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

Wei Chen[1], Yanying Li[1], Chang-Er Chen[1], Andrew J. Sweetman[1], Hao Zhang[1*] and Kevin C. Jones[1*]

1. Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, UK

*: corresponding authors

Email: h.zhang@lancaster.ac.uk and k.c.jones@lancaster.ac.uk; Tel: +44 1524 593899 (HZ) and +44 1524 510230 (KCJ).

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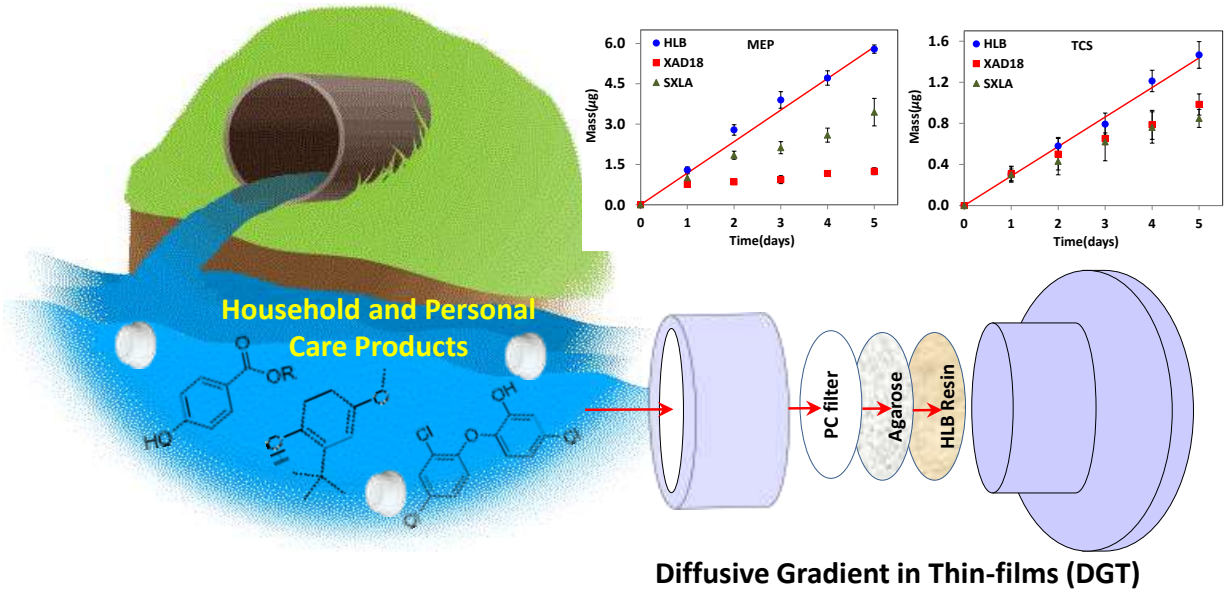
Household and Personal Care Products
HLB
XAD18
SXLA
MEP
Mass(μg)
Time(days)
TCS
PC filter
Agarose
HLB Resin
Diffusive Gradient in Thin-films (DGT)

ABSTRACT:

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

1. INTRODUCTION

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

Performance reference compounds (PRCs) are therefore used to provide calibration data to assess the difference between *in situ* sampling rates (R_S) and laboratory derived values,[14, 17, 18] but this is still problematic for polar chemicals.

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

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

where M is the measured mass of target chemical accumulated in the binding gel, Δg is the thickness of the diffusive gel layer, δ is the thickness of diffusive boundary layer (DBL), D is the diffusion coefficient of target chemical in the diffusive gel layer, t is the exposure time and A is the exposure area of the sampler. Δg is much thicker than the typical environmental DBL thickness under most conditions, so the influence of the environmental DBL becomes negligible, making the DGT measurement fairly insensitive to hydrodynamic conditions.[20, 21] Equation (1) therefore simplifies to:

$$C_{DGT} = \frac{M\Delta g}{DAt} \quad (2)$$

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

other polar organic contaminants in WWTPs.[30] Thus, the possibility of a DGT sampler for the wide family of HPCPs-preservatives, antioxidants and disinfectants is of great interest.

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

2. MATERIALS AND METHODS

2.1 Chemicals and Reagents

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

2.2 Diffusive and Binding Gel Preparation

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

2.3 Chemical Analysis and Detection Limits

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

2.4 Performance Testing of DGT in the Laboratory

2.4.1 Adsorption by DGT holders, diffusive gels and membrane filters

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

2.4.2 Optimisation of binding gel extraction recoveries

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

2.4.3 Uptake capacity of DGT and binding gel uptake kinetics

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

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

2.4.4 Diffusion coefficient measurements

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

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

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

2.4.5 Time and diffusion layer thickness dependence

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

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

2.4.6 Effect of pH, IS and DOM

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

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

2.5 *In situ* Measurements in a WWTP

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

3. RESULTS AND DISCUSSIONS

3.1 Adsorption by DGT Holders, Diffusive Gels and Membrane Filters

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

3.2 Optimisation of Gel Extraction Recoveries

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

3.3 Binding Capacity of DGT and Uptake Kinetics of Binding Gel

The results obtained from the capacity experiments showed that the uptake of all test chemicals increased linearly up to about 2 mg L^{-1} 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) μg; 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) $\mu g\ L^{-1}$ 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) $\mu g\ L^{-1}$. In most situations, HPCP concentrations in waters would be <10 $\mu g\ L^{-1}$. 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.

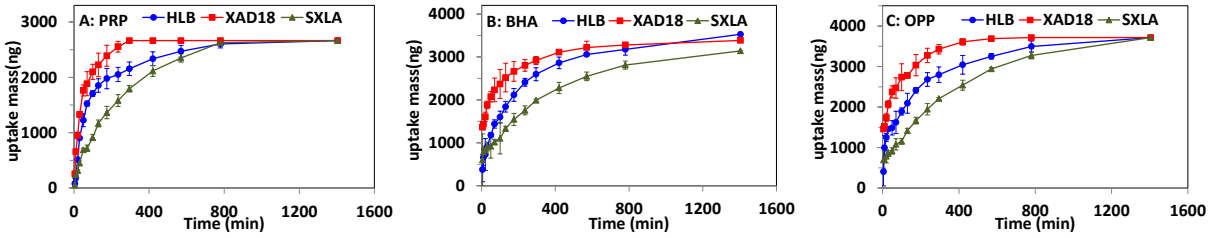

Figure 1: Binding kinetics of PRP, BHA and OPP by HLB, XAD18 and SXLA resin gels in 20 mL solutions of ca. 200 μg L^{-1} test chemicals (IS = 0.01 M, pH = 6.8±0.1, T = 20±2 ℃; n=3). Error bars were calculated from the standard deviation (SD) of three replicates.

3.4 Diffusion Coefficient Measurement

The measured D values of test chemicals at 25 ℃ (D_{25}) were calculated using Equation (3), based on the k values obtained from the diffusion cell experiments (**Figure S6)**. The D values at other temperatures (D_T) can be estimated using Equation (4)[20].

$$\log D_T = \frac{1.37023(T-25)+8.35\times10^{-4}(T-25)^2}{109+T} + \log\frac{D_{25}(273+T)}{298} \quad (4)$$

D values were calculated from 1 to 35 ℃ and these are listed in **Table S7**. Measurements at 15 and 20 ℃ were also carried out to compare with the calculated values. The measured D values at both 15 and 20 ℃ (**Table S7**) were within 10% of the calculated values, indicating the accuracy of D measurement in this study. For D value variations of +/- 10%, the effect on the weighted average calculations is between +11% and -9%.

3.5 Time and Diffusion Layer Thickness Dependence

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

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

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

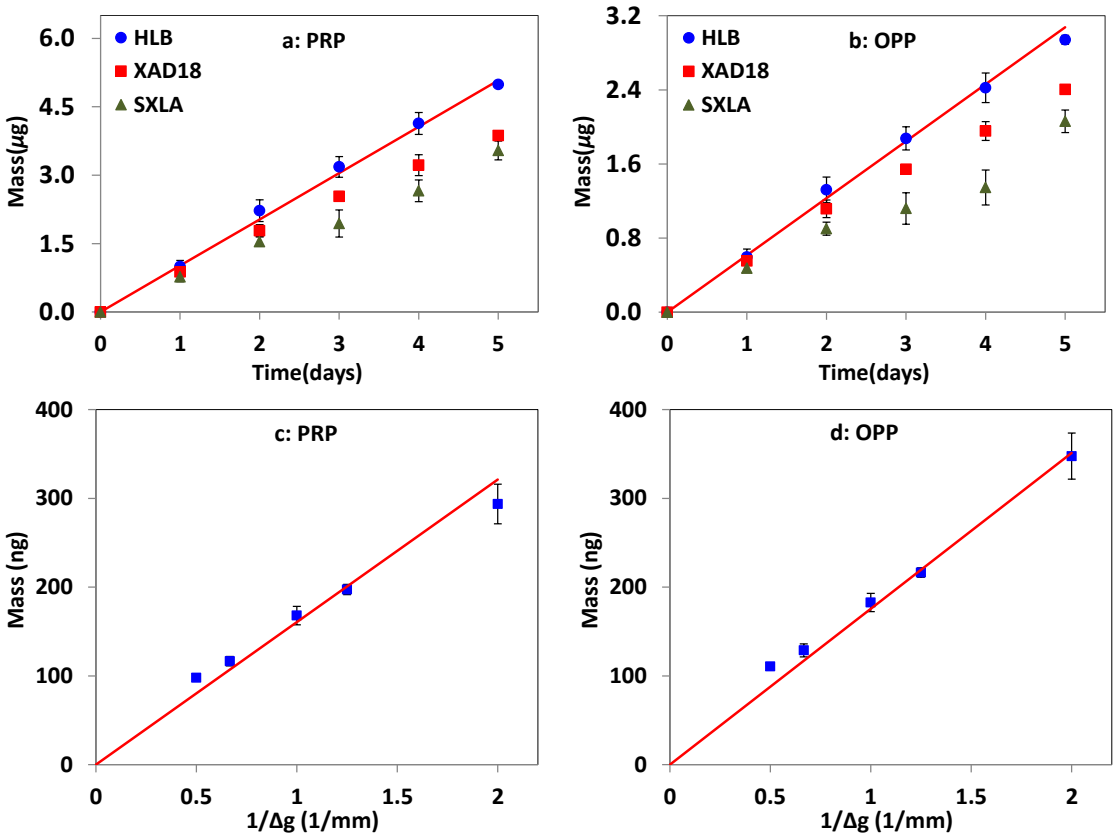

Figure 2: Measured masses of PRP and OPP in HLB, XAD18 and SXLA-DGT devices deployed in well stirred solution for different time (a-b, n=3) and in HLB-DGT devices with various diffusion layer thicknesses after 20 hours (c-d, n=3). The solid lines are theoretical lines predicted by Equation (2). Error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

3.6 Effect of pH, Ionic Strength and DOM

No significant pH effect on DGT uptake of test chemicals was observed (**Figure S9**). For the 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 averages of C_{DGT}/C_b values at all pH for individual chemicals were in the range of 0.97-1.08, **Table S8**). No significant difference (ANOVA, $p>0.05$) of the C_{DGT}/C_b was observed, although there was a slight decline of C_{DGT}/C_b at the highest pH (9.5). The only exception was for TCS (**Table S8**): the 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

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

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

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

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

3.7 Effect of DBL

DGT devices with various thicknesses of diffusive gel layer were deployed at the same time in influent and effluent to determine the *in situ* DBL thickness (δ). The following Equation (5)[20] (derived from Equation (1)) was used:

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

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

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) for the effluent. The DBL thickness in the influent was very similar to a previous study conducted at the same location of the same WWTP.[24] The smaller DBL thickness in the effluent was consistent with more turbulent flow. To reduce the errors on the TWA concentrations, 0.25 and 0.07 mm were used as the DBL thicknesses when calculating the C_{DGT} in the influent and effluent, respectively. With other passive samplers for organics (i.e. POCIS and Chemcatcher), the effect of DBL would be much greater, capable of producing several-fold errors on measured concentrations.[14]

3.8 Field Trial Application at the WWTP

3.8.1 HPCPs in the grab and auto-sampler samples

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

3.8.2 Uptake of HPCPs by the DGT devices

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

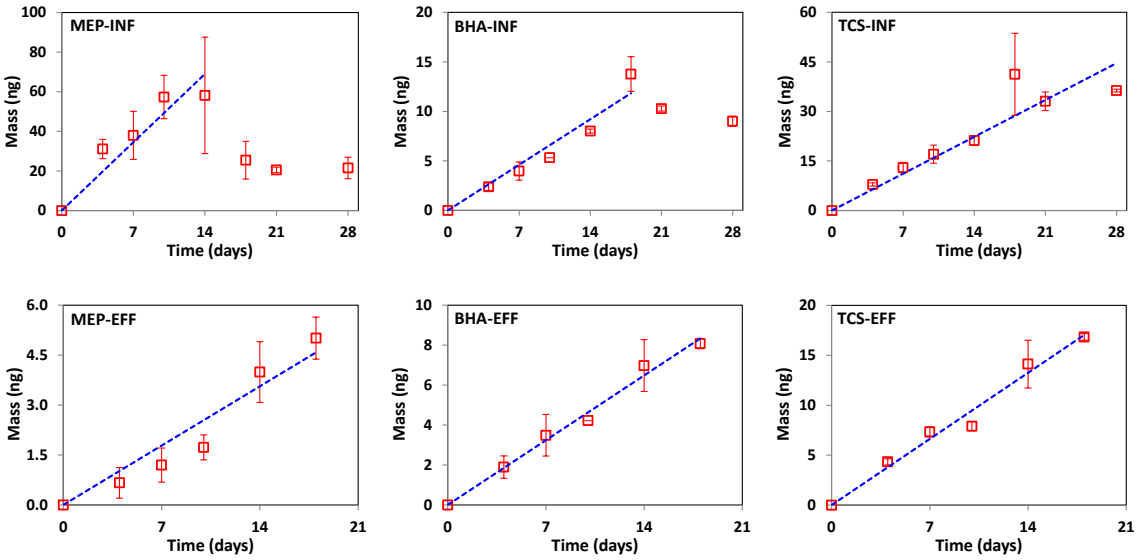

Figure 3: Uptake of typical HPCPs by HLB-DGT (n=3) in the influent (INF) and effluent (EFF) of a UK WWTP (The dotted blue line is the linear regression line through those points with continuous uptake). This Figure shows that deployment times of 7-14 days would be ideal for deriving TWA values. Error bars: 1 SD.

This is consistent with studies where DGT and POCIS were used to sample for antibiotics and drugs in WWTPs.[24, 44] There would appear to be three possible reasons for a reduction in sampling rate or decline in mass retained on the resin gel. One possibility is biofouling, where growth on the sampler surface inhibits uptake or enhances degradation of the compound in the biofilm. The second is degradation of HPCPs in the resins. The third is possible uptake and retention of co-existing/competing substances. Differences in compound properties will influence their susceptibility to degradation. Biofouling is not significant for the DGT samplers in either the influent or effluent in this study, as can be seen in **Figure S14** which shows DGT samplers retrieved after 14 days. Considering the detection limits and the fouling effects, 1 to 2 weeks deployment time is recommended for practical application.

3.8.3 Comparison of concentrations derived by DGT and active sampling

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

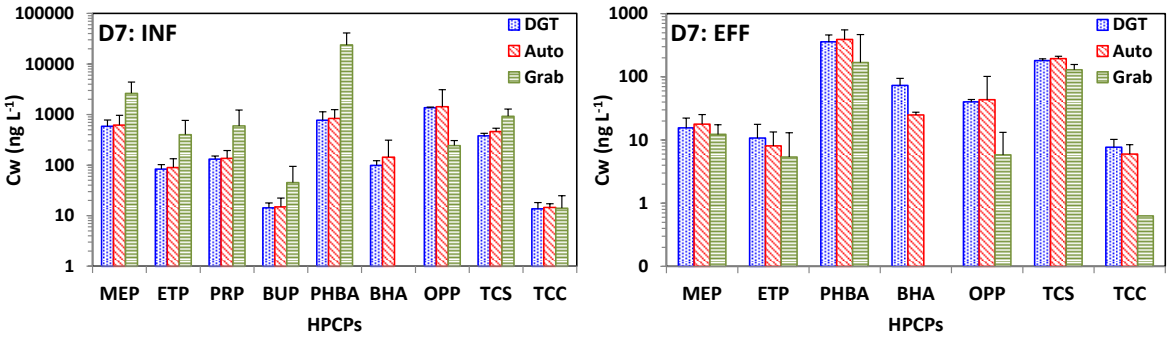

Figure 4: TWA concentrations measured by DGT samplers during 7 days deployment and average concentrations of the same compounds by auto samplers and grab samples in both influent (INF) and effluent (EFF). Error bars: 1 SD.

3.8.4 Analytical advantage of DGT measurements

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

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

3.9 Recommendations and perspectives

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

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

SUPPORTING INFORMATION

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

AUTHOR INFORMATION

Corresponding Author

* Email: h.zhang@lancaster.ac.uk and k.c.jones@lancaster.ac.uk; Tel: +44 1524 593899 (HZ) and +44 1524 510230 (KCJ).

Notes

The authors declare no competing financial interest.

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