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1 **How do PDMS-coated stir bars used as passive samplers integrate**
2 **concentration peaks of pesticides in freshwater?**

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6

7
8 **Abstract**

9 Passive samplers are theoretically capable of integrating variations of concentrations of
10 micropollutants in freshwater and providing accurate average values. However, this property
11 is rarely verified and quantified experimentally. In this study, we investigated, in controlled
12 conditions, how the polydimethylsiloxane-coated stir bars (passive Twisters) can integrate
13 fluctuating concentrations of 20 moderately hydrophilic to hydrophobic pesticides ($2.18 <$
14 $\text{Log } K_{ow} < 5.51$). In the first two experiments, we studied the pesticide accumulation in the
15 passive Twisters during high concentration peaks of various durations in tap water. We then
16 followed their elimination from the passive Twisters placed in non-contaminated water
17 (Experiment n°1), or in water spiked at low concentrations (Experiment n°2) for one week. In
18 the third experiment, we assessed the accuracy of the time-weighted average concentrations
19 (TWAC) obtained from the passive Twisters exposed for four days to several concentration
20 variations scenarios. We observed little to no elimination of hydrophobic pesticides from the
21 passive Twisters placed in non-contaminated water, and additional accumulation when placed
22 in water spiked at low concentrations. Moreover, passive Twisters allowed determining
23 accurate TWAC (accuracy, determined by TWAC-average measured concentrations ratios,
24 ranged from 82 to 127 %) for the pesticides with $\text{Log } K_{ow}$ higher than 4.2. In contrast, fast and
25 large elimination was observed for the pesticides with $\text{Log } K_{ow}$ lower than 4.2 and poorer
26 TWAC accuracy (ranging from 32 to 123 %) was obtained.

27 **Keywords:** Passive sampling, passive SBSE, variations of concentrations, time-weighted
28 average concentrations (TWAC)

29

30

31 **Introduction**

32

33 Passive sampling allows the determination of representative time-weighted average
34 concentrations (TWAC) of micropollutants such as pesticides in freshwater, for lower
35 logistical and analytical costs than spot sampling at high sampling frequency (Poulier et al.
36 2014). In case of periodic concentration peaks, such as during flood events in small
37 agricultural watersheds, greater attention to the determination of accurate TWAC is needed
38 for ecological risk assessment and decision making. Indeed, floods are a major pathway for
39 the transport of pesticides in rivers located in vineyard watershed (Kreuger 1998; Rabiet et al.
40 2010). Recent studies demonstrated that the lambda-cyhalothrin peak exposure scenario (10-
41 fold higher concentrations for 10-fold shorter exposure duration) could result in a higher
42 ecotoxicity to aquatic invertebrates such as *Gammarus fossarum* than a longer exposure
43 period at lower concentrations (Bundschuh et al. 2013).

44 Based on the commercial laboratory extraction technique Stir Bar Sorptive Extraction
45 (SBSE), the passive SBSE was recently developed for the passive sampling of pesticides in
46 river waters (Assoumani et al. 2013; Assoumani et al. 2014; Assoumani et al. 2015),
47 especially for the integration of transient concentration peaks resulting from flood events.
48 Gerstel Twisters® (herein called “passive Twisters”) were exposed without membrane
49 directly in small rivers to accumulate pesticides and integrate transient variations of pesticide
50 concentrations.

Mis en forme : Anglais (États Unis)

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51 The theory of passive sampling is well established and documented (Vrana et al. 2005;
52 Huckins et al. 2006; Greenwood et al. 2007); and the passive SBSE follows the same theory
53 as described by these authors. Assuming isotropic exchange, the accumulation of a
54 micropollutant in a passive Twister over time with constant ambient water concentration
55 obeys a first-order kinetics, described by Eq. 1 (Assoumani et al. 2014):

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

56 where M_s (ng) is the mass of micropollutant accumulated in the receiving phase; C_w (ng L⁻¹)
57 is the concentration of micropollutant in the water phase; K_{sw} (adimensional) described by the
58 ratio of the concentration at equilibrium of micropollutant in the receiving phase C_s (ng L⁻¹)
59 and the concentration at equilibrium of micropollutant in the water phase C_w (ng L⁻¹), is the
60 receiving phase/water partition coefficient; V_s (L) is the volume of the receiving phase; R_s is
61 the sampling rate (L d⁻¹); and t (d) is the duration of exposure.

62 The accumulation kinetics is composed of a linear phase, and then, a curvilinear phase, before
63 reaching the equilibrium. In the initial phase, the linear accumulation is integrative, and
64 defined as follows (Eq. 2):

$$M_s(t) = C_w R_s t \quad (2)$$

65 During this period, the fluctuations of concentrations are theoretically integrated by the
66 sampler with negligible elimination of micropollutant after the peak events. The accumulation
67 half-life of the micropollutants ($t_{1/2}$) is commonly defined as the limit of this linear period, and
68 samplers exposed in the field during this period are therefore expected to provide TWAC
69 (Vrana et al. 2005; Huckins et al. 2006; Greenwood et al. 2007).

70 In case of linear integrative accumulation, the TWAC (C_w) is calculated with the following
71 equation (Eq. 3), derived from Eq. 2:

$$C_w = \frac{M_s}{R_s t} \quad (3)$$

72 In case of curvilinear accumulation, for instance for exposure periods larger than $t_{1/2}$, TWAC
73 can still be determined with the following equation (Eq. 4):

$$C_w = \frac{M_s}{K_{sw} V_s (1 - \exp(-\frac{R_s t}{K_{sw} V_s}))} \quad (4)$$

74 However, during the curvilinear accumulation period, the uptake of micropollutants is not
75 integrative (Vrana et al. 2005; Huckins et al. 2006; Greenwood et al. 2007), and these TWAC
76 might be less accurate, in case the passive sampler is exposed to fluctuating concentrations.

77 Lately, the behavior of passive samplers regarding fluctuating concentrations has been
78 investigated through modeling and laboratory studies. Gourlay-Francé et al. (2008) modeled
79 the impact of the duration of the linear accumulation period (i.e., the $t_{1/2}$ value) of polycyclic
80 aromatic hydrocarbons (PAH) in semipermeable membrane device (SPMD) on the accuracy
81 of the TWAC. Shaw and Mueller (2009) investigated the integration of the pesticides
82 concentration fluctuations by Chemcatcher and the accuracy of TWAC through modeling and
83 laboratory experiments. Hawker (2010) modeled the responses of passive samplers to several
84 patterns of concentration variations of organic micropollutants. On the one hand, these studies
85 showed the capabilities of different passive samplers for integrating various patterns of
86 concentration fluctuations. On the other hand, deviation between the TWAC and the
87 theoretical concentration or the average spot sample concentration reached up to 100 %,
88 depending on the passive sampler, the half-life of monitored micropollutants, and the
89 magnitude, time and duration of concentration variations. This shows that (i) further
90 knowledge about how passive samplers integrate concentration peaks is needed, (ii) the
91 deviation of TWAC from the actual average concentrations is sampler- and micropollutant-
92 dependent, and (iii) concentration peak experiments in controlled conditions need to be

93 performed for new tools such as passive SBSE to fully assess the deviation of the derived
94 TWAC in a context of fluctuating concentrations.

95 To this end, we designed three laboratory experiments and exposed the passive Twisters to
96 several scenarios of concentration variations. In Experiment n°1 and n°2, we exposed the
97 passive Twisters to fast and high integration peaks, and then to low concentration levels for
98 seven days. We observed how the passive Twisters integrated the concentration peaks of
99 pesticides, and then, how the pesticides eliminated from the passive Twisters exposed in low
100 concentration level water. And in Experiment n°3, we exposed the passive Twisters to several
101 scenarios of low magnitude variations of concentrations through a four-day flow-through
102 kinetic study and we assessed the accuracy of the derived TWAC.

103

104 **Experimental**

105

106 **Chemicals and materials.** The 20 pesticides selected for this study belong to different use
107 classes (herbicides, insecticides, and fungicides) and chemical classes (triazines, substituted
108 ureas, triazoles, and organophosphate compounds); they have various physical chemical
109 properties, such as their octanol-water partition coefficient (Log K_{ow}) (Table 1). We selected
110 acetochlor, atrazine, azoxystrobin, chlorfenvinphos, chlorpyrifos, chlorpyrifos-methyl,
111 chlortoluron, 3,4-dichloroaniline (metabolite of diuron), diflufenican, dimethomorph,
112 flufenoxuron, fenitrothion, isoproturon, linuron, metolachlor, norflurazon, procymidon,
113 simazine, spiroxamine, and tebuconazole (all with purity $\geq 92.5\%$), purchased from Dr.
114 Ehrenstorfer GmbH (Augsburg, Germany).

115 For chemical analyses, diuron-d6 (used as internal standard) was provided by Dr. Ehrenstorfer
116 (purity $\geq 98.5\%$). Ultrapure water was produced by a MilliQ water purification system

117 equipped with an LC-Pak cartridge and purchased from Millipore (Billerica, MA, USA). For
118 passive SBSE, we used Twisters® (20 mm x 1-mm thick polydimethylsiloxane (PDMS) film)
119 purchased from Gerstel (Mülheim a/d Ruhr, Germany). For all experiments, the passive
120 Twisters were placed in water in deployment bags, as described elsewhere (Assoumani et al.
121 2014).

122

123 **Flow-through experiments.** For the flow-through experiments, three levels of pesticides
124 concentrations were selected. In Experiment n°1 and n°2, a high level of concentrations called
125 10C (from 2 to 800 $\mu\text{g L}^{-1}$) was selected for the concentration peaks simulations (in
126 Supplementary Data section, see the nominal and measured pesticide concentrations during
127 the six-hour concentration peak exposure in Experiment n°1 and Experiment n°2 in Table S1
128 and Table S2). In Experiment n°3, two lower levels of concentrations called 1C (from 0.20 to
129 80 $\mu\text{g L}^{-1}$) and 2C (from 0.40 to 160 $\mu\text{g L}^{-1}$) were selected for the evaluation of TWAC
130 accuracy (in Supplementary Data section, see the nominal and measured pesticide
131 concentrations in the contaminated waters at 1C and 2C concentration levels in Experiment
132 n°3 in Table S5). The 1C concentration level was chosen as low as possible to approach
133 environment conditions while allowing direct injection analysis of all the pesticides.

134 To simulate variations of concentrations, different durations of passive Twister exposure as
135 well as different concentration levels were applied. For Experiments n°1 and n°2, we studied
136 the exposure of the passive Twisters to high concentration (10C) for a short period (two, four
137 and six hours), in order to investigate the capabilities of the passive Twisters to integrate fast
138 and high concentration peaks, as encountered during flood events in small agricultural
139 watersheds. Then, we measured the elimination of the pesticides from the passive Twisters in
140 non-contaminated (0C) or contaminated water (1C) for seven days, to determine how long the
141 passive Twisters would keep the pesticide accumulated after the fast concentration peak. In

142 Experiment n°3, we studied different scenarios of exposure of the passive Twisters to lower
143 concentrations (1C and 2C) for a longer period (four days). And then, we assessed the
144 accuracy of the derived TWAC for each scenario and each pesticide.

145 All experiments were realized in glass aquariums filled with 17 L of tap water either non-
146 spiked or spiked at different concentration levels, depending on the experiment. The
147 experiments were realized either in open circuit, i.e., with a continuous renewal of water
148 (spiked or not) in the aquariums, or in closed circuit, i.e., without renewal of the water, as
149 described for each experiment. For the renewal of non-spiked water, tap water flow was 71
150 mL.min⁻¹ for each aquarium, ensuring six renewals of the water a day (in Supplementary Data
151 section, see the schematized systems of Experiment n°1 in Figure S1). For the renewal of spiked
152 water, the pesticide stock solution and tap water were continuously brought into a mixing
153 vessel (in Supplementary Data section, see the schematized systems of Experiment n°2 in Figure
154 S2). Then, the flow of freshly prepared spiked tap water in each aquarium was 71 mL.min⁻¹,
155 ensuring six renewals of the water a day. The aquariums were equipped with one or two
156 diffusion ramps -each one connected to an immersed pump (New Jet 1200, Aquarium
157 Systems NEWA, Italy) creating the water flows (in Supplementary Data section, see Figure
158 S3). Each ramp was composed of four holes, through which the water went out at 20 cm.s⁻¹.
159 The passive Twisters were placed in deployment bags. The deployment bags were attached to
160 stainless steel sticks, which were plunged in the water so that the passive Twisters were
161 placed in front of each hole of the diffusion ramp, in the water flow during the experiment
162 (Figure S3). All three experiments were realized at 20 ± 1 °C; all aquariums were placed in a
163 bath of temperature-controlled water. The temperature of the water of each aquarium was
164 monitored continuously with a data logger (Tiny tag Aquatic 2).

165 In Experiment n°1, three batches of 10 passive Twisters were placed simultaneously in an
166 aquarium filled with tap water spiked with the target pesticides at high concentration level

167 (10C) (Figure S1). To simulate concentration peaks of different durations and to assess their
168 integration of the concentration peaks, one batch of 10 passive Twisters was exposed for two
169 hours to high pesticide concentration (10C), another one for 4 hours, and the last batch for 6
170 hours. Water samples were collected at the beginning of the experiment, and then every 15
171 min for 6 hours to monitor the water concentration of the pesticides (in Supplementary Data
172 section, see the nominal and measured pesticide concentrations during the six-hour
173 concentration peak exposure in Experiment n°1 and Experiment n°2 in Table S1 and Table
174 S2). The concentration peak exposures were realized in a closed circuit. We spiked the tap
175 water with a stock solution of the 20 pesticides at the beginning of the six-hour experiment.
176 According to a previous study (unpublished data), besides the initial spiking of all pesticides,
177 additional spiking of chlorpyrifos, chlorpyrifos-methyl, and diflufenican was realized every
178 hour to keep their concentration constant.

179 After the concentration peak exposures, for the three batches of passive Twisters, seven
180 passive Twisters out of ten were placed (in the same deployment bags) in three aquariums
181 filled with non-contaminated tap water to study the elimination kinetics of the target
182 pesticides for seven days. One passive Twister was collected every day, for seven days, and
183 placed at -18 °C until chemical analysis, to determine the mass of remaining sorbed
184 pesticides. The three remaining passive Twisters of each batch were placed directly at -18 °C
185 before chemical analysis; they constituted the initial point of the elimination kinetics. For the
186 study of the elimination kinetics in Experiment n°1, the three aquariums were in open circuit.
187 Fresh tap water was provided at a flow rate of 71 mL min⁻¹, to replace the water of the
188 aquarium (17 L) six times a day. After one hour of exposure of the passive Twisters in non-
189 contaminated tap water (0C), a water sample was collected in the three aquariums and
190 analyzed directly by solid phase extraction and ultra-high performance liquid chromatography
191 coupled to tandem mass spectrometry (SPE-UHPLC-MS/MS) (in Chemical analysis of water

192 samples and passive Twisters section, see the analysis conditions). The concentrations of the
193 pesticides in the water were checked once, soon after the deployment of the passive Twisters.
194 We supposed this was the moment when the elimination of the pesticides was the largest. This
195 was to check that, with the elimination of the pesticides, the volume of the non-contaminated
196 water and renewal rate of water were sufficient to ensure negligible pesticide concentrations
197 (0C) in comparison with 1C concentrations.

198 Experiment n°2 was similar to Experiment n°1 regarding the concentration peak exposures,
199 but for the elimination kinetics, the passive Twisters were plunged in tap water spiked at low
200 concentration level 1C (in Supplementary Data section, see the schematized systems of
201 Experiment n°2 in Figure S2). To ensure constant water concentrations for seven days, a
202 continuous spiking of all target pesticides was realized. Water samples were collected every
203 day for seven days in the three aquariums, and stored at -18 °C until the chemical analysis.

204 In Experiment n°3, seven batches of passive Twisters were exposed to seven scenarios of low
205 concentration level exposures from 0C to 2C during four days (Table 2) (in Supplementary
206 Data section, see the schematized system of Experiment n°3 in Figure S4). For scenarios n°1, 2
207 and 7, the passive Twisters were exposed for four days to constant concentrations of
208 pesticides, at 0C, 1C and 2C, respectively. For scenarios n°3 to 6, the passive Twisters were
209 exposed to daily variations of concentrations. Three aquariums in flow-through mode were
210 used for this experiment, with a continuous spiking of the pesticides for concentration levels
211 1C and 2C, to ensure constant concentrations. Water samples were taken every day for seven
212 days in the aquariums. For each scenario, six passive Twisters were used to follow the
213 accumulation kinetics of the pesticides. One passive Twister was collected on the first three
214 days, and a triplicate of passive Twisters was collected on the last day to determine the mass
215 of accumulated pesticides and calculate the TWAC.

216

217 **Treatment of passive Twisters.** Prior to the three experiments, the passive Twisters were
218 placed at 300 °C for an hour for thermal conditioning in the Tube Conditioner from Gerstel.
219 The passive Twisters collected during the experiments were taken out of their deployment
220 bags, gently rinsed with ultrapure water, dried with Kimwipes® precision paper, and then
221 stored at -18 °C until chemical analysis.

222
223 **Chemical analysis of water samples and passive Twisters.** Pesticide concentrations in
224 water samples at 1C, 2C and 10C concentration levels were determined in direct injection by
225 UHPLC-MS/MS. Water samples at 0C concentration level were analyzed by SPE-UHPLC-
226 MS/MS. Before extraction and determination of pesticide concentrations, all water samples
227 were filtered with 0.7 µm GF/F glass fiber membranes. The SPE was realized with Oasis
228 HLB cartridges from Waters (3 mL, 60 mg). Briefly, the cartridges were first conditioned
229 with subsequently 3 mL of acetonitrile, 3 mL of methanol, and 3 mL of ultrapure water. Then,
230 250 mL of water sample was charged on the cartridges at 10 mL.min⁻¹ flow rate. Then 2 mL
231 of ultrapure water was passed through the cartridge, before the elution with 6 mL of
232 acetonitrile. The extract was then evaporated to dryness, and the sample was reconstituted in
233 250 µL of a water-acetonitrile mix (80/20, v/v) spiked with diuron-d6 at 10 µg.L⁻¹; the
234 concentration factor was 1000. Pesticides accumulated in the passive Twisters were desorbed
235 and determined by an analytical method that has been published elsewhere (Margoum et al.
236 2013). Briefly, the passive Twisters were then placed in 200 µL of methanol/acetonitrile
237 (50/50, v/v), and the pesticides were desorbed under sonication for 15 min. Finally, 150 µL of
238 ultrapure water and 10 µL of diuron-d6 at 200 µg L⁻¹, in acetone, were added to 40 µL of the
239 desorbate to constitute the sample for chemical analysis.

240 The chemical analyses were performed with a LC Nexera apparatus from Shimadzu (Marne-
241 la-Vallée, France) coupled with a MS triple quadrupole API 4000 from AB Sciex (Les Ulis,

242 France), equipped with an electrospray ionization source (ESI) that was operated in the
243 positive ionization mode. An HSS T3 column (2.1 mm x 100 mm; $d_p = 1.8 \mu\text{m}$) purchased
244 from Waters (St Quentin-en-Yvelines, France) was used for the chromatographic separation
245 of the analytes in 15 min. Acetonitrile and ultrapure water both with formic acid (0.1 %) were
246 used in an analytical gradient from 10 to 90 % acetonitrile in 10 min (Margoum et al. 2013).

247

248 **Results and discussion**

249 **Accumulation and desorption kinetics (Experiment n°1 and n°2).** Figure 1a and Figure 1b
250 show the accumulation kinetics of simazine and chlorpyrifos, respectively, in passive
251 Twisters exposed to a six-hour concentration peak. Simazine and chlorpyrifos present
252 different hydrophobicities and will be taken as examples in this study to graphically illustrate
253 the behaviors we observed from one pesticide to another. Fast accumulation in the passive
254 Twisters was observed for both pesticides. The masses of pesticides measured in the passive
255 Twisters after two, four, and six hours at 10C showed fast accumulation of all pesticides
256 without lag-time, as reported in our previous study (Assoumani et al. 2014). In both
257 experiments, the 10C concentration level caused saturation of the passive Twister PDMS
258 phase for hydrophilic pesticides with $\text{Log } K_{ow} < 3$ after two or four hours of exposure,
259 depending on the hydrophobicity of the micropollutant. The measured water concentrations at
260 10C level for both six hour-accumulation experiments and the accumulation kinetics of all
261 pesticides in both experiments are presented in Supplementary Data section in Table S1 and
262 in Figure S5, respectively. So, for these hydrophilic pesticides, the passive Twisters could not
263 integrate concentration peaks for more than two or four hours, depending on the
264 hydrophobicity of the micropollutant. In contrast, in Experiment n°1, linear accumulations
265 were observed for more hydrophobic micropollutants such as spiroxamine, fenitrothion,
266 diflufenican, chlorpyrifos, chlorpyrifos-methyl, and flufenoxuron. Therefore, passive Twisters

267 were capable of rapidly integrating high concentration peaks of these pesticides for up to six
268 hours. In Experiment n°2, linear accumulations were observed only for chlorpyrifos and
269 flufenoxuron. Slightly faster accumulation rates than Experiment n°1, possibly due to higher
270 average water temperature (21 °C instead of 20 °C in Experiment n°1), might explain faster
271 saturation for spiroxamine, fenitrothion, diflufenican, and chlorpyrifos-methyl. Indeed, Booij
272 et al. (2003) showed that the sampling rates of PAH and polychlorobiphenyls (PCB) in SPMD
273 and low-density polyethylene (LDPE) stripes increased by a 1.5 factor with a 10 °C increase
274 in water temperature.

275 After exposure to concentration peaks, different behaviors were observed for the target
276 pesticides, depending on their hydrophobicity and the experiment. In this paper, we discuss
277 only the results regarding the passive Twisters exposed to 10C concentration level for six
278 hours, since, for all pesticides except spiroxamine, chlorpyrifos-methyl, fenitrothion,
279 diflufenican, chlorfenvinphos (all in Experiment n°2), similar behaviors were obtained after
280 four hours and two hours of exposure (in the Supplementary Data section, see the monitoring
281 of all pesticides sorbed in the passive Twisters exposed for seven days to non-contaminated water
282 and contaminated water in Figure S6 and Figure S7). Figure 2a and 2b show the results of both
283 seven-day kinetic experiments for simazine and chlorpyrifos, after the six-hour exposure at
284 10C concentration level. In Experiment n°1, up to 78 % of the mass of simazine was
285 eliminated from the passive Twisters in three days and 92 % in seven days, due to the low
286 affinity of this hydrophilic pesticide with the PDMS phase of the passive Twisters. In
287 Experiment n°2, 30 % of simazine initially sorbed in the passive Twisters was eliminated in
288 four days. No further elimination was observed because the concentration of simazine
289 remaining in the passive Twister probably was in equilibrium with the concentration of
290 simazine in the water (in the Supplementary Data section, see the water concentrations during
291 the elimination kinetics of Experiment n°1 and Experiment n°2 in Table S3 and Table S4,

292 respectively). In contrast, chlorpyrifos was not eliminated from the passive Twisters in
293 Experiment n°1, and additional accumulation was observed in Experiment n°2 (Figure 2b), in
294 accordance with passive sampling theory, as described in the Introduction section (Vrana et
295 al. 2005; Huckins et al. 2006; Greenwood et al. 2007).

296 Table 1 shows the trend of the elimination kinetics of all target pesticides in Experiments n°1
297 and n°2 after six hours of exposure at 10C concentration level. Results of Experiment n°1
298 showed that most pesticides previously accumulated in the passive Twisters were eliminated
299 rapidly within one to four days and were completely eliminated after being exposed for seven
300 days to non-contaminated water (in the Supplementary Data section, see the monitoring of all
301 tested pesticides sorbed in the passive Twisters exposed for seven days to non-contaminated water in
302 Figure S6). Only the masses of chlorpyrifos and flufenoxuron sorbed in the PDMS phase
303 remained relatively constant, with elimination rates of 0 and 24 %, respectively.

304 In the case of Experiment n°2, acetochlor, 3,4-dichloroaniline, linuron, metolachlor,
305 procymidon were eliminated rapidly but only partially from the passive Twisters exposed for
306 seven days to contaminated water (1C); their concentration in the receiving phase reached
307 equilibrium with the water phase concentration within one to two days (in the Supplementary
308 Data section, see the monitoring of all tested pesticides sorbed in the passive Twisters exposed for
309 seven days to contaminated water in Figure S7). Slower elimination was observed for atrazine,
310 azoxystrobine, simazine, chlorfenvinphos, chlorpyrifos-methyl, chlortoluron, diflufenican,
311 fenitrothion, norflurazon, and tebuconazole. The mass of dimethomorph, isoproturon, and
312 spiroxamine sorbed in the passive Twisters remained relatively constant over the whole
313 experiment; with elimination rates ranging from 0 to 10 %. This confirms the saturation
314 observed during the concentration peak simulations. Finally, the masses of chlorpyrifos and
315 flufenoxuron sorbed in the PDMS phase increased for seven days.

316 Hence, passive Twisters showed the ability to integrate fast and high concentration peaks of
317 spiroxamine, fenitrothion, diflufenican, chlorpyrifos, chlorpyrifos-methyl, and flufenoxuron,
318 and to possibly provide accurate TWAC after 7 days exposed in non-contaminated or
319 contaminated water for chlorpyrifos and flufenoxuron.

320

321 **Evaluation of TWAC accuracy (Experiment n°3).** Water concentrations of all pesticides
322 for 1C and 2C concentration levels dropped over the four-day experiments despite the
323 continuous spiking (in the Supplementary Data section, see the water concentrations of the 1C
324 and 2C levels during the accumulation kinetics in Table S5). Decreases rates ranged from 16
325 % for chlorpyrifos-methyl up to 74 % for flufenoxuron for the 1C concentration level, and
326 from 10 % for diflufenican to 65 % for flufenoxuron for the 2C concentration level. The
327 scenario n°2 and n°7 were used to study the accumulation kinetics of all pesticides passive
328 Twisters exposed to constant 1C and 2C concentration levels, respectively, for four days. The
329 accumulation kinetics of simazine and chlorpyrifos in passive Twisters exposed to 1C and 2C
330 concentration levels are showed in Figure 3a and Figure 3b, respectively. For all pesticides
331 except for spiroxamine, chlorpyrifos, chlorpyrifos-methyl, flufenoxuron, and diflufenican,
332 equilibrium (or saturation) was reached on the first or second day at 1C concentration level,
333 and even faster at 2C concentration level (in Supplementary Data section, see the
334 accumulation kinetics of all pesticides in the passive Twisters exposed to constant 1C and 2C
335 concentration levels for four days in Figure S8). Water concentrations were chosen as low as
336 possible while allowing direct injection analysis. The level of water concentrations, however
337 probably too high, the small volume of PDMS phase of the passive Twisters, and the decrease
338 in the water concentrations can explain that equilibrium was reached surprisingly fast. Indeed,
339 Booij and Tucca (2015) recently showed that the decrease of the ambient concentration can
340 make the accumulation of micropollutant in a passive sampler reach the equilibrium faster. In

341 contrast, linear and curvilinear accumulations were observed for more hydrophobic
342 spiroxamine, diflufenican, chlorpyrifos, chlorpyrifos-methyl and flufenoxuron.

343 For scenarios n°2 to n°6, the TWAC (C_w) were calculated with the mass of all pesticides
344 accumulated in the passive Twisters at the end of the experiment (day 4) and with Eq. 4. The
345 sampling rate (R_s) and the partition coefficient (K_{sw}) of all studied pesticides were determined
346 with the accumulation kinetics obtained from scenario n°2, Eq. 1 and the Solver tool in
347 Microsoft Excel software. To evaluate the accuracy of the TWAC derived from the passive
348 SBSE in scenarios n°2 to n°6, we calculated the ratios between the TWAC (C_w) and the
349 average value of the measured water concentrations (\bar{C}) during the four-day exposure,
350 obtained by the analysis of the spot samples (in Supplementary Data section, see the
351 measured pesticide concentrations in the contaminated waters at 1C and 2C concentration
352 levels in Table S5).

353 Figure 4a shows the distribution of the accuracy of all pesticides for the five scenarios. As
354 expected for scenario n°2, we observed accuracy close to 100 % for all pesticides. Scenarios
355 n°3 and n°6 ended with one or two days of exposure at 2C concentration level; the passive
356 Twisters accumulated the target pesticides while little to no elimination occurred. Therefore,
357 average accuracy of 124 % for scenario n°3 and 106 % for scenario n°6 were observed,
358 although with large variability. Average accuracy of 53 % and 46 % were observed for
359 scenario n°4 and scenario n°5, respectively, which ended with one or two days of exposure to
360 non-contaminated tap water. In these cases, the most hydrophilic pesticides were rapidly
361 eliminated from the passive Twisters, as observed in Experiment n°1 (Figure S6). The
362 observed average accuracy imply that the scenario has an impact on the value of average
363 concentration. When the variation of concentration occurs just before the end of the sampling
364 period, the average concentration is closer to the actual value. These results are in good
365 agreement with the work of Shaw and Mueller (2009) with the Chemcatcher. The authors

366 predicted through simulation that a herbicide concentration peak event is better represented by
367 the sampler (under curvilinear accumulation kinetics) when it occurs towards the end of the
368 sampling period. Figure 4b displays the distribution of the accuracy for the five scenarios for
369 spiroxamine, diflufenican, chlorpyrifos, chlorpyrifos-methyl, and flufenoxuron. Better
370 accuracy was observed for these five hydrophobic pesticides, with average accuracy ranging
371 from 82 to 127 % depending on the scenario. In that case, the moment when the variation of
372 concentration occurred during the sampling period had less impact on the average
373 concentrations because the sampling of these pesticides by the passive Twisters was more
374 integrative. Indeed, they showed little to no elimination in four days in Experiment n° 1
375 (except for chlorpyrifos-methyl) (Figure S6), and their accumulation kinetics were more
376 linear (Experiment n°3) (Figure S8).

377

378 **Can passive SBSE determine accurate TWAC?** Linear accumulation and integrative
379 sampling are obviously preferable for the determination of accurate TWAC by passive SBSE
380 (Greenwood et al. 2007; Assoumani et al. 2014). However in practice, curvilinear
381 accumulation might occur because, for instance, passive Twisters might be exposed for
382 periods longer than the linear accumulation period. The integration of a concentration peak or
383 the exposure of the sampler to decreasing water concentrations could also lower the $t_{1/2}$ value,
384 and shorten the linear accumulation period (Hawker 2010; Booij and Tuca 2015). Therefore,
385 the ability of the passive Twisters in curvilinear sampling for providing accurate enough
386 concentrations needs to be assessed for future field applications of the passive SBSE.

387 In case passive Twisters are exposed to constant concentrations, Eq. 4 allows calculating
388 TWAC with good accuracy. Indeed, we obtained an average accuracy of 95 % for the TWAC
389 of 20 studied pesticides in the scenario n°2 of the Experiment n°3. The error in the TWAC
390 accuracy comes from the difference between the model and the real mass of micropollutant

391 accumulated, which is determined with an analytical uncertainty. Scenario n°2 showed that,
392 for the 20 pesticides with different physical chemical properties and kinetic patterns, this error
393 was lower than 20 %. Considering an average analytical uncertainty of 20 % for the
394 determination of pesticides in water samples (Margoum et al. 2013), this error on the TWAC
395 accuracy is satisfactory.

396 In case of fluctuating concentrations at the daily scale, the present investigation allowed us to
397 highlight two groups of pesticides, in relation with their hydrophobicity. First, on the basis of
398 the results of Experiment n°3, the pesticides with $\text{Log } K_{ow} < 4.2$ might provide TWAC with
399 poor average accuracy (33 % for scenario n°5 and 39 % for scenario n°4) in case the
400 concentration variation occurred at the beginning of the sampling campaign. Nevertheless,
401 although these pesticides showed short accumulation periods in laboratory conditions, in field
402 conditions, passive Twisters may accumulate linearly these hydrophilic pesticides for a period
403 larger than 2 days. A field calibration of the passive Twisters is needed to confirm this
404 hypothesis. Second, linear and curvilinear accumulations, and average accuracy ranging from
405 82 to 127 % depending on the scenario (Experiment n°3) for diflufenican, spiromaxime,
406 chlorpyrifos, chlorpyrifos-methyl, flufenoxuron showed that the passive SBSE could provide
407 concentrations with an error comparable to the analytical uncertainty in case of fluctuating
408 concentrations.

409

410 **Conclusion**

411

412 Pesticide concentrations in rivers of small vineyard watersheds generally vary according to
413 fluctuation of hydrological conditions, and especially during storm events. This works aimed
414 at determining the capabilities of the passive Twisters for integrating variations of
415 concentrations of 20 moderately hydrophilic to hydrophobic pesticides, and their accuracy for

416 the determination of TWAC. In the first two experiments, we observed integration of fast and
417 high concentration peaks for spiroxamine, fenitrothion, diflufenican, chlorpyrifos,
418 chlorpyrifos-methyl, and flufenoxuron. We also observed little to no elimination from the
419 passive Twisters when exposed to non-contaminated water and additional accumulation when
420 exposed to water spiked at low concentrations for chlorpyrifos and flufenoxuron. The results
421 of the third experiment showed that passive Twisters could provide TWAC of hydrophobic
422 pesticides such as diflufenican, spiroxamine, chlorpyrifos, chlorpyrifos-methyl, flufenoxuron
423 with average accuracy ranging from 82 to 127 %, depending on the scenario. In contrast,
424 TWAC with average accuracy ranging from 33 to 123 %, depending on the scenario, were
425 obtained for the pesticides with $\text{Log } K_{ow} < 4.2$, due to fast and great elimination from the
426 passive Twisters.

427

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431

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