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

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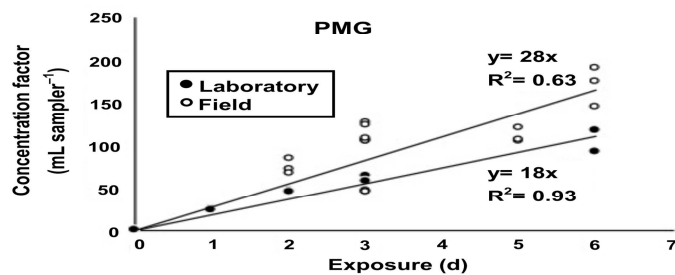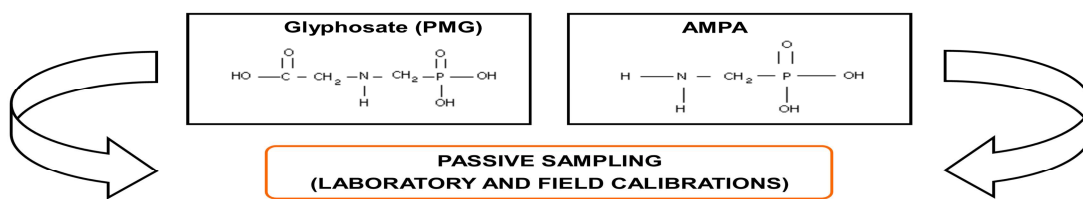
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Glyphosate (PMG)

AMPA

PASSIVE SAMPLING
(LABORATORY AND FIELD CALIBRATIONS)

MPT (Microporous
polyethylene tube + TiO₂ gel)

PMG

Concentration factor (mL sampler^{-1})

Exposure (d)

● Laboratory
○ Field

y= 28x
R²= 0.63

y= 18x
R²= 0.93

1   # Glyphosate and AMPA passive sampling in

2   # freshwater using a microporous polyethylene

3   # diffusion sampler

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14

15 **ABSTRACT**

16 Glyphosate (PMG) is one of the most widely used herbicides with a reported 8.6 million tons

17 applied globally in 2016. Due to widespread use and limited understanding of long-term

18 environmental impacts, it is expected that future monitoring requirements for PMG and its

19 primary metabolite aminomethyl phosphonic acid (AMPA) in aquatic environments will increase,

20 along with the need for low cost monitoring and risk assessment strategies. The aim of this study

21 was to investigate a microporous polyethylene tube (MPT; 2-mm thickness, 17.6 cm^2 surface

22 area, 35 % porosity, 2.5 μm pore size) as a diffusive layer for the passive sampling of PMG and

23 AMPA. Levels of PMG and AMPA sorbed to MPT were low (K_{mw} close to 1 mL g^{-1}), validating

24 MPT as a diffusive layer. Uptake experiments were conducted first under controlled laboratory

25 conditions (pH = 6.8, 6 days) followed by an in situ freshwater lake system deployment (pH =

26 7.3, 11 days). PMG and AMPA accumulated linearly (slope relative standard deviation < 6 %)

27 under laboratory conditions with sampling rates (R_s) of 18 and 25 mL d^{-1}, respectively. PMG in

28 situ R_s was 28 mL d^{-1}, and was not different from the one found in laboratory. AMPA was below

29 the limit of quantification (LOQ, 1 ng mL^{-1}) in grab water samples, but was detected (> LOQ) in

30 all passive samplers. Results illustrate the gain in sensitivity provided by the passive sampling

31 technique, and the applicability of the device developed for the passive sampling of PMG and

32 AMPA.

2

1. INTRODUCTION

Glyphosate (*N*-phosphonomethyl glycine, i.e. PMG) is the active substance of more than 750

commercial formulation (i.e., glyphosate-based herbicides, GBHs) and the most widly used

herbicide for agricultural and non-crop uses, both in Australia (15,000 tons y^{-1}) and worldwide

(826,000 tons y^{-1}) (Benbrook, 2016). The primary breakdown pathway of this polar (log K_{ow} = -

4.59 to -1.70) and ionic (zwitterion at all pH) organic compound is through microbial

degradation, resulting in the production of aminomethyl phosphonic acid, i.e. AMPA (Annett et

al., 2014). After spraying onto land of GBHs, the leaching of PMG and AMPA and consequent

transport into waterways will depend on application rates, soil properties and rainfall (Borggaard

and Gimsing, 2008). Another crucial parameter affecting PMG transport, degradation and

availability is the formation of complexes with natural occurring metal cations (Magbanua et al.,

2013; Shushkova et al., 2010; Zhou et al., 2013). However, due to the high solubility of PMG

(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 usually found together in most water bodies (Annett et al., 2014; Aparicio et al., 2013;

Battaglin et al., 2014; Comoretto et al., 2007; Coupe et al., 2012; Mercurio et al., 2014; Stewart et

al., 2014).

PMG and AMPA present complex chemical properties (i.e., high water solubility, poor solubility

in organic solvents, high complexation capacity) which complicate their extraction and analysis

in water at environmental trace levels. Accordingly, a derivatization step is needed to increase the

selectivity and sensitivity of the analysis (Arkan and Molnár-Perl, 2015; Dong et al., 2015). Thus,

PMG and AMPA are often not included in routine monitoring programs, as they require

specialized analysis which increases the costs of monitoring programs, although PMG and

AMPA are prioritized by the European network Norman (www.normandata.eu). Otherwise, these

3

56   substances were recently the subject of a considerable debate concerning their carcinogenic effect

57   on human health (Portier et al., 2016). Due to limited knowledge of the effects of chronic

58   exposure to low levels of PMG and AMPA (i.e., low ng L^{-1} range in aquatic systems), it is

59   expected that future monitoring requirements for these compounds in aquatic environments will

60   increase, along with the need for reliable, highly-sensitive and low-cost monitoring techniques.

61   Passive sampling may address these three fundamental requirements.

62   Since their development in the early 2000's (Alvarez et al., 2004; Kingston et al., 2000), passive

63   sampling techniques of polar compounds (i.e., the Polar Organic Chemical Integrative Sampler

64   (POCIS) and Chemcatchers) have been successfully used for the measurement of a wide range of

65   organic compounds in aquatic systems. Subsequently, passive sampling methods were adapted

66   for the monitoring of ionizable organic compounds in water systems (Fauvelle et al., 2014, 2012,

67   Kaserzon et al., 2014, 2012; Li et al., 2011). Aiming to target PMG and AMPA, a previous study

68   adapted the Diffusive Gradient in Thin-film (DGT) passive sampling technique with a TiO_2

69   receiving phase (Fauvelle et al., 2015), while another adapted the POCIS design using

70   molecularly imprinted polymer (MIP) as a receiving phase (Berho et al., 2017). Both TiO_2 and

71   MIP sorption phases successfully accumulated these analytes. However, limitations of the

72   developed sampling tools include:

73   i)   the low sampling rates (R_s) achieved for PMG and AMPA with the DGT based

74   sampler, i.e. around 10 mL day^{-1} (Fauvelle et al., 2015), which affects the sensitivity

75   and applicability of the sampler under environmental conditions

76   ii)   the dependency of the analytes flux and sampling rates on the external water velocity

77   (i.e., water boundary layer thickness; WBL) with the POCIS based sampler, which

4

78   can increase the uncertainty of water concentration estimates (Berho et al., 2017;

79   Fauvelle et al., 2017)

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

81   A higher R_s (Eq. 1) can be obtained by increasing the product of the exposure surface area of the

82   sampler (A) and the overall mass transfer coefficient (k_o):

83    $$R_s = A \times k_o \qquad (1)$$

84   k_o (Eq. 2) is dependent on the MTCs (mass transfer coefficients) of each successive compartment

85   of the sampler (Booij et al., 2017), as evidenced by the expression of the resistance to mass

86   transfer ($1/k_o$):

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

88   Where k_w, k_m, k_s are the MTC for the WBL, the membrane (microporous polyethylene tube in our

89   case, MPT), and the sorbent respectively, and K_{mw}, K_{sw} are the sorption coefficients of the

90   membrane and the sorbent. When $K_{mw} = 1$, and transport through the membrane (MPT) is only

91   via the pore space (i.e., filled with water), Eq. 2 becomes (Fauvelle et al., 2017):

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

93   Where δ and d are WBL and membrane thicknesses, D_w is the contaminant diffusion coefficient

94   in water, θ is the tortuosity, and ϕ is the membrane porosity.

5

95 Otherwise, a promising way to limit the influence of WBL thickness can be found in increasing

96 the second term of Eq. 3, e.g. increasing d (Belles et al., 2017; Chen et al., 2013; Fauvelle et al.,

97 2017).

98 In the present study, we propose to assess MPT ($d = 2$ mm thick, $A = 17.6$ cm^2, $\phi = 35\%$ porosity,

99 2.5 μm pore size) as a diffusion barrier filled with a receiving phase consisting of TiO$_2$ particles

100 embedded in an agarose gel. Compared to the conventional DGT, A is increased from 3.14 to

101 17.6 cm^2 (factor of 5.6), d is increased from 0.8 to 2 mm (factor of 2.5), ϕ is decreased from

102 almost 100 % to 35 % (factor of 3), and θ^2 could be also decreased from 3 to 1. Indeed, θ^2 is

103 supposed to be much higher in a gel than in MPT, as Belles et al. observed lower (factor of 3 to

104 factor of 9) diffusion coefficients for polar organic substances in hydrogels than in water (Belles

105 et al., 2017). Therefore, in light of Eq. 3, MPT could increase R_s by a factor of 2, and as R_s is

106 proportional to A, increasing MPT length will increase R_s accordingly when required. Otherwise,

107 resistance to mass transfer induced by MPT should be 4 times higher than the one induced by the

108 WBL, considering a worst case δ value of 1.50 ± 0.013 mm in an unstirred medium (Warnken et

109 al., 2006; with $d = 2$ mm, $\theta^2 = 1$, $\phi = 35$ %), suggesting a full MPT control (i.e., low dependency

110 to flowing conditions) of the diffusion of PMG and AMPA across the sampler.

111 The objectives of this study were i) to determine K_{mw} for PMG and AMPA to ensure their

112 transport is occurring only via the pore space and to avoid any interferences during the sampling,

113 ii) to verify that MPT is the compartment of the sampler providing the higher resistance to mass

114 transfer, and iii) to evaluate the performances of the sampler in situ.

115 **2. EXPERIMENTAL SECTION**

116 **2.1. Chemicals and reagents**

6

117   Acetonitrile (ACN), methanol (MeOH) and dichloromethane (DCM) were purchased from Merck

118   (Darmstadt, Germany) and their purity were higher than 99.8%. Trimethylamine (TEA) was

119   obtained from Atifina Chemicals Inc. (USA) and its purity was 99.5%. Water with resistivity >

120   18.2 MΩ (MQ) was produced by a Millipore system. Glyphosate (PMG),

121   aminomethylphosphonic acid (AMPA), $^{13}C_2$-^{15}N-PMG, ^{13}C-^{15}N-D_2-AMPA, agarose, titanium

122   dioxide (325 mesh, TiO_2), sodium borate, ethylenediaminetetraacetic acid disodium (EDTA),

123   fluorenylmethyloxycarbonyl chloride (FMOC) were purchased from Sigma-Aldrich (China).

124   NaOH pellets were obtained from Selby Biolab (Calyton, Victoria, 97% purity).

125   **2.2. Passive sampler procedure**

126   *Passive sampler assembly*

127   Microporous Polyethylene Tubes (MPTs) were purchased from Pall Corp. Crailsheim, Germany

128   (Filtroplast®, 12 mm O.D., 8 mm I.D., 35% porosity, 2.5 μm pore size, 0.6 g cm^{-3} density).

129   Tubes were cut in cylinders (8 cm length), solvent cleaned in a 400-mL jar with MeOH for 2

130   hours and stored in MQ until assembly. 200 mg of agarose gel, 216 mg of TiO_2 and 10 mL of

131   MQ were mixed together at 90°C for 10 min in single-use 15-mL polyethylene conical centrifuge

132   tubes. The mixture was immediately cast into a nonporous plastic tube (8 mm I.D.; 25 cm

133   length), and then placed in an ice bath for 1 h to get a homogeneous distribution of the TiO_2

134   particles in the agarose matrix. Tubes were stored in the fridge for ~ 2 hours (until the mixture

135   solidified). The TiO_2 + agarose gels were removed from the plastic tubes, cut in 7 cm length

136   pieces, and then allowed to sit for 30 min at ambient temperature to shrink (i.e., through

137   desiccation) and facilitate their subsequent introduction into the MPTs. Plastic tube inserts (5 mm

138   length each, Stockcap, Sydney, Australia) were used to cap the tubes at both ends. Assembled

7

139   MPT samplers (see Supplementary Material Figure 1) were stored in MQ until deployment. A

140   total sampler exposure area of 17.6 cm^2 (vs. 3.14 for a DGT housing) was considered for each

141   MPT device i.e., considering the internal diameter of the MPT in contact with the receiving phase

142   (Cristale et al., 2013).

143   *Extraction of passive samplers*

144   After deployment, samplers were stored in the fridge at 4 °C until extraction within a week.

145   Entire MPT samplers were placed in 15-mL polyethylene conical centrifuge tubes with 4 mL of

146   0.3 M NaOH. Tubes were placed on a shaker (60 rpm) in the darkness. Different extraction times

147   (i.e. 24, 48 and 96 h) were tested with the passive samplers deployed in situ for 11 days. No

148   significant differences were found in PMG and AMPA concentrations measured at different

149   extraction times, and thus, hereafter, a 24 h elution step was performed with the all samplers.

150   After extraction, a derivatization step was performed (see section 2.4). As only 400 μL were used

151   for the derivatization step, a correction factor (22.5) was finally applied according to the overall

152   water content of the extract (9 mL): selectively the NaOH extraction fraction (4 mL), the gel

153   water content (i.e., total gel volume 3.5 mL, consisting of more than 95% of water) and the MPT

154   pore water content (i.e., tube volume $\times \phi = 1.5$ mL).

155   **2.3. Water samples procedure**

156   Grab water samples (20 mL) were filtered through 0.45 μm regenerated-cellulose filters (Agilent)

157   and were not pre-concentrated prior to the derivatization step (see section 2.4). When not

158   analyzed the same day, samples were stored at –18°C.

159   **2.4. Derivatization step**

8

160   In order to reach sufficient retention on a C_{18} reversed phase chromatographic analytical column,

161   analytes were derivatized using FMOC-Cl, as suggested in ISO 16308:2014. Briefly, 400 μL of

162   sample (i.e. passive sampler eluate or grab water sample) was transferred in a 15-mL

163   polyethylene falcon tube, together with 480 μL of borate buffer (10 g L^{-1} of sodium tetraborate in

164   MQ). Then, 20 μL of internal standard solution (1 ng $μL^{-1}$ $^{13}C_2$-^{15}N-PMG and ^{13}C-^{15}N-D_2-

165   AMPA), 40 μL of EDTA (29.2 g L^{-1} of EDTA-Na_2 in MQ, pH adjusted to 8 with NaOH for

166   improved dissolution) and 60 μL of FMOC (12 g L^{-1} of FMOC-Cl in ACN) was added (final pH

167   was 9). Samples were shaken after each addition and then left overnight at room temperature in

168   the dark for complete derivatization of the analytes. Next day, the excess of FMOC was removed

169   by adding 300 μL of DCM, shaking, and recovering the upper aqueous phase (~ 500 μL). Final

170   eluents were placed in amber glass LC vials and stored in the fridge (4 °C) until analysis (within

171   3-4 days).

172   **2.5. Analytical method**

173   Sample analysis methodology was adapted from previous studies (Fauvelle et al., 2015; Freuze et

174   al., 2007). Briefly, analysis was performed on HPLC-MS/MS using an AB/Sciex API6500+Q

175   mass spectrometer (Sciex, Concord, Ontario, Canada) equipped with an electrospray (TurboV)

176   interface coupled to a Shimadzu Nexera HPLC system (Shimadzu Corp., Kyoto, Japan).

177   Glyphosate, AMPA and their analogues, derivatized with FMOC-Cl, were separated by a

178   Phenomenex Gemini-NX column (50 mm length, 3 μm particle size, 2.1 mm diameter). Mobile

179   phase consisted of a 0.1 % TEA aqueous solution pH adjusted to 9.5 with acetic acid (A), and

180   MeOH/ACN 50:50 (v/v) (B). The analytical gradient was set at 92:8 (A/B) for 1.5 min; B was

181   then increased linearly to 95% during 1.5 min and kept constant for another 1.5 min. B was

182   decreased thereafter to initial conditions during 1.5 min, and a final 5 min equilibrating phase was

9

183   applied at the end of the gradient (11 min run). The mobile phase flow rate was set at 400 µL

184   min^{-1}, and the column oven temperature was 40 °C. Mass acquisition was performed using

185   selected reaction monitoring (SRM) and negative ESI mode (Fauvelle et al., 2015). A 6-point

186   calibration curve (from 1 to 200 ng mL^{-1}) was prepared and derivatized according to the protocol

187   described above (section 2.4). Instrumental limits of quantification were estimated at 0.5 ng mL^{-1}

188   for PMG and 1 ng mL^{-1} for AMPA. It is noteworthy that TEA resulted in the contamination of

189   the mass spectrometer. This can be mitigated by flushing the system with a mix of solvents

190   (isopropanol/ACN/MeOH) for 24 h. However, low levels of TEA remained detectable. Replacing

191   TEA by ammonium acetate will avoid contaminations, at the expense of chromatographic

192   parameters (worst peak shape and lower retention time).

193   **2.6. Adsorption on MPT**

194   To ensure transport is only occurring via the pore space, and is not delayed because of the

195   diffusive material (Fauvelle et al., 2017), MPT to water partition coefficient ($K_{mw} = C_{MPT}.C_{w}^{-1}$,

196   with C_{MPT} the concentration in MPT and C_{w} the concentration in water) values for PMG and

197   AMPA were determined. To this end, 8 cm MPTs (n = 3) were conditioned (see section 2.2), and

198   immersed individually for 72 h in 10 mL of a 10 µg L^{-1} aqueous solution of both analytes. Three

199   controls with no MPT ensured the solution stability for the whole experiment duration. Water

200   concentration was measured at the end of the experiment in the 3 above mentioned controls and

201   in the 3 samples containing MPT. K_{mw} after 72 h of exposure (mL g^{-1}) was determined as the

202   concentration ratio in the MPT (i.e., deduced from water concentration balance before and after

203   exposure, ng g^{-1}) and in the water (ng mL^{-1}).

204   **2.7. MPT sampler laboratory calibration**

205   Laboratory calibration of TiO$_2$ gels, naked or inserted in MPTs, was performed in two separated 3

206   L plastic beakers filled with ultrapure water (one for 8 MPT samplers, another one for 8 naked

207   TiO$_2$ gels). The calibration system was spiked with PMG and AMPA and allowed to equilibrate

208   for 24 h before samplers' exposure. Water concentrations were measured daily (5 ± 0.8 and $10 \pm$

209   2.7 µg L^{-1} for PMG and AMPA, respectively). Duplicates of TiO$_2$ gels, naked and enclosed in

210   MPTs, were retrieved after 1, 2, 3 and 6 days, and treated according to the method described

211   above. Naked TiO$_2$ gels and MPT samplers were enclosed in a nylon mesh (2 mm mesh) together

212   with a PTFE weight to ensure that samplers were completely submerged throughout the

213   experiment (Supplementary material Figure 2). Shaking was performed using a rotary shaker (60

214   rpm) and beakers were completely covered in aluminum foil. The temperature and pH of the

215   system were periodically checked and were in the range 22-25°C and 6.8-7, respectively. Non-

216   linear regressions were fitted using Addinsoft XL-STAT software 19.02.

217   **2.8. MPT sampler in situ calibration**

218   A field calibration was performed in a drinking water reservoir in South East Queensland,

219   Australia (Wappa Dam, 26.572105 °S, 152.922028 °E) in May 2016 (Supplementary material

220   Figure 3). Triplicate MPT samplers were deployed in staggered configuration for 2, 3, 5, 6 and 11

221   days. Each triplicate was deployed in stainless steel cages (5 mm mesh). Grab samples for water

222   concentration measurements (see section 2.3) were taken every 2 or 3 days, together with the

223   passive sampler replacement or retrieval. Wappa Dam, along with many other freshwater bodies

224   in South East Queensland, are subject to excessive growth of aquatic weeds (e.g., *Salvinia*, water

225   lettuce, water hyacinth) that may affect water quality (e.g., depleting dissolved oxygen,

226   increasing nutrient load) and wildlife habitat. Therefore, one type of chemical control that is

227   routinely implemented, to restrain weed growth, consists of spraying glyphosate onto newly

11

228 grown weeds. The MPT samplers were deployed about 2 h post spraying of glyphosate in the

229 dam. Physico-chemical parameters (i.e., temperature, conductivity, pH, turbidity, dissolved

230 oxygen) and total and dissolved concentrations of major and trace elements (i.e., Ca, Mg, Al, Cd,

231 Co, Cu, Fe, Mn, Zn) were measured every 3 days (Supplementary material Table 1).

232 **2.9. Quality assurance and quality control**

233 Passive sampler blanks, MQ blanks, analytical blanks, and non-extracted spikes were prepared

234 and treated along with passive and water samples. Positive controls were made by checking the

235 intensity of internal standards (PMG and AMPA ^{13}C) spiked in all the samples and QA/QC

236 samples (always between 81 and 115% recoveries). A 6-point calibration curve ensured the

237 efficiency of the derivatization protocol for native PMG and AMPA. No PMG or AMPA were

238 detected in any blanks or negative controls, relative standard deviation (RSD) of passive

239 samplers' replicates were within 3 and 18% for both laboratory and field deployments.

240 **3. RESULTS AND DISCUSSION**

241 **3.1. PMG and AMPA adsorption on MPT**

242 K_{mw} values (see section 2.6) for PMG and AMPA were found to be close to 1 (1.07 ± 0.17 and

243 0.76 ± 0.07 mL g^{-1}, respectively), meaning comparable quantities are found in MPT and in water.

244 Therefore, adsorption at the MPT surface can be expected to be minimal for the diffusive layer

245 selected and consequently, it is assumed that diffusion only occurs via the MPT pores. The

246 diffusive material of a passive sampler should otherwise have a low affinity towards the analytes

247 of interest to avoid any interferences during the sampling that may complicate data interpretation,

248 e.g. delayed accumulation in the receiving phase (Belles et al., 2014; Vermeirssen et al., 2012).

12

249   The low K_{mw} for the compounds of interest suggests that the surface of the MPT will interact only

250   minimally with the compounds and thus not affect their diffusion into the sampling phase which

251   simplifies modelling.

252   **3.2. Uptake of PMG and AMPA in TiO$_2$ gels and MPT passive samplers**
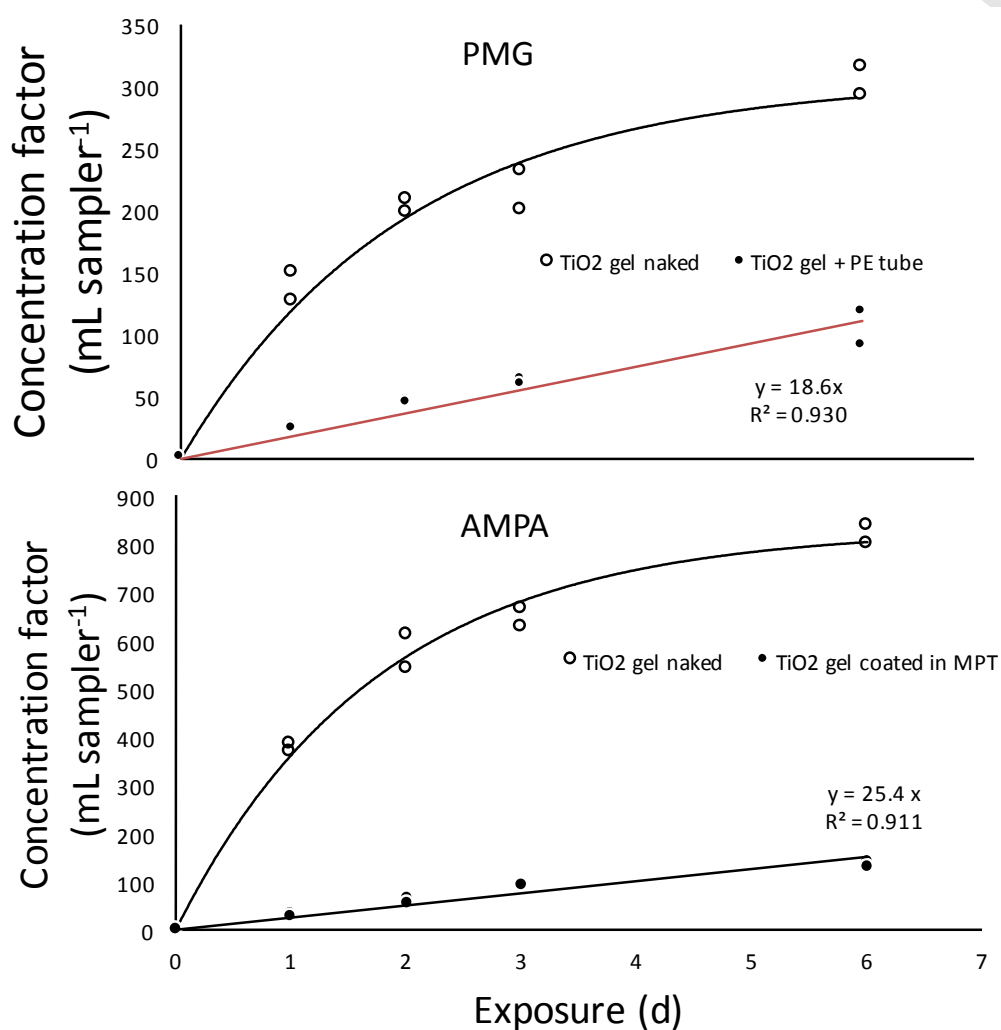
253

254   Figure 1. Uptake of PMG and AMPA in naked TiO$_2$ + agarose gels (open circles) and in TiO$_2$ +

255   agarose gels inserted in microporous polyethylene tubes (MPTs) (full circles), under laboratory

13

256   controlled conditions. An indicative first order kinetic [y=K(1-e$^{-k \times t}$)] was fitted to the non-linear

257   data.

258   A second experiment was set up to evaluate the uptake kinetic of PMG and AMPA in the TiO_2 +

259   agarose gel both with and without the MPT housing. In both cases, no measurable lag phase was

260   observed at the beginning of the sampling, confirming no high interactions analytes and MPT.

261   Looking at the first order kinetics [y=K(1-e$^{-k \times t}$)], the mass of analyte sampled reached a pseudo-

262   plateau ($K = 307 \pm 21$ and 831 ± 29 mL sampler^{-1} for PMG and AMPA respectively) within a

263   couple of days without MPT. Kinetics seem however, on the basis of our data, increasing beyond

264   those pseudo-plateaux. Thus, the actual TiO_2 to water distribution coefficient could be higher

265   than those values. The slope at $t = 0$ (i.e., k) gave otherwise an estimation of the analytes fluxes in

266   TiO_2 gels naked of 156 ± 28 and 475 ± 46 mL day^{-1} for PMG and AMPA respectively. These

267   data are to be compared with the analytes fluxes in the case of TiO_2 gels covered by MPT: we

268   observed experimental R_s values of 18.4 ± 0.9 and 25.4 ± 1.4 mL day^{-1} for PMG and AMPA,

269   respectively (Fig. 1; Eq 1). Thus, the mass transfer resistance by the MPT is almost 10 times

270   higher than the receiving phase alone. We can therefore consider a large control of contaminants

271   fluxes by MPT to the receiving phase. R_s values measured with MPT are otherwise twice higher

272   than those reported for o-DGT (Chen et al., 2013, 2012; Fauvelle et al., 2015), which shows the

273   ability of MPT based passive sampler to increase R_s, which was identified a main issue of o-

274   DGT. Considering Eq 1 and 3 with $A = 17.6$ cm^2, $\phi = 35\%$, $d = 2$ mm, and adopting $\theta = 1$, and a

275   typical D_w value for organic acids of 5 to 10×10^{-10} m^2 s^{-1}, we can predict a generic R_s between 13

276   and 27 mL day^{-1}, which is in good agreement with the experimental data mentioned above. The

277   difference in R_s estimates between PMG and AMPA is likely to be attributed to the higher D_w of

278   AMPA related to its lower molecular weight and steric hindrance. The same pattern was also

279   observed in a previous study (Fauvelle et al., 2015).

280   The role of the water boundary layer, whose thickness depends on hydrodynamics, was not

281   investigated here. Nevertheless, assuming no water advection phenomena within the MPT matrix,

282   the 2-mm thick MPT with $\phi = 35\%$ (d/$\phi = 5.71$, Eq. 3 with $\theta = 1$) used here should be able to

283   minimize the effect of the WBL with typical thicknesses between 0.230 ± 0.032 mm under stirred

284   conditions, increasing up to 1.50 ± 0.013 mm in an unstirred medium (Warnken et al., 2006).

285   Thereby, the maximum error on sampling rates would be lower than 20% whatever the flowing

286   conditions (except in the theoretical case of zeroflow where δ is infinite).

287   **3.3. Calibration of MPT passive samplers for PMG and AMPA in freshwater lake**

288   MPT samplers were deployed in overlapping and consecutive periods (Fig. 2) in order to check

289   the accuracy and consistency of the PMG and AMPA uptake in the samplers (Allan et al., 2008).

290   If uptake over time is uniform, all three bars should show the same level of mass accumulated

291   after 11 days of exposure. Similar uptake was observed at the shortest deployment times (i.e. 3+3

292   d and 6 d), but contaminant fluxes seem to decrease with increasing exposure duration (3 bars

293   statistically different, Kruskal-Wallis test, $\alpha = 0.05$). This might be explained by i) the increased

294   pathway thickness due to the equilibrium reached with the surface TiO_2 particles of the receiving

295   phase, and ii) the addition of an increasing resistance attributed to biotic or abiotic fouling (i.e.,

296   additional thickness of the MPT layer due to the development of biofilm at the surface of the

297   sampler or pore clogging by natural particles, increasing d or lowering ϕ, respectively). Another

298   possibility is the potential degradation of the compounds sequestered inside the sampler, since

299   MPT pore size is big enough to allow the passage of microorganisms. These phenomena may

15

300   imply an underestimation of the time-weighted average concentrations and require further

301   investigation.
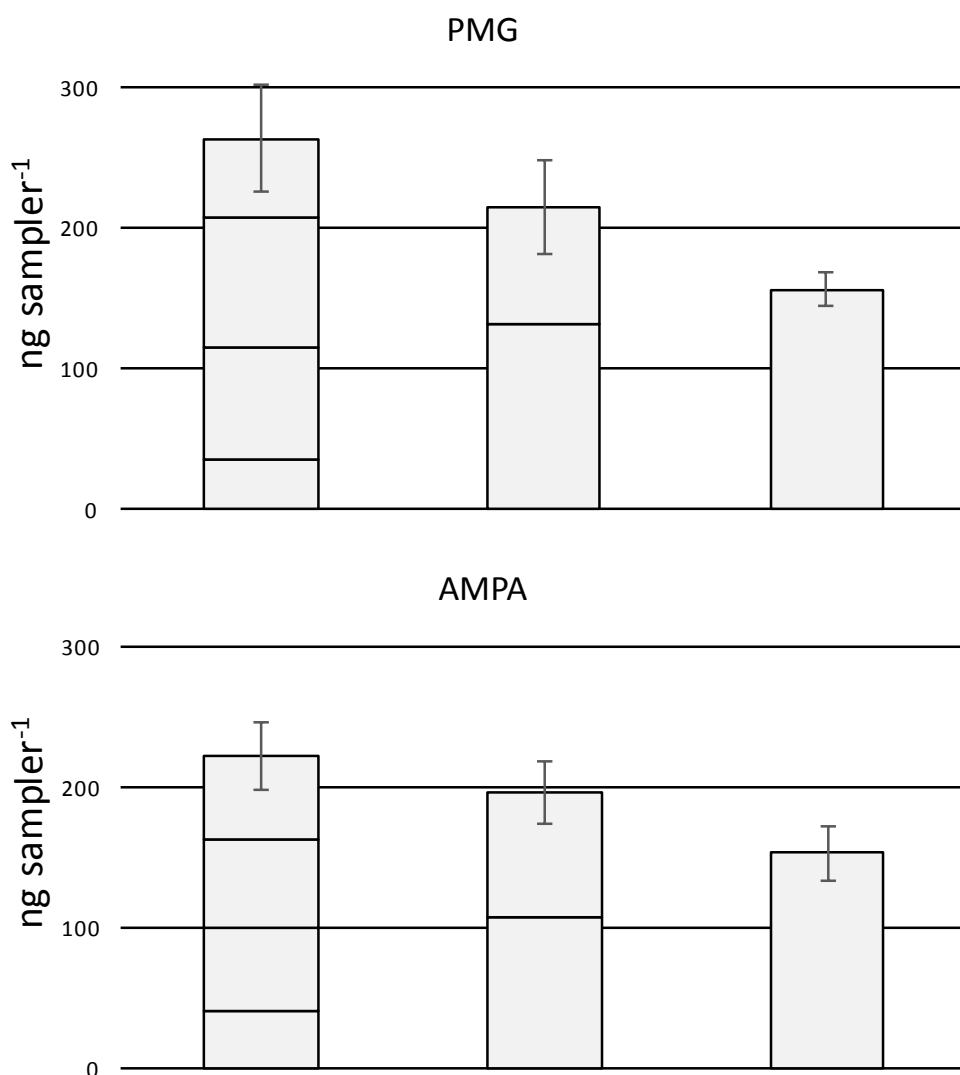
303   Figure 2. Mass of PMG and AMPA accumulated in MTP passive samplers deployed in Wappa

304   dam. Left bar represents the sum of 4 x triplicate samplers exposed successively for 3 or 2 days.

305   Middle bar is the sum of 2 x triplicate samplers exposed successively for 6 and 5 days. Right bar

306   is the analyte mass found in the single triplicate sampler exposed for the entire 11 days. Error

307   bars are the square roots of the sums of squared standard deviations (n = 3).

16

308   Uptake results for PMG and AMPA in MPT samplers deployed in Wappa dam are presented in

309   Fig. 2 and 3. The concentration of PMG directly measured in grab water samples (collected every

310   3 days) was found to be relatively constant (0.77 ± 0.12 ng mL^{-1}, Supplementary Material Figure

311   4, LOQ = 0.5 ng mL^{-1}), whereas AMPA concentration in grab samples was always below the

312   LOQ (1 ng mL^{-1}). In MPT passive samplers, a linear relationship between the analyte mass

313   accumulated in the sampler and the exposure duration was observed (Fig. 3) for both PMG and

314   AMPA. The PMG mass accumulated after 11 days of exposure is below the linear regression,

315   which can be partially explained by the lower concentration reported at the end of the experiment

316   (Supplementary Material Figure 4). Although AMPA was not detected in grab samples, linear

317   uptake of the analyte in the MPT passive samplers was observed (Fig. 3), which demonstrate the

318   better sensitivity of MPT technique compare to grab sample directly injected. Taking into

319   account the previously determined R_s for AMPA (Fig. 1, 25.4 ± 1.4 mL day^{-1}), and the slope of

320   Fig. 3 (i.e. average mass of AMPA accumulated per day, 15.9 ± 0.7 ng day^{-1}), we can estimate a

321   hypothetical time averaged AMPA concentration of 0.63 ng mL^{-1} during the experiment, which is

322   below the analytical LOQ of grab water samples.
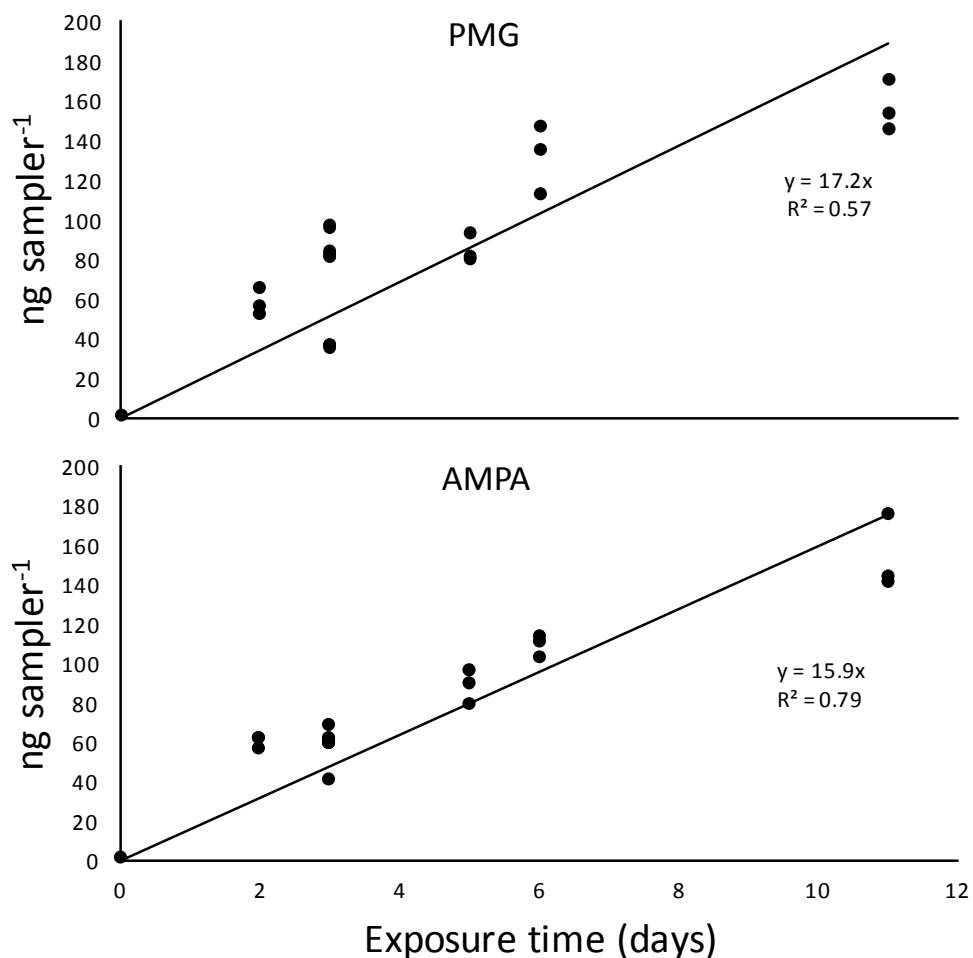
Figure 3. Mass of PMG and AMPA accumulated in MTP passive samplers in Wappa dam as a function of exposure duration.

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

18

331 A previous study mentioned the presence of metal cations as a potential interfering factor with

332 the accumulation of PMG and AMPA in passive samplers (Fauvelle et al., 2015). That

333 interference was not observed in the current study, because similar concentration factors were

334 observed in the laboratory and in situ. An explanation can be found in the different bivalent

335 cation composition of each study, which may differ by an order of magnitude (see Supplementary

336 Material Table 1). A special attention should then be paid to the inorganic composition of each

337 medium sampled.
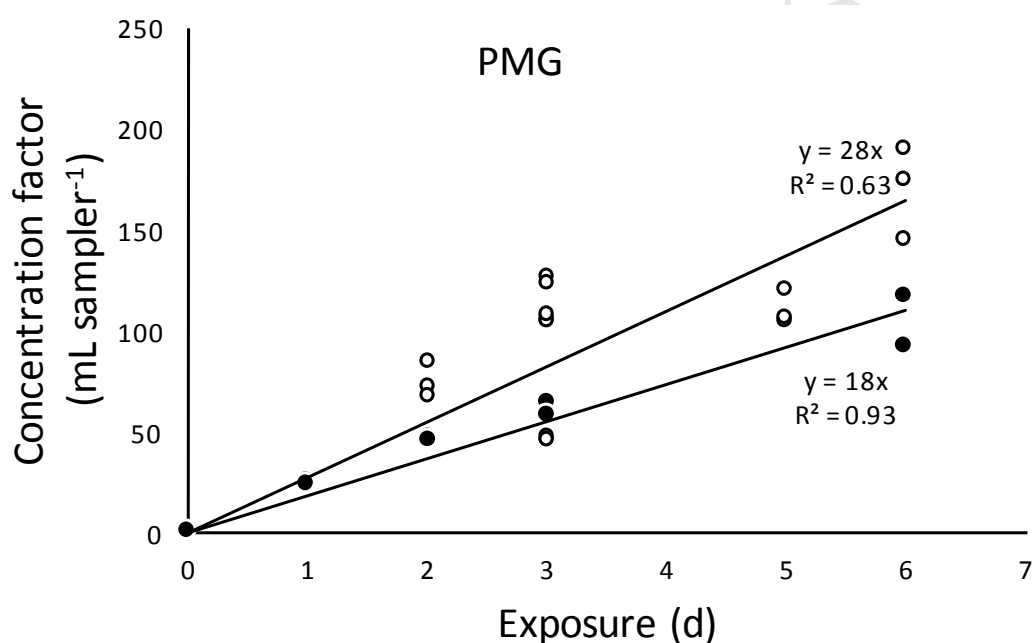
338

339 Figure 4. Concentration factor (mL sampler^{-1}) of PMG in MPT passive samplers in surface water

340 (open circles) and in MQ water (full circles). Slopes represent the sampling rates over the 6-day

341 period.

342 The use of MPT samplers allowed the measurement of low PMG and AMPA concentrations in

343 the aquatic environment. This study is part of several recent studies aimed at improving the

19

344 passive sampling of polar organic compounds. It opens the possibility of applying them in other

345 complex systems, presenting low concentrations, such as the marine environment. Accordingly,

346 future studies would focus on testing the reliability and robustness of the performance of MPT

347 passive samplers under different environmental conditions.

348 **ACKNOWLEDGMENTS**

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483

484 **SUPPLEMENTARY MATERIAL**

485 Supplementary material Table 1. Physico-chemical parameters measured at Wappa Dam with a

486 YSI 650 MDS multiparameter probe. Dissolved metal concentrations refer to water filtered

487 through 0.45 µm regenerated cellulose filters measured by inductively coupled plasma-mass

488 spectrometer.

	0.2 m depth	RSD (%)	1.5 m depth	RSD (%)
Average temperature (°C)	23	4	22	3
Conductivity ($\mu s\ cm^{-1}$)	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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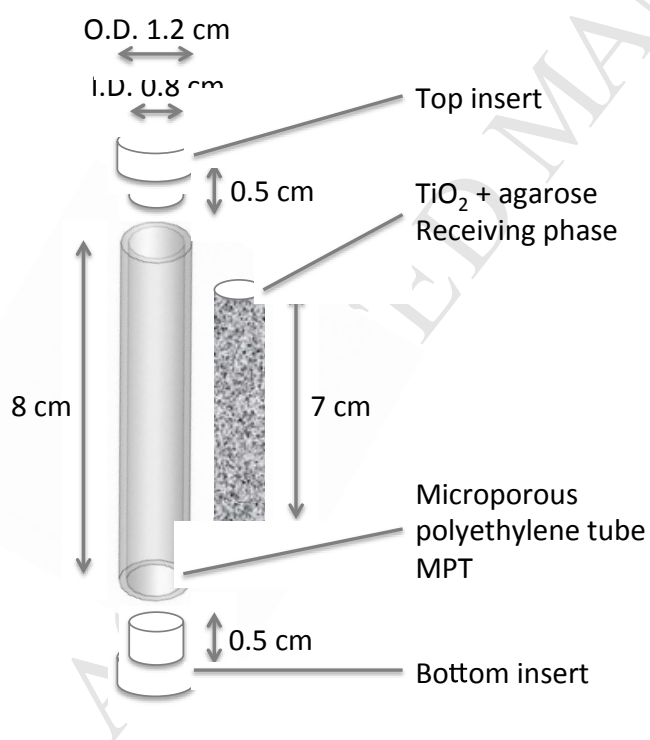
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491 Supplementary material Figure 1. Schematic view of the microporous polyethylene tube (MPT)

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

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

25

Plastic Beaker

Contaminated water

TiO_2 + agarose
Receiving phase

MPT passive sampler

Nylon bag (2 mm mesh)

PTFE weight

Rotary shaker
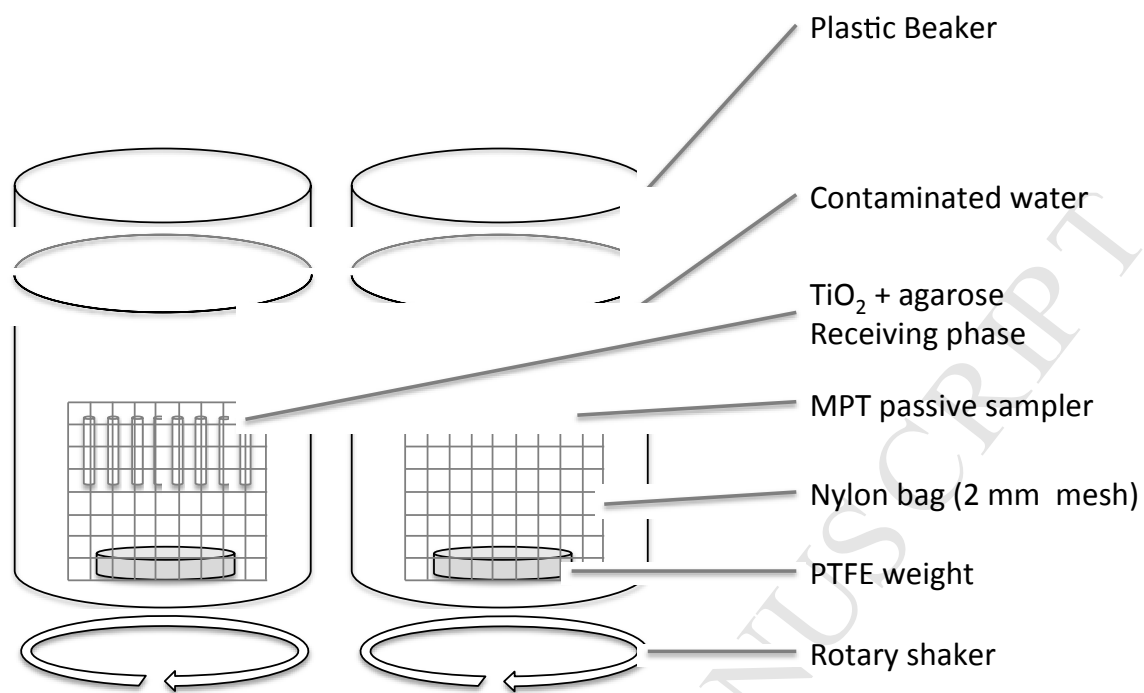
494

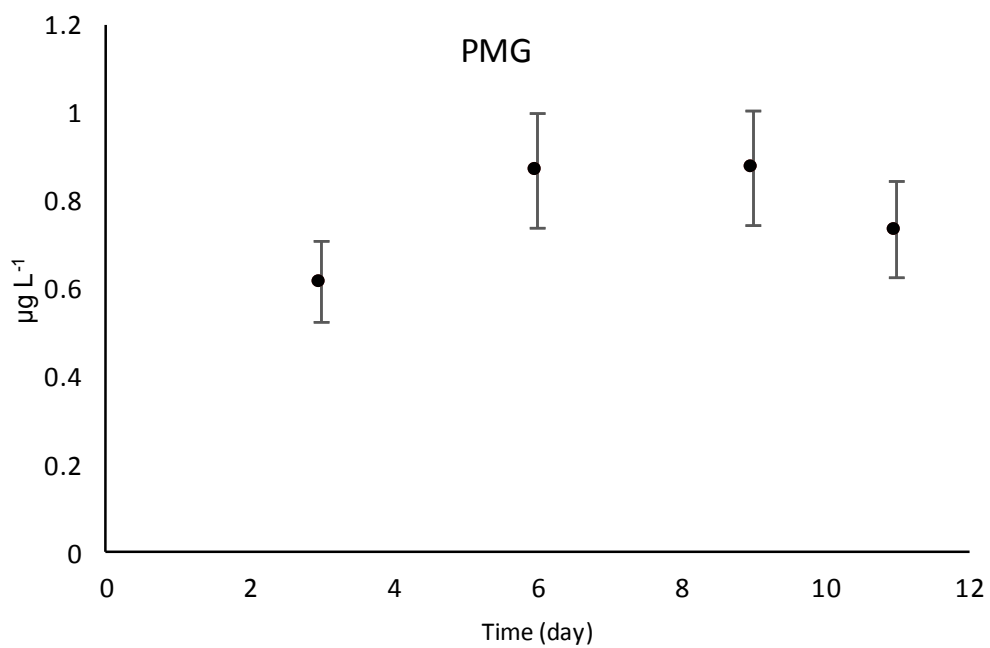495   Supplementary material Figure 2. Laboratory calibration system for MPT passive samplers and

496   TiO_2 + agarose receiving phases naked.
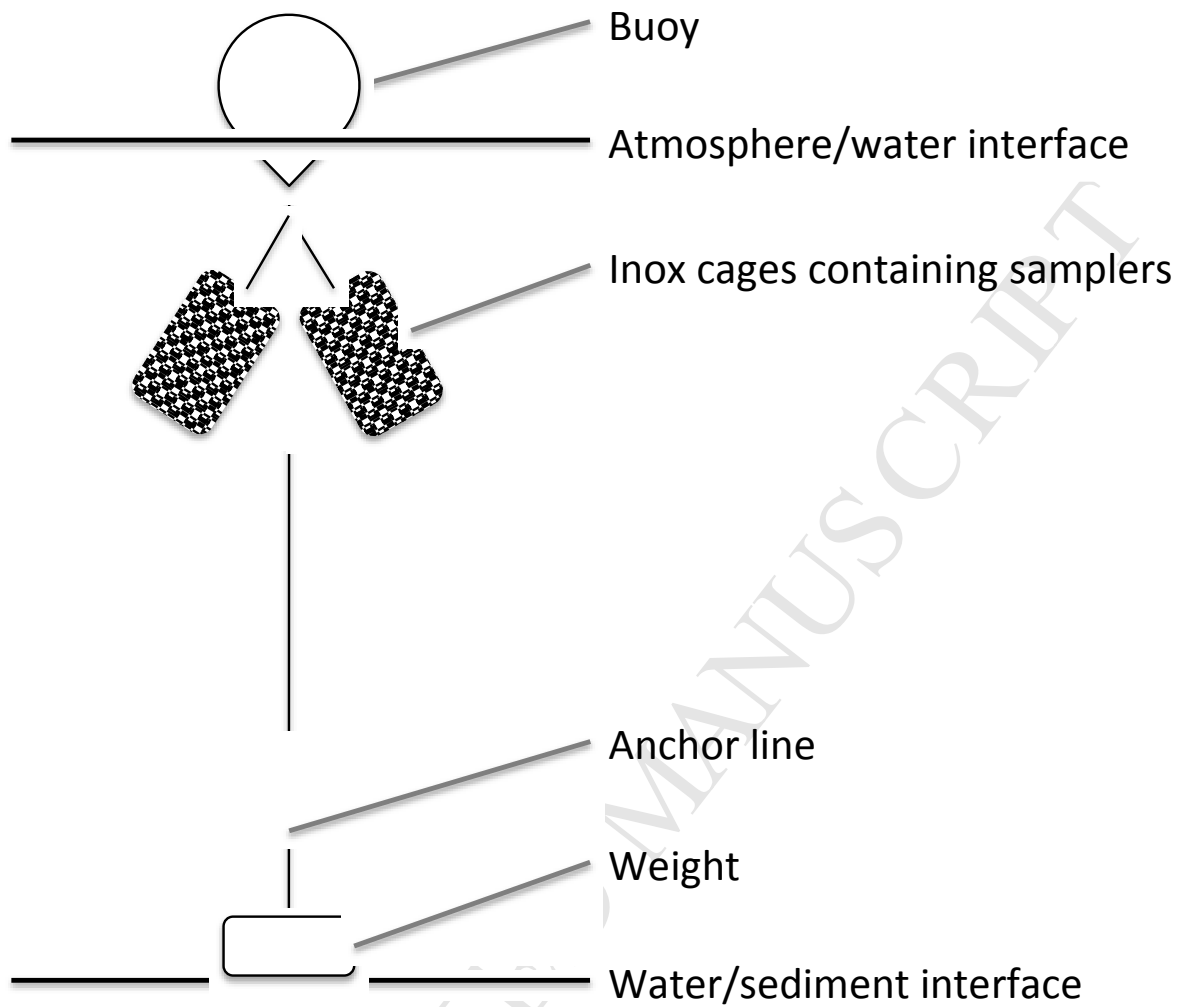
Supplementary material Figure 3. Scheme of in situ deployment system.

PMG

500

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

calibration of MPT samplers.

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

Vincent Fauvelle, Natalia Montero, Jochen Mueller, Andrew Banks, Nicolas Mazzella, Sarit Kaserzon

Highlights

- A novel passive sampler based on diffusion through microporous polyethylene was developed
- A novel passive sampler was adapted for glyphosate and its transformation product AMPA
- The first in situ application of passive sampler for glyphosate is described
- The cylindrical geometry of the sampler allows adapting sampling rates

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