

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

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

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

#### 44 Highlights

- 45 In-situ calibration of POCIS
- Sampling rate determination of pesticides and metabolites
- 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

## 31

#### 52 **1.** Introduction

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

In order to estimate the TWA water concentrations of pollutants from accumulated amounts in 77 a passive sampler used in kinetic mode, laboratory or in-situ calibration data are required for 78 estimating the sampling rate (Rs) for each compound. The Rs of passive samplers depends on 79 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 rate/turbulence [7, 8, 16] and dissolved organic carbon [17-19]. The challenge is to obtain 82 TWA concentrations that are sufficiently representative of the real pollution levels in the 83 aquatic medium. This goal is mainly dependent upon the calibration of the passive sampler, 84

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

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

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

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The aim of the present work was threefold: 1) Study the uptake kinetics in surface water of a range of polar pesticides and metabolites by pharm-POCIS samplers, in order to determine sampling rates by in-situ calibration. 2) Compare these results with those obtained previously under laboratory conditions for assessing the impact of environmental conditions on POCIS field performance. 3) Evaluate the
 effectiveness of POCIS for determining TWA concentrations in the aquatic medium,
 compared with the classical spot sampling method.

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## 2. Experimental work

#### 124 2.1. <u>Materials and chemicals</u>

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

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## 139 2.2. Site selection and sampling strategy

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

The present field campaign took place at Pichegu station for three weeks (20 February to 14 March 2012). On the day of deployment, the samplers were placed in homemade cages built with a mesh that lets water run through without changing the water flow within the cage. Each cage contained two POCIS. During transport to the field, the cages were covered with aluminum-foil sheets in order to minimize contamination. On site, the six cages were
submerged simultaneously at a depth of 1 m. In order to maintain this position, each cage was
tied with a rope fixed to a metal barrier.

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

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#### 162 2.3. <u>Sampler retrieval and water sampling</u>

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

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## 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<sup>™</sup> HLB cartridge. 187

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

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#### 203 2.5. Chemical analysis

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

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#### 218 2.6. <u>R<sub>s</sub> calculation</u>

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

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Ms = Rs  $C_{TWA}$  t + Ms<sub>0</sub> (1) where Ms is the amount of the analyte accumulated in the sampler (ng) after exposure, Ms<sub>0</sub> the amount of the analyte in the sampler before exposure,  $C_{TWA}$  is the time-weighted average (TWA) concentration of the compound in water (ng L<sup>-1</sup>) during the sampling time t (day), Rs is the sampling rate of the sampler (L day<sup>-1</sup>) representing the equivalent extracted water volume per unit of time for a given compound.

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

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

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## 239 3. <u>Results and discussion</u>

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

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

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

considerable variation was observed for the metolachlor concentration (CV=69%) and tebuconazole (CV=41%) over the exposure period (Table 1). The concentration profile of 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 the 10<sup>th</sup> day of exposure, after which the concentration decreased to 10 ng L<sup>-1</sup> (Fig.1a).

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

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

Linear regression correlation coefficients ( $\mathbb{R}^2$ ) were in the range of 0.8302–0.9860 (Table 1). 271 When looking at the accumulation trend of atrazine and its metabolite DIA (Fig. 1b and 1c), 272 273 we see a linear accumulation of atrazine in POCIS for the 21 days, while the accumulation of DIA follows a curvilinear pattern. In fact, DIA is linearly accumulated during the first seven 274 days of exposure, after which its accumulation curve tends to a curvilinear phase, modeled 275 with a second-order polynomial function ( $R^2=0.7844$ ). A similar observation was made 276 during laboratory calibration of POCIS for sampling polar pesticides and metabolites [32]. 277 For the metolachlor, accumulation in the sampler followed a linear pattern with a slight 278 increase in accumulation between days 10 and 14, which is the interval corresponding to the 279 appearance of the metolachlor concentration peak in the aqueous phase. As the duration of the 280 pollution event was quite short compared to the total exposure time of the sampler, this peak 281 of concentration was smoothed and integrated by the POCIS. It could be noted that the mass 282 283 of metolachlor in POCIS for 3 days exposure was under the limit of quantification (Fig. 1a).

284

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

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

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

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

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

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

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

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

338

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

350

#### 351 **3.4** Applicability of Rs for determining C<sub>TWA</sub>

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

354

The results of the analysis of POCIS and water samples revealed the presence 8 compounds in the aqueous phase, including triazines and metabolites (atrazine, simazine, terbuthylazine and 357 DEA), phenylureas (diuron, chlortoluron), chloroacetanilides (metolachlor), phenylamides358 (metalaxyl).

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

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

371

## 372 **4.** Conclusions

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

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

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

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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 Rs with average of spot sampling measurements. Average spot sampling (n=3) and CTWA (n=3)



Compounds	LogKow	Linear regression lines of uptake curve	Correlation coefficient (R <sup>2</sup> )	Mean Cw (CV) (n=12)	$\begin{array}{c} Rs \pm SD \\ (mL \ g^{-1} \ day^{-1}) \\ In-situ \ (n=2) \end{array}$	$\begin{array}{c} \text{Rs} \pm \text{SD} \\ (\text{mL } g^{\text{-1}} \text{ day}^{\text{-1}}) \\ \text{Laboratory} \\ (n=3) \end{array}$	Rs-Lab/Rs in-situ ratio
Atrazine	zine $2.70$ $y = 1,38x + 7$ 0.		0.9531	4.1 (6%)	333±24	$1269 \pm 174$	4
DEA 1.51		y = 1,50x + 9,2	0.8695	6.4 (11%)	$236{\pm}26$	$665\pm91$	3
Simazine	2.18	y = 0,66x + 2,1	0.9685	2.5 (16%)	$267 \pm 26$	$1088 \pm 1601$	4
Terbuthylazine	3.21	y = 0,67x - 0,1	0.9696	2.1 (9%)	$319\pm 62$	$816\pm112$	3
DET	2.30	y = 0,34x + 6,8	0.8337	2	$169\pm47$	$^*1025\pm31$	7.5
Chlortoluron	2.41	y = 1,36x + 5,3	0.9275	5.6 (19%)	$240\pm22$	$1257 \pm 157$	5
Diuron	2.68	y = 0.97x + 1	0.8302	2.4 (14%)	$401\pm86$	$1284\pm217$	3
IPU	2.80	y = 0,65x + 0,3	0.9860	2	$273\pm25$	$1182 \pm 166$	4
Metalaxyl	1.65	y = 1,12x + 6	0.8811	3.9 (12%)	$289\pm46$	$1320\pm200$	5
Metolachlor	3.13	y = 6,53x + 3,5	0.9218	13.6 (69%)	$479\pm49$	$1341 \pm 184.6$	3
Propiconazole	3.72	-	-	2	-	-	-
Tebuconazole	3.7	-	-	4.1 (41%)	-	-	-

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].

#### SUPPLEMENTARY MATERIAL

Physicochemical prope	erties of the water o	column during the campaign
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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
pН	-	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	$mg L^{-1}$	4.7	4.5	4.8	4.8	4.5	4.8	4.6
NO <sub>3</sub> -	mg L <sup>-1</sup>	4.6	4.7	5.4	4.9	5.4	5.1	5
$SO_4$	mg L <sup>-1</sup>	71.1	62.6	66.8	58.2	58.2	50.3	59.9