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# Evidence and Recommendations to Support the Use of a Novel Passive Water Sampler to Quantify Antibiotics in Wastewaters

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Supporting Information

**ABSTRACT:** A novel passive water sampler (diffusive gradients in thin-films for organics, o-DGT) was previously developed and successfully tested in the laboratory, but has not yet been validated in the field. Here, o-DGT samplers were deployed in the influent and effluent of a typical UK wastewater treatment plant (WWTP); the influent was also sampled with a conventional automatic sampler (Auto) and by grab (Grab) sampling. All the samples were analyzed by LC-MS/MS for 40 target antibiotics (including 16 sulfonamides (SAs), 12 fluoroquinolones, 6 macrolides, 2 ionophores, 2 diaminopyimidines, 1 aminocoumarin, and 1 lincosamide). The diffusion coefficients ($D$) of these antibiotics in o-DGT, measured in the laboratory, ranged from $0.58 \times 10^{-06}$ to $6.24 \times 10^{-06}$ cm$^2$ s$^{-1}$. The derived surface area normalized sampling rates ($R_{S/A}$, 0.54−5.74 mL d$^{-1}$ cm$^{-2}$) were comparable with those for another passive sampler called POCIS. Fourteen antibiotics were detected in the actively sampled water samples, with 10 of the 14 detected in o-DGT devices deployed for more than 7 days. Most of the antibiotics detected in o-DGT, except sulfapyridine, were continually accumulated by o-DGT for ∼10 days. Deployment for 7 days is recommended to integrate ambient concentrations over time, without risks of reaching capacity and significant biofouling. Diffusive boundary layer (DBL) thickness had less effect on the o-DGT measurement than reported for other passive samplers. The comparison between o-DGT and Auto and Grab samplings showed that o-DGT was more efficient in terms of cost, time, and labor. This study demonstrates for the first time in a real environment that o-DGT is an effective tool for the routine monitoring of antibiotics in wastewaters and provides a powerful approach to studying their occurrence, fate, and behavior in the environment.


## INTRODUCTION

There are many potential benefits of passive rather than active sampling for trace organic contaminants in waters. Passive sampling can yield time-weighted average (TWA) concentrations and can be more effective in terms of time, labor, and costs,[1−3] although few studies have attempted to quantify the savings.[4,5] Passive samplers can be deployed continuously at many sites simultaneously in a water body (catchments, rivers, or wastewater treatment plants - WWTPs). However, a recognized problem is whether such samplers can yield reliable quantitative data, because for many designs, the measurements are flow-rate dependent.[6] If samplers could perform independently of water flow rate, their use in replacing more expensive active samplers as a routine tool would become more widely accepted. For example, they could be used for routine monitoring of effluents, of surface waters, and to conduct mass balance studies of WWTPs. The usual approach, to simply take a grab sample, has many well-documented limitations,[2,3,7] while programmable active samplers are expensive, which limits their use.

Of the range of existing passive water samplers, the diffusive gradients in thin-films (DGT)[8,9] technique has been extensively used. The analyte diffuses through a membrane filter and fairly thick (∼1 mm) gel layer before accumulating on a binding phase. As the accumulation is driven by the concentration gradient, it is a dynamic (or kinetic) sampler which depends on a flux that is proportional to concentration. The thickness of the well-defined diffusive gel is more important than the diffusive boundary layer (DBL) in solution in controlling the mass transfer of chemicals. The sampling rate is therefore relatively independent of the rate of water flow.[8] These features have been systematically investigated for the measurement of inorganic components, including metals. In consideration of these advantages, we recently developed the first configuration of DGT for measuring organic chemicals (o-DGT).[10] However, in our previous study, we only tested its principle in the

Received: June 17, 2013
Revised: November 4, 2013
Accepted: November 15, 2013
Published: November 15, 2013

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laboratory with one organic chemical as an example and reported results from a simple trial in the field. In this study we undertook a comprehensive set of laboratory and field measurements to assess the performance and suitability of o-DGT for the widespread screening of antibiotics in the field. Comparisons with traditional automatic and grab sampling approaches were a key part of the trials.

Antibiotics with diverse physiochemical and structural properties are among the most important and widely used classes of pharmaceuticals and personal care products (PPCPs) in our daily life. Their prevalence in the environment[11−13] can promote antibiotic resistance[14,15] and might have adverse effects on aquatic organisms.[16−18] These compounds have been considered emerging contaminants, and increasing attention has been paid to their fate and behavior in the environment over the past decade.[12,19]

This study had the following objectives: (1) to measure the diffusion coefficients in the o-DGT devices for various classes of antibiotics in the laboratory since they are the key parameters required to calculate aqueous concentrations from the mass of compound retained by the sampler; (2) to test the o-DGT sampler for its ability to measure quantitatively the concentrations of trace organic contaminants (antibiotics) in a challenging 'real world' situation − WWTP; (3) to investigate *in situ* the effect of the DBL on o-DGT sampling. Recommendations for future applications of o-DGT are also discussed.

## METHOD AND MATERIALS

**Chemicals and Reagents.** Target standards—sulfapyridine (SPD), sulfadiazine (SDZ), sulfamethazine (SMZ), sulfamethoxazole (SMX), sulfacetamide (SCT), sulfisoxazole (SSX), sulfadimethoxine (SDM), sulfathiazole (STZ), sulfachlorpyridazine (SCP), sulfamonomethoxine (SMM), sulfameter (SM), sulfamerazine (SMR), sulfanilamide (SNM), sulfaguanidine (SGD), sulfadoxine (SDX), sulfaquinoxaline (SQX), trimethoprim (TMP), ormetoprim (OMP), norfloxacin (NFX), ciprofloxacin (CFX), ofloxacin (OFX), lomefloxacin (LFX), enrofloxacin (EFX), fleroxacin (FLX), danofloxacin (DAX), pefloxacin (PFX), marbofloxacin (MFX), difloxacin (DIX), sarafloxacin (SFX), carbadox (CBX), oleandomycin (OLM), leucomycin (LEM), clarithromycin (CLM), lincomycin (LIM), salinomycin (SAM), monensin (MON), and novobiocin (NOV)—were purchased from Dr. Ehrenstorfer GmbH (Germany). Roxithromycin (ROM), tylosin (TYL), and erythromycin (ETM) were obtained from Sigma−Aldrich (St. Louis, MO, USA). Erythromycin-$H_2O$ (ETM-$H_2O$) was prepared according to the previous study.[20] Details of the properties of all antibiotics are given in Supporting Information (SI) Table S1. An internal standard of $^{13}C_3$-caffeine was purchased from Sigma-Aldrich (Poole, UK).

Methanol and acetonitrile of HPLC grade were purchased from Merck (Darmstadt, Germany), formic acid from Tedia Company (Fairfield, OH, USA), and ammonium acetate from Sigma-Aldrich (St. Louis, MO, USA).

**o-DGT and Active Sampling.** The o-DGT configuration and its optimization are described elsewhere.[10] Briefly, a 0.5 mm XAD18 agarose binding gel, a 0.8 mm standard agarose diffusive gel, and a 0.14 mm polyethersulfone (PES) membrane filter were used in the standard o-DGT plastic body, with an exposure area of 3.1 $cm^2$. Previous experiments have shown no detectable adsorption of antibiotics to the plastic body of DGT.[10] The standard samplers (triplicate) were deployed in the influent and effluent of the WWTP for 4, 7, 10, 14, and 18 days, respectively, to investigate the antibiotics uptake kinetics by the o-DGT. o-DGT samplers with different thicknesses of diffusive gels (0.5, 0.8, 1.0, and 1.3 mm) were deployed (triplicate for each thickness and each site) for the same time period (10 days) in order to estimate the thickness of the DBL.

A weather-refrigerated automatic sampler (SIGMA SD900) was installed to sample the influent to the WWTP. It was set to continuous mode (106 mL $h^{-1}$) and used to collect 24-h composite samples (Auto). In addition, daily grab samples were taken with 1 L PP bottles at around 10:00 a.m. each day. All water samples were spiked with 8 M HCl and methanol to adjust the pH to 3 and suppress microbial activity. They were transferred to the laboratory as soon as possible, stored at 4 °C, and treated within 24 h. The water temperature was 12.2−15.0 °C (mean 14.3 °C) and pH was 7.4−8.0 (mean 7.7). No rain was recorded until after 2 weeks.

**Water Pretreatment and o-DGT Extraction.** The antibiotics in the filtered water samples (Whatman GF/F filters) were measured using a standard approach (see SI for details). They were concentrated by solid-phase extraction (SPE) using an HLB cartridge (200 mg, 6 mL, Sigma-Aldrich, Gillingham, UK) with $^{13}C_3$-caffeine as a surrogate standard,[21] according to the procedures of Zhou et al.[20] and Xu et al.[21]

Extraction of compounds from the o-DGTs was described in our previous study.[10] In brief, the retrieved o-DGTs were disassembled and the binding gel was transferred into a 15 mL prebaked and washed amber glass vial. 100 ng of internal standard ($^{13}C_3$-caffeine) was spiked, followed by addition of 5 mL methanol and extraction for 20 min in an ultrasonic bath. This extraction procedure was repeated again. The combined extract was blown down to dryness under a gentle flow of $N_2$, then redissolved in 1 mL of methanol, followed by filtering (0.22 $\mu$m) to an amber GC vial, storage at −18 °C, and finally analysis on a rapid resolution liquid chromatography-tandem mass spectrometry (RRLC-MS/MS).

**Diffusion Coefficient Measurement.** The diffusion coefficients ($D$) of all the antibiotics were measured at 25 °C using a 0.8-mm-thick diffusive gel layer in a two compartment diffusion cell[22] equipped with twin stirrers. The transfer of analyte between the two compartments is driven solely by the concentration gradient which is related to the flux by Fick's law of diffusion. The background solution was 0.02 M NaCl, pH 6.5. The source cell was spiked with 200 ng $mL^{-1}$ of each antibiotic. At 20−30 min intervals, 300 $\mu$L of solution was sampled from the receiving cell to measure the diffused masses (10 samples). Five samples were also taken from the source cell. All the samples were analyzed by RRLC-MS/MS. The values of $D$ were calculated from the slope of the plots of mass versus time, as described in our previous study.[10] $D$ values ($cm^2$ $s^{-1}$) at other temperatures, $D_T$, were calculated from the value at 25 °C, $D_{25}$, using eq 1.

$$\log D_T = \frac{1.37023(T-25) + 8.36\times 10^{-4}(T-25)^2}{109+T} + \log\frac{D_{25}(273+T)}{298} \quad (1)$$

**Instrumental Analysis.** The target compounds in the extracts of samples were analyzed by RRLC-MS/MS following the chromatographic separation procedures given by Zhou[20] and Zhang.[23] Details are provided in the SI.

**Calculation of o-DGT Measured Concentrations.** The concentration of antibiotics in the water ($C_w$) was calculated by using eq 2.

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

where $M$ is the mass of antibiotics accumulated in the binding gel, $\Delta g$ is the diffusion layer thickness which includes the diffusive gel and PES membrane, $D$ is the diffusion coefficient of the analyte in the diffusive gel, $A$ is the exposure area, and $t$ is the exposure time.

**Quality Control and Quality Assurance.** Blanks (tap water), spiked blanks (tap water spiked to two levels), spiked recoveries (environmental samples spiked to two levels),[20] and o-DGT blanks were measured to assess potential contamination and loss. The recoveries of spiked target compounds were, with one exception, in the range of 70−130% (Table S2), comparable with a previous study.[20] The limit of quantification (LOQ) was based on blanks or the minimum measured concentration and extrapolating to S/N values of 10.[20] Details are given in Table S3. Only if the qualifier ion ratio of a compound fell in the range ±20% and the retention time was within ±5% of its calibration standard was the compound considered detected. For antibiotics that failed these critera, LOQ was calculated from the low level of standards with S/N > 10 (details are given in Table S3). Independent check standards and blanks (initial mobile phases) were injected approximately every 10 injections; the resulting calculated concentration was required to be within 20% of the expected value for the analysis to be acceptable.

## RESULTS AND DISCUSSION

**Diffusion Coefficients (*D*).** Of the physical quantities required by eq 2 to calculate the concentrations of antibiotics in water, only $D$ is compound-dependent and not readily available. It was determined here at 25 °C for 37 of the 40 target compounds (see Table 1). Values for DAX, MFX, and SFX could not be obtained, due to poor linearity in the plots of concentration versus time. However, according to previous studies,[22,24] eq 3 can be used to estimate diffusion coefficients ($D_e$) from the values in water ($D_w$).

$$D_e = D_w\varepsilon^m = \frac{3.3 \times 10^{-5}\varepsilon^m}{\sqrt[3]{M_w}} \quad (3)$$

The molecular weight of each chemical is represented by $M_W$, $\varepsilon$ is the porosity of the porous media (here 0.98), and $m$ is Archie's law exponent, which in porous media usually ranges 1.5−2.5. A value of 2 was used.[24] A good linear relationship was found between these calculated $D_e$ values and the measured $D$ values (Figure S1), justifying the use of eq 4 for estimating the values of $D$ for the 3 antibiotics without measured values, although further work is required to validate fully this approach for organic compounds.

$$D = \frac{8.1 \times 10^{-5}\varepsilon^m}{\sqrt[3]{M_w}} - 7.3 \times 10^{-6} \quad (4)$$

Equation 5 can be used to calculate the sampling rate per unit area of o-DGT ($R_{S/A}$), enabling comparison with values obtained using other passive samplers:

**Table 1. Measured Diffusion Coefficients ($D$) of Antibiotics through the o-DGT Diffusive Gel at 25 °C and Corresponding Sampling Rates ($R_{S/A}$) per Unit Area for o-DGT**

| Compound | $D$ ($\times 10^{-6}$ cm$^2$ s$^{-1}$) | $R_{S/A}$ (mL d$^{-1}$ cm$^{-2}$) | Compound | $D$ ($\times 10^{-6}$ cm$^2$ s$^{-1}$) | $R_{S/A}$ (mL d$^{-1}$ cm$^{-2}$) |
|---|---|---|---|---|---|
| SCT | 4.76 | 4.38 | DIX | 3.20 | 2.94 |
| SCP | 3.59 | 3.30 | EFX | 2.96 | 2.72 |
| SDZ | 4.23 | 3.89 | FLX | 1.03 | 0.95 |
| SDX | 3.85 | 3.54 | LFX | 3.07 | 2.52 |
| SDM | 3.84 | 3.53 | NFX | 2.46 | 2.26 |
| SMZ | 4.01 | 3.69 | OFX | 2.24 | 2.06 |
| SMX | 5.10 | 4.69 | PFX | 1.92 | 1.76 |
| SM | 4.01 | 3.69 | CBX | 3.79 | 3.48 |
| SMM | 4.08 | 3.75 | LIM | 3.10 | 2.85 |
| SPD | 4.75 | 4.37 | CLM | 1.95 | 1.79 |
| SQX | 3.50 | 3.22 | LEM | 1.43 | 1.31 |
| SSX | 3.79 | 3.48 | OLM | 1.66 | 1.53 |
| STZ | 4.61 | 4.24 | ROM | 1.49 | 1.37 |
| SNM | 6.24 | 5.74 | TYL | 1.09 | 1.00 |
| SMR | 3.79 | 3.48 | ETM-$H_2O$ | 1.85 | 1.70 |
| SGD | 4.51 | 4.15 | SAM | 0.61 | 0.56 |
| TMP | 3.79 | 3.48 | MON | 0.58 | 0.54 |
| OMP | 3.94 | 3.62 | NOV | 0.80 | 0.73 |
| CFX | 2.75 | 2.53 | | | |

$$R_{S/A} = \frac{D}{\Delta g} \quad (5)$$

The sampling rates of these antibiotics by o-DGT (surface area of 3.1 cm$^2$) are given in Table 1, which are comparable with the $R_{S/A}$ values of POCIS (1.9−8.3 mL d$^{-1}$ cm$^{-2}$) with a surface area of ∼18 cm$^2$.[1,6] Larger molecules diffuse more slowly, resulting in lower sampling rates. Measurement of the diffusion coefficients effectively calibrates the sampler for each compound, enabling the time weighted average concentrations of antibiotics in waters to be calculated using eq 2. Previously, we measured the diffusion coefficients of SMX at different pH values and showed they were independent of pH above 6. We have assumed this is the case for other antibiotics, although we cannot exclude effects associated with charge associated speciation.

**Uptake of Antibiotics by o-DGT.** Fourteen antibiotics (SDZ, STZ, SMR, SMZ, LIM, TMP, SPD, SMX, SDX, SDM, OFX, CFX, ETM-$H_2O$, and CLM) were detected in the actively sampled waters from the influent. No antibiotics were detected in the blank o-DGT samplers. Ten of the 14 antibiotics were detected (>LOQ) in the o-DGT samplers. The exceptions of SDZ, STZ, SMR, and SMZ had low concentrations in the water and/or high LOQs for o-DGT (Table S3). Most antibiotics detected in o-DGT were continuously accumulated by o-DGT from the water over about 10 days, with a few antibiotics (e.g., LIM and CFX) accumulated over at least 18 days. Figure 1A gives some examples from each class of antibiotics. The full data sets are given in SI Figure S2.

Four days' deployment was not long enough to detect some compounds in the water such as SMX (Figure 1A). A 7-day deployment was sufficient for all 10 antibiotics to be detected in the o-DGT. Ten days' deployment is also effective for most antibiotics except SPD (Figure S2). Plateauing of the plots may be due to fouling, as observed in the influent, particularly after 10 d, an approach to equilibrium with the binding phase or

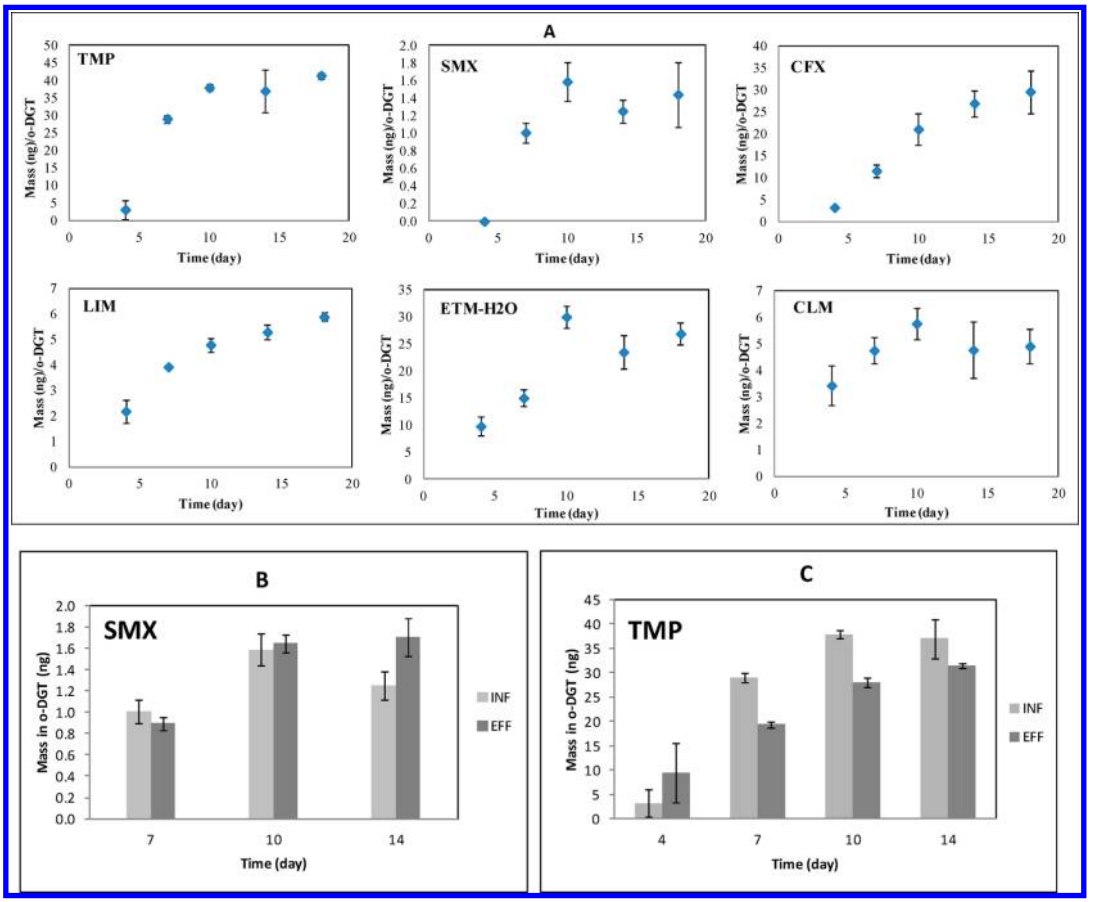


**Figure 1.** Uptake of typical antibiotics by o-DGT ($n$ = 3) in (A) the influent of a British WWTP over 18 days and (B) SMX (data at 4 d were <LOQ) and (C) TMP accumulated in the o-DGT deployed in influent (INF) and effluent (EFF) of the WWTP. Error bars: 1 s.d.

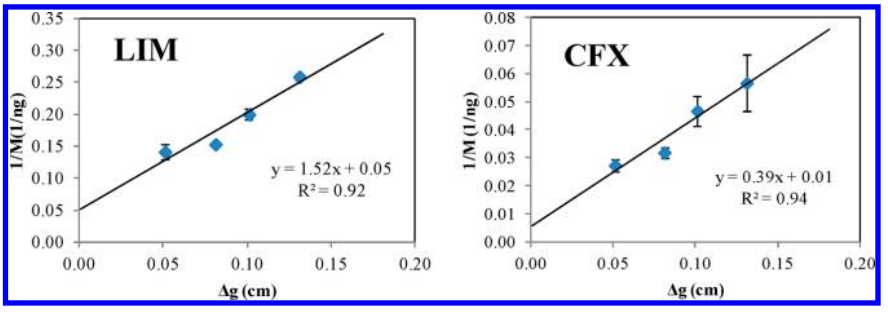


**Figure 2.** Plot of 1/mass (1/$M$) of typical antibiotics (1/ng)—LIM and CFX accumulated by o-DGT deployed in the influent of a UK WWTP versus diffusive layer thickness ($\Delta g$, cm).

simply reflect the concentrations in water declining with time. These explanations cannot account for a decline of the accumulated masses after 10 days, observed for SPD and nonsignificantly some other antibiotics. Similar declines have been observed for some organic compounds using POCIS[1] and for some metals using DGT.[9] A possible explanation is that coexisting substances (e.g., dissolved organic matter - DOM) in the influent can compete with some antibiotics for adsorption sites on the resin gel, resulting in release of the weakly adsorbed antibiotics. The effluent was sampled at the same time as the influent, but the 18 d samples were lost. It is cleaner (with lower DOM), which probably resulted in the o-DGT deployed in the effluent continuing to accumulate some antibiotics over 14 days (Figure 1B,C), as shown by there being no significant temporal loss of SMX (or TMP) in the effluent compared with the influent whether or not concentrations were generally higher (TMP) or the same (SMX) as the in the effluent (except 4 d). A recent study with POCIS also observed a longer kinetic uptake time in cleaner water than in wastewater.[25] Further studies, particularly controlled laboratory experiments, are warranted to establish the controlling effects and are being undertaken.

For this configuration of o-DGT for domestic WWTP, 7-day exposure is long enough to sample detectable levels of the main antibiotics. Bailly et al.[25] also documented for POCIS that without a longer deployment time, the reliability of the short term deployment measurement would be questionable. Having established the reliability of the 7-day data, they were used in comparison with traditional sampling approaches.

**Effect of DBL.** The DBL at the solid/liquid interface can control the uptake rate; if its thickness varies with water flow rate, then the sampling rate can be affected. Theoretically, at a

given flow rate, the DBL thickness should be the same for all analytes, as it is a common physical parameter. If o-DGT samplers with various thicknesses of diffusive gel layer are deployed simultaneously, the effective DBL thickness ($\delta$) can be estimated *in situ* using eq 6:[26]

$$\frac{1}{M} = \frac{\Delta g}{DC_{DGT}At} + \frac{\delta}{DC_{DGT}At} \quad (6)$$

The reciprocal of the accumulated masses of antibiotics varied linearly with the thickness of the diffusion layer ($\Delta$g), with examples, for LIM and CFX, given in Figure 2. Values for $\delta$ and $C_{DGT}$ were calculated using eqs 7 and 8 from the intercept, $I$, and slope, $S$.

$$\delta = \frac{I}{S} \quad (7)$$

$$C_{DGT} = \frac{M(\Delta g + \delta)}{DAt} \quad (8)$$

The calculated $\delta$ had a mean value of 0.23 mm in the influent. The DBL thickness will vary with hydrodynamic conditions. The value of 0.23 mm is less than determined for metals in poorly stirred and unstirred solution,[27] for SMX in unstirred solution,[10] and for metals in Runaway Bay marina and Jabiru Island,[26] but comparable with values found for metals in moderate to well stirred solution.[27,28] If this 0.23 mm DBL was disregarded in the calculations of concentrations in the water, for devices with the 0.8-mm-thick diffusive gel, the concentration would be underestimated by <25%. This potential bias can be avoided by deploying simultaneously devices with multiple diffusion layer thicknesses and calculating the concentrations of analytes in the water ($C_{DGT}$) using eq 8, but additional precision errors will be introduced. Where sensitivity and/or fouling are not issues, deployment of o-DGT samplers with thicker diffusion layer (e.g., >1 mm) can further minimize the effect of an unknown DBL. The effect of DBL on measurement of antibiotics in water using o-DGT can be controlled and minimized. Here we assumed that the DBL in the influent was 0.23 mm when calculating o-DGT derived concentrations of antibiotics in the wastewater.

**Comparison of o-DGT and Active Sampling Methods.** *Performance.* The daily concentrations of antibiotics in the influent from both the Auto and Grab samplings over two weeks are shown in Figure S2. In order to compare with the o-DGT data, the 7-day averaged concentrations corresponding to the o-DGT deployment were calculated for both Auto and Grab samplings, and are shown in Figure 3. Overall, the three sampling methods resulted in similar patterns of the antibiotics (see Figure 3). The time integrated active sampler and the o-DGT sampler gave very good agreement of absolute levels (sum of all detected antibiotics - Σ10, for o-DGT = 2800 ng/L); Σ14, for autosampling - 2870 ng/L). In contrast, the Grab sampling result was about a factor of 3 higher (Σ14, 7600 ng/L).

Auto sampling (particularly at continuous flow-proportional mode), with an automatic sampler, is the most appropriate method to assess loads of PPCPs.[7] Although we did not set the sampler at the continuous flow proportional mode in our study, according to the WWTP operator, the flow rate in the influent was almost constant, so our data should be very similar to the continuous flow proportional mode. Therefore, o-DGT sampling was compared with this auto sampling. Excluding those samples where antibiotics could not be detected (SDZ, STZ, SMR, and SMZ), the individual antibiotic mean concentrations measured by o-DGT were, within error, similar to values derived from the auto sampling data (Figure 3). Furthermore, where measurements of means measured by o-DGT for different time periods were available and reliable (within the kinetic uptake regime), they agreed well with the values derived from the auto sampling measurements, as shown for two antibiotics (LIM and CFX) in Figure 4. This is consistent with the theory that o-DGT provides continuous time-proportional data, similar to the auto sampler.

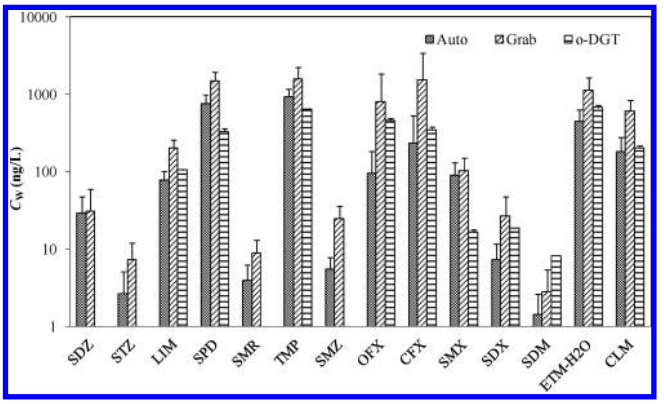


**Figure 3.** Comparison of mean antibiotic concentrations by o-DGT with active samplings (Auto and Grab) for 7 days. Error bar, 1 s.d.

There are differences between Auto and o-DGT sampling which should be recognized. o-DGT is an in situ technique, which does not affect water properties, so that pH remains at its natural value of around 7.7. By contrast, auto sampling utilizes SPE after adjusting the pH to 3, which might change the fractions available (usually improves the recoveries). There is a possibility that storage of the water samples before analysis might change the antibiotic concentrations in the water sample,[29] affecting the auto sampling data. Conversely, there is a possibility that coexisting substances, such as DOM and metals could together or separately affect the antibiotics' behavior,[30] which might have some effect on their uptake by o-DGT.

Grab sampling is still the most commonly used method,[31] since it is easy to use and requires no special equipment. However, as has been increasingly realized, conclusions drawn from data obtained using this sampling (if not high frequency) method may be suspect because of the higher variations.[7,32] As also observed in this study, the high variations in Figure 3 could be associated with missing or recording only a peak event in Figure 4. This issue is often a concern for river sampling, where fluctuation might be very big due to, for example, point sources and rain events. Grab sampling might miss the discharge events; for example, an industry might discharge in the evening when samples are not usually collected.

*Costs of Different Sampling Approaches.* As discussed above, auto sampling could give comparable results to o-DGT; however, in terms of the cost, time, and labor involved to obtain a 7-day TWA concentration, o-DGT passive sampling is more efficient, even without considering the autosampler equipment cost. An estimation of costs involved in these sampling methods is given in Table S4. For just one measurement by each sampling method, the cost for o-DGT is higher (<a factor of 2) than that for active sampling. This is mainly attributed to the return travel necessary to retrieve the

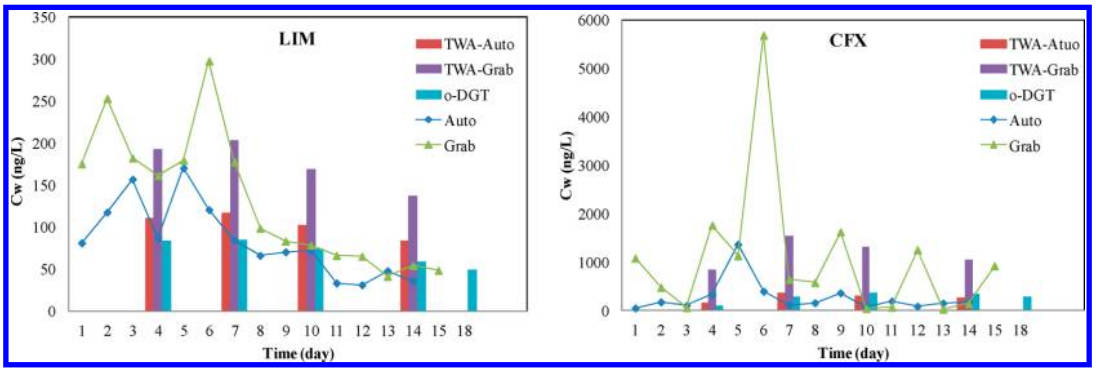


**Figure 4.** o-DGT vs Auto and Grab samplings in concentration measurements of LIM and CFX in wastewaters.

samplers. However, when a TWA concentration is required/desired (e.g., 7-day TWA concentration), more active samples are needed with more travel associated with the necessary active sampling, while the o-DGT cost is unaffected. The result indicates a higher (>a factor of 3) cost for active sampling than o-DGT passive sampling. The most pronounced difference is the cost of sampler equipment and the need to travel regularly to the sampling site. It is worth noting that these figures assume no problems with the active sampling approach. In fact, clogging of filters is common, which would result in more time/labor involved. Although o-DGT is generally a little less sensitive than the active sampling methods, due to its low sampling rate, sensitivity could be increased, if necessary, by further concentration of the sample or pooling binding layers from parallel samplers.

**Recommendations and Perspectives.** This study has demonstrated several virtues of o-DGT. Measurements using o-DGT are less dependent than other passive samplers on water flow rate and the dependency can be minimized and controlled. They provide comparable results to those obtained using Auto sampling, with both these approaches being better than Grab sampling. Moreover, o-DGT is efficient in terms of time, labor, and cost. The general pros and cons of using passive and grab sampling have been discussed at length elsewhere.[6,7] This work simply demonstrates that passive sampling using o-DGT is an alternative sampling method to traditional active sampling techniques for investigating the fate and behavior of PPCPs in the environment. However, o-DGT was unable to detect some antibiotics if deployment times were short (4 d), while it can suffer from (bio)fouling with 'long' deployment times. It has a lower total sampling rate compared to other samplers (such as POCIS) and, like other passive samplers, site visits are required for both deployment and retrieval. To achieve its potential and avoid the shortcomings, o-DGT should be used in accordance with the following recommendations.

(1) Although the ideal for a passive sampler would be that it provided TWA concentrations irrespective of deployment time, in practice this is not possible. Deployment times of less than 20 days are recommended, particularly in raw wastewater, to avoid significant (bio)fouling effects. Two different deployment times (e.g., 7 days and 10/14 days) are recommended in order to check if the sampler is working in the kinetic uptake regime throughout the deployment. However, for rivers and lakes where there are low levels of DOM or these antibiotics, just one time period of deployment is likely to be sufficient.

(2) For sampling in the environment where there are very low levels of antibiotics, parallel o-DGT devices can be deployed and pooled as one sample, to ensure detection of the target compounds.

(3) In calculations of concentrations in the water from o-DGT accumulated amounts, assuming a DBL thickness of 0.2 mm of DBL provides a reasonable approximation for most situations. Deployment of o-DGT samplers with various thicknesses of diffusion layers provides a mean to calculate the DBL for the chosen samples and improves, where appropriate, the accuracy of derived concentrations.

o-DGT is not only promising for routine monitoring of the dissolved fractions of antibiotics, but can also be used to explore the *in situ* interactions of antibiotics with coexisting substances such as DOM and inorganic chemicals (e.g., heavy metals). This will advance our understanding of their fate, behavior, and effects in the environment, with corresponding improvements to predictive fate models and risk assessment.

## ■ ASSOCIATED CONTENT

### Supporting Information

Water sample pretreatment; Instrumental Analysis; Figure S1. Measured diffusion coefficient values vs calculated values of diffusion coefficient ($D_e$) using equation $D_e = (3.3 \times 10^{-5}\varepsilon^m)/(3(M_w)^{1/2})$; Figure S2. Uptake in o-DGT and water concentrations ($C_w$) of detected antibiotics in the influent of a UK WWTP over 18 days; Table S1. Physiochemical properties of the antibiotics used in the study; Table S2. Recoveries of representative antibiotics in spiked tap water, influent and effluent; Table S3. Calibration curves of the target antibiotics and instrumental detection limitations and limitations of quantification (LOQ) for active and o-DGT samplings; Table S4. Comparison between active (Auto and Grab) and passive sampling (o-DGT) in terms of costs, time, and labor. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors thank D. Abbott, R. Wain, V. Booker, W. Chen, C. Graf, C. Halsall, and A. Sweetman for supporting and helping

sampling in the WWTP. We also thank LJ Zhou and FJ Peng from GIG CAS for helping in analyzing samples by RRLC-MS/MS. We are grateful to the Chinese Scholarship Council (CSC) for sponsorship of Chang-Er Chen. Kevin Jones is grateful to the Chinese Academy of Sciences (CAS) for a Senior Visiting International Scientist Professorship position. This study was also supported by the UK-China Bridge Project.

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