

1 DGT passive sampling for quantitative *in situ* measurements of  
2 compounds from household and personal care products in waters

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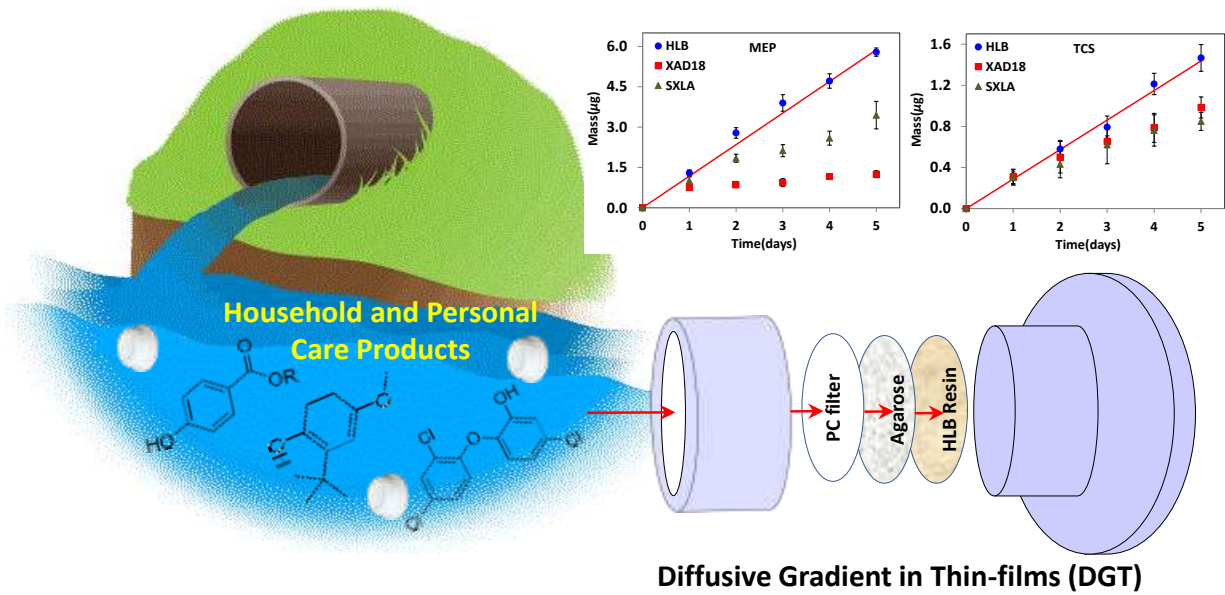
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19 **ABSTRACT:**

20 Widespread use of organic chemicals in household and personal care product (HPCPs) and their  
21 discharge into aquatic systems means reliable, robust techniques to monitor environmental  
22 concentrations are needed. The passive sampling approach of diffusive gradients in thin-films (DGT)  
23 is developed here and demonstrated to provide *in situ* quantitative and time-weighted average (TWA)  
24 measurement of these chemicals in waters. The novel technique is developed for HPCPs, including  
25 preservatives, antioxidants and disinfectants, by evaluating the performance of different binding  
26 agents. Ultrasonic extraction of binding resin gels in acetonitrile gave good and consistent recoveries  
27 for all test chemicals. Uptake by DGT with HLB (hydrophilic-lipophilic-balanced) as the binding  
28 agent was relatively independent of pH (3.5-9.5), ionic strength (0.001-0.1 M) and dissolved organic  
29 matter (0-20 mg L<sup>-1</sup>), making it suitable for applications across a wide range of environments.  
30 Deployment time and diffusion layer thickness dependence experiments confirmed DGT  
31 accumulated chemicals masses are consistent with theoretical predictions. The technique was further  
32 tested and applied in the influent and effluent of a wastewater treatment plant. Results were compared  
33 with conventional grab-sampling and 24-hour-composited samples from auto-samplers. DGT provided  
34 TWA concentrations over up to 18 days deployment, with minimal effects from biofouling or the diffusive  
35 boundary layer. The field application demonstrated advantages of the DGT technique: it gives *in*  
36 *situ* analyte pre-concentration in a simple matrix, with more quantitative measurement of the  
37 HPCP analytes.

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## 39 1. INTRODUCTION

40 Household and personal care products (HPCPs) and pharmaceuticals contain a broad range of trace  
41 organic chemicals (TOrCs),<sup>1</sup> including preservatives, antioxidants and disinfectants that are designed  
42 to enhance the quality of life.<sup>2</sup> With worldwide consumer spending and the availability of these  
43 products increasing, the global production and usage of many of these chemicals has continued to  
44 increase. For example, >10 million tonnes of pharmaceuticals were sold in 2012 and \$213 billion was  
45 spent on HPCPs in 2013 (estimated from ESRI 2012<sup>3</sup> and ChinaIRN 2012<sup>4</sup>). The organic chemicals  
46 used in these products can potentially enter the environment via wastewater treatment plants  
47 (WWTPs) or direct discharge of household wastewater<sup>5</sup> and are considered to effectively and  
48 constantly be emitted into the environment via wastewater streams.<sup>6</sup> Possible adverse effects<sup>7</sup> on  
49 aquatic organisms is a potential concern. Measurement and monitoring are essential to understand  
50 their fate and behaviour,<sup>8</sup> to provide data to evaluate potential risks to ecosystems and human health.  
51 Passive sampling has seen a rise in availability and popularity for monitoring programmes,<sup>9, 10</sup>  
52 although conventional grab sampling is still considered ‘the norm’.<sup>11</sup> It provides an *in situ*  
53 measurement of time-weighted average (TWA) concentrations.<sup>9, 12</sup> There are other advantages, such  
54 as increased sensitivity,<sup>12</sup> reducing/eliminating matrix interferences, saving time and solvent  
55 consumption.<sup>13</sup> It can minimise sample contamination due to pre-concentration, and minimise  
56 decomposition/degradation or loss/change in post-sampling transport and storage.<sup>12</sup> Many existing  
57 passive samplers require *in situ* and/or laboratory calibration,<sup>9, 14</sup> and are dependent on the  
58 hydrodynamic conditions.<sup>15, 16</sup> Such factors can result in considerable measurement uncertainty.<sup>9, 14</sup>

59 Performance reference compounds (PRCs) are therefore used to provide calibration data to assess the  
60 difference between *in situ* sampling rates ( $R_s$ ) and laboratory derived values,<sup>14, 17, 18</sup> but this is still  
61 problematic for polar chemicals.

62 The technique of diffusive gradients in thin-films (DGT) has provided quantitative *in situ*  
63 measurements of trace chemicals in aqueous systems without calibration because transport of the  
64 analyte from water to the sampler's binding gel is controlled by molecular diffusion through the  
65 diffusive layer.<sup>19, 20</sup> The principle of the DGT sampler, based on Fick's first law of diffusion, has been  
66 widely reported previously.<sup>20, 21</sup> The analyte concentration in the sampled water derived from DGT,  
67  $C_{DGT}$ , is expressed using Equation (1):<sup>20</sup>

$$68 \quad C_{DGT} = \frac{M(\Delta g + \delta)}{DA t} \quad (1)$$

69 where  $M$  is the measured mass of target chemical accumulated in the binding gel,  $\Delta g$  is the thickness  
70 of the diffusive gel layer,  $\delta$  is the thickness of diffusive boundary layer (DBL),  $D$  is the diffusion  
71 coefficient of target chemical in the diffusive gel layer,  $t$  is the exposure time and  $A$  is the exposure  
72 area of the sampler.  $\Delta g$  is much thicker than the typical environmental DBL thickness under most  
73 conditions, so the influence of the environmental DBL becomes negligible, making the DGT  
74 measurement fairly insensitive to hydrodynamic conditions.<sup>20, 21</sup> Equation (1) therefore simplifies to:

$$75 \quad C_{DGT} = \frac{M\Delta g}{DA t} \quad (2)$$

76 Theoretically, DGT can be applied to any inorganic or organic diffusing species,<sup>19</sup> although most  
77 research so far has focused on the measurement of inorganic substances,<sup>21, 22</sup> More recently, some  
78 studies have demonstrated applications for organic substances such as antibiotics,<sup>23-25</sup> phenol and  
79 4-chlorophenol (4-CP),<sup>26, 27</sup> bisphenols (BPs),<sup>28</sup> glyphosate and aminomethyl phosphonic acid,<sup>29</sup> and

80 other polar organic contaminants in WWTPs.<sup>30</sup> Thus, the possibility of a DGT sampler for the wide  
81 family of HPCPs-preservatives, antioxidants and disinfectants is of great interest.

82 The aim of this study was to develop and apply a new DGT technique for a wide range of organic  
83 chemicals in waters. Thirteen different chemicals were used to systematically test different gels and  
84 DGT samplers under various conditions of pH, ionic strength (IS) and dissolved organic matter  
85 (DOM). The developed DGT sampler was deployed in a WWTP, alongside conventional sampling  
86 techniques, to assess its application under challenging conditions.

## 87 **2. MATERIALS AND METHODS**

### 88 **2.1 Chemicals and Reagents**

89 Compounds were selected to represent a range of HPCP ingredients. High purity chemical standards  
90 were purchased from Sigma-Aldrich (UK). They covered 7 preservatives and one of their metabolites,  
91 2 antioxidant and 3 disinfectants, as follows: methylparaben (MEP), ethylparaben (ETP),  
92 propylparaben (PRP), isopropylparaben (IPRP), butylparaben (BUP), benzylparaben (BEP), heptyl  
93 paraben (HEP) and 4-hydroxybenzoic acid (PHBA), butylated hydroxyanisole (BHA) and butylated  
94 hydroxytoluene (BHT), and ortho-phenylphenol (OPP), triclosan (TCS) and triclocarban (TCC). Six  
95 of them - MEP, PRP, IPRP, BHA, OPP and TCS - were selected as the test chemicals for the  
96 laboratory performance tests. Stable isotope-labelled internal standards (SIL-ISs) were purchased  
97 from Sigma-Aldrich (UK) and QMX Laboratories (UK). Details of the chemicals, SIL-ISs, reagents,  
98 materials and sample handling are given in the Supporting Information ([SI text and Table S1](#)).

## 99 2.2 Diffusive and Binding Gel Preparation

100 Three resins, HLB (Waters, UK), XAD18 (Dow, USA) and Strata-XL-A (SXLA, Phenomenex, UK),  
101 were tested for their suitability as the binding gel. Information on the three resins is given in **Table**  
102 **S2**. The resins were thoroughly washed with Milli-Q (MQ) water and then immersed in methanol  
103 followed by MQ water wash before using them to make binding gels. Polyacrylamide diffusive gels  
104 (PA), agarose diffusive gels (AG, 1.5%) and binding gels were prepared according to well  
105 documented procedures.<sup>23, 31</sup> All the gel sheets were then cut into 2.5 cm diameter disks and stored in  
106 0.01 M NaCl solution at 4 °C before use.

## 107 2.3 Chemical Analysis and Detection Limits

108 A Thermo Finnigan high performance liquid chromatography (HPLC) system coupled with a  
109 photodiode array detector (DAD) was employed to analyse the test chemicals in both water and DGT  
110 samples for all the laboratory experiments, where higher levels with cleaner matrices were used  
111 (details of analysis provided in **SI**). Wastewater and field DGT samples were analysed by liquid  
112 chromatography-tandem mass spectrometry (LC-MS/MS, Waters, UK) using published procedures<sup>32</sup>  
113 for all HPCPs (details of pre-treatment and instrumental analysis given in the **SI**). The instrumental  
114 detection limits (IDLs) for HPLC-DAD and LC-MS/MS were calculated based on the signal/noise  
115 ratio (S/N) >3; method detection limits (MDLs) were calculated based on IDLs, the concentration  
116 factors and the absolute recoveries for water and DGT samples.<sup>32</sup> Both IDLs and MDLs are listed in  
117 **Table S3**.

## 118 2.4 Performance Testing of DGT in the Laboratory

### 119 2.4.1 Adsorption by DGT holders, diffusive gels and membrane filters

120 Materials which were used for making DGT devices were assessed for possible adsorption of test  
121 chemicals. The plastic DGT holder (piston and cap), two diffusive gels (PA and AG), five membrane  
122 filters (polyethenesulfone membrane, PES; Nuclepore track-etch membrane, PC; cyclopore track  
123 etched membrane, PC1; Nuclepore polycarbonate membrane, PC2; cellulose nitrate membrane,  
124 CNM; details given in [SI](#)) were immersed in solution containing ca.  $100 \mu\text{g L}^{-1}$  of test chemicals and  
125 shaken for 24 h on an orbital shaker at 80 rpm (Orbital, DOS-20L, Sky Line, ELMI). The amounts of  
126 chemicals adsorbed by these materials were calculated by mass balance from concentrations in the  
127 solutions before and after exposure.

### 128 2.4.2 Optimisation of binding gel extraction recoveries

129 HLB binding gel was used to optimise the extraction procedure. HLB binding gels were added into  
130 10 mL of ca.  $250 \mu\text{g L}^{-1}$  test chemicals and shaken for 24 h. They were then taken out and placed into  
131 15 mL vials with 5 mL ACN added each time before ultrasonic extraction for 15 or 30 min with  
132 either one or two extractions. Once the extraction procedure was optimised for HLB binding gel, the  
133 extraction recoveries were further tested at two other concentrations (ca.  $100$  and  $500 \mu\text{g L}^{-1}$ ) with all  
134 three binding gels (HLB, XAD18 and SXLA), to confirm whether stable recoveries could be  
135 achieved with a wide range of exposure concentrations.



136 *2.4.3 Uptake capacity of DGT and binding gel uptake kinetics*

137 DGT devices with binding gel in front of the diffusive gel were exposed to 50 mL solutions of  
138 various concentrations of test chemicals up to ca. 10 mg L<sup>-1</sup>. All the solutions (pH = 6 or 8) were  
139 shaken for 24 h at room temperature (20±2 °C). The amounts of test chemicals adsorbed by binding  
140 gels were calculated according to the concentration differences before and after the experiment.

141 The kinetics of HPCP uptake to the binding gels was investigated by immersing gel discs in solutions  
142 for different times. Gel discs were placed in 20 mL of ca. 200 µg L<sup>-1</sup> HPCPs solutions (IS = 0.01 M  
143 and pH = 6.8±0.1) and shaken at 80 rpm (Orbital, DOS-20L, Sky Line, ELMI), and 0.1 mL samples  
144 were collected at different times for a period of 24 h.

145 *2.4.4 Diffusion coefficient measurements*

146 A diffusion cell containing two compartments (source and receptor) connected by a circular window  
147 (1.5 cm diameter) with a 0.8 mm diffusive gel (AG gel without filter) was used to measure the  
148 diffusion coefficients (*D*) of test chemicals according to a published procedure.<sup>31</sup> Both compartments  
149 were filled with 100 mL of 0.01 M NaCl solution (pH = 6.8±0.1). The test chemicals were spiked  
150 into the source compartment (ca. 3000 µg L<sup>-1</sup> for each chemical). The solutions in both compartments  
151 were well-stirred during the experiment. Samples (0.1 mL) from both compartments were collected  
152 and analysed by HPLC-DAD at intervals of 60 min for the first 3 h and then subsequently at 30 min  
153 intervals for the next 8-9 h. The slope (*k*) of the linear plot of the test chemical mass (*M*) diffused into  
154 the receiving compartment *versus* time (*t*) was used to calculate *D*, according to Equation (3):

155 
$$D = \frac{k\Delta g'}{C_s A_s} \quad (3)$$

156 where  $C_s$  is the test chemical concentration in the source solution,  $A_s$  is the window area of the  
157 diffusion cell, and  $\Delta g'$  is the thickness of the diffusion gel. The experiments were conducted in a  
158 temperature-controlled room at 15, 20 and 25 °C (any temperature change during the experiment was  
159 <0.5 °C).

#### 160 *2.4.5 Time and diffusion layer thickness dependence*

161 DGT devices were deployed in stirred solutions (IS = 0.01 M, pH = 6.8±0.2 at 24±2 °C) of ca. 50 µg  
162 L<sup>-1</sup> test chemicals for different durations up to 5 days. After retrieval the resin gel layer was extracted  
163 using the optimised procedure in *Section 2.4.2*. The mass of test chemicals accumulated in binding  
164 gels was then determined.

165 HLB-DGT devices with various thicknesses of diffusive gels (0.5 to 2.0 mm) were used to test the  
166 DGT principle. They were deployed in a well-stirred solution (IS = 0.01 M, pH = 6.8±0.2 at 24±2 °C)  
167 of ca. 60 µg L<sup>-1</sup> HPCPs for 20 h. After the experiment, the test chemicals in the resin gels were  
168 extracted and analysed.

#### 169 *2.4.6 Effect of pH, IS and DOM*

170 The performance of DGT was tested at a wide range of pH (3.5-9.5), IS (0.001-0.5 M) and DOM  
171 (0-20 mg L<sup>-1</sup>). The devices were deployed in 2 L of ca. 100 µg L<sup>-1</sup> test chemical solutions (20±2 °C)  
172 for 20 h. The  $C_{DGT}$  was calculated using Equation (2), and the ratio of  $C_{DGT}$  to the directly measured  
173 concentration ( $C_b$ ) of test chemicals in the bulk solution was used to evaluate the performance of

174 DGT. The ratio of  $C_{DGT}/C_b$  ranged from 0.9 to 1.1 indicating the good performance of DGT.

## 175 **2.5 *In situ* Measurements in a WWTP**

176 To test the applicability of DGT in field conditions, DGT devices were deployed *in situ* at a WWTP  
177 in the UK. The devices were located ca. 30 cm below the water surface in influent and effluent  
178 channels for up to 4 weeks. DGT samplers were retrieved at day 4, 7, 10, 14, 18, 21 and 28 from each  
179 site (if the samplers were not lost), rinsed with MQ water and then sealed in a clean plastic bag for  
180 transport. The DBL thicknesses were estimated by deploying DGT devices with different thicknesses  
181 of diffusive gels (0.35, 0.5, 1, 1.5 and 2 mm) at the same sites for 8 days. On arrival at the laboratory,  
182 the binding gels of DGT devices were taken out and extracted. Field blanks of DGT were prepared  
183 and taken to the WWTP without deployment. All-weather refrigerated automatic samplers (SIGMA  
184 SD900) were also installed to collect the influent and effluent in the WWTP. They were set on  
185 constant flow mode ( $\sim 100 \text{ mL h}^{-1}$ ) to provide a 24-hour composite water sample (auto-sample, 2.4 L  
186 sample<sup>-1</sup>) every day for 3 weeks. Grab samples were also collected at about 10~11 am on the first and  
187 last day of the week during the DGT deployment for 2 weeks, using 1 L pre-cleaned amber bottles.  
188 The water temperature, pH and weather conditions were recorded when samples were taken (see  
189 **Table S4** for details). Detailed description of the pre-treatment of wastewater and field DGT samples  
190 and LC- MS/MS analysis is given in the **SI**.

## 191 **3. RESULTS AND DISCUSSIONS**

### 192 3.1 Adsorption by DGT Holders, Diffusive Gels and Membrane Filters

193 The results of the adsorption experiments ([Figure S1](#)) demonstrate that there was no significant  
194 adsorption (ANOVA,  $p > 0.05$ ) by the DGT holders for all the test chemicals. No significant  
195 adsorption by PA or AG diffusive gels was observed; AG gel also showed no significant adsorption  
196 and gave the best reproducibility when all the test compounds were considered (see [Figure S1](#)). PES  
197 filters (those typically used for POCIS and Chemcatcher<sup>33</sup>) and CNM filters, significantly adsorbed  
198 all the test chemicals (nearly 100% absorbed by PES and 50% by CNM), while moderate adsorption  
199 was observed for PC1 filters (34%), PC2 filters (12%) and very slight adsorption by PC filter (< 5%  
200 on average). Thus, AG gel (1.5%) and the PC filter were selected as the diffusive gel and filter in the  
201 subsequent experiments.

### 202 3.2 Optimisation of Gel Extraction Recoveries

203 Optimisation of the extraction procedure based on HLB binding gels demonstrated that, for most of  
204 the test chemicals, the average extraction recoveries were in the order: a single 15 min extraction <  
205 two 15 min extractions < one 30 min extraction = two 30 min extractions ([Figure S2](#)). Thus, a simple  
206 procedure of a single 30 min ultrasonic extraction by 5 mL ACN was selected since it provides good  
207 and stable recoveries across a range of exposure concentrations ([Table S5 and Figure S3](#)).

### 208 3.3 Binding Capacity of DGT and Uptake Kinetics of Binding Gel

209 The results obtained from the capacity experiments showed that the uptake of all test chemicals  
210 increased linearly up to about 2 mg L<sup>-1</sup> solution concentration for both pH 6 and 8 ([Figure S4](#)). No

211 significant differences were observed between the two pHs and between the three resins.

212 The linear parts of the curves were used to estimate the capacities of the DGT devices. Results

213 (**Table S6**) ranged from 11 (MEP) to 97 (TCS)  $\mu\text{g}$ ; no systematic difference was observed between

214 DGT devices with different binding gels or between two different pH values for most test chemicals.

215 Based on these capacities, the maximum HPCPs concentrations in waters that could be measured by

216 DGT were calculated using Equation (2). Results ranged from 44 (MEP) to 670 (TCS)  $\mu\text{g L}^{-1}$  if the

217 deployment time was 2 weeks. If the deployment time was 1 month, they would range from 21 (MEP)

218 to 310 (TCS)  $\mu\text{g L}^{-1}$ . In most situations, HPCP concentrations in waters would be  $<10 \mu\text{g L}^{-1}$ . The

219 capacities of DGT devices are therefore more than adequate for monitoring HPCPs chemicals in

220 polluted environments.

221 The results of binding kinetics (**Figure 1** and **Figure S5**) showed that the uptake of test chemicals by

222 each resin gel increased rapidly with time for the first hour (ca. 60% uptake), followed by more

223 gradual uptake. The uptake onto XAD18 resin gel was slightly faster than that of the HLB resin gel

224 and much faster than that of SXLA resin gel (except for MEP). The rapid initial uptake is the key

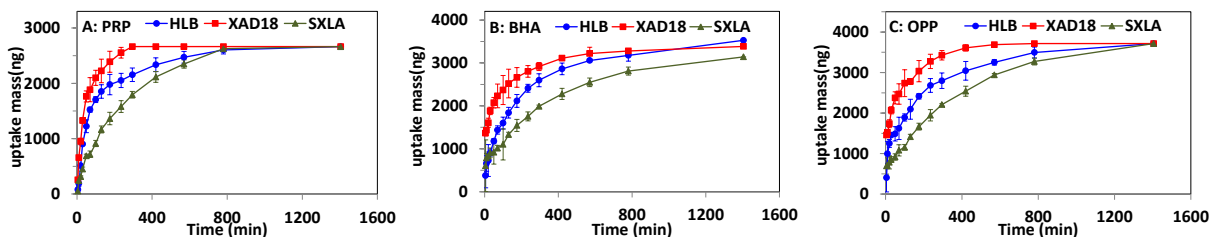
225 aspect to enable fully quantitative performance of DGT, which requires zero concentration at the

226 resin gel/diffusive gel interface. According to Fick's law of diffusion, the minimum uptake amount

227 by the resin gel for the first 5 minutes is about 10 ng. The results presented in **Figure 1** show minima

228 of 50 ng for all test chemicals and for all three types of resin gels; higher values for XAD18 and HLB

229 gels indicate they are more suitable for use as the binding phases than SXLA.



230  
 231 **Figure 1:** Binding kinetics of PRP, BHA and OPP by HLB, XAD18 and SXLA resin gels in 20 mL solutions of ca.  
 232  $200 \mu\text{g L}^{-1}$  test chemicals (IS = 0.01 M, pH =  $6.8 \pm 0.1$ ,  $T = 20 \pm 2 \text{ }^\circ\text{C}$ ; n=3). Error bars were calculated from the  
 233 standard deviation (SD) of three replicates.

### 234 3.4 Diffusion Coefficient Measurement

235 The measured  $D$  values of test chemicals at  $25 \text{ }^\circ\text{C}$  ( $D_{25}$ ) were calculated using Equation (3), based on  
 236 the  $k$  values obtained from the diffusion cell experiments (**Figure S6**). The  $D$  values at other  
 237 temperatures ( $D_T$ ) can be estimated using Equation (4)<sup>20</sup>.

$$238 \log D_T = \frac{1.37023(T - 25) + 8.35 \times 10^{-4}(T - 25)^2}{109 + T} + \log \frac{D_{25}(273 + T)}{298} \quad (4)$$

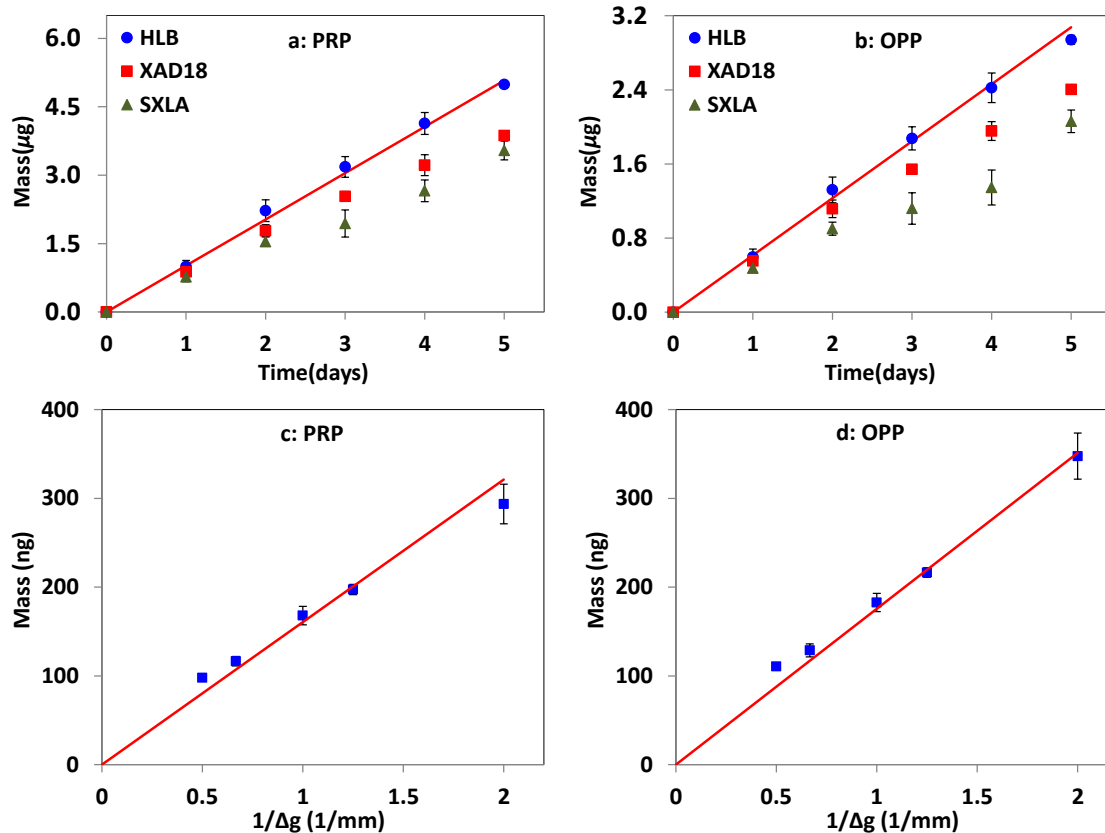
239  $D$  values were calculated from 1 to  $35 \text{ }^\circ\text{C}$  and these are listed in **Table S7**. Measurements at 15 and  
 240  $20 \text{ }^\circ\text{C}$  were also carried out to compare with the calculated values. The measured  $D$  values at both 15 and  
 241  $20 \text{ }^\circ\text{C}$  (**Table S7**) were within 10% of the calculated values, indicating the accuracy of  $D$  measurement in  
 242 this study. For  $D$  value variations of  $\pm 10\%$ , the effect on the weighted average calculations is between  
 243  $+11\%$  and  $-9\%$ .

### 244 3.5 Time and Diffusion Layer Thickness Dependence

245 The experiments of DGT time dependence and diffusion layer thickness dependence are important  
 246 for confirming the validity of the DGT principle for the test chemicals. The results (**Figures 2a-b**  
 247 **and S7**) showed that DGT with HLB resin gel can simultaneously accumulate test chemicals linearly

248 with the deployment time ( $R^2$  ranged from 0.9853 to 0.9995,  $p < 0.001$ ) and agreed well with the  
249 theoretical prediction. DGT devices with XAD and SXLA gels also accumulate the chemicals  
250 linearly with deployment time, but accumulating lesser amounts than theoretical prediction (**Figure**  
251 **S7**, discussion in **SI**). The possible reasons could be competitive binding of chemicals on XAD18  
252 and SXLA resin gels (it has been confirmed by the time dependence experiment using individual  
253 compound). These results indicate that only DGT with HLB can measure the test chemicals  
254 accurately with confidence. Therefore, DGT with HLB as binding phase was selected for the  
255 subsequent laboratory tests and field applications.

256 According to the principles of DGT, the accumulated mass on the resin gel should be inversely  
257 proportional to the diffusion layer thickness when DGT devices were exposed to a well-stirred  
258 solution for a fixed duration. Data for PRP and OPP are shown in **Figure 2c-d** as examples (full data  
259 given in **Figure S8**) and agreed well with theoretical predictions. The results also demonstrate that  
260 the DBL effect can be ignored in a well-stirred solution. The good fits of measured mass to the  
261 predicted line confirm the use of appropriate D values in water.



262  
 263 **Figure 2:** Measured masses of PRP and OPP in HLB, XAD18 and SXLA-DGT devices deployed in well stirred  
 264 solution for different time (a-b, n=3) and in HLB-DGT devices with various diffusion layer thicknesses after 20  
 265 hours (c-d, n=3). The solid lines are theoretical lines predicted by Equation (2). Error bars: 1 SD.

### 266 3.6 Effect of pH, Ionic Strength and DOM

267 No significant pH effect on DGT uptake of test chemicals was observed (**Figure S9**). For the  
 268 majority of test chemicals,  $C_{DGT}/C_b$  was between 0.9 and 1.1 when pH ranged from 3.5 to 9.5 (the  
 269 averages of  $C_{DGT}/C_b$  values at all pH for individual chemicals were in the range of 0.97-1.08, **Table**  
 270 **S8**). No significant difference (ANOVA,  $p>0.05$ ) of the  $C_{DGT}/C_b$  was observed, although there was a  
 271 slight decline of  $C_{DGT}/C_b$  at the highest pH (9.5). The only exception was for TCS (**Table S8**): the  
 272  $C_{DGT}/C_b$  values at all pH were  $<0.90$ , but no significant difference (ANOVA,  $p>0.05$ ) of the  $C_{DGT}/C_b$



273 was found between different pH values (0.85 on average). These findings demonstrate that DGT  
274 performance is generally independent of solution pH between 3.5 and 9.5 for the majority of test  
275 chemicals and DGT can be directly applied to their measurements in most of the field conditions  
276 across this range of pH values.

277 The effect of IS on DGT performance is shown in [Figure S10](#). No significant differences (ANOVA,  
278  $p>0.05$ ) of  $C_{DGT}/C_b$  were observed for the majority of test chemicals when the IS concentration was  
279 0.001-0.1 M, and the values fell between 0.9-1.1 (data in [Table S8](#)), except for BHA and TCS. A  
280 significant reduction in  $C_{DGT}/C_b$  (>10%) was observed when IS increased to 0.5 M. A possible reason  
281 for the decline was that the test chemicals were less bound to the resin gels due to competition with  
282 other major ions (e.g. Cl<sup>-</sup>). A similar phenomenon was previously observed when XAD18 was used  
283 as the resin for antibiotics,<sup>23</sup> when uptake to the binding gel decreased with increasing IS. This result  
284 is also consistent with Togola and Budzinski's study on POCIS uptake of pharmaceuticals<sup>34</sup> and  
285 Zheng *et al.*'s study on DGT performance for BPs when IS increased to 0.5 M.<sup>28</sup> However, the results  
286 are not consistent with Zhang *et al.*'s study of HLB-POCIS on endocrine disrupting chemicals (EDCs)  
287 where  $R_s$  did not vary significantly with changing salinity from 0-3.5%<sup>35</sup> and also contrasts with  
288 Dong *et al.*'s research on 4-CP; they demonstrated that the ratio of  $C_{DGT}/C_b$  increased when IS  
289 concentration increased from 0.1 to 0.7 M.<sup>27</sup> Our results indicate that the DGT device with HLB resin  
290 as binding phase is suitable for use in freshwater, but further work is needed on the effect of IS  
291 before quantitative applications in seawater.

292 There was no significant effect of DOM on DGT measurements in this study. The ratios of  $C_{DGT}/C_b$   
293 for most test chemicals were within the range of 0.9-1.1, when the DOM concentrations increase

294 from 0 to 20 mg L<sup>-1</sup> (**Figure S11**). However, for TCS, the ratios of  $C_{DGT}/C_b$  were always <0.9 and  
295 decreased with increasing DOM. DOM tends to bind relatively hydrophobic organic compounds  
296 (HOCs)<sup>36,37</sup> (log Kow for TCS is 4.66, see **Table S1**); this makes it difficult for the bound compound  
297 to pass through the diffusive layer<sup>38</sup> (smaller  $C_{DGT}$ ). The other test chemicals are less hydrophobic,  
298 with log Kow values in the range 2 to 3.3 (see **Table S1**), so less effect of DOM is expected. This  
299 result for the majority of test chemicals is consistent with Charlestra *et al*'s<sup>19</sup> study on pesticides  
300 uptake by HLB-POCIS with varying dissolved organic carbon (DOC) contents. They demonstrated  
301 no significant differences when DOC varied between <0.1 and 4.5 mg L<sup>-1</sup>. Li *et al.*<sup>39</sup> demonstrated an  
302 increase in uptake of polar organic chemicals by HLB-POCIS when DOM increased from 3.3 to 4.9  
303 mg L<sup>-1</sup>. However, Dong *et al*<sup>27</sup> demonstrated reduced ratios of  $C_{DGT}/C_b$  for 4-CP at high DOC  
304 contents (9.8-36.5 mg L<sup>-1</sup>), similar to the result for TCS from this study. These results indicate that  
305 DGT can quantitatively measure the majority of the chemicals tested across typical environmental  
306 DOM values.

### 307 **3.7 Effect of DBL**

308 DGT devices with various thicknesses of diffusive gel layer were deployed at the same time in  
309 influent and effluent to determine the *in situ* DBL thickness ( $\delta$ ). The following Equation (5)<sup>20</sup>  
310 (derived from Equation (1)) was used:

$$311 \quad \frac{1}{M} = \frac{\Delta g}{DC_{DGT}At} + \frac{\delta}{DC_{DGT}At} \quad (5)$$

312 The reciprocal of accumulated masses of HPCPs ( $1/M$ ) were then plotted against the thickness of the  
313 diffusive layer ( $\Delta g$ ) (see **Figure S12**). The results show the DBL thickness (calculation in **SI**) was in

314 the range of 0.20 to 0.29 mm (mean 0.25 mm) for the influent and 0.05 to 0.09 mm (mean 0.07 mm)  
315 for the effluent. The DBL thickness in the influent was very similar to a previous study conducted at  
316 the same location of the same WWTP.<sup>24</sup> The smaller DBL thickness in the effluent was consistent  
317 with more turbulent flow. To reduce the errors on the TWA concentrations, 0.25 and 0.07 mm were  
318 used as the DBL thicknesses when calculating the  $C_{DGT}$  in the influent and effluent, respectively.  
319 With other passive samplers for organics (i.e. POCIS and Chemcatcher), the effect of DBL would be  
320 much greater, capable of producing several-fold errors on measured concentrations.<sup>14</sup>

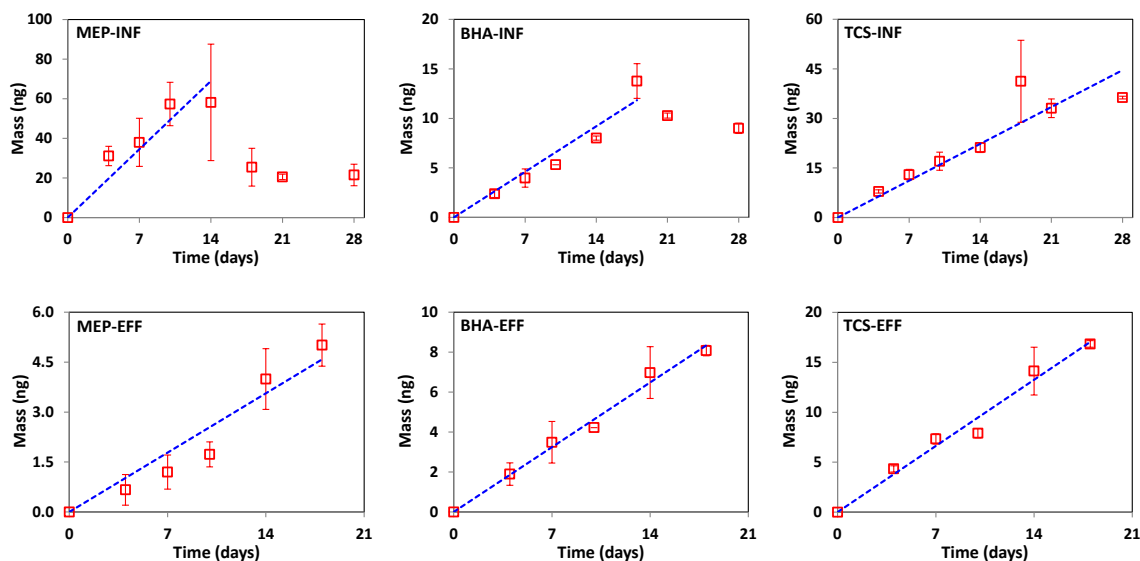
### 321 **3.8 Field Trial Application at the WWTP**

#### 322 *3.8.1 HPCPs in the grab and auto-sampler samples*

323 The results obtained by the conventional samplers are presented in **Figure S13**. The concentrations of  
324 the individual compounds are in the range of 10s->10,000 ng L<sup>-1</sup> in the influent and 1-100s ng L<sup>-1</sup> in  
325 the effluent. They are in agreement with other published studies.<sup>40-42</sup> As expected, the grab samples  
326 show higher variability than the auto-samples. Consistent with other studies,<sup>24, 42, 43</sup> the  
327 concentrations in the effluent are typically 1-2 orders of magnitude lower than the influent, indicating  
328 removal during the water treatment process.

#### 329 *3.8.2 Uptake of HPCPs by the DGT devices*

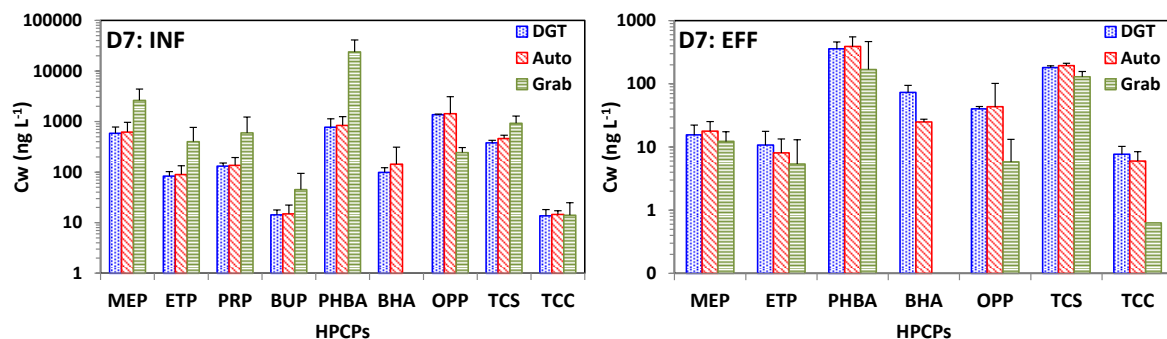
330 Of the analysed HPCPs, all except BEP and HEP were detected in DGT devices deployed in the  
331 influent. **Figure 3** gives some examples of uptake over time in DGT devices for typical HPCPs; the  
332 full data set is given in **Figure S13**. Most compounds accumulated in the DGT binding gel linearly  
333 for about 18 days and plateaued or declined after that, with the exception of MEP, PHBA and BHT.



334  
 335 **Figure 3:** Uptake of typical HPCPs by HLB-DGT (n=3) in the influent (INF) and effluent (EFF) of a UK WWTP  
 336 (The dotted blue line is the linear regression line through those points with continuous uptake). This Figure shows  
 337 that deployment times of 7-14 days would be ideal for deriving TWA values. Error bars: 1 SD.  
 338 This is consistent with studies where DGT and POCIS were used to sample for antibiotics and drugs  
 339 in WWTPs.<sup>24,44</sup> There would appear to be three possible reasons for a reduction in sampling rate or  
 340 decline in mass retained on the resin gel. One possibility is biofouling, where growth on the sampler  
 341 surface inhibits uptake or enhances degradation of the compound in the biofilm. The second is  
 342 degradation of HPCPs in the resins. The third is possible uptake and retention of  
 343 co-existing/competing substances. Differences in compound properties will influence their  
 344 susceptibility to degradation. Biofouling is not significant for the DGT samplers in either the influent  
 345 or effluent in this study, as can be seen in **Figure S14** which shows DGT samplers retrieved after 14  
 346 days. Considering the detection limits and the fouling effects, 1 to 2 weeks deployment time is  
 347 recommended for practical application.

### 348 3.8.3 Comparison of concentrations derived by DGT and active sampling

349 The DGT concentrations of HPCPs were calculated for 7 days sampling period and they were  
350 compared with concentrations obtained by auto and grab sampling methods (**Figure 4**). For most  
351 HPCPs the concentrations detected by DGT are similar to those obtained by auto-sampling. The  
352 concentrations obtained for different deployment times (presented in **Figure S15**) also agreed well  
353 with the average concentrations of auto-samples. The grab sample results are not always consistent  
354 with DGT and auto-sample results. It is well known that grab samples lack representativeness and  
355 they may miss any episodic events during the sampling period, such as peak, point source, rain or  
356 discharge events (or only record these events inversely).<sup>45</sup> The differences could also have resulted  
357 from the ionisability of compounds and the fractions being measured. DGT accumulates the  
358 dissolved fraction (nm range due to the diffusive gel pore size) of chemicals *in situ* at the natural pH  
359 (6.8-7.4, **Table S4**) of the wastewater, whilst the active samples contain some particulate fraction  
360 through filters (0.7  $\mu\text{m}$ ) and more neutral fractions (pH adjusted to 2.5 for better recoveries of  
361 solid-phase extraction). Similar results were found in previous studies when HLB-POCIS was used  
362 for sampling pharmaceuticals in seawater<sup>34</sup> and for sampling endocrine disrupting chemicals (EDCs)  
363 in river and wastewater,<sup>35</sup> and when DGT was used for sampling antibiotics<sup>24</sup> and 4-CP in  
364 wastewater.<sup>27</sup>



365  
 366 **Figure 4:** TWA concentrations measured by DGT samplers during 7 days deployment and average concentrations of  
 367 the same compounds by auto samplers and grab samples in both influent (INF) and effluent (EFF). Error bars: 1 SD.

### 368 3.8.4 Analytical advantage of DGT measurements

369 There are significant advantages of the DGT sampler for trace organic analysis. DGT lowers the detection  
 370 limit by pre-concentrating compounds *in situ*. Larger molecules, humic, fulvic and colloidal material do  
 371 not pass through the nano-pore size of the diffusive gel layer, while the resin gel selectively retains  
 372 targeted chemicals; these factors both reduce matrix interference. Hence, DGT extracts are cleaner than  
 373 those from active sampling. The samples from active sampling have high background interference signals  
 374 on LC-MS/MS, as WWTP influents are highly complex matrices that normally require extensive  
 375 sample clean-up. This is apparent from the total ion chromatograms obtained in selected ion  
 376 monitoring (SIM) scan mode (see **Figure S16 A and B**). More non-target peaks were detected in  
 377 extracts from grab and auto-sampler samplers than the DGT extract. When a target ion was selected,  
 378 more interference peaks appear in the auto-sample extract than in the DGT extract. **Figure S16 C**  
 379 **and D** gives an example for  $m/z$  151, the target ion of MEP; three significant interference peaks were  
 380 detected in the active sample extract.

381 Summaries of the IDLs and the MDLs of the studied chemicals for LC-DAD and LC-MS/MS are  
382 presented in **Table S3** for both water and DGT samples. For a 7-day deployment in the field at 25 °C,  
383 the MDLs for DGT were typically in the low ng L<sup>-1</sup> range, low enough for environmental analysis.  
384 Of course, if necessary, the MDLs for DGT can be further improved by combining the extracts from  
385 duplicate DGT devices and reducing solvent extract volume prior to LCMS analysis.

### 386 **3.9 Recommendations and perspectives**

387 A novel DGT sampler has been successfully developed for *in situ* measurement of HPCPs, based on  
388 systematic tests and comparative evaluation of different binding resins. DGT with HLB resin is  
389 recommended for its robustness in environmental conditions, with little effect from biofouling or  
390 water flow rates. Good agreement between DGT measurements and auto-sampling concentrations  
391 indicates that DGT can provide reliable *in situ* TWA concentrations of HPCPs and it can be used for  
392 studying the fate and behaviour of HPCPs in the aquatic environment. The thickness of the DBL is  
393 ~0.2 mm in typical field conditions with flowing (or moving) water, as shown in previous studies.  
394 Therefore, the recommended minimum diffusive layer thickness for DGT device (diffusive gel plus filter  
395 membrane) should be ~1 mm. Some potential applications of DGT are recommended according to the  
396 virtues demonstrated in this study. DGT could be used for assessing chemical removal efficiency in  
397 WWTPs and for screening of illegal discharge of industrial compounds in rivers and lakes.  
398 Auto-samplers may be too costly for multiple sites, while grab-sampling may miss the  
399 peak/discharge events. DGT can also be applied for target or non-target screening of emerging

400 contaminants and their metabolites in aquatic environments, due to its high sensitivity and low matrix  
401 interferences for analysis.

## 402 **SUPPORTING INFORMATION**

403 Information including chemical standards, reagents, experiment control, analytical method,  
404 supplementary tables and figures, and some additional discussion is given in the Supporting  
405 Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### 410 **Notes**

411 The authors declare no competing financial interest.

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