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Prediction of the accumulation behavior of pesticides in PDMS-coated stir bars used as passive samplers in freshwaters

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Abstract

Passive samplers accumulate organic contaminants at rates that depend on in-field exposure conditions such as freshwater flow velocity, water temperature and water quality. Time-weighted average concentrations can be determined by using a correction process such as the performance reference compound (PRC) method. This study presented a new approach to predict the accumulation behavior of pesticides in polydimethylsiloxane-coated stir bars under different exposure conditions and assign a specific PRC to each pesticide for quantitative purposes. We used an experimental design with eight simultaneous accumulation kinetics of 13 pesticides and elimination kinetics of three PRC candidates run in a flow-through system to determine the effects of flow velocity, water temperature and dissolved organic matter on the kinetic constants. We identified the parameters that had a significant effect on the accumulation of each pesticide and assigned a PRC candidate to each pesticide. We then used a discriminant function analysis to find the parameters that had a significant effect on accumulation of the 13 pesticides via their physical-chemical properties and to predict through a stochastic approach the parameters for seven other pesticides. This approach provides a better framework for identifying a PRC than conventional methods to determine unbiased concentrations in future monitoring efforts.

Key words: Passive sampling, River, Accumulation kinetics, Performance Reference Compound, Experimental designs, Exposure conditions

Highlights

- Different accumulation and elimination patterns were observed depending on the target pesticides and PRC candidates, and on the experimental conditions
- A change between membrane control and WBL control for the pesticide uptake was observed for $\log K_{ow}$ of around 3.3
- A discriminant function analysis showed the link between the accumulation behaviors of the 13 studied pesticides in changing experimental conditions and their physical-chemical properties
- The accumulation behaviors of seven other pesticides were predicted from their physical-chemical properties through a stochastic approach

Introduction

Passive sampling has proven to be an efficient alternative to conventional active sampling for monitoring contaminants in the aquatic environment.¹⁻⁴ Passive samplers afford a more accurate assessment of contamination in water bodies that are characterized by strong temporal variations.⁵ Over the last three decades, several passive samplers have been developed for determining organic contaminants with different polarities in the aquatic environment.^{6, 7} Passive stir-bar sorptive extraction (passive SBSE) is a passive sampling technique using polydimethylsiloxane (PDMS)-coated stir bars called ‘Twisters’ that has proven particularly

efficient during flood events for identifying pesticide increases in surface waters draining agricultural areas.^{8,9} Twisters were also used as passive samplers in a laboratory calibration study for monitoring polychlorobiphenyls, polycyclic aromatic hydrocarbons, and organochlorine pesticides in water.¹⁰

Passive samplers need to be calibrated in controlled laboratory conditions prior to field deployment to determine time-weighted average concentrations (TWAC) of organic contaminants.¹ The calibration is the study of the kinetics of contaminant accumulation in the passive sampler to determine their corresponding sampling rates (R_s). However, differences between field and laboratory conditions may affect the accumulation kinetics of some contaminants and therefore the corresponding R_s . Studies have shown that flow velocity, water temperature, and dissolved organic matter (DOM) are the parameters that most impact the accumulation kinetics of organic contaminants in several passive samplers.⁷ Field R_s may therefore be different from laboratory R_s and consequently introduce a bias in TWAC calculations.¹¹ This makes it necessary to identify the contaminants for which accumulation kinetics depend on exposure conditions and to correct their sampling rates in order to determine unbiased TWAC values.

Performance reference compounds (PRCs) are used to determine accurate field R_s ¹⁰ based on the assumption of isotropic kinetic exchanges. A PRC is an analytically non-interfering compound that is loaded into the passive sampler prior to field exposure. Measurements of PRC dissipation during both laboratory calibration and field exposures of the passive sampler serve to calculate an adjustment factor for determining field R_s . The most common PRC are deuterium analogs of some of the target contaminants,¹¹⁻¹³ and they are often used to correct the R_s of compounds other than their native analogs. To qualify as a PRC, the PRC candidate also needs to behave like the target contaminants over the course of changing exposure conditions. This

means that the elimination kinetics of the PRC candidate and the accumulation kinetics of the target contaminants need to both depend on the same parameters.

The impact of exposure conditions such as flow velocity, water temperature and DOM concentration on the accumulation kinetics and R_s of pesticides, pharmaceuticals and polycyclic aromatic hydrocarbons has been assessed in laboratory¹⁴⁻¹⁸ and field¹⁹⁻²¹ studies, but these studies have only dealt with one parameter at a time and were unable to assess the impact of several parameters in interaction.^{22, 23}

The aim of this study was to predict the accumulation behavior (i.e., the parameters that have a significant effect on accumulation) of several pesticides in Twisters under different exposure conditions, and to assign a PRC to each one of them. With that vision, we first assessed the simultaneous impact of flow velocity, water temperature and DOM concentration on the accumulation kinetics of 13 pesticides in Twisters and on the elimination kinetics of three PRC candidates, by means of a screening design of experiments. This comprehensive study allowed to (i) identify the pesticides for which kinetics depend on exposure conditions, (ii) identify exactly which experimental parameters have a significant impact, and (iii) assign each pesticide with a PRC candidate for which the elimination kinetics depends on the same experimental parameters. We then used a discriminant function analysis (DFA) to discriminate the behavior of the 13 target pesticides via their physical-chemical properties. Finally, we used the results of this DFA to predict how seven other pesticides would behave in response to the same experimental parameters.

Theory of passive sampling

The theory of passive sampling is well established and documented^{1, 3, 24}. Assuming isotropic exchange, the uptake of a contaminant in a Twister used as a passive sampler at constant ambient water concentration obeys a first-order kinetics⁸, described by Eq. 1:

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

where M_s (ng) is mass of contaminant accumulated in the receiving phase, C_w (ng L⁻¹) is concentration of contaminant in the water phase, K_{sw} (dimensionless) described by the ratio at equilibrium of the concentration of contaminant in the sampler C_s (ng L⁻¹) and concentration of contaminant in the water phase, C_w (ng L⁻¹) is receiving phase/water partition coefficient, V_s (L) is volume of the receiving phase, R_s is sampling rate (L d⁻¹), and t (d) is duration of exposure.

The elimination of PRC is deduced from Eq. 1 when PRC is not present in the water ($C_w = 0$):

$$M_s(t) = M_0 \exp(-k_e \cdot t) \quad (2)$$

where M_s (ng) is mass of PRC remaining in the receiving phase of the sampler and M_0 (ng) is initial mass of PRC spiked in the receiving phase, with the elimination rate constant k_e (d⁻¹) defined as follows (Eq. 3):

$$k_e = \frac{R_s}{K_{sw} V_s} \quad (3)$$

The sampling rate is proportional to the passive sampler surface area (A) and the overall mass transfer coefficient (k_o) as follow (Eq. 4):

$$R_s = k_o A \quad (4)$$

The overall resistance to mass transfer ($1/k_o$) comprises each individual resistance to mass transfer and is calculated with k_w and k_s as the mass transfer coefficients in the water and the PDMS respectively, and K_{sw} the silicone/water partition coefficient (Eq. 5):

$$\frac{1}{k_0} = \frac{1}{k_w} + \frac{1}{K_{sw}k_s} \quad (5)$$

The individual resistance to mass transfer is calculated with the ratio of the thickness (δ) of each compartment (water or PDMS, respectively noted with subscripts w and s) contributing to the mass transfer and the diffusion coefficient of the compound (D). The individual resistance for each compartment is calculated as follows (Eq. 6 and 7):

$$\frac{1}{k_w} = \frac{\delta_w}{D_w} \quad (6)$$

$$\frac{1}{k_s} = \frac{\delta_s}{D_s} \quad (7)$$

By combining Eq. 4, 5, 6 and 7, R_s can be estimated by Eq. 8:

$$R_s = \frac{A}{\frac{\delta_w}{D_w} + \frac{\delta_s}{K_{sw}D_s}} \quad (8)$$

Experimental

Chemicals and materials. For this study, we selected 13 wine-growing-related pesticides from different use classes (herbicides, insecticides, and fungicides) that are frequently monitored and quantified in rivers located in agricultural watersheds.^{25, 26} The 13 pesticides selected atrazine, chlorfenvinphos, chlorpyrifos, chlorpyrifos-methyl, chlortoluron, diflufenican, dimethomorph, fenitrothion, isoproturon, linuron, norflurazon, simazine, and spiroxamine, (purity $\geq 92.5\%$) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). This panel of pesticides covers different chemical classes (triazines, substituted ureas, triazoles, and organophosphate compounds) and presents a range of physical-chemical properties, such as octanol-water

partition coefficient ($2.18 < \log K_{ow} < 5.50$) (Table 1). Further three deuterated PRC candidates, i.e. chlorpyrifos methyl-d6 ($\log K_{ow} = 4.31$), fenitrothion-d6 ($\log K_{ow} = 3.32$) and tebuconazole-d6 ($\log K_{ow} = 3.70$), were selected. We expected a change in the accumulation behavior for compounds with $\log K_{ow}$ greater than 3.3 according to our previous work⁹. So, we selected these PRC candidates to investigate on their elimination under changing experimental conditions. These PRC candidates were also purchased from Dr. Ehrenstorfer (purity > 95%).

For chemical analyses, diuron-d6 (used as internal standard), linuron-d6 and chlorpyrifos-ethyl-d10 (used as surrogates) were purchased from by Dr. Ehrenstorfer (purity $\geq 98.5\%$). Sodium chloride NaCl (purity = 99.5%), dichloromethane for pesticide residue analysis, and liquid chromatography–mass spectrometry (LC-MS)-grade acetonitrile and methanol were purchased from VWR (Strasbourg, France). Humic acids (technical grade) for spiking water with DOM, and formic acid (purity = 98%) for LC-MS analysis were purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France). Ultrapure water produced by a Milli-Q® water purification system equipped with an LC-Pak® cartridge was purchased from Millipore (Billerica, MA). For passive SBSE, we used Twisters® (20 mm x 1-mm-thick PDMS film, film volume: 126 μ L) purchased from Gerstel (Mülheim a/d Ruhr, Germany).

Design of experiments. We assessed the simultaneous impact of flow velocity, water temperature and DOM on the accumulation kinetics of 13 pesticides in Twisters and on the elimination kinetics of three PRC candidates, using a 2^3 -model full factorial design for screening. Three factors with two levels (low and high) were investigated, thus representing eight experiments (Experiment #1 to Experiment #8). The low-level and high-level values of each factor are presented in Table 2. For DOM, dissolved organic carbon concentration (DOC) was determined according to standard method NF EN 1484²⁷ (limit of quantification = 0.5 mgC.L^{-1}). We selected this design to evaluate the effect of the factors and the effect of two-

factor interactions. Data was processed using Statgraphics software (Centurion XVII) from SigmaPlus.

The flow-through system used for this study made it possible to perform all eight experiments of the design simultaneously (Figure S1 in the Supplementary Data section). The eight experiments were carried out in four aquariums (i.e., two experiments per aquarium) filled with 17 L of tap water spiked with the target pesticides. In two of these aquariums, tap water was also spiked with humic acids (HA) to reach the DOC concentration of 20 mgC L⁻¹ (Aquariums #2 and #4). The DOC concentration in the other two aquariums was 2 mgC L⁻¹ (Aquariums #1 and #3). Aquariums #1 and #2 were placed in a bath at 10°C while Aquariums #3 and #4 were placed in a bath at 23°C. In each of these four aquariums, the water flows were generated via two diffusion ramps, each connected to an immersion pump (Figure S2 in the Supplementary Data section). Each ramp was composed of four holes through which the water exited at a set flow velocity. Two Twisters were placed in a deployment bag⁸ positioned in front of each hole of the diffusion ramp to hold the Twisters® in the water flow during the experiment. For each aquarium, one diffusion ramp provided a flow velocity of 4 cm s⁻¹ and the other ramp provided a flow velocity of 20 cm s⁻¹.

Tap water was spiked with the target pesticides at nominal concentrations ranging from 0.25 to 2.5 µg L⁻¹. To offset the adsorption of the pesticides onto the inner surfaces of the calibration system (e.g., glass aquarium and silicone and polyvinyl chloride pipes) and ensure constant concentrations, a system was set up to continuously spike the water by diluting a stock solution of the target pesticides in two mixing vessels run in parallel. The stock solution was brought into each mixing vessel at 2.1 mL h⁻¹, while tap water flow was 140 mL min⁻¹. The flow of freshly-prepared spiked tap water in each aquarium was set to 70 mL min⁻¹ to ensure six water renewals per day. Continuous spiking with a stock solution of HA was also performed in a mixing vessel at 7.1 mL h⁻¹ to ensure a constant concentration of DOC in both DOC-

supplemented aquariums (Figure S1). The system was run without the Twisters for two days for equilibration purposes. Then, the eight experiments were run for 7 days, and for each experiment, one Twister was collected at each timepoint (6 h, and 1, 2, 3, 4, 5, 6 and 7 days) to track the time-course accumulation kinetics of the 13 pesticides and the elimination kinetics of the three PRC candidates.

Treatment of Twisters. Prior to the experiment, the Twisters were placed at 300°C for one hour for thermal conditioning. Then, each Twister was loaded separately with the PRC candidates (i.e., chlorpyrifos-methyl-d6, fenitrothion-d6, and tebuconazole-d6) by extraction for 3 h at 800 rpm of 20 mL of ultrapure water spiked at 32, 40, and 16 $\mu\text{g L}^{-1}$, respectively, and with 2.0 g of NaCl.⁹ The Twisters were then gently rinsed with ultrapure water, dried with Kimwipes® precision-cleaning task wipes, and placed at -18°C until use. For the experiment, the Twisters were placed in deployment bags made of two pieces of plastic mesh in order to expose the membrane-free PDMS phase to the spiked water.^{8,9} The Twisters collected during the experiment were taken out of their deployment bags, gently rinsed with ultrapure water, dried with Kimwipes® cleaning task wipes, then stored in their original vials at -18°C until chemical analysis.

Monitoring of exposure conditions. A water sample was collected with a glass bottle at the beginning of the study at the same time as collecting Twisters (6 h, and 1, 2, 3, 4, 5, 6 and 7 days). Eighteen water samples were collected from Aquariums #1 and #4 to measure pesticide concentrations in water (i.e., controls) with low and high concentrations of DOC, respectively. Pesticide concentrations in water and relative standard deviations (RSDs) are reported in Table S1 in the Supplementary Data section. DOC concentration was also measured every day in Aquariums #1 and #2 (Table S2 in the Supplementary Data section). Water temperature was

monitored every 6 hours in every aquarium via four temperature dataloggers (Tinytag Aquatic 2 from Gemini Data Loggers Ltd, UK) (Table S3). Flow velocity was measured at the beginning and at the end of the experiment on every diffusion ramp using an ultrasonic flowmeter (Flo-Mate 2000 from Marsh-McBirney, Loveland, CO) (Table S4 in the Supplementary Data section).

Chemical analysis. Before extraction and determination of pesticide concentrations, all water samples were filtered with 0.7- μm GF/F-grade glass fiber membranes (Millipore). Pesticide concentrations 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).²⁸ The accumulated pesticides in the Twisters as well as the remaining amounts of PRC candidates were desorbed in a methanol/acetonitrile mix (50/50, v/v) by sonication for 15 min. The amounts of the desorbed pesticides and PRC candidates were determined by an analytical method published elsewhere.²⁹ Briefly, the chemical analyses were performed with an LC 1100 series apparatus from Agilent (Massy, France) coupled with a MS triple quadrupole API 4000 system from AB Sciex (Les Ulis, France) equipped with an electrospray ionization (ESI) source that was operated in positive ion mode. An HSS T3 column (2.1 mm x 100 mm; $d_p = 1.8 \mu\text{m}$; 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 a 15-minute analytical gradient.

Data processing. Accumulation and elimination kinetics were modeled by estimating the parameters of Eq. 1 and Eq. 2, respectively, using BaRatin, which is an application based on the Bayesian paradigm that was originally developed to estimate rating curve parameters in hydraulics sciences.³⁰ Here, for each target pesticide and each experiment in the design plan,

we determined the parameters for accumulation and elimination kinetics by fitting the respective models on the experimental data. BaRatin considered the individual uncertainty of each datum (i.e., the amount of pesticides accumulated in the Twisters and the remaining amounts of PRC candidates) to adjust the models and output optimal graphical representations of the accumulation and elimination curves (corresponding to optimal parameters). BaRatin also computed uncertainty intervals resulting from the uncertainty in parameter estimates as well as the imperfect representation of accumulation/elimination by Eq. 1 and Eq. 2. The uncertainty of the data used for modeling the accumulation and elimination kinetics in BaRatin was the expanded uncertainty of the LC-MS/MS method for each studied pesticide and PRC candidate as determined in previous studies,^{30, 31} i.e., ranging from 11% to 24%. A relation between the physical-chemical parameters of the pesticides (Table 1) and their dependency on experimental conditions was investigated using DFA in RStudio software.

Results and discussion

Determination of sampling rates. Sampling rates, R_s , with their relative standard deviations, RSDs, were determined for the 13 pesticides in all experiments and presented in Table 3. Sampling rates ranged from 0.7 mL d⁻¹ for spiroxamine in Experiment #2 to 879 mL d⁻¹ for chlorfenvinphos in Experiment #7, with RSDs between 14% for chlorpyrifos-methyl in Experiments #3, #4, #5 and #7 and 50% for spiroxamine in Experiment #8. Higher RSD values were found for the R_s of chlorpyrifos (80%) and diflufenican (119%) in Experiment #8 with all experimental parameters at the higher level. High RSD values were also obtained for the R_s of spiroxamine in Experiments #4 (133%) and #5 (131%), probably because of short linear accumulation periods (one day).

Experiment #3 (water at 23°C, 2 mgC L⁻¹ for DOM, and flow velocity of 4 cm s⁻¹) was performed in conditions close to a previous laboratory calibration of Twisters⁹ (tap water at

20°C and flow velocity of 2.5 cm s⁻¹) and resulted in similar R_s values for all targets except chlorfenvinphos; values higher by a factor of 1.3 for atrazine to 4.4 for chlortoluron were obtained in this study in comparison with the previous calibration. Martin et al.³² determined the R_s of 23 pesticides, including the 13 studied here, in silicon rubber rods under two flow velocities (5 and 20 cm s⁻¹). The R_s of the 13 pesticides obtained in Experiments #3 and #7 (water at 23°C, 2 mgC L⁻¹ for DOM, and flow velocities of 4 and 20 cm s⁻¹) were of the same order of magnitude as the R_s found by Martin et al.³²

Determination of partition coefficients. Chlorfenvinphos, chlorpyrifos-methyl and fenitrothion showed a curvilinear accumulation pattern in all eight experiments, and so their partition coefficients between water and the PDMS, K_{sw}, were also determined by BaRatin (Table 3). K_{sw} values ranged from 244 for fenitrothion in Experiment #2 to 4915 for chlorpyrifos-methyl in Experiment #3, with RSDs ranging from 11% for chlorpyrifos-methyl to 44% for fenitrothion. K_{sw} values for chlorfenvinphos (3626), chlorpyrifos-methyl (4851) and fenitrothion (1995) in Experiment #7 (water at 23°C, 2 mgC L⁻¹ for DOM, and flow velocity of 20 cm s⁻¹) were the same order of magnitude as those determined by Martin et al.³² in close experimental conditions (water at 20°C, 3.5 mgC L⁻¹ for TOC, and flow velocity of 20 cm s⁻¹). According to the theory,¹ flow velocity has no impact on K_{sw}, so the K_{sw} values obtained should be similar between Experiments #1 and #5 for which water temperature and DOC concentration were similar and only flow velocity was different (Table 2). Likewise, K_{sw} values should be similar between Experiments #2 and #6, between Experiments #3 and #7, and between Experiments #4 and #8. These similar experiment-to-experiment K_{sw} values were confirmed (given the uncertainty of the K_{sw} values) in all cases (three pesticides and eight experiments) except for chlorpyrifos-methyl in Experiments #2 and #6, thus demonstrating the repeatability and robustness of our flow-through system. Contrary to flow velocity, temperature seemed to

have an effect on the K_{sw} values of chlorfenvinphos, chlorpyrifos-methyl and fenitrothion: higher K_{sw} values were determined as temperature increased from 10°C to 23°C. This is a quite surprising result, which could be explained by the equilibrium not really reached in the seven-day experiments carried out at 10°C, thus leading to a calculation of biased lower K_{sw} . The experiments should be repeated and performed for more than seven days to make sure equilibrium is reached. Moreover, lower K_{sw} values were determined as DOC concentration increased from 2 to 20 mg L⁻¹. This was in fact an artifact due to lower concentrations of freely-dissolved pesticides when DOC concentration was high. We could not measure the concentrations the freely-dissolved pesticides only, so we used the total concentrations in the data treatment, which resulted in apparent lower K_{sw} .

Determination of elimination constants. Elimination constants, k_e , with their relative standard deviations, RSDs, were determined for three PRC candidates in all experiments (Table 3). The k_e values ranged from 0.04 d⁻¹ for chlorpyrifos-methyl-d6 in Experiment #2 to 0.87 d⁻¹ for fenitrothion-d6 in Experiment #7, with RSDs ranging from 14% for chlorpyrifos-methyl-d6 to 67% for tebuconazole-d6. The k_e value of fenitrothion-d6 obtained during a previous laboratory calibration (0.26 d⁻¹)⁹ was in the same order of magnitude as that obtained in Experiment #3 here (0.66 ± 0.35 d⁻¹), in similar experimental conditions.

Effect of exposure conditions on accumulation and elimination kinetics. Accumulation kinetics were found to be either linear or curvilinear depending on experiment and pesticide, due to the effect of different exposure conditions on the R_s and the small volume of the Twister PDMS phase. To illustrate, Figure 1a shows a linear accumulation of spiroxamine for Experiment #2 (water at 10°C, 20 mgC L⁻¹ for DOM, and a flow velocity of 4 cm s⁻¹) and a curvilinear accumulation for Experiment #7 (water at 23°C, 2 mgC L⁻¹ for DOM, and a flow

velocity of 20 cm s⁻¹). This paper presents the kinetics of Experiments #2 and #7 as they represented the most divergent cases in terms of experimental conditions (Table 2), i.e., low water temperature, low flow velocity, and high DOC concentration for Experiment #2 versus high water temperature, high flow velocity, and low DOC concentration for Experiment #7, and the most divergent results in terms of accumulation kinetics. The accumulation patterns of the other pesticides in Experiments #2 and #7 are reported in Figure S3 in the Supplementary Data section. Experiment #2 and Experiment #7 also showed the most divergent patterns of accumulation for the other pesticides. Some more hydrophobic pesticides such as chlorfenvinphos, chlorpyrifos-methyl and fenitrothion showed curvilinear uptake in the Twisters, whereas more hydrophilic pesticides such as chlortoluron, isoproturon and atrazine showed more linear uptake. This might be due to high R_s (compared to those of the polar pesticides) and small PDMS volume. Curvilinear uptake over seven days for these three hydrophobic pesticides under similar conditions was also observed by Martin et al.³² Elimination kinetics also varied depending on experiment and PRC candidate. Figure 1b shows that fenitrothion-d6 elimination from the Twisters was slow for Experiment #2, as only about half the initial PRC candidate amount disappeared after 7 days, but fast in Experiment #7 as almost all the initial PRC candidate amount disappeared after 3 days. The elimination patterns of chlorpyrifos methyl-d6 and tebuconazole-d6 in Experiment #2 and Experiment #7 are shown in Figure S4 in the Supplementary Data section. Both these PRC candidates showed faster elimination in Experiment #7 than in Experiment #2. The amounts of the target pesticides and the PRC candidates determined in the Twisters during all eight experiments are presented in Table S5 in the Supplementary Data section. Results from these eight experiments confirmed that flow velocity, water temperature and/or DOM have an impact on the accumulation of all 13 target pesticides and on the elimination of the three PRC candidates, although to different extents depending on pesticide and PRC candidate.

Moreover, Figure 1a plots the accumulation kinetics of spiroxamine in Twisters and Figure 1b plots the elimination kinetics of fenitrothion-d6 as modeled using the BaRatin application, with the corresponding modeled standard deviation. Considering the uncertainty of each datum, BaRatin gave less weight to the less certain observations.

Control of the pesticide uptake. According to the theory¹, the uptake of the target pesticides in the Twisters is controlled either by the PDMS (membrane control) or the water boundary layer (WBL control), or a combination of both. Plotting the sampling rate as a function of K_{ow} should highlight the pesticides of which the accumulation in the Twisters is under membrane control or under WBL control. K_{ow} values were used instead of K_{sw} values because the latter could not be determined for the pesticides that displayed linear accumulation patterns. For more hydrophilic pesticides, theoretically under membrane control, R_s values were expected to increase with increasing K_{ow} . In contrast, for more hydrophobic compounds, under WBL control, R_s values were expected to be constant and slowly decrease with increasing K_{ow} ¹⁴. The change from membrane control to WBL control was expected to occur for hydrophobic compounds with $\log K_{ow}$ of 3.3, according to our previous work⁹.

Figure S5 in the Supplementary Data section shows two plots of the $\log R_s$ of the 13 target pesticides (normalized for 100 cm²) versus $\log K_{ow}$ determined from the experiments carried out at 2 flow velocities (4 and 20 cm s⁻¹), one at water temperature of 23°C and one at 10°C. Both plots show for polar pesticides (with $\log K_{ow}$ up to 2.87) that the $\log R_s$ values increased with the $\log K_{ow}$, and were equivalent for the two flow velocities, suggesting an uptake controlled by the PDMS. For more hydrophobic pesticides (with $\log K_{ow}$ from 3.81), $\log R_s$ values decreased with $\log K_{ow}$. Moreover, both plots show a separation of the $\log R_s$ values obtained at the two flow velocities, to a greater extent for the experiments performed at 10°C. This suggests the uptake of these pesticides were controlled by the WBL. For fenitrothion (with

$\log K_{ow} = 3.3$), flow velocity did not have an effect on the R_s value at 23°C, but it did at 10°C possibly due to increased water viscosity, although to a lesser extent than for the more hydrophobic pesticides. This does not clearly suggest a WBL control for this pesticide.

For the pesticides that accumulate under WBL control (chlorfenvinphos, diflufenican, chlorpyrifos methyl, chlorpyrifos and spiroxamine), hydrodynamics has an impact on their R_s value, through its impact on the WBL thickness δ_w . We estimated the two δ_w corresponding to the two experiments performed in water with low DOM concentration at 23°C and at flow velocities of 4 and 20 cm s^{-1} . To this end, we adjusted simultaneously the two δ_w values by fitting the R_s values of the five pesticides calculated with Eq. 8 to the experimental R_s corresponding to the two flow velocities. Diffusion coefficients in water (D_w) were calculated using the method of Hayduk and Laudie³³ from the molar volume of pesticides. D_s values were estimated at the same time as δ_w . We estimated $\delta_{w4} = 67 \mu\text{m}$ and $\delta_{w20} = 14 \mu\text{m}$, and D_s values between 1.6×10^{-13} and $1.5 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. We plotted our 2 estimated δ_w against flow velocities together with values estimated by Martin et al.³² and Rusina et al.³⁴ during studies carried out at close water temperatures (20°C and 18°C, respectively) (Figure S6 in the Supplementary Data section). We observed a power function correlation between δ_w values and v ($n = 6$, $\delta_w = 107.9v^{-0.66}$, $r^2 = 0.994$), like the one observed by Martin et al.³²

Significant effects of exposure conditions on sampling rates. The three factors and the three two-factor interactions had significant effects on R_s values. The Pareto diagrams showed that the type and number of factors with significant effects on accumulation varied depending on target pesticide, as illustrated in Figure S7 in the Supplementary Data section for dimethomorph, atrazine, chlorfenvinphos, simazine and spiroxamine. These five pesticides represent the five types of Pareto diagrams obtained. The Pareto diagrams of the other target pesticides are reported in Figure S8 in the Supplementary Data section. The 13 pesticides

investigated were sorted into five groups according to type and number of factors that had significant effects on their accumulation kinetics (Table 4). We then explored these groups to further assign a PRC candidate to each of the target pesticides. Group #1 comprised dimethomorph (Figure S7a) and chlortoluron, for which only temperature had a significant positive effect. Moreover, for chlortoluron, there was a significant negative effect of flow velocity (standardized effect of 2.4) but an even stronger positive effect of temperature (standardized effect of 3.2) (Figure S8). This negative effect of flow velocity was probably due to very low and similar R_s values (ranging from 1.2 to 3.5 mL d⁻¹ with RSDs up to 46%) found for this pesticide in the eight experiments (Table 3). Group #2 comprised atrazine (Figure S7b), azoxystrobin, fenitrothion and isoproturon, for which there was a positive effect of temperature and a negative effect of DOM (Figure S8). For isoproturon, there was no significant effect of DOM *per se* but there was a significant DOM × temperature interaction effect (AB). We therefore considered DOM as a significant factor for this pesticide. Moreover, the effect of DOM × temperature interaction (AB) was significant for all Group #2 pesticides except atrazine. These results could only be observed with the design-of-experiments method. Group #3 comprised norflurazon, chlorfenvinphos (Figure S7c), chlorpyrifos, chlorpyrifos-methyl and diflufenican, for which temperature and flow velocity had a positive effect, and DOM had a negative effect. The effects of DOM × temperature (AB) and DOM × flow velocity (AC) interactions were significant for all Group #3 pesticides. For norflurazon (Figure S8), the effect of temperature was just under the threshold for significance. Nevertheless, since the effect of temperature × DOM interaction (AB) was significant, temperature was considered as a significant factor for this pesticide. Moreover, the significant effect of flow velocity was contrary to a membrane control for this pesticide suggested in the study of the R_s values against the K_{ow} , as, in theory, flow velocity does not have a significant effect on R_s values for substances under membrane control. Like for chlortoluron, this result might be due to low and similar R_s

values (ranging from 2.8 to 7.7 mL d⁻¹ with RSDs up to 38%) obtained for norflurazon in the eight experiments (Table 3). Group #4 comprised only simazine (Figure S7d), with a surprising positive effect of DOM. Again, this result might be due to very low and similar R_s values (ranging from 1.2 to 4.1 mL d⁻¹ with RSDs up to 46%) obtained for simazine in the eight experiments (Table 3). Group #5 comprised only spiroxamine (Figure S7e), for which the effect of DOM \times flow velocity interaction was significant. We thus considered a positive effect of flow velocity and a negative effect of DOM on this pesticide. There was no significant effect of temperature, although the sampling rates determined for Experiments #3, #4 and #8 performed at 23°C were larger than those of Experiments #1, #2 and #6 performed at 10°C (Table 3). This surprising result might be explained by an artifact caused by the sampling rate determined for Experiment #5 performed at 10°C being larger -and more uncertain- (77.3 mL d⁻¹ and RSD = 131%) than the one determined for Experiment #7 performed at 23°C (71.8 mL d⁻¹ and RSD = 34%).

Interpretation of the effects of the factors. Temperature had a significant effect on the accumulation of pesticides in Groups #1, #2 and #3. Pesticides in Groups #1 (chlortoluron, dimethomorph) and #2 (atrazine, azoxystrobin, fenitrothion, isoproturon) were characterized by membrane-controlled uptake, as flow velocity had no significant effect on their R_s . Norflurazon might also be characterized by membrane-controlled uptake, if we consider the results of the plots of R_s against K_{ow} determined earlier. For these compounds, when neglecting the mass transfer resistance of the water boundary layer (WBL), the sampling rate R_s is linked to the partition coefficient, K_{sw} , and to diffusion in the PDMS phase, D_s , (Eq. 9), which is temperature-dependent.³⁵

$$R_s = \frac{D_s K_{sw}}{\delta_s} A \quad (9)$$

Group #3 pesticides (chlorfenvinphos, chlorpyrifos, chlorpyrifos-methyl, diflufenican) were characterized by WBL-controlled uptake, as flow velocity had a significant effect on their R_s . For these four compounds, when neglecting the mass transfer resistance of the membrane, R_s can be expressed as (Eq. 10):

$$R_s = k_w A \approx D_w^{\frac{2}{3}} A \quad (10)$$

The R_s is linked to the aqueous diffusion coefficient D_w , which is temperature-dependent because the kinematic viscosity of water is strongly temperature-dependent.³⁵

DOM had a significant effect on the accumulation of pesticides in Groups #2, #3, #4 (simazine) and #5 (spiroxamine). The DOM effect was negative for all these pesticides except simazine. Lower R_s values were determined at a high level of DOC concentration. This could be partly due to slower diffusion of the pesticides in slightly more viscous water and especially in the WBL. Moreover, the sorption of organic compounds to DOM had an indirect impact on R_s values determined. So, lower R_s values were also probably due to an artifact caused by lower concentrations of freely-dissolved pesticides when DOC concentration was high. Indeed, the target pesticides partly sorbed to the DOM³⁵ were unable to accumulate in the PDMS phase. Therefore, lower R_s values for the pesticides in Groups #2, #3 and #5 at high level of DOC concentration may be due to an overestimation of their freely-dissolved aqueous concentrations. This suggests that passive SBSE only samples freely-dissolved organic compounds. Prokeš et al.³⁶ successfully linked the fall in R_s values to the adsorption of hydrophobic compounds on colloids and the overestimation of their dissolved concentrations, and they reported this relation for compounds accumulated under WBL control. In fact, the impact of DOM is independent of the type of accumulation control, as here it affected both compounds accumulated under membrane control (Group #2) and compounds accumulated under WBL control (Groups #3 and #5). It is most likely due to the structure and physical-chemical properties of the pesticides. Indeed, DOM had very little effect on the accumulation of chlortoluron and isoproturon, two

urea herbicides, whereas it had a strong effect on the accumulation of chlorpyrifos and chlorpyrifos methyl, two more hydrophobic organochlorine insecticides. The indirect effect of DOM was also observed on K_{sw} values for fenitrothion in Group #2 and for chlorfenvinphos and chlorpyrifos in Group #3 (Table 3). For these three target pesticides, we determined lower K_{sw} values at higher DOC concentrations, for the same reasons as for the R_s .

Moreover, as seen in Figure 2 for chlorfenvinphos, the negative effect of DOC concentration is stronger at high temperature than at low temperature. This might be explained by higher K_{DOC} values at higher temperature, resulting in lower amounts of freely-dissolved pesticides. The negative effect of the DOM \times flow velocity interaction could be explained by a thicker WBL at 20 cm s^{-1} when the water is slightly more viscous (i.e., when DOC concentration is at 20 mgC L^{-1}).

Flow velocity had a significant effect on the accumulation of pesticides in Groups #3 and #5. For these pesticides, which are characterized by WBL-controlled uptake, the R_s is proportional to the mass transfer coefficient in the WLB k_w (Eq. 2), which is linked to flow rate and turbulence.³⁶ Flow velocity surprisingly had a significant effect on the relatively polar norflurazon ($\log K_{ow} = 2.3$) (Figure S8). According to the theory,^{1, 3, 37} the accumulation of norflurazon in the Twister should be membrane-controlled, and so flow velocity should not have a significant effect on its R_s . This result might be due to low and similar R_s values (ranging from 2.8 to 7.7 mL d^{-1} with RSDs up to 38%) obtained for norflurazon in the eight experiments (Table 3). The effect of flow velocity on fenitrothion R_s was not significant, contrary to the results obtained in the previous laboratory calibration.⁹ This might be due to a difference in flow velocities between the two studies, i.e., 4 and 20 cm s^{-1} here against 0, 0.1 and 2.5 cm s^{-1} in the previous study. It is possible that our flow velocity was too high and/or the range was too narrow (flow velocities 5-fold as high between 4 cm s^{-1} and 20 cm s^{-1} as opposed to 25-fold as

high between 0.1 cm s^{-1} and 2.5 cm s^{-1} in the previous study⁹) to result in an increase in R_s values of fenitrothion.

Significant effects of experimental conditions on elimination constants. We found significant effects of factors and two-factor interactions on the elimination constants for the three PRC candidates (Table 3). Figure S9 in the Supplementary Data section shows the Pareto diagrams for tebuconazole-d6, fenitrothion-d6, and chlorpyrifos-d6. These Pareto diagrams allowed us to assign each PRC candidate to one of the groups previously composed for R_s (Table 4). Tebuconazole-d6 was assigned to Group #1, as only temperature had a significant effect on its elimination from the Twisters. Likewise, fenitrothion-d6 was assigned to Group #2, as both temperature and DOM were factors with significant effects. Finally, chlorpyrifos-d6 was assigned to Group #3, as each of the three factors and DOM \times flow velocity interaction had significant effects. Deuterium-labeled fenitrothion-d6 and chlorpyrifos-d6 were logically assigned to the same groups as their native homologs. These results show that the elimination of a compound sorbed in the Twister not only depends on flow velocity but also on temperature and the presence of DOM. Regarding the effect of DOM on the elimination of the sorbed compound, one explanation could be that DOM increased the water viscosity, and as a result, the diffusion of the pesticide through the water boundary layer was slower. Therefore, the PRCs could be used to correct the effects of these three factors, providing that isotropic exchange is confirmed. This also applies for simazine and spiroxamine in Groups #4 and 5, for which we found no assignable PRC candidates. The deuterated analogs of these two pesticides would need to be tested as PRC candidates.

Discriminant function analysis. In this part, we performed a DFA ($\alpha = 0.05$) on a total of 20 pesticides, i.e., on the 13 target pesticides used in the design of experiments and on another 7

pesticides that had not been used in the first part of this study. A similar statistical study was successfully performed to elucidate the adsorption pattern of various organic compounds in POCIS.³⁸ First we identified the physical-chemical properties that were able to discriminate the 13 target pesticides into the groups determined in the design of experiments, and then we predicted the accumulation behavior (i.e., Group number) of the 7 other pesticides to determine which PRC would be the most appropriate to use. The physical-chemical properties able to impact accumulation in the PDMS phase and interactions with the DOM were selected as quantitative variables for the DFA based on previous studies,^{38, 39} i.e., $\log K_{ow}$ at pH 7, polar surface area, molecular volume, maximal projection area, molar mass, and polarizability (Table 1). The qualitative variables were three of the groups of target pesticides determined in the first part of this study, i.e., Groups #1, #2, and #3 (Table 4). The DFA could not process Group #4 and Group #5 because they were composed of only one pesticide each. Therefore, simazine and spiroxamine were added to the set of 7 pesticides for which groups were predicted, to not influence the construction of the DFA model.

The p-value of the Wilk's lambda test was 0.011, and thus validated the DFA results. Figure 2a presents the quantitative variables (i.e., the physical-chemical properties). The F1 and F2 axes explained 96% and 4% of the variability of the data, respectively. The most discriminant physical-chemical properties were $\log K_{ow}$ at pH 7 and polar surface area, and to a lesser extent molar mass and maximal projection area. In their study on the differences in the accumulation models of micropollutants in POCIS, Morin et al.³⁸ also observed that the most discriminant physical-chemical properties were the $\log D_{ow}$ at pH 7,6 and polar surface area. Figure 2b represents the observations as three homogeneous sets of clearly-separated points (each set of points is composed of pesticides from only one Group). The Group #1 pesticides were anti-correlated with $\log K_{ow}$ at pH 7 and polar surface area on the F2 axis. This corroborates the membrane-controlled uptake for these pesticides with low $\log K_{ow}$ values, and suggests weak

polar interactions with the polar sites of humic acids composed of polysaccharides, proteins and lipids.^{40, 41} The Group #2 pesticides were correlated with polar surface area and anti-correlated with $\log K_{ow}$ at pH 7 and molar mass on the F1 axis. This confirms the membrane-controlled uptake for these moderately polar pesticides ($\log K_{ow}$ values ranging from 2.50 to 3.32), and suggests polar interactions with the humic acids.³⁵ Finally, the Group #3 pesticides were correlated with $\log K_{ow}$ at pH 7 and molar mass on the F1 axis and with polar surface area on the F2 axis. This confirms the WBL-controlled uptake of these moderately polar-to-hydrophobic pesticides and the polar interactions with humic acids. Norflurazon appeared close to the other pesticides of Group #3 although the plots of R_s against K_{ow} suggested a membrane-controlled uptake for this pesticide. This DFA result may probably be due to the high molar mass of norflurazon (303.7 g mol^{-1}) compared to the other polar pesticides. Further investigation of the effect of the flow velocity on the accumulation of norflurazon could confirm the control mechanism for this pesticide.

Figure 2b also shows the groups predicted by the DFA for the 7 pesticides, and spiroxamine and simazine, based on their physical-chemical properties. All predictions were performed with 100% probability of affiliation (i.e., likelihood of the prediction). Predictions assigned linuron and 3,4-dichloroaniline to Group #1, acetochlor, metolachlor, tebuconazole, simazine, and spiroxamine to Group #2, and flufenoxuron and procymidon to Group #3. The DFA predicted tebuconazole to belong to Group #2 whereas tebuconazole d6 was assigned to Group #1. This might be due to anisotropic exchange of tebuconazole with the PDMS of the Twisters.

The fact that the three sets of points on Figure 2b were homogeneous and well-separated corroborates the interpretation of the results of the DFA in terms of power to discriminate the groups based on the physical-chemical properties of the target pesticides. Our results demonstrated the feasibility of predicting the exposure factors that could have an impact on accumulation kinetics based on physical-chemical properties of the pesticides. Moreover, the

DFA approach provides a better identification than more conventional approaches of appropriate PRC candidates to determine unbiased TWAC by passive SBSE for undocumented pesticides. Also, it allowed us to observe that some physical-chemical properties might have a role in the impact of the experimental conditions on the uptake of pesticides in Twisters, while others do not. Further laboratory research could be carried out to confirm the predictions made and complete them with a mechanistic investigation.

Prospects on field application of passive SBSE. This passive sampling technique could be applied for monitoring concentrations of pesticides in surface waters, using PRC, like other silicone-based passive samplers. The laboratory experiments showed that a seven-day period could be suitable for field exposures and determination of time-weighted average concentrations, as pesticides accumulate quickly in Twisters exposed in water without a membrane. To be fully operational for field monitoring, further calibration of Twisters is needed to confirm for which compounds integrative sampling could be performed during a seven-day exposure period. For those compounds, the laboratory sampling rates determined in the present study must be confirmed and isotropic exchange must be verified for the PRC candidates. Equilibrium sampling could also be investigated in further work for the pesticides that reach equilibrium in less than seven days.

Our previous work⁴² showed that Twisters can integrate very quick variations of concentrations of pesticides in water (a few hours or days), which can occur in small rivers located in agricultural watersheds. Seven-day exposures of Twisters could then allow to integrate those variations and provide accurate time-weighted average concentrations of the pesticides under integrative uptake. Twisters used as passive samplers could then provide a better temporal representativity than grab sampling and could be complementary to other passive samplers that would not be able to integrate quick concentration variations.

Conclusion

Our experiments demonstrated the effects of flow velocity, temperature, and DOM on the accumulation of the 13 target pesticides in Twisters. It suggested that correction of R_s might be needed in case of differences in flow velocities but also in water temperatures and DOC concentrations. The experiments performed with high concentration of DOC confirmed that freely-dissolved compounds can accumulate in the Twisters. The differences in the sampling rates confirmed that estimation of in situ sampling rates by measuring the dissipation rates of performance reference compounds (PRC) is needed. We proposed a stochastic approach through PDA to help select the adapted PRC.

This study also allowed to confirm passive SBSE could be applied in field research, using PRC, as it is done for other silicone-based passive samplers. Further calibration of Twisters will confirm for which compounds integrative sampling could be performed and determine for those compounds the laboratory sampling rates and PRC. Because Twisters are exposed directly in water, passive SBSE is more suitable than more conventional passive samplers for hydrosystems where pesticides concentrations can vary very quickly, such as small rivers located in agricultural watersheds. Seven-day exposures of Twisters could allow to integrate fast variations of concentrations in water and provide accurate time-weighted average concentrations of the pesticides under integrative uptake.

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Supporting information

Supporting information containing additional figures and tables are available free of charge via the internet.

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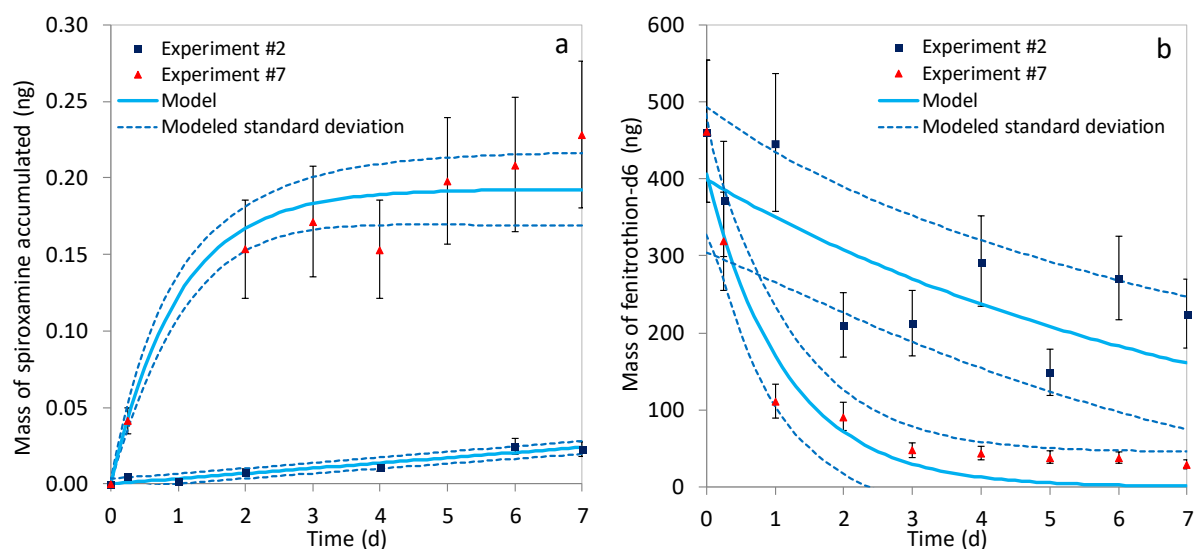


Figure 1 (a) Accumulation kinetics of spiroxamine in Twisters, and (b) elimination kinetics of fenitrothion-d6 over seven days in Experiment #2 (water at 10°C, 20 mgC L⁻¹ for DOM, and flow velocity of 4 cm s⁻¹) and Experiment #7 (water at 23°C, 2 mgC L⁻¹ for DOM, and flow velocity of 20 cm s⁻¹). Error bars represent the expanded uncertainty as determined in previous studies^{28, 29}.

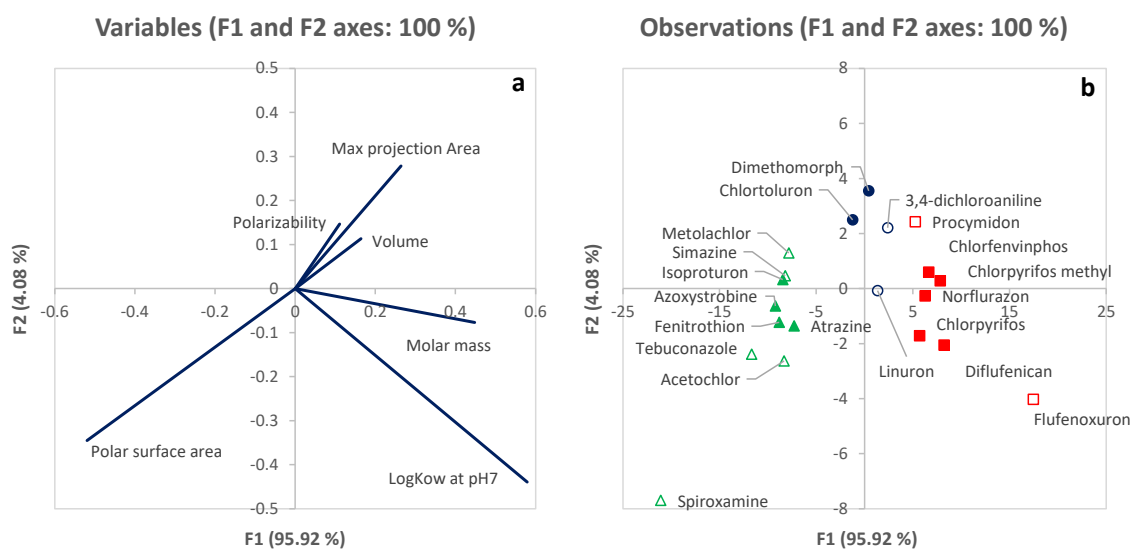


Figure 2 Graphical representations of (a) the variables and (b) the observations of the discriminant function analysis performed with the physical-chemical properties of the target pesticides as quantitative data and the groups determined during the design-of-experiments stage as qualitative data. Group #1 (blue circles): effect of temperature, Group #2 (green triangles): effects of DOM and temperature, Group #3 (red squares): effects of DOM, temperature, and flow velocity. Full circles, triangles and squares stand for the 13 pesticides used in the experimental design. Empty circles, triangles and squares stand for the predictions of groups for the 9 pesticides.

Table 1 Physical-chemical properties of the 13 pesticides used in the discriminant function analysis (DFA) and the 7 pesticides selected for the prediction of parameters that had a significant effect on their accumulation in Twisters (source: www.chemicalize.com)

| Use in the DFA | Pesticide | Log K_{ow} at pH 7 | Polar surface area (Å ²) | Molar mass (g mol ⁻¹) | Maximal projection area (Å ²) | Volume (Å ³) | Polarizability (Å ³) |
|----------------|---------------------|-------------------------|---|--------------------------------------|--|-----------------------------|-------------------------------------|
| Modeling | Atrazine | 2.61 | 62.7 | 215.7 | 66.1 | 190.9 | 21.2 |
| | Azoxystrobin | 2.50 | 103.6 | 403.4 | 100.4 | 347.4 | 41.5 |
| | Chlorfenvinphos | 3.81 | 44.8 | 359.6 | 81.2 | 272.7 | 32.4 |
| | Chlorpyrifos | 4.96 | 40.6 | 350.6 | 84.4 | 252.2 | 31.5 |
| | Chlorpyrifos-methyl | 4.31 | 40.6 | 322.5 | 68.9 | 218.3 | 27.9 |
| | Chlortoluron | 2.41 | 32.3 | 212.7 | 66.6 | 190.0 | 21.8 |
| | Diflufenican | 4.20 | 51.2 | 394.3 | 84.0 | 300.5 | 33.0 |
| | Dimethomorph | 2.68 | 48.0 | 387.9 | 103.5 | 342.2 | 40.7 |
| | Fenitrothion | 3.32 | 70.8 | 277.2 | 38.0 | 220.8 | 26.5 |
| | Isoproturon | 2.87 | 32.3 | 206.3 | 72.1 | 210.2 | 23.6 |
| | Norflurazon | 2.30 | 44.7 | 303.7 | 78.3 | 266.6 | 24.8 |
| | Simazine | 2.18 | 62.7 | 201.7 | 64.6 | 173.9 | 19.4 |
| | Spiroxamine | 5.50 | 21.7 | 297.5 | 95.4 | 326.9 | 35.3 |
| Prediction | Acetochlor | 4.14 | 29.5 | 269.8 | 78.3 | 255.5 | 28.6 |
| | 3,4-dichloroaniline | 2.69 | 26.0 | 162.0 | 48.4 | 120.9 | 15.3 |
| | Flufenoxuron | 5.11 | 67.4 | 488.8 | 108.1 | 354.1 | 38.7 |
| | Linuron | 3.20 | 45.1 | 249.1 | 70.4 | 195.7 | 22.7 |
| | Metolachlor | 3.13 | 29.5 | 283.8 | 72.8 | 272.9 | 30.5 |
| | Procymidon | 3.08 | 37.4 | 284.1 | 80.1 | 222.3 | 26.9 |
| | Tebuconazole | 3.70 | 50.9 | 307.8 | 81.5 | 287.9 | 32.9 |

Table 2 Experimental matrix of the full factorial design with three factors (exposure conditions) investigated on pesticide accumulation and elimination kinetics in Twisters.

| Experiment number | DOC concentration (mgC L⁻¹) | Temperature (°C) | Flow velocity (cm s⁻¹) |
|--------------------------|---|-------------------------|--|
| 1 | 2 | 10 | 4 |
| 2 | 20 | 10 | 4 |
| 3 | 2 | 23 | 4 |
| 4 | 20 | 23 | 4 |
| 5 | 2 | 10 | 20 |
| 6 | 20 | 10 | 20 |
| 7 | 2 | 23 | 20 |
| 8 | 20 | 23 | 20 |

Table 3 Sampling rates R_s , partition coefficients K_{sw} , elimination coefficients k_e , and the corresponding RSDs obtained for the target pesticides and PRC candidates during the eight accumulation and elimination experiments of the full factorial design.

| Exp. | R_s (mL d ⁻¹) (RSD (%)) ^a | | | | | | | | | | | | |
|---------------|--|----------|-----------|----------------|-----------|----------|----------------|----------|-----------|----------|----------|----------|------------|
| | ATZ | AZS | CFV | CPE | CPM | CTU | DFE | DMM | FNT | IPU | NFZ | SMZ | SPX |
| 1 | 2.2 (22) | 3.4 (24) | 56.6 (20) | 8.3 (20) | 70.8 (22) | 1.7 (28) | 19.6 (37) | 2.8 (34) | 70.9 (36) | 1.4 (25) | 2.8 (23) | 1.3 (38) | 3.1 (39) |
| 2 | 1.8 (16) | 3.1 (26) | 27.4 (20) | - ^b | 30.8 (16) | 2.0 (19) | - ^b | 3.0 (33) | 32.3 (26) | 2.2 (31) | 3.0 (23) | 2.8 (46) | 0.7 (31) |
| 3 | 3.4 (25) | 5.0 (23) | 600 (22) | 47.2 (22) | 258 (14) | 3.5 (26) | 98.7 (19) | 5.2 (26) | 413 (34) | 3.4 (39) | 4.6 (26) | 1.8 (30) | 30.1 (32) |
| 4 | 3.0 (24) | 3.7 (24) | 151 (22) | 5.1 (18) | 61.7 (14) | 2.3 (46) | 8.2 (20) | 4.4 (28) | 87.7 (38) | 3.0 (39) | 3.3 (19) | 4.1 (33) | 43.0 (133) |
| 5 | 3.2 (28) | 3.6 (23) | 295 (27) | 51.8 (18) | 307 (14) | 1.2 (18) | 175 (19) | 4.3 (40) | 178 (32) | 1.0 (28) | 5.1 (26) | 1.6 (40) | 77.3 (131) |
| 6 | 1.9 (21) | 3.5 (25) | 104 (35) | - ^b | 94.8 (18) | 1.4 (15) | 18.9 (26) | 2.4 (22) | 88.2 (41) | 2.1 (28) | 3.9 (23) | 3.2 (43) | 2.1 (34) |
| 7 | 4.1 (26) | 7.3 (27) | 879 (45) | 78.7 (21) | 360 (14) | 1.8 (36) | 215 (33) | 5.1 (44) | 463 (48) | 4.4 (35) | 7.7 (33) | 1.2 (42) | 71.8 (34) |
| 8 | 2.3 (25) | 3.1 (23) | 286 (26) | 18.4 (80) | 141 (15) | 2.4 (28) | 84.5 (119) | 3.4 (41) | 162 (38) | 2.8 (40) | 3.4 (38) | 4.1 (23) | 18.4 (50) |
| Max/Min Ratio | 2.3 | 2.4 | 32.1 | 15.4 | 11.7 | 2.9 | 26.2 | 2.2 | 14.3 | 4.4 | 2.8 | 3.2 | 110 |

| Exp. | K_{sw} (RSD (%)) | | | k_e (d ⁻¹) (RSD (%)) | | |
|---------------|--------------------|-----------|-----------|------------------------------------|-----------|-----------|
| | CFV | CPM | FNT | CPM-d6 | FNT-d6 | TBZ-d6 |
| 1 | 1219 (24) | 3073 (38) | 1076 (44) | 0.06 (37) | 0.14 (29) | 0.08 (44) |
| 2 | 299 (19) | 328 (13) | 244 (23) | 0.04 (66) | 0.13 (43) | 0.10 (47) |
| 3 | 3554 (16) | 4915 (14) | 2033 (26) | 0.17 (26) | 0.66 (53) | 0.14 (67) |
| 4 | 990 (18) | 1429 (16) | 723 (32) | 0.11 (25) | 0.31 (31) | 0.21 (47) |
| 5 | 1046 (19) | 4083 (13) | 1368 (26) | 0.15 (26) | 0.34 (36) | 0.14 (33) |
| 6 | 337 (18) | 542 (14) | 322 (23) | 0.06 (43) | 0.13 (61) | 0.09 (48) |
| 7 | 3626 (16) | 4851 (12) | 1995 (27) | 0.22 (14) | 0.87 (46) | 0.18 (40) |
| 8 | 926 (16) | 1207 (11) | 659 (27) | 0.11 (22) | 0.44 (50) | 0.24 (49) |
| Max/Min Ratio | 12.1 | 15.0 | 8.3 | 5.5 | 6.7 | 3.0 |

^a: RSD, relative standard deviation determined by the BaRatin application

^b: masses of pesticides were lower than the limits of quantification, so no accumulation kinetics could be plotted

ATZ: atrazine, AZS: azoxystrobin, CPE: chlorpyrifos, CPM: chlorpyrifos-methyl, CTU: chlortoluron, DFE: diflufenican, FNT: fenitrothion, IPU: isoproturon, NFZ: norflurazon, SMZ: simazine, SPX: spiroxamine

Table 4 Pesticides and PRC candidates sorted into groups according to factors with significant effects on their accumulation and elimination.

| Group | Factors with significant effects | Pesticides | PRC candidates |
|--------------|---|---|------------------------|
| 1 | Temperature (+) | Chlortoluron Dimethomorph | Tebuconazole-d6 |
| 2 | Temperature (+) DOM (-) | Atrazine Azoxystrobin Fenitrothion Isoproturon | Fenitrothion-d6 |
| 3 | Temperature (+) DOM (-) Flow velocity (+) | Norflurazon Chlorfenvinphos Chlorpyrifos Chlorpyrifos methyl Diflufenican | Chlorpyrifos-methyl-d6 |
| 4 | DOM (+) | Simazine | |
| 5 | Flow velocity (+) DOM (-) | Spiroxamine | |

Prediction of the accumulation behavior of pesticides in PDMS-coated stir bars used as passive samplers in freshwaters

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Supplementary Data section

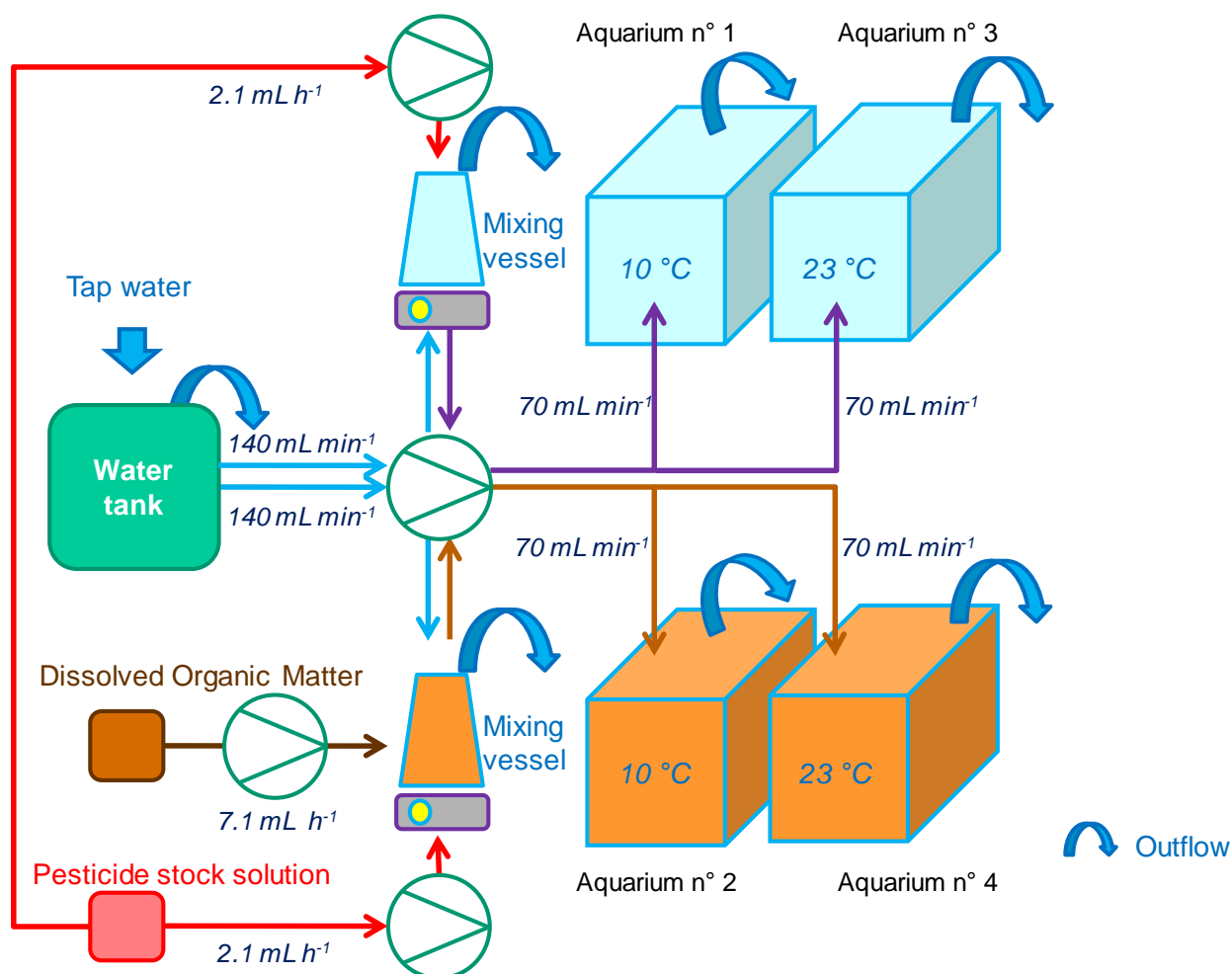
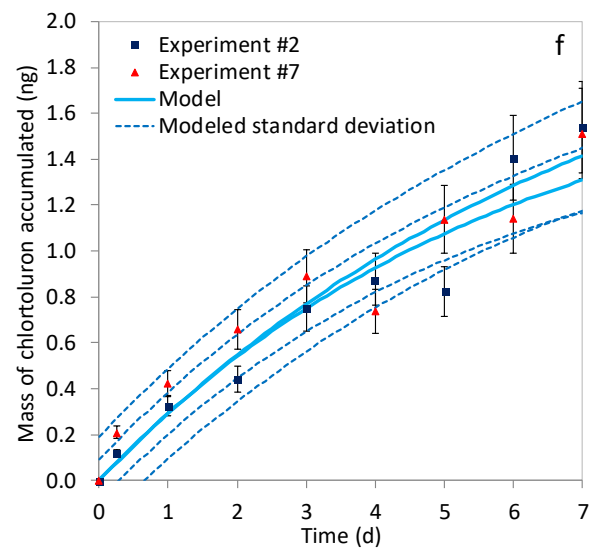
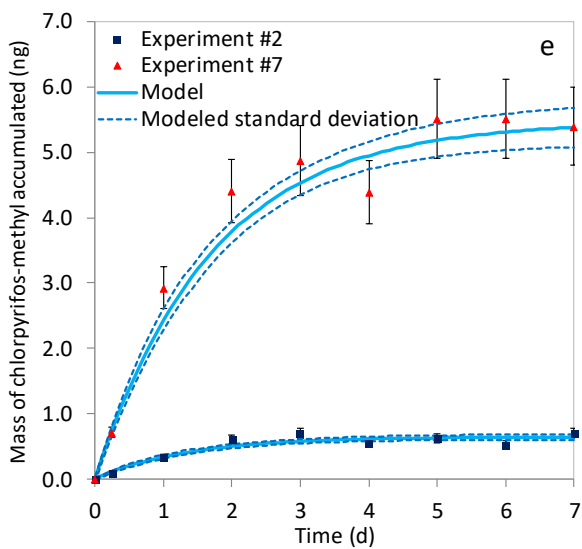
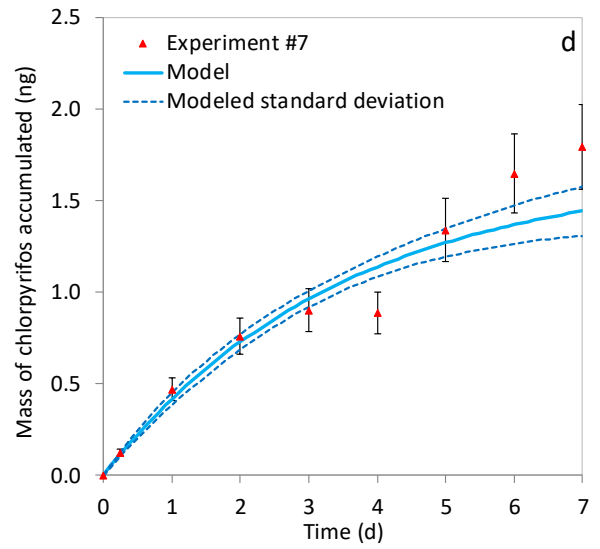
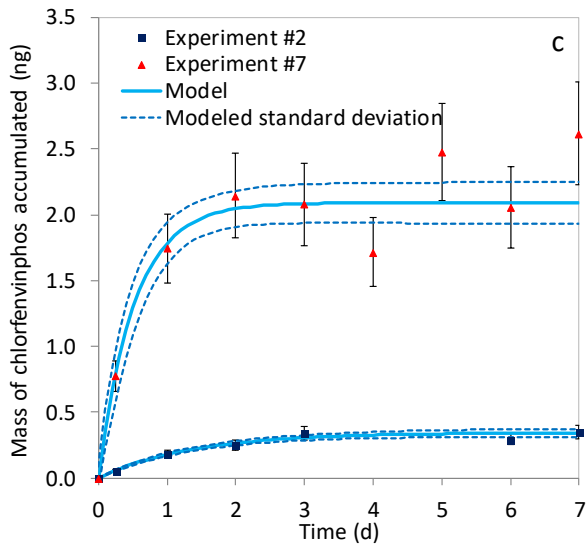
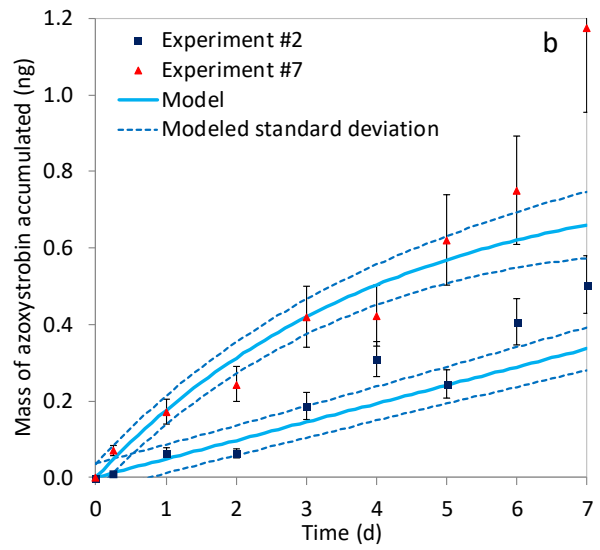
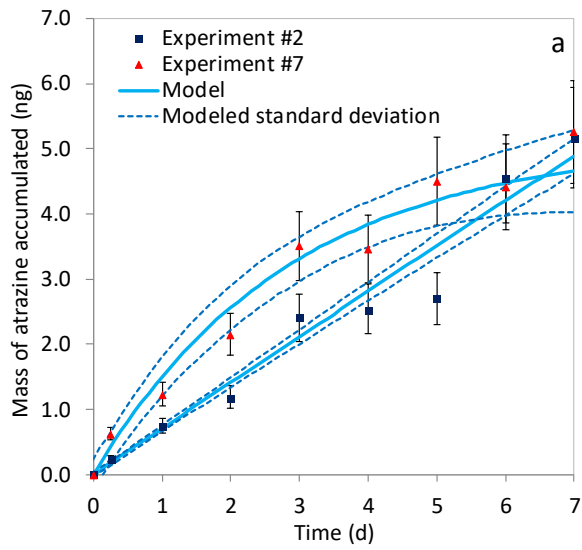


Figure S1 Schematized flow-through system for simultaneously evaluating the effects of temperature, flow velocity and dissolved organic matter (DOM) on the accumulation of the target pesticides in Twisters and on the elimination of the PRC candidates.



Figure S2 Two diffusion ramps and an aquarium used in the experiments (20*40*25 (w*L*h) cm, 20 L)



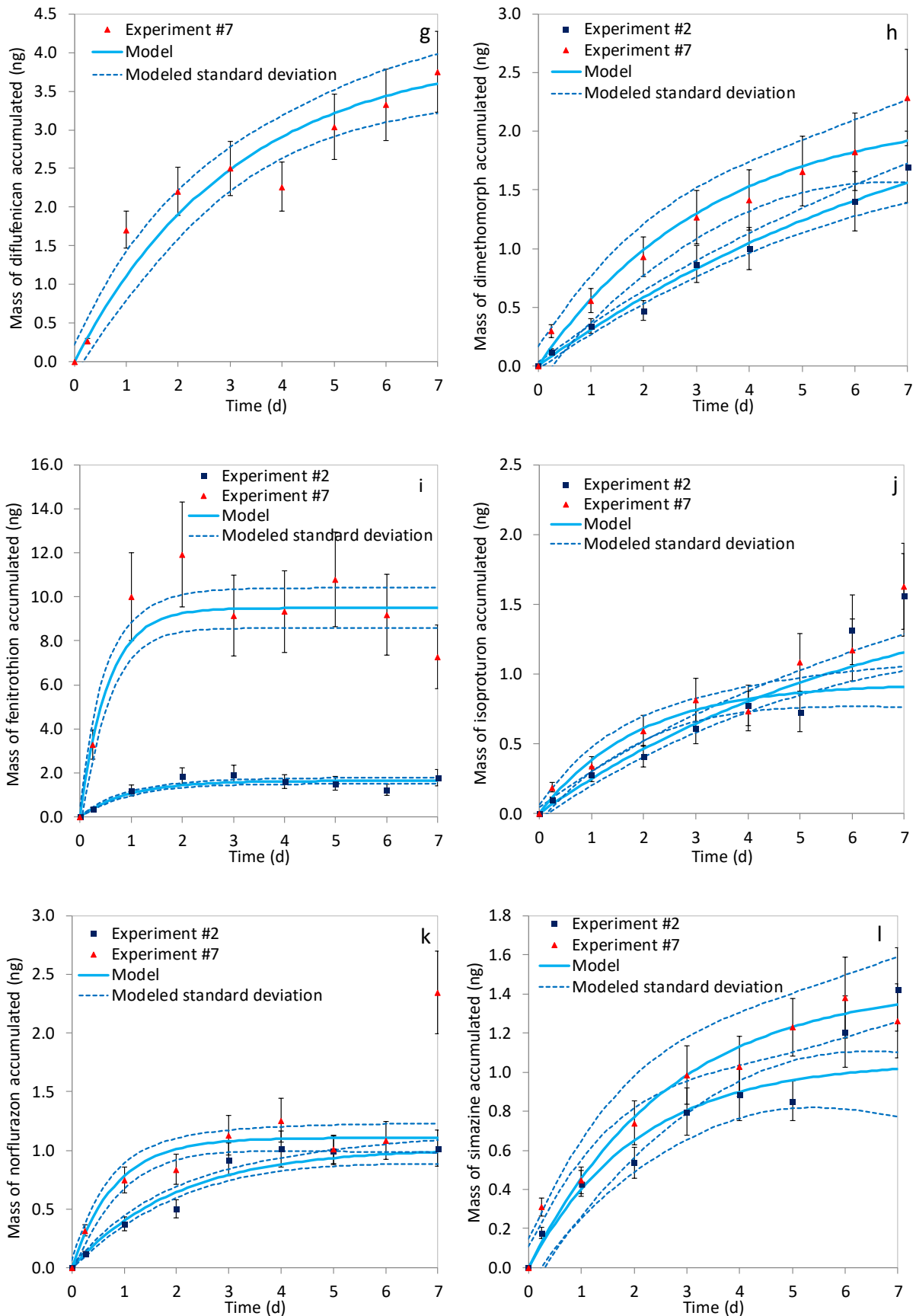


Figure S3 Accumulation kinetics of (a) atrazine, (b) azoxystrobin, (c) chlorfenvinphos, (d) chlorpyrifos, (e) chlorpyrifos-methyl, (f) chlortoluron, (g) diflufenican, (h) dimethomorph, (i)

fenitrothion, (j) isoproturon, (k) norflurazon, and (l) simazine in Twisters over seven days in Experiment #2 (water at 10°C, 20 mgC L⁻¹ for DOM, and flow velocity of 4 cm s⁻¹) and Experiment #7 (water at 23°C, 2 mgC L⁻¹ for DOM, and flow velocity of 20 cm s⁻¹). The points are the experimental data, the solid line is the modeled accumulation, and the dotted lines plot the modeled standard deviation. Error bars represent the expanded uncertainty as determined in previous studies (Guillemain et al., 2014; Margoum et al., 2013). Chlorpyrifos and diflufenican did not accumulate enough in the Twisters over the course of Experiment # 2, so their accumulation kinetics cannot be shown.

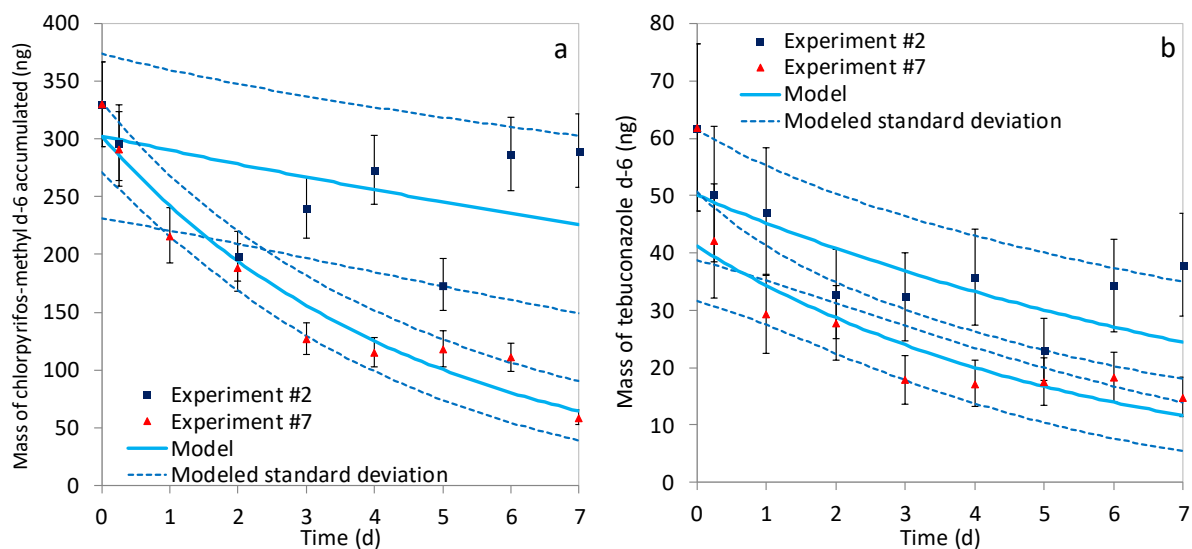


Figure S4 Elimination kinetics of (a) chlorpyrifos methyl-d6 and (b) tebuconazole-d6 from Twisters over seven days during Experiment #2 (water at 10°C, 20 mgC L⁻¹ for DOM, and flow velocity of 4 cm s⁻¹) and Experiment # 7 (water at 23°C, 2 mgC L⁻¹ for DOM, and flow velocity of 20 cm s⁻¹). The points are the experimental data, the solid line is the modeled accumulation, and the dotted lines plot the modeled standard deviation. Error bars represent the expanded uncertainty as determined in previous studies (Guillemain et al., 2014; Margoum et al., 2013).

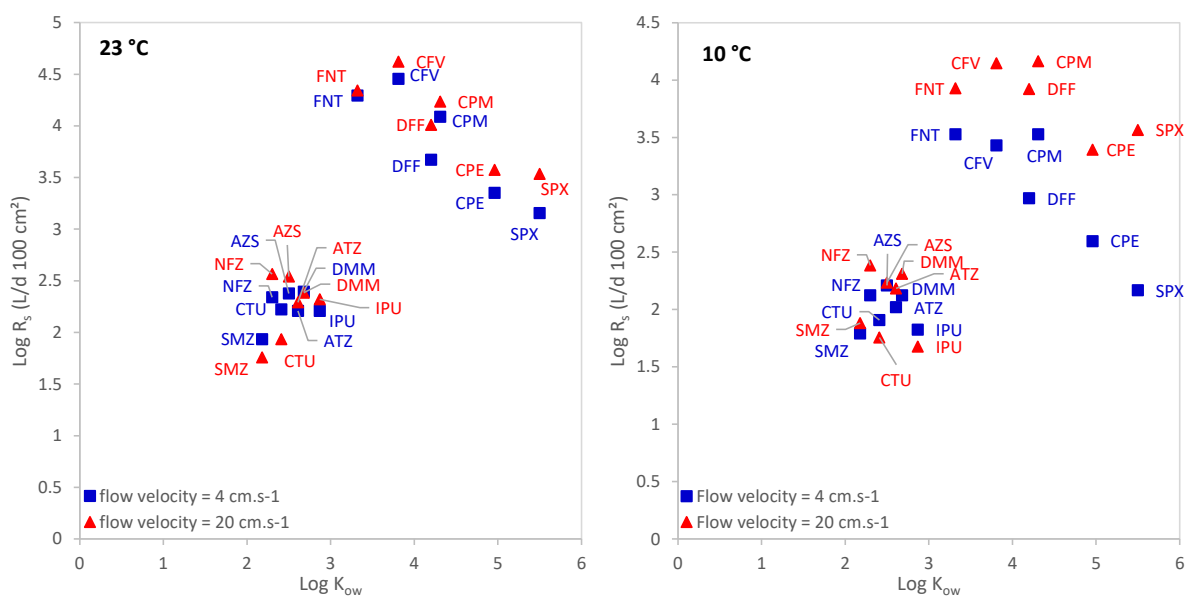


Figure S5 Plot of log R_s normalized for 100 cm² versus log K_{ow} determined from experiments at 2 flow velocities (4 and 20 cm s⁻¹) and at 2 water temperatures 23°C (left) and 10°C (right).

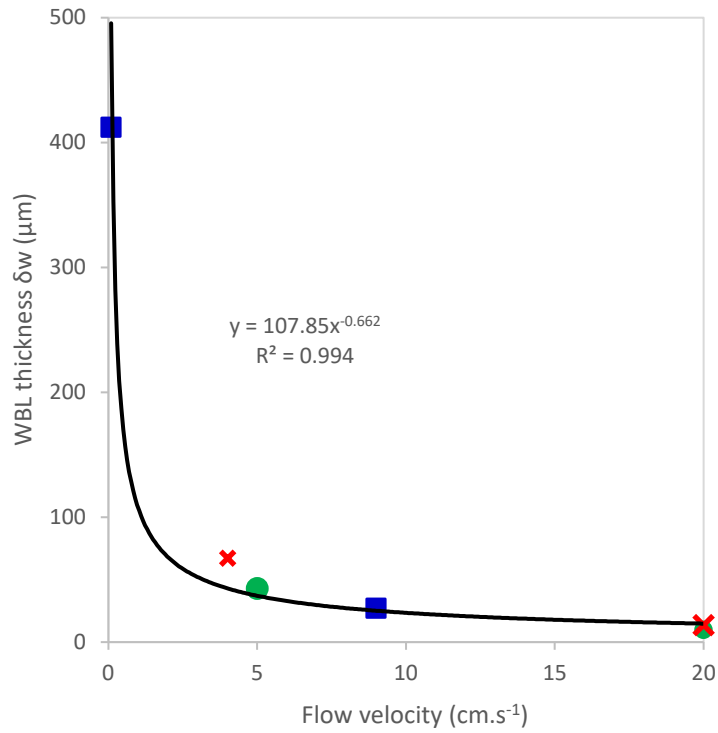
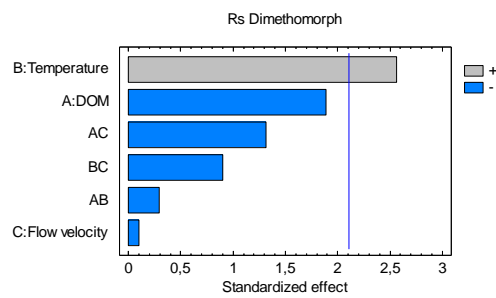


Figure S6 Plot of water boundary layer thickness (δ_w) estimated by theoretical model against water flow velocity from the present study (crosses), Martin et al. (2018) (dots) and Rusina et al. (2010) (squares).



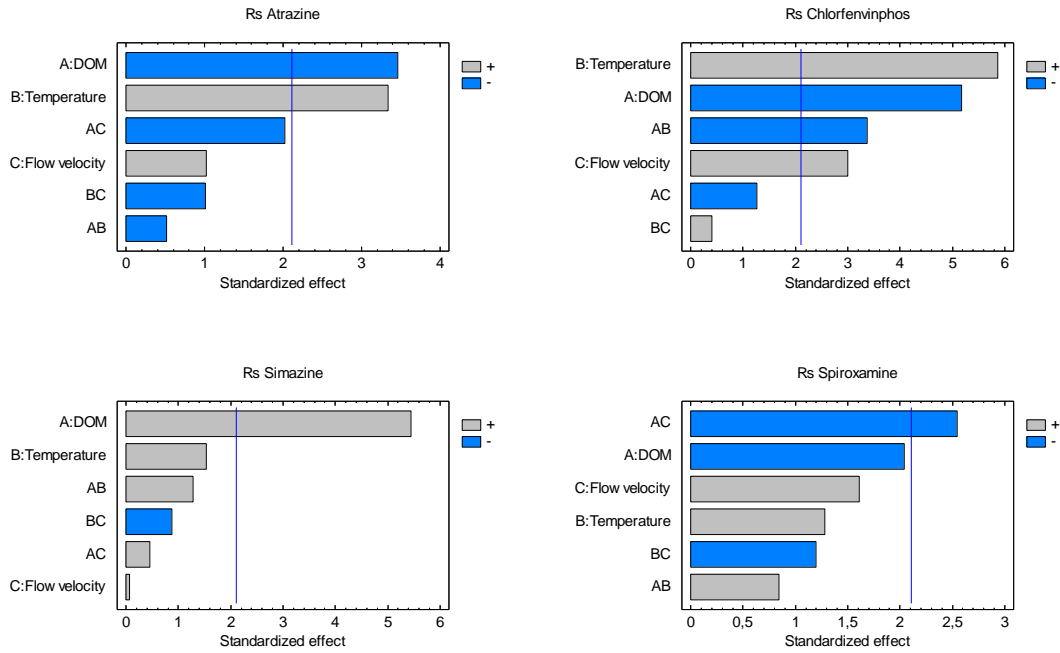


Figure S7 Pareto diagrams of the effects of dissolved organic matter (DOM, factor A), temperature (factor B), flow velocity (factor C), and their interactions (AB, AC, BC) on the sampling rates (R_s) of (a) dimethomorph, (b) atrazine, (c) chlorfenvinphos, (d) simazine, and (e) spiroxamine. The vertical line represents the limit of significance at 2.1; factors with standardized effect larger than the limit are significant. Bars in blue represent negative effects, and bars in grey represent positive effects.

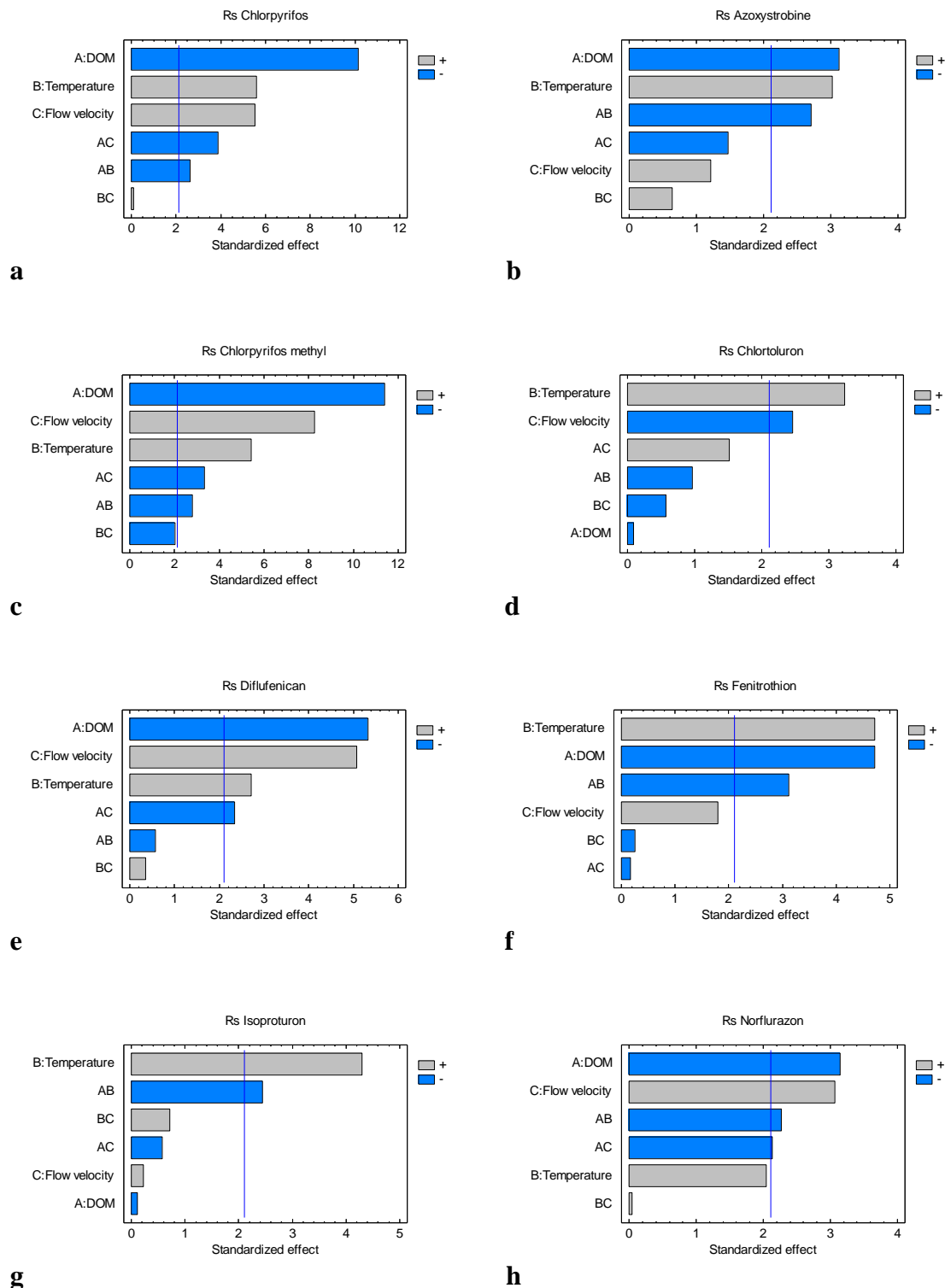
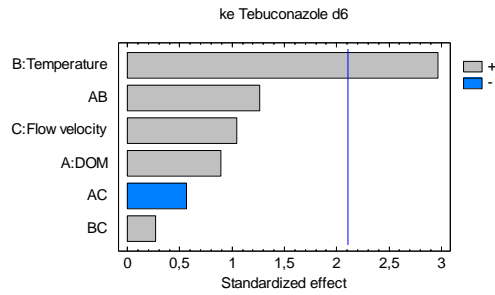
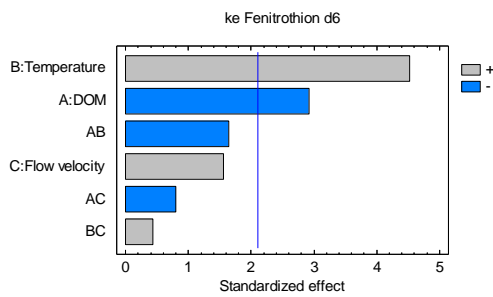


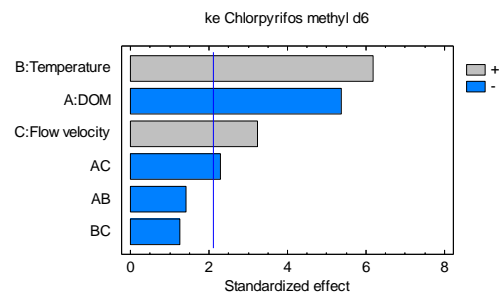
Figure S8 Pareto diagrams of the effects of dissolved organic matter (DOM), temperature, flow velocity and their interactions on sampling rates (R_s) in Twisters for (a) azoxystrobin, (b) chlorpyrifos, (c) chlorpyrifos-methyl, (d) chlortoluron, (e) diflufenican, (f) fenitrothion, (g) isoproturon, and (h) norflurazon. The vertical line represents the limit of significance.



a



b



c

Figure S9 Pareto diagrams of the effects of DOM, temperature, flow velocity and their interactions on the elimination constant (k_e) of (a) tebuconazole-d6, (b) fenitrothion-d6, and (c) chlorpyrifos-methyl-d6. The vertical line represents the limit of significance.

Table S1 Concentration of the 13 target pesticides measured in the grab water samples collected in aquarium #1 and aquarium #4 during the exposure of the Twisters

| Pesticide | Water concentrations in Aquarium #4 (ng L ⁻¹) | | | | | | | | | | |
|---------------------|---|------|------|------|------|------|------|------|------|------|---------|
| | Start | 6 h | 1 d | 2 d | 3 d | 4 d | 5 d | 6 d | 7 d | Mean | RSD (%) |
| Atrazine | 118 | 181 | 269 | 293 | 407 | 907 | 981 | 342 | 93.3 | 399 | 81.6 |
| Azoxystrobin | 5.4 | 5.7 | 6.6 | 8.6 | 18.4 | 19.4 | 22.5 | 22.8 | 30.9 | 15.6 | 59.5 |
| Chlorfenvinphos | 20.9 | 20.0 | 8.8 | 9.2 | 21.6 | 7.7 | 6.6 | 6.1 | 7.1 | 12.0 | 55.9 |
| Chlorpyrifos | 2.4 | 4.8 | 7.0 | 6.4 | 13.3 | 6.9 | 5.6 | 5.3 | 6.8 | 6.5 | 45.0 |
| Chlorpyrifos-methyl | 6.0 | 14.1 | 15.8 | 14.1 | 23.8 | 18.6 | 18.1 | 18.9 | 17.9 | 16.4 | 29.9 |
| Chlortoluron | 93.2 | 99.3 | 97.9 | 163 | 183 | 206 | 211 | 212 | 262 | 170 | 35.8 |
| Diflufenican | a.i. | a.i. | a.i. | a.i. | a.i. | a.i. | a.i. | a.i. | a.i. | a.i. | a.i. |
| Dimethomorph | 99.0 | 91.6 | 104 | 164 | 201 | 143 | 140 | 138 | 180 | 140 | 26.8 |
| Fenitrothion | 54.3 | 59.5 | 62.7 | 55.0 | 69.6 | 58.1 | 56.2 | 53.7 | 55.5 | 58.3 | 8.7 |
| Isoproturon | 57.4 | 72.7 | 98.7 | 107 | 157 | 160 | 176 | 178 | 185 | 132 | 36.8 |

| Pesticide | Water concentrations in Aquarium #1 (ng L ⁻¹) | | | | | | | | | | RSD (%) |
|---------------------|---|------|------|------|------|------|------|------|------|------|---------|
| | Start | 6 h | 1 d | 2 d | 3 d | 4 d | 5 d | 6 d | 7 d | Mean | |
| Norflurazon | 86.0 | 88.7 | 112 | 159 | 227 | 187 | 195 | 184 | 207 | 161 | 32.7 |
| Simazine | 177 | 139 | 107 | 138 | 277 | 158 | 173 | 294 | 165 | 181 | 34.9 |
| Spiroxamine | 0.3 | 10.0 | 1.1 | 0.4 | 1.0 | 10.3 | 1.5 | 11.2 | 1.5 | 4.2 | 115 |
| Atrazine | 132 | 169 | 245 | 394 | 596 | 546 | 620 | 623 | 475 | 422 | 46.5 |
| Azoxystrobin | 7.7 | 5.2 | 6.8 | 20.9 | 41.7 | 37.0 | 50.4 | 41.9 | 52.4 | 29.3 | 65.8 |
| Chlorfenvinphos | 5.1 | 5.0 | 4.5 | 4.5 | 4.8 | 4.3 | 4.0 | 3.3 | 3.8 | 4.4 | 13.9 |
| Chlorpyrifos | 4.0 | 4.4 | 6.1 | 6.3 | 7.0 | 5.2 | 6.2 | 6.1 | 7.7 | 5.9 | 19.9 |
| Chlorpyrifos-methyl | 4.4 | 6.6 | 6.3 | 7.9 | 10.1 | 6.9 | 9.8 | 9.1 | 9.1 | 7.8 | 24.4 |
| Chlortoluron | 110 | 106 | 107 | 175 | 220 | 189 | 225 | 224 | 263 | 180 | 33.0 |
| Diflufenican | 6.4 | 5.8 | 4.8 | 4.6 | 6.1 | 6.8 | 6.4 | 8.2 | 6.9 | 6.2 | 17.5 |
| Dimethomorph | 120 | 125 | 145 | 103 | 172 | 121 | 147 | 149 | 179 | 140 | 17.9 |
| Fenitrothion | 41.0 | 29.4 | 35.8 | 29.2 | 35.8 | 35.8 | 36.6 | 35.2 | 33.6 | 34.7 | 10.5 |
| Isoproturon | 90.4 | 68.2 | 71.3 | 89.5 | 107 | 85.2 | 175 | 167 | 208 | 118 | 43.6 |
| Norflurazon | 85.6 | 95.6 | 114 | 174 | 228 | 182 | 198 | 206 | 232 | 168 | 33.4 |
| Simazine | 265 | 314 | 367 | 485 | 531 | 461 | 499 | 523 | 505 | 439 | 22.4 |
| Spiroxamine | 2.5 | 1.9 | 0.6 | 1.0 | 2.3 | 3.0 | 5.2 | 5.2 | 1.7 | 2.6 | 63.5 |

a.i: Analytical issue when determining diflufenican concentration in water from Aquarium #4. R_s calculated using a theoretical concentration of 16.2 ng L⁻¹

Table S2 Concentrations of DOC in the water of four aquariums during the study

| | DOC concentrations (mg L ⁻¹) | | | | | | | | | | | |
|-------------|--|------|------|------|-----|------|------|------|------|------|--------------------|---------|
| | Start | 6 h | 1 d | 2 d | 3 d | 4 d | 5 d | 6 d | 7 d | Mean | Standard deviation | RSD (%) |
| Aquarium #1 | 2.1 | 2.0 | 2.1 | 2.3 | 2.3 | 2.0 | 2.1 | 2.1 | 2.1 | 2.1 | 0.12 | 5.5 |
| Aquarium #2 | 25.8 | 11.3 | 17.0 | 19.0 | 2.6 | 16.5 | 27.2 | 34.0 | 28.5 | 20.2 | 9.70 | 48.0 |
| Aquarium #3 | 2.0 | - | - | - | - | - | - | - | 1.6 | 1.8 | | - |
| Aquarium #4 | 23.0 | - | - | - | - | - | - | - | 28.9 | 26.0 | | - |

h: hour; d: day

Table S3 Water temperatures in the four aquariums during the study

| Date and hour of the measurement | Water temperature (°C) | | | |
|----------------------------------|------------------------|-------------|-------------|-------------|
| | Aquarium #1 | Aquarium #2 | Aquarium #3 | Aquarium #4 |
| 15/11/2013 06:00 | 10.5 | 10.7 | 23.2 | 23.2 |
| 15/11/2013 12:00 | 10.5 | 10.9 | 23.2 | 23.1 |
| 15/11/2013 18:00 | 10.6 | 11.0 | 23.3 | 23.2 |
| 16/11/2013 00:00 | 10.7 | 11.1 | 23.2 | 23.2 |
| 16/11/2013 06:00 | 10.5 | 10.9 | 23.1 | 23.1 |
| 16/11/2013 12:00 | 10.4 | 10.9 | 23.1 | 23.1 |
| 16/11/2013 18:00 | 10.5 | 11.0 | 23.1 | 23.1 |
| 17/11/2013 00:00 | 10.4 | 10.9 | 23.2 | 23.1 |
| 17/11/2013 06:00 | 10.0 | 10.3 | 22.6 | 22.5 |
| 17/11/2013 12:00 | 10.0 | 10.4 | 22.5 | 22.5 |
| 17/11/2013 18:00 | 10.0 | 10.3 | 22.4 | 22.4 |
| 18/11/2013 00:00 | 9.9 | 10.2 | 22.3 | 22.3 |
| 18/11/2013 06:00 | 9.9 | 10.3 | 22.8 | 22.6 |
| 18/11/2013 12:00 | 10.0 | 10.5 | 23.0 | 22.8 |
| 18/11/2013 18:00 | 10.4 | 10.9 | 23.1 | 23.0 |
| 19/11/2013 00:00 | 10.5 | 11.0 | 23.0 | 23.0 |
| 19/11/2013 06:00 | 10.5 | 11.0 | 23.0 | 23.0 |
| 19/11/2013 12:00 | 10.5 | 11.0 | 23.1 | 23.0 |
| 19/11/2013 18:00 | 10.5 | 11.0 | 23.1 | 23.0 |
| 20/11/2013 00:00 | 10.4 | 10.9 | 23.0 | 22.9 |
| 20/11/2013 06:00 | 10.3 | 10.8 | 22.9 | 22.9 |
| 20/11/2013 12:00 | 10.4 | 10.8 | 23.0 | 22.9 |
| 20/11/2013 18:00 | 10.3 | 10.8 | 23.0 | 22.9 |
| 21/11/2013 00:00 | 10.5 | 11.0 | 23.0 | 23.0 |
| 21/11/2013 06:00 | 10.5 | 11.0 | 23.0 | 23.0 |
| 21/11/2013 12:00 | 10.4 | 10.9 | 23.0 | 22.9 |
| 21/11/2013 18:00 | 10.3 | 10.8 | 23.0 | 22.9 |
| 22/11/2013 00:00 | 10.4 | 11.0 | 23.1 | 23.1 |
| 22/11/2013 06:00 | 10.4 | 10.9 | 23.1 | 23.1 |
| Mean | 10.4 | 10.8 | 23.0 | 22.9 |
| Standard deviation | 0.20 | 0.30 | 0.21 | 0.21 |
| RSD (%) | 1.9 | 2.8 | 0.9 | 0.9 |

Table S4 Flow velocities measured at the beginning (t= 0) and end of the study (t = 7d) at each hole of each diffusion ramp in the four aquariums

| Flow velocity in cm s ⁻¹ | Diffusion ramp 1 | | | | Diffusion ramp 2 | | | |
|-------------------------------------|------------------|--------|--------|--------|------------------|--------|--------|--------|
| | Hole 1 | Hole 2 | Hole 3 | Hole 4 | Hole 1 | Hole 2 | Hole 3 | Hole 4 |
| Start of the study | | | | | | | | |
| Aquarium #1 | 20 | 18 | 19 | 20 | 3.4 | 3.8 | 4.0 | 4.2 |
| Aquarium #2 | 20 | 19 | 18 | 18 | 4.0 | 3.7 | 3.5 | 4.3 |
| Aquarium #3 | 21 | 20 | 18 | 19 | 3.9 | 4.4 | 3.8 | 4.1 |
| Aquarium #4 | 19 | 19 | 18 | 17 | 4.3 | 3.8 | 4.1 | 3.9 |
| | | | | | | | | |
| | Diffusion ramp 1 | | | | Diffusion ramp 2 | | | |
| End of the study | Hole 1 | Hole 2 | Hole 3 | Hole 4 | Hole 1 | Hole 2 | Hole 3 | Hole 4 |
| Aquarium #1 | 19 | 19 | 19 | 21 | 4.0 | 3.0 | 3.0 | 2.5 |
| Aquarium #2 | 19 | 19 | 19 | 19 | 3.0 | 4.0 | 4.0 | 4.0 |
| Aquarium #3 | 17 | 19 | 17 | 17 | 4.0 | 4.0 | 4.0 | 4.0 |
| Aquarium #4 | 18 | 18 | 17 | 17 | 3.0 | 3.0 | 3.0 | 3.0 |

Table S5 Amounts of target pesticides and PRC candidates determined in Twisters during the eight experiments

| Substance | Time | Amount of substance determined in Twisters (ng) | | | | | | | |
|-----------------|------|---|---------|---------|---------|---------|---------|---------|---------|
| | | Exp. #1 | Exp. #2 | Exp. #3 | Exp. #4 | Exp. #5 | Exp. #6 | Exp. #7 | Exp. #8 |
| Atrazine | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6h | 0.46 | 0.24 | 0.53 | 0.35 | 0.46 | 0.27 | 0.63 | 0.28 |

| | | | | | | | | | |
|---------------------|-------------|--|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| | 1d | 1.14 | 0.74 | 1.23 | 0.91 | 1.21 | 0.70 | 1.23 | 0.78 |
| | 2d | 1.85 | 1.19 | 2.25 | 1.30 | 1.84 | 1.35 | 2.15 | 1.26 |
| | 3d | 2.83 | 2.41 | 3.29 | 2.79 | 2.54 | 2.45 | 3.51 | 2.38 |
| | 4d | 3.38 | 2.54 | 3.61 | 2.41 | 3.38 | 2.20 | 3.46 | 2.18 |
| | 5d | 3.79 | 2.70 | 4.29 | 3.69 | 4.10 | 3.94 | 4.50 | 2.90 |
| | 6d | 4.79 | 4.54 | 4.90 | 4.15 | 4.22 | 3.84 | 4.42 | 3.30 |
| | 7d | 6.39 | 5.17 | 5.72 | 3.69 | 4.51 | 5.53 | 5.26 | 4.07 |
| | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6h | 0.04 | 0.01 | 0.06 | 0.03 | 0.06 | 0.01 | 0.07 | 0.02 |
| | 1d | 0.09 | 0.07 | 0.14 | 0.07 | 0.10 | 0.04 | 0.17 | 0.05 |
| | 2d | 0.14 | 0.06 | 0.27 | 0.10 | 0.15 | 0.10 | 0.24 | 0.08 |
| Azoxystrobin | 3d | 0.27 | 0.19 | 0.43 | 0.25 | 0.29 | 0.13 | 0.42 | 0.20 |
| | 4d | 0.40 | 0.31 | 0.61 | 0.22 | 0.47 | 0.22 | 0.42 | 0.16 |
| | 5d | 0.63 | 0.24 | 0.77 | 0.29 | 0.48 | 0.39 | 0.62 | 0.20 |
| | 6d | 0.79 | 0.41 | 0.85 | 0.45 | 0.70 | 0.43 | 0.75 | 0.36 |
| | 7d | 1.01 | 0.50 | 1.10 | 0.43 | 0.73 | 0.62 | 1.18 | 0.48 |
| | | Amount of substance determined in Twisters (ng) | | | | | | | |
| Substance | Time | Exp. #1 | Exp. #2 | Exp. #3 | Exp. #4 | Exp. #5 | Exp. #6 | Exp. #7 | Exp. #8 |

| | | | | | | | | | |
|------------------------|----|------|---------|------|------|------|------|------|------|
| | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6h | 0.06 | 0.05 | 0.52 | 0.33 | 0.29 | 0.17 | 0.78 | 0.53 |
| | 1d | 0.27 | 0.18 | 1.45 | 0.84 | 0.59 | 0.34 | 1.75 | 1.18 |
| | 2d | 0.34 | 0.25 | 1.90 | 0.87 | 0.56 | 0.29 | 2.15 | 0.97 |
| Chlorfenvinphos | 3d | 0.50 | 0.34 | 1.92 | 1.43 | 0.68 | 0.35 | 2.08 | 1.40 |
| | 4d | 0.42 | 0.19 | 2.01 | 1.18 | 0.66 | 0.36 | 1.72 | 1.12 |
| | 5d | 0.77 | 0.19 | 1.87 | 1.22 | 0.70 | 0.43 | 2.48 | 1.16 |
| | 6d | 0.64 | 0.30 | 1.97 | 1.36 | 0.71 | 0.41 | 2.06 | 1.23 |
| | 7d | 0.78 | 0.35 | 2.26 | 1.20 | 0.82 | 0.54 | 2.62 | 1.13 |
| | 0 | 0.00 | no data | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6h | 0.00 | no data | 0.01 | 0.00 | 0.07 | 0.04 | 0.12 | 0.00 |
| | 1d | 0.07 | no data | 0.32 | 0.07 | 0.25 | 0.05 | 0.47 | 0.14 |
| | 2d | 0.08 | no data | 0.44 | 0.08 | 0.38 | 0.00 | 0.76 | 0.20 |
| Chlorpyrifos | 3d | 0.18 | no data | 0.67 | 0.32 | 0.46 | 0.01 | 0.90 | 0.16 |
| | 4d | 0.10 | no data | 0.61 | 0.13 | 0.70 | 0.05 | 0.89 | 0.02 |
| | 5d | 0.27 | no data | 0.93 | 0.16 | 0.75 | 0.06 | 1.34 | 0.34 |
| | 6d | 0.25 | no data | 0.69 | 0.24 | 0.57 | 0.00 | 1.65 | 0.24 |
| | 7d | 0.44 | no data | 1.20 | 0.25 | 0.79 | 0.04 | 1.79 | 0.31 |

| | | | | | | | | | |
|---------------------------------|----|------|------|------|------|------|------|------|------|
| | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6h | 0.15 | 0.10 | 0.47 | 0.23 | 0.56 | 0.32 | 0.71 | 0.52 |
| | 1d | 0.72 | 0.34 | 2.01 | 0.83 | 1.69 | 0.89 | 2.92 | 1.66 |
| | 2d | 0.87 | 0.61 | 2.86 | 1.37 | 2.59 | 0.67 | 4.41 | 2.19 |
| Chlorpyrifos- methyl | 3d | 1.34 | 0.70 | 4.21 | 2.50 | 2.65 | 1.15 | 4.88 | 2.02 |
| | 4d | 1.21 | 0.56 | 3.55 | 1.91 | 3.79 | 0.91 | 4.39 | 1.96 |
| | 5d | 2.03 | 0.63 | 4.73 | 2.28 | 3.86 | 1.52 | 5.52 | 2.93 |
| | 6d | 2.13 | 0.53 | 3.98 | 2.82 | 3.28 | 1.01 | 5.51 | 2.78 |
| | 7d | 2.58 | 0.70 | 4.93 | 2.68 | 4.05 | 1.23 | 5.40 | 3.14 |

| Substance | Time | Amount of substance determined in Twisters (ng) | | | | | | | |
|---------------------|------|---|---------|---------|---------|---------|---------|---------|---------|
| | | Exp. #1 | Exp. #2 | Exp. #3 | Exp. #4 | Exp. #5 | Exp. #6 | Exp. #7 | Exp. #8 |
| | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6h | 0.18 | 0.12 | 0.19 | 0.16 | 0.18 | 0.13 | 0.21 | 0.13 |
| | 1d | 0.35 | 0.32 | 0.40 | 0.42 | 0.37 | 0.29 | 0.42 | 0.35 |
| Chlortoluron | 2d | 0.43 | 0.44 | 0.69 | 0.46 | 0.46 | 0.53 | 0.66 | 0.42 |
| | 3d | 0.67 | 0.75 | 0.73 | 0.82 | 0.63 | 0.78 | 0.89 | 0.77 |
| | 4d | 0.78 | 0.88 | 0.91 | 0.69 | 0.74 | 0.68 | 0.74 | 0.67 |
| | 5d | 0.84 | 0.82 | 0.99 | 1.14 | 0.90 | 1.28 | 1.14 | 0.84 |

| | | | | | | | | | |
|---------------------|----|------|---------|---------|------|------|------|------|---------|
| | 6d | 0.98 | 1.41 | 1.12 | 1.17 | 0.98 | 1.33 | 1.14 | 0.93 |
| | 7d | 1.41 | 1.54 | 1.33 | 1.02 | 1.05 | 1.62 | 1.51 | 1.14 |
| | 0 | 0.00 | no data | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6h | 0.00 | no data | 0.14 | 0.00 | 0.30 | 0.06 | 0.26 | 0.12 |
| | 1d | 0.66 | no data | no data | 0.21 | 0.84 | 0.12 | 1.70 | no data |
| | 2d | 0.18 | no data | 1.28 | 0.24 | 1.16 | 0.00 | 2.20 | 0.67 |
| Diflufenican | 3d | 0.46 | no data | 1.83 | 0.76 | 1.28 | 0.15 | 2.50 | 0.64 |
| | 4d | 0.38 | no data | 1.74 | 0.48 | 1.87 | 0.21 | 2.26 | 0.57 |
| | 5d | 0.95 | no data | 2.41 | 0.58 | 1.69 | 0.23 | 3.04 | 1.00 |
| | 6d | 0.71 | no data | 1.96 | 0.82 | 1.44 | 0.13 | 3.32 | 0.82 |
| | 7d | 0.89 | no data | 2.92 | 0.77 | 1.79 | 0.15 | 3.75 | 0.99 |
| | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6h | 0.21 | 0.12 | 0.25 | 0.20 | 0.21 | 0.13 | 0.30 | 0.16 |
| | 1d | 0.43 | 0.34 | 0.51 | 0.49 | 0.54 | 0.30 | 0.56 | 0.37 |
| Dimethomorph | 2d | 0.65 | 0.47 | 1.00 | 0.56 | 0.58 | 0.51 | 0.93 | 0.53 |
| | 3d | 0.86 | 0.87 | 1.16 | 1.17 | 0.87 | 0.89 | 1.27 | 0.96 |
| | 4d | 1.11 | 1.00 | 1.81 | 0.96 | 1.04 | 0.83 | 1.42 | 0.71 |
| | 5d | 1.38 | 0.84 | 1.57 | 1.29 | 1.27 | 1.36 | 1.66 | 1.03 |

| | 6d | 1.41 | 1.41 | 1.93 | 1.62 | 1.33 | 1.40 | 1.82 | 1.35 |
|---------------------|------|---|---------|---------|---------|---------|---------|---------|---------|
| | 7d | 1.90 | 1.70 | 2.13 | 1.33 | 1.39 | 2.03 | 2.29 | 1.21 |
| | | Amount of substance determined in Twisters (ng) | | | | | | | |
| Substance | Time | Exp. #1 | Exp. #2 | Exp. #3 | Exp. #4 | Exp. #5 | Exp. #6 | Exp. #7 | Exp. #8 |
| | | | | | | | | | |
| Fenitrothion | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6h | 0.61 | 0.36 | 3.09 | 1.22 | 1.56 | 0.94 | 3.28 | 1.87 |
| | 1d | 2.05 | 1.19 | 8.16 | 3.35 | 3.45 | 2.08 | 10.00 | 4.85 |
| | 2d | 2.23 | 1.86 | 8.11 | 3.99 | 5.12 | 1.73 | 11.94 | 4.75 |
| | 3d | 3.17 | 1.94 | 8.67 | 6.79 | 4.89 | 2.42 | 9.15 | 5.44 |
| | 4d | 3.30 | 1.61 | 9.15 | 4.90 | 6.25 | 2.28 | 9.33 | 4.90 |
| | 5d | 3.39 | 1.52 | 10.1 | 5.73 | 5.80 | 3.24 | 10.80 | 5.07 |
| | 6d | 5.16 | 1.24 | 9.86 | 5.86 | 5.99 | 2.13 | 9.18 | 5.41 |
| | 7d | 5.53 | 1.78 | 8.85 | 5.41 | 6.45 | 2.36 | 7.27 | 5.16 |
| Isoproturon | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6h | 0.15 | 0.10 | 0.16 | 0.15 | 0.14 | 0.11 | 0.19 | 0.12 |
| | 1d | 0.18 | 0.28 | 0.33 | 0.41 | 0.23 | 0.25 | 0.34 | 0.32 |
| | 2d | 0.25 | 0.41 | 0.60 | 0.44 | 0.25 | 0.82 | 0.59 | 0.41 |
| | 3d | 0.37 | 0.61 | 0.73 | 0.85 | 0.35 | 0.68 | 0.82 | 0.75 |

| | | | | | | | | | |
|--------------------|-------------|--|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| | 4d | 0.48 | 0.77 | 0.90 | 0.78 | 0.42 | 0.61 | 0.73 | 0.69 |
| | 5d | 0.64 | 0.72 | 1.02 | 1.03 | 0.59 | 1.13 | 1.08 | 0.82 |
| | 6d | 0.70 | 1.32 | 1.22 | 1.24 | 0.69 | 1.24 | 1.17 | 1.05 |
| | 7d | 1.16 | 1.57 | 1.46 | 1.08 | 0.79 | 1.50 | 1.63 | 1.11 |
| | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6h | 0.29 | 0.12 | 0.27 | 0.15 | 0.20 | 0.16 | 0.32 | 0.21 |
| | 1d | 0.52 | 0.37 | 0.55 | 0.58 | 0.62 | 0.44 | 0.75 | 0.39 |
| | 2d | 0.76 | 0.50 | 0.97 | 0.66 | 0.81 | 0.76 | 0.84 | 0.47 |
| Norflurazon | 3d | 0.86 | 0.92 | 1.11 | 1.19 | 0.73 | 1.10 | 1.13 | 0.83 |
| | 4d | 1.40 | 1.01 | 1.47 | 1.16 | 1.11 | 0.97 | 1.26 | 0.80 |
| | 5d | 0.97 | 1.00 | 1.41 | 1.18 | 0.97 | 1.33 | 1.01 | 0.93 |
| | 6d | 2.05 | 1.32 | 1.30 | 1.58 | 1.35 | 1.04 | 1.09 | 1.17 |
| | 7d | 2.00 | 1.02 | 2.11 | 1.62 | 1.25 | 1.62 | 2.35 | 0.82 |
| | | Amount of substance determined in Twisters (ng) | | | | | | | |
| Substance | Time | Exp. #1 | Exp. #2 | Exp. #3 | Exp. #4 | Exp. #5 | Exp. #6 | Exp. #7 | Exp. #8 |
| | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Simazine | 6h | 0.26 | 0.18 | 0.26 | 0.24 | 0.27 | 0.20 | 0.31 | 0.22 |
| | 1d | 0.43 | 0.43 | 0.43 | 0.45 | 0.44 | 0.41 | 0.45 | 0.46 |

| | | | | | | | | | |
|-------------------------------|----|------|------|------|------|------|------|---------|------|
| | 2d | 0.71 | 0.54 | 0.79 | 0.61 | 0.68 | 0.66 | 0.74 | 0.60 |
| | 3d | 0.87 | 0.80 | 0.89 | 0.82 | 0.98 | 0.74 | 0.99 | 0.98 |
| | 4d | 1.00 | 0.89 | 1.07 | 1.03 | 0.78 | 0.78 | 1.03 | 0.39 |
| | 5d | 1.17 | 0.85 | 1.14 | 1.00 | 1.04 | 1.15 | 1.23 | 0.94 |
| | 6d | 1.24 | 1.21 | 1.20 | 1.13 | 1.07 | 1.26 | 1.38 | 0.96 |
| | 7d | 1.50 | 1.42 | 1.33 | 1.05 | 1.13 | 1.29 | 1.26 | 1.08 |
| | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6h | 0.00 | 0.01 | 0.03 | 0.03 | 0.04 | 0.01 | 0.04 | 0.02 |
| | 1d | 0.04 | 0.00 | 0.07 | 0.03 | 0.09 | 0.02 | no data | 0.04 |
| | 2d | 0.02 | 0.01 | 0.09 | 0.02 | 0.07 | 0.01 | 0.15 | 0.05 |
| Spiroxamine | 3d | 0.03 | 0.03 | 0.13 | 0.05 | 0.07 | 0.03 | 0.17 | 0.06 |
| | 4d | 0.03 | 0.01 | 0.13 | 0.03 | 0.22 | 0.17 | 0.15 | 0.03 |
| | 5d | 0.20 | 0.01 | 0.14 | 0.03 | 0.09 | 0.04 | 0.20 | 0.05 |
| | 6d | 0.05 | 0.02 | 0.12 | 0.04 | 0.09 | 0.04 | 0.21 | 0.05 |
| | 7d | 0.05 | 0.02 | 0.14 | 0.03 | 0.10 | 0.03 | 0.23 | 0.04 |
| | 0 | 330 | 330 | 330 | 330 | 330 | 330 | 330 | 330 |
| Chlorpyrifos-methyl-d6 | 6h | 291 | 297 | 337 | 293 | 334 | 331 | 292 | 260 |
| | 1d | 288 | 369 | 237 | 304 | 301 | 263 | 217 | 277 |

| | 2d | 326 | 199 | 192 | 243 | 210 | 276 | 189 | 201 |
|--|------|---|---------|---------|---------|---------|---------|---------|---------|
| | 3d | 234 | 240 | 122 | 190 | 257 | 222 | 127 | 192 |
| | 4d | 247 | 273 | 164 | 230 | 126 | 162 | 115 | 78 |
| | 5d | 169 | 174 | 108 | 138 | 126 | 252 | 118 | 150 |
| | 6d | 233 | 287 | 160 | 213 | 189 | 246 | 111 | 158 |
| | 7d | 261 | 290 | 125 | 158 | 154 | 228 | 59 | 154 |
| Amount of substance determined in Twisters (ng) | | | | | | | | | |
| Substance | Time | Amount of substance determined in Twisters (ng) | | | | | | | |
| | | Exp. #1 | Exp. #2 | Exp. #3 | Exp. #4 | Exp. #5 | Exp. #6 | Exp. #7 | Exp. #8 |
| | 0 | 462 | 462 | 462 | 462 | 462 | 462 | 462 | 462 |
| | 6h | 389 | 374 | 402 | 339 | 401 | 318 | 319 | 269 |
| | 1d | 295 | 447 | 140 | 285 | 263 | 212 | 111 | 211 |
| | 2d | 310 | 210 | 113 | 164 | 166 | 244 | 91.2 | 109 |
| Fenitrothion-d6 | 3d | 192 | 213 | 48.6 | 104 | 138 | 168 | 47.8 | 90.3 |
| | 4d | 253 | 293 | 80.5 | 133 | 80.9 | 131 | 43.7 | 48.7 |
| | 5d | 173 | 149 | 40.6 | 71.0 | 68.2 | 173 | 38.7 | 51.5 |
| | 6d | 164 | 272 | 60.0 | 98.5 | 100 | 191 | 38.0 | 63.6 |
| | 7d | 199 | 225 | 40.9 | 60.9 | 66.0 | 169 | 29.5 | 45.3 |
| Tebuconazol-d6 | 0 | 61.9 | 61.9 | 61.9 | 61.9 | 61.9 | 61.9 | 61.9 | 61.9 |

| | | | | | | | | |
|----|------|------|------|------|------|------|------|------|
| 6h | 43.9 | 50.3 | 43.4 | 43.9 | 47.4 | 50.8 | 42.1 | 41.5 |
| 1d | 31.5 | 47.2 | 26.3 | 33.6 | 41.3 | 36.3 | 29.3 | 32.9 |
| 2d | 37.3 | 32.8 | 26.0 | 32.9 | 35.9 | 49.0 | 27.8 | 24.3 |
| 3d | 31.7 | 32.4 | 16.8 | 17.8 | 38.3 | 28.7 | 17.9 | 25.8 |
| 4d | 35.0 | 35.8 | 22.2 | 24.8 | 23.2 | 24.3 | 17.2 | 10.7 |
| 5d | 25.6 | 23.2 | 19.3 | 14.5 | 23.3 | 32.7 | 17.6 | 16.5 |
| 6d | 25.9 | 34.4 | 20.5 | 18.0 | 26.8 | 33.3 | 18.4 | 14.7 |
| 7d | 33.7 | 37.9 | 16.4 | 13.7 | 23.9 | 35.4 | 14.9 | 15.4 |

Technical specifications

Quality assurance and quality control of the analytical method:

The pesticides analytical method was evaluated during a previous study (Margoum et al., 2013) following a procedure inspired from reference standards (ISO/IEC 17025:2005, AFNOR NF T90-210:2009, SANCO/10684/2009). The limits of quantification of the method are presented in that study.

Modelling of the accumulation kinetics

The uncertainty affecting each mass datum is a given input of the calibration process: highly uncertain points had less weight than more certain points.

The uncertainty affecting the measurement times shown on the x-axis was considered negligible.

At time $t=0$, the mass of accumulated pesticides is forced to zero, as there is no intercept in the accumulation kinetics model as shown in equation (1).