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# Polar organic chemical integrative sampler (POCIS) uptake rates for 17 polar pesticides and degradation products: laboratory calibration

Intiaz Ibrahim, Anne Togola, Catherine Gonzalez

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1 **Polar-Organic-Chemical-Integrative Sampler**  
2 **(POCIS) uptake rates for 17 polar pesticides**  
3 **and degradation products: laboratory**  
4 **calibration**

5 Imtiaz Ibrahim<sup>a,b</sup>, Anne Togola<sup>a</sup>, Catherine Gonzalez<sup>b</sup>.

6

7 Authors

8

9 I.Ibrahim

10 *<sup>a</sup>Bureau de recherche géologiques et minières (BRGM), Laboratory Division, 3*  
11 *avenue Claude Guillemin, 45100 Orléans, France*

12 *<sup>b</sup>Ecole des mines d'Alès (EMA), LGEI Center, 6 Avenue de Clavieres, 30319 Alès,*  
13 *France*

14 [i.imtiaz@mines-ales.fr](mailto:i.imtiaz@mines-ales.fr)

15 Tel: (+33)4.66.78.27.22; Fax: (+33)4.66.78.27.01

16

17 A.Togola

18 *<sup>a</sup>Bureau de recherche géologiques et minières (BRGM), Laboratory Division, 3*  
19 *avenue Claude Guillemin, 45100 Orléans, France*

20 [a.togola@brgm.fr](mailto:a.togola@brgm.fr)

21 Tel: (+33)2.38.64.38.36 ; Fax: (+33)2.38.64.39.25.

22 C. Gonzalez

23 *<sup>b</sup>Ecole des mines d'Alès (EMA), LGEI Center, 6 Avenue de Clavieres, 30319 Alès,*  
24 *France*

25 [catherine.gonzalez@mines-ales.fr](mailto:catherine.gonzalez@mines-ales.fr)

26 Tel: (+33)4.66.78.27.65; Fax: (+33)4.66.78.27.01

27 **Abstract**

28 Polar organic chemical integrative samplers (POCIS) are useful for monitoring a wide range of  
29 chemicals, including polar pesticides, in water bodies. However, few calibration data are available,  
30 which limits the use of these samplers for time-weighted average concentration measurements in  
31 an aquatic medium. This work deals with the laboratory calibration of the pharmaceutical

32 configuration of a polar organic chemical-integrative sampler (pharm-POCIS) for calculating the  
33 sampling rates of 17 polar pesticides ( $1.15 \leq \log K_{ow} \leq 3.71$ ) commonly found in water. The  
34 experiment, conducted for 21 days in a continuous water flow-through exposure system, showed  
35 an integrative accumulation of all studied pesticides for 15 days. 3 compounds (metalaxyl,  
36 azoxystrobin and terbuthylazine) remained integrative for the 21-day experiment. The sampling  
37 rates measured ranged from 67.9 to 279 mLday<sup>-1</sup> and increased with the hydrophobicity of the  
38 pesticides until reaching a plateau where no significant variation in sampling rate is observed when  
39 increasing the hydrophobicity.

40

41 ***Keywords:*** laboratory calibration, passive sampling, POCIS, polar pesticides

42

43 Abbreviations

Polar organic chemical integrative sampler	POCIS
Pharmaceutical polar organic integrative sampler	Pharm-POCIS
Pesticide polar organic chemical integrative sampler	Pest-POCIS
Time weighted average	TWA
Desethylatrazine	DEA
Desisopropylatrazine	DIA
Desethylterbuthylazine	DET
Solid phase extraction	SPE
Polyethersulfone	PES
Ultra performance liquid chromatography	UPLC
Relative standard deviation	RSD
Reaction monitoring mode	MRM

44

## 45 **Introduction**

46 Over the past decades, many organic contaminants have been found in different aquatic  
47 environments. Among these pollutants, pesticides are mainly derived from agricultural activities  
48 (Schwarzenbach et al. 2006). Runoff over fields and infiltration caused by precipitation are the  
49 major causes of the presence of these agrochemicals in surface- and ground waters (Beltran et al.  
50 1993). Pesticide pollution can be not only problematic for human health, considering drinking  
51 water, but also for aquatic organisms.

52 Continuous monitoring of pesticide concentrations in aquatic environments is necessary for  
53 assessing the water quality (Liess et al. 1999), whereby sampling is a crucial step. The  
54 conventional methods of screening for aquatic pollutants rely on the analysis of grab samples, but  
55 these techniques generally do not provide appropriate information on variability of micro-  
56 pollutants concentration in water. Spot sampling provides only a snapshot of pollutant  
57 concentrations at the time of sampling and is often insufficient for detecting and quantifying trace  
58 levels of contaminants in water. In addition, the concentration of pollutants can fluctuate  
59 depending on environmental conditions, and frequent sampling is required to monitor contaminant  
60 levels. However, increasing the sampling frequency means taking a larger number of water  
61 samples, which is time consuming, laborious and expensive.

62 In environmental analysis, the development and application of monitoring techniques based on  
63 passive sampling offer a new and alternative approach to monitoring programmes that rely on  
64 collecting spot samples. Passive sampling, in contrast to spot sampling, enables determination of  
65 the time-weighted average (TWA) concentration of water contaminants over long sampling  
66 periods, permits the detection of trace and ultra-trace contaminants by the *in-situ* pre-concentration  
67 of pollutants, and finally offers significant handling, use and economic benefits compared with  
68 conventional grab-sampling techniques (Kot et al. 2000).

69 Various types of samplers exist with different design characteristics for the sampling of aquatic  
70 organic pollutants of different polarities. Among the passive samplers available, the most widely  
71 used for sampling polar organic pollutants are the Chemcatchers®(Kingston et al. 2000,  
72 Greenwood et al. 2007, Vrana et al. 2007) and polar organic chemical integrative samplers  
73 (POCIS). POCIS consists of a solid sequestration phase (sorbent) enclosed between two  
74 hydrophilic microporous polyethersulfone (PES) membranes (porosity 0.1  $\mu\text{m}$ ). The surface area of  
75 POCIS is 41  $\text{cm}^2$ , and two configurations are commercially available: pharmaceutical-POCIS  
76 (pharm-POCIS) and pesticide-POCIS (pest-POCIS) (Alvarez et al. 2004).

77 The sorbent in POCIS samplers is usually based on polystyrene divinylbenzene combined with  
78 active carbon in the case of pest-POCIS, or Oasis™ HLB sorbent in pharm-POCIS. This sampler  
79 can retain a large range of polar organic pollutants from different classes of organic compounds,  
80 such as pesticides, non-ionic detergents, polar pharmaceuticals, or natural and synthetic hormones  
81 (Alvarez et al. 2004; MacLeod et al. 2007; Li et al. 2011; Pesce et al. 2011). Alvarez et al.  
82 (2004) reported that pharm-POCIS is more suitable for organic polar compounds with multiple  
83 functional groups, and Mazzella et al. (2007) mentioned that it is more convenient for the sampling  
84 of basic and neutral herbicides. There are some practical advantages in using pharm-POCIS for  
85 monitoring polar organic contaminants, including the use of less solvents than for recovering  
86 analytes from pest-POCIS (Li et al. 2011).

87 A detailed description of these tools and their respective applications is available in the literature  
88 (Alvarez 1999; Alvarez et al. 2004; Petty et al. 2004; MacLeod et al. 2007; Mazzella et al.  
89 2007; Arditsoglou and Voutsas 2008; Li et al. 2011; Pesce et al. 2011).

90 The POCIS approach has been used as a screening tool for determining the presence of possible  
91 sources and relative amounts of organic contaminants in surface water and wastewater This  
92 approach allows the detection of new compounds such as pharmaceuticals, detergent identified as  
93 “emerging pollutants”, that cannot be detected by spot sampling, (Petty et al. 2004).

94 However, the use of POCIS as a quantitative tool for determining TWA concentrations requires  
95 calibration studies for the estimation of sampling rates of the targeted compounds. To date, POCIS  
96 sampling rates have been determined for only few pesticides(Mazzella et al. 2007; Togola and  
97 Budzinski 2007;Arditsoglou and Voutsas 2008; Li et al. 2011). The theory of passive sampling was  
98 described earlier as well (Alvarez et al. 2004;Mazzella et al. 2007; Togola and Budzinski 2007).

99 The objective of this study was to determine the sampling rates of 17 polar pesticides (Table 1) by  
100 pharm-POCIS in a laboratory-calibration experiment, in order to use this sampler as a quantitative  
101 tool for TWA concentration measurements in different aquatic environments. The studied  
102 compounds were atrazine, simazine, desethylatrazine (DEA), desisopropylatrazine (DIA),  
103 desethylterbuthylazine (DET), terbuthylatrazine, diuron, isoproturon, chlortoluron, linuron,  
104 propyzamide, alachlor, metolachlor, acetochlor, metalaxyl, penconazole and azoxystrobin.

## 105 **Material and methods**

### 106 **Chemicals and materials**

107 All pesticides analytical standards (purity >98%) were provided by Dr.Ehrenstorfer (CIL, Sainte  
108 Foy La Grande, France). Individual solutions of pesticides ( $500 \text{ mg L}^{-1}$ ) were prepared in  
109 acetonitrile and stored in the dark at  $-18^\circ \text{C}$ . Standard working mixtures of pesticides ( $3 \text{ mg L}^{-1}$ )  
110 prepared in acetonitrile were used for the experiment. Deuterated labelled compounds, simazine-  
111  $\text{d}_{10}$  (98%) and atrazine- $\text{d}_5$  (97.5%) were obtained from Dr.Ehrenstorfer (see above) and were used  
112 for recovery control and analytical control, respectively. Acetonitrile and methanol (HPLC grade)  
113 were obtained from Fisher Chemical (Illkirch, France) and formic acid was from Avantor  
114 (Deventer, the Netherlands).Water used for experimental processes was generated by a Millipore  
115 direct-ultrapure water system with a specific resistance of  $18.2 \text{ M}\Omega\text{cm}^{-1}$ . Oasis™ HLB extraction  
116 cartridges (500 mg,  $60 \mu\text{m}$ ) were purchased from Waters Corporation (Guyancourt, France).  
117 Exposmeter SA (Tavelsjö, Sweden) provided the pharmaceutical POCIS samplers. Empty  
118 polypropylene solid-phase extraction (SPE) tubes with polyethylene frits were purchased from  
119 Supelco (Saint-Quentin Fallavier, France). An HPLC pump (ProStar 220, Varian, LesUlis, France)  
120 and a peristaltic pump (Labcraft) were used in the experimental set-up for supplying water. An  
121 Autotrace SPE workstation (Caliper Life Sciences, Villepinte, France) was used for the water-  
122 sample processing and a Visiprep SPE Manifold (Supelco) was used for POCIS processing.

### 123 **Experiment design**

124 The POCIS calibration experiment was conducted in a 100 L stainless steel tank filled with tap  
125 water ( $\text{pH} = 8.3$ ) initially fortified at  $1.1 \mu\text{g L}^{-1}$  of each target pesticide. The tank was designed to

126 contain an inert Teflon carousel, connected to an electric motor with an adjustable rotation speed  
127 for simulating turbulent conditions in water. For determining the sampling rates, 12 pharm-POCIS  
128 were initially immersed in the tank, attached to the carousel. To study the kinetic accumulation of  
129 pesticides in the POCIS, the samplers were successively removed from the tank in triplicate at set  
130 time intervals (5, 9, 15 and 21 days) and analysed to determine the amount of accumulated  
131 chemicals. In order to maintain the concentration of pesticides in water constant, the tank was  
132 continuously supplied with tap water spiked with pesticides at  $1.1 \mu\text{g L}^{-1}$  with flow rate of  
133  $7 \text{ mLmin}^{-1}$ . The volume of methanol added in the tank for the initial supplementation was very low  
134 (less than 0.03% of the total volume) and the volume of methanol added all along the experiment  
135 was estimated to 0.004% and doesn't change significantly the DOC value. The monitoring of  
136 pesticide concentrations in the tank during the experiment was done by sampling 200 mL of water  
137 in triplicate from the outlet of the tank at each time the POCIS were removed. The water  
138 temperature and pH in the tank were monitored during the experimental period and remained  
139 stable with a mean of  $21^\circ\text{C}$  (from  $20.8^\circ\text{C}$  to  $21.5^\circ\text{C}$ ) for temperature and from 8.2 to 8.4 with a  
140 mean of 8.3 for pH. The carousel rotation speed was fixed at 10 rpm ( $0.115 \text{ ms}^{-1}$ ). Blank POCIS  
141 have been deployed during exposure in parallel, showing no contamination by targeted compounds  
142 during the experiment.

### 143 **Sample treatment**

144 After exposure, each POCIS was opened and the sorbent was recovered from the PES membranes  
145 with ultrapure water and transferred into a 1 mL empty SPE tube with a polyethylene frit and  
146 packed under vacuum by using the Visiprep SPE manifold. The sorbent was dried for 30 min  
147 under vacuum. Prior to extraction,  $75 \mu\text{L}$  of atrazin-d5 ( $0.5 \text{ mg L}^{-1}$ ) was added during the  
148 sequestering phase. Pesticides were extracted by eluting under vacuum with 10 mL of acetonitrile.  
149 The eluate was evaporated under a gentle stream of nitrogen and the volume of the extract was  
150 reduced to 1 mL. After elution, the sorbent was dried at  $40^\circ\text{C}$  and weighted. All results were  
151 corrected by using the real mass of sorbent in each exposed sampler.

152  
153 Water samples (200 mL) were extracted via SPE using the autotrace SPE workstation. The HLB  
154 cartridges were successively pre-conditioned with 5 mL acetonitrile, 5 mL methanol and then  
155 5 mL of ultrapure water at  $5 \text{ ml min}^{-1}$ . Prior to extraction, each sample was fortified with 125 ng of  
156 atrazine-d5. The samples were passed through the cartridges under vacuum at a flow rate of  
157  $10 \text{ mlmin}^{-1}$ . Before elution, the cartridges were dried under vacuum for 1 h. Analytes were  
158 recovered by eluting the cartridges with 8 mL of acetonitrile at a flow rate of  $3 \text{ mLmin}^{-1}$ . The  
159 sample volume was reduced to 1.5 mL under a gentle stream of nitrogen and transferred to an  
160 autosampler vial.

161 All sample extracts were spiked before analysis with  $50 \mu\text{L}$  of the deuterated internal standard  
162 simazine-d10 ( $2 \text{ mg L}^{-1}$ ).

## 163 **Pesticide analyses**

164 All POCIS and cartridges extracts were analysed by UPLC-MS/MS. Liquid chromatography  
165 separations were done in a Waters ACQUITY UPLC system (Waters, Guyancourt, France) using a  
166 150 mm × 2.1 mm × 1.7 μm ACQUITY BEH C18 column. The mobile phase was composed of  
167 solvent A (0.05% formic acid in water) and solvent B (0.05% formic acid in acetonitrile) at a  
168 constant flow of 0.4 mLmin<sup>-1</sup>. The gradient was programmed to increase the amount of B from 0 %  
169 to 100% in 7.5 min, with stabilization at 100% for 1.5 min before returning to the initial conditions  
170 (0% B) in 0.3 min. These conditions were maintained for 15 min. Mass spectrometry detection  
171 was done with a Quattro Premier XE MS/MS (Waters, Guyancourt, France) fitted with an ESI  
172 interface and controlled by MassLynx software. Typical interface conditions were optimized for  
173 maximum intensity of the precursor ions as follows: nebulizer and desolvation (drying gas, N<sub>2</sub>)  
174 flows were set at 650 and 150 Lh<sup>-1</sup>, respectively; source block and desolvation temperatures were  
175 100 and 350 °C, respectively. The ESI polarity ionization mode was set individually for each target  
176 compound. Argon was used as collision gas at a pressure of 3.7×10<sup>-3</sup> mBar. Mass spectra were  
177 performed in the multiple reaction-monitoring mode (MRM). The mass-spectrum acquisition of  
178 each compound was done by recording two characteristic fragments: a transition one was used for  
179 quantitation and the other for confirmation.

## 180 **Stability of pesticides in the aqueous phase**

181 During the 21 days of the experiment, the aqueous concentration of pesticides in the tank was  
182 monitored at each time the POCIS were removed. If concentrations are kept relatively constant  
183 during laboratory calibration, the sampling rate for each pesticide can be calculated when  
184 accumulation in the sampler follows a linear pattern. The results showed a relatively constant  
185 chemical concentration (R.S.D = 3–12%) in the exposure tank throughout the experiment, with  
186 average concentrations ranging from 568 ng L<sup>-1</sup> (penconazole) to 1337 ng L<sup>-1</sup> (DIA) (Table  
187 2). Average concentrations presented in table 2 concern mean values calculated from water  
188 sampled in triplicate at the 5<sup>th</sup>, 9<sup>th</sup> and 15<sup>th</sup> day of exposure (9 water samples) and used for  
189 calculations.

## 190 **Sampling rate calculation**

191 Accumulation of contaminants by passive samplers typically follows first-order kinetics, which  
192 includes an initial integrative phase, followed by curvilinear and equilibrium-partitioning phases.  
193 POCIS requires a relatively long sampling time before reaching equilibrium, and accumulation  
194 thus tends to remain for a long period after deployment in the integrative phase when analyte  
195 uptake is linear. In the linear region of POCIS uptake, the amount of a chemical accumulated in  
196 the sampler (M) is described by equation (1):

$$197 \quad M = CwRst \quad (1)$$

198 where R<sub>s</sub> is the sampling rate (Lday<sup>-1</sup>), C<sub>w</sub> is the concentration of the compound in water (ngL<sup>-1</sup>)  
199 and t the exposure time (day).

200 The experimental data obtained from the laboratory calibration tests were used for calculating the  
201 sampling rates ( $R_s$ ) of the target pesticides according to equation (1). To simplify the calculation of  
202  $R_s$ , the regression line for each pesticide was fitted through the origin. A linear regression model  
203 with zero intercept was also used in other studies (Mazzella et al. 2007; Arditoglou and Voutsas  
204 2008; Martínez Bueno et al. 2009). For each pesticide, the sampling rate was determined by  
205 dividing the slope of the linear regression curve by the mean aqueous concentration for the  
206 selected compounds during the first 15-days exposure.

207 The sampling rate of each compound was calculated by dividing the slope of the uptake curve  
208 plotted for 15 days exposure by the mean aqueous concentration of the corresponding compound  
209 computed for the similar exposure time, which corresponds to an average of 9 water samples. As  
210 the experience of analytes uptake by POCIS has been done in triplicate, the mean and standard  
211 deviation of  $R_s$  for each compound was calculated by taking in account the values obtained for the  
212 POCIS in triplicate.

213

## 214 **Results and discussion**

### 215 **Pesticide uptake kinetics by POCIS**

216 Characteristic pesticide uptake curves for the pharm-POCIS after an exposure of 5, 9, 15 and 21  
217 days in the spiked tap water under water flow over the POCIS conditions are shown in figure 1.  
218 The results showed that for most of the studied compounds, the uptake in POCIS follows a linear  
219 pattern until 15 days with an equilibrium state reached after a 21-day exposure. However, for three  
220 compounds (metalaxyl, azoxystrobin, terbuthylazine), the accumulation in POCIS remained  
221 linear for the whole 21-day experiment.

### 222 **Determining sampling rates**

223 The correlation coefficients of the linear regressions for most pesticides were acceptable, with  
224 values from 0.7924 (DEA) to 0.9706 (azoxystrobin) (Table 3). Pesticide sampling rates expressed  
225 in  $\text{mL g}^{-1} \text{d}^{-1}$  and  $\text{mL day}^{-1}$  (computed for 200 mg of HLB sorbent phase) are given in Table 3. The  
226 calculated  $R_s$  values ranged from 67.9 to 279  $\text{mL day}^{-1}$  with  $\text{RSD} \leq 17\%$ . The lowest sampling rate  
227 value was obtained for the most polar compound DIA ( $\log K_{ow} = 1.2$ ), demonstrating that POCIS is  
228 less effective for sequestering this molecule. A similar result was observed by Mazzella et al.  
229 (2007) when calibrating pharm-POCIS in the laboratory. Penconazole showed the highest  $R_s$  value  
230 ( $279 \text{ mL day}^{-1}$ ).

### 231 **Comparison of sampling rates**

232 An overview of our sampling rates and those of previous studies is given in Table 4 concerning  
233 only experiments fitting with our own experiment in term of exposure conditions (water renewal  
234 and non-quiescent exposure). For several pesticides, the sampling-rate values from our study were



235 similar to those obtained by authors (Mazzella et al. 2007;Hernando et al. 2007; Lissalde et al.  
236 2011) who used a similar experimental set-up for pharm-POCIS calibration as ours. The  $R_s$  values  
237 we obtained for terbuthylazine and linuron were 1.5 and 1.7 times lower, respectively, than those  
238 reported by Mazzella et al. (2007) and Lissalde et al. (2011) even if the results for the other  
239 compounds are very closed. This difference cannot be explained and those both results seem to be  
240 not reliable because of the important difference of sampling rate compared to the other compounds  
241 owing to the same chemical group (140ml day for linuron instead of respectively 256.7 and 236.5  
242 for diuron and isoproturon). Our sampling rates were of the same order of magnitude as those  
243 obtained by Thomatou et al. (2011), even though these authors used a pest-POCIS in a stirred-  
244 renewal exposure design for a calibration experiment using natural lake water. Sampling-rate  
245 values for diuron from other studies were systematically below our values: 3 times lower for  
246 Martínez Bueno et al. (2009) and 5.7 times lower for Alvarez et al. (2004), respectively. The  
247 experimental set-ups used by these authors use a static system stirred by a magnetic bar, but their  
248 salinity values were quite different.

249 It is thus clear that great disparities exist between the methods used for calibrating POCIS.  
250 Detailed descriptions of experimental parameters and  $R_s$  comparisons during POCIS calibrations  
251 for several pesticides and other chemicals are given by Munaron et al. (2011) and Morin et al.  
252 (2012). For the pesticides,  $R_s$  values are comparable to the present study and the observed  
253 differences can be explained by considering the different parameters, such as the experimental set-  
254 up for calibration (such as water renewal..), water-temperature and turbulence conditions that  
255 affect the sampling rate, the POCIS configuration and the value of its surface area - sorbent-phase  
256 ratio. Large differences between the experimental conditions used may lead to large variations in  
257  $R_s$  values. As described by Morin et al. (2012), there is a lot of studies in which all the needed  
258 information (speed of rotation, water temperature, calibration methods...) are not clearly  
259 expressed. These discrepancies highlight the need for standardized POCIS manufacture and  
260 calibration procedures in order to compare and use  $R_s$  data obtained in the different studies. A first  
261 EN-ISO document (EN-ISO 2011) is already available, but this document gives a general guidance  
262 and could not constitute a basis for use as a standard. It should be implemented by definitions of  
263 exposure conditions that need to be respected or explicated to enhance reliability of obtained data.

264

## 265 **Relationship between sampling rates and physical-chemical** 266 **properties**

267 A non-linear regression was performed for sampling rates determined from the calibration  
268 experiments, using a second-order polynomial function of  $\log K_{ow}$  ( $Y = -44.701 X^2 + 289.14 X -$   
269  $199.69; r^2=0.9221$ ) (Fig. 2). To obtain a better correlation, the  $R_s$  values of metalaxyl,  
270 propyzamide and azoxystrobine were not plotted, even though their mean  $R_s$  values are included in  
271 the graph. The quadratic curve shows an increase of the sampling rates with the hydrophobicity  
272 ( $\log K_{ow}$ ), reaching a plateau for compounds with  $\log K_{ow}$  ranging from 1.15 to 3.7. Mazzella et al.

273 (2007) and Thomatou et al. (2011) when calibrating POCIS for polar pesticides established a  
274 similar relationship. Arditsoglou and Voutsas (2008) when working with steroid and phenolic  
275 compounds found no clear correlation, but they showed a similarity in sampling-rate values across  
276 a range of hydrophobic molecules. The observed plateau from our study, which describes a  
277 similarity of POCIS uptake over a range of hydrophobicity ( $\log K_{ow}$ : 1.7-3.7), was also reported for  
278 pesticides on polar Chemcatchers<sup>®</sup> (Shaw et al. 2009) for the uptake by the RPS-SDB sorbent  
279 phase for the compounds studied ( $\log K_{ow}$ : 1.78–4.0). According to Alvarez et al. (2007b), POCIS  
280 are able to accumulate compounds with  $\log K_{ow} < 3$ . The selected pesticides in this work have  
281  $\log K_{ow}$  values that range from 1.15 (DIA) to 3.72 (penconazole). For all compounds studied except  
282 DIA, we obtained sampling rates of over 100 mL day<sup>-1</sup>. The sampling rates generated by  
283 Arditsoglou and Voutsas (2008) when working with steroid and phenolic compounds ( $\log K_{ow}$ :  
284 2.81-4.67) ranged from 90 to 221 mL day<sup>-1</sup>; their experimental data suggest that POCIS can be  
285 used even with compounds whose  $\log K_{ow}$  is over 4. The limits of POCIS performance and  
286 sampling efficiency should be defined by considering compounds from the same chemical groups.  
287 Fig. 3 focuses on the range of compound sampling rates on the plateau of the curve described  
288 above (Fig. 2). The mean sampling rate calculated for the 13 compounds is 239 mL day<sup>-1</sup> with a  
289 relative standard deviation of 14%. Considering that the determination of average concentrations  
290 by passive sampling with an RSD of 20 % in environmental measurements is acceptable, the main  
291 idea could be to use a unique sampling rate value for calculating the TWA concentration of any  
292 pesticide in the aquatic environment whose polarity falls in the  $\log K_{ow}$  interval determined above.  
293 In order to further develop this point, other experiments are needed with a large number of  
294 compounds belonging to different chemical classes and with a wide range of polarity values.  $R_s$   
295 variability for molecules falling in the proposed  $\log K_{ow}$  interval is much lower than the  $R_s$   
296 variability for various conditions of temperature and agitation. The demonstration is highlighted  
297 by the result presented in figure 3. It is also possible to consider an “average global”  $R_s$  for all  
298 compound owing to the  $\log K_{ow}$  intervals and to focus the research on developing correction of  
299 lab- $R_s$  to fit with environmental conditions. Different ways could be investigated: use of PRC  
300 compounds (Mazzella 2007), use of passive flow monitor (O'Brien, 2012) already applied for  
301 SPMD (semipermeable membrane device) and PDMS (polydimethylsiloxan) passive samplers and  
302 which could be useful for POCIS. It will be more interesting to focus the research on developing  
303 correction of lab- $R_s$  to fit with environmental conditions with a validation by in-situ calibrations.

304

## 305 **Conclusions**

306 The quantitative use of POCIS requires suitable sampling-rate values for each compound of  
307 interest. Very few sampling-rate data are available for estimating ambient contaminant  
308 concentrations from analyte levels in exposed POCIS.

309 A laboratory experiment based on a flow-through exposure system was designed and implemented  
310 for the calibration of POCIS (pharmaceutical configuration), and the sampling rates of 17 polar

311 pesticides were determined. The calibration revealed integrative uptakes of the target pesticides for  
312 15 and 21 days. The obtained sampling rates ranged from 67.9 to 279 mL day<sup>-1</sup> and demonstrated  
313 the effectiveness of POCIS for achieving a lower quantification limit for the selected compounds,  
314 compared to standard active-sampling methods. For an exposure duration of 15 days, we have the  
315 equivalence of a 1 to 4 L grab water sample, depending on the targeted compounds.

316 The calibration results obtained showed a similar POCIS sampling capacity for several compounds  
317 belonging to different chemical classes, with a logK<sub>ow</sub> ranging from 1.7 to 3.7. The use of an  
318 average laboratory-R<sub>s</sub> could be considered for determining the TWA concentration in water for a  
319 given compound, whose polarity falls within a defined interval with other compounds that have  
320 similar sampling-rate values. This Lab-R<sub>s</sub> need to be improved and corrected (by PRC or passive  
321 flow monitor) to fit better with realistic environmental conditions.

322

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328

329

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413 Table 1 Physico-chemical properties of selected compounds

Compound	Cas number	type	Chemical class	Chemical formula	Molecular weight (g/mol)	LogK <sub>ow</sub>	pKa
Azoxystrobine	131860-33-8	fungicide	strobilurine	C <sub>22</sub> H <sub>17</sub> N <sub>3</sub> O <sub>5</sub>	403,4	2,5	nd
Metalaxyl	57837-19-1	fungicide	amide	C <sub>15</sub> H <sub>21</sub> NO <sub>4</sub>	279,3	1,7	nd
Penconazole	66246-88-6	fungicide	azole	C <sub>13</sub> H <sub>15</sub> Cl <sub>2</sub> N <sub>3</sub>	284,2	3,7	1,5
Acetochlor	34256-82-1	herbicide	chloracetanilide	C <sub>14</sub> H <sub>20</sub> ClNO <sub>2</sub>	269,8	3,0	nd
Alachlor	15972-60-8	herbicide	chloracetanilide	C <sub>14</sub> H <sub>20</sub> ClNO <sub>2</sub>	269,8	3,5	nd
Atrazin	1912-24-9	herbicide	triazine	C <sub>8</sub> H <sub>14</sub> ClN <sub>5</sub>	215,7	2,6	1,7
Chlortoluron	15545-48-9	herbicide	urea	C <sub>10</sub> H <sub>13</sub> ClN <sub>2</sub> O	212,7	2,4	nd
DEA	6190-65-4	herbicide	triazine metabolite	C <sub>6</sub> H <sub>10</sub> ClN <sub>5</sub>	187,6	1,5	nd
DET	30125-63-4	herbicide	triazine metabolite	C <sub>7</sub> H <sub>12</sub> ClN <sub>5</sub>	201,7	2,3	nd
DIA	1007-28-9	herbicide	triazine metabolite	C <sub>5</sub> H <sub>8</sub> ClN <sub>5</sub>	173,6	1,2	nd
Diuron	330-54-1	herbicide	urea	C <sub>9</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O	233,1	2,7	nd
Isoproturon	34123-59-6	herbicide	urea	C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O	206,3	2,9	nd
Linuron	330-55-2	herbicide	urea	C <sub>9</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	249,1	3,2	nd
Metolachlor	51218-45-2	herbicide	chloracetanilide	C <sub>15</sub> H <sub>22</sub> ClNO <sub>2</sub>	283,8	3,1	nd
Propyzamide	23950-58-5	herbicide	amide	C <sub>12</sub> H <sub>11</sub> Cl <sub>2</sub> NO	256,1	3,4	nd
Simazin	122-34-9	herbicide	triazine	C <sub>7</sub> H <sub>12</sub> ClN <sub>5</sub>	201,7	2,2	1,6
terbuthylazin	5915-41-3	herbicide	triazine	C <sub>9</sub> H <sub>16</sub> ClN <sub>5</sub>	229,7	3,2	2

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Table 2 Selected pesticides mean aqueous concentrations in the tank for 15 days experiment

	<b>average concentration (µg/L) (n=9)</b>	<b>RSD (%)</b>
acetochlor	0,843	<b>7%</b>
alachlor	0,790	<b>6%</b>
atrazin	0,880	<b>3%</b>
diuron	0,890	<b>12%</b>
linuron	1,020	<b>8%</b>
chlortoluron	1,045	<b>8%</b>
desethylatrazin	1,220	<b>4%</b>
desethylterbutylazin	0,971	<b>3%</b>
desisopropylatrazin	1,337	<b>5%</b>
isoproturon	1,199	<b>7%</b>
metolachlor	0,964	<b>5%</b>
propyzamide	1,047	<b>6%</b>
simazin	0,918	<b>4%</b>
terbutylazin	0,973	<b>4%</b>
azoxystrobine	0,586	<b>7%</b>
metalaxyl	0,658	<b>6%</b>
penconazole	0,568	<b>4%</b>

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420 Table 3 Sampling rates of pesticides determined in the flow-through experiment

Compounds	logKow	Rs (mLday <sup>-1</sup> g <sup>-1</sup> ) (n=3)	Rs (mLday <sup>-1</sup> ) (n=3)	RSD (%)	Correlation coefficient (r <sup>2</sup> )
DIA	1,2	339,4	67,9	12	0,9221
DEA	1,5	664,7	132,9	14	0,7924
Simazine	2,2	1088,6	217,7	15	0,8377
DET	2,3	1268,5	253,7	14	0,8404
Atrazine	2,7	1269,1	253,8	14	0,8588
Terbutylazine	3,2	816,3	163,3	14	0,8726
Acetochlor	3	1115,7	223,1	9	0,9599
Metolachlor	3,1	1341	268,2	14	0,8655
Alachlor	3,5	1277,7	255,5	12	0,8572
Chlortoluron	2,4	1257,4	251,5	12	0,876
Isoproturon	2,5	1182,5	236,5	14	0,8378
Diuron	2,7	1283,7	256,7	17	0,8092
Linuron	3,2	702,5	140,5	14	0,9231
Metalaxyl	1,7	1321	264,2	15	0,8497
Azoxystrobine	2,5	768,8	153,8	14	0,9706
Propyzamide	3,4	973,9	194,8	15	0,9038
Penconazole	3,7	1394,8	279	8	0,9429



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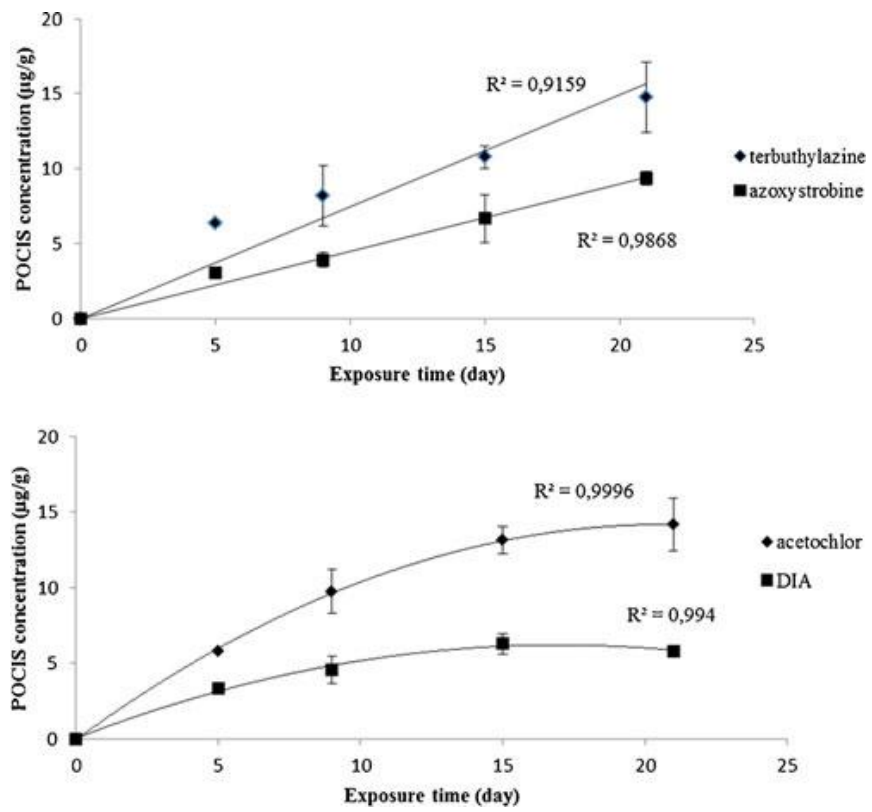
Table 4 Comparison of our sampling rates ( $R_s$  in mLday<sup>-1</sup>) and previous studies using water renewal conditions

Compounds	This study	(Mazzella et al. 2007)	(Lissalde et al. 2011)	Hernando et al. (2007)	(Thomatou et al. 2011)	(Martínez Bueno et al. 2009)	(Alvarez et al. 2007a)
Experimental set-up	Tank with a rotary exposure system	Aquarium for static exposure	Aquarium for static exposure	Aquarium for static exposure	Beaker under stirring conditions	Beaker under stirring conditions	Beaker under stirring conditions
Type of water and sampler	Tap water pharm-POCIS	Tap water pharm-POCIS	Tap water pharm-POCIS	Sea water pharm-POCIS	Lake water pest-POCIS	Sea water pharm-POCIS	Water quality not specified pest-POCIS
<b>Atrazine</b>	253.8	239	228	192	245	214	-
<b>DEA</b>	132.9	121.5	173	146	162	-	-
<b>DET</b>	253.7	205	213	-	-	-	-
<b>Simazine</b>	217.7	210.3	199	239	178	223	-
<b>DIA</b>	67.9	63.6	176	-	-	-	-
<b>Acetochlor</b>	223.1	225.2	241	-	-	-	-
<b>Diuron</b>	256.7	247.3	199	256	-	86	45
<b>Isoproturon</b>	236.5	217.6	167	-	-	-	86
<b>Alachlor</b>	255.5	-	205	247	230	-	-
<b>Metolachlor</b>	268.2	-	182	232	230	-	-
<b>Azoxystrobin</b>	153.8	-	179	-	-	-	-
<b>Propyzamide</b>	194.8	-	-	-	-	-	-
<b>Terbuthylazine</b>	163.3	250.7	238	-	-	-	-
<b>Linuron</b>	140.5	235.9	204	-	-	-	-

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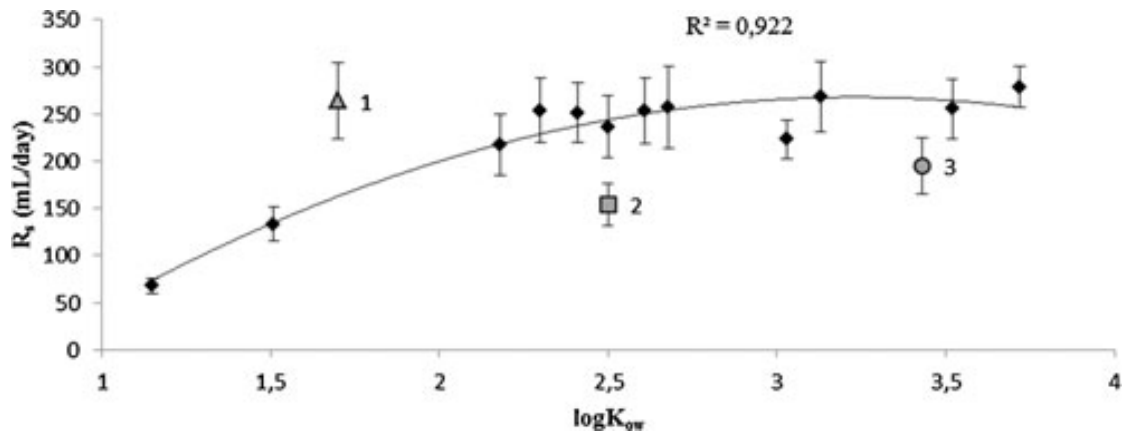
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Fig 1 Some examples of pesticides uptake by POCIS over a period of 21 days exposure



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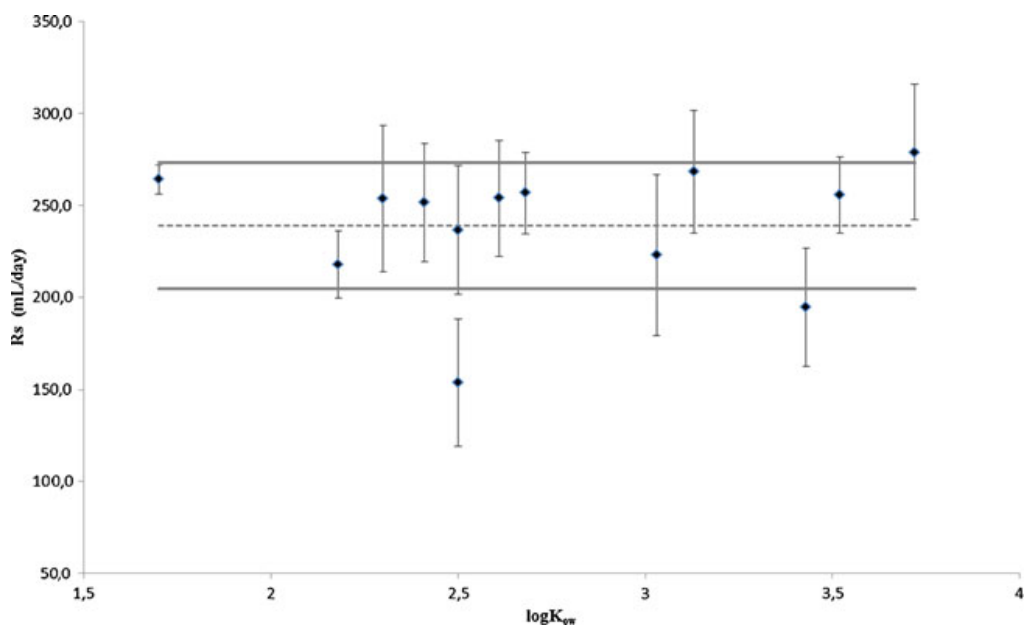
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Fig 2 Relationship between sampling rates ( $R_s$ ) and  $\log K_{ow}$ . Metalaxyl (1), azoxystrobin (2), and propryzamide (3)



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Fig 3 Average sampling rate of POCIS for pesticides whose polarity varies from 1.7 to 3.7. Discontinuous line of the figure represents the mean Rs value. Continuous lines represent the 20% of RSD calculated from the 13 Rs values