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## Calibration of silicone rubber rods as passive samplers for pesticides at two different flow velocities: Modeling of sampling rates under water boundary layer and polymer control

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6 **Running Head:** Silicone rubber rods as passive samplers for pesticides

7

8 **Calibration of silicone rubber rods as passive samplers for pesticides at two**  
9 **different flow velocities: modelling of sampling rates under water boundary**  
10 **layer and polymer control**

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17

18 **Abstract**

19 There is a need to determine time-weighted average concentrations of polar contaminants  
20 such as pesticides by passive sampling in environmental waters. Calibration data for silicone  
21 rubber (SR)-based passive samplers are lacking for this class of compounds. The calibration  
22 data, sampling rate ( $R_s$ ) and partition coefficient between SR and water ( $K_{sw}$ ) were precisely  
23 determined for 23 pesticides and 13 candidate performance reference compounds (PRCs) in a  
24 laboratory calibration system over 14 d for two water flow velocities,  $5 \text{ cm s}^{-1}$  and  $20 \text{ cm s}^{-1}$ .  
25 Results showed that an in situ exposure duration of 7 d left a SR rod passive sampler  
26 configuration in the linear or curvilinear uptake period for 19 of the pesticides studied. A  
27 change in the transport mechanism from polymer control to water boundary layer control was  
28 observed for pesticides with a  $\log K_{sw}$  of around 3.3. The PRC candidates were not fully  
29 relevant to correct the impact of water flow velocity on  $R_s$ . We therefore propose an  
30 alternative method based on an overall resistance to mass transfer model to adjust  $R_s$  from  
31 laboratory experiments to in situ hydrodynamic conditions. We estimated diffusion  
32 coefficients ( $D_s$ ) and thickness of water boundary layer ( $\delta_w$ ) as adjustable model parameters.  
33  $\log D_s$  values ranged from  $-12.13$  to  $-10.07 \text{ m}^2 \text{ s}^{-1}$ . The estimated  $\delta_w$  value showed a power  
34 function correlation with water flow velocity.

35

36 **Keywords:** pesticides, polydimethylsiloxane, freshwaters, mass transfer model, monitoring

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## 42 1 Introduction

43 The monitoring of trace levels of pesticides with a wide range of physical and chemical  
44 properties is a challenge for sampling and analysis to evaluate water resource quality. The  
45 variability in the discharge of pesticides into the environment, such as during flood events in  
46 small agricultural watersheds, requires the development of suitable methods that take  
47 temporal variations into account [1]. Passive sampling offers a promising alternative to  
48 classical grab sampling. It allows the determination of representative time-weighted average  
49 concentrations of contaminants, such as pesticides in freshwaters, at lower logistical and  
50 analytical costs [2].

51 Passive sampling community experts recently recommended monophasic polymers (e.g.  
52 silicone rubber (SR) or low density polyethylene (LDPE) as passive sampler materials of  
53 choice for hydrophobic and non-ionised organic compounds [3]. These passive samplers are  
54 available in a large variety of shapes: sheets, tubes, rods or coated stir bars named “Passive  
55 SBSE” (Stir Bar Sorptive Extraction) [4]. Modelling of contaminant uptake mechanisms in  
56 monophasic polymers, such as SR, is now well-documented for passive sampling of  
57 hydrophobic contaminants (PAHs and PCBs) [5-11]. Although SRs are strongly hydrophobic  
58 [12], they can extract organic compounds with a broad range of polarities ( $\log K_{ow} > 1-2$ ) from  
59 water but only a few studies have focused on pesticides [13-17]. Sorption properties of SRs  
60 for polar contaminants have mainly been assessed by determining partition coefficients  
61 between the SR and water at equilibrium ( $K_{sw}$ ), but if equilibrium is not attained, the  
62 determination of representative time-weighted average concentrations in water requires  
63 determining uptake kinetic parameters such as sampling rates ( $R_s$ ) or diffusion coefficients  
64 ( $D_s$ ) in the SR for every compound studied [18-20]. The uptake kinetic parameters are  
65 dependent on the variation of environmental factors including water flow velocity [5, 7, 8],

66 temperature, salinity [21] and biofouling [22, 23]. To correct for environmental variability,  
67 and especially water flow velocity,  $R_s$  can be estimated from the dissipation rates of  
68 performance reference compounds (PRCs) with which the passive sampler is spiked  
69 beforehand [24]. A second method, described by Estoppey et al. [7] with SR sheets, is based  
70 on correction factors derived from a power function relationship between the compound  
71 uptake and water flow velocity. This new method was introduced to correct PCB  
72 concentrations among sites with great differences in water flow velocity, where PRC-based  $R_s$   
73 overcorrected the impact of varying flow velocities. Estoppey et al. [8] recently improved  
74 their method for PCBs by using a simple linear correlation between  $R_s$  and flow velocity. For  
75 SRs, a close agreement between this second method and PRC correction was reported for  
76 flow velocities from 10 cm s<sup>-1</sup> to 60 cm s<sup>-1</sup> [8], and a similar linear correlation was observed  
77 by O'Brien et al. [25] using a passive flow monitor. This method has the advantages of being  
78 accessible by the operator applying passive samplers, less time consuming, less expensive  
79 than PRC-based methods and not influenced by uncertainties in log  $K_{sw}$  and  $R_s$  determination  
80 [8].

81 The determination of  $R_s$  requires a calibration experiment with a constant concentration of  
82 contaminants and controlled experimental parameters (constant temperature and adjustable  
83 flow velocity) [26]. For SRs, few calibrations have been conducted for pesticides and  
84 especially for polar pesticides [6, 14, 17, 27]. These calibration studies highlighted the need  
85 for an experimental design adapted to pesticide properties with short exposure monitoring  
86 (<15 d). Emelogu et al. [27] quantified urea herbicide in field studies with SR-based passive  
87 samplers, but lacked calibration data to convert mass accumulated by the SR into water  
88 concentration.

89 The main goal of this study was to determine  $R_s$  and  $K_{sw}$  for 24 polar and non-polar pesticides  
90 ( $0.6 < \log K_{ow} < 5.5$ ) with an experimental calibration, in order to estimate an appropriate

91 deployment period for linear uptake in freshwaters. We also assessed the impact of water flow  
92 velocity on the uptake of pesticides. The use of 13 deuterated pesticides as PRC candidates  
93 was evaluated to correct  $R_s$  for differences in flow velocity. The kinetic variables were  
94 determined using a home-made calibration system with adjustable water flow velocity and a  
95 diffusive source of pesticides. The theoretical model of overall resistance to mass transfer [28]  
96 was first applied to estimate  $D_s$  values. In a second step, we then used this model to predict  $R_s$   
97 of pesticides for other water flow velocities in order to simplify the calculation of time-  
98 weighted average concentrations in different field applications.

99

## 100 2 Mass transfer resistance model in silicone rubber- 101 based passive samplers

102 The mass transfer of contaminants into a passive sampler depends mainly on both the  
103 characteristics of the device and the physical and chemical properties of the sampled analytes,  
104 but it depends also on environmental factors. We focused only on the theory for membrane-  
105 free or monophasic samplers, such as SR plates. In this configuration, the exchange process is  
106 driven by different transport mechanisms involving transport of the compound by diffusion  
107 through the water, diffusion across the thickness of the receiving phase/ polymer. The  
108 transport across the biofilm layer for long exposure in water was neglected in the present  
109 work. Each transport mechanism contributes to the resistance to mass transfer ( $1/k_o$ ),  
110 calculated using Eq. 1, with  $k_w$  and  $k_s$  as the mass transfer coefficients in the water and the SR  
111 polymer respectively, and  $K_{sw}$  the silicone-water partition coefficient [26, 29, 30].

$$\frac{1}{k_o} = \frac{1}{k_w} + \frac{1}{K_{sw}k_s} \quad (1)$$

112 According to Greenwood et al. [26] and Huckins et al. [28], the individual mass transfer for a  
113 specific compound is related to the ratio of the compound's diffusion coefficient ( $D$ ) and the  
114 thickness ( $\delta$ ) of each compartment (water or SR, respectively noted with subscripts  $w$  and  $s$ )  
115 contributing to  $k_o$ . The mass-transfer coefficients for each compartment are calculated as  
116 follows (Eq. 2 and Eq. 3):

117

$$k_s = \frac{D_s}{\delta_s}, \quad (2) \quad k_w = \frac{D_w}{\delta_w}. \quad (3)$$

118 If diffusion occurs from both sides for a plate configuration of a SR-based passive sampler,  
119 the barrier thickness ( $\delta_s$ ) is considered as the half-thickness. Using the very simplified  
120 approach of Zhao et al. [31], where a linear concentration profile is assumed within the  
121 polymer cylinder or rod configuration, the barrier thickness ( $\delta_s$ ) is considered as the half-  
122 diameter or radius. For the water compartment, the notion of water boundary layer (WBL) of  
123 thickness  $\delta_w$  was assumed for convenience, considering the complexity of the hydrodynamics.  
124 In this work, we chose to use a mass transfer resistance model with linear concentration  
125 profiles in both the WBL and the SR. It is a simple and approximated model, contrary to the  
126 two-phase Fickian model [29] (considering a time-dependent  $D_s$  and resulting in non-linear  
127 diffusion profiles in the polymer) that would lead to more accurate results.

128 Assuming that elimination and uptake of compounds obey first-order kinetics (isotropic  
129 exchanges), the uptake of compounds in an SR-based passive sampler over time with constant  
130 ambient water concentration (and free of compounds at deployment), is described by Eq. 4:

$$C_s(t) = C_w K_{sw} (1 - \exp(-k_e t)), \quad (4)$$

131 where  $C_s$  ( $\text{ng L}^{-1}$ ) is the concentration of the compound accumulated in the receiving phase;  
132  $C_w$  ( $\text{ng L}^{-1}$ ) the concentration of the compound in the water phase, and  $t$  (d) the duration of



133 exposure. Elimination and uptake rate constants, respectively  $k_e$  ( $d^{-1}$ ) and  $k_u$  ( $d^{-1}$ ) are linked by  
134 a proportional constant  $K_{sw}$  ( $L L^{-1}$ ), the silicone-water partition coefficient. It is described by  
135 the ratio of concentration at equilibrium of the compound in the sampler  $C_{s,eq}$  ( $ng L^{-1}$ ) to the  
136 concentration at equilibrium of the compound in the water phase  $C_{w,eq}$  ( $ng L^{-1}$ ). The  
137 elimination rate constant  $k_e$  is expressed by:

$$k_e = \frac{R_s}{K_{sw} V_s} = \frac{k_o A}{K_{sw} V_s}, \quad (5)$$

138 where  $V_s$  (L) is the volume of the receiving phase,  $R_s$  is the sampling rate ( $L d^{-1}$ ) and  $A$  ( $cm^2$ )  
139 is the exposed surface area of the sampler. The calculation of time of sorption half-  
140 equilibrium ( $t_{1/2} = \ln 2 / k_e$ ) is also used to describe the calibration regime as linear ( $t < t_{1/2}$ ),  
141 curvilinear ( $t_{1/2} < t < 4t_{1/2}$ ) or equilibrium ( $t > 4t_{1/2}$ ) state for the exposure period ( $t$ ) [28].  
142 Combining Eq. 1, Eq. 2, Eq. 3 and Eq. 5, and neglecting biofilm resistance,  $R_s$ , based on the  
143 properties of the compounds, is estimated by:

$$R_s = \frac{A}{\frac{\delta_w}{D_w} + \frac{\delta_s}{K_{sw} D_s}}. \quad (6)$$

## 144 3 Materials and methods

### 145 3.1 Chemicals

146 The 24 pesticides selected, including two metabolites, covered a broad polarity range ( $0.6 <$   
147  $\log K_{ow} < 5.5$ ) and were listed in Table 1. Among them, 13 additional deuterated pesticides  
148 were used as PRCs (SI-1). Pesticides, PRCs and one internal standard (diuron-d6) used for  
149 quantification were purchased from Dr Ehrenstorfer (Augsburg, Germany) and Sigma Aldrich  
150 (Saint-Quentin Fallavier, France). Acetone and dichloromethane for pesticide residue  
151 analysis, UHPLC grade acetonitrile, ethyl acetate and methanol were purchased from  
152 Biosolve (Dieuze, France). LC-MS grade formic acid (purity 98%) was supplied by Waters

153 (Guyancourt, France). Ultrapure water was obtained using a Millipore water purification  
154 system equipped with an LC-Pak cartridge (Billerica, MA, USA). Nitrogen gas (purity  
155 99.995%) used for thermal decontamination was purchased from Messer (Saint-Georges-  
156 d'Espéranche, France).

### 157 3.2 Passive samplers

158 The passive samplers used in this study were made of SR shaped into small rods. The shape  
159 of rod was preferred to the classic sheet because of the convenience of handling and storage,  
160 the lower volume of solvent required for back extraction and the possibility to use  
161 thermodesorption (TD)-GC/MS analysis. Translucent SR was obtained as flexible cord from  
162 Goodfellow (Lille, France). This SR had been selected in an earlier study for its sorption  
163 properties for pesticides [13]. The SR was cut with a clean cutter blade into rods ( $20 \times 3$  mm),  
164 with a surface area of  $2.03 \text{ cm}^2$  and a volume of  $141 \mu\text{L}$ . Silicone rubber rods (SR rods) were  
165 selected by weight ( $165 \text{ mg} \pm 2.5\%$ ,  $d = 1.2$ ) to ensure repeatability.

166 Before use, SR rods were chemically and thermally cleaned to remove most residues such as  
167 oligomers that could interfere with the instrumental analysis [13]. First the SR rods were  
168 chemically conditioned by immersion in dichloromethane/methanol (50/50, v/v) under  
169 sonication for 15 min. They were then wiped with a lint-free tissue and dried at  $70 \text{ }^\circ\text{C}$  for 1 h,  
170 and thermally treated in a Gerstel tube conditioner TC (Mülheim a/d Ruhr, Germany) under a  
171 nitrogen flow ( $75 \text{ mL min}^{-1}$ ) with a temperature ramp of  $10 \text{ }^\circ\text{C min}^{-1}$  to  $300 \text{ }^\circ\text{C}$  maintained  
172 constant for 1 h.

173 Cleaned SR rods ( $n = 34$ ) were preloaded with PRCs by agitation at 600 rpm for 48 h in  
174 650 mL of ultrapure water spiked with a mixture of 13 PRCs (water concentrations ranging  
175 from 150 to  $220 \mu\text{g L}^{-1}$ ). The SR rods were then gently rinsed with ultrapure water, dried with  
176 a lint-free tissue and stored at  $-18 \text{ }^\circ\text{C}$  until deployed in the calibration system. Before

177 deployment each SR rod was inserted into a stainless steel spring ( $30 \times 5$  mm, wire diameter  
178 0.4 mm) to simplify handling.

### 179 3.3 *Characteristics of the calibration system*

180 The calibration system was custom-made (Colas & Gire, Saint-Genis-les-Ollières, France). It  
181 consisted of a stainless steel cylindrical tank (diameter 40 cm, height 35 cm), with a stirring  
182 system and hooks fixed on the inner wall of the tank at 4 levels, each level enabling the  
183 experimenter to expose 8 SR rods or 8 SR dosing sheets (Figure 1). Two copper wire hoops  
184 were fitted in the middle of the tank. Eight magnetic stir bars, wrapped in aluminium foil,  
185 were fixed on the copper wire between each hook; in this way the SR rods in their springs  
186 were retained magnetically at each position. The stainless steel tank was filled with 31.4 L of  
187 tap water and placed in a thermostatic bath at 20 °C. The tank was covered with an aluminium  
188 plate to prevent evaporation and photo-degradation in the water compartment. A Tinytag self-  
189 recording thermometer (Gemini Data Loggers Ltd, Chichester, United Kingdom) was  
190 immersed in the thermostatic bath to continuously follow the water temperature during the  
191 experiment.

192 Stirring was done by a four-blade motor-driven propeller composed of an agitator motor  
193 (RZR 2020 Control from Heidolph Instrument, Schwabach, Germany) and a propeller with a  
194 diameter of 10 cm (type R1345 from IKA, Staufen, Germany). The rotation generated a water  
195 flow velocity near the SR rod positions (set at 5 and 20 cm s<sup>-1</sup>). These flow velocities were  
196 measured with a propeller-type current meter (Streamflo430, Nixon, Cheltenham, United  
197 Kingdom) in the same way for all positions in the tank. All dimensions of the calibration  
198 system are availables in SI-2.

199 Constant concentrations of pesticides of about 1 µg L<sup>-1</sup> in the water were ensured by two  
200 methods. Some polar pesticides (CBZ, CTU, DIU, IMD, IPU, NFZ) (Table 1) were directly

201 added to the water using 5 mL of a highly concentrated solution in acetone. For more apolar  
202 pesticides, spiked SR sheets acted as diffusive contaminant sources in the water [5, 10]. Eight  
203 SR sheets ( $2 \times 7.5 \times 0.3$  cm, Goodfellow) were fixed with hooks at the bottom of the tank.  
204 The total volume of the dosing sheets was 20 times that of the SR rods, ensuring that  
205 depletion caused by uptake would be negligible. Before being spiked, the sheets were cleaned  
206 by shaking in ethyl acetate and then rinsing in ultrapure water [32]. The quantity of pesticides  
207 absorbed by the sheets was assessed with partition coefficients determined by Martin et al.  
208 [13]. For the spiking step, the SR sheets were placed in a bottle containing 2.5 L of ultrapure  
209 water contaminated with 5 mL of highly concentrated pesticide solutions (concentrations  
210 ranging from 56 to 923 mg L<sup>-1</sup> in acetone) and the bottle was shaken for 72 h at 300 rpm.  
211 Before the exposure of PRC preloaded passive samplers, the system was run for 72 h to allow  
212 the stabilization of the pesticide concentrations by reaching equilibrium between water and  
213 the spiked sheets for all the compounds (including added polar pesticides).

#### 214 3.4 Experimental design

215 Two calibration experiments lasting 14 days were performed with SR rods spiked with PRCs  
216 to simultaneously follow uptake and elimination of compounds at an effective water flow  
217 velocity of  $5.5 \pm 2.3$  cm s<sup>-1</sup> ( $n = 14$ ) and  $19.9 \pm 3.5$  cm s<sup>-1</sup> ( $n = 19$ ). A total of 20 SR rods were  
218 exposed for each experiment. Three SR rods spiked with PRCs were analysed to determine  
219 the initial concentrations of PRCs. The first SR rod was removed from the tank 30 min after  
220 the beginning of the experiment and then after 1, 2, 4, 8 h, and 1, 2, 3, 4, 5, 6, 7, 10, 14 days.  
221 Additional triplicates of SR rods were also exposed and analysed to evaluate overall  
222 repeatability for both uptake of pesticides and elimination of PRCs. The triplicates of SR rods  
223 exposed are detailed in the spreadsheet file (SI-7) compiling results of the calibration  
224 experiments. During the experiments, a 10 mL water sample was taken in an amber flask

225 every time a SR rod was collected from the tank to measure concentrations of pesticides. All  
226 the SR rods and water samples were stored at  $-18\text{ }^{\circ}\text{C}$  before analysis. Moreover, total organic  
227 carbon (TOC) was measured at the start and the end of each experiment in acidified water  
228 samples (HCl 2N, 1%, v/v) with TOC analyser (multi N/C® 3100, Analytik Jena) using  
229 thermal oxidation ( $850^{\circ}\text{C}$ ) and NDIR (Non-Dispersive Infrared) sensor.

### 230 3.5 Analytical procedure

231 Pesticides were desorbed from SR rods by chemical extraction according to the protocol  
232 developed by Martin et al. [13]. The solvent back-extraction recoveries of this step were  
233 between 60 and 98% depending on the compounds (listed in Table 1). Briefly, SR rods were  
234 rinsed with ultrapure water, wiped with lint-free tissue and stored at  $-18\text{ }^{\circ}\text{C}$ . Before analysis  
235 the pesticides absorbed in the SR rods were desorbed in 200  $\mu\text{L}$  of acetonitrile/methanol  
236 (50/50) for 15 minutes under sonication. Finally, 40  $\mu\text{L}$  of the desorbate was added to 150  $\mu\text{L}$   
237 of ultrapure water and 10  $\mu\text{L}$  of a diuron-d6 solution ( $200\text{ }\mu\text{g L}^{-1}$ ) to prepare the extract for  
238 analysis by UHPLC-MS/MS (Nexera X2 UHPLC system, Shimadzu and API 4000, AB  
239 Sciex). For calibration experiments, the analysis of the water samples was performed by direct  
240 injection. An aliquot of water of 1 mL was spiked with diuron-d6 at a concentration of  $10\text{ }\mu\text{g}$   
241  $\text{L}^{-1}$  as for the SR rod extract analysis. Chromatographic parameters, limit of quantification  
242 (LOQ) and settings for MS/MS (SI-1) analysis are reported elsewhere by Martin et al. [13].

## 243 4 Results and discussion

### 244 4.1 Monitoring of experimental parameters

245 During the two 14-day exposure experiments, the mean water temperature recorded was  $19.7$   
246  $\pm 0.5\text{ }^{\circ}\text{C}$ . Considering two measures per experiment and the results of both experiments, we  
247 observed a slight variation of pH, from  $7.9 \pm 0.6$  at the start of the calibration to  $8.6 \pm 0.1$  at

248 the end. No influence of pH on the properties of the selected pesticides or the range of  
249 fluctuation was expected. A mean value of TOC for the two experiments was measured at 3.5  
250  $\pm 1.1 \text{ mg L}^{-1}$  ( $n = 4$ ).

251 The mean pesticide concentrations in the water of the tank ranged from  $0.4 \text{ }\mu\text{g L}^{-1}$  to  $3.1 \text{ }\mu\text{g L}^{-1}$   
252 (Table 1). We opted to work at higher concentrations for some pesticides (TBZ at  $23.9 \text{ }\mu\text{g L}^{-1}$   
253  $^1$ , FNT at  $24.1 \text{ }\mu\text{g L}^{-1}$  and PCM at  $9.6 \text{ }\mu\text{g L}^{-1}$ ) that had a higher LOQ or could be partly  
254 degraded or absorbed by our experimental calibration system. The concentrations of the 23  
255 pesticides remained stable (RSD between 8% and 27%,  $n = 30$ ). By contrast, a higher RSD  
256 was obtained for PCM (41%), which may have been partly degraded (aqueous hydrolysis  
257  $DT_{50}$  of PCM: 25 d). Nevertheless, the SR sheets added into the tank acted as a contaminant  
258 source as expected for the other pesticides. The PRC concentrations in the water of the tank at  
259 the end of either experiment were below LOQ.

#### 260 4.2 Determination of kinetic parameters

261 Considering the two experiments, repeatability of sorbed mass on triplicates of SR rods  
262 sampled in experiments, expressed as RSD ( $n = 3$ ), ranged from an average value of 3.6% for  
263 dimethomorph (DMM) to 14.5% for spiroxamine (SPX), except for PCM (21.5 %). These  
264 RSD values take into account the accumulation of target pesticides in the SR rods, the liquid  
265 desorption process and the UHPLC-MS/MS analysis. We therefore excluded PCM from this  
266 study owing to high variability in uptake into SRs and in the water of the tank (cf. §4.1). All  
267 calibration results are detailed in an additional spreadsheet (SI-7).

268 For each pesticide, the concentration factor ( $C_s/C_w$ ) was calculated according to the ratio  
269 between the concentration in the SR rod ( $\text{ng L}^{-1}$ ) and the mean concentration in water ( $\text{ng L}^{-1}$ )  
270 from the beginning of the experiment to the same sampling time. The concentration factors of  
271 the pesticides for various time periods were fitted to a first order uptake model (Eq. 7 derived

272 from Eq. 4 and Eq. 5) using  $R_s$  and  $K_{sw}$  as adjustable variables. We optimised the sum of the  
273 squared differences between the experimental and calculated values to a minimum using non-  
274 linear regression with XLSTAT software (version 2015.3.01.19703). The RSD values of the  
275 kinetic parameters were calculated using the derivative of the function for each parameter.

$$\frac{C_s}{C_w}(t) = K_{sw} \left( 1 - \exp\left(-\frac{R_s t}{K_{sw} V_s}\right) \right). \quad (7)$$

276 We obtained satisfactory coefficients of determination ( $r^2$ ) of fitted data with the first order  
277 uptake model, ranging from 0.938 to 0.993. The calculation of parameters ( $R_s$ ,  $K_{sw}$ ,  $t_{1/2}$ ) took  
278 into account solvent back extraction recoveries determined in Martin et al. [13]. The  
279 calculated parameters are detailed in Table 1, and the fitted curves are illustrated in SI-3. The  
280 constants of elimination of pesticides in uptake experiments ( $k_{e\ up}$ ) were calculated using their  
281 associated  $R_s$  and  $K_{sw}$  values according to Eq. 5.

282 The times of sorption half-equilibrium ( $t_{1/2}$ ) ranged from 0.2 d for DCA, reaching equilibrium  
283 very quickly in SR rods, up to nearly 15.2 d for CPE at 5 cm s<sup>-1</sup>. Comparing DCA properties  
284 with DMM, which has an equivalent log  $K_{ow}$ , the fast uptake kinetic of DCA may be related to  
285 its low molecular volume (121 Å<sup>3</sup> and log  $K_{ow}$  of 2.69). DMM has a larger molecular volume  
286 (342 Å<sup>3</sup> and log  $K_{ow}$  of 2.68), and we observed a longer  $t_{1/2}$  (6.4 d) at 5 cm s<sup>-1</sup>. Thus, mainly  
287 curvilinear and equilibrium patterns were observed for the uptake of pesticides in SR rods at 5  
288 cm s<sup>-1</sup> for 14 d exposure. Equilibrium state was reached more frequently in the calibration  
289 experiment at 20 cm s<sup>-1</sup>. The impact of flow velocity is discussed in section 4.3.

290 According to low flow velocities measured near passive samplers in freshwaters (close to 5  
291 cm s<sup>-1</sup> with a deployment system), we found that an in situ exposure duration of 7 d was a  
292 good compromise in this SR rod passive sampler configuration to stay within the linear or  
293 curvilinear uptake period for 19 out of 23 pesticides ( $4t_{1/2} > 7$  d except for DCA, FNT, MTC  
294 and TBZ).

295 Those  $t_{1/2}$  values are greater than those previously reported for a selection of 19 pesticides  
296 with “Passive SBSE” [4]. The authors obtained a  $t_{1/2}$  ranging from 1.5 to 4 d in an experiment  
297 with flow velocity at  $2.5 \text{ cm s}^{-1}$ . This difference is because of the use of different geometries  
298 (area and volume) between the two passive samplers ( $A/V=17.0 \text{ cm}^{-1}$  and  $14.3 \text{ cm}^{-1}$   
299 respectively for Passive SBSE and SR rod) [9] or differences in diffusion coefficients ( $D_s$ ).  
300 Pesticides potentially diffuse into the half-diameter of SR rods (1.5 mm), whereas the  
301 thickness of the SBSE coating is only 1 mm.  
302 Calculated sampling rates ( $R_s$ ) for the two experiments are reported in Table 1 with their  
303 relative standard deviations (RSD). Sampling rates ranged between  $0.039 \text{ mL d}^{-1}$  (IMD) and  
304  $812 \text{ mL d}^{-1}$  (CPE), with RSD ranging from 8% to 27%. In comparison, “Passive SBSE”  
305 exhibited lower  $R_s$  values by a mean factor of 4.7 for 19 pesticides studied in common,  
306 excluding DCA, which differed by a factor of 68 [4]. Differences in  $D_s$  due to a specific SR  
307 formulation could explain this difference for DCA, as no differences in sorption at  
308 equilibrium were found for this compound by Martin et al. [13].  
309 The partition coefficients calculated in both experiments were compared with results obtained  
310 on the same SR in an earlier study by sorption isotherm experiments reported by Martin et al.  
311 [13] (SI-4). For pesticides with  $\log K_{sw} < 3$ ,  $K_{sw}$  values obtained in the present study were 1.8  
312 to 8.9 times greater than  $K_{sw}$  previously determined. Martin et al. [13] suggested a possible  
313 adsorption of the pesticides on the SR following a non-linear sorption isotherm depending on  
314 water concentration (Freundlich model). However,  $K_{sw \text{ Freundlich}}$  calculated with the mean  
315 concentration in water does not match the  $K_{sw}$  values obtained in the present study. This  
316 difference could be due to different experimental approaches and calculation methods, or to  
317 the influence of water characteristics on adsorption (Evian® water vs. tap water). We adopted  
318  $K_{sw}$  values derived from Eq. 7 in the experiment at  $20 \text{ cm}^{-1}$  as reference values (Table 1),  
319 because equilibrium state was reached more frequently in calibration experiments at  $20 \text{ cm s}^{-1}$



320 than at  $5 \text{ cm s}^{-1}$  for most pesticides after 14-d exposure (Cf. § 4.3), leading to more accurate  
321 values.

### 322 4.3 Impact of flow velocity on uptake of pesticides

323 As predicted by the theoretical model (Cf. § 2.0), a correlation of sampling rate, expressed as  
324  $\log R_s$  normalised per  $100 \text{ cm}^2$ , with  $\log K_{sw}$  should highlight the control of uptake kinetics by  
325 the WBL or by the polymer. This change in transport mechanism was expected for  
326 hydrophobic compounds with  $\log K_{ow}$  in the range 3.5–5 [11, 33]. For hydrophilic compounds  
327 theoretically under polymer control ( $R_s \approx AK_{sw}D_s/\delta_s$ ),  $R_s$  values were expected to increase  
328 with increasing  $K_{sw}$ . On the contrary, for more hydrophobic compounds, such as PCBs and  
329 PAHs (with  $\log K_{ow} > 3.3$ ) not investigated in the present study,  $R_s$  values were expected to be  
330 constant and slowly decrease with increasing  $K_{sw}$  [5], in accordance with WBL control theory  
331 ( $R_s \approx AD_w/\delta_w$ ) (compounds with high  $K_{sw}$  also have a lower  $D_w$ ).

332 In our experiments (Figure 2), for polar pesticides with a low affinity for SR, we observed  
333 that the  $R_s$  values increased with increasing values of  $\log K_{sw}$  up to around 3, whereas for  
334 more hydrophobic pesticides,  $R_s$  remained constant irrespective of the  $\log K_{sw}$  values.  
335 The plot of  $\log R_s$  at the two velocities (Figure 2) shows similar  $R_s$  values for polar pesticides,  
336 and highlights a significant separation of the two curves at  $\log K_{sw}$  around 3.3, defined as  
337 graphical intersection of tangents from both ends, with higher values of  $R_s$  for the experiments  
338 at  $20 \text{ cm s}^{-1}$ . This change in behaviour demonstrates the impact of hydrodynamics on the  
339 thickness of the WBL and on  $R_s$  values. A higher flow velocity leads to a thinner WBL,  
340 resulting in an increase in  $R_s$  proportional to  $1/\delta_w$ . To our knowledge, this is the first time that  
341 the change from polymer control to WBL control for  $\log K_{sw} > 3.3$  has been experimentally  
342 confirmed with polar and non-polar compounds ( $0.6 < \log K_{ow} < 5.5$ ) using different flow

343 velocities. This result is consistent with those of Assoumani et al. [4], suggesting a WBL  
344 control for pesticides with  $\log K_{ow}$  above 3.3 (FNT) in “Passive SBSE” (coated with SR).

#### 345 4.4 PRCs desorption kinetics: isotropic exchanges?

346 The elimination of PRC obeys first-order kinetics described by:

$$m_s(t) = m_0 \exp(-k_{e\ PRC} t), \quad (8)$$

347 where  $m_s$  (ng) is the mass of PRC remaining in the receiving phase of the sampler, and  $m_0$   
348 (ng) is the initial mass of spike PRC in the receiving phase. The repeatability of mass  
349 measurement on triplicates of SR rods sampled in experiments was similar for the release of  
350 13 PRCs and for the uptake of pesticides (RSD from 4.3% to 12.2%). The release of PRCs  
351 from the SR rods was fitted by nonlinear regression of PRCs fractions ( $f = m_s(t)/m_0$ )  
352 remaining in the SR rod as a function of exposure time ( $t$ ) using Eq. 8 (XLSTAT), with the  
353 elimination constant ( $k_{e\ PRC}$ ) as an adjustable parameter (fitted curves are available in SI-3).  
354 Unlike in uptake experiments, not all coefficients of determination ( $r^2$ ) were satisfactory  
355 (ranging from 0.15 to 0.91). Some PRCs (ATZ-d5, CBZ-d4, IPU-d6, MTC-d6 at 5  $\text{cm s}^{-1}$  and  
356 CBZ-d4, FNT-d6 at 20  $\text{cm s}^{-1}$ ) seemed to obey elimination kinetics with an inflexion point (or  
357 two slopes) that could not be described by Eq. 8. This was also observed for some compounds  
358 with another passive sampler (POCIS) by Morin et al. [34]. Accordingly only PRCs obeying  
359 first order kinetics were considered for the present study and the data for above mentioned  
360 PRC were removed.

361 Several hypotheses can be ventured to explain these deviations from the first order kinetic  
362 model. Adsorption on SR could be involved instead of absorption for these strongly polar  
363 PRCs. Another explanation is that the geometry of SR rods with a half-thickness of 1.5 mm  
364 makes them thicker than the silicone plates (0.25 mm), for which isotropic exchanges have  
365 been demonstrated [5]. It is possible that the two-phase Fickian model was more adapted in

366 this case with a time-dependency of  $D_s$  [29, 35]. It may be that the distribution of PRCs within  
367 this thicker SR-based passive sampler was not homogeneous because SR rods were preloaded  
368 with PRCs without methanol, which allows fast and homogeneous equilibrium by swelling  
369 the polymeric structure [36].

370 Calculated values of  $k_e$   $_{PRC}$  for the two experiments are reported in Figure 3. RSD ranged from  
371 7% to 34% similarly to  $k_e$   $_{up}$  derived from the uptake experiments.

372 The use of several pairs of deuterated (PRCs) and non-deuterated pesticides allowed direct  
373 comparison of the uptake and release processes. We opted to use the graphical comparison of  
374 uptake/release instead of checking the equality of elimination constants ( $k_e$   $_{up}$  and  $k_e$   $_{PRC}$ ), due  
375 to different calculation methods ( $k_e$   $_{up}$  was calculated from Eq. 5. and  $k_e$   $_{PRC}$  from Eq. 8. with  
376 lower  $r^2$ ). We considered a confidence interval of 10% for the intersection of uptake/release:  
377 isotropic exchanges were thus validated for an intercept between 40% and 60%.

378 As shown in Figure 3, curves describing the uptake of CPM and LINU and the release of  
379 CPM-d6 and LINU-d6 at  $5 \text{ cm s}^{-1}$  intersect at about 50% of the concentration interval,  
380 indicating that the exchange process is isotropic. These profiles were observed for the  
381 following deuterated analogues: ATC, CPM, CPE, FNT, and LINU (SI-3). Isotropic exchange  
382 of FNT and FNT-d6 with “Passive SBSE” was also confirmed by Assoumani et al. [4] by  
383 comparison of  $k_e$  values determined by elimination experiments for the two compounds.  
384 Therefore, regarding data at  $5 \text{ cm s}^{-1}$ , the release of the 5 selected PRCs seems pertinent for  
385 the correction of  $R_s$  in in situ applications.

386 In Figure 4, the  $\log k_e$   $_{PRC}$  at the two flow velocities are plotted against  $\log K_{sw}$  of non-  
387 deuterated corresponding pesticides. A change of transport mechanism is again highlighted by  
388 a global increase and then a decrease in  $k_e$   $_{PRC}$  with increasing  $K_{sw}$  values. However, in  
389 contrast to uptake, no differences in the release of hydrophobic PRCs ( $k_e$   $_{PRC}$ ) (ATC, CFV,  
390 CPM, CPE, DFF) were observed between the two flow velocities studied (Figure 4). This is

391 surprising considering the impact of flow velocity on uptake for these hydrophobic pesticides.  
392 The cause of this discrepancy might arise from (i) a non-isotropic exchange for the two  
393 velocities or (ii) ill-suited design of the calibration system for the elimination experiments.  
394 The graphical comparison of uptake/release of PRCs at  $20 \text{ cm s}^{-1}$  showed non-isotropic  
395 exchange for all pesticides; the uptake was faster than the release of PRCs (SI-3). The  
396 alternative explanation is that the static calibration system design (without continuous renewal  
397 of water) was not suited to following elimination kinetics.  
398 Hence it is difficult to conclude on the use of selected deuterated pesticides as PRC candidates  
399 in this study to take into account variation of flow velocity for  $R_s$  correction. Other  
400 experiments in continuous flow calibration systems will be needed to validate this statement.  
401 Considering these results from PRCs, we propose an alternative method based on an overall  
402 resistance to mass transfer model to adjust  $R_s$  from laboratory experiments to other  
403 hydrodynamic conditions by measuring in situ flow velocity.

#### 404       4.5       *Application of the overall resistance to mass transfer model*

405 We first applied the overall resistance to mass transfer model on our experimental results. The  
406 application of Eq. 6 required knowledge of diffusion parameters ( $D_w$  and  $D_s$ ) for the pesticides  
407 studied. Diffusion coefficients in water ( $D_w$ ) were calculated using the method of Hayduk and  
408 Laudie [37] from the molar volume of pesticides (SI-5). We chose this method according to  
409 the recommendation of the US Environmental Protection Agency and the conclusions of  
410 Pintado-Herrera et al. [19]. Experimental  $D_s$  values in SR are scarce in the literature, and have  
411 been estimated only for a few classes of contaminants (PCBs and PAHs [20], PBDEs [18] and  
412 emerging contaminants [19]) and unfortunately not determined for pesticides. We therefore  
413 opted to estimate  $D_s$  values for pesticides by simultaneously fitting the data at the two flow

414 velocities to the overall resistance to mass transfer model. The WBL thickness ( $\delta_w$ ), not  
415 available by direct measurement, was defined as an adjustment factor for the model.  
416 To estimate the initial  $\delta_w$  parameters for the model, we used the approximation of a theoretical  
417 WBL control model ( $R_s \approx AD_w / \delta_w$ ) with six pesticides that had  $\log K_{sw} > 3.3$  and were  
418 considered in WBL control (FNT, CFV, CPM, SPX, DFF, CPE) for both experiments. We  
419 obtained  $\delta_w$  values of 60  $\mu\text{m}$  at 5  $\text{cm s}^{-1}$  ( $\delta_{w5\text{ ini}}$ ) and 19  $\mu\text{m}$  at 20  $\text{cm s}^{-1}$  ( $\delta_{w20\text{ ini}}$ ). These values  
420 are in the range of typical values (from a few  $\mu\text{m}$  to 1 mm) reported by Huckins et al. [28] for  
421 SPMD.  
422 We then used  $R_s$  and  $K_{sw}$  for all pesticides at the two flow velocities ( $n = 48$ ) to calculate more  
423 accurate  $\delta_w$  values ( $\delta_{w5}$  and  $\delta_{w20}$ ) and  $D_s$  values for 23 pesticides according to Eq. 6. Predicted  
424  $R_s$  values were fitted simultaneously to the experimental  $R_s$  values with adjustable parameters  
425 ( $\delta_w$  values and  $D_s$  values) by minimising the sum of the squares of the residuals weighted by  
426 the average of the residuals with the “optim” function of R software (version 2.15.2) and a  
427 limited memory algorithm for bound constrained optimisation (L-BFGS-B). The initial values  
428 of adjustable parameters were  $\delta_{w\text{ ini}}$  values and a  $\log D_s$  value of  $-11\text{ m}^2\text{ s}^{-1}$  for all pesticides  
429 (approximated mean value for PAHs and PCBs as initial parameters), and lower and upper  
430 bounds were respectively 0 and 1000 mm for  $\delta_w$ , and  $-10$  and  $-14$  for  $\log D_s$ .  
431 Predicted  $R_s$  values (normalised to 100  $\text{cm}^2$ ) adjusted to our experimental data were plotted  
432 against  $\log K_{sw}$  (Figure 5). Estimated  $\delta_w$  values ( $\delta_{w5} = 43\text{ }\mu\text{m}$  and  $\delta_{w20} = 10\text{ }\mu\text{m}$ ) were slightly  
433 lower than those evaluated initially. Estimated  $\log D_s$  for pesticides are given in Table 1.  
434 Estimated  $\log D_s$  values in the present study were in the range  $-12.13$  (IMD) to  $-10.07$  (CPE)  
435  $\text{m}^2\text{ s}^{-1}$ . The lowest  $\log D_s$  for pesticides ( $-12.13\text{ m}^2\text{ s}^{-1}$ ) was for IMD, the most hydrophilic  
436 compound studied ( $\log K_{ow} = 0.6$ ) with the lowest affinity for SR ( $\log K_{sw} = 0.71$ ). By  
437 contrast, the highest  $\log D_s$  was for CPE, the second most hydrophobic pesticide ( $\log K_{ow} =$

438 4.7) with the highest affinity for SR ( $\log K_{sw} = 4.60$ ). The most hydrophobic pesticide, SPX  
439 ( $\log K_{ow} = 5.5$ ), also had a high molar volume reported to influence the diffusion of  
440 compounds in polymers [20, 38] and resulting in a decreased diffusivity in SR. Other trends  
441 of the diffusion coefficients related to chemical structures are illustrated in SI-6 with  $\log D_s$   
442 plotted to molar volumes and molar mass.  
443 This is a first evaluation of  $D_s$  values for pesticides using calibration data instead of direct  
444 measurement. They therefore need to be validated with further experiments. In regard to other  
445 experimental values for PAHs and PCBs for another SR formulation (supplied by Altec) [20],  
446 ranging from  $-9.8$  to  $-11.0 \text{ m}^2 \text{ s}^{-1}$ ; our data seem reasonable. In comparison, diffusion  
447 coefficient values for the studied pesticides were lower and with a wider range (2 orders of  
448 magnitude) than for PCBs and PAHs (1 order of magnitude).

#### 449 4.6 *Modelling of the influence of water flow velocity on sampling rates*

450 The knowledge of  $D_s$  for each pesticide and  $\delta_w$  values related to flow velocity enabled us to  
451 estimate  $R_s$  for other hydrodynamic conditions. Also, the change from the polymer control to  
452 the WBL control could be predicted. This model aims at estimating  $\delta_w$  by a correlation related  
453 to a hydrodynamic parameter such as water flow velocity. Such a correlation was proposed by  
454 Estoppey et al. [7, 8] for PCBs by in situ passive sampler exposures using LDPE and SR  
455 plates.

456 Our estimated  $\delta_w$  values for two different measured flow velocities were insufficient to  
457 demonstrate such a correlation; we therefore used calibration data for which water flow  
458 velocities were only estimated to determine complementary  $\delta_w$  values. The study of Rusina et  
459 al. [5] describes calibration experiments for PAHs and PCBs with SR flat plate passive  
460 samplers at two calculated flow velocities (Exp A =  $0.14 \text{ cm s}^{-1}$  and Exp B =  $9 \text{ cm s}^{-1}$ ),  
461 assuming that uptake was controlled by diffusion in the WBL in both cases. We applied the

462 overall resistance to mass transfer model with the available experimental values of  $D_s$  for  
463 PAHs and PCBs [20]. The estimated  $\delta_w$  values were  $\delta_{w,0.1} = 412 \mu\text{m}$  and  $\delta_{w,9} = 27 \mu\text{m}$ . In  
464 quasi-static hydrodynamics conditions ( $0.14 \text{ cm s}^{-1}$ ), the WBL thickness was more than 7  
465 times greater than at  $5 \text{ cm s}^{-1}$  in our experiment.

466 The estimated  $\delta_w$  values from the two studies ( $n = 4$ ) were plotted against the flow velocities  
467 ( $v$ ) reported in experiments in Figure 6. A power function correlation was observed between  
468  $\delta_w$  values and  $v$  ( $n = 4$ ,  $\delta_w = 111.6 v^{-0.71}$ ,  $r^2 = 0.98$ ). Such a correlation was indirectly  
469 demonstrated by Estoppey et al. [7] with power function relations between amounts of PCB  
470 accumulated and flow velocity in the range  $1.9$  to  $37.7 \text{ cm s}^{-1}$ . They then provided individual  
471 linear correlations for 6 PCBs between PRC-based  $R_s$  and water flow velocities above  $10 \text{ cm}$   
472  $\text{s}^{-1}$  for SR: assuming that PCB uptake was under WBL control, the  $R_s$  is proportional to  $1/\delta_w$ ,  
473 which was indirectly linked to  $v$ . Our results confirm that this relationship could also be  
474 approximated by a linear correlation for flow velocities above  $5 \text{ cm s}^{-1}$  ( $n = 3$ ,  $\delta_w = -2.1 v +$   
475  $51$ ,  $r^2 = 0.93$ ).

476 These results acquired using different SR based passive sampler designs (plate or cylinder)  
477 suggest that the effect of flow velocity on the water boundary layer thickness calculated from  
478 Eq.6 could be weakly influenced by the geometry of the passive samplers used. Considering  
479 the complexity of hydrodynamic conditions near a passive sampler, and the different positions  
480 of the passive sampler in the fluid, this approximation yields a simple model that will need to  
481 be validated with further data including measurement of water flow velocities.

482 In Figure 5, we calculated  $R_s$  values for pesticides with SR rods at flow velocities recorded by  
483 Rusina et al. [5]. At low flow velocity ( $v = 0.14 \text{ cm s}^{-1}$ ), the estimated  $R_s$  values for WBL  
484 controlled pesticides ( $\log K_{sw} > 2.7$ ) were lower by a mean factor of 10 than those  
485 experimentally determined at  $5 \text{ cm s}^{-1}$ , and the change in transport mechanism occurred at  $\log$   
486  $K_{sw}$  around 2.7 instead of 3.3. These extrapolated data could be used to calculate time-

487 weighted average concentrations of pesticides in freshwaters with only a representative field  
488 measurement of water flow velocity. Another way to calculate  $\delta_w$  could be to use an  
489 adaptation of the PRCs model with deuterated PAHs or PCBs as described by Booij et al.  
490 [36].

## 491 5 Conclusion

492 The calibration data for SR rods,  $R_s$  and  $K_{sw}$  were determined for 23 pesticides and 13  
493 candidate PRCs in a laboratory calibration system over 14 d at two flow velocities. The  
494 results show that an in situ exposure duration of 7 d kept the SR rod passive sampler  
495 configuration in the linear or curvilinear uptake period for 19 pesticides. A change in transport  
496 mechanism from polymer control to WBL control was observed for a log  $K_{sw}$  of around 3.3.  
497 The isotropic exchange of candidate PRCs was demonstrated for 5 PRCs at 5 cm s<sup>-1</sup>.  
498 However, the influence of water flow velocity on elimination was not demonstrated. Hence,  
499 the use of these PRCs was not validated to correct  $R_s$  for pesticides with WBL-controlled  
500 uptake kinetics.

501 Considering the PRC results, we propose an alternative method based on the overall  
502 resistance to mass transfer model to adjust  $R_s$  from laboratory experiments to other  
503 hydrodynamic conditions by measuring in situ flow velocities. The theoretical model of  
504 overall resistance to mass transfer was applied to our experimental data using log  $D_s$  values  
505 and  $\delta_w$  as adjustable parameters. The estimated log  $D_s$  values ranging from -12.13 to -10.07  
506 m<sup>2</sup> s<sup>-1</sup> for pesticides were consistent with values previously determined for PAHs and PCBs.  
507 Nonetheless, the application of a two-phase Fickian model could lead to more accurate  
508 results; for this purpose, calibration results are detailed in an additional spreadsheet (SI-7).  
509 Moreover, we demonstrated a power function correlation between  $\delta_w$  and water velocity using  
510 a compilation of data from the present study and from Rusina et al. [5]. This correlation is



511 apparently not influenced by passive sampler geometry. Thus, the estimation of new  $R_s$   
512 requires only direct measurements of flow velocity in the deployment location of the SR-  
513 based passive sampler. Considering isotropic exchanges,  $\delta_w$  values could also be estimated  
514 with WBL-controlled PRCs (PAHs, PCBs). However, further experiments are required to  
515 address isotropic exchange and significant dissipation of PRCs with the SR rod configuration.

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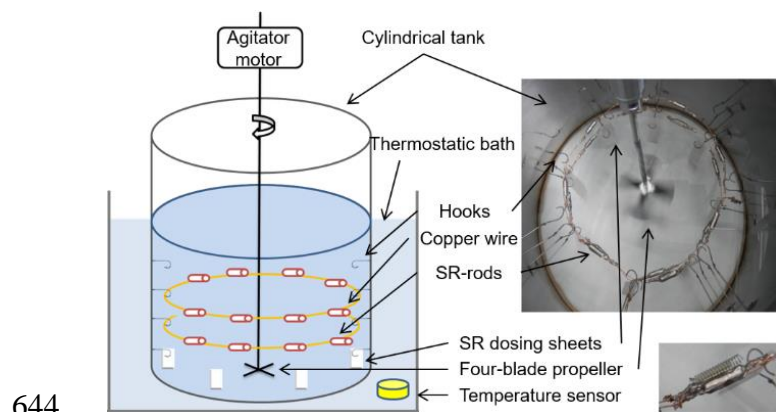
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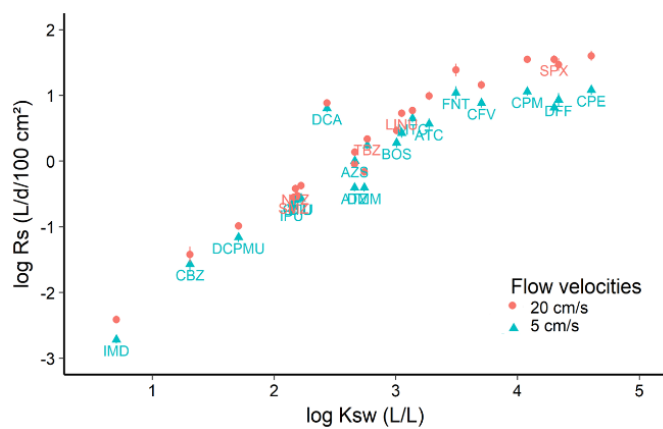
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- 640

641 Figure 1. Schematic diagram of the laboratory static calibration system (a), depiction of the  
642 inside of the calibration tank with the SR rods (b) and zoom on SR-rods inserted in a spring  
643 (c)



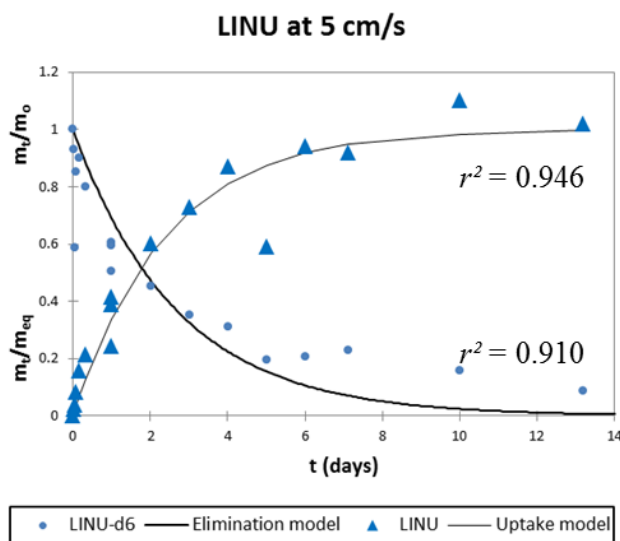
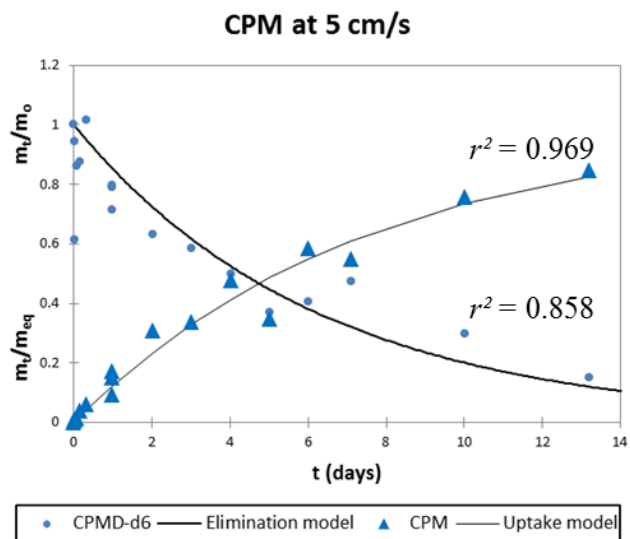
646 Figure 2. Plot of  $\log R_s$  normalised per 100  $\text{cm}^2$  versus  $\log K_{sw}$  in our experiment at two flow  
647 velocities. Error is expressed as standard deviation.



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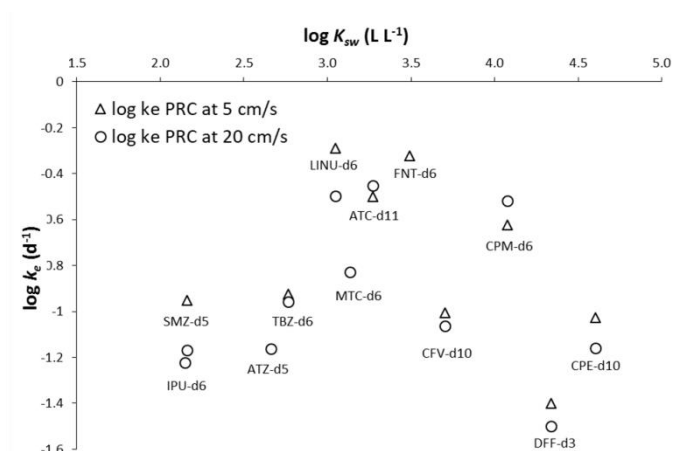
650 Figure 3. The uptake of CPM and LINU and release of corresponding deuterated pesticides  
651 (CPM-d6 and LINU-d6) by SR rods. Mass ratios are plotted relative to the initial mass for the  
652 release ( $m_0$ ) and to the predicted equilibrium mass for the uptake ( $m_{eq}$ ) with triangles for 5 cm  
653  $s^{-1}$  and circles for 20  $cm s^{-1}$ .



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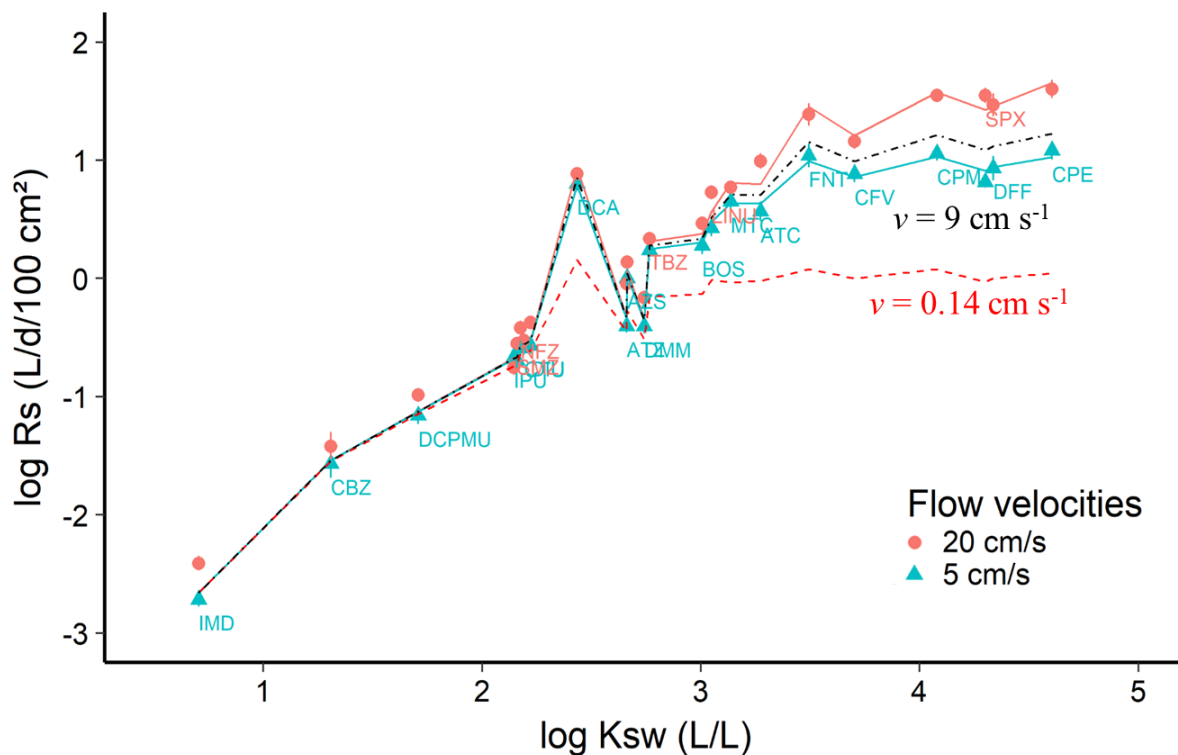
656 Figure 4. Plot of  $\log k_e PRC$  versus  $\log K_{sw}$  in experiments at two flow velocities (5 and 20 cm  
657  $s^{-1}$ ).



658

659

660 Figure 5. Plot of  $\log R_s$  normalised per 100  $\text{cm}^2$  versus  $\log K_{sw}$  in experiments at two flow  
661 velocities (5 and 20  $\text{cm s}^{-1}$ ) with theoretical model (solid lines) and estimated by theoretical  
662 model (dotted lines) for other flow velocities (0.14 and 9  $\text{cm s}^{-1}$  with data from Rusina et al.  
663 [5]).

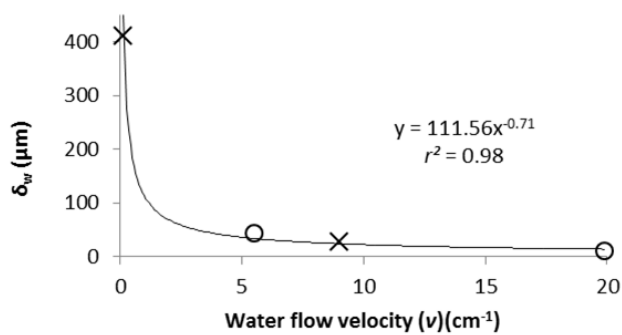


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666 Figure 6. Plot of water boundary layer thickness ( $\delta_w$ ) estimated by theoretical model (Eq. 6)  
667 versus water flow velocity ( $v$ ) from this present study (circles) and Rusina et al. [5] (crosses).



668

669 **Table 1. Physico-chemical properties, kinetic parameters at two flow velocities and estimated diffusion coefficients of the**  
 670 **studied pesticides.**

Pesticide name	Abbreviation	Log $K_{ow}$ <sup>a</sup>	Water concentration	Solvent back	Log $K_{sw}$	Log $K_{sw}$	$R_s$	$R_s$	$t_{1/2}$	$t_{1/2}$	Log $D_s$
			( $\mu\text{g L}^{-1}$ )	extraction	( $\text{L L}^{-1}$ )	( $\text{L L}^{-1}$ )	( $\text{mL d}^{-1}$ )	( $\text{mL d}^{-1}$ )	(d)	(d)	( $\text{m}^2 \text{s}^{-1}$ )
			Mean value	Mean value	5 $\text{cm s}^{-1}$	20 $\text{cm s}^{-1}$	5 $\text{cm s}^{-1}$	20 $\text{cm s}^{-1}$	5 $\text{cm s}^{-1}$	20 $\text{cm s}^{-1}$	Estimated
			$n = 30$ , RSD (%)	$n = 3$ , sd.	$n = 20$ , sd.	$n = 20$ , sd.	$n = 20$ , RSD (%)	$n = 20$ , RSD (%)			values
Acetochlor	ATC	4.1	2.8 (13)	69 (9)	3.18 (0.03)	3.27 (0.01)	75 (19)	200 (14)	2.3	0.9	-11.17
Atrazine	ATZ	2.7	1.5 (24)	86 (4)	2.47 (0.04)	2.66 (0.02)	8.0 (12)	18 (8)	5.3	2.3	-11.75
Azoxystrobin	AZS	2.5	1.2 (15)	95 (6)	2.87 (0.03)	2.66 (0.02)	20 (10)	28 (10)	2.1	1.5	-11.35
Boscalid	BOS	3.0	1.8 (16)	80 (7)	2.89 (0.03)	3.01 (0.02)	38 (16)	59 (12)	2.4	1.6	-11.36
Carbendazim	CBZ	1.5	0.4 (16)	82 (21)	1.41 (0.04)	1.31 (0.03)	0.5 (27)	0.8 (27)	3.4	2.4	-11.61
Chlorfenvinphos	CFV	3.8	2.7 (9)	82 (10)	3.82 (0.04)	3.70 (0.01)	155 (16)	293 (14)	3	1.6	-11.05
Chlorpyrifos-ethyl	CPE	4.7	1.6 (14)	60 (10)	-	4.60 (0.03)	245 (17)	812 (17)	15.2	4.6	-10.07
Chlorpyrifos-methyl	CPM	4	1.9 (12)	68 (6)	4.12 (0.05)	4.08 (0.01)	231 (13)	714 (10)	4.8	1.5	-10.67
Chlortoluron	CTU	2.5	1.8 (11)	90 (9)	1.76 (0.02)	2.19 (0.01)	5.5 (17)	6.1 (12)	2.6	2.4	-11.50
3,4-dichloroaniline	DCA	2.7	0.9 (20)	87 (6)	2.19 (0.01)	2.43 (0.01)	129 (13)	156 (11)	0.2	0.2	-10.20
3-(3,4-dichlorophenyl)- 1-methylurea	DCPMU	2.9*	1.5 (19)	91 (10)	1.53 (0.03)	1.71 (0.02)	1.4 (16)	2.1 (13)	3.4	2.2	-11.59
Diflufenican	DFE	4.2	1.4 (15)	69 (15)	4.37 (0.14)	4.34 (0.02)	174 (24)	598 (22)	11.5	3.3	-11.15
Diuron	DIU	2.9	2.0 (12)	87 (8)	2.13 (0.03)	2.22 (0.02)	5.5 (16)	8.6 (13)	2.8	1.8	-11.50
Dimethomorph	DMM	2.7	1.8 (16)	96 (12)	2.81 (0.04)	2.74 (0.02)	8.0 (14)	14 (14)	6.4	3.7	-11.84
Fenitrothion	FNT	3.3	24.1 (15)	76 (13)	3.37 (0.02)	3.49 (0.01)	222 (22)	495 (21)	1.3	0.6	-10.45
Imidacloprid	IMD	0.6	1.1 (8)	91 (11)	0.42 (0.04)	0.71 (0.04)	0.04 (13)	0.08 (13)	12	5.9	-12.13
Isoproturon	IPU	2.5	1.8 (11)	96 (12)	2.22 (0.03)	2.15 (0.02)	4.4 (16)	3.6 (13)	2.9	3.6	-11.58
Linuron	LINU	3.0	3.1 (13)	73 (6)	2.99 (0.03)	3.05 (0.01)	54 (16)	109 (13)	1.9	0.9	-11.21
Metolachlor	MTC	3.4	2.2 (10)	75 (5)	3.17 (0.02)	3.14 (0.01)	91 (14)	120 (10)	1.4	1.1	-11.02
Norflurazon	NFZ	2.5	1.9 (17)	98 (8)	2.04 (0.02)	2.18 (0.02)	5.2 (13)	7.8 (12)	2.6	1.8	-11.48
Procymidone	PCM	3.3	9.6 (41)	69 (19)	-	-	-	-			-
Simazine	SMZ	2.3	1.5 (21)	97 (8)	2.09 (0.03)	2.16 (0.02)	4.1 (14)	5.7 (11)	3.2	2.3	-11.58
Spiroxamine	SPX	5.5*	0.5 (27)	88 (9)	-	4.30 (0.03)	133 (11)	717 (14)	13.9	2.6	-11.15
Tebuconazole	TBZ	3.7	23.9 (15)	87 (6)	2.95 (0.03)	2.77 (0.01)	35 (12)	44 (10)	1.5	1.2	-11.19

671 <sup>a</sup> University of Hertfordshire. Pesticide Properties DataBase: <http://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm>

672 \* Predicted by ChemAxon: <http://www.chemicalize.org/structure>

## **Calibration of silicone rubber rods as passive samplers for pesticides at two different flow velocities: Modelling of sampling rates under water boundary layer and polymer control**

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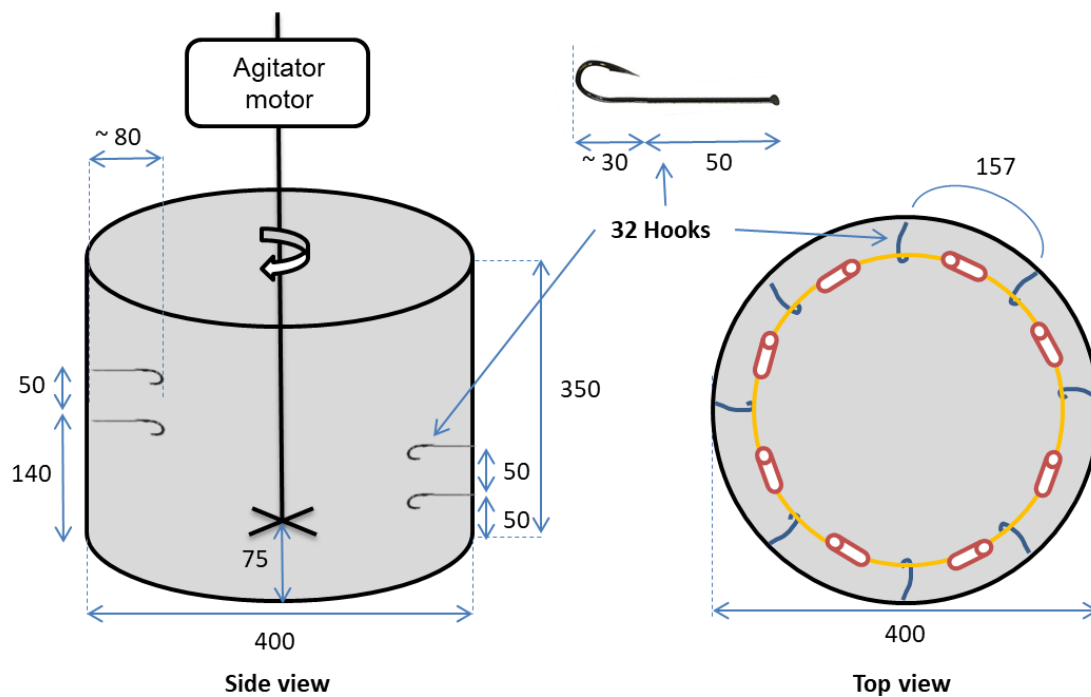
## **Supplementary Information**

### SI-1. Pesticide parameters for UHPLC-MS/MS analysis.

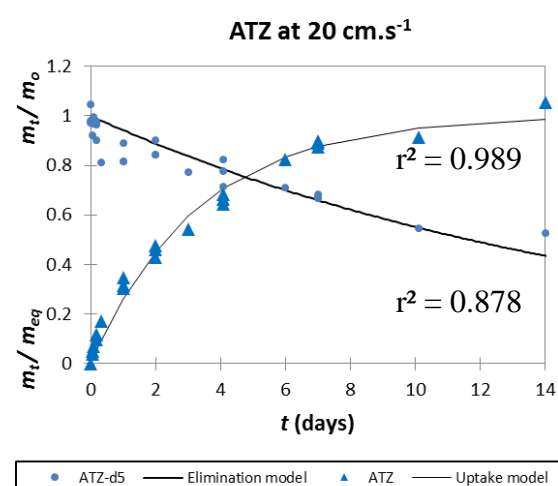
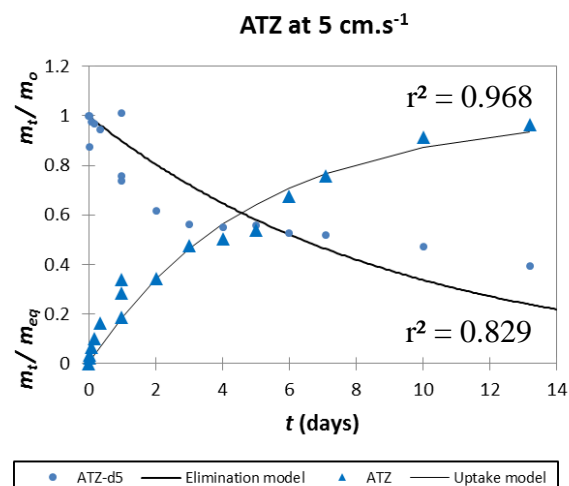
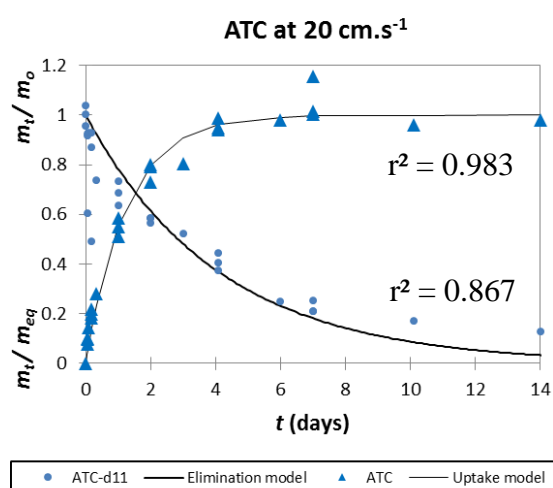
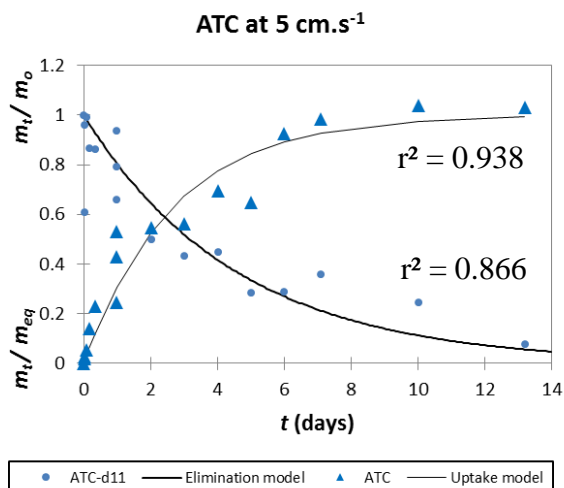
Compound	LOQ ( $\mu\text{g L}^{-1}$ )	Quantification transitions ( $m/z$ )	Declustering potential (V)	Collision energy (V)	Collision exit potential (V)
ATC	0.40	269.9 > 224.2 ;	31	15	16
		269.9 > 148.1	31	27	14
ATZ	0.10	215.9 > 174.1 ;	66	25	16
		215.9 > 104.1	66	41	8
AZS	0.02	404 > 372 ;	61	33	26
		404 > 344	61	35	28
BOS	0.20	343 > 307 ;	81	25	28
		343 > 140	81	29	8
CBZ	0.02	192 > 160 ;	56	25	16
		192 > 132	56	41	24
CFV	0.16	359 > 155 ;	76	17	20
		359 > 99	76	43	8
CPE	0.40	352 > 200 ;	45	30	38
		350 > 97	61	55	4
CPM	0.40	322 > 125 ;	71	29	22
		322 > 290	71	23	54
CTU	0.40	213 > 72 ;	51	25	12
		213 > 140	51	37	6
DCA	0.40	162 > 127 ;	51	31	24
		162 > 74	51	73	14
DCPMU	0.16	219 > 162 ;	66	21	26
		219 > 127	66	37	22
DFE	0.40	395 > 266 ;	86	35	28
		395 > 246	86	47	40
DIU	0.40	233 > 72 ;	46	51	6
		233 > 46	46	37	8
DMM	0.16	388 > 301 ;	76	31	36
		388 > 165	76	43	28
FNT	4.00	278 > 125 ;	71	29	22
		278 > 109	71	25	16
IMD	0.10	256 > 209.1 ;	61	23	38
		256 > 175.1	61	27	12
IPU	0.16	207 > 72 ;	51	37	8
		207 > 165	51	19	28
LINU	0.16	249 > 160 ;	61	25	32
		249 > 182	61	19	12
MTC	0.04	284.1 > 252.2 ;	46	21	20
		284.1 > 176.2	46	37	4
NFZ	0.40	304 > 284 ;	101	35	26
		304 > 88	101	61	16
PCM	1.60	284 > 256	76	25	46
SMZ	0.02	202.1 > 132.2 ;	56	29	10
		202.1 > 124.1	56	27	10
SPX	0.16	298 > 144 ;	51	31	8
		298 > 100	51	45	18
TBZ	0.16	308 > 70 ;	76	51	12
		308 > 125	76	57	12

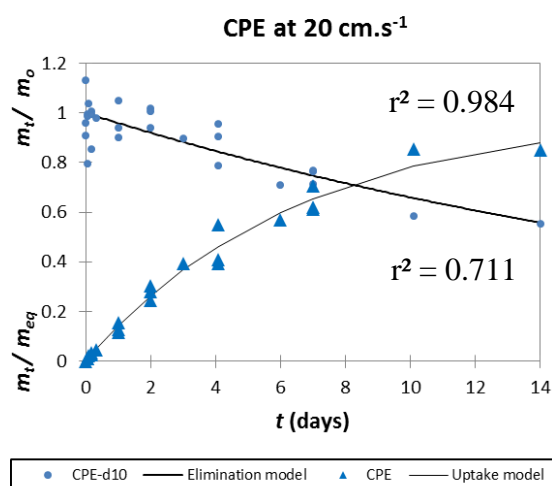
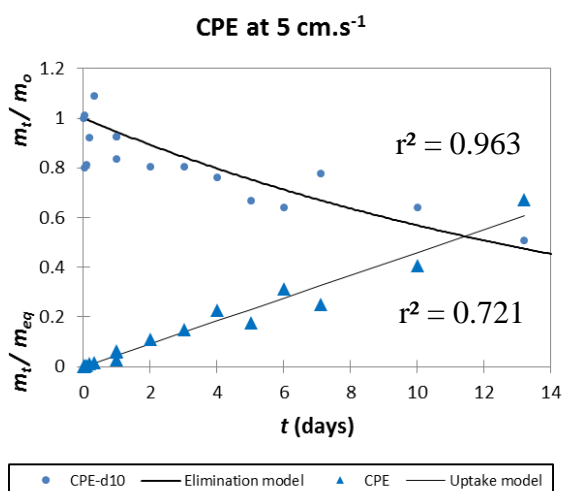
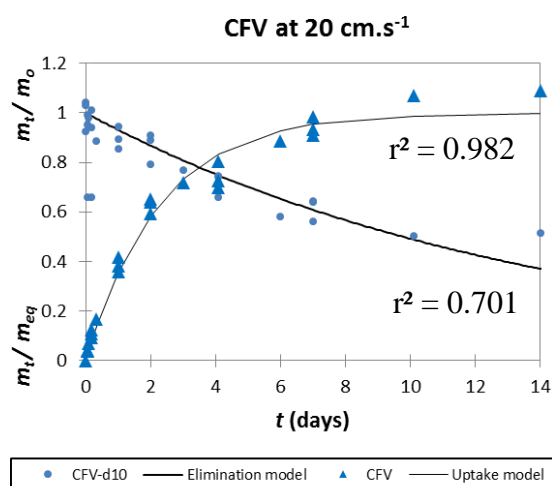
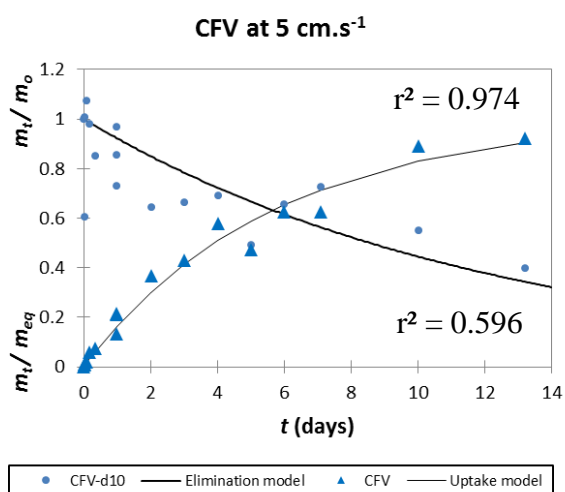
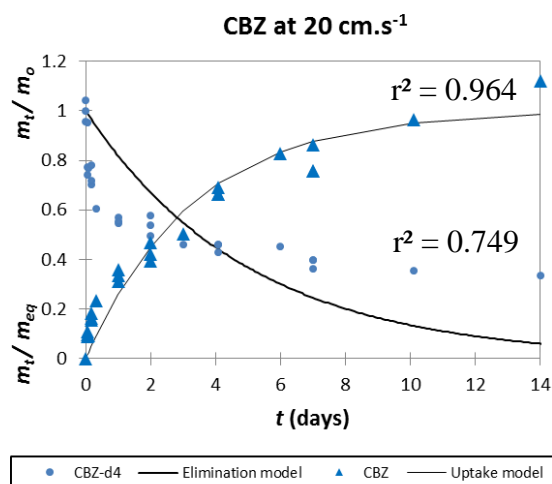
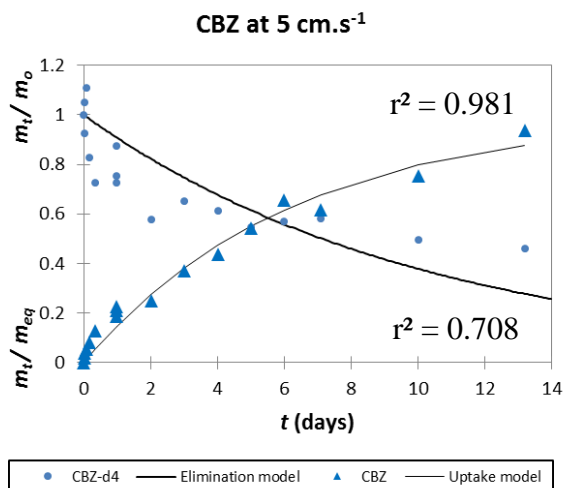
<b>Compound</b>	<b>LOQ (<math>\mu\text{g L}^{-1}</math>)</b>	<b>Quantification transitions (<math>m/z</math>)</b>	<b>Declustering potential (V)</b>	<b>Collision energy (V)</b>	<b>Collision exit potential (V)</b>
<b>ATC-d11</b>	0.40	281.1 > 235.1 ;	31	13	20
		281.1 > 159.1	31	29	12
<b>ATZ-d5</b>	0.10	221.06 > 179.1 ;	46	27	18
		221.06 > 101.1	46	35	18
<b>CBZ-d4</b>	0.02	196 > 164.1 ;	61	29	12
		196 > 138.1	61	41	8
<b>CFV-d10</b>	0.16	369.1 > 165.2 ;	56	19	10
		369.1 > 101.2	56	45	10
<b>CPE-d10</b>	0.40	360 > 199 ;	66	29	14
		360 > 163	66	21	14
<b>CPM-d6</b>	0.40	328 > 131.2 ;	66	31	8
		328 > 292.9	66	23	22
<b>DFP-d3</b>	0.40	398 > 268 ;	76	31	16
		398 > 248	76	49	20
<b>DIU d6</b>	0.40	239 > 78 ;	66	43	14
		239 > 52	66	37	10
<b>FNT-d6</b>	4.00	284 > 131 ;	61	27	18
		284 > 249	61	25	12
<b>IPU-d6</b>	0.16	213.1 > 78.3 ;	66	27	24
		213.1 > 171.2	66	21	10
<b>LINU-d6</b>	0.16	255 > 159.9 ;	56	25	8
		255 > 185	56	21	14
<b>MTC-d6</b>	0.04	290.1 > 258.1 ;	65	21	22
		290.1 > 182.2	65	35	32
<b>SMZ-d5</b>	0.02	207 > 129.1 ;	71	29	6
		207 > 137.1	71	27	8
<b>TBZ-d6</b>	0.16	314 > 72 ;	81	77	12
		314 > 125	81	53	10

**SI-2. Schematic diagrams (top and side view) of the laboratory static calibration system with dimensions in mm.**

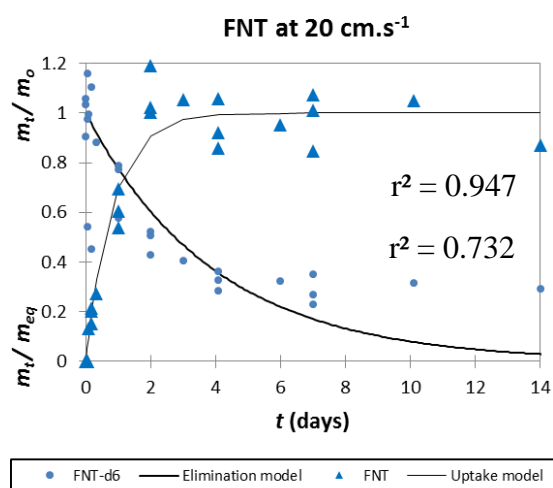
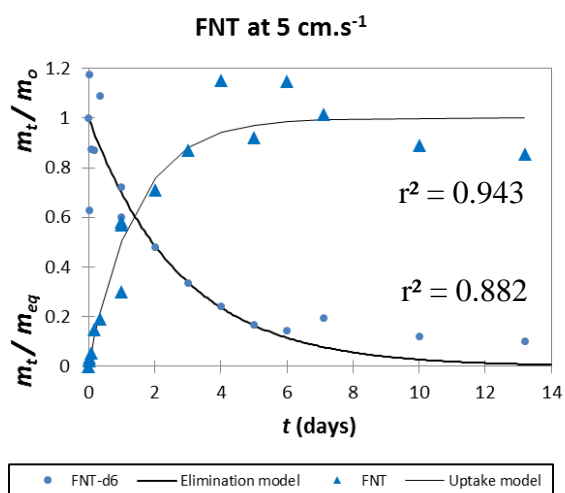
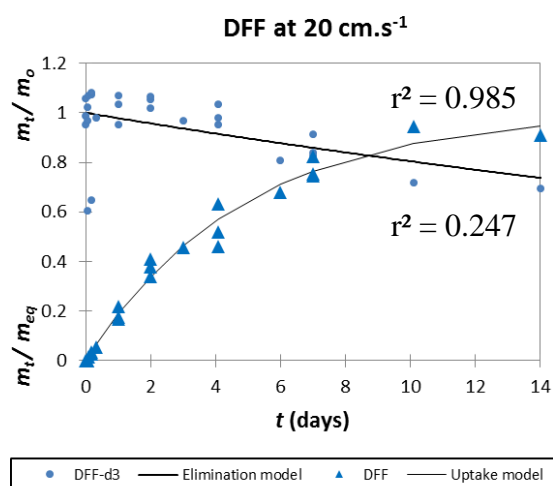
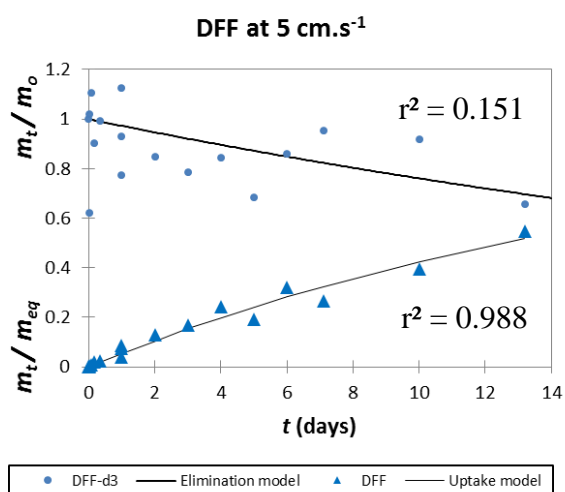
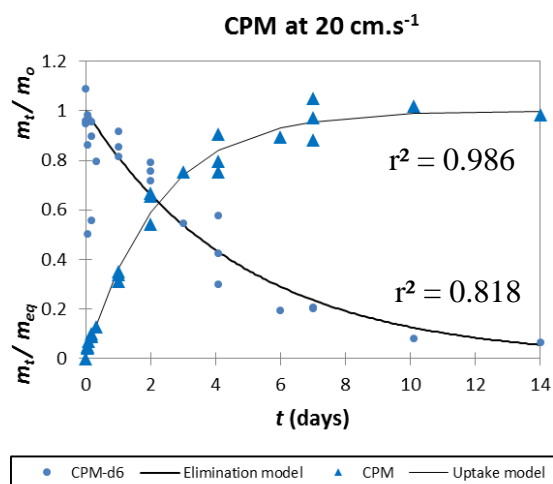
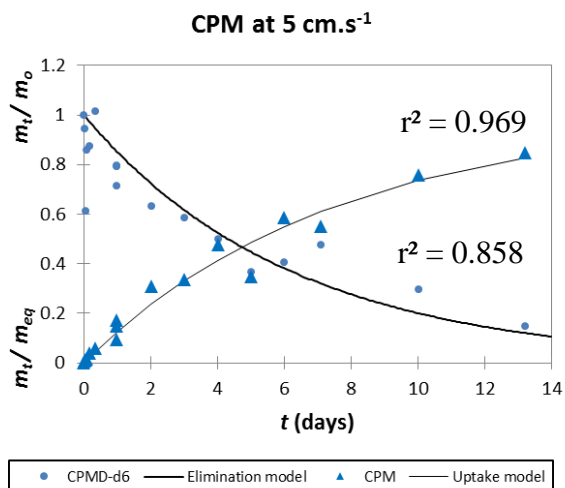


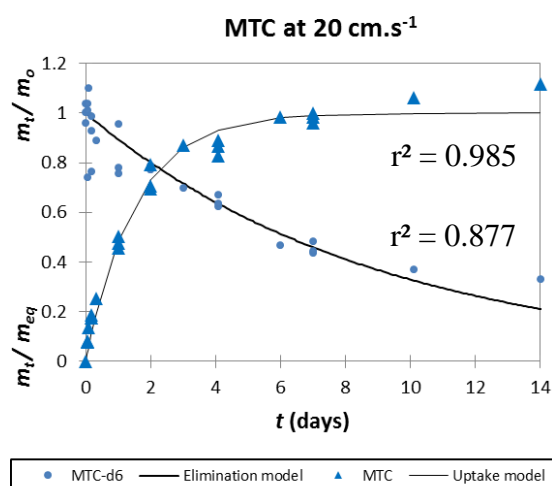
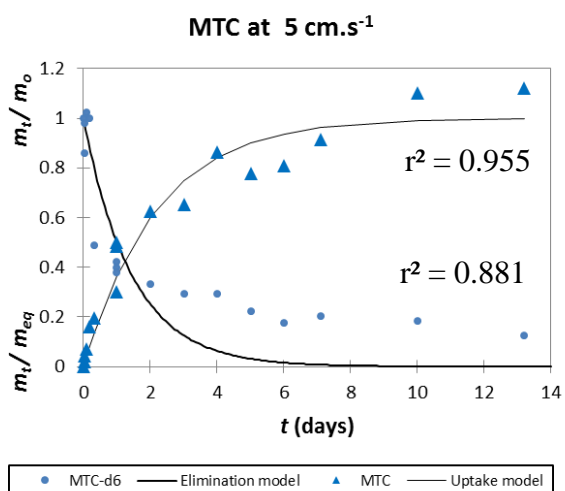
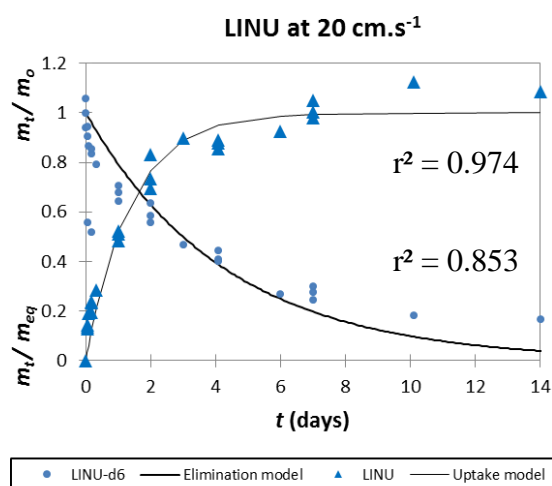
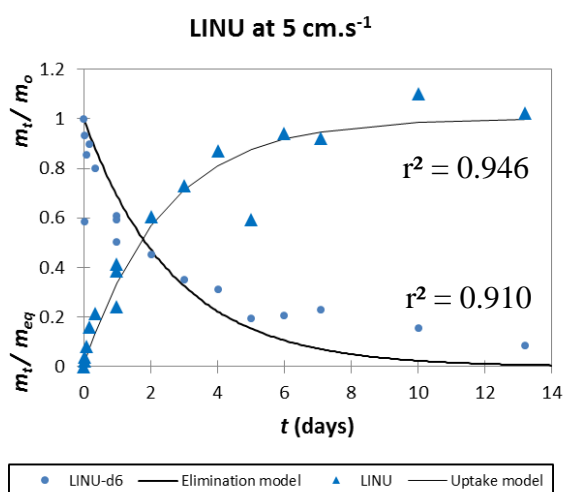
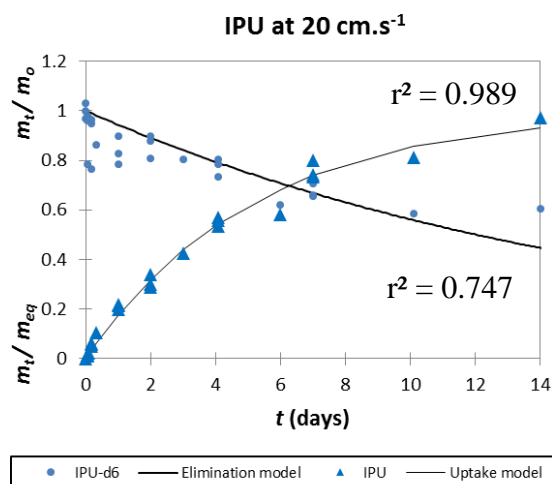
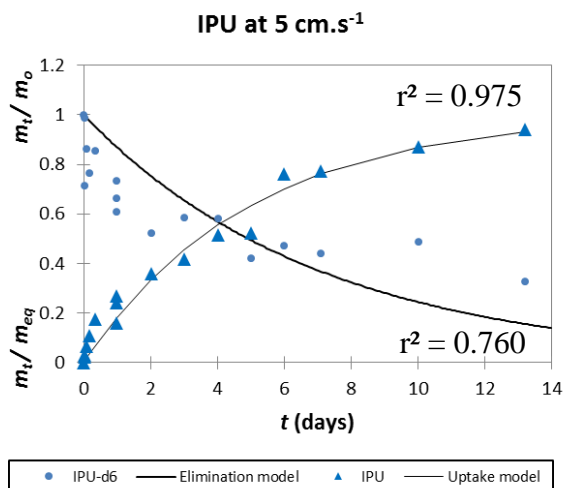
**SI-3. Uptake of pesticides and release of corresponding deuterated pesticide**  
(candidate PRCs) by the silicone rods (SRs) at two flow velocities (5 and 20  $\text{cm}\cdot\text{s}^{-1}$ ).  
Accumulated mass ( $m$ ) is plotted relative to the initial mass for the release ( $m_0$ ) and to  
the predicted equilibrium mass for the uptake ( $m_{eq}$ ).

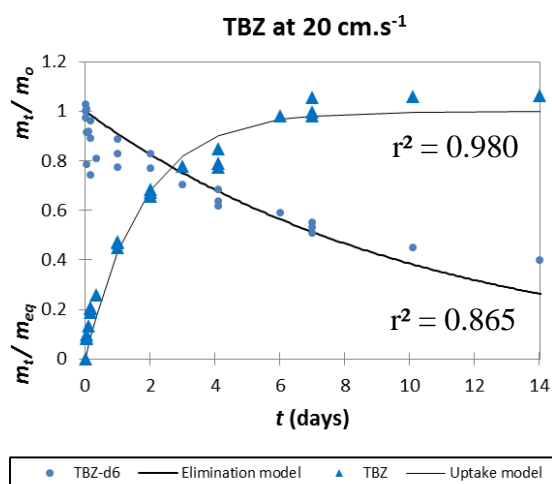
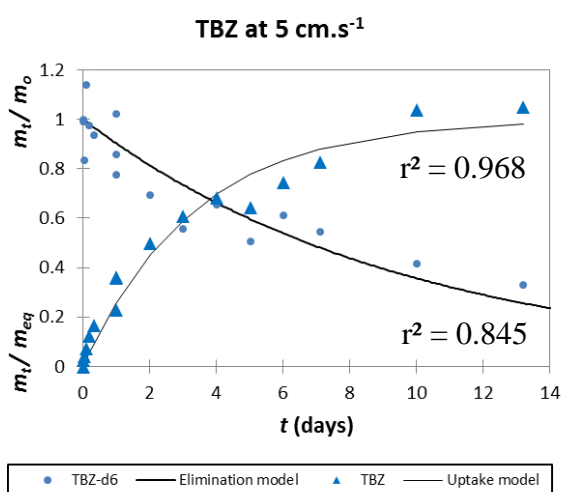
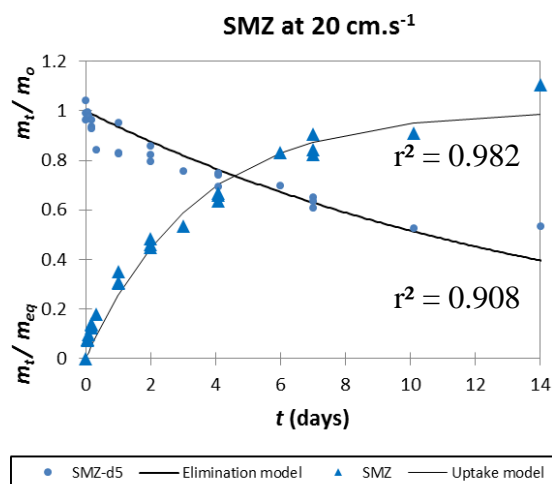
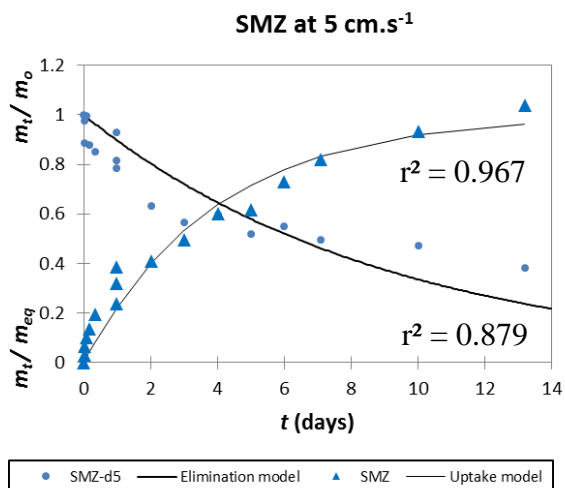




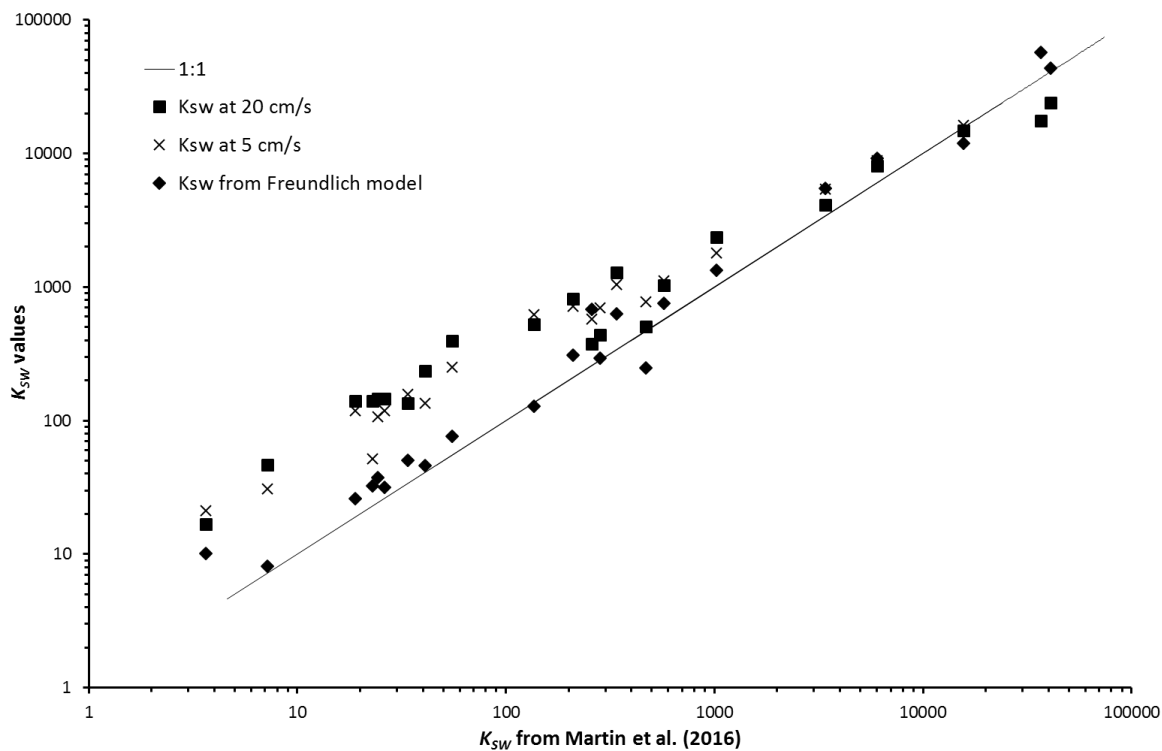








**SI-4. Plot of  $K_{sw}$  values from the experiments at two flow velocities (Eq.7) and estimated by the Freundlich model ( $K_{sw} = K_f C_w eq^{1/n-1}$  with parameters from Martin et al. [1]) at the concentration of this experiment against  $K_{sw}$  estimated in Martin et al. [1].**



**SI-5. Molecular properties ( $M$ ,  $V_m$ ,  $\text{Log } D_w$ ) of pesticides.**

Pesticide	$M^a$	$V_m^a$	$\text{Log } D_w^b$
	( $\text{g mol}^{-1}$ )	( $\text{cm}^3 \text{mol}^{-1}$ )	( $\text{m}^2 \text{s}^{-1}$ )
ATC	269.8	240.9	-9.28
ATZ	215.7	163.1	-9.18
AZS	403.4	300.1	-9.34
BOS	342.2	262.1	-9.3
CBZ	191.2	137.5	-9.14
CFV	359.6	261.8	-9.30
CPE	350.6	236.8	-9.28
CPM	322.5	203.8	-9.24
CTU	212.7	184.5	-9.21
DCA	162.0	115.6	-9.09
DCPMU	219.1	152.1	-9.16
DFE	394.3	274.0	-9.31
DIU	233.1	178.6	-9.21
DMM	387.9	315.1	-9.35
FNT	277.2	202.8	-9.24
IMD	255.7	160.1	-9.18
IPU	206.3	196.3	-9.23
LINU	249.1	185.2	-9.21
MTC	283.8	257.8	-9.30
NFZ	303.7	208.8	-9.24
PCM	284.1	189.1	-9.22
SMZ	201.7	147.9	-9.16
SPX	297.5	308.2	-9.34
TBZ	307.8	268.1	-9.31

<sup>a</sup> Predicted by ACD/Labs: <http://www.chemspider.com/>

<sup>b</sup> Calculated from Hayduk and Laudie (1974)



4 **SI-7. Spreadsheet file compiling results from the two calibration experiments for 24**  
5 **pesticides and 13 candidate PRCs at two flow velocities (5 and 20 cm·s<sup>-1</sup>). Accumulated**  
6 **mass of pesticides (*m*, ng) were not corrected by corresponding solvent back extraction**  
7 **recoveries (Table 1). Concentrations of pesticides in water (*C<sub>w</sub>*) was expressed in µg L<sup>-1</sup>.**

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