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Use of passive stir bar sorptive extraction as a simple integrative sampling technique of pesticides in freshwaters: determination of sampling rates and lag-phases

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Abstract

Passive sampling represents a cost-effective approach and is more representative than grab sampling for the determination of contaminant concentrations in freshwaters. In this study, we performed the calibration of a promising tool, the passive Stir Bar Sorptive Extraction (SBSE), which has previously shown good performances for semi-quantitative monitoring of pesticides in a field study. We determined the sampling rates and lag-phases of 18 moderately hydrophobic to hydrophobic agricultural pesticides ($2.18 < \log K_{ow} < 5.11$) from different chemical classes including triazines, substituted ureas, triazoles and organophosphate compounds. We also realised an elimination experiment to identify a performance reference compound (PRC). A flow-through calibration experiment was realised for 7 days at constant concentrations of target pesticides in tap water, under controlled temperature (20 °C) and flow velocity (2.5 cm s^{-1}). Sampling rates were between 1.3 and 121 mL d^{-1} with satisfactory RSD for most pesticides (9-47%), and poor repeatability for 3 hydrophobic pesticides (59-83%). Lag-phases for all target pesticides were shorter than 2 h, demonstrating the efficiency of passive SBSE for the integration of transient concentration peaks of these contaminants in surface waters. The role of flow velocity on pesticide uptakes was investigated and we assumed a water boundary layer-controlled mass transfer for 5 pesticides with $\log K_{ow} > 3.3$. Among these pesticides, we selected fenitrothion to evaluate its elimination, along with its deuterated analogue. Results showed 82% elimination of both compounds over the 7-day

experiment and isotropic exchange for fenitrothion, making fenitrothion-d6 a promising PRC candidate for *in situ* applications.

Keywords: Passive sampling, Stir bar sorptive extraction (SBSE), Calibration, Performance reference compound (PRC), Agricultural pesticides

1. Introduction

Passive samplers have been recently developed for the monitoring of various organic contaminants in the aquatic environment. These devices represent a cost-effective alternative to grab and automated sampling for the determination of concentration of target organic contaminants in surface and ground waters, as they require less logistical needs. Additionally, the integrative sampling of the dissolved fraction of target pollutants over days to weeks generally results in low quantification limits [1, 2]. A passive sampler is typically composed of a receiving phase, where the target organic contaminants are accumulated, and a membrane, which separates the receiving phase from the aquatic medium. This is the case for the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) [3, 4]. For other passive samplers, such as the Silicone Rubber (SR) and Low-density Polyethylene (LDPE) strips [5, 6], the polymer itself is both the membrane and the receiving phase. After convective transport of the contaminants from bulk solution to the water boundary layer (WBL) at the surface of the membrane, the sampling process is governed by diffusion to the receiving phase [7, 8]. For the determination of time-weighted average (TWA) concentrations, a calibration of the passive sampler has to be performed prior to field exposition. In other words, the accumulation kinetics of each target organic contaminant is studied in controlled conditions in order to determine the corresponding

sampling rate (R_s). However, it is well known that laboratory-derived R_s may differ from *in situ* R_s because of the difference in the exposition conditions (flow velocity, biofouling and temperature). Therefore, the determination of TWA concentrations may be biased [7]. The use of a performance reference compound (PRC) [9] during *in situ* applications has shown to be an efficient approach to determine more realistic R_s and calculate unbiased TWA concentrations of polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) for SPMD and SR [3, 5]; also, it has shown promising determination of estimates of polar pesticides with POCIS [10]. For well-described non polar samplers (SPMD, LDPE, SR and Chemcatcher for hydrophobic compounds), laboratory calibration could be avoided, since R_s can be modelled as a function of octanol-water partition coefficient (K_{ow}) [7, 11–13]. However, PRC are still needed for adjustment of the R_s modelled values [14].

Depending on the types of membrane and receiving phase of the passive sampler, chemicals with different polarities can be sampled, from polar contaminants such as pharmaceuticals and pesticides [4, 15], to hydrophobic organic contaminants such as PAH and PCB [16–20]. However, to our knowledge, sampling of moderately hydrophobic to hydrophobic pesticides ($2 < \log K_{ow} < 5$) is still poorly documented [2, 19, 20]. Moreover, some passive samplers equipped with a membrane (e.g., Membrane-Enclosed Sorptive Coating - MESCO, Chemcatcher and POCIS) might not be able to integrate short variations of concentration of moderately hydrophobic to hydrophobic pesticides (concentration peaks), as lag-phases would be relatively long (up to several days) [21–24]. The lag-phase is the time required to attain steady state accumulation flux in the passive sampler; it generally depends on the diffusion of contaminants through the membrane [7]. Finally, for most passive samplers, the sample treatment to recover the contaminants sequestered in the receiving phase is complex, time-consuming and organic solvent-consuming, and may be a source of poor repeatability [19].

Recently, we successfully applied stir bar sorptive extraction (SBSE), a fast, simple and solvent-free analytical sampling technique [25], directly *in situ* as a membrane-free passive sampling technique for the semi-quantitative monitoring of moderately hydrophobic to hydrophobic pesticides in two rivers (therein named “Passive SBSE”) [26]. The extraction device (Twister) is composed of a magnet enclosed in a glass tube coated with a thick film of polydimethylsiloxane (PDMS). In that field study, only qualitative and semi-quantitative performances of the passive sampler were compared to automated average sampling, as R_s of target pesticides had not been determined.

Hence, the aim of the present study was to obtain calibration data of passive SBSE for 18 agricultural pesticides in waters. We studied the accumulation kinetics of the target pesticides in Twisters with a flow-through system for 7 days, to determine the corresponding R_s and lag-phases. In addition, we studied the effect of flow velocity on the pesticide uptakes to assess which pesticide accumulation kinetics were controlled by the exposition conditions. Finally, we studied the elimination kinetics of selected pesticides to identify a PRC candidate.

2. Theory of passive sampling

To determine TWA concentrations of organic contaminants dissolved in the water column, a calibration of the passive sampler is generally performed in controlled conditions to study the accumulation kinetics of each contaminant and to determine the corresponding R_s . This section describes the theory of accumulation kinetics of organic contaminants in Twister used as membrane-free passive samplers. Similarly to SR and LDPE, the PDMS coating of the Twister is both membrane and receiving phase. Twister used as a passive sampler obeys the same kinetic laws as these other well-known devices [2, 7]. Mass transfer of a contaminant in the Twister includes several diffusion and interfacial transport steps across all barriers, *i.e.*,

the aqueous boundary layer, the possible biofilm layer and then, the receiving phase. Assuming isotropic exchange, the corresponding uptake in the sampler -initially empty- over time with constant ambient concentration can be described as follows (Eq. 1) [7, 8]:

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

where M_s (ng) is the mass of contaminant accumulated in the receiving phase; V_s (L) is the volume of the receiving phase; K_{sw} (adimensional), described by the ratio of the concentration at equilibrium of contaminant in the sampler C_s (ng mL⁻¹) and the concentration at equilibrium of contaminant in the water phase C_w (ng mL⁻¹), is the receiving phase/water partitioning coefficient; and t (d) equals the duration of exposition. The elimination rate constant k_e (d⁻¹) is defined as follows (Eq. 2):

$$k_e = \frac{R_s}{K_{sw} V_s} = \frac{\lambda A}{K_{sw} V_s} \quad (2)$$

where R_s is the sampling rate (mL d⁻¹); A (cm²) is the sampler surface area and λ (cm d⁻¹) is the overall mass transfer coefficient.

The graphical representation of Eq. 1 is curvilinear with a plateau corresponding to an equilibrium phase (described by K_{sw}). In the initial uptake phase, when the exponential term is small ($\ll 1$), chemical uptake is linear and integrative. Thus, in the initial uptake phase, Eq. 1 is reduced to Eq. 3:

$$M_s(t) = C_w \lambda A t \quad (3)$$

The overall mass transfer coefficient λ describes the movement of the contaminant 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:

$$\frac{1}{\lambda} = \frac{\delta_w}{D_w} + \frac{\delta_b}{D_b K_{bw}} + \frac{\delta_s}{D_s K_{sw}} \quad (4)$$

with δ (cm) the thickness of the particular barrier (in subscripts, w stands for water, b for the possible biofilm, and s for the receiving phase), D_w ($\text{cm}^2 \text{d}^{-1}$) the diffusion coefficient of the contaminant in water (*i.e.*, aqueous boundary layer), D_b ($\text{cm}^2 \text{d}^{-1}$) the diffusion coefficient of the contaminant in the possible biofilm, K_{bw} (adimensional) the partitioning coefficient between water and the possible biofilm, and K_{sw} (adimensional) the partitioning coefficient between water and the receiving phase.

For passive SBSE, we refer to two kinetic limitations of the contaminant uptakes as receiving phase and WBL 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, as previously discussed by Allan et al. for other non polar samplers such as SPMD, Chemcatchers for hydrophobic compounds, LDPE membranes, two types of MESCO, and silicone rods [27].

For contaminants with accumulation kinetics controlled by the WBL, the exposition conditions can have an impact on the R_s . Therefore, the difference between laboratory calibration conditions and field exposition conditions can lead to biased determinations of TWA concentrations. Spiking the receiving phase with a PRC prior to field exposition of the sampler has been used to calculate *in situ* R_s and determine unbiased TWA concentrations [3, 10]. PRC is an analytically non-interfering organic compound which can be loaded in a large amount in the receiving phase of the sampler, with moderate to high elimination and for which isotropic exchange kinetics is verified. The elimination of PRC is deduced from Eq. 1, when PRC is not present in water ($C_w = 0$):

$$M_s(t) = M_0 \exp(-k_e \cdot t) \quad (5)$$

where M_s (ng) is the mass of PRC remaining in the receiving phase of the sampler and M_0 (ng) is the initial mass of PRC spiked in the receiving phase of the sampler.

3. Experimental

3.1 Chemicals and materials

The 18 pesticides selected for this study belong to different use classes (herbicides, insecticides, and fungicides) and chemical classes (including triazines, substituted ureas, triazoles and organophosphate compounds), and have different physical chemical properties, such as their log K_{ow} (Table 1). They were provided by Dr. Ehrenstorfer GmbH (Augsburg, Germany): acetochlor, atrazine, azoxystrobin, chlorfenvinphos, chlorpyrifos-ethyl, chlortoluron, diflufenican, dimethomorph, 3,4-dichloroaniline (metabolite of diuron), fenitrothion, flufenoxuron, isoproturon, linuron, metolachlor, norflurazon, procymidon, simazine, and tebuconazole (purity $\geq 92.5\%$). For chemical analyses, diuron-d6, used as internal standard, was also provided by Dr. Ehrenstorfer (purity $\geq 98.5\%$). For the study of elimination kinetics, fenitrothion-d6 was purchased from Dr. Ehrenstorfer. 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 a LC-Pak cartridge and purchased from Millipore (Billerica, MA, USA).

3.2 Sampler design and preparation

The devices used for passive SBSE in this study were Twisters (20 mm x 1-mm thick PDMS film, with a surface area of 2.14 cm^2 and a volume of $126 \text{ }\mu\text{L}$) from Gerstel (Mülheim a/d Ruhr, Germany). For exposition purposes, the Twisters were placed in deployment bags made

of plastic mesh, to directly expose the sorption phase to the aquatic medium (*i.e.*, no membrane used).

Prior to use, the Twisters were treated following a method published elsewhere [28]. Briefly, the Twisters were placed overnight at 50 °C, then they were rinsed with 10 mL methanol/dichloromethane (50:50, v/v) for 30 min by sonication, gently dried with Kimwipes® precision paper and placed at 50 °C until use. For the calibration, the Twisters were placed in the deployment bags directly after treatment; whereas, for the elimination study, they were first loaded with fenitrothion and fenitrothion-d6. Twisters were loaded by extraction at 800 rpm for 3 h of 20 mL of ultrapure water spiked with each compound at 40 µg L⁻¹ and with 2.0 g of NaCl. Twisters were then gently rinsed with ultrapure water, dried with Kimwipes® precision paper, then placed at -18 °C until the elimination study.

After deployment, the Twisters were then gently rinsed with ultrapure water, dried with Kimwipes® precision paper, then stored at -18 °C until chemical analysis.

3.3 Flow-through experiments

3.3.1 Passive SBSE calibration

For the calibration of passive SBSE, 15 triplicates of Twisters were immersed in 15 glass channels (3 L each) supplied by means of individual pumps with 70 L of tap water spiked with the target pesticides at nominal concentrations ranging from 0.20 to 40 µg L⁻¹ located in a glass aquarium (Fig. 1). We selected these concentrations as low as possible, while allowing direct chemical analysis without pre-concentration. In order to offset the adsorption of the pesticides onto the surfaces of the calibration system (glass aquarium, and silicone and PVC pipes) and to ensure constant concentrations, a continuous spiking of the water in the

aquarium was realised. The experiment was performed for 7 days at 20 °C and flow velocity was 2.5 cm s⁻¹. Triplicates of Twisters were collected at different times (2, 4, 6, 8, 10, 24, 28, 32, 48, 56, 72, 80, 96 and 168 h) to follow the accumulation kinetics.

3.3.2 Effect of flow velocity on pesticide uptakes

To investigate the effect of flow velocity on the uptakes of the target pesticides, we immersed two triplicates of Twisters in two channels supplied with tap water spiked at the same concentrations as those applied for the calibration. This study was performed for 4 days at 25 °C with the same flow-through system and with continuous spiking. In the first channel, flow velocity was 2.5 cm s⁻¹, whereas in the second channel, flow velocity was 0.1 cm s⁻¹. Also, to determine pesticide uptakes in static conditions, we immersed a Twister in a 1-L amber glass flask filled with the same pesticide solution (flow velocity = 0 cm s⁻¹). For the accumulation in static conditions, the spiked water was replaced daily by 1 L of freshly prepared pesticide solution. All Twisters were collected at the same time after the 4 days of accumulation.

3.3.3 Elimination kinetics

Based on the study of the effect of flow velocity on pesticide uptakes, we selected fenitrothion and fenitrothion-d6 for elimination kinetic experiment with the same flow-through system and under the same conditions as for the calibration, *i.e.*, at 20 °C and 2.5 cm s⁻¹. In this case, however, the Twisters, previously loaded with fenitrothion and fenitrothion-d6, were immersed in triplicates in non-spiked tap water. Triplicates of loaded Twisters were immersed in 9 channels and were collected at different times (6, 10, 24, 48, 72, 96, 120, 144, 168 h) to follow the elimination kinetics.

3.3.4 Monitoring of experimental conditions

Every time a triplicate of Twisters was collected during the calibration and every day during the study of the effect of flow velocity on the pesticide uptakes, a water sample was collected from the channels and from the amber glass flask to measure concentrations of pesticides. Moreover, water temperature was checked every day during the calibration and elimination experiments, and the study of the effects of flow velocity on pesticide uptakes. Finally, flow velocity was measured at the beginning and at the end of all three experiments.

3.4 Chemical analysis

The target pesticides were analyzed by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) in two types of samples called the “Twister extracted samples” and the “water samples”. On the one hand, pesticides were desorbed from Twisters according to an analytical method published elsewhere [28]. Briefly, after storage at -18 °C, Twisters were placed in 200 µL of methanol/acetonitrile (50:50, v/v), and pesticides were desorbed under sonication for 15 min (*i.e.*, liquid desorption - LD). Then, 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 Twister extracted sample for analysis. On the other hand, for the verification of constant pesticide concentrations, the water samples were constituted with 990 µL aliquots of spiked tap water collected from the channels and from the amber glass flask and 10 µL of diuron-d6 at 1000 µg L⁻¹, in acetone. For both types of samples, the concentration of the internal standard diuron-d6 was 10 µg L⁻¹.

The analyses of the Twister extracted samples and of the water samples were performed using an LC 1100 Series apparatus from Agilent (Massy, France) coupled with an MS triple quadrupole API4000 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; $d_p = 3 \mu\text{m}$), purchased from Waters (St Quentin-en-Yvelines, France) was used for the chromatographic separation of the contaminants. Acetonitrile and ultrapure water both with formic acid (0.1%) were used in an analytical gradient (from 10% to 90% acidic acetonitrile) of 15 min.

4. Results and discussion

4.1 Passive SBSE calibration

4.1.1 Uptake kinetics

Mean measured pesticide concentrations in water (between 0.17 and 14.3 $\mu\text{g L}^{-1}$) were lower than nominal spiked concentrations (from 0.20 to 40 $\mu\text{g L}^{-1}$). Relative standard deviations (RSD) ranged from 12 to 44%, except for diflufenican, flufenoxuron, and fenitrothion, for which RSD ranged from 60 to 85% (Table 1). High RSD were observed for water concentrations of these 3 pesticides because, in spite of continuous spiking, their concentrations decreased dramatically (46 to 72% decrease) between the start of the calibration and the first sampling time ($t = 2 \text{ h}$). This decrease was due to massive adsorption of these 3 hydrophobic pesticides ($\log K_{ow} > 3.3$, Table 1) onto the surfaces of the calibration system, composed of a glass aquarium, and silicone and PVC pipes. This phenomenon

explains why measured pesticide concentrations were lower than nominal pesticide concentrations.

Uptake kinetic curves of insecticides, fungicides and herbicides are presented in Fig. 2a, Fig. 2b and Fig. 2c, respectively. Satisfactory to relatively poor repeatability for the masses of all target pesticides accumulated in Twisters and for all sampling times was obtained since RSD ranged from 0.5 to 41% ($n = 3$) for most pesticides and ranged from 51 to 59% for metolachlor, dimethomorph and flufenoxuron (data not shown). These RSD take into account the accumulation of target pesticides in the Twisters, the liquid desorption process and the LC-MS/MS analysis. The relatively poor repeatability was caused by the variations in the water concentrations. However, these repeatability results are in good agreement with previous field application of passive SBSE in river water [26].

Curvilinear patterns were observed for the uptake of insecticides, fungicides and herbicides. For all target pesticides, equilibrium was reached before the end of the calibration (7 days), and the linear accumulation periods ranged from 1.5 to 4 days. This means that for 1-week field application of Twisters, the TWA concentrations might not be considered as integrative, but only indicative. However, these results are in the same order of magnitude as those of the study of Zhao et al. [29], although the authors studied the accumulation kinetics of PAH such as pyrene ($\log K_{ow} = 4.88$) in PDMS rods, which are similar to our device. In that study, equilibrium regime for pyrene was reached in about 100 h for PDMS rods placed in a flow-through system supplied by spiked deionized water. In contrast, linear accumulation periods up to 14 days have been reported for the passive sampling of PAH and PCB with MESCO [20]. However, the MESCO is composed of a Twister as receiving phase and a low density polyethylene (LDPE) membrane that separates the receiving phase from the medium. This LDPE membrane constitutes an additional kinetic barrier regarding the accumulation of

organic contaminants in the Twister and probably slows down the uptake rates, resulting in longer accumulation periods.

In the present study, we performed the calibration of the passive SBSE for a broad range of pesticides ($2.18 < \log K_{ow} < 5.11$). Previous lab or *in situ* studies have focused on some of these pesticides such as acetochlor, simazine, atrazine, isoproturon, chlortoluron, linuron, metolachlor, chlorfenvinphos, fenitrothion, chlorpyrifos-ethyl, and organochlorine and organophosphate pesticides [1, 2, 4, 6, 10, 18, 20, 30-35]. Nevertheless, to our knowledge, the passive sampling of moderately hydrophobic to hydrophobic pesticides targeted in our study such as flufenoxuron, diflufenican, tebuconazole, procymidon, dimethomorph, azoxystrobin and norflurazon has scarcely been reported in the literature [26].

4.1.2 Lag-phases and sampling rates (R_s)

The first triplicate of Twisters was collected after 2 h of exposition in spiked water. Even after this short exposition, the target pesticides accumulated in the Twisters; masses were 10 to 114-fold larger than the corresponding limits of quantification, estimated at signal-to-noise ratios of 10 (Table 1). This means that the lag-phases for all target pesticides were shorter than 2 h. Indeed, without a membrane, mass transfer of target pesticides was faster than for membrane-equipped passive samplers such as MESCO [20] or SPMD [7]. Thus, passive SBSE could be an efficient technique for the monitoring of transient concentration peaks of the target pesticides in surface waters such as small dynamic rivers located in vineyard watersheds [26, 36]. For these pesticides, one could use larger samplers such as LPDE, SR, or SPMD, as they would behave similarly as Twisters regarding lag-phases, and linear accumulation periods would be longer. Nevertheless, Twister used as a passive sampler allows simple handling, preparation before deployment, *in situ* deployment and sample

treatment after exposition. Moreover, as Twister is originally an efficient analytical extraction device, the recovery of contaminants sequestered in the PDMS phase implies a faster, easier and less organic solvent-consuming treatment process [25].

Sampling rates (R_s) were calculated according to Eq. 2 and Eq. 3, by dividing the slope of the linear accumulation by the average pesticide concentration relative to this period. The linear accumulation periods were defined so that the correlation coefficients r^2 were higher than 0.8. Sampling rates were between 1.3 mL d^{-1} and 121 mL d^{-1} , with RSD ranging from 9 to 47%, except for fenitrothion, diflufenican, and flufenoxuron, for which RSD were between 59 and 83% (Table 2). The RSD of R_s of each pesticide was calculated by propagation of variance with the variance of the slope of the linear accumulation and the variance of the pesticide concentration in water. The high RSD for the R_s of fenitrothion, diflufenican, and flufenoxuron were caused by the high variance of water concentrations of the corresponding pesticides, reported in section 4.1.1.

In Table 2, pesticides are sorted by increasing values of $\log K_{ow}$. The highest R_s value was obtained for fenitrothion with $\log K_{ow} = 3.32$. Then, R_s values decreased for tebuconazole, chlorfenvinphos, acetochlor, diflufenican, chlorpyrifos-ethyl and flufenoxuron. The control of the accumulation kinetics by the WBL at the Twister surface might explain this decrease. Indeed, studies have suggested the uptake control by the WBL for compounds with $\log K_{ow}$ values higher than 4.5 to 5.0, regarding non-polar passive samplers with membrane such as SPMD [7], MESCO and Chemcatcher, as well as for samplers without membrane such as LDPE membranes and silicon strips [27]. Our experimental results might corroborate the WBL control reported in the literature [27], although in our case this would be for compounds with $\log K_{ow}$ higher than 3.3. Therefore, the accumulation kinetics of the target pesticides with $\log K_{ow}$ larger than 3.3 may be controlled by the WBL; so exposition conditions, especially flow velocity, may have an impact on their uptakes in Twisters.

4.2 Effect of flow velocity on pesticide uptakes

Mean pesticide concentrations in water were between 0.13 and 19.6 $\mu\text{g L}^{-1}$ with satisfactory to relatively high RSD, ranging from 21 to 73% (data not shown). Nevertheless, satisfactory RSD were obtained for the masses of pesticides accumulated in the Twisters at the end of the 4-day experiment. For the Twisters placed in the channel with flow velocity at 2.5 cm s^{-1} , RSD ranged from 2 to 32%, whereas RSD were between 10 and 44% for the Twisters placed in the channel with flow velocity at 0.1 cm s^{-1} (data not shown). Fig. 3 presents the masses of pesticides for which an ANOVA ($\alpha = 0.05$) confirmed a significant effect of flow velocity on the uptakes. Pesticide uptakes in static conditions were similar to those at 0.1 cm s^{-1} for fenitrothion and chlorfenvinphos, and relatively close for diflufenican, chlorpyrifos-ethyl and flufenoxuron. But, a significant increase of the masses of fenitrothion, chlorfenvinphos, diflufenican, chlorpyrifos-ethyl and flufenoxuron was observed with an increase in flow velocity from 0.1 cm s^{-1} to 2.5 cm s^{-1} . Therefore, the accumulation kinetics of these hydrophobic compounds ($\log K_{ow} > 3.3$) in the Twisters was controlled by the WBL. Faster flow decreased the thickness of the WBL, so that the transfer of these organic contaminants to the receiving phase was faster. These results confirm, except for tebuconazole and acetochlor, the assumption made in section 4.1.2 that the accumulation kinetics of the target pesticides with $\log K_{ow}$ larger than 3.3 are controlled by the WBL. Moreover, this suggests that PRC might be needed for the determination of unbiased TWA concentrations of these compounds. In contrast, for less hydrophobic compounds ($2.18 < \log K_{ow} < 3.3$), no effect of flow velocity was observed. Therefore, we can assume accumulation kinetics controlled by the receiving phase, and also that the uptakes of these pesticides might be less dependent or independent

from exposition conditions. As a result, no PRC might be required for determination of TWA concentration of these pesticides.

4.3 Elimination kinetics

Fenitrothion showed an uptake strongly dependent on flow velocity, *i.e.*, WBL-controlled accumulation kinetics, and was accumulated in the Twister 3 to 5 times more than chlorfenvinphos, diflufenican, chlorpyrifos-ethyl and flufenoxuron (Fig. 3). Moderate to high elimination of fenitrothion from the receiving phase of the Twister and isotropic exchange still had to be verified for fenitrothion-d6 to be a PRC candidate. Therefore, the elimination kinetics of fenitrothion and fenitrothion-d6 was followed for 7 days (Fig. 4). The pesticide and its deuterated analogue showed very similar elimination kinetics and high elimination from the PDMS phase of the sampler. Over the 7 days of exposition, 82% of the initial mass of the two compounds were eliminated.

Knowing that the calibration and the elimination studies were conducted under the same conditions (temperature and flow velocity), we compared the elimination rate constant of fenitrothion derived from the calibration (k_{e-Cal}) with the directly measured elimination rate constant (k_e), as it is a useful way to verify isotropic exchange kinetics [3]. Calibration-derived elimination rate constant of fenitrothion was calculated using Eq. 2, where K_{sw} was determined with the calibration data, since all target pesticides reached equilibrium by the end of the 7-day experiment. Calibration-derived elimination rate constant k_{e-Cal} (0.297 d^{-1}) was slightly larger than directly measured k_e (0.253 d^{-1}) for fenitrothion. Therefore, since fenitrothion-d6 (0.260 d^{-1}) showed similar elimination kinetics as fenitrothion, we can assume isotropic exchange for both compounds and we identified fenitrothion-d6 as a PRC candidate. Field exposition of the Twisters spiked with fenitrothion-d6 will allow us to evaluate this

compound as PRC for the determination of unbiased TWA concentrations of target pesticides with accumulation kinetics under WBL control. To do so, since one PRC candidate has been identified so far, the exposure adjustment factor (EAF) methodology would be used [3].

5. Conclusion

This study focused on the calibration of passive SBSE for the monitoring of 18 moderately hydrophobic to hydrophobic pesticides in waters. Firstly, we determined sampling rates of the target pesticides ranging from 1.3 to 121 mL d⁻¹ and observed linear accumulation periods between 1.5 to 4 days. Secondly, results revealed that flow velocity had an effect on the uptakes of 5 of the most hydrophobic target pesticides ($\log K_{ow} > 3.3$), due to WBL control, and we assumed receiving phase-controlled accumulation kinetics for the moderately hydrophobic pesticides ($2.18 < \log K_{ow} < 3.3$). Thirdly, among these 5 hydrophobic pesticides, we selected fenitrothion for the elimination study, along with its deuterated analogue fenitrothion-d6. We observed similar elimination kinetics of the two compounds and verified isotropic exchange for fenitrothion. Therefore, fenitrothion-d6 is a promising PRC candidate for the determination of TWA concentrations for *in situ* applications. Future work will focus on the implementation of the calibration data and use of fenitrothion-d6 for quantitative purposes.

Passive SBSE is a simple and environmentally friendly passive sampling technique for the monitoring of target pesticides in freshwaters. Very small volumes of organic solvents are required to recover the absorbed contaminants by liquid desorption, and the small size of the Twisters allows simple handling, preparation before deployment and *in situ* deployment. Moreover, without a membrane, lag-phases of passive SBSE are shorter than most samplers equipped with membranes such as POCIS and MESCO. Thus, passive SBSE could be

efficient for the monitoring of transient concentration peaks of the target pesticides in
freshwaters.

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Table 1 Mean water concentrations (n = 16), limits of quantification (LQ) reached by the analytical system and mass of target pesticides accumulated in the Twisters (n = 3) after 2-h exposition during flow-through calibration for 7 days at 20 °C and flow rate of 2.5 cm s⁻¹

Pesticide	Log K _{ow}	Use	Water concentration (n = 16)			Mass of pesticides accumulated (ng)	
			Nominal (µg L ⁻¹)	Mean (µg L ⁻¹)	RSD (%)	LQ	After 2 h of exposition (n = 3)
Simazine	2.18	H	0.20	0.30	13	0.01	0.14
Chlortoluron	2.41	H	4.0	4.3	14	0.2	1.9
Norflurazon	2.30	H	16.0	14.3	21	0.8	8.1
Azoxystrobin	2.50	F	4.0	2.9	16	0.2	6.1
Atrazine	2.61	H	1.0	0.9	13	0.1	1.1
Dimethomorph	2.68	F	4.0	3.7	14	0.2	2.4
3,4-dichloroaniline	2.69	M	20.0	11.3	26	1.0	44.4
Isoproturon	2.87	H	8.0	8.1	12	0.4	4.3
Procymidon	3.08	F	40.0	6.5	44	2.0	120
Metolachlor	3.13	H	0.40	0.17	24	0.02	1.31
Linuron	3.20	H	8.0	3.8	25	0.4	3.1
Fenitrothion	3.32	I	40.0	2.3	85	2.0	102
Tebuconazole	3.70	F	5.0	3.2	18	0.3	14.1
Chlorfenvinphos	3.81	I	8.0	2.0	34	0.4	33.1
Acetochlor	4.14	H	20.0	7.7	27	2.0	76.5
Diflufenican	4.20	H	4.0	0.2	60	0.2	6.1
Chlorpyrifos-ethyl	4.96	I	4.0	0.2	21	0.2	4.3
Flufenoxuron	5.11	I	40.0	10.5	74	0.4	45.4

H: herbicide, F: fungicide, M: metabolite, I: insecticide

Table 2 Passive SBSE sampling rates (R_s) derived from flow-through calibration for 7 days at 20 °C and flow rate of 2.5 cm s⁻¹ (n = 3)

Pesticide	R _s (mL d ⁻¹)	RSD (n = 3) (%)
Simazine	1.4	9
Chlortoluron	0.8	17
Norflurazon	1.5	15
Azoxystrobin	4.3	17
Atrazine	2.6	16
Dimethomorph	1.7	18
3,4-dichloroaniline	1.9	25
Isoproturon	1.3	14
Procymidon	34.1	47
Metolachlor	21.9	19
Linuron	23.2	25
Fenitrothion	121	83
Tebuconazole	10.7	20
Chlorfenvinphos	62.5	34
Acetochlor	26.2	23
Diflufenican	59.2	59
Chlorpyrifos-ethyl	27.6	22
Flufenoxuron	6.6	75

Fig. 1 Schematized flow-through system for calibration of passive SBSE. Triplicates of Twisters are immersed in tap water at 20 °C spiked with the target pesticides, located in a glass aquarium and flowing by means of individual pumps in all channels at 2.5 cm s⁻¹

Fig. 2 Uptake curves of (a) insecticides, (b) fungicides and (c) herbicide in Twisters during flow-through calibration for 7 days at 20 °C and 2.5 cm s⁻¹. Errors bars represent $\pm s$ (n = 3)

Fig. 3 Effect of flow velocity on uptakes of selected pesticides in Twisters during flow-through and static experiments for 4 days at 25 °C. Errors bars represent $\pm s$ (n = 3)

Fig. 4 Elimination curves of fenitrothion and fenitrothion-d6 from Twisters during flow-through experiment for 7 days at 20 °C and flow rate of 2.5 cm s⁻¹. Errors bars represent $\pm s$ (n = 3)

References

- [1] J. Namieśnik, B. Zabiegała, A. Kot-Wasik, M. Partyka, A. Wasik, *Anal. Bioanal. Chem.* 381 (2005) 279.
- [2] B. Vrana, G. Mills, I. Allan, E. Dominiak, K. Svensson, J. Knutsson, G. Morrison, R. Greenwood, *TrAC - Trends Anal. Chem.* 24 (2005) 845.
- [3] J.N. Huckins, J.D. Petty, J.A. Lebo, F.V. Almeida, K. Booij, D.A. Alvarez, W.L. Cranor, R.C. Clark, B.B. Mogensen, *Environ. Sci. Technol.* 36 (2002) 85.
- [4] D.A. Alvarez, J.D. Petty, J.N. Huckins, T.L. Jones-Lepp, D.T. Getting, J.P. Goddard, S.E. Manahan, *Environ. Toxicol. Chem.* 23 (2004) 1640.
- [5] F. Smedes, in: R. Greenwood, G. Mills, B. Vrana (Eds.), *Comprehensive Analytical Chemistry*, Vol. 48: Passive sampling techniques in environmental monitoring, Elsevier Science, Amsterdam, 2007, pp. 407.
- [6] K. Booij, F. Smedes, E. van Weerlee, *Chemosphere* 46 (2002) 1157.
- [7] J.N. Huckins, J.D. Petty, K. Booij, *Monitors of Organic Chemicals in the Environment: Semipermeable Membrane Devices*, Springer Science+Business Media, New York, 1st ed., 2006.
- [8] R. Greenwood, G. Mills, B. Vrana, *Comprehensive Analytical Chemistry*, Vol. 48: Passive sampling techniques in environmental monitoring, Elsevier Science, Amsterdam, 1st ed., 2007.
- [9] K. Booij, H.M. Sleiderink, F. Smedes, *Environ Toxicol Chem.* 17 (1998) 1236-1245.
- [10] N. Mazzella, S. Lissalde, S. Moreira, F. Delmas, P. Mazellier, J.N. Huckins, *Environ. Sci. Technol.* 44 (2010) 1713.
- [11] K. Booij, H.E. Hofmans, C.V. Fischer, E.M. Van Weerlee, *Environmental Science & Technology*, 37 (2003) 361-366.
- [12] B. Vrana, G.A. Mills, M. Kotterman, P. Leonards, K. Booij, R. Greenwood, *Environmental Pollution*, 145 (2007) 895-904.
- [13] T.P. Rusina, F. Smedes, M. Koblizkova, J. Klanova, *Environmental Science & Technology*, 44 (2010) 362-367.
- [14] K. Booij, F. Smedes, *Environmental Science & Technology*, 44 (2010) 6789-6794.
- [15] N. Mazzella, T. Debenest, F. Delmas, *Chemosphere* 73 (2008) 545.
- [16] J.N. Huckins, M.W. Tubergen, G.K. Manuweera, *Chemosphere* 20 (1990) 533.
- [17] J.N. Huckins, G.K. Manuweera, J.D. Petty, D. Mackay, J.A. Lebo, *Environ. Sci. Technol.* 27 (1993) 2489.
- [18] B. Vrana, P. Popp, A. Paschke, G. Schüürmann, *Anal. Chem.* 73 (2001) 5191.

- 507 [19] B. Vrana, A. Paschke, P. Popp, *Environ. Pollut.* 144 (2006) 296.
- 508 [20] A. Paschke, K. Schwab, J. Brümmer, G. Schüürmann, H. Paschke, P. Popp, J.
509 *Chromatogr. A* 1124 (2006) 187.
- 510 [21] E.L.M. Vermeirssen, N. Bramaz, J. Hollender, H. Singer, B.I. Escher, *Water Res.* 43
511 (2009) 903.
- 512 [22] E.L.M. Vermeirssen, C. Dietschweiler, B.I. Escher, J. van der Voet, J. Hollender,
513 *Environ. Sci. Technol.* 46 (2012) 6759.
- 514 [23] I.J. Allan, K. Booij, A. Paschke, B. Vrana, G. Mills, R. Greenwood, J. *Environ. Monitor.*
515 12 (2010) 696.
- 516 [24] C. Harman, K.-E. Tollefsen, O. Bøyum, K. Thomas, M. Grung, *Chemosphere* 72 (2008)
517 1510.
- 518 [25] E. Baltussen, P. Sandra, F. David, C. Cramers, J. *Microcol. Sep.* 11 (1999) 737.
- 519 [26] A. Assoumani, S. Lissalde, C. Margoum, N. Mazzella, M. Coquery, *Sci. Total Environ.*
520 463–464 (2013) 829.
- 521 [27] I.J. Allan, K. Booij, A. Paschke, B. Vrana, G. Mills, R. Greenwood, *Environ. Sci.*
522 *Technol.* 43 (2009) 5383.
- 523 [28] C. Margoum, C. Guillemain, X. Yang, M. Coquery, *Talanta* 116 (2013) 1.
- 524 [29] W. Zhao, G. Ouyang, M. Alaei, J. Pawliszyn, J. *Chromatogr. A* 1124 (2006) 112.
- 525 [30] D.A. Alvarez, P.E. Stackelberg, J.D. Petty, J.N. Huckins, E.T. Furlong, S.D. Zaugg, M.T.
526 Meyer, *Chemosphere* 61 (2005) 610.
- 527 [31] D.A. Alvarez, J.N. Huckins, J.D. Petty, T. Jones-Lepp, F. Stuer-Lauridsen, D.T. Getting,
528 J.P. Goddard, A. Gravell, in: R. Greenwood, G. Mills, B. Vrana (Eds.), *Comprehensive*
529 *Analytical Chemistry*, Vol. 48: Passive sampling techniques in environmental monitoring,
530 Elsevier Science, Amsterdam, 2007, pp. 171.
- 531 [32] I.J. Allan, A. Ruus, M.T. Schaanning, K.J. Macrae, K. Næs, *Sci. Total Environ.* 423
532 (2012) 125.
- 533 [33] A. Jahnke, M. McLachlan, P. Mayer, *Chemosphere* 73 (2008) 1575.
- 534 [34] R. Prokeš, B. Vrana, J. Klánová, *Environ. Pollut.* 166 (2012) 157.
- 535 [35] F. Stuer-Lauridsen, *Environ. Pollut.* 136 (2005) 503.
- 536 [36] M. Rabiet, C. Margoum, V. Gouy, N. Carlier, M. Coquery, *Environ. Pollut.* 158 (2010)
537 737.
538
539