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Field application of passive SBSE for the monitoring of pesticides in surface waters

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Abstract

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

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

1 Introduction

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

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

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

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

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

2 Experimental

2.1 Chemicals and materials

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

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

2.2 Field experiments

Two monitoring campaigns took place along two rivers of a French vineyard watershed (220 km²) located about 70 km north of Lyon in the Beaujolais region, the Morcille River and the Ardières River (Figure 1). The Morcille River is a tributary of the Ardières River and is located in a subwatershed of 8 km². In spring, the typical flow of the Morcille River is 5 L s⁻¹ (Figure S1 in Supplementary data section), and the typical flow of the Ardières River is 350 L s⁻¹ (Figure S2). Typical flood events last 5 h for the Morcille River and 24 h for the Ardières

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

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

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

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

2.3 Chemical analysis of water samples and passive Twisters

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

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

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

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

3 Theory

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

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

where M_s (ng) is the mass of contaminant accumulated in the receiving phase, C_w (ng mL⁻¹) the concentration of contaminant in the water phase, R_s the sampling rate (mL d⁻¹), and t (d) the exposure time.

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

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

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

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

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

where V_s (L) is the volume of the receiving phase, K_{sw} (adimensional), described as the ratio of the concentration at equilibrium of contaminant in the passive Twister C_s (ng mL⁻¹) to the concentration at equilibrium of contaminant in the water phase C_w (ng mL⁻¹). When the passive Twister is deployed in the field for longer than the linear accumulation period, TWA 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 (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 ng L^{-1}) and 3,4-dichloroaniline (165 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 azoxystrobin, 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 cm s⁻¹) and
296 temperature (10 and 25 °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.

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

4.2 Determination of pesticide contamination with passive SBSE

4.2.1 Spatial variations in pesticide concentrations

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

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

4.2.2 Temporal variations in pesticide concentrations

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

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

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

5 Conclusion

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

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References

- Alvarez DA, Petty JD, Huckins JN, et al. (2004) Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. *Environ Toxicol Chem* 23:1640–1648. doi: 10.1897/03-603
- Assoumani A, Lissalde S, Margoum C, et al. (2013) In situ application of stir bar sorptive extraction as a passive sampling technique for the monitoring of agricultural pesticides in surface waters. *Sci Total Environ* 463–464:829–835. doi: 10.1016/j.scitotenv.2013.06.025
- Assoumani A, Margoum C, Chataing S, et al. (2014) Use of passive stir bar sorptive extraction as a simple integrative sampling technique of pesticides in freshwaters: Determination of sampling rates and lag-phases. *J Chromatogr A* 1333:1–8. doi: 10.1016/j.chroma.2014.01.063
- Bailly E, Levi Y, Karolak S (2013) Calibration and field evaluation of polar organic chemical integrative sampler (POCIS) for monitoring pharmaceuticals in hospital wastewater. *Environ Pollut* 174:100–105. doi: 10.1016/j.envpol.2012.10.025
- Baltussen E, Sandra P, David F, Cramers C (1999) Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: Theory and principles. *J Microcolumn Sep* 11:737–747. doi: 10.1002/(SICI)1520-667X(1999)11:10<737::AID-MCS7>3.0.CO;2-4
- Booij K, Sleiderink HM, Smedes F (1998) Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards. *Environ Toxicol Chem* 17:1236–1245. doi: 10.1002/etc.5620170707
- Dalton RL, Pick FR, Boutin C, Saleem A (2014) Atrazine contamination at the watershed scale and environmental factors affecting sampling rates of the polar organic chemical integrative sampler (POCIS). *Environ Pollut* 189:134–142. doi: 10.1016/j.envpol.2014.02.028
- Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing the framework for Community action in the field of water policy. *OJ L* 327, 22.12.2000, pp.1-73.
- Greenwood R, Mills GA, Vrana B (2007a) Passive sampling techniques in environmental monitoring (*Comprehensive analytical chemistry*, Vol. 48).
- Greenwood R, Mills GA, Roig B (2007b) Introduction to emerging tools and their use in water monitoring. *TrAC - Trends Anal Chem* 26:263–267. doi: 10.1016/j.trac.2006.12.006
- Huckins JN, Petty JD, Booij K (2006) *Monitors of Organic Chemicals in the Environment: Semipermeable Membrane Devices*. New York, NY

- 437 Huckins JN, Petty JD, Lebo JA, et al. (2002) Development of the Permeability/Performance
438 Reference Compound Approach for In Situ Calibration of Semipermeable Membrane
439 Devices. *Environ Sci Technol* 36:85–91. doi: 10.1021/es010991w
- 440 Hyne RV, Aistrope M (2008) Calibration and field application of a solvent-based cellulose
441 membrane passive sampling device for the monitoring of polar herbicides.
442 *Chemosphere* 71:611–620. doi: 10.1016/j.chemosphere.2007.11.017
- 443 Ibrahim I, Togola A, Gonzalez C (2013) In-situ calibration of POCIS for the sampling of
444 polar pesticides and metabolites in surface water. *Talanta* 116:495–500. doi:
445 10.1016/j.talanta.2013.07.028
- 446 Kaserzon SL, Kennedy K, Hawker DW, et al. (2012) Development and Calibration of a
447 Passive Sampler for Perfluorinated Alkyl Carboxylates and Sulfonates in Water.
448 *Environ Sci Technol* 46:4985–4993. doi: 10.1021/es300593a
- 449 Kreuger J (1998) Pesticides in stream water within an agricultural catchment in southern
450 Sweden, 1990–1996. *Sci Total Environ* 216:227–251. doi: 10.1016/S0048-
451 9697(98)00155-7
- 452 Lohmann R, Booij K, Smedes F, Vrana B (2012) Use of passive sampling devices for
453 monitoring and compliance checking of POP concentrations in water. *Environ Sci*
454 *Pollut Res* 19:1885–1895. doi: 10.1007/s11356-012-0748-9
- 455 Louchart X, Voltz M, Andrieux P, Moussa R (2001) Herbicide Transport to Surface Waters at
456 Field and Watershed Scales in a Mediterranean Vineyard Area. *J Environ Qual*
457 30:982. doi: 10.2134/jeq2001.303982x
- 458 Madrid Y, Zayas ZP (2007) Water sampling: Traditional methods and new approaches in
459 water sampling strategy. *TrAC Trends Anal Chem* 26:293–299. doi:
460 10.1016/j.trac.2007.01.002
- 461 Margoum C, Guillemain C, Yang X, Coquery M (2013) Stir bar sorptive extraction coupled to
462 liquid chromatography-tandem mass spectrometry for the determination of pesticides
463 in water samples: Method validation and measurement uncertainty. *Talanta* 116:1–7.
464 doi: 10.1016/j.talanta.2013.04.066
- 465 Mazzella N, Lissalde S, Moreira S, et al. (2010) Evaluation of the Use of Performance
466 Reference Compounds in an Oasis-HLB Adsorbent Based Passive Sampler for
467 Improving Water Concentration Estimates of Polar Herbicides in Freshwater. *Environ*
468 *Sci Technol* 44:1713–1719. doi: 10.1021/es902256m
- 469 Morin N, Miège C, Coquery M, Randon J (2012) Chemical calibration, performance,
470 validation and applications of the polar organic chemical integrative sampler (POCIS)
471 in aquatic environments. *TrAC Trends Anal Chem* 36:144–175. doi:
472 10.1016/j.trac.2012.01.007
- 473 Namieśnik J, Zabiegała B, Kot-Wasik A, et al. (2005) Passive sampling and/or extraction
474 techniques in environmental analysis: a review. *Anal Bioanal Chem* 381:279–301. doi:
475 10.1007/s00216-004-2830-8

- 476 Petersen J, Grant R, Larsen SE, Blicher-Mathiesen G (2012) Sampling of herbicides in
477 streams during flood events. *J Environ Monit* 14:3284–3294. doi:
478 10.1039/C2EM30771E
- 479 Rabiet M, Margoum C, Gouy V, et al. (2010) Assessing pesticide concentrations and fluxes in
480 the stream of a small vineyard catchment - Effect of sampling frequency. *Environ*
481 *Pollut* 158:737–748. doi: 10.1016/j.envpol.2009.10.014
- 482 Roig B, Valat C, Allan IJ, et al. (2007) The use of field studies to establish the performance of
483 a range of tools for monitoring water quality. *TrAC - Trends Anal Chem* 26:274–282.
484 doi: 10.1016/j.trac.2007.02.005
- 485 Smedes F (2007) Monitoring of chlorinated biphenyls and polycyclic aromatic hydrocarbons
486 by passive sampling in concert with deployed mussels. *Passive Sampl. Tech. Environ.*
487 *Monit.* Greenwood, R., Mills, G., Vrana, B., pp 407–447
- 488 Taghavi L, Merlina G, Probst J-L (2011) The role of storm flows in concentration of
489 pesticides associated with particulate and dissolved fractions as a threat to aquatic
490 ecosystems - Case study: the agricultural watershed of Save river (Southwest of
491 France). *Knowl Manag Aquat Ecosyst* 06. doi: 10.1051/kmae/2011002
- 492 Vrana B, Mills G, Allan I, et al. (2005) Passive sampling techniques for monitoring pollutants
493 in water. *TRAC-TRENDS Anal Chem* 24:845–868. doi: 10.1016/j.trac.2005.06.006
- 494 Vrana B, Popp P, Paschke A, Schüürmann G (2001) Membrane-Enclosed Sorptive Coating.
495 An Integrative Passive Sampler for Monitoring Organic Contaminants in Water. *Anal*
496 *Chem* 73:5191–5200. doi: 10.1021/ac010630z

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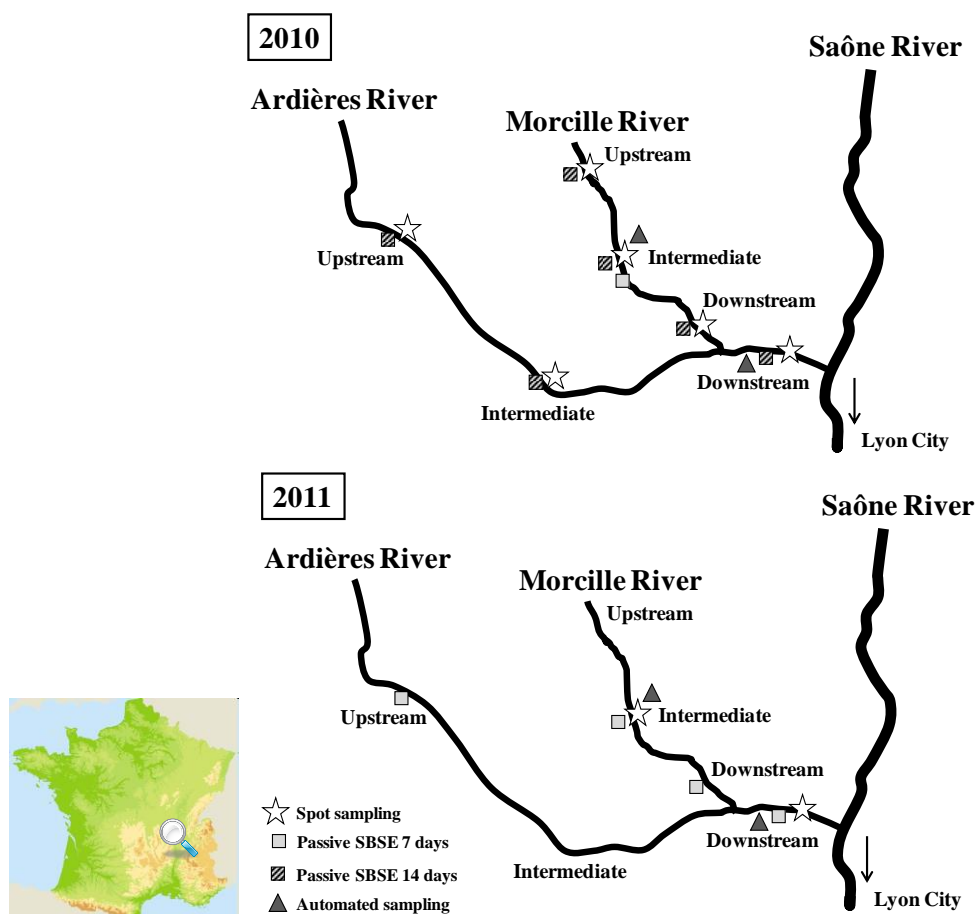
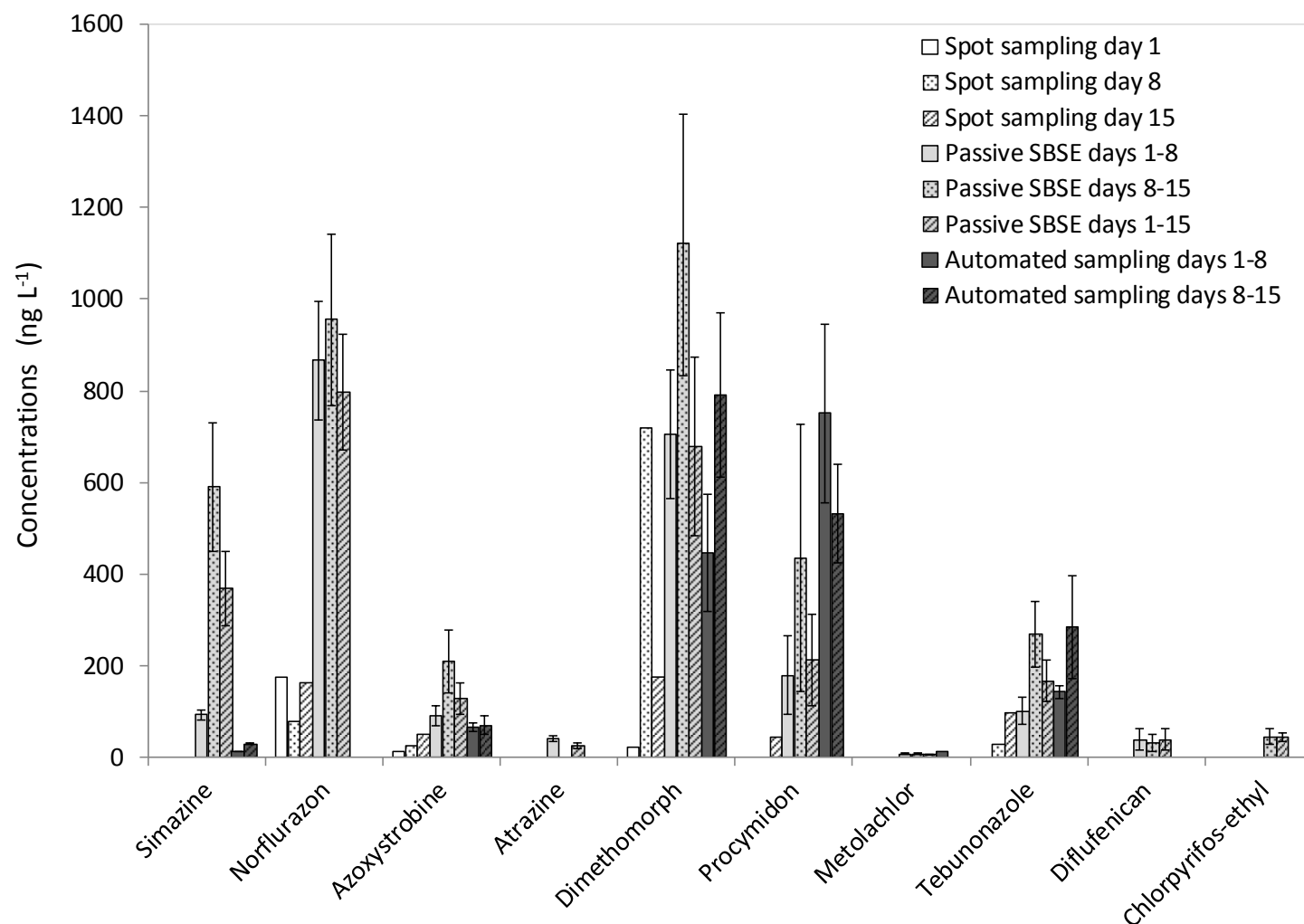


Figure 1. Locations of the deployment and sampling sites along the Morcille River and the Ardières River, for the spring 2010 and spring 2011 field campaigns (Beaujolais region, France).



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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.

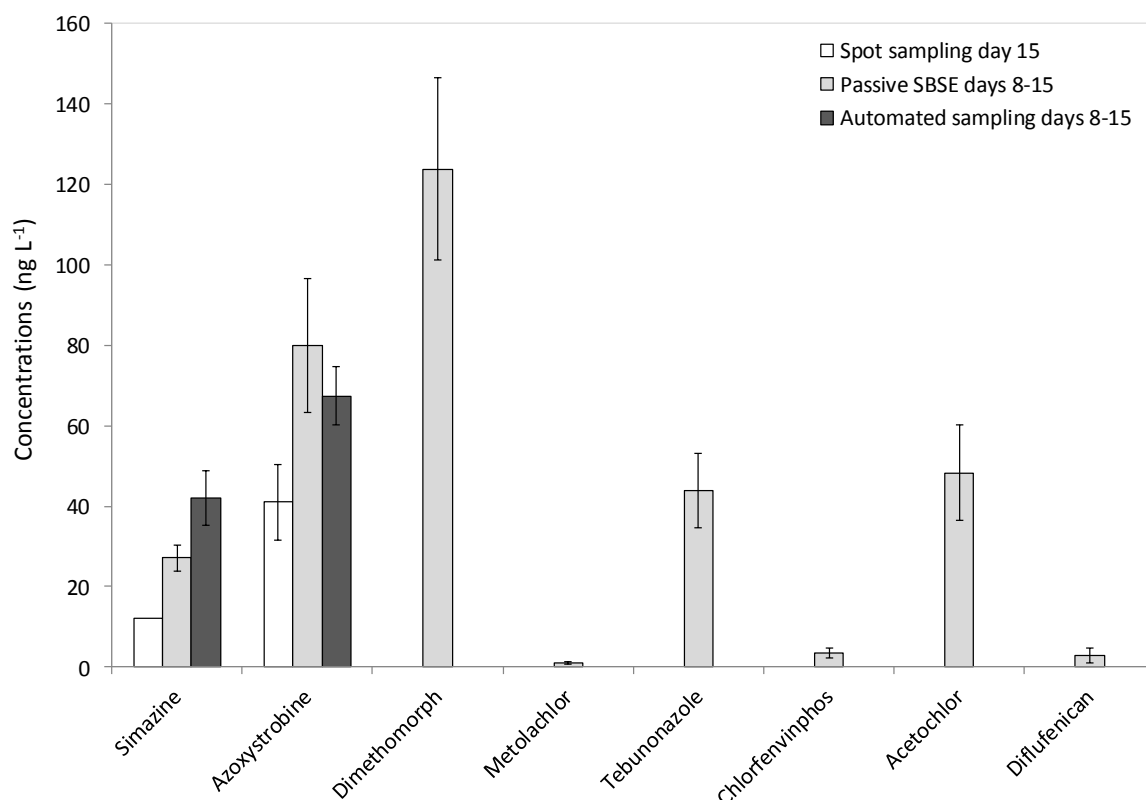


Figure 3. Comparison of passive SBSE ($n = 3$), spot sampling ($n = 1$) and automated sampling ($n = 3$) for the determination of the concentrations of the target pesticides at the downstream site of the Ardières River, during the third week of the spring 2011 field campaign. Pesticides are sorted by increasing values of $\log K_{ow}$. Error bars represent the standard deviation. Only the quantified pesticides are displayed.

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_{ow}	Limits of quantification (ng L ⁻¹)		
				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 Ardères 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 ⁻¹)											
		Standard deviation (ng L ⁻¹)											
		SMZ	NFZ	AZS	ATZ	DMM	PCM	MTC	TBZ	ATC	DFF	CPE	FFX
Upstream	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
Intermediate	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
Downstream	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 ⁻¹)											
		Standard deviation (ng L ⁻¹)											
		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				
Morcille River	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
	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
		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
Intermediate	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		
	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	

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536 Table 2. (continued)

Site	Samples	Pesticide concentrations (ng L ⁻¹) Standard deviation (ng L ⁻¹)											
		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
		1		10		128	196	-	15				
	Automated sampling days 8-15	28	< LQ	70	< LQ	792	531	< LQ	285	< LQ	< LQ	< LQ	< LQ
		2		21		180	108		112				
	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
		31		37		66	132	0.8	75				
	Passive SBSE days 22-29	132	869	85	< LQ	349	328	4.5	230	< LQ	< LQ	< LQ	< LQ
		43	130	51		64	194	1.0	107				
	Passive SBSE days 15-29	198	< LQ	91	< LQ	< LQ	323	3.8	250	< LQ	< LQ	< LQ	< LQ
		22		20			155	0.7	73				
	Automated sampling days 15-22	408	329	73	< LQ	459	< LQ	< LQ	116	< LQ	< LQ	< LQ	< LQ
		72	59	6		43			8				
	Automated sampling days 22-29	106	487	72	< LQ	331	< LQ	< LQ	126	< LQ	< LQ	< LQ	< LQ
		20	238	10		26			13				
	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
		86	176	86		651	116	1.1	243		21	2227	
	Spot sampling day 1	nt	52	17	nt	36	< LQ	nt	20	nt	< LQ	< LQ	< LQ

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539 Table 2. (end)

Site	Samples	Pesticide concentrations (ng L ⁻¹)											
		<i>Standard deviation (ng L⁻¹)</i>											
		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
Downstream	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 ⁻¹)												
		Standard deviation (ng L ⁻¹)												
		SMZ	NFZ	AZS	ATZ	DMM	DCA	PCM	MTC	TBZ	CFV	ATC	DFP	CPE
Ardières River	Upstream													
		< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	2.6	< LQ
		< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	816	2.3	< LQ
	Downstream													
		< LQ	< LQ	< LQ	8.6	< LQ	< LQ	< LQ	0.4	< LQ	< LQ	429	1.7	12
		< LQ	< LQ	< LQ	2.2	< LQ	< LQ	< LQ	0.2	< LQ	< LQ	115	1.1	3
	Automated sampling	< LQ	< LQ	< LQ	9.0	< LQ	< LQ	< LQ	< LQ	< LQ	4.1	216	3.1	< LQ
Morcille River	Upstream													
		10	< LQ	70	< LQ	< LQ	< LQ	< LQ	< LQ	21	< LQ	< LQ	2.3	< LQ
		3		22						8			1.4	
		< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
	Downstream	< LQ	< LQ	61	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
		61	< LQ	18	< LQ	93	< LQ	< LQ	< LQ	58	< LQ	< LQ	10	< LQ
		10		4		42				14			12	
	Automated sampling	108	< LQ	25	< LQ	< LQ	61	< LQ	< LQ	< LQ	< LQ	104	< LQ	< LQ
		3		2			-					2		
Morcille River	Upstream													
		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	
		12	< LQ	41	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
	Downstream													
		-		10										
		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 ⁻¹)													
		<i>Standard deviation (ng L⁻¹)</i>													
		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
			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	Intermediate	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
		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								
		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								

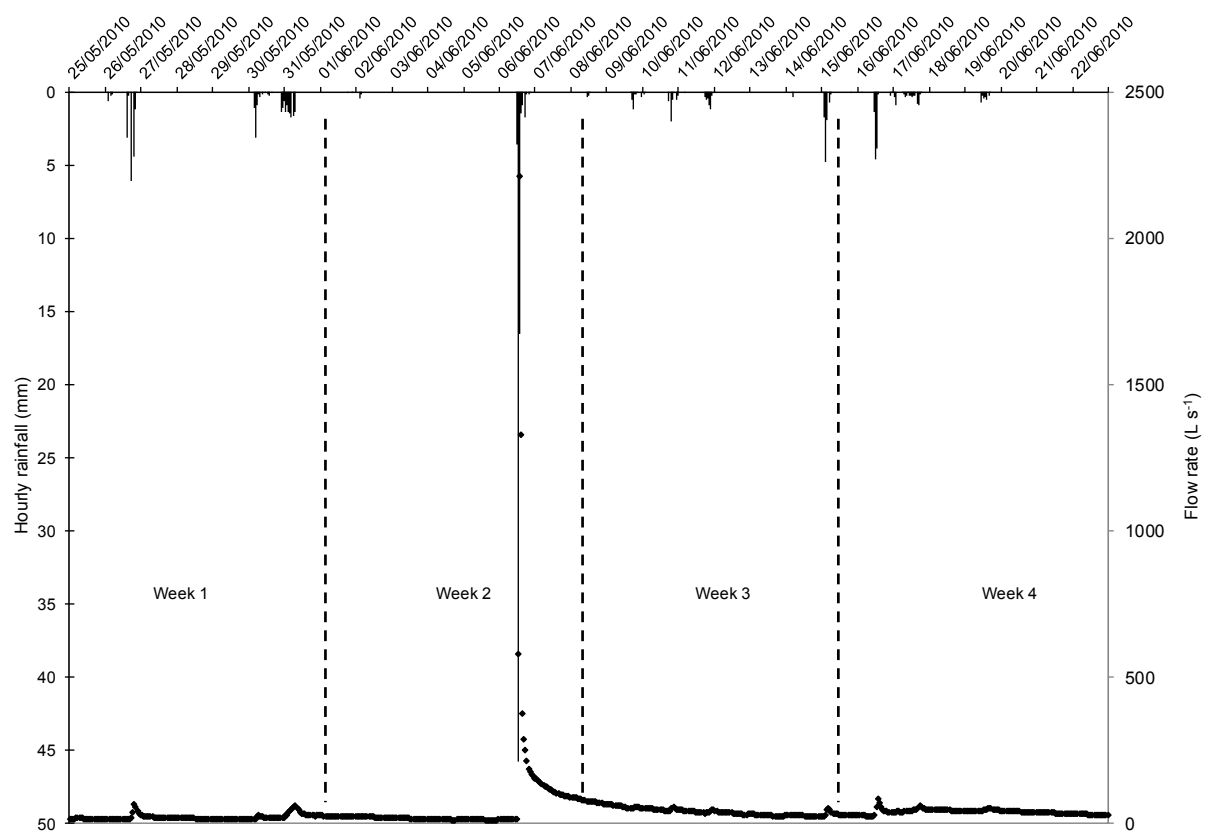
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546 Table 3. (continued)

Site	Samples	Pesticide concentrations (ng L ⁻¹)												
		<i>Standard deviation (ng L⁻¹)</i>												
		SMZ	NFZ	AZS	ATZ	DMM	DCA	PCM	MTC	TBZ	CFV	ATC	DFF	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				
Downstream	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	

LQ: limit of quantification; nt: non targeted.

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.
553

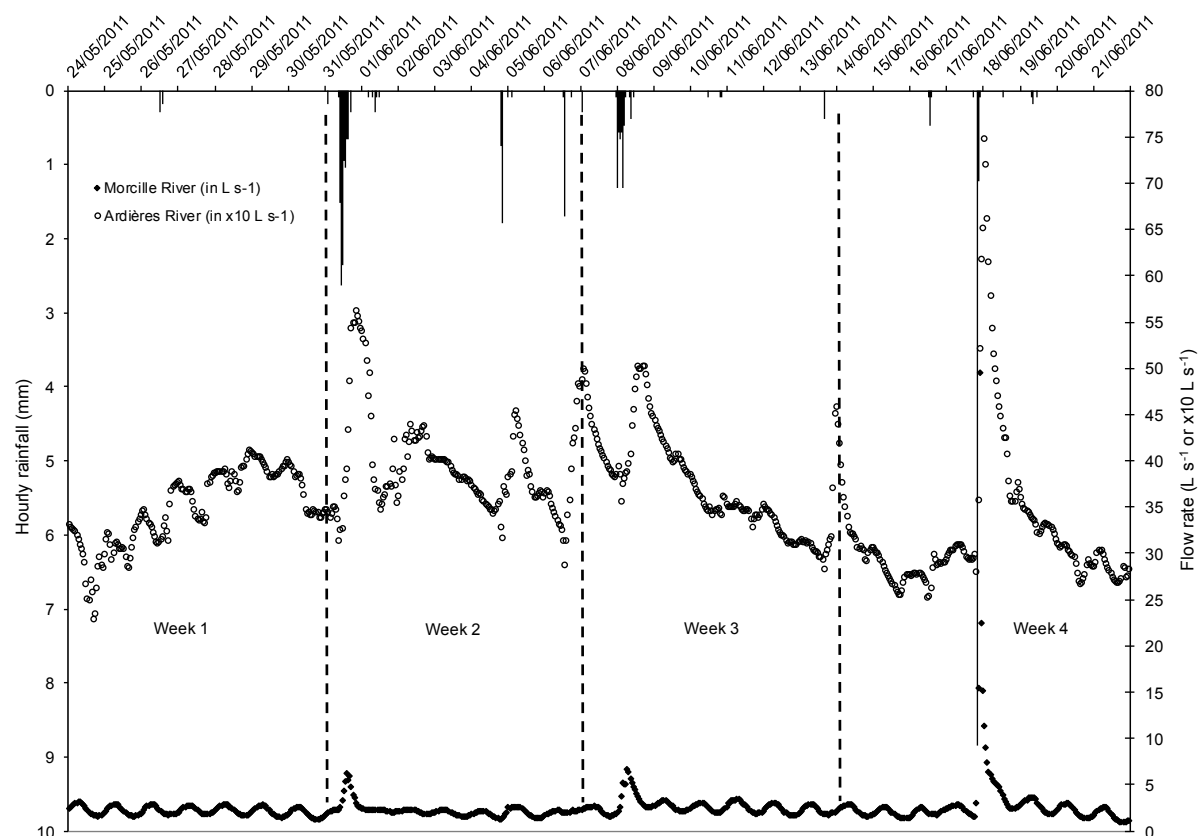


Figure S2. Hourly rainfall (in mm) and flow rate at the intermediate site of the Morcille River (in $L s^{-1}$) and at the downstream site of the Ardères River (in $x10 L s^{-1}$) during the spring 2011 campaign.