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2 In-Situ calibration of POCIS for the sampling of polar  
3 pesticides and metabolites in surface water  
4

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31

32 **Abstract**

33 Over the past years, passive sampling devices have been successfully used for the monitoring  
34 of various pollutants in water. The present work studied the uptake kinetics in surface  
35 water of ten polar pesticides and metabolites, using pharmaceutical POCIS samplers.  
36 The aim was to determine sampling rates from in-situ calibration and to compare results  
37 with those obtained earlier under laboratory conditions, with the final objective of  
38 assessing the impact of environmental conditions on POCIS field performance. Field  
39 results showed a low efficiency of POCIS uptake capacity for moderately polar compounds,  
40 such as propiconazole ( $\log K_{ow}=3.72$ ) and tebuconazole ( $\log K_{ow}=3.7$ ), that were present in the  
41 aqueous phase at very low levels. The in-situ sampling rates obtained in this study ranged  
42 from 169 to 479 mL g<sup>-1</sup> day<sup>-1</sup> and differ by a factor of 3 to 7.5 from Rs determined under  
43 laboratory conditions.

44 **Highlights**

- 45 • In-situ calibration of POCIS
- 46 • Sampling rate determination of pesticides and metabolites
- 47 • Comparison of sampling rate obtained under in-situ and laboratory conditions
- 48 • Environmental factors influencing the uptake rate of POCIS samplers

49 **Keywords**

50 POCIS, in-situ calibration, pesticides and metabolites

51

## 52 **1. Introduction**

53 Pesticide pollution of the aquatic environment is among the most widely discussed topics in  
54 environmental issues. The determination of ecotoxicological risk for these compounds  
55 requires regular monitoring for assessing the water quality. Traditional environmental  
56 monitoring programs are based on the collection of several spot samples at specific sites at  
57 fixed time intervals and using expensive analytical methods. Contaminant concentrations can  
58 vary over time and such traditional monitoring strategies may miss fluctuations in pollutant  
59 levels; moreover, they are sometimes not efficient for detecting and quantifying  
60 micropollutants present in ultra-trace to trace levels in water[1]. Over the past years, passive  
61 sampling devices have been successfully used for the monitoring of various pollutants in  
62 surface- and ground-waters [1]. The principle of passive sampling in water has been well  
63 described in the literature [2]. Several designs of such devices are available either as  
64 experimental prototypes or as commercial [3]. Today, two main passive samplers are used for  
65 polar organic contaminants: the polar organic integrative sampler (POCIS) and the  
66 Chemcatcher with a polar configuration, but other tools are under investigation, such as O-  
67 DGT [4] or silicon [5]. Chemcatcher is composed of a polytetrafluoroethylene or  
68 polycarbonate body with a polyethersulfone (PES) hydrophilic microporous membrane,  
69 coupled with various receiving phases, such as C18 Empore disk [3, 6], SDB-XC [7, 8], or  
70 SDB-RPS [9, 10]. The POCIS consists of a solid sequestration phase (sorbent) between two  
71 PES membranes [11]. This sampler can retain a wide range of polar organic pollutants, such  
72 as pesticides, non-ionic detergents, polar pharmaceuticals, or natural and synthetic hormones  
73 [12, 13]. Due to their high capacity for accumulating target pollutants, passive samplers have  
74 contributed to decreasing the detection limits of analytical methods, and can be used as a  
75 quantitative tool for determining time-weighted average (TWA) concentrations for a given  
76 compound and over a specific period [14].

77 In order to estimate the TWA water concentrations of pollutants from accumulated amounts in  
78 a passive sampler used in kinetic mode, laboratory or in-situ calibration data are required for  
79 estimating the sampling rate (Rs) for each compound. The Rs of passive samplers depends on  
80 the physico-chemical properties of the chemicals (e.g. molecular weight, structure and  
81 hydrophobicity) and on environmental conditions, such as temperature [6, 15], water flow  
82 rate/turbulence [7, 8, 16] and dissolved organic carbon [17-19]. The challenge is to obtain  
83 TWA concentrations that are sufficiently representative of the real pollution levels in the  
84 aquatic medium. This goal is mainly dependent upon the calibration of the passive sampler,

85 generally done under controlled conditions at laboratory scale. However, as the field  
86 environment could be variable and also very different from fixed laboratory conditions, the  
87 use of inappropriate laboratory-derived sampling rates for calculating TWA concentrations  
88 from passive samplers exposed in the field, can lead to an inaccurate evaluation of the real  
89 pollution levels [20-24] with higher (about 4 times) or lower (about 3 times) concentrations  
90 when comparing TWA and grab concentrations. In order to obtain representative  
91 concentrations from a passive sampler, it is necessary to correct the laboratory-sampling rates  
92 (Lab-Rs) for considering the exposure conditions. The proposed rectification tools are still  
93 under investigation to correct laboratory sampling rate or determining in-situ sampling rates,  
94 that are representative of the uncontrolled and variable field conditions, allowing to calculate  
95 realistic TWA concentrations [2, 25, 26].

96 Performance reference compound (PRC) approach was first proposed and demonstrated for  
97 semi-permeable membrane devices (SPMDs[28, 29]) [27, 28]. The possibility of using PRCs  
98 for Chemcatcher has been evaluated and validated for its hydrophobic configuration [26]. So  
99 far no field studies have evaluated the performance of these compounds for correcting the  
100 laboratory-sampling rates and for obtaining reliable concentrations from the polar  
101 Chemcatcher configurations. Up to now, very few PRCs have been tested for POCIS samplers  
102 [11, 22]. However, further improvement and validation are needed for using PRC.

103 The Passive Flow monitor [29] is another approach for considering environmental variations.  
104 This tool is based on the dissolution of gypsum for measuring the average water velocity to  
105 which a sampler has been exposed.

106  
107 In order to understand the influence of environmental conditions on passive sampling, and to  
108 validate in-situ POCIS performance, another approach consists in deploying the samplers in  
109 the field for determining the in-situ Rs values by measuring simultaneously target-compound  
110 concentrations in water and in the samplers during the exposure period. However, this method  
111 requires the presence of quantifiable levels of target compounds in the studied medium that  
112 should remain relatively constant throughout the exposure period. To date, only few values of  
113 in-situ Rs for POCIS have been published [12, 23, 30, 31].

114  
115 The aim of the present work was threefold: 1) Study the uptake kinetics in surface  
116 water of a range of polar pesticides and metabolites by pharm-POCIS samplers, in  
117 order to determine sampling rates by in-situ calibration. 2) Compare these results  
118 with those obtained previously under laboratory conditions for assessing the impact

119 of environmental conditions on POCIS field performance. 3) Evaluate the  
120 effectiveness of POCIS for determining TWA concentrations in the aquatic medium,  
121 compared with the classical spot sampling method.

122

## 123 **2. Experimental work**

### 124 **2.1. Materials and chemicals**

125

126 All analytical standards (purity >98%) were purchased from Dr. Ehrenstorfer (CIL, Sainte-  
127 Foy-La Grande, France), including deuterated labeled compounds, and atrazine-d5 (97.5%)  
128 and simazine-d10 (98%) that were used for recovery and analytical control, respectively.  
129 Acetonitrile and methanol (HPLC reagent grade) were obtained from Fisher Chemical. Water  
130 used for experimental processes was generated from a Millipore Direct-Ultrapure Water  
131 Systems. Oasis™ HLB extraction cartridges (500 mg, 60 µm) were purchased from Waters  
132 Corporation and a Visiprep SPE vacuum manifold was used for water samples extractions..  
133 GF/F glass-fiber filters (0.7 µm pore size) were from Whatman (Maidstone, England), and the  
134 POCIS were purchased from Exposmeter SA (Tavelsjö, Sweden). These were of the  
135 pharmaceutical configuration, each filled with approximately 230 mg Oasis™ HLB sorbent  
136 and having a sampling surface area of 41 cm<sup>2</sup>. Empty polypropylene SPE tubes with  
137 polyethylene frits were purchased from Supelco (Bellefonte, USA).

138

### 139 **2.2. Site selection and sampling strategy**

140 The sampling area for the study is located in the Bas-Rhône Languedoc (BRL) canal, in a  
141 water-pumping station on the Rhône River in Bellegard (Gard Dept). The BRL canal is an  
142 irrigation canal bringing water from the Rhône River to the south of the Gard and the east  
143 of the Hérault departments. The Rhône water is taken upstream of Arles city and is led by a  
144 12-km channel to the pumping station. This station allows the irrigation of more than 36,000  
145 hectares of agricultural land in southern France. This water is also used in six water-  
146 treatment plants for the production of drinking water. Water quality monitoring realized by  
147 BRL revealed the presence of some pesticides in the water at relatively constant levels over a  
148 long enough period to provide reliable sampling rates.

149 The present field campaign took place at Pichegu station for three weeks (20 February to 14  
150 March 2012). On the day of deployment, the samplers were placed in homemade cages built  
151 with a mesh that lets water run through without changing the water flow within the cage.  
152 Each cage contained two POCIS. During transport to the field, the cages were covered with

153 aluminum-foil sheets in order to minimize contamination. On site, the six cages were  
154 submerged simultaneously at a depth of 1 m. In order to maintain this position, each cage was  
155 tied with a rope fixed to a metal barrier.

156 In order to validate the applicability of the laboratory and the in situ sampling rates (Lab-Rs  
157 and in situ-Rs) for the determination of reliable  $C_{TWA}$ , an independent campaign was run from  
158 29 June to 19 July 2012. During this period, Pharm-POCIS were deployed in triplicates for 20  
159 days in the Aristide Dumont pumping station, and three water samples were taken at different  
160 times during the campaign.

161

### 162 **2.3. Sampler retrieval and water sampling**

163 On the day of deployment, two grab water samples of one liter were collected in cleaned  
164 amber glass bottles on the spot where each cage was immersed. In order to study the  
165 pesticide-uptake kinetics of the samplers, one cage was removed from the water after 3, 7,  
166 10, 14, 17 and 21 days after deployment. A duplicate water sample was collected at the same  
167 time. A field blank was used as quality control, being transported to the site and exposed to  
168 the air each time the immersed samplers were retrieved from water. The retrieved POCIS  
169 samplers were rinsed with ultrapure water, wrapped in aluminum foil, placed in a plastic bag  
170 and stored under cooled conditions during transport to the laboratory. In order to assess the  
171 influence of environmental conditions on the POCIS sampling efficiency, the water flow  
172 velocity -measured by current meter (HYDREKA, model 801, Saint Cyr au Mont d'Or,  
173 France)- and the physico-chemical parameters of the water were monitored during the  
174 different field visits. The physico-chemical parameters were obtained with a Pastel UV  
175 portable spectrophotometer (SECOMAM), which, through spectral deconvolution,  
176 simultaneously estimates general (COD, BOD, TOC, SM) parameters. The simultaneous  
177 analysis of nitrate and orthophosphate was done by ionic chromatography with an IC-PAK A  
178 HR WATERS column with borate/gluconate as eluent at  $1.0 \text{ mL min}^{-1}$ , detected with a  
179 conductivity detector (WATERS). Conductivity and pH were measured in-situ with specific  
180 probes.

181

### 182 **2.4. Extraction of analytes from water samples and POCIS samplers**

183 The pesticides were usually extracted on the same day the samplers were retrieved. The  
184 collected 1 L water samples were filtered through GF/F filters to eliminate suspended matter,  
185 spiked with 100 ng of d5-atrazine, and extracted via solid phase extraction (SPE) using an  
186 Oasis™ HLB cartridge.

187  
188 Prior to extraction, the Oasis HLB cartridges were activated with 5 mL of acetonitrile under  
189 vacuum, followed by 5 mL of methanol and 5 mL of ultrapure water. The water samples were  
190 percolated through the cartridges at a flow rate of 20 mL min<sup>-1</sup> with a Visiprep SPE manifold.  
191 The cartridges were then dried under vacuum for one hour before eluting the pesticides with  
192 8 mL of acetonitrile, which was concentrated to 1 mL under a nitrogen stream. In the  
193 laboratory, each POCIS was opened on one side by cutting the PES membrane. The sorbent  
194 was then transferred into an empty solid-phase extraction tube packed with polyethylene (PE)  
195 frits of 20 µm porosity. The SPE tubes were then put on a Visiprep SPE vacuum manifold for  
196 drying the Oasis™ HLB solid phase for 30 minutes under vacuum. Prior to extraction, 75 µL  
197 of atrazin-d5 (0.5 mg L<sup>-1</sup>) was added to the sorbent. The pesticides were extracted by eluting  
198 under vacuum with 8 mL of acetonitrile. The eluate was reduced to 1 mL in a gentle stream of  
199 nitrogen and transferred to an autosampler vial for analysis. Field blanks were treated in the  
200 same manner as the deployed samplers. All extracts were spiked with 50 µL of deuterated  
201 internal standard simazine-d5 (2 mg L<sup>-1</sup>) and analyzed by UPLC-MS/MS.

## 202 203 **2.5. Chemical analysis**

204 The passive samplers and spot water-sample extracts were analyzed by UPLC-MS/MS.  
205 Chromatographic separation was done with a Waters ACQUITY UPLC system (Waters,  
206 Guyancourt, France) using a 150 mm × 2.1 mm × 1.7 µm ACQUITY BEH C18 column. The  
207 mobile phase was composed of water (0.05% formic acid) and acetonitrile (0.05% formic  
208 acid) at a constant flow of 0.4 mLmin<sup>-1</sup>. The gradient was programmed to increase the amount  
209 of acetonitrile from 0% to 100% in 7.5 min, with stabilization at 100% for 1.5 min before  
210 returning to the initial conditions in 0.3 min. These conditions were maintained for 15 min.  
211 Mass spectrometry detection was done with a Quattro Premier XE MS/MS (Waters,  
212 Guyancourt, France), equipped with an ESI interface and controlled by MassLynx software.  
213 The ESI polarity ionization was set to the positive mode (ESI+). Mass spectra were generated  
214 in the multiple reaction-monitoring mode (MRM); their acquisition for each compound was  
215 done by registering two characteristic fragments; one transition was used for quantitation and  
216 the other one for confirmation.

## 217 218 **2.6. R<sub>s</sub> calculation**

219 For an exposure time corresponding to the linear uptake region, the amount of analyte  
220 accumulated in the sampler can be resumed by equation (1):

221



222  $M_s = R_s C_{TWA} t + M_{s_0}$  (1)  
223 where  $M_s$  is the amount of the analyte accumulated in the sampler (ng) after exposure,  $M_{s_0}$   
224 the amount of the analyte in the sampler before exposure,  $C_{TWA}$  is the time-weighted average  
225 (TWA) concentration of the compound in water ( $\text{ng L}^{-1}$ ) during the sampling time  $t$  (day),  $R_s$   
226 is the sampling rate of the sampler ( $\text{L day}^{-1}$ ) representing the equivalent extracted water  
227 volume per unit of time for a given compound.

228 If analyte concentrations in the aqueous medium remain constant during the calibration  
229 campaign, the sampling rate for each compound can be calculated with equation (1). This is  
230 done by dividing the slope of the linear curves describing the pollutant accumulation in  
231 POCIS samplers by their respective mean concentrations in the aqueous phase calculated  
232 from the 14 water samples taken during the 21 days of campaign.

233  
234 The time-weighted average concentrations ( $C_{TWA} \text{ ng L}^{-1}$ ) of pesticides and their metabolites  
235 are calculated with equation (1) from the amount of analyte accumulated in the sampler  
236 exposed in the aqueous phase for 21 days, which is determined after extraction and UPLC-  
237 MS/MS analysis.

238

### 239 **3. Results and discussion**

#### 240 **3.1 Water sample analyses**

241 The water temperature and conductivity measured during the field experiment ranged  
242 respectively from 5 to 10 °C (average temperature of  $8.4 \pm 2.4$ ;  $n=7$ ) and from 410 to 464  $\mu\text{S}$   
243  $\text{cm}^{-1}$ . The quality of the aqueous medium did not significantly change during the 21-day trial  
244 (data presented in Supplementary Materials). The average water velocity measured near the  
245 cages at a depth of 1 m was around  $2.6 \text{ cm s}^{-1}$ .

246

247 Overall, 13 compounds were detected in the water samples, including triazines (atrazine,  
248 simazine, terbuthylazine), phenylureas (isoproturon IPU; diuron, chlortoluron), conazoles  
249 (tebuconazole, propiconazole), chloroacetanilides (metolachlor), phenylamides (metalaxyl)  
250 and triazine metabolites (deethylatrazine DEA, deisopropylatrazine DIA,  
251 deethylterbuthylazine DET). Most of these compounds occurred at very low levels ( $<8 \text{ ng L}^{-1}$ )  
252 in the water samples. Among the quantified compounds, reasonably stable water  
253 concentrations were obtained for most during the 21-day trial (Table 1). Five compounds had  
254 very stable concentrations in water ( $C_w$ ) with a coefficient of variation (CV) below 10% and  
255 six compounds had fairly stable  $C_w$  values, with a CV between 10 and 20%. However,

256 considerable variation was observed for the metolachlor concentration (CV=69%) and  
257 tebuconazole (CV=41%) over the exposure period (Table 1). The concentration profile of  
258 metolachlor showed a variation between 2.5 and 27 ng L<sup>-1</sup> with a peak detected from the 7<sup>th</sup> to  
259 the 10<sup>th</sup> day of exposure, after which the concentration decreased to 10 ng L<sup>-1</sup> (Fig.1a).

260

261

262

### 263 **3.2 Accumulation of pesticides in POCIS samplers**

264 At the end of the field trial, POCIS analyses showed the presence of the 13 compounds  
265 previously quantified in the water samples. For most of those compounds, their accumulation  
266 by the POCIS samplers was gradual and linear over the experimental 21-day period (Table 1).  
267 Uptake in POCIS was fitted with a simple linear regression model without zero-intercept.  
268 Linear fits were not forced through zero in order to well describe the accumulation of targeted  
269 compounds in the sampler. Linear fits were not forced through zero in order to well describe  
270 the accumulation of target compounds in the sampler.

271 Linear regression correlation coefficients ( $R^2$ ) were in the range of 0.8302–0.9860 (Table 1).

272 When looking at the accumulation trend of atrazine and its metabolite DIA (Fig. 1b and 1c),  
273 we see a linear accumulation of atrazine in POCIS for the 21 days, while the accumulation of  
274 DIA follows a curvilinear pattern. In fact, DIA is linearly accumulated during the first seven  
275 days of exposure, after which its accumulation curve tends to a curvilinear phase, modeled  
276 with a second-order polynomial function ( $R^2=0.7844$ ). A similar observation was made  
277 during laboratory calibration of POCIS for sampling polar pesticides and metabolites [32].  
278 For the metolachlor, accumulation in the sampler followed a linear pattern with a slight  
279 increase in accumulation between days 10 and 14, which is the interval corresponding to the  
280 appearance of the metolachlor concentration peak in the aqueous phase. As the duration of the  
281 pollution event was quite short compared to the total exposure time of the sampler, this peak  
282 of concentration was smoothed and integrated by the POCIS. It could be noted that the mass  
283 of metolachlor in POCIS for 3 days exposure was under the limit of quantification (Fig. 1a).

284

285 The two less polar compounds, propiconazole (logK=3.72) and tebuconazole (logK<sub>ow</sub>=3.7),  
286 were only found at quantifiable levels in POCIS sampled during 17th and the 21th exposure  
287 days, respectively, for which reason it was not possible to determine in-situ  $R_s$  values for  
288 these compounds. However, different phenomena could explain these results. The sorption of  
289 these compounds onto natural organic matter, generally controlled by their hydrophobicity

290 and characterized by the octanol-water partition coefficient ( $K_{ow}$ ), could limit their  
291 accumulation by the sampler membrane surface (pore size 100 nm), although several studies  
292 [7, 26] have classified compounds with  $\log K_{ow}$  between 2.5 and 4.3 as slightly hydrophilic  
293 with a medium sorption potential onto organic matter. Among the 13 compounds detected in  
294 water, seven compounds have a  $\log K_{ow} > 2.5$  (diuron, atrazin, IPU, metolachlor,  
295 terbuthylazine, tebuconazole, propiconazole) with a  $\log K_{ow}$  in the range of 2.68-3.72.  
296 However, the  $K_{ow}$  does not only drive the sorption of chemicals onto organic matter. Other  
297 parameters, such as the nature and chemical structure of the organic matter and the pH of the  
298 aqueous phase, can affect the sorption process of pollutants onto natural organic matter in  
299 water [33].

300

301 Another phenomenon that can limit the accumulation of these compounds by POCIS is the  
302 different barrier resistance to the mass transfer of contaminants in the sampler, for instance,  
303 the water boundary layer (WBL), the diffusion membrane resistance and the biofilm  
304 resistance in a case of biofouling phenomenon [6]. [35] An increase in hydrodynamic  
305 turbulence reduces the resistance of the WBL and thus increases the accumulation of analyte  
306 in the sampler.

307

308 A lag time is attributed to the time it takes for the compound to pass through the diffusive  
309 barriers (WBL, PES diffusion membrane and biofilm in case of bio-fouling) before it can be  
310 detected in the sorbent phase.

311 A lag time occurs if a steady-state condition across these layers is not rapidly established.  
312 Vermeirssen et al. [34] noticed an increase in the  $C_{PES}/C_{sorbent}$  ratios with  $\log K_{ow}$  of studied  
313 compounds. Compounds with higher  $\log K_{ow}$  values tended to be retained more by the PES  
314 membrane. High levels of absorption into PES correlated with a delay in transfer of the  
315 compound from water through the PES to the sorbent. For POCIS, [35] reported the  
316 occurrence of a lag-phase for compounds with  $\log K_{ow}$  values exceeding 3.1.

317

### 318 **3.3 In-situ sampling rates and comparison with lab- $R_s$**

319 Table 1 presents the in-situ sampling rates expressed in  $\text{mL g}^{-1} \text{day}^{-1}$  of pesticides and those  
320 determined previously under controlled laboratory conditions [32]. The calculated in-situ- $R_s$   
321 values ranged from 169 to 479  $\text{mL g}^{-1} \text{day}^{-1}$ . The  $R_s$  of metolachlor was calculated: despite a  
322 significant variability of its aqueous concentration during the experiment caused by a  
323 pollution peak, accumulation of this pesticide in the sampler followed a linear pattern

324 (Fig. 1a). For most of the compounds, the field-sampling rates were significantly lower—by a  
325 factor of 3-5—than those of the laboratory experiment, except DET that had a ratio of 7.5  
326 (Table 1). During the field experiment, the accumulation of DET by POCIS was very slow  
327 compared to the other compounds, which explains the obtained ratio ( $R_{s\text{-lab}}/R_{s\text{ in-situ}}$ ). The  
328 laboratory calibration experiment was conducted at 21 °C with a relatively high flow velocity  
329 ( $11.5\text{ cm s}^{-1}$ ) [32]. The low water turbulence observed in the field, ( $2.6\text{ cm s}^{-1}$ ), can affect  
330 analyte accumulation in POCIS. Previous studies at laboratory scale showed that  
331 hydrodynamics significantly affect analyte uptake by POCIS, particularly between exposure  
332 conditions conducted while stirring or under quiescent conditions [17].[38]  $R_s$  values  
333 calculated from these two exposure conditions differ by a factor of 3-6 for most of the tested  
334 compounds. [17] Water turbulence increases the mass-transfer coefficient ( $k_0$ ), and thus  $R_s$ , by  
335 reducing the thickness of the diffusion boundary layer. An effect of hydrodynamic variation  
336 on  $R_s$  was observed in several earlier studies involving SPMD and Chemcatcher samplers [7,  
337 8, 26, 28].

338

339 A low water temperature can affect the mass transfer of analytes from water to POCIS  
340 through decreasing their uptake kinetics. The water-temperature dependency of uptake for  
341 polar compounds was investigated for the polar Chemcatcher, which demonstrated an  
342 increase in sampling rates by a factor of 2 over a 20 °C temperature range [36]. Few studies,  
343 concerning the effect of temperature on the uptake of organic contaminants by POCIS  
344 samplers has been published in the literature [40][37], showing an increase in the POCIS  
345 sampling rate for most of the pharmaceutical compounds tested between 5 and 21 °C. [41]  
346 The type of water used for the calibration may also influence the accumulation of target  
347 compounds in POCIS. The impact of the water matrix effect on POCIS sampling rates for  
348 pharmaceuticals showed great differences when comparing deionized water, tap water and  
349 natural lake water [19].

350

### 351 **3.4 Applicability of $R_s$ for determining $C_{TWA}$**

352 The water velocity during this second campaign was below  $2.5\text{ cm s}^{-1}$  and the mean value of  
353 the water temperature was  $27.2^\circ\text{C}$  ( $27.2 \pm 1$ ;  $n=3$ ).

354

355 The results of the analysis of POCIS and water samples revealed the presence 8 compounds in  
356 the aqueous phase, including triazines and metabolites (atrazine, simazine, terbuthylazine and

357 DEA), phenylureas (diuron, chlortoluron), chloroacetanilides (metolachlor), phenylamides  
358 (metalaxyl).

359 The  $C_{TWA}$  of the detected compounds was calculated from the mass accumulated in POCIS  
360 samplers after 20 days exposure using  $R_s$ -lab and  $R_s$  in-situ. The values were compared with  
361 the average water concentrations obtained from spot samples over the 20 days (Fig. 2).

362 Comparison of the data obtained from these two sampling methods shows that the use of  $R_s$   
363 Lab does not permit to obtain reliable values of concentrations. This is certainly due to the  
364 high difference of the water turbulence between field and laboratory conditions. Because lab  
365 conditions (in particular flow velocity) influence uptake rates, the calculated concentrations  
366 are not in accordance with the spot sampling concentrations (average water concentrations  
367 over 20 days). In this case, concentrations are underestimated by a factor ranging between 3  
368 and 5. The applicability of POCIS sampling rates determined under field conditions to  
369 calculate reliable  $C_{TWA}$  of pesticides in the channel BRL showed good results. The use of in-  
370 situ  $R_s$  permits to obtain a better representativity of the real levels of pesticides in water.

371

#### 372 **4. Conclusions**

373 The field calibration of pharmaceutical configuration POCIS samplers was done in a channel  
374 network where water comes from Rhône river water. The BRL canal was used as a full-scale  
375 pilot site, where physico-chemical parameters, flow velocity and temperature were monitored.  
376 Based on those experimental conditions, we determined the in-situ sampling rates of some  
377 polar pesticides and their associated metabolites found in the water. Calibration results  
378 revealed integrative linear uptakes of ten compounds over a 21-day exposure period, except  
379 DIA, whose accumulation in POCIS followed a curvilinear pattern. The low variability of  
380 water temperature during the exposure period did not affect the integrative uptake of the  
381 POCIS sampler, and thus the linear model for determining the accumulation rate ( $R_s$ ) was  
382 successfully applied. Field results showed a low efficiency of the POCIS uptake capacity for  
383 moderately polar compounds such as propiconazole ( $\log K_{ow}=3.72$ ) and tebuconazole  
384 ( $\log K_{ow}=3.7$ ), which were present in the aqueous phase at very low levels. The in-situ  
385 sampling rates obtained in this study range from 169 to 479 mL g<sup>-1</sup> day<sup>-1</sup> and differ from a  
386 factor of 3 to 7.5 with the  $R_s$  values determined under laboratory conditions [32].

387 As shown by this study, the use of laboratory sampling rates for calculating TWA  
388 concentrations may lead to a significant underestimation of the real concentration values.

389 POCIS samplers can give reliable estimates of ambient pesticide concentrations in water and  
390 can provide a holistic picture of the presence of these compounds in the aquatic medium by  
391 the use of in-situ sampling rates. Application of in-situ Rs on the same site but on different  
392 period has been validated. However, in-situ calibration is still an exploratory approach that  
393 needs more data and fieldwork to evaluate its performance and applicability for measuring  
394 TWA concentrations in various waters and under different environmental conditions. One line  
395 of investigation could be to correct lab-sampling rates by considering the main factor that  
396 seems to affect passive sampling accumulation capacity: i.e. flow velocity. The use of a  
397 passive flow monitor needs further investigation as well, and a channel with flow control and  
398 natural water is a good setting for developing and validating passive samplers as suitable  
399 tools.

400

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Fig 1 a : Concentrations of metolachlor in water and POCIS over during the 21 day field deployment. Uptake in POCIS was fitted with a simple linear regression model without intercept.

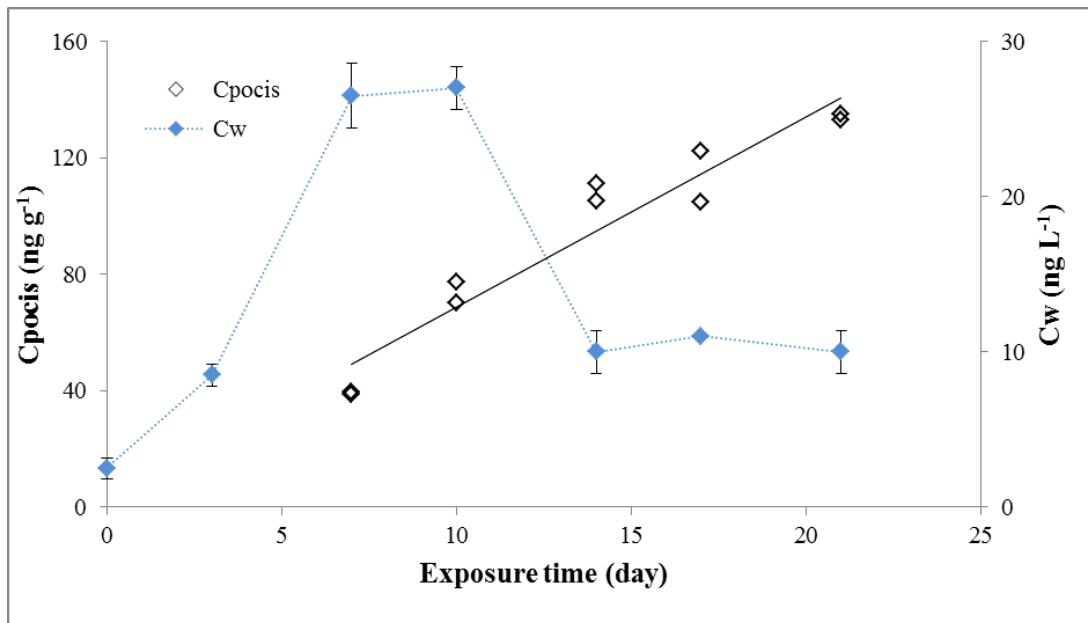


Fig 1 b: Concentrations of atrazine in water and POCIS over during the 21 day field deployment. Uptake in POCIS was well fitted with a simple linear regression model without intercept.

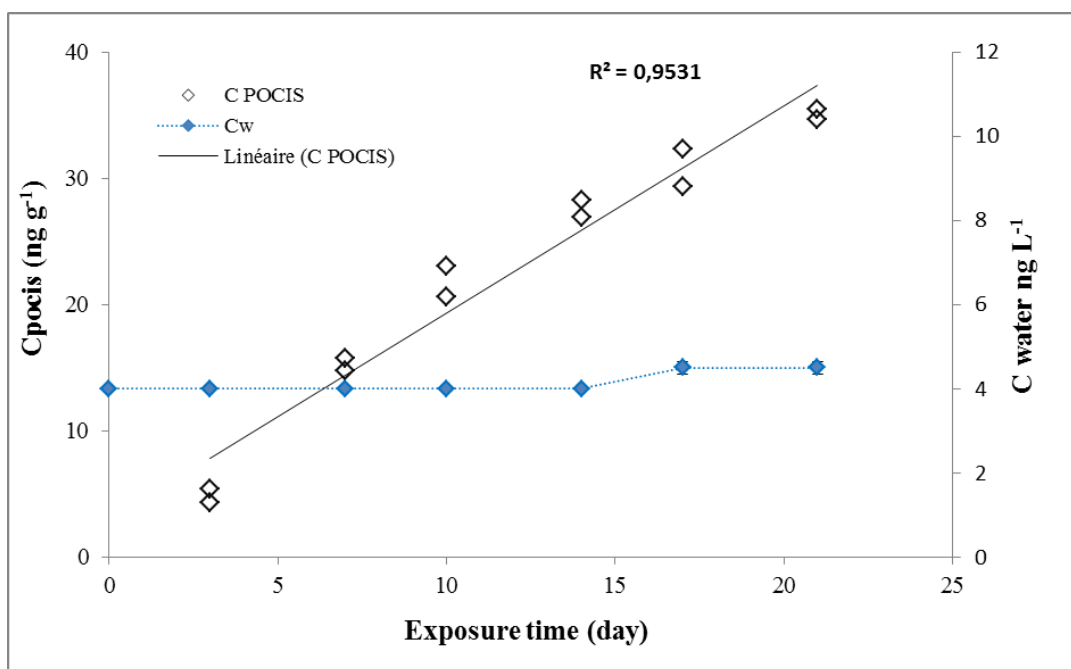




Fig 1 c: Concentration of DIA in water and curvilinear uptake by POCIS during the calibration experiment. Uptake in POCIS was modeled with a second-order polynomial function.

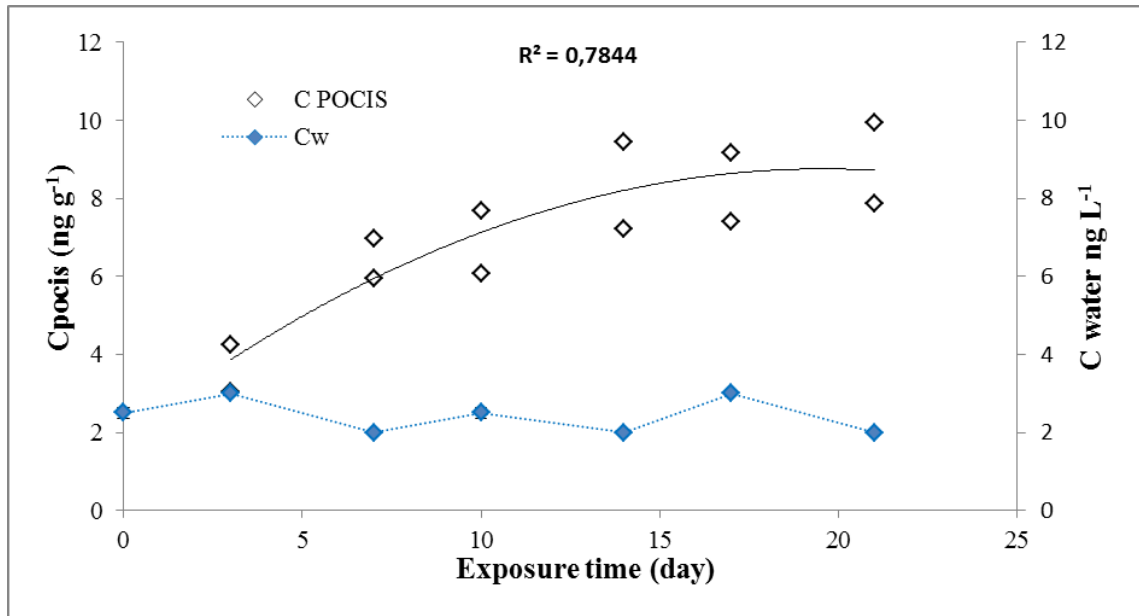


Fig 2: Comparison of TWA concentration from POCIS, calculated from in lab and in situ R<sub>s</sub> with average of spot sampling measurements. Average spot sampling (n=3) and CTWA (n=3)

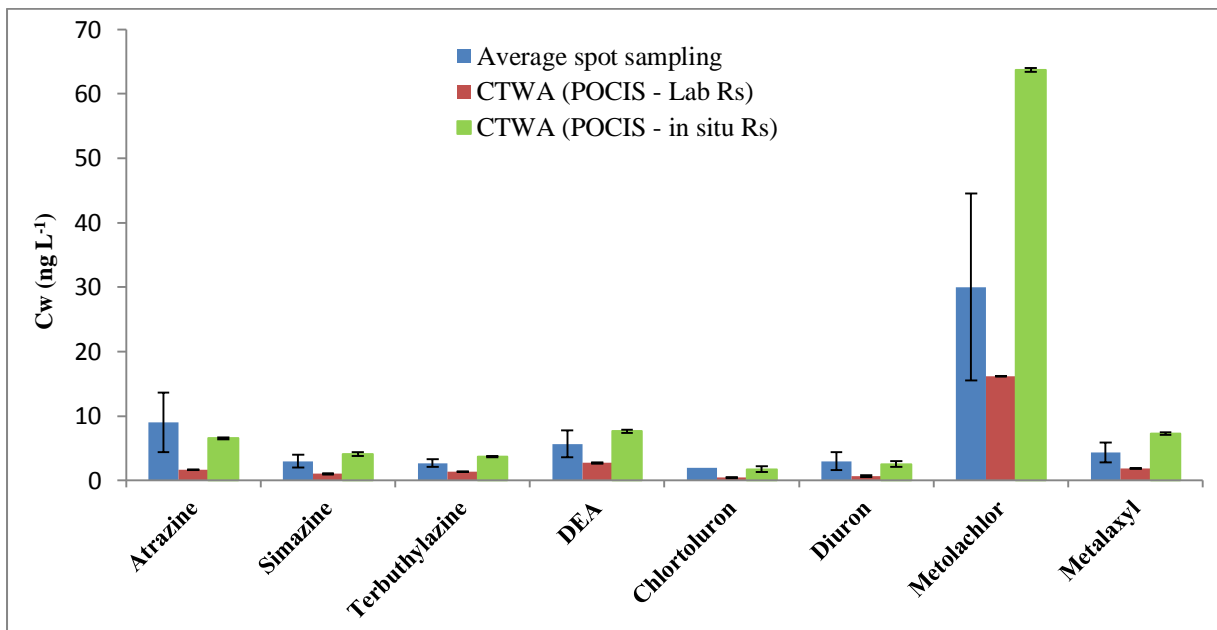


Table 1. Regression lines characterizing analytes uptake in POCIS and average water concentration during in situ calibration study and the Rs –Lab from previous study [37].

Compounds	LogKow	Linear regression lines of uptake curve	Correlation coefficient (R <sup>2</sup> )	Mean Cw (CV) (n=12)	Rs ± SD (mL g <sup>-1</sup> day <sup>-1</sup> ) In-situ (n=2)	Rs ± SD (mL g <sup>-1</sup> day <sup>-1</sup> ) Laboratory (n=3)	Rs-Lab/Rs in-situ ratio
Atrazine	2.70	y = 1,38x + 7	0.9531	4.1 (6%)	333± 24	1269 ± 174	4
DEA	1.51	y = 1,50x + 9,2	0.8695	6.4 (11%)	236± 26	665 ± 91	3
Simazine	2.18	y = 0,66x + 2,1	0.9685	2.5 (16%)	267± 26	1088 ± 1601	4
Terbuthylazine	3.21	y = 0,67x - 0,1	0.9696	2.1 (9%)	319 ± 62	816 ± 112	3
DET	2.30	y = 0,34x + 6,8	0.8337	2	169 ± 47	*1025 ± 31	7.5
Chlortoluron	2.41	y = 1,36x + 5,3	0.9275	5.6 (19%)	240 ± 22	1257 ± 157	5
Diuron	2.68	y = 0,97x + 1	0.8302	2.4 (14%)	401 ± 86	1284 ± 217	3
IPU	2.80	y = 0,65x + 0,3	0.9860	2	273 ± 25	1182 ± 166	4
Metalaxyl	1.65	y = 1,12x + 6	0.8811	3.9 (12%)	289 ± 46	1320 ± 200	5
Metolachlor	3.13	y = 6,53x + 3,5	0.9218	13.6 (69%)	479 ± 49	1341 ± 184.6	3
Propiconazole	3.72	-	-	2	-	-	-
Tebuconazole	3.7	-	-	4.1 (41%)	-	-	-

## SUPPLEMENTARY MATERIAL

### Physicochemical properties of the water column during the campaign

Parameter	Unit	20/02/2012	23/02/2012	27/02/2012	01/03/2012	05/03/2012	08/03/2012	12/03/2012
Temperature	°C	4.9	5.5	8.3	10.8	10.5	10.1	8.7
pH	-	8.3	8.4	8.2	8.1	8.1	7.7	7.7
Conductivity	µS cm <sup>-1</sup>	422	428	430	410	420	430	464
Suspend matter (SM)	mg L <sup>-1</sup>	3.8	3.6	4.7	4.2	6.7	5.7	4
TOC	mg L <sup>-1</sup>	3.6	3.4	3.6	3.4	3.6	3.5	3.5
DCO	mg L <sup>-1</sup>	6.2	6.4	6.8	6.4	6.9	6.3	6.3
DBO5	mg L <sup>-1</sup>	4.7	4.5	4.8	4.8	4.5	4.8	4.6
NO <sub>3</sub> <sup>-</sup>	mg L <sup>-1</sup>	4.6	4.7	5.4	4.9	5.4	5.1	5
SO <sub>4</sub> <sup>-</sup>	mg L <sup>-1</sup>	71.1	62.6	66.8	58.2	58.2	50.3	59.9