and/or reducing the thickness of the diffusive gel layer.

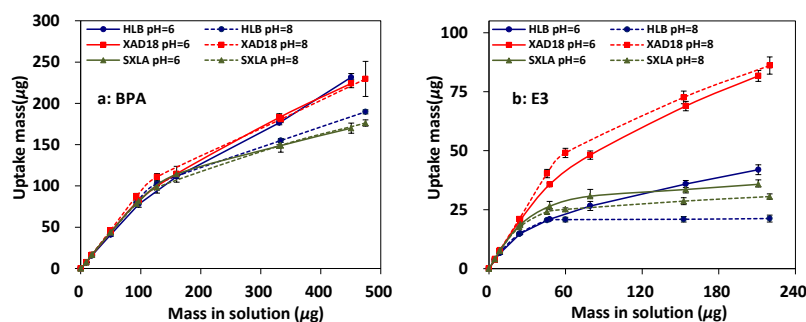
### 232 **3.2 Adsorption Properties of DGT Components**

233 No significant adsorption of EDCs occurred for the DGT holder, PC filter (10  $\mu$ m thickness,  
234 0.2  $\mu$ m of pore size, track-etch membrane, Nuclepore, Whatman) and agarose diffusive gels  
235 (AG gel) (**Figure SD3**). Thus, the AG gel (1.5%) and PC filter were selected as the diffusive  
236 layer and pre-filter for this study.

### 237 3.3 Extraction Recovery, Binding Capacity and Kinetic Uptake

238 Pre-experimental tests using MeOH as the extraction solvent showed recoveries of HLB  
239 binding gel for estrogenic chemicals were <60%, so ACN was selected instead. The results  
240 showed a single extraction using 5 mL ACN for 30 minutes in an ultrasonic bath achieved  
241 satisfactory extraction recovery for all test chemicals (see **Figure SD4** and associated  
242 discussion in **SD**). There was no significant difference (ANOVA,  $p>0.05$ ) between the three  
243 resin gels (see **Figure SD5** and associated discussion in **SD**). However, there was a marked  
244 difference between chemicals, with lowest recovery for E1 (71%), followed by E2 (88%) and  
245 about 100% for E3, EE2 and BPA (**Table SD5**).

246 All three resin gels demonstrated linear uptake of the EDCs initially up to 50-100  $\mu\text{g}$  of  
247 individual EDCs at both pH 6 and 8, except for E3 which had a shorter linear range (**Figures**  
248 **1** and **SD6**, and associated discussion in **SD**). The linear components of the uptake curves were  
249 used to estimate the maximum linear accumulation capacities of the binding gels, which ranged  
250 from 17.6 (E3) to 142 (EE2)  $\mu\text{g}$  per disc (**Table SD6**). Based on these uptake capacities and a  
251 practical deployment time of 2 weeks to 1 month, the maximum chemical concentrations that  
252 can be measured using DGT are in the range 50 to 1000  $\mu\text{g L}^{-1}$  (**Table SD6**) (i.e. far greater  
253 than concentrations encountered in natural/field environments).



254  
255 **Figure 1:** Masses ( $\mu\text{g}$ ) of BPA (a) and E3 (b) taken up by HLB, XAD18 and SXLA resin gels in 50 mL EDC  
256 solutions of various concentration at pH 6 and 8 (IS=0.01M,  $T=20\pm 2$  °C; n=3). Error bars: 1 standard deviation.

257 HLB and XAD18 gels took up the test EDCs at a similar rate (**Figure SD7**), but faster than the  
258 SXLA gel. According to Fick's law of diffusion, the rapid initial uptake (>100 ng in the first  
259 10 minutes in this study) is the key aspect to enable fully quantitative performance of DGT,  
260 which requires zero concentration at the binding gel/diffusive gel interface. This suggested that  
261 HLB and XAD18 gels were more suitable for use in the field (**Figure SD6**).

### 262 **3.4 Measured Diffusion Coefficients and Sampling Rate**

263 Measurements of  $D$  at 15°C and 20°C (**Table SD2**) compared well with the calculated values  
264 (a difference within 10%). This confirmed that the calculated  $D$  can be directly applied to  
265 calculate the TWA concentrations. This is consistent with **Zheng et al. (2015)** who suggested  
266 that the  $D$  for BPA was  $4.71 \text{ E-06 cm}^2 \text{ s}^{-1}$  (IS=0.01 M, pH=7,  $T=25^\circ\text{C}$ ), within 2% of the results  
267 presented here.

268 Sampling rates ( $R_s$ ) are a useful performance parameter for the evaluation of many passive  
269 sampling devices (**Harman et al. 2012**). For POCIS and Chemcatcher,  $R_s$  is normally measured  
270 or calibrated using laboratory or field data and then used to calculate TWA concentrations.  
271 Although the  $R_s$  was not used when calculating the TWA concentrations for DGT sampler  
272 (DGT only needs the  $D$  value), the DGT  $R_s$  has been estimated using Equation (3) for  
273 comparison purposes (**Chen et al. 2012**):

$$274 \quad R_s = \frac{D_e A}{\Delta g} \quad (3)$$

275 Due to the different designs and exposure areas ( $3.14 \text{ cm}^2$  for DGT, typically  $45.8 \text{ cm}^2$  for  
276 POCIS and  $15.9 \text{ cm}^2$  for Chemcatcher), the sampling rate per unit area ( $R_{s/A}$ ) was calculated. For  
277 the DGT sampler, the  $R_{s/A}$  can be estimated by Equation (4) below (**Chen et al. 2013**):

$$278 \quad R_{s/A} = \frac{D_e}{\Delta g} \quad \text{or} \quad R_{s/A} = \frac{R_s}{A} \quad (4)$$

279 The  $R_{SA}$  of selected EDCs for standard DGT samplers (1 mm diffusion layer) were calculated  
280 using  $D_e$  at 25 °C for individual chemicals measured using a diffusion cell (**Table SD7**). The  
281  $R_{SA}$  for POCIS and Chemcatcher were also calculated using published data for  $R_s$  (see **Table**  
282 **SD7**). The  $R_{SA}$  for DGT at 25 °C ranged from 2.94 to 4.18 mL (d cm<sup>2</sup>)<sup>-1</sup>, within a similar range  
283 for POCIS and Chemcatcher samplers. For BPA, the calculated  $R_{SA}$  for DGT, POCIS and  
284 Chemcatcher was 4.15 (or 4.07), 6.78 (ranged from 1.92 to 19.05) and 4.23 (ranged from 1.95-  
285 6.54) mL (d cm<sup>2</sup>)<sup>-1</sup>, respectively. These comparisons indicate that DGT can provide comparable  
286 sampling rates to POCIS and Chemcatcher. The large differences of  $R_{SA}$  between the different  
287 studies for POCIS and Chemcatcher may be because of varying DBL conditions in the field.

### 288 **3.5 Effect of pH, Ionic Strength and DOM**

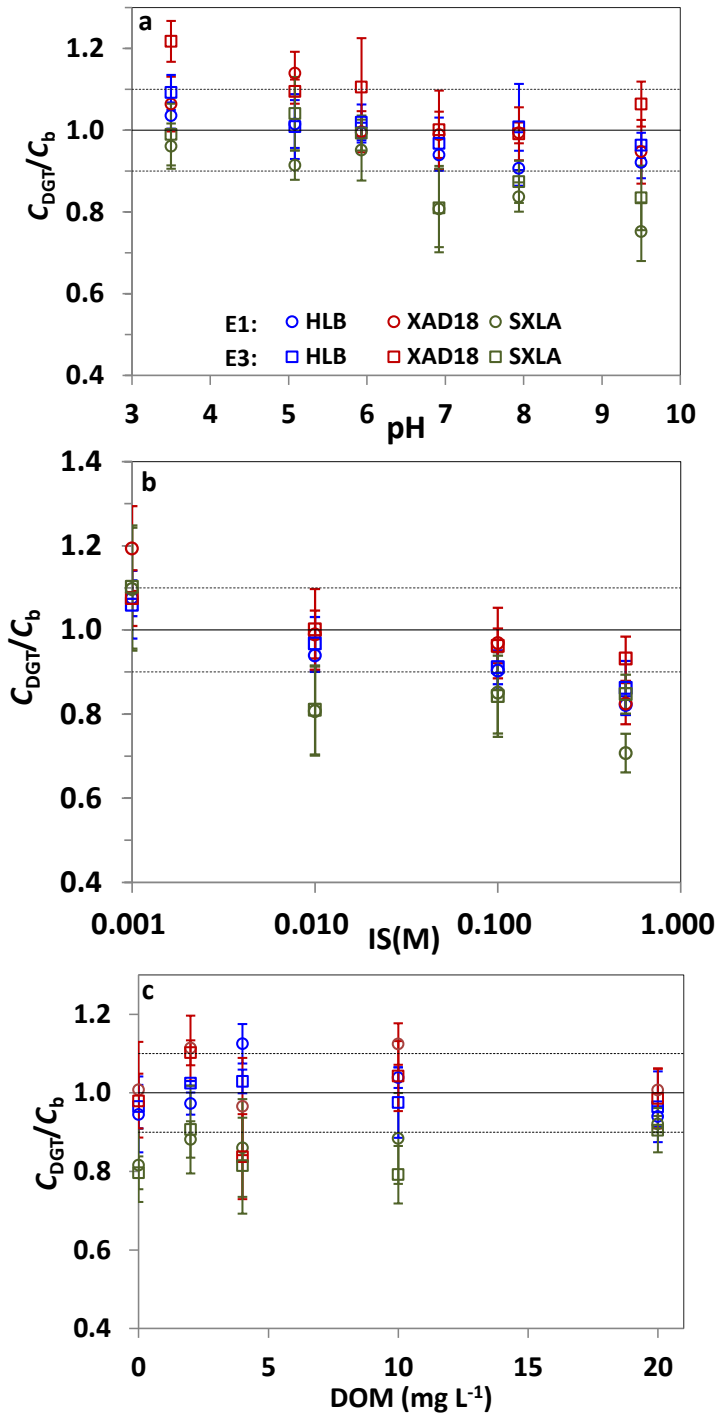
289 Most  $C_{DGT}/C_b$  values fell into the range 0.9-1.1 for XAD18 and HLB devices when the pH was  
290 3.5-9.5, indicating high accuracy and precision of the DGT measurements (**Figure 2a** and  
291 **Table SD8**). No significant difference was observed throughout the pH range investigated. A  
292 declining trend was observed for HLB-POCIS used for sampling similar EDCs (BPA, E1, E2  
293 and EE2), and for MAX-POCIS (MAX, similar to SXLA, a mixed-mode anion-exchange and  
294 reversed-phase sorbents) for phenols and estrogens (Li et al. 2011). Chen et al. (2012) reported  
295 similar findings using XAD18 as a resin for DGT to accumulate ionic antibiotics in water. The  
296 anionic proportion of EDCs increases at high pH so they may be less bound to the resin gels  
297 due to electrostatic repulsion (Domínguez et al. 2011), but this did not impact our results.

298 The effect of ionic strength (IS) on DGT performance was negligible, with most values of  
299  $C_{DGT}/C_b$  also falling between 0.9-1.1 (**Figures 1b** and **Table SD9**) for XAD18 and HLB devices  
300 between 0.001-0.1 M. A slight reduction of  $C_{DGT}/C_b$  occurred when IS increased to 0.5 M from  
301 0.1 M for all three types of DGT devices (**Figures 2b** and **SD9**), indicating that further work  
302 may be required for deployment in seawater. The possible reason could be competition from  
303 other ions for binding sites. This phenomenon has also been observed when XAD18 was used

304 as a resin for antibiotics (Chen et al. 2012), a range of pharmaceutical compounds (Togola and  
305 Budzinski 2007) and bisphenols (slight decline but all within acceptable limits) from 0.001 to  
306 0.5 M (Zheng et al. 2015).

307 Dissolved organic matter had no effect on DGT performance in the range of 0 to 20 mg DOM  
308  $L^{-1}$ .  $C_{DGT}/C_b$  values were within 0.9-1.1 for most compounds for all three types of DGT devices,  
309 with generally lower values (<1.0) for SXLA-DGT (Figure 2c and Table SD10). This again  
310 gives re-assurance that DGT samplers can be employed to derive quantitative information on  
311 the selected EDCs in a range of natural environments.

312 Considering the above results, DGT devices with HLB and XAD18 binding gels are a better  
313 choice for making measurements under a wide range of pH, IS and DOM conditions.



314

315 **Figure 2:** Effect of pH (a), IS (b) and DOM (c) on measurement for three types of DGT devices (n=3) for E1

316 and E3. The solid horizontal lines represent the value of 1 and the dotted horizontal lines represent the values at

317 0.9 and 1.1. Error bars were calculated from the standard deviation of three replicates.

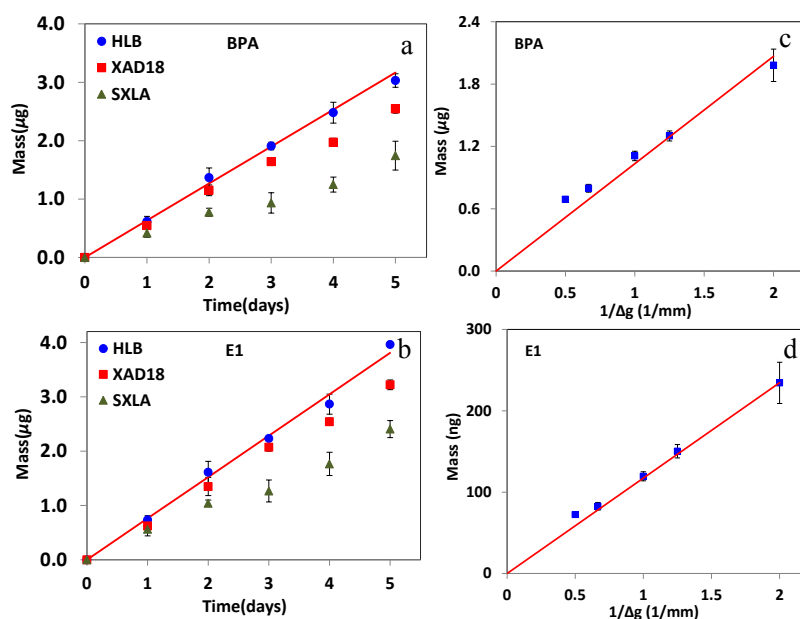


### 318 3.6 Validation of DGT for EDCs

319 Two validation experiments of EDCs uptake with deployment time and diffusion layer  
320 thicknesses were conducted in a standard solution in the laboratory, to confirm the samplers  
321 follow the DGT theory. The general order of accumulated mass for the three types of DGT  
322 devices was:  $HLB \geq XAD18 > SXLA$  (**Figures 3a-b** and **SD11**). Uptake by HLB-DGT devices  
323 agreed well with theoretical prediction according to Equation (1), with measured to predicted  
324 ratios close to 1. The XAD18-DGT devices accumulated similar amounts of EDCs to the HLB-  
325 DGT devices, just slightly lower than the theoretical predictions. Although the SXLA- DGT  
326 devices could accumulate the chemicals linearly with the deployment time, only ~60% of the  
327 theoretical predictions were accumulated after 5 days. There was no significant difference in  
328 accumulated mass in 24 h between the three ( $p > 0.05$ ), but a difference appeared after 24 h  
329 (**Figure 3a-b**). The possible reasons for different performance of three types of DGT devices  
330 could be: 1) different uptake efficiencies of the binding resins (slowest uptake by SXLA) and  
331 this difference will only appear after a period of time (>24 h); 2) competitive binding of  
332 chemicals on SXLA resin gels (this has been confirmed by the time dependence for individual  
333 compounds such as E3). Thus, both HLB and XAD18-DGT devices can be used for  
334 measurement of the selected EDCs in aquatic systems directly and accurately, while SXLA-  
335 DGT devices are not suitable unless “effective”  $D$  values are applied to calibrate the results.

336 The amounts of chemicals accumulated on the resin gels should be inversely proportional to  
337 the diffusion layer thickness, when DGT devices are exposed to a well-stirred EDC solution  
338 for a fixed immersion time. The data obtained for the HLB-DGT devices agreed well with  
339 theoretical predictions (**Figures 3c-d** and **SD12**). The results also demonstrated that the DBL  
340 effect could be ignored in the well-stirred solution, and the fit of measured data to the predicted  
341 concentration line confirmed that the use of diffusion coefficients in water was appropriate.  
342 Both results on time and diffusion layer thickness dependence confirm the DGT theory and

343 validated the direct use of HLB-DGT devices for simultaneous measurements of EDCs in  
344 waters.



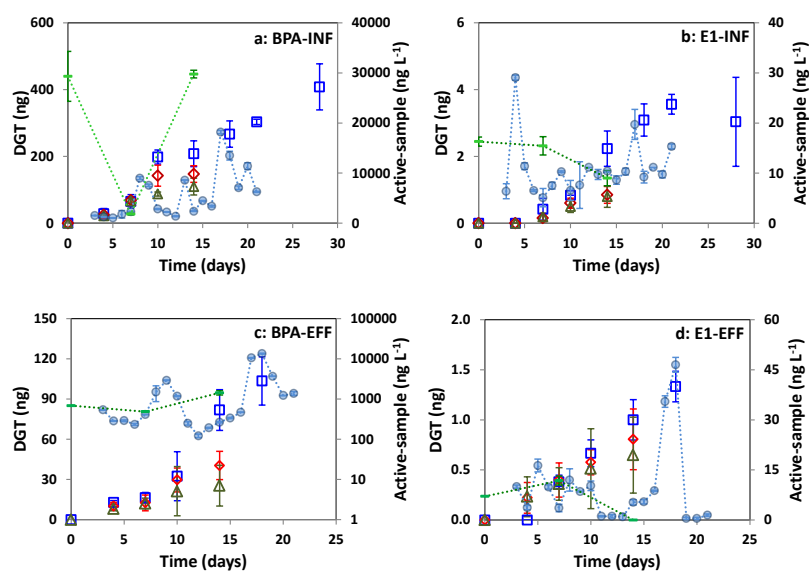
345  
346 **Figure 3:** Measured masses ( $M$ ,  $\mu\text{g}$ ) of BPA and E1 in HLB, XAD18 and SXLA-DGT devices deployed in well-  
347 stirred solution for different times (a-b,  $n=3$ ) and in HLB-DGT with various diffusion layer thicknesses (c-d,  $n=3$ ).  
348 The solid lines are theoretical lines predicted by Equation (1). Error bars: 1 standard deviation.

### 349 3.7 Field Applications

#### 350 3.7.1 DGT deployments

351 DGT devices were deployed at the WWTP to test their performance on 8 EDCs under real  
352 conditions alongside the conventional active sampling. The concentrations of E3, BPA, 4-*t*-OP  
353 and NP obtained by the conventional active samplers were in the range of 10s – >10, 000s ng  
354  $\text{L}^{-1}$  in the influent, together with relatively low concentrations (<MDLs – 10s ng  $\text{L}^{-1}$ ) of E1, E2,  
355 EE2 and DES. The concentrations of E1, EE2, BPA, 4-*t*-OP from active samples were in the  
356 range of 1s – 1000s ng  $\text{L}^{-1}$  in the effluent, while concentrations of E2, E3, and DES were below  
357 MDLs for most samples (NP for nearly half of all samples). Among the 8 target EDCs, the data  
358 from DGT samples showed that the concentrations of DES, E2 and EE2 (and E3 in the effluent)

359 were often below the MDLs in both influent and effluent. These findings were similar to the  
 360 active sampling results. In the first 2 weeks, DGT devices with the 3 different resins were  
 361 observed to continuously take up EDCs from wastewater (**Figure 4**, full set in **Figure SD13**),  
 362 with the general order of  $HLB \geq XAD18 > SXLA$ , similar to the results from the laboratory  
 363 experiments. Differences between uptake rates became greater with increasing deployment  
 364 time. The HLB-DGT devices accumulated the EDCs for least 18 days, after which a plateau or  
 365 decline was observed. Similar observations of a period of accumulation followed by a  
 366 plateau/decline were observed when DGT and POCIS were used to sample for antibiotics,  
 367 household and personal care products, and pharmaceuticals in WWTPs ([Chen et al. 2013](#), [Chen](#)  
 368 [et al. 2017](#), [Harman et al. 2011](#)). This could be a result of biofouling, degradation of EDCs on  
 369 the resin, or the uptake and retention of co-existing/competing substances. Lack of uptake of  
 370 E1 by DGT deployed in the influent for the first 4 days could be the results of varying  
 371 concentrations or competition of much higher concentration of chemicals on the binding sites.



372  
 373 **Figure 4:** Uptake of BPA and E1 by the three types of DGT device (ng, n=3, blue square for HLB-DGT, red  
 374 rhomboid for XAD18-DGT and green triangle for SXLA-DGT) and average active-sample concentrations of BPA  
 375 and E1 ( $\text{ng L}^{-1}$ , blue circles for auto-samples and green dash for grab-samples) in both influent (INF) and effluent  
 376 (EFF) in a WWTP. Error bar: 1 standard deviation.

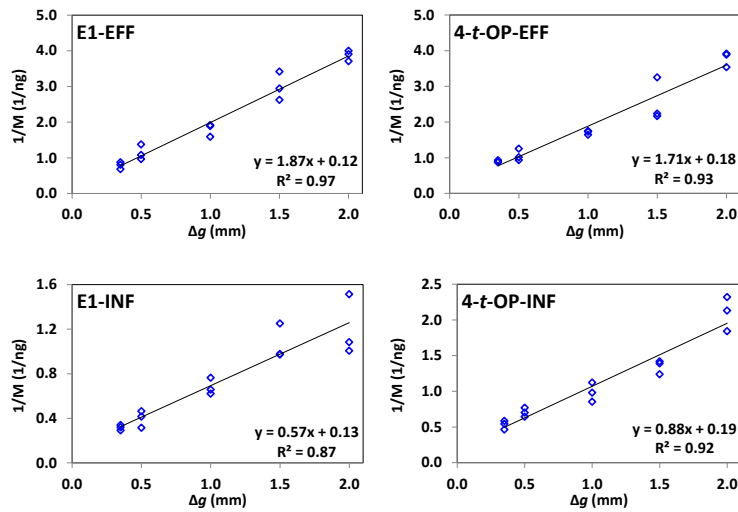
### 377 3.7.2 Effect of DBL

378 To estimate the effect of DBL on the accuracy of the measurements, the thickness of the DBL  
379 ( $\delta$ ) was obtained by deploying devices with different thicknesses of the diffusive layer in the  
380 WWTPs. The following Equation (5) was used for calculations (Zhang and Davison 1995): the  
381 reciprocal of accumulated masses of test EDCs ( $1/M$ ) was plotted against the thickness of the  
382 diffusive layer ( $\Delta g$ );  $\delta$  can then be calculated using the ratio of the intercept and the slope of  
383 the regression line.

$$384 \frac{1}{M} = \frac{\Delta g}{D_e C_{DGT} At} + \frac{\delta}{D_e C_{DGT} At} \quad (5)$$

385 The DBL thickness for the influent and effluent (Figure 5 and Figure SD14) was in the range  
386 of 0.21-0.29 mm (mean 0.24 mm) and from 0.06-0.11 mm (mean 0.08 mm), respectively. The  
387 result in the influent is very similar to previous studies conducted at the same WWTP (0.23  
388 mm (Chen et al. 2013) and 0.25 mm (Chen et al. 2017)). If this DBL thickness was not  
389 considered when calculating the  $C_{DGT}$  for DGT devices with a diffusive layer of 1 mm thickness,  
390 the TWA concentration will be ca. 20% underestimated. A comparison with other passive  
391 samplers such as POCIS and Chemcatcher (ca. 70% underestimation in this condition),  
392 suggests that the effect of DBL on DGT is much lower, as there are much thinner diffusive gels  
393 in POCIS and Chemcatcher (the thickness of typical PES filter used for these samplers was ca.  
394 110  $\mu$ m). The average thickness of the DBL in the effluent was 0.08 mm, which was similar to  
395 that in a study of household and personal care products (Chen et al. 2017), and much less than  
396 in a recent study of WWTP effluent from Canada (0.45 mm on average (Challis et al. 2016)).  
397 The small thickness of the DBL in this study could result from the high and turbulent flow in  
398 the effluent. The smaller DBL thickness will only cause ca. 7% underestimation of the  
399 measured concentration. Values of 0.24 and 0.08 mm were subsequently used as the DBL

400 thicknesses to calculate the  $C_{DGT}$  according to Equation (2), to have accurate TWA  
401 concentrations in the influent and effluent for this study, respectively.

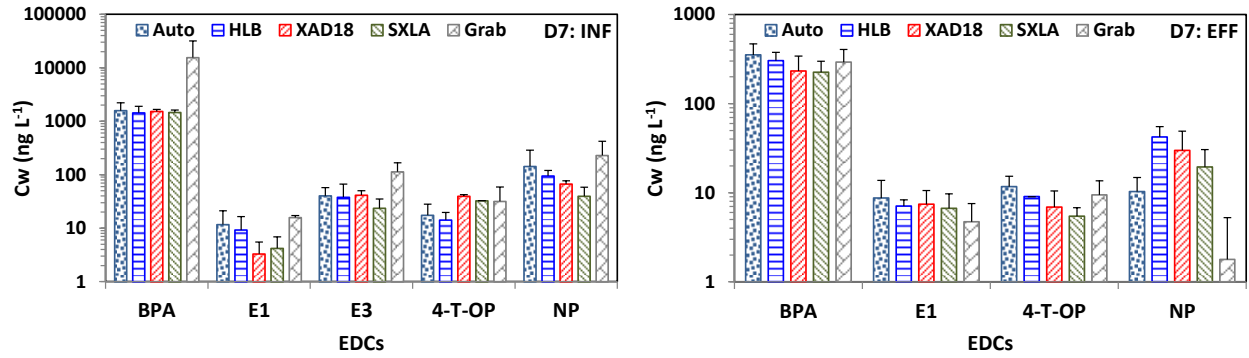


402

403 **Figure 5:** Plot of 1/mass (1/M, 1/ng) of E1 and 4-*t*-OP accumulated by DGT deployed in both influent (INF) and  
404 effluent (EFF) versus different diffusive gel thickness (Δg, mm)

### 405 3.7.3 DGT versus Active Sampling

406 Conventional auto-sampler and grab-sampling methods were used alongside DGT  
407 deployments and the results compared (see **Figures 6** and **SD15**). For most of the detected  
408 compounds, DGT measured concentrations were similar to those obtained with auto-samplers.  
409 For individual EDCs, the DGT TWA concentrations also agreed well with the average  
410 concentrations provided by auto-samplers. The similar results between DGT samples (HLB  
411 and XAD18) and the auto-samplers confirmed that DGT could provide continuous  
412 measurements of TWA concentrations in the wastewaters.



413

414 **Figure 6:** 7-day TWA concentrations of DGT samples and average concentrations of auto and grab samples for  
 415 compounds detected by DGT in both influent (INF) and effluent (EFF). Error bar: 1 standard deviation.

416 Results from the grab-samples showed significant differences when compared to DGT and the  
 417 auto-samplers. Grab sampling only gives a snapshot of concentrations at the time of collection  
 418 (Arditsoglou and Voutsas 2008); it may miss or only partially record events such as time varying  
 419 point source discharge (short-term high concentrations) or rainfall events (dilution of normal  
 420 concentrations).

421 The DGT sampler can be used as a tool to assess the chemical removal efficiency in WWTPs,  
 422 as it can provide reliable TWA concentrations for a period (days to weeks) easily, while the  
 423 grab-sampling may miss the peak/discharge events and auto-sampling devices may not be  
 424 available at most sites due to their high cost. The total removal efficiency (*Removal*, %) of the  
 425 EDCs in the WWTP of this study could be roughly estimated using Equation (6) below:

426 
$$Removal = \frac{C_{inf} - C_{eff}}{C_{inf}} \times 100\% \quad (6)$$

427 where  $C_{inf}$  and  $C_{eff}$  are the TWA concentrations of EDCs measured by DGT in the influent and  
 428 effluent, respectively. When using the 7-day average concentrations measured by DGT, the  
 429 overall removal efficiencies for E1 and BPA were 24% and 79%, which were very similar to  
 430 the estimations obtained based on auto-sampler measurements (26% for E1 and 78% for BPA)

431 However, the grab samples in this study over-estimated the removal efficiencies of EDCs with  
432 70% for E1 and 98% for BPA.

#### 433 **4 CONCLUSIONS AND IMPLICATIONS**

434 The systematic investigation of three types (HLB, XAD18 and SXLA) of DGT samplers  
435 demonstrated that the devices with HLB and XAD18 can be used for measuring EDCs in both  
436 laboratory and field conditions with high accuracy, high sensitivity and good precision. DGT  
437 performance is independent of a wide range of pH, ionic strength and dissolved natural organic  
438 matter. Therefore, the DGT sampler can constitute a viable and attractive alternative to  
439 conventional grab and active water sampling for routine monitoring of EDCs in wastewaters  
440 and natural waters, and for studying the fate and behaviour of EDCs in the aquatic environment.  
441 The HLB resins are widely-used binding agents for other POCs and provide the potential for  
442 future development of DGT for more POCs.

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#### 447 **REFERENCES**

448 Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P. and  
449 Manahan, S.E. (2004) Development of a passive, in situ, integrative sampler for hydrophilic  
450 organic contaminants in aquatic environments. *Environmental Toxicology and Chemistry*  
451 23(7), 1640-1648.

452 Arditoglou, A. and Voutsas, D. (2008) Passive sampling of selected endocrine disrupting  
453 compounds using polar organic chemical integrative samplers. *Environmental Pollution*  
454 156(2), 316-324.

455 Belles, A., Tapie, N., Pardon, P. and Budzinski, H. (2014) Development of the performance  
456 reference compound approach for the calibration of "polar organic chemical integrative  
457 sampler" (POCIS). *Analytical and Bioanalytical Chemistry* 406(4), 1131-1140.

458 Challis, J.K., Hanson, M.L. and Wong, C.S. (2016) Development and Calibration of an  
459 Organic-Diffusive Gradients in Thin Films Aquatic Passive Sampler for a Diverse Suite of  
460 Polar Organic Contaminants. *Analytical Chemistry*.

461 Chen, C.-E., Chen, W., Ying, G.-G., Jones, K.C. and Zhang, H. (2015a) In situ measurement  
462 of solution concentrations and fluxes of sulfonamides and trimethoprim antibiotics in soils  
463 using o-DGT. *Talanta* 132(0), 902-908.

464 Chen, C.-E., Zhang, H. and Jones, K.C. (2012) A novel passive water sampler for in situ  
465 sampling of antibiotics. *Journal of Environmental Monitoring* 14(6), 1523-1530.

466 Chen, C.-E., Zhang, H., Ying, G.-G. and Jones, K.C. (2013) Evidence and recommendations  
467 to support the use of a novel passive water sampler to quantify antibiotics in wastewaters.  
468 *Environmental Science & Technology* 47(23), 13587-13593.

469 Chen, C.-E., Zhang, H., Ying, G.-G., Zhou, L.-J. and Jones, K.C. (2015b) Passive sampling: a  
470 cost-effective method for understanding antibiotic fate, behaviour and impact. *Environment*  
471 *International* 85, 284-291.

472 Chen, W., Huang, H., Chen, C.-E., Qi, S., Price, O.R., Zhang, H., Jones, K.C. and Sweetman,  
473 A.J. (2016) Simultaneous determination of 20 trace organic chemicals in waters by solid-phase  
474 extraction (SPE) with triple-quadrupole mass spectrometer (QqQ-MS) and hybrid quadrupole  
475 Orbitrap high resolution MS (Q-Orbitrap-HRMS). *Chemosphere* 163, 99-107.

476 Chen, W., Li, Y., Chen, C.-E., Sweetman, A.J., Zhang, H. and Jones, K.C. (2017) DGT Passive  
477 Sampling for Quantitative in Situ Measurements of Compounds from Household and Personal  
478 Care Products in Waters. *Environmental Science & Technology* 51(22), 13274-13281.

479 Davison, W. and Zhang, H. (1994) In-situ speciation measurements of trace components in  
480 natural-wasters using thin-film gels. *Nature* 367(6463), 546-548.

481 Davison, W. and Zhang, H. (2012) Progress in understanding the use of diffusive gradients in  
482 thin films (DGT) - back to basics. *Environmental Chemistry* 9(1), 1-13.

483 Diamanti-Kandarakis, E., Bourguignon, J.-P., Giudice, L.C., Hauser, R., Prins, G.S., Soto,  
484 A.M., Zoeller, R.T. and Gore, A.C. (2009) Endocrine-Disrupting Chemicals: An Endocrine  
485 Society Scientific Statement. *Endocrine Reviews* 30(4), 293-342.

486 Domínguez, J.R., González, T., Palo, P. and Cuerda-Correa, E.M. (2011) Removal of common  
487 pharmaceuticals present in surface waters by Amberlite XAD-7 acrylic-ester-resin: Influence  
488 of pH and presence of other drugs. *Desalination* 269(1-3), 231-238.

489 Dong, J., Fan, H., Sui, D., Li, L. and Sun, T. (2014a) Sampling 4-chlorophenol in water by  
490 DGT technique with molecularly imprinted polymer as binding agent and nylon membrane as  
491 diffusive layer. *Analytica Chimica Acta* 822(0), 69-77.

492 Dong, J., Li, L., Jiang, Z., Zhang, G. and Sun, T. (2014b) Sampling of phenol in water by  
493 diffusive gradients using thin film technique. *Chemistry Letters* 43(7), 1164-1166.

494 Fauvelle, V., Nhu-Trang, T.T., Feret, T., Madarassou, K., Randon, J. and Mazzella, N. (2015)  
495 Evaluation of titanium dioxide as a binding phase for the passive sampling of glyphosate and



496 aminomethyl phosphonic acid in an aquatic environment. *Analytical Chemistry* 87(12), 6004-  
497 6009.

498 Guibal, R., Buzier, R., Charriau, A., Lissalde, S. and Guibaud, G. (2017) Passive sampling of  
499 anionic pesticides using the Diffusive Gradients in Thin films technique (DGT). *Analytica*  
500 *Chimica Acta* 966, 1-10.

501 Guo, C., Zhang, T., Hou, S., Lv, J., Zhang, Y., Wu, F., Hua, Z., Meng, W., Zhang, H. and Xu,  
502 J. (2017) Investigation and Application of a New Passive Sampling Technique for in Situ  
503 Monitoring of Illicit Drugs in Waste Waters and Rivers. *Environmental Science & Technology*  
504 51(16), 9101-9108.

505 Harman, C., Allan, I.J. and Vermeirssen, E.L.M. (2012) Calibration and use of the polar  
506 organic chemical integrative sampler-a critical review. *Environmental Toxicology and*  
507 *Chemistry* 31(12), 2724-2738.

508 Harman, C., Reid, M. and Thomas, K.V. (2011) In situ calibration of a passive sampling device  
509 for selected illicit drugs and their metabolites in wastewater, and subsequent year-long  
510 assessment of community drug usage. *Environmental Science & Technology* 45(13), 5676-  
511 5682.

512 Huckins, J.N., Tubergen, M.W. and Manuweera, G.K. (1990) Semipermeable membrane  
513 devices containing model lipid: a new approach to monitoring the bioavailability of lipophilic  
514 contaminants and estimating their bioconcentration potential. *Chemosphere* 20(5), 533-552.

515 Kingston, J.K., Greenwood, R., Mills, G.A., Morrison, G.M. and Bjorklund Persson, L. (2000)  
516 Development of a novel passive sampling system for the time-averaged measurement of a  
517 range of organic pollutants in aquatic environments. *Journal of Environmental Monitoring* 2(5),  
518 487-495.

519 Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B. and  
520 Buxton, H.T. (2002) Pharmaceuticals, Hormones, and Other Organic Wastewater  
521 Contaminants in U.S. Streams, 1999–2000: A National Reconnaissance. *Environmental*  
522 *Science & Technology* 36(6), 1202-1211.

523 Li, H., Helm, P.A., Paterson, G. and Metcalfe, C.D. (2011) The effects of dissolved organic  
524 matter and pH on sampling rates for polar organic chemical integrative samplers (POCIS).  
525 *Chemosphere* 83(3), 271-280.

526 Li, H., Vermeirssen, E.L.M., Helm, P.A. and Metcalfe, C.D. (2010) Controlled field evaluation  
527 of water flow rate effects on sampling polar organic compounds using polar organic chemical  
528 integrative samplers. *Environmental Toxicology and Chemistry* 29(11), 2461-2469.

529 Liu, S., Ying, G.G., Zhao, J.L., Chen, F., Yang, B., Zhou, L.J. and Lai, H.J. (2011) Trace  
530 analysis of 28 steroids in surface water, wastewater and sludge samples by rapid resolution  
531 liquid chromatography-electrospray ionization tandem mass spectrometry. *Journal of*  
532 *Chromatography A* 1218(10), 1367-1378.

533 MacLeod, S.L., McClure, E.L. and Wong, C.S. (2007) Laboratory calibration and field  
534 deployment of the polar organic chemical integrative sampler for pharmaceuticals and personal

535 care products in wastewater and surface water. *Environmental Toxicology and Chemistry*  
536 26(12), 2517-2529.

537 Miège, C., Mazzella, N., Allan, I., Dulio, V., Smedes, F., Tixier, C., Vermeirssen, E., Brant, J.,  
538 O'Toole, S., Budzinski, H., Ghestem, J.-P., Staub, P.-F., Lardy-Fontan, S., Gonzalez, J.-L.,  
539 Coquery, M. and Vrana, B. (2015) Position paper on passive sampling techniques for the  
540 monitoring of contaminants in the aquatic environment – achievements to date and  
541 perspectives. *Trends in Environmental Analytical Chemistry* 8, 20-26.

542 Mills, G.A., Gravell, A., Vrana, B., Harman, C., Budzinski, H., Mazzella, N. and Ocelka, T.  
543 (2014) Measurement of environmental pollutants using passive sampling devices - an updated  
544 commentary on the current state of the art. *Environmental Science: Processes & Impacts* 16(3),  
545 369-373.

546 Mills, G.A., Vrana, B., Allan, I., Alvarez, D.A., Huckins, J.N. and Greenwood, R. (2007)  
547 Trends in monitoring pharmaceuticals and personal-care products in the aquatic environment  
548 by use of passive sampling devices. *Analytical and Bioanalytical Chemistry* 387(4), 1153-  
549 1157.

550 Soedergren, A. (1987) Solvent-filled dialysis membranes simulate uptake of pollutants by  
551 aquatic organisms. *Environmental Science & Technology* 21(9), 855-859.

552 Tijani, J.O., Fatoba, O.O. and Petrik, L.F. (2013) A Review of pharmaceuticals and endocrine-  
553 disrupting compounds: sources, effects, removal, and detections. *Water Air and Soil Pollution*  
554 224(11).

555 Togola, A. and Budzinski, H. (2007) Development of polar organic integrative samplers for  
556 analysis of pharmaceuticals in aquatic systems. *Analytical Chemistry* 79(17), 6734-6741.

557 Vallejo, A., Prieto, A., Moeder, M., Usobiaga, A., Zuloaga, O., Etxebarria, N. and Paschke, A.  
558 (2013) Calibration and field test of the polar organic chemical integrative samplers for the  
559 determination of 15 endocrine disrupting compounds in wastewater and river water with  
560 special focus on performance reference compounds (PRC). *Water Research* 47(8), 2851-2862.

561 Vrana, B., Mills, G.A., Allan, I.J., Dominiak, E., Svensson, K., Knutsson, J., Morrison, G. and  
562 Greenwood, R. (2005) Passive sampling techniques for monitoring pollutants in water. *Trac-*  
563 *Trends in Analytical Chemistry* 24(10), 845-868.

564 Xu, N., Xu, Y.-F., Xu, S., Li, J. and Tao, H.-C. (2012) Removal of estrogens in municipal  
565 wastewater treatment plants: a Chinese perspective. *Environmental Pollution* 165, 215-224.

566 Zhang, H. and Davison, W. (1995) Performance characteristics of diffusion gradients in thin-  
567 films for the in-situ measurements of trace metals in aqueous solution. *Analytical Chemistry*  
568 67(19), 3391-3400.

569 Zhang, H. and Davison, W. (1999) Diffusional characteristics of hydrogels used in DGT and  
570 DET techniques. *Analytica Chimica Acta* 398(2-3), 329-340.

571 Zhang, H. and Davison, W. (2015) Use of diffusive gradients in thin-films for studies of  
572 chemical speciation and bioavailability. *Environmental Chemistry* 12(2), 85-101.

573 Zheng, J.-L., Guan, D.-X., Luo, J., Zhang, H., Davison, W., Cui, X.-Y., Wang, L.-H. and Ma,  
574 L.Q. (2015) Activated charcoal based diffusive gradients in thin films for in situ monitoring of  
575 bisphenols in waters. *Analytical Chemistry* 87(1), 801-807.

576 Zhu, Y., Price, O.R., Kilgallon, J., Rendal, C., Tao, S., Jones, K.C. and Sweetman, A.J. (2016)  
577 A Multimedia Fate Model to Support Chemical Management in China: A Case Study for  
578 Selected Trace Organics. *Environmental Science & Technology* 50(13), 7001-7009.

579 Zoeller, R.T., Brown, T.R., Doan, L.L., Gore, A.C., Skakkebaek, N.E., Soto, A.M., Woodruff,  
580 T.J. and Vom Saal, F.S. (2012) Endocrine-Disrupting Chemicals and Public Health Protection:  
581 A Statement of Principles from The Endocrine Society. *Endocrinology* 153(9), 4097-4110.

582

583