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Development of a Passive Sampling Technique for Measuring Pesticides in Waters and Soils

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ABSTRACT

It is essential to monitor pesticides in the environment to help ensure water and soil quality. The diffusive gradients in thin-films (DGT) technique can measure quantitative in-situ labile (available) concentrations of chemicals in water, soil and sediments. This study describes the systematic development of the DGT technique for 9 current pesticides, selected to be representative of different classes with a wide range of properties, with two types of resins (HLB (hydrophilic-lipophilic-balanced) and XAD 18) as binding layer materials. The masses of pesticides accumulated by DGT devices were proportional to the deployment time and in inverse proportion to the thickness of the diffusive layer, in line with DGT theoretical predictions. DGT with both resin gels were tested in the laboratory for the effects of typical environmental factors on the DGT measurements. DGT performance was independent of: pH in the range of 4.7 - 8.2; dissolved organic matter concentrations <20 mg L$^{-1}$; and ionic strength from 0.01 to 0.25 M, although it was slightly affected at 0.5 M in some cases. This confirms DGT as a sampler suitable for controlled studies of environmental processes affecting pesticides. Field applications of DGT to measure pesticides in situ in waters and controlled laboratory measurements on five different soils (prepared at fixed soil:water ratios) demonstrated DGT is a suitable tool for environmental monitoring in waters and for investigating chemical processes in soils.
INTRODUCTION

Pesticides contribute significantly to food production. However, their potential adverse effects on the environment, biodiversity, food quality and human health have raised concerns. Pesticides enter soil systems through direct application,\(^1\) or indirect pathways such as wash-off from treated foliage,\(^2\) crop residues, leaf fall and root exudates.\(^3\) Only a small proportion of applied pesticides reach the target pests,\(^4\) with typically >99% remaining in soils. This may cause unintended environmental effects as pesticides can be hazardous to the indigenous microorganisms, including beneficial competitors, predators and parasites of target pest insects.\(^5\) Studies have shown that pesticides inhibit soil microbial diversity and activities,\(^6, 7\) adversely influence soil biochemical processes and disturb soil ecosystems.\(^8\) In recent decades there has been increasing concern that pesticides constitute a risk to humans by entering the food chain,\(^9\) through direct contact with soil, inhalation of volatile pesticides,\(^10\) and through groundwater contamination by pesticides leaching from soils.

It is clear that measurements of pesticides in soils are needed to understand their fate and dissipation. These are usually performed using various extraction methods,\(^11\) which can be complicated, expensive, laborious and time-consuming.\(^12\) These extraction methods usually focus on the ‘total concentration’, although some of them could be related to the bioavailable fraction, which is more relevant in risk assessment. However, they cannot provide any kinetic parameters of \textit{in situ} soil processes of pesticides, such as i) exchange between soil solution and solid phase and ii) resupply kinetics in response to biological uptake. Therefore, a technique which considers kinetic aspects and bioavailability would be of great benefit.

Pesticides can enter surface waters through diffuse pollution and leaching.\(^13\) There are requirements to monitor pesticides to assess water quality. Grab sampling, which is widely used
in water monitoring, is an effective way to measure the occurrence of organic contaminants in aquatic systems, but it only provides snapshot information at the time of sample collection; episodic contaminant events may be missed.\textsuperscript{14, 15} The development of passive sampling approaches, which can give time-weighted average (TWA) concentrations, has therefore increased in recent years.

Passive samplers are able to retain trace analytes by pre-concentration; the \textit{in situ} sampling does not affect the environment.\textsuperscript{16} Passive samplers also limit the degradation of trapped chemicals during transport and storage.\textsuperscript{17} Techniques such as POCIS (polar organic chemical integrative sampler), Chemcatcher\textsuperscript{18, 19}, ceramic dosimeters\textsuperscript{20} and microporous samplers\textsuperscript{21} are currently used for the measurement of pesticides in waters. However, they are dependent on hydrodynamic conditions during field deployment and/or rely on a laboratory calibration and losses of performance reference compounds to estimate sampling rates.\textsuperscript{22} DGT (diffusive gradients in thin-films) is a passive sampling technique which can be used for field deployment without calibration.\textsuperscript{23} It is also a ‘dynamic’ technique that can be used in soils for measuring bioavailable species.\textsuperscript{24}

The development and use of DGT for inorganics has a long and well-published pedigree. The principles were first published in 1994 in Nature\textsuperscript{25} and now over 800 peer-reviewed papers have been published on testing and applying the technique in different environmental media, such as waters,\textsuperscript{26, 27} soils\textsuperscript{28} and sediments.\textsuperscript{29} Until recently, the focus has been on metals, nutrients and radionuclides. DGT typically utilizes a three-layer system: a resin-impregnated hydrogel layer, a hydrogel diffusion-layer and a filter membrane. The thick diffusion gel layer which controls the uptake of analytes into the receiving phase limits the influence of hydrodynamic conditions by making the effect of the diffusive boundary layer (DBL) negligible.\textsuperscript{30} Uptake and pre-
concentration is balanced with exposure time to yield sufficient time-integrated mass of analytes(s) for detection.\textsuperscript{25}

The principle of DGT is based on Fick’s first law,\textsuperscript{25} such that the DGT measured-concentration ($C_{\text{DGT}}$) of target chemicals in solution can be calculated using Equation 1:

$$
C_{\text{DGT}} = \frac{M(\Delta g + \delta)}{D_e A_t}
$$

where, $M$ is the mass of analyte accumulated in the binding gel, $t$ is the exposure time, $D_e$ is the diffusion coefficient of the analyte in the diffusive layer, $A$ represents the sampling area of DGT, $\Delta g$ is the diffused length through which the analyte passes before being taken up by the binding phase, and $\delta$ is the thickness of the diffusive boundary layer (DBL).

There is great potential for applications of DGT to organic chemicals, but the first application to organic compounds was not until 2012 by Chen et al.\textsuperscript{23} They investigated the performance characteristics of DGT for quantifying polar organic compounds (with log$K_{ow}$ value <4). The newly developed DGT for organics was applied in rivers, wastewater treatment plants and soils to sample antibiotics with XAD18 as the binding gel.\textsuperscript{31, 32} Zheng et al.\textsuperscript{33} subsequently applied activated charcoal as the binding layer for DGT to detect bisphenols (BPs) in the aquatic environment. Fauvelle et al.\textsuperscript{34} extended the application of DGT to glyphosate (PMG) and amino methyl phosphonic acid (AMPA) using titanium dioxide (TiO2) as the binding layer. Weng et al. explored the bioavailability of glyphosate in soils using DGT.\textsuperscript{35} Recently, more research has been carried out developing DGT techniques for household and personal care products, illicit drugs, organophosphorus flame retardants and pesticides.\textsuperscript{36-40} Although there are two publications\textsuperscript{36, 38} on DGT measurements for pesticides, the technique has not been developed for many important and widely-used pesticides nor solved some essential technical issues, notably the choice of filter membrane, diffusive and resin gels. DGT devices in these two recent papers were deployed...
without a filter membrane, probably due to significant adsorption of the target chemicals on to the
filter, which can affect the accuracy of the measurements. However, there is little use for a DGT
sampler without a filter membrane, as the hydrogel must be protected and cannot be directly
exposed in waters and soils, otherwise particulates/microbes may become embedded in it.\textsuperscript{41}
The aim of this study was to develop the DGT technique to measure the available concentration of
a wide range of pesticides in waters and soils. In evaluating the performance characteristics of the
new DGT device, 9 pesticides were selected as test chemicals and two kinds of binding material
were tested. The binding kinetics and capacity of the binding gels were determined, and the effects
of deployment time, diffusive gel thickness, pH, ionic strength, and organic matter were studied.
A field study deploying DGT in waters and the application of DGT in a defined soil:water ratio
were also undertaken to demonstrate the performance and applicability of the technique.
The 9 target chemicals were selected from various pesticides in use in the UK and China and
chosen to cover a range of different classifications (pesticides, insecticides and fungicides) and
different functional groups (detailed properties are listed in Table S1). They represent most of the
classes of polar pesticides in use.\textsuperscript{42} The method was also tested for some of the metabolites of
atrazine, to demonstrate its utility for fate studies.\textbf{MATERIALS AND METHODS}

\textbf{Chemicals and reagents}

High purity (≥98.5\%) standards of the 9 pesticides (pyrimethanil (PYR), ethofumesate (ETH),
fluometuron (FLU), chloridazon (CHL), clomazone (CLO), thiabendazole (THI), atrazine (ATR),
linuron (LIN) and pirimicarb (PIR)), atrazine metabolites (hydroxyatrazine (HA), deethylatrazine
(DEA), desisopropylatrazine (DIA), diaminochlorotriazine (DACT), cyanuric acid (CYA)) and 2
internal standards (atrazine-d5 and linuron-d6) were purchased from Sigma-Aldrich or Dr.
Ehrenstorfer. The details of the 9 target compounds are listed in Table S1, including their
classification, use and some of their physicochemical properties. Two different materials -
Amberlite™ XAD 18 (Rohm and Haas Company) and Oasis HLB (Waters, UK) were used as
binding material. Details of the chemicals, reagents and materials are given in the Supporting
Information (SI).

**Gel preparation and DGT assemblies**

Polyacrylamide resin gels were made by mixing 4 g HLB binding resin or 1.5 g XAD18 binding
resins (wet weight), 10 mL gel solution (made by appropriate amounts of acrylamide solution,
cross-linker and MQ water), 60 μL of ammonium persulphate and 15 μL of TEMED (N,N,N′,N′-
Tetramethylethylenediamine). The solutions were then pipetted between two glass plates separated
by spacers with a certain thickness and allowed to set at 42 - 45 °C for about 45 min.23, 25, 43

Agarose diffusive gel (containing 1.5% agarose) was prepared by dissolving an appropriate
amount of agarose in an appropriate volume of pre-heated MQ water in a boiling water bath until
all the agarose was dissolved and the solution became transparent. The hot gel solution was
immediately pipetted into a preheated, gel-casting assembly and left to cool down to room
temperature.23 All gels were hydrated in MQ water and stored in 0.01M NaCl solution. The DGT
device was assembled using the standard plastic base housing consisting of a base and a cap,30
the diffusive gel was sandwiched between the binding gel and a filter membrane.

**Adsorption by DGT holder, filter membranes and diffusive gels**

All materials used for DGT devices were assessed for possible adsorption of the target compounds.
Plastic DGT holders (piston and cap) (rinsed with methanol, followed by MQ water),
polyacrylamide gels (PA), agarose gels (AG), 6 different filter membranes obtained from
Whatman® (UK) (polyethenesulfone membrane, PES; nucleopore track-etch membrane, PC;
nylon membrane, NL; Cellulose Acetate membrane, OE; mixed celluse ester membrane, ME;
hydrophilic polypropylene membrane, GHP) were exposed to 50 µg L\(^{-1}\) of the mixture of compounds in 10 mL solutions (DGT holders were in 100 mL solution). They were shaken for 20 h (Orbital, DOS-20L, Sky Line, ELMI). All materials were immersed in MQ water as blanks and the pesticides solution alone served as controls. The concentrations in the solution before and after experiment were measured to obtain the mass adsorbed.

**Binding capacity and uptake kinetics of resin gels**

To measure the binding capacity of the resin gels for accumulating the target pesticides, the resin gel disc was immersed for 21 h in well-stirred solutions containing 0.01 M NaCl and a range of concentrations of mixed compounds (1, 2, 4, 6, 8, 10 mg L\(^{-1}\)). The resin gel disc was immersed in 40 mL of 200 µg L\(^{-1}\) mixed compounds solution with a matrix of 0.01 M NaCl and shaken for 33 h. Samples were taken out at various times from 5 min to 33 h to measure the sorption kinetics of target compounds on two types of resin gels.

**Diffusion coefficient measurements**

The diffusion coefficients of the pesticides were measured using a diffusion cell that has been reported previously.\(^4\) It comprises two compartments, each with an interconnecting 1.5 cm diameter connecting window. A 2.5 cm diameter disc of 1 mm thick diffusive gel was placed between the windows and the whole assembly clamped together. Both compartments were rinsed with methanol and subsequently MQ water. The source compartment contained 100 mL of 1 mg L\(^{-1}\) mixed pesticides in 0.01 M NaCl solution; 100 mL of 0.01 M NaCl only solution was introduced into the other compartment as the receptor solution. The water levels in both compartments were exactly the same to ensure no difference in hydrostatic-head pressure. Both compartments were stirred continuously using an overhead stirrer. Sub-samples of 0.2 mL were
taken from each compartment at various intervals. The temperature during the experiment was 21.5 ± 1.6 °C.

The slope of the linear plot of the mass of the measured chemical compound which diffused into the receptor compartment versus time was used to calculate $D_e$

$$D_e = \frac{\text{slope} \times \Delta g}{C_s \times A_s}$$  \hspace{1cm} (2)

where $\Delta g$ is the thickness of the diffusive gel; $C_s$ is the concentration of compounds in the source compartment; and $A_s$ is the area of the connecting window of the diffusion cell.

**Time dependence**

The DGT devices with both binding layers were deployed in 10 µg L\(^{-1}\) mixed pesticides solution (0.01 M NaCl, pH 6.9 ± 0.2, Temperature 24 ± 2 °C) for different time periods up to 84 h. The devices were on a floating holder, and the solution was stirred by a magnetic bar.

**Diffusive layer thickness dependence**

DGTs with HLB binding gel and containing diffusive gel of different thicknesses (0.5 to 1.5 mm) were immersed in 2 L of 10 µg L\(^{-1}\) mixed pesticides solution (0.01 M NaCl, pH 6.9 ± 0.2, Temperature 21 ± 2°C) for 15 h to determine the relationship between mass accumulated by DGT and diffusive gel thickness. All DGT test experiments were carried out in minimum 2 litre solutions to prevent any significant depletion in concentration of the targeted chemicals.

**Effect of pH, ionic strength and DOM**

To investigate whether pH and ionic strength had any effect on DGT performance, DGT devices were deployed in solutions of various pH and ionic strength. As the pH for natural water is normally between 5 and 8,44,45 DGT devices were deployed in 2 L of 10 µg L\(^{-1}\) mixed pesticides solution (0.01 M NaCl) of pH range from 4.7 to 8.2 for 17.8 h at 20 ± 1°C. For the effect of ionic strength, DGT devices were exposed to 2 L of 10 µg L\(^{-1}\) mixed pesticides solution with NaCl
ranging from 0.01 to 0.5 M (pH 6.9 ± 0.2, temperature 20 ± 2 °C). Effects of DOM were tested by deploying DGT devices in 2 L of 10 µg L\(^{-1}\) mixed pesticides solution with DOM ranging from 0 - 20 mg L\(^{-1}\) (0.01 M NaCl, pH 6.9 ± 0.2, temperature 21 ± 1 °C) for 16 h.

DGT extraction, analytical methods and detection limits

After deployment, all the devices were rinsed with MQ water thoroughly before they were disassembled. The diffusive gel was peeled off, and the binding gel was placed in a pre-cleaned amber vial. 50 ng of internal standards (ATR-d5 and LIN-d6) were added before extraction. Two consecutive 5 mL portions of MeOH were added to the vial to extract target pesticides from the binding gel by 30 min ultrasonic bath. The concentrations of the pesticides were then determined following the procedure described below.

The separation of the target chemicals was performed with a Phenomenex Kinetex Biphenyl column (50×2.1 mm, 2.6 µm). Liquid chromatography with mass spectrometry (LC–MS) was used for laboratory samples of the 9 pesticides, with an Agilent LC coupled with a HP single quadrupole mass spectrometer detector with an ESI interface. It is adequate as all the target chemicals were added to laboratory testing solutions at reasonably high levels. Details of analysis are provided in the SI. Field samples including atrazine metabolites were analysed on a Shimadzu Nexera X2 LC coupled with a Shimadzu LCMS-8030 triple quadrupole mass spectrometer detector (details in SI).
The instrumental detection limits (IDLs) for LS-MS were calculated according to the standard deviation from a measured concentration of standard (8 times) and method detection limits (MDLs) were calculated based on IDLs, the recoveries for water samples and DGT samples and the dilution factors. The results are given in Table 1 (details of the calculation are shown in Table S3(a), Table S3(b) summarises the IDLs and MDLs of ATR and its metabolites in water and soils samples for LC-MS/MS). DGT for pesticide metabolites

Verification of DGT measurement for pesticide metabolites was carried out in solution of pH 7 and ionic strength 0.01M containing atrazine and its metabolites (HA, DEA, DIA, DACT, CYA). DGT devices with HLB resin gel were deployed in the solution for 24 hours at 21 ± 1°C. After deployment, the binding gel was extracted with 10 mL ACN by 30 min ultrasonic bath.

Field applications in waters and soils

A field trial was undertaken by deploying DGT devices in two sampling sites of the She River in Fushun, China, for *in situ* measurement of pesticides. Each site had 3 sampling locations. DGT devices were deployed in triplicate, 30 cm below the water surface for 4 and 7 days. Traditional grab samples were also taken on day 4 and day 7 of the DGT deployment using 1 L amber bottles. They were filtered and pre-concentrated using a well-established solid-phase extraction (SPE) method. Detailed information is shown in the SI. At the end of the deployment, the DGT devices were retrieved and rinsed with MQ water and then placed in clean plastic bags for transport. The sample treatments and analysis were the same as the methods above.

To test the DGT applicability in soils, five soils of different properties collected from the UK and China were spiked with ATR at the concentration of 100 mg kg⁻¹. The deployment was carried out after 23 days when ATR reached equilibrium between soil solution and the solid phase. Soils were hydrated with MQ water to a fixed soil:water ratios (>80% of Maximum Water Holding Capacity)
before deployment. The details of soil properties, soil collection and treatments, and DGT deployment in soils are listed in SI and Table S5.

Quality assurance/control (QA/QC)

All DGT deployments in laboratory and field were carried out in triplicates and the results were expressed as the average ± standard deviation (SD). 3 DGT devices were retrieved prior to each deployment as blank samples. Control samples (test solution without DGT devices) were performed in each experiment to prevent the possible interference during the experiment. All the SPE samples were replicated, no target compounds were found in the blank SPE samples.

RESULTS AND DISCUSSION

Sorption by DGT holder, filter membrane and diffusive gels

There was no appreciable sorption of target compounds on the two types of diffusive gels or DGT mouldings as shown in Figure S1(a). However, compounds were sorbed substantially by PES, NL, OE and ME filter membranes (Figure S1(b)). Sorption to the PES filters was marked (>50%) – this filter type has been used for POCIS\textsuperscript{16} and Chemcatcher; \textsuperscript{19} loss on the ME filter was also considerable. The PES filters were also used in DGT devices for other medium polar chemicals in other studies and the adsorption effect was negligible. PC and GHP showed little sorption of the compounds; PC membrane performed the best, with <5% for 5 compounds and <15% for the other four. It was therefore selected for the subsequent experiments.

The results on sorption to membranes/filters are important. Some studies have encountered problems of retention of medium polarity compounds onto filters with DGT, leading them to advocate that no filters be used. However, use of a filter is an intrinsic and key feature of DGT, being needed to protect the gel from particle intrusion and to limit biofouling effects on uptake. A
wide array of filter materials are available on the market and these can be screened/tested, to help
selection of the best type for different analytes.
Agarose gel (thickness of 1 mm) was chosen as the diffusive gel as it is cheaper compared to the
polyacrylamide gel and easier to prepare.

**Binding capacity of resin gels**

DGT samplers are normally deployed in the environment to accumulate target compounds over
periods of weeks or more. Knowledge of the binding capacity of the resin gel is important, to help
determine optimum sampling times for accurate measurements. For the HLB binding gel, the
uptake masses of all 9 pesticides increased linearly with increasing concentration in the bulk
solutions (see Figure 1 and Figure S2). The binding capacity is dependent on the amount of resin
used. According to the test concentration, the capacity of these pesticides on the HLB gel disc was
at least within the range of 19-44 µg per disc (the lowest for CHL and the highest for PYR),
assuming only half of the resin would be available during DGT deployment (the other half
embedded deeper in the gel was not considered). If the devices are deployed for 2 weeks, from
equation 1, the concentration of CHL that can be accurately measured (within the binding capacity)
would be at least 75 µg L^{-1} and that of PYR would be at least 200 µg L^{-1}. These are much higher
than reported environmental concentrations. \(^{47, 48}\) The amount of XAD18 which could be
incorporated in the gel solution of the standard DGT configuration was less than HLB resin. The
masses of pesticides bound to the XAD18 gel increased linearly with increasing solution
concentrations for all compounds except ATR and CHL. This could be caused by the competition
between the compounds.\(^{49}\) The mass of CHL did not increase with solution concentration,
indicating that there was no significant binding of CHL on the XAD18 resin. Although the binding
capacity of XAD18 gel is lower than HLB in the present configuration, it is still enough for at least
2 weeks deployment in a polluted environment. Increased capacity for longer sampling is easily obtained by different configurations of DGT (e.g. by using smaller size of resin to increase the specific surface area for binding). Caution needs to be taken when using the capacity values to estimate the deployment time in the field. The above capacity measurements were carried out in solutions of targeted pesticides only, without the presence of other competing chemicals. As it is not practical to test all the competing chemicals for all the possible scenarios in the laboratory condition, multiple deployment times should be carried out when DGT is used in an unknown environment for the first time.

**Uptake kinetics of the resin gels**

To ensure fully quantitative measurement by DGT, it is crucial to have rapid uptake of the target chemical by the resin gel, to create close to zero concentration at the resin gel/diffusive gel interface. The uptake of target compounds by XAD18 gel increased sharply and linearly within 2 h (Figure 2 and Figure S3), then slowly increased up to 8 hours. After 8 hours interaction, 6 compounds were adsorbed by >80% of the total amount added; most of the target chemicals (near 100%) were adsorbed within 12 h, showing the effective pre-concentration nature of the device. The kinetics of the uptake by the HLB gel was slower than that of the XAD18 gel, but was still completed within 24 h. According to Fick’s law of diffusion, the minimum uptake amount of target pesticide by the resin gel is about 10 ng at the first 5 minutes. The results presented in Figure 2 show minima of 99 ng for all test chemicals and for both resin gels. The results show that the target compounds bound onto these two types of gels sufficiently rapidly to ensure the concentration of these compounds at the diffusive/ binding gel interface will be zero, which enables good performance of DGT.
**Diffusion coefficient measurement**

The diffusion coefficient of a targeted chemical, $D_e$, is an essential parameter to calculate its concentration, $C_{DGT}$, using Equation (1). It is measured independently using the diffusion cell.\(^{43}\)

Based on the methods mentioned above, the diffusion coefficients of the 9 pesticides were measured at 21.5 °C and the standard diffusion coefficient at 25 °C was obtained from Equation (3):

$$\log D_t = \frac{1.37023(t - 25) + (8.36 \times 10^{-4})(t - 25)^2}{10^9 + t} + \log \frac{D_{25}(273 + t)}{298}$$

The diffusion coefficient of the target compound at the solution temperature $t$ (°C) during the diffusion cell experiment is $D_t$, and $D_{25}$ is the diffusion coefficient of the target compound at 25 °C.

The typical plots of mass diffused versus experiment time for the target pesticides in the diffusion cell gave the slopes shown in Figure S4. All the data are shown in Table S4.

In order to compare with POCIS and Chemcatcher passive samplers, the sampling rate per unit area for DGT was calculated using Equation (4).\(^{31}\)

$$R_{S/A} = \frac{D_e}{\Delta g}$$

Table 2 shows that the $R_{S/A}$ values for the DGT sampler ranged from 0.76 to 32.7 mL (d cm\(^2\))\(^{-1}\).

For THI, ATR and LIN, the $R_{S/A}$ values for DGT were comparable with $R_{S/A}$ values reported in the literature for POCIS and Chemcatcher.

**Effect of deployment time and diffusive gel thickness**

Two experiments, testing the relationships of accumulated mass versus deployment time and diffusion layer thickness, were carried out to validate the principle of DGT for measuring pesticides. The masses of targeted chemicals accumulated by DGT increased linearly (for 7 chemicals sorbed by HLB and 5 chemicals with XAD18, $R^2$ values were higher than 0.99) with time up to 87 h and agreed well with the theoretical line calculated by Equation (1) for most
chemicals (see Figure S5). For DGT devices with HLB resin gel, the results for ETH showed significant deviation from the theoretical line after deployment for 36 hours. For devices with XAD resin gel, only three target chemicals, ATR, THI and CLO, followed the theoretical line. The other six chemicals showed different degrees of deviation at different deployment times. These results indicate that the performance of DGT with HLB is better than that with XAD18 gel for measuring pesticides. A further test of the DGT principle for pesticides was carried out using HLB DGT devices with different thicknesses of diffusive gel in a well stirred solution. The measured mass of the target compounds that diffused through the diffusive gel layer was inversely proportional to the diffusion layer thickness (Figure S6). The experimental data agreed well with the theoretical line obtained from the Equation (1). Both results of time dependence and diffusion layer thickness confirm the principle and mechanism of the DGT technique for pesticides in solution.

The results obtained from the different diffusion layer thicknesses also indicate the DBL at the surface of the device is insignificant during the experiment under stirred conditions and it can be neglected in calculations.

**Effect of pH, ionic strength and DOM**

Pesticides can be neutral, cationic, anionic or zwitterionic, depending on the pH of the solution. Their physicochemical properties may change with the environmental conditions, which can also affect the performance of DGT. It is therefore important to confirm that uptake to DGT is independent of the normal range of environmental variables.

To assess the pH effect on the DGT measurement, DGT devices were immersed in solutions with the pH ranged from 4.7 to 8.2. The ratio of the target compound concentrations measured by DGT (\(C_{DGT}\)) to their concentrations in the bulk solutions (\(C_b\)) were plotted against pH values (Figure...
The results indicate that pH of the solution had no marked effect on the measurement by DGT with HLB binding gel as most of the ratios ($C_{\text{DGT}}/C_b$) were between 0.9 and 1.1. However, for DGT with XAD18 binding gel, the $C_{\text{DGT}}/C_b$ ratios were below 0.9 at pH 7 for all tested compounds and at pH 6 and 7.5 for most compounds. This could be due to less efficient and less effective uptake of chemicals by XAD resin at more neutral pH range. These results demonstrate that DGT with HLB binding gel can accurately measure concentrations of pesticides in the aquatic environment with a wide range of pH, whereas DGT with XAD 18 binding gel has its limitations.

The effect of IS on DGT measurements was investigated in solutions with ionic strength similar to freshwater, estuary water and seawater, ranging from 0.01 M to 0.5 M. For DGT with HLB binding gel, there was no significant effect observed in the range of 0.01 M to 0.25 M, as shown in Figure S8. The ratios of $C_{\text{DGT}}$ to $C_b$ were within 0.9 and 1.1 for all tested chemicals. At the IS of 0.5 M (close to seawater), the DGT measured concentrations were slightly lower than expected. The ratio of $C_{\text{DGT}}$ to $C_b$ was <0.9 for ATR, THI and CLO, and close to 0.9 for other six chemicals.

The viscosity of the solution is higher on addition of a large amount of NaCl, which impedes the mass transfer process. The effect of DOM on measurements of target chemicals by DGT devices with HLB resin as binding phase is demonstrated in Figure S9. The ratios of $C_{\text{DGT}}/C_b$ were between 0.9 and 1.1 for majority of the chemicals at various DOM concentrations up to 20 mg L$^{-1}$. The $C_{\text{DGT}}/C_b$ ratios of some chemicals, such as CHL, FLU, PIR and CLO were <0.9, but similar to the ratios for the control solution where the DOM concentration was zero. These findings suggest that the performance of DGT is independent of DOM concentration. Similar phenomena have been observed in the study of Li et al. using POCIS for pharmaceuticals and personal care products.
(PPCPs) and endocrine disrupting chemicals (EDCs), where $R_s$ was not affected by DOM. Li et al.’s research on perfluorinated chemicals has also shown similar results.\textsuperscript{52} In general, the performance of DGT devices with HLB resin gel was better than the DGT devices with XAD18 resin as the binding gel. DGT with HLB resin gel was therefore selected as suitable for the future experiments and measurements.

**DGT for atrazine metabolites**

All the metabolites except CYA were detected and measured quantitatively by DGT devices. CYA could be taken up by DGT with HLB binding gel, but could not be eluted effectively from the HLB resin using the present elution reagents. The results are expressed as the ratio of the DGT measured concentration ($C_{DGT}$) and the concentration in solution by conventional method ($C_b$) (Figure S10). The ratios for all compounds were between 0.9 and 1.1 and most of them were close to 1.0. The results indicate that DGT can be used for measuring not only the pesticides, but also metabolites. This opens up important opportunities for detailed fate studies.

**Field applications in waters and soils**

**In situ DGT deployments in river water**

The results of DGT deployments in the She River and Dahuofang Reservoir, north China are presented in Figure 3. ATR was the only detectable target compound in both grab samples and in DGT samplers. DGT provides TWA concentrations of ATR over the exposure period. The similar concentrations in the 3 locations of the river (Figure 3a) between two different deployment periods, 4 days and 7 days, indicate: i) the concentration of ATR during the 7 days was consistent without significant variation; ii) the distribution of ATR in the 3 locations (about 50 meters apart) was similar and iii) DGT performance was good during the long deployment period and not affected by environmental
factors, such as biofouling. The deployment time could be extended longer as the DGT device has a great capacity for all the targeted chemicals. However, the common problems for all passive samplers such as biofouling and possible degradations may affect the accuracy of the measurements for longer time deployments. As the river water flow was fast, the DBL was neglected in calculating $C_{DGT}$ as the DBL thickness was estimated to be much smaller than the thickness of the diffusive gel. Deployment in the reservoir showed slightly greater variation in DGT measured concentrations of ATR between three different locations and between two different deployment times (Figure 3b), notably for locations L5 and L6. This is reasonable as the mixing in the reservoir may be less efficient compared to the river. The concentrations of ATR in grab samples were higher than DGT measured in situ concentrations. Although the differences were small, relative to the measurements made and the techniques used, DGT usually gives lower values than bulk water sampling because DGT only measures the available fraction which is dissolved and able to diffuse through the diffusive gel. The measurement from the grab samples gives the total concentration, including colloids and complexed fractions that may not be measured by DGT. Several studies have also shown the advantage of DGT over grab sampling when measuring chemical concentration in a changing environment.\textsuperscript{27, 53}

**DGT measurements in soils**

DGT devices were deployed in five different soils after wetting with water (Table S5) to test the applicability of the technique for measuring pesticides and their metabolites in soils. ATR and its metabolites were chosen as test compounds. The results are shown in Table 3. HA and DEA were the primary metabolites measured and DIA and DACT were not detected in these soils, the concentration of HA was much higher than that of DEA, indicating that the chemical degradation pathway was favoured, rather than biological degradation.\textsuperscript{,} Although CYA was detected in soil F,
the result was not presented here since CYA could not be eluted efficiently from HLB resin in the DGT performance test experiment. The extremely low concentration of ATR in soil F indicates the fast degradation of ATR in that soil. Soil F was collected from highly productive agricultural land with regular addition of fertilisers and pesticides; this is likely to make the microbial activity much higher than in the other test soils,\textsuperscript{54, 55} and therefore with much faster ATR degradation. Although ATR was spiked to the same total concentration for all the soils, DGT measured concentrations, $C_{\text{DGT}}$, varied between soils. The available ATR concentrations in soils M and D were similar, but less than concentrations in soils R and K. This is likely due to much lower pH in soils M and D, since adsorption of ATR to soil increases at lower pH.\textsuperscript{56} The concentrations of metabolites in soils M and D were greater than those in soils R and K, consistent with findings by other researchers that hydrolysis of ATR decreases with increasing soil pH.\textsuperscript{57} Although organic matter content enhanced degradation of ATR,\textsuperscript{13} pH seemed to have more influence due to the big range in pH in those soils.

**CONCLUSIONS**

A novel DGT sampling technique on measurement for 9 pesticides has been successfully developed through systematic performance tests, HLB resin was selected as binding agent and agarose as diffusive gel. The DGT sampler can provide comparable sampling rate per unit area ($R_{S/A}$) to other passive samplers. The measurement of these pesticides using DGT was independent of pH 4.7 - 8.2, ionic strength 0.01 – 0.25 M, and DOM up to 20 mg L$^{-1}$, extending its utility for a wide range of environmental conditions. It is capable of measuring pesticide metabolites, implying its potential of exploring the environmental fate and behaviour of organic chemicals. It has also been assessed under field conditions. This study has demonstrated that DGT sampler with HLB
resin gel is a reliable technique for in situ measurement of several groups of pesticides in waters and soils.

SUPPORTING INFORMATION

Information on analytical method, sampling sites, supplementary tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES


Sun, L.; Lee, H. K., Optimization of microwave-assisted extraction and supercritical fluid extraction of carbamate pesticides in soil by experimental design methodology. *Journal of Chromatography A 2003*, 1014 (1), 165-177.


Table 1. IDLs of test chemicals for LC-MS and MDLs of test chemicals for lab and field samples

<table>
<thead>
<tr>
<th>Test Chemicals</th>
<th>IDL (µg L⁻¹)</th>
<th>Lab sample MDL (µg L⁻¹)</th>
<th>Field sample MDL (ng L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water</td>
<td>DGT</td>
</tr>
<tr>
<td>CHL</td>
<td>0.08</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>THI</td>
<td>0.23</td>
<td>0.26</td>
<td>0.14</td>
</tr>
<tr>
<td>FLU</td>
<td>0.11</td>
<td>0.13</td>
<td>0.06</td>
</tr>
<tr>
<td>ATR</td>
<td>0.05</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>PIR</td>
<td>0.29</td>
<td>0.33</td>
<td>0.19</td>
</tr>
<tr>
<td>LIN</td>
<td>0.09</td>
<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>PYR</td>
<td>0.14</td>
<td>0.15</td>
<td>0.09</td>
</tr>
<tr>
<td>CLO</td>
<td>0.10</td>
<td>0.11</td>
<td>0.07</td>
</tr>
<tr>
<td>ETH</td>
<td>0.05</td>
<td>0.06</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 2. Comparison of $R_{S/A}$ (mL(d cm⁻²)⁻¹) for DGT at 25°C and some other passive samplers

<table>
<thead>
<tr>
<th></th>
<th>CHL</th>
<th>THI</th>
<th>FLU</th>
<th>ATR</th>
<th>PIR</th>
<th>LIN</th>
<th>PYR</th>
<th>CLO</th>
<th>ETH</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGT $R_{S/A}$</td>
<td>5.68</td>
<td>5.33</td>
<td>5.51</td>
<td>4.90</td>
<td>4.88</td>
<td>4.92</td>
<td>4.95</td>
<td>4.89</td>
<td>4.59</td>
</tr>
<tr>
<td>POCIS $R_{S/A}$</td>
<td>$^{a}$</td>
<td>$^{3.975^{50c} - 16.775^{50c}}$</td>
<td>-</td>
<td>$^{0.765^{50c} - 5.835^{50d}}$</td>
<td>-</td>
<td>$^{3.435^{50c} - 23.125^{50c}}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chemcatcher $R_{S/A}$</td>
<td>-</td>
<td>-</td>
<td>$^{4.786^{50e} - 32.706^{50f}}$</td>
<td>$^{6.296^{50e} - 23.963^{50h}}$</td>
<td>$^{3.276^{50e} - 8.186^{50h}}$</td>
<td>-</td>
<td>-</td>
<td>$^{5.036^{50g}}$</td>
<td></td>
</tr>
</tbody>
</table>

- a: no data available
- b: $R_{S/A}$ values were calculated according to $R_{S/A} = R_S / A$ where $R_S$ is sampling rate and $A$ is exposure area of the sampler. The values for $A$ were: c: 45.8 cm²; d: 41 cm²; e, f, g, h: 15.9 cm².
- The temperature values were: c: 29±3 °C; d: 17±1 °C; e: 20 °C; f: 16.4-17.4 °C; g: 5-20 °C; h: 14.25 °C
Table 3. DGT measured concentrations of ATR and its metabolites in soils expressed in mg L$^{-1}$

<table>
<thead>
<tr>
<th></th>
<th>Soil M</th>
<th>Soil D</th>
<th>Soil F</th>
<th>Soil R</th>
<th>Soil K</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATR</td>
<td>3.430</td>
<td>3.305</td>
<td>0.001</td>
<td>4.059</td>
<td>4.034</td>
</tr>
<tr>
<td>HA</td>
<td>0.331</td>
<td>0.406</td>
<td>0.029</td>
<td>0.269</td>
<td>0.141</td>
</tr>
<tr>
<td>DEA</td>
<td>0.042</td>
<td>0.039</td>
<td>&lt;MDL</td>
<td>0.007</td>
<td>0.003</td>
</tr>
</tbody>
</table>

CYA was detected in samples from soil F. As CYA cannot be eluted effectively from the HLB resin gel, the data in soil F would not be accurate and meaningful. Therefore, it is not presented here.
Figure 1. Masses of four pesticides (ATR, LIN, PIR and PYR) taken up by two types of binding gels with HLB and XAD18 resins at different concentrations (1-10 mg L\(^{-1}\)) (IS = 0.01 M, pH = 5.8 ± 0.2, \(T= 20 \pm 2 \, ^\circ\text{C}; \, n=3\)). Error bars were calculated from the standard deviation (SD) of three replicates.
Figure 2. Binding kinetics of selected test chemicals by HLB and XAD18 resin gels in 40 mL solutions of 200 μg L⁻¹ test chemicals (IS = 0.01 M, pH = 6.0 ± 0.1, T = 21 ± 1 °C; n = 3). Error bars were calculated from the standard deviation (SD) of three replicates.
**Figure 3.** Average concentration of ATR measured by DGT devices *in situ* during two different deployment times (4 days, in green, and 7 days, in orange) in (a) She River (in three different locations, L1, L2, and L3) and (b) Hahuofang Reservoir (in three different locations (L4, L5, and L6). Grab samples were taken for both deployment period.