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# 1 Use of passive stir bar sorptive extraction as a simple integrative sampling 2 technique of pesticides in freshwaters: determination of sampling rates and 3 lag-phases

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## 10 Abstract

11 Passive sampling represents a cost-effective approach and is more representative than grab  
12 sampling for the determination of contaminant concentrations in freshwaters. In this study, we  
13 performed the calibration of a promising tool, the passive Stir Bar Sorptive Extraction  
14 (SBSE), which has previously shown good performances for semi-quantitative monitoring of  
15 pesticides in a field study. We determined the sampling rates and lag-phases of 18 moderately  
16 hydrophobic to hydrophobic agricultural pesticides ( $2.18 < \log K_{ow} < 5.11$ ) from different  
17 chemical classes including triazines, substituted ureas, triazoles and organophosphate  
18 compounds. We also realised an elimination experiment to identify a performance reference  
19 compound (PRC). A flow-through calibration experiment was realised for 7 days at constant  
20 concentrations of target pesticides in tap water, under controlled temperature (20 °C) and flow  
21 velocity ( $2.5 \text{ cm s}^{-1}$ ). Sampling rates were between 1.3 and 121  $\text{mL d}^{-1}$  with satisfactory RSD  
22 for most pesticides (9-47%), and poor repeatability for 3 hydrophobic pesticides (59-83%).  
23 Lag-phases for all target pesticides were shorter than 2 h, demonstrating the efficiency of  
24 passive SBSE for the integration of transient concentration peaks of these contaminants in  
25 surface waters. The role of flow velocity on pesticide uptakes was investigated and we  
26 assumed a water boundary layer-controlled mass transfer for 5 pesticides with  $\log K_{ow} > 3.3$ .  
27 Among these pesticides, we selected fenitrothion to evaluate its elimination, along with its  
28 deuterated analogue. Results showed 82% elimination of both compounds over the 7-day

29 experiment and isotropic exchange for fenitrothion, making fenitrothion-d6 a promising PRC  
30 candidate for *in situ* applications.

31

32 **Keywords:** Passive sampling, Stir bar sorptive extraction (SBSE), Calibration, Performance  
33 reference compound (PRC), Agricultural pesticides

34

## 35 **1. Introduction**

36

37 Passive samplers have been recently developed for the monitoring of various organic  
38 contaminants in the aquatic environment. These devices represent a cost-effective alternative  
39 to grab and automated sampling for the determination of concentration of target organic  
40 contaminants in surface and ground waters, as they require less logistical needs. Additionally,  
41 the integrative sampling of the dissolved fraction of target pollutants over days to weeks  
42 generally results in low quantification limits [1, 2]. A passive sampler is typically composed  
43 of a receiving phase, where the target organic contaminants are accumulated, and a  
44 membrane, which separates the receiving phase from the aquatic medium. This is the case for  
45 the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative  
46 Sampler (POCIS) [3, 4]. For other passive samplers, such as the Silicone Rubber (SR) and  
47 Low-density Polyethylene (LDPE) strips [5, 6], the polymer itself is both the membrane and  
48 the receiving phase. After convective transport of the contaminants from bulk solution to the  
49 water boundary layer (WBL) at the surface of the membrane, the sampling process is  
50 governed by diffusion to the receiving phase [7, 8]. For the determination of time-weighted  
51 average (TWA) concentrations, a calibration of the passive sampler has to be performed prior  
52 to field exposition. In other words, the accumulation kinetics of each target organic  
53 contaminant is studied in controlled conditions in order to determine the corresponding

54 sampling rate ( $R_s$ ). However, it is well known that laboratory-derived  $R_s$  may differ from *in*  
55 *situ*  $R_s$  because of the difference in the exposition conditions (flow velocity, biofouling and  
56 temperature). Therefore, the determination of TWA concentrations may be biased [7]. The use  
57 of a performance reference compound (PRC) [9] during *in situ* applications has shown to be  
58 an efficient approach to determine more realistic  $R_s$  and calculate unbiased TWA  
59 concentrations of polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls  
60 (PCB) for SPMD and SR [3, 5]; also, it has shown promising determination of estimates of  
61 polar pesticides with POCIS [10]. For well-described non polar samplers (SPMD, LDPE, SR  
62 and Chemcatcher for hydrophobic compounds), laboratory calibration could be avoided, since  
63  $R_s$  can be modelled as a function of octanol-water partition coefficient ( $K_{ow}$ ) [7, 11–13].  
64 However, PRC are still needed for adjustment of the  $R_s$  modelled values [14].

65 Depending on the types of membrane and receiving phase of the passive sampler, chemicals  
66 with different polarities can be sampled, from polar contaminants such as pharmaceuticals  
67 and pesticides [4, 15], to hydrophobic organic contaminants such as PAH and PCB [16–20].  
68 However, to our knowledge, sampling of moderately hydrophobic to hydrophobic pesticides  
69 ( $2 < \log K_{ow} < 5$ ) is still poorly documented [2, 19, 20]. Moreover, some passive samplers  
70 equipped with a membrane (e.g., Membrane-Enclosed Sorptive Coating - MESCO,  
71 Chemcatcher and POCIS) might not be able to integrate short variations of concentration of  
72 moderately hydrophobic to hydrophobic pesticides (concentration peaks), as lag-phases would  
73 be relatively long (up to several days) [21–24]. The lag-phase is the time required to attain  
74 steady state accumulation flux in the passive sampler; it generally depends on the diffusion of  
75 contaminants through the membrane [7]. Finally, for most passive samplers, the sample  
76 treatment to recover the contaminants sequestered in the receiving phase is complex, time-  
77 consuming and organic solvent-consuming, and may be a source of poor repeatability [19].

78 Recently, we successfully applied stir bar sorptive extraction (SBSE), a fast, simple and  
79 solvent-free analytical sampling technique [25], directly *in situ* as a membrane-free passive  
80 sampling technique for the semi-quantitative monitoring of moderately hydrophobic to  
81 hydrophobic pesticides in two rivers (therein named “Passive SBSE”) [26]. The extraction  
82 device (Twister) is composed of a magnet enclosed in a glass tube coated with a thick film of  
83 polydimethylsiloxane (PDMS). In that field study, only qualitative and semi-quantitative  
84 performances of the passive sampler were compared to automated average sampling, as  $R_s$  of  
85 target pesticides had not been determined.

86 Hence, the aim of the present study was to obtain calibration data of passive SBSE for 18  
87 agricultural pesticides in waters. We studied the accumulation kinetics of the target pesticides  
88 in Twisters with a flow-through system for 7 days, to determine the corresponding  $R_s$  and lag-  
89 phases. In addition, we studied the effect of flow velocity on the pesticide uptakes to assess  
90 which pesticide accumulation kinetics were controlled by the exposition conditions. Finally,  
91 we studied the elimination kinetics of selected pesticides to identify a PRC candidate.

92

## 93 **2. Theory of passive sampling**

94

95 To determine TWA concentrations of organic contaminants dissolved in the water column, a  
96 calibration of the passive sampler is generally performed in controlled conditions to study the  
97 accumulation kinetics of each contaminant and to determine the corresponding  $R_s$ . This  
98 section describes the theory of accumulation kinetics of organic contaminants in Twister used  
99 as membrane-free passive samplers. Similarly to SR and LDPE, the PDMS coating of the  
100 Twister is both membrane and receiving phase. Twister used as a passive sampler obeys the  
101 same kinetic laws as these other well-known devices [2, 7]. Mass transfer of a contaminant in  
102 the Twister includes several diffusion and interfacial transport steps across all barriers, *i.e.*,

103 the aqueous boundary layer, the possible biofilm layer and then, the receiving phase.  
104 Assuming isotropic exchange, the corresponding uptake in the sampler -initially empty- over  
105 time with constant ambient concentration can be described as follows (Eq. 1) [7, 8]:

$$M_s(t) = C_w K_{sw} V_s (1 - \exp(-k_e \cdot t)) \quad (1)$$

106  
107 where  $M_s$  (ng) is the mass of contaminant accumulated in the receiving phase;  $V_s$  (L) is the  
108 volume of the receiving phase;  $K_{sw}$  (adimensional), described by the ratio of the concentration  
109 at equilibrium of contaminant in the sampler  $C_s$  (ng mL<sup>-1</sup>) and the concentration at  
110 equilibrium of contaminant in the water phase  $C_w$  (ng mL<sup>-1</sup>), is the receiving phase/water  
111 partitioning coefficient; and  $t$  (d) equals the duration of exposition. The elimination rate  
112 constant  $k_e$  (d<sup>-1</sup>) is defined as follows (Eq. 2):

$$k_e = \frac{R_s}{K_{sw} V_s} = \frac{\lambda A}{K_{sw} V_s} \quad (2)$$

113  
114 where  $R_s$  is the sampling rate (mL d<sup>-1</sup>);  $A$  (cm<sup>2</sup>) is the sampler surface area and  $\lambda$  (cm d<sup>-1</sup>) is  
115 the overall mass transfer coefficient.

116 The graphical representation of Eq. 1 is curvilinear with a plateau corresponding to an  
117 equilibrium phase (described by  $K_{sw}$ ). In the initial uptake phase, when the exponential term is  
118 small ( $\ll 1$ ), chemical uptake is linear and integrative. Thus, in the initial uptake phase, Eq. 1  
119 is reduced to Eq. 3:

$$M_s(t) = C_w \lambda A t \quad (3)$$

120  
121 The overall mass transfer coefficient  $\lambda$  describes the movement of the contaminant out of the  
122 bulk solution, across multiple barriers, to the receiving phase. The overall resistance ( $1/\lambda$ ) is  
123 given by sum of all particular barrier resistances:

$$\frac{1}{\lambda} = \frac{\delta_w}{D_w} + \frac{\delta_b}{D_b K_{bw}} + \frac{\delta_s}{D_s K_{sw}} \quad (4)$$

124

125 with  $\delta$  (cm) the thickness of the particular barrier (in subscripts, w stands for water, b for the  
126 possible biofilm, and s for the receiving phase),  $D_w$  ( $\text{cm}^2 \text{d}^{-1}$ ) the diffusion coefficient of the  
127 contaminant in water (*i.e.*, aqueous boundary layer),  $D_b$  ( $\text{cm}^2 \text{d}^{-1}$ ) the diffusion coefficient of  
128 the contaminant in the possible biofilm,  $K_{bw}$  (adimensional) the partitioning coefficient  
129 between water and the possible biofilm, and  $K_{sw}$  (adimensional) the partitioning coefficient  
130 between water and the receiving phase.

131 For passive SBSE, we refer to two kinetic limitations of the contaminant uptakes as receiving  
132 phase and WBL controls, and we assume that the transition from one mass transfer control to  
133 the other occurs for compounds with  $\log K_{ow}$  between 4.5 and 5.0, as previously discussed by  
134 Allan et al. for other non polar samplers such as SPMD, Chemcatchers for hydrophobic  
135 compounds, LDPE membranes, two types of MESCO, and silicone rods [27].

136 For contaminants with accumulation kinetics controlled by the WBL, the exposition  
137 conditions can have an impact on the  $R_s$ . Therefore, the difference between laboratory  
138 calibration conditions and field exposition conditions can lead to biased determinations of  
139 TWA concentrations. Spiking the receiving phase with a PRC prior to field exposition of the  
140 sampler has been used to calculate *in situ*  $R_s$  and determine unbiased TWA concentrations [3,  
141 10]. PRC is an analytically non-interfering organic compound which can be loaded in a large  
142 amount in the receiving phase of the sampler, with moderate to high elimination and for  
143 which isotropic exchange kinetics is verified. The elimination of PRC is deduced from Eq. 1,  
144 when PRC is not present in water ( $C_w = 0$ ):

$$M_s(t) = M_0 \exp(-k_e \cdot t) \quad (5)$$

145  
146 where  $M_s$  (ng) is the mass of PRC remaining in the receiving phase of the sampler and  $M_0$   
147 (ng) is the initial mass of PRC spiked in the receiving phase of the sampler.

148

### 149 **3. Experimental**

150

### 151 3.1 Chemicals and materials

152

153 The 18 pesticides selected for this study belong to different use classes (herbicides,  
154 insecticides, and fungicides) and chemical classes (including triazines, substituted ureas,  
155 triazoles and organophosphate compounds), and have different physical chemical properties,  
156 such as their log  $K_{ow}$  (Table 1). They were provided by Dr. Ehrenstorfer GmbH (Augsburg,  
157 Germany): acetochlor, atrazine, azoxystrobin, chlorfenvinphos, chlorpyrifos-ethyl,  
158 chlortoluron, diflufenican, dimethomorph, 3,4-dichloroaniline (metabolite of diuron),  
159 fenitrothion, flufenoxuron, isoproturon, linuron, metolachlor, norflurazon, procymidon,  
160 simazine, and tebuconazole (purity  $\geq 92.5\%$ ). For chemical analyses, diuron-d6, used as  
161 internal standard, was also provided by Dr. Ehrenstorfer (purity  $\geq 98.5\%$ ). For the study of  
162 elimination kinetics, fenitrothion-d6 was purchased from Dr. Ehrenstorfer. Sodium chloride  
163 NaCl (purity = 99.5%) was purchased from VWR (Strasbourg, France). Dichloromethane for  
164 pesticide residue analysis, and liquid chromatography-mass spectrometry (LC-MS) grade  
165 acetonitrile and methanol were purchased from VWR (Strasbourg, France). Formic acid  
166 (purity = 98%) for LC-MS analysis was provided by Sigma-Aldrich (Saint-Quentin-Fallavier,  
167 France). Ultrapure water was produced by a MilliQ water purification system equipped with a  
168 LC-Pak cartridge and purchased from Millipore (Billerica, MA, USA).

169

### 170 3.2 Sampler design and preparation

171

172 The devices used for passive SBSE in this study were Twisters (20 mm x 1-mm thick PDMS  
173 film, with a surface area of 2.14 cm<sup>2</sup> and a volume of 126  $\mu$ L) from Gerstel (Mülheim a/d  
174 Ruhr, Germany). For exposition purposes, the Twisters were placed in deployment bags made



175 of plastic mesh, to directly expose the sorption phase to the aquatic medium (*i.e.*, no  
176 membrane used).

177 Prior to use, the Twisters were treated following a method published elsewhere [28]. Briefly,  
178 the Twisters were placed overnight at 50 °C, then they were rinsed with 10 mL  
179 methanol/dichloromethane (50:50, v/v) for 30 min by sonication, gently dried with  
180 Kimwipes® precision paper and placed at 50 °C until use. For the calibration, the Twisters  
181 were placed in the deployment bags directly after treatment; whereas, for the elimination  
182 study, they were first loaded with fenitrothion and fenitrothion-d6. Twisters were loaded by  
183 extraction at 800 rpm for 3 h of 20 mL of ultrapure water spiked with each compound at 40  
184  $\mu\text{g L}^{-1}$  and with 2.0 g of NaCl. Twisters were then gently rinsed with ultrapure water, dried  
185 with Kimwipes® precision paper, then placed at -18 °C until the elimination study.

186 After deployment, the Twisters were then gently rinsed with ultrapure water, dried with  
187 Kimwipes® precision paper, then stored at -18 °C until chemical analysis.

188

### 189 3.3 Flow-through experiments

190

#### 191 3.3.1 Passive SBSE calibration

192

193 For the calibration of passive SBSE, 15 triplicates of Twisters were immersed in 15 glass  
194 channels (3 L each) supplied by means of individual pumps with 70 L of tap water spiked  
195 with the target pesticides at nominal concentrations ranging from 0.20 to 40  $\mu\text{g L}^{-1}$  located in  
196 a glass aquarium (Fig. 1). We selected these concentrations as low as possible, while allowing  
197 direct chemical analysis without pre-concentration. In order to offset the adsorption of the  
198 pesticides onto the surfaces of the calibration system (glass aquarium, and silicone and PVC  
199 pipes) and to ensure constant concentrations, a continuous spiking of the water in the

200 aquarium was realised. The experiment was performed for 7 days at 20 °C and flow velocity  
201 was 2.5 cm s<sup>-1</sup>. Triplicates of Twisters were collected at different times (2, 4, 6, 8, 10, 24, 28,  
202 32, 48, 56, 72, 80, 96 and 168 h) to follow the accumulation kinetics.

203

### 204 3.3.2 Effect of flow velocity on pesticide uptakes

205

206 To investigate the effect of flow velocity on the uptakes of the target pesticides, we immersed  
207 two triplicates of Twisters in two channels supplied with tap water spiked at the same  
208 concentrations as those applied for the calibration. This study was performed for 4 days at 25  
209 °C with the same flow-through system and with continuous spiking. In the first channel, flow  
210 velocity was 2.5 cm s<sup>-1</sup>, whereas in the second channel, flow velocity was 0.1 cm s<sup>-1</sup>. Also, to  
211 determine pesticide uptakes in static conditions, we immersed a Twister in a 1-L amber glass  
212 flask filled with the same pesticide solution (flow velocity = 0 cm s<sup>-1</sup>). For the accumulation  
213 in static conditions, the spiked water was replaced daily by 1 L of freshly prepared pesticide  
214 solution. All Twisters were collected at the same time after the 4 days of accumulation.

215

### 216 3.3.3 Elimination kinetics

217

218 Based on the study of the effect of flow velocity on pesticide uptakes, we selected fenitrothion  
219 and fenitrothion-d6 for elimination kinetic experiment with the same flow-through system and  
220 under the same conditions as for the calibration, *i.e.*, at 20 °C and 2.5 cm s<sup>-1</sup>. In this case,  
221 however, the Twisters, previously loaded with fenitrothion and fenitrothion-d6, were  
222 immersed in triplicates in non-spiked tap water. Triplicates of loaded Twisters were immersed  
223 in 9 channels and were collected at different times (6, 10, 24, 48, 72, 96, 120, 144, 168 h) to  
224 follow the elimination kinetics.

225

#### 226 3.3.4 Monitoring of experimental conditions

227

228 Every time a triplicate of Twisters was collected during the calibration and every day during  
229 the study of the effect of flow velocity on the pesticide uptakes, a water sample was collected  
230 from the channels and from the amber glass flask to measure concentrations of pesticides.  
231 Moreover, water temperature was checked every day during the calibration and elimination  
232 experiments, and the study of the effects of flow velocity on pesticide uptakes. Finally, flow  
233 velocity was measured at the beginning and at the end of all three experiments.

234

#### 235 3.4 Chemical analysis

236

237 The target pesticides were analyzed by liquid chromatography coupled with tandem mass  
238 spectrometry (LC-MS/MS) in two types of samples called the “Twister extracted samples”  
239 and the “water samples”. On the one hand, pesticides were desorbed from Twisters according  
240 to an analytical method published elsewhere [28]. Briefly, after storage at -18 °C, Twisters  
241 were placed in 200  $\mu\text{L}$  of methanol/acetonitrile (50:50, v/v), and pesticides were desorbed  
242 under sonication for 15 min (*i.e.*, liquid desorption - LD). Then, 150  $\mu\text{L}$  of ultrapure water  
243 and 10  $\mu\text{L}$  of diuron-d6 at 200  $\mu\text{g L}^{-1}$ , in acetone, were added to 40  $\mu\text{L}$  of the desorbate to  
244 constitute the Twister extracted sample for analysis. On the other hand, for the verification of  
245 constant pesticide concentrations, the water samples were constituted with 990  $\mu\text{L}$  aliquots of  
246 spiked tap water collected from the channels and from the amber glass flask and 10  $\mu\text{L}$  of  
247 diuron-d6 at 1000  $\mu\text{g L}^{-1}$ , in acetone. For both types of samples, the concentration of the  
248 internal standard diuron-d6 was 10  $\mu\text{g L}^{-1}$ .

249 The analyses of the Twister extracted samples and of the water samples were performed using  
250 an LC 1100 Series apparatus from Agilent (Massy, France) coupled with an MS triple  
251 quadrupole API4000 from AB SCIEX (Les Ulis, France), equipped with an electrospray  
252 ionization source (ESI) that was operated in the positive ionization mode. An Atlantis T3 (2.1  
253 mm x 100 mm;  $d_p = 3 \mu\text{m}$ ), purchased from Waters (St Quentin-en-Yvelines, France) was  
254 used for the chromatographic separation of the contaminants. Acetonitrile and ultrapure water  
255 both with formic acid (0.1%) were used in an analytical gradient (from 10% to 90% acidic  
256 acetonitrile) of 15 min.

257

## 258 **4. Results and discussion**

259

### 260 4.1 Passive SBSE calibration

261

#### 262 4.1.1 Uptake kinetics

263

264 Mean measured pesticide concentrations in water (between 0.17 and 14.3  $\mu\text{g L}^{-1}$ ) were lower  
265 than nominal spiked concentrations (from 0.20 to 40  $\mu\text{g L}^{-1}$ ). Relative standard deviations  
266 (RSD) ranged from 12 to 44%, except for diflufenican, flufenoxuron, and fenitrothion, for  
267 which RSD ranged from 60 to 85% (Table 1). High RSD were observed for water  
268 concentrations of these 3 pesticides because, in spite of continuous spiking, their  
269 concentrations decreased dramatically (46 to 72% decrease) between the start of the  
270 calibration and the first sampling time ( $t = 2 \text{ h}$ ). This decrease was due to massive adsorption  
271 of these 3 hydrophobic pesticides ( $\log K_{ow} > 3.3$ , Table 1) onto the surfaces of the calibration  
272 system, composed of a glass aquarium, and silicone and PVC pipes. This phenomenon

273 explains why measured pesticide concentrations were lower than nominal pesticide  
274 concentrations.

275 Uptake kinetic curves of insecticides, fungicides and herbicides are presented in Fig. 2a, Fig.  
276 2b and Fig. 2c, respectively. Satisfactory to relatively poor repeatability for the masses of all  
277 target pesticides accumulated in Twisters and for all sampling times was obtained since RSD  
278 ranged from 0.5 to 41% ( $n = 3$ ) for most pesticides and ranged from 51 to 59% for  
279 metolachlor, dimethomorph and flufenoxuron (data not shown). These RSD take into account  
280 the accumulation of target pesticides in the Twisters, the liquid desorption process and the  
281 LC-MS/MS analysis. The relatively poor repeatability was caused by the variations in the  
282 water concentrations. However, these repeatability results are in good agreement with  
283 previous field application of passive SBSE in river water [26].

284 Curvilinear patterns were observed for the uptake of insecticides, fungicides and herbicides.  
285 For all target pesticides, equilibrium was reached before the end of the calibration (7 days),  
286 and the linear accumulation periods ranged from 1.5 to 4 days. This means that for 1-week  
287 field application of Twisters, the TWA concentrations might not be considered as integrative,  
288 but only indicative. However, these results are in the same order of magnitude as those of the  
289 study of Zhao et al. [29], although the authors studied the accumulation kinetics of PAH such  
290 as pyrene ( $\log K_{ow} = 4.88$ ) in PDMS rods, which are similar to our device. In that study,  
291 equilibrium regime for pyrene was reached in about 100 h for PDMS rods placed in a flow-  
292 through system supplied by spiked deionized water. In contrast, linear accumulation periods  
293 up to 14 days have been reported for the passive sampling of PAH and PCB with MESCO  
294 [20]. However, the MESCO is composed of a Twister as receiving phase and a low density  
295 polyethylene (LDPE) membrane that separates the receiving phase from the medium. This  
296 LDPE membrane constitutes an additional kinetic barrier regarding the accumulation of

297 organic contaminants in the Twister and probably slows down the uptake rates, resulting in  
298 longer accumulation periods.

299 In the present study, we performed the calibration of the passive SBSE for a broad range of  
300 pesticides ( $2.18 < \log K_{ow} < 5.11$ ). Previous lab or *in situ* studies have focused on some of  
301 these pesticides such as acetochlor, simazine, atrazine, isoproturon, chlortoluron, linuron,  
302 metolachlor, chlorfenvinphos, fenitrothion, chlorpyrifos-ethyl, and organochlorine and  
303 organophosphate pesticides [1, 2, 4, 6, 10, 18, 20, 30-35]. Nevertheless, to our knowledge, the  
304 passive sampling of moderately hydrophobic to hydrophobic pesticides targeted in our study  
305 such as flufenoxuron, diflufenican, tebuconazole, procymidon, dimethomorph, azoxystrobin  
306 and norflurazon has scarcely been reported in the literature [26].

307

#### 308 4.1.2 Lag-phases and sampling rates ( $R_s$ )

309

310 The first triplicate of Twisters was collected after 2 h of exposition in spiked water. Even after  
311 this short exposition, the target pesticides accumulated in the Twisters; masses were 10 to  
312 114-fold larger than the corresponding limits of quantification, estimated at signal-to-noise  
313 ratios of 10 (Table 1). This means that the lag-phases for all target pesticides were shorter  
314 than 2 h. Indeed, without a membrane, mass transfer of target pesticides was faster than for  
315 membrane-equipped passive samplers such as MESCO [20] or SPMD [7]. Thus, passive  
316 SBSE could be an efficient technique for the monitoring of transient concentration peaks of  
317 the target pesticides in surface waters such as small dynamic rivers located in vineyard  
318 watersheds [26, 36]. For these pesticides, one could use larger samplers such as LPDE, SR, or  
319 SPMD, as they would behave similarly as Twisters regarding lag-phases, and linear  
320 accumulation periods would be longer. Nevertheless, Twister used as a passive sampler  
321 allows simple handling, preparation before deployment, *in situ* deployment and sample

322 treatment after exposition. Moreover, as Twister is originally an efficient analytical extraction  
323 device, the recovery of contaminants sequestered in the PDMS phase implies a faster, easier  
324 and less organic solvent-consuming treatment process [25].

325 Sampling rates ( $R_s$ ) were calculated according to Eq. 2 and Eq. 3, by dividing the slope of the  
326 linear accumulation by the average pesticide concentration relative to this period. The linear  
327 accumulation periods were defined so that the correlation coefficients  $r^2$  were higher than 0.8.  
328 Sampling rates were between  $1.3 \text{ mL d}^{-1}$  and  $121 \text{ mL d}^{-1}$ , with RSD ranging from 9 to 47%,  
329 except for fenitrothion, diflufenican, and flufenoxuron, for which RSD were between 59 and  
330 83% (Table 2). The RSD of  $R_s$  of each pesticide was calculated by propagation of variance  
331 with the variance of the slope of the linear accumulation and the variance of the pesticide  
332 concentration in water. The high RSD for the  $R_s$  of fenitrothion, diflufenican, and  
333 flufenoxuron were caused by the high variance of water concentrations of the corresponding  
334 pesticides, reported in section 4.1.1.

335 In Table 2, pesticides are sorted by increasing values of  $\log K_{ow}$ . The highest  $R_s$  value was  
336 obtained for fenitrothion with  $\log K_{ow} = 3.32$ . Then,  $R_s$  values decreased for tebuconazole,  
337 chlorfenvinphos, acetochlor, diflufenican, chlorpyrifos-ethyl and flufenoxuron. The control of  
338 the accumulation kinetics by the WBL at the Twister surface might explain this decrease.  
339 Indeed, studies have suggested the uptake control by the WBL for compounds with  $\log K_{ow}$   
340 values higher than 4.5 to 5.0, regarding non-polar passive samplers with membrane such as  
341 SPMD [7], MESCO and Chemcatcher, as well as for samplers without membrane such as  
342 LDPE membranes and silicon strips [27]. Our experimental results might corroborate the  
343 WBL control reported in the literature [27], although in our case this would be for compounds  
344 with  $\log K_{ow}$  higher than 3.3. Therefore, the accumulation kinetics of the target pesticides with  
345  $\log K_{ow}$  larger than 3.3 may be controlled by the WBL; so exposition conditions, especially  
346 flow velocity, may have an impact on their uptakes in Twisters.

347

#### 348 4.2 Effect of flow velocity on pesticide uptakes

349

350 Mean pesticide concentrations in water were between 0.13 and 19.6  $\mu\text{g L}^{-1}$  with satisfactory to  
351 relatively high RSD, ranging from 21 to 73% (data not shown). Nevertheless, satisfactory  
352 RSD were obtained for the masses of pesticides accumulated in the Twisters at the end of the  
353 4-day experiment. For the Twisters placed in the channel with flow velocity at 2.5  $\text{cm s}^{-1}$ ,  
354 RSD ranged from 2 to 32%, whereas RSD were between 10 and 44% for the Twisters placed  
355 in the channel with flow velocity at 0.1  $\text{cm s}^{-1}$  (data not shown). Fig. 3 presents the masses of  
356 pesticides for which an ANOVA ( $\alpha = 0.05$ ) confirmed a significant effect of flow velocity  
357 on the uptakes. Pesticide uptakes in static conditions were similar to those at 0.1  $\text{cm s}^{-1}$  for  
358 fenitrothion and chlorfenvinphos, and relatively close for diflufenican, chlorpyrifos-ethyl and  
359 flufenoxuron. But, a significant increase of the masses of fenitrothion, chlorfenvinphos,  
360 diflufenican, chlorpyrifos-ethyl and flufenoxuron was observed with an increase in flow  
361 velocity from 0.1  $\text{cm s}^{-1}$  to 2.5  $\text{cm s}^{-1}$ . Therefore, the accumulation kinetics of these  
362 hydrophobic compounds ( $\log K_{ow} > 3.3$ ) in the Twisters was controlled by the WBL. Faster  
363 flow decreased the thickness of the WBL, so that the transfer of these organic contaminants to  
364 the receiving phase was faster. These results confirm, except for tebuconazole and acetochlor,  
365 the assumption made in section 4.1.2 that the accumulation kinetics of the target pesticides  
366 with  $\log K_{ow}$  larger than 3.3 are controlled by the WBL. Moreover, this suggests that PRC  
367 might be needed for the determination of unbiased TWA concentrations of these compounds.  
368 In contrast, for less hydrophobic compounds ( $2.18 < \log K_{ow} < 3.3$ ), no effect of flow velocity  
369 was observed. Therefore, we can assume accumulation kinetics controlled by the receiving  
370 phase, and also that the uptakes of these pesticides might be less dependent or independent



371 from exposition conditions. As a result, no PRC might be required for determination of TWA  
372 concentration of these pesticides.

373

#### 374 4.3 Elimination kinetics

375

376 Fenitrothion showed an uptake strongly dependent on flow velocity, *i.e.*, WBL-controlled  
377 accumulation kinetics, and was accumulated in the Twister 3 to 5 times more than  
378 chlorfenvinphos, diflufenican, chlorpyrifos-ethyl and flufenoxuron (Fig. 3). Moderate to high  
379 elimination of fenitrothion from the receiving phase of the Twister and isotropic exchange  
380 still had to be verified for fenitrothion-d6 to be a PRC candidate. Therefore, the elimination  
381 kinetics of fenitrothion and fenitrothion-d6 was followed for 7 days (Fig. 4). The pesticide  
382 and its deuterated analogue showed very similar elimination kinetics and high elimination  
383 from the PDMS phase of the sampler. Over the 7 days of exposition, 82% of the initial mass  
384 of the two compounds were eliminated.

385 Knowing that the calibration and the elimination studies were conducted under the same  
386 conditions (temperature and flow velocity), we compared the elimination rate constant of  
387 fenitrothion derived from the calibration ( $k_{e-Cal}$ ) with the directly measured elimination rate  
388 constant ( $k_e$ ), as it is a useful way to verify isotropic exchange kinetics [3]. Calibration-  
389 derived elimination rate constant of fenitrothion was calculated using Eq. 2, where  $K_{sw}$  was  
390 determined with the calibration data, since all target pesticides reached equilibrium by the end  
391 of the 7-day experiment. Calibration-derived elimination rate constant  $k_{e-Cal}$  ( $0.297\text{ d}^{-1}$ ) was  
392 slightly larger than directly measured  $k_e$  ( $0.253\text{ d}^{-1}$ ) for fenitrothion. Therefore, since  
393 fenitrothion-d6 ( $0.260\text{ d}^{-1}$ ) showed similar elimination kinetics as fenitrothion, we can assume  
394 isotropic exchange for both compounds and we identified fenitrothion-d6 as a PRC candidate.  
395 Field exposition of the Twisters spiked with fenitrothion-d6 will allow us to evaluate this

396 compound as PRC for the determination of unbiased TWA concentrations of target pesticides  
397 with accumulation kinetics under WBL control. To do so, since one PRC candidate has been  
398 identified so far, the exposure adjustment factor (EAF) methodology would be used [3].

399

## 400 **5. Conclusion**

401

402 This study focused on the calibration of passive SBSE for the monitoring of 18 moderately  
403 hydrophobic to hydrophobic pesticides in waters. Firstly, we determined sampling rates of the  
404 target pesticides ranging from 1.3 to 121 mL d<sup>-1</sup> and observed linear accumulation periods  
405 between 1.5 to 4 days. Secondly, results revealed that flow velocity had an effect on the  
406 uptakes of 5 of the most hydrophobic target pesticides ( $\log K_{ow} > 3.3$ ), due to WBL control,  
407 and we assumed receiving phase-controlled accumulation kinetics for the moderately  
408 hydrophobic pesticides ( $2.18 < \log K_{ow} < 3.3$ ). Thirdly, among these 5 hydrophobic  
409 pesticides, we selected fenitrothion for the elimination study, along with its deuterated  
410 analogue fenitrothion-d6. We observed similar elimination kinetics of the two compounds and  
411 verified isotropic exchange for fenitrothion. Therefore, fenitrothion-d6 is a promising PRC  
412 candidate for the determination of TWA concentrations for *in situ* applications. Future work  
413 will focus on the implementation of the calibration data and use of fenitrothion-d6 for  
414 quantitative purposes.

415 Passive SBSE is a simple and environmentally friendly passive sampling technique for the  
416 monitoring of target pesticides in freshwaters. Very small volumes of organic solvents are  
417 required to recover the absorbed contaminants by liquid desorption, and the small size of the  
418 Twisters allows simple handling, preparation before deployment and *in situ* deployment.  
419 Moreover, without a membrane, lag-phases of passive SBSE are shorter than most samplers  
420 equipped with membranes such as POCIS and MESCO. Thus, passive SBSE could be

421 efficient for the monitoring of transient concentration peaks of the target pesticides in  
422 freshwaters.

423

424 **Acknowledgements**

425

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429 support.

430

431 **Table 1** Mean water concentrations (n = 16), limits of quantification (LQ) reached by the  
 432 analytical system and mass of target pesticides accumulated in the Twisters (n = 3) after 2-h  
 433 exposition during flow-through calibration for 7 days at 20 °C and flow rate of 2.5 cm s<sup>-1</sup>

| Pesticide           | Log K <sub>ow</sub> | Use | Water concentration (n = 16)  |                            |         | Mass of pesticides accumulated (ng) |                                 |
|---------------------|---------------------|-----|-------------------------------|----------------------------|---------|-------------------------------------|---------------------------------|
|                     |                     |     | Nominal (µg L <sup>-1</sup> ) | Mean (µg L <sup>-1</sup> ) | RSD (%) | LQ                                  | After 2 h of exposition (n = 3) |
| Simazine            | 2.18                | H   | 0.20                          | 0.30                       | 13      | 0.01                                | 0.14                            |
| Chlortoluron        | 2.41                | H   | 4.0                           | 4.3                        | 14      | 0.2                                 | 1.9                             |
| Norflurazon         | 2.30                | H   | 16.0                          | 14.3                       | 21      | 0.8                                 | 8.1                             |
| Azoxystrobin        | 2.50                | F   | 4.0                           | 2.9                        | 16      | 0.2                                 | 6.1                             |
| Atrazine            | 2.61                | H   | 1.0                           | 0.9                        | 13      | 0.1                                 | 1.1                             |
| Dimethomorph        | 2.68                | F   | 4.0                           | 3.7                        | 14      | 0.2                                 | 2.4                             |
| 3,4-dichloroaniline | 2.69                | M   | 20.0                          | 11.3                       | 26      | 1.0                                 | 44.4                            |
| Isoproturon         | 2.87                | H   | 8.0                           | 8.1                        | 12      | 0.4                                 | 4.3                             |
| Procymidon          | 3.08                | F   | 40.0                          | 6.5                        | 44      | 2.0                                 | 120                             |
| Metolachlor         | 3.13                | H   | 0.40                          | 0.17                       | 24      | 0.02                                | 1.31                            |
| Linuron             | 3.20                | H   | 8.0                           | 3.8                        | 25      | 0.4                                 | 3.1                             |
| Fenitrothion        | 3.32                | I   | 40.0                          | 2.3                        | 85      | 2.0                                 | 102                             |
| Tebuconazole        | 3.70                | F   | 5.0                           | 3.2                        | 18      | 0.3                                 | 14.1                            |
| Chlorfenvinphos     | 3.81                | I   | 8.0                           | 2.0                        | 34      | 0.4                                 | 33.1                            |
| Acetochlor          | 4.14                | H   | 20.0                          | 7.7                        | 27      | 2.0                                 | 76.5                            |
| Diflufenican        | 4.20                | H   | 4.0                           | 0.2                        | 60      | 0.2                                 | 6.1                             |
| Chlorpyrifos-ethyl  | 4.96                | I   | 4.0                           | 0.2                        | 21      | 0.2                                 | 4.3                             |
| Flufenoxuron        | 5.11                | I   | 40.0                          | 10.5                       | 74      | 0.4                                 | 45.4                            |

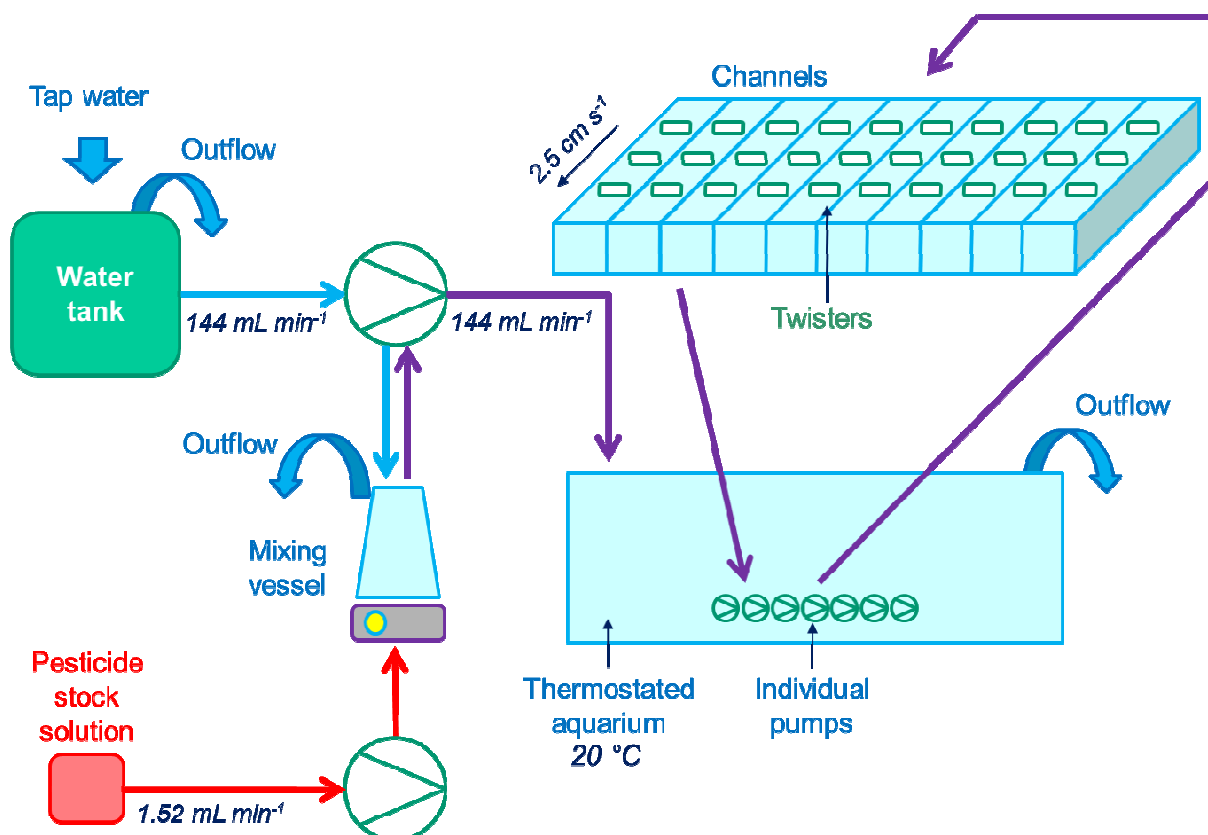
H: herbicide, F: fungicide, M: metabolite, I: insecticide

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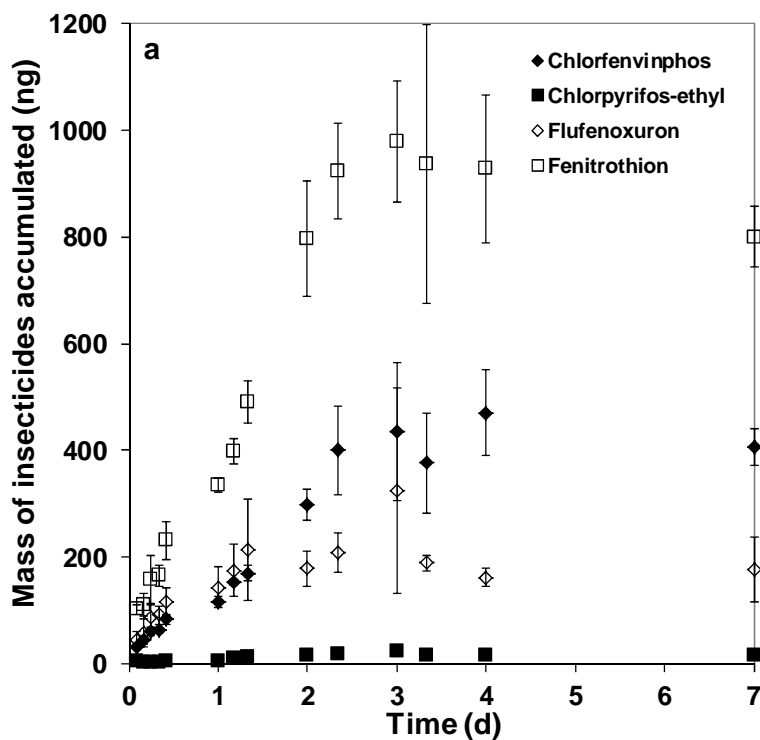
438 **Table 2** Passive SBSE sampling rates (R<sub>s</sub>) derived from flow-through calibration for 7 days at  
 439 20 °C and flow rate of 2.5 cm s<sup>-1</sup> (n = 3)

| Pesticide           | R <sub>s</sub> (mL d <sup>-1</sup> ) | RSD (n = 3) (%) |
|---------------------|--------------------------------------|-----------------|
| Simazine            | 1.4                                  | 9               |
| Chlortoluron        | 0.8                                  | 17              |
| Norflurazon         | 1.5                                  | 15              |
| Azoxystrobin        | 4.3                                  | 17              |
| Atrazine            | 2.6                                  | 16              |
| Dimethomorph        | 1.7                                  | 18              |
| 3,4-dichloroaniline | 1.9                                  | 25              |
| Isoproturon         | 1.3                                  | 14              |
| Procymidon          | 34.1                                 | 47              |
| Metolachlor         | 21.9                                 | 19              |
| Linuron             | 23.2                                 | 25              |
| Fenitrothion        | 121                                  | 83              |
| Tebuconazole        | 10.7                                 | 20              |
| Chlorfenvinphos     | 62.5                                 | 34              |
| Acetochlor          | 26.2                                 | 23              |
| Diflufenican        | 59.2                                 | 59              |
| Chlorpyrifos-ethyl  | 27.6                                 | 22              |
| Flufenoxuron        | 6.6                                  | 75              |

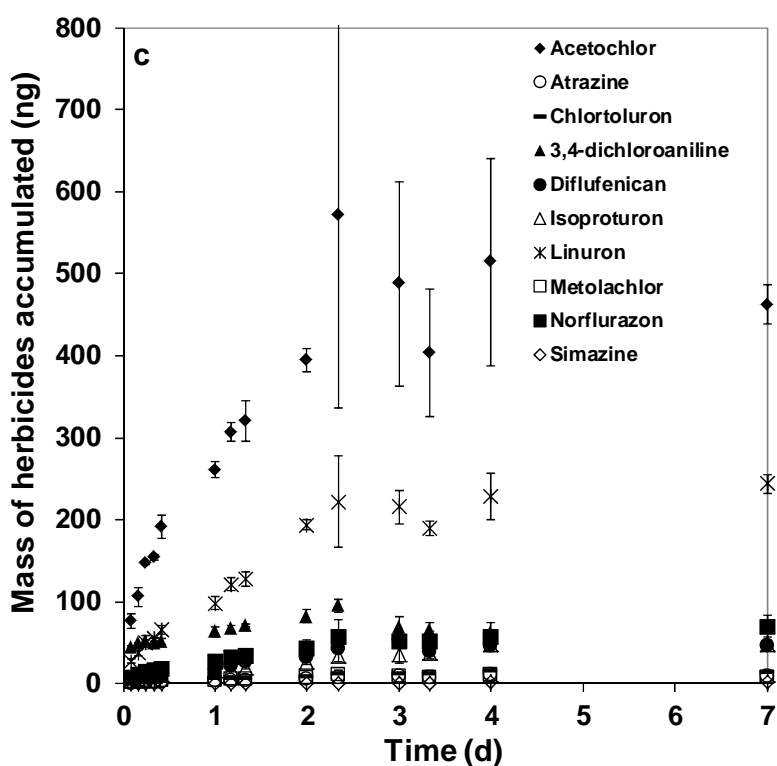
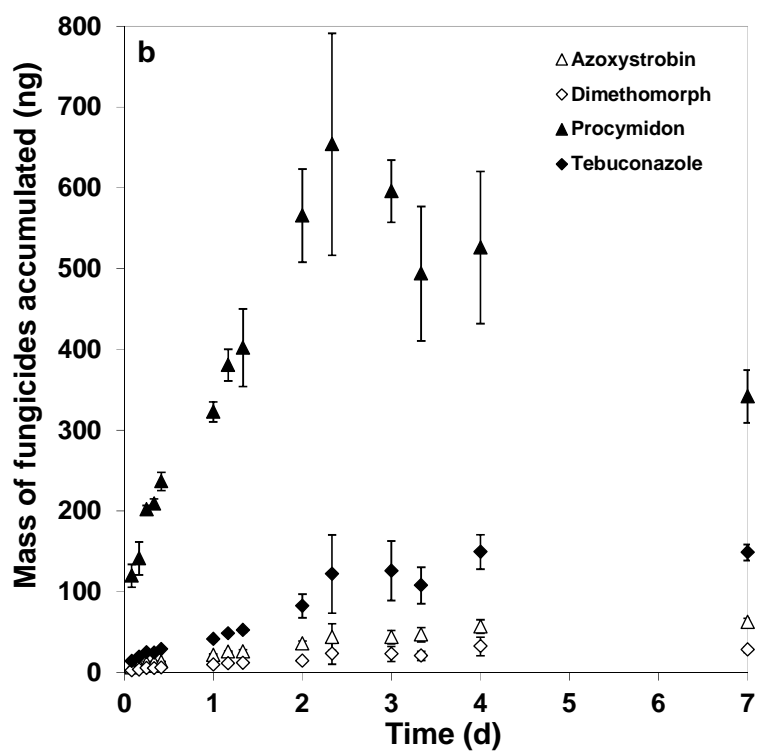
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453 **Fig. 1** Schematized flow-through system for calibration of passive SBSE. Triplicates of  
454 Twisters are immersed in tap water at  $20 \text{ }^\circ\text{C}$  spiked with the target pesticides, located in a  
455 glass aquarium and flowing by means of individual pumps in all channels at  $2.5 \text{ cm s}^{-1}$   
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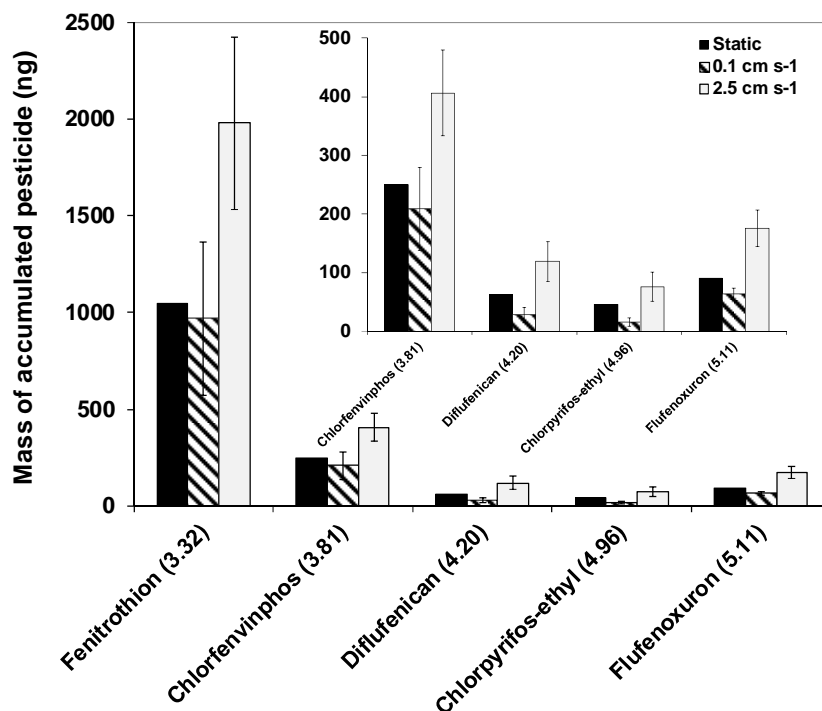
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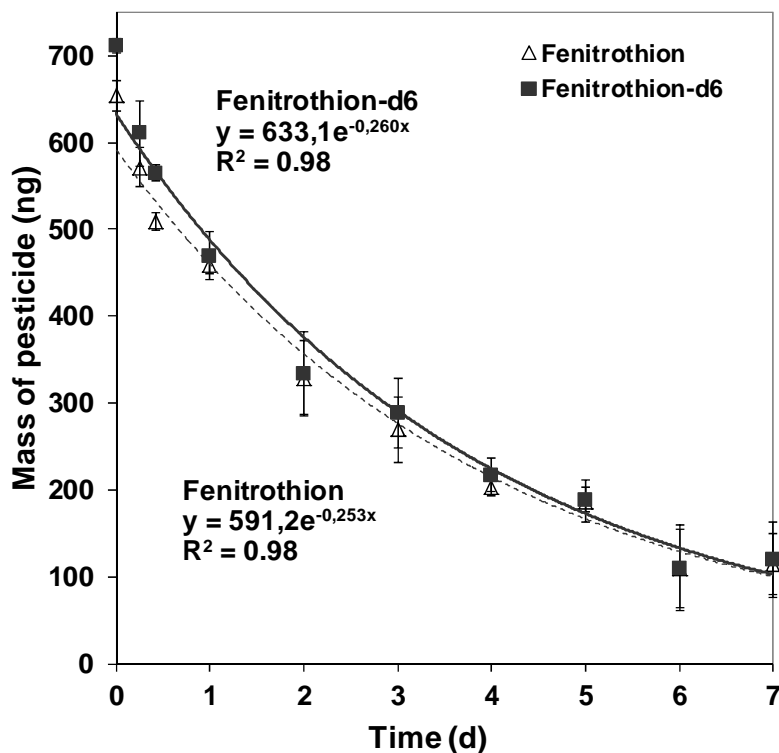
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**Fig. 2** Uptake curves of (a) insecticides, (b) fungicides and (c) herbicide in Twisters during flow-through calibration for 7 days at 20 °C and 2.5 cm s<sup>-1</sup>. Errors bars represent ± s (n = 3)



464  
 465 **Fig. 3** Effect of flow velocity on uptakes of selected pesticides in Twisters during flow-  
 466 through and static experiments for 4 days at 25 °C. Errors bars represent  $\pm s$  (n = 3)  
 467



468  
 469 **Fig. 4** Elimination curves of fenitrothion and fenitrothion-d6 from Twisters during flow-  
 470 through experiment for 7 days at 20 °C and flow rate of 2.5 cm s<sup>-1</sup>. Errors bars represent  $\pm s$  (n  
 471 = 3)  
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