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

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Measuring Pesticides in Waters and Soils

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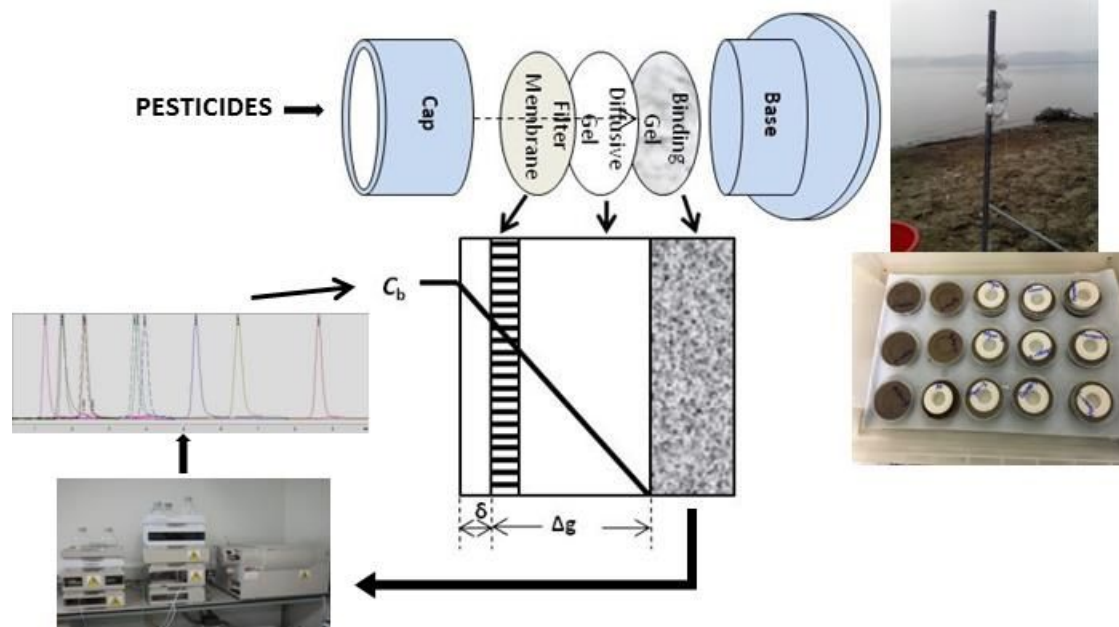
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22 **ABSTRACT**

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

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 *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

4

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

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).

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.

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.

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.

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    $21.5 \pm 1.6\,°C$.

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

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.

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 $24 \pm 2\,°C$) 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.

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 $21 \pm 2°C$) 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.

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 $20 \pm 1°C$. 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).

11

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 $21 \pm 1°C$. 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)

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

14

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

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
$$R_{S/A} = \frac{D_e}{\Delta g} \tag{4}$$

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

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

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

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

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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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 ($\mu g\ L^{-1}$)	Lab sample MDL ($\mu g\ L^{-1}$)		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

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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.
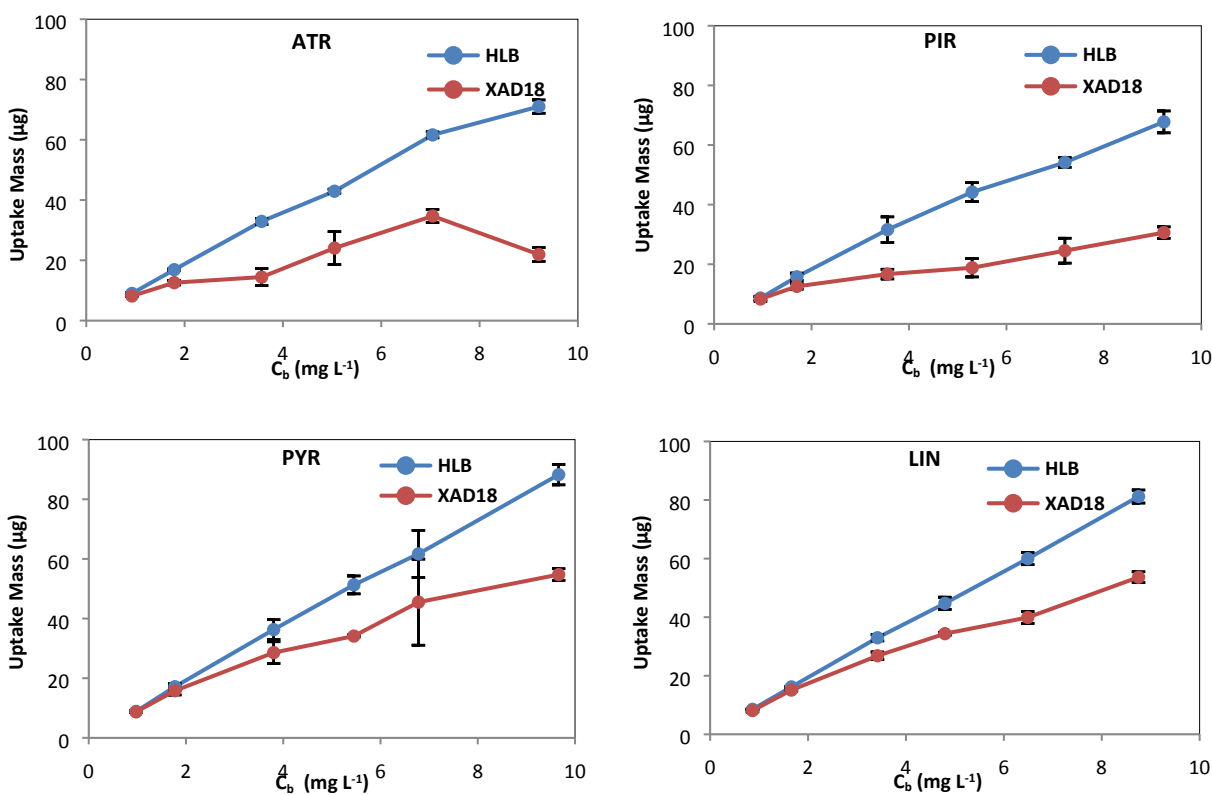
655   **Figure 1.** Masses of four pesticides (ATR, LIN, PIR and PYR) taken up by two types of binding

656   gels with HLB and XAD18 resins at different concentrations (1-10 mg L^{-1}) (IS = 0.01 M, pH = 5.8

657   $\pm$ 0.2, T = 20 $\pm$ 2 °C; n=3). Error bars were calculated from the standard deviation (SD) of three

658   replicates.
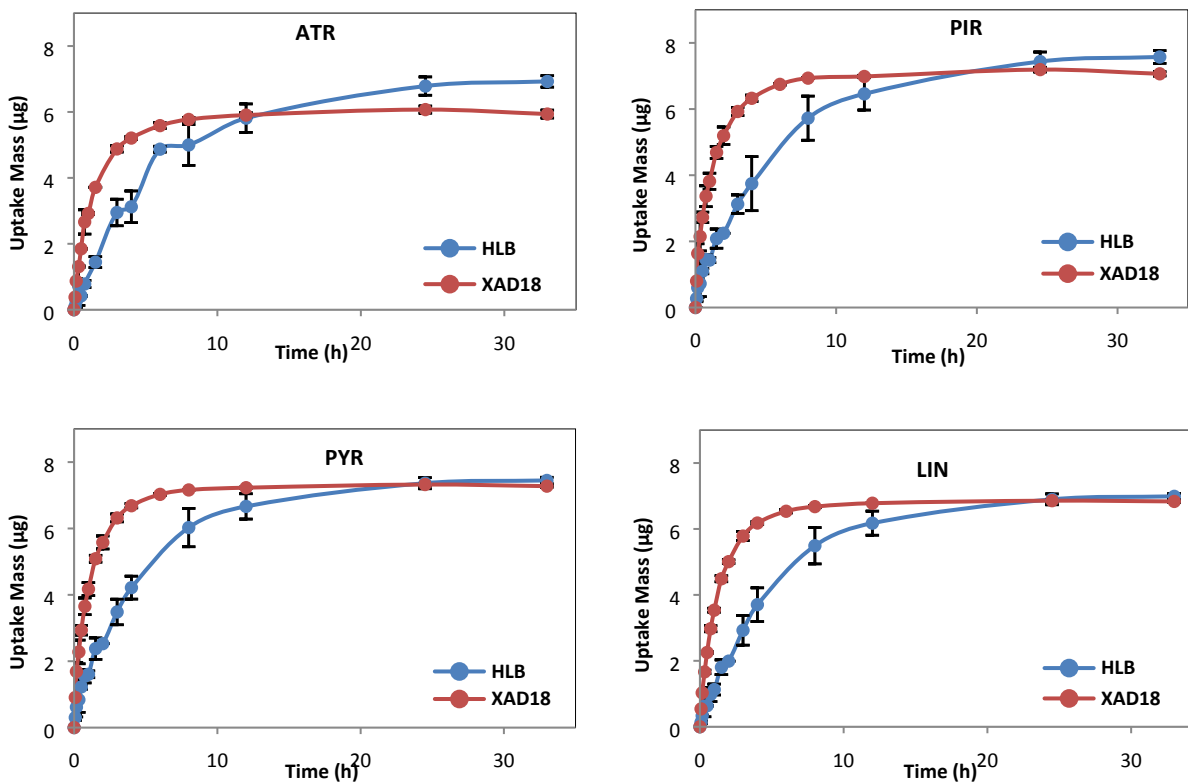
659   **Figure 2.** Binding kinetics of selected test chemicals by HLB and XAD18 resin gels in 40 mL

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.

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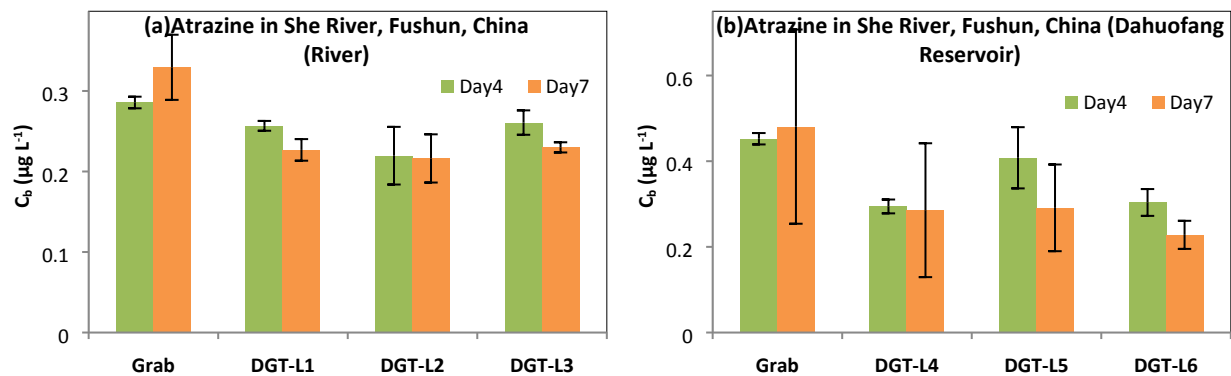
662   **Figure 3.** Average concentration of ATR measured by DGT devices *in situ* during two different

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.