Diffusive Gradients in Thin-films (DGT) for *in situ* Measurement of Neonicotinoid Insecticides (NNIs) in Waters

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21 ABSTRACT

Neonicotinoid insecticides (NNIs) are among the most widely-used insecticides, 22 23 although their threat to non-target organisms has attracted attention in recent years. In 24 this study, a diffusive gradient in thin-films (DGT) passive sampling technique was 25 developed for in situ monitoring of time-weighted average (TWA) concentrations of 26 NNIs in groundwater and wastewater. Systematic studies demonstrated that DGT with 27 HLB as binding gels (HLB-DGT) is suitable for quantitative sampling of NNIs under 28 a wide range of conditions, independent of pH (5–9.5), ionic strength (0.001–0.5 M) 29 and dissolved organic matter (0–10 mg/L). The performance of HLB-DGT devices was 30 also independent of the typical groundwater ionic environments. The thicknesses of in-31 situ measured diffusive boundary layer were 0.35 and 0.25 mm in the groundwater and 32 effluent, respectively. HLB-DGT can provide TWA concentrations over 14-18 days 33 deployment with linear uptake in both groundwater and wastewater. Concentrations and 34 occurrence patterns of NNIs obtained by HLB-DGT were in accordance with those 35 measured from grab samples. The reliability and stability of the HLB-DGT for 36 measuring NNIs in the groundwater and wastewater were confirmed and can be used to improve understanding of the occurrence and fate of NNIs in surface water and 37 38 groundwater.

39 Keywords: Neonicotinoid insecticides, Passive sampling, Diffusive gradients in thin-

40 films (DGT), Groundwater, Wastewater

41 SYNOPSIS

- 42 A diffusive gradient thin-films (DGT) passive sampler for *in-situ* monitoring of 9 NNIs
- 43 in groundwater and wastewater was developed and the reliability of the technique was
- 44 demonstrated in field trials.

45 **GRAPHIC FOR TABLE OF CONTENTS (TOC)**



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48 **1. INTRODUCTION**

Neonicotinoid insecticides (NNIs) are selective systemic insecticides synthesized 49 by modifying the structures of natural nicotinoids.¹ Compared to traditional insecticides 50 51 (e.g., organophosphates, aminomethyl and pyrethroids), NNIs are considered to be 52 relatively less toxic to mammals, fish and birds². Therefore, NNIs rapidly became one 53 of the most widely used insecticides, accounting for > 25% of the global insecticide market³. However, some NNIs (e.g., Imidacloprid (IMI)) have been shown to be highly 54 toxic to non-target pollinators and invertebrate insects,⁴ threatening biodiversity.⁵ The 55 56 extensive use and potential ecological risks of NNIs are therefore causing increasing 57 concerns. Recently, the European Commission completely banned the application of 3 NNIs (IMI, Clothianidin (CLO) and Thiamethoxam (TMX))⁶⁻⁸ and the US restricts the 58 use of Dinotefuran (DIN).9 59

60 After application, a high proportion of the active ingredients of NNIs remain in soils,¹⁰ or can leach out and contaminate surface water and groundwater during heavy 61 62 storm events, due to their high water solubility. In addition, non-agricultural 63 applications such as horticulture and pet flea control also consume large amounts of 64 NNIs, which are not effectively removed when they enter wastewater treatment plants (WWTPs) and are subsequently discharged to receiving water.^{11, 12} NNIs have been 65 detected in surface water,^{13, 14} groundwater,¹⁵ and drinking water¹⁶ around the world. 66 Therefore, it is crucial to maintain regular monitoring of NNIs in waters. Meanwhile, > 67 50% of global water demand is currently supplied by groundwater,¹⁷ and the frequent 68

detection of NNIs in groundwater is a matter of concern.^{18, 19} However, it is difficult to
assess the contamination levels and trends of NNIs in aquifers because NNIs exist at
low concentrations that are analytically challenging.

72 Effective monitoring methods are crucial for accurately quantifying the behaviour and potential risks of NNIs in the aquatic environment. Currently, active sampling such 73 as grab sampling, remains the dominant sampling method for NNIs.¹⁸⁻²¹ However, grab 74 sampling can be affected by short-term events (e.g., flooding, heavy rainfall and tidal 75 changes), so can only provide a "snapshot concentration" which is not representative.²² 76 77 Passive sampling can overcome these problems by providing *in-situ* time-weighted average (TWA) concentrations,²³ with the following advantages: high sensitivity while 78 avoiding tedious pre-treatment, cleaner matrices,²⁴ and avoidance of target compound 79 losses due to morphological changes during transport or storage.²⁵ So far, only semi-80 81 quantification of 7 NNIs (i.e., IMI, CLO, TMX, DIN, acetamiprid (ACE), Nitenpyram 82 (NIT) and thiacloprid (THI)) has been conducted using the polar organic chemical integrative samplers (POCIS) and Chemcatcher passive samplers.^{26, 27} It is known that 83 the sampling rates (R_s) of POCIS and Chemcatcher are strongly influenced by 84 85 hydrodynamic conditions, so field or laboratory calibration is required, which is not 86 always effective.²⁸ This could particularly be a problem in groundwater with near-static 87 flow rates, where even the most accurate calibration method of POCIS, performance reference compounds, may fail to achieve accurate quantification.²⁹ In contrast to other 88 89 passive samplers, the diffusive gradients in thin-films (DGT) technique, based on Fick's

90	first law of diffusion with a defined diffusion path length, ³⁰ is more quantitative and
91	relatively unaffected by hydrodynamic conditions. ³¹ Owing to these advantages, DGT
92	is becoming popular for monitoring organic pollutants associated with industrial and
93	household products, ³² including antibiotics, ³³ household and personal care products
94	(HPCPs), ²⁴ synthetic musks (SMs), ³⁴ denatonium benzoate (DB), ³⁵ per- and
95	polyfluoroalkyl substances (PFASs), ³⁶ artificial sweeteners (ASs), ³⁷ polycyclic
96	aromatic hydrocarbons,38 etc. DGT devices for surface water monitoring are well
97	established, while only a few DGT studies have been carried out in groundwaters. ³⁹⁻⁴¹
98	Thus, their effectiveness in detecting organic contaminants in groundwater under the
99	near-static hydrodynamic conditions with ion-rich hydrochemical environments
100	requires further investigation and validation.

101 The objectives of this study were to (1) evaluate the performance of 3 kinds of 102 resins as binding gels for development of DGT technique to accurately quantify 9 NNIs, 103 (2) assess the effects of typical environmental factors (ionic strength (IS), pH and 104 dissolved organic matter (DOM)) and typical ions in groundwater on the performance 105 of DGT, and (3) validate the suitability of developed DGT for *in-situ* measurement of 106 NNIs in groundwater and wastewater.

107 2. MATERIALS AND METHODS

108 2.1 Standards and Reagents

High-purity standards of 9 commercial NNIs, IMI, CLO, TMX, DIN, THI, ACE,
NIT, Flonicamid (FLO), and Imidaclothiz (IMIT), were selected for DGT testing in this

study. 4 deuterated NNIs, namely CLO-d₃, TMX-d₃, IMI-d₄ and ACE-d₃, were
purchased and used as isotope-labelled internal standards (ISs) for NNIs quantification.
Acetonitrile and methanol were used to extract NNIs from the binding gels. Details of
the standards, chemicals and reagents are given in the Supporting Information (SI
Text S1 and Table S1).

116 **2.2 DGT Preparation**

117 The DGT (Figure S1) utilizes a sandwich design comprising a standard plastic 118 moulding (base and cap) for securing the gel layers, a binding gel to adsorb the target 119 chemicals, a diffusive gel to allow free diffusion, and a filter membrane to guard against particle damage to the gel layers during long-term deployment.⁴² Three resins, namely 120 121 PLS (Dikma, China), HLB and WCX (Waters, US) were investigated for their suitability as the binding gels. HLB and WCX resins have been used in solid phase 122 extraction (SPE) for the enrichment of NNIs in water,^{18, 26} while PLS resin possesses 123 124 similar properties to HLB resin (Text S1). The resins were thoroughly cleaned with 125 Ultrapure water (UPW) and methanol before gel making. Polyacrylamide (PA) 126 diffusive gels, agarose (AG) diffusive gels (1.5%) and binding gels were prepared according to well-documented procedures.43,44 127

128 2.3 Sample Extraction, Analysis and Concentration Calculation

Acetonitrile and methanol were compared as extraction solvents, based on the previous SPE procedures.^{18, 19} Extraction recoveries with different extraction conditions were then further evaluated to find the best extraction solvents, as detailed in **Text S2**. An efficient extraction method was achieved with a single ultrasonic extraction for 30min with 5 mL acetonitrile.

134 High-performance liquid chromatography coupled with a photodiode array 135 detector (HPLC-DAD, Thermo U3000, US) was employed to analyse the matrix-clean 136 laboratory samples. A liquid chromatography-tandem mass spectrometer (LC-MS/MS, 137 Waters Xevo TQS, UK) was used to analyse the field samples. Details of the sample pre-treatment procedures and specific methods for both instruments are given in Text 138 139 **S3.** Table S2 provides instrumental detection limits (IDL), calculated based on the 140 signal/noise ratio $(S/N) \ge 3$ and method detection limits (MDL), according topublished methods.²⁴ Details of the quality assurance and quality control (QA/QC) procedures for 141 142 full experimental procedures are listed in Text S4.

143 DGT measures the TWA concentration of NNIs during deployment (C_{DGT}), which 144 can be expressed as eq 1:⁴²

145
$$C_{\rm DGT} = \frac{M(\Delta g + \delta)}{DAt}$$
(1)

146 where *M* represents the mass of target chemical accumulated in the binding gel layer 147 (mg), Δg is the thickness of the diffusive layer (cm), δ expresses the thickness of the 148 diffusive boundary layer (DBL, cm), *D* is the diffusion coefficient of the target chemical 149 in the diffusive gel (cm² s⁻¹), *t* is the exposure time (s) and A is the exposure window 150 area of the cap (cm²). When the thickness of DBL can be neglected compared to Δg , 151 C_{DGT} can be expressed as eq 2:⁴²

152
$$C_{\rm DGT} = \frac{M\Delta g}{DAt}$$
(2)

153 2.4 Performance Testing of DGT in the Laboratory

154 2.4.1 Adsorption by DGT Components

155 The materials used to assemble the DGT device were evaluated for possible adsorption of target NNIs (Details in Text S3). The plastic DGT mouldings, 3 resin-156 based binding gels (HLB, PLS and WCX), 2 diffusive gels (PA and AG) and 5 filter 157 membranes (polyethenesulfone (PES), hydrophilic polypropylene (GHP), cellulose 158 acetate (CA), polyamide (NL16) and water wettable polytetrafluoroethylene 159 160 (wwPTFE), details in Figure S2) were exposed to a solution containing ca. 200 μ g/L 161 of NNIs and shaken for 20 hours (h). 2.4.2 Uptake Capacity of DGT and Binding Gel Uptake Kinetics 162 163 Adequate capacity for absorbing the target chemicals is an essential requirement of a binding gel in the DGT device. Gel discs were exposed to 10 mL of solutions with 164 165 different NNI concentrations up to about 12 mg/L and then shaken for 20 h (Details in

166 Text S3). Rapid adsorption of target chemicals by binding gels is a precondition for

- accurate measurement of DGT. To test for this, gel discs were placed in 10 mL of 200
- 168 μ g/L NNIs solutions and shaken for 24 h (Details in Text S3).

169 2.4.3 D and Rs Measurement

- 170 A diffusion cell with 2 compartments (i.e., source and receiver)²⁴ was used to
- 171 measure the diffusion coefficients (D) of 9 NNIs through AG gels at 25 and 30 °C.
- 172 Details of the experiments and calculation of *D* are given in Text S5.
- $R_{\rm S}$ is an important parameter for assessing the performance of passive samplers; it

174 is necessary to calculate TWA concentrations with POCIS and Chemcatcher.^{27, 45} 175 Although $R_{\rm S}$ is not used for DGT, to further quantitatively assess the sampling capacity 176 of the 3 passive samplers with different principles, the sampling rate per unit area ($R_{\rm S/A}$) 177 was introduced to standardise the data. The $R_{\rm S/A}$ of POCIS and Chemcatcher were 178 calculated using published $R_{\rm S}$ data and $R_{\rm S/A}$ of DGT was calculated using eq 3:²⁴

179
$$R_{S/A} = \frac{D}{\Delta g}$$
(3)

180 2.4.4 Time Dependence

181 DGT devices were deployed in 2.5 L of 50 μ g/L NNIs solutions for various times 182 up to 60 h (Details in Text S3), to check whether DGT devices can continuously 183 accumulate NNIs from water, in line with the theoretical prediction of eq 2.

184 2.4.5 Effects of IS, pH and DOM

185 The performance of DGT devices was evaluated across a wide range of IS (0.001–

186 0.5 M), pH (3.5–9.5) and DOM (0–20 mg/L). DGT devices were deployed in 2.5 L of

187 100 μ g/L NNI solutions for 20 h with different IS, pH and DOM concentrations

188 (Details in Text S3). To evaluate the performance of the DGT device under different

- 189 conditions more intuitively, the ratio of C_{DGT} (calculated by eq 2) to the directly
- 190 measured NNI solutions concentration ($C_{\rm S}$) was applied.²⁴ When $C_{\rm DGT}/C_{\rm S}$ falls within
- 191 0.9 to 1.1, it indicates good DGT performance.

192 2.4.6 Effect of Typical ions in Groundwater

193 The abundance of ions in groundwater is generally higher than in surface water,

194 due to mineral dissolution, resulting in different chemical compositions of groundwater,⁴⁶ which may affect the adsorption of target analytes by DGT.⁴⁷ To verify 195 196 the DGT applicability in groundwater, DGT devices were deployed (Details in Text S3) in a synthetic groundwater environment containing 6 major ions (Ca²⁺, Mg²⁺, Na⁺, 197 HCO₃⁻, SO₄²⁻, and Cl⁻) at different concentrations (Table S3). Groundwater ionic 198 species were selected according to the Shukarev classification⁴⁸ and 4 different groups 199 200 of the concentrations were set up based on typical concentration ranges in groundwater. 201 DGT devices were deployed in approximately 2.5 L of 100 μ g/L NNI simulated 202 groundwater solutions for 20 h.

203 2.5 Field Trials in Groundwater and Wastewater

204 To further confirm the applicability of DGT devices in the aquatic environment, 205 two of the most challenging conditions, namely groundwater and wastewater, were 206 selected. HLB-DGT devices were deployed for up to 28 days in groundwater 207 environmental monitoring wells in an agricultural area and the effluent from a WWTP 208 in Wuhan, central China, to check whether the HLB-DGT devices were continuing to 209 accumulate NNIs in waters (Text S6). 500 mL active grab water samples were collected 210 (in duplicate), and water temperature and pH (Table S4) were measured at each DGT deployment and retrieval. HLB-DGT devices with different thicknesses of diffusive 211 gels were deployed simultaneously in the groundwater and effluent to determine the in-212 213 situ DBL thickness (Text S6). Detailed procedures of sample treatment and analysis are 214 presented in Text S2.

215 **3. RESULTS AND DISCUSSION**

216 3.1 Pre-evaluation of DGT components and binding gels, and 217 optimisation of binding gel extraction

218 Full details of results and discussion for this section were given in SI, key results 219 are shown here. Briefly, no significant adsorption (ANOVA, p > 0.05) was found for 9 NNIs to the DGT mouldings (Figure S2). AG and PA diffusive gels both showed < 10% 220 221 adsorption of NNIs. Considering their accessibility, AG gels were therefore preferred 222 and used in subsequent studies. PES membranes showed severe adsorption of major 223 NNIs (average 26%). CA and NL16 membranes presented moderate adsorption (average 12%) of 9 NNIs, while GHP and wwPTFE caused only slight adsorption 224 225 (average 6.4%). Due to the discontinuing supply for GHP filters, wwPTFE filters were 226 chosen for the subsequent experiments.

227 HLB and PLS showed better adsorption for NNIs than WCX (Figure S3). 228 Therefore, HLB and PLS resins were selected for further evaluation. Acetonitrile was 229 selected as the extraction solvent because of stable extraction recoveries > 80% for 230 NNIs, based on pre-experiments for HLB binding gel extraction. Increasing extraction solvent to 10 mL or two times of 30 min ultrasonic extractions did not significantly 231 (ANOVA, p > 0.05) improve the recoveries, so a simple and effective extraction method 232 of ultrasonic extraction of the binding gels with 5 mL acetonitrile for 30 min (Figure 233 **S4**) was selected, which could reliably extract NNIs from both HLB and PLS gels 234 235 (Table S5 and Figure S5).

236 3.2 Adsorption Capacity and Absorption Kinetics of the Binding Gel

237 No significant difference (ANOVA, p > 0.05) in adsorption capacities was 238 observed between HLB and PLS resin gels for all NNIs (Figure S6). The adsorption of 239 8 NNIs by the resins increased linearly in the solution concentrations range of at least 6 mg/L (except for DIN at 1 mg/L). Based on the linear portion of the curves, the 240 241 maximum adsorption capacities per gel disc were estimated. Then, the maximum concentrations of NNIs measured by DGT in water were calculated using eq 2. Table 242 243 **S6** shows that the DGT devices can be deployed for 1 month at concentrations ranging 244 from ~10 (DIN) to ~80 (THI) μ g/L in the environment. Concentrations of NNIs reported in the aquatic environment are typically $< 1 \mu g/L$, ^{12, 18-21} confirming that both 245 246 HLB and PLS-DGT devices are suitable for the long-term monitoring of NNIs in the 247 field.

248 The adsorption of all NNIs by the 2 binding gels increased rapidly with time during 249 the initial 120 min (ca. 50% uptake), followed by slower linear adsorption (Figure S7). 250 The rapid adsorption during the initial 120 min demonstrated the effective 251 preconcentration properties of both binding gels. This indicates that once NNIs have 252 diffused across the diffusive layer to the interface between the diffusive layer and the 253 binding gel, they can be rapidly adsorbed by both binding gels. DGT achieves complete 254 quantification of the targets based on 0 concentration at the interface between the binding and diffusive gels, so rapid initial uptake is essential.³⁰ 255

256 **3.3** *D* and *Rs* Measurement

The D values were measured with a diffusion cell at 25 °C and 30 °C, then 257 258 calculated using eq S1 in SI, based on the slope of the mass versus time of tested NNIs 259 within the receiving compartment (Figure S8). D values at other temperatures (1-35 °C)were calculated using eq S2 (listed in Table S7). The difference between the directly 260 261 measured (eq S1) and the calculated (using eq S2 based on values at 25 °C) D values at 30 °C is within 20% for all NNIs studied, indicating the reliability of the D262 263 measurement in this experiment. $R_{S/A}$ values (Table S8) of NNIs for the developed DGT 264 ranged from 4.78 (NIT and IMIT) to 6.10 mL / (d cm²) (TMX), generally greater than 265 those of POCIS and Chemcatcher. Notably, the $R_{S/A}$ values of NNIs for POCIS and 266 Chemcatcher showed considerable variability in different studies, which may be because their $R_{\rm S}$ are strongly influenced by hydrodynamic conditions.²⁸ The $R_{\rm S/A}$ values 267 for DGT vary less,⁴⁹ which indicates it'slower hydrodynamic dependence. 268

269 **3.4 Time dependence**

Time dependence experiments are important to confirm the effectiveness of the DGT principle for the target chemicals. Overall, both HLB and PLS-DGT devices adsorbed most NNIs linearly over 60 h deployment time (except DIN), which is in good agreement with the theoretical line calculated using eq 2 (Figure 1 and Figure S9). However, the HLB-DGT maintained theoretical linear adsorption better for all NNIs than PLS-DGT. DIN was the only exception; itaccumulated linearly and in line with the theoretical line for the first 24 h and then showed a slightly decreasing linear

adsorption after 24 h. Despite the excellent retention ability of HLB and PLS for polar compounds, the retention for strongly polar targets remains unsatisfactory. DIN was the most polarized ($\log K_{OW} = -0.19$, in **Table S1**) among 9 NNIs, which may explain the slight decrease in its adsorption by binding gels after 24 h. Modification of the existing DGT configuration or further calculation with additional parameters are needed to improve the performance for DIN.



Figure 1: Measured masses (M, μ g) of IMI, CLO, and TMX by DGT devices with HLB and PLS binding gels deployed in well-stirred solution for different durations (IS = 0.01 M, pH = 6.0 ± 0.2, T = 22 ± 1 °C;

n = 3). The solid lines are theoretical lines predicted by eq 1. Error bars: 1 standard deviation (SD).

287 **3.5 Effect of IS, pH, and DOM**

The IS affects the diffusion of charged species in the diffusive layer by influencing the surface charge of the diffusive layer (Donnan potential)⁵⁰ and also affects the solubility of organic matter through the "salting-out effect".⁵¹ $C_{\text{DGT}}/C_{\text{S}}$ of HLB-DGT for 9 NNIs were mostly between 0.9 and 1.1 over the IS range of 0.001–0.5 M, indicating the accuracy of HLB-DGT for the NNI quantification was not significantly (ANOVA, p > 0.05) affected by the IS (**Figure 2a** and **Table S9**). Although it has been 294 shown previously that the adsorption of target chemicals on HLB decreased significantly at IS of 0.5 M,²⁴ this was not seen in this study. For PLS-DGT, $C_{\text{DGT}}/C_{\text{S}}$ 295 296 values for all NNIs were generally lower than 0.9 at 0.5 M IS (Figure S10), similar to the case when XAD-18 was used as a binding gel for antibiotics.⁴³ The results indicated 297 298 that PLS-DGT was not suitable for applications in environments with high IS (e.g., 299 seawater). Therefore, in subsequent experiments, only HLB-DGT was tested. For ionisable organic compounds, their speciation in the aqueous environment is 300 301 regulated by pH and pKa, which may influence the diffusion behaviour of the chemicals in the DGT.⁴³ $C_{\text{DGT}}/C_{\text{S}}$ values of the tested NNIs ranged from approximately 0.9 to 1.1 302 for the pH range of 5.0-9.5 (Figure 2b and Table S10), indicating HLB-DGT 303 performance was unaffected by pH of natural waters (ANOVA, p > 0.05). However, 304 305 $C_{\text{DGT}}/C_{\text{S}}$ values for 9 NNIs were higher than 1.1 at pH 3.5. This may be due to changes 306 in the speciation of the NNIs under acidic conditions, resulting in different 307 physicochemical properties (e.g., K_{OW}, adsorption behaviour, photo reactivity). Similar phenomena were observed when MCX-DGT was used to measure DB35 and 308 melamine⁵² under acidic conditions and WAX-DGT for PFASs³⁶ under alkaline 309 310 conditions. These findings demonstrated that for the tested NNIs, the performance of 311 DGT is generally independent of the pH of the solution between 5 and 9.5, so that DGT 312 can be applied directly to most field conditions in this pH range.



Figure 2: Effect of IS (a), pH (b), DOM (c) and typical groundwater ions (d) on HLB-DGT measurement (IS = 0.01 M, $T = 25.0 \pm 0.5$ °C, pH = 7.0 ± 1.0; n = 3). The dotted horizontal lines represent the values at 0.9 and 1.1. Error bars: 1SD.

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317 DOM can complex with the chemicals to alter their diffusion, or compete with the chemicals for adsorption sites on the binding gel.⁵³ $C_{\text{DGT}}/C_{\text{S}}$ values of most of the tested 318 319 NNIs were in the range of 0.9–1.1 when the DOM concentrations were between 0 to 10 320 mg/L. However, when the concentration of DOM was increased to 20 mg/L, C_{DGT}/C_{S} 321 were > 1.1 for most of NNIs (Figure 2c and Table S11). The overall results of C_{DGT}/C_S showed a slight positive correlation as the concentration of DOM increased. Generally, 322 DOM can compete or form complexes with the analytes, resulting in a decrease in 323 $C_{\text{DGT}}/C_{\text{S}}$.³² Interestingly, in this study, $C_{\text{DGT}}/C_{\text{S}}$ values increased with increasing DOM 324 325 concentrations, possibly due to DOM enhancing the diffusion and adsorption of NNIs 326 to DGT. Similar phenomena were also found in the sorption of dibutyl phthalate by

soil⁵⁴ and in the development of DGT for melamine.⁵² Overall, the developed HLBDGT was accurate for the NNI quantification in the concentration range of 0–10 mg/L
DOM.

330 **3.6 Effect of Typical Groundwater Ions**

331 DGT applications in groundwater have so far only focused on the effects of nearstatic hydrodynamic conditions, ignoring the potential effects of the ions in 332 groundwater.^{29, 55} Ions may affect the sampling performance of DGT by competing for 333 adsorption, reacting with target compounds⁴⁷ and influencing diffusion.⁵⁰ C_{DGT}/Cs 334 335 values ranged from 0.9 to 1.1 (Figure 2d and Table S12) for almost all NNIs in 4 groups 336 of concentration gradients (Table S3), indicating that HLB-DGT performance for NNIs 337 is independent of the ionic environment of groundwater. The exception is DIN, slightly 338 below 0.9 with an average of 0.84. The HLB adsorption of DIN is lower compared to 339 other NNIs (Figures S6 and S7) and the competing of ions from the groundwater may 340 further reduce the adsorption of DIN by HLB resins. Overall, HLB-DGT is insensitive to typical groundwater ionic environments, and this feature makes HLB-DGT 341 342 potentially suitable for monitoring NNIs in groundwater.

343 3.7 In-Situ Measurement of DBL

Details of the DBL calculation based on the DGT measurements can be found in **Text S6.** The *in-situ* DBL thickness was in the range of 0.05–0.44 mm (**Figure S11**) for the effluent and 0.30–0.40 mm (**Figure S12**) for the groundwater in this study. To ensure the accuracy of the DGT TWA concentration calculation, average DBL thicknesses of 0.35 and 0.25 mm were applied to eq 1 for the groundwater and effluent,
respectively.

350 The average *in-situ* DBL thickness (0.35 mm) for the groundwater in this study 351 was much less than that in tube wells (average DBL ranged from 1.98 to 3.03 mm) when measuring nitrate concentrations in a bioreactor,⁵⁶ and was lower than the DBL 352 353 range (0.76-1.05 mm) when DGT devices were staticly suspended in groundwater wells of different diameters for nitrate measurement in New Zealand.⁵⁵ The lower DBL 354 355 thickness in the wells of this study may be caused by the groundwater flow, due to 356 pumping for irrigation by farmers during DGT deployment, which is similar to the impact of the universal DGT monitoring system⁵⁵ on the DBL. The in-situ DBL 357 358 thickness (average 0.25 mm) for the effluent was lower than it in a WWTP (0.29-1.28 mm, average 0.62 mm) from Canada,⁵⁷ but was higher than it in the effluent stream of 359 a WWTP (0.05-0.09 mm, average 0.07 mm; 0.06-0.11 mm, average 0.08 mm) in 360 England.^{24, 49} The difference of DBL probably reflects the different flow rates in 361 different WWTPs. 362

Under these hydrodynamic conditions of the groundwater and the effluent, C_{DGT} would be underestimated by 28% and 22% when using 0.8 mm AG as diffusive gels plus 0.1 mm wwPTFE membranes as protective filters, respectively, if the effects of DBL is not taken into account. Evenso, the underestimation by DGT is much smaller than that from POCIS and Chemcatcher, which can produce several-fold underestimations or overestimations on TWA concentrations.²⁴

369 3.8 Field Validation

370 **3.8.1 Application in Groundwater**

371 To our knowledge, there have been no DGT monitoring studies of organic contaminants in groundwater before this study; DGT applications in groundwater were 372 only conducted for inorganic elements.^{39, 55} The usual size of the housing for DGT 373 devices (40 mm)⁴² has been suggested to be a disadvantage, compared with other 374 passive samplers, such as the POCIS (70-90 mm)²⁵ and Chemcatcher (52 mm).⁵⁸ 375 376 However, it could be seen as an advantage during groundwater sampling, especially in 377 groundwater monitoring wells. The minimum inner diameter is 50 mm and 76 mm for shallow (< 20 m) groundwater environmental monitoring wells⁵⁹ and hydrological 378 monitoring wells⁶⁰ in China, respectively, both of which are suitable for DGT 379 380 deployment. Neither POCIS nor Chemcatcher can be deployed in such groundwater 381 environmental monitoring wells, even without the deployment canister, and it would be 382 difficult to deploy or retrieve them, due to the limited space since there is normally 383 other equipment in the wells for long-term regulation monitoring that cannot be 384 removed for the passive sampler deployment.

The NNIs in the groundwater from the groundwater monitoring wells in the agricultural area of Wuhan were determined by both grab sampling and HLB-DGT. Only IMI, ACE and THI were detected by both methods. As listed in **Table S13**, IMI and ACE are among the most commonly used NNIs in China. The concentrations of individual compounds ranged from < MDL to 2.27 ng/L (**Figure 3a-c**) in the grab 390 samples, which were comparable to NNI concentrations of the shallow groundwater in





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Figure 3: Uptake of selected NNIs by HLB-DGT (n = 3, the blue line is the regression line through those points with continuous uptake) and active-sample (grab) concentrations of selected NNIs (n = 2, green circles and dash for grab-samples) in the groundwater (GW, a-c) and in the effluent of a WWTP (d-f). Error bar: 1 SD.

397 All NNIs detected by DGT accumulated linearly for 14-18 days and then showed 398 a slower accumulation or plateau (Figure 3a-c). A similar phenomenon was observed when DGT was deployed at WWTPs for measurement of HPCPs,²⁴ EDCs⁴⁹ and SMs³⁴ 399 and for NNIs in this study (see *Section 3.8.2*). The plateau or slower accumulation after 400 401 14-18 days may be due to several reasons: (1) biofouling during long-term DGT 402 deployment in the water is common (Figure S13a-c), and biofilm formation on the surface of the filter membrane may inhibit the adsorption or accelerate the degradation 403 of the target analytes;^{24, 61} (2) degradation or hydrolysis of NNIs may happen in binding 404 405 gels (see water photolysis in Table S1), that will counteract the further uptake of the NNIs after 18 days; and (3) competitive adsorption of coexisting substances or $ions^{24}$, 406

407 ³⁵ can also reduce the uptake or retention of target compounds. Considering the
408 detection limit and the quantitative accuracy over a linear period of DGT, a deployment
409 period of 7–14 days is recommended for groundwater.

A lag time in accumulation by DGT for all detected NNIs was observed in the initial deployment (**Figure 3a-c**), which was similar to the results of DGT sampling for antibiotics,³³ SMs³⁴ and NNIs (see *Section 3.8.2*) in WWTPs. This phenomenon can be explained by the adsorption of target chemicals on the filter membrane that slowed the supply of these chemicals to the binding gel and prolonged the time to establish a linear adsorption steady state.⁶²



416

Figure 4: TWA concentrations measured by DGT during 10 days deployment time and concentrations
of the same compounds in grab samples in WWTP effluent and groundwater (GW). Note the log scale.
Error bars: 1 SD.

420 The DGT concentrations of NNIs in the groundwater during the different 421 deployment periods were calculated and compared with those from active grab 422 sampling (Figure 4 for 10 days and Figure S14 for the other days). A similar 423 distribution pattern of NNIs concentrations was observed between the two sampling 424 methods, while the DGT samples showed slightly lower concentrations than the grab 425 samples. Two main reasons may account for this: (1) two different principles of sampling (TWA concentration or instantaneous concentration) and (2) DGT is 426 427 considered to quantify dissolved chemical species in water, whereas active grab sampling may include chemical species adsorbed in the particulate phase in addition to 428 dissolved phase.²⁴ For the grab sampling, the SPE pre-treatment is normally necessary 429 430 to enrich the NNIs to increase their detection limits, since the NNIs are typically present 431 at ng/L in the groundwater, which makes monitoring cumbersome and costly. However, 432 HLB-DGT can be used to monitor the NNIs in the groundwater with MDLs of 0.11-433 0.63 ng/L (for 14-day in-situ deployment, Table S2). This is low enough and comparable to the MDLs (0.06–0.34 ng/L, Table S2) for active grab sampling of 500 434 435 mL after 2000-fold concentrating after extraction in this study. These results demonstrate that HLB-DGT devices perform well in the groundwater for in-situ 436 437 monitoring of NNIs.

438 **3.8.2 Application in Wastewater**

All the tested NNIs were detected in both grab and DGT samples (**Figures 3** and **S15**), except NIT and IMIT. The concentrations of individual compounds ranged from 0.89 to 77.9 ng/L in the grab samples during the sampling period, with IMI having the highest average concentrations (67.6 ng/L) followed by TMX (19.3 ng/L) and ACE (16.5 ng/L), comparable to concentrations reported in effluent from other WWTPs.^{11, 63}
This is generally consistent with the application preference of NNIs in China (Table
S13), with the highest registration of products for IMI, ACE and TMX, but the lowest
for IMIT and NIT. The results also indicated the limited removal efficiencies for IMI
and ACE in the WWTPs.¹¹

448 Most NNIs accumulated in DGT binding gels linearly with time for up to 14-18 449 days, after which they plateaued or accumulated more slowly. This was consistent with the DGT results for HPCPs,²⁴ EDCs⁴⁹ and SMs³⁴ in WWTPs, and the results of NNIs 450 451 in the groundwater (see *Section 3.8.1*). Similar to the results of DGT for NNIs in the groundwater and for SMs and antibiotics in the WWTPs,^{33, 34} a lag time in accumulation 452 453 of all detected NNIs by DGT was observed in the initial deployment (Figure 3d-f and 454 Figure S15). The initial delay in adsorption, and the plateau or decline in uptake rate after 14-18 days may be due to the adsorption of NNIs by filter membranes,62 455 biofouling (Figure S13d-f).^{24, 61} degradation (including photolysis or hydrolysis) and 456 competing adsorption.²⁴ 457

Concentrations of NNIs measured by the DGT during different sampling periods were calculated and compared with those obtained by active grab sampling (**Figures 4** and **S16**). The overall distribution patterns of NNIs in grab and DGT samples are similar. However, the concentrations obtained by the two methods are different (fluctuating within an order of magnitude). It is believed that this is due to the different principles between grab sampling and DGT sampling. DGT measures integrated concentrations 464 over the deployment time, whereas active grab sampling yields snapshot concentrations 465 susceptible to irregular wastewater discharges.²³ The results of this study are similar to 466 those for HPCPs,²⁴ PFASs,³⁶ and ASs³⁷ following DGT deployments at WWTPs over 467 the past few years. These results showed that the HLB-DGT can be applied in the most 468 challenging conditions of the complex wastewater matrix, as well as in the groundwater 469 with the near-static flow rates and high concentrations of ions.

470 **3.9 Environmental Implications**

471 A novel DGT technique has been developed and demonstrated for in-situ 472 monitoring of 9 globally important commercial NNIs in aquatic environments. It has 473 been verified through systematic testing in the laboratory and field applications in the 474 most challenging conditions, groundwater and wastewater. HLB-DGT devices performed well across a wide range of environmental conditions. Comparable 475 476 concentrations and distribution patterns of NNIs obtained by HLB-DGT devices and 477 grab samples confirmed the reliability of the DGT technique in both groundwater and 478 surface water. This is the first demonstration that the DGT technique can be used to in-479 situ sample NNIs, a type of trace organic contaminants, in groundwater. Thus, further systematic studies of interactions and behaviours of NNIs between surface water and 480 481 groundwater can be achieved, to provide a better understanding of the fate and biogeochemical processes of these compounds. 482

483 SUPPORTING INFORMATION

484 Information includes standards, reagents, quality control, analytical methods, extraction

- 485 method optimization, measurement of diffusion coefficients, measurement of DBL,
- 486 supplementary tables and figures.

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490 Notes

491 The authors declare no competing financial interest.

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