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Journal:	*Analytical Chemistry*
Manuscript ID	ac-2019-025712.R1
Manuscript Type:	Article
Date Submitted by the Author:	n/a
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Investigating potential limitations of current diffusive gradients in thin films (DGT) samplers for measuring organic chemicals

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ABSTRACT: The diffusive gradients in thin films (DGT) passive sampler has emerged as a powerful tool for measuring *in situ* concentrations of organic contaminants in waters with appropriate spatial and temporal resolution at low cost. This study addresses the property range of compounds which can be routinely sampled with the present design of DGT device. Sorption experiments and DGT deployment with 9 model chemicals [organophosphate esters with a wide range of log K_{OW} (0.8–9.5), molecular weight (182–435 Da)] and different functional groups showed compounds with high hydrophobicity and aromatic rings are prone to retention on membrane filters, which slows the supply of chemical to the binding resin of the sampler. The current DGT sampler (PTFE membrane filter, agarose gel diffusion layer and HLB binding layer) is potentially reliable for measuring hydrophilic [log K_{OW} (0.8–2.6)] and non-aromatic-ring chemicals. For compounds of higher values of K_{OW} or with aromatic rings, knowledge of the lag phase is necessary to optimize sampling times to avoid biasing subsequent laboratory analyses. A standard procedure is used to measure lag times (from minutes to days), by exposing a series of DGT samplers in waters until linear mass accumulation in samplers is achieved. We discuss how monitoring of a wide array of organic contaminants across classes should be possible in future, with a range of validated new DGT devices, optimized for the choice of membrane filter, diffusive material and binding resin.

The organic chemical status of water bodies is crucial to water supply, human health, natural ecosystems and biodiversity. However, organic pollutants are ubiquitous and have often been poorly controlled.[1] Many of them are continuously discharged into aquatic systems, as waste water treatment plants (WWTPs) are normally not designed to remove them from the dissolved phase. Regulation is still limited, especially in developing countries; for example, there are no specific organic compounds on the compulsory control list of the current discharge standard of pollutants for municipal WWTPs in China (GB 18918–2002). Water management authorities need surface water monitoring networks to properly monitor contaminants and report long-term trends. Surveillance, operational monitoring and investigative monitoring programmes need different monitoring designs, taking account of the spatial and temporal variability within a water body. Sufficient samples need to be taken to identify sources and to give a coherent, comprehensive overview of the chemical status of the water body. When monitoring trace level organic pollutants, the balance between costs and sufficient coverage of samples in time and space is challenging. Preservation, storage and transport of water samples and sufficient education and training for field personnel are all essential to the quality of sampling activities, but also increase the challenge. Spot sampling is used for most monitoring in water bodies. However, at places where contaminant concentrations are heavily influenced by flow conditions and temporal variation, flow-proportional or time-proportional samples may be needed for more representative sampling.[2] State-of-the-art passive water sampling techniques, such as diffusive gradients in thin films (DGT), the polar organic chemical integrative sampler (POCIS) and Chemcatcher, give ecotoxicologically relevant, time-weighted average (TWA) concentrations and enable cost-effective multiple site sampling.[2] Hence they have attracted increasing attention over the past decades as water authorities seek to balance their financial resources against a tendency to monitor using traditional grab or spot sampling. Considerable research now supports: using

passive water sampling with accuracy and reliability; increasing the range of chemicals and sampling environments; and procedures to improve real-world applications, with varying water flow rates, biofouling and physicochemical conditions (Table S1). Yet our understanding of sampling mechanisms of organic chemicals should be further explored for a broader use of passive samplers.

A significant advantage of the DGT technique over other passive sampling techniques is that contaminant uptake by DGT is independent of hydrodynamic conditions above a low flow threshold, so no extra calibration is needed for *in situ* monitoring.[3] It was invented and first applied to inorganics over 20 years ago and is built on a solid scientific foundation.[4] There are now over 800 peer reviewed papers on developments and applications of the DGT technique for metals and nutrients in waters, soils and sediments since the 1990s. In contrast, research and development of DGT for organic chemicals only started in 2012, but it has already attracted considerable interest and is developing rapidly.[5] To date, sampler development and testing of 136 organic compounds has been reported in the literature (a few from personal communication), with more being conducted.[5-38] Compound classes include pharmaceuticals and personal care products, illicit drugs, endocrine disrupting chemicals and pesticides etc. Table S1 summarizes these publications. Different sampler configurations have been optimized for different groups of chemicals. Seventeen types of binding layers with 15 different binding agents, 5 types of diffusion layers and 9 types of membrane filters have been described in the literature. Apart from those membranes recommended so far, a few others have also been tested. Some membrane filters give problems of retention of some compounds. This led a few studies to propose using DGT without a membrane filter,[23-27, 33] but this is inadvisable because a filter is not only protecting the inner system from clogging

by particles in water, the 0.45 μm pore size membranes are also stopping microorganisms entering the system.

As we seek to extend the use of DGT to organic chemicals, it is critical to understand any limitations of the standard sampler design and any constraints to the range of possible analytes. This can inform future developments and applications. The objectives of this study were therefore to: i). characterize sorption of target chemicals on the standard DGT device and investigate the effects of physicochemical properties of those compounds on sorption; ii). delineate limitations of the standard DGT configuration for measuring organic chemicals; and iii) recommend practical criteria for using DGT in monitoring organics in waters.

EXPERIMENTAL SECTION

Choice of compounds for study

Five hydrophilic organophosphate esters (OPEs: TCEP, TCPP, TDCPP, TPrP and TBP) were tested for *in situ* monitoring in aquatic systems using the DGT technique in a previous study.[20] In this study, a group of 9 OPEs was chosen to expand the range of functional group diversity and range of physicochemical properties (Figure 1). Details of the compounds are given in Supporting Information (SI, Table S2 and Figure S1). The 9 chemicals can be sub-divided into three groups: four with alkyl moieties of different lengths (TEP, TPrP, TBP and TEHP); three with chlorinated alkyl moieties (TCEP, TCPP and TDCPP) and two with phenyl moieties (TPP and ToCP). Their log K_{OW} (a parameter describing hydrophobicity) and molecular weight vary from 0.8 to 9.5 and from 182 to 435 Da. These ranges cover ≈75% of the organic chemicals for which the DGT technique has been developed (Table S1). Whilst log K_{OW} is clearly not the only physicochemical property controlling compound behavior, it is a primary marker of compound behavior, routinely measured for chemicals of commerce and

environmental pollutants and an excellent surrogate to represent aqueous solubility and partitioning behaviour.[39]

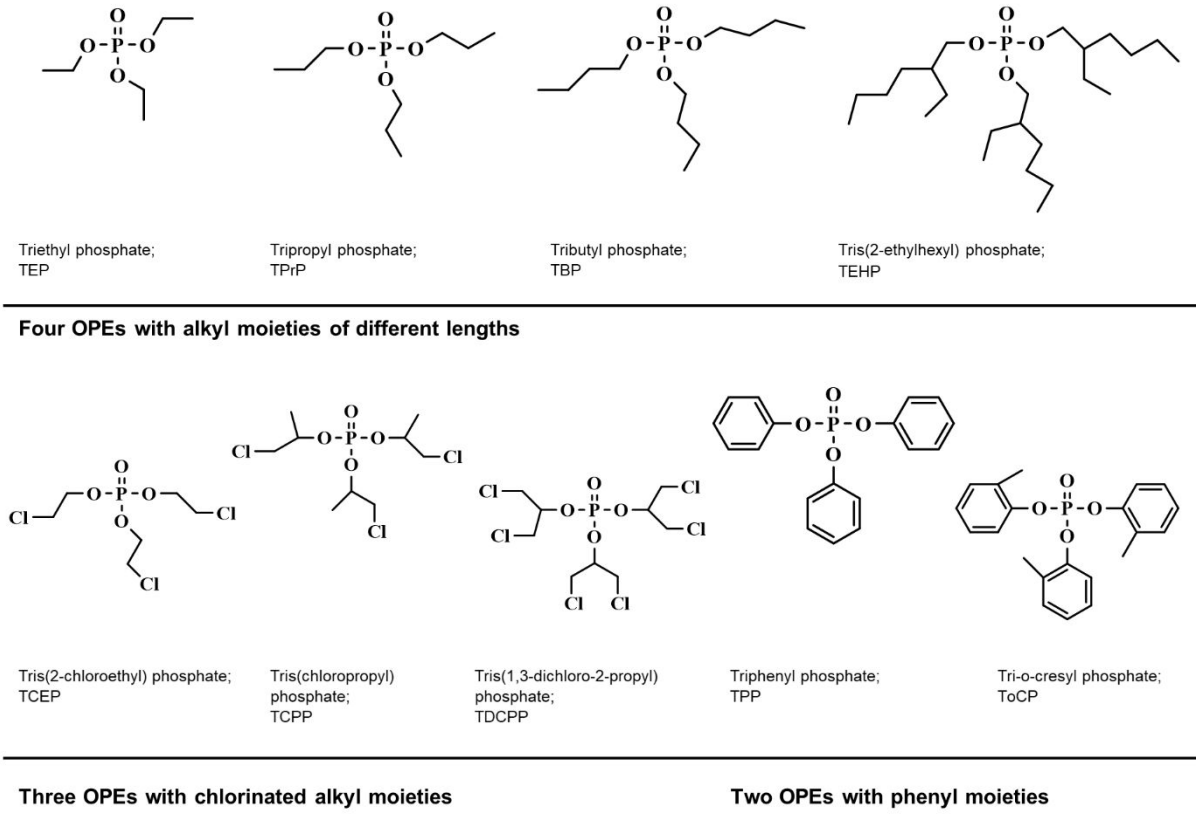

Figure 1. Chemical structures of nine organophosphate esters (OPEs) selected for this study.

Chemicals and Reagents.

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

Sampler details.

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

membrane (0.45 μm pore size, 150 μm thickness) as the standard filter. More details about the DGT sampler and the technique were first described previously.[40]

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 binary pumps, an autosampler, a degasser and a column oven connected to a Phenomenex Kinetex Biphenyl column (50×2.1 mm, 2.6 μm). Detections were conducted by a triple quadrupole mass spectrometer (Shimadzu LCMS-8040, Kyoto, Japan), with an electrospray ionisation source operated in positive ion mode. Details about the instrument, the LC gradient method, MS source parameters, an illustrative chromatogram (Figure S2), MRM parameters (Table S3), calibration curves (Table S4), instrumental limits of detection (LOD), limits of quantitation (LOQ) and method detection limits (MDL) (Table S5) are given in the SI.

Sorption experiments.

Before laboratory experiments, all containers including tubes, vials, beakers, DGT holders, pipette tips used in the study were tested for possible contamination. Since OPEs are widely used compounds, e.g. they could be found in new vials from plastic packing procedures, all glassware used in this study was ultrasonically cleaned for 30 min in a 5% (w/v) non-ionic surfactant solution, then extensively rinsed with tap water followed by MQ water, and then followed by methanol. Plastic materials were replaced with metal or glassware as much as possible for the experiment to avoid chemical losses by adsorption. HLB resins from the cartridges were thoroughly washed with acetonitrile. All solvents are carefully checked to be OPE-free.

For any DGT testing experiments using standard solutions, the concentrations of the targeted chemicals should be approximately constant. There should not be significant losses in mass

during experiments due to adsorption on the container walls. In order for the DGT technique to work optimally, all the materials for the sampler, except the binding gel, should have no significant affinity for adsorbing the targeted chemicals.

Different standard solutions (2.5, 20, 200, 1000 μg/L) of OPEs prepared in 0.01 M NaCl were used in the following experiments. They were placed in appropriate containers (5 L glass beakers, 15 mL and 50 mL glass vials and the diffusion cells) and were shaken on a horizontal shaker for suitable times in an air-conditioned room (25 °C) at a speed of 150 rpm. Solution concentrations were measured frequently to check for any changes compared to the initial concentrations. Samples of 0.2 mL solution were collected and spiked with 0.1 mL acetonitrile and 0.1 mL SIS solution and then filtered through a 0.2 μm PTFE syringe filter into LC amber vials before analysis by LC-MS/MS.

DGT sampler materials such as moldings, diffusive gels and membrane filters were tested for possible sorption losses separately. They were immersed in a 25 mL solution containing ca. 200 μg/L OPEs and 0.01 M NaCl for 6 hours. After spiking of 50 ng SIS, DGT moldings, diffusive gels and membrane filters were separately eluted with 3 × 2 mL aliquots of acetonitrile and sonicated for 5 minutes between each elution. The elution solution was evaporated to dryness by gentle nitrogen and reconstituted in 1 mL of acetonitrile and water (v:v = 50:50) and then filtered through a 0.2 μm PTFE syringe filter into LC amber vials. Samples were stored at 4 °C before analysis by LC-MS/MS. Solution concentrations were measured to calculate the mass losses from mass balance. The detailed sample treatment procedure is given in Extraction efficiency in SI.

The sorption and permeation properties of polymeric membranes are governed by their molecular characteristics and membrane structures (pore size, distribution and density, surface roughness, thickness, etc.).[41] Although there is great potential for materials science and industry to improve membrane properties for passive samplers,[42] one aim of this study is

to characterize the present available membrane filters to find the most suitable one for DGT devices for measuring organic contaminants and to investigate their influences on the DGT sampler. Three types of membrane filters were tested for possible sorption of model compounds. They were hydrophilic polyethersulfone (PES) membranes (thickness: 140 μm, diameter: 25 mm, pore size: 0.45 μm, PALL), which is a well-studied membrane filter;[23, 42] hydrophilic polytetrafluoroethylene (PTFE) membranes (thickness: 150 μm, diameter: 25 mm, pore size: 0.45 μm, ANPEL); and hydrophilic polypropylene (GHP) membranes (thickness: 114 μm, diameter: 25 mm, pore size: 0.45 μm, PALL)—two of the most commonly used membrane filters for organic DGT samplers (Table S1). Sorption to PTFE membrane filters was also investigated in *DGT deployment* for 7 days. Solutions in DGT deployment were renewed every 12 hours to ensure stable concentrations. Further details are in the SI.

Diffusion coefficient measurements.

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

The masses of analyte in the receptor compartment were plotted as a function of time to obtain a linear line with a slope that equals the first-order diffusion rate constant, k (mass, M, over time t). Equation (1) below was then used to calculate D (cm^2/s), where Δg is the diffusive gel thickness, c_s is the initial analyte concentration in the source compartment, and A_s is the area of the connecting window:

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

It is assumed that the thickness of the diffusive boundary layer (DBL) (δ) in the diffusion cell is negligible under the vigorously mixed conditions used in the experimental set-up.[43]

Uptake kinetics.

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

DGT deployment.

To test the DGT principle for measuring OPEs, DGT devices were deployed in 2.5 L solution containing ca. 20 μg/L OPEs and 0.01 M NaCl for various deployment times up to 45 hours at 19 ± 1 °C. According to the DGT equation (2), the mass of OPEs accumulated in the devices (M_{DGT}) should be increased linearly with deployment time (t).

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

Further test was conducted for longer deployment time up to 7 days in solution with lower OPEs concentration. Devices were exposed in 2.5 L solution containing around 2.5 μg/L

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

QA/QC

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

RESULTS AND DISCUSSION

Sorption.

Sorption on glassware walls.

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

much lower water solubility (360 and 600 μg/L) were stable at low concentrations such as 2.5 and 20 μg/L but decreased sharply at high concentration 200 μg/L (Figure S5).

Sorption on DGT materials.

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

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

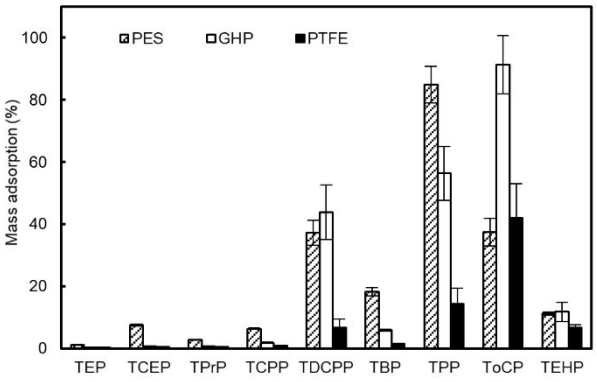

Figure 2. Adsorption of tested OPEs by 3 types of membrane filters in 25 mL solutions containing ca. 200 μg/L OPEs and 0.01 M NaCl for 6 hours. Error bars were calculated from the standard deviation of triplicates. Note, TPP, ToCP and TEHP appeared to have not reached sorption equilibrium after 6 hours,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

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

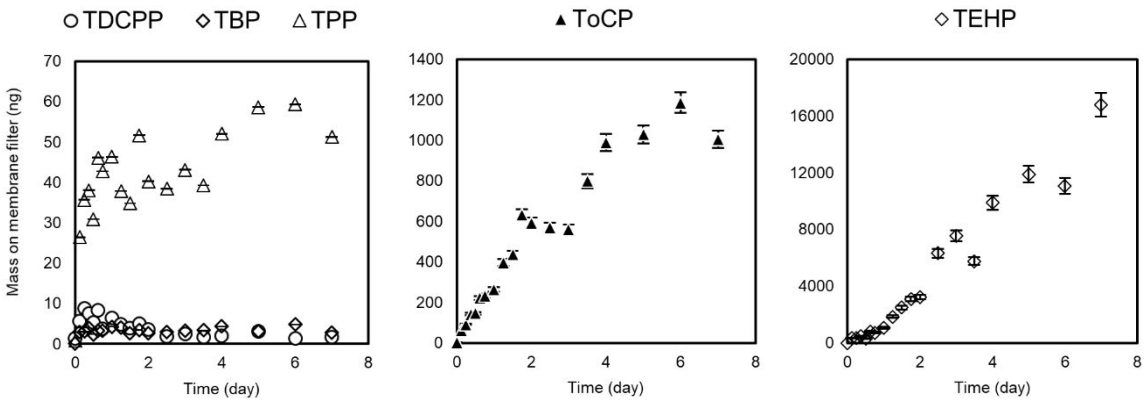

Figure 3. Sorption profiles of 5 OPEs on PTFE membrane filters from DGT samplers exposed in solution with a few micrograms per liter OPEs (Figure S8) and 0.01 M NaCl from 3 hours to 7 days (note that the solution was renewed every 12 hours to keep the concentrations approximately constant), error bars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

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

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

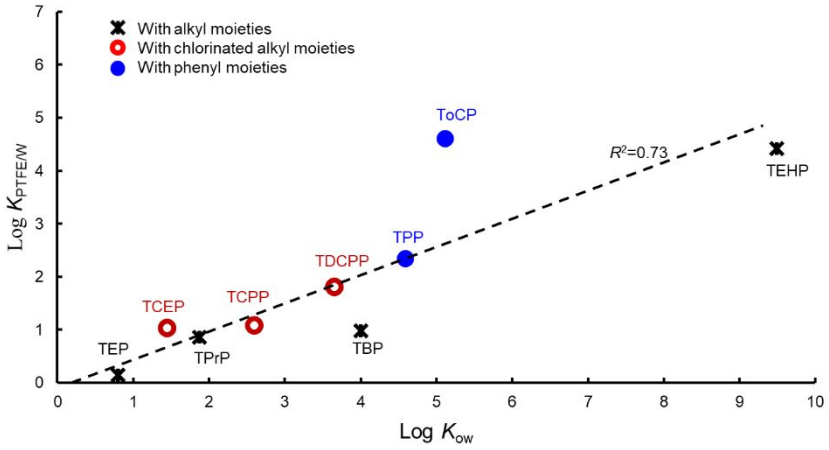

Figure 4. Log $K_{PTFE/W}$ vs log K_{OW} (note that $K_{PTFE/W}$ of TEHP were estimated based on membrane filters sorption study the sorption capacity of PTFE membrane filter for TEHP was higher than 16 µg). The dashed line indicates the linear regression for studied chemicals (log $K_{PTFE/W} = 0.52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

Diffusion coefficients.

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

The diffusion coefficients (D) at 25 °C were 6.77×10^{-6}, 6.19×10^{-6}, 5.47×10^{-6}, 6.17×10^{-6}, 5.26×10^{-6}, 4.46×10^{-6} and 5.61×10^{-6} cm^2/s for TEP, TCEP, TPrP, TCPP, TDCPP, TBP and TPP, respectively, which agreed well with D of 5 OPEs (TCEP, TCPP, TDCPP, TPrP and TBP) published before.[20] The ratios of D in this study to those published by Zou et al were in the range of 0.9–1.1.

Uptake kinetics.

When the DGT binding layer rapidly and irreversibly binds target chemicals, this ensures the concentration of the analyte at the interface between the binding layer and diffusion layer is effectively zero. Then the mass transport of the analyte through the diffusion layer can achieve a steady state and the DGT equation (2) can be used to accurately determine the DGT concentration (c_{DGT}) of the analyte in the solution.

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

As the DGT principle only works within the linear accumulation range of the resin gel, it is important to verify the DGT performance by deploying devices in a solution at constant concentration for different times. For all 9 OPEs tested, 7 of them (except ToCP and TEHP) showed linear increase in accumulated mass with deployment time. The linear relationship was compared with a theoretical line of mass versus time predicted using DGT equation (2). At initial stages of the deployment, analytes have to diffuse through the membrane filter and then the diffusive gel layer. For chemicals with high affinity to the membrane filter, the resulting lag times cause the actual mass accumulation line to deviate from the theoretical line as shown in Figure 5 except ToCP. The greater the sorption onto the membrane filter, the

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

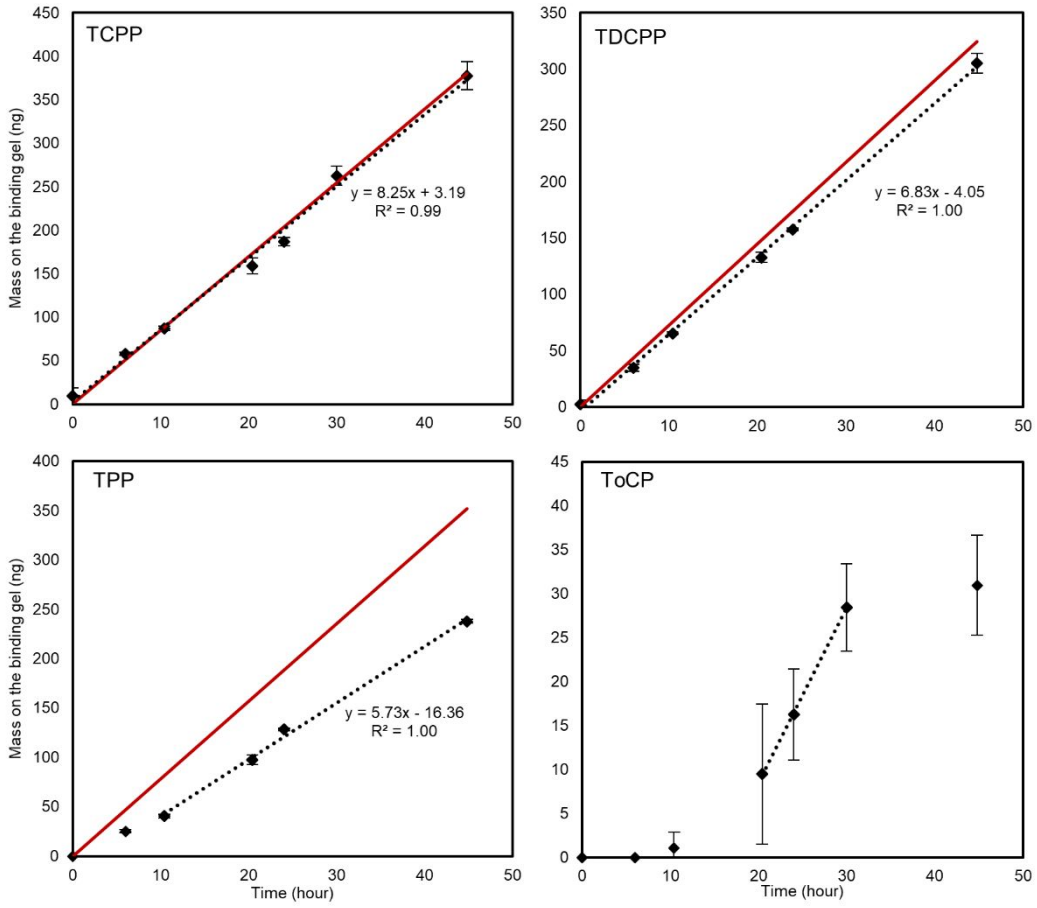

Figure 5. Linear mass accumulation of 4 selected OPEs over time by DGT samplers exposed in 2.5 L solution containing ca. 20 µg/L OPEs and 0.01 M NaCl for various deployment times up to 45 hours. The solid red line is the theoretical mass accumulation line, assuming δ = 0.3 mm. Error bars were calculated from the standard deviation (SI) of triplicates. (Figure S6 presents all the compounds).

Establishing steady state.

The time to achieve linear mass accumulation (steady state), t_{ss}, can be estimated using equation (3).[47] Here Δg represents the diffusion layer thickness, with the diffusion coefficient being an aggregated value for the diffusive gel and membrane filter.

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

If the overlaid membrane filter had negligible adsorption effect, the transient times for OPEs (except ToCP and TEHP) were about 16 minutes, which would be consistent with previous works.[48-50] However, the interactions of analytes with the membrane filter substantially extend the time needed to reach steady state. This study provides a standard procedure to measure it by exposing a series of DGT samplers at environmental concentration levels (nanograms to micrograms per liter)[51, 52] of a testing solution until linear mass accumulation is achieved.

Figure 6 illustrates the masses accumulated in binding gels for the longer deployment time of 7 days. Black dotted lines show the establishment of steady state in the binding gels and intercepts of the time-axis are the lag times required for establishing it. For DGT device with a 0.8 mm thick diffusive gel and a 0.14 mm thick PTFE membrane filter under the testing solution conditions (a few micrograms per liter OPEs, Figure S8), steady state was effectively reached within 18 minutes for TEP and 42 minutes for TCEP. The errors caused by lag time are <3% for deployments of 24 h or greater for shorter sampling windows. Longer deployment times of >24 h for TPrP and more than a week for TCPP are necessary to ensure <10% error. For TDCPP, TBP, TPP, ToCP and TEHP, the recommended minimum deployment time would be 2 weeks to 2 months due their long lag times (Table S8). As shown in Figure 7, DGT measured concentrations of TEP, TCEP, TPrP and TCPP agreed well with the bulk solution concentrations, with c_{DGT}/c^{soln} ranging from 0.95–0.99, whereas the deviation of DGT measurement from the solution concentration increased for TDCPP, TBP and TPP. The theoretical method quantitation limits (MQLs) of the DGT technique can be converted from MDLs [1.05 ng/L (TEP), 0.49 ng/L (TCEP) and 0.43 ng/L (TPrP), refer Table S5, M_{DGT} equals 1.05, 0.49 and 0.43 ng, respectively] to a concentration by equation (2), depending on the deployment time. For 24 hour deployment, using D = 6.77E-06 cm^2/s (TEP), 6.19E-06 cm^2/s (TCEP), 5.47E-06 cm^2/s (TPrP), Δg = 0.125 cm, A_s = 3.14 cm^2, the

MQLs are 71 ng/L (TEP), 36 ng/L (TCEP) and 36 ng/L (TPrP) and for 1 week deployment, the MQLs are 10 ng/L (TEP), 5 ng/L (TCEP) and 5 ng/L (TPrP). The single-digit ng/L sensitivity agrees well with this field study.[26] It's worth mentioning that the lag time was tested at a general environmental concentration level (a few micrograms per liter). In the case where the adsorption of the chemicals on the membrane filter is significant, the lag time is dependent on not only the *D* value, but also the concentration of the chemicals in the environment due to the adsorption capacity of the membrane filter. If the testing solution is at very high concentrations or the environmental concentrations are extraordinary high (>10s µg/L or even >100s µg/L), the lag time could be negligible.

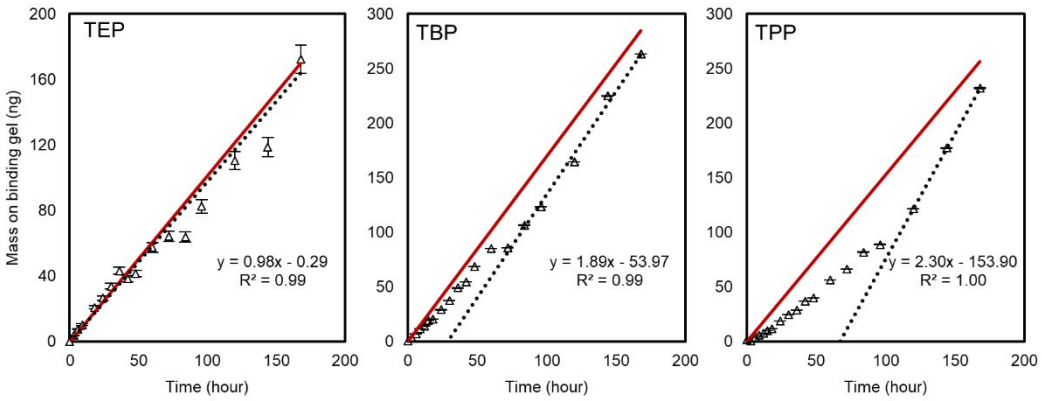

Figure 6. Mass accumulation of 3 selected OPEs over time by DGT samplers exposed in 2.5 L solution containing a few micrograms per liter OPEs (Figure S8) and 0.01 M NaCl from 3 hours up to 7 days. The solid red line is a theoretical mass accumulation line, δ = 0.3 mm. Error bars were calculated from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

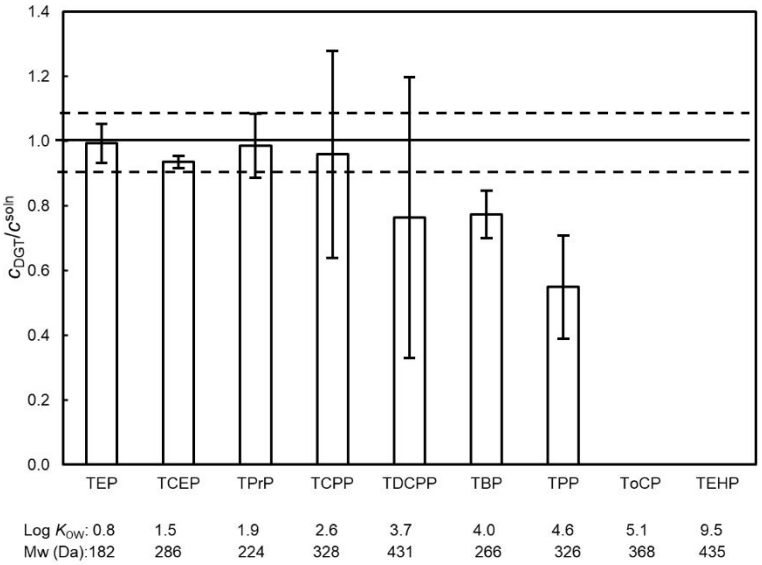

Figure 7. Ratios of DGT-measured OPEs concentrations, c_{DGT}, to their concentrations in the bulk solution, c^{soln}, during *DGT deployment* in which DGT samplers were exposed in 2.5 L solution containing a few micrograms per liter OPEs (Figure S8) and 0.01 M NaCl from 3 hours up to 7 days. The solid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

CONCLUSIONS

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

determine lag times is presented, by deploying a series of DGT devices in waters until linear mass accumulation with time in the devices is achieved and the time-axis intercepts are treated as lag times. In practice, a deployment time of 24 hours in an experiment or field monitoring situation would have a sampling time error of <3% for compounds TEP and TCEP; when the deployment time is 2 weeks, the sampling time error is <10% for most compounds (TEP, TCEP, TPrP, TCPP, TDCPP and TBP) but is higher for TPP (≈20%), ToCP (≈40%) and TEHP (>40%). Although a membrane filter could cause retention from minutes to days, it is necessary to protect the diffusive gel from clogging by particles and to prevent organisms going into the DGT device. This study focuses on the limitation of the current DGT sampler for measuring organic chemicals and we have identified the absolute limitation to use the current DGT device for organics is adsorption in the diffusion layer, mainly in membrane filters. However, it is possible to extend the DGT technique for a wider range of chemicals, for example, by replacing the current DGT membrane filter with a new type of membrane filter which does not interact with compounds such as ToCP and TEHP. New configurations of DGT devices using different materials for housing the binding and diffusion layers, new types of diffusion layer and membrane filters should be developed for both fields of research and monitoring. Studies are being undertaken to address concerns over effects of biofouling and compound degradation/loss during sample handling/storage on the sampler performance and will be the subject of a separate article.

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Funding

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

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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

SUPPORTING INFORMATION

Detailed list of studies on the DGT technique, further details of chemicals and reagents, detailed information on tested chemicals, analytical methods, experimental details, statistical analysis, supplementary results and discussion (PDF)

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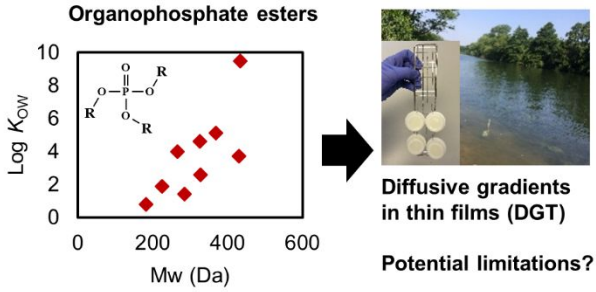
Organophosphate esters
Log K_{OW}
10
8
6
4
2
0
0
200
400
600
Mw (Da)
Diffusive gradients
in thin films (DGT)
Potential limitations?

615