

1 ***In situ* measurement of an emerging persistent, mobile and toxic**
2 **(PMT) substance - melamine and related triazines in waters by**
3 **Diffusive Gradient in Thin-films**

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16

17 **Abstract**

18 Melamine has received increasing public attention as a persistent, mobile and toxic
19 (PMT) substance. To better assess environmental exposure and risks of melamine and
20 related triazines (cyromazine, ammeline, and atrazine), a new passive sampling method
21 based on the diffusive gradients in thin films (DGT) technique has been developed and
22 validated in this study. The studied triazines were adsorbed quickly and strongly by the
23 selected mixed cation exchange (MCX) binding gels. This MCX-DGT can linearly
24 accumulate these chemicals over at least 5 days, with neither significant individual
25 influence from pH (6–8), ionic strength (0.01–0.5 M) or dissolved organic matter (0–
26 10 M), or interaction effects. Field applications in Southern China showed that DGT
27 performed well in both sewage treatment plant (STP) and river samples. Melamine was
28 found to be the dominant triazine with the concentrations at $\mu\text{g}\cdot\text{L}^{-1}$ in the STP and
29 receiving river. Surprisingly, much higher concentration of melamine was found in the
30 STP effluent than influent, and appeared to be some of the highest concentrations
31 reported in STPs worldwide to date. Comparable melamine and atrazine concentraions
32 in the STP effluent and receiving river suggested other sources to the river. The MCX-
33 DGT sampler developed here was demonstrated to be reliable and robust for measuring
34 the triazines in waters, and is promising as an in situ tool in understanding the
35 occurrence, sources, and fate of the emerging PMT substances in aquatic environment.

36 **Keywords:** Melamine, Triazines; Passive Sampling; Aquatic Environment; Active
37 Sampling; Wastewater.

38

39 1. Introduction

40 Melamine is an *s*-triazine with three amino groups and is mainly used to synthesize
41 melamine-formaldehyde (MF) resins, which are added to kitchenware, textiles, foamed
42 plastics, electric appliances, and flooring to impart fire resistance. Aside from MF resins,
43 melamine is also used in paints and coatings, flooring, machine wash liquids, leather
44 treatment products. It is a high-production-volume chemical with an import volume of
45 up to 1,000,000 tonnes per year into the EU (ECHA, 2019). Due to its high nitrogen
46 content (66.7%), melamine has been reported to have been deliberately added into milk
47 and feed ingredients. In 2008, a melamine-contaminated milk substitute was given to
48 300,000 Chinese infants, out of which more than 50,000 were hospitalized and six died
49 due to kidney failure (WHO, 2008). Since then, the potential health risks of melamine
50 as well as its ecotoxicological risks have raised concerns worldwide.

51 Melamine is hydrophilic and highly mobile (Table 1). It has been shown to migrate
52 from MF plastics and other melamine products (Kim et al., 2021; Lund and Petersen,
53 2006), and more than 90% can be excreted via urine when humans and animals
54 consume melamine-contaminated diets (Bhalla et al., 2009).

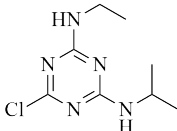
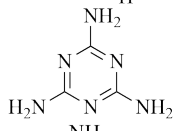
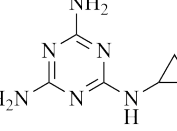
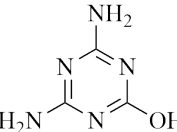
55 The main source of melamine to aquatic environments is via effluent discharge from
56 sewage treatment plants (STPs) (Qin et al., 2010). Melamine can also be derived from
57 the metabolism of cyromazine, a triazine pesticide (Li et al., 2011). Once discharged,
58 melamine is stable in water with a predicated degradation half-life of 37.5 d (Table 1).
59 There is limited evidence of hydrolysis, but it can occur yielding cyanuric acid, where
60 ammeline and ammelide are the intermediates (Bann and Miller, 1958).

61 Melamine and related triazines have frequently been detected in various aquatic
62 environments such as wastewaters, rivers, lakes, and seawaters (Qin et al., 2010; Zhu
63 and Kannan, 2020), with concentrations reported to be as high as several $\mu\text{g}\cdot\text{L}^{-1}$. Current

64 evidence has demonstrated that these triazines may result in adverse impacts to both
 65 human health and aquatic organisms (Arnold, 1990; Bolden et al., 2017). For example,
 66 low-level, continuous exposure to melamine and its analogues in humans has been
 67 linked to the risk of uric acid formation and calcium urolithiasis (Li et al., 2010; Liu
 68 et al., 2011). Similar consequences were also observed in fish (Phromkunthong et al.,
 69 2015a; Phromkunthong et al., 2015b). Cyromazine has high toxicity to eggs or early-
 70 instar larvae of *Chironomus* (Robinson and Scott, 1995). As a result, melamine has
 71 been recently suggested as a persistent, mobile and toxic (PMT) substance (Anna,
 72 2020; Hale et al., 2020) and has gained increasing public attention worldwide. In order
 73 to protect public health and aquatic ecosystems and improve water quality, it is
 74 essential to understand the occurrence and fate of melamine and its related triazines
 75 (i.e., atrazine, cyromazine, ammeline, etc.) in waters.

76

77 **Table 1.** Basic physicochemical properties of the target compounds in this study.

Compound	Molecular Formula	CAS number	Solubility (g/L) ^a	Log <i>K</i> _{ow} ^b	Half-life in water (d) ^c	Molecular Structure
Atrazine	C ₈ H ₁₄ ClN ₅	1912-24-9	0.035	2.61	60	
Melamine	C ₃ H ₆ N ₆	108-78-1	3.23	-1.37	37.5	
Cyromazine	C ₆ H ₁₀ N ₆	66215-27-8	13.6	0.96	60	
Ammeline	C ₃ H ₅ N ₅ O	645-92-1	0.075	-3.65	15	

78 ^a estimated using WSKOW v 1.41 in the USEPA EPI Suite 4.1.

79 ^b estimated using KOWWIN v 1.68 in the USEPA EPI Suite 4.1.

80 ^c estimated based on a level-III fugacity model *via* WOVWINTM in the USEPA EPI
 81 Suite 4.1.

82

83 Currently, water quality monitoring campaigns mostly adopt grab sampling
84 approaches as they are easy to implement and require no specialized equipment.
85 However, target chemicals may adsorb onto the container surface or degrade during
86 transportation and storage, which can lead to measurement errors. For example,
87 melamine gradually hydrolyses to ammeline, ammelide, and cyanuric acid under acidic
88 or basic conditions (Zhu and Kannan, 2019). In light of this, passive sampling
89 techniques offer a suitable alternative as they provide *in situ* pre-filtration and pre-
90 concentration. Moreover, they measure time-weighted average (TWA) concentrations
91 over the entire deployment period and thus provide a more medium- to long-term
92 assessment of contamination compared to traditional “snapshot” sampling (Mutzner et
93 al., 2019). This characteristic can also be important for monitoring rivers susceptible to
94 variable flows resulting from floods, rainstorms and tidal variation.

95 Over the past decade, organic diffusive gradient in thin-films (DGT) technique, as
96 an emerging passive sampling technique, has become increasingly popular for
97 monitoring polar organic pollutants (Challis et al., 2016; Chen et al., 2012a; Chen et al.,
98 2013; Liu et al., 2021a; Liu et al., 2021b). It belongs to the group of kinetic samplers
99 which depend on a flux that is proportional to concentration (Williams, 2016). Besides
100 the aforementioned advantages, DGT can save approximately two-thirds of costs
101 compared to grab sampling (Chen et al., 2013), be independent of hydrodynamic
102 conditions, and does not require field calibration (Chen et al., 2020). Therefore, DGT
103 is recommended by the European Union Water Framework Directive as a
104 complementary monitoring tool alongside grab sampling (Directive 2013/39/UE;
105 Hanke et al., 2009). Currently, several DGT configurations have been validated for
106 atrazine using HLB and Septra ZT as binding agents (Challis et al., 2016; Stroski et al.,

107 2018). However, no published study has yet assessed suitable DGT configurations and
108 validation for melamine and other triazines.

109 Therefore, the main objectives of this study are: (i) to develop and evaluate a DGT
110 passive sampler for determining melamine and related triazines in waters; (ii) to
111 validate the DGT performance in field environments along with grab sampling; and (iii)
112 to understand the occurrence and patterns of these chemicals in an STP and receiving
113 river in Southern China. Atrazine, a well-known triazine herbicide, is also included in
114 the target compounds to facilitate comparison with other studies.

115

116 **2. Materials and Methods**

117 **2.1 DGT preparation and Configuration**

118 A standard DGT device was assembled and used in this study, comprising an ABS
119 moulding, a binding gel layer, an APA (polyacrylamide with agarose-derivative cross
120 linker) diffusive gel layer, and a nylon filter membrane. Considering the alkalinity of
121 these amino-triazines, mixed cation exchange (MCX) resins were selected as a potential
122 binding agent for the binding gel layer.

123 APA diffusive gels were prepared according to the procedure of a previous study
124 (Zhang and Davison, 1995), and details are described in the *Supplemental Materials*.
125 To prepare MCX binding gels, 10 mL of 19% (v/v) polyacrylamide gel solution were
126 well mixed with 4 g wet weight of MCX resins. 80 μ L of ammonium persulfate and 25
127 μ L of *N,N,N',N'*-tetramethylethylenediamine were sequentially added to induce
128 reaction. The well-mixed solutions were carefully pipetted into the space separated by
129 a polytetrafluoroethylene (PTFE) spacer between two glass plates and then oven-dried

130 at 43 °C until they were completely set. After hydration in MQ water, the expanded
131 binding gels (0.5 mm) were cut into 25 mm diameter circular discs and stored in 0.01
132 M NaCl solution in a fridge (4°C).

133 **2.2 Adsorption and Elution Efficiencies**

134 To assess potential adsorption of the triazines included in this study by different DGT
135 components (i.e., APA gels, nylon filter membrane, and DGT moulding), representative
136 materials were immersed in 10 mL of 100 µg·L⁻¹ solution containing 0.01 M NaCl in
137 triplicate and shaken for 24 h. The solution concentrations before and after the
138 experiment were directly measured by LC-MS/MS. The adsorption percentages were
139 calculated from the mass differences during the experiment.

140 To investigate adsorption kinetics by MCX binding gels, MCX gels were also
141 immersed in well-stirred solutions spiked with 10 mL of 100 µg·L⁻¹ containing 0.01 M
142 NaCl. At 0, 0.08, 0.25, 0.5, 1, 2, 4, 8, 12, and 24 h, the concentrations of the solutions
143 were analysed and the adsorption percentages at different times calculated. The MCX
144 binding gels were transferred into 5 mL clean glass tubes and spiked with atrazine-d5
145 (as internal standard for atrazine) and melamine-¹³C₃, ¹⁵N₃ (as internal standard for the
146 other target chemicals). 2.5 mL of 5% ammonium hydroxide (v/v)-methanol was added
147 into the tubes, and then ultrasonic extraction took place for 30 min. The same step was
148 repeated again. The extracts were combined, concentrated, redissolved in 1 mL of
149 acetonitrile-water (8: 2, v/v), and filtered for LC-MS/MS analysis.

150 **2.3 Measurements of Diffusion Coefficients**

151 A diffusion cell method with two compartments (i.e., source compartment – A and
152 receiving compartment – B) was used to measure diffusion coefficients (D_{PA}) of the
153 selected triazines through an APA gel. The A and B cells were filled with 50 mL

154 solutions containing $20 \mu\text{g}\cdot\text{L}^{-1}$ of each target chemicals and 0.01 M NaCl, and the same
155 background solutions but without target chemicals, respectively. They were
156 magnetically stirred with a glass coated stirrer. After 2 h, aliquots of the solutions from
157 both sides were sampled in duplicate at a time interval of 15 min until 10 time points
158 were achieved. The solution temperature was recorded using a mercurial thermometer.
159 D_{PA} was then calculated from the slope (k) of linear plot of accumulated mass versus
160 time as follow (Chen et al., 2012a):

$$161 \quad D = \frac{k\Delta g}{C_w A} \quad (1)$$

162 where A is the exposure area, Δg is the thickness of diffusive layer, C_w is the
163 concentration of target chemical in the source compartment.

164 To further compare data from this study with sampling rates (R_s) of other passive
165 samplers such as polar organic chemical integrative sampler (POCIS), sampling rate
166 per unit area of sampler ($R_{s/A}$) was calculated as follows:

$$167 \quad R_{s/A} = \frac{D_{\text{PA}}}{\Delta g} \text{ or } R_{s/A} = \frac{R_s}{A} \quad (2)$$

168 **2.4 Time Dependence**

169 In total 15 DGT devices were immersed into 2 L of $100 \mu\text{g}\cdot\text{L}^{-1}$ well-stirred solutions
170 containing 0.01 M NaCl for different time periods up to 120 h. Although the
171 deployment time (5 days) was slightly shorter than that recommended in field
172 environments (1–2 weeks), it was still sufficient to confirm whether linear uptake
173 occurred because the solution concentration of the target triazines were higher by at
174 least two orders of magnitude than their environmental concentrations, even for
175 melamine ($\sim\mu\text{g}\cdot\text{L}^{-1}$). Three DGT devices were retrieved every day. Their external
176 surfaces were rinsed with MQ water and stored in plastic bags at 4°C for further elution.

177 Meanwhile, solution concentrations were measured daily and remained stable with
178 coefficient of variations less than 12%. The solution temperature was 27 ± 0.4 °C during
179 the deployment. The MCX gels from all the retrieved DGTs were taken off and
180 extracted as detailed above.

181 **2.5 Effects of Ionic Strength (IS), pH and Dissolved Organic Matter (DOM)**

182 IS, pH and DOM are key water chemistry parameters that might affect the
183 performance of DGT measurement on the analytes of interests, they are therefore tested
184 in this study as individual parameters or interactions.

185 **Single-Factor Experiments:** Individual effects of IS, pH and DOM on DGT
186 performance were studied by immersing DGT devices into 500 mL of $20 \mu\text{g}\cdot\text{L}^{-1}$ well-
187 stirred solutions for 24 h under different conditions. The IS (0.01, 0.1, and 0.5 M) in
188 the bulk solutions was maintained by adding appropriate amounts of NaCl. The solution
189 pH (6, 7, and 8) was adjusted by 0.5 mM sodium acetate or sodium bicarbonate and left
190 overnight prior to the experiment. The experiment on the effect of DOM on sampler
191 performance was conducted at two different DOM concentrations (5 and $10 \text{ mg}\cdot\text{L}^{-1}$),
192 along with a control ($0 \text{ mg}\cdot\text{L}^{-1}$). During the experiments, the solution temperature was
193 recorded with a temperature logger and averaged 22 ± 0.5 °C. The concentrations in the
194 bulk solutions were sampled and analyzed directly by LC-MS/MS.

195 **Factorial Design Experiment:** A two-level full factorial design experiment (2^3) was
196 designed in order to evaluate interactions of IS, pH and DOM on DGT performance.
197 The input variables and their levels in the experiment are presented in Table 2. Each
198 design was conducted in triplicate. Other test conditions and DGT treatment were the
199 same as those of the single-factor experiments.

200 Table 2 Ranges and levels of the factors used in the factorial design.

Independent variable	Coded symbol	Range and Level
----------------------	--------------	-----------------

		-1	0	1
IS (M)	X_1	0.01	0.255	0.5
pH	X_2	6	7	8
DOM concentration (mg·L ⁻¹)	X_3	0	5	10

201

202 In both the single-factor experiments and the factorial design experiments, melamine
203 was selected as the test compound.

204 2.6 Field Application

205 **STP Deployment:** To validate the reliability of the developed DGT under field
206 environments, a 4-day DGT deployment campaign was conducted in April 2021 in the
207 influent and effluent of a sewage treatment plant (STP) in Southern China. Three DGT
208 devices were retrieved every day at each site, rinsed with MQ water and then transferred
209 to the laboratory within a plastic bag. Simultaneously, 50 mL of water were collected
210 daily from the influent; due to limited access, no effluent water was sampled. Water
211 temperatures and pH values in the influent were measured by using a portable YSI
212 multiparameter water meter (YSI, Inc., Ohio, USA). Details on treatment of the grab
213 samples are provided in the *Supplementary Materials*.

214 **River Deployment:** DGT performance in a tidal river downstream from the STP was
215 also tested. Six DGT devices were deployed for 7 days, and three were retrieved at day
216 3 and day 7, respectively. In addition, 50 mL grab samples were collected daily. Other
217 details were the same as those in the STP deployment.

218 2.7 Chemical Analysis

219 Chemical analysis for the target compounds was performed using a Waters Acquity
220 ultra-performance liquid chromatograph (UPLC) connected to a Waters Xevo TQS
221 triple-quadrupole tandem mass spectrometer (Waters Corp., Milford, MA, USA).
222 Melamine and ammeline are highly hydrophilic and cannot be retained in a reverse

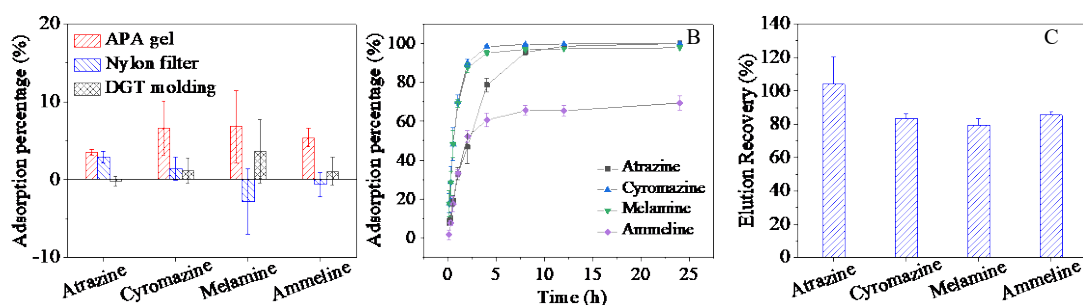
223 chromatographic column such as C18 column. A Waters Acquity UPLC BEH
224 hydrophilic interaction (HILIC) column (2.1 × 100 mm, 1.7 μm) was selected in this
225 study as it has been demonstrated to provide good peak shapes enabling confident
226 quantification of melamine and ammeline (Andersen et al., 2008; Benvenuti and
227 O'Connor, 2009; Braekevelt et al., 2011). The column temperature was set at 35 °C and
228 the injection volume was 5 μL. The mobile phases consisted of 0.1% (v/v) formic acid
229 in water containing 2 mM ammonium formate (A) and acetonitrile (B) with a flow rate
230 of 0.3 mL/min. The gradient elution programme was initiated with 98% B, ramped to
231 90% B at 4 min, then to 40% B at 6 min, re-equilibrated to the initial phase in 1 min
232 and held further for 2 min. The analytes were monitored using an electrospray
233 ionization source (ESI+) in multiple reaction monitoring (MRM) mode. The retention
234 times, MRM transitions, optimized collision energies and cone voltages are given in
235 Table S1 in the Supplementary Materials. Other MS conditions were: Capillary voltage,
236 3.0 kV; Source temperature, 150 °C; Desolvation gas temperature, 400 °C; Desolvation
237 gas, 800 L·h⁻¹; Cone gas, 150 L·h⁻¹; Collision gas, 0.17 mL·min⁻¹; and Nebuliser gas, 7
238 bar. Quantification of the target chemicals was based on a 6-point (0.1–100 ng·mL⁻¹)
239 calibration curve for each chemical and an internal standard method (atrazine-d₅ for
240 atrazine and melamine-¹³C₃, ¹⁵N₃ for the remaining chemicals) with $R^2 > 0.99$ for all
241 chemicals. Other details on detection limits, quality assurance and control (QA/QC) are
242 provided in the Supplementary Materials.

243 **3. Results and Discussion**

244 **3.1 Adsorption by DGT Components**

245 A standard DGT piston is manufactured from ABS resins and has been found to
246 exhibit little adsorption of a wide range of chemicals (Guan et al., 2021; Zhang et al.,

247 2019). APA diffusive gels have previously been demonstrated to exhibit much higher
 248 strength than agarose gels (Liu et al., 2021a) and resistance to biodegradation, therefore
 249 APA gel is preferable and tested first here. The results show that no significant
 250 adsorption of these triazines (less than 10%) occurred for APA gels, nylon filter
 251 membrane, and ABS pistons (Figure 1A). This confirms the suitability of these
 252 materials as the diffusive layer, filter, and moulding, respectively, for studying the
 253 triazines.
 254



256 **Figure 1.** Plot A: Adsorption percentages (%) of target compounds by different DGT
 257 components (APA gels, nylon filter, and DGT moulding) in $100 \mu\text{g}\cdot\text{L}^{-1}$ solutions
 258 containing $0.01 \text{ mol}\cdot\text{L}^{-1}$ NaCl; Plot B: Adsorption kinetics of target compounds by
 259 MCX gels in $100 \mu\text{g}\cdot\text{L}^{-1}$ solutions containing $0.01 \text{ mol}\cdot\text{L}^{-1}$ NaCl; Plot C: Elution
 260 recoveries (%) of MCX gels for target compounds using repeated ultrasonic
 261 extraction for 30 min with 2.5 mL of 5% (v/v) ammonium hydroxide-methanol. Error
 262 bars: 1 SD ($n = 3$).
 263

264 3.2 Adsorption Kinetics and Elution Efficiencies of the MCX Gels

265 To address the practical performance aspects of using MCX resins (kinetics and
 266 capacity), the adsorption kinetics of the triazines is illustrated in Figure 1B. The
 267 adsorption of all the compounds increased rapidly within the first 2 h and then the rates
 268 plateaued after 8 h. The maximum adsorption percentages for the triazines were close
 269 to 100%, except for ammeline, which had a lower value of 69.4%. It is likely that the

270 substitution of hydroxyl group weakens the alkalinity of ammeline and thus the
271 adsorption of ammeline onto MCX gels. The uptake rates by the MCX gels ranged from
272 0.01 s^{-1} to 0.02 s^{-1} (a pseudo-first order model was assumed). They are about two orders
273 of magnitudes higher than the ratios of diffusion coefficients of analytes through the
274 diffusion layer over the square of its thickness ($D/\Delta g^2$, $2 \times 10^{-4} \text{ s}^{-1}$ – $3 \times 10^{-4} \text{ s}^{-1}$) (Dong
275 et al., 2014), and are on the same order of magnitude as those of other organics
276 chemicals in previous DGT studies (Liu et al., 2021a; Wei et al., 2019). This implies
277 that the MCX gels exhibit strong and fast adsorption of the triazines that once they
278 diffuse across the diffusive layer, they are immediately adsorbed onto the MCX gels
279 without reverse-diffusion. This may suggest that chemical concentrations at the
280 interface between the diffusive gel and binding gel would be close to zero and thus a
281 steady diffusion gradient would be established during DGT sampling.

282 Stable and efficient elution is an essential precondition for DGT measurement. As
283 shown in Figure 1C, extraction recoveries ranged from 79% for melamine to 104% for
284 atrazine with the $SD < 16\%$, suggesting the selected extraction method performs well.

285 **3.3 Diffusion Coefficients**

286 Diffusion coefficients are one of the key parameters in determining the TWA
287 concentrations in DGT measurements. In this study, good correlations between
288 accumulated mass and time were obtained for all triazines with $R^2 \geq 0.94$ (see Table 3).
289 The resultant D_{PA} values were the highest for melamine ($2.41 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$), followed
290 by atrazine ($1.65 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$), ammeline ($1.58 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$) and cyromazine (1.54
291 $\times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$). The D_{PA} value for atrazine was lower by a factor of 2–3 compared those
292 measured in agarose gels by [Challis et al. \(2016\)](#) ($3.74 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$) and [Li et al. \(2019\)](#)
293 ($5.19 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$). The much smaller pore size of APA gels compared to agarose gels
294 should have contributed to the lower D_{PA} value of atrazine measured in this study

295 (Zhang and Davison, 1999). This result is in accordance with our earlier findings for
 296 other chemicals using APA and agarose gels (Liu et al., 2021a; Liu et al., 2021b). The
 297 measurement for atrazine in this study was lower than that measured by Stroski et al.
 298 (2018) ($2.96 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$) in a PA gel with 15% acrylamine monomer and 0.1% cross-
 299 linker (total monomer concentration, $T\%$: 15.1%). The higher $T\%$ (19.3%) of the APA
 300 diffusive gels used in this study might decrease the pore size (Zhang and Davison, 1999),
 301 resulting in the lower measurements than that by Stroski et al. (2018).

302

303 **Table 3.** Measured diffusion coefficients (D_{PA} , 25 °C) of atrazine, cyromazine,
 304 melamine, and ammeline through APA gels using a diffusion cell and corresponding
 305 sampling rates per unit area of DGT derived from diffusion coefficient measurement
 306 experiment ($R_{S/A}$) and time dependence experiment ($R'_{S/A}$), respectively. Error bars: 1
 307 SD ($n = 2$).

Compound	Molecular Weight	$D_{PA} \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$	R^2	$R_{S/A} / \text{mL} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$	$R'_{S/A} / \text{mL} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$
Atrazine	215.7	1.65 ± 0.04	0.99	1.62 ± 0.03	1.50
Cyromazine	166.2	1.54 ± 0.02	0.98	1.52 ± 0.01	1.62
Melamine	126.1	2.41 ± 0.07	0.96	2.36 ± 0.07	2.34
Ammeline	127.1	1.58 ± 0.08	0.94	1.55 ± 0.06	1.23

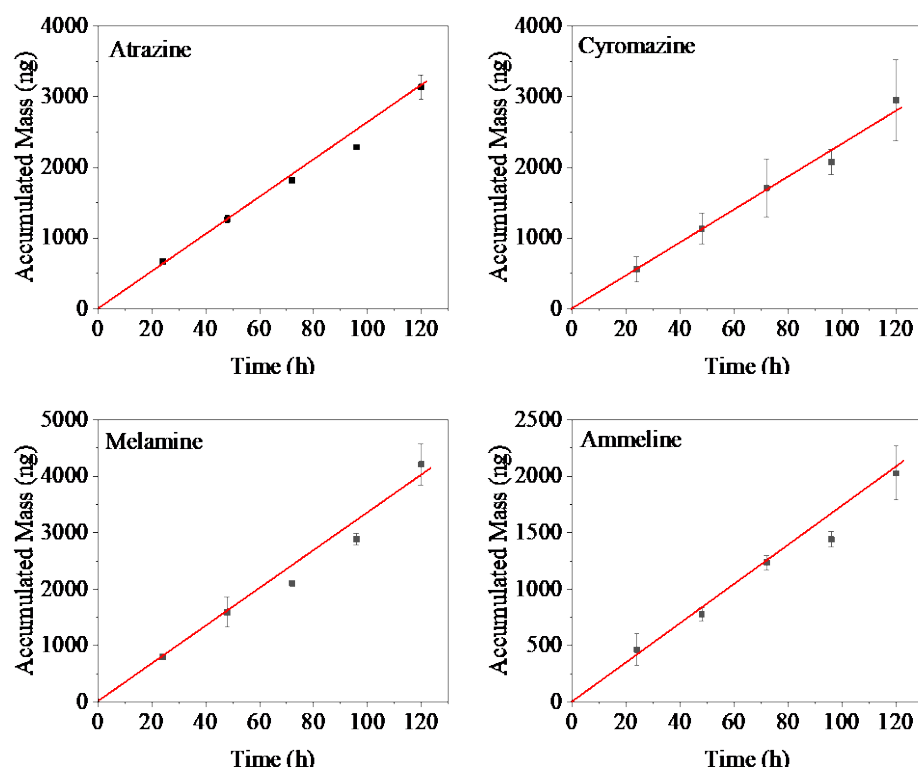
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309 The $R_{S/A}$ values of the studied triazines for DGT ranged from $1.52 \text{ mL} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ for
 310 cyromazine to $2.36 \text{ mL} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ for melamine, and were very close to those measured
 311 by the time dependence experiment ($R'_{S/A}$: $1.23\text{--}2.34 \text{ mL} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$) (Table 3), suggesting
 312 the accuracy of the former experiment. The $R_{S/A}$ values of atrazine by POCIS with an
 313 exposure area of $42\text{--}45.8 \text{ cm}^2$ were reported to be $3.2\text{--}5.6 \text{ mL} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ (Booij et al.,
 314 2020; Dalton et al., 2014), which was similar to those by DGT with agarose gels (3.7--
 315 $5.1 \text{ mL} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$), but lower than those by DGT with APA gels. This is because the
 316 sampling rates by DGT depend on the diffusive layer, and APA diffusive gels have a

317 smaller pore size compared to agarose gels.

318 3.4 Time Dependence

319 In order to obtain reliable TWA concentrations, a DGT device must operate in its
320 linear accumulation regime during the field deployment. Therefore, uptake kinetics of
321 DGT devices were investigated under laboratory conditions to confirm whether linear
322 uptake process occurs and over what period it is maintained.



324 **Figure 2.** Time-series accumulations (M) of atrazine (A), cyromazine (B), melamine
325 (C), and ammeline (D) by DGT devices deploying in 2 L of $100 \mu\text{g}\cdot\text{L}^{-1}$ well-stirred
326 solutions containing $0.01 \text{ mol}\cdot\text{L}^{-1}$ NaCl ($27 \pm 0.4 \text{ }^\circ\text{C}$). Solid red lines indicate
327 theoretical lines predicated by equation: $M = DCA t / \Delta g$ (C is the solution
328 concentration, A is the exposure area, t is the deployment time, Δg is the thickness of
329 diffusive layer). Error bars: 1 SD ($n = 3$).

330

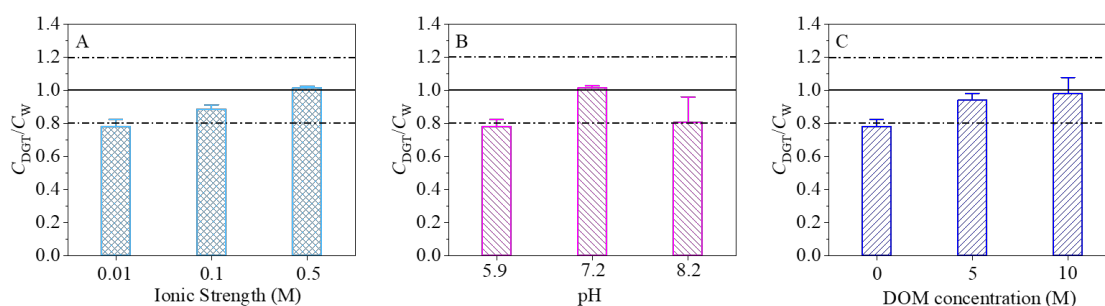
331 All of the studied triazines were accumulated linearly in DGT devices over the 5-d

332 deployment, and there was no evidence of uptake approaching equilibrium.
333 Furthermore, the measured masses in DGT devices agreed well with the theoretically
334 derived values. These results demonstrated that a linear uptake regime was established
335 using the currently configured DGT sampler. In addition, the accumulated masses in
336 DGT devices were as high as 2.0–4.2 $\mu\text{g}\cdot\text{disc}^{-1}$. Assuming environmentally relevant
337 concentrations are $\leq 10 \mu\text{g}\cdot\text{L}^{-1}$ for melamine and $\leq 200 \text{ ng}\cdot\text{L}^{-1}$ for the other triazines,
338 sampler uptake would continue for at least 53 d for melamine and several years for the
339 other triazines. However, it is not recommended to carry out deployments for these
340 periods, as in natural waters (bio)fouling and potential competitive adsorption of DOM
341 and other coexisting pollutants including the other triazines will occur. Generally,
342 deployment timeframes of between 1 and 2 weeks (dependent on chemicals) could be
343 considered ideal (Chen et al., 2013).

344 **3.5 Effects of pH, Ionic Strength and DOM**

345 In natural waters, pH, IS, and DOM are key environmental factors which could
346 significantly alter DGT performance. Figure 3 shows the individual effects of these
347 parameters on the ratio of DGT-measured melamine concentrations compared to bulk
348 solution concentrations ($C_{\text{DGT}}/C_{\text{water}}$). The ratios increased slightly with increasing IS
349 (0.01–0.5 M) and DOM concentrations (0–10 M), whereas the ratios were close to 1 at
350 neutral pH and decreased in acidic or basic conditions. The slightly positive impact of
351 IS on DGT measurements was also observed in our earlier study (Liu et al., 2021a),
352 which could be explained by a possible salting-out effect. It is important to note that
353 melamine is in the amide form in neutral solution but converted into triamide structure
354 with addition of acid or base (Bann and Miller, 1958), which might alter the interaction
355 of melamine with MCX gels. Thus, alteration of the melamine structure as well as the
356 adsorption on the binding phase at acidic or basic pH values could possibly explain the

357 underestimation of DGT measurements at pH = 5.9 or 8.2. Generally, DOM competes
 358 for binding sites with analytes or lowers the freely dissolved species of the analytes
 359 (Guibal et al., 2019; Liu et al., 2021b). But interestingly, more melamine was
 360 accumulated in DGT when DOM concentrations increased in the present study, which
 361 might be attributed to additional binding sites of the DOM supramolecules adsorbed
 362 onto MCX gels. A similar phenomenon was observed by Wu et al. (2018). Nevertheless,
 363 no significant effects ($p > 0.05$) were observed for pH, IS, and DOM concentrations.
 364 This demonstrates that the DGT performance is reliable and robust under the tested
 365 range of pH (6–8), IS (0.01–0.5 M), and DOM concentrations ranging from 0–10 M.
 366

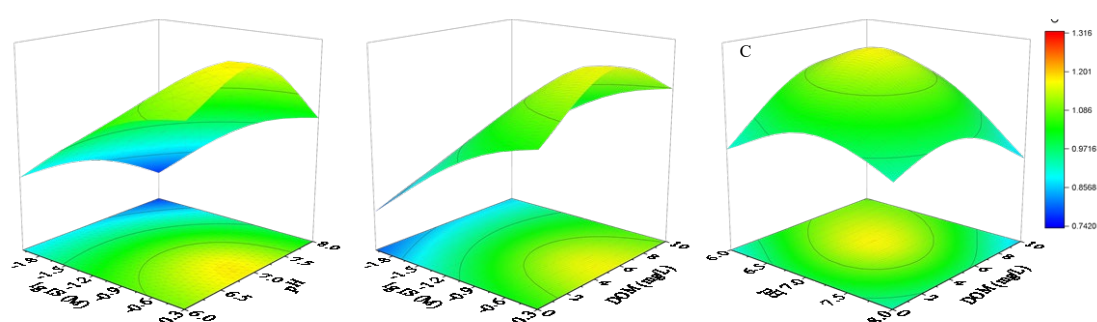


368 **Figure 3.** Individual effects of ionic strength (A), pH (B), and DOM concentrations
 369 (C) on the ratios of DGT-measured concentrations to measured concentrations of
 370 melamine in bulk solutions (C_{DGT}/C_{water}). Error bars: 1 SD ($n = 3$).
 371

372 The interaction effects between each pair of pH, IS, and DOM were also explored
 373 by using a two-level full factorial design experiment and are illustrated by 3D surface
 374 and contour plots (Figure 4). The elliptical contour plot indicates the interaction is
 375 significant while a circular contour plot means the opposite (Chen et al., 2012b). As
 376 shown in Figure 4, all interactions displayed quadratic effects on the DGT performance.
 377 Taking the interaction of IS and pH for example (Figure 4A), when keeping IS (X_1) at
 378 a high level, the DGT measurements increased at first and then decreased with

379 increasing pH (X_2) from 6 to 8. However, the contour for IS and pH tended towards the
 380 circular, suggesting their quadratic interaction was not significant. This might be
 381 explained by the findings by Pommier et al. (2021) who observed little Donnan effect
 382 on DGT measurements at high IS ($\geq 10^{-3}$ M) regardless of the pH. Briefly, the immobile
 383 charges in gels are mainly shielded by the predominant ions (cations/anions) from
 384 solution at high IS ($\geq 10^{-3}$ M), thereby preventing a significant change of the analyte's
 385 concentration at the gel-solution interface. The circular contour plots for DOM vs IS
 386 (Figure 4B) and DOM vs pH (Figure 4C) also indicated their interactions were not
 387 significant. These results were also supported by the results of a regression analysis
 388 (Table S4).

389



391 **Figure 4.** Contour plots for interaction effects of pH vs lg IS (A), dissolved organic
 392 matter (DOM) vs lg IS (B), and DOM vs pH (C) on MCX-DGT performance
 393 (C_{DGT}/C_{water}) of melamine.

394

395 **3.6 Field Application**

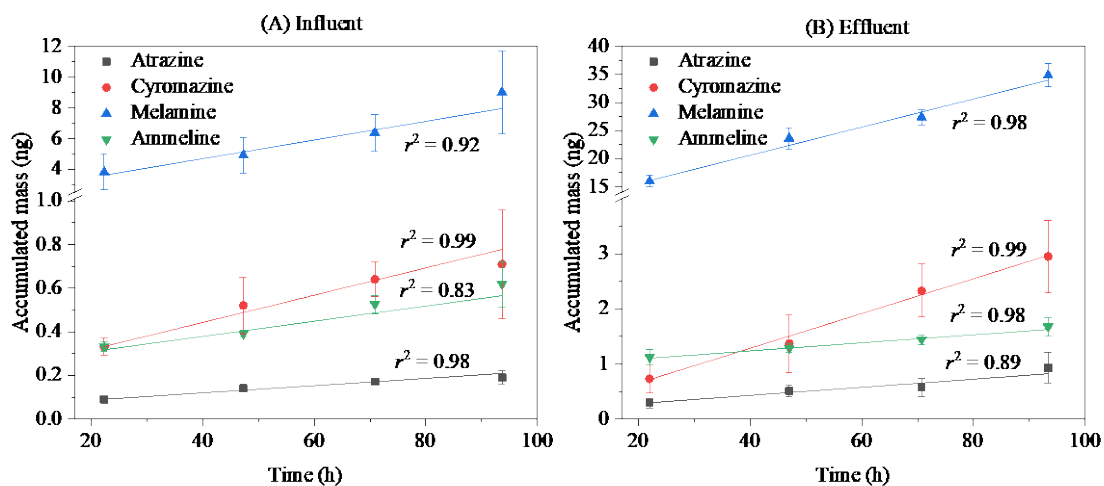
396 ***Performance in the STP***

397 All of the target triazines were detected in the grab samples from the influent (Figure
 398 S1). The triazine profiles in the STP influent were melamine (mean: 2450 ± 370 ng·L⁻¹)
 399 ¹) > ammeline (135 ± 36 ng·L⁻¹) > cyromazine (58.9 ± 4.7 ng·L⁻¹) > atrazine (8.1 ± 0.8

400 ng·L⁻¹). The average concentrations of melamine measured in the influent were higher
 401 by at least one order of magnitude than those of the other triazines. The melamine
 402 concentrations in the influent were also four times higher than those reported in STPs
 403 in the United States (mean: 653 ng·L⁻¹, median: 389 ng·L⁻¹) (Zhu and Kannan, 2020).
 404 To the best of our knowledge, these are the highest concentrations reported in STPs
 405 worldwide.

406 The major source of melamine to the STP might not be domestic wastewater, as there
 407 are numerous family clothing workshops around the STP. Textile dye wastewaters may
 408 contain MF resins as the polymers are widely used in fabric impregnation (El-Sayed et
 409 al., 2006; Tian et al., 2012), and are likely to be discharged directly along with domestic
 410 wastewaters. MF resins are generally synthesized by the polymerization of melamine
 411 and formaldehyde under alkaline conditions (pH = 8–10) (Li et al., 2018) and hydrolyse
 412 under acidic conditions (Bauer, 1982; Farmakis et al., 2020). Given that the pH in the
 413 influent was neutral (7.4–7.8) during the deployment, MF resins should be stable.
 414 Therefore, we hypothesized that the high concentrations of melamine found in the
 415 present study are likely to have resulted from the acidic hydrolysis of MF resins during
 416 sample treatment with acids.

417



419 **Figure 5.** Uptake kinetics of atrazine, cyromazine, melamine, and ammeline by DGT
420 devices in influent (A) and effluent (B) of a STP from Southern China within a 4-d
421 deployment. Error bars: 1 SD ($n = 3$). The solid lines indicate the regression lines that
422 are not forced to pass through the origin.

423
424 All of the studied triazines were detected at concentrations higher than the method
425 detection limits (MDLs) in DGT samples. For both influent and effluent samples, the
426 accumulation of the chemicals in DGT correlated well ($r^2 \geq 0.83$) with the deployment
427 timeframes (Figure 5). These data indicate that DGT sampling performs well in the STP
428 environment, suggesting that DGT measurements are reliable. DGT-measured
429 concentrations are given in Table S6. It is worth noting that the DGT measurements
430 were much higher in the effluent than those in the influent, which is similar to the
431 antibiotics reported in previous studies (Chen et al., 2013, 2015). Possible reasons for
432 this include: (i) re-transformation/release of metabolite/complexed species (e.g. with
433 coexisting DOM or particulate matter), and (ii) biotic hydrolysis of MF resins. In
434 addition, comparison with the results from grab sampling shows comparable DGT
435 measurements in the influent for atrazine and cyromazine (Figure 6A). However, for
436 melamine and ammeline, the concentrations measured in the DGT samples were much
437 lower than those in the grab samples, which might be explained by discrepancies
438 between grab sampling and DGT technique (Chen et al., 2013; Dong et al., 2014).
439 Generally, the results of grab samples (which were not pre-filtered in this study) are
440 thought to represent the total concentrations of freely dissolved fractions and bound
441 fractions (including as part of MF resins), especially for melamine, whereas DGT
442 measures the freely dissolved fraction only (Dong et al., 2014). Also, DGT sampling
443 integrates concentrations during the whole period, whereas grab sampling provides
444 snapshot contamination information that might miss or only record peak events

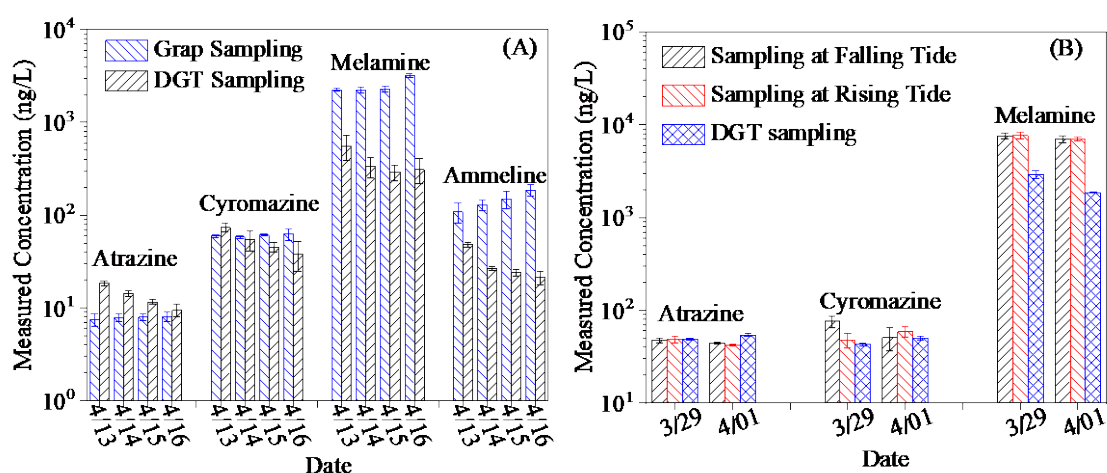
445 unintentionally (Chen et al., 2013), especially when possible textile industrial sources
446 exist.

447 In this study, the DGT devices were deployed in the STP for at least one day and at
448 most five days, which was slightly less than the deployment timeframes (1–2 weeks)
449 that we recommended earlier (Chen et al., 2013), since they were long enough for
450 chemical detection. Generally, DGT deployment time depends on the target chemical
451 concentration. The concentrations of melamine in the STP ($\sim\mu\text{g}\cdot\text{L}^{-1}$) were so high that
452 it took only several hours to reach the method detection limits (*MDLs*: 0.09–1.76 $\text{ng}\cdot\text{L}^{-1}$,
453 Table S3) of DGT and the concentration gradient in the diffusive gel would be quickly
454 established. Furthermore, it is necessary to shorten the deployment time to avoid
455 significant fouling, particularly in the influent of STP.

456 *In the River*

457 The grab sampling campaign was conducted during both periods of rising and falling
458 tides. Atrazine, cyromazine, and melamine were detected in all the river samples
459 (Figure S2). Compared to the quite stable concentrations in the STP, triazine
460 concentrations in the river samples varied greatly, which could be related to fluctuations
461 in river flow and/or emissions. Unlike the concentration profiles in the STP influent,
462 the triazine profiles in the river samples were melamine > cyromazine \geq atrazine >
463 ammeline (not detected). Similarly to the STP measurements, Melamine was the
464 dominant triazine in the river water samples (range: 6,420–11,330 $\text{ng}\cdot\text{L}^{-1}$, median:
465 7,560 $\text{ng}\cdot\text{L}^{-1}$, mean: 7,760 $\text{ng}\cdot\text{L}^{-1}$). Its concentrations in the river samples were 4–5
466 times higher than those in the grab samples from the STP influent. The melamine
467 concentrations in the river were also much higher than those reported in rivers in the
468 United States (median: 235 $\text{ng}\cdot\text{L}^{-1}$, mean: 469 $\text{ng}\cdot\text{L}^{-1}$) (Zhu and Kannan, 2020), but
469 much lower than those in melamine-contaminated irrigation water from China (range:

470 21,000–100,000 ng·L⁻¹) (Qin et al., 2010). In addition, the tidal effects on the
 471 concentration patterns of the triazines appear to be variable (Figure S2). This may be
 472 because factors such as increased wastewater discharge during the rising tide period
 473 cancelled out the effects of flow fluctuations (caused by tide) on the triazine
 474 concentrations in the river.
 475



477 **Figure 6.** Comparison of results from grab sampling and DGT measurements in the
 478 influent of a STP (A) and a receiving river (B), respectively. Error bars: 1 SD ($n = 3$).
 479

480 The DGT concentrations for ammeline were below the MDLs in the river samples,
 481 which was similar to the results from grab sampling. The time-dependent mass
 482 accumulation by DGT in the river for the other triazines was similar to that in the STP
 483 (Figure S3). As illustrated in Figure 6B, DGT-measured concentrations for atrazine and
 484 cyromazine in the river samples were comparable to the results from grab sampling.
 485 For melamine, the DGT measurements were a factor of 2–3 lower than the
 486 concentrations in the grab samples.

487 Pollutant concentrations are often considerably diluted by river waters after
 488 discharge from the effluent. However, for atrazine and melamine, the DGT-measured
 489 concentrations in the river were comparable to those in the STP effluent (atrazine:

490 45–56 ng·L⁻¹ vs 31–83 ng·L⁻¹, melamine: 1,820–3,170 ng·L⁻¹ vs 1,140–2,480 ng·L⁻¹).

491 Therefore, other inputs of atrazine and melamine in addition to wastewater effluents are
492 likely to have contributed to the apparent weak dilution effect. In addition, when taking
493 into account missing information on the concentration fluctuation, especially in tidal
494 rivers, concentrations obtained by grab sampling are likely to lack representativeness,
495 whilst the DGT measurements could more accurately reflect actual concentrations.

496

497 **4. Conclusions**

498 In this study, a new passive sampler based on the DGT technique has been developed
499 for in situ measurement of melamine and related triazines (atrazine, cyromazine, and
500 ammeline) in waters. The DGT accumulates linearly with deployment time both in the
501 laboratory and in the field. Over a wide range of pH, IS, and DOM values neither
502 individual effects nor interaction effects were observed on DGT performance.
503 Compared to grab sampling, comparable or lower DGT measurements were obtained
504 in samples from an STP and a downstream river. Melamine was the dominant triazine
505 in both the STP and river samples with the highest reported levels in STPs to date. In
506 addition, since their high mobility in aquatic systems, it is possible that they might
507 contaminate groundwater which requires further investigation. Subchronic toxicities
508 have not been reported yet in aquatic organisms exposed to melamine with
509 concentrations close to those reported in this study. Nevertheless, evidence suggests
510 that melamine exposure may have a toxic effect on female reproductive system and
511 impair fertilization (Dai et al., 2015; Duan et al., 2015). Thus, the health and ecological
512 risks posed by melamine with the highest concentrations being over ten µg·L⁻¹ in the
513 STP samples and surrounding waters should be evaluated further. DGT therefore

514 represents a promising and reliable passive sampler to provide in-situ information on
515 the occurrence and fate of triazine chemicals in the aquatic environment, and
516 particularly as a complementary tool to grab sampling in screening and monitoring of
517 further new PMT substances.

518

519 **Appendix A. Supplementary data**

520 Supplementary materials to this article can be found online.

521

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529

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