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1   Glyphosate and AMPA passive sampling in  
2   freshwater using a microporous polyethylene  
3   diffusion sampler

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16

17 **ABSTRACT**

18 Glyphosate (PMG) is one of the most widely used herbicides with a reported 8.6 million tons  
19 applied globally in 2016. Due to widespread use and limited understanding of long-term  
20 environmental impacts, it is expected that future monitoring requirements for PMG and its  
21 primary metabolite aminomethyl phosphonic acid (AMPA) in aquatic environments will increase,  
22 along with the need for low cost monitoring and risk assessment strategies. The aim of this study  
23 was to investigate a microporous polyethylene tube (MPT; 2-mm thickness, 17.6 cm<sup>2</sup> surface  
24 area, 35 % porosity, 2.5 μm pore size) as a diffusive layer for the passive sampling of PMG and  
25 AMPA. Levels of PMG and AMPA sorbed to MPT were low ( $K_{ow}$  close to 1 mL g<sup>-1</sup>), validating  
26 MPT as a diffusive layer. Uptake experiments were conducted first under controlled laboratory  
27 conditions (pH = 6.8, 6 days) followed by an in situ freshwater lake system deployment (pH =  
28 7.3, 11 days). PMG and AMPA accumulated linearly (slope relative standard deviation < 6 %)  
29 under laboratory conditions with sampling rates ( $R_s$ ) of 18 and 25 mL d<sup>-1</sup>, respectively. PMG in  
30 situ  $R_s$  was 28 mL d<sup>-1</sup>, and was not different from the one found in laboratory. AMPA was below  
31 the limit of quantification (LOQ, 1 ng mL<sup>-1</sup>) in grab water samples, but was detected (> LOQ) in  
32 all passive samplers. Results illustrate the gain in sensitivity provided by the passive sampling  
33 technique, and the applicability of the device developed for the passive sampling of PMG and  
34 AMPA.

## 35 1. INTRODUCTION

36 Glyphosate (*N*-phosphonomethyl glycine, i.e. PMG) is the active substance of more than 750  
37 commercial formulation (i.e., glyphosate-based herbicides, GBHs) and the most widely used  
38 herbicide for agricultural and non-crop uses, both in Australia (15,000 tons y<sup>-1</sup>) and worldwide  
39 (826,000 tons y<sup>-1</sup>) (Benbrook, 2016). The primary breakdown pathway of this polar (log  $K_{ow}$  = -  
40 4.59 to -1.70) and ionic (zwitterion at all pH) organic compound is through microbial  
41 degradation, resulting in the production of aminomethyl phosphonic acid, i.e. AMPA (Annett et  
42 al., 2014). After spraying onto land of GBHs, the leaching of PMG and AMPA and consequent  
43 transport into waterways will depend on application rates, soil properties and rainfall (Borggaard  
44 and Gimsing, 2008). Another crucial parameter affecting PMG transport, degradation and  
45 availability is the formation of complexes with natural occurring metal cations (Magbanua et al.,  
46 2013; Shushkova et al., 2010; Zhou et al., 2013). However, due to the high solubility of PMG  
47 (10.1-15.7 g L<sup>-1</sup> at 25°C) and AMPA (5.8 g L<sup>-1</sup> at 25°C) in water, they are typically mobile and are  
48 usually found together in most water bodies (Annett et al., 2014; Aparicio et al., 2013; Battaglin  
49 et al., 2014; Comoretto et al., 2007; Coupe et al., 2012; Mercurio et al., 2014; Stewart et al.,  
50 2014).

51 PMG and AMPA present complex chemical properties (i.e., high water solubility, poor solubility  
52 in organic solvents, high complexation capacity) which complicate their extraction and analysis  
53 in water at environmental trace levels. Accordingly, a derivatization step is needed to increase the  
54 selectivity and sensitivity of the analysis (Arkan and Molnár-Perl, 2015; Dong et al., 2015). Thus,  
55 PMG and AMPA are often not included in routine monitoring programs, as they require  
56 specialized analysis which increases the costs of monitoring programs, although PMG and  
57 AMPA are prioritized by the European network Norman ([www.normandata.eu](http://www.normandata.eu)). Otherwise, these

58 substances were recently the subject of a considerable debate concerning their carcinogenic effect  
59 on human health (Portier et al., 2016). Due to limited knowledge of the effects of chronic  
60 exposure to low levels of PMG and AMPA (i.e., low ng L<sup>-1</sup> range in aquatic systems), it is  
61 expected that future monitoring requirements for these compounds in aquatic environments will  
62 increase, along with the need for reliable, highly-sensitive and low-cost monitoring techniques.  
63 Passive sampling may address these three fundamental requirements.

64 Since their development in the early 2000's (Alvarez et al., 2004; Kingston et al., 2000), passive  
65 sampling techniques of polar compounds (i.e., the Polar Organic Chemical Integrative Sampler  
66 (POCIS) and Chemcatchers) have been successfully used for the measurement of a wide range of  
67 organic compounds in aquatic systems. Subsequently, passive sampling methods were adapted  
68 for the monitoring of ionizable organic compounds in water systems (Fauvelle et al., 2014, 2012,  
69 Kaserzon et al., 2014, 2012; Li et al., 2011). Aiming to target PMG and AMPA, a previous study  
70 adapted the Diffusive Gradient in Thin-film (DGT) passive sampling technique with a TiO<sub>2</sub>  
71 receiving phase (Fauvelle et al., 2015), while another adapted the POCIS design using  
72 molecularly imprinted polymer (MIP) as a receiving phase (Berho et al., 2017). Both TiO<sub>2</sub> and  
73 MIP sorption phases successfully accumulated these analytes. However, limitations of the  
74 developed sampling tools include:

- 75 i) the low sampling rates ( $R_s$ ) achieved for PMG and AMPA with the DGT based  
76 sampler, i.e. around 10 mL day<sup>-1</sup> (Fauvelle et al., 2015), which affects the sensitivity  
77 and applicability of the sampler under environmental conditions
- 78 ii) the dependency of the analytes flux and sampling rates on the external water velocity  
79 (i.e., water boundary layer thickness; WBL) with the POCIS based sampler, which

80 can increase the uncertainty of water concentration estimates (Berho et al., 2017;  
81 Fauvelle et al., 2017)

82 iii) the absence of in situ testing of the devices developed

83 A higher  $R_s$  (Eq. 1) can be obtained by increasing the product of the exposure surface area of the  
84 sampler ( $A$ ) and the overall mass transfer coefficient ( $k_o$ ):

$$85 \quad R_s = A \times k_o \quad (1)$$

86  $k_o$  (Eq. 2) is dependent on the MTCs (mass transfer coefficients) of each successive compartment  
87 of the sampler (Booij et al., 2017), as evidenced by the expression of the resistance to mass  
88 transfer ( $1/k_o$ ):

$$89 \quad \frac{1}{k_o} = \frac{1}{k_w} + \frac{1}{K_{mw}k_m} + \frac{1}{K_{sw}k_s} \quad (2)$$

90 Where  $k_w$ ,  $k_m$ ,  $k_s$  are the MTC for the WBL, the membrane (microporous polyethylene tube in our  
91 case, MPT), and the sorbent respectively, and  $K_{mw}$ ,  $K_{sw}$  are the sorption coefficients of the  
92 membrane and the sorbent. When  $K_{mw} = 1$ , and transport through the membrane (MPT) is only via  
93 the pore space (i.e., filled with water), Eq. 2 becomes (Fauvelle et al., 2017):

$$94 \quad \frac{1}{k_o} = \frac{\delta}{D_w} + \frac{d\theta^2}{\phi D_w} + \frac{1}{K_{sw}k_s} \quad (3)$$

95 Where  $\delta$  and  $d$  are WBL and membrane thicknesses,  $D_w$  is the contaminant diffusion coefficient  
96 in water,  $\theta$  is the tortuosity, and  $\phi$  is the membrane porosity.

97 Otherwise, a promising way to limit the influence of WBL thickness can be found in increasing  
98 the second term of Eq. 3, e.g. increasing  $d$  (Belles et al., 2017; Chen et al., 2013; Fauvelle et al.,  
99 2017).

100 In the present study, we propose to assess MPT ( $d = 2$  mm thick,  $A = 17.6$  cm<sup>2</sup>,  $\phi = 35\%$  porosity,  
101  $2.5$   $\mu$ m pore size) as a diffusion barrier filled with a receiving phase consisting of TiO<sub>2</sub> particles  
102 embedded in an agarose gel. Compared to the conventional DGT,  $A$  is increased from  $3.14$  to  
103  $17.6$  cm<sup>2</sup> (factor of  $5.6$ ),  $d$  is increased from  $0.8$  to  $2$  mm (factor of  $2.5$ ),  $\phi$  is decreased from  
104 almost  $100\%$  to  $35\%$  (factor of  $3$ ), and  $\theta$  could be also decreased from  $3$  to  $1$ . Indeed,  $\theta$  is  
105 supposed to be much higher in a gel than in MPT, as Belles et al. observed lower (factor of  $3$  to  
106 factor of  $9$ ) diffusion coefficients for polar organic substances in hydrogels than in water (Belles  
107 et al., 2017). Therefore, in light of Eq. 3, MPT could increase  $R$ , by a factor of  $2$ , and as  $R$ , is  
108 proportional to  $A$ , increasing MPT length will increase  $R$ , accordingly when required. Otherwise,  
109 resistance to mass transfer induced by MPT should be  $4$  times higher than the one induced by the  
110 WBL, considering a worst case  $\delta$  value of  $1.50 \pm 0.013$  mm in an unstirred medium (Warnken et  
111 al., 2006; with  $d = 2$  mm,  $\theta = 1$ ,  $\phi = 35\%$ ), suggesting a full MPT control (i.e., low dependency  
112 to flowing conditions) of the diffusion of PMG and AMPA across the sampler.

113 The objectives of this study were i) to determine  $K_{mv}$  for PMG and AMPA to ensure their  
114 transport is occurring only via the pore space and to avoid any interferences during the sampling,  
115 ii) to verify that MPT is the compartment of the sampler providing the higher resistance to mass  
116 transfer, and iii) to evaluate the performances of the sampler in situ.

## 117 **2. EXPERIMENTAL SECTION**

### 118 **2.1. Chemicals and reagents**

119 Acetonitrile (ACN), methanol (MeOH) and dichloromethane (DCM) were purchased from Merck  
120 (Darmstadt, Germany) and their purity were higher than 99.8%. Trimethylamine (TEA) was  
121 obtained from Atifina Chemicals Inc. (USA) and its purity was 99.5%. Water with resistivity >  
122 18.2 M $\Omega$  (MQ) was produced by a Millipore system. Glyphosate (PMG),  
123 aminomethylphosphonic acid (AMPA), <sup>13</sup>C<sub>2</sub>-<sup>15</sup>N-PMG, <sup>13</sup>C-<sup>15</sup>N-D<sub>2</sub>-AMPA, agarose, titanium dioxide  
124 (325 mesh, TiO<sub>2</sub>), sodium borate, ethylenediaminetetraacetic acid disodium (EDTA),  
125 fluorenylmethyloxycarbonyl chloride (Fmoc) were purchased from Sigma-Aldrich (China).  
126 NaOH pellets were obtained from Selby Biolab (Calyton, Victoria, 97% purity).

## 127 **2.2. Passive sampler procedure**

### 128 *Passive sampler assembly*

129 Microporous Polyethylene Tubes (MPTs) were purchased from Pall Corp. Crailsheim, Germany  
130 (Filtroplast®, 12 mm O.D., 8 mm I.D., 35% porosity, 2.5  $\mu$ m pore size, 0.6 g cm<sup>-3</sup> density). Tubes  
131 were cut in cylinders (8 cm length), solvent cleaned in a 400-mL jar with MeOH for 2 hours and  
132 stored in MQ until assembly. 200 mg of agarose gel, 216 mg of TiO<sub>2</sub> and 10 mL of MQ were  
133 mixed together at 90°C for 10 min in single-use 15-mL polyethylene conical centrifuge tubes.  
134 The mixture was immediately cast into a nonporous plastic tube (8 mm I.D.; 25 cm length), and  
135 then placed in an ice bath for 1 h to get a homogeneous distribution of the TiO<sub>2</sub> particles in the  
136 agarose matrix. Tubes were stored in the fridge for ~ 2 hours (until the mixture solidified). The  
137 TiO<sub>2</sub> + agarose gels were removed from the plastic tubes, cut in 7 cm length pieces, and then  
138 allowed to sit for 30 min at ambient temperature to shrink (i.e., through desiccation) and facilitate  
139 their subsequent introduction into the MPTs. Plastic tube inserts (5 mm length each, Stockcap,  
140 Sydney, Australia) were used to cap the tubes at both ends. Assembled MPT samplers (see



141 Supplementary Material Figure 1) were stored in MQ until deployment. A total sampler exposure  
142 area of 17.6 cm<sup>2</sup> (vs. 3.14 for a DGT housing) was considered for each MPT device i.e.,  
143 considering the internal diameter of the MPT in contact with the receiving phase (Cristale et al.,  
144 2013).

#### 145 *Extraction of passive samplers*

146 After deployment, samplers were stored in the fridge at 4 °C until extraction within a week.  
147 Entire MPT samplers were placed in 15-mL polyethylene conical centrifuge tubes with 4 mL of  
148 0.3 M NaOH. Tubes were placed on a shaker (60 rpm) in the darkness. Different extraction times  
149 (i.e. 24, 48 and 96 h) were tested with the passive samplers deployed in situ for 11 days. No  
150 significant differences were found in PMG and AMPA concentrations measured at different  
151 extraction times, and thus, hereafter, a 24 h elution step was performed with the all samplers.  
152 After extraction, a derivatization step was performed (see section 2.4). As only 400 µL were used  
153 for the derivatization step, a correction factor (22.5) was finally applied according to the overall  
154 water content of the extract (9 mL): selectively the NaOH extraction fraction (4 mL), the gel  
155 water content (i.e., total gel volume 3.5 mL, consisting of more than 95% of water) and the MPT  
156 pore water content (i.e., tube volume  $\times \phi = 1.5$  mL).

#### 157 **2.3. Water samples procedure**

158 Grab water samples (20 mL) were filtered through 0.45 µm regenerated-cellulose filters (Agilent)  
159 and were not pre-concentrated prior to the derivatization step (see section 2.4). When not  
160 analyzed the same day, samples were stored at -18°C.

#### 161 **2.4. Derivatization step**

162 In order to reach sufficient retention on a  $C_{18}$  reversed phase chromatographic analytical column,  
163 analytes were derivatized using FMOC-Cl, as suggested in ISO 16308:2014. Briefly, 400  $\mu\text{L}$  of  
164 sample (i.e. passive sampler eluate or grab water sample) was transferred in a 15-mL  
165 polyethylene falcon tube, together with 480  $\mu\text{L}$  of borate buffer (10  $\text{g L}^{-1}$  of sodium tetraborate in  
166 MQ). Then, 20  $\mu\text{L}$  of internal standard solution (1  $\text{ng } \mu\text{L}^{-1}$   $^{13}\text{C}_2$ - $^{15}\text{N}$ -PMG and  $^{13}\text{C}$ - $^{15}\text{N}$ -D<sub>2</sub>-AMPA), 40  
167  $\mu\text{L}$  of EDTA (29.2  $\text{g L}^{-1}$  of EDTA- $\text{Na}_3$  in MQ, pH adjusted to 8 with NaOH for improved  
168 dissolution) and 60  $\mu\text{L}$  of FMOC (12  $\text{g L}^{-1}$  of FMOC-Cl in ACN) was added (final pH was 9).  
169 Samples were shaken after each addition and then left overnight at room temperature in the dark  
170 for complete derivatization of the analytes. Next day, the excess of FMOC was removed by  
171 adding 300  $\mu\text{L}$  of DCM, shaking, and recovering the upper aqueous phase ( $\sim 500 \mu\text{L}$ ). Final  
172 eluents were placed in amber glass LC vials and stored in the fridge (4 °C) until analysis (within  
173 3-4 days).

## 174 **2.5. Analytical method**

175 Sample analysis methodology was adapted from previous studies (Fauvelle et al., 2015; Freuze et  
176 al., 2007). Briefly, analysis was performed on HPLC-MS/MS using an AB/Sciex API6500+Q  
177 mass spectrometer (Sciex, Concord, Ontario, Canada) equipped with an electrospray (TurboV)  
178 interface coupled to a Shimadzu Nexera HPLC system (Shimadzu Corp., Kyoto, Japan).  
179 Glyphosate, AMPA and their analogues, derivatized with FMOC-Cl, were separated by a  
180 Phenomenex Gemini-NX column (50 mm length, 3  $\mu\text{m}$  particle size, 2.1 mm diameter). Mobile  
181 phase consisted of a 0.1 % TEA aqueous solution pH adjusted to 9.5 with acetic acid (A), and  
182 MeOH/ACN 50:50 (v/v) (B). The analytical gradient was set at 92:8 (A/B) for 1.5 min; B was  
183 then increased linearly to 95% during 1.5 min and kept constant for another 1.5 min. B was  
184 decreased thereafter to initial conditions during 1.5 min, and a final 5 min equilibrating phase was

185 applied at the end of the gradient (11 min run). The mobile phase flow rate was set at 400  $\mu\text{L min}^{-1}$ , and the column oven temperature was 40  $^{\circ}\text{C}$ . Mass acquisition was performed using selected  
186 reaction monitoring (SRM) and negative ESI mode (Fauvelle et al., 2015). A 6-point calibration  
187 curve (from 1 to 200  $\text{ng mL}^{-1}$ ) was prepared and derivatized according to the protocol described  
188 above (section 2.4). Instrumental limits of quantification were estimated at 0.5  $\text{ng mL}^{-1}$  for PMG  
189 and 1  $\text{ng mL}^{-1}$  for AMPA. It is noteworthy that TEA resulted in the contamination of the mass  
190 spectrometer. This can be mitigated by flushing the system with a mix of solvents  
191 (isopropanol/ACN/MeOH) for 24 h. However, low levels of TEA remained detectable. Replacing  
192 TEA by ammonium acetate will avoid contaminations, at the expense of chromatographic  
193 parameters (worst peak shape and lower retention time).

## 195 **2.6. Adsorption on MPT**

196 To ensure transport is only occurring via the pore space, and is not delayed because of the  
197 diffusive material (Fauvelle et al., 2017), MPT to water partition coefficient ( $K_{\text{mw}} = C_{\text{MPT}} \cdot C_{\text{w}}^{-1}$ , with  
198  $C_{\text{MPT}}$  the concentration in MPT and  $C_{\text{w}}$  the concentration in water) values for PMG and AMPA  
199 were determined. To this end, 8 cm MPTs ( $n = 3$ ) were conditioned (see section 2.2), and  
200 immersed individually for 72 h in 10 mL of a 10  $\mu\text{g L}^{-1}$  aqueous solution of both analytes. Three  
201 controls with no MPT ensured the solution stability for the whole experiment duration. Water  
202 concentration was measured at the end of the experiment in the 3 above mentioned controls and  
203 in the 3 samples containing MPT.  $K_{\text{mw}}$  after 72 h of exposure ( $\text{mL g}^{-1}$ ) was determined as the  
204 concentration ratio in the MPT (i.e., deduced from water concentration balance before and after  
205 exposure,  $\text{ng g}^{-1}$ ) and in the water ( $\text{ng mL}^{-1}$ ).

## 206 **2.7. MPT sampler laboratory calibration**

207 Laboratory calibration of TiO<sub>2</sub> gels, naked or inserted in MPTs, was performed in two separated 3  
208 L plastic beakers filled with ultrapure water (one for 8 MPT samplers, another one for 8 naked  
209 TiO<sub>2</sub> gels). The calibration system was spiked with PMG and AMPA and allowed to equilibrate  
210 for 24 h before samplers' exposure. Water concentrations were measured daily ( $5 \pm 0.8$  and  $10 \pm$   
211  $2.7 \mu\text{g L}^{-1}$  for PMG and AMPA, respectively). Duplicates of TiO<sub>2</sub> gels, naked and enclosed in  
212 MPTs, were retrieved after 1, 2, 3 and 6 days, and treated according to the method described  
213 above. Naked TiO<sub>2</sub> gels and MPT samplers were enclosed in a nylon mesh (2 mm mesh) together  
214 with a PTFE weight to ensure that samplers were completely submerged throughout the  
215 experiment (Supplementary material Figure 2). Shaking was performed using a rotary shaker (60  
216 rpm) and beakers were completely covered in aluminum foil. The temperature and pH of the  
217 system were periodically checked and were in the range 22-25°C and 6.8-7, respectively. Non-  
218 linear regressions were fitted using Addinsoft XL-STAT software 19.02.

## 219 **2.8. MPT sampler in situ calibration**

220 A field calibration was performed in a drinking water reservoir in South East Queensland,  
221 Australia (Wappa Dam, 26.572105 °S, 152.922028 °E) in May 2016 (Supplementary material  
222 Figure 3). Triplicate MPT samplers were deployed in staggered configuration for 2, 3, 5, 6 and 11  
223 days. Each triplicate was deployed in stainless steel cages (5 mm mesh). Grab samples for water  
224 concentration measurements (see section 2.3) were taken every 2 or 3 days, together with the  
225 passive sampler replacement or retrieval. Wappa Dam, along with many other freshwater bodies  
226 in South East Queensland, are subject to excessive growth of aquatic weeds (e.g., *Salvinia*, water  
227 lettuce, water hyacinth) that may affect water quality (e.g., depleting dissolved oxygen,  
228 increasing nutrient load) and wildlife habitat. Therefore, one type of chemical control that is  
229 routinely implemented, to restrain weed growth, consists of spraying glyphosate onto newly

230 grown weeds. The MPT samplers were deployed about 2 h post spraying of glyphosate in the  
231 dam. Physico-chemical parameters (i.e., temperature, conductivity, pH, turbidity, dissolved  
232 oxygen) and total and dissolved concentrations of major and trace elements (i.e., Ca, Mg, Al, Cd,  
233 Co, Cu, Fe, Mn, Zn) were measured every 3 days (Supplementary material Table 1).

## 234 **2.9. Quality assurance and quality control**

235 Passive sampler blanks, MQ blanks, analytical blanks, and non-extracted spikes were prepared  
236 and treated along with passive and water samples. Positive controls were made by checking the  
237 intensity of internal standards (PMG and AMPA <sup>13</sup>C) spiked in all the samples and QA/QC  
238 samples (always between 81 and 115% recoveries). A 6-point calibration curve ensured the  
239 efficiency of the derivatization protocol for native PMG and AMPA. No PMG or AMPA were  
240 detected in any blanks or negative controls, relative standard deviation (RSD) of passive  
241 samplers' replicates were within 3 and 18% for both laboratory and field deployments.

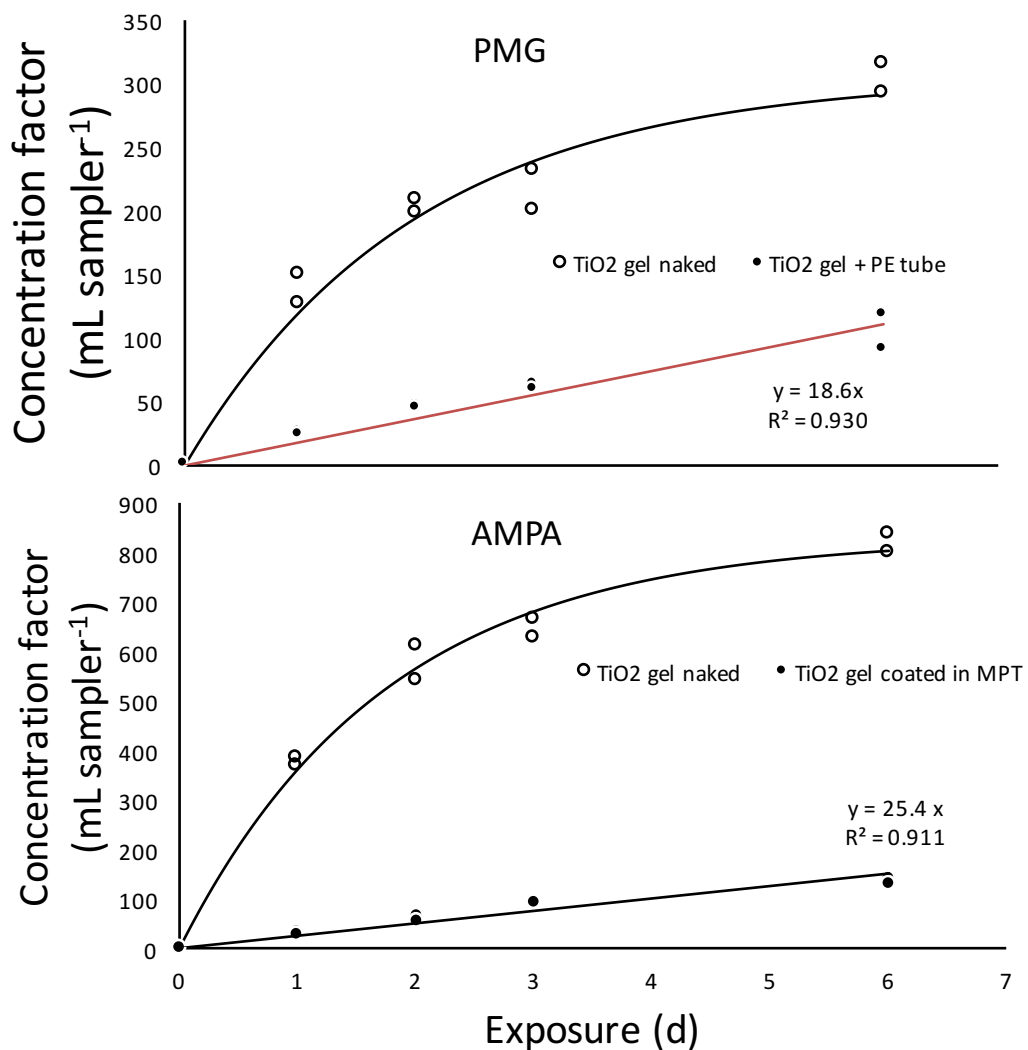
## 242 **3. RESULTS AND DISCUSSION**

### 243 **3.1. PMG and AMPA adsorption on MPT**

244  $K_{mw}$  values (see section 2.6) for PMG and AMPA were found to be close to 1 ( $1.07 \pm 0.17$  and  
245  $0.76 \pm 0.07$  mL g<sup>-1</sup>, respectively), meaning comparable quantities are found in MPT and in water.  
246 Therefore, adsorption at the MPT surface can be expected to be minimal for the diffusive layer  
247 selected and consequently, it is assumed that diffusion only occurs via the MPT pores. The  
248 diffusive material of a passive sampler should otherwise have a low affinity towards the analytes  
249 of interest to avoid any interferences during the sampling that may complicate data interpretation,  
250 e.g. delayed accumulation in the receiving phase (Belles et al., 2014; Vermeirssen et al., 2012).

251 The low  $K_{mw}$  for the compounds of interest suggests that the surface of the MPT will interact only  
252 minimally with the compounds and thus not affect their diffusion into the sampling phase which  
253 simplifies modelling.

### 254 3.2. Uptake of PMG and AMPA in TiO<sub>2</sub> gels and MPT passive samplers



255  
256 Figure 1. Uptake of PMG and AMPA in naked TiO<sub>2</sub> + agarose gels (open circles) and in TiO<sub>2</sub> +  
257 agarose gels inserted in microporous polyethylene tubes (MPTs) (full circles), under laboratory

258 controlled conditions. An indicative first order kinetic [ $y=K(1-e^{-kx})$ ] was fitted to the non-linear  
259 data.

260 A second experiment was set up to evaluate the uptake kinetic of PMG and AMPA in the  $\text{TiO}_2$  +  
261 agarose gel both with and without the MPT housing. In both cases, no measurable lag phase was  
262 observed at the beginning of the sampling, confirming no high interactions analytes and MPT.

263 Looking at the first order kinetics [ $y=K(1-e^{-kx})$ ], the mass of analyte sampled reached a pseudo-  
264 plateau ( $K = 307 \pm 21$  and  $831 \pm 29$  mL sampler<sup>-1</sup> for PMG and AMPA respectively) within a  
265 couple of days without MPT. Kinetics seem however, on the basis of our data, increasing beyond  
266 those pseudo-plateaux. Thus, the actual  $\text{TiO}_2$  to water distribution coefficient could be higher than  
267 those values. The slope at  $t = 0$  (i.e.,  $k$ ) gave otherwise an estimation of the analytes fluxes in  $\text{TiO}_2$   
268 gels naked of  $156 \pm 28$  and  $475 \pm 46$  mL day<sup>-1</sup> for PMG and AMPA respectively. These data are  
269 to be compared with the analytes fluxes in the case of  $\text{TiO}_2$  gels covered by MPT: we observed  
270 experimental  $R_s$  values of  $18.4 \pm 0.9$  and  $25.4 \pm 1.4$  mL day<sup>-1</sup> for PMG and AMPA, respectively  
271 (Fig. 1; Eq 1). Thus, the mass transfer resistance by the MPT is almost 10 times higher than the  
272 receiving phase alone. We can therefore consider a large control of contaminants fluxes by MPT  
273 to the receiving phase.  $R_s$  values measured with MPT are otherwise twice higher than those  
274 reported for o-DGT (Chen et al., 2013, 2012; Fauvelle et al., 2015), which shows the ability of  
275 MPT based passive sampler to increase  $R_s$ , which was identified a main issue of o-DGT.

276 Considering Eq 1 and 3 with  $A = 17.6$  cm<sup>2</sup>,  $\phi = 35\%$ ,  $d = 2$  mm, and adopting  $\theta = 1$ , and a typical  
277  $D_w$  value for organic acids of  $5$  to  $10 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup>, we can predict a generic  $R_s$  between  $13$  and  $27$   
278 mL day<sup>-1</sup>, which is in good agreement with the experimental data mentioned above. The  
279 difference in  $R_s$  estimates between PMG and AMPA is likely to be attributed to the higher  $D_w$  of

280 AMPA related to its lower molecular weight and steric hindrance. The same pattern was also  
281 observed in a previous study (Fauvelle et al., 2015).

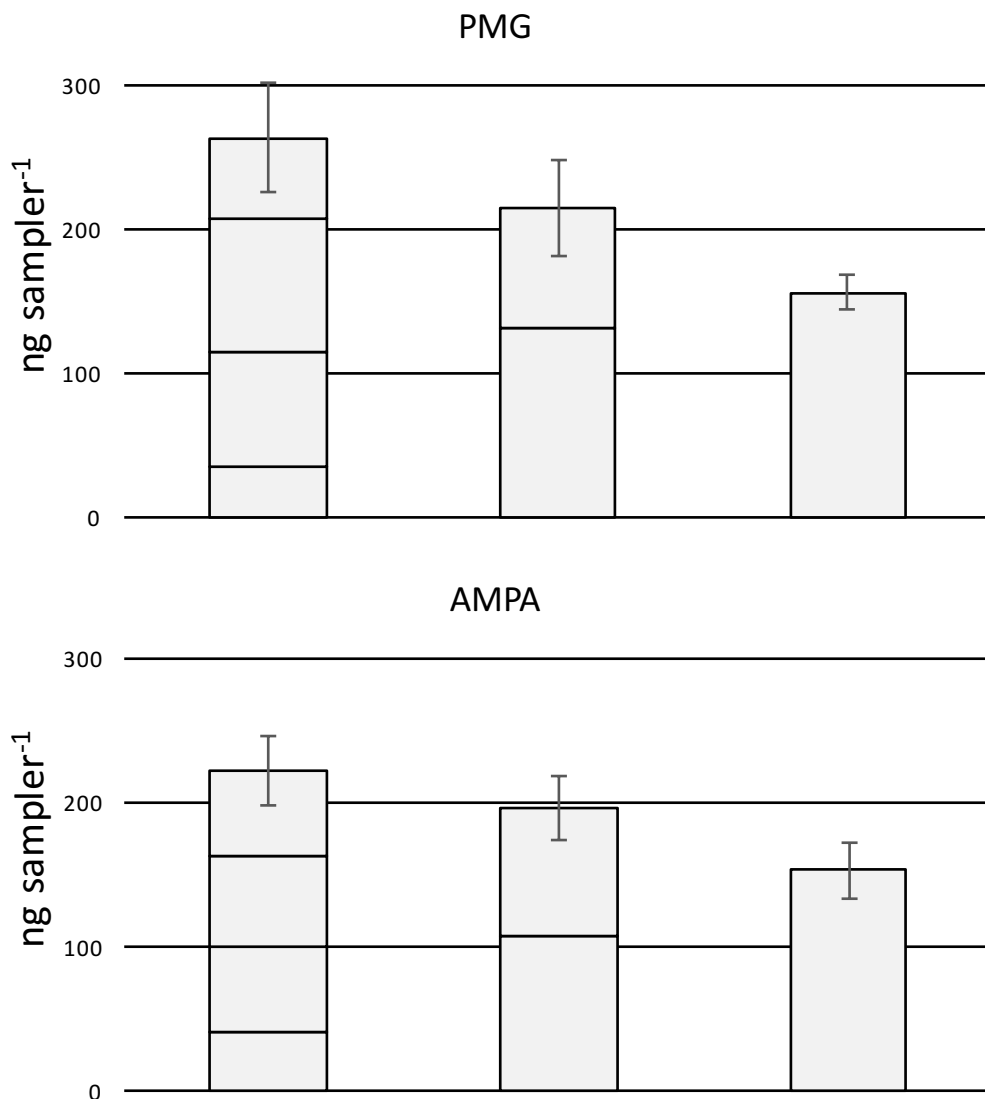
282 The role of the water boundary layer, whose thickness depends on hydrodynamics, was not  
283 investigated here. Nevertheless, assuming no water advection phenomena within the MPT matrix,  
284 the 2-mm thick MPT with  $\phi = 35\%$  ( $d/\phi = 5.71$ , Eq. 3 with  $\theta = 1$ ) used here should be able to  
285 minimize the effect of the WBL with typical thicknesses between  $0.230 \pm 0.032$  mm under stirred  
286 conditions, increasing up to  $1.50 \pm 0.013$  mm in an unstirred medium (Warnken et al., 2006).  
287 Thereby, the maximum error on sampling rates would be lower than 20% whatever the flowing  
288 conditions (except in the theoretical case of zero flow where  $\delta$  is infinite).

### 289 **3.3. Calibration of MPT passive samplers for PMG and AMPA in freshwater lake**

290 MPT samplers were deployed in overlapping and consecutive periods (Fig. 2) in order to check  
291 the accuracy and consistency of the PMG and AMPA uptake in the samplers (Allan et al., 2008).  
292 If uptake over time is uniform, all three bars should show the same level of mass accumulated  
293 after 11 days of exposure. Similar uptake was observed at the shortest deployment times (i.e. 3+3  
294 d and 6 d), but contaminant fluxes seem to decrease with increasing exposure duration (3 bars  
295 statistically different, Kruskal-Wallis test,  $\alpha = 0.05$ ). This might be explained by i) the increased  
296 pathway thickness due to the equilibrium reached with the surface  $\text{TiO}_2$  particles of the receiving  
297 phase, and ii) the addition of an increasing resistance attributed to biotic or abiotic fouling (i.e.,  
298 additional thickness of the MPT layer due to the development of biofilm at the surface of the  
299 sampler or pore clogging by natural particles, increasing  $d$  or lowering  $\phi$ , respectively). Another  
300 possibility is the potential degradation of the compounds sequestered inside the sampler, since  
301 MPT pore size is big enough to allow the passage of microorganisms. These phenomena may

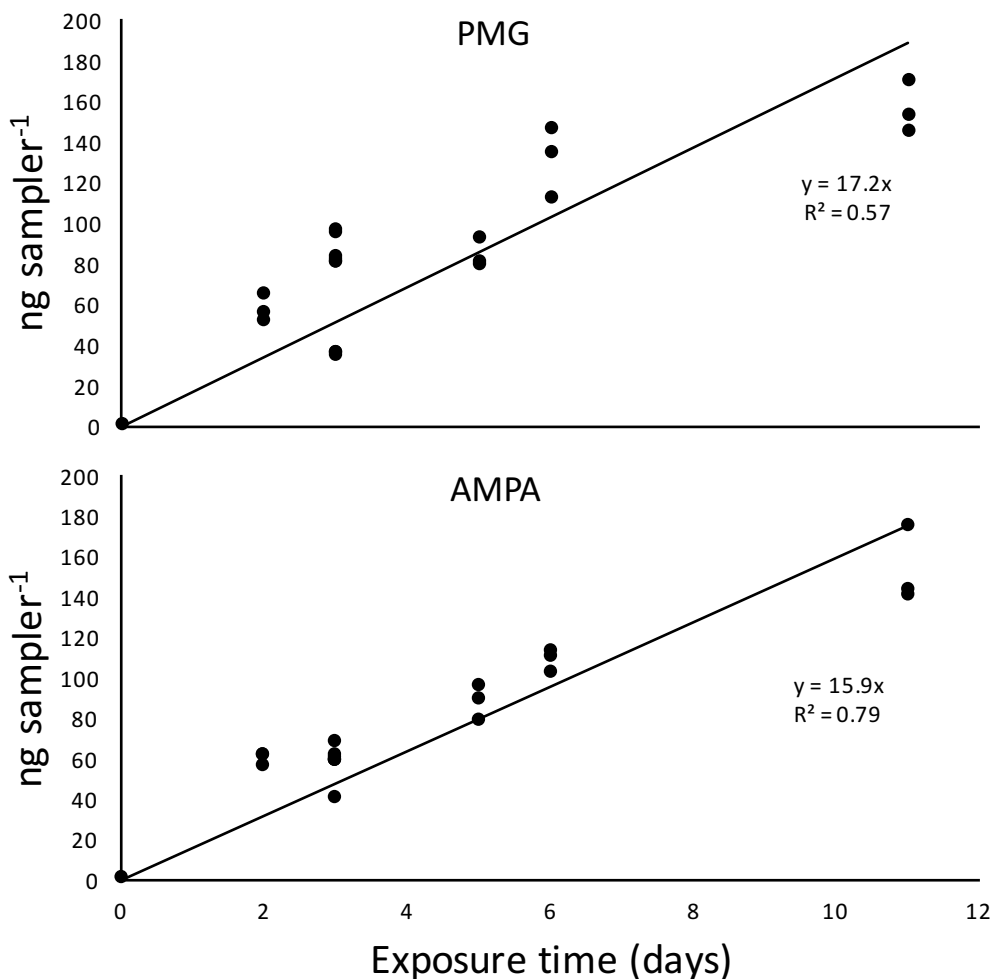


302 imply an underestimation of the time-weighted average concentrations and require further  
303 investigation.



304  
305 Figure 2. Mass of PMG and AMPA accumulated in MTP passive samplers deployed in Wappa  
306 dam. Left bar represents the sum of 4 x triplicate samplers exposed successively for 3 or 2 days.  
307 Middle bar is the sum of 2 x triplicate samplers exposed successively for 6 and 5 days. Right bar  
308 is the analyte mass found in the single triplicate sampler exposed for the entire 11 days. Error  
309 bars are the square roots of the sums of squared standard deviations (n = 3).

310 Uptake results for PMG and AMPA in MPT samplers deployed in Wappa dam are presented in  
311 Fig. 2 and 3. The concentration of PMG directly measured in grab water samples (collected every  
312 3 days) was found to be relatively constant ( $0.77 \pm 0.12 \text{ ng mL}^{-1}$ , Supplementary Material Figure  
313 4, LOQ =  $0.5 \text{ ng mL}^{-1}$ ), whereas AMPA concentration in grab samples was always below the  
314 LOQ ( $1 \text{ ng mL}^{-1}$ ). In MPT passive samplers, a linear relationship between the analyte mass  
315 accumulated in the sampler and the exposure duration was observed (Fig. 3) for both PMG and  
316 AMPA. The PMG mass accumulated after 11 days of exposure is below the linear regression,  
317 which can be partially explained by the lower concentration reported at the end of the experiment  
318 (Supplementary Material Figure 4). Although AMPA was not detected in grab samples, linear  
319 uptake of the analyte in the MPT passive samplers was observed (Fig. 3), which demonstrate the  
320 better sensitivity of MPT technique compare to grab sample directly injected. Taking into  
321 account the previously determined  $R_v$  for AMPA (Fig. 1,  $25.4 \pm 1.4 \text{ mL day}^{-1}$ ), and the slope of  
322 Fig. 3 (i.e. average mass of AMPA accumulated per day,  $15.9 \pm 0.7 \text{ ng day}^{-1}$ ), we can estimate a  
323 hypothetical time averaged AMPA concentration of  $0.63 \text{ ng mL}^{-1}$  during the experiment, which is  
324 below the analytical LOQ of grab water samples.

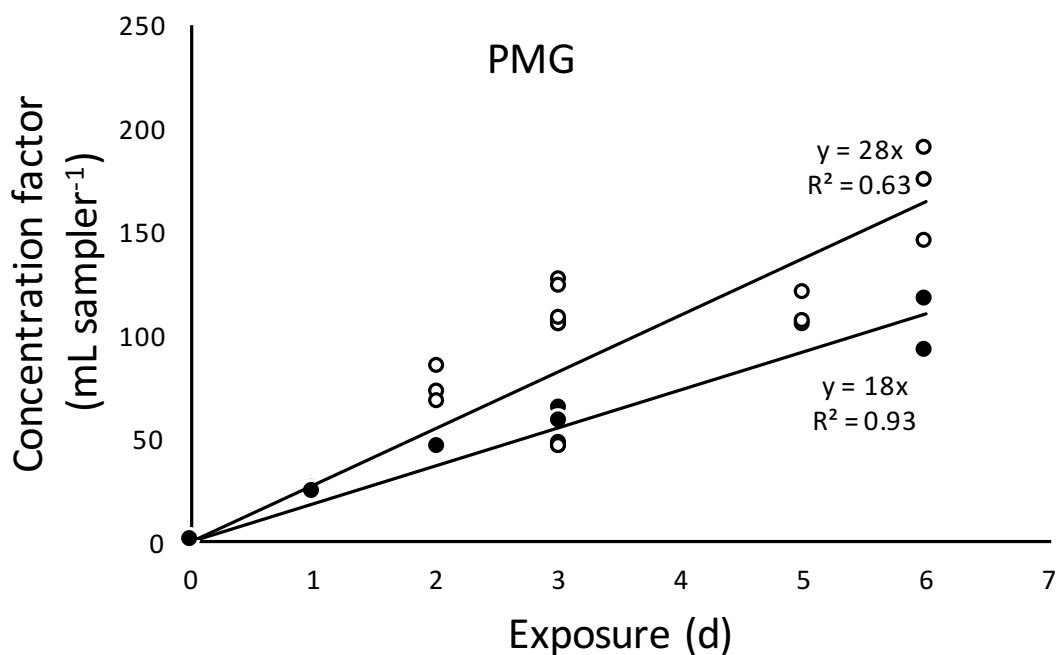


325

326 Figure 3. Mass of PMG and AMPA accumulated in MTP passive samplers in Wappa dam as a  
 327 function of exposure duration.

328 PMG accumulation in MTP passive samplers deployed in surface water (in situ experiment) and  
 329 in MQ (laboratory experiment) is illustrated in Fig. 4. The slopes indicate the sampling rates in  
 330 each exposure environment. The 6-day averaged sampling rates are 50 % higher in the field than  
 331 in the laboratory. However, the distribution of the in situ data points is scattered, and slopes are  
 332 rather close to the theoretical one determined in section 3.2 (13 to 27 mL day<sup>-1</sup>).

333 A previous study mentioned the presence of metal cations as a potential interfering factor with  
334 the accumulation of PMG and AMPA in passive samplers (Fauvelle et al., 2015). That  
335 interference was not observed in the current study, because similar concentration factors were  
336 observed in the laboratory and in situ. An explanation can be found in the different bivalent  
337 cation composition of each study, which may differ by an order of magnitude (see Supplementary  
338 Material Table 1). A special attention should then be paid to the inorganic composition of each  
339 medium sampled.



340  
341 Figure 4. Concentration factor (mL sampler<sup>-1</sup>) of PMG in MPT passive samplers in surface water  
342 (open circles) and in MQ water (full circles). Slopes represent the sampling rates over the 6-day  
343 period.

344 The use of MPT samplers allowed the measurement of low PMG and AMPA concentrations in  
345 the aquatic environment. This study is part of several recent studies aimed at improving the

346 passive sampling of polar organic compounds. It opens the possibility of applying them in other  
347 complex systems, presenting low concentrations, such as the marine environment. Accordingly,  
348 future studies would focus on testing the reliability and robustness of the performance of MPT  
349 passive samplers under different environmental conditions.

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## 357 **REFERENCES**

- 358 Allan, I.J., Knutsson, J., Guigues, N., Mills, G.A., Fouillac, A.-M., Greenwood, R., 2008.  
359 Chemcatcher® and DGT passive sampling devices for regulatory monitoring of trace metals  
360 in surface water. *J. Environ. Monit.* 10. doi:10.1039/b802581a
- 361 Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P.,  
362 Manahan, S.E., 2004. Development of a passive, in situ, integrative sampler for hydrophilic  
363 organic contaminants in aquatic environments. *Environ. Toxicol. Chem.* 23, 1640–1648.
- 364 Annett, R., Habibi, H.R., Hontela, A., 2014. Impact of glyphosate and glyphosate-based  
365 herbicides on the freshwater environment. *J. Appl. Toxicol.* 34. doi:10.1002/jat.2997
- 366 Aparicio, V.C., De Gerónimo, E., Marino, D., Primost, J., Carriquiriborde, P., Costa, J.L., 2013.  
367 Environmental fate of glyphosate and aminomethylphosphonic acid in surface waters and  
368 soil of agricultural basins. *Chemosphere* 93, 1866–73.  
369 doi:10.1016/j.chemosphere.2013.06.041
- 370 Arkan, T., Molnár-Perl, I., 2015. The role of derivatization techniques in the analysis of  
371 glyphosate and aminomethyl-phosphonic acid by chromatography. *Microchem. J.* 121.

372 doi:10.1016/j.microc.2015.02.007

373 Battaglin, W.A., Meyer, M.T., Kuivila, K.M., Dietze, J.E., 2014. Glyphosate and its degradation  
374 product AMPA occur frequently and widely in U.S. soils, surface water, groundwater, and  
375 precipitation. *J. Am. Water Resour. Assoc.* 50. doi:10.1111/jawr.12159

376 Beeton, R., Buckley, K., Jones, G., Morgan, D., Reichelt, R., Trewin, D., 2006. Australia State of  
377 the Environment.

378 Belles, A., Alary, C., Aminot, Y., Readman, J.W., Franke, C., 2017. Calibration and response of  
379 an agarose gel based passive sampler to record short pulses of aquatic organic pollutants.  
380 *Talanta* 165, 1–9. doi:10.1016/j.talanta.2016.12.010

381 Belles, A., Pardon, P., Budzinski, H., 2014. Development of an adapted version of polar organic  
382 chemical integrative samplers (POCIS-Nylon). *Anal. Bioanal. Chem.* 406, 1099–1110.  
383 doi:10.1007/s00216-013-7286-2

384 Benbrook, C.M., 2016. Trends in glyphosate herbicide use in the United States and globally.  
385 *Environ. Sci. Eur.* 28. doi:10.1186/s12302-016-0070-0

386 Berho, C., Claude, B., Coisy, E., Togola, A., Bayouhd, S., Morin, P., Amalric, L., 2017.  
387 Laboratory calibration of a POCIS-like sampler based on molecularly imprinted polymers  
388 for glyphosate and AMPA sampling in water. *Anal. Bioanal. Chem.* doi:10.1007/s00216-  
389 016-0150-4

390 Booij, K., Maarsen, N.L., Theeuwes, M., van Bommel, R., 2017. A method to account for the  
391 effect of hydrodynamics on polar organic compound uptake by passive samplers. *Environ.*  
392 *Toxicol. Chem.* doi:10.1002/etc.3700

393 Borggaard, O.K., Gimsing, A.L., 2008. Fate of glyphosate in soil and the possibility of leaching  
394 to ground and surface waters: A review. *Pest Manag. Sci.* 64. doi:10.1002/ps.1512

395 Chen, C.-E., Zhang, H., Jones, K.C., 2012. A novel passive water sampler for in situ sampling of  
396 antibiotics. *J. Environ. Monit.* 14, 1523–30. doi:10.1039/c2em30091e

397 Chen, C.-E., Zhang, H., Ying, G.-G., Jones, K.C., 2013. Evidence and recommendations to  
398 support the use of a novel passive water sampler to quantify antibiotics in wastewaters.  
399 *Environ. Sci. Technol.* 47, 13587–93. doi:10.1021/es402662g

400 Comoretto, L., Arfib, B., Chiron, S., 2007. Pesticides in the Rhône river delta (France): basic data  
401 for a field-based exposure assessment. *Sci. Total Environ.* 380, 124–32.  
402 doi:10.1016/j.scitotenv.2006.11.046

403 Coupe, R.H., Kalkhoff, S.J., Capel, P.D., Gregoire, C., 2012. Fate and transport of glyphosate  
404 and aminomethylphosphonic acid in surface waters of agricultural basins. *Pest Manag. Sci.*  
405 68. doi:10.1002/ps.2212

406 Cristale, J., Katsoyiannis, A., Chen, C., Jones, K.C., Lacorte, S., 2013. Assessment of flame  
407 retardants in river water using a ceramic dosimeter passive sampler. *Environ. Pollut.* 172,  
408 163–169. doi:10.1016/j.envpol.2012.08.014

409 Dong, Y.-L., Guo, D.-Q., Cui, H., Li, X.-J., He, Y.-J., 2015. Magnetic solid phase extraction of  
410 glyphosate and aminomethylphosphonic acid in river water using  
411  $\text{Ti}^{4+}$ -immobilized  
412  $\text{Fe}_3\text{O}_4$  nanoparticles by capillary  
413 electrophoresis. *Anal. Methods* 7. doi:10.1039/c5ay00109a

414 Fauvelle, V., Kaserzon, S.L., Montero, N., Lissalde, S., Allan, I.J., Mills, G., Mazzella, N.,  
415 Mueller, J.F., Booij, K., 2017. Dealing with Flow Effects on the Uptake of Polar  
416 Compounds by Passive Samplers. *Environ. Sci. Technol.* 51, 2536–2537.  
417 doi:10.1021/acs.est.7b00558

418 Fauvelle, V., Mazzella, N., Belles, A., Moreira, A., Allan, I.J., Budzinski, H., 2014. Optimization  
419 of the polar organic chemical integrative sampler for the sampling of acidic and polar  
420 herbicides. *Anal. Bioanal. Chem.* 406, 3191-3199. doi:10.1007/s00216-014-7757-0

421 Fauvelle, V., Mazzella, N., Delmas, F., Madarassou, K., Eon, M., Budzinski, H., 2012. Use of  
422 mixed-mode ion exchange sorbent for the passive sampling of organic acids by polar  
423 organic chemical integrative sampler (POCIS). *Environ. Sci. Technol.* 46, 13344–13353.

424 Fauvelle, V., Nhu-Trang, T.-T., Feret, T., Madarassou, K., Randon, J., Mazzella, N., 2015.  
425 Evaluation of Titanium Dioxide as a Binding Phase for the Passive Sampling of Glyphosate  
426 and Aminomethyl Phosphonic Acid in an Aquatic Environment. *Anal. Chem.* 87, 6004–9.  
427 doi:10.1021/acs.analchem.5b00194

428 Freuze, I., Jadas-Hecart, A., Royer, A., Communal, P.-Y., 2007. Influence of complexation  
429 phenomena with multivalent cations on the analysis of glyphosate and aminomethyl  
430 phosphonic acid in water. *J. Chromatogr. A* 1175, 197–206.  
431 doi:10.1016/j.chroma.2007.10.092

432 Kaserzon, S.L., Hawker, D.W., Booij, K., O'Brien, D.S., Kennedy, K., Vermeirssen, E.L.M.,  
433 Mueller, J.F., 2014. Passive sampling of perfluorinated chemicals in water: in-situ  
434 calibration. *Environ. Pollut.* 186, 98–103. doi:10.1016/j.envpol.2013.11.030

435 Kaserzon, S.L., Kennedy, K., Hawker, D.W., Thompson, J., Carter, S., Roach, A.C., Booij, K.,  
436 Mueller, J.F., 2012. Development and calibration of a passive sampler for perfluorinated  
437 alkyl carboxylates and sulfonates in water. *Environ. Sci. Technol.* 46, 4985–93.  
438 doi:10.1021/es300593a

439 Kingston, J.K., Greenwood, R., Mills, G.A., Morrison, G.M., Björklund Persson, L., 2000.  
440 Development of a novel passive sampling system for the time-averaged measurement of a

441 range of organic pollutants in aquatic environments. *J. Environ. Monit.* 2, 487–495.  
442 doi:10.1039/b003532g

443 Li, H., Helm, P. a, Paterson, G., Metcalfe, C.D., 2011. The effects of dissolved organic matter  
444 and pH on sampling rates for polar organic chemical integrative samplers (POCIS).  
445 *Chemosphere* 83, 271–80. doi:10.1016/j.chemosphere.2010.12.071

446 Magbanua, F.S., Townsend, C.R., Hageman, K.J., Lange, K., Lear, G., Lewis, G.D., Matthaei,  
447 C.D., 2013. Understanding the combined influence of fine sediment and glyphosate  
448 herbicide on stream periphyton communities. *Water Res.* 47, 5110–20.  
449 doi:10.1016/j.watres.2013.05.046

450 Mercurio, P., Flores, F., Mueller, J.F., Carter, S., Negri, A.P., 2014. Glyphosate persistence in  
451 seawater. *Mar. Pollut. Bull.* 1, 1–6. doi:10.1016/j.marpolbul.2014.01.021

452 Portier, C.J., Armstrong, B.K., Baguley, B.C., Baur, X., Belyaev, I., Bellé, R., Belpoggi, F.,  
453 Biggeri, A., Bosland, M.C., Bruzzi, P., Budnik, L.T., Bugge, M.D., Burns, K., Calaf, G.M.,  
454 Carpenter, D.O., Carpenter, H.M., López-Carrillo, L., Clapp, R., Cocco, P., Consonni, D.,  
455 Comba, P., Craft, E., Dalvie, M.A., Davis, D., Demers, P.A., De Roos, A.J., DeWitt, J.,  
456 Forastiere, F., Freedman, J.H., Fritschi, L., Gaus, C., Gohlke, J.M., Goldberg, M., Greiser,  
457 E., Hansen, J., Hardell, L., Hauptmann, M., Huang, W., Huff, J., James, M.O., Jameson,  
458 C.W., Kortenkamp, A., Kopp-Schneider, A., Kromhout, H., Larramendy, M.L., Landrigan,  
459 P.J., Lash, L.H., Leszczynski, D., Lynch, C.F., Magnani, C., Mandrioli, D., Martin, F.L.,  
460 Merler, E., Michelozzi, P., Miligi, L., Miller, A.B., Mirabelli, D., Mirer, F.E., Naidoo, S.,  
461 Perry, M.J., Petronio, M.G., Pirastu, R., Portier, R.J., Ramos, K.S., Robertson, L.W.,  
462 Rodriguez, T., Röösli, M., Ross, M.K., Roy, D., Rusyn, I., Saldiva, P., Sass, J., Savolainen,  
463 K., Scheepers, P.T.J., Sergi, C., Silbergeld, E.K., Smith, M.T., Stewart, B.W., Sutton, P.,  
464 Tateo, F., Terracini, B., Thielmann, H.W., Thomas, D.B., Vainio, H., Vena, J.E., Vineis, P.,  
465 Weiderpass, E., Weisenburger, D.D., Woodruff, T.J., Yorifuji, T., Yu, I.J., Zambon, P.,  
466 Zeeb, H., Zhou, S.-F., 2016. Differences in the carcinogenic evaluation of glyphosate  
467 between the international agency for research on cancer (IARC) and the european food  
468 safety authority (EFSA). *J. Epidemiol. Community Health* 70. doi:10.1136/jech-2015-  
469 207005

470 Shushkova, T., Ermakova, I., Leontievsky, A., 2010. Glyphosate bioavailability in soil.  
471 *Biodegradation* 21. doi:10.1007/s10532-009-9310-y

472 Stewart, M., Olsen, G., Hickey, C.W., Ferreira, B., Jelić, A., Petrović, M., Barcelo, D., 2014. A  
473 survey of emerging contaminants in the estuarine receiving environment around Auckland,  
474 New Zealand. *Sci. Total Environ.* 468–469, 202–10. doi:10.1016/j.scitotenv.2013.08.039

475 Vermeirssen, E.L.M., Dietschweiler, C., Escher, B.I., van der Voet, J., Hollender, J., 2012.  
476 Transfer kinetics of polar organic compounds over polyethersulfone membranes in the



477 passive samplers POCIS and Chemcatcher. *Environ. Sci. Technol.* 46, 6759–66.  
 478 doi:10.1021/es3007854

479 Warnken, K., Zhang, H., Davison, W., 2006. Accuracy of the diffusive gradients in thin-films  
 480 technique: Diffusive boundary layer and effective sampling area considerations. *Anal.*  
 481 *Chem.* 78, 3780–3787. doi:10.1021/ac060139d

482 Zhou, C.-F., Wang, Y.-J., Li, C.-C., Sun, R.-J., Yu, Y.-C., Zhou, D.-M., 2013. Subacute toxicity  
 483 of copper and glyphosate and their interaction to earthworm (*Eisenia fetida*). *Environ.*  
 484 *Pollut.* 180, 71–7. doi:10.1016/j.envpol.2013.05.016

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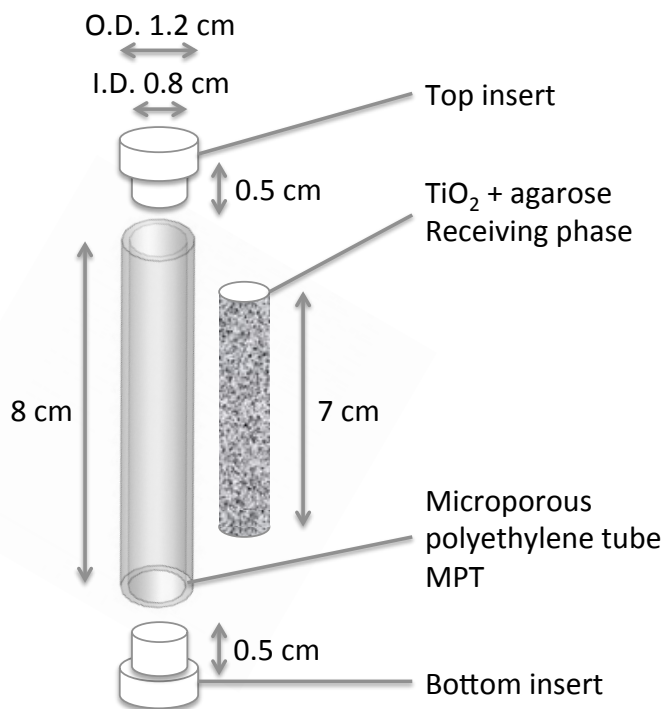
486 **SUPPLEMENTARY MATERIAL**

487 Supplementary material Table 1. Physico-chemical parameters measured at Wappa Dam with a  
 488 YSI 650 MDS multiparameter probe. Dissolved metal concentrations refer to water filtered  
 489 through 0.45  $\mu\text{m}$  regenerated cellulose filters measured by inductively coupled plasma-mass  
 490 spectrometer.

	0.2 m depth	RSD (%)	1.5 m depth	RSD (%)
Average temperature ( $^{\circ}\text{C}$ )	23	4	22	3
Conductivity ( $\mu\text{s cm}^{-1}$ )	226	6	229	5
pH	7	1	7	2
Turbidity (NTU)	3	32	4	22
Dissolved Oxygen (%)	63	28	24	45
Dissolved Oxygen ( $\text{mg L}^{-1}$ )	6	20	2	46
Ca total ( $\text{mg L}^{-1}$ )	7.8	49	-	-
Ca dissolved ( $\text{mg L}^{-1}$ )	7.3	49	-	-
Mg total ( $\text{mg L}^{-1}$ )	7.8	49	-	-
Mg dissolved ( $\text{mg L}^{-1}$ )	7.6	50	-	-
Al total ( $\text{mg L}^{-1}$ )	0.13	128	-	-
Al dissolved ( $\text{mg L}^{-1}$ )	0.015	55	-	-

Cd total (mg L <sup>-1</sup> )	0	-	-	-
Cd dissolved (mg L <sup>-1</sup> )	0	-	-	-
Co total (mg L <sup>-1</sup> )	0	-	-	-
Co dissolved (mg L <sup>-1</sup> )	0	-	-	-
Cu total (mg L <sup>-1</sup> )	0.001	78	-	-
Cu dissolved (mg L <sup>-1</sup> )	0	-	-	-
Fe total (mg L <sup>-1</sup> )	0.26	60	-	-
Fe dissolved (mg L <sup>-1</sup> )	0.06	52	-	-
Mn total (mg L <sup>-1</sup> )	0.061	81	-	-
Mn dissolved (mg L <sup>-1</sup> )	0.008	143	-	-

491

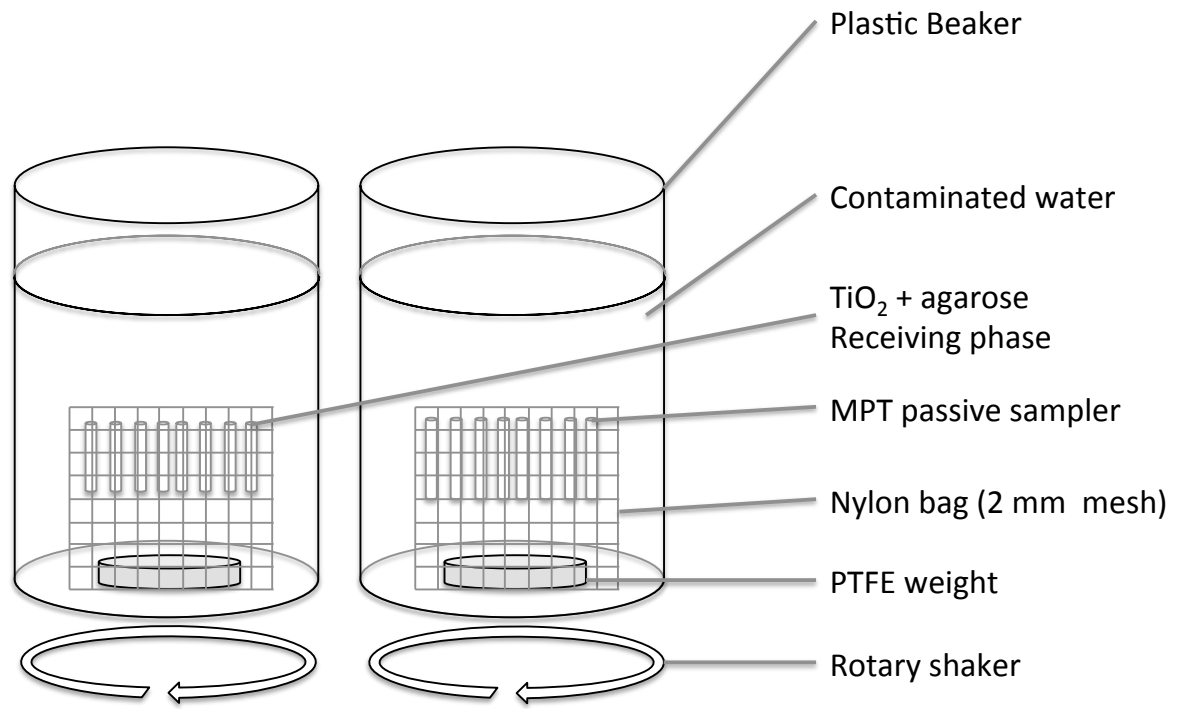


492

493 Supplementary material Figure 1. Schematic view of the microporous polyethylene tube (MPT)

494 sampler developed for the sampling of glyphosate and its transformation product

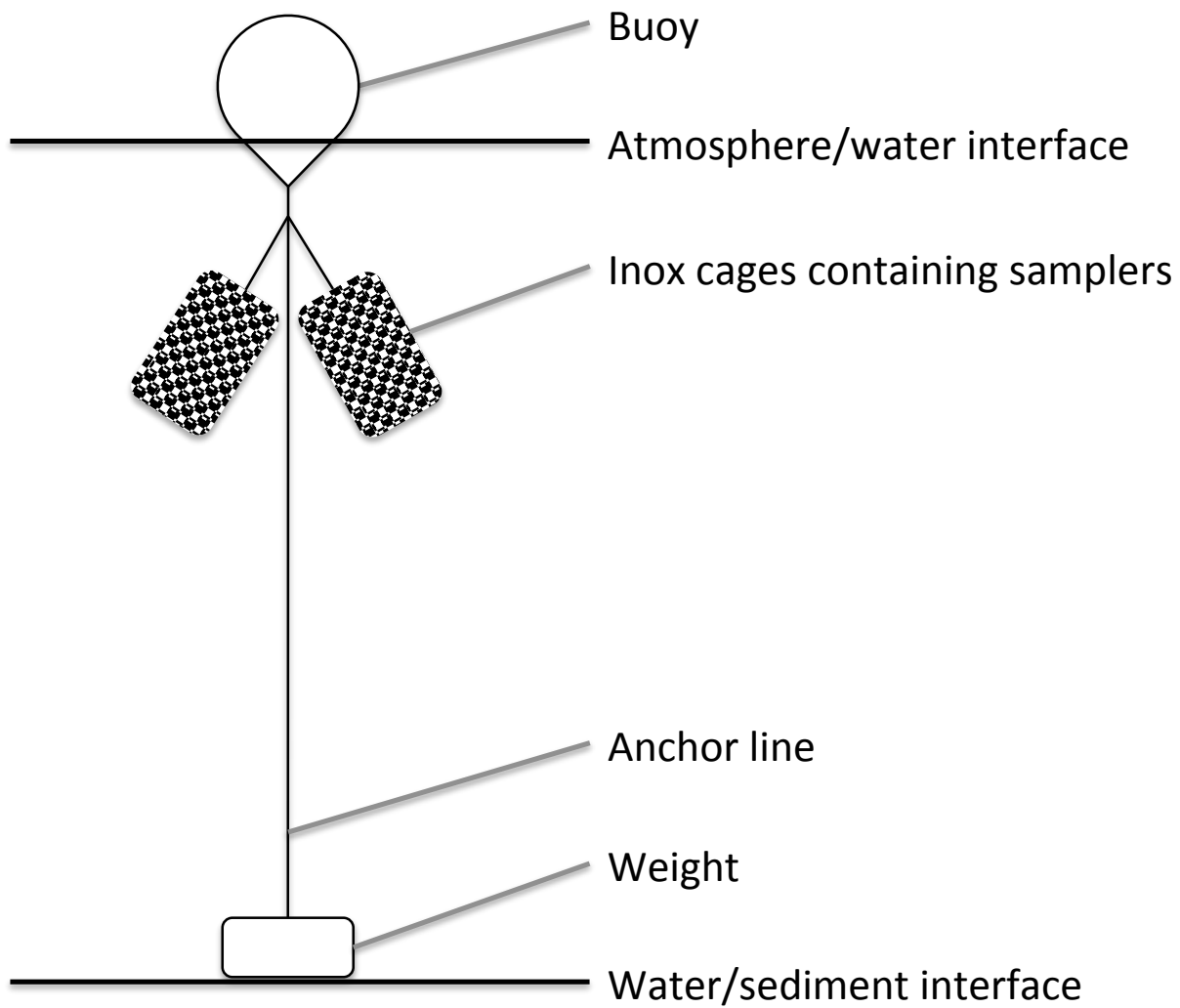
495 aminomethylphosphonic acid. O.D. is outside diameter, I.D. is internal diameter.



496

497 Supplementary material Figure 2. Laboratory calibration system for MPT passive samplers and

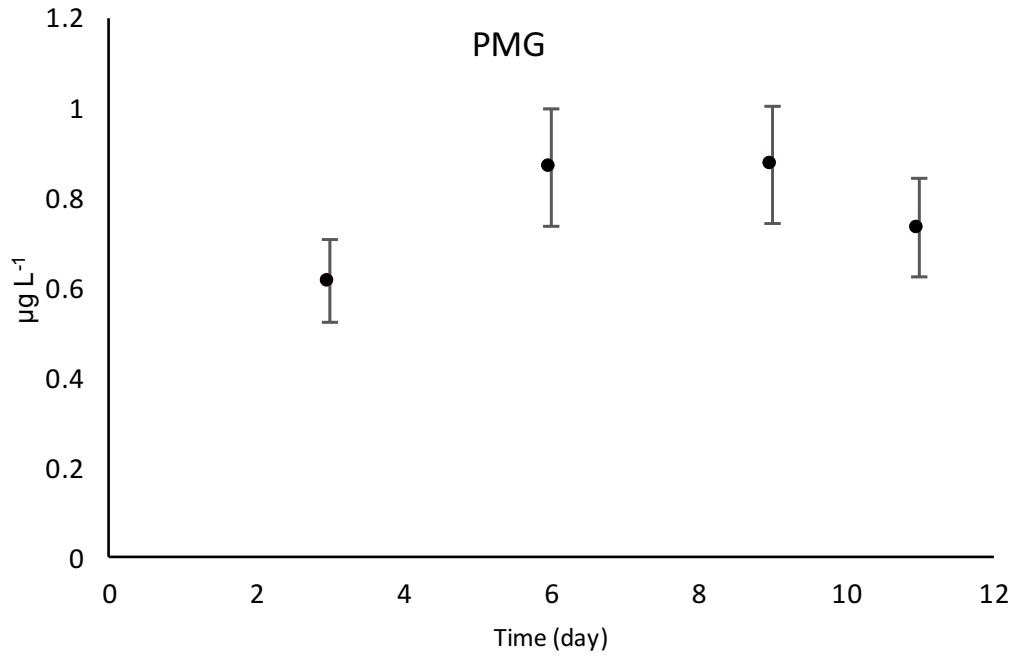
498 TiO<sub>2</sub> + agarose receiving phases naked.



499

500 Supplementary material Figure 3. Scheme of in situ deployment system.

501



502

503 Supplementary material Figure 4. PMG concentration in spot samples during the in situ

504 calibration of MPT samplers.