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

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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+/-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-convectional 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 ($\delta$; *cm*) and the diffusion coefficient in agarose gel ($D_{gel}$;

121  cm² s$^{-1}$):

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

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

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

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

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 $3.10^{-10}$ m² 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 µm), 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 µg

237     of each target compound. Recovery rates for the target compounds ranged between 77 % and 150 %

238     and the typical variability was of ± 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 thorough 20 µm 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 m$^2$ s$^{-1}$ with $\eta$ (cP) as

277    the viscosity of water at the considered temperature and $V_m$ (cm$^3$ 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    $$D_w = 13.26 \frac{10^{-5}}{\eta^{1.4} V_m^{0.589}}$$    (5)

281    A reduced diffusion coefficient below the unit (σ <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 ($r_s$) of 60 nm, the obstruction model described by Johnson et al. (1996) ($\sigma =$

286    $\exp(-\Phi^{\frac{1}{2}} . \frac{r_s}{r_f})$; with $\Phi$ 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 σ=62 ± 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-bound 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

302
$$\ln D_{gel\,T1} - \ln D_{gel\,T2} = -\frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (6)$$

303     where $D_{gel\,T1}$ and $D_{gel\,T2}$ are the diffusivity at temperatures $T_1$ and $T_2$, $R$ (kJ mol$^{-1}$ 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 $47 \pm 14$ 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 ± 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: sampled amount reduction=[initial concentration-final concentration]/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 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
$$t_{max} \ll \frac{K_{Strata-X}\delta}{D_{gel}A} \qquad (7)$$

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 m² 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 min <

427     $t_{lag}$ < 14 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 ≥ 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. Furthers study remain necessary for large scale validation of device

486    in filed conditions and through comparative study with other passive sampling techniques.

487

488                                    **ACKNOWLEDGMENTS**

492

# BIBLIOGRAPHY

Addeck A., Croes K., Van Langenhove K., Denison M., Elskens M., Baeyens W. Dioxin analysis in water by using a passive sampler and CALUX bioassay. *Talanta* **2012**; 88:73-78.

http://dx.doi.org/10.1016/j.talanta.2011.10.009

Bailly E., Levi Y., Karolak S. Calibration and field evaluation of polar organic chemical integrative sampler (POCIS) for monitoring pharmaceuticals in hospital wastewater. *Environmental Pollution* **2013**; 174:100-105. http://dx.doi.org/10.1016/j.envpol.2012.10.025

Bäuerlein P.S., Mansell J.E., ter Laak T.L., de Voogt P. Sorption Behavior of Charged and Neutral Polar Organic Compounds on Solid Phase Extraction Materials: Which Functional Group Governs Sorption? *Environ. Sci. Technol.* **2012**; 46 (2): 954-961. http://dx.doi.org/10.1021/es203404x

Belles A., Tapie N., Pardon P., Budzinski H. Development of the performance reference compound approach for the calibration of "polar organic chemical integrative sampler" (POCIS). *Anal Bioanal Chem.* **2014a**; 406(4):1131-1140.  http://dx.doi.org/10.1007/s00216-013-7297-z

Belles A., Pardon P., Budzinski H. Development of an adapted version of polar organic chemical integrative samplers (POCIS-Nylon). *Anal Bioanal Chem.* **2014b**; 406(4):1099-1110.

http://dx.doi.org/10.1007/s00216-013-7286-2

Belles A, Mamindy-Pajany Y, Alary C, Simulation of aromatic polycyclic hydrocarbons remobilization from a river sediment using laboratory experiments supported by passive sampling techniques. *Environ Sci Pollut Res Int*. **2016a**; 23(3):2426-36. http://dx.doi.org/10.1007/s11356-015-5462-y

Belles A., Alary C., Mamindy-Pajany Y. Thickness and material selection of polymeric passive samplers for polycyclic aromatic hydrocarbons in water: Which more strongly affects sampler properties? *Environ Toxicol Chem.* **2016b**; 35(7):1708-1717.  http://dx.doi.org/10.1002/etc.3326

Booij K., Sleiderink H., Smedes F. Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards. *Environ Toxicol Chem.* **1998**; 17(7):1236-1245. http://dx.doi.org/10.1002/etc.5620170707

Carpinteiro I., Schopfer A., Estoppey N., Fong C., Grandjean D., de Alencastro L.F. Evaluation of performance reference compounds (PRCs) to monitor emerging polar contaminants by polar organic chemical integrative samplers (POCIS) in rivers. *Anal Bioanal Chem.* **2016**; 408(4):1067-78. http://dx.doi.org/10.1007/s00216-015-9199-8

Chang W-T, Lee C-L, Brimblecombe P, Fang M-D, Chang K-T, Liu J.T. The effects of flow rate and temperature on SPMD measurements of bioavailable PAHs in seawater. *Marine Pollution Bulletin* **2015**; 97(1–2):217-223. http://dx.doi.org/10.1016/j.marpolbul.2015.06.013

Charriau A., Lissalde S., Poulier G., Mazzella N., Buzier R., Guibaud G. Overview of the Chemcatcher® for the passive sampling of various pollutants in aquatic environments Part A: Principles, calibration, preparation and analysis of the sampler. *Talanta* **2016**; 148:556-571. http://dx.doi.org/10.1016/j.talanta.2015.06.064

Chen C.-E., Zhang H., Jones K.C., A novel passive water sampler for in situ sampling of antibiotics. *J. Environ. Monit.*, **2012**, 14: 1523-1530. http://dx.doi.org/10.1039/c2em30091e

Chen C-E., Zhang H., Ying G-G., Jones K.C., Evidence and Recommendations to Support the Use of a Novel Passive Water Sampler to Quantify Antibiotics in Wastewaters. *Environ. Sci. Technol.*, **2013**, 47(23):13587-13593.  http://dx.doi.org/10.1021/es402662g

Chen C.-E., Zhang H., Ying G.-G., Zhou L.-J., Jones K.C., Passive sampling: A cost-effective method for understanding antibiotic fate, behaviour and impact. *Environ. Int*.,**2015**, 85: 284-291. http://dx.doi.org/10.1016/j.envint.2015.10.001

Cheng T., Zhao Y., Li X., Lin F., Xu Y., Zhang X., Li Y., Wang R. Computation of Octanol−Water Partition Coefficients by Guiding an Additive Model with Knowledge. *J. Chem. Inf. Model*. **2007**; 47(6):2140-2148. http://dx.doi.org/10.1021/ci700257y

Crank J. 1975. The Mathematics of Diffusion. Oxford University Press Inc., New York, USA.

Fatin-Rouge N., Starchev K., Buffle J. Size Effects on Diffusion Processes within Agarose Gels. *Biophys J*. **2004**; 86(5):2710-2719. http://dx.doi.org/10.1016/S0006-3495(04)74325-8

Fauvelle V., Mazzella N., Belles A., Moreira A., Allan I.J., Budzinski H.Optimization of the polar organic chemical integrative sampler for the sampling of acidic and polar herbicides. *Anal Bioanal Chem.* **2014**; 406(13):3191-3199. http://dx.doi.org/10.1007/s00216-014-7757-0

Garcia-Rodríguez A., Fontàs C., Matamoros V., Almeida M.I.G.S., Cattrall R.W., Kolev S.D. Development of a polymer inclusion membrane-based passive sampler for monitoring of sulfamethoxazole in natural waters. Minimizing the effect of the flow pattern of the aquatic system. *Microchemical Journal* **2016**; 124:175-180. http://dx.doi.org/10.1016/j.microc.2015.08.017

Gourlay-Francé C., Lorgeoux C., Tusseau-Vuillemin M-H. Polycyclic aromatic hydrocarbon sampling in wastewaters using semipermeable membrane devices: Accuracy of time-weighted average concentration estimations of truly dissolved compounds. *Chemosphere* **2008**; 73(8):1194–1200. http://dx.doi.org/10.1016/j.chemosphere.2008.07.049

Harman C., Allan IJ, Bäuerlein PS, The Challenge of Exposure Correction for Polar Passive Samplers—The PRC and the POCIS. *Environ. Sci. Technol*. **2011**; 45(21):9120–9121. http://dx.doi.org/10.1021/es2033789

Hayduk W., Laudie H. Prediction of Diffusion Coefficients for Non-Electrolytes in Dilute Aqueous Solutions *AIChE Journal* **1974**; 20(3):611-615.  http://dx.doi.org/10.1002/aic.690200329

Huckins J., Petty J., Booij K. Monitors of Organic Chemicals in the Environment: Semipermeable Membrane Devices. Springer, New York, **2006**, NY, USA.

Johnson E.M., Berk D.A., Rakesh A., Jain K., Deen W.M. Hindered Diffusion in Agarose Gels: Test of Effective Medium Model. *Biophys J*. **1996**; 70(2):1017-1023. http://dx.doi.org/10.1016/S0006-3495(96)79645-5

Li H., Vermeirssen E.L., Helm P.A., Metcalfe C.D., Controlled field evaluation of water flow rate effects on sampling polar organic compounds using polar organic chemical integrative samplers. *Environ Toxicol Chem*. **2010**, 29(11):2461-2469. http://dx.doi.org/10.1002/etc.305

Liu H-H., Wong C.S. Zeng E.Y. Recognizing the Limitations of Performance Reference Compound (PRC)-Calibration Technique in Passive Water Sampling. *Environ. Sci. Technol*., **2013**, 47(18):10104-10105. http://dx.doi.org/10.1021/es403353d

Lohmann R, Booij K, Smedes F, Vrana B. Use of passive sampling devices for monitoring and compliance checking of POP concentrations in water. *Environ Sci Pollut Res.* **2012**, 19:1885-95. http://dx.doi.org/10.1007/s11356-012-0748-9

O'Brien D., Komarova T., Mueller J.F. Determination of deployment specific chemical uptake rates for SPMD and PDMS using a passive flow monitor. *Marine Pollution Bulletin*, **2012**; 64(5):1005-1011. http://dx.doi.org/10.1016/j.marpolbul.2012.02.004

Partington, J.: An advanced treatise on physical chemistry, Longmans Green, London, New York, **1949**.

Pluen A., Netti P.A., Jain R.K., Berk D.A. Diffusion of Macromolecules in Agarose Gels: Comparison of Linear and Globular Configurations. *Biophys J.* **1999**; 77(1):542-552. http://dx.doi.org/10.1016/S0006-3495(99)76911-0

Rusina T., Smedes F., Klánová J. Diffusion coefficients of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in some polymers. *Journal of applied polymer science*, **2010**; 116(3)1803-1810. http://dx.doi.org/10.1002/app.31704

Sathyanarayana M. Upadrashta, Bert O. Häglund, Lars-Olof Sundelöf. Diffusion and Concentration Profiles of Drugs in Gels. *Journal of pharmaceutical sciences* **1993**; 82(11):1094-1098. http://dx.doi.org/10.1002/jps.2600821106

Thompson J.M., Hsieh C.H., Luthy R.G., Modeling uptake of hydrophobic organic contaminants into polyethylene passive samplers. *Environ Sci Technol.* **2015**; 49(4):2270-2277. http://dx.doi.org/10.1021/es504442s

Vermeirssen E.L.M., Dietschweiler C., Escher B.I., van der Voet J., Hollender J. Transfer Kinetics of Polar Organic Compounds over Polyethersulfone Membranes in the Passive Samplers Pocis and Chemcatcher. *Environ. Sci. Technol*. **2012**; 46(12)6759-6766. http://dx.doi.org/10.1021/es3007854

Vrana B., Smedes F., Prokeš R., Loos R., Mazzella N., Miege C., Budzinski H., Vermeirssen E.,

Ocelka T., Gravell A., Kaserzon S. An interlaboratory study on passive sampling of emerging water

pollutants. *TrAC Trends in Analytical Chemistry*, **2016**; 76:153-165.

http://dx.doi.org/10.1016/j.trac.2015.10.013

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

| | Log P [a] | Log $D_w$ (m² s$^{-1}$)[b] | log $D_{gel}$ $^{4°C}$ (m² s$^{-1}$) | log $D_{gel}$ $^{20°C}$ (m² s$^{-1}$) | Ea (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., Dw = (13.26×10-9)/(η1.4Vm0.589), 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.
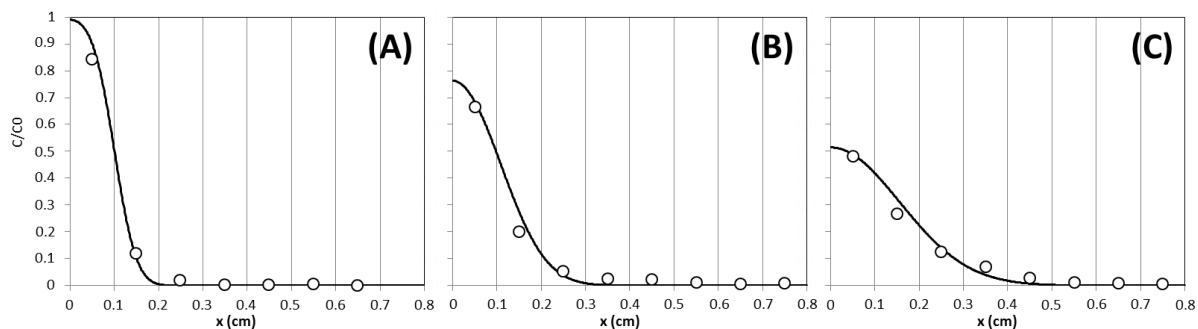
**Figure 1** Concentration distribution of galaxolide in agarose gel stack after 5 min (A), 20 min (B) and 2 h (C) of contact time. Black curves represent the fit of Equation 4 with $D_{gel}$ used as the adjustment factor. Vertical lines represent the boundaries between two gel slabs of the stack.
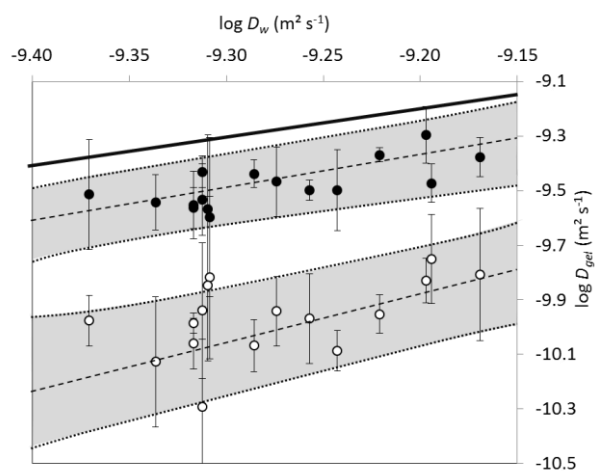


**Figure 2** double logarithmic scaled plots $D_{gel}$ against $D_w$. Filled symbols refer to the average $D_{gel}$ determined at 20 °C, and the open symbols refer to the average $D_{gel}$ determined at 4 °C. Full lines refer to the diffusion coefficient in water estimated following Hayduk and Laudie (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.
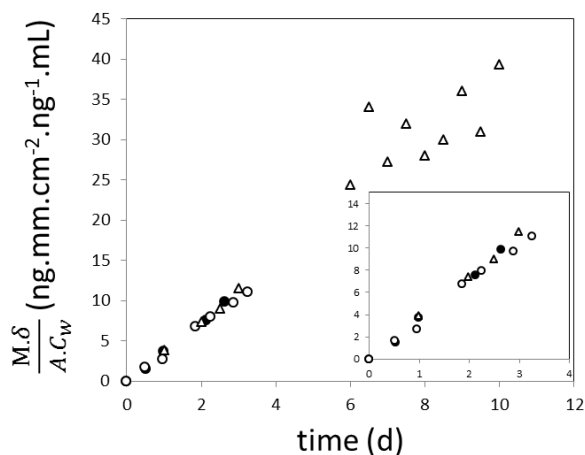
**Figure 3** Uptake of atrazine in both experiments simulating 2 water flow rates and contamination

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 ($\delta$) and divided by the

sampling area ($A$)] is normalized by the water contamination level ($C_w$). The inset provides a zoomed
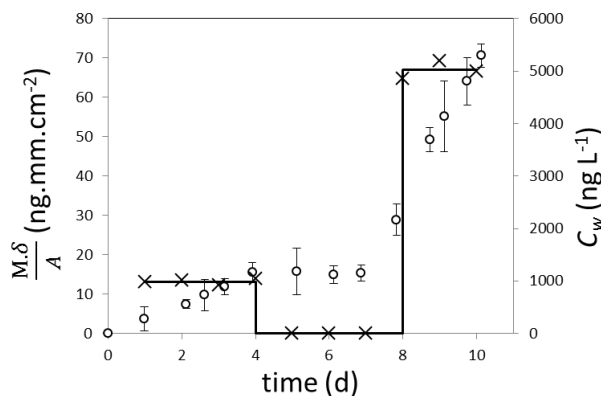
in view of the short time.



**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

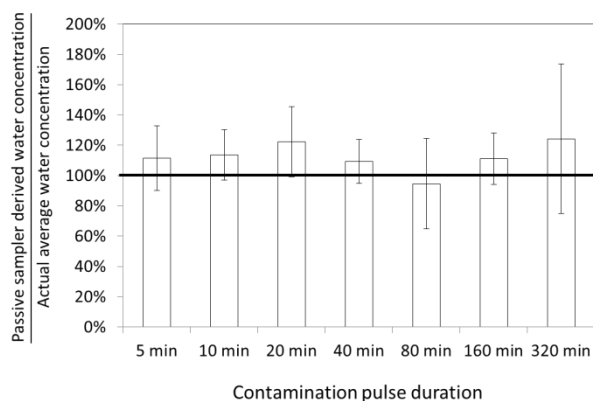circles are the amount of compounds sampled by the device.

**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).
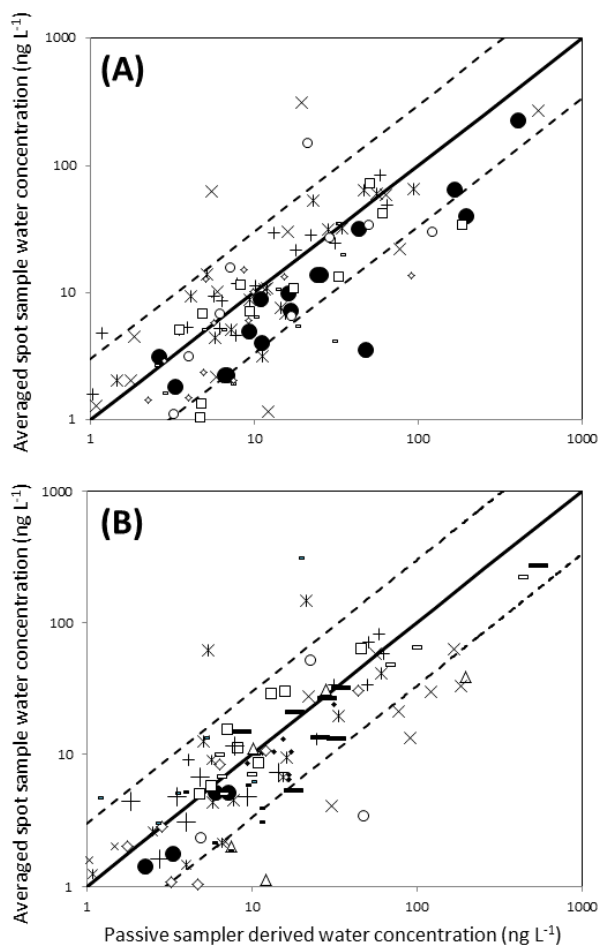
**Figure 6** Average spot sampling measured water concentrations against the passive sampler derived water concentrations. In part (A), the different markers indicate different exposure sites (filled circles represent the WWTP sampling site which is the only site to show a systematic deviation). In part (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.