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Comparison between the polar organic chemical integrative sampler and the solid-phase extraction for estimating herbicide time-weighted average concentrations during a microcosm experiment

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10 **Comparison between the polar organic chemical integrative sampler**
11 **and the solid-phase extraction for estimating herbicide time-weighted**
12 **average concentrations during a microcosm experiment**
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41

42 **Abstract**

43

44 Polar organic chemical integrative samplers (POCIS) were exposed for 9 days in two
45 different microcosms that contained river waters spiked with deethylterbuthylazine,
46 terbuthylazine and isoproturon. The experiment was performed with natural light and strong
47 turbulence (flow velocities of about 15-50 cm s⁻¹) for reproducing natural conditions. The
48 concentrations were kept relatively constant in the first microcosm (2.6-3.6 µg L⁻¹) and were
49 variable in the second microcosm (peak concentrations ranged from 15-24 µg L⁻¹ during the 3
50 day pulse phase). The time-weighted average (TWA) concentrations were determined with both
51 POCIS and repetitive grab sampling followed by solid phase extraction. The results showed a
52 systematic and significant overestimation of the TWA concentrations with the POCIS most
53 probably due to the use of sampling rates derived under low flow scenario. The results showed
54 also that peak concentrations of pollutants are fully integrated by this passive sampler. Even if the
55 POCIS should not provide very accurate concentration estimates without the application of
56 adequate sampling rate values or the use of performance reference compounds, it can be a really
57 useful tool for detecting episodic or short-term pollution events (e.g. increased herbicide
58 concentrations during a flood), which may be missed with classical and low frequency grab
59 sampling.

60

61 **Keywords:** GC-MS, phenylureas, triazines, passive sampler, water monitoring.

62 **1. Introduction**

63

64 The European framework directive in the field of water policy 2000/60/EC seeks to
65 prevent deterioration, to enhance and to restore bodies of surface water, to achieve good chemical
66 and ecological status of such water and to reduce pollution from discharges and emissions of
67 hazardous substances. The evaluation of surface water chemical status requires reliable
68 concentration estimates of various organic pollutants such as herbicides. For this purpose, two
69 approaches can be considered: active sampling (grab or automated) or passive sampling. Grab
70 and low frequency sampling (every week or month) is the easiest and most common method,
71 however, it seldom accurately tracks concentration fluctuations of targeted compounds in natural
72 aqueous environments. Time-weighted average (TWA) concentrations can be estimated by the
73 collection of several repetitive grab samples with automatic samplers. However, the use of such
74 equipment is often physically and logistically difficult, and it generates a large number of
75 samples with a corresponding increase in analytical cost. For monitoring polar herbicides in
76 freshwater, the use of polar organic chemical integrative samplers (POCIS) allows estimates of
77 TWA concentrations (Alvarez *et al.*, 2004; Alvarez *et al.*, 2005). Nevertheless, the accuracy and
78 the precision of these passive samplers for determining the ambient concentrations in rivers have
79 not been fully demonstrated.

80 This work assessed POCIS reliability for sampling selected polar herbicides
81 (deethylterbuthylazine, terbuthylazine and isoproturon) in natural aqueous environments. We
82 spiked triplicates of POCIS with the chemicals of interest and determined their elimination into
83 river water after 9 days. Afterwards, the POCIS were immersed within two microcosms filled
84 with the same river water but fortified at different concentration level; a relatively constant

85 concentration and pulsed concentration event scenarios were considered. In fact, transient, high
86 environmental concentration events were simulated in one microcosm in order to determine the
87 capacity of the POCIS for integrating short-term large concentration increases. We also studied
88 the effects of turbulence and the eventual biofouling on both the precision and accuracy of TWA
89 concentrations estimated with the POCIS.

90

91 **2. Experimental**

92

93 **2.1. Chemicals and materials**

94

95 Acetonitrile supragradient, methanol gradient and water gradient (HPLC grade) were
96 purchased from ICS-Science Groupe (Gradignan, France), ethyl acetate (HPLC grade) was
97 provided by Riedel-de Haën (Saint-Quentin-Fallavier, France). 1 mL empty polypropylene solid-
98 phase extraction (SPE) tubes with polyethylene (PE) frits (20 μm porosity) and Oasis HLB bulk
99 sorbent (60 μm) were purchased from Supelco (Saint-Quentin-Fallavier, France) and Waters
100 (Guyancourt, France), respectively. Hydrophilic polyethersulfone (PES) SUPOR 100 Membrane
101 Disc Filters (0.1 μm , 90 mm membrane diameter) were purchased from Pall (Saint-Germain-en-
102 Laye, France). Oasis HLB cartridges (6 mL, 500 mg, 60 μm) were provided by Waters (France).
103 Pharmaceutical POCIS were provided by Exposmeter (Tavelsjö, Sweden). All analytical
104 standards (purity \geq 98%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany):
105 deethylterbuthylazine (DET), terbuthylazine, isoproturon and atrazine d5.

106

107 **2.2. Solid-phase extraction of water**

108

109 Preconcentration of the analytes from water samples was accomplished by using SPE
110 with Oasis HLB cartridges. Prior to SPE, 200-mL water samples (pH adjusted to 7) were filtered
111 using GF/F glass microfibre filters (0.7 μm pore size). Afterwards, 10 μL of a stock solution
112 (acetonitrile) containing 100 ng μL^{-1} of atrazine d5 (surrogate), was added to the water samples,
113 resulting in fortification level of 5 $\mu\text{g L}^{-1}$. SPE was conducted using a VisiPrep 12-port manifold

114 (Supelco, France). The conditioning, extraction and rinsing steps were carried out under a 53.33
115 kPa vacuum. The SPE cartridges were successively washed with 10 mL of methanol, conditioned
116 with 10 mL of HPLC grade water, loaded with 200-mL water samples, then rinsed with 20 mL of
117 HPLC grade water and dried with a stream of nitrogen for 30 minutes. Elutions were achieved
118 with 5 mL of methanol. The 5-mL extracts were blown under a gentle stream of nitrogen and
119 dissolved within 1 mL of ethyl acetate prior to the GC-MS analyses. The final concentration of
120 the surrogate was about 1 mg L⁻¹ after SPE extractions. The recoveries (Table 1) were optimized
121 with the extraction of 200 mL of both tap and river waters fortified with 5 µg L⁻¹ of DET,
122 terbuthylazine, isoproturon and atrazine d5 (n=10).

123

124 **2.3. Recoveries from POCIS**

125

126 “Pharmaceutical” POCIS (Alvarez *et al.*, 2004) contains 200 mg of Oasis HLB sorbent
127 enclosed between two polyethersulfone (PES) membranes. The membrane-sorbent-membrane
128 layers are compressed between two holder washers (5.1 cm I.D., 8.9 cm O.D.). The total
129 exchanging surface area of the membrane (both sides) is approximately 41 cm² and the surface
130 area per mass of sorbent ratio is approximately 200 cm² g⁻¹. After the exposure in water, each
131 POCIS was opened and the sequestration medium (i.e. Oasis HLB) was transferred in a 50 mL
132 glass beaker with 2×20 mL washes of HPLC grade water. The sorbent was transferred into a 1
133 mL empty SPE tube with a PE frit and packed under vacuum by using a Visiprep SPE Manifold.
134 Afterwards, another polyethylene frit was added to the top of the SPE cartridge. All the cartridges
135 were washed with 20 mL of HPLC grade water and dried with a stream of nitrogen for 30
136 minutes. Elutions were achieved with 5 mL of methanol. 10 µL of a stock solution (acetonitrile)
137 containing 100 ng µL⁻¹ of atrazine D5 was added before the evaporation of the methanol with a

138 gentle stream of nitrogen. The final extract was dissolved within 1 mL of ethyl acetate prior to
 139 the GC-MS analyses.

140 Table 1. Analytical parameters and sampling rates of DET, terbuthylazine and isoproturon.

141

Herbicides	DET	Terbuthylazine	Isoproturon
Classes	Triazine metabolite	Triazine	Phenylurea
Retention times (min)	21.85	24.05	12.90 ^a
Fragments (m/z)	145, 186 ^b , 201	173, 214 ^b , 229	146 ^b , 161
SPE recoveries (%) ^c	95 (3)	100 (7)	106 (5)
log K _{ow} ^d	1.98	3.21	2.87
k _u (mL g ⁻¹ d ⁻¹) ^e	1025 (28)	1253 (48)	1088 (51)
R _s (mL d ⁻¹) ^e	205 (6)	251 (10)	218 (10)

142

143 ^a Isoproturon was analyzed as 4-(isopropyl)phenyl isocyanate degradation product (Carabias-Martínez *et al.*, 2003).

144 ^b Base peak.

145 ^c Fortification of tap and river waters (± 1 S.D, n=10).

146 ^d log K_{ow} for pH=7-8 (Barceló & Hennion, 1997; Hansch & Leo, 1987)

147 ^e Data (± 1 S.D) from (Mazzella *et al.*, 2007)

148

149 **2.4. GC-MS determination of herbicides**

150

151 DET, terbuthylazine and isoproturon were analyzed using a TRACE GC 2000 gas
 152 chromatograph (Thermo Electron Corporation, MA, USA) equipped with a Zebron ZB-5
 153 (Phenomenex, Le Pecq, France) capillary column (60 m, 0.25 mm, 0.25 μ m) and an AS 800
 154 autosampler (Thermo Electron Corporation, MA, USA). The TRACE GC 2000 gas
 155 chromatograph was coupled to a GCQ/POLARIS ion trap mass spectrometer (Thermo Electron
 156 Corporation, MA, USA). The transfer line was held at 280 °C and the source at 240 °C. Electron
 157 impact mass spectra were acquired at 70 eV. Quantitative analysis were acquired in full scan

158 mode from 100 to 350 amu. The total scan time was set to 0.68 s (6 microscans) and the max ion
159 time was kept constant at 25 ms. Retention times, and quantitative and characteristic fragments of
160 DET, terbuthylazine and isoproturon are given in Table 1. Atrazine d5 was used as internal
161 standard (retention time: 23.30 min, m/z = 205). A volume of 2 μ L (samples dissolved within
162 ethyl acetate) was injected on a splitless injector (270 °C, 138 kPa pressure pulse for 1.2 min).
163 Helium was used as carrier gas at a constant flow rate of 1 mL min⁻¹. The temperature program
164 was 40 °C for 1.2 min, then 15 °C min⁻¹ up to 160 °C and 4°C min⁻¹ to 270 °C followed by a 3.3
165 min isotherm (total running time: 40 min).

166

167 **2.5. Dissolved organic carbon measurements**

168

169 The water samples were filtered using GF/F glass microfibre filters (0.7 μ m pore size) and
170 the concentrations of dissolved organic carbon (DOC) were measured using a model 1010 OI
171 Analytical carbon analyzer with a 1051 auto-sampler (Bioritech, France). The total organic
172 carbon analyses were performed with an high-temperature persulfate oxidation technology and
173 according the European standard ISO 8245:1999 (1999).

174

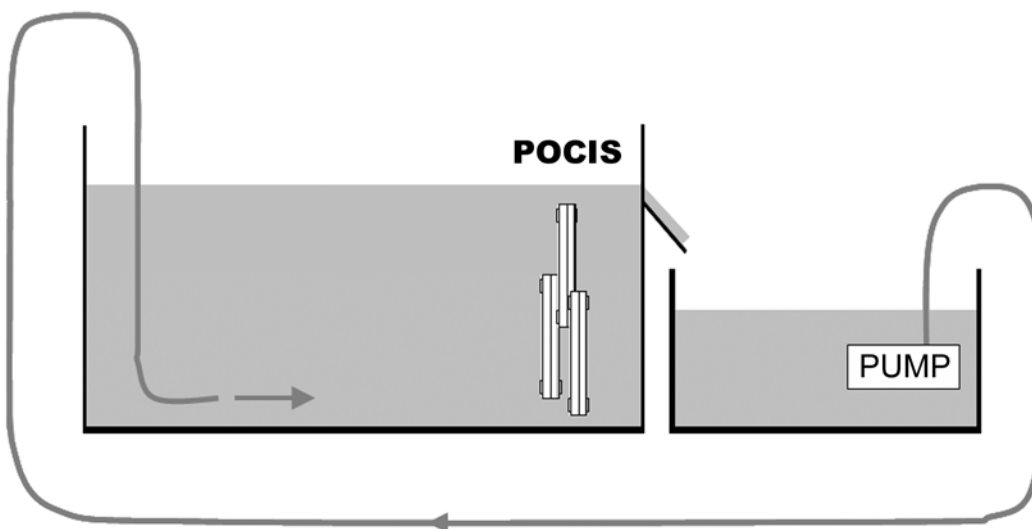
175 **2.6. Microcosm experimental design and POCIS exposure**

176

177 As shown in Figure 3, the POCIS (n=3) were immersed into two different glass
178 microcosms A and B each filled with 50 L of river water from Anan (southwest part of France).
179 The river water was characterized by a pH 7.67 and a low dissolved organic carbon content
180 (DOC = 1.69±0.03 mg L⁻¹). Prior to use, concentrations of isoproturon, DET and terbuthylazine

181 were determined in the river water. Background concentrations of the chemicals of interest were
182 lower than the LODs ($0.05\text{-}0.15\ \mu\text{g L}^{-1}$). The microcosms A and B were initially spiked with
183 approximately $5\ \mu\text{g L}^{-1}$ and $25\ \mu\text{g L}^{-1}$ of test compounds, respectively. Another microcosm with
184 unfortified river water was used as a blank control for the POCIS. During the exposure,
185 concentrations were relatively constant in microcosm A (i.e. standard addition was not required
186 after the initial spiking), whereas the river water was fully changed in microcosm B after 3 days.
187 Turbulent conditions were obtained by using submersible pumps. Flow velocities in the
188 microcosms varied from $15\ \text{to}\ 50\ \text{cm s}^{-1}$. The temperature was kept constant ($21\pm 1\ ^\circ\text{C}$) and the
189 experiment was carried out with natural light. SPE were performed at time zero (t_0) and every 3
190 days (t_0 , 3-d, 6-d and 9-d), resulting in 4 grab samples per microcosm. Both concentration and
191 standard deviation values were recovery corrected. The time weighted average concentrations
192 (Figure 2) were expressed for 3-day intervals and then for the whole exposure period (9 days).
193 All the triplicates of POCIS were sampled after 9 days of exposure.

194



195

196

197 Figure 1. Experimental design of microcosms A and B. Triplicate POCIS were immersed into
198 river water for 9 days and exposed to flow velocities ranging from 15 to 50 cm s⁻¹.

199

200 **2.7. Spiking of POCIS sorbent with DET, terbuthylazine and isoproturon**

201

202 A solution of 1 mg L⁻¹ of DET, terbuthylazine and isoproturon was prepared in methanol.

203 50 mL of this solution was added to 5 g of Oasis HLB bulk sorbent and sonicated for 5 min. The

204 solvent was eliminated with a rotary evaporator and the sorbent was dried at 60 °C for 1 h. We

205 obtained 5 g of Oasis HLB bulk sorbent spiked with 10 µg g⁻¹ of each of the test chemicals.

206 Three reference cartridges were prepared by transferring 200 mg of the fortified sorbent into 1

207 mL empty polypropylene SPE tubes with PE frits. The elution (5 mL of methanol) and the GC-

208 MS analysis of the reference cartridges revealed initial concentrations (C₀) of 8.3 µg g⁻¹ (7.8%

209 RSD), 7.4 µg g⁻¹ (4.1% RSD) and 7.7 µg g⁻¹ (4.4% RSD) for DET, terbuthylazine and

210 isoproturon, respectively. Three POCIS were prepared with 200 mg of the same fortified sorbent.

211 The POCIS were exposed in a microcosm filled with 50 L of river water. The flow and

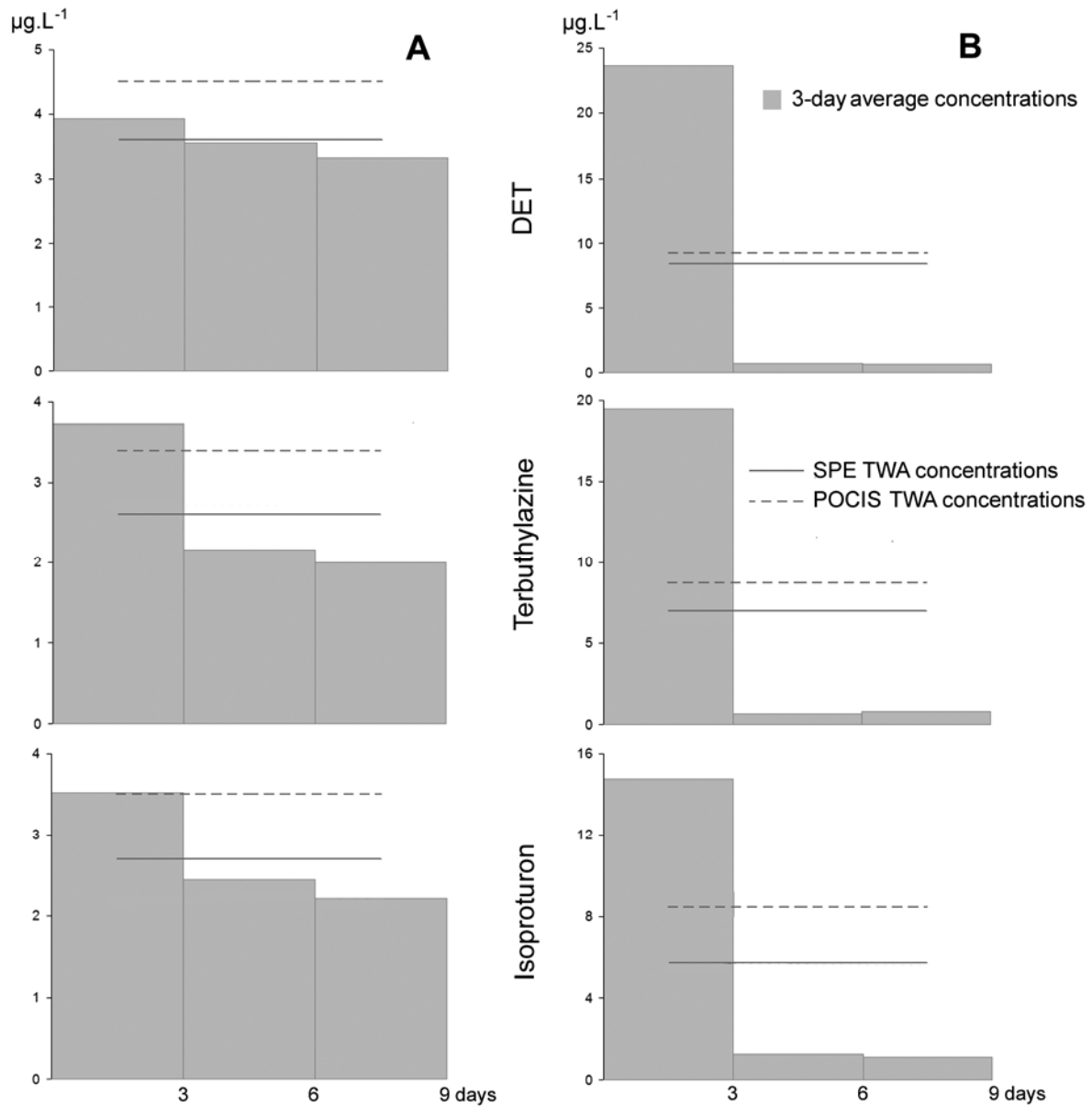
212 temperature conditions were as described above. The 3 POCIS were sampled after 9 days of

213 exposure. The sorbents were transferred into 1 mL empty SPE tubes with PE frits, eluted with 5

214 mL of methanol and dried under a gentle stream of nitrogen (1 µg of atrazine D5 was added as

215 internal standard before the solvent elimination). The extracts were dissolved within 1 mL of

216 ethyl acetate prior to the GC-MS analysis.



217

218 Figure 2. Time-weighted average concentrations of DET, terbuthylazine and isoproturon
 219 (microcosms A and B) calculated from repetitive grab sampling and from POCIS.

220

221 3. Theory and modelling

222
223 Assuming isotropic exchange, ambient concentrations of the contaminants can be
224 estimated from the amounts of these chemicals within the POCIS. Eq. 1 (Huckins *et al.*, 1993;
225 Huckins *et al.*, 1999; Stuer-Lauridsen, 2005; Vrana *et al.*, 2005):

$$226 C_{POCIS} = C_w K_{sw} (1 - e^{-k_e t}) \quad (1)$$

227 Where C_{POCIS} is the concentration ($\mu\text{g g}^{-1}$) of the analyte in the sorbent, C_w the TWA
228 concentration ($\mu\text{g L}^{-1}$) of the analyte in water, K_{sw} the POCIS-water partition constant (L g^{-1}) and
229 k_e the elimination rate constant (d^{-1}). Details of the model development and the conditions have
230 been presented and discussed for the semipermeable membrane devices (SPMDs) (Huckins *et al.*,
231 1993; Huckins *et al.*, 1999) and applied to the POCIS (Alvarez, 1999; Alvarez *et al.*, 2004;
232 Mazzella *et al.*, 2007). If the elimination rate k_e is negligible compared to the uptake rate k_u (L g^{-1}
233 d^{-1} or $\text{mL g}^{-1} \text{d}^{-1}$), then the POCIS acts as an infinite sink for the chemical of interest and analyte
234 uptake is linear for several weeks ($t \leq (\ln 2)/k_e$) (Alvarez *et al.*, 2004). In this case, Eq. 1 can be
235 reduced to:

$$236 C_{POCIS} = C_w k_u t \quad (2)$$

237 If we introduce the mass of the sorbent M_{POCIS} (g), we can rearrange Eq. 2 to an equivalent
238 relationship with the sampling rate R_s (mL d^{-1}), instead of the uptake rate constant k_u :

$$239 C_{POCIS} = \frac{C_w R_s t}{M_{POCIS}} \quad (3)$$

240 Eq. 3 and R_s values derived from a previous calibration experiment (Mazzella *et al.*, 2007; Table
241 4) were used for TWA concentration estimates with the POCIS.

242 4. Results and discussion

243

244 4.1. Desorption of DET, terbuthylazine and isoproturon from POCIS

245

246 We studied the desorption of DET, terbuthylazine and isoproturon. As reported in Table
247 5, elimination was negligible (3%) for DET and relatively low for both terbuthylazine and
248 isoproturon (11-12%) after 9 days. These results are in good agreement with previous works
249 indicating a strong retention for some polar herbicides such as atrazine, diazinon, diuron,
250 isoproturon (Alvarez *et al.*, 2004) and simazine (Mazzella *et al.*, 2007). However, the POCIS are
251 frequently deployed for several weeks in the field (Alvarez *et al.*, 2004; Alvarez *et al.*, 2005;
252 Macleod *et al.*, 2007; Matthiessen *et al.*, 2006) and for long exposure times, the desorption
253 phenomena are probably not negligible. In this case we have to investigate the elimination rates
254 in further detail.

255 Table 2. Desorption of the chemical of interest.

256

Herbicides	C_{9-d}/C_0^a	% RSD
DET	0.97	1.4
Terbuthylazine	0.88	12.5
Isoproturon	0.89	18.0

257

258 ^a Ratio between the concentrations after 9 days and the initial concentrations.

259 Table 3. Parametric Z-test (critical Z value of 1.960 and 95 % confidence interval) for comparing
260 the time-weighted average (TWA) concentrations calculated from repetitive grab sampling and
261 from the POCIS in the microcosms A and B.

262

Herbicides	DET	Terbuthylazine	Isoproturon	DET	Terbuthylazine	Isoproturon
Microcosms	A			B		
Differences ($\mu\text{g L}$) ^a	0.90	0.77	0.77	0.90	1.77	2.80
Overestimation (%)	+ 25	+ 29.5	+ 28.5	+ 11	+ 25	+ 49
Z ^b (Observed value)	3.402	2.203	1.000	1.372	1.919	2.750
p-values ^b (Two-tailed)	0.001	0.028	0.317	0.170	0.055	0.006

263
264
265
266

^a Differences between the means of the TWA concentrations calculated from POCIS and from grab samples.

^b Z-tests and p-values were calculated with XLSTAT-PRO (Addinsoft).

267 4.2. Comparison between solid-phase extraction and POCIS with various conditions

268

269 In order to facilitate the comparison between the two approaches, the same sorbent (i.e.
270 Oasis HLB) was used for grab and passive sampling. In regard to the microcosm A, the
271 concentration of DET was relatively constant while a steep decrease of both terbuthylazine and
272 isoproturon concentrations was observed between 3 and 6 days (Figure 4). This decrease may be
273 due to the adsorption of isoproturon and terbuthylazine on suspended particulate matter since
274 these chemicals are characterized by a higher hydrophobicity ($\log K_{ow}=2.87$ and 3.21 ,
275 respectively) than DET ($\log K_{ow}=1.98$). Concerning the microcosm B, we simulated a peak
276 exposure scenario by replacing the initial spiked medium by clear river water after 3 days (Figure
277 4).

278 The TWA concentrations (Figure 4) were determined with both SPE of grab samples and
279 the POCIS exposed during 9 days. The results of a parametric test are reported in Table 6 (z-test,
280 $p = 0.05$). For DET and terbuthylazine (microcosm A), the TWA concentrations calculated with
281 the SPE ($n=10$) and estimated with the POCIS ($n=3$) were significantly different. In regard to the
282 microcosm B, the reference concentrations (SPE) and the estimated concentrations (POCIS) are

283 significantly different for isoproturon only. In the other cases (isoproturon in microcosm A and
284 both DET and terbuthylazine in microcosm B), there were no significant differences between the
285 two sampling methods. This may be due to both a slight overestimation (especially for DET in
286 the microcosm B with + 11%) and a high standard deviation. Globally, the concentrations were
287 systematically and significantly overestimated with the POCIS (from + 11 to + 49%; Table 6) in
288 comparison with the SPE procedure. This result is most likely due to the application of
289 inadequate R_s values previously determined during the calibration (Mazzella et al., 2007).

290 In this study, we used river water with a low DOC content ($1.69 \pm 0.03 \text{ mg L}^{-1}$) and we
291 observed a growth of algae on the glass wall of the microcosms whereas the biofilm formation
292 was barely visible on the membranes of the POCIS. Consequently, we assumed that the PES
293 membranes were probably not affected by the biofouling (Vrana *et al.*, 2005) and the
294 concentration overestimation should be attributed to the higher flow velocities for this experiment
295 (from 15 to 50 cm s^{-1}) than for the calibration (2-3 cm s^{-1}) (Mazzella et al., 2007).

296 As suggested by some authors (Alvarez *et al.*, 2004), the solute mass transfer is mainly
297 controlled by the aqueous boundary layer. In other words, the sampling rates depend on the flow
298 velocities and the turbulence. Some works (Gunold *et al.*, In Press) showed for Empore SDB-XC
299 disks that the influence of flow velocity on the sampling rates seems to play a minor role for
300 hydrophilic substances such as herbicides. However, the authors performed calibrations only at
301 relatively high flow velocities (13.5 cm s^{-1} and 40 cm s^{-1}) and they did not use diffusion-limiting
302 membranes. The comparison with the POCIS is tenuous but such data indicates an increase of the
303 sampling rates with flow velocity until a certain threshold only. For polar chemicals sampled
304 with Empore SDB-RPS disks, Vermeirssen et al. (Vermeirssen et al., 2008) observed an
305 increase of accumulated amounts with increasing flow velocities (from 2.6 to 37 cm s^{-1}). Their
306 results showed also curvilinear uptakes and earlier equilibriums for polar chemicals at flow

307 velocities higher than 10 cm s^{-1} , indicating a rapid increase of k_e with flow velocity. However, a
308 direct comparison is still difficult since no diffusion-limiting membrane was used in this work as
309 well. If bulk flow rates in test microcosms are good predictors of chemical uptake rates in
310 boundary layer controlled passive samplers, then the relative differences in TWA concentrations
311 obtained from SPE and POCIS approaches should be relatively constant as shown in Figure 4 and
312 Table 6 for microcosm A. Regarding to microcosm B, the results were more variable with
313 overestimates ranging from + 11% to +49%. We observed during the POCIS calibration a slight
314 and variable increase in sampling rates occurring in the first five days (Mazzella et al., 2007).
315 Such a phenomenon is generally reduced with the POCIS presoaking (Alvarez, 1999) but it can
316 explain the variation of the sampling rates during the 3 day pulse experiment only. In this case,
317 short-term pollution peaks may be imprecisely integrated by the POCIS if such a phenomenon
318 occurs at the beginning of the exposure. Lastly, the concordance between the reference SPE
319 measurements and the POCIS concentration estimates could obviously be improved with the
320 application of microcosm-calibrated R_s . We can also use an appropriate performance reference
321 compounds (PRCs). The PRC approach was successfully developed and applied for the SPMDs
322 (Booij *et al.*, 2002; Huckins *et al.*, 2002) and in a previous work (Mazzella et al., 2007) we
323 suggested the use of the deisopropylatrazine as PRC since we observed isotropic exchanges and a
324 strong release of this chemical from the POCIS sorbent after only 10 days. The application of
325 such a PRC will be further investigated with *in situ* experiments.

326
327 In general, there is a paucity of studies on the uptake of short-term fluctuations with
328 passive samplers (Greenwood *et al.*, 2007), especially for polar compounds. For the microcosm B
329 (Figure 4), unlike SPE of grab samples, passive samplers do not instantaneously reflect changes
330 in the environmental concentrations of chemicals, as response time must be considered. However,

331 the results showed that the peaks of DET, terbuthylazine and isoproturon concentrations were
332 integrated by the POCIS. The largest differences in values derived from the two approaches
333 should be observed for comparisons where the time resolution for grab samples is low (i.e.,
334 several days or some weeks between samples) and the concentrations measured change relatively
335 fast such as observed for microcosm B. Such conditions are frequently observed with small
336 drainage basin ($\leq 1000 \text{ km}^2$) and in this case the POCIS may be a really useful tool for detecting
337 episodic and short-term events (e.g. herbicide concentration increase during a rise in the water
338 level) which may be missed with classical and low frequency grab sampling.

339

340 **5. Conclusion**

341

342 The POCIS method likely works well when appropriate sampling rates for analytes are
343 available. Unfortunately, the PRC approach for *in situ* calibration is not fully developed for
344 POCIS, which necessitated the use of sampling rates for test compounds measured at lower flow
345 velocities than the present study. Use of these inappropriate sampling rates for calculating water
346 concentrations of analytes from POCIS concentrations resulted in an expected systematic and
347 significant overestimation of water concentrations relative to SPE grab samples. Although,
348 POCIS derived water concentrations estimates were significantly overestimated relative to SPE
349 grab samples, the bias in the concentration values was not large as they ranged from 11 to 49%
350 greater. Further studies with various real-world conditions (i.e. quiescent or highly turbulent
351 environments, variable temperature, occurrence of organic matter and biofouling, etc.) are
352 compulsory for determining the reliability of the POCIS for a quantitative approach.

353

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355

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358

359

360 **Tables**

361

362 Table 4. Analytical parameters and sampling rates of DET, terbuthylazine and isoproturon.

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364 Table 5. Desorption of the chemical of interest.

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366 Table 6. Parametric Z-test (critical Z value of 1.960 and 95% confidence interval) for comparing

367 the time-weighted average (TWA) concentrations calculated from repetitive grab sampling and

368 from the POCIS in the microcosms A and B.

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373 **Figures**

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375 Figure 3. Experimental design of microcosms A and B. Triplicate POCIS were immersed into
376 river water for 9 days and exposed to flow velocities ranging from 15 to 50 cm s⁻¹.

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378 Figure 4. Time-weighted average concentrations of DET, terbuthylazine and isoproturon
379 (microcosms A and B) calculated from repetitive grab sampling and from POCIS.

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