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In situ application of stir bar sorptive extraction as a passive sampling technique for the monitoring of agricultural pesticides in surface waters

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Abstract

Grab sampling and automated sampling are not suitable or logistically too constraining for the monitoring of pesticides in dynamic streams located in agricultural watersheds. In this work, we applied stir bar sorptive extraction (SBSE) Twisters® directly in two small rivers of a French vineyard (herein referred to as "passive SBSE"), for periods of one or two weeks during a month, for the passive sampling of 19 agricultural pesticides. We performed qualitative and semi-quantitative comparisons of the performances of passive SBSE firstly to automated sampling coupled to analytical SBSE, and secondly to the polar organic chemical integrative sampler (POCIS), a well-known passive sampler for hydrophilic micropollutants. Applying passive SBSE in river waters allowed the quantification of more pesticides and in greater amounts than analytical SBSE as shown for samples collected concurrently. Also, passive SBSE and POCIS proved to be complementary techniques in terms of detected molecules; but only passive SBSE was able to integrate a concentration peak triggered by a quick flood event that lasted 5 hours. Passive SBSE could be an interesting tool for the monitoring of moderately hydrophobic to hydrophobic organic micropollutants in changing hydrosystems. In this purpose, further studies will focus on the accumulation kinetics of target pesticides and the determination of their sampling rates.

Keywords: Passive sampling, Field study, SBSE, POCIS, Pesticides, Water monitoring

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1. Introduction

Monitoring of organic micropollutant contamination in surface waters has become a challenging issue in Europe since the Water Framework Directive (European Commission, 2000), which general aim is to improve and protect European water quality. The evaluation of the chemical quality of surface waters requires reliable measurements of concentrations for priority pollutants including several pesticides (Coquery et al., 2005). Floods are a major pathway for the transport of pesticides in surface waters located in agricultural watersheds and can induce concentration peaks that can vary over several orders of magnitude (Rabiet et al., 2010). In dynamic hydrosystems like small rivers located in agricultural watersheds, flood-induced concentration peaks can be very quick (down to a few hours); therefore low frequency grab sampling is not suitable for the monitoring of the pesticide contamination. Moreover, this sampling technique does not allow the determination of ultra trace levels of some fungicides, which may have an impact on aquatic microbial life (Artigas et al., 2012). Numerous grab samples or automated samples are necessary to assess the time variability of the contamination. Moreover, these sampling techniques would trigger a large number of analyses, and the use and maintenance of an automated sampler are costly.

Passive (or integrative) sampling has recently been developed as an alternative to grab or automated sampling in order to obtain, at lower cost, more realistic estimates of the average concentrations of micropollutants in surface waters (Greenwood et al., 2007; Namieśnik et al., 2005; Vrana et al., 2005). In addition, the passive accumulation of chemicals from large volumes of water results in ultra trace level detection and smoothed integrative sampling over periods ranging from days to months. Passive samplers can monitor a broad range of micropollutants, depending on their physical chemical properties. The polar organic chemical integrative sampler (POCIS) is one of the main devices used for the passive sampling of the

moderately polar organic compounds (Alvarez et al., 2004). Its efficiency for the determination of time-weighted average (TWA) concentrations of hydrophilic pesticides in natural waters has been reported in the literature (Greenwood et al., 2007; Vrana et al., 2005). Moreover, numerous studies have been dedicated to the passive sampling of hydrophobic organic micropollutants such as polycyclic aromatic hydrocarbons (PAH), polychlorobiphenyl (PCB) congeners, and highly hydrophobic organochlorine and organophosphate pesticides (Allan et al., 2012; Booij et al., 2002; Jahnke et al., 2008; Paschke et al., 2006; Prokeš et al., 2012; Stuer-Lauridsen, 2005; Vrana et al., 2001). To our knowledge, however, the sampling of moderately hydrophobic to hydrophobic pesticides ($2 < \log K_{ow} < 5$) is poorly documented.

Stir bar sorptive extraction (SBSE) is a solvent free sample preparation technique dedicated to moderately hydrophobic to hydrophobic compounds in aqueous and gaseous samples. The extraction device, named Twister®, is composed of a magnet enclosed in a glass tube coated with a thick film of polydimethylsiloxane (PDMS) (Baltussen et al., 1999a). The extraction is performed with a Twister by immersion in the aqueous sample (SBSE) or by headspace sampling (headspace sorptive extraction, HSSE) (Baltussen et al., 1999a; Tienpont et al., 2000). This novel sample treatment technique has been successfully used for the analytical extraction of several compounds, such as hormones, pesticides, PAH and PCB in air, soil, and various liquid matrices (David and Sandra, 2007; Prieto et al., 2010). The application of SBSE on site has been reported in the literature, but only for the analysis of PAH (Roy et al., 2005).

In this work, we applied SBSE directly *in situ* as a passive sampling technique for the monitoring of fugacious agricultural pesticides in dynamic streams (herein named “passive SBSE”). For this purpose, we first compared the performances of passive SBSE and automated sampling coupled with analytical SBSE, i.e., the extraction with Twisters of water

samples collected concurrently in a French river located in an agricultural watershed and performed in the laboratory. Secondly, we compared the qualitative and semi-quantitative performances of the passive SBSE and the POCIS during base flow and a flood event of a second dynamic stream located in the same watershed.

2. Experimental

2.1 Chemicals and materials

The 19 pesticides selected for this study belong to different chemical classes (herbicides, insecticides, and fungicides) and have different physical chemical properties, such as their octanol-water partitioning coefficient log K_{ow} (Table 1). They were provided by Dr. Ehrenstorfer GmbH (Augsburg, Germany): acetochlor, atrazine, azoxystrobin, chlorfenvinphos, chlorpyrifos-ethyl, diflufenican, dimethomorph, diuron, 3,4-dichloroaniline (metabolite of diuron), 1-(3,4-dichlorophenyl)-3-methyl urea (metabolite of diuron), fenitrothion, flufenoxuron, isoproturon, metolachlor, norflurazon, procymidon, simazine, spiroxamine, and tebuconazole (purity $\geq$ 92.5%). For chemical analyses, atrazine-d5, chlorpyrifos-ethyl-d10, diuron-d6, isoproturon-d6, and metolachlor-d6, used as internal standard or surrogate, were also provided by Dr. Ehrenstorfer (purity $\geq$ 98.5%).

For both passive SBSE and analytical SBSE techniques, LC-MS grade acetonitrile and methanol, and dichloromethane for pesticide residue analysis were purchased from VWR (Strasbourg, France). Formic acid (purity = 98%) for LC-MS analysis was provided by Fischer Bioblock (Illkirch, France). Ultrapure water was produced by a MilliQ water purification system purchased from Millipore (Billerica, MA, USA). The Twisters (20 mm x

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104 1-mm thick PDMS film, with an external surface area of 2.1 cm^2 and a PDMS phase volume
105 of 126 µL) were purchased from Gerstel (Mülheim a/d Ruhr, Germany).
106 For the POCIS technique, all solvents (HPLC grade) were obtained from Sharlau (Sentmenat,
107 Spain) except ethyl acetate, which was purchased from Fluka (St. Louis, MO, USA).
108 Ultrapure water was produced by a Synergy UV system from Millipore (Billerica, MA, USA).
109 All eluents were filtered through 0.45 µm regenerated cellulose filters from Whatman
110 (Versailles, France). Ammonium acetate was purchased from Fluka (St Louis, MO, USA).
111 POCIS (Alvarez et al., 2004; Mazzella et al., 2007) contains about 200 mg of Oasis HLB
112 sorbent, purchased from Waters (St Quentin-en-Yvelines, France), weighted with accuracy
113 and enclosed between two hydrophilic polyethersulfone (PES) SUPOR 100 membrane disc
114 filters (0.1 µm, 90 mm membrane diameter), purchased from Pall (Saint-Germain-en-Laye,
115 France). The total exchanging surface area of the membrane (both sides) is approximately 41
116 cm^2 and the surface area per mass of sorbent ratio is approximately 200 cm^2 g^{-1}.
117
118 2.2 Field experiments
119
120 The passive samplers were deployed in two rivers of a French vineyard watershed located
121 about 70 km north of Lyon in the Beaujolais region, the Ardières and the Morcille Rivers.
122 Two deployment sites -one per river- were selected for a one-month exposition campaign. For
123 the comparison of the performances of passive SBSE and analytical SBSE, Twisters were
124 immersed in triplicates for 4 periods of one week in the Morcille River (herein named
125 “passive Twisters”). During the same period, passive Twisters and POCIS were deployed,
126 both in triplicates, for two periods of two weeks in the Ardières River. The passive Twisters
127 were placed in deployment bags, made of two pieces of plastic mesh, in order to expose the
128 PDMS phase directly to the aquatic medium, and protect it from small rocks, pieces of wood

or coarse sand. The POCIS orientation was vertical with the PES membranes perpendicular to the water surface and the flow (Mazzella et al., 2010). The two passive samplers were placed in the same cages for deployment in the rivers. Field blanks for passive Twisters and POCIS were systematically used.

Simultaneously, at both sites, weekly time-averaged water samples were collected with a refrigerated automated sampler (Bühler 4010, Hach-Lange) in amber glass bottles. The water samples and the passive Twisters were brought to the laboratory in Lyon for chemical analysis, whereas the POCIS were sent in an isothermal case to the laboratory in Bordeaux for the determination of the pesticide concentrations.

2.3 Chemical analysis of water samples and passive Twisters

The pesticide concentrations of the Ardières River water 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). For the Morcille River water samples, pesticide concentrations were determined by analytical SBSE followed by liquid desorption and liquid chromatography coupled with tandem mass spectrometry (SBSE-LD-LC-MS/MS). The development and the validation of the extraction of the selected pesticides by SBSE and analysis by LC-MS/MS have been published elsewhere (Margoum et al., 2013). Briefly, the extraction was performed at 800 rpm for 3 hours on 20 mL of the weekly averaged water samples filtered with 0.7 µm GF/F glass fiber membranes. The Twisters (herein 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 µg L^{-1}, in acetone, were added to 40 µL of the desorbate to constitute the sample for LC-MS/MS analysis.

After exposure, the passive Twisters were taken out of their deployment bags, gently rinsed and dried, then placed overnight at -18 °C. Afterwards, the pesticides sorbed in the passive Twisters were extracted 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 a MS triple quadrupole API 4000 from AB Sciex (Les Ulis, France), equipped with an electrospray ionization source (ESI) that was operated in the positive ionization mode. An Atlantis T3 (2.1 mm x 100 mm; d_p = 3 µm) purchased from Waters (St 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.

2.4 Recovery from POCIS and extract analysis

Full details of the treatment of the POCIS and the analysis of pesticides performed after exposure can be found elsewhere (Lissalde et al., 2011; Mazzella et al., 2010). Briefly, the POCIS was open and the sorbent was transferred into a 3-mL empty SPE tube with a PE frit and packed under vacuum by using a Visiprep SPE Manifold. Analytes were eluted with 3 mL of methanol, then with 3 mL of a methanol:ethyl acetate mix (75:25, v/v). The solvent was then evaporated under a gentle stream of nitrogen for 30 min. Finally, the dried extract was dissolved in 1 mL of the injection solvent (ultrapure water:acetonitrile, 90:10, v/v) for LC-MS/MS analysis.

An HPLC Ultimate 3000 apparatus from Dionex (Voisin Le Bretonneux, France) was used (solvent rack SRD-3600 6 degasser channels, DGP-3600M pump, WPS-3000 TSL Micro autosampler, TCC-3100 HP 1xRH 2P-6P thermostated column oven). Acetonitrile and 5 mM ammonium acetate solution were used with an analytical gradient of 15 min.

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Chromatographic separation was performed with a Gemini-NX C18 3 µm, 110 Å, 2.0 mm x 100 mm with a SecurityGuard cartridge Gemini-NX C18 2.0 mm x 4 mm, both from Phenomenex (Le Pecq, France). The detector was an API 2000 triple quadrupole mass spectrometer from AB Sciex. It was equipped with an ESI source operated in the positive ionization mode.

3. Theory and modeling

3.1 Stir Bar Sorptive Extraction

Stir Bar Sorptive Extraction is a sampling technique governed by diffusion of the analytes. This technique relies on equilibrium, and the extraction of solutes from the aqueous samples into the extraction phase is controlled by the partitioning coefficient of the solutes between the PDMS phase and the aqueous phase (K_{sw}) (Baltussen et al., 2002; David and Sandra, 2007). Baltussen et al. (1999a, 1999b) have correlated the partitioning coefficient of hydrophobic analytes (K_{sw}) with their octanol-water distribution coefficient (K_{ow}). The partitioning coefficient of a compound is linked to the concentration in the Twister and the concentration in the water sample (Eq. 1):

$$K_{ow} \approx K_{sw} = \frac{C_s}{C_w} = \frac{m_s}{m_w} \text{ x } \frac{V_w}{V_s} = \frac{m_s}{m_w} \text{ x } \beta \quad (1)$$

where C_w (µg L^{-1}) is the concentration of analyte in the water sample at equilibrium; C_s (µg L^{-1}) is the concentration of analyte in the extraction phase at equilibrium; m_w (µg) is the mass of analyte remaining in the water sample; m_s (µg) is the mass of analyte in the extraction phase; V_w (L) is the volume of water sample; V_s (L) is the volume of the extraction phase; β (adimensional) is the phase ratio.

The extraction recovery η is expressed as the ratio of the mass of analyte in the extraction phase (m_s) over the initial mass of analyte in the water sample ($m_0 = m_s + m_w$). It is determined by the partitioning coefficient K_{sw} and by the phase ratio β, as described in Eq. 2.

$$\eta = \frac{m_s}{m_0} = \frac{K_{sw}/\beta}{1+(K_{sw}/\beta)} \quad (2)$$

From Eq. 2, it is easily deduced that the extraction recovery increases with K_{sw}. Since K_{sw} is approached by K_{ow} (Eq. 1), extraction recovery on PDMS, in general, decreases with increasing polarity. Moreover, the phase ratio β can also affect the extraction recovery. When the volume of the PDMS extraction phase is increased, β decreases, and the extraction efficiency increases.

3.2 Passive sampling

The mass transfer of an analyte in a sampler includes several diffusion and interfacial transport steps across all barriers, i.e., the stagnant aqueous boundary layer, possible biofilm layer, the membrane and then, the receiving phase. Assuming isotropic exchange, the corresponding uptake in the sampler over time with constant ambient concentration can be described as follows (Eq. 3):

$$N(t) = M_s K'_{sw} C_w (1 - \exp(-k_e.t)) \quad (3)$$

where N (µg) is the mass of analytes accumulated in the receiving phase; M_s (g) is the mass of the receiving phase; K'_{sw} (mL g^{-1}), described by the ratio of the concentration of analytes in the sampler C'_s (µg g^{-1}) and the concentration of the analytes in the water phase C_w (µg mL^{-1}), is the receiving phase/water partitioning coefficient; and t (d) equals time.

The elimination constant k_e (d^{-1}) is defined as follows (Eq. 4):

$$k_e = \frac{R_s}{K'_{sw} M_s} = \frac{\lambda A}{K'_{sw} M_s} \quad (4)$$

where R_s is the sampling rate (mL d^{-1}) and A (cm^2) is the sampler surface area.

The overall mass transfer coefficient λ (cm d^{-1}) describes the movement of the analytes out of the bulk solution, across multiple barriers, to the receiving phase. The overall resistance ($1/\lambda$) is given by sum of all particular barrier resistances:

$$\frac{1}{\lambda} = \frac{\delta_w}{D_w} + \frac{\delta_b}{D_b K_{bw}} + \frac{\delta_m}{D_m K_{mw}} + \frac{\delta_s}{D_s K_{sw}} \quad (5)$$

with δ the thickness of the particular barrier, D_w the diffusion coefficient of the analyte in water (i.e., stagnant aqueous boundary layer), D_i the diffusion coefficient of the analyte in the *i*th barrier (i.e., biofilm, membrane, etc.), and K_{iw} the partitioning coefficient between water and the *i*th barrier or receiving phase (in subscripts, w stands for the water, b the possible biofouling, m the membrane, and s the receiving phase).

In passive SBSE, the receiving phase/water partitioning coefficient K_{sw} is adimensional, since it is described by the ratio of the concentration in the Twisters C_s (µg mL^{-1}) and the concentration in the water phase C_w (µg mL^{-1}). With POCIS, K'_{sw} (mL g^{-1}) is used, since the receiving phase is a powder and the concentration of analytes in the sampler C'_s is expressed in µg g^{-1}. For comparison of passive SBSE with the POCIS, one can convert K_{sw} into K'_{sw} with the mass density of PDMS ρ_s, which is 1.15 g mL^{-1} according to Rusina et al. (2007), as follows (Eq. 6):

$$K'_{sw} = \frac{K_{sw}}{\rho_s} = \frac{K_{sw}}{M_s} V_s \quad (6)$$

For POCIS, the overall mass transfer coefficient highly depends on δ_w as it is assumed that the analyte uptakes are mainly under aqueous boundary layer control (Alvarez et al., 2004; Mazzella et al., 2008; Vrana et al., 2005). In passive SBSE, no membrane separates the

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Twister from the aqueous medium. Hence, the analyte uptakes are limited either by the resistance in the water boundary layer or by the resistance in the receiving phase (PDMS) (Vrana et al., 2006). Eq. 5 shows that the resistance in the receiving phase decreases with increasing K_{sw} value for substances having similar diffusion coefficient D_s in this material. Nevertheless, since K_{sw} is approached by K_{ow} (Eq. 1), there will be a critical K_{ow} value where the analyte uptakes will turn to be controlled by the water boundary layer, likely due to decreasing diffusivity of more hydrophobic molecules, with increasing size/volume. Studies have suggested that uptake control switches from membrane to water boundary layer for compounds with log K_{ow} values in the range of 4.5 to 5.0, for non polar compound passive samplers with membrane such as semipermeable membrane device (SPMD) (Huckins et al., 2006), membrane enclosed sorptive coating (MESCO) and Chemcatcher, as well as for samplers without membrane such as low density polyethylene (LDPE) membranes and silicon strips (Allan et al., 2009). Therefore, for passive SBSE, we refer to the two kinetic limitations of the compound uptakes as membrane and water boundary layer controls, and we assume that the transition from one mass transfer control to the other occurs for compounds with log K_{ow} between 4.5 and 5.0.

4. Results and discussion

4.1 Comparison of the passive SBSE and automated sampling coupled with analytical SBSE

We first compared the accumulation of 19 target pesticides in the Twisters deployed in the Morcille River (passive Twisters) and in those used for the analytical extraction of weekly averaged river water samples (analytical Twisters), collected at the same site. The masses of

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pesticides accumulated in either the passive Twisters or analytical Twisters for 4 consecutive periods of one week are presented in Table 1. Firstly, the two techniques showed similar repeatability; the relative standard deviations (RSD) calculated (with n = 3) ranged from 4.0 to 57.5% for passive SBSE and from 5.7 to 48.9% for analytical SBSE. Secondly, over the 4 weeks of the study, passive Twisters accumulated 6 pesticides more frequently than analytical Twisters, including atrazine, diflufenican and chlorpyrifos-ethyl, which were accumulated only by passive Twisters. This was not caused by a difference in limits of quantification (LOQ) since the two techniques reached similar LOQ in ng, estimated with signal-to-noise ratios. For most pesticides quantified by both techniques, accumulation in the passive Twisters was 1.3 to 8 times higher in average. In contrast, dimethomorph, norflurazon and simazine were accumulated in passive Twisters to a lower extent (about 1.6 times less in average). Considering the lower log K_{ow} values for these compounds (Table 1), we can assume lower log K_{sw} values (Eq. 1), thus a lower affinity for the PDMS phase. As a result, lower masses of these 3 pesticides in the passive Twisters in comparison with analytical Twisters could be due to desorption phenomena during the one-week exposition periods. Nevertheless, for the most hydrophobic pesticides, our results imply that lower LOQ could be reached by passive SBSE, in agreement with the theory of passive sampling (Greenwood et al., 2007; Huckins et al., 2006).

4.2 Comparison of passive SBSE and POCIS

During both two-week exposition periods, passive Twisters and POCIS were deployed simultaneously at the same site, thus they were exposed to the same concentrations of pesticides. After recovery of both samplers, no biofilm was observed. Consequently, we assume that the determination of the masses of pesticides accumulated in the samplers was

not biased by biofouling. Moreover, concentrations of the target pesticides in the river water were monitored for both exposition periods by means of automated samplings and SPE-LC-MS/MS analyses. After recovery of the samplers and chemical analyses, we performed qualitative and semi-quantitative comparisons of the two devices. For the qualitative comparison, we focused only on the 7 pesticides quantified in the two passive samplers and in the weekly averaged water samples, i.e., simazine, azoxystrobin, dimethomorph, diuron, 1-(3,4-dichlorophenyl)-3-methyl urea, metolachlor, and chlorpyrifos-ethyl. As shown in Figure 1, the most polar compounds (simazine, dimethomorph, azoxystrobin, diuron, and 1-(3,4-dichlorophenyl)-3-methyl urea) were either accumulated only by the POCIS or sorbed by the POCIS to a higher extent than by the passive Twisters. In contrast, the most hydrophobic pesticides (metolachlor and chlorpyrifos-ethyl) were accumulated only by the passive Twisters. Similar results were obtained from passive Twisters and POCIS deployed concurrently in 2 other sites on the same river and one site on the Morcille River (data not shown). Thus, passive SBSE and POCIS could be used as two complementary techniques for the monitoring of a broad range of pesticides in natural waters. This conclusion was quite expected since SBSE is originally an analytical sample preparation technique for moderately hydrophobic to hydrophobic contaminants (log K_{ow} > 3) (Baltussen et al., 1999a, 1999b; David and Sandra, 2007), and POCIS are known to target more hydrophilic contaminants (log K_{ow} < 4) (Alvarez et al., 2007, 2004; Mazzella et al., 2007; Morin et al., 2012). Over the 7 pesticides presented in Figure 1, azoxystrobin, simazine and dimethomorph were accumulated in both passive samplers. Interestingly, in the case of simazine, log K'_{sw} values for SBSE (1.90) deduced from Eqs. 1 and 6, and for POCIS (4.68) available in the literature (Mazzella et al., 2010), indicate the higher affinity of this polar compound for the receiving phase of the POCIS. This comparison is possible only for simazine, because it is the only pesticide for which we have log K'_{sw} values for both samplers.

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For semi-quantitative comparison, we chose to normalize the masses of accumulated analytes to the respective device surface areas (2.1 cm^2 for passive Twisters and 41 cm^2 for POCIS), as shown in Figure 1. The normalization of the mass of a pesticide accumulated in the sampler by its surface area is a useful way to approach its overall mass transfer coefficient λ (Eq. 4). The weekly averaged pesticide concentrations, obtained from the automated sampler, were similar during the two exposition periods (Figure 1). But average normalized masses of accumulated pesticides and RSD (n = 3) varied between samplers and from one exposition period to the other. Larger RSD for the pesticides accumulated in the POCIS exposed during the first two-week exposition period compared to the second exposition period (7 to 27 times larger) may be attributed to a 5-hour flood event that occurred two days before retrieval of the samplers (on day 12). In other words, high turbulences and a short and brutal change in flow velocity probably made each POCIS of the triplicates accumulate pesticides with a different accumulation rate. Indeed, measurements of the flow rate revealed a two hundred-fold increase at the peak of the flood event (from 11.5 to 2210 L s^{-1} in less than 5 hours). For the same reasons, larger normalized masses of pesticides accumulated in POCIS during the second exposition period (from 1.5 to 2.8 larger) could be attributed to a two-fold increase of the flow rate of the river between the first and the second two-week exposition period (average flow rate increased from 18 L s^{-1} to 37 L s^{-1}). Hence, we assume that the increased flow velocity probably triggered faster chemical accumulations in the POCIS. These observations suggest two distinct behaviors for the devices. Indeed, δ_s, D_s and K'_{sw} of the pesticides studied are different for the two devices (Eq. 5); also, the mass transfer of the solute into the POCIS is controlled by the aqueous boundary layer, i.e., it depends on the hydrodynamic conditions during the exposition (Alvarez et al., 2004; Mazzella et al., 2008).

On the other hand, 1.5 to 11 times more simazine, azoxystrobin, dimethomorph, metolachlor and chlorpyrifos-ethyl were quantified in passive Twisters exposed during the first exposition

348 period in comparison to those deployed for the second exposition period. This could be
349 attributed to a quick concentration peak which occurred during the flood event (on day 12)
350 (Rabiet et al., 2010). Response times of the passive Twisters -without membranes- with
351 respect to pesticide accumulation were probably short enough to integrate the concentration
352 peak, which was not integrated by the automated sampler. Moreover, as mentioned in the
353 section 3.2, the mass transfer of simazine, azoxystrobin, dimethomorph, diuron, 1-(3,4-
354 dichlorophenyl)-3-methyl urea, metolachlor, chlorfenvinphos and chlorpyrifos-ethyl into the
355 passive Twisters was probably controlled by the membrane, since their log K_{ow} values are
356 below 5.0. Therefore, unlike the POCIS, the hydrodynamic conditions during this flood event
357 had little impact on the repeatability of the accumulation of the target pesticides into the
358 passive Twisters. For instance, for the first exposition period, the RSD for the normalized
359 masses of pesticides (simazine, azoxystrobin, dimethomorph, metolachlor and chlorpyrifos-
360 ethyl) accumulated in the passive Twisters ranged from 4.1 to 10.5% whereas, for the
361 pesticides accumulated in POCIS (simazine, azoxystrobin, dimethomorph, diuron, and 1-(3,4-
362 dichlorophenyl)-3-methyl urea), RSD ranged from 34.7 to 56.2%. Moreover as a comparison
363 of the two samplers, the RSD of the accumulation of simazine, azoxystrobin and
364 dimethomorph in the passive Twisters were 6 to 8 times lower than those for the same
365 pesticides accumulated in the POCIS.
366 In this study, we focused on the performances of passive SBSE for the sampling of a broad
367 range of pesticides ($2.18 < \log K_{ow} < 5.11$). Several pesticides among those have been
368 targeted by POCIS via laboratory or *in situ* studies: for instance, acetochlor, 1-(3,4-
369 dichlorophenyl)-3-methyl urea, diuron, simazine, atrazine, isoproturon, metolachlor,
370 chlorfenvinphos, fenitrothion, and chlorpyrifos-ethyl (Alvarez et al., 2007, 2005, 2004;
371 Mazzella et al., 2010). Moreover, performances of passive samplers for hydrophobic
372 organochlorine or organophosphate pesticides, such as SPMD, LDPE, silicon rubbers, PDMS

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membranes or MESCO have been reported in several studies (Allan et al., 2012; Booij et al., 2002; Jahnke et al., 2008; Namieśnik et al., 2005; Paschke et al., 2006; Prokeš et al., 2012; Stuer-Lauridsen, 2005; Vrana et al., 2005, 2001). Nevertheless, to our knowledge, the passive sampling of moderately hydrophobic to hydrophobic pesticides targeted in our study such as spiroxamine, flufenoxuron, diflufenican, tebuconazole, procymidon, dimethomorph, azoxystrobin and norflurazon has not been reported in the literature.

5. Conclusion

This study focused on the passive sampling of 19 moderately hydrophobic to hydrophobic pesticides in surface waters by passive SBSE. Firstly, results showed that this technique could allow to reach lower LOQ than automated sampling coupled with analytical SBSE for most hydrophobic studied pesticides. Secondly, passive SBSE and POCIS were shown complementary regarding the ranges of polarity for the chemicals targeted. The two techniques, when the masses of accumulated pesticides are normalized to the respective surface areas of the devices, showed, however, different accumulation performances. Thirdly, the passive SBSE and POCIS revealed two different behaviors in changing hydrodynamics, due to different analyte uptake controls. Flow velocity seemed to impact the accumulation of the target pesticides in POCIS only. An additional way to compare these two samplers would be the calculation of time-weighted averaged concentrations using the sampling rates of the target pesticides obtained from kinetic studies and laboratory calibration of the passive Twisters.

One of the advantages of the passive SBSE technique is the simple handling, preparation before deployment, *in situ* deployment and sample treatment after exposition of the Twisters. Moreover, in case of analysis by liquid chromatography, passive SBSE is environmentally

398 friendly and cost-effective with respect to solvent consumption, since small solvent volumes
399 (50 to 200 µL) are generally used for the desorption of the chemicals accumulated in the
400 Twisters. In case of thermal desorption and analysis by gas chromatography, passive SBSE
401 seems even more promising regarding the reduction of the use of organic solvents and the
402 improvement of LOQ. Finally, since no membrane separates the Twister from the aquatic
403 medium in passive SBSE, response times to concentration peaks may be shorter than most
404 samplers equipped with a membrane, such as SPMD, POCIS and MESCO. Hence, this first
405 study proves that passive SBSE is an interesting technique for monitoring chemicals in
406 hydrosystems with high concentration variations and needs further work for the determination
407 of sampling rates in order to calculate time-weighted averaged concentrations.
408

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410

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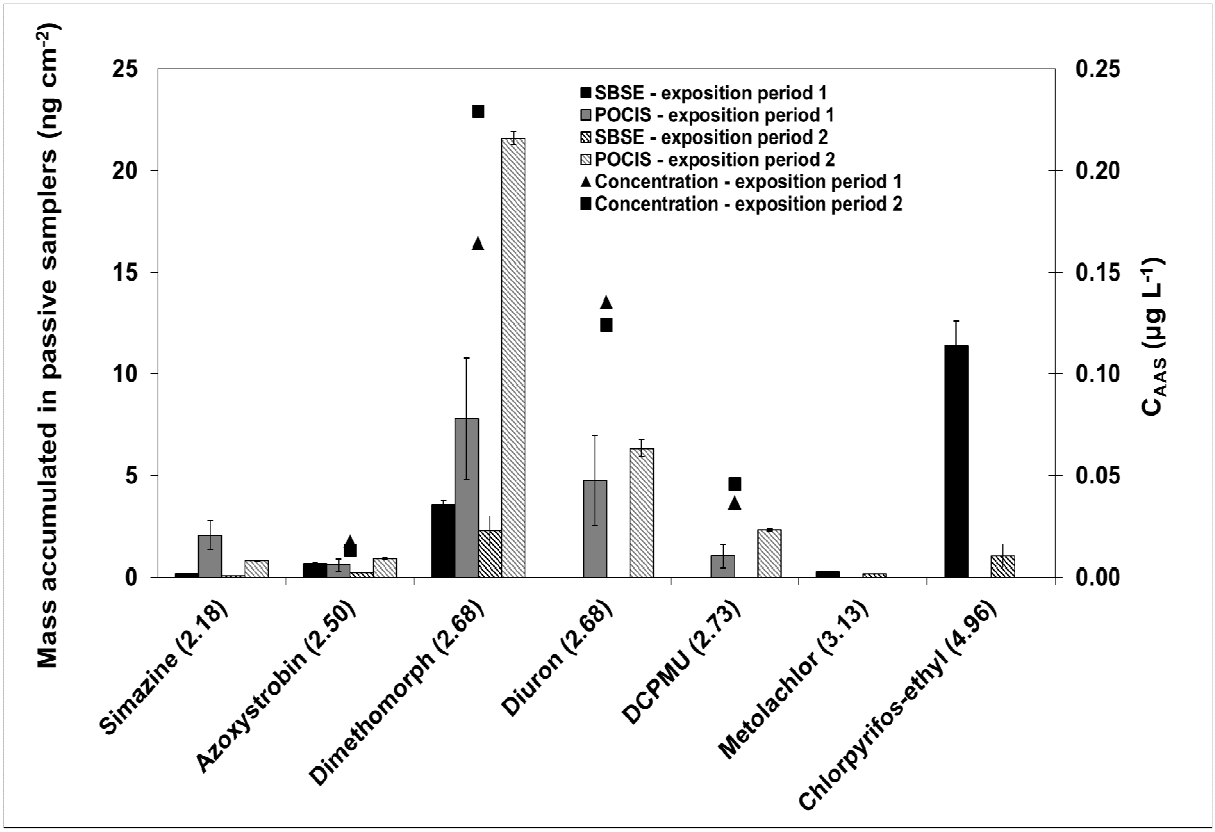

Figure 1. Comparison of masses of pesticides accumulated in POCIS and passive Twisters normalized to the respective surface area of the devices, for the two exposition periods of two weeks; and weekly average water concentration obtained via automated sampler (C_{AAS}). Numbers in brackets on the x axis are the log K_{ow} of the pesticides, sorted by increasing values. DCPMU stands for 1-(3,4-dichlorophenyl)-3-methyl urea. Error bars represent ± standard deviation, n = 3 for passive samplers.

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Table 1. Masses of pesticides accumulated in Twisters for comparison of passive SBSE and automated sampling coupled with analytical SBSE. Passive Twisters were exposed in triplicates (n = 3) for 4 periods of 1 week. Analytical Twisters were used in triplicates (n = 3) for the extraction of 4 weekly-averaged river water samples, collected during the same period.

Pesticides	log K_{ow}	LOQ (ng)	Passive SBSE					Analytical SBSE				
			Week 1 (ng) RSD (%)	Week 2 (ng) RSD (%)	Week 3 (ng) RSD (%)	Week 4 (ng) RSD (%)	Average[a] (ng)	Week 1 (ng) RSD (%)	Week 2 (ng) RSD (%)	Week 3 (ng) RSD (%)	Week 4 (ng) RSD (%)	Average[a] (ng)
Simazine	2.18	0.2	0.4 (9.7)	2.3 (22.1)	0.8 (11.6)	0.5 (31.6)	1.0	0.3 -	0.6 (5.9)	8.2 (17.7)	2.1 (18.7)	2.8
Norflurazon	2.30	4.0	4.1 -	4.5 (12.7)	nq -	4.1 -	4.2	nq -	nq -	6.6 (18.6)	9.7 (48.9)	8.2
Azoxystrobin	2.50	0.4	1.5 (15.7)	3.4 (28.3)	1.5 (35.8)	1.4 (57.5)	1.9	1.3 (14.4)	1.4 (30.4)	1.5 (7.7)	1.4 (14.3)	1.4
Atrazine	2.61	0.2	0.3 (5.1)	nq -	nq -	nq -	0.3	nq -	nq -	nq -	nq -	nq
Dimethomorph	2.68	2.0	4.3 (7.5)	6.8 (17.6)	2.2 -	2.1 -	3.9	8.9 (28.8)	15.8 (22.7)	7.2 (11.8)	4.7 (11.1)	9.2
Diuron	2.68	20	nq -	nq -	nq -	nq -	nq	nq -	nq -	nq -	nq -	nq
3,4-dichloroaniline	2.69	1.0	nq -	nq -	nq -	nq -	nq	nq -	nq -	nq -	nq -	nq
1-(3,4-dichlorophenyl)-3-methyl urea	2.73	20	nq -	nq -	nq -	nq -	nq	nq -	nq -	nq -	nq -	nq
Isoproturon	2.87	2.0	nq -	nq -	nq -	nq -	nq	nq -	nq -	nq -	nq -	nq
Spiroxamine	2.89	0.4	4.8 (4.3)	9.8 (47.1)	13.1 (15.6)	10.7 (13.7)	9.6	0.3 (13.5)	2.8 (21.7)	1.0 (16.8)	0.5 (5.7)	1.2
Procymidon	3.08	4.0	9.7 (11.9)	23.7 (48.3)	14.0 (21.5)	17.9 (36.5)	16.3	15.0 (26.0)	10.6 (20.3)	nq -	nq -	12.8
Metolachlor	3.13	0.2	0.4 (11.4)	0.3 (8.1)	0.2 -	0.2 (12.3)	0.3	0.2 -	nq -	nq -	nq -	0.2
Fenitrothion	3.32	10	nq -	nq -	nq -	nq -	nq	nq -	nq -	nq -	nq -	nq
Tebuconazole	3.70	2.0	3.7 (19.8)	9.9 (18.1)	8.3 (26.2)	8.5 (41.8)	7.6	2.8 (10.3)	5.7 (39.3)	2.3 (7.2)	2.5 (10.6)	3.3
Chlorfenvinphos	3.81	2.0	3.2 (4.0)	nq -	nq -	nq -	3.2	2.2 -	nq -	nq -	nq -	2.2
Acetochlor	4.14	2.0	nq -	nq -	nq -	nq -	nq	nq -	nq -	nq -	nq -	nq
Diflufenican	4.20	4.0	6.6 (10.3)	5.3 (5.8)	nq -	nq -	6.0	nq -	nq -	nq -	nq -	nq
Chlorpyrifos-ethyl	4.96	1.0	nq -	2.8 (33.8)	nq -	nq -	2.8	nq -	nq -	nq -	nq -	nq
Flufenoxuron	5.11	4.0	nq -	nq -	nq -	nq -	nq	nq -	nq -	nq -	nq -	nq

[a]: Average masses of pesticides were calculated with only the values above the LOQ; nq: not quantified