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**Investigating potential limitations of current diffusive gradients in thin films (DGT) samplers for measuring organic chemicals**

Journal:	<i>Analytical Chemistry</i>
Manuscript ID	ac-2019-025712.R1
Manuscript Type:	Article
Date Submitted by the Author:	n/a
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3 **1 Investigating potential limitations of current diffusive gradients in thin films (DGT)**  
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5 **2 samplers for measuring organic chemicals**  
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3 20 ABSTRACT: The diffusive gradients in thin films (DGT) passive sampler has emerged as a  
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5 21 powerful tool for measuring *in situ* concentrations of organic contaminants in waters with  
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7 22 appropriate spatial and temporal resolution at low cost. This study addresses the property  
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9 23 range of compounds which can be routinely sampled with the present design of DGT device.  
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11 24 Sorption experiments and DGT deployment with 9 model chemicals [organophosphate esters  
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13 25 with a wide range of log  $K_{OW}$  (0.8–9.5), molecular weight (182–435 Da)] and different  
14  
15 26 functional groups showed compounds with high hydrophobicity and aromatic rings are prone  
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17 27 to retention on membrane filters, which slows the supply of chemical to the binding resin of  
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19 28 the sampler. The current DGT sampler (PTFE membrane filter, agarose gel diffusion layer  
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21 29 and HLB binding layer) is potentially reliable for measuring hydrophilic [ $\log K_{OW}$  (0.8–2.6)]  
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23 30 and non-aromatic-ring chemicals. For compounds of higher values of  $K_{OW}$  or with aromatic  
24  
25 31 rings, knowledge of the lag phase is necessary to optimize sampling times to avoid biasing  
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27 32 subsequent laboratory analyses. A standard procedure is used to measure lag times (from  
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29 33 minutes to days), by exposing a series of DGT samplers in waters until linear mass  
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31 34 accumulation in samplers is achieved. We discuss how monitoring of a wide array of organic  
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33 35 contaminants across classes should be possible in future, with a range of validated new DGT  
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35 36 devices, optimized for the choice of membrane filter, diffusive material and binding resin.  
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3 37 The organic chemical status of water bodies is crucial to water supply, human health, natural  
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5 38 ecosystems and biodiversity. However, organic pollutants are ubiquitous and have often been  
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7 39 poorly controlled.<sup>1</sup> Many of them are continuously discharged into aquatic systems, as waste  
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10 40 water treatment plants (WWTPs) are normally not designed to remove them from the  
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12 41 dissolved phase. Regulation is still limited, especially in developing countries; for example,  
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14 42 there are no specific organic compounds on the compulsory control list of the current  
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17 43 discharge standard of pollutants for municipal WWTPs in China (GB 18918–2002). Water  
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19 44 management authorities need surface water monitoring networks to properly monitor  
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21 45 contaminants and report long-term trends. Surveillance, operational monitoring and  
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23 46 investigative monitoring programmes need different monitoring designs, taking account of  
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26 47 the spatial and temporal variability within a water body. Sufficient samples need to be taken  
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28 48 to identify sources and to give a coherent, comprehensive overview of the chemical status of  
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30 49 the water body. When monitoring trace level organic pollutants, the balance between costs  
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33 50 and sufficient coverage of samples in time and space is challenging. Preservation, storage and  
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35 51 transport of water samples and sufficient education and training for field personnel are all  
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37 52 essential to the quality of sampling activities, but also increase the challenge. Spot sampling  
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40 53 is used for most monitoring in water bodies. However, at places where contaminant  
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42 54 concentrations are heavily influenced by flow conditions and temporal variation, flow-  
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44 55 proportional or time-proportional samples may be needed for more representative sampling.<sup>2</sup>  
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47 56 State-of-the-art passive water sampling techniques, such as diffusive gradients in thin films  
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49 57 (DGT), the polar organic chemical integrative sampler (POCIS) and Chemcatcher, give  
50  
51 58 ecotoxicologically relevant, time-weighted average (TWA) concentrations and enable cost-  
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53 59 effective multiple site sampling.<sup>2</sup> Hence they have attracted increasing attention over the past  
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56 60 decades as water authorities seek to balance their financial resources against a tendency to  
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58 61 monitor using traditional grab or spot sampling. Considerable research now supports: using  
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3 62 passive water sampling with accuracy and reliability; increasing the range of chemicals and  
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5 63 sampling environments; and procedures to improve real-world applications, with varying  
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7 64 water flow rates, biofouling and physicochemical conditions (Table S1). Yet our  
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9 65 understanding of sampling mechanisms of organic chemicals should be further explored for a  
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11 66 broader use of passive samplers.  
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15 67 A significant advantage of the DGT technique over other passive sampling techniques is that  
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17 68 contaminant uptake by DGT is independent of hydrodynamic conditions above a low flow  
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19 69 threshold, so no extra calibration is needed for *in situ* monitoring.<sup>3</sup> It was invented and first  
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21 70 applied to inorganics over 20 years ago and is built on a solid scientific foundation.<sup>4</sup> There  
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23 71 are now over 800 peer reviewed papers on developments and applications of the DGT  
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25 72 technique for metals and nutrients in waters, soils and sediments since the 1990s. In contrast,  
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27 73 research and development of DGT for organic chemicals only started in 2012, but it has  
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29 74 already attracted considerable interest and is developing rapidly.<sup>5</sup> To date, sampler  
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31 75 development and testing of 136 organic compounds has been reported in the literature (a few  
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33 76 from personal communication), with more being conducted.<sup>5-38</sup> Compound classes include  
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35 77 pharmaceuticals and personal care products, illicit drugs, endocrine disrupting chemicals and  
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37 78 pesticides etc. Table S1 summarizes these publications. Different sampler configurations  
38  
39 79 have been optimized for different groups of chemicals. Seventeen types of binding layers  
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41 80 with 15 different binding agents, 5 types of diffusion layers and 9 types of membrane filters  
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43 81 have been described in the literature. Apart from those membranes recommended so far, a  
44  
45 82 few others have also been tested. Some membrane filters give problems of retention of some  
46  
47 83 compounds. This led a few studies to propose using DGT without a membrane filter,<sup>23-27, 33</sup>  
48  
49 84 but this is inadvisable because a filter is not only protecting the inner system from clogging  
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3 85 by particles in water, the 0.45  $\mu\text{m}$  pore size membranes are also stopping microorganisms  
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5 86 entering the system.  
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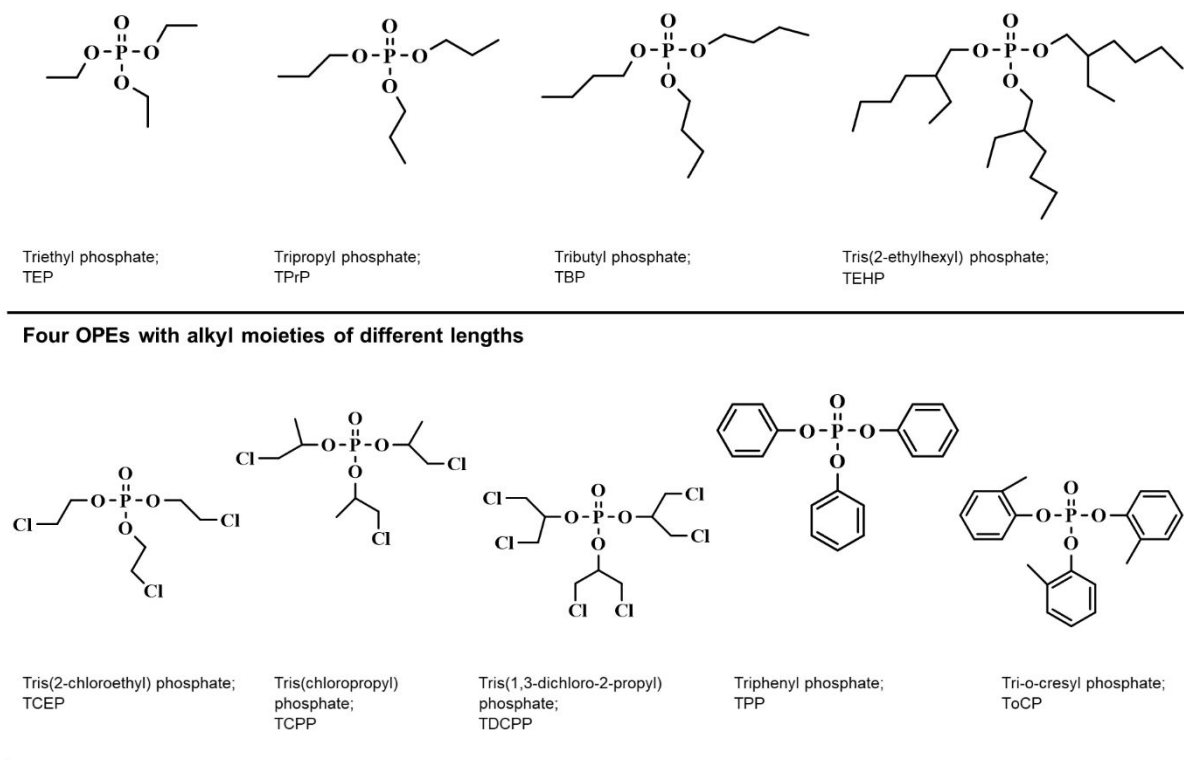
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9 87 As we seek to extend the use of DGT to organic chemicals, it is critical to understand any  
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11 88 limitations of the standard sampler design and any constraints to the range of possible  
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13 89 analytes. This can inform future developments and applications. The objectives of this study  
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15 90 were therefore to: i). characterize sorption of target chemicals on the standard DGT device  
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17 91 and investigate the effects of physicochemical properties of those compounds on sorption; ii).  
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19 92 delineate limitations of the standard DGT configuration for measuring organic chemicals; and  
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21 93 iii) recommend practical criteria for using DGT in monitoring organics in waters.  
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## 24 94 **EXPERIMENTAL SECTION**

### 25 95 **Choice of compounds for study**

26  
27 96 Five hydrophilic organophosphate esters (OPEs: TCEP, TCPP, TDCPP, TPrP and TBP) were  
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29 97 tested for *in situ* monitoring in aquatic systems using the DGT technique in a previous  
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31 98 study.<sup>20</sup> In this study, a group of 9 OPEs was chosen to expand the range of functional group  
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33 99 diversity and range of physicochemical properties (Figure 1). Details of the compounds are  
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35 100 given in Supporting Information (SI, Table S2 and Figure S1). The 9 chemicals can be sub-  
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37 101 divided into three groups: four with alkyl moieties of different lengths (TEP, TPrP, TBP and  
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39 102 TEHP); three with chlorinated alkyl moieties (TCEP, TCPP and TDCPP) and two with  
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41 103 phenyl moieties (TPP and ToCP). Their  $\log K_{\text{OW}}$  (a parameter describing hydrophobicity) and  
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43 104 molecular weight vary from 0.8 to 9.5 and from 182 to 435 Da. These ranges cover  $\approx 75\%$  of  
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45 105 the organic chemicals for which the DGT technique has been developed (Table S1). Whilst  
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47 106  $\log K_{\text{OW}}$  is clearly not the only physicochemical property controlling compound behavior, it is  
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49 107 a primary marker of compound behavior, routinely measured for chemicals of commerce and  
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108 environmental pollutants and an excellent surrogate to represent aqueous solubility and  
 109 partitioning behaviour.<sup>39</sup>



110 **Three OPEs with chlorinated alkyl moieties**

110 **Two OPEs with phenyl moieties**

111 Figure 1. Chemical structures of nine organophosphate esters (OPEs) selected for this study.

### 112 **Chemicals and Reagents.**

113 Stock solutions of all 9 chemicals and a mixture of 7 chemicals (all except for ToCP and  
 114 TEHP) were prepared in acetonitrile at 100 mg/L. A surrogate internal standard (SIS) mixture  
 115 was prepared in acetonitrile at 500 µg/L. Further details of these and other reagents are  
 116 provided in the SI.

### 117 **Sampler details.**

118 The DGT configuration in this study comprised a 0.4 mm thickness of hydrophilic-lipophilic-  
 119 balanced (HLB) resin gel as the binding layer (7 mg HLB per disc, nominal), a 0.8 mm  
 120 thickness of agarose gel (AG gel) as the diffusion layer and a polytetrafluoroethylene (PTFE)

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3 121 membrane (0.45  $\mu\text{m}$  pore size, 150  $\mu\text{m}$  thickness) as the standard filter. More details about  
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5 122 the DGT sampler and the technique were first described previously.<sup>40</sup>  
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### 8 123 **Instrumental analysis.**

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10 124 An ultra-high-performance liquid chromatography-tandem mass spectrometer (UHPLC-  
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12 125 MS/MS) was used to determine the target compounds. Separations were achieved by a  
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14 126 Shimadzu Nexera UHPLC (Kyoto, Japan) equipped with two binary pumps, an autosampler,  
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16 127 a degasser and a column oven connected to a Phenomenex Kinetex Biphenyl column (50 $\times$ 2.1  
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18 128 mm, 2.6  $\mu\text{m}$ ). Detections were conducted by a triple quadrupole mass spectrometer  
19  
20 129 (Shimadzu LCMS-8040, Kyoto, Japan), with an electrospray ionisation source operated in  
21  
22 130 positive ion mode. Details about the instrument, the LC gradient method, MS source  
23  
24 131 parameters, an illustrative chromatogram (Figure S2), MRM parameters (Table S3),  
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26 132 calibration curves (Table S4), instrumental limits of detection (LOD), limits of quantitation  
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28 133 (LOQ) and method detection limits (MDL) (Table S5) are given in the SI.  
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### 33 134 **Sorption experiments.**

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35 135 Before laboratory experiments, all containers including tubes, vials, beakers, DGT holders,  
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37 136 pipette tips used in the study were tested for possible contamination. Since OPEs are widely  
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39 137 used compounds, e.g. they could be found in new vials from plastic packing procedures, all  
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41 138 glassware used in this study was ultrasonically cleaned for 30 min in a 5% (w/v) non-ionic  
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43 139 surfactant solution, then extensively rinsed with tap water followed by MQ water, and then  
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45 140 followed by methanol. Plastic materials were replaced with metal or glassware as much as  
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47 141 possible for the experiment to avoid chemical losses by adsorption. HLB resins from the  
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49 142 cartridges were thoroughly washed with acetonitrile. All solvents are carefully checked to be  
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51 143 OPE-free.  
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55 144 For any DGT testing experiments using standard solutions, the concentrations of the targeted  
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57 145 chemicals should be approximately constant. There should not be significant losses in mass  
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3 146 during experiments due to adsorption on the container walls. In order for the DGT technique  
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5 147 to work optimally, all the materials for the sampler, except the binding gel, should have no  
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8 148 significant affinity for adsorbing the targeted chemicals.

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10 149 Different standard solutions (2.5, 20, 200, 1000  $\mu\text{g/L}$ ) of OPEs prepared in 0.01 M NaCl were  
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12 150 used in the following experiments. They were placed in appropriate containers (5 L glass  
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14 151 beakers, 15 mL and 50 mL glass vials and the diffusion cells) and were shaken on a  
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17 152 horizontal shaker for suitable times in an air-conditioned room (25  $^{\circ}\text{C}$ ) at a speed of 150 rpm.  
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19 153 Solution concentrations were measured frequently to check for any changes compared to the  
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21 154 initial concentrations. Samples of 0.2 mL solution were collected and spiked with 0.1 mL  
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23 155 acetonitrile and 0.1 mL SIS solution and then filtered through a 0.2  $\mu\text{m}$  PTFE syringe filter  
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26 156 into LC amber vials before analysis by LC-MS/MS.

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28 157 DGT sampler materials such as moldings, diffusive gels and membrane filters were tested for  
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30 158 possible sorption losses separately. They were immersed in a 25 mL solution containing ca.  
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33 159 200  $\mu\text{g/L}$  OPEs and 0.01 M NaCl for 6 hours. After spiking of 50 ng SIS, DGT moldings,  
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35 160 diffusive gels and membrane filters were separately eluted with  $3 \times 2$  mL aliquots of  
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37 161 acetonitrile and sonicated for 5 minutes between each elution. The elution solution was  
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39 162 evaporated to dryness by gentle nitrogen and reconstituted in 1 mL of acetonitrile and water  
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41 163 ( $v:v = 50:50$ ) and then filtered through a 0.2  $\mu\text{m}$  PTFE syringe filter into LC amber vials.  
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43 164 Samples were stored at 4  $^{\circ}\text{C}$  before analysis by LC-MS/MS. Solution concentrations were  
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45 165 measured to calculate the mass losses from mass balance. The detailed sample treatment  
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47 166 procedure is given in Extraction efficiency in SI.

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51 167 The sorption and permeation properties of polymeric membranes are governed by their  
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53 168 molecular characteristics and membrane structures (pore size, distribution and density,  
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55 169 surface roughness, thickness, etc.).<sup>41</sup> Although there is great potential for materials science  
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58 170 and industry to improve membrane properties for passive samplers,<sup>42</sup> one aim of this study is

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3 171 to characterize the present available membrane filters to find the most suitable one for DGT  
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5 172 devices for measuring organic contaminants and to investigate their influences on the DGT  
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7 173 sampler. Three types of membrane filters were tested for possible sorption of model  
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10 174 compounds. They were hydrophilic polyethersulfone (PES) membranes (thickness: 140  $\mu\text{m}$ ,  
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12 175 diameter: 25 mm, pore size: 0.45  $\mu\text{m}$ , PALL), which is a well-studied membrane filter;<sup>23, 42</sup>  
13  
14 176 hydrophilic polytetrafluoroethylene (PTFE) membranes (thickness: 150  $\mu\text{m}$ , diameter: 25  
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17 177 mm, pore size: 0.45  $\mu\text{m}$ , ANPEL); and hydrophilic polypropylene (GHP) membranes  
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19 178 (thickness: 114  $\mu\text{m}$ , diameter: 25 mm, pore size: 0.45  $\mu\text{m}$ , PALL)—two of the most  
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21 179 commonly used membrane filters for organic DGT samplers (Table S1). Sorption to PTFE  
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23 180 membrane filters was also investigated in *DGT deployment* for 7 days. Solutions in DGT  
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25 181 deployment were renewed every 12 hours to ensure stable concentrations. Further details are  
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27 182 in the SI.

### 183 **Diffusion coefficient measurements.**

184 One of the advantages of the DGT technique (compared to other passive sampling  
185 techniques) is that temperature specific diffusion coefficients ( $D$ ) through the diffusion layer  
186 are well established in the laboratory, generating more reliable field measurements without  
187 the need for further field calibration. The  $D$  values of targeted compounds were measured  
188 with a cast glass two-compartments diffusion cell (source and receptor) connected by a  
189 circular window (1.6 cm diameter) with a 0.8 mm thick diffusive gel (AG gel without filter).  
190 Both compartments were filled with 50 mL of 0.01 M NaCl solution. A 0.5 mL volume of  
191 stock solution containing 7 OPEs (100 mg/L) was spiked into the source compartment and  
192 the same volume of acetonitrile without OPEs was spiked into the receptor compartment. The  
193 solutions in both compartments were well stirred with mini glass-coated stirrer bars during  
194 the experiment. Solutions of 0.2 mL from both compartments were collected for analysis,  
195 after 5 minutes and then at intervals of 15 minutes for 3 hours.

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3 196 The masses of analyte in the receptor compartment were plotted as a function of time to  
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5 197 obtain a linear line with a slope that equals the first-order diffusion rate constant,  $k$  (mass,  $M$ ,  
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7 198 over time  $t$ ). Equation (1) below was then used to calculate  $D$  ( $\text{cm}^2/\text{s}$ ), where  $\Delta g$  is the  
9  
10 199 diffusive gel thickness,  $c_s$  is the initial analyte concentration in the source compartment, and  
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12 200  $A_s$  is the area of the connecting window:

$$D = \frac{k\Delta g}{c_s A_s} \quad (1)$$

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15 201  
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17 202 It is assumed that the thickness of the diffusive boundary layer (DBL) ( $\delta$ ) in the diffusion cell  
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19 203 is negligible under the vigorously mixed conditions used in the experimental set-up.<sup>43</sup>

#### 204 **Uptake kinetics.**

205 The binding agent (Oasis HLB, 60  $\mu\text{m}$  particle size, 80  $\text{\AA}$  pore size, 830  $\text{m}^2/\text{g}$  surface area)  
206 used in the DGT devices is a water-wettable polymer, with high capacity for a wide range of  
207 compounds and is stable at pH 0–14. Uptake kinetics of the binding layer were investigated  
208 by immersing binding gel discs in 40 mL solutions containing ca. 200  $\mu\text{g}/\text{L}$  OPEs and 0.01 M  
209 NaCl at  $21 \pm 2$   $^\circ\text{C}$  (in triplicate), and shaken horizontally for 24 hours. Solution samples (0.2  
210 mL) were collected at different times up to 24 hours, for further instrumental analysis, and the  
211 mass taken up by the binding gels was derived from the mass balance calculation.

#### 212 **DGT deployment.**

213 To test the DGT principle for measuring OPEs, DGT devices were deployed in 2.5 L solution  
214 containing ca. 20  $\mu\text{g}/\text{L}$  OPEs and 0.01 M NaCl for various deployment times up to 45 hours  
215 at  $19 \pm 1$   $^\circ\text{C}$ . According to the DGT equation (2), the mass of OPEs accumulated in the  
216 devices ( $M_{\text{DGT}}$ ) should be increased linearly with deployment time ( $t$ ).

$$c_{\text{DGT}} = \frac{M_{\text{DGT}}\Delta g}{tAD} \quad (2)$$

217  
218 Further test was conducted for longer deployment time up to 7 days in solution with lower  
219 OPEs concentration. Devices were exposed in 2.5 L solution containing around 2.5  $\mu\text{g}/\text{L}$

220 OPEs and 0.01 M NaCl and the solution was renewed every 12 hours to keep the  
221 concentrations approximately constant. The solution temperature ranged from 19 to 22 °C  
222 over the course of the experiment. To minimize the diffusive boundary layer, samplers were  
223 fixed on a steel frame in the solution and the solution was well stirred at 300 rpm by a glass-  
224 coated stirrer bar. Solution samples were collected before, during and after renewing the  
225 solution and samplers were retrieved at different times from 3 hours to 7 days. Binding gels,  
226 diffusive gels and membrane filters from every DGT device were extracted by acetonitrile  
227 immediately after deployment to obtain the mass of chemicals on them.

### 228 *QA/QC*

229 Quality control standards (50 µg/L) were prepared using independent weighing and they were  
230 run every 10 samples (concentration to be within 20% of target). Linearity ( $R^2$ ) of calibration  
231 standards was >0.99 over all analyses and all compounds. Matrix matched calibrators made  
232 by blank DGT extracts and 0.01 M NaCl solution were compared with calibrators made by  
233 pure acetonitrile and water. As a result, the matrix effects were negligible. The instrumental  
234 limit of detection (LOD) was from 0.01 (TEP) to 0.62 (TDCPP) µg/L (more details in SI).  
235 Where concentrations were below the detection limit, in statistical analyses, these values  
236 were substituted with LOD divided by the square root of 2.

## 237 **RESULTS AND DISCUSSION**

### 238 **Sorption.**

#### 239 **Sorption on glassware walls.**

240 There was negligible sorption of 7 OPEs [TEP, TCEP, TPrP, TCPP, TDCPP, TBP, TPP, log  
241  $K_{OW}$  (0.8–4.6), water solubility ( $1.9–5.0 \times 10^5$  mg/L)] in all glass containers and diffusion cells  
242 as their concentrations were stable at all 4 levels (2.5, 20, 200, 1000 µg/L). The  
243 concentrations of the 2 most hydrophobic OPEs [ToCP and TEHP, log  $K_{OW}$  (5.11, 9.49)] with

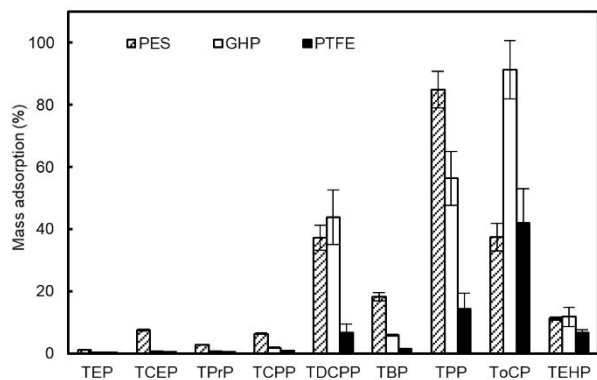
244 much lower water solubility (360 and 600  $\mu\text{g/L}$ ) were stable at low concentrations such as 2.5  
245 and 20  $\mu\text{g/L}$  but decreased sharply at high concentration 200  $\mu\text{g/L}$  (Figure S5).

#### 246 **Sorption on DGT materials.**

247 i) DGT moldings and gels: Seven OPEs (except ToCP and TEHP) reached sorption  
248 equilibrium quickly (<3 hours), on the DGT plastic moldings and diffusive agarose gels, with  
249 negligible sorption (<1% of total mass in the solution) observed, as the concentrations in test  
250 solution hardly decreased. When extracting OPEs from DGT plastic moldings and diffusive  
251 agarose gels by acetonitrile, very small amounts (<1% of total mass in the solution) of  
252 chemicals, including ToCP and TEHP, were detected. This is consistent with studies on other  
253 organic chemicals<sup>5, 18, 32</sup> and it is encouraging, as the application of the current DGT  
254 moulding units and diffusive agarose gels are becoming widespread for the environmental  
255 sampling of trace organic chemicals.

256 ii) Membrane filters: Sorption varied considerably between membrane filters and compounds,  
257 but one finding was consistent: more hydrophobic compounds (TDCPP, TBP, TPP, ToCP  
258 and TEHP,  $\log K_{\text{OW}}$  from 3.7 to 9.5) were always more prone to sorption onto the 3 types of  
259 membrane filters than more hydrophilic compounds (TEP, TCEP, TPrP and TCPP,  $\log K_{\text{OW}}$   
260 is from 0.8 to 2.6). However, less sorption occurred with PTFE than with the other two  
261 membrane filter types (Figure 2). In detail, there was little adsorption of TEP (0.28%  $\pm$   
262 0.02% of total mass 5  $\mu\text{g}$ ), TCEP (0.38%  $\pm$  0.01%), TPrP (0.42%  $\pm$  0.04%) and TCPP (0.78%  
263  $\pm$  0.03%) onto the PTFE membrane filter; slightly higher adsorption of TDCPP (6.8%  $\pm$   
264 2.7%) and TBP (1.5%  $\pm$  0.11%) onto PTFE membrane filters was found; TPP (14.2%  $\pm$   
265 5.1%) and ToCP (41.9%  $\pm$  11.2%) were significantly absorbed by PTFE membrane (see later  
266 for the detailed sorption profiles). PTFE was therefore chosen to be the filter for further  
267 study.

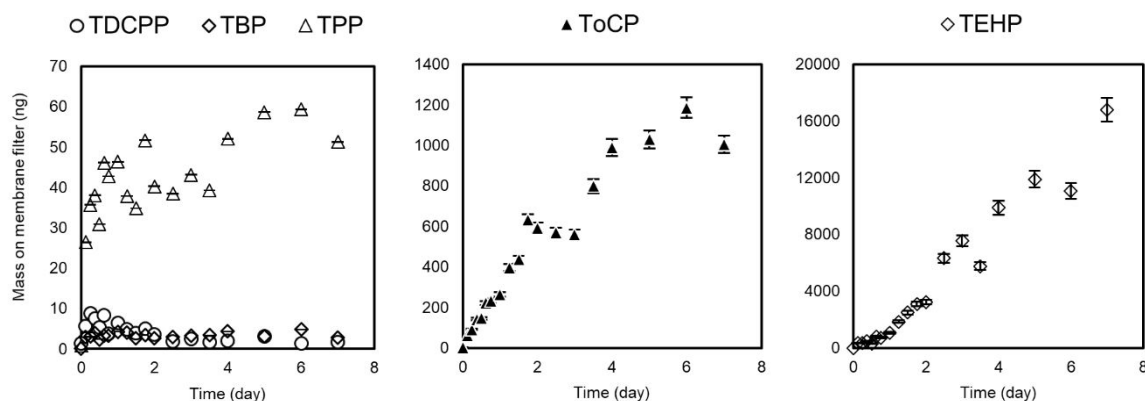
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269

270 Figure 2. Adsorption of tested OPEs by 3 types of membrane filters in 25 mL solutions  
 271 containing ca. 200  $\mu\text{g/L}$  OPEs and 0.01 M NaCl for 6 hours. Error bars were calculated from  
 272 the standard deviation of triplicates. Note, TPP, ToCP and TEHP appeared to have not  
 273 reached sorption equilibrium after 6 hours, the time of this experiment.

274 For three chemicals (TPP, ToCP and TEHP) sorption equilibrium to membrane filters had not  
 275 reached equilibrium after 6 hours, as the solution concentrations of those chemicals continued  
 276 to decrease in the test solution. Experiments over much longer time were carried out and the  
 277 results showed that TPP did not reach equilibrium until about 4 days, while ToCP and TEHP  
 278 needed  $>6$  days (Figure 3 for sorption profiles of OPEs on PTFE membrane filters). Endo and  
 279 Matsuura did a sorption experiment which also showed that 6 out of 14 chemicals did not  
 280 reach apparent equilibrium on PES polymer over 7 days.<sup>42</sup>



281

282 Figure 3. Sorption profiles of 5 OPEs on PTFE membrane filters from DGT samplers  
283 exposed in solution with a few micrograms per liter OPEs (Figure S8) and 0.01 M NaCl from  
284 3 hours to 7 days (note that the solution was renewed every 12 hours to keep the  
285 concentrations approximately constant), error bars were calculated from the standard  
286 deviation of triplicates. The other 4 compounds (TEP, TCEP, TPrP and TCPP) showed  
287 negligible sorption on PTFE membrane filters and are not present here.

288  
289  $K_{\text{PTFE/W}}$  values (the ratio of the concentration of a studied chemical in PTFE membrane filter  
290 and water at equilibrium at the temperature in this study) were plotted against  $K_{\text{OW}}$  to  
291 compare the sorption strength of the PTFE membrane filter across studied chemicals (Figure  
292 4).  $\log K_{\text{PTFE/W}}$  was significantly correlated with  $\log K_{\text{OW}}$  ( $\log K_{\text{PTFE/W}} = 0.52 \log K_{\text{OW}} - 0.02$ ,  
293  $R^2 = 0.73$ ,  $p < 0.05$ ). Note that for TEHP, which didn't reach equilibrium after 7 days, a  
294 sorption mass of 16.8  $\mu\text{g}$  on the 7th day was used ( $R^2 = 0.76$  if estimated sorption mass was 2  
295 times of 16.8  $\mu\text{g}$ ,  $R^2 = 0.82$  if estimated sorption mass was 10 times of 16.8  $\mu\text{g}$ ). Although  
296 sorption by PTFE in comparison to  $K_{\text{OW}}$  has been conducted before with, e.g., carcinogens,  
297 industry additives, solvents and pharmaceuticals,<sup>42, 44</sup> no significant correlations between  $\log$   
298  $K_{\text{PTFE/W}}$  and  $\log K_{\text{OW}}$  were found. We consider the chemical property ranges were not wide  
299 enough to see a correlation.  $\log K_{\text{PTFE/W}}$  was  $< 1.78$  for all studied chemicals in the study by  
300 Leggett and Parker,<sup>44</sup>  $\log K_{\text{PTFE/W}}$  was  $< 1.65$  for all studied chemicals in study by Endo and  
301 Matsuura,<sup>42</sup> while this study substantially pushed the boundary to 4.61 ( $\log K_{\text{PTFE/W}}$  of ToCP).  
302 Thus, hydrophobicity (as reflected by  $\log K_{\text{OW}}$ ) seems one factor influencing chemicals  
303 sorption on PTFE polymer and this slow equilibration (Figure 4). Diffusion through the filter  
304 pores is strongly retarded by sorption to the polymeric matrix. However, this cannot explain  
305 that relatively hydrophilic chemicals, like caffeine ( $\log K_{\text{OW}} = -0.07$ , 194.2 Da) showed slow  
306 sorption equilibration ( $> 7$  d) on the PES matrix.<sup>42</sup> ToCP stands out of the regression line in

Figure 4, which seems also to suggest hydrophobicity is not the only factor influencing this slow equilibration. We speculate that aromatic rings in caffeine (imidazole ring) cause slow equilibration, by increasing electrostatic interactions between electron-rich  $\pi$  systems and the polymeric matrix,<sup>39</sup> the same as ToCP (benzene ring) in this study.

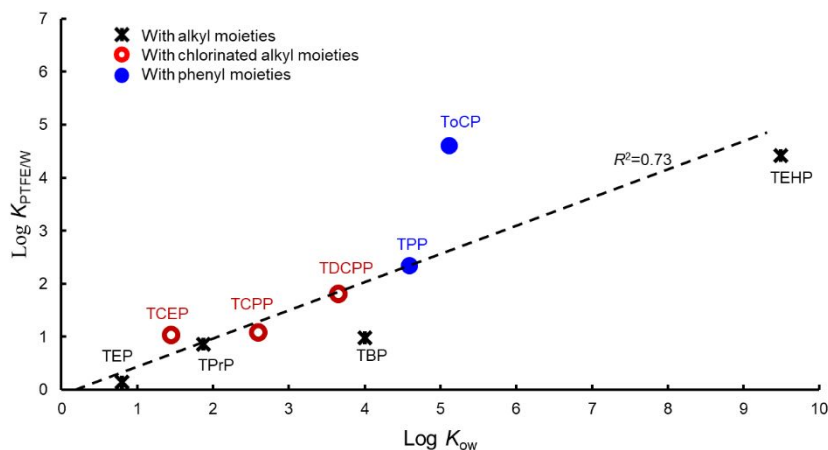


Figure 4. Log  $K_{PTFE/W}$  vs log  $K_{OW}$  (note that  $K_{PTFE/W}$  of TEHP were estimated based on membrane filters sorption study the sorption capacity of PTFE membrane filter for TEHP was higher than 16  $\mu\text{g}$ ). The dashed line indicates the linear regression for studied chemicals ( $\log K_{PTFE/W} = 0.52 \log K_{OW} - 0.02$ ,  $R^2 = 0.73$ ,  $p < 0.05$ ).

### Diffusion coefficients.

Diffusion coefficients of seven OPEs in diffusive gel measured using the diffusion cell are presented in Table S7. Good linear relationships ( $R^2$  from 0.97 to 0.99) of diffused masses versus time were obtained (Figure S3). The two least water soluble compounds ToCP and TEHP (360 and 600  $\mu\text{g/L}$ , respectively) showed significant sorption to the diffusion cell wall, which made it impossible to keep the concentrations in source compartment stable with the normal diffusion cell system used here. The difficulties of working with very low aqueous solubility compounds in laboratory experiments is well known;<sup>45, 46</sup> different approaches, such as the use of a generator column or a loaded stirrer bar, may be useful in future studies on these types of chemicals.



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2  
3 326 The diffusion coefficients ( $D$ ) at 25 °C were  $6.77 \times 10^{-6}$ ,  $6.19 \times 10^{-6}$ ,  $5.47 \times 10^{-6}$ ,  $6.17 \times 10^{-6}$ ,  
4  
5 327  $5.26 \times 10^{-6}$ ,  $4.46 \times 10^{-6}$  and  $5.61 \times 10^{-6}$  cm<sup>2</sup>/s for TEP, TCEP, TPrP, TCPP, TDCPP, TBP and  
6  
7 328 TPP, respectively, which agreed well with  $D$  of 5 OPEs (TCEP, TCPP, TDCPP, TPrP and  
8  
9 329 TBP) published before.<sup>20</sup> The ratios of  $D$  in this study to those published by Zou et al were in  
10  
11 330 the range of 0.9–1.1.

### 14 331 **Uptake kinetics.**

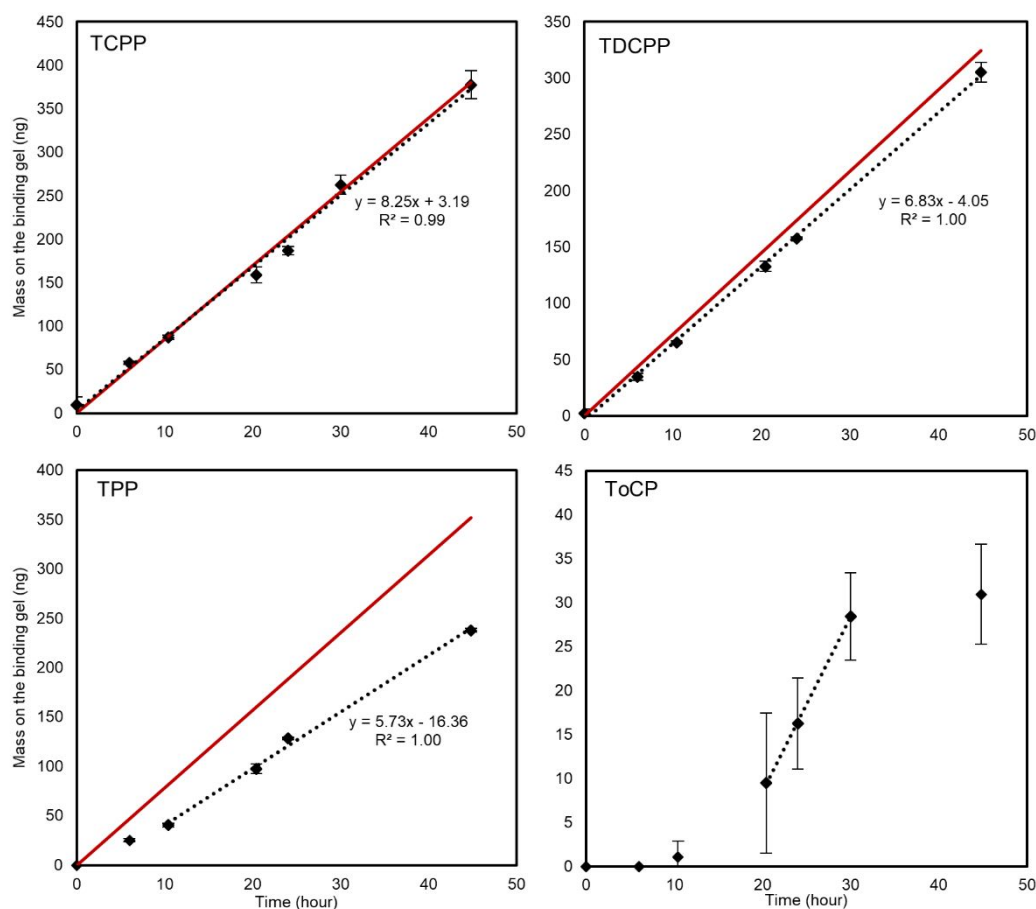
16 332 When the DGT binding layer rapidly and irreversibly binds target chemicals, this ensures the  
17  
18 333 concentration of the analyte at the interface between the binding layer and diffusion layer is  
19  
20 334 effectively zero. Then the mass transport of the analyte through the diffusion layer can achieve  
21  
22 335 a steady state and the DGT equation (2) can be used to accurately determine the DGT  
23  
24 336 concentration ( $c_{\text{DGT}}$ ) of the analyte in the solution.

26 337 The OPEs were taken up rapidly (ca. 40% uptake in 1 hour) by the binding gels, followed by  
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28 338 more gradual uptake (Figure S4) for all the compounds except ToCP and TEHP. The  
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30 339 concentration of ToCP and TEHP decreased sharply, due to rapid sorption to the glassware  
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32 340 (Figure S5). Further procedures mentioned earlier are needed to keep ToCP and TEHP water  
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34 341 concentrations relatively constant, in order to assess uptake kinetics.

35 342 As the DGT principle only works within the linear accumulation range of the resin gel, it is  
36  
37 343 important to verify the DGT performance by deploying devices in a solution at constant  
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39 344 concentration for different times. For all 9 OPEs tested, 7 of them (except ToCP and TEHP)  
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41 345 showed linear increase in accumulated mass with deployment time. The linear relationship  
42  
43 346 was compared with a theoretical line of mass versus time predicted using DGT equation (2).

44 347 At initial stages of the deployment, analytes have to diffuse through the membrane filter and  
45  
46 348 then the diffusive gel layer. For chemicals with high affinity to the membrane filter, the  
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48 349 resulting lag times cause the actual mass accumulation line to deviate from the theoretical  
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50 350 line as shown in Figure 5 except ToCP. The greater the sorption onto the membrane filter, the

351 greater the deviation from the theoretical linear line. This point is demonstrated by the results  
 352 of TPP, ToCP and TEHP (Figures 5, S6).



353  
 354 Figure 5. Linear mass accumulation of 4 selected OPEs over time by DGT samplers exposed  
 355 in 2.5 L solution containing ca. 20  $\mu\text{g/L}$  OPEs and 0.01 M NaCl for various deployment  
 356 times up to 45 hours. The solid red line is the theoretical mass accumulation line, assuming  $\delta$   
 357 = 0.3 mm. Error bars were calculated from the standard deviation (SI) of triplicates. (Figure  
 358 S6 presents all the compounds).

### 359 Establishing steady state.

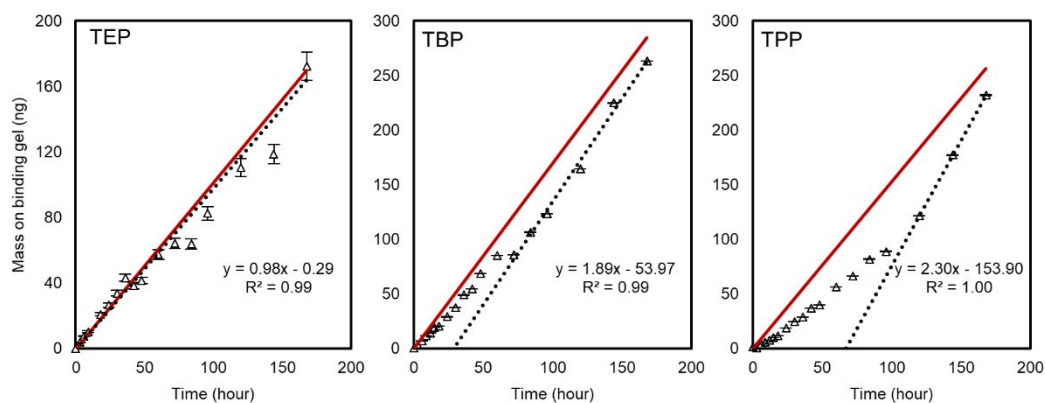
360 The time to achieve linear mass accumulation (steady state),  $t_{ss}$ , can be estimated using  
 361 equation (3).<sup>47</sup> Here  $\Delta g$  represents the diffusion layer thickness, with the diffusion coefficient  
 362 being an aggregated value for the diffusive gel and membrane filter.

$$363 \quad t_{ss} = \Delta g^2 / 2D \quad (3)$$

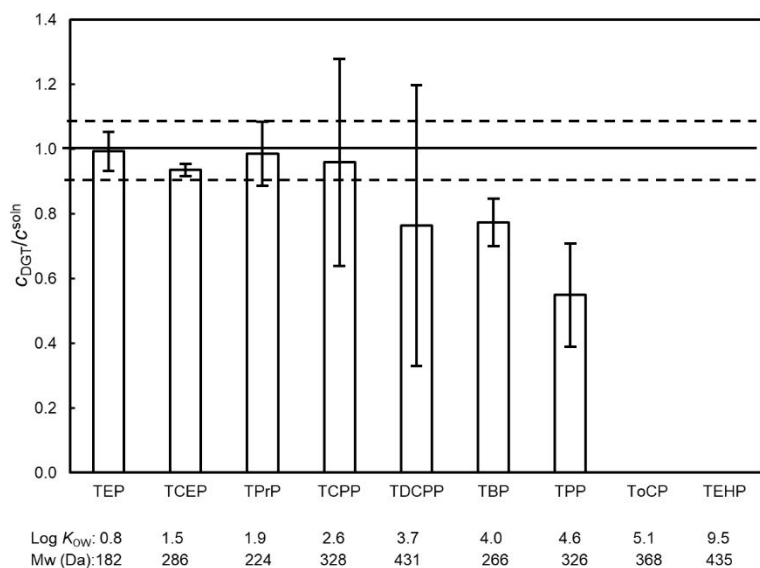
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3 364 If the overlaid membrane filter had negligible adsorption effect, the transient times for OPEs  
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5 365 (except ToCP and TEHP) were about 16 minutes, which would be consistent with previous  
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7 366 works.<sup>48-50</sup> However, the interactions of analytes with the membrane filter substantially  
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9  
10 367 extend the time needed to reach steady state. This study provides a standard procedure to  
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12 368 measure it by exposing a series of DGT samplers at environmental concentration levels  
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14 369 (nanograms to micrograms per liter)<sup>51, 52</sup> of a testing solution until linear mass accumulation  
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16  
17 370 is achieved.

18  
19 371 Figure 6 illustrates the masses accumulated in binding gels for the longer deployment time of  
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21 372 7 days. Black dotted lines show the establishment of steady state in the binding gels and  
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23 373 intercepts of the time-axis are the lag times required for establishing it. For DGT device with  
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25 374 a 0.8 mm thick diffusive gel and a 0.14 mm thick PTFE membrane filter under the testing  
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27 375 solution conditions (a few micrograms per liter OPEs, Figure S8), steady state was effectively  
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29 376 reached within 18 minutes for TEP and 42 minutes for TCEP. The errors caused by lag time  
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31 377 are <3% for deployments of 24 h or greater for shorter sampling windows. Longer  
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33 378 deployment times of >24 h for TPrP and more than a week for TCPP are necessary to ensure  
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35 379 <10% error. For TDCPP, TBP, TPP, ToCP and TEHP, the recommended minimum  
36  
37 380 deployment time would be 2 weeks to 2 months due their long lag times (Table S8). As  
38  
39 381 shown in Figure 7, DGT measured concentrations of TEP, TCEP, TPrP and TCPP agreed  
40  
41 382 well with the bulk solution concentrations, with  $c_{\text{DGT}}/c^{\text{soln}}$  ranging from 0.95–0.99, whereas  
42  
43 383 the deviation of DGT measurement from the solution concentration increased for TDCPP,  
44  
45 384 TBP and TPP. The theoretical method quantitation limits (MQLs) of the DGT technique can  
46  
47 385 be converted from MDLs [1.05 ng/L (TEP), 0.49 ng/L (TCEP) and 0.43 ng/L (TPrP), refer  
48  
49 386 Table S5,  $M_{\text{DGT}}$  equals 1.05, 0.49 and 0.43 ng, respectively] to a concentration by equation  
50  
51 387 (2), depending on the deployment time. For 24 hour deployment, using  $D = 6.77\text{E-}06 \text{ cm}^2/\text{s}$   
52  
53 388 (TEP),  $6.19\text{E-}06 \text{ cm}^2/\text{s}$  (TCEP),  $5.47\text{E-}06 \text{ cm}^2/\text{s}$  (TPrP),  $\Delta g = 0.125 \text{ cm}$ ,  $A_s = 3.14 \text{ cm}^2$ , the  
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3 389 MQLs are 71 ng/L (TEP), 36 ng/L (TCEP) and 36 ng/L (TPrP) and for 1 week deployment,  
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5 390 the MQLs are 10 ng/L (TEP), 5 ng/L (TCEP) and 5 ng/L (TPrP). The single-digit ng/L  
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7 391 sensitivity agrees well with this field study.<sup>26</sup> It's worth mentioning that the lag time was  
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9 392 tested at a general environmental concentration level (a few micrograms per liter). In the case  
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11 393 where the adsorption of the chemicals on the membrane filter is significant, the lag time is  
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13 394 dependent on not only the  $D$  value, but also the concentration of the chemicals in the  
14  
15 395 environment due to the adsorption capacity of the membrane filter. If the testing solution is at  
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17 396 very high concentrations or the environmental concentrations are extraordinary high (>10s  
18  
19 397  $\mu\text{g/L}$  or even >100s  $\mu\text{g/L}$ ), the lag time could be negligible.



398  
399 Figure 6. Mass accumulation of 3 selected OPEs over time by DGT samplers exposed in 2.5  
400 L solution containing a few micrograms per liter OPEs (Figure S8) and 0.01 M NaCl from 3  
401 hours up to 7 days. The solid red line is a theoretical mass accumulation line,  $\delta = 0.3$  mm.  
402 Error bars were calculated from the standard deviation (SI) of triplicates (Figure S7 for all the  
403 compounds).



404

405 Figure 7. Ratios of DGT-measured OPEs concentrations,  $c_{DGT}$ , to their concentrations in the  
 406 bulk solution,  $c^{soln}$ , during *DGT deployment* in which DGT samplers were exposed in 2.5 L  
 407 solution containing a few micrograms per liter OPEs (Figure S8) and 0.01 M NaCl from 3  
 408 hours up to 7 days. The solid line represents the target value of 1.0. Values were expressed as  
 409 mean  $\pm$  standard deviation of 18 DGT samplers.

### 410 CONCLUSIONS

411 DGT integrated with UHPLC-MS/MS can be used to monitor trace organic pollutants in  
 412 aquatic systems. This study used 9 OPEs as model chemicals, which covered  $\approx 75\%$  of the  
 413 organic chemicals (in terms of  $\log K_{ow}$  and molecular weight) for which the DGT technique  
 414 has been developed, to investigate limitations of the standard DGT configuration for  
 415 measuring organic chemicals. We have demonstrated that DGT is potentially reliable for  
 416 measuring hydrophilic [ $\log K_{ow}$  (0.8–2.6)] and non-aromatic-ring chemicals at short and long  
 417 deployment times. Organic chemicals with high hydrophobicity or aromatic rings are prone  
 418 to retention on membrane filters, which delays their diffusion, causing a lag time before  
 419 linear mass accumulation in the DGT sampler. For those compounds, a standard procedure to

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3 420 determine lag times is presented, by deploying a series of DGT devices in waters until linear  
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5 421 mass accumulation with time in the devices is achieved and the time-axis intercepts are  
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7 422 treated as lag times. In practice, a deployment time of 24 hours in an experiment or field  
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9 423 monitoring situation would have a sampling time error of <3% for compounds TEP and  
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11 424 TCEP; when the deployment time is 2 weeks, the sampling time error is <10% for most  
12  
13 425 compounds (TEP, TCEP, TPrP, TCPP, TDCPP and TBP) but is higher for TPP ( $\approx 20\%$ ),  
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15 426 ToCP ( $\approx 40\%$ ) and TEHP ( $>40\%$ ). Although a membrane filter could cause retention from  
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17 427 minutes to days, it is necessary to protect the diffusive gel from clogging by particles and to  
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19 428 prevent organisms going into the DGT device. This study focuses on the limitation of the  
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21 429 current DGT sampler for measuring organic chemicals and we have identified the absolute  
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23 430 limitation to use the current DGT device for organics is adsorption in the diffusion layer,  
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25 431 mainly in membrane filters. However, it is possible to extend the DGT technique for a wider  
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27 432 range of chemicals, for example, by replacing the current DGT membrane filter with a new  
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29 433 type of membrane filter which does not interact with compounds such as ToCP and TEHP.  
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31 434 New configurations of DGT devices using different materials for housing the binding and  
32  
33 435 diffusion layers, new types of diffusion layer and membrane filters should be developed for  
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35 436 both fields of research and monitoring. Studies are being undertaken to address concerns over  
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37 437 effects of biofouling and compound degradation/loss during sample handling/storage on the  
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39 438 sampler performance and will be the subject of a separate article.  
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13  
14 449 **Funding**

15  
16 450 Runmei Wang is grateful to the financial support from China Scholarship Council (CSC) for  
17  
18 451 pursuing her study in the UK as a Ph.D. Student.

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20  
21 452 **Notes**

22  
23 453 The authors declare no competing financial interest.

24  
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26 454 **ACKNOWLEDGMENTS**

27  
28 455 The authors thank DGT Research Ltd. (Lancaster, UK) for providing DGT devices.

29  
30  
31 456 **SUPPORTING INFORMATION**

32  
33 457 Detailed list of studies on the DGT technique, further details of chemicals and reagents,  
34  
35 458 detailed information on tested chemicals, analytical methods, experimental details, statistical  
36  
37 459 analysis, supplementary results and discussion (PDF)

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