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# 1 **Field application of passive SBSE for the monitoring of pesticides in surface** 2 **waters**

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## 8 **Abstract**

9 Spot sampling lacks representativeness for monitoring organic contaminants in most surface  
10 waters. Passive sampling has emerged as a cost-effective complementary sampling technique.  
11 We recently developed passive stir bar sorptive extraction (passive SBSE), with Twister from  
12 Gerstel, for monitoring moderately hydrophilic to hydrophobic pesticides ( $2.18 < \log K_{ow} <$   
13  $5.11$ ) in surface water. The aim of the present study was to assess this new passive sampler for  
14 the determination of representative average concentrations and to evaluate the contamination  
15 levels of two French rivers. Passive SBSE was evaluated for the monitoring of 16 pesticides  
16 in two rivers located in a small vineyard watershed during two one-month field campaigns in  
17 spring 2010 and spring 2011. Passive SBSE was applied for periods of one or two weeks  
18 during the field campaigns, and compared with spot sampling and weekly average automated  
19 sampling. Results showed that passive SBSE could achieve better time-representativeness  
20 than spot sampling, and lower limits of quantification than automated sampling coupled to  
21 analytical SBSE for the pesticides studied. Finally, passive SBSE proved useful for revealing  
22 spatial and temporal variations in pesticide contamination of both rivers, and the impact of  
23 rainfall and runoff on the river water quality.

24

25

26

27 **Keywords:** Freshwater monitoring, Passive sampling, Spot sampling, Pesticides

## 28 **1 Introduction**

29

30 Monitoring organic contaminants in the aquatic environment is a critical issue, as many of  
31 them can cause adverse effects. Currently, spot sampling is the most commonly used method  
32 for monitoring water quality (Greenwood et al. 2007b; Madrid and Zayas 2007); 4–12 spot  
33 samples per year are required to implement monitoring programs for the Water Framework  
34 Directive (European Commission, 2000). For most hydrosystems, frequent spot sampling is  
35 necessary for good time-representativeness. However, the cost can be high because of the  
36 labor and transport involved in sampling, and the need for a large number of analyses (Roig et  
37 al. 2007). Automated sampling achieves better time-representativeness than spot sampling,  
38 with lower logistical cost, and also with lower analytical cost when composite samples are  
39 collected and analyzed. However, this technique is costly for purchase and maintenance,  
40 cannot be used at all sites, and can only be used to monitor stable molecules (Morin et al.  
41 2012). Alternative sampling methods, such as passive sampling, are being developed, and  
42 may provide more representative data than spot sampling. However, the reliability,  
43 reproducibility and sensitivity of these methods first need to be assessed in both laboratory  
44 and field studies before they can be applied (Greenwood et al. 2007b).

45 Passive sampling is a recently developed sampling method for monitoring contaminants in  
46 surface waters (Namieśnik et al. 2005; Vrana et al. 2005; Greenwood et al. 2007a). This  
47 technique allows smoothed integrative sampling over periods ranging from days to months,  
48 and ultra-trace levels of detection for a broad range of organic contaminants (Huckins et al.  
49 2006; Greenwood et al. 2007a). For determining time-weighted average (TWA)  
50 concentrations, the passive sampler has to be calibrated prior to field exposure. In fact, the  
51 accumulation kinetics of the target organic contaminants are studied in controlled conditions  
52 to determine the corresponding sampling rates ( $R_s$ ). The efficiency of passive samplers for the

53 determination of TWA concentrations in natural waters is generally assessed by comparison  
54 with active sampling (Vrana et al. 2005; Greenwood et al. 2007a). In most cases, passive  
55 sampling has been compared with spot sampling with globally positive results. For instance,  
56 Alvarez et al. (2004) obtained an agreement in the concentrations of diuron and isoproturon in  
57 two rivers with a less than 1.7-fold difference between the POCIS and spot sampling.  
58 Kaserzon et al. (2012) also observed a close agreement between perfluorinated chemicals  
59 measured by repeated spot sampling and POCIS in Sidney Harbor water. However, fewer  
60 studies report comparisons with automated sampling, although this provides better time-  
61 representativeness (Hyne and Aistropé 2008; Mazzella et al. 2010; Morin et al. 2012; Bailly et  
62 al. 2013).

63 Floods are a major pathway for the transport of pesticides into dynamic rivers located in small  
64 agricultural watersheds (Kreuger 1998; Taghavi et al. 2011; Petersen et al. 2012), when spot  
65 sampling usually under-estimates the contamination levels (Rabiet et al. 2010; Dalton et al.  
66 2014). Recently, we used Gerstel Twisters® (commercially available devices used for stir bar  
67 sorptive extraction (SBSE)) to develop passive SBSE as a simple passive sampling technique  
68 for moderately hydrophilic to hydrophobic pesticides ( $2.18 < \log K_{ow} < 5.11$ ) (Assoumani et  
69 al. 2013). Stir bar sorptive extraction is originally an analytical sample preparation technique  
70 for liquid and gaseous samples (Baltussen et al. 1999). Vrana et al. (2001) also used  
71 Twisters® and developed the membrane-enclosed sorptive coating (MESCO) for the passive  
72 sampling of polycyclic aromatic hydrocarbons (PAH) and polychlorobiphenyls (PCB) in  
73 water. Equipped with a membrane, the accumulation kinetics of organic contaminants in the  
74 MESCO might not be fast enough to integrate transient variations of concentrations. In  
75 contrast, for membrane-free passive SBSE, we reported fast accumulation kinetics for the 18  
76 target pesticides in laboratory conditions (Assoumani et al. 2014). This new passive sampler  
77 needed to be assessed in field conditions and compared with conventional active sampling

78 techniques. Hence, the aim of the present work was, first, to evaluate passive SBSE for the  
79 determination of representative pesticide concentrations and, second, to assess the  
80 contamination levels of two French rivers. We conducted two one-month monitoring  
81 campaigns, in spring 2010 and spring 2011, to assess the time-representativeness and  
82 sensitivity of passive SBSE for the monitoring of 16 pesticides in river waters. Firstly, we  
83 compared the results of passive SBSE with those of spot sampling and weekly average  
84 automated sampling. We focused on qualitative and quantitative results, and on the limits of  
85 quantification allowed by the three sampling techniques. Secondly, passive SBSE results were  
86 used to assess the pesticide contamination of two river waters. Spatial and temporal variations  
87 in the pesticide concentrations were assessed in the two rivers in relation to agrochemical and  
88 hydrological conditions.

89

## 90 **2 Experimental**

91

### 92 **2.1 Chemicals and materials**

93

94 The 16 pesticides selected for this study were acetochlor (ATC), atrazine (ATZ), azoxystrobin  
95 (AZS), chlorfenvinphos (CFV), chlorpyrifos-ethyl (CPE), diflufenican (DFF), dimethomorph  
96 (DMM), 3,4-dichloroaniline (DCA) (metabolite of diuron), fenitrothion (FNT), flufenoxuron  
97 (FFX), isoproturon (IPU), metolachlor (MTC), norflurazon (NFZ), procymidon (PCM),  
98 simazine (SMZ), and tebuconazole (TBZ) (purity  $\geq$  92.5%) (Dr. Ehrenstorfer GmbH,  
99 Augsburg, Germany). They belong to different use classes (herbicides, insecticides and  
100 fungicides) and chemical classes (triazines, substituted ureas, triazoles and organophosphate  
101 compounds); their physical and chemical properties, including their octanol-water partitioning  
102 coefficient ( $\log K_{ow}$ ), range widely (Table 1).

103 For chemical analyses, diuron-d6 (used as internal standard), linuron-d6 and chlorpyrifos-  
104 ethyl-d10 (used as surrogates), were provided by Dr. Ehrenstorfer (purity  $\geq 98.5\%$ ). Sodium  
105 chloride NaCl (purity = 99.5%) was purchased from VWR (Strasbourg, France).  
106 Dichloromethane for pesticide residue analysis, and liquid chromatography-mass  
107 spectrometry (LC-MS) grade acetonitrile and methanol were purchased from VWR  
108 (Strasbourg, France). Formic acid (purity = 98%) for LC-MS analysis was provided by  
109 Sigma-Aldrich (Saint-Quentin-Fallavier, France). Ultrapure water was produced by a MilliQ  
110 water purification system equipped with an LC-Pak cartridge purchased from Millipore  
111 (Billerica, MA, USA). For passive SBSE, we used Twisters® (20 mm  $\times$  1 mm thick  
112 polydimethylsiloxane (PDMS) film) as passive sampling tools, hereafter named passive  
113 Twisters, purchased from Gerstel (Mülheim a/d Ruhr, Germany). For the field application, the  
114 passive Twisters were placed in deployment bags, made of two pieces of plastic mesh, in  
115 order to expose the PDMS phase directly to the aquatic medium, and protect it from small  
116 rocks, pieces of wood or coarse sand (Assoumani et al. 2013). The deployment bags with  
117 passive Twisters were placed in cases with holes (40 cm  $\times$  30 cm  $\times$  20 cm), which were  
118 placed in the river.

119

## 120 2.2 Field experiments

121

122 Two monitoring campaigns took place along two rivers of a French vineyard watershed  
123 (220 km<sup>2</sup>) located about 70 km north of Lyon in the Beaujolais region, the Morcille River and  
124 the Ardières River (Figure 1). The Morcille River is a tributary of the Ardières River and is  
125 located in a subwatershed of 8 km<sup>2</sup>. In spring, the typical flow of the Morcille River is 5 L s<sup>-1</sup>  
126 (Figure S1 in Supplementary data section), and the typical flow of the Ardières River is 350 L  
127 s<sup>-1</sup> (Figure S2). Typical flood events last 5 h for the Morcille River and 24 h for the Ardières

128 River. The proportion of land devoted to vineyards increases along both rivers. This  
129 proportion increases up to 40% and to 70% for the Ardières and the Morcille watersheds,  
130 respectively (Rabiet et al. 2010). Six deployment sites, three per river, were selected for two  
131 one-month exposure campaigns, in spring 2010 and spring 2011.

132 For the performance evaluation of passive SBSE, the sampling strategy varied depending on  
133 the campaign year and the deployment site (Figure 1). In spring 2010, triplicate passive  
134 Twisters were deployed for two periods of two weeks at all the sites. Further triplicate passive  
135 Twisters were deployed for four periods of one week at the intermediate site of the Morcille  
136 River. Simultaneously, to assess the time-representativeness of passive SBSE, spot sampling  
137 and weekly average automated sampling were carried out every week. Spot samples were  
138 collected in 1-L amber polyethylene bottles rinsed twice with the river water. The weekly  
139 average samples were collected with a refrigerated automated sampler (Bühler 4010, Hach-  
140 Lange) in a single 5 L amber glass container (i.e. composite sample) every week at the  
141 intermediate site of the Morcille River and at the downstream site of the Ardières River. The  
142 automated samplers were set to collect 100 mL of river water every 3.5 h. The time interval  
143 was short enough to allow the integration of typical floods of the two rivers, and the water  
144 volume collected at each time point was selected to allow the operation of the automated  
145 samplers for 7 days (48 samples collected) while ensuring satisfactory repeatability.

146 In spring 2011, triplicate passive Twisters were deployed for four periods of one week at the  
147 intermediate site and the downstream site of the Morcille River, and at the upstream site and  
148 downstream site of the Ardières River. During the same period, spot samples and weekly  
149 average samples (via automated samplers) were collected every week at the intermediate site  
150 of the Morcille River and at the downstream site of the Ardières River (Figure 1).

151 Field blanks for passive Twisters were systematically used. All the passive Twisters were  
152 placed individually in deployment bags, made of two pieces of plastic mesh, in order to  
153 expose the PDMS phase directly to the aquatic medium, while protecting it from small rocks,  
154 pieces of wood or coarse sand. The water samples and the passive Twisters were brought back  
155 to the laboratory in a refrigerated case for subsequent pesticide assays. Hourly rainfall and  
156 flow rate were measured at the intermediate site of the Morcille River in spring 2010, and at  
157 the intermediate site of the Morcille River and at the downstream site of the Ardières River in  
158 spring 2011.

159

### 160 2.3 Chemical analysis of water samples and passive Twisters

161

162 Before extraction and determination of pesticide concentrations, all the water samples were  
163 filtered with 0.7  $\mu\text{m}$  GF/F glass fiber membranes. In spring 2010, pesticide concentrations in  
164 spot samples were determined by solid phase extraction (6 mL Oasis HLB cartridges, Waters)  
165 followed by liquid chromatography coupled with tandem mass spectrometry (SPE-LC-  
166 MS/MS). The extraction was carried out with 250 mL of water sample, and the concentration  
167 factor was 1000. For the weekly average samples, pesticides were assayed in triplicate by  
168 analytical SBSE followed by liquid desorption and liquid chromatography coupled with  
169 tandem mass spectrometry (SBSE-LD-LC-MS/MS). In spring 2011, this analytical method  
170 was applied for pesticide assay in the spot samples and in the weekly average samples, both in  
171 triplicate. The development and validation of the SBSE-LD-LC-MS/MS analytical method  
172 have been described elsewhere (Margoum et al., 2013). Briefly, the extraction of 20 mL of  
173 water samples was performed at 800 rpm for 3 h. The Twisters (hereafter named analytical  
174 Twisters) were then placed in 200  $\mu\text{L}$  of methanol/acetonitrile (50/50, v/v), and the pesticides  
175 were desorbed under sonication for 15 min. Finally, 150  $\mu\text{L}$  of ultrapure water and 10  $\mu\text{L}$  of



176 diuron-d6 at 200  $\mu\text{g L}^{-1}$  in acetone, were added to 40  $\mu\text{L}$  of the desorbate to constitute the  
177 sample for LC-MS/MS analysis. The concentration factor was 20.

178 After exposure, the passive Twisters were taken out of their deployment bags, gently rinsed  
179 with ultrapure water and dried with lint-free tissue, and then left at least overnight at  $-18\text{ }^{\circ}\text{C}$ .  
180 The pesticides sorbed in the passive Twisters were then extracted in the same way as for the  
181 analytical Twisters.

182 The chemical analyses were performed with an LC 1100 Series apparatus from Agilent  
183 (Massy, France) coupled with an MS triple quadrupole API 4000 from AB Sciex (Les Ulis,  
184 France), equipped with an electrospray ionization source (ESI) operated in the positive  
185 ionization mode. An Atlantis T3 (2.1 mm  $\times$  100 mm;  $d_p = 3\text{ }\mu\text{m}$ ) purchased from Waters  
186 (Saint-Quentin-en-Yvelines, France) was used for the chromatographic separation of the  
187 analytes. Acetonitrile and ultrapure water both with formic acid (0.1%) were used in an  
188 analytical gradient of 15 min.

189

### 190 **3 Theory**

191

192 The theory of passive sampling is well established and documented (Vrana et al. 2005;  
193 Huckins et al. 2006; Greenwood et al. 2007a). For passive SBSE, assuming isotropic  
194 exchange, the uptake of a contaminant in a passive Twister over time with constant ambient  
195 water concentration obeys first-order kinetics (Assoumani et al. 2014). In the initial phase, the  
196 chemical uptake is linear and integrative, and defined as follows (Eq. 1):

$$M_s(t) = C_w R_s t, \quad (1)$$

197 where  $M_s$  (ng) is the mass of contaminant accumulated in the receiving phase,  $C_w$  (ng mL<sup>-1</sup>)  
198 the concentration of contaminant in the water phase,  $R_s$  the sampling rate (mL d<sup>-1</sup>), and  $t$  (d)  
199 the exposure time.

200 When a passive Twister is deployed in the field and then retrieved within the linear  
201 accumulation period, integrative TWA concentrations can be calculated by Eq. 2:

$$C_w = \frac{M_s}{R_s t} = \frac{M_s}{V_e} \quad (2)$$

202  
203 The product  $R_s t$  provides a link between batch extraction, such as SPE or analytical SBSE,  
204 and passive sampling, as it equals the extracted water volume  $V_e$  (Huckins et al. 2006;  
205 Lohmann et al. 2012). The limit of quantification (LQ) of the contaminant in the water for the  
206 passive SBSE (in ng.L<sup>-1</sup>) can be calculated by dividing the corresponding LQ in the passive  
207 Twister (in ng) by  $V_e$ , and then compared with the LQ achieved by the batch extraction.

208 Eq. 1 is a special case of the general uptake (Eq. 3):

$$M_s(t) = C_w K_{sw} V_s (1 - \exp(-\frac{R_s t}{K_{sw} V_s})), \quad (3)$$

209 where  $V_s$  (L) is the volume of the receiving phase,  $K_{sw}$  (adimensional), described as the ratio  
210 of the concentration at equilibrium of contaminant in the passive Twister  $C_s$  (ng mL<sup>-1</sup>) to the  
211 concentration at equilibrium of contaminant in the water phase  $C_w$  (ng mL<sup>-1</sup>). When the  
212 passive Twister is deployed in the field for longer than the linear accumulation period, TWA  
213 concentrations can be calculated with Eq. 4, but they are considered non-integrative.

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

214

215 With Eq. 4,  $V_e$ , and therefore the LQ in water for the passive SBSE, can be estimated at any  
216 time of the deployment (Lohmann et al. 2012).

217

## 218 **4 Results and discussion**

219

220 4.1 Comparison of passive SBSE with spot sampling and weekly average automated sampling

221

222 4.1.1 Comparison of limits of quantification

223 Table 1 presents the LQ achieved by the SPE-LC-MS/MS analysis of the spot samples, the  
224 SBSE-LD-LC-MS/MS analysis of the samples collected by the automated sampler, and the  
225 LD-LC-MS/MS analysis of the passive Twisters. The LQ values for water concentrations  
226 using passive Twisters ( $\text{ng L}^{-1}$ ) were calculated with Eq. 4 and the LQ in the sampler (ng),  
227 determined with a signal-to-noise ratio of 10 in a previous study (Assoumani et al. 2014), and  
228 for a 7-day deployment of the passive Twisters. We first observed that passive SBSE allowed  
229 achieving lower LQ than analytical SBSE for all the target pesticides (factor 1.2 to 167),  
230 except for atrazine ( $11 \text{ ng L}^{-1}$ ) and 3,4-dichloroaniline ( $165 \text{ ng L}^{-1}$ ). Passive SBSE LQ values  
231 for fenitrothion, chlorfenvinphos and diflufenican, which were among the most hydrophobic  
232 target pesticides, were 45 to 167 times lower than analytical SBSE; large  $R_s$ , thus  $V_e$  3 to 6  
233 times greater than the batch extraction volume (20 mL) were obtained for these compounds  
234 during the laboratory calibration (Assoumani et al. 2014). Nonetheless, SPE gave a value of  
235 LQ 1.6 to 34 times lower than passive SBSE for the most hydrophilic pesticides (norflurazon,  
236 azoxystrobine, dimethomorph, 3,4-dichloroaniline, isoproturon, procymidon, tebuconazole)  
237 and flufenoxuron, but required sample volumes 12 times larger.

238

#### 239 4.1.2 Quantification frequencies of the target pesticides

240 Figure 2 and Figure 3 show the concentrations of the pesticides quantified at the intermediate  
241 site of the Morcille River in spring 2010 and at the downstream site of the Ardières River in  
242 spring 2011, respectively. The pesticide concentrations were obtained from passive SBSE,  
243 spot sampling and weekly average automated sampling. For passive SBSE, TWA  
244 concentrations were calculated with Eq. 4, and the mass of the pesticides accumulated in the  
245 passive Twisters retrieved after 7 or 14 days in the river waters. In Figure 2, out of the 10  
246 pesticides quantified via at least one sampling technique, four were quantified through spot  
247 sampling, 10 through passive SBSE, and six through automated sampling. In spring 2010,  
248 3,4-dichloroaniline, isoproturon, fenitrothion and chlorfenvinphos were never quantified by  
249 any sampling technique. Over the whole spring 2010 campaign, for the eight pesticides  
250 quantified at least once via the three sampling techniques, spot sampling gave a quantification  
251 frequency of 35%, whereas passive SBSE and automated sampling gave 52% and 53%,  
252 respectively.

253 Likewise, out of the eight pesticides quantified via at least one sampling technique, two were  
254 quantified through spot sampling, eight through passive SBSE, and two through automated  
255 sampling (Figure 3). In spring 2011, isoproturon, fenitrothion and flufenoxuron were never  
256 quantified by any sampling technique. Over the whole spring 2011 campaign, for the 13  
257 pesticides quantified at least once via the three sampling techniques, spot sampling gave a  
258 quantification frequency of 5%, whereas passive SBSE and automated sampling gave 36%  
259 and 17%, respectively. Hence for both campaigns, passive SBSE and automated sampling  
260 achieved better time-representativeness of the target pesticide concentrations than spot  
261 sampling.

262

#### 263 4.1.3 Concentrations of the target pesticides

264 Concentrations of pesticides quantified from spot sampling were generally lower than those  
265 obtained from passive SBSE and automated sampling. For instance, in spring 2010,  
266 concentrations of norflurazon in the spot samples were five times lower than those calculated  
267 from passive SBSE data (Figure 2). The same trend was observed for azoxystrobin and  
268 procymidon in spring 2010, and for simazine and azoxystrobin in spring 2011 (Figure 3).  
269 Also, several pesticides that were not quantified in the spot samples were quantified by  
270 passive SBSE and automated sampling. Diflufenican and chlorpyrifos-ethyl in spring 2010,  
271 and dimethomorph, tebuconazole, chlorfenvinphos, acetochlor and diflufenican in spring  
272 spring 2011 were not quantified in the spot samples, but were quantified through passive  
273 SBSE. The same trend was observed for most results obtained in both campaigns, as shown in  
274 Table 2 and Table 3, which present all the concentrations of the target pesticides in the  
275 Morcille River and Ardières River during spring 2010 and spring 2011, respectively. Spot  
276 samples did not integrate variations of concentrations that probably occurred during the  
277 campaigns. These results confirm the observations of Dalton et al. (2014). In that study, low  
278 frequency spot sampling systematically gave lower atrazine concentrations than the POCIS  
279 deployed for 56 days in rivers located in an agricultural watershed. However, in rare cases,  
280 concentrations obtained from spot samples were higher than those determined with passive  
281 SBSE, or the number of quantified pesticides was higher for spot samples. This could be due  
282 to lower LQ for SPE-LC-MS/MS analysis of the spot samples (e.g. norflurazon and  
283 dimethomorph concentrations at the upstream site of the Morcille River in spring 2010), or to  
284 high pesticide concentrations in the river water at the precise time of the spot sampling (i.e.

285 dimethomorph at the downstream site of the Ardières River on Day 22 (June 15) of the spring  
286 2010 campaign).

287 The concentrations of the target pesticides obtained from the passive SBSE matched those  
288 obtained from automated sampling (e.g. dimethomorph, procymidon and tebuconazole in  
289 spring 2010, Figure 2). No performance reference compound (PRC) (Booij et al. 1998;  
290 Huckins et al. 2002; Smedes 2007) was used for the calculations of the TWA concentrations  
291 obtained from passive SBSE. During both field campaigns, TWA concentrations of the  
292 pesticides with  $\log K_{ow}$  values below 3.3 were similar to those determined via automated  
293 sampling (i.e. from simazine to metolachlor, Table 1) (Figure 2 and Figure 3). Therefore, for  
294 those pesticides, it seems that TWA concentrations calculated without using a PRC were  
295 accurate. Recently, we investigated the influence of flow velocity (up to  $2.5 \text{ cm s}^{-1}$ ) and  
296 temperature (10 and  $25 \text{ }^{\circ}\text{C}$ ) on pesticide uptake in passive Twisters for the same pesticides as  
297 in the present study (Assoumani et al. 2014). No significant effect of either parameter was  
298 observed for the pesticides with  $\log K_{ow}$  lower than 3.3; we therefore assumed membrane-  
299 controlled accumulation kinetics. This means that no PRC would be required for the  
300 determination of accurate TWA concentrations of these pesticides. The results obtained in this  
301 field study confirm the observations made in that previous laboratory study. Good agreement  
302 between concentrations derived from passive sampling and active sampling were also  
303 obtained in previous studies. Hyne and Aistrophe (2008) observed concentrations of pesticides  
304 in 24-hour composite water samples within two fold of the TWA concentrations derived for  
305 their cellulose sampling device. Also, although only spot sampling was used as a comparison,  
306 Ibrahim et al. (2013) reported good representativeness for TWA concentrations of pesticides  
307 derived from POCIS.

308 Hence (i) spot sampling lacked temporal representativeness and tended to under-estimate  
309 contaminant concentrations in rivers, and (ii) passive SBSE gave a representative insight into  
310 pesticide contamination in both rivers, as shown by the close agreement of passive SBSE with  
311 automated sampling results.

312

## 313 4.2 Determination of pesticide contamination with passive SBSE

314

### 315 4.2.1 Spatial variations in pesticide concentrations

316 In spring 2010, concentration gradients were observed from the upstream site to the  
317 downstream site of both rivers (Table 2). During the first 14 days of the field campaign, the  
318 concentrations of all the quantified pesticides except diflufenican and acetochlor increased  
319 along the Ardières River. Neither herbicide is used for wine-growing, and so is not expected  
320 at increasing concentrations along a river of a vineyard watershed. The presence of  
321 diflufenican in water might be due to residues from earlier use remaining in the soil, given its  
322 relatively high  $\log K_{ow}$  (4.20) and high  $K_{oc}$  values (3186 mL g<sup>-1</sup>) (Petersen et al. 2012). A  
323 dilution effect could then explain the decrease in the diflufenican concentration at the  
324 downstream site. Also, there was a maize field near the upstream site, so applications of  
325 herbicides might explain the presence of acetochlor in the river. In the Morcille River, the  
326 concentrations of all the quantified pesticides, except norflurazon, atrazine, metolachlor and  
327 diflufenican, increased from upstream to downstream. These four herbicides were not  
328 expected to increase along the Morcille River, since norflurazon was banned in 2004 and  
329 atrazine in 2003, and metolachlor and diflufenican are not used for wine-growing. The  
330 observed pesticide concentration gradients can be explained by the strong increase in the  
331 proportion of land devoted to vineyards along both rivers (Rabiet et al. 2010).

332 In spring 2011, similar concentration gradients were observed, although water sampling was  
333 carried out at only two sites per river (Table 3). The concentrations of all the quantified  
334 pesticides except chlorfenvinphos and diflufenican increased along the Ardières River for all  
335 the weeks of the campaign. Likewise, the concentrations of all quantified pesticides except  
336 dimethomorph increased along the Morcille River. Therefore, passive SBSE is sensitive  
337 enough to highlight concentration gradients of the target pesticides at ultra-trace levels.

338

#### 339 4.2.2 Temporal variations in pesticide concentrations

340 Regarding temporal variations in TWA concentrations, decreases of 10–91% were observed  
341 for all the quantified pesticides between the first period (Days 1–15) and the second period  
342 (Days 15–29) for the spring 2010 campaign at the upstream site and the downstream site of  
343 the Ardières River (Table 2). The data at the intermediate site are missing because of onsite  
344 vandalism during the second sampling period. These decreases can be linked to heavy rainfall  
345 during the first half of the campaign, and especially on Day 13 (June 6) when precipitations  
346 lasted 3 h with a peak at 46 mm h<sup>-1</sup> (Figure S1). Hence runoff from the vineyards to the rivers  
347 was probably responsible for the high pesticide TWA concentrations measured during this  
348 period. The same trend was observed in the Morcille River, presumably for the same reasons.  
349 The concentrations of all quantified pesticides except procymidon decreased from the first to  
350 the second period of the campaign at the upstream site and the downstream site (decreases of  
351 11–91%, depending on the pesticide). At the intermediate site, all the quantified pesticides  
352 except procymidon and tebuconazole were quantified at lower concentrations during the last  
353 14 days of the campaign (decreases of 25–45%). Spring 2011 was drier than spring 2010  
354 (Figure S2), and pesticide TWA concentrations were generally lower than in spring 2010.  
355 However, some rainfall caused increases in the river flows, which may be related to the



356 increases in some pesticide concentrations (Kreuger 1998; Louchart et al. 2001; Rabiet et al.  
357 2010; Taghavi et al. 2011; Petersen et al. 2012). At the downstream site of the Ardières River,  
358 the increases in the concentrations of simazine, dimethomorph, tebuconazole and diflufenican  
359 from the first week to the second week of the campaign could be linked to rainfall that  
360 occurred on Day 8 (May 31) (Table 3). Similarly, increases in the concentrations of simazine,  
361 atrazine, dimethomorph, metolachlor, tebuconazole and diflufenican from the third week to  
362 the fourth week, at the downstream site of the Ardières River, may have been caused by  
363 rainfall that occurred on Day 24 (June 16).

364 A few events of severe spot contaminations were detected via passive SBSE during both  
365 campaigns. In spring 2010, the rainfall on Day 13 (June 6) probably triggered a concentration  
366 peak of chlorpyrifos-ethyl, quantified at  $9011 \text{ ng L}^{-1}$ , at the downstream site of the Morcille  
367 River during the first week of the field campaign. Interestingly, this could also explain the  
368 high chlorpyrifos-ethyl concentration ( $356 \text{ ng L}^{-1}$ ) obtained during the same period at the  
369 downstream site of the Ardières River: this site is close (at about 800 m) to the downstream  
370 site of the Morcille River (Figure 1). Likewise, on Day 23 (June 16), rainfall caused an  
371 increase in dimethomorph concentration at the downstream site of the Morcille River (up to  
372  $969 \text{ ng L}^{-1}$ ), and also an increase in the concentration of the same pesticide at the downstream  
373 site of the Ardières River (up to  $668 \text{ ng L}^{-1}$ ). Finally, as observed in spring 2010, an  
374 acetochlor contamination at the upstream site of the Ardières River, linked to the maize field  
375 upstream from this sampling site, was quantified in spring 2011 for 3 weeks (from 816 to 216  
376  $\text{ng L}^{-1}$ ).

377

## 378 **5 Conclusion**

379

380 The time-representativeness of this new passive sampling technique over periods of one or  
381 two weeks was better than spot sampling. Moreover, while presenting results similar to those  
382 obtained from automated sampling at lower cost, the passive SBSE gave lower LQ for most  
383 hydrophobic compounds, allowing the quantification of lower concentrations of the target  
384 pesticides in water. This simple, cost-effective and environmentally friendly sampling  
385 technique is therefore well suited to determining average estimates of pesticides in dynamic  
386 rivers. The small size of the passive Twisters allows extensive deployment in field studies,  
387 with simple handling and preparation before deployment, and *in situ* use. Lastly, passive  
388 SBSE designed for the study of pesticide contamination can tell us not only the spatial and  
389 temporal variations in pesticide concentrations, but also the impact of rainfall and runoff on  
390 the chemical quality of small rivers located in an agricultural watershed.

391

## 392 **6 Acknowledgments**

393

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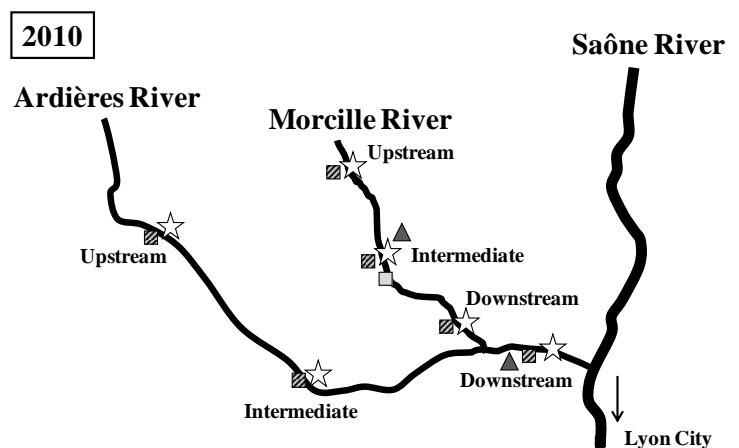
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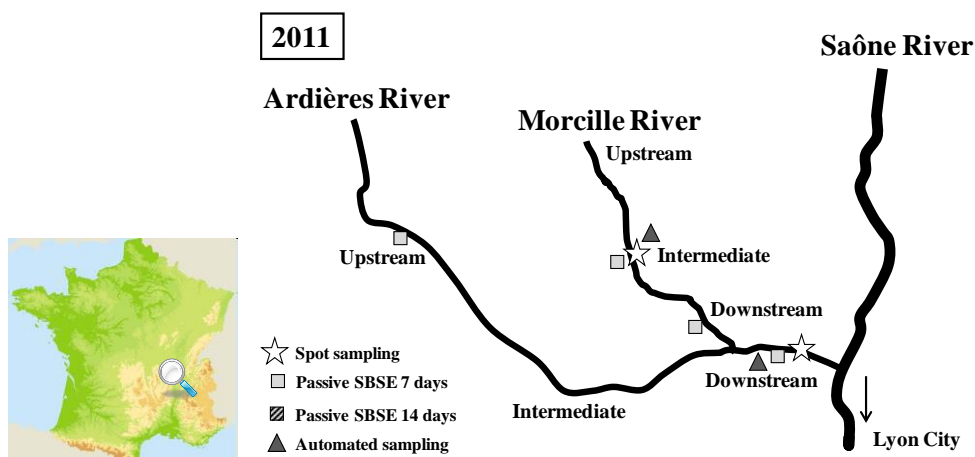
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502



503 Figure 1. Locations of the deployment and sampling sites along the Morcille River and the  
504 Ardières River, for the spring 2010 and spring 2011 field campaigns (Beaujolais region,  
505 France).

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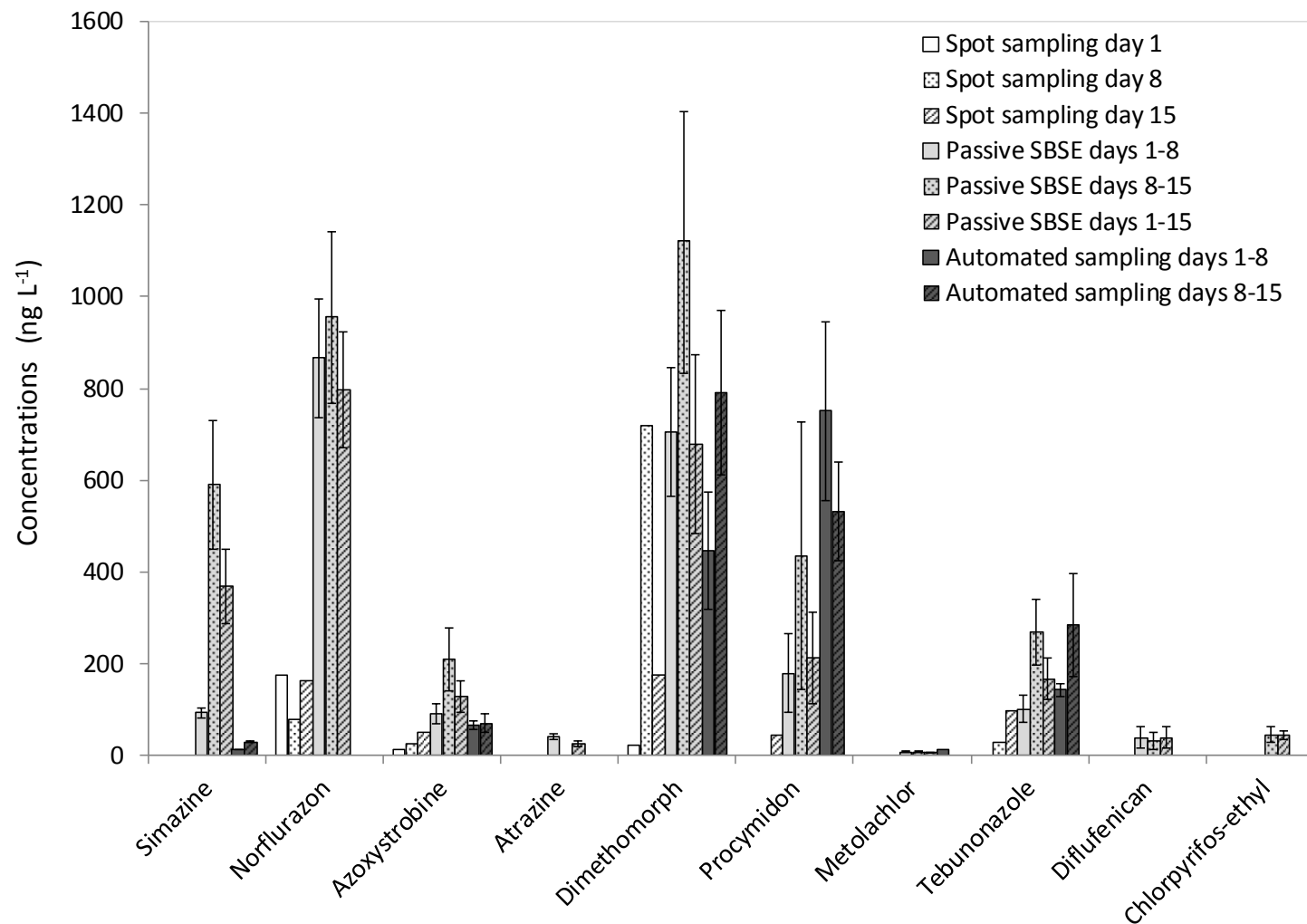
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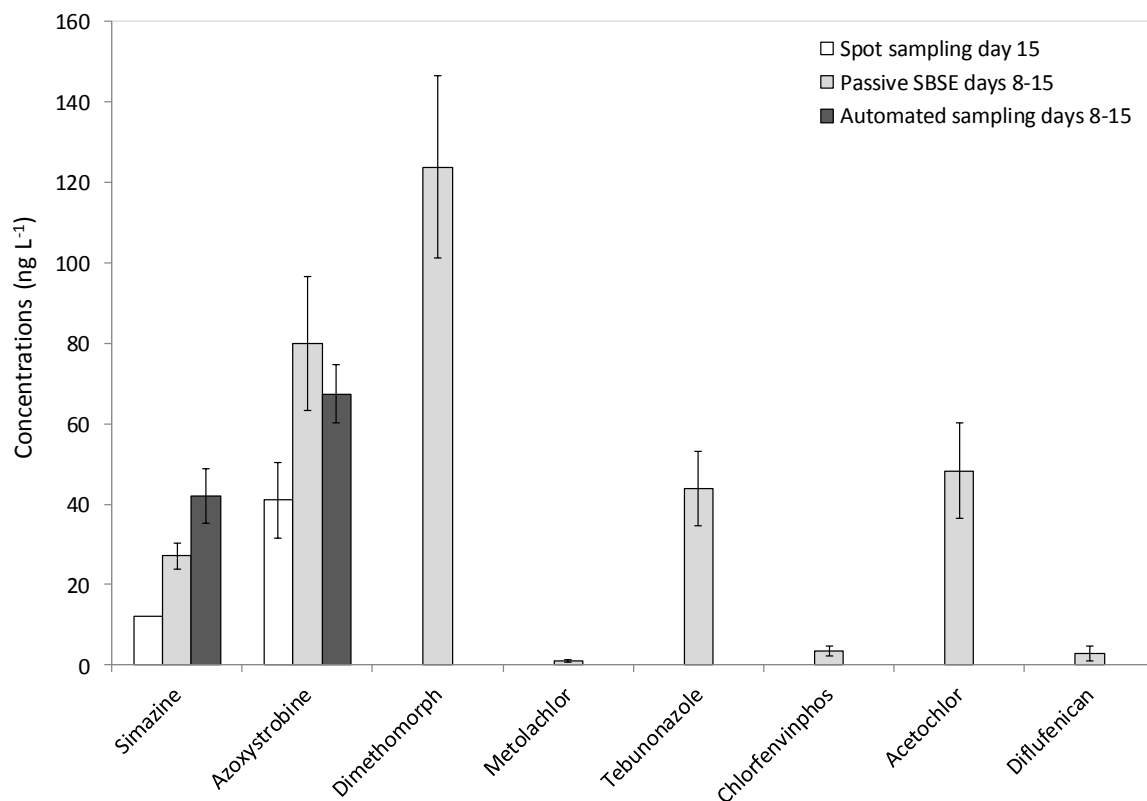
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517 Figure 2. Comparison of passive SBSE (n = 3), spot sampling (n = 1) and automated sampling (n = 3) for the determination of the concentrations  
518 of the target pesticides at the intermediate site of the Morcille River, during the first 2 weeks of the spring 2010 field campaign. Pesticides are  
519 sorted by increasing values of  $\log K_{ow}$ . Error bars represent the standard deviation. Only the quantified pesticides are displayed.



520

521 Figure 3. Comparison of passive SBSE (n = 3), spot sampling (n = 1) and automated sampling  
522 (n = 3) for the determination of the concentrations of the target pesticides at the downstream  
523 site of the Ardières River, during the third week of the spring 2011 field campaign. Pesticides  
524 are sorted by increasing values of log K<sub>ow</sub>. Error bars represent the standard deviation. Only  
525 the quantified pesticides are displayed.

526



527 Table 1. Limits of quantification of the 16 studied pesticides obtained for passive SBSE  
 528 followed by LD-LC-MS/MS analysis, for analytical SBSE-LD-LC-MS/MS of water samples  
 529 and for SPE-LC-MS/MS analysis of water samples.

Pesticide	Abbreviation	Use	log K <sub>ow</sub>	Limits of quantification (ng L <sup>-1</sup> )		
				Passive SBSE	SBSE-LD-LC-MS/MS	SPE-LC-MS/MS
Simazine	SMZ	H	2.18	2.5	10	nt
Norflurazon	NFZ	H	2.30	171	200	5.0
Azoxystrobin	AZS	F	2.50	12	20	5.0
Atrazine	ATZ	H	2.61	11	10	nt
Dimethomorph	DMM	F	2.68	33	100	10
3,4-dichloroaniline	DCA	M	2.69	165	50	10
Isoproturon	IPU	H	2.87	86	100	5.0
Procymidon	PCM	F	3.08	37	200	20
Metolachlor	MTC	H	3.13	0.4	10	nt
Fenitrothion	FNT	I	3.32	6.6	500	50
Tebuconazole	TBZ	F	3.70	8.1	100	5.0
Chlorfenvinphos	CFV	I	3.81	2.3	100	20
Acetochlor	ATC	H	4.14	32	100	nt
Diflufenican	DFF	H	4.20	1.2	200	20
Chlorpyrifos-ethyl	CPE	I	4.96	3.1	50	20
Flufenoxuron	FFX	I	5.11	25	200	20

530 H: herbicide; F: fungicide; M: metabolite; I: insecticide; nt: non targeted

531 Table 2. Concentrations of pesticides in the Ardières River and the Morcille River obtained from passive SBSE (n = 3), spot sampling (n= 1) and  
 532 automated sampling (n = 3) during the spring 2010 campaign. Only pesticides quantified at least once are displayed.

Site	Samples	Pesticide concentrations (ng L <sup>-1</sup> )											
		<i>Standard deviation (ng L<sup>-1</sup>)</i>											
		SMZ	NFZ	AZS	ATZ	DMM	PCM	MTC	TBZ	ATC	DFP	CPE	FFX
<b>Upstream</b>	Passive SBSE days 1-15	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	8.7	22	36	26	20	<LQ
								2.8	5	10	15	5	
	Spot sampling day 1	nt	<LQ	<LQ	nt	<LQ	<LQ	nt	<LQ	nt	<LQ	<LQ	<LQ
	Spot sampling day 15	nt	<LQ	<LQ	nt	215	<LQ	nt	<LQ	nt	<LQ	<LQ	<LQ
	Passive SBSE days 15-29	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	4.8	<LQ	<LQ	<LQ	<LQ	<LQ
								1.4					
Spot sampling day 29	nt	<LQ	<LQ	nt	<LQ	<LQ	nt	<LQ	nt	<LQ	<LQ	<LQ	
<b>Intermediate</b>	Passive SBSE days 1-15	50	<LQ	34	<LQ	661	153	7.7	402	<LQ	79	45	<LQ
		7		10		365	76	3.6	166		48	15	
	Spot sampling day 1	nt	21	<LQ	nt	15	<LQ	nt	<LQ	nt	<LQ	<LQ	<LQ
	Spot sampling day 15	nt	69	<LQ	nt	185	<LQ	nt	123	nt	<LQ	<LQ	<LQ
	Passive SBSE days 15-29	-	-	-	-	-	-	-	-	-	-	-	-
		-	-	-	-	-	-	-	-	-	-	-	-
Spot sampling day 29	nt	28	<LQ	nt	55	<LQ	nt	<LQ	nt	<LQ	<LQ	<LQ	
<b>Downstream</b>	Passive SBSE days 1-15	89	<LQ	71	<LQ	1030	182	11	463	<LQ	50	356	<LQ
		9		14		199	86	2	97		30	87	
	Automated sampling days 1-8	<LQ	<LQ	27	<LQ	148	703	13	462	<LQ	266	74	<LQ
				2		38	131	1	15		2	13	
	Automated sampling days 8-15	69	290	365	<LQ	5087	513	<LQ	1626	<LQ	258	<LQ	<LQ
		3	98	22		635	105		70		1		
Spot sampling day 1	nt	28	<LQ	nt	19	<LQ	nt	<LQ	nt	<LQ	<LQ	<LQ	
Spot sampling day 8	nt	27	<LQ	nt	50	<LQ	nt	27	nt	<LQ	<LQ	<LQ	

533 Table 2. (continued)

Site	Samples	Pesticide concentrations (ng L <sup>-1</sup> )											
		SMZ	NFZ	AZS	ATZ	DMM	PCM	MTC	TBZ	ATC	DFP	CPE	FFX
Ardières River	Spot sampling day 15	nt	72.1	18.3	nt	23.5	<LQ	nt	97.0	nt	<LQ	<LQ	<LQ
	Passive SBSE days 15-29	42	<LQ	64	<LQ	668	157	7.1	303	<LQ	28	33	<LQ
		5		57		243	75	2.2	67		16	19	
	Automated sampling days 15-22	66	<LQ	11	<LQ	592	<LQ	<LQ	180	<LQ	<LQ	<LQ	<LQ
		33		-		111			49				
	Automated sampling days 22-29	<LQ	<LQ	12	<LQ	881	<LQ	<LQ	130	<LQ	<LQ	<LQ	<LQ
				8		195			76				
Spot sampling day 22	nt	105	88	nt	2113	28	nt	493	nt	<LQ	<LQ	<LQ	
Spot sampling day 29	nt	34	<LQ	nt	72	<LQ	nt	21	nt	<LQ	<LQ	<LQ	
Morcille River	Passive SBSE days 1-15	45	<LQ	<LQ	<LQ	<LQ	<LQ	4.9	33	<LQ	<LQ	<LQ	<LQ
		5						1.0	7				
	Spot sampling day 1	nt	12	<LQ	nt	11	<LQ	nt	<LQ	nt	<LQ	<LQ	<LQ
	Spot sampling day 15	nt	19	<LQ	nt	11	<LQ	nt	<LQ	nt	<LQ	<LQ	<LQ
	Passive SBSE days 15-29	<LQ	<LQ	<LQ	<LQ	<LQ	126	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
							59						
	Spot sampling day 29	nt	17	<LQ	nt	<LQ	<LQ	nt	<LQ	nt	<LQ	<LQ	<LQ
Passive SBSE days 1-8	92	867	91	40	706	178	7.4	101	<LQ	39	<LQ	<LQ	
	12	129	21	7	140	86	1.6	29		23			
Intermediate	Passive SBSE days 8-15	589	956	210	<LQ	1120	435	6.8	268	<LQ	31	44	<LQ
		140	187	69		286	292	1.4	73		18	18	
Passive SBSE days 1-15		369	796	128	25	678	212	5.5	167	<LQ	39	43	<LQ
		81	127	35	6	196	99	1.2	45		24	10	

534  
535

536 Table 2. (continued)

Site	Samples	Pesticide concentrations (ng L <sup>-1</sup> )												
		SMZ	NFZ	AZS	ATZ	DMM	PCM	MTC	TBZ	ATC	DFP	CPE	FFX	
Morcille River	Automated sampling days 1-8	13	<LQ	66	<LQ	446	751	12	142	<LQ	<LQ	<LQ	<LQ	
		<i>1</i>		<i>10</i>		<i>128</i>	<i>196</i>	-	<i>15</i>					
	Automated sampling days 8-15	28	<LQ	70	<LQ	792	531	<LQ	285	<LQ	<LQ	<LQ	<LQ	
		<i>2</i>		<i>21</i>		<i>180</i>	<i>108</i>		<i>112</i>					
	Spot sampling day 1	nt	173	11	nt	23	<LQ	nt	<LQ	nt	<LQ	<LQ	<LQ	
	Spot sampling day 8	nt	78	27	nt	718	<LQ	nt	30	nt	<LQ	<LQ	<LQ	
	Spot sampling day 15	nt	163	49	nt	176	44	nt	96	nt	<LQ	<LQ	<LQ	
	Passive SBSE days 15-22	213	<LQ	93	<LQ	360	257	4.2	225	<LQ	<LQ	<LQ	<LQ	
		<i>31</i>		<i>37</i>		<i>66</i>	<i>132</i>	<i>0.8</i>	<i>75</i>					
	Intermediate	Passive SBSE days 22-29	132	869	85	<LQ	349	328	4.5	230	<LQ	<LQ	<LQ	<LQ
			<i>43</i>	<i>130</i>	<i>51</i>		<i>64</i>	<i>194</i>	<i>1.0</i>	<i>107</i>				
	Passive SBSE days 15-29	198	<LQ	91	<LQ	<LQ	323	3.8	250	<LQ	<LQ	<LQ	<LQ	
		<i>22</i>		<i>20</i>			<i>155</i>	<i>0.7</i>	<i>73</i>					
	Automated sampling days 15-22	408	329	73	<LQ	459	<LQ	<LQ	116	<LQ	<LQ	<LQ	<LQ	
		<i>72</i>	<i>59</i>	<i>6</i>		<i>43</i>			<i>8</i>					
	Automated sampling days 22-29	106	487	72	<LQ	331	<LQ	<LQ	126	<LQ	<LQ	<LQ	<LQ	
<i>20</i>		<i>238</i>	<i>10</i>		<i>26</i>			<i>13</i>						
Spot sampling day 22	nt	129	84	nt	167	24	nt	129	nt	<LQ	<LQ	<LQ		
Spot sampling day 29	nt	105	29	nt	56	26	nt	38	nt	<LQ	<LQ	<LQ		
Downstream	Passive SBSE days 1-15	293	862	200	<LQ	1248	222	5.8	469	<LQ	35	9011	<LQ	
		<i>86</i>	<i>176</i>	<i>86</i>		<i>651</i>	<i>116</i>	<i>1.1</i>	<i>243</i>		<i>21</i>	<i>2227</i>		
	Spot sampling day 1	nt	52	17	nt	36	<LQ	nt	20	nt	<LQ	<LQ	<LQ	

537  
538

539 Table 2. (end)

Site	Samples	Pesticide concentrations (ng L <sup>-1</sup> )											
		Standard deviation (ng L <sup>-1</sup> )											
		SMZ	NFZ	AZS	ATZ	DMM	PCM	MTC	TBZ	ATC	DFP	CPE	FFX
	Spot sampling day 15	nt	148	75	nt	242	35	nt	102	nt	< LQ	< LQ	< LQ
<b>Downstream</b>	Passive SBSE days 15-29	103	< LQ	72	< LQ	969	240	5.1	418	< LQ	33	783	596
		31		23		429	159	1.4	198		20	471	448
	Spot sampling day 29	nt	116	29	nt	137	27	nt	57	nt	< LQ	< LQ	< LQ

540 LQ: limit of quantification; nt: non targeted.

541

542 Table 3. Concentrations of pesticides in the Ardières River and the Morcille River obtained from passive SBSE (n = 3), spot sampling (n = 3) and  
 543 automated sampling (n = 3) during the spring 2011 campaign. Only pesticides quantified at least once are displayed.

Site	Samples	Pesticide concentrations (ng L <sup>-1</sup> )														
		Standard deviation (ng L <sup>-1</sup> )														
		SMZ	NFZ	AZS	ATZ	DMM	DCA	PCM	MTC	TBZ	CFV	ATC	DFP	CPE		
Ardières River	Upstream	Passive SBSE days 1-8	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	2.6	<LQ	
														1.5		
		Passive SBSE days 8-15	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	816	2.3	<LQ
														196	1.4	
		Passive SBSE days 15-22	<LQ	<LQ	<LQ	8.6	<LQ	<LQ	<LQ	0.4	<LQ	<LQ	429	1.7	12	
					2.2				0.2			115	1.1	3		
	Passive SBSE days 22-29	<LQ	<LQ	<LQ	9.0	<LQ	<LQ	<LQ	<LQ	<LQ	4.1	216	3.1	<LQ		
					2.4						1.8	64	3.0			
	Downstream	Passive SBSE days 1-8	10	<LQ	70	<LQ	<LQ	<LQ	<LQ	<LQ	21	<LQ	<LQ	2.3	<LQ	
			3		22						8			1.4		
Spot sampling day 8		<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ		
Automated sampling days 1-8		<LQ	<LQ	61	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ		
				6												
Passive SBSE days 8-15		61	<LQ	18	<LQ	93	<LQ	<LQ	<LQ	58	<LQ	<LQ	10	<LQ		
		10		4		42				14			12			
Automated sampling days 8-15		108	<LQ	25	<LQ	<LQ	61	<LQ	<LQ	<LQ	<LQ	104	<LQ	<LQ		
	3		2			-					2					
Passive SBSE days 15-22	27	<LQ	80	<LQ	124	<LQ	<LQ	1.1	44	3.4	48	2.9	<LQ			
	3		17		23			0.3	9	1.2	12	1.8				
Spot sampling day 22	12	<LQ	41	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ			
	-		10													
Automated sampling days 15-22	42	<LQ	67	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ			
	7		7													

544 Table 3. (continued)

Site	Samples	Pesticide concentrations (ng L <sup>-1</sup> )													
		Standard deviation (ng L <sup>-1</sup> )													
		SMZ	NFZ	AZS	ATZ	DMM	DCA	PCM	MTC	TBZ	CFV	ATC	DFF	CPE	
Ardières River	Downstream	Passive SBSE days 22-29	111	<LQ	79	7.9	494	<LQ	<LQ	2.6	169	3.4	<LQ	11	<LQ
			29		30	1.4	91			0.6	51	1.2		8	
	Spot sampling day 29	31	<LQ	22	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
		6		-											
	Automated sampling days 22-29	31	294	38	<LQ	317	<LQ	<LQ	<LQ	111	<LQ	<LQ	<LQ	<LQ	
		5	115	2		29				3					
Morcille River	Downstream	Passive SBSE days 1-8	10	<LQ	<LQ	<LQ	71	<LQ	<LQ	<LQ	20	<LQ	<LQ	<LQ	<LQ
			1				13				5				
		Spot sampling day 8	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
		Automated sampling days 1-8	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
	Intermediate	Passive SBSE days 8-15	11	<LQ	<LQ	<LQ	393	<LQ	<LQ	<LQ	44	<LQ	<LQ	<LQ	<LQ
			4				149				21				
		Automated sampling days 8-15	<LQ	<LQ	<LQ	<LQ	477	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
						43									
Upstream	Passive SBSE days 15-22	13	<LQ	<LQ	<LQ	181	<LQ	<LQ	0.5	60	4.2	<LQ	1.1	3.5	
		1				33			0.2	13	1.6		0.7	0.8	
	Spot sampling day 22	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
	Automated sampling days 15-22	<LQ	<LQ	<LQ	<LQ	111	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
					2										

545

546 Table 3. (continued)

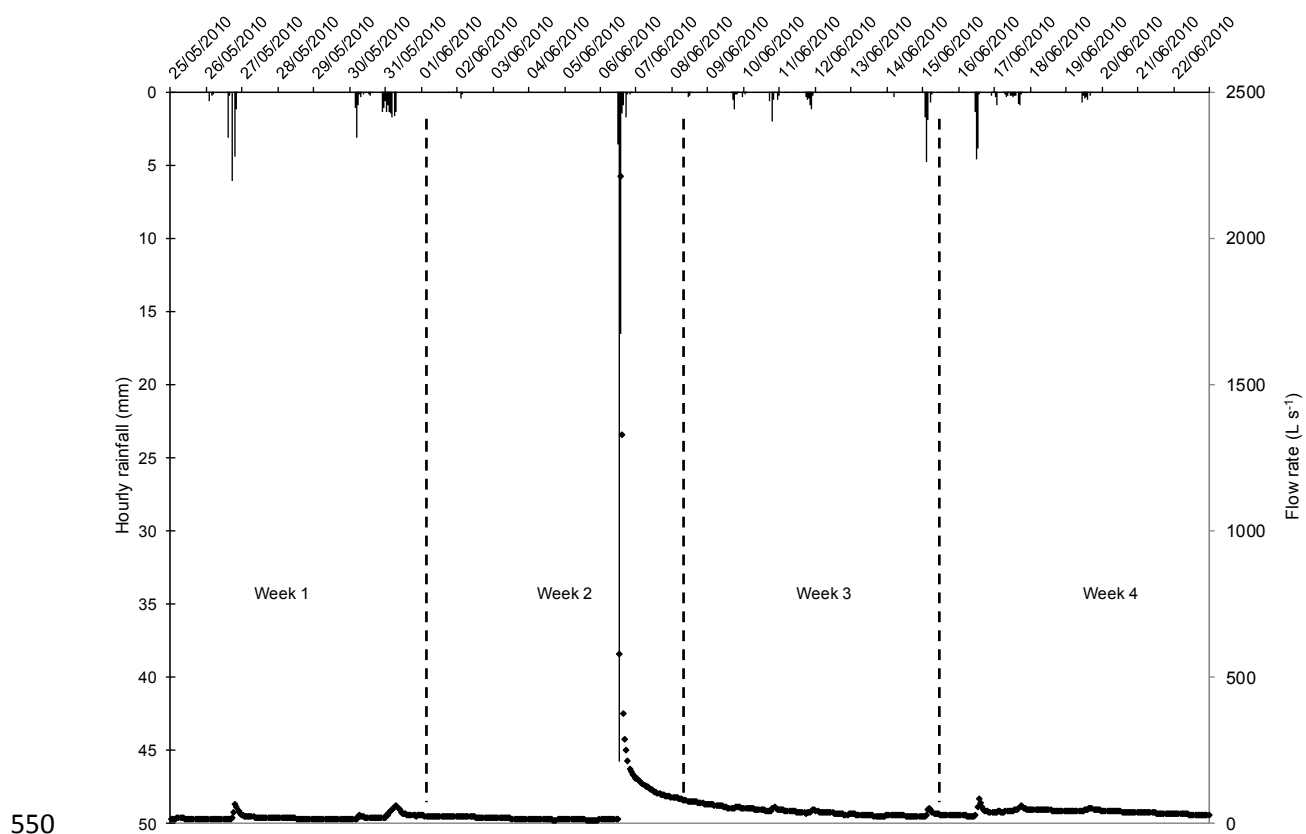
Site	Samples	Pesticide concentrations (ng L <sup>-1</sup> )												
		Standard deviation (ng L <sup>-1</sup> )												
		SMZ	NFZ	AZS	ATZ	DMM	DCA	PCM	MTC	TBZ	CFV	ATC	DFP	CPE
	Passive SBSE days 22-29	26	<LQ	43	<LQ	<LQ	<LQ	48	0.9	249	<LQ	<LQ	2.5	<LQ
		2		12				23	0.3	59			1.6	
	Spot sampling day 29	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
	Automated sampling days 22-29	13	<LQ	22	<LQ	169	<LQ	<LQ	<LQ	197	<LQ	<LQ	<LQ	<LQ
		-		-		88				26				
<b>Downstream</b>	Passive SBSE days 1-8	16	<LQ	77	<LQ	99	<LQ	<LQ	<LQ	113	<LQ	<LQ	2.5	<LQ
		2		23		19				38			2.1	
	Passive SBSE days 8-15	12	<LQ	24	<LQ	82	<LQ	<LQ	<LQ	112	<LQ	<LQ	12	<LQ
		3		20		60				41			7	

547 LQ: limit of quantification; nt: non targeted.

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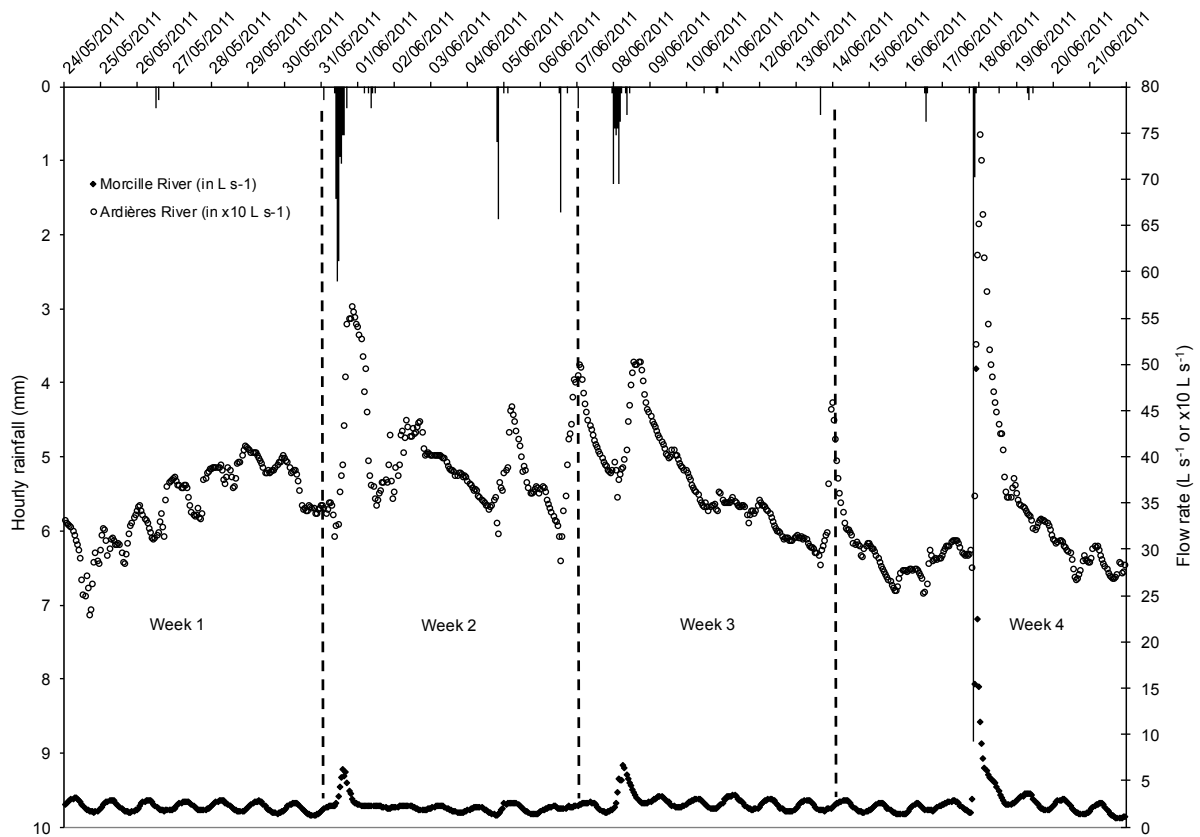


549 **Supplementary Data**



551 Figure S1. Hourly rainfall (in mm) and flow rate at the intermediate site of the Morcille River  
552 (in  $L s^{-1}$ ) during the spring 2010 campaign.

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Figure S2. Hourly rainfall (in mm) and flow rate at the intermediate site of the Morcille River (in  $L s^{-1}$ ) and at the downstream site of the Ardières River (in  $x10 L s^{-1}$ ) during the spring 2011 campaign.