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1 Glyphosate and AMPA passive sampling in
2 freshwater using a microporous polyethylene
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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 cm² 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⁻¹), 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⁻¹, respectively. PMG in
30 situ R_s was 28 mL d⁻¹, and was not different from the one found in laboratory. AMPA was below
31 the limit of quantification (LOQ, 1 ng mL⁻¹) 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⁻¹) and worldwide
39 (826,000 tons y⁻¹) (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⁻¹ at 25°C) and AMPA (5.8 g L⁻¹ 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). 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⁻¹ 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 TiO₂
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 TiO₂ 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⁻¹ (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, MPPT), 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 (MPPT) 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 δ and d are WBL and membrane thicknesses, D_w is the contaminant diffusion coefficient
96 in water, θ is the tortuosity, and ϕ 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, $A = 17.6$ cm², $\phi = 35\%$ porosity,
101 2.5 μ m pore size) as a diffusion barrier filled with a receiving phase consisting of TiO₂ particles
102 embedded in an agarose gel. Compared to the conventional DGT, A is increased from 3.14 to
103 17.6 cm² (factor of 5.6), d is increased from 0.8 to 2 mm (factor of 2.5), ϕ is decreased from
104 almost 100% to 35% (factor of 3), and θ could be also decreased from 3 to 1 . Indeed, θ 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 δ value of 1.50 ± 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 $K_{m,w}$ 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 MΩ (MQ) was produced by a Millipore system. Glyphosate (PMG),
123 aminomethylphosphonic acid (AMPA), ¹³C₂-¹⁵N-PMG, ¹³C-¹⁵N-D₂-AMPA, agarose, titanium dioxide
124 (325 mesh, TiO₂), 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 μm pore size, 0.6 g cm⁻³ 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 TiO₂ 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 TiO₂ particles in the
136 agarose matrix. Tubes were stored in the fridge for ~ 2 hours (until the mixture solidified). The
137 TiO₂ + 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 cm² (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 × ϕ = 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 μL 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 μL of borate buffer (10 g L^{-1} of sodium tetraborate in
166 MQ). Then, 20 μL of internal standard solution (1 $\text{ng } \mu\text{L}^{-1}$ $^{13}\text{C}_2$ - ^{15}N -PMG and ^{13}C - ^{15}N -D₂-AMPA), 40
167 μL of EDTA (29.2 g L^{-1} of EDTA- Na_3 in MQ, pH adjusted to 8 with NaOH for improved
168 dissolution) and 60 μL of FMOC (12 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 μL 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 μm 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 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 ng mL^{-1} for PMG
189 and 1 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_{MPT} the concentration in MPT and C_{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_{mw} after 72 h of exposure (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, ng g^{-1}) and in the water (ng mL^{-1}).

206 **2.7. MPT sampler laboratory calibration**

207 Laboratory calibration of TiO₂ 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 TiO₂ 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 ± 0.8 and $10 \pm$
211 $2.7 \mu\text{g L}^{-1}$ for PMG and AMPA, respectively). Duplicates of TiO₂ 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 TiO₂ 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 ¹³C) 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.

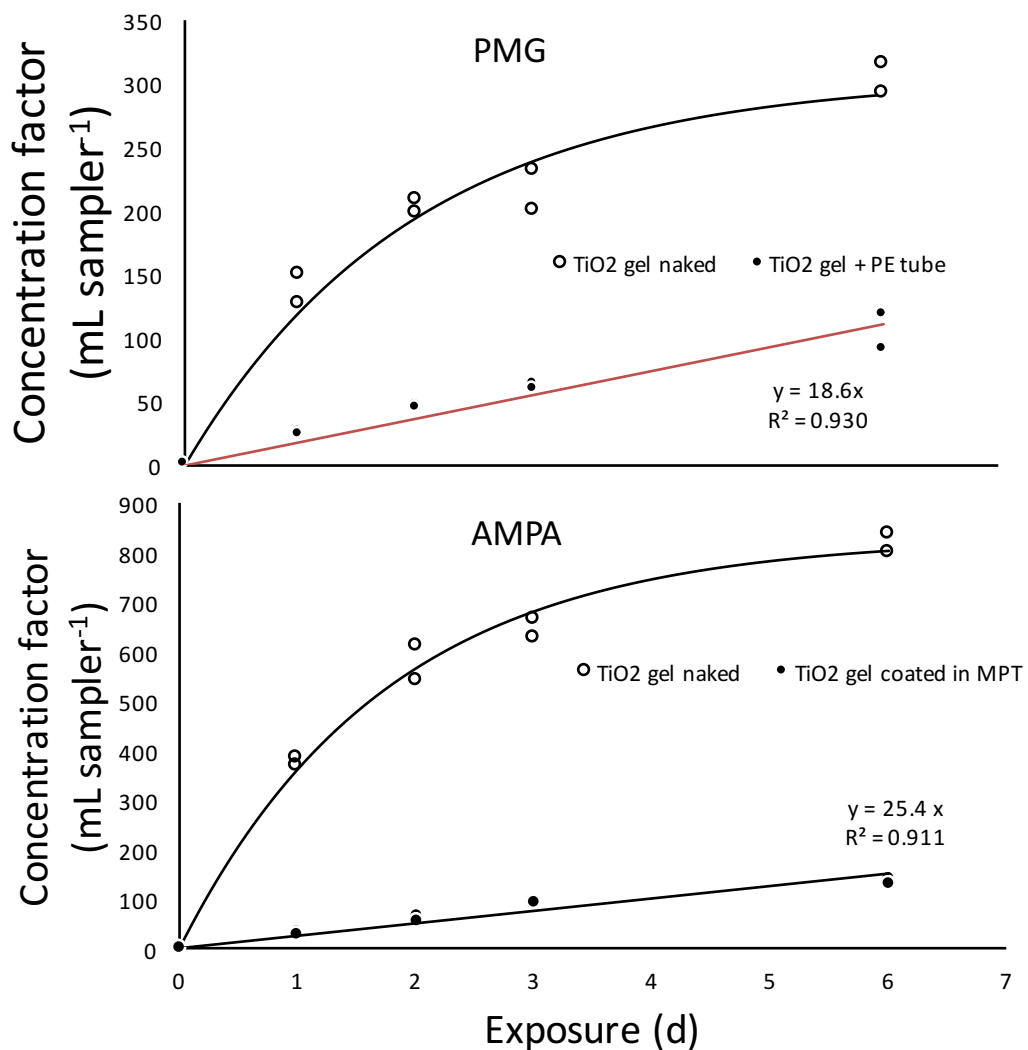
242 **3. RESULTS AND DISCUSSION**

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 ± 0.17 and
245 0.76 ± 0.07 mL g⁻¹, 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 TiO₂ gels and MPT passive samplers



255
256 Figure 1. Uptake of PMG and AMPA in naked TiO₂ + agarose gels (open circles) and in TiO₂ +
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 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 ± 29 mL sampler⁻¹ 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 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 TiO_2
268 gels naked of 156 ± 28 and 475 ± 46 mL day⁻¹ for PMG and AMPA respectively. These data are
269 to be compared with the analytes fluxes in the case of TiO_2 gels covered by MPT: we observed
270 experimental R_s values of 18.4 ± 0.9 and 25.4 ± 1.4 mL day⁻¹ 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 $A = 17.6$ cm², $\phi = 35\%$, $d = 2$ mm, and adopting $\theta = 1$, and a typical
277 D_w value for organic acids of 5 to 10×10^{-10} m² s⁻¹, we can predict a generic R_s between 13 and 27
278 mL day⁻¹, 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

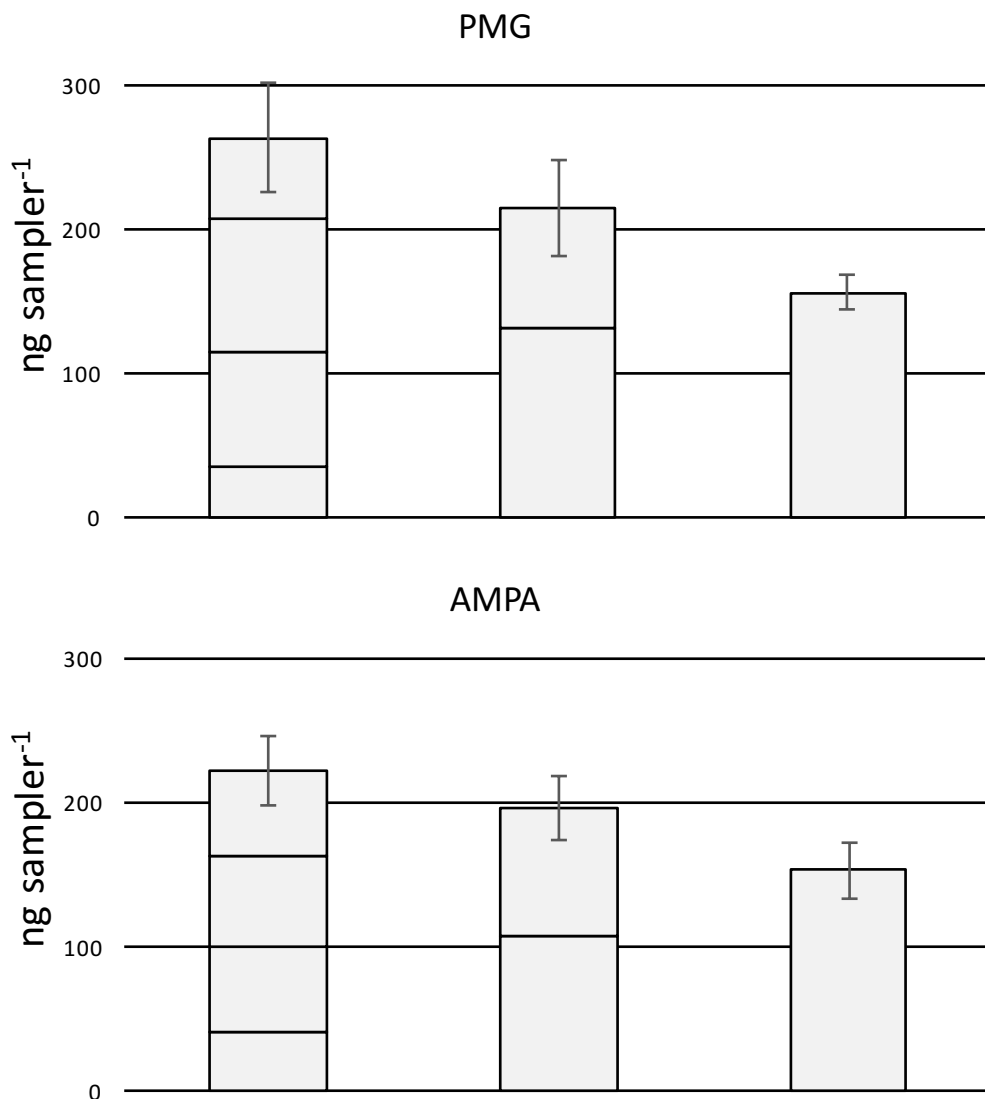
280 AMPA related to its lower molecular weight and steric hindrance. The same pattern was also
281 observed in a previous study (Fauvelle et al., 2015).

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 ± 0.032 mm under stirred
286 conditions, increasing up to 1.50 ± 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 δ is infinite).

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

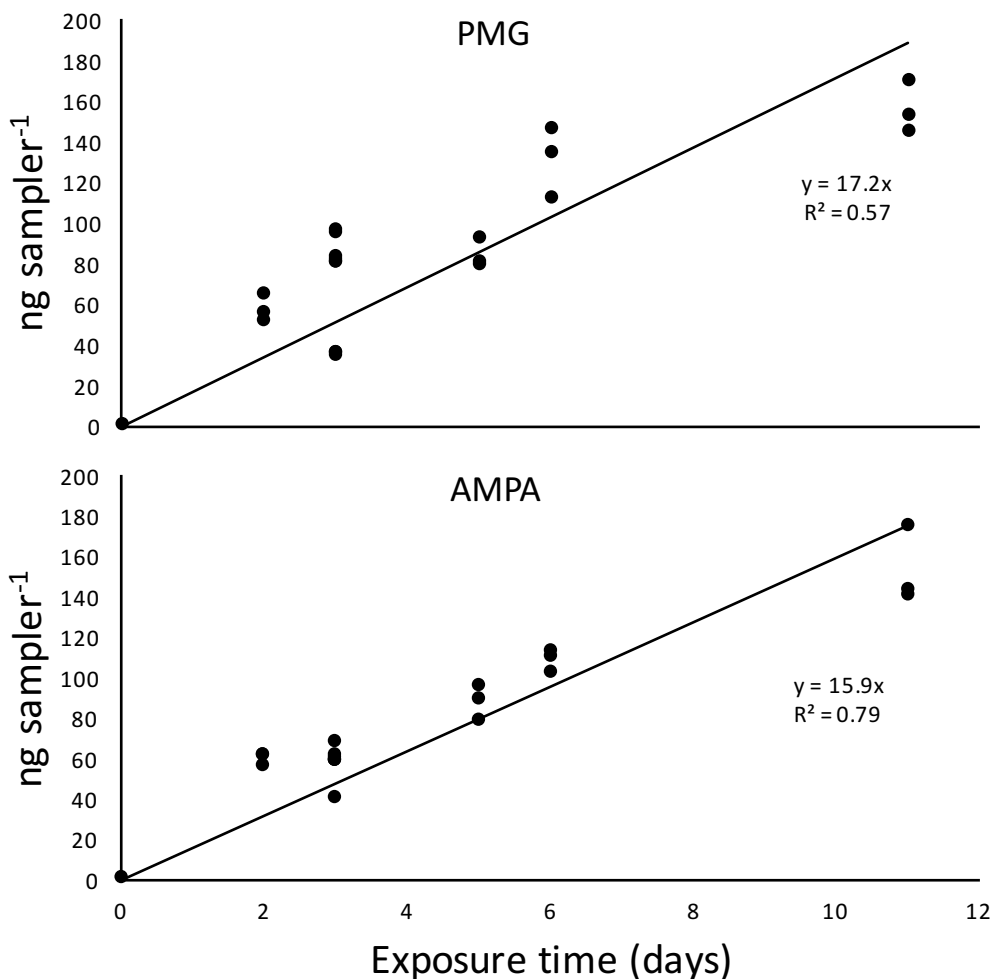
290 MPT samplers were deployed in overlapping and consecutive periods (Fig. 2) in order to check
291 the accuracy and consistency of the PMG and AMPA uptake in the samplers (Allan et al., 2008).
292 If uptake over time is uniform, all three bars should show the same level of mass accumulated
293 after 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 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 ϕ , 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 ng mL^{-1}), whereas AMPA concentration in grab samples was always below the
314 LOQ (1 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_s 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 ng mL^{-1} during the experiment, which is
324 below the analytical LOQ of grab water samples.

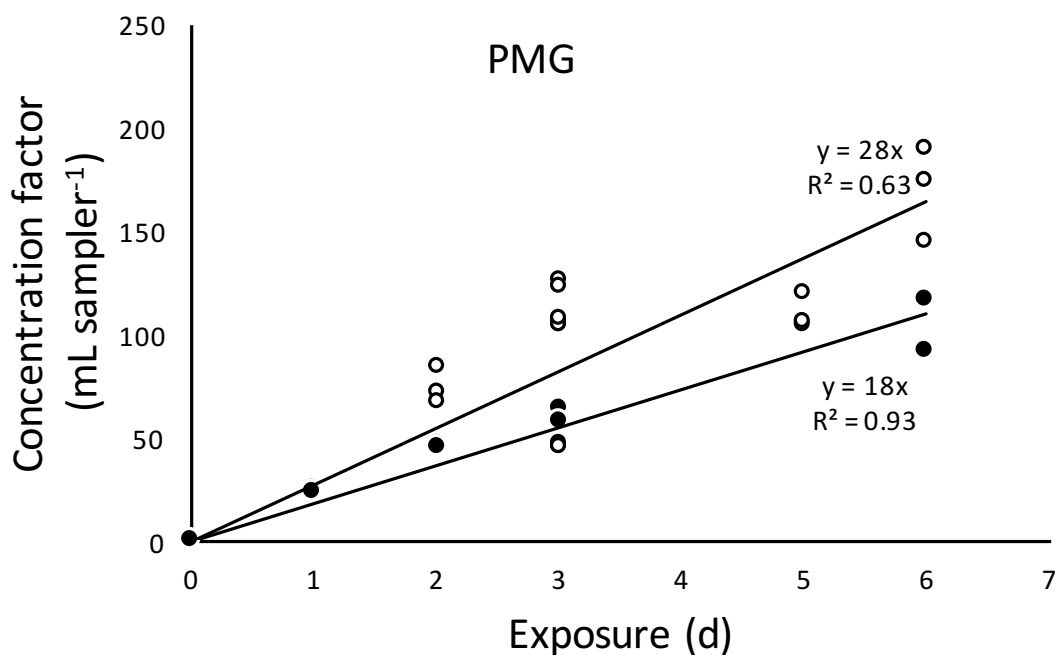


325

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⁻¹).

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⁻¹) 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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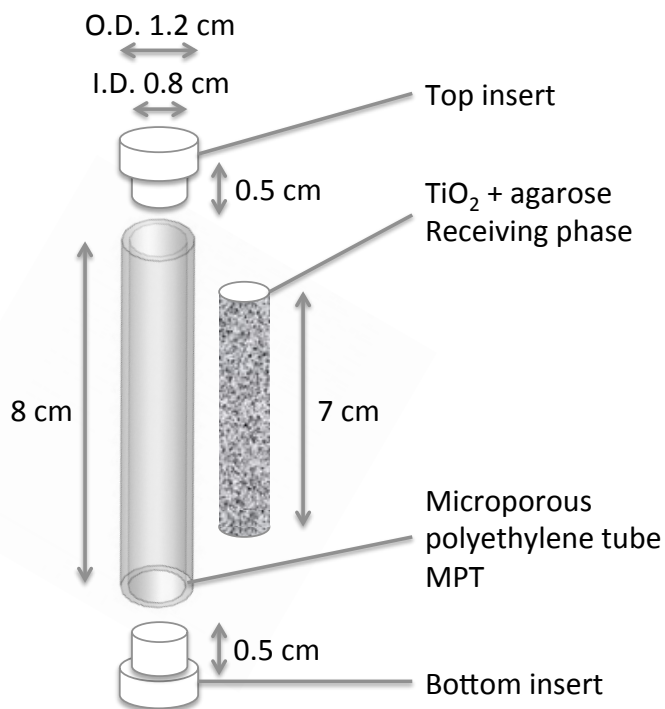
486 **SUPPLEMENTARY MATERIAL**

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 μm 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 (mg L^{-1})	6	20	2	46
Ca total (mg L^{-1})	7.8	49	-	-
Ca dissolved (mg L^{-1})	7.3	49	-	-
Mg total (mg L^{-1})	7.8	49	-	-
Mg dissolved (mg L^{-1})	7.6	50	-	-
Al total (mg L^{-1})	0.13	128	-	-
Al dissolved (mg L^{-1})	0.015	55	-	-

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

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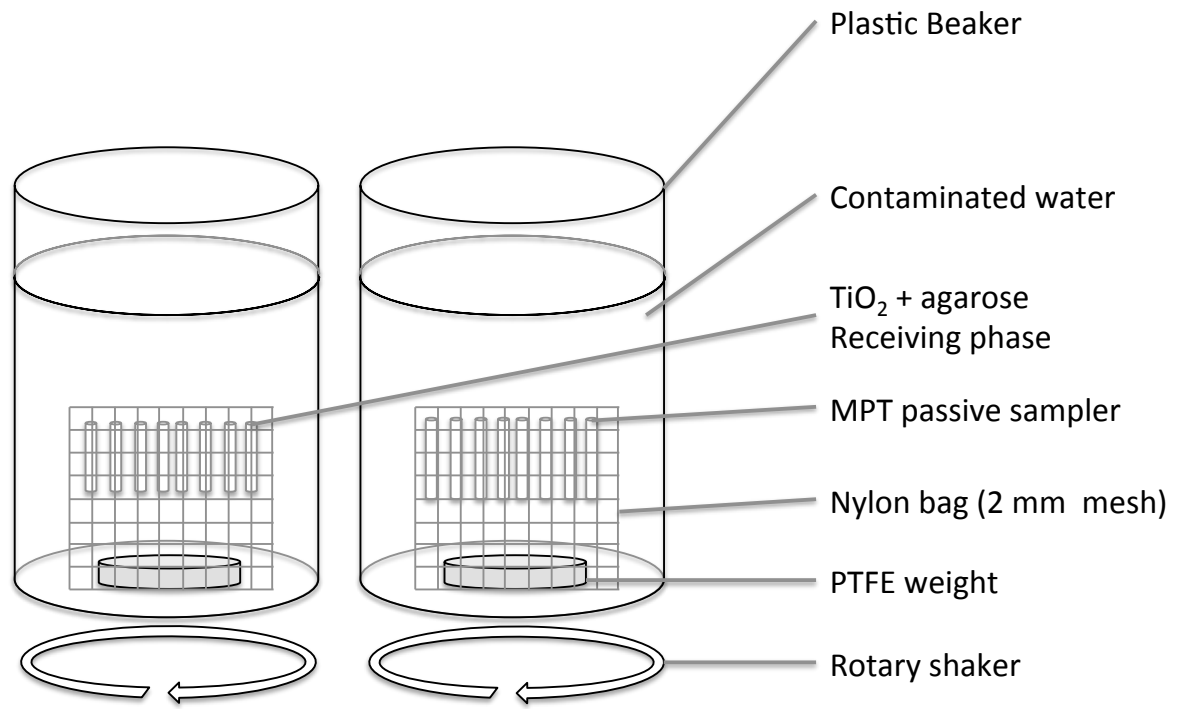


492

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

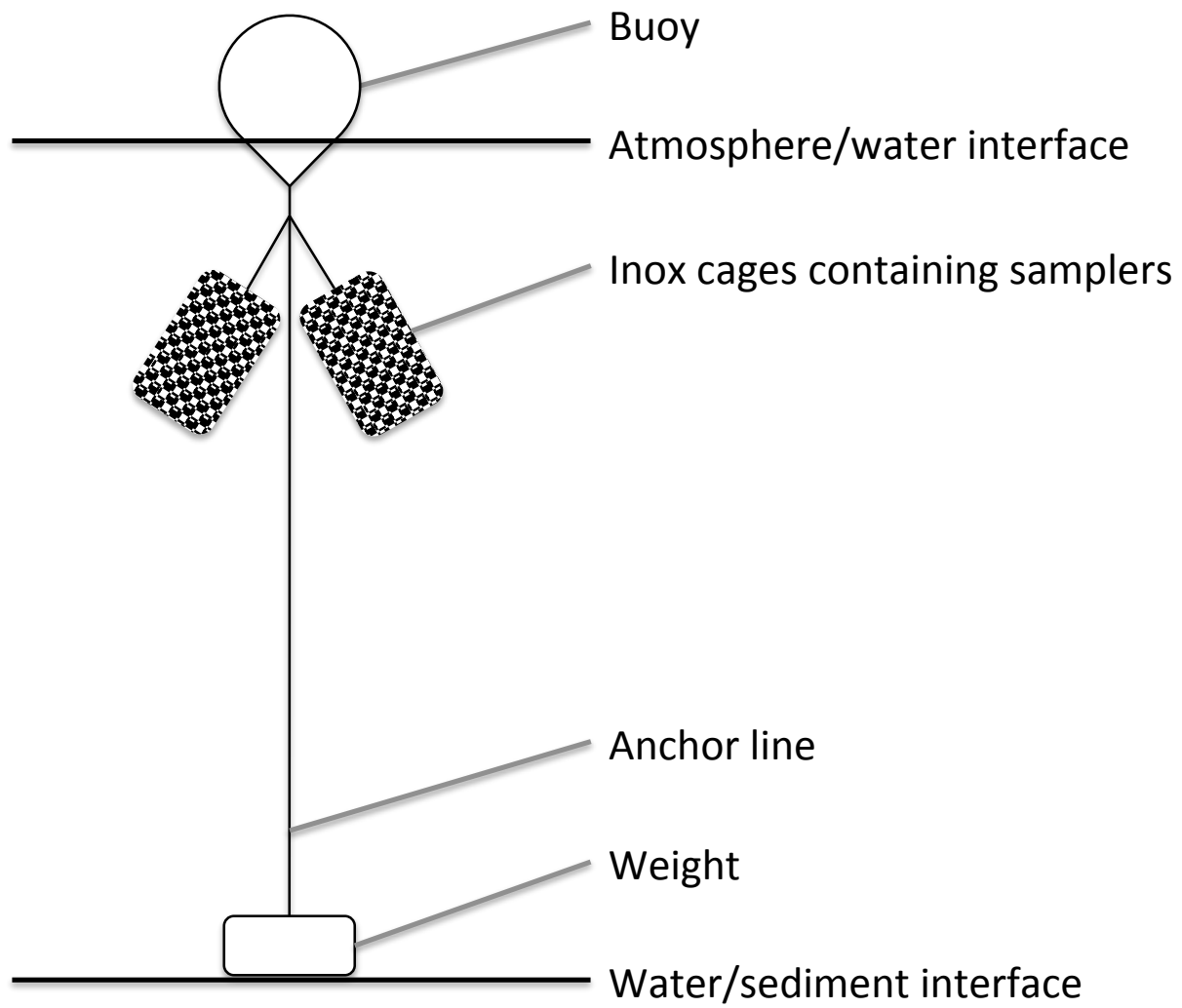
495 aminomethylphosphonic acid. O.D. is outside diameter, I.D. is internal diameter.



496

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

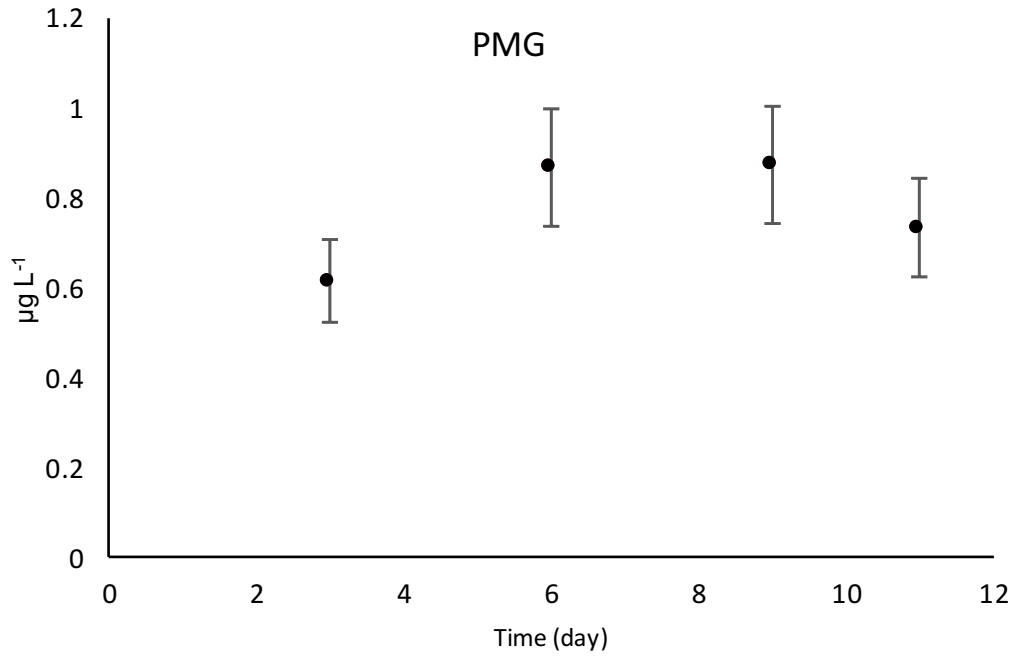
498 TiO₂ + agarose receiving phases naked.



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.