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

Journal:	*Journal of Agricultural and Food Chemistry*
Manuscript ID	Draft
Manuscript Type:	Article
Date Submitted by the Author:	n/a
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1 # Development of a Passive Sampling Technique for
2 # Measuring Pesticides in Waters and Soils

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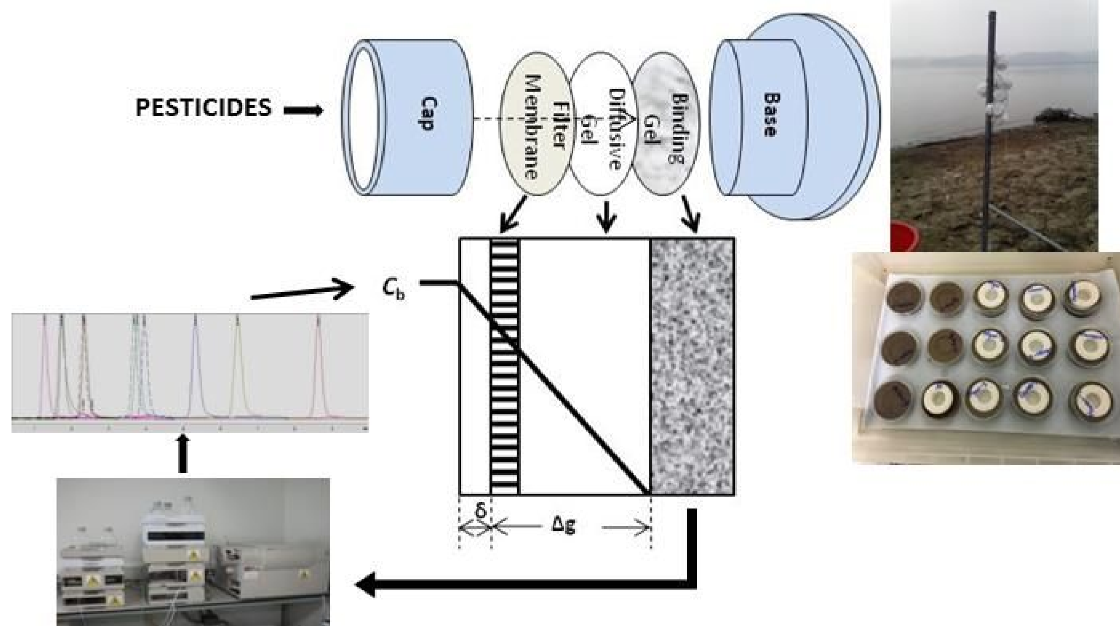

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22 **ABSTRACT**

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

39

40 **INTRODUCTION**

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

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

61 Pesticides can enter surface waters through diffuse pollution and leaching.[13] There are
62 requirements to monitor pesticides to assess water quality. Grab sampling, which is widely used

63 in water monitoring, is an effective way to measure the occurrence of organic contaminants in
64 aquatic systems, but it only provides snapshot information at the time of sample collection;
65 episodic contaminant events may be missed.[14, 15] The development of passive sampling approaches,
66 which can give time-weighted average (TWA) concentrations, has therefore increased in recent
67 years.

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

78 The development and use of DGT for inorganics has a long and well-published pedigree. The
79 principles were first published in 1994 in Nature[25] and now over 800 peer-reviewed papers have
80 been published on testing and applying the technique in different environmental media, such as
81 waters,[26, 27] soils[28] and sediments.[29] Until recently, the focus has been on metals, nutrients and
82 radionuclides. DGT typically utilizes a three-layer system: a resin-impregnated hydrogel layer, a
83 hydrogel diffusion-layer and a filter membrane. The thick diffusion gel layer which controls the
84 uptake of analytes into the receiving phase limits the influence of hydrodynamic conditions by
85 making the effect of the diffusive boundary layer (DBL) negligible.[30] Uptake and pre-

86 concentration is balanced with exposure time to yield sufficient time-intergated mass of analytes(s)
87 for detection.[25]
88 The principle of DGT is based on Fick's first law,[25] such that the DGT measured-concentration
89 (C_{DGT}) of target chemicals in solution can be calculated using Equation 1:

90 $$C_{DGT} = \frac{M\,(\Delta g + \delta)}{D_e A t} \quad (1)$$

91 where, M is the mass of analyte accumulated in the binding gel, t is the exposure time, D_e is the
92 diffusion coefficient of the analyte in the diffusive layer, A represents the sampling area of DGT,
93 Δg is the diffused length through which the analyte passes before being taken up by the binding
94 phase, and δ is the thickness of the diffusive boundary layer (DBL).
95 There is great potential for applications of DGT to organic chemicals, but the first application to
96 organic compounds was not until 2012 by Chen et al.[23] They investigated the performance
97 characteristics of DGT for quantifying polar organic compounds (with $\log K_{ow}$ value <4). The
98 newly developed DGT for organics was applied in rivers, wastewater treatment plants and soils to
99 sample antibiotics with XAD18 as the binding gel.[31, 32] Zheng et al.[33] subsequently applied
100 activated charcoal as the binding layer for DGT to detect bisphenols (BPs) in the aquatic
101 environment. Fauvelle et al.[34] extended the application of DGT to glyphosate (PMG) and amino
102 methyl phosphonic acid (AMPA) using titanium dioxide (TiO2) as the binding layer. Weng et al.
103 explored the bioavailability of glyphosate in soils using DGT.[35] Recently, more research has been
104 carried out developing DGT techniques for household and personal care products, illicit drugs,
105 organophosphorus flame retardants and pesticides.[36-40] Although there are two publications[36, 38] on
106 DGT measurements for pesticides, the technique has not been developed for many important and
107 widely-used pesticides nor solved some essential technical issues, notably the choice of filter
108 membrane, diffusive and resin gels. DGT devices in these two recent papers were deployed

109 without a filter membrane, probably due to significant adsorption of the target chemicals on to the
110 filter, which can affect the accuracy of the measurements. However, there is little use for a DGT
111 sampler without a filter membrane, as the hydrogel must be protected and cannot be directly
112 exposed in waters and soils, otherwise particulates/microbes may become embedded in it.[41]
113 The aim of this study was to develop the DGT technique to measure the available concentration of
114 a wide range of pesticides in waters and soils. In evaluating the performance characteristics of the
115 new DGT device, 9 pesticides were selected as test chemicals and two kinds of binding material
116 were tested. The binding kinetics and capacity of the binding gels were determined, and the effects
117 of deployment time, diffusive gel thickness, pH, ionic strength, and organic matter were studied.
118 A field study deploying DGT in waters and the application of DGT in a defined soil:water ratio
119 were also undertaken to demonstrate the performance and applicability of the technique.
120 The 9 target chemicals were selected from various pesticides in use in the UK and China and
121 chosen to cover a range of different classifications (pesticides, insecticides and fungicides) and
122 different functional groups (detailed properties are listed in Table S1). They represent most of the
123 classes of polar pesticides in use.[42] The method was also tested for some of the metabolites of
124 atrazine, to demonstrate its utility for fate studies.**MATERIALS AND METHODS**

125 **Chemicals and reagents**

126 High purity (≥98.5%) standards of the 9 pesticides (pyrimethanil (PYR), ethofumesate (ETH),
127 fluometuron (FLU), chloridazon (CHL), clomazone (CLO), thiabendazole (THI), atrazine (ATR),
128 linuron (LIN) and pirimicarb (PIR)), atrazine metabolites (hydroxyatrazine (HA), deethylatrazine
129 (DEA), desisopropylatrazine (DIA), diaminochlorotriazine (DACT), cyanuricacid (CYA)) and 2
130 internal standards (atrazine-d5 and linuron-d6) were purchased from Sigma-Aldrich or Dr.
131 Ehrenstorfer. The details of the 9 target compounds are listed in Table S1, including their

132 classification, use and some of their physicochemical properties. Two different materials - 133 Amberlite™ XAD 18 (Rohm and Haas Company) and Oasis HLB (Waters, UK) were used as 134 binding material. Details of the chemicals, reagents and materials are given in the Supporting 135 Information (SI).

136 **Gel preparation and DGT assemblies**

137 Polyacrylamide resin gels were made by mixing 4 g HLB binding resin or 1.5 g XAD18 binding 138 resins (wet weight), 10 mL gel solution (made by appropriate amounts of acrylamide solution, 139 cross-linker and MQ water), 60 μL of ammonium persulphate and 15 μL of TEMED (N,N,N′,N′- 140 Tetramethylethylenediamine). The solutions were then pipetted between two glass plates separated 141 by spacers with a certain thickness and allowed to set at 42 - 45 °C for about 45 min.[23, 25, 43] 142 Agarose diffusive gel (containing 1.5% agarose) was prepared by dissolving an appropriate 143 amount of agarose in an appropriate volume of pre-heated MQ water in a boiling water bath until 144 all the agarose was dissolved and the solution became transparent. The hot gel solution was 145 immediately pipetted into a preheated, gel-casting assembly and left to cool down to room 146 temperature.[23] All gels were hydrated in MQ water and stored in 0.01M NaCl solution. The DGT 147 device was assembled using the standard plastic base housing consisting of a base and a cap,[30] 148 the diffusive gel was sandwiched between the binding gel and a filter membrane.

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

150 All materials used for DGT devices were assessed for possible adsorption of the target compounds. 151 Plastic DGT holders (piston and cap) (rinsed with methanol, followed by MQ water), 152 polyacrylamide gels (PA), agarose gels (AG), 6 different filter membranes obtained from 153 Whatman® (UK) (polyethenesulfone membrane, PES; nucleopore track-etch membrane, PC; 154 nylon membrane, NL; Cellulose Acetate membrane, OE; mixed celluse ester membrane, ME;

155 hydrophilic polypropylene membrane, GHP) were exposed to 50 μg L^{-1} of the mixture of
156 compounds in 10 mL solutions (DGT holders were in 100 mL solution). They were shaken for 20
157 h (Orbital, DOS-20L, Sky Line, ELMI). All materials were immersed in MQ water as blanks and
158 the pesticides solution alone served as controls. The concentrations in the solution before and after
159 experiment were measured to obtain the mass adsorbed.

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

161 To measure the binding capacity of the resin gels for accumulating the target pesticides, the resin
162 gel disc was immersed for 21 h in well-stirred solutions containing 0.01 M NaCl and a range of
163 concentrations of mixed compounds (1, 2, 4, 6, 8, 10 mg L^{-1}).

164 The resin gel disc was immersed in 40 mL of 200 μg L^{-1} mixed compounds solution with a matrix
165 of 0.01 M NaCl and shaken for 33 h. Samples were taken out at various times from 5 min to 33 h
166 to measure the sorption kinetics of target compounds on two types of resin gels.

167 **Diffusion coefficient measurements**

168 The diffusion coefficients of the pesticides were measured using a diffusion cell that has been
169 reported previously.[43] It comprises two compartments, each with an interconnecting 1.5 cm
170 diameter connecting window. A 2.5 cm diameter disc of 1 mm thick diffusive gel was placed
171 between the windows and the whole assembly clamped together. Both compartments were rinsed
172 with methanol and subsequently MQ water. The source compartment contained 100 mL of 1 mg
173 L^{-1} mixed pesticides in 0.01 M NaCl solution; 100 mL of 0.01 M NaCl only solution was
174 introduced into the other compartment as the receptor solution. The water levels in both
175 compartments were exactly the same to ensure no difference in hydrostatic-head pressure. Both
176 compartments were stirred continuously using an overhead stirrer. Sub-samples of 0.2 mL were

177 taken from each compartment at various intervals. The temperature during the experiment was
178 21.5 ± 1.6 °C.

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

181 $$D_e = \frac{\text{slope} \times \Delta g}{C_s \times A_s} \quad (2)$$

182 where Δg is the thickness of the diffusive gel; C_s is the concentration of compounds in the source
183 compartment; and A_s is the area of the connecting window of the diffusion cell.

184 **Time dependence**

185 The DGT devices with both binding layers were deployed in 10 μg L^{-1} mixed pesticides solution
186 (0.01 M NaCl, pH 6.9 ± 0.2, Temperature 24 ± 2 °C) for different time periods up to 84 h. The
187 devices were on a floating holder, and the solution was stirred by a magnetic bar.

188 **Diffusive layer thickness dependence**

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

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

195 To investigate whether pH and ionic strength had any effect on DGT performance, DGT devices
196 were deployed in solutions of various pH and ionic strength. As the pH for natural water is
197 normally between 5 and 8,[44, 45] DGT devices were deployed in 2 L of 10 μg L^{-1} mixed pesticides
198 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
199 strength, DGT devices were exposed to 2 L of 10 μg L^{-1} mixed pesticides solution with NaCl

200 ranging from 0.01 to 0.5 M (pH 6.9 ± 0.2, temperature 20 ± 2 °C). Effects of DOM were tested by
201 deploying DGT devices in 2 L of 10 μg L^{-1} mixed pesticides solution with DOM ranging from 0 -
202 20 mg L^{-1} (0.01 M NaCl, pH 6.9 ± 0.2, temperature 21 ± 1 °C) for 16 h.

203 **DGT extraction, analytical methods and detection limits**

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

210 The separation of the target chemicals was performed with a Phenomenex Kinetex Biphenyl
211 column (50×2.1 mm, 2.6 μm). Liquid chromatography with mass spectrometry (LC–MS) was used
212 for laboratory samples of the 9 pesticides, with an Agilent LC coupled with a HP single quadrupole
213 mass spectrometer detector with an ESI interface. It is adequate as all the target chemicals were
214 added to laboratory testing solutions at reasonably high levels. Details of analysis are provided in
215 the SI. Field samples including atrazine metabolites were analysed on a Shimadzu Nexera X2 LC
216 coupled with a Shimadzu LCMS-8030 triple quadrupole mass spectrometer detector (details in
217 SI).

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218 **The instrumental detection limits (IDLs) for LS-MS were calculated according to the**
219 **standard deviation from a measured concentration of standard (8 times) and method**
220 **detection limits (MDLs) were calculated based on IDLs, the recoveries for water samples and**
221 **DGT samples and the dilution factors. The results are given in Table 1 (details of the**
222 **calculation are shown in Table S3(a), Table S3(b) summarises the IDLs and MDLs of ATR**
223 **and its metabolites in water and soils samples for LC-MS/MS).DGT for pesticide metabolites**
224 Verification of DGT measurement for pesticide metabolites was carried out in solution of pH 7
225 and ionic strength 0.01M containing atrazine and its metabolites (HA, DEA, DIA, DACT, CYA).
226 DGT devices with HLB resin gel were deployed in the solution for 24 hours at 21 ± 1°C. After
227 deployment, the binding gel was extracted with 10 mL ACN by 30 min ultrasonic bath.
228 **Field applications in waters and soils**
229 A field trial was undertaken by deploying DGT devices in two sampling sites of the She River in
230 Fushun, China, for *in situ* measurement of pesticides. Each site had 3 sampling locations. DGT
231 devices were deployed in triplicate, 30 cm below the water surface for 4 and 7 days. Traditional
232 grab samples were also taken on day 4 and day 7 of the DGT deployment using 1 L amber bottles.
233 They were filtered and pre-concentrated using a well-established solid-phase extraction (SPE)
234 method.[46] Detailed information is shown in the SI. At the end of the deployment, the DGT devices
235 were retrieved and rinsed with MQ water and then placed in clean plastic bags for transport. The
236 sample treatments and analysis were the same as the methods above.
237 To test the DGT applicability in soils, five soils of different properties collected from the UK and
238 China were spiked with ATR at the concentration of 100 mg kg^{-1}. The deployment was carried out
239 after 23 days when ATR reached equilibrium between soil solution and the solid phase. Soils were
240 hydrated with MQ water to a fixed soil:water ratios (>80% of Maximum Water Holding Capacity)

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241 before deployment. The details of soil properties, soil collection and treatments, and DGT
242 deployment in soils are listed in SI and Table S5.

243 **Quality assurance/control (QA/QC)**

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

249 **RESULTS AND DISCUSSION**

250 **Sorption by DGT holder, filter membrane and diffusive gels**

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

259 The results on sorption to membranes/filters are important. Some studies have encountered
260 problems of retention of medium polarity compounds onto filters with DGT, leading them to
261 advocate that no filters be used. However, use of a filter is an intrinsic and key feature of DGT,
262 being needed to protect the gel from particle intrusion and to limit biofouling effects on uptake. A

263 wide array of filter materials are available on the market and these can be screened/tested, to help
264 selection of the best type for different analytes.
265 Agarose gel (thickness of 1 mm) was chosen as the diffusive gel as it is cheaper compared to the
266 polyacrylamide gel and easier to prepare.

267 **Binding capacity of resin gels**

268 DGT samplers are normally deployed in the environment to accumulate target compounds over
269 periods of weeks or more. Knowledge of the binding capacity of the resin gel is important, to help
270 determine optimum sampling times for accurate measurements.[30] For the HLB binding gel, the
271 uptake masses of all 9 pesticides increased linearly with increasing concentration in the bulk
272 solutions (see Figure 1 and Figure S2). The binding capacity is dependent on the amount of resin
273 used. According to the test concentration, the capacity of these pesticides on the HLB gel disc was
274 at least within the range of 19-44 μg per disc (the lowest for CHL and the highest for PYR),
275 assuming only half of the resin would be available during DGT deployment (the other half
276 embedded deeper in the gel was not considered). If the devices are deployed for 2 weeks, from
277 equation 1, the concentration of CHL that can be accurately measured (within the binding capacity)
278 would be at least 75 μg L^{-1} and that of PYR would be at least 200 μg L^{-1}. These are much higher
279 than reported environmental concentrations.[47, 48] The amount of XAD18 which could be
280 incorporated in the gel solution of the standard DGT configuration was less than HLB resin. The
281 masses of pesticides bound to the XAD18 gel increased linearly with increasing solution
282 concentrations for all compounds except ATR and CHL. This could be caused by the competition
283 between the compounds.[49] The mass of CHL did not increase with solution concentration,
284 indicating that there was no significant binding of CHL on the XAD18 resin. Although the binding
285 capacity of XAD18 gel is lower than HLB in the present configuration, it is still enough for at least

286 2 weeks deployment in a polluted environment. Increased capacity for longer sampling is easily
287 obtained by different configurations of DGT (e.g. by using smaller size of resin to increase the
288 specific surface area for binding). Caution needs to be taken when using the capacity values to
289 estimate the deployment time in the field. The above capacity measurements were carried out in
290 solutions of targeted pesticides only, without the presence of other competing chemicals. As it is
291 not practical to test all the competing chemicals for all the possible scenarios in the laboratory
292 condition, multiple deployment times should be carried out when DGT is used in an unknown
293 environment for the first time.

294 **Uptake kinetics of the resin gels**

295 To ensure fully quantitative measurement by DGT, it is crucial to have rapid uptake of the target
296 chemical by the resin gel, to create close to zero concentration at the resin gel/diffusive gel
297 interface. The uptake of target compounds by XAD18 gel increased sharply and linearly within 2
298 h (Figure 2 and Figure S3), then slowly increased up to 8 hours. After 8 hours interaction, 6
299 compounds were adsorbed by >80% of the total amount added; most of the target chemicals (near
300 100%) were adsorbed within 12 h, showing the effective pre-concentration nature of the device.
301 The kinetics of the uptake by the HLB gel was slower than that of the XAD18 gel, but was still
302 completed within 24 h. According to Fick's law of diffusion, the minimum uptake amount of target
303 pesticide by the resin gel is about 10 ng at the first 5 minutes. The results presented in Figure 2
304 show minima of 99 ng for all test chemicals and for both resin gels. The results show that the target
305 compounds bound onto these two types of gels sufficiently rapidly to ensure the concentration of
306 these compounds at the diffusive/ binding gel interface will be zero, which enables good
307 performance of DGT.

308 **Diffusion coefficient measurement**

309 The diffusion coefficient of a targeted chemical, D_e, is an essential parameter to calculate its
310 concentration, C_{DGT}, using Equation (1). It is measured independently using the diffusion cell.[43]
311 Based on the methods mentioned above, the diffusion coefficients of the 9 pesticides were
312 measured at 21.5 °C and the standard diffusion coefficient at 25 °C was obtained from Equation
313 (3):

314 $$\log D_t = \frac{1.37023(t-25) + (8.36 \times 10^{-4})(t-25)^2}{109 + t} + \log\frac{D_{25}(273 + t)}{298} \quad (3)$$

315 The diffusion coefficient of the target compound at the solution temperature *t* (°C) during the
316 diffusion cell experiment is D_t, and D_{25} is the diffusion coefficient of the target compound at 25°C.
317 The typical plots of mass diffused versus experiment time for the target pesticides in the diffusion
318 cell gave the slopes shown in Figure S4. All the data are shown in Table S4.
319 In order to compare with POCIS and Chemcatcher passive samplers, the sampling rate per unit
320 area for DGT was calculated using Equation (4).[31]

321 $$R_{S/A} = \frac{D_e}{\Delta g} \quad (4)$$

322 Table 2 shows that the $R_{S/A}$ values for the DGT sampler ranged from 0.76 to 32.7 mL (d cm^2)$^{-1}$.
323 For THI, ATR and LIN, the $R_{S/A}$ values for DGT were comparable with $R_{S/A}$ values reported in the
324 literature for POCIS and Chemcatcher.

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

326 Two experiments, testing the relationships of accumulated mass versus deployment time and
327 diffusion layer thickness, were carried out to validate the principle of DGT for measuring
328 pesticides. The masses of targeted chemicals accumulated by DGT increased linearly (for 7
329 chemicals sorbed by HLB and 5 chemicals with XAD18, R^2 values were higher than 0.99) with
330 time up to 87 h and agreed well with the theoretical line calculated by Equation (1) for most

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331 chemicals (see Figure S5). For DGT devices with HLB resin gel, the results for ETH showed
332 significant deviation from the theoretical line after deployment for 36 hours. For devices with
333 XAD resin gel, only three target chemicals, ATR, THI and CLO, followed the theoretical line. The
334 other six chemicals showed different degrees of deviation at different deployment times. These
335 results indicate that the performance of DGT with HLB is better than that with XAD18 gel for
336 measuring pesticides. A further test of the DGT principle for pesticides was carried out using HLB
337 DGT devices with different thicknesses of diffusive gel in a well stirred solution. The measured
338 mass of the target compounds that diffused through the diffusive gel layer was inversely
339 proportional to the diffusion layer thickness (Figure S6). The experimental data agreed well with
340 the theoretical line obtained from the Equation (1). Both results of time dependence and diffusion
341 layer thickness confirm the principle and mechanism of the DGT technique for pesticides in
342 solution.

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

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

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

351 To assess the pH effect on the DGT measurement, DGT devices were immersed in solutions with
352 the pH ranged from 4.7 to 8.2. The ratio of the target compound concentrations measured by DGT
353 (C_{DGT}) to their concentrations in the bulk solutions (C_b) were plotted against pH values (Figure

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354 S7). The results indicate that pH of the solution had no marked effect on the measurement by DGT
355 with HLB binding gel as most of the ratios (C_{DGT}/C_b) were between 0.9 and 1.1. However, for
356 DGT with XAD18 binding gel, the C_{DGT}/C_b ratios were below 0.9 at pH 7 for all tested compounds
357 and at pH 6 and 7.5 for most compounds. This could be due to less efficient and less effective
358 uptake of chemicals by XAD resin at more neutral pH range. These results demonstrate that DGT
359 with HLB binding gel can accurately measure concentrations of pesticides in the aquatic
360 environment with a wide range of pH, whereas DGT with XAD 18 binding gel has its limitations.
361 The effect of IS on DGT measurements was investigated in solutions with ionic strength similar
362 to freshwater, estuary water and seawater, ranging from 0.01 M to 0.5 M. For DGT with HLB
363 binding gel, there was no significant effect observed in the range of 0.01 M to 0.25 M, as shown
364 in Figure S8. The ratios of C_{DGT} to C_b were within 0.9 and 1.1 for all tested chemicals. At the IS
365 of 0.5 M (close to seawater), the DGT measured concentrations were slightly lower than expected.
366 The ratio of C_{DGT} to C_b was <0.9 for ATR, THI and CLO, and close to 0.9 for other six chemicals.
367 The viscosity of the solution is higher on addition of a large amount of NaCl, which impedes the
368 mass transfer process.[50]
369 The effect of DOM on measurements of target chemicals by DGT devices with HLB resin as
370 binding phase is demonstrated in Figure S9. The ratios of C_{DGT}/C_b were between 0.9 and 1.1 for
371 majority of the chemicals at various DOM concentrations up to 20 mg L^{-1}. The C_{DGT}/C_b ratios of
372 some chemicals, such as CHL, FLU, PIR and CLO were <0.9, but similar to the ratios for the
373 control solution where the DOM concentration was zero. These findings suggest that the
374 performance of DGT is independent of DOM concentration. Similar phenomena have been
375 observed in the study of Li et al.[51] using POCIS for pharmaceuticals and personal care products

376 (PPCPs) and endocrine disrupting chemicals (EDCs), where R_s was not affected by DOM. Li et
377 al.'s research on perfluorinated chemicals has also shown similar results.[52]
378 In general, the performance of DGT devices with HLB resin gel was better than the DGT devices
379 with XAD18 resin as the binding gel. DGT with HLB resin gel was therefore selected as suitable
380 for the future experiments and measurements.

381 **DGT for atrazine metabolites**

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

389 **Field applications in waters and soils**

390 ***In situ DGT deployments in river water***

391 The results of DGT deployments in the She River and Dahuofang Reservoir, north China are
392 presented in Figure 3. ATR was the only detectable target compound in both grab samples and in
393 DGT samplers.
394 DGT provides TWA concentrations of ATR over the exposure period. The similar concentrations
395 in the 3 locations of the river (Figure 3a) between two different deployment periods, 4 days and 7
396 days, indicate: i) the concentration of ATR during the 7 days was consistent without significant
397 variation; ii) the distribution of ATR in the 3 locations (about 50 meters apart) was similar and iii)
398 DGT performance was good during the long deployment period and not affected by environmental

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399 factors, such as biofouling. The deployment time could be extended longer as the DGT device has
400 a great capacity for all the targeted chemicals. However, the common problems for all passive
401 samplers such as biofouling and possible degradations may affect the accuracy of the
402 measurements for longer time deployments. As the river water flow was fast, the DBL was
403 neglected in calculating C_{DGT} as the DBL thickness was estimated to be much smaller than the
404 thickness of the diffusive gel. Deployment in the reservoir showed slightly greater variation in
405 DGT measured concentrations of ATR between three different locations and between two different
406 deployment times (Figure 3b), notably for locations L5 and L6. This is reasonable as the mixing
407 in the reservoir may be less efficient compared to the river. The concentrations of ATR in grab
408 samples were higher than DGT measured in situ concentrations. Although the differences were
409 small, relative to the measurements made and the techniques used, DGT usually gives lower values
410 than bulk water smpling because DGT only measures the available fraction which is dissolved and
411 able to diffuse through the diffusive gel. The measurement from the grab samples gives the total
412 concentration, including colloids and complexed fractions that may not be measured by DGT.
413 Several studies have also shown the advantage of DGT over grab sampling when measuring
414 chemical concentration in a changing environment.[27, 53]

415 ***DGT measurements in soils***

416 DGT devices were deployed in five different soils after wetting with water (Table S5) to test the
417 applicability of the technique for measuring pesticides and their metabolites in soils. ATR and it
418 metabolites were chosen as test compounds. The results are shown in Table 3. HA and DEA were
419 the primary metabolites measured and DIA and DACT were not detected in these soils, the
420 concentration of HA was much higher than that of DEA, indicating that the chemical degradation
421 pathway was favoured, rather than biological degradation., Although CYA was detected in soil F,

422 the result was not presented here since CYA could not be eluted efficiently from HLB resin in the
423 DGT performance test experiment. The extremely low concentration of ATR in soil F indicates
424 the fast degradation of ATR in that soil. Soil F was collected from highly productive agricultural
425 land with regular addition of fertilisers and pesticides; this is likely to make the microbial activity
426 much higher than in the other test soils,[54, 55] and therefore with much faster ATR degradation.
427 Although ATR was spiked to the same total concentration for all the soils, DGT measured
428 concentrations, C_{DGT}, varied between soils. The available ATR concentrations in soils M and D
429 were similar, but less than concentrations in soils R and K. This is likely due to much lower pH in
430 soils M and D, since adsorption of ATR to soil increases at lower pH.[56] The concentrations of
431 metabolites in soils M and D were greater than those in soils R and K, consistent with findings by
432 other researchers that hydrolysis of ATR decreases with increasing soil pH.[57] Although organic
433 matter content enhanceddegradation of ATR,[13] pH seemed to have more influence due to the big
434 range in pH in those soils.

435 **CONCLUSIONS**

436 A novel DGT sampling technique on measurement for 9 pesticides has been successfully
437 developed through systematic performance tests, HLB resin was selected as binding agent and
438 agarose as diffusive gel. The DGT sampler can provide comparable sampling rate per unit area
439 ($R_{S/A}$) to other passive samplers. The measurement of these pesticides using DGT was independent
440 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
441 wide range of environmental conditions. It is capable of measuring pesticide metabolites, implying
442 its potential of exploring the environmental fate and behaviour of organic chemicals. It has also
443 been assessed under field conditions. This study has demonstrated that DGT sampler with HLB

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444 resin gel is a reliable technique for *in situ* measurement of several groups of pesticides in waters
445 and soils.

446 **SUPPORTING INFORMATION**

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

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453 **ACKNOWLEDGEMENT**

454 The authors thank Dr. Hao Cheng for assistance in making gels, Dr. Shane Rothwell for assistance
455 in soil sampling, and Mr. Chunlong Xia and Mr. Puyu Xi for helping in water sampling. We are
456 grateful to the Chinese Scholarship Council (CSC) for sponsorship of Yanying Li.

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638

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

Test Chemicals	IDL (μg L^{-1})	Lab sample MDL (μg L^{-1})		Field sample MDL (ng L^{-1})	
		Water	DGT	Water	DGT
CHL	0.08	0.09	0.04	0.17	0.61
THI	0.23	0.26	0.14	0.64	1.94
FLU	0.11	0.13	0.06	0.23	0.91
ATR	0.05	0.06	0.03	0.11	0.48
PIR	0.29	0.33	0.19	0.63	2.73
LIN	0.09	0.09	0.06	0.17	0.79
PYR	0.14	0.15	0.09	0.31	1.29
CLO	0.10	0.11	0.07	0.23	0.97
ETH	0.05	0.06	0.03	0.12	0.50

641
642
643
644 **Table 2.** Comparison of $R_{S/A}$[b] (mL(d cm^2)$^{-1}$) for DGT at 25°C and some other passive samplers

	CHL	THI	FLU	ATR	PIR	LIN	PYR	CLO	ETH
DGT $R_{S/A}$	5.68	5.33	5.51	4.90	4.88	4.92	4.95	4.89	4.59
POCIS $R_{S/A}$	-[a]	3.97[58c] - 16.77[58c]	-	0.76[58c] – 5.83[59d]	-	3.43[58c] – 23.12[58c]	-	-	-
Chemcatcher $R_{S/A}$	-	-	-	4.78[60e] – 32.70[61f]	6.29[62g] – 23.9[63h]	3.27[60e] – 8.18[63h]	-	-	5.03[62g]

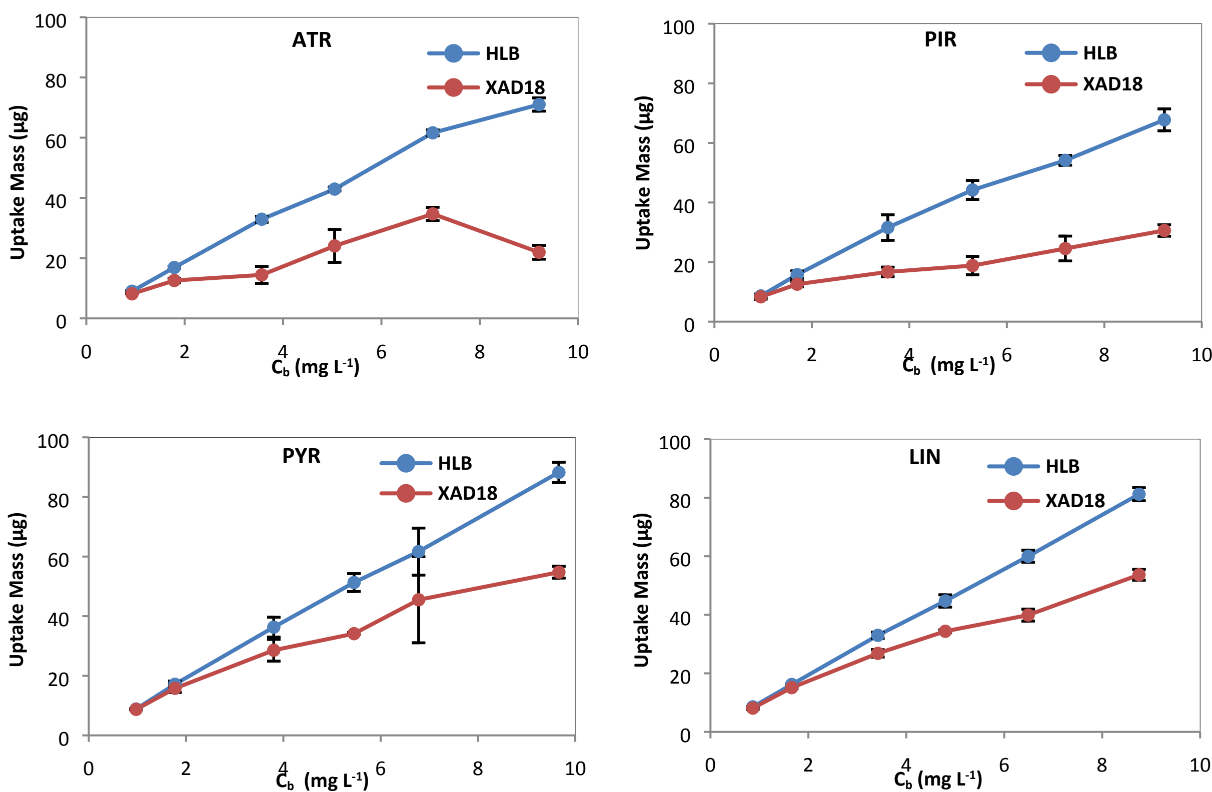
645 a: no data available
646 b: $R_{S/A}$ values were calculated according to $R_{S/A} = R_S /A$ where R_S is sampling rate and A is
647 exposure area of the sampler. The values for A were: c: 45.8 cm^2; d: 41 cm^2; e, f, g, h: 15.9 cm^2.
648 The temperature values were: c: 29±3 ºC; d: 17±1 ºC; e: 20 ºC; f: 16.4-17.4 ºC; g: 5-20 ºC; h: 14.25
649 ºC
650

651

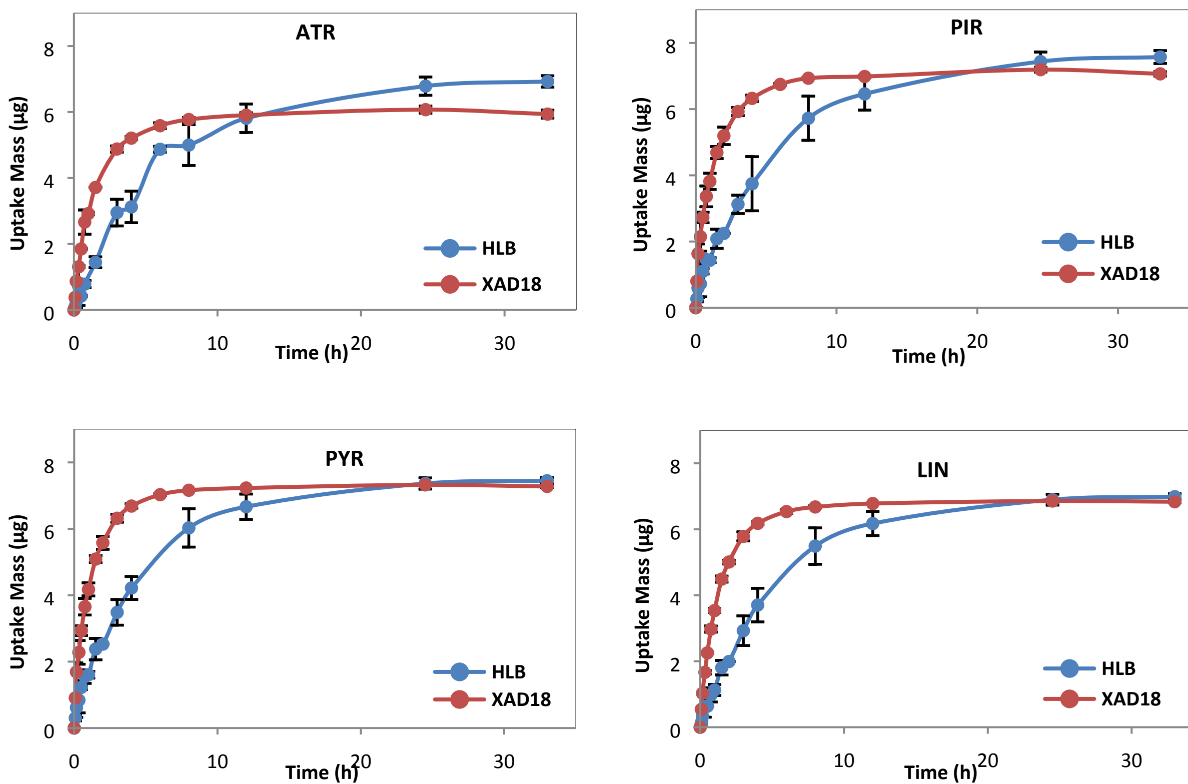
652 **Table 3.** DGT measured concentrations of ATR and its metabolites in soils expressed in mg L^{-1}

	Soil M	Soil D	Soil F	Soil R	Soil K
ATR	3.430	3.305	0.001	4.059	4.034
HA	0.331	0.406	0.029	0.269	0.141
DEA	0.042	0.039	<MDL	0.007	0.003

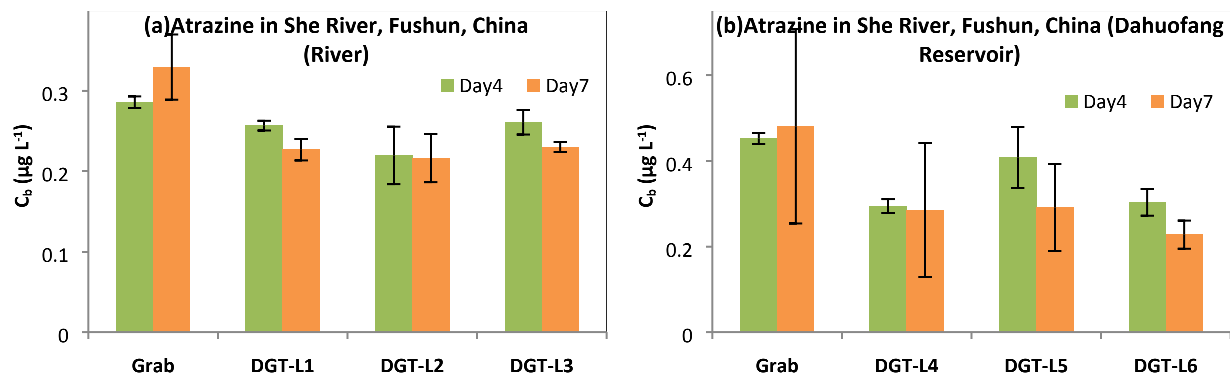
653 CYA was detected in samples from soil F. As CYA cannot be eluted effectively from the HLB
654 resin gel, the data in soil F would not be accurate and meaningful. Terfore, it is not presented here.



655 **Figure 1.** Masses of four pesticides (ATR, LIN, PIR and PYR) taken up by two types of binding
656 gels with HLB and XAD18 resins at different concentrations (1-10 mg L^{-1}) (IS = 0.01 M, pH = 5.8
657 ± 0.2, T = 20 ± 2 °C; n=3). Error bars were calculated from the standard deviation (SD) of three
658 replicates.



659 **Figure 2.** Binding kinetics of selected test chemicals by HLB and XAD18 resin gels in 40 mL
660 solutions of 200 μg L^{-1} test chemicals (IS = 0.01 M, pH = 6.0 ±0 .1, T = 21 ± 1 ℃; n = 3). Error
661 bars were calculated from the standard deviation (SD) of three replicates.



662 **Figure 3.** Average concentration of ATR measured by DGT devices *in situ* during two different
663 deployment times (4 days, in green, and 7 days, in orange) in (a) She River (in three different
664 locations, L1, L2, and L3) and (b) in Dahuofang Reservoir (in three different locations (L4, L5,
665 and L6). Grab samples were taken for both deployment period.