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1 Calibration and response of an agarose gel based passive sampler 2 to record short pulses of aquatic organic pollutants

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12

13 ABSTRACT

14 A passive sampler inspired from previous devices was developed for the integrative sampling
15 of a broad range of contaminants in the water column. Our primary objective was to improve the
16 performance of the device to provide accurate and averaged pollutant water concentrations. For this
17 purpose, an agarose diffusive gel was used as the boundary layer that drives the analyte uptake rate.
18 Contrary to conventional passive samplers, the developed device does not require the sampling rates to
19 be corrected for exposure conditions (*e.g.* hydrodynamic flow) because the diffusive gel boundary
20 layer selected was sufficiently large to control the pollutant diffusion rate from the aqueous phase. The
21 compounds diffusion coefficients in agarose gel and the gel thickness are the only required data to
22 accurately calculate the time weighted averaged water concentration of pollutants. The performance of
23 the developed sampler was evaluated in the laboratory under two contamination scenarios and in the
24 field in 8 contrasting exposure sites for a selection of 16 emerging pollutants and pesticides. The
25 results show that detection limits of this method are environmentally relevant and allow the
26 determination of the averaged pollutant concentrations. Additionally, the ability of the device to sense

27 very short contamination pulses (5 to 320 min) was evaluated through a theoretical approach and
28 laboratory tests. Results show that the device is suitable for sampling contamination pulses as short as
29 5 min without deviation from the actual average concentrations of pollutants.

30

31 **KEYWORDS**

32 Passive sampler; polar contaminant; agarose gel; contamination pulse; water

33

34

35 **HIGHLIGHTS**

36 A novel agarose gel-based passive sampler was developed for polar pollutants

37 The compounds uptake rates do not depend on water flow conditions

38 The devices are able to accurately record very short contamination pulses (< 10 min)

39 The sampling rates determined in laboratory are suitable for field exposure

40

41 **1. INTRODUCTION**

42 One of the main advantages of water passive samplers is their integrative sampling giving
43 access to a time weighted averaged (TWA) water concentration over its exposure period. This
44 averaged water concentration is a suitable indicator for compliance monitoring of regulated
45 substances, such as in the European Water Framework Directive. However, the use of samplers in
46 their integrative regime for determining the TWA concentration requires maintenance of the pollutant
47 accumulation far from equilibrium between the water and the samplers and to evaluate the uptake rate
48 of compounds in the passive samplers (Lohman et al. 2012). Unfortunately, many studies report the
49 exposure condition-dependence of the uptake rate leading to difficulties in deriving the TWA water
50 concentration (O'Brien et al. 2012; Chang et al. 2015). To correct the sampling rate for the
51 environmental conditions, such as hydrodynamic flow or temperature, a performance reference
52 compounds (PRC) approach was successfully developed for partitioning-based passive samplers (*e.g.*
53 SPMD, polymeric passive samplers) (Booij et al. 1998, Belles et al. 2016a). Problems arise, however,

54 when sampling relatively polar compounds for which such devices have limited affinities.
55 Alternatively, numerous studies have demonstrated the ability of sorbent-based passive samplers (*e.g.*
56 POCIS, Chemcatcher) to efficiently trap the more polar compounds unsuitable for the partitioning-
57 based passive samplers (Bailly et al. 2013; Charriau et al. 2016; Vrana et al. 2016). However, reliable
58 quantitative TWA water concentrations are difficult to achieve as with the partitioning-based passive
59 samplers, the uptake rates of such devices are highly dependent on the exposure conditions (Li et al.
60 2010; Belles et al. 2014a). Unlike the partitioning-based passive samplers, however, the PRC approach
61 should not be implemented to improve the quantitative reliability of the sorbent-based devices because
62 they are driven by surface sorption processes rather than partitioning (Harman et al. 2011; Liu et al.
63 2013). Typically, the hydrodynamic flow is by far the most critical parameter driving the uptake rate
64 of the sorbent-based passive samplers by controlling the thickness of the stagnant water film at the
65 samplers surface, the so called water boundary layer (WBL) (Li et al. 2010; Belles et al. 2014a;
66 Carpinteiro et al. 2016). In this context, the development of samplers with a kinetic accumulation that
67 is not controlled by the compound diffusion through the WBL is a promising evolution of passive
68 sampler tools for accurately deriving the TWA water concentration of the polar pollutants without
69 needing a hydrodynamic flow correction for compound uptake rate (Garcia-Rodríguez et al. 2016).

70 The strategy introduced by Chen et al. (2012, 2013, 2015) aimed at reducing the compound
71 uptake rate by adding a diffusion step through a gel layer of known thickness. Ultimately, the process
72 of mass transfer through the diffusive gel is the limiting process and controls the uptake rate. The
73 kinetic of accumulation is then expected to be independent of the hydrodynamic flow and the uptake
74 rate measured in laboratory conditions should be close to the field values. This strategy was first
75 successfully applied by Chen et al. (2012, 2013, 2015) for waste water treatment plants by using an
76 agarose gel diffusing layer in the DGT housing leading to a small sampling surface area (3.14 cm²) at
77 the expense of sensitivity. Similar devices were tested by Fauvelle et al. (2014) through a set of
78 laboratory experiments for the sampling of polar and ionic pesticides. However two questions remain:
79 is the performance of such devices environmentally relevant for trace level analyses? How do such
80 devices integrate contamination pulses?

81 The overall objectives of this study were to adapt the agarose gel passive sampler design for
82 the measurement of TWA water concentrations by improving its detection limit and its integrative
83 sampling ability including the case of short contamination pulses. Firstly, the devices were calibrated
84 in the laboratory by measuring the diffusion coefficients of the targeted compounds in the agarose gel
85 and by measuring the actual uptake rates of compounds in the whole samplers immersed in water
86 under various exposure conditions. The sampler's ability for sensing short contamination pulses was
87 then theoretically evaluated and measured under laboratory conditions. Finally, the devices were tested
88 through various field exposures for examining their environmental robustness.

89

90 **2. MATERIALS AND METHODS**

91 *2.1. Chemicals*

92 Standards of target compounds and labeled internal standards (listed in Table 1 and S1) were
93 supplied by Sigma Aldrich (France) and LGC standards (United-Kingdom). All solvents and
94 chemicals were of analytical grade or better (Fisher Scientific, France). Strata-X polymeric reversed
95 phase (30 μm) was obtained from 500 mg-solid phase extraction (SPE) cartridges (Phenomenex,
96 United-Kingdom). Low electro-endosmosis agarose powder (for molecular biology (3,6-Anhydro- α -L-
97 galacto- β -galactan) and glass petri dishes (used as sampler bodies) were provided by Sigma Aldrich
98 (France). Gel strength for a 1% agarose gel (w/w) is 1200 g/cm², the gelling point for 1.5 % gel (w/w)
99 is 36 \pm 1.5 °C and the sulfate content of the dried powder is below 0.15%. Prior to use, all glassware
100 was combusted for 12 h at 400 °C. The Strata X sorbent was cleaned by passing 10 mL of
101 dichloromethane (DCM) through the SPE cartridges under vacuum.

102

103 *2.2. Passive sampler design and kinetic accumulation model*

104 The designed devices used a receiving medium consisting of Strata-X reversed phase sorbent
105 immobilized in agarose gel which is separated from the sampled water only by a 1.2 mm diffusive
106 layer of unfilled agarose gel (Figure 1). To improve the predictability of the kinetic exchange between
107 the device and the sampled water, no additional membranes were used to protect the diffusive gel
108 (Vermeirssen et al. 2012). The diffusion coefficient of pollutants in agarose gel is expected to be lower

109 than in water (Pluen et al. 1999) and the 1.2 mm gel thickness is several times higher than the typical
110 WBL thickness which ranges between 10 and 1000 μm (Huckins et al. 2006; Belles et al. 2016b). Both
111 properties ensure that the mass transfer through the diffusive gel layer is slower than across the WBL
112 so that the compounds uptake rate should be fully controlled by the diffusive gel. Because the gel is an
113 un-convective diffusive medium, for which the thickness is not dependent on the hydrodynamic
114 flow, the uptake rates measured in the laboratory are expected to be the same than in the field
115 providing that other parameters do not affect the kinetics of accumulation (*e.g.* temperature).

116 Owing to the affinity of compounds for the Strata-X sorbent, the concentration in the diffusive
117 gel at its interface with the binding gel, where diffusing compounds emerge is maintained effectively
118 at a null concentration. In this case, Crank et al. (1975) found that the compound accumulated in the
119 binding gel (M , ng) is a function of the water concentration (C_w ; ng mL⁻¹), the surface exchange area
120 (A ; cm²), the thickness of the diffusive gel (δ ; cm) and the diffusion coefficient in agarose gel (D_{gel} ;
121 cm² s⁻¹):

$$122 \quad C_w = \frac{M \delta}{D_{gel} A t} \quad (1)$$

123 Equation 1 is a useful indicator for a long exposure time and was adopted by several authors in the
124 field of passive samplers (Addeck et al. 2012; Chen et al. 2013; Fauvelle et al. 2014). If we consider
125 the early stage of accumulation kinetics, *e.g.* for studying the passive sampler's response to a very
126 short contamination pulse, it makes more sense to consider the general equation (Equation 2) for
127 kinetic uptake (Crank et al. 1975):

$$128 \quad M = \delta C_w A \left(\frac{D_{gel} t}{\delta^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{D_{gel} n^2 \pi^2 t}{\delta^2}\right) \right) \quad (2)$$

129 Equation 2 takes into account the transient stage for establishment of the steady state flow rate of
130 compounds through the diffusive gel (commonly called "lag phase"), leading to a delay in the
131 effective compound accumulation (Huckins et al. 2006). Usually, the characteristic time needed to
132 achieve the steady state flow rate is expressed as the intercept on the time-axis of the accumulation
133 curve given by Equation 3:

$$134 \quad t_{lag} = \frac{\delta^2}{6D_{gel}} \quad (3)$$

135 2.3. *Passive sampler preparation*

136 Passive samplers were built in the bottom half of a glass petri dish (11.5 cm internal diameter)
137 by successive deposition of a 0.7 mm-thick layer of binding gel and a 1.2 mm-thick layer of diffusive
138 gel (Figure 1). During the exposure of the samplers, both gels were held together with a plastic
139 housing (acrylonitrile-butadiene-styrene) built using a 3D printer (MakerBot Replicator 2X) and
140 protected with an aluminium screen (28 % open area; 12 Mesh). The binding gel was prepared by
141 mixing 10 mL of water, 0.15 g of ultrapure agarose powder and 1 g of Strata-X sorbent. After
142 homogenization, the preparation was heated in a water bath for 3 minutes, transferred into a pre-heated
143 petri dish (90 °C) and left to cool at room temperature for 1 h. Because D_{gel} depends to a large extent
144 on the cooling rate during gelification, the cooling time and temperature were carefully controlled
145 when preparing the passive samplers (Fatin-Rouge et al. 2004). Only the center part of the binding gel
146 disk was kept by removing a 7 mm ring, resulting in a final sampling area of 78 cm². The sampling
147 surface of the designed device is significantly higher than the standard POCIS configuration which
148 shows an exposure window of 46 cm². POCIS also overestimates the effective sampling area owing to
149 the surface of membrane which is not in contact with the POCIS sorbent (Fauvelle et al. 2014). After
150 cooling of the binding gel, the diffusive gel (20 mL of water and 0.3 g of agarose powder; 1.5 % w/w)
151 was cast in one time over the binding gel. The resulting diffusive gel thickness is of approximately 1.2
152 mm (Figure 1). After exposure of the passive samplers, the binding gel of each device was removed
153 for analysis and the effective thicknesses of the diffusive gel (δ) were measured with a micrometer
154 screw gauge for the calculation of the TWA water concentration (Equation 1).

155

156 2.4. *Determination of the compound diffusion coefficient in the agarose gel*

157 The diffusion coefficients in agarose gel of the target compounds were evaluated by the slice
158 stacking method (Rusina et al. 2010, Thomson et al. 2015). Agarose gel disks of 2 cm diameter and 1
159 mm thickness were prepared as described previously for the diffusive gel of passive samplers by
160 casting the warmed liquid agarose gel between 2 glass plates. After cooling, 15 disks were spiked by
161 immersing them into 250 mL of water spiked at 2.5 mg L⁻¹ with all selected chemicals. After 12 h of
162 immersion, 9 spiked disk were retrieved and capped with 7 un-spiked disk each. The 6 last spiked

163 disks were analysed as a blank for determining the initial compound concentrations (see section 2.9).
164 Three stacks were disassembled after a contact time of 5 min, 20 min and 2 h, were extracted and each
165 disk was analyzed separately. The diffusion coefficient (D_{gel}) was calculated for each contact time
166 experiment by fitting the measured concentration in each disk of the stack with the model in Equation
167 4, derived from Crank et al. (1975):

$$168 \quad C = C_0 \left(\frac{h}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left(\frac{n\pi h}{l} \right) \exp \left(-\frac{D_{gel} n^2 \pi^2 t}{l^2} \right) \cos \left(\frac{n\pi x}{l} \right) \right) \quad (4)$$

169 In Equation 4, C (ng g^{-1}) is the compound concentration at the distance x (cm) from the top of the
170 stack, C_0 (ng g^{-1}) is the measured initial contamination of the spiked disks, h (cm) is the total thickness
171 of the stack, l (cm) is the thickness of the spiked disk, t (s) is the contact time and n is the summation
172 index. The measured D_{gel} were averaged for all contact time experiments where the final
173 concentrations of the spiked disks are within the range 35-85 % of the initial concentrations
174 (conditions of a significant concentration gradient). Outside this range, the values were discarded to
175 minimize the uncertainty. In addition, the same experiments were conducted at 4°C to evaluate the
176 dependence of D_{gel} on temperature. Details of the D_{gel} values determined for each contact time
177 experiment and the averaged numerical values are available in the supplemental data section (Table
178 S2-S3).

179

180 2.5. Strata-X to water sorption isotherms of compounds

181 The sorption isotherms of selected compounds between the Strata-X sorbent and the water
182 were determined by mixing 50 mg of sorbent in 1 liter of contaminated water during a period of 15 d.
183 Nine contamination levels were simulated by adding to the aqueous phase 40, 100, 200, 400, 600,
184 2500, 10000, 20000 and 50000 μg of each polar compound as a concentrated methanolic solution (3
185 order of magnitude are spanned). After the equilibration period, the sorbent and aqueous phases were
186 separated by filtration through polypropylene frits (nominal pore size 0.7 μm) and separately analyzed.
187

188 2.6. Laboratory calibration of the devices

189 To ensure that the accumulation kinetics of compounds is fully controlled by the diffusion
190 across the gel and that D_{gel} is the only value required for calibrating the devices, the compound uptake
191 rates by the samplers were measured in the laboratory through 2 experiments simulating different
192 contamination sequences and hydrodynamic conditions. A first exposure simulated a constant water
193 concentration (5000 ng L⁻¹) and a strong water flow rate of 150 cm s⁻¹ (estimated from the velocity of
194 a float left in the experimental unit). A second condition simulated a low water flow rate (20 cm s⁻¹)
195 with a discontinuous water contamination composed of an initial 4 days of continuous contamination
196 (1000 ng L⁻¹) followed by 3 days with no contamination and 3 days of strongly contaminated water
197 (5000 ng L⁻¹). During the uncontaminated period, granular activated carbon was placed in the bottom
198 of the experimental unit to keep the background water contamination close to zero (Thompson et al.
199 2015). In both experiments, the setting consisted of a 27 L exposure tank mixed with an overhead
200 stirrer and contaminated by spiking water with a concentrated methanolic solution (2 mg L⁻¹) to reach
201 the target aqueous concentration. To keep the aqueous concentration constant, the water was renewed
202 and spiked every day. For both experiments, 26 passive samplers were exposed in the water and 2
203 were retrieved once or twice a day. After exposure, the devices were rinsed with Milli-Q water and
204 analyzed (see section 2.9). In addition, water samples of 800 mL from the experimental setting were
205 collected at least every day and analyzed for monitoring the actual water concentration (see section
206 2.9).

207

208 *2.7. Response of the devices to a short contamination pulse*

209 The ability of the device to account for the contamination variability over a short
210 contamination pulse was evaluated under laboratory conditions in moderately stirred water (50 cm s⁻¹).
211 For this purpose, 3 devices were exposed to un-contaminated water during 3 days including a brief
212 immersion after 24 h in a second water tank contaminated with the target compounds listed in Table 1.
213 The experiment was replicated for increasing contamination pulse periods of 5, 10, 20, 40, 80, 165 and
214 320 min. The water concentration during the contamination pulse periods was selected in order to
215 expose all devices in all experiments to the same TWA water concentrations (*i.e.* 50, 28, 12.5, 6, 3, 1.5
216 and 0.8 µg L⁻¹). For evaluating the actual water contamination, 1 L of water was sampled during the

217 simulated contamination pulse for analysis (see section 2.9.). The shortest contamination pulse period
218 was chosen in the order of the characteristic time needed to achieve the steady state flow rate through
219 the agarose gel (Equation 3) assuming a D_{gel} value of $3 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (a common value for the considered
220 compounds, see section 3.1).

221

222 2.8. Field testing

223 The field performance of the device for evaluating water contamination in contrasting
224 exposure conditions was evaluated by exposing devices in 8 aquatic sites including: marine water,
225 canals, lake and a waste water treatment plant. Details on the sample site properties are provided in
226 Table S4. At each site, 3 devices were simultaneously exposed for a period ranging from 8 to 15 days.
227 During the exposure period, at least 3 discrete water samples were collected for comparison to the
228 TWA water concentration derived from the passive samplers. The water temperature was continuously
229 monitored during the sampler exposure using a data logger (Onset HOBO data logger) and the
230 conductivity and pH were measured at each discrete sample recovery.

231

232 2.9. Analysis

233 After filtration (GF/F; $0.7 \mu\text{m}$), the collected water samples were spiked with an internal
234 standard solution (Table S1) and treated by liquid-liquid extraction using 3 times 30 mL of
235 dichloromethane as the organic extraction solvent. Recoveries of the extraction procedure were
236 evaluated by analyzing 14 artificial samples consisting of 1 L of Milli-Q water spiked with 0.1 to $5 \mu\text{g}$
237 of each target compound. Recovery rates for the target compounds ranged between 77 % and 150 %
238 and the typical variability was of $\pm 20 \%$ (Table S5).

239 To extract the passive sampler devices, the Strata-X sorbent of the binding gel was recovered
240 by freeze-drying the hydrated gel. Internal standards and 40 mL of dichloromethane were added to the
241 dried sorbent. After 24 h, the extract was collected and replaced by 40 mL of fresh dichloromethane
242 and left for an additional 24 hours. Both extracts were combined and filtered through $20 \mu\text{m}$ PE frits.
243 The recovery rates of the passive sampler extraction procedure were examined by analyzing a third
244 fraction of dichloromethane extracts for a set of 6 samples randomly selected. The average peak area

245 of the compounds from the 3rd fraction reached typically 1.5 % of the signal area of the combined first
246 2 fractions, confirming the performance of the extraction procedure developed (Table S5).

247 The final products of the liquid-liquid extractions and of passive sampler extractions were
248 blown down under a gentle stream of ultra-pure grade nitrogen at 55 °C and the solvent was changed
249 to 100 µL of ethyl-acetate for the chromatographic analysis.

250 All extracts were analyzed by gas chromatography coupled to mass spectrometry detector
251 (GC-MS; Agilent Technology 7890B series coupled to 5977 A mass spectrometer). One µL splitless
252 was injected at 250°C on a 30 m column (HP5MS-UI 30 m × 0.25 mm i.d. × 0.25 µm film thickness)
253 using Helium as a carrier gas at 1.3 mL min⁻¹ (constant flow rate). The oven temperature programme
254 was 55 °C for 0.5 min and then increased at 10 °C/min to a final temperature of 300 °C, where it was
255 held for 10 min. The GC-MS transfer line temperature was set at 300 °C. The MS was operated in
256 selected ion monitoring mode with electronic impact ionization with source temperature at 270 °C and
257 quadrupole temperature at 150 °C (details of the characteristic ion monitored for each analyte are
258 provided in Table S1).

259 Analyses of field control passive samplers showed no trace of any target compound (n=3).
260 Analysis of blanks of the liquid-liquid extraction procedures showed occasionally some traces of
261 galaxolide, benzophenone, tris(phenyl)phosphate and octicizer and were subtracted as background
262 from the corresponding field samples (Table S5).

263

264 **3. RESULTS AND DISCUSSION**

265 *3.1. Diffusion coefficients in agarose gel*

266 An example of the galaxolide distribution over the gel stack after 5, 20 min and 2 h of contact
267 time at 20 °C is shown in Figure 2. Similar distributions were observed for all of the selected
268 compounds. D_{gel} was estimated by fitting the experimental points with Equation 4. Depending on the
269 compounds, the measured diffusion coefficients ranged between -9.4 and -9.6 log unit (m² s⁻¹) and the
270 variability is typically 0.2 log unit (factor 1.3). The measured diffusivities D_{gel} are in the order of the
271 one measured for chlorpheniramine in 1 % agarose gel at 25 °C (-9.26 m² s⁻¹ log unit), as reported by
272 Sathynarayana et al. (1993).

273 The reduced diffusion coefficient (σ) within the gel, defined as the diffusion coefficient ratio
274 in the gel relative to the water (D_{gel}/D_w), is a key parameter for characterizing the compounds mobility
275 in the gel matrix (Pluen et al. 1999). The diffusivity in free solution (D_w) could be easily estimated by
276 Equation 5 formulated by Hayduk and Laudie (1974) where D_w is expressed as $\text{m}^2 \text{s}^{-1}$ with η (cP) as
277 the viscosity of water at the considered temperature and V_m ($\text{cm}^3 \text{mol}^{-1}$) is the so-called Le Bas
278 estimate of the molar volume of compounds estimated using the Schroeder additive method
279 (Partington et al. 1949):

$$280 \quad D_w = 13.26 \frac{10^{-5}}{\eta^{1.4} V_m^{0.589}} \quad (5)$$

281 A reduced diffusion coefficient below the unit ($\sigma < 1$) is typically observed in gel, because of a
282 combination of chemical interactions with agarose polymer and steric factors. In this study, the
283 hydrodynamic volume of selected compounds is too low for that steric interaction to prevail in the
284 reduced diffusion coefficient. Effectively, assuming an average compound radius (r_s) of 10 Å and
285 agarose fiber radius (r_f) of 60 nm, the obstruction model described by Johnson et al. (1996) ($\sigma =$
286 $\exp(-\Phi^{\frac{1}{2}} \cdot \frac{r_s}{r_f})$); with Φ for the agarose volume fraction, predicts that the reduced diffusion coefficient
287 should be about 99 % in the presence of the steric interaction alone. By comparison, the
288 experimentally measured D_{gel} gives an average reduced diffusion coefficient of $\sigma = 62 \pm 9$ % which was
289 for numerous compounds insignificant with respect to the error on the D_w estimate (0.2 log unit) and
290 measured D_{gel} (Table 1). Even though, according to the obstruction model, D_{gel} is expected to be equal
291 to D_w , our results suggest that D_{gel} is lower than D_w , but due to the variability of the compared values
292 we were not able to clearly provide evidence that σ differs from unity. In addition, it should be noted
293 that agarose gel is subject to H-bond interaction due to hydroxyl group and ionic interactions with
294 charged groups, in particular pyruvate and sulfate which could reduce the mobility of some
295 charged/polar compounds.

296 A significant temperature effect on D_{gel} was observed for all compounds with an average
297 increase of 0.4 log units (factor 2.5) between 4 °C and 20 °C (Figure 3, Table S2 and S3). This value is
298 comparable to the one of the pharmaceutical ibuprofen which increases by a factor of 1.6 between 26

299 and 45 °C in 1 % agarose gel (Sathynarayana et al. 1993). The temperature dependence of D_{gel} can be
300 evaluated from an Arrhenius type relationship as:

301

$$\ln D_{gel T1} - \ln D_{gel T2} = -\frac{Ea}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (6)$$

302

303 where $D_{gel T1}$ and $D_{gel T2}$ are the diffusivity at temperatures T_1 and T_2 , R ($\text{kJ mol}^{-1} \text{K}^{-1}$) is the gas
304 constant and Ea (kJ mol^{-1}) is the apparent activation energy of compound diffusion within the gel.
305 The value of the Ea is a direct measurement of the temperature dependence of the compound
306 diffusivity D_{gel} (Table 1). Under our selected conditions, the average Ea was $47 \pm 14 \text{ kJ mol}^{-1}$ which
307 indicates that the diffusivity of compounds in agarose gel and subsequently the compounds uptake rate
308 strongly depends on temperature, suggesting a variation by a factor 3.9 for typical field temperature
309 values (5-25 °C).

310

311 3.2. Laboratory calibration of passive sampler devices

312 The time series of the amount of atrazine sampled by the devices in the two water flow
313 conditions trialed in the laboratory experiments is given in Figure 4. For a direct comparison
314 regardless of the difference in the water contamination levels, the results are given as the amount of
315 compound sampled divided by the sampling surface area and the atrazine water concentration and
316 further multiplied by the diffusive gel thickness (Equation 1). After normalization by the water
317 concentration, the accumulated amounts of the compounds in both water flow conditions were similar.
318 The hydrodynamic conditions do not affect the compounds uptake rate, confirming that it is driven by
319 the diffusion across the diffusive gel rather than across the WBL (Li et al. 2010; Belles et al.2014b).
320 This unique result illustrates the interest of our device in comparison to some other passive sampler
321 configurations dedicated to the sampling of polar compounds (*e.g.* POCIS, Chemcatcher)..

322 An overview of atrazine kinetic uptake when devices were exposed to a discontinuous
323 contamination is given in Figure 5. For atrazine and all other target compounds in this study, the
324 sampled amounts were directly proportional to the average water concentration indicating that the D_{gel}
325 values are independent of the contamination level (Equation 1). Thus, the tested sampler is integrative

326 and the final amount sampled by the device is consistent with the average water contamination. In
327 most cases, the sampled compounds are not significantly released from the device during the
328 uncontaminated exposure period (analyses of water samples collected during the uncontaminated
329 period confirmed that background contamination levels remained below the detection limits). This
330 underlines the ability of the samplers to integrate a contamination peak without losing the chemical
331 information over the following exposure days. Compound release can become a problem when
332 samplers are exposed to a lower water concentration during the last days of deployment as desorption
333 will induce a loss of analytes and provide an underestimation of the TWA water contamination
334 (Gourlay-Francé et al. 2008). In our study, only the most hydrophilic selected compounds (atrazine-
335 desethyl; $\log P = 1.5 \pm 0.26$; XLOGP3 estimate (Cheng et al. 2007)) were significantly released during
336 the 4 days of the uncontaminated water period with a sampled amount reduction of 13 % (calculated
337 as: $\text{sampled amount reduction} = [\text{initial concentration} - \text{final concentration}] / \text{initial concentration}$). Similar
338 results were previously reported for POCIS passive samplers by Belles et al. (2014b) for a set of
339 pesticides and pharmaceuticals with $\log P$ ranging between -1.7 and 2.0. By comparison, the usual
340 partitioning-based passive samplers such as the polymeric sheets are more prone to compound release
341 of similar hydrophobicity (Fluorene, Acenaphthene, Acenaphthylene and Naphthalene) for which full
342 dissipation is common (Huckins et al. 2006; Belles et al. 2016b).

343

344 *3.3. Practical application of agarose gel based passive samplers*

345 D_{gel} are required for all compounds to estimate the TWA concentration in water from the
346 amount of compounds sampled by the device. The diffusivity coefficients D_{gel} , used to derive the TWA
347 concentrations, are a key parameter which should be determined with the highest accuracy to improve
348 method suitability. For this purpose, the D_{gel} determined in the laboratory experiments (using Equation
349 4 for the gel stack experiments and Equation 1 for the passive sampler calibration experiments) were
350 used to determine an average value and for evaluating its variability. At a given temperature, the
351 measured D_{gel} values were not significantly different D_{gel} between the gel stack experiments and the
352 laboratory calibrations despite different calculation methods (Table 1, S2 and S3). Ultimately, the

353 observed variability of D_{gel} , similar to the variability on the calculated water concentration, ranged
354 between 0.1 and 0.3 log units depending on the compounds (Table 1).

355 If the sampling rate of a passive sampler is a function of the compound's hydrophobicity [as
356 most notably for the partitioning based passive samplers for single compound classes (Booij et al.
357 1998; Belles et al. 2016b)], several publications have demonstrated that the same does not apply for
358 sorption based passive samplers such as POCIS (Carpinteiro et al. 2016). Effectively, uptake kinetics
359 of POCIS devices are controlled by many processes that are not a function of a compound's
360 hydrophobicity, such as the diffusion of compounds into the sorbent pores (Belles et al 2014b). This
361 negates tentative correlations of log P with uptake rate. For the present device, the sampler design is
362 specifically adapted for kinetic accumulations controlled by diffusion through the agarose gel which
363 has been demonstrated to be proportional to the diffusivity in water and subsequently to the molecular
364 volume (Fatin-Rouge et al. 2004). Based on this assumption, it is appropriate to evaluate the uptake
365 rate of samplers (D_{gel}) from the compounds diffusivity in water and the molecular volume. In addition,
366 it is of primary interest to estimate the D_{gel} value without performing full calibration experiments
367 under laboratory conditions. For that purpose, the reduced diffusion coefficient relationship between
368 D_{gel} and D_w ($\sigma=D_{gel}/D_w$), derived from the results of the laboratory experiments, provides a simple
369 relationship indicating that the expected value of D_{gel} should reach 62 % of the diffusion coefficient in
370 pure water (Figure 3). For the set of selected compounds, the relationship yields a typical error of 0.2
371 log units based on the averaged standard error between the predicted and measured values of D_{gel} (0.2
372 log unit error on log D_{gel} results in a 14 % error in the calculated water concentrations). Also, this
373 relationship provides an initial estimate of D_{gel} for dosing additional compounds without the need of
374 specific time consuming calibration experiments. Alternatively, the slice stacking technique could be
375 used to determine a field suitable uptake rate through a laboratory measurement with a contact time of
376 about 1 h. In addition, to avoid a deviation from the calculated water concentration during the field
377 deployment of passive samplers, D_{gel} determined in the laboratory (usually at 20 or 25 °C) requires a
378 correction by using Equation 6 and the temperature measured in the field at least at the deployment
379 and retrieval of the samplers.

380 Another aspect to consider when using passive samplers is the detection limit of the method,
381 especially when monitoring low trace levels. In our study, the amount of compounds detected in the
382 fabrication control and field control samplers were negligible (see section 2.9.) and do not drive the
383 detection limit of the method (Lohmann et al. 2012). In such cases, the detection limit is rather
384 controlled by the analytical detection limit than by the blank level. Owing to the measured D_{gel} value
385 and an assumed analytical detection limit of 1 ng per sample, we expect that the detection limit of the
386 passive sampler, including all steps of the sampling, would be in the order of 3 ng L⁻¹ for 1 d of
387 exposure (given $A=78$ cm²; $\delta=1.2$ mm; $\log D_{gel}=-9.2$ m² s⁻¹). This estimated detection limit should be
388 divided by the number of exposure days to provide the final detection limit of a given exposed sampler
389 (i.e. 0.3 ng L⁻¹ for a typical exposure period of 10 d).

390

391 3.4. Maximum exposure time for integrative sampling

392 To ensure that the passive sampler remains far from equilibrium and to evaluate the maximum
393 exposure time for integrative sampling of the device, the sorption isotherm of compounds between the
394 Strata-X sorbent and water was measured and the distribution constant values ($K_{Strata-X}$) was calculated
395 by fitting the experimental value to the linear sorption model $C_s=K_{Strat-X}.C_w$ (where C_s refers to the
396 concentration of sorbed compounds). For many of the compounds the linear sorption model deviates
397 from the experimental value, notably for the most polar compounds and the lower contamination
398 levels. This result in lower correlation coefficients between the model and the experimental values
399 reported in Table 1. For these compounds more complex sorption models (such as freundlich,
400 langmuir or dual mode) should improve the predictability of the experimental values (Bäuerlein et al.
401 2012). However, as a first approach to evaluate the sampler's equilibrium, the adopted linear model is
402 appropriate. To ensure fully integrative sampling, the devices should remain at all times far from
403 equilibrium conditions and subsequently the concentration ratio C_s/C_w should remain far below the
404 calculated value of $K_{Strata-X}$. Combined with equation 1, this assumption could be rearranged as
405 follows:

406

407
$$t_{max} \ll \frac{K_{Strata-x}\delta}{D_{gel}A} \quad (7)$$

408 For each compound, the t_{max} values below which the exposure period should remain to ensure
409 correct integrative sampling, is reported in Table 1. Atrazine-desethyl is the compound exhibiting the
410 lowest t_{max} with a value of 4 d. To ensure good device performance, it is reasonable to adopt an
411 exposure period 10 times lower than this threshold. For atrazine-desethyl the threshold is rapidly
412 reached and as suggested by the $K_{Strata-x}$ dependency with log P (Figure S1), it is probable that all
413 compounds with a log P lower than atrazine-desethyl (log P=1.5) are in a similar position. Note that
414 the establishment of an equilibrium state for atrazine-desethyl was not formally observed during the
415 laboratory calibration, most probably due to the underestimation of the $K_{Strata-x}$ value owing to the non-
416 linear sorption isotherm. However the equilibrium is probably almost reached as is suggested by the
417 release of atrazine-desethyl during the uncontaminated period (see section 3.2.)

418

419 *3.4. Response of passive samplers exposed to a short contamination pulse*

420 According to Crank et al. (1975), a lag time period is expected in the compounds uptake
421 before the establishment of a steady flow of compounds across the diffusive agarose gel. This may
422 result in a non-linear accumulation curve and delay in integration of a short contamination pulse
423 (Equations 2 and 3). Ultimately, a very short contamination pulse could not be sampled by this type of
424 device. For a common compound with $\log D_{gel} = -9.2 \text{ m}^2 \text{ s}^{-1}$ (e.g. galaxolide) sampled by a device with
425 1.2 mm diffusive gel thickness, the estimated lag time is about 10 min (Equation 3). It is noteworthy
426 that similar t_{lag} are expected for all compounds, because their D_{gel} are within a narrow range ($7 \text{ min} <$
427 $t_{lag} < 14 \text{ min}$, Table 1). In addition to the theoretical estimate of t_{lag} , a set of laboratory experiments
428 was conducted to evaluate the effective lag time which represents the minimal period threshold for
429 samplers to sense a contamination event. The results, illustrated in Figure 6, showed that the water
430 concentrations estimated by the device were close to the actual averaged concentration, even for short
431 contamination periods (in the range 5 min - 320 min). In the case of short contamination pulses, the
432 deviations between the passive samplers estimate and the actual TWA water concentration were in the
433 order of the D_{gel} variability, suggesting that any potential deviation coming from the lag effect for the

434 short time would remain lower than the uncertainty on D_{gel} . These results indicate that the calculated
435 water concentration of a contamination pulse longer than 5 min is accurately recorded by the device
436 without significant deviation. However, the ability of the samplers to detect a short contamination
437 pulse decreases with the pulse duration. Therefore, the shorter the contamination peak, the higher is
438 the detection limit of the method (Figure S2).

439

440 3.5. Field validation

441 Using the averaged D_{gel} determined in laboratory (see section 3.3.), the TWA water
442 concentrations of the selected compounds in the exposure sites were calculated. Because water
443 contamination is expected to vary with time, comparison between the TWA water concentration
444 derived from the passive samplers and the average of conventional spot samples ($n \geq 3$) may differ.
445 However, by replicating the comparison many times and through different exposure scenarios (8 sites
446 were monitored), the accuracy of the approach can be assessed if no systematic deviation is observed
447 between the passive samplers and the grab sample analyses. Punctual differences, for a given
448 compounds at a given site, does not invalidate the developed approach. However, a systematic
449 overestimation or underestimation for a given site or a given compound is critical and poses a potential
450 problem for sampler calibration. The large number of compounds assessed and of sampled sites in this
451 study increase robust evaluation of the comparison. However, selection of larger sets of exposure
452 scenarios, beyond the scope of this study, could improve field validation.. As indicated in Figure 7A
453 and Table S4, no systematic deviation was observed for a given site, suggesting that the device
454 performances are not dependent on the water body properties (*e.g.* salinity, temperature,
455 hydrodynamic flow). In the only case of the “WWTP” sampling site, water concentrations derived
456 from the passive samplers were overestimated (approximately by a factor 2). Because a contamination
457 pulse is not expected to induce a simultaneous increase of concentration of pollutants belonging to
458 unrelated compound classes (*i.e.* personal care products, herbicides), the observed systematic
459 overestimation was not attributed to a contamination pulse. Temperature, conductivity and pH,
460 comparable in the “WWTP” samples to the average values measured in the others sampling sites, do
461 not seem to be the cause for this deviation (Table S4). The origin of this overestimation requires

462 further investigations, notably with regard to the dissolved organic matter that is undoubtedly higher in
463 WWTP sampling site and could play an important role in the sampler's performance. Within the
464 exception of propazine, no systematic deviation was observed per compound, indicating that the D_{gel}
465 determined in the laboratory calibration experiments were suitable for the field exposures (Figure 7B;
466 Table S4). However, such deviation as observed for propazine show that laboratory calibration should
467 be replicated for improving the accuracy of the measured D_{gel} .

468

469 **4. CONCLUSIONS**

470 The interest of using an agarose gel as an anticonvective medium at the exchange surface of
471 the sampler is to precisely define the thickness of the diffusive boundary layer controlling the
472 compounds uptake rate, contrary to the standard configuration of POCIS and polar Chemcatcher. We
473 demonstrate that such diffusive gel passive samplers have a robust uptake rate that allows the use of
474 laboratory calibration data for field monitoring, yielding to relative errors between 30 and 100 %
475 depending on the compounds. With the only exception of atrazine-desethyl, the selected compounds in
476 this study are integratively sampled by the developed device (with compound uptake proportional to
477 the water contamination) which provides quantitative values of the water contamination. In addition,
478 the determination of the compound uptake rates, needed to derive the TWA water contamination from
479 the amount of compounds taken up, is straightforward by using the gel-slice stacking technique.
480 Diffusive gel-based passive samplers are a very promising approach for the improvement of passive
481 samplers dedicated to comparatively polar compounds dosing. Furthermore, the suitability of the
482 samplers for integrating the concentration fluctuations, even for very short contamination pulses, have
483 been experimentally demonstrated. In the light of these results, such passive samplers should be
484 considered for monitoring simultaneously the TWA water concentrations of exposure periods ranging
485 from a few hours to several days. Further study remain necessary for large scale validation of device
486 in field conditions and through comparative study with other passive sampling techniques.

487

488

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492

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Table 1: Agarose gel diffusion coefficient ($\log D_{gel}$) determined in laboratory at 4 °C and 20 °C and apparent activation energy (E_a ; kJ mol^{-1}) of compounds diffusion within the gel.

	Log P ^a	Log D_w ($\text{m}^2 \text{s}^{-1}$) ^b	$\log D_{gel}^{4^\circ\text{C}}$ ($\text{m}^2 \text{s}^{-1}$)	$\log D_{gel}^{20^\circ\text{C}}$ ($\text{m}^2 \text{s}^{-1}$)	E_a (kJ mol^{-1})
Atrazine	2.6	-9.27	-10.0 ± 0.1	-9.4 ± 0.1	57
Atrazine-desethyl	1.5	-9.21	-9.8 ± 0.2	-9.4 ± 0.1	42
Benzophenone	3.4	-9.25	-9.7 ± 0.2	-9.5 ± 0.1	27
Diflufenican	4.6	-9.42	-10.1 ± 0.2	-9.5 ± 0.1	57
Galaxolide	4.8	-9.36	-10.3 ± 0.2	-9.5 ± 0.1	74
Irgarol	3.9	-9.32	-9.9 ± 0.1	-9.5 ± 0.1	46
Lilial	3.9	-9.31	-10.0 ± 0.2	-9.5 ± 0.1	46
Metazachlore	2.7	-9.33	-10.1 ± 0.1	-9.4 ± 0.1	61
Metolachlore	3.1	-9.36	-9.9 ± 0.2	-9.4 ± 0.1	49
Octicizer	6.3	-9.44	-10.0 ± 0.1	-9.5 ± 0.2	45
Propazine	2.9	-9.29	-10.1 ± 0.1	-9.5 ± 0.1	57
Simazine	2.2	-9.24	-9.8 ± 0.1	-9.3 ± 0.1	52
Tonalid	5.3	-9.36	-10.1 ± 0.1	-9.6 ± 0.1	48
Tri(n-butyl)phosphate	3.7	-9.22	-9.8 ± 0.3	-9.6 ± 0.3	27
Triisobutyl phosphate	3.0	-9.22	-9.8 ± 0.3	-9.6 ± 0.3	21
Tris(phenyl)phosphate	4.6	-9.38	-10.0 ± 0.1	-9.6 ± 0.1	42

^a estimated by XLOGP3 calculator (Cheng et al. 2007)

^b D_w was estimated using the relationship developed by Hayduk and Laudie (1974) i.e., $D_w = (13.26 \times 10^{-9}) / (\eta 1.4 V_m 0.589)$, using molar volume as estimated by incremental method as described in Partington et al. 1949. The average error on the estimation is 0,2 log unit.

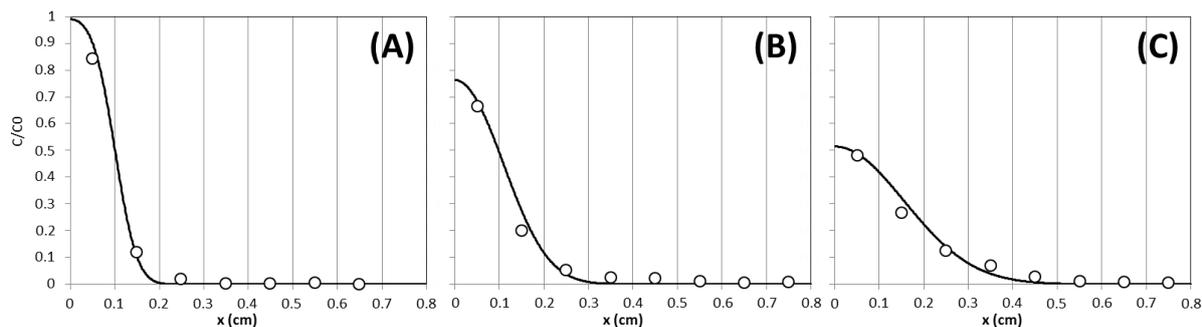


Figure 1 Concentration distribution of galaxolide in agarose gel stack after 5 min (A), 20 min (B) and 2 h (C) of contact time. Black curves represent the fit of Equation 4 with D_{gel} used as the adjustment factor. Vertical lines represent the boundaries between two gel slabs of the stack.

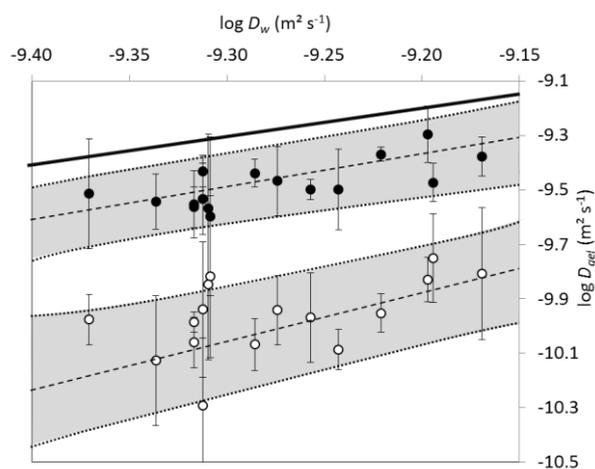


Figure 2 double logarithmic scaled plots D_{gel} against D_w . Filled symbols refer to the average D_{gel} determined at 20 °C, and the open symbols refer to the average D_{gel} determined at 4 °C. Full lines refer to the diffusion coefficient in water estimated following Hayduk and Laudie (1974) at 20 °C (1:1 agreement line). Dashed line represents the linear regression of each data set; the dotted lines represent the 95 % confidence interval.

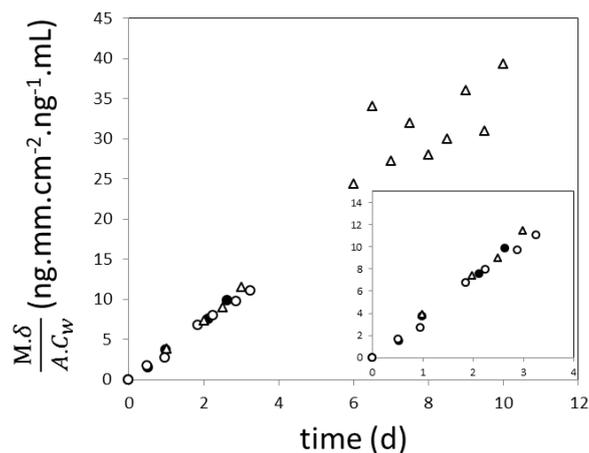


Figure 3 Uptake of atrazine in both experiments simulating 2 water flow rates and contamination levels. Triangles refer to the strong water flow and constant water contamination experiment. Circles refer to the variable water contamination experiment (filled symbols refer to the first contamination period and open symbols to the second contamination period). For a direct comparison, the accumulation curve [sampled amount (M) multiplied by the gel thickness (δ) and divided by the sampling area (A)] is normalized by the water contamination level (C_w). The inset provides a zoomed in view of the short time.

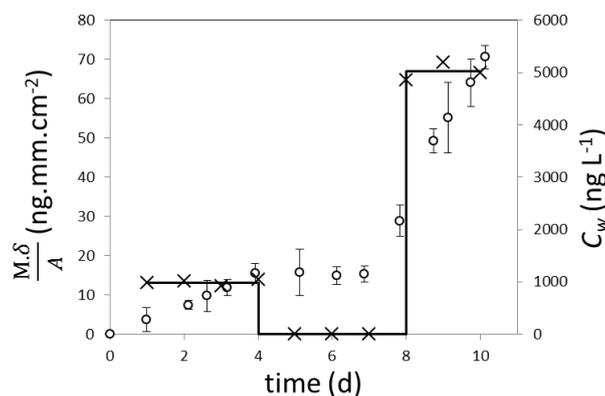


Figure 4 Uptake of atrazine during the discontinuous water contamination simulation. Left-axis refers to the accumulated amount of compounds. Right-axis refers to the aqueous concentration. Full line represents the nominal water concentration, cross symbols are the measured water contaminations and circles are the amount of compounds sampled by the device.

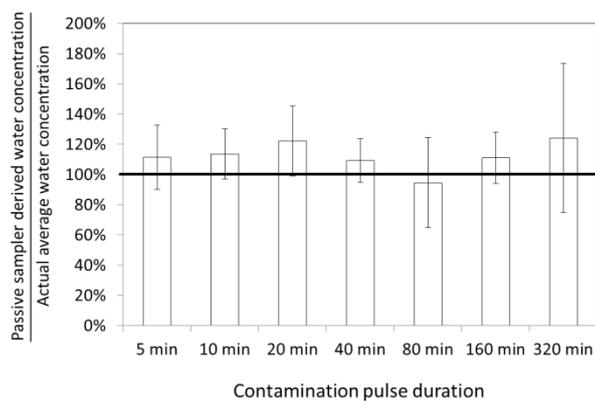


Figure 5 Comparison between the passive samplers derived water concentration and the actual average water contamination for the various simulated contamination pulses. Contamination pulse levels and durations are selected in order to expose all devices to the same TWA water contamination. The results are expressed as the average of all the selected compounds. Error bars refer to the standard deviation (n=16).

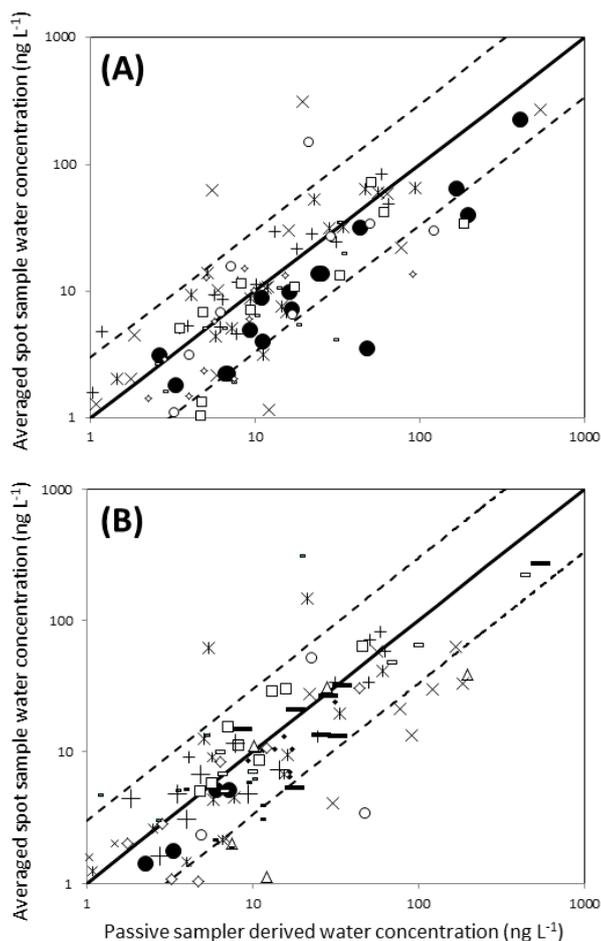


Figure 6 Average spot sampling measured water concentrations against the passive sampler derived water concentrations. In part (A), the different markers indicate different exposure sites (filled circles represent the WWTP sampling site which is the only site to show a systematic deviation). In part (B), the same date is plotted with symbols indicating different compounds (filled circles represent propazine which is the only compound to show a systematic deviation). Full lines refer to the 1:1 agreement line and dotted lines to the factor 3 deviation lines.

