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**Calibration of silicone rubber rods as passive samplers for pesticides at two
different flow velocities: modelling of sampling rates under water boundary
layer and polymer control**

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Abstract

There is a need to determine time-weighted average concentrations of polar contaminants such as pesticides by passive sampling in environmental waters. Calibration data for silicone rubber (SR)-based passive samplers are lacking for this class of compounds. The calibration data, sampling rate (R_s) and partition coefficient between SR and water (K_{sw}) were precisely determined for 23 pesticides and 13 candidate performance reference compounds (PRCs) in a laboratory calibration system over 14 d for two water flow velocities, 5 cm s⁻¹ and 20 cm s⁻¹. Results showed that an in situ exposure duration of 7 d left a SR rod passive sampler configuration in the linear or curvilinear uptake period for 19 of the pesticides studied. A change in the transport mechanism from polymer control to water boundary layer control was observed for pesticides with a log K_{sw} of around 3.3. The PRC candidates were not fully relevant to correct the impact of water flow velocity on R_s . We therefore propose an alternative method based on an overall resistance to mass transfer model to adjust R_s from laboratory experiments to in situ hydrodynamic conditions. We estimated diffusion coefficients (D_s) and thickness of water boundary layer (δ_w) as adjustable model parameters. Log D_s values ranged from -12.13 to -10.07 m² s⁻¹. The estimated δ_w value showed a power function correlation with water flow velocity.

Keywords: pesticides, polydimethylsiloxane, freshwaters, mass transfer model, monitoring

1 Introduction

The monitoring of trace levels of pesticides with a wide range of physical and chemical properties is a challenge for sampling and analysis to evaluate water resource quality. The variability in the discharge of pesticides into the environment, such as during flood events in small agricultural watersheds, requires the development of suitable methods that take temporal variations into account [1]. Passive sampling offers a promising alternative to classical grab sampling. It allows the determination of representative time-weighted average concentrations of contaminants, such as pesticides in freshwaters, at lower logistical and analytical costs [2].

Passive sampling community experts recently recommended monophasic polymers (e.g. silicone rubber (SR) or low density polyethylene (LDPE) as passive sampler materials of choice for hydrophobic and non-ionised organic compounds [3]. These passive samplers are available in a large variety of shapes: sheets, tubes, rods or coated stir bars named “Passive SBSE” (Stir Bar Sorptive Extraction) [4]. Modelling of contaminant uptake mechanisms in monophasic polymers, such as SR, is now well-documented for passive sampling of hydrophobic contaminants (PAHs and PCBs) [5-11]. Although SRs are strongly hydrophobic [12], they can extract organic compounds with a broad range of polarities ($\log K_{ow} > 1-2$) from water but only a few studies have focused on pesticides [13-17]. Sorption properties of SRs for polar contaminants have mainly been assessed by determining partition coefficients between the SR and water at equilibrium (K_{sw}), but if equilibrium is not attained, the determination of representative time-weighted average concentrations in water requires determining uptake kinetic parameters such as sampling rates (R_s) or diffusion coefficients (D_s) in the SR for every compound studied [18-20]. The uptake kinetic parameters are dependent on the variation of environmental factors including water flow velocity [5, 7, 8],

temperature, salinity [21] and biofouling [22, 23]. To correct for environmental variability, and especially water flow velocity, R_s can be estimated from the dissipation rates of performance reference compounds (PRCs) with which the passive sampler is spiked beforehand [24]. A second method, described by Estoppey et al. [7] with SR sheets, is based on correction factors derived from a power function relationship between the compound uptake and water flow velocity. This new method was introduced to correct PCB concentrations among sites with great differences in water flow velocity, where PRC-based R_s overcorrected the impact of varying flow velocities. Estoppey et al. [8] recently improved their method for PCBs by using a simple linear correlation between R_s and flow velocity. For SRs, a close agreement between this second method and PRC correction was reported for flow velocities from 10 cm s⁻¹ to 60 cm s⁻¹ [8], and a similar linear correlation was observed by O'Brien et al. [25] using a passive flow monitor. This method has the advantages of being accessible by the operator applying passive samplers, less time consuming, less expensive than PRC-based methods and not influenced by uncertainties in log K_{sw} and R_s determination [8].

The determination of R_s requires a calibration experiment with a constant concentration of contaminants and controlled experimental parameters (constant temperature and adjustable flow velocity) [26]. For SRs, few calibrations have been conducted for pesticides and especially for polar pesticides [6, 14, 17, 27]. These calibration studies highlighted the need for an experimental design adapted to pesticide properties with short exposure monitoring (<15 d). Emelogu et al. [27] quantified urea herbicide in field studies with SR-based passive samplers, but lacked calibration data to convert mass accumulated by the SR into water concentration.

The main goal of this study was to determine R_s and K_{sw} for 24 polar and non-polar pesticides ($0.6 < \log K_{ow} < 5.5$) with an experimental calibration, in order to estimate an appropriate

deployment period for linear uptake in freshwaters. We also assessed the impact of water flow velocity on the uptake of pesticides. The use of 13 deuterated pesticides as PRC candidates was evaluated to correct R_s for differences in flow velocity. The kinetic variables were determined using a home-made calibration system with adjustable water flow velocity and a diffusive source of pesticides. The theoretical model of overall resistance to mass transfer [28] was first applied to estimate D_s values. In a second step, we then used this model to predict R_s of pesticides for other water flow velocities in order to simplify the calculation of time-weighted average concentrations in different field applications.

2 Mass transfer resistance model in silicone rubber-based passive samplers

The mass transfer of contaminants into a passive sampler depends mainly on both the characteristics of the device and the physical and chemical properties of the sampled analytes, but it depends also on environmental factors. We focused only on the theory for membrane-free or monophasic samplers, such as SR plates. In this configuration, the exchange process is driven by different transport mechanisms involving transport of the compound by diffusion through the water, diffusion across the thickness of the receiving phase/ polymer. The transport across the biofilm layer for long exposure in water was neglected in the present work. Each transport mechanism contributes to the resistance to mass transfer ($1/k_o$), calculated using Eq. 1, with k_w and k_s as the mass transfer coefficients in the water and the SR polymer respectively, and K_{sw} the silicone-water partition coefficient [26, 29, 30].

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

According to Greenwood et al. [26] and Huckins et al. [28], the individual mass transfer for a specific compound is related to the ratio of the compound's diffusion coefficient (D) and the thickness (δ) of each compartment (water or SR, respectively noted with subscripts w and s) contributing to k_o . The mass-transfer coefficients for each compartment are calculated as follows (Eq. 2 and Eq. 3):

$$k_s = \frac{D_s}{\delta_s}, \quad (2) \quad k_w = \frac{D_w}{\delta_w}. \quad (3)$$

If diffusion occurs from both sides for a plate configuration of a SR-based passive sampler, the barrier thickness (δ_s) is considered as the half-thickness. Using the very simplified approach of Zhao et al. [31], where a linear concentration profile is assumed within the polymer cylinder or rod configuration, the barrier thickness (δ_s) is considered as the half-diameter or radius. For the water compartment, the notion of water boundary layer (WBL) of thickness δ_w was assumed for convenience, considering the complexity of the hydrodynamics. In this work, we chose to use a mass transfer resistance model with linear concentration profiles in both the WBL and the SR. It is a simple and approximated model, contrary to the two-phase Fickian model [29] (considering a time-dependent D_s and resulting in non-linear diffusion profiles in the polymer) that would lead to more accurate results.

Assuming that elimination and uptake of compounds obey first-order kinetics (isotropic exchanges), the uptake of compounds in an SR-based passive sampler over time with constant ambient water concentration (and free of compounds at deployment), is described by Eq. 4:

$$C_s(t) = C_w K_{sw} (1 - \exp(-k_e t)), \quad (4)$$

where C_s (ng L^{-1}) is the concentration of the compound accumulated in the receiving phase; C_w (ng L^{-1}) the concentration of the compound in the water phase, and t (d) the duration of

exposure. Elimination and uptake rate constants, respectively k_e (d^{-1}) and k_u (d^{-1}) are linked by a proportional constant K_{sw} (L L^{-1}), the silicone-water partition coefficient. It is described by the ratio of concentration at equilibrium of the compound in the sampler $C_{s,eq}$ (ng L^{-1}) to the concentration at equilibrium of the compound in the water phase $C_{w,eq}$ (ng L^{-1}). The elimination rate constant k_e is expressed by:

$$k_e = \frac{R_s}{K_{sw} V_s} = \frac{k_o A}{K_{sw} V_s}, \quad (5)$$

where V_s (L) is the volume of the receiving phase, R_s is the sampling rate (L d^{-1}) and A (cm^2) is the exposed surface area of the sampler. The calculation of time of sorption half-equilibrium ($t_{1/2} = \ln 2 / k_e$) is also used to describe the calibration regime as linear ($t < t_{1/2}$), curvilinear ($t_{1/2} < t < 4t_{1/2}$) or equilibrium ($t > 4t_{1/2}$) state for the exposure period (t) [28]. Combining Eq. 1, Eq. 2, Eq. 3 and Eq. 5, and neglecting biofilm resistance, R_s , based on the properties of the compounds, is estimated by:

$$R_s = \frac{A}{\frac{\delta_w}{D_w} + \frac{\delta_s}{K_{sw} D_s}}. \quad (6)$$

3 Materials and methods

3.1 Chemicals

The 24 pesticides selected, including two metabolites, covered a broad polarity range ($0.6 < \log K_{ow} < 5.5$) and were listed in Table 1. Among them, 13 additional deuterated pesticides were used as PRCs (SI-1). Pesticides, PRCs and one internal standard (diuron-d6) used for quantification were purchased from Dr Ehrenstorfer (Augsburg, Germany) and Sigma Aldrich (Saint-Quentin Fallavier, France). Acetone and dichloromethane for pesticide residue analysis, UHPLC grade acetonitrile, ethyl acetate and methanol were purchased from Biosolve (Dieuze, France). LC-MS grade formic acid (purity 98%) was supplied by Waters

(Guyancourt, France). Ultrapure water was obtained using a Millipore water purification system equipped with an LC-Pak cartridge (Billerica, MA, USA). Nitrogen gas (purity 99.995%) used for thermal decontamination was purchased from Messer (Saint-Georges-d'Espéranche, France).

3.2 Passive samplers

The passive samplers used in this study were made of SR shaped into small rods. The shape of rod was preferred to the classic sheet because of the convenience of handling and storage, the lower volume of solvent required for back extraction and the possibility to use thermodesorption (TD)-GC/MS analysis. Translucent SR was obtained as flexible cord from Goodfellow (Lille, France). This SR had been selected in an earlier study for its sorption properties for pesticides [13]. The SR was cut with a clean cutter blade into rods (20×3 mm), with a surface area of 2.03 cm^2 and a volume of $141 \text{ }\mu\text{L}$. Silicone rubber rods (SR rods) were selected by weight ($165 \text{ mg} \pm 2.5\%$, $d = 1.2$) to ensure repeatability.

Before use, SR rods were chemically and thermally cleaned to remove most residues such as oligomers that could interfere with the instrumental analysis [13]. First the SR rods were chemically conditioned by immersion in dichloromethane/methanol (50/50, v/v) under sonication for 15 min. They were then wiped with a lint-free tissue and dried at $70 \text{ }^\circ\text{C}$ for 1 h, and thermally treated in a Gerstel tube conditioner TC (Mülheim a/d Ruhr, Germany) under a nitrogen flow (75 mL min^{-1}) with a temperature ramp of $10 \text{ }^\circ\text{C min}^{-1}$ to $300 \text{ }^\circ\text{C}$ maintained constant for 1 h.

Cleaned SR rods ($n = 34$) were preloaded with PRCs by agitation at 600 rpm for 48 h in 650 mL of ultrapure water spiked with a mixture of 13 PRCs (water concentrations ranging from 150 to $220 \text{ }\mu\text{g L}^{-1}$). The SR rods were then gently rinsed with ultrapure water, dried with a lint-free tissue and stored at $-18 \text{ }^\circ\text{C}$ until deployed in the calibration system. Before

deployment each SR rod was inserted into a stainless steel spring (30×5 mm, wire diameter 0.4 mm) to simplify handling.

3.3 *Characteristics of the calibration system*

The calibration system was custom-made (Colas & Gire, Saint-Genis-les-Ollières, France). It consisted of a stainless steel cylindrical tank (diameter 40 cm, height 35 cm), with a stirring system and hooks fixed on the inner wall of the tank at 4 levels, each level enabling the experimenter to expose 8 SR rods or 8 SR dosing sheets (Figure 1). Two copper wire hoops were fitted in the middle of the tank. Eight magnetic stir bars, wrapped in aluminium foil, were fixed on the copper wire between each hook; in this way the SR rods in their springs were retained magnetically at each position. The stainless steel tank was filled with 31.4 L of tap water and placed in a thermostatic bath at 20 °C. The tank was covered with an aluminium plate to prevent evaporation and photo-degradation in the water compartment. A Tinytag self-recording thermometer (Gemini Data Loggers Ltd, Chichester, United Kingdom) was immersed in the thermostatic bath to continuously follow the water temperature during the experiment.

Stirring was done by a four-blade motor-driven propeller composed of an agitator motor (RZR 2020 Control from Heidolph Instrument, Schwabach, Germany) and a propeller with a diameter of 10 cm (type R1345 from IKA, Staufen, Germany). The rotation generated a water flow velocity near the SR rod positions (set at 5 and 20 cm s⁻¹). These flow velocities were measured with a propeller-type current meter (Streamflo430, Nixon, Cheltenham, United Kingdom) in the same way for all positions in the tank. All dimensions of the calibration system are availables in SI-2.

Constant concentrations of pesticides of about 1 µg L⁻¹ in the water were ensured by two methods. Some polar pesticides (CBZ, CTU, DIU, IMD, IPU, NFZ) (Table 1) were directly

added to the water using 5 mL of a highly concentrated solution in acetone. For more apolar pesticides, spiked SR sheets acted as diffusive contaminant sources in the water [5, 10]. Eight SR sheets ($2 \times 7.5 \times 0.3$ cm, Goodfellow) were fixed with hooks at the bottom of the tank. The total volume of the dosing sheets was 20 times that of the SR rods, ensuring that depletion caused by uptake would be negligible. Before being spiked, the sheets were cleaned by shaking in ethyl acetate and then rinsing in ultrapure water [32]. The quantity of pesticides absorbed by the sheets was assessed with partition coefficients determined by Martin et al. [13]. For the spiking step, the SR sheets were placed in a bottle containing 2.5 L of ultrapure water contaminated with 5 mL of highly concentrated pesticide solutions (concentrations ranging from 56 to 923 mg L⁻¹ in acetone) and the bottle was shaken for 72 h at 300 rpm. Before the exposure of PRC preloaded passive samplers, the system was run for 72 h to allow the stabilization of the pesticide concentrations by reaching equilibrium between water and the spiked sheets for all the compounds (including added polar pesticides).

3.4 Experimental design

Two calibration experiments lasting 14 days were performed with SR rods spiked with PRCs to simultaneously follow uptake and elimination of compounds at an effective water flow velocity of 5.5 ± 2.3 cm s⁻¹ ($n = 14$) and 19.9 ± 3.5 cm s⁻¹ ($n = 19$). A total of 20 SR rods were exposed for each experiment. Three SR rods spiked with PRCs were analysed to determine the initial concentrations of PRCs. The first SR rod was removed from the tank 30 min after the beginning of the experiment and then after 1, 2, 4, 8 h, and 1, 2, 3, 4, 5, 6, 7, 10, 14 days. Additional triplicates of SR rods were also exposed and analysed to evaluate overall repeatability for both uptake of pesticides and elimination of PRCs. The triplicates of SR rods exposed are detailed in the spreadsheet file (SI-7) compiling results of the calibration experiments. During the experiments, a 10 mL water sample was taken in an amber flask

every time a SR rod was collected from the tank to measure concentrations of pesticides. All the SR rods and water samples were stored at -18°C before analysis. Moreover, total organic carbon (TOC) was measured at the start and the end of each experiment in acidified water samples ($\text{HCl } 2\text{N}$, 1%, v/v) with TOC analyser (multi N/C® 3100, Analytik Jena) using thermal oxidation (850°C) and NDIR (Non-Dispersive Infrared) sensor.

3.5 Analytical procedure

Pesticides were desorbed from SR rods by chemical extraction according to the protocol developed by Martin et al. [13]. The solvent back-extraction recoveries of this step were between 60 and 98% depending on the compounds (listed in Table 1). Briefly, SR rods were rinsed with ultrapure water, wiped with lint-free tissue and stored at -18°C . Before analysis the pesticides absorbed in the SR rods were desorbed in 200 μL of acetonitrile/methanol (50/50) for 15 minutes under sonication. Finally, 40 μL of the desorbate was added to 150 μL of ultrapure water and 10 μL of a diuron-d6 solution ($200\text{ }\mu\text{g L}^{-1}$) to prepare the extract for analysis by UHPLC-MS/MS (Nexera X2 UHPLC system, Shimadzu and API 4000, AB Sciex). For calibration experiments, the analysis of the water samples was performed by direct injection. An aliquot of water of 1 mL was spiked with diuron-d6 at a concentration of $10\text{ }\mu\text{g L}^{-1}$ as for the SR rod extract analysis. Chromatographic parameters, limit of quantification (LOQ) and settings for MS/MS (SI-1) analysis are reported elsewhere by Martin et al. [13].

4 Results and discussion

4.1 Monitoring of experimental parameters

During the two 14-day exposure experiments, the mean water temperature recorded was $19.7 \pm 0.5^{\circ}\text{C}$. Considering two measures per experiment and the results of both experiments, we observed a slight variation of pH, from 7.9 ± 0.6 at the start of the calibration to 8.6 ± 0.1 at

the end. No influence of pH on the properties of the selected pesticides or the range of fluctuation was expected. A mean value of TOC for the two experiments was measured at $3.5 \pm 1.1 \text{ mg L}^{-1}$ ($n = 4$). The mean pesticide concentrations in the water of the tank ranged from $0.4 \mu\text{g L}^{-1}$ to $3.1 \mu\text{g L}^{-1}$ (Table 1). We opted to work at higher concentrations for some pesticides (TBZ at $23.9 \mu\text{g L}^{-1}$, FNT at $24.1 \mu\text{g L}^{-1}$ and PCM at $9.6 \mu\text{g L}^{-1}$) that had a higher LOQ or could be partly degraded or absorbed by our experimental calibration system. The concentrations of the 23 pesticides remained stable (RSD between 8% and 27%, $n = 30$). By contrast, a higher RSD was obtained for PCM (41%), which may have been partly degraded (aqueous hydrolysis DT_{50} of PCM: 25 d). Nevertheless, the SR sheets added into the tank acted as a contaminant source as expected for the other pesticides. The PRC concentrations in the water of the tank at the end of either experiment were below LOQ.

4.2 Determination of kinetic parameters

Considering the two experiments, repeatability of sorbed mass on triplicates of SR rods sampled in experiments, expressed as RSD ($n = 3$), ranged from an average value of 3.6% for dimethomorph (DMM) to 14.5% for spiromaxamine (SPX), except for PCM (21.5 %). These RSD values take into account the accumulation of target pesticides in the SR rods, the liquid desorption process and the UHPLC-MS/MS analysis. We therefore excluded PCM from this study owing to high variability in uptake into SRs and in the water of the tank (cf. §4.1). All calibration results are detailed in an additional spreadsheet (SI-7). For each pesticide, the concentration factor (C_s/C_w) was calculated according to the ratio between the concentration in the SR rod (ng L^{-1}) and the mean concentration in water (ng L^{-1}) from the beginning of the experiment to the same sampling time. The concentration factors of the pesticides for various time periods were fitted to a first order uptake model (Eq. 7 derived

from Eq. 4 and Eq. 5) using R_s and K_{sw} as adjustable variables. We optimised the sum of the squared differences between the experimental and calculated values to a minimum using non-linear regression with XLSTAT software (version 2015.3.01.19703). The RSD values of the kinetic parameters were calculated using the derivative of the function for each parameter.

$$\frac{C_s}{C_w}(t) = K_{sw} \left(1 - \exp\left(-\frac{R_s t}{K_{sw} V_s}\right) \right). \quad (7)$$

We obtained satisfactory coefficients of determination (r^2) of fitted data with the first order uptake model, ranging from 0.938 to 0.993. The calculation of parameters (R_s , K_{sw} , $t_{1/2}$) took into account solvent back extraction recoveries determined in Martin et al. [13]. The calculated parameters are detailed in Table 1, and the fitted curves are illustrated in SI-3. The constants of elimination of pesticides in uptake experiments ($k_{e\ up}$) were calculated using their associated R_s and K_{sw} values according to Eq. 5.

The times of sorption half-equilibrium ($t_{1/2}$) ranged from 0.2 d for DCA, reaching equilibrium very quickly in SR rods, up to nearly 15.2 d for CPE at 5 cm s⁻¹. Comparing DCA properties with DMM, which has an equivalent log K_{ow} , the fast uptake kinetic of DCA may be related to its low molecular volume (121 Å³ and log K_{ow} of 2.69). DMM has a larger molecular volume (342 Å³ and log K_{ow} of 2.68), and we observed a longer $t_{1/2}$ (6.4 d) at 5 cm s⁻¹. Thus, mainly curvilinear and equilibrium patterns were observed for the uptake of pesticides in SR rods at 5 cm s⁻¹ for 14 d exposure. Equilibrium state was reached more frequently in the calibration experiment at 20 cm s⁻¹. The impact of flow velocity is discussed in section 4.3.

According to low flow velocities measured near passive samplers in freshwaters (close to 5 cm s⁻¹ with a deployment system), we found that an in situ exposure duration of 7 d was a good compromise in this SR rod passive sampler configuration to stay within the linear or curvilinear uptake period for 19 out of 23 pesticides ($4t_{1/2} > 7$ d except for DCA, FNT, MTC and TBZ).

Those $t_{1/2}$ values are greater than those previously reported for a selection of 19 pesticides with “Passive SBSE” [4]. The authors obtained a $t_{1/2}$ ranging from 1.5 to 4 d in an experiment with flow velocity at 2.5 cm s^{-1} . This difference is because of the use of different geometries (area and volume) between the two passive samplers ($A/V=17.0 \text{ cm}^{-1}$ and 14.3 cm^{-1} respectively for Passive SBSE and SR rod) [9] or differences in diffusion coefficients (D_s). Pesticides potentially diffuse into the half-diameter of SR rods (1.5 mm), whereas the thickness of the SBSE coating is only 1 mm.

Calculated sampling rates (R_s) for the two experiments are reported in Table 1 with their relative standard deviations (RSD). Sampling rates ranged between 0.039 mL d^{-1} (IMD) and 812 mL d^{-1} (CPE), with RSD ranging from 8% to 27%. In comparison, “Passive SBSE” exhibited lower R_s values by a mean factor of 4.7 for 19 pesticides studied in common, excluding DCA, which differed by a factor of 68 [4]. Differences in D_s due to a specific SR formulation could explain this difference for DCA, as no differences in sorption at equilibrium were found for this compound by Martin et al. [13].

The partition coefficients calculated in both experiments were compared with results obtained on the same SR in an earlier study by sorption isotherm experiments reported by Martin et al. [13] (SI-4). For pesticides with $\log K_{sw} < 3$, K_{sw} values obtained in the present study were 1.8 to 8.9 times greater than K_{sw} previously determined. Martin et al. [13] suggested a possible adsorption of the pesticides on the SR following a non-linear sorption isotherm depending on water concentration (Freundlich model). However, $K_{sw \text{ Freundlich}}$ calculated with the mean concentration in water does not match the K_{sw} values obtained in the present study. This difference could be due to different experimental approaches and calculation methods, or to the influence of water characteristics on adsorption (Evian® water vs. tap water). We adopted K_{sw} values derived from Eq. 7 in the experiment at 20 cm^{-1} as reference values (Table 1), because equilibrium state was reached more frequently in calibration experiments at 20 cm s^{-1}

than at 5 cm s^{-1} for most pesticides after 14-d exposure (Cf. § 4.3), leading to more accurate values.

4.3 Impact of flow velocity on uptake of pesticides

As predicted by the theoretical model (Cf. § 2.0), a correlation of sampling rate, expressed as $\log R_s$ normalised per 100 cm^2 , with $\log K_{sw}$ should highlight the control of uptake kinetics by the WBL or by the polymer. This change in transport mechanism was expected for hydrophobic compounds with $\log K_{ow}$ in the range 3.5–5 [11, 33]. For hydrophilic compounds theoretically under polymer control ($R_s \approx AK_{sw}D_s/\delta_s$), R_s values were expected to increase with increasing K_{sw} . On the contrary, for more hydrophobic compounds, such as PCBs and PAHs (with $\log K_{ow} > 3.3$) not investigated in the present study, R_s values were expected to be constant and slowly decrease with increasing K_{sw} [5], in accordance with WBL control theory ($R_s \approx AD_w/\delta_w$) (compounds with high K_{sw} also have a lower D_w).

In our experiments (Figure 2), for polar pesticides with a low affinity for SR, we observed that the R_s values increased with increasing values of $\log K_{sw}$ up to around 3, whereas for more hydrophobic pesticides, R_s remained constant irrespective of the $\log K_{sw}$ values. The plot of $\log R_s$ at the two velocities (Figure 2) shows similar R_s values for polar pesticides, and highlights a significant separation of the two curves at $\log K_{sw}$ around 3.3, defined as graphical intersection of tangents from both ends, with higher values of R_s for the experiments at 20 cm s^{-1} . This change in behaviour demonstrates the impact of hydrodynamics on the thickness of the WBL and on R_s values. A higher flow velocity leads to a thinner WBL, resulting in an increase in R_s proportional to $1/\delta_w$. To our knowledge, this is the first time that the change from polymer control to WBL control for $\log K_{sw} > 3.3$ has been experimentally confirmed with polar and non-polar compounds ($0.6 < \log K_{ow} < 5.5$) using different flow

velocities. This result is consistent with those of Assoumani et al. [4], suggesting a WBL control for pesticides with $\log K_{ow}$ above 3.3 (FNT) in “Passive SBSE” (coated with SR).

4.4 PRCs desorption kinetics: isotropic exchanges?

The elimination of PRC obeys first-order kinetics described by:

$$m_s(t) = m_0 \exp(-k_{e\text{ PRC}} t), \quad (8)$$

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 spike PRC in the receiving phase. The repeatability of mass measurement on triplicates of SR rods sampled in experiments was similar for the release of 13 PRCs and for the uptake of pesticides (RSD from 4.3% to 12.2%). The release of PRCs from the SR rods was fitted by nonlinear regression of PRCs fractions ($f = m_s(t)/m_0$) remaining in the SR rod as a function of exposure time (t) using Eq. 8 (XLSTAT), with the elimination constant ($k_{e\text{ PRC}}$) as an adjustable parameter (fitted curves are available in SI-3). Unlike in uptake experiments, not all coefficients of determination (r^2) were satisfactory (ranging from 0.15 to 0.91). Some PRCs (ATZ-d5, CBZ-d4, IPU-d6, MTC-d6 at 5 cm s⁻¹ and CBZ-d4, FNT-d6 at 20 cm s⁻¹) seemed to obey elimination kinetics with an inflexion point (or two slopes) that could not be described by Eq. 8. This was also observed for some compounds with another passive sampler (POCIS) by Morin et al. [34]. Accordingly only PRCs obeying first order kinetics were considered for the present study and the data for above mentioned PRC were removed.

Several hypotheses can be ventured to explain these deviations from the first order kinetic model. Adsorption on SR could be involved instead of absorption for these strongly polar PRCs. Another explanation is that the geometry of SR rods with a half-thickness of 1.5 mm makes them thicker than the silicone plates (0.25 mm), for which isotropic exchanges have been demonstrated [5]. It is possible that the two-phase Fickian model was more adapted in

this case with a time-dependency of D_s [29, 35]. It may be that the distribution of PRCs within this thicker SR-based passive sampler was not homogeneous because SR rods were preloaded with PRCs without methanol, which allows fast and homogeneous equilibrium by swelling the polymeric structure [36].

Calculated values of $k_{e\ PRC}$ for the two experiments are reported in Figure 3. RSD ranged from 7% to 34% similarly to $k_{e\ up}$ derived from the uptake experiments.

The use of several pairs of deuterated (PRCs) and non-deuterated pesticides allowed direct comparison of the uptake and release processes. We opted to use the graphical comparison of uptake/release instead of checking the equality of elimination constants ($k_{e\ up}$ and $k_{e\ PRC}$), due to different calculation methods ($k_{e\ up}$ was calculated from Eq. 5. and $k_{e\ PRC}$ from Eq. 8. with lower r^2). We considered a confidence interval of 10% for the intersection of uptake/release: isotropic exchanges were thus validated for an intercept between 40% and 60%.

As shown in Figure 3, curves describing the uptake of CPM and LINU and the release of CPM-d6 and LINU-d6 at 5 cm s^{-1} intersect at about 50% of the concentration interval, indicating that the exchange process is isotropic. These profiles were observed for the following deuterated analogues: ATC, CPM, CPE, FNT, and LINU (SI-3). Isotropic exchange of FNT and FNT-d6 with “Passive SBSE” was also confirmed by Assoumani et al. [4] by comparison of k_e values determined by elimination experiments for the two compounds. Therefore, regarding data at 5 cm s^{-1} , the release of the 5 selected PRCs seems pertinent for the correction of R_s in in situ applications.

In Figure 4, the $\log k_{e\ PRC}$ at the two flow velocities are plotted against $\log K_{sw}$ of non-deuterated corresponding pesticides. A change of transport mechanism is again highlighted by a global increase and then a decrease in $k_{e\ PRC}$ with increasing K_{sw} values. However, in contrast to uptake, no differences in the release of hydrophobic PRCs ($k_{e\ PRC}$) (ATC, CFV, CPM, CPE, DFF) were observed between the two flow velocities studied (Figure 4). This is

surprising considering the impact of flow velocity on uptake for these hydrophobic pesticides. The cause of this discrepancy might arise from (i) a non-isotropic exchange for the two velocities or (ii) ill-suited design of the calibration system for the elimination experiments. The graphical comparison of uptake/release of PRCs at 20 cm s^{-1} showed non-isotropic exchange for all pesticides; the uptake was faster than the release of PRCs (SI-3). The alternative explanation is that the static calibration system design (without continuous renewal of water) was not suited to following elimination kinetics. Hence it is difficult to conclude on the use of selected deuterated pesticides as PRC candidates in this study to take into account variation of flow velocity for R_s correction. Other experiments in continuous flow calibration systems will be needed to validate this statement. Considering these results from PRCs, we propose an alternative method based on an overall resistance to mass transfer model to adjust R_s from laboratory experiments to other hydrodynamic conditions by measuring in situ flow velocity.

4.5 *Application of the overall resistance to mass transfer model*

We first applied the overall resistance to mass transfer model on our experimental results. The application of Eq. 6 required knowledge of diffusion parameters (D_w and D_s) for the pesticides studied. Diffusion coefficients in water (D_w) were calculated using the method of Hayduk and Laudie [37] from the molar volume of pesticides (SI-5). We chose this method according to the recommendation of the US Environmental Protection Agency and the conclusions of Pintado-Herrera et al. [19]. Experimental D_s values in SR are scarce in the literature, and have been estimated only for a few classes of contaminants (PCBs and PAHs [20], PBDEs [18] and emerging contaminants [19]) and unfortunately not determined for pesticides. We therefore opted to estimate D_s values for pesticides by simultaneously fitting the data at the two flow

velocities to the overall resistance to mass transfer model. The WBL thickness (δ_w), not
 available by direct measurement, was defined as an adjustment factor for the model.
 To estimate the initial δ_w parameters for the model, we used the approximation of a theoretical
 WBL control model ($R_s \approx AD_w / \delta_w$) with six pesticides that had $\log K_{sw} > 3.3$ and were
 considered in WBL control (FNT, CFV, CPM, SPX, DFF, CPE) for both experiments. We
 obtained δ_w values of 60 μm at 5 cm s^{-1} ($\delta_{w5\text{ ini}}$) and 19 μm at 20 cm s^{-1} ($\delta_{w20\text{ ini}}$). These values
 are in the range of typical values (from a few μm to 1 mm) reported by Huckins et al. [28] for
 SPMD.
 We then used R_s and K_{sw} for all pesticides at the two flow velocities ($n = 48$) to calculate more
 accurate δ_w values (δ_{w5} and δ_{w20}) and D_s values for 23 pesticides according to Eq. 6. Predicted
 R_s values were fitted simultaneously to the experimental R_s values with adjustable parameters
 (δ_w values and D_s values) by minimising the sum of the squares of the residuals weighted by
 the average of the residuals with the “optim” function of R software (version 2.15.2) and a
 limited memory algorithm for bound constrained optimisation (L-BFGS-B). The initial values
 of adjustable parameters were $\delta_{w\text{ ini}}$ values and a $\log D_s$ value of $-11\text{ m}^2\text{ s}^{-1}$ for all pesticides
 (approximated mean value for PAHs and PCBs as initial parameters), and lower and upper
 bounds were respectively 0 and 1000 mm for δ_w , and -10 and -14 for $\log D_s$.
 Predicted R_s values (normalised to 100 cm^2) adjusted to our experimental data were plotted
 against $\log K_{sw}$ (Figure 5). Estimated δ_w values ($\delta_{w5} = 43\text{ }\mu\text{m}$ and $\delta_{w20} = 10\text{ }\mu\text{m}$) were slightly
 lower than those evaluated initially. Estimated $\log D_s$ for pesticides are given in Table 1.
 Estimated $\log D_s$ values in the present study were in the range -12.13 (IMD) to -10.07 (CPE)
 $\text{m}^2\text{ s}^{-1}$. The lowest $\log D_s$ for pesticides ($-12.13\text{ m}^2\text{ s}^{-1}$) was for IMD, the most hydrophilic
 compound studied ($\log K_{ow} = 0.6$) with the lowest affinity for SR ($\log K_{sw} = 0.71$). By
 contrast, the highest $\log D_s$ was for CPE, the second most hydrophobic pesticide ($\log K_{ow} =$

4.7) with the highest affinity for SR ($\log K_{sw} = 4.60$). The most hydrophobic pesticide, SPX ($\log K_{ow} = 5.5$), also had a high molar volume reported to influence the diffusion of compounds in polymers [20, 38] and resulting in a decreased diffusivity in SR. Other trends of the diffusion coefficients related to chemical structures are illustrated in SI-6 with $\log D_s$ plotted to molar volumes and molar mass. This is a first evaluation of D_s values for pesticides using calibration data instead of direct measurement. They therefore need to be validated with further experiments. In regard to other experimental values for PAHs and PCBs for another SR formulation (supplied by Altec) [20], ranging from -9.8 to $-11.0 \text{ m}^2 \text{ s}^{-1}$; our data seem reasonable. In comparison, diffusion coefficient values for the studied pesticides were lower and with a wider range (2 orders of magnitude) than for PCBs and PAHs (1 order of magnitude).

4.6 *Modelling of the influence of water flow velocity on sampling rates*

The knowledge of D_s for each pesticide and δ_w values related to flow velocity enabled us to estimate R_s for other hydrodynamic conditions. Also, the change from the polymer control to the WBL control could be predicted. This model aims at estimating δ_w by a correlation related to a hydrodynamic parameter such as water flow velocity. Such a correlation was proposed by Estoppey et al. [7, 8] for PCBs by in situ passive sampler exposures using LDPE and SR plates.

Our estimated δ_w values for two different measured flow velocities were insufficient to demonstrate such a correlation; we therefore used calibration data for which water flow velocities were only estimated to determine complementary δ_w values. The study of Rusina et al. [5] describes calibration experiments for PAHs and PCBs with SR flat plate passive samplers at two calculated flow velocities (Exp A = 0.14 cm s^{-1} and Exp B = 9 cm s^{-1}), assuming that uptake was controlled by diffusion in the WBL in both cases. We applied the

overall resistance to mass transfer model with the available experimental values of D_s for PAHs and PCBs [20]. The estimated δ_w values were $\delta_{w\ 0.1} = 412\ \mu\text{m}$ and $\delta_{w\ 9} = 27\ \mu\text{m}$. In quasi-static hydrodynamics conditions ($0.14\ \text{cm s}^{-1}$), the WBL thickness was more than 7 times greater than at $5\ \text{cm s}^{-1}$ in our experiment.

The estimated δ_w values from the two studies ($n = 4$) were plotted against the flow velocities (v) reported in experiments in Figure 6. A power function correlation was observed between δ_w values and v ($n = 4$, $\delta_w = 111.6\ v^{-0.71}$, $r^2 = 0.98$). Such a correlation was indirectly demonstrated by Estoppey et al. [7] with power function relations between amounts of PCB accumulated and flow velocity in the range 1.9 to $37.7\ \text{cm s}^{-1}$. They then provided individual linear correlations for 6 PCBs between PRC-based R_s and water flow velocities above $10\ \text{cm s}^{-1}$ for SR: assuming that PCB uptake was under WBL control, the R_s is proportional to $1/\delta_w$, which was indirectly linked to v . Our results confirm that this relationship could also be approximated by a linear correlation for flow velocities above $5\ \text{cm s}^{-1}$ ($n = 3$, $\delta_w = -2.1\ v + 51$, $r^2 = 0.93$).

These results acquired using different SR based passive sampler designs (plate or cylinder) suggest that the effect of flow velocity on the water boundary layer thickness calculated from Eq.6 could be weakly influenced by the geometry of the passive samplers used. Considering the complexity of hydrodynamic conditions near a passive sampler, and the different positions of the passive sampler in the fluid, this approximation yields a simple model that will need to be validated with further data including measurement of water flow velocities.

In Figure 5, we calculated R_s values for pesticides with SR rods at flow velocities recorded by Rusina et al. [5]. At low flow velocity ($v = 0.14\ \text{cm s}^{-1}$), the estimated R_s values for WBL controlled pesticides ($\log K_{sw} > 2.7$) were lower by a mean factor of 10 than those experimentally determined at $5\ \text{cm s}^{-1}$, and the change in transport mechanism occurred at $\log K_{sw}$ around 2.7 instead of 3.3. These extrapolated data could be used to calculate time-

weighted average concentrations of pesticides in freshwaters with only a representative field measurement of water flow velocity. Another way to calculate δ_w could be to use an adaptation of the PRCs model with deuterated PAHs or PCBs as described by Booij et al. [36].

5 Conclusion

The calibration data for SR rods, R_s and K_{sw} were determined for 23 pesticides and 13 candidate PRCs in a laboratory calibration system over 14 d at two flow velocities. The results show that an in situ exposure duration of 7 d kept the SR rod passive sampler configuration in the linear or curvilinear uptake period for 19 pesticides. A change in transport mechanism from polymer control to WBL control was observed for a log K_{sw} of around 3.3. The isotropic exchange of candidate PRCs was demonstrated for 5 PRCs at 5 cm s⁻¹. However, the influence of water flow velocity on elimination was not demonstrated. Hence, the use of these PRCs was not validated to correct R_s for pesticides with WBL-controlled uptake kinetics.

Considering the PRC results, we propose an alternative method based on the overall resistance to mass transfer model to adjust R_s from laboratory experiments to other hydrodynamic conditions by measuring in situ flow velocities. The theoretical model of overall resistance to mass transfer was applied to our experimental data using log D_s values and δ_w as adjustable parameters. The estimated log D_s values ranging from -12.13 to -10.07 m² s⁻¹ for pesticides were consistent with values previously determined for PAHs and PCBs. Nonetheless, the application of a two-phase Fickian model could lead to more accurate results; for this purpose, calibration results are detailed in an additional spreadsheet (SI-7). Moreover, we demonstrated a power function correlation between δ_w and water velocity using a compilation of data from the present study and from Rusina et al. [5]. This correlation is

apparently not influenced by passive sampler geometry. Thus, the estimation of new R_s requires only direct measurements of flow velocity in the deployment location of the SR-based passive sampler. Considering isotropic exchanges, δ_w values could also be estimated with WBL-controlled PRCs (PAHs, PCBs). However, further experiments are required to address isotropic exchange and significant dissipation of PRCs with the SR rod configuration.

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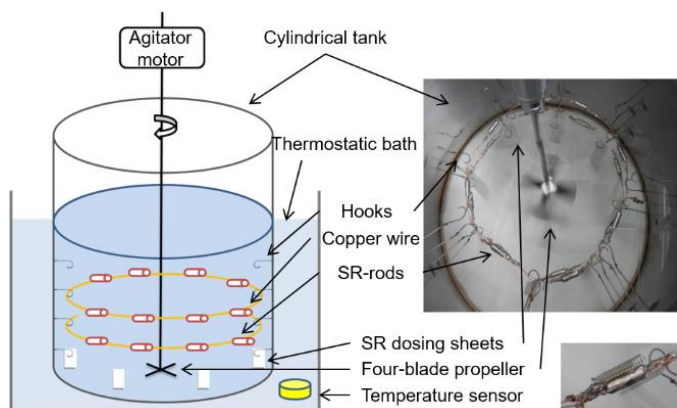
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Figure 1. Schematic diagram of the laboratory static calibration system (a), depiction of the
inside of the calibration tank with the SR rods (b) and zoom on SR-rods inserted in a spring
(c)



646 Figure 2. Plot of $\log R_s$ normalised per 100 cm² versus $\log K_{sw}$ in our experiment at two flow
647 velocities. Error is expressed as standard deviation.

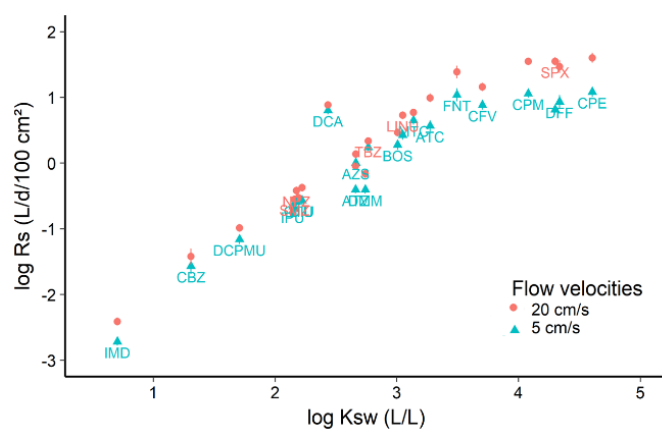
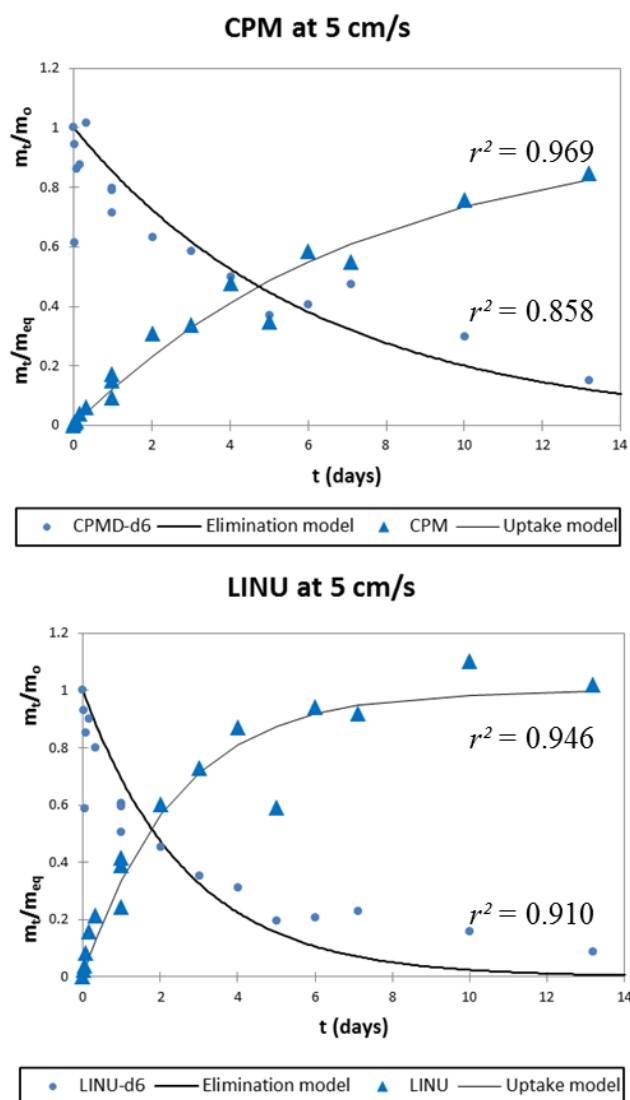
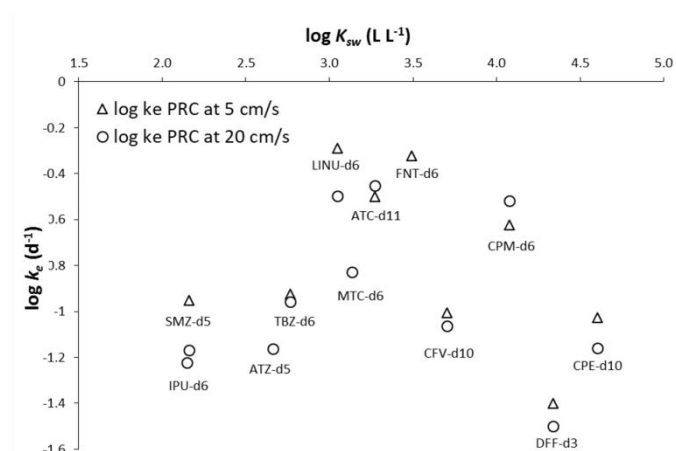


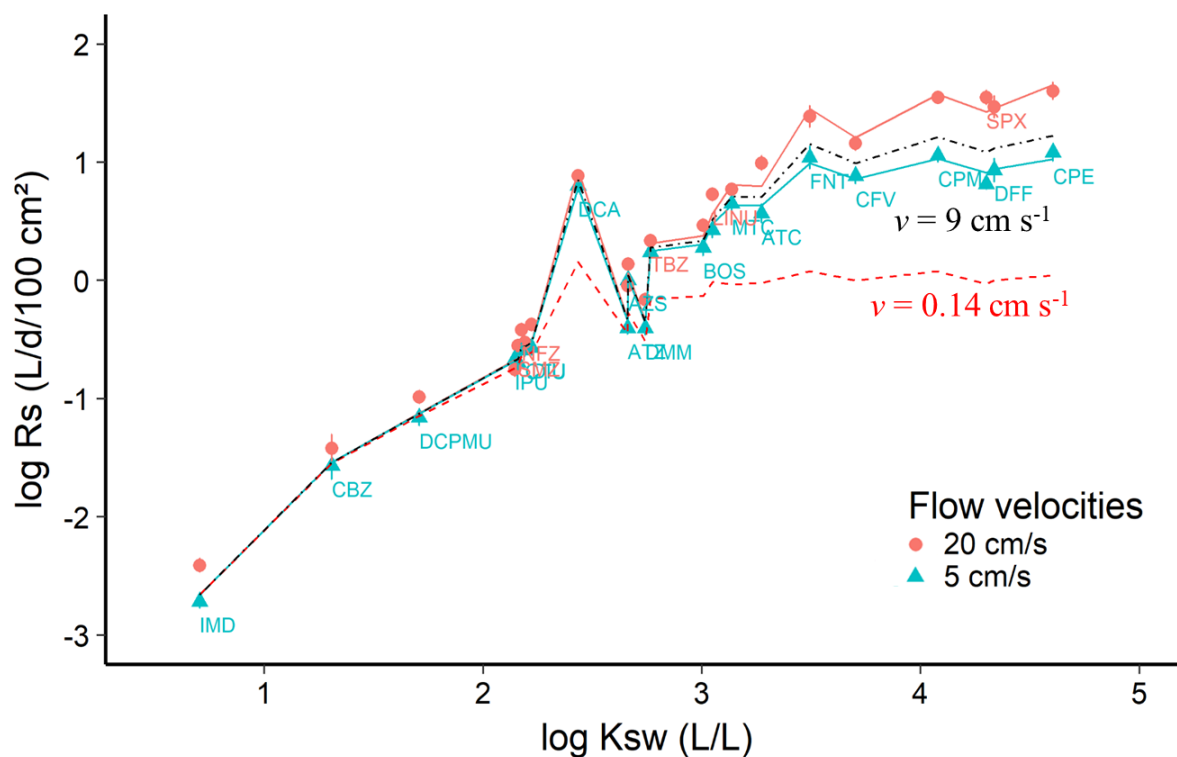
Figure 3. The uptake of CPM and LINU and release of corresponding deuterated pesticides (CPM-d6 and LINU-d6) by SR rods. Mass ratios are plotted relative to the initial mass for the release (m_0) and to the predicted equilibrium mass for the uptake (m_{eq}) with triangles for 5 cm s^{-1} and circles for 20 cm s^{-1} .



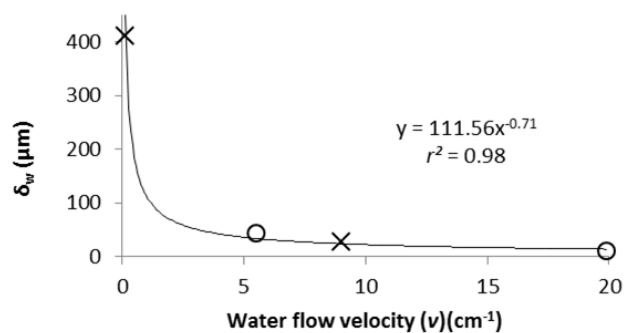
656 Figure 4. Plot of $\log k_e$ PRC versus $\log K_{sw}$ in experiments at two flow velocities (5 and 20 cm
657 s⁻¹).



660 Figure 5. Plot of $\log R_s$ normalised per 100 cm² versus $\log K_{sw}$ in experiments at two flow
661 velocities (5 and 20 cm s⁻¹) with theoretical model (solid lines) and estimated by theoretical
662 model (dotted lines) for other flow velocities (0.14 and 9 cm s⁻¹ with data from Rusina et al.
663 [5]).



666 Figure 6. Plot of water boundary layer thickness (δ_w) estimated by theoretical model (Eq. 6)
667 versus water flow velocity (v) from this present study (circles) and Rusina et al. [5] (crosses).



669 **Table 1. Physico-chemical properties, kinetic parameters at two flow velocities and estimated diffusion coefficients of the**
670 **studied pesticides.**

Pesticide name	Abbreviation	Log K_{ow} ^a	Water concentration ($\mu\text{g L}^{-1}$)	Solvent back extraction recovery (%)	Log K_{sw} (L L^{-1})	Log K_{sw} (L L^{-1})	R_s (mL d^{-1})	R_s (mL d^{-1})	$t_{1/2}$ (d)	$t_{1/2}$ (d)	Log D_s ($\text{m}^2 \text{s}^{-1}$)
			Mean value <i>n</i> = 30, RSD (%)	Mean value <i>n</i> = 3, sd.	5 cm s^{-1} <i>n</i> = 20, sd.	20 cm s^{-1} <i>n</i> = 20, sd.	5 cm s^{-1} <i>n</i> = 20, RSD (%)	20 cm s^{-1} <i>n</i> = 20, RSD (%)	5 cm s^{-1}	20 cm s^{-1}	Estimated values
Acetochlor	ATC	4.1	2.8 (13)	69 (9)	3.18 (0.03)	3.27 (0.01)	75 (19)	200 (14)	2.3	0.9	-11.17
Atrazine	ATZ	2.7	1.5 (24)	86 (4)	2.47 (0.04)	2.66 (0.02)	8.0 (12)	18 (8)	5.3	2.3	-11.75
Azoxystrobin	AZS	2.5	1.2 (15)	95 (6)	2.87 (0.03)	2.66 (0.02)	20 (10)	28 (10)	2.1	1.5	-11.35
Boscalid	BOS	3.0	1.8 (16)	80 (7)	2.89 (0.03)	3.01 (0.02)	38 (16)	59 (12)	2.4	1.6	-11.36
Carbendazim	CBZ	1.5	0.4 (16)	82 (21)	1.41 (0.04)	1.31 (0.03)	0.5 (27)	0.8 (27)	3.4	2.4	-11.61
Chlorfenvinphos	CFV	3.8	2.7 (9)	82 (10)	3.82 (0.04)	3.70 (0.01)	155 (16)	293 (14)	3	1.6	-11.05
Chlorpyrifos-ethyl	CPE	4.7	1.6 (14)	60 (10)	-	4.60 (0.03)	245 (17)	812 (17)	15.2	4.6	-10.07
Chlorpyrifos-methyl	CPM	4	1.9 (12)	68 (6)	4.12 (0.05)	4.08 (0.01)	231 (13)	714 (10)	4.8	1.5	-10.67
Chlortoluron	CTU	2.5	1.8 (11)	90 (9)	1.76 (0.02)	2.19 (0.01)	5.5 (17)	6.1 (12)	2.6	2.4	-11.50
3,4-dichloroaniline	DCA	2.7	0.9 (20)	87 (6)	2.19 (0.01)	2.43 (0.01)	129 (13)	156 (11)	0.2	0.2	-10.20
3-(3,4-dichlorophenyl)- 1-methylurea	DCPMU	2.9*	1.5 (19)	91 (10)	1.53 (0.03)	1.71 (0.02)	1.4 (16)	2.1 (13)	3.4	2.2	-11.59
Diiflufenican	DFF	4.2	1.4 (15)	69 (15)	4.37 (0.14)	4.34 (0.02)	174 (24)	598 (22)	11.5	3.3	-11.15
Diuron	DIU	2.9	2.0 (12)	87 (8)	2.13 (0.03)	2.22 (0.02)	5.5 (16)	8.6 (13)	2.8	1.8	-11.50
Dimethomorph	DMM	2.7	1.8 (16)	96 (12)	2.81 (0.04)	2.74 (0.02)	8.0 (14)	14 (14)	6.4	3.7	-11.84
Fenitrothion	FNT	3.3	24.1 (15)	76 (13)	3.37 (0.02)	3.49 (0.01)	222 (22)	495 (21)	1.3	0.6	-10.45
Imidacloprid	IMD	0.6	1.1 (8)	91 (11)	0.42 (0.04)	0.71 (0.04)	0.04 (13)	0.08 (13)	12	5.9	-12.13
Isoproturon	IPU	2.5	1.8 (11)	96 (12)	2.22 (0.03)	2.15 (0.02)	4.4 (16)	3.6 (13)	2.9	3.6	-11.58
Linuron	LINU	3.0	3.1 (13)	73 (6)	2.99 (0.03)	3.05 (0.01)	54 (16)	109 (13)	1.9	0.9	-11.21
Metolachlor	MTC	3.4	2.2 (10)	75 (5)	3.17 (0.02)	3.14 (0.01)	91 (14)	120 (10)	1.4	1.1	-11.02
Norflurazon	NFZ	2.5	1.9 (17)	98 (8)	2.04 (0.02)	2.18 (0.02)	5.2 (13)	7.8 (12)	2.6	1.8	-11.48
Procymidone	PCM	3.3	9.6 (41)	69 (19)	-	-	-	-	-	-	-
Simazine	SMZ	2.3	1.5 (21)	97 (8)	2.09 (0.03)	2.16 (0.02)	4.1 (14)	5.7 (11)	3.2	2.3	-11.58
Spiroxamine	SPX	5.5*	0.5 (27)	88 (9)	-	4.30 (0.03)	133 (11)	717 (14)	13.9	2.6	-11.15
Tebuconazole	TBZ	3.7	23.9 (15)	87 (6)	2.95 (0.03)	2.77 (0.01)	35 (12)	44 (10)	1.5	1.2	-11.19

671 ^a University of Hertfordshire. Pesticide Properties DataBase: <http://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm>

672 * Predicted by ChemAxon: <http://www.chemicalize.org/structure>

Calibration of silicone rubber rods as passive samplers for pesticides at two different flow velocities: Modelling of sampling rates under water boundary layer and polymer control

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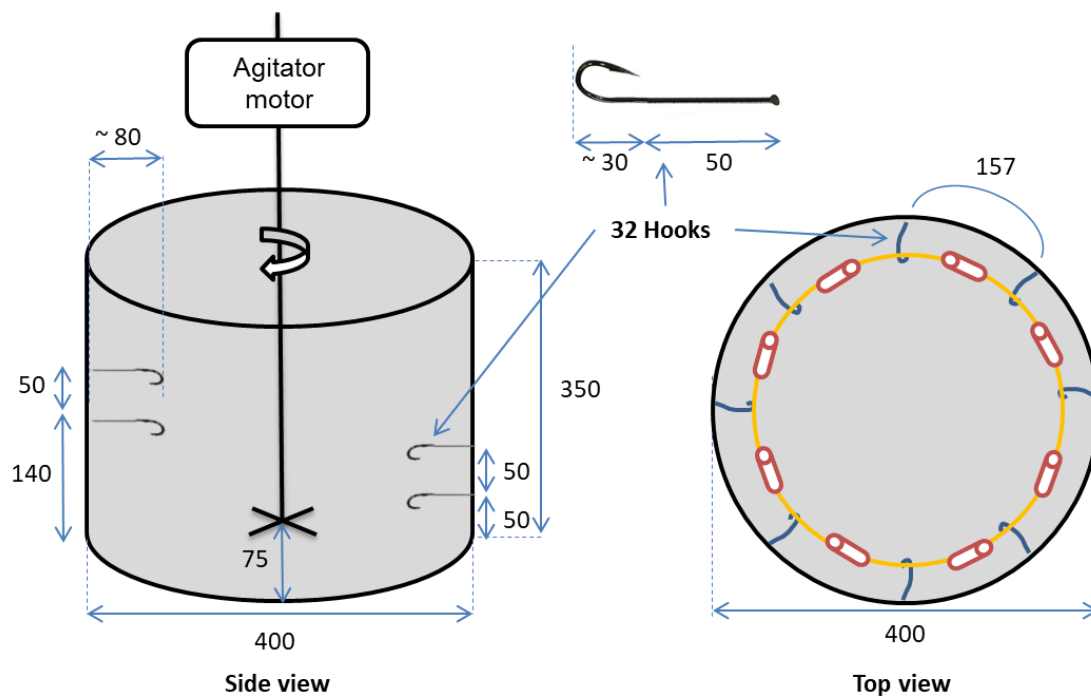
Supplementary Information

SI-1. Pesticide parameters for UHPLC-MS/MS analysis.

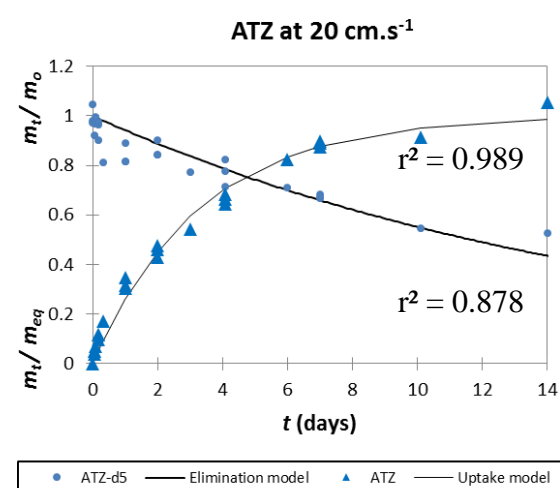
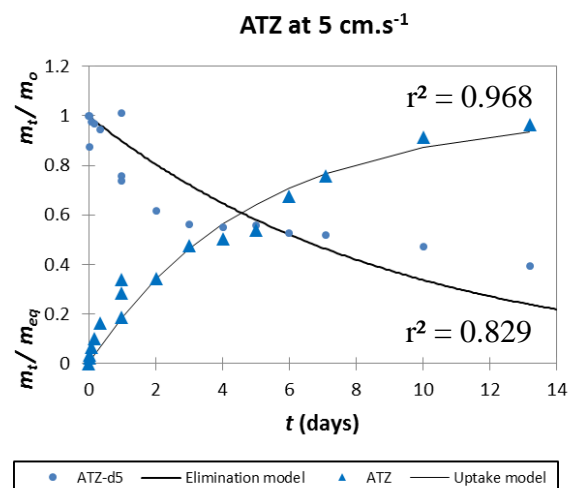
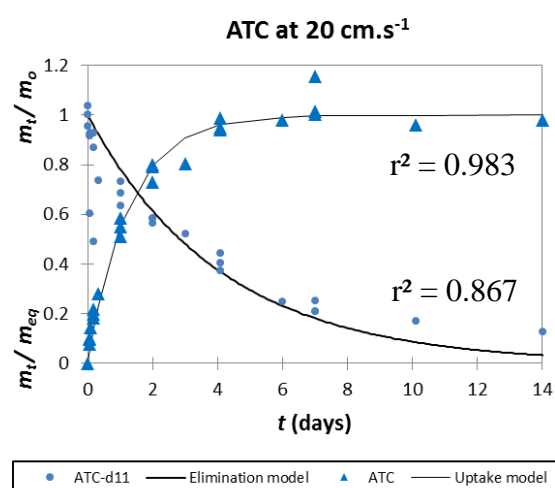
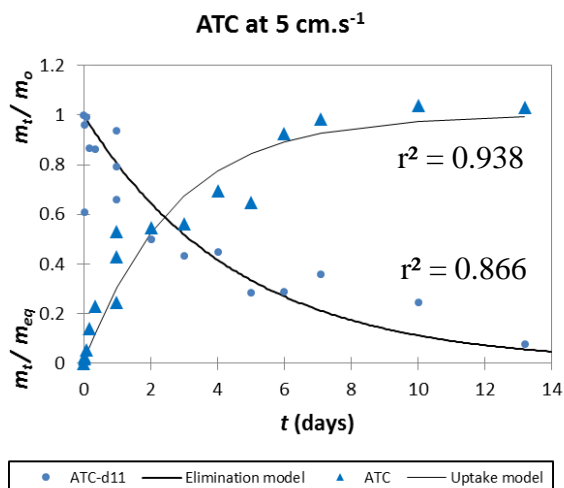
Compound	LOQ ($\mu\text{g L}^{-1}$)	Quantification transitions (m/z)	Declustering potential (V)	Collision energy (V)	Collision exit potential (V)
ATC	0.40	269.9 > 224.2 ;	31	15	16
		269.9 > 148.1	31	27	14
ATZ	0.10	215.9 > 174.1 ;	66	25	16
		215.9 > 104.1	66	41	8
AZS	0.02	404 > 372 ;	61	33	26
		404 > 344	61	35	28
BOS	0.20	343 > 307 ;	81	25	28
		343 > 140	81	29	8
CBZ	0.02	192 > 160 ;	56	25	16
		192 > 132	56	41	24
CFV	0.16	359 > 155 ;	76	17	20
		359 > 99	76	43	8
CPE	0.40	352 > 200 ;	45	30	38
		350 > 97	61	55	4
CPM	0.40	322 > 125 ;	71	29	22
		322 > 290	71	23	54
CTU	0.40	213 > 72 ;	51	25	12
		213 > 140	51	37	6
DCA	0.40	162 > 127 ;	51	31	24
		162 > 74	51	73	14
DCPMU	0.16	219 > 162 ;	66	21	26
		219 > 127	66	37	22
DFF	0.40	395 > 266 ;	86	35	28
		395 > 246	86	47	40
DIU	0.40	233 > 72 ;	46	51	6
		233 > 46	46	37	8
DMM	0.16	388 > 301 ;	76	31	36
		388 > 165	76	43	28
FNT	4.00	278 > 125 ;	71	29	22
		278 > 109	71	25	16
IMD	0.10	256 > 209.1 ;	61	23	38
		256 > 175.1	61	27	12
IPU	0.16	207 > 72 ;	51	37	8
		207 > 165	51	19	28
LINU	0.16	249 > 160 ;	61	25	32
		249 > 182	61	19	12
MTC	0.04	284.1 > 252.2 ;	46	21	20
		284.1 > 176.2	46	37	4
NFZ	0.40	304 > 284 ;	101	35	26
		304 > 88	101	61	16
PCM	1.60	284 > 256	76	25	46
SMZ	0.02	202.1 > 132.2 ;	56	29	10
		202.1 > 124.1	56	27	10
SPX	0.16	298 > 144 ;	51	31	8
		298 > 100	51	45	18
TBZ	0.16	308 > 70 ;	76	51	12
		308 > 125	76	57	12

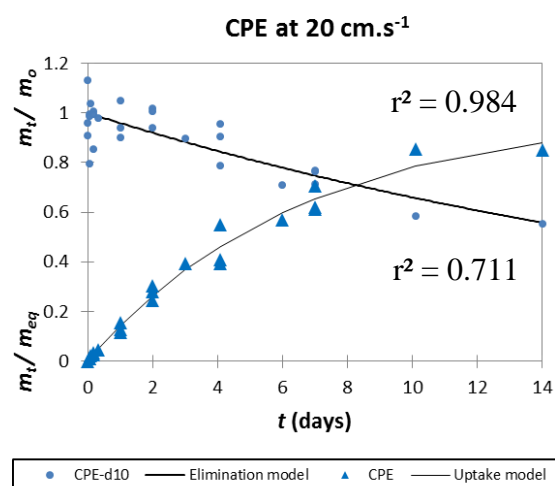
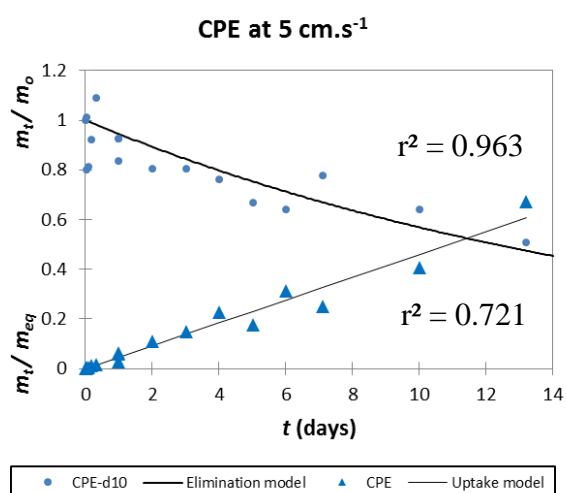
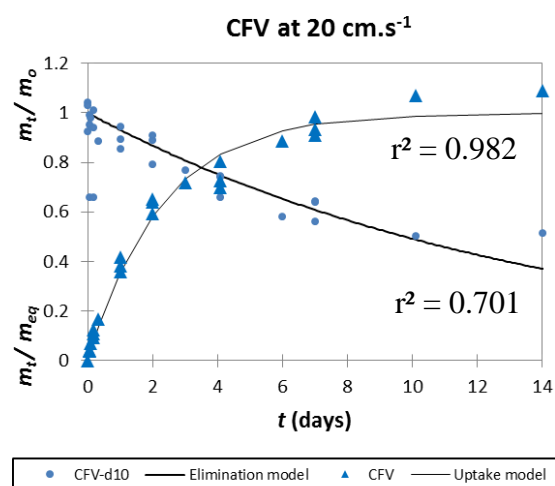
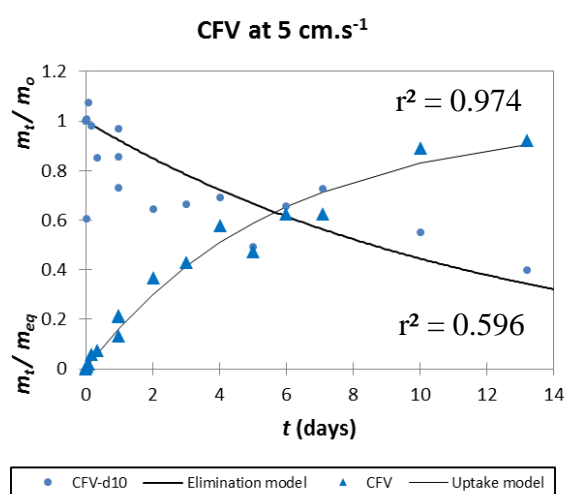
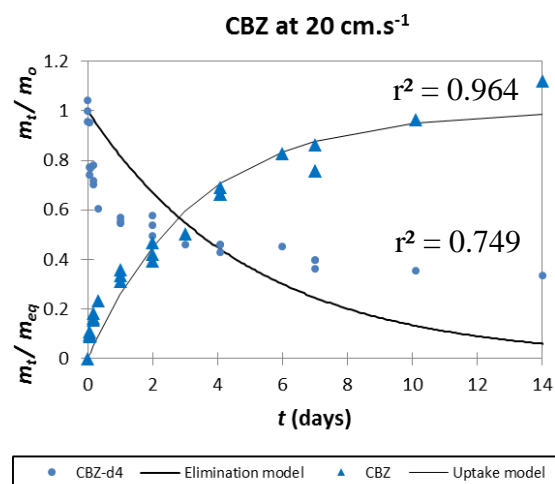
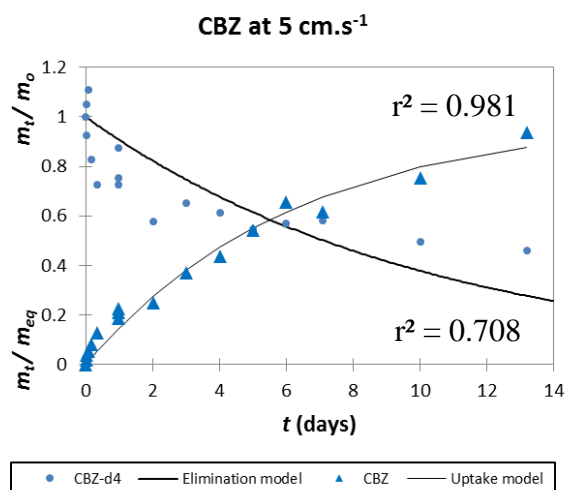
Compound	LOQ ($\mu\text{g L}^{-1}$)	Quantification transitions (m/z)	Declustering potential (V)	Collision energy (V)	Collision exit potential (V)
ATC-d11	0.40	281.1 > 235.1 ;	31	13	20
		281.1 > 159.1	31	29	12
ATZ-d5	0.10	221.06 > 179.1 ;	46	27	18
		221.06 > 101.1	46	35	18
CBZ-d4	0.02	196 > 164.1 ;	61	29	12
		196 > 138.1	61	41	8
CFV-d10	0.16	369.1 > 165.2 ;	56	19	10
		369.1 > 101.2	56	45	10
CPE-d10	0.40	360 > 199 ;	66	29	14
		360 > 163	66	21	14
CPM-d6	0.40	328 > 131.2 ;	66	31	8
		328 > 292.9	66	23	22
DFF-d3	0.40	398 > 268 ;	76	31	16
		398 > 248	76	49	20
DIU d6	0.40	239 > 78 ;	66	43	14
		239 > 52	66	37	10
FNT-d6	4.00	284 > 131 ;	61	27	18
		284 > 249	61	25	12
IPU-d6	0.16	213.1 > 78.3 ;	66	27	24
		213.1 > 171.2	66	21	10
LINU-d6	0.16	255 > 159.9 ;	56	25	8
		255 > 185	56	21	14
MTC-d6	0.04	290.1 > 258.1 ;	65	21	22
		290.1 > 182.2	65	35	32
SMZ-d5	0.02	207 > 129.1 ;	71	29	6
		207 > 137.1	71	27	8
TBZ-d6	0.16	314 > 72 ;	81	77	12
		314 > 125	81	53	10

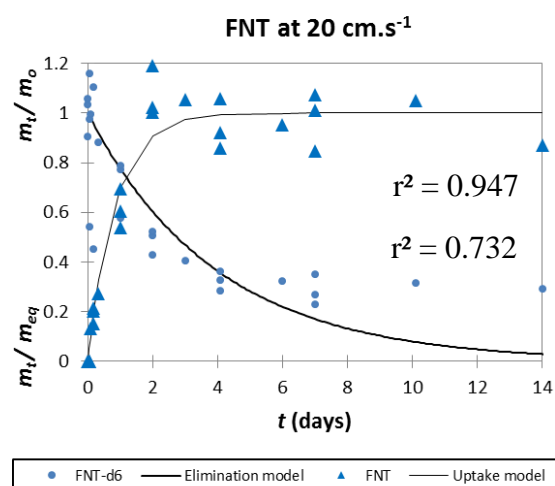
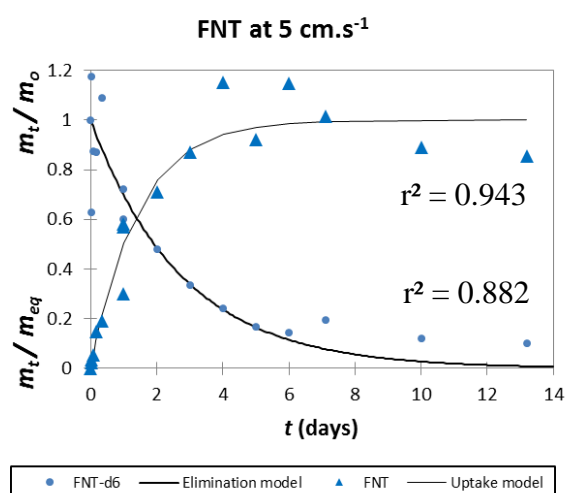
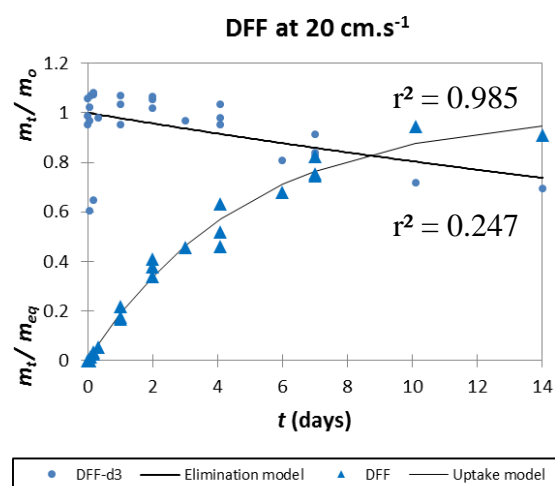
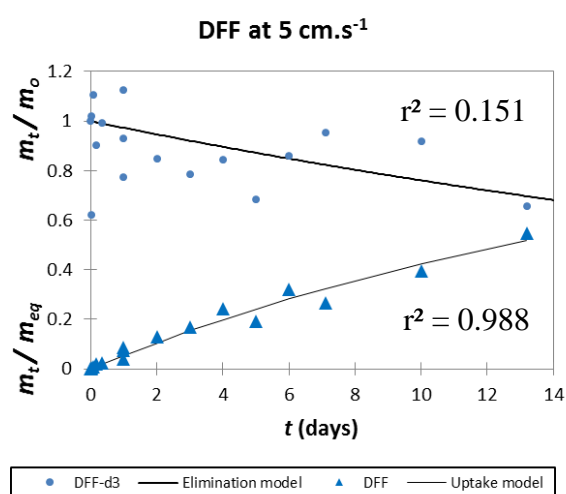
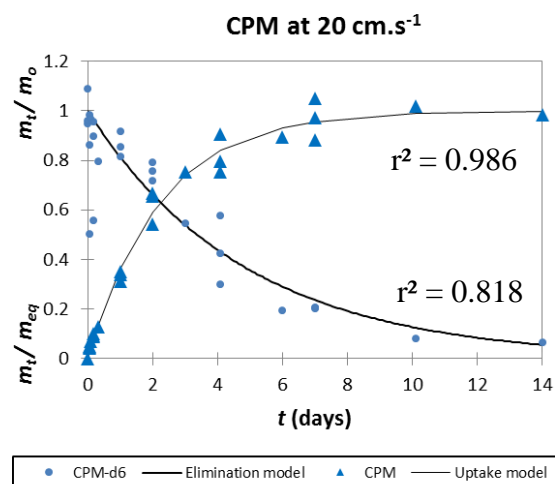
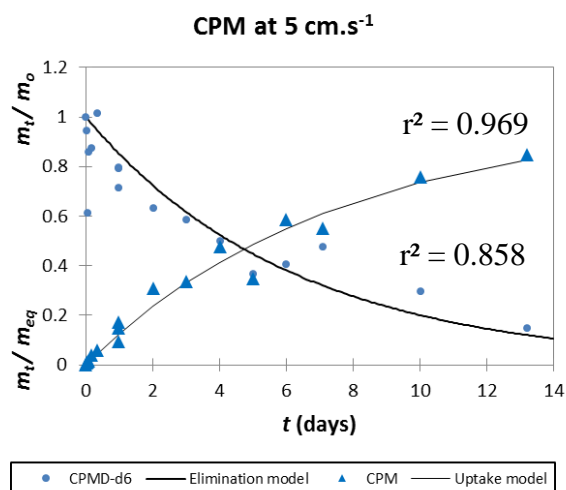
SI-2. Schematic diagrams (top and side view) of the laboratory static calibration system with dimensions in mm.

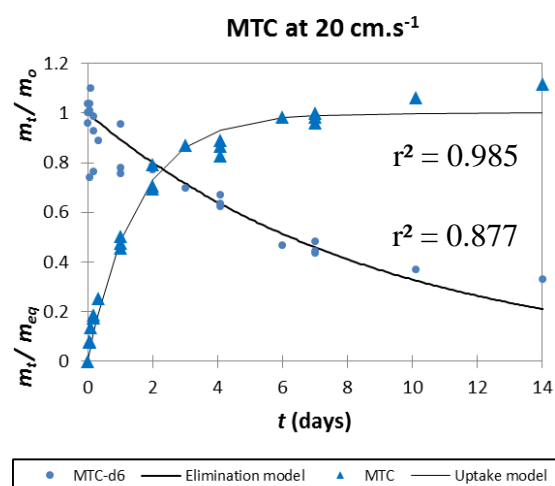
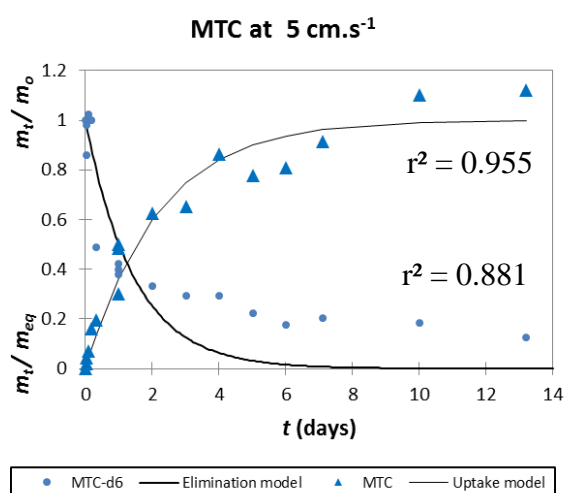
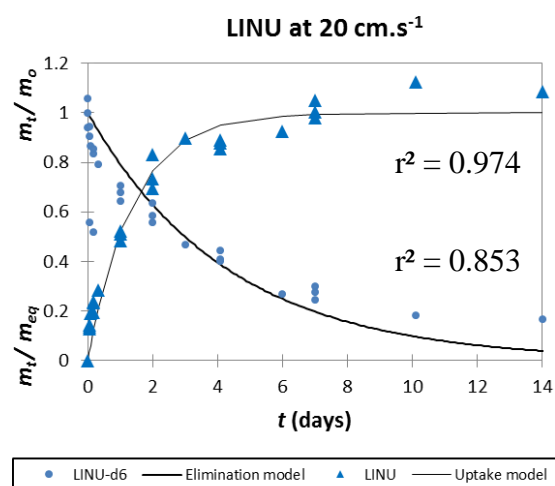
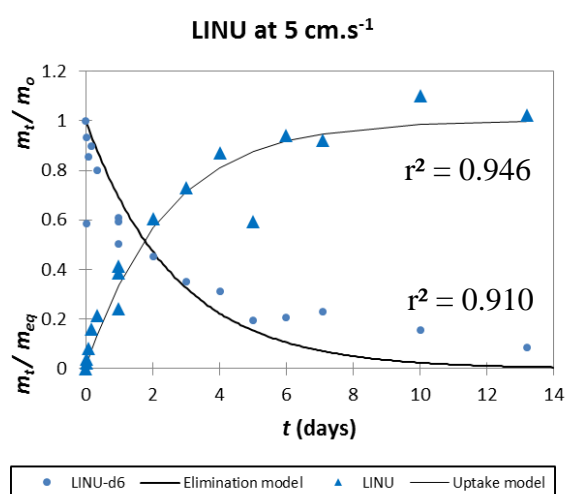
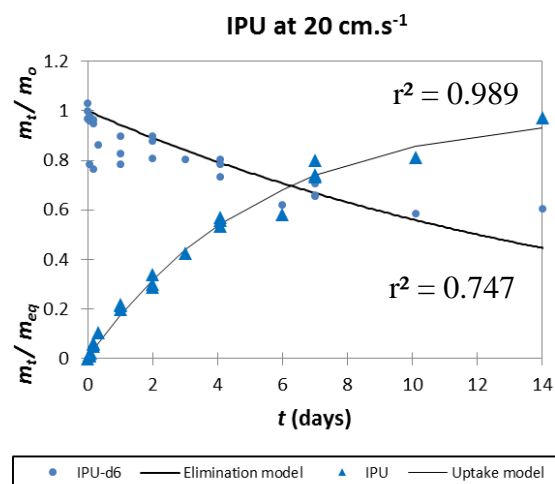
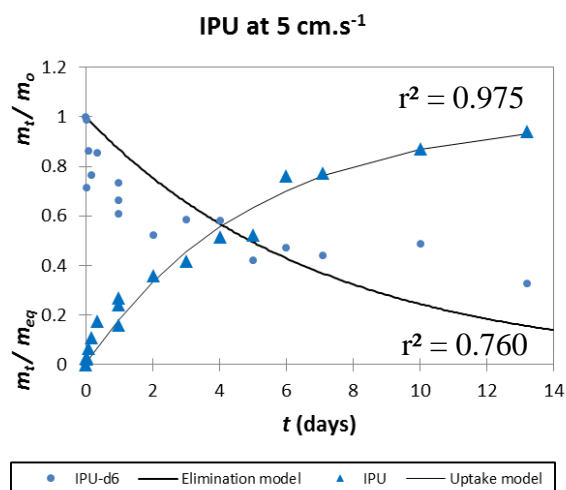


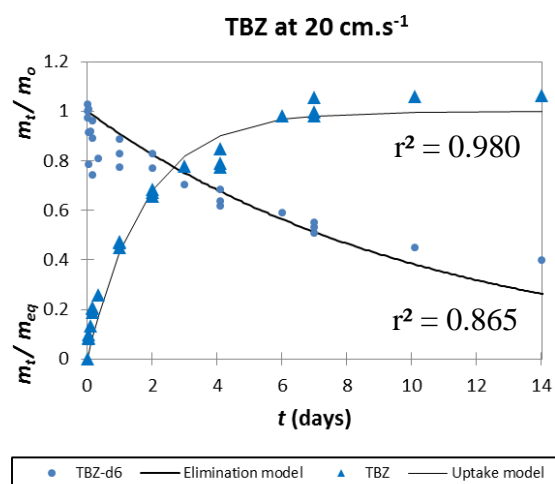
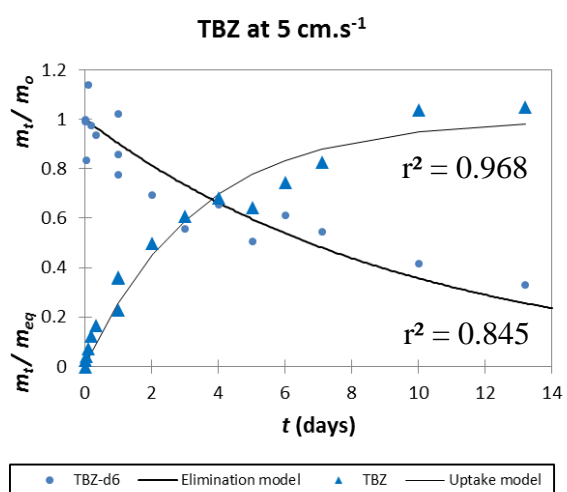
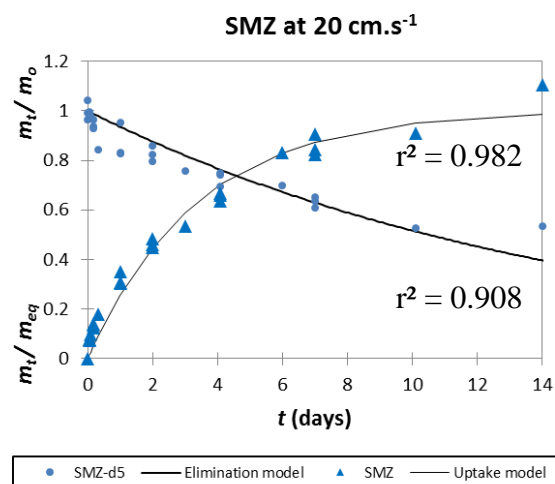
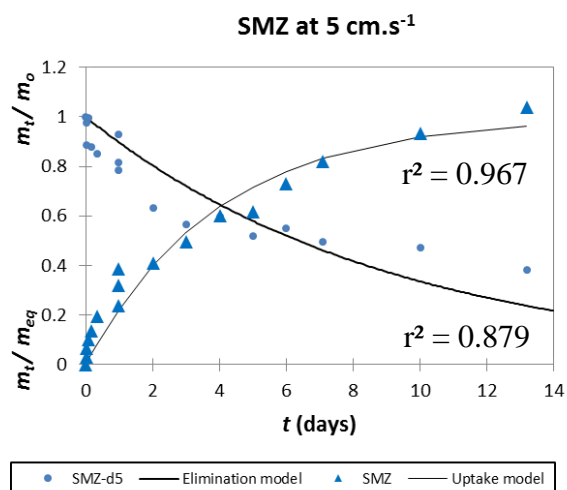
SI-3. Uptake of pesticides and release of corresponding deuterated pesticide
(candidate PRCs) by the silicone rods (SRs) at two flow velocities (5 and 20 $\text{cm}\cdot\text{s}^{-1}$).
Accumulated mass (m) is plotted relative to the initial mass for the release (m_0) and to the predicted equilibrium mass for the uptake (m_{eq}).



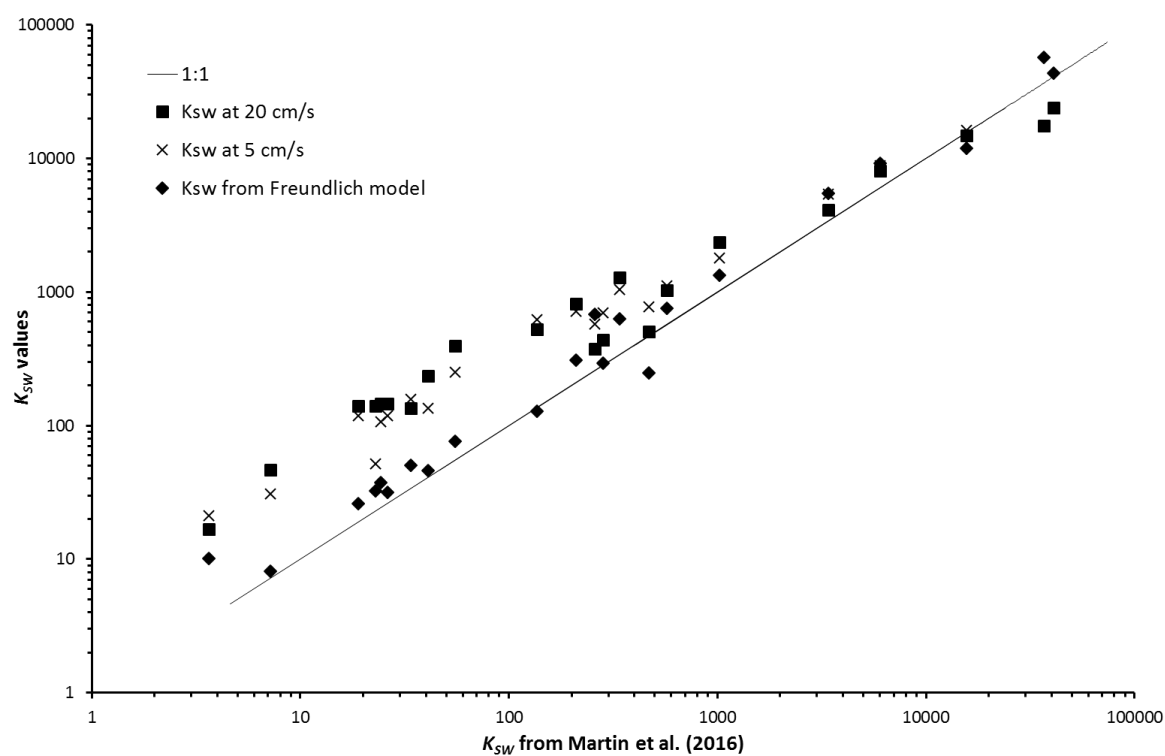








SI-4. Plot of K_{sw} values from the experiments at two flow velocities (Eq.7) and estimated by the Freundlich model ($K_{sw} = K_f C_w eq^{1/n-1}$ with parameters from Martin et al. [1]) at the concentration of this experiment against K_{sw} estimated in Martin et al. [1].



SI-5. Molecular properties (M , V_m , $\text{Log } D_w$) of pesticides.

Pesticide	M^a	V_m^a	$\text{Log } D_w^b$
	(g mol ⁻¹)	(cm ³ mol ⁻¹)	(m ² s ⁻¹)
ATC	269.8	240.9	-9.28
ATZ	215.7	163.1	-9.18
AZS	403.4	300.1	-9.34
BOS	342.2	262.1	-9.3
CBZ	191.2	137.5	-9.14
CFV	359.6	261.8	-9.30
CPE	350.6	236.8	-9.28
CPM	322.5	203.8	-9.24
CTU	212.7	184.5	-9.21
DCA	162.0	115.6	-9.09
DCPMU	219.1	152.1	-9.16
DFF	394.3	274.0	-9.31
DIU	233.1	178.6	-9.21
DMM	387.9	315.1	-9.35
FNT	277.2	202.8	-9.24
IMD	255.7	160.1	-9.18
IPU	206.3	196.3	-9.23
LINU	249.1	185.2	-9.21
MTC	283.8	257.8	-9.30
NFZ	303.7	208.8	-9.24
PCM	284.1	189.1	-9.22
SMZ	201.7	147.9	-9.16
SPX	297.5	308.2	-9.34
TBZ	307.8	268.1	-9.31

^a Predicted by ACD/Labs: <http://www.chemspider.com/>

^b Calculated from Hayduk and Laudie (1974)

SI-7. Spreadsheet file compiling results from the two calibration experiments for 24 pesticides and 13 candidate PRCs at two flow velocities (5 and 20 cm·s⁻¹). Accumulated mass of pesticides (*m*, ng) were not corrected by corresponding solvent back extraction recoveries (Table 1). Concentrations of pesticides in water (*C_w*) was expressed in µg L⁻¹.

References

- [1] Martin A, Margoum C, Randon J, Coquery M. 2016. Silicone rubber selection for passive sampling of pesticides in water. *Talanta* 160:306-313.
- [2] Rusina TP, Smedes F, Klanova J. 2010. Diffusion Coefficients of Polychlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons in Polydimethylsiloxane and Low-Density Polyethylene Polymers. *Journal of Applied Polymer Science* 116:1803-1810.
- [3] Rusina TP, Smedes F, Koblizkova M, Klanova J. 2010. Calibration of silicone rubber passive samplers: experimental and modeled relations between sampling rate and compound properties. *Environmental Science & Technology* 44:362-367.