In situ catchment scale sampling of emerging contaminants using diffusive gradients in thin films (DGT) and traditional grab sampling: a case study of the River Thames, UK

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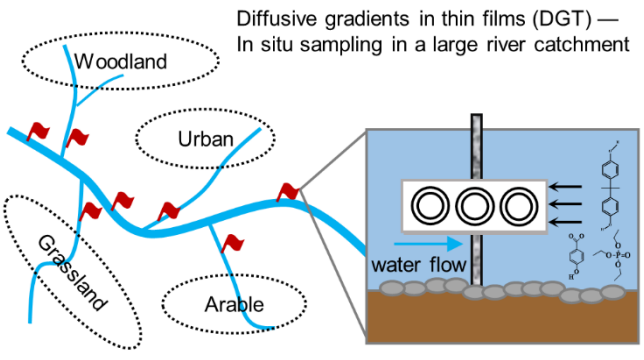

ABSTRACT: The in situ passive sampling technique, diffusive gradients in thin films (DGT), confronts many of the challenges associated with current sampling methods used for emerging contaminants (ECs) in aquatic systems. This study compared DGT and grab sampling for their suitability to screen and monitor ECs at the catchment scale in the River Thames system (U.K.) and explored their sources and environmental fate. The ubiquitous presence of endocrine disrupting chemicals, parabens and their metabolites is of concern. This study is the first to report organophosphate esters (OPEs) in the study area. TEP (summer 13–160 and winter 18–46, ng/L) and TCPP (summer 242–4282 and winter 215–854, ng/L) were the main OPEs. For chemicals which were relatively stable in the rivers, DGT and grab sampling were in good agreement. For chemicals which showed high variation in water bodies, DGT provided a better integral of loadings and exposure than grab sampling. DGT was not as sensitive as grab sampling under the procedures employed here, but there are several options to improve it to give comparable/better performance. DGT samples take less time to prepare for analysis in the laboratory than grab samples. Overall, DGT can be a powerful tool to characterize ECs throughout a large dynamic water system.

INTRODUCTION

Emerging contaminants (ECs), or contaminants of emerging concern, are synthetic or naturally occurring substances that are not commonly monitored in the environment but have the potential to enter the environment and cause adverse ecological and/or human health effects.[1,2] They are a large and expanding array of relatively polar organic compounds such as pharmaceuticals, pesticides, chemicals in household and personal care products (HPCPs), endocrine disrupting chemicals (EDCs) and flame retardants, which are often found in water systems. [1,3] Until now, these substances are not adequately considered in legislation for several reasons, including a lack of knowledge of contaminant sources and pathways, properties and effects of substances and analytical detection techniques.[3] Sampling programs for ECs in dynamic water systems involve several challenges, owing to low concentrations and variations in time and space. Concentrations of ECs range widely in water bodies, from pg/L to mg/L.[4] As current mass spectrometry instruments can provide sub- to single-digit μg/L instrumental detection limits, a pre-concentration approach is needed for ECs at ultra-trace and trace levels (pg/L to ng/L). Sampling methods with good temporal and spatial resolution are needed as ECs in water bodies could vary markedly.[5,6] Thus, reliable and representative samples are necessary for monitoring and studying the sources, transport, fate and environmental impact of ECs.

Grab or spot sampling is the most commonly used method to collect samples due to its simplicity.[7] Over 50 ECs, including pharmaceuticals and potential EDCs, were screened from 2 L samples of U.S. drinking waters.[8] Grab samples of 1 L water were collected from 40 rivers around the Bohai Sea, China to understand the occurrence and spatial distribution of organophosphate esters (OPEs).[9] Samples of 1 L can be concentrated to 1 mL, so when pollutants are at sub-ng/L or even lower levels, large volumes (10–100 L) of water need to be collected. The subsequent laboratory analysis of grab samples only provides a snapshot of the

pollutants at the time of sampling. The drawbacks of this approach are obvious when the contaminant concentrations vary over time and with flow rate, which is the case for most ECs[5,6] and episodic pollution events could be missed. Field studies with high temporal resolution showed that, during rainfall events, concentrations of agricultural pesticides in small streams (in catchments <10 km^2) can increase by a factor of 10–100 or more within hours.[10,11] One solution to this issue is to increase the sampling frequency, or to use automatic sampling devices that can take time-proportional composite samples over a time period. Some regulations, such as the current national Discharge Standard of Pollutants for Municipal Wastewater Treatment Plants (WWTPs) in China (GB 18918–2002), require 24-hour time-proportional (2 h × 12) samples for monitoring regulated pollutants [e.g., chemical oxygen demand (COD), the 5 day biochemical oxygen demand (BOD_5), total nitrogen, etc.].[12] Half-day time-proportional composite site samples (45 min × 16) were taken for studying 213 pesticides in small streams with an automatic sampling device.[13] Such systems are costly, complex for end-users and are rarely used in widespread monitoring campaigns.[7] In addition, collecting, preserving, transporting and preparation of these samples in the laboratory is laborious and time consuming and samples in glass bottles are also subject to degradation and contamination.

Passive sampling has become an increasingly accepted alternative to address many of these challenges. It pre-concentrates analytes in situ and provides time-weighted average (TWA) concentrations for the sampling window.[14] The most common aquatic passive sampler for polar organic chemicals—the polar organic chemical integrative sampler (POCIS)—is highly dependent on environmental conditions, such as water flow rates, because of the effect of the diffusive boundary layer (DBL).[15] Because measuring or predicting DBL is complex, in situ correction for POCIS using performance reference compounds (PRC) has been proposed in the

77 literature.[16] This approach corrects the target compound sampling rate relative to the in situ
78 desorption rate of a PRC according to isotropic exchange. Nevertheless, this is expensive and
79 subject to the availability of the isotope-labelled compounds, especially for ECs. The diffusive
80 gradients in thin films (DGT) sampler—widely used for inorganic contaminants and
81 increasingly used for organic chemicals—is largely independent of water flow rate.[17,18]
82 Because of the fairly long diffusive path of the DGT system (≈1 mm in a standard DGT device),
83 DBL is negligible when water flow is above a low threshold (0.02 m/s).[19] This has been shown
84 by controlled laboratory experiments[16,19] and field evaluations.[18,20] One of the examples was
85 the field application and assessment of POCIS and DGT for a total of 34 polar organic
86 chemicals, including organophosphates and antibiotics.[18] Because of the large body of
87 literature and the solid foundation of DGT,[21-23] its research and applications to organics are
88 attracting considerable interest and growing rapidly. At the time of writing, DGT has been
89 developed and validated for over 150 organic compounds, including pharmaceuticals, HPCPs,
90 flame retardants, estrogens, pesticides, drugs, etc.[24-28] Until now, research into DGT for
91 organics has mainly focused on laboratory development and calibration,[20,22,29,30] with a few
92 field evaluations conducted mostly in raw or treated wastewaters.[26,31,32] Applying DGT to
93 rivers at a catchment scale is necessary to test and demonstrate its reliability and challenges in
94 a dynamic water system, with different environmental conditions. Exploring sources and
95 environmental fate of ECs using DGT provides a 'real world' field testing of the technique for
96 environmental monitoring of trace organics.
97 The River Thames and its tributaries play an important role in supporting ~13 million
98 inhabitants, including London, the capital of the United Kingdom.[33] The river system is the
99 main source of drinking water in this area. It is also actively influenced by anthropogenic
100 activities, with 352 WWTPs discharging into it.[34] The River Thames is one of the most

monitored and studied rivers in the world. Some water quality parameters, such as phosphorus and nitrogen, have been continuously monitored.[35] It therefore offers a unique study area with high-quality data support, such as river flow, catchment area, land cover, wastewater treatment systems, and population density. From a practical perspective, there are intensive ongoing monitoring programs to build on.[34,36] The field campaigns in this study were built on the Thames Initiative research platform operated by the Centre for Ecology and Hydrology (CEH, U.K.) (see details in Supplementary Information).

Large numbers of unregulated ECs, such as pharmaceuticals and drugs have been found in rivers, groundwater and drinking water across the United Kingdom,[37-43] while their occurrence in the River Thames catchment is largely unknown. A limited number of pharmaceuticals were investigated in the River Thames and its tributaries by grab sampling (500 mL water sample)[44,45] and automatic sampling (500 mL 24-hour composite sample).[46] Organophosphate esters (OPEs), as an alternative, have been increasingly used as flame retardants since the use of polybrominated diphenyl ethers (PBDEs) is restricted and declining.[9] However, data from monitoring, toxicity testing, epidemiological studies and risk assessments all suggest that there are concerns at current exposure levels for OPEs.[9,47] Although they are important ECs in waterways, no information is available about OPEs in the Thames catchment.

The objectives of this study were therefore to: (i) compare DGT and grab sampling approaches to establish the applicability of DGT for measuring ECs in field conditions, (ii) obtain DGT concentration data for a range of ECs at selected established sites in the rivers across the Thames catchment in two different seasons, (iii) use the data generated by DGT to characterize fate processes of ECs in the aquatic system and understand better the sources, transport and fate throughout the large dynamic watershed, and (iv) assess the significance of the

concentrations detected for aquatic organisms and the implications for monitoring contaminants.

MATERIALS AND METHODS

Study area and sampling sites

The River Thames in south England extends 354 km from its source in the Cotswold Hills to its tidal limit at Teddington, covering a catchment area of 9948 km^2, with a population density of 960 people km^{-2}.[36] The mean annual runoff is 245 mm.[36] A total of 345 WWTPs are located before the tidal limit.[34] A more detailed catchment description can be found elsewhere.[36] This study focused on the River Thames from Swinford to Runnymede, above the tidal reach (Figure S1 for study area and sampling sites). Three sampling sites are on the main channel of the River Thames—upstream (Swinford, TS), midstream (Wallingford, TW), downstream (Runnymede, TR)—and the others selected are on six tributaries—Cherwell (Ch), Ray (Ra), Ock (Oc), Thame (Th), Pang (Pa) and the Cut (Cu). The catchment area, distance to source, land cover and WWTPs population equivalent (PE) upstream of each sampling site and the corresponding WWTPs population equivalent density are listed in Table S1. The study area has a big variety of sub-catchments, from the predominantly rural River Pang (with WWTPs PE densities of <30 PE/km^2 and <5% urban and semi-urban land cover) to rivers that are predominantly urban and receiving high WWTPs effluent loadings, such as the Cut (with WWTPs PE density of over 1500 PE/km^2, which is five-fold of the average WWTPs PE density in the study area). DGT samplers were deployed for one week (in summer and winter) and grab samples were collected twice during the DGT deployment in the first field campaign. With this sampling site design, each field campaign could be effectively done within one day. Two seasons of field campaigns were carried out, one in summer (June 25–July 02, 2018) and one in winter (Feb 11–Feb18, 2019). River flow data at the sampling sites or the nearest gauging stations were

obtained from the National River Flow Archive and are shown in Table S2 and Figure S2. The river flow over the whole sampling duration was slightly below the long-term average.

Analytes of interest

An essential issue faced by scientists and regulators is which compounds to investigate. More than 200 pharmaceuticals alone have been reported in river waters globally in 2015,[4] while approximately 2000 pharmaceuticals are registered in the United Kingdom and more than 3000 are approved for prescription in the United States.[8] Selection of the target chemicals in this study was based on several criteria:[8] (a) prescription drug status, (b) volume of use, (c) toxicity, (d) occurrence and public concerns, (e) chemical classes, and (f) availability of the DGT and analytical methods. They are important ECs in river systems with well-developed DGT methods[23] and can be monitored using one DGT configuration (see sampler details later).[24,26,27,48-50] Thirteen target chemicals were selected across EC types, as follows: pharmaceuticals [sulfapyridine (SPD), sulfamerazine (SMR), sulfadoxine (SDX), trimethoprim (TMP), methylparaben (MEP), propylparaben (PRP), butylparaben (BUP), 4-hydroxybenzoic acid (PHBA)], EDC [estriol (E3)], and OPE flame retardants [triethyl phosphate (TEP), tris(2-chloroethyl) phosphate (TCEP), tripropyl phosphate (TPrP) and tris(chloropropyl) phosphate (TCPP)]. Their physicochemical properties and descriptions are given in Table S3 and their structures in Figure S3. Isotope-labelled chemicals were used as surrogate internal standards (SIS): SMX-d4, CAF-13C3, MEP-13C6, PRP-13C6, BUP-13C6, PHBA-d4 and E3-d2. Most compounds were calibrated with SIS, although the external method was used for the OPEs due to lack of SIS.

The studied pharmaceuticals and an EDC are ionic organic chemicals, which contain at least one polar functional group, such as amino, hydroxyl and carboxyl. These chemicals can be neutral, cationic, anionic or zwitterionic under different pH conditions. It has been shown that

the DGT measurement is unaffected by pH in the range 6.2–9.0 for SPD, SMR, SDX and TMP,[22,51] and in the range 3.5–9.5 for MEP, PRP, BUP, PHBA and E3.[26,27] OPEs with alkyl groups (TEP in this study, Figure S3) and with chlorinated groups (TCEP and TCPP in this study, Figure S3) exhibit great hydrolytic stability and are stable at neutral and basic conditions (pH 7.0–11.0) for up to 35 days.[52] The DGT measurement of the studied OPEs is independent of pH 3.1–9.7.[24,53] The above literature also showed the DGT measurement of these target chemicals is independent of ionic strength (0.001–0.1 M) and dissolved organic matter (0−20 mg/L). Overall, DGT measurement of these target chemicals in the rivers of the Thames catchment is not expected to be affected by pH (pH = 7.9±0.2 in sampling periods), ionic strength (average 0.01 M) and dissolved organic matter (DOM = 7.2±2.6 mg/L in sampling periods) (pH and DOM measured and provided by CEH).

Sampler details

The plastic housing moldings for DGT were provided by DGT Research Ltd. (Lancaster, U.K.) and the binding gels and diffusive gels were made in the laboratory in one batch before the fieldwork. The DGT samplers in this study comprised a 0.4 mm thickness of hydrophilic-lipophilic-balanced (HLB) resin gel as the binding layer (50 mg wet weight HLB per disc), a 0.8 mm thickness of agarose gel (1.5% agarose) as the diffusion layer and a hydrophilic polypropylene (GHP) membrane (thickness: 0.11 mm, diameter: 25 mm, pore size: 0.45 μm, PALL) as the membrane filter. More details about the DGT sampler and the technique were first described in Zhang and Davison.[54]

Field campaigns

Grab sampling

Water samples (1.2 L) from the main river flow were collected in solvent cleaned amber glass bottles rinsed with the water from the sampling site prior to the sample collection. Following

collection, samples were placed in the dark cool-boxes containing frozen icepacks and transported back to a sample store walk-in refrigerator (4 °C) within 12 hours. Three amber glass bottles with deionized water from the laboratory were taken to the field sites and used as field blanks for each field campaign. Duplicate samples at two random sites (the River Thames at Wallingford and Swinford) were taken to check the repeatability of the sampling and analytical methods.

DGT sampling

The DGT samplers were deployed in flowing water, 0.3 m below the water surface, but in positions which would avoid high turbulence (see more detail in SI, Figure S4). Three standard DGT samplers (HLB resin + 0.8 mm agarose gel + GHP membrane filter) were deployed simultaneously at each site. Three new DGT samplers were used for field blanks. The exposure time of DGT samplers was recorded exactly, but was ~1 week at each site. After retrieval, the sampler surface was examined carefully; there was no obvious biofouling on any of the DGT samplers (Figure S5). After rinsing the DGT sampler with deionized water and shaking off obvious surface water, samplers were placed in polyethylene bags in the dark cool-boxes containing frozen icepacks, following a method detailed elsewhere.[50] After transporting back to the CEH laboratory, samplers were disassembled and resin gels were carefully put in amber glass vials separately. SIS mixtures (50 µL, containing 50 ng of each isotopically labelled chemicals) were spiked onto the resin gel in each vial and 5 mL of acetonitrile was added in each vial within the sampling day. They were stored in a refrigerator (4 °C) before sonication extraction at Lancaster laboratory within one week, following a method detailed elsewhere.[50] In total, 25 grab samples and 66 DGT samplers were collected (summarized in Table S4).

Sample treatments

Grab samples were filtered and solid-phase extracted on the second day of the sampling. Briefly, water samples (1 L) were filtered through glass fiber filters (GF/F, 0.45 μm, Whatman, U.K.), and spiked with SIS mixtures (50 μL, containing 50 ng of each isotopically labelled chemicals). Oasis HLB cartridges (200 mg, 6cc, Waters, U.K.) were then used for concentrating water samples (see details in SI). After storage (see details in SI), the cartridges were eluted with 5 mL methanol twice and 5 mL acetonitrile. The combined elution solution was evaporated to dryness under gentle stream of nitrogen, reconstituted in 1 mL acetonitrile and water (v:v = 20:80) and then filtered through a 0.2 μm PTFE syringe filter into LC amber vials. All samples were stored at 4 °C before analysis by LC-MS/MS within a week.

Resin gel of the DGT sampler was eluted twice with 5 mL aliquots of acetonitrile each time followed by 30 minutes sonication and then rinsed by another 2 mL acetonitrile. The combined elution solution was then processed as above (for the grab samples).

Instrumental analysis

An ultra-high-performance liquid chromatography-tandem mass spectrometer (UHPLC-MS/MS) was used to determine the target compounds. Separations were achieved by a Shimadzu Nexera UHPLC (Kyoto, Japan) equipped with two LC-30AD pumps, a CTO-20AC column oven, a DGU-30A5 degasser, an SIL-30AC auto-sampler and a column oven connected to a LC column. A Waters Xbridge C18 column (2.1 × 100 mm, 2.5 μm) was used for SPD, SMR, SDX, TMP, MEP, PRP, BUP, PHBA and E3 (more details in SI). A Phenomenex Kinetex Biphenyl column (50 × 2.1 mm, 2.6 μm) was used for separating TEP, TCEP, TPrP and TCPP; Details about MRM parameters are in SI and other details are elsewhere.[50,53]

QA/QC

Field blanks of grab samples and DGT samplers were collected to assess any contamination from field conditions (i.e., sample handling, transport and storage) and sample preparation (i.e.

243 filtration and solid phase extraction). SIS were used in both grab samples and DGT samplers
244 to correct for any chemical loss during sample processing (filter, transfer, extraction and
245 nitrogen blowdown) and to calibrate instrument fluctuation. DGT samplers were deployed in
246 triplicate at all the sampling sites and grab samples were taken in duplicate at two random
247 sampling sites, to check the reproducibility of the sampling methods. QC standards (10 and 50
248 µg/L) were prepared using independent weighing and they were analyzed with every 10
249 samples. Instrumental limits of detection (LOD) were between 0.01 (TEP) and 0.50 (PHBA)
250 µg/L. Detailed information about the LOD and method quantification limit (MQL) of the SPE
251 method (grab samples) and the DGT method is given in Table S5 (see more details later).

252 **Calculation of DGT measured concentrations**

253 When the concentration of the analyte in the surrounding solution changes, as may occur in a
254 river, DGT provides TWA concentration (c_{TWA}) of the fully dissolved analytes during the
255 deployment time (t). The diffusion coefficient (D) of the analyte through the diffusion layer is
256 well established in the laboratory. The exposure area (A) of a standard DGT device is 3.14 cm^2.
257 After quantifying mass of the analyte accumulated in the binding gel, M_{DGT}, c_{TWA} (or c_{DGT}) can
258 be calculated using eq 1:

259 $$c_{DGT} = \frac{M_{DGT}(\Delta g + \delta)}{tAD} \qquad (1)$$

260 Diffusion coefficients of the analytes at 25 °C (D_{25}) were measured under controlled conditions
261 elsewhere[26,27,31] and those at other temperatures calculated using eq 2 (see Table S6):[31]

262 $$\log D_{t_2} = \frac{1.37023(t_2-25) + 8.36 \times 10^{-4}(t_2-25)^2}{109 + t_2} + \log\frac{D_{25}(273 + t_2)}{298} \qquad (2)$$

263 It is suggested that δ = 0.2 mm should be applied when DGT samplers used in naturally flowing
264 streams and rivers (flow rate ≥ ≈ 2 cm/s). [18-20,55] Thus, δ = 0.2 mm is applied in the calculation.

265 **RESULTS AND DISCUSSION**

266 **Comparison of DGT and grab sampling performance**

Biofouling should have little effect on the DGT measurement of the target chemicals in the sampling conditions, based on a previous study.[50] The analytes were also shown to have little degradation/loss in the sampling, transport and storage conditions of this study.[50] Therefore, the passive sampling system here is shown to have good QC. DGT sampling provides in situ TWA concentrations for the deployment period, e.g. from hours[56] to weeks[18], while grab sampling only gives concentrations at one time point. To compare DGT and grab sampling in fulfilling the objective of assessing the applicability of DGT in field conditions, grab samples were collected twice during the DGT deployment in the first field campaign (i.e., in summer). The following discussion is presented in three aspects: sensitivity, representativeness and practicality.

Sensitivity

DGT sampling rate (*R*s) for an analyte can be estimated by eq 3 using its temperature-specific *D*:

$$R_s = \frac{DA}{\Delta g + \delta} \qquad (3)$$

In this study, temperatures in the river system ranged from 7 to 22 °C. Average *R*s for the analytes was ~8 mL/day at 7 °C and ~12 mL/day at 22 °C. These were close to the average DGT *R*s for 34 organic chemicals of ~12 mL/day at 23 °C.[20] The pre-concentration factor (i.e., sample volume divided by final sample volume, V_0, for analysis) of the grab sampling (1 L/1 mL) was 1000 while for DGT sampling with one-week exposure time (*t*) it was ~50 at 7 °C and ~90 at 22 °C [pre-concentration factor of the DGT sampling = ($R_s \times t$)/V_0]. With the same LC-MS/MS instrument, the MQL of the sampling approach depends on the pre-concentration factor. Therefore, MQLs for DGT sampling (3–23 ng/L) are higher than those of grab sampling (0.03–1.5 ng/L). Although the MQLs of 7 days DGT sampling in this study were sufficient to detect chemicals at or higher than single- to double-digit ng/L, it can miss chemicals with TWA

concentrations lower than their MQLs. This explains lower detection frequencies of the analytes from DGT sampling than from grab sampling (Table 1). For chemicals such as SMR, MEP, PRP, PHBA, E3 and TCEP, where greater sensitivity (sub- or low-single digit ng/L) is needed, the current DGT sampler with 7 days deployment time is not sufficient. Options including use of a sampler with larger exposure area (A), longer deployment time (t), smaller final sample volume (V_0) and combination of multiple samplers could be considered for future work.

Table 1. Detection frequencies of the target ECs from grab samples and the DGT samplers

Year	Sample type	N (Sampling site)	Detection rate (%)												
			SPD	SMR	SDX	TMP	MEP	PRP	BUP	PHBA	E3	TEP	TCEP	TPrP	TCPP
2018	Grab sample (June 25)	9	100	22	0	89	100	56	0	100	44	100	89	100	100
	Grab sample (June 28)	8	100	25	0	88	100	38	0	100	38	100	88	100	100
	DGT sampler (June 25–July 02)	7	86	0	0	71	0	0	0	43	0	86	14	57	100
2019	DGT sampler (Feb 11–Feb 18)	5	100	100	0	80	0	0	0	40	0	100	80	100	100

Representativeness

Figure 1 shows ratios of concentrations measured by grab sampling (c_1, c_2) to those measured by DGT sampling (c_{DGT}). The two grab samples at each site were collected at different day. For example, grab samples at Thame (Th) were collected at 16:35 on June 25 and 13:28 on June 28, 2019. Variations in levels of pharmaceuticals (SPD, TMP and PHBA) between c_1 and c_2 were generally quite low across the seven sampling sites (c_1/c_2 = 0.4–2.4). As effluents of WWTPs are considered the main source of pharmaceuticals in these streams,[26] comparable values of the grab samples suggest that discharges of these pharmaceuticals from the effluents varied by less than a factor of ~2. For these pharmaceuticals (SPD, TMP and PHBA), c_{DGT} was comparable with c_1 and c_2, with ratios of c_1 and c_2 to c_{DGT} ranging from ~0.5 to 2.3 (mean: 1.2).

Thus, for chemicals which were relatively stable in the river, DGT and grab sampling were in a reasonable agreement.

The OPEs (TEP, TCEP, TPrP and TCPP) showed a different picture. Their ratios of c_1 to c_2 (c_1/c_2 = 0.2–7.9) varied more than for pharmaceuticals. Greater differences between c_{DGT} and c_1 (c_2) were also evident, with ratios of c_1 and c_2 to c_{DGT} ranging from <0.1 to 3.7 (mean: 0.8). This was most noticeable for all the OPEs at the sampling site on the Cut (Cu) and for TCPP at all seven sampling sites (see Figure 1). At the Cut, c_1 (c_2) of OPEs (TEP, TCEP, TPrP and TCPP) were 0.04 (0.04), 0.2 (0.2), 0.1 (0.1) and 0.5 (0.1) of c_{DGT}. The c_{DGT} of TCPP at the seven sites was 100s to 1000s ng/L, while for concentrations measured by grab sampling only c_2 for the Thames at Wallingford (TW) (320 ng/L, 60% of c_{TWA}) and c_1 at the Cut (Cu) (1910 ng/L, 50% of c_{TWA}) were close to c_{DGT}. The difference between the two grab samples suggested that the inputs of OPEs were not as constant as the pharmaceuticals. For chemicals which showed higher variations in water bodies, DGT with one-week sampling window integrated varying levels, while grab sampling cannot fully capture this. It is interesting that OPEs varied more than pharmaceuticals, since it might have been assumed that WWTPs are the main sources for both these classes of chemicals.[26,49]

Thus, DGT can integrate fluctuating pollutant concentrations and better represent the general water quality status, especially for those chemicals with fluctuating concentrations in highly dynamic water bodies.

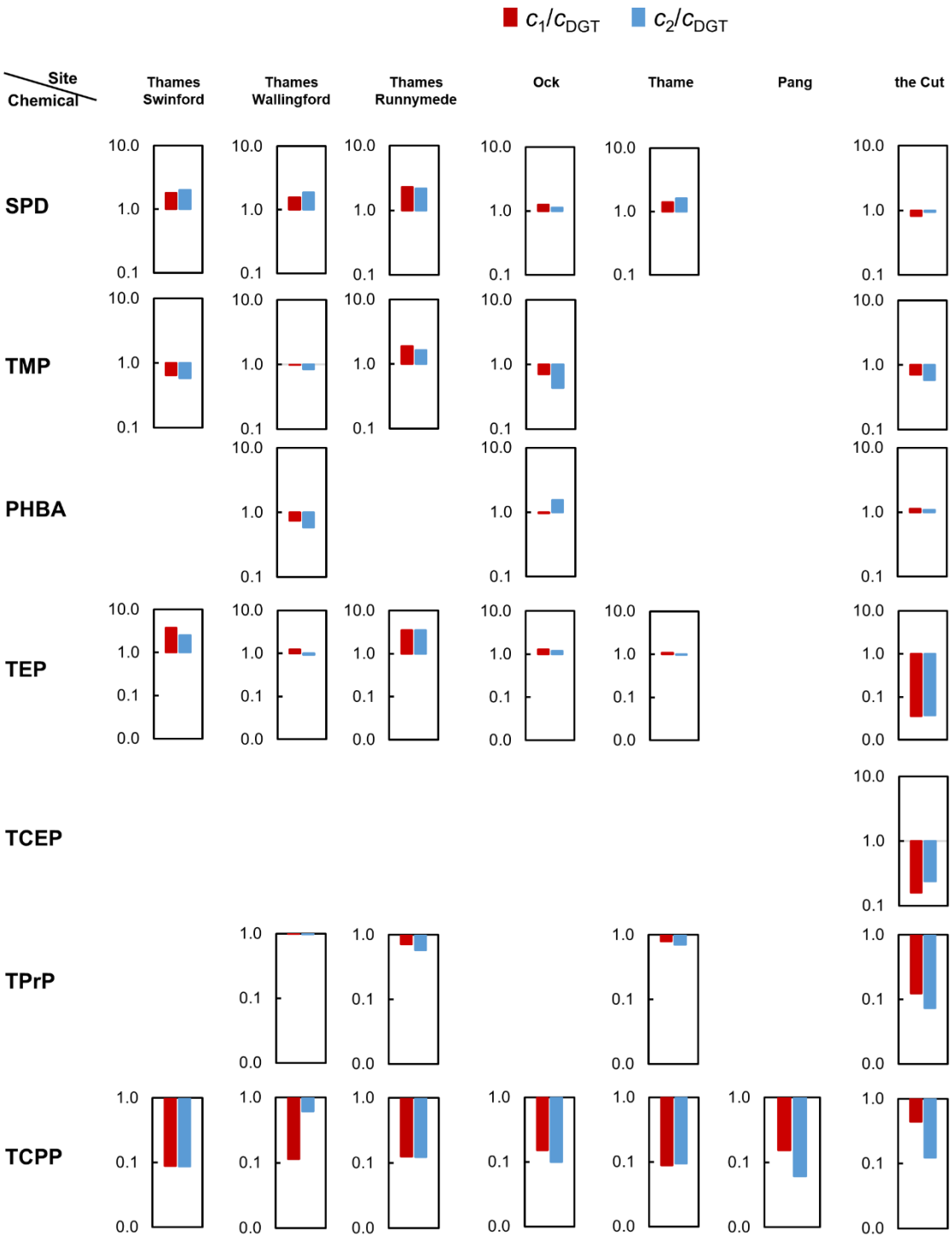

Figure 1. Ratios of c_1 (c_2) (concentrations in water measured by grab samples) and c_{DGT} (measured by DGT samplers) at the sampling sites in the River Thames catchment in summer. DGT samplers were exposed for approximately one week and grab samples were collected twice during DGT deployment. When <MQL of DGT, it was regarded as not detectable and is not shown in the figure.

Practicality

An accessible and secure site to deploy the passive sampling system is fundamental for DGT sampling, otherwise the samplers may be subject to damage or loss. In this study, no DGT samplers were recovered at two sampling sites in the summer campaign and four in the winter campaign, because of either sample loss, interference by the public or lack of accessibility to the sampling site (Table S4). It took 10 minutes per site to set up and collect the DGT passive sampling system and 5 minutes to collect grab samples. However, for later storage and sample preparation, the DGT method is much more space- and time-effective. The space for a 1 L glass bottle could contain at least 20 DGT samplers with bagging. A key point is that the pretreatment of 1L grab samples is much more time consuming with 6 samples per day and 100 DGT samples can be treated for the same time.

DGT allows repeated measurements without greatly increasing the overall cost and laboratory workload. Triplicate DGT samplers were deployed at each of the sampling sites and showed good repeatability across the detected analytes, with coefficients of variation (CV, or relative standard deviation) ranging from 1% to 33% (mean: 10%).

Profiles of chemicals detected in the Thames catchment

Most of the analytes were detected at least once in the grab samples, although SDX and BUP were lower than detection limits in all the retrieved grab samples. Table S8 shows the detection frequencies of analytes in the main stream of the River Thames and tributaries. The detection frequencies of all the target ECs, pharmaceuticals, EDCs and OPEs were consistent, with the highest values in three tributaries (Cherwell, Thame and the Cut), the lowest values in one tributary (Pang) and median values in the main stream of the River Thames and the other two tributaries (Ray and Ock). Given the types of compounds and their primary uses, sources to the river are most likely to be linked to human-related effluents (i.e., WWTPs).[26,49] It was evident

that the dilution effect in the main stream was much higher than in the tributaries, because of the much higher flow rate (mean: 15–60 m^3/s) in the main stream than in the tributaries (0.4–4 m^3/s). Interestingly, in the tributaries where the dilution effect was weak, the WWTPs population equivalent density appeared to be most relevant. For example, the Cut with the highest WWTPs population equivalent density (>1500 PE/km^2) had one of the highest values of detection frequency, while the Pang with the lowest WWTPs population equivalent density (~30 PE/km^2) had the lowest values of detection frequency. However, in the main channel where the dilution effect was stronger, the value of detection frequency didn't increase from upstream to downstream with the increasing population density. This suggested that tributaries (mean flow rate <4 m^3/s) were more affected by population density than the main stream because of less dilution effect in smaller streams. An evaluation of scientific literature on pesticides in fresh water bodies showed that only a small percentage of studies examined small streams (catchments of less than 10 km^2), although they make up the majority of the river network length (e.g., an estimated 80% in Europe).[13] Therefore, priority should be given to smaller waterways when attempting the detection of ECs, where they are more likely to be concentrated due to less dilution. Other mechanisms such as sedimentation and re-suspension may also have an influence. As expected, there was no evidence to link sub-catchments with high agricultural activity (e.g. Ock) to higher occurrences of the target ECs.

Parabens (MEP, PRP, BUP) are widely used in cosmetics and personal care products, such as creams, lotions, shampoos and bath products. Their common metabolite (PHBA) is used as a preservative in food, pharmaceuticals, and personal care products. These substances mimic estrogen and can act as potential hormone (endocrine) system disruptors. They belong to category 1 (at least one in vivo study providing clear evidence for endocrine disruption in an intact organism) of the European Endocrine Disrupter Priority List for wildlife and human

384 health. Three parabens (MEP, PRP, BUP) were not detected by the DGT sampler; their 7-day
385 TWA concentrations were lower than their MQLs (12, 11 and 4 ng/L). MEP and PRP were
386 detected in 100% and 38% of grab samples, respectively, while BUP was not detected in grab
387 samples. The highest MEP concentrations were found in the Cut (31 ng/L), with other sampling
388 sites in the range 2–12 ng/L. Three high points of PRP were found in the Cherwell (148 ng/L),
389 the Thames at Swinford (77 ng/L) and the Cut (70 ng/L), with other sampling sites lower than
390 32 ng/L. Their metabolite (PHBA) was detected at all the sampling sites, in the range 14–46
391 ng/L (mean: 26 ng/L). These substances are ubiquitous in the Thames river system, which is a
392 source for drinking water supplies, after passing through drinking water treatment processes.
393 All of the target OPEs were routinely detected across the studied sites (only in the Pang was
394 the detection frequency <100%) at relatively high concentrations (see later). This is the first
395 report of OPEs in the River Thames catchment. They are on the list of High Production Volume
396 Chemicals (HPVC) (>1000 tons/year in Europe) and used as flame retardants and plasticizers
397 in plastics, textiles, furniture and many other materials.[9] However, they tend to be released
398 from their host materials.[57] They have been found to now be ubiquitous in water, especially
399 wastewater, and air, particularly associated with airborne particulate matter.[49,58] Four OPEs
400 (16–26000 ng/L) were found in the River Aire (U.K.), with TCPP ranging from 2900–6700
401 ng/L.[59] However, before this study, no data were available for OPEs in the Thames catchment.
402 TEP (13–160 ng/L in summer, 18–46 ng/L in winter) and TCPP (242–4282 ng/L in summer,
403 215–854 ng/L in winter) were the main OPEs, according to the 7-day TWA concentrations
404 obtained by DGT. The comparison between data generated by DGT and grab sampling
405 indicated that the input patterns of OPEs were different from pharmaceuticals. High TWA
406 concentrations of OPEs (c_{DGT}, Figure 1) were found in the Cut, which receives the highest
407 WWTPs effluent loadings, indicating effluents from WWTPs are important sources of OPEs.

The generally high c_{DGT} of TCPP found across the sampling sites in both summer and winter imply higher levels occurred in the time period not covered by grab sampling. The photodegradation or photo transformation of most OPEs (except TCEP which is recalcitrant) occurs mainly by indirect mechanisms and the presence of inorganic constituents (nitrite, nitrate, carbonate and some iron species) in river water increases the photodegradation rates.[60] One possible explanation for the lower levels of OPEs measured by grab sampling could be the active indirect photodegradation pathways of OPEs in the day time (i.e., the sampling time of grab samples), especially for TCPP. There were 5 analytes (SDX, MEP, PRP, BUP and E3) not detected by DGT sampling. The other 8 were detected at least once at all the sampling sites. Figure 2 shows the composition of the analytes, mean concentrations of TCPP and the mean sum concentrations of ECs from the sampling sites in the Thames catchment. The mean sum of 8 ECs concentrations ranged from 242 ng/L (Pang) to 4890 ng/L (the Cut) in summer and from 372 ng/L (Pang) to 1001 ng/L (Thames at Swinford) in winter, indicating large variability between the sampling sites. Tributaries (242–4890 ng/L in summer) showed larger variability than the main stream (316–643 ng/L in summer, 482–1001 ng/L in winter), showing that tributaries were affected more by local discharges, while the main stream had a greater dilution effect and 'smoothed' concentrations.

There were five sampling sites where both summer and winter data were obtained. The composition of ECs was more diverse in winter than in summer, with TCPP dominant in summer (81–100%) and lower in winter (45–85%). At two sites (i.e., one on the main stream at Wallingford and one on the Ock) ECs in summer were higher than those in winter by factors of 1.3 and 2.0. This was due to the lower river flow rate in summer than in winter (Figure S2). At the other three sites (i.e., two on the main stream at Swinford and Runnymede, one on the tributary of Pang) ECs in winter were higher than those in summer all by a factor of ~1.5. River

flow rate in the winter sampling period (Feb 11–Feb 18, 2019) was approximately 5-fold greater than of it in the summer sampling period (June 25–July 02, 2018) in the main channel (Figure S2). Although the seasonality of river flow was evident, seasonal differences of ECs were not consistent across the catchment. This presumably reflected differences in the impact of local discharges.

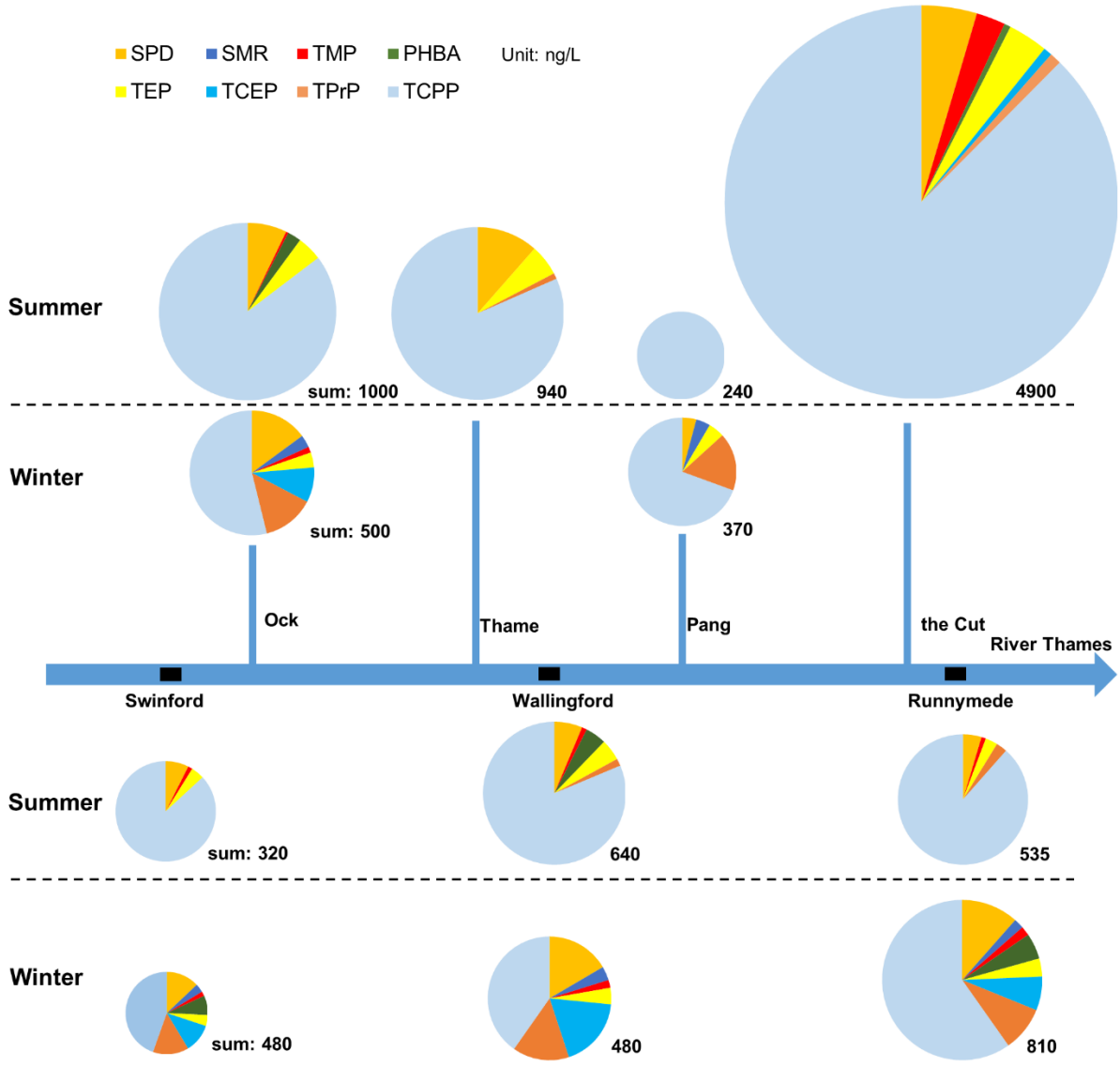

Figure 2. Composition and mean sum concentration of ECs (on the right corner) by DGT sampling from the sampling sites in the Thames catchment.

Preliminary risk assessment for aquatic organisms

A preliminary risk assessment of the studied chemicals for aquatic organisms was carried out, following the EU's technical guidance document on risk assessment (see more information in SI and Table S9).[61] RQs (risk quotient calculated as measured environmental concentration divided by predicted no effect concentration) were <1 for most target ECs and the exposure point concentrations were less than the risk screening benchmarks, indicating no significant risk. RQs of TCPP were ≥1 at 5 out of 7 sampling sites where c_{DGT} were available and the highest RQ = 7 at the Cut. This risk assessment is highly restricted by the lack of toxicity data of the target ECs. For target ECs which are believed to have continuous inputs from effluents of WWTPs, a long-term risk assessment is necessary. Potential adverse effects of the breakdown products should also be taken into account. The endocrine disrupting effects of E3 should also be taken into account. However, existing knowledge does not allow a more standardized approach for risk assessment of such substances at present.[61] Studies showed that tributaries were likely to provide distinct physical habitat conditions and increase biodiversity.[62] Because of the high detection frequencies and concentrations of EC found in tributaries, they are probably the locations to look for possible ecotoxicological effects.

Implications and recommendations for use of DGT in catchment studies

This work has demonstrated the applicability of DGT as an effective in situ monitoring tool for ECs in large dynamic aquatic environments. Comparisons of DGT and traditional grab sampling showed important advantages and challenges with DGT. DGT with a continuous sampling period can integrate pollutant concentrations and better represent the general water quality status, especially for chemicals with fluctuating concentrations in highly dynamic water bodies. For the one-week deployment in this study, DGT sensitivity was lower than that of grab sampling (1 L of sample). Longer deployment time, larger surface area samplers or combining

samplers and greater pre-concentration in elution solution prior to injection to the MS, are options to increase the sensitivity of DGT. A pilot DGT reconnaissance/surveillance exercise would allow screening of ranges of compounds and their approximate concentrations. This can then be used to inform the fuller monitoring program, as to the likely levels and therefore the deployment times and conditions needed/pre-concentrations required. DGT and grab sampling took comparable time and effort at the sampling stage, while DGT had higher requirements for accessibility and security of field sites. DGT sampling effectively pre-cleans the sample during passage through the membrane filter and diffusive gel, while grab samples needed an additional laboratory clean-up step. Hence, in the storage and sample preparation stages, DGT is more space- and time-efficient, i.e. require less storage space and shorter sample treatment time.

ASSOCIATED CONTENT

Supporting Information

Detailed information on study area, field campaigns, chemicals, reagents, sample preparation, instrumental analysis, supplementary tables and figures, and some additional discussion is given in the Supporting Information.

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