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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HIGHLIGHTS

- Stir bar sorptive extraction was used as a passive sampler in rivers (passive SBSE).
- Passive SBSE was compared to polar organic chemical integrative sampler (POCIS).
- The two passive samplers were complementary in terms of detected molecules.
- Passive SBSE showed good accumulation repeatability in changing hydrodynamics.

ARTICLE INFO

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 h. 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.

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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

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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 ≥ 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 ≥ 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 × 1-mm thick PDMS film, with an external surface

area of 2.1 cm² and a PDMS phase volume of 126 μL) were purchased from Gerstel (Mülheim a/d Ruhr, Germany).

For the POCIS technique, all solvents (HPLC grade) were obtained from Sharlau (Sentmenat, Spain) except ethyl acetate, which was purchased from Fluka (St. Louis, MO, USA). Ultrapure water was produced by a Synergy UV system from Millipore (Billerica, MA, USA). All eluents were filtered through 0.45 μm regenerated cellulose filters from Whatman (Versailles, France). Ammonium acetate was purchased from Fluka (St Louis, MO, USA). POCIS (Alvarez et al., 2004; Mazzella et al., 2007) contains about 200 mg of Oasis HLB sorbent, purchased from Waters (St Quentin-en-Yvelines, France), weighted with accuracy and enclosed between two hydrophilic polyethersulfone (PES) SUPOR 100 membrane disk filters (0.1 μm, 90 mm membrane diameter), purchased from Pall (Saint-Germain-en-Laye, France). The total exchanging surface area of the membrane (both sides) is approximately 41 cm² and the surface area per mass of sorbent ratio is approximately 200 cm² g⁻¹.

2.2. Field experiments

The passive samplers were deployed in two rivers of a French vineyard watershed located about 70 km north of Lyon in the Beaujolais region, the Ardières and the Morcille Rivers. Two deployment sites – one per river – were selected for a one-month exposition campaign. For the comparison of the performances of passive SBSE and analytical SBSE, Twisters were immersed in triplicates for 4 periods of one week in the Morcille River (herein named "passive Twisters"). During the same period, passive Twisters and POCIS were deployed, both in triplicates, for two periods of two weeks in the Ardières River. 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. 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 h 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