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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⁻¹ day⁻¹ and differ by a factor of 3 to 7.5 from Rs determined under
43 laboratory conditions.

44 **Highlights**

- 45
- 46 • In-situ calibration of POCIS
 - 47 • Sampling rate determination of pesticides and metabolites
 - 48 • Comparison of sampling rate obtained under in-situ and laboratory conditions
 - 49 • 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 cm². 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 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⁻¹ 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⁻¹) 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⁻¹) 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⁻¹. 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_s 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 (ng L^{-1}) during the sampling time t (day), R_s
226 is the sampling rate of the sampler (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 ± 2.4 ; $n=7$) and from 410 to 464 μS
243 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 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⁻¹ with a peak detected from the 7th to
259 the 10th day of exposure, after which the concentration decreased to 10 ng L⁻¹ (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 (logKow=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 cm s^{-1}) [32]. The low water turbulence observed in the field, (2.6 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 cm s^{-1} and the mean value of
353 the water temperature was 27.2°C (27.2 ± 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⁻¹ day⁻¹ 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

401 **References**

- 402 [1] F. Stuer-Lauridsen, *Environ. Pollut.* 136 (2005) 503-524.
403 [2] K. Booij, B. Vrana, J.N. Huckins, In: R. Greenwood, G. Mills and B. Vrana, Editor(s),
404 *Comprehensive Analytical Chemistry*, Elsevier, 2007, Volume 48 p. 141-169.
405 [3] B. Vrana, I.J. Allan, R. Greenwood, G.A. Mills, E. Dominiak, K. Svensson, J.
406 Knutsson, G. Morrison, *TrAC, Trends Anal. Chem.* 24 (2005) 845-868.
407 [4] C.E. Chen, H. Zhang, K.C. Jones, *J. Environ. Monit.* 14 (2012) 1523-1530.
408 [5] K. Wille, M. Claessens, K. Rappé, E. Monteyne, C.R. Janssen, H.F. De Brabander, L.
409 Vanhaecke, *J. Chromatogr. A*, 1218 (2011) 9162-9173.
410 [6] R. Greenwood, G. Mills, and B. Vrana (eds), *Passive Sampling Techniques in*
411 *Environmental Monitoring. Comprehensive Analytical Chemistry Series*, Elsevier,
412 Amsterdam, 2007.
413 [7] R. Gunold, R.B. Schafer, A. Paschke, G. Schuurmann, M. Liess, *Environ. Pollut.* 155
414 (2008) 52-60.
415 [8] E.L.M. Vermeirssen, N. Bramaz, J. Hollender, H. Singer, B.I. Escher, *Wat. Res.* 43
416 (2009) 903-914.
417 [9] M. Shaw, G. Eaglesham, J.F. Mueller, *Chemosphere*, 75 (2009) 1-7.
418 [10] B.S. Stephens, A.P. Kapernick, G. Eaglesham, J.F. Mueller, *Mar. Pollut. Bull.* 58
419 (2009) 1116-1122.
420 [11] D.A. Alvarez, J.D. Petty, J.N. Huckins, T.L. Jones-Lepp, D.T. Getting, J.P. Goddard,
421 S.E. Manahan, *Environ. Toxicol. Chem.* 23 (2004) 1640-1648.
422 [12] C. Harman, I.J. Allan, E.L. Vermeirssen, *Environ. Toxicol. Chem.* 31 (2012) 2724-
423 2738.
424 [13] N. Morin, C. Miège, M. Coquery, J. Randon, *TrAC, Trends Anal. Chem.* 36 (2012)
425 144-175.
426 [14] A. Kot-Wasik, B. Zabiegata, M. Urbanowicz, E. Dominiak, A. Wasik, J. Namiesnik,
427 *Anal. Chim. Acta*, 602 (2007) 141-163.
428 [15] B. Vrana, G.A. Mills, M. Kotterman, P. Leonards, K. Booij, R. Greenwood, *Ozone at*
429 *the Intensive Monitoring Plots in SW Europe*, 145 (2007) 895-904.
430 [16] H. Li, E.L. Vermeirssen, P.A. Helm, C.D. Metcalfe, *Environ. Toxicol. Chem.* 29
431 (2010) 2461-2469.

- 432 [17] L. Charlestra, A. Amirbahman, D.L. Courtemanch, D.A. Alvarez, H. Patterson,
433 Environ. Pollut. 169 (2012) 98-104.
- 434 [18] J.N. Huckins, K. Booij, J.D. Petty, Monitors of organic chemicals in the environment:
435 Semipermeable Membrane Devices, Springer Verlag, New York (2006).
- 436 [19] H. Li, P.A. Helm, G. Paterson, C.D. Metcalfe, Chemosphere, 83 (2011) 271-280.
- 437 [20] A. Arditoglou, D. Voutsas, Environ. Pollut. 156 (2008) 316-324.
- 438 [21] S. Lissalde, N. Mazzella, V. Fauvelle, F. Delmas, P. Mazellier, B. Legube, J.
439 Chromatogr. A, 1218 (2011) 1492-1502.
- 440 [22] C. Miege, N. Mazzella, S. Schiavone, A. Dabrin, C. Berho, J.P. Ghestem, C.
441 Gonzalez, J.L. Gonzalez, B. Lalere, S. Lardy-Fontan, B. Lepot, D. Munaron, C. Tixier, A.
442 Togola, M. Coquery, TrAC, Trends Anal. Chem. 36 (2012) 128-143.
- 443 [23] Z. Zhang, A. Hibberd, J.L. Zhou, Anal. Chim. Acta, 607 (2008) 37-44.
- 444 [24] M.J. Martínez Bueno, M.D. Hernando, A. Agüera, A.R. Fernández-Alba, Talanta, 77
445 (2009) 1518-1527.
- 446 [25] N. Mazzella, J.-F. Dubernet, F. Delmas, J. Chromatogr. A, 1154 (2007) 42-51.
- 447 [26] B. Vrana, G.A. Mills, E. Dominiak, R. Greenwood, Environ. Pollut. 142 (2006) 333-
448 343.
- 449 [27] K. Booij, H.M. Sleiderink, F. Smedes, Environ. Toxicol. Chem. 17 (1998) 1236-1245.
- 450 [28] J.N. Huckins, J.D. Petty, J.A. Lebo, F.V. Almeida, K. Booij, D.A. Alvarez, W.L.
451 Cranor, R.C. Clark, B.B. Mogensen, Environ. Sci. Technol. 36 (2002) 85-91.
- 452 [29] D. O'Brien, T. Komarova, J.F. Mueller, Mar. Pollut. Bull. 64 (2012) 1005-1011.
- 453 [30] R. Jacquet, C. Miège, P. Bados, S. Schiavone, M. Coquery, Environ. Toxicol. Chem.
454 31 (2012) 279-288.
- 455 [31] N. Mazzella, S. Lissalde, S. Moreira, F. Delmas, P. Mazellier, J.N. Huckins, Environ.
456 Sci. Technol. 44 (2010) 1713-1719.
- 457 [32] I. Ibrahim, A. Togola, C. Gonzalez, Environ. Sci. Pollut. R. 20 (2013) 3679-3687.
- 458 [33] A. Nikolaou, S. Meric, D. Fatta, Anal. Bioanal. Chem. 387 (2007) 1225-1234.
- 459 [34] E.L.M. Vermeirssen, C. Dietschweiler, B.I. Escher, J. Van Der Voet, J. Hollender,
460 Environ. Sci. Technol. 46 (2012) 6759-6766.
- 461 [35] C. Harman, K.E. Tollefsen, O. Bøyum, K. Thomas, M. Grung, Chemosphere, 72
462 (2008) 1510-1516.
- 463 [36] R. Greenwood, G.A. Mills, B. Vrana, I. Allan, R. Aguilar-Martinez, G. Morrison, in
464 Passive Sampling Techniques in Environmental Monitoring (Comprehensive Analytical
465 Chemistry), R. Greenwood (Ed.), Elsevier, 2007, p. 199-229.
- 466 [37] A. Togola, H. Budzinski, Anal. Chem. 79 (2007) 6734-6741.
- 467

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.

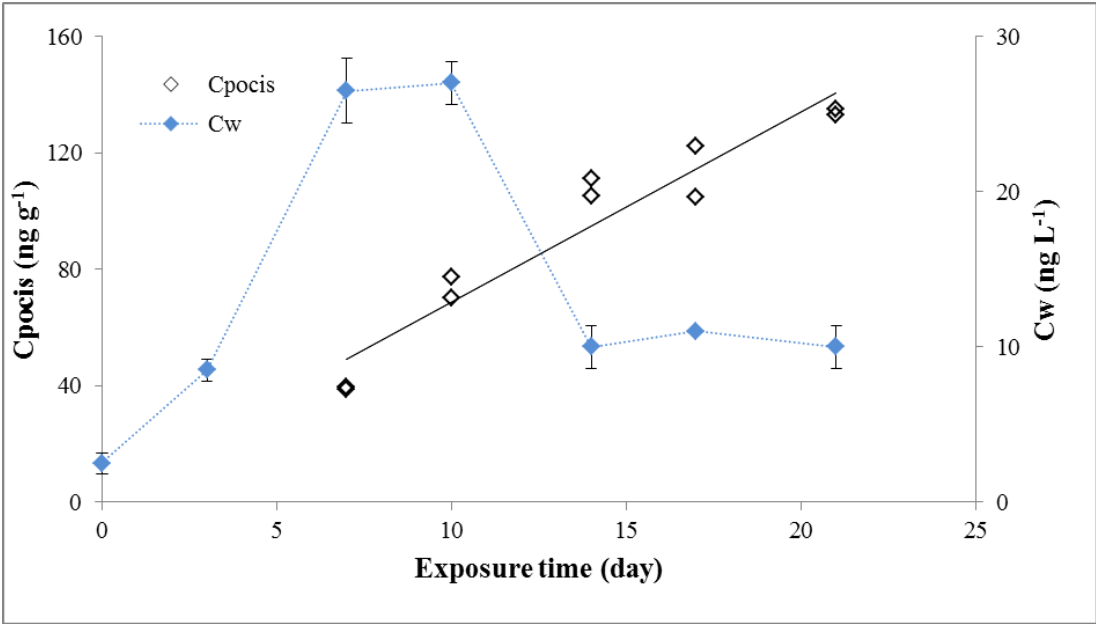


Fig 1 b: Concentrations of atrazine in water and POCIS over during the 21 day field deployment. Uptake in POCIS was well fitted with a simple linear regression model without intercept.

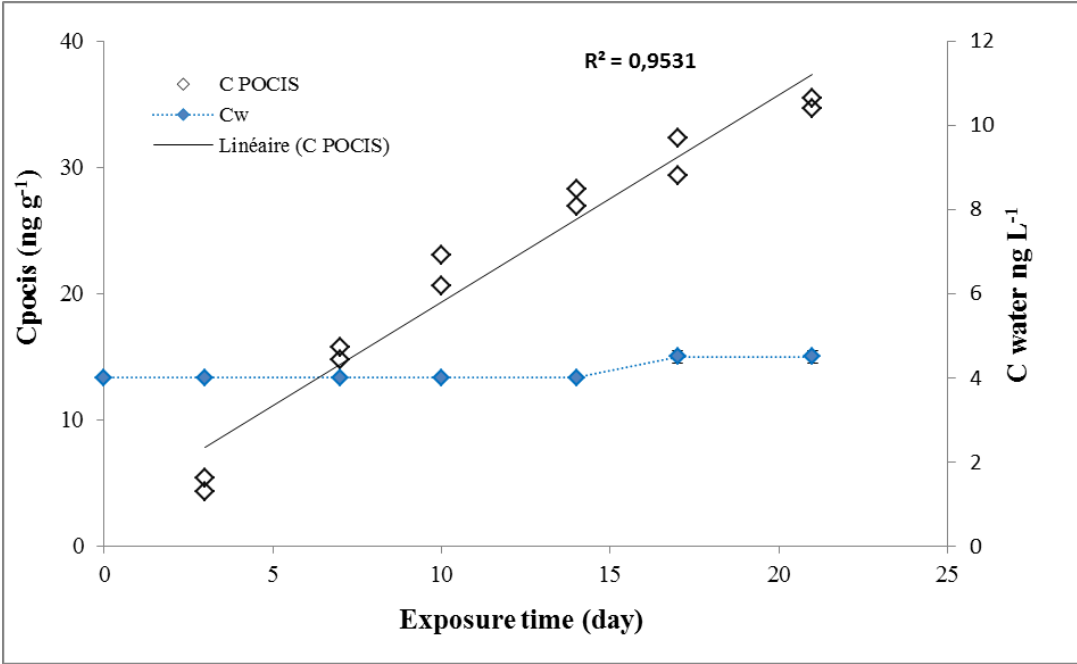


Fig 1 c: Concentration of DIA in water and curvilinear uptake by POCIS during the calibration experiment. Uptake in POCIS was modeled with a second-order polynomial function.

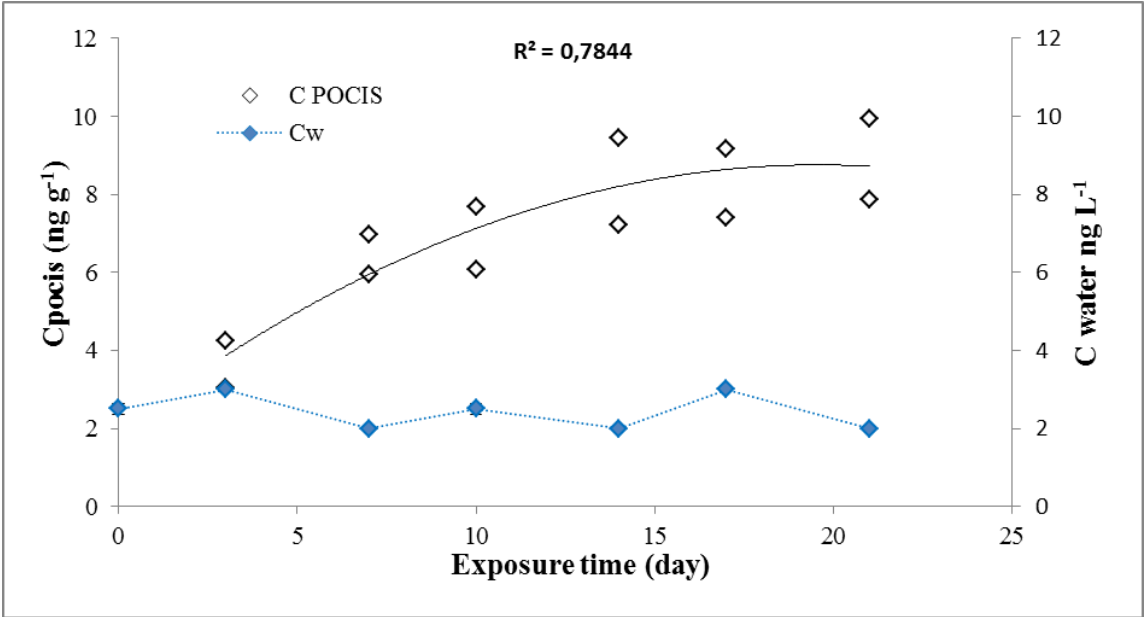


Fig 2: Comparison of TWA concentration from POCIS, calculated from in lab and in situ R_s with average of spot sampling measurements. Average spot sampling (n=3) and CTWA (n=3)

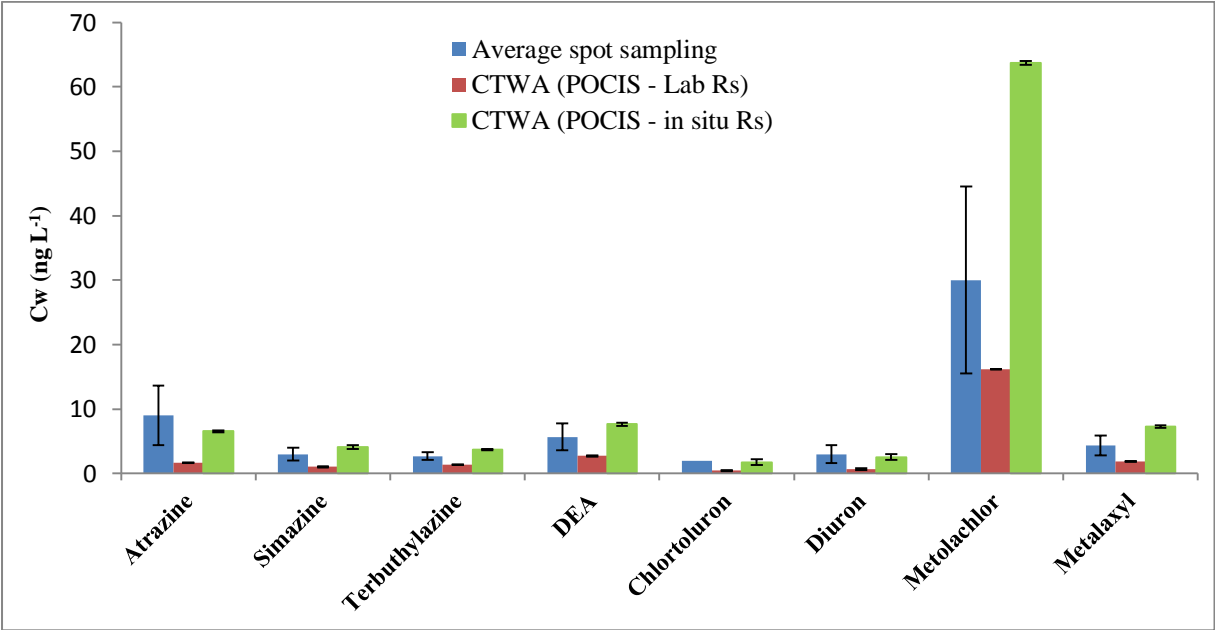


Table 1. Regression lines characterizing analytes uptake in POCIS and average water concentration during in situ calibration study and the Rs –Lab from previous study [37].

Compounds	LogKow	Linear regression lines of uptake curve	Correlation coefficient (R ²)	Mean Cw (CV) (n=12)	Rs ± SD (mL g ⁻¹ day ⁻¹) In-situ (n=2)	Rs ± SD (mL g ⁻¹ day ⁻¹) 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 ⁻¹	422	428	430	410	420	430	464
Suspend matter (SM)	mg L ⁻¹	3.8	3.6	4.7	4.2	6.7	5.7	4
TOC	mg L ⁻¹	3.6	3.4	3.6	3.4	3.6	3.5	3.5
DCO	mg L ⁻¹	6.2	6.4	6.8	6.4	6.9	6.3	6.3
DBO5	mg L ⁻¹	4.7	4.5	4.8	4.8	4.5	4.8	4.6
NO ₃ ⁻	mg L ⁻¹	4.6	4.7	5.4	4.9	5.4	5.1	5
SO ₄ ⁻	mg L ⁻¹	71.1	62.6	66.8	58.2	58.2	50.3	59.9