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## Do pesticides degrade in surface water receiving runoff from agricultural catchments? Combining passive samplers (POCIS) and compound-specific isotope analysis

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1 **Do pesticides degrade in surface water receiving runoff from agricultural**  
2 **catchments?**

3 **Combining passive samplers (POCIS) and compound-specific isotope analysis**  
4  
5

6 Tetyana Gilevska<sup>1</sup>, Jeremy Masbou<sup>1</sup>, Baptiste Baumlin<sup>1</sup>, Betty Chaumet<sup>2</sup>, Cedric Chaumont<sup>3</sup>,  
7 Sylvain Payraudeau<sup>1</sup>, Julien Tournebize<sup>3</sup>, Anne Probst<sup>2</sup>, Jean Luc Probst<sup>2</sup>, Gwenaël Imfeld<sup>1\*</sup>  
8

9 <sup>1</sup> Université de Strasbourg, CNRS/ENGEES, ITES UMR 7063, Institut Terre et Environnement  
10 de Strasbourg, Strasbourg, France

11 <sup>2</sup> Laboratoire Ecologie fonctionnelle et Environnement, Université de Toulouse, CNRS, 31326  
12 Castanet Tolosan, France

13 <sup>3</sup> UR HYCAR, INRAE / Univ. Paris-Saclay, Antony, France  
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15 \*Correspondence  
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20 **Highlights:**

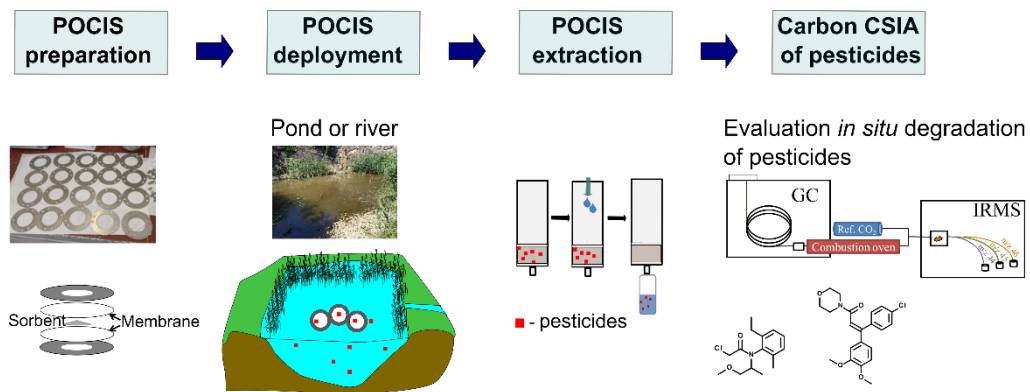
- 21 • POCIS-CSIA approach enables recording  $\delta^{13}\text{C}$  of pesticides at  $\text{ng.L}^{-1}$  range
- 22 • Uptake and extraction from POCIS cause no isotope effect for pesticides
- 23 •  $\delta^{13}\text{C}$  values recorded in water confirmed degradation of *S*-metolachlor in soil
- 24 •  $\delta^{13}\text{C}$  values indicate *in situ* degradation of dimethomorph Z in pond water
- 25 • Fresh applications of *S*-metolachlor were recorded by POCIS-CSIA approach

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29 **Graphical abstract (13 x 5 cm)**



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33

34 **Abstract**

35 Pesticides lead to surface water pollution and ecotoxicological effects on aquatic biota. Novel  
36 strategies are required to evaluate the contribution of degradation to the overall pesticide  
37 dissipation in surface waters. Here, we combined polar organic chemical integrative samplers  
38 (POCIS) with compound-specific isotope analysis (CSIA) to trace *in situ* pesticide degradation in  
39 artificial ponds and agricultural streams. The application of pesticide CSIA to surface waters is  
40 currently restricted due to environmental concentrations in the low  $\mu\text{g.L}^{-1}$  range, requiring  
41 processing of large water volumes. A series of laboratory experiments showed that POCIS  
42 enables preconcentration and accurate recording of the carbon isotope signatures ( $\delta^{13}\text{C}$ ) of  
43 common pesticides under simulated surface water conditions and for various scenarios.  
44 Commercial and in-house POCIS did not significantly ( $\Delta\delta^{13}\text{C}<1\%$ ) change the  $\delta^{13}\text{C}$  of pesticides  
45 during uptake, extraction, and  $\delta^{13}\text{C}$  measurements of pesticides, independently of the pesticide  
46 concentrations (1–10  $\mu\text{g.L}^{-1}$ ) or the flow speeds (6 or 14  $\text{cm.s}^{-1}$ ). However, simulated rainfall  
47 events of pesticide runoff affected the  $\delta^{13}\text{C}$  of pesticides in POCIS. In-house POCIS coupled  
48 with CSIA of pesticides were also tested under different field conditions, including three flow-  
49 through and off-stream ponds and one stream receiving pesticides from agricultural catchments.  
50 The POCIS-CSIA method enabled to determine whether degradation of *S*-metolachlor and  
51 dimethomorph mainly occurred in agricultural soil or surface waters. Comparison of  $\delta^{13}\text{C}$  of *S*-  
52 metolachlor in POCIS deployed in in a stream with  $\delta^{13}\text{C}$  of *S*-metolachlor in commercial  
53 formulations suggested runoff of fresh *S*-metolachlor in the midstream sampling site, which was  
54 not recorded in grab samples. Altogether, our study highlights that the POCIS-CSIA approach  
55 represents a unique opportunity to evaluate the contribution of degradation to the overall  
56 dissipation of pesticides in surface waters.

57 Keywords: Isotope analysis, pesticides, agricultural catchments, surface water, passive samplers

## 58 **1. Introduction**

59 The continuous and partially increasing use of pesticides in agriculture jeopardizes the ecological  
60 and chemical status of water resources and associated aquatic ecosystems, threatening human  
61 health (Mateo-Sagasta et al., 2017). In recent decades, efforts to reduce the use of pesticides have  
62 mostly failed, while global warming is expected to expand the prevalence of pests in the future  
63 and increase the societal dependence on chemical crop protection (Stokstad, 2018). In this  
64 context, novel strategies are needed to track the occurrence and transformation of pesticides in  
65 the environment and to guide the deployment of efficient and targeted strategies to reduce the  
66 use and harmfulness of pesticides.

67 The extent of pesticide transport from the application site toward surface waters depends on the  
68 complex interplay between pesticides and soil properties, hydroclimatic conditions, and site  
69 characteristics (e.g., drainage system) (Reichenberger et al., 2007). Small streams may be  
70 particularly at high risk of pesticide contamination because of adjacent agricultural areas, low  
71 dilution potential, and large runoff inputs after heavy rainfall events (Posthuma et al., 2020;  
72 Szöcs et al., 2017; Taghavi et al., 2011, 2010). Artificial ponds and constructed wetlands in  
73 agricultural landscapes are also often the first structures intercepting pesticide runoff events  
74 following applications (Reichenberger et al., 2007, Imfeld et al., 2021). Therefore, runoff events  
75 in agricultural catchments drive pesticide peaks in surface waters (Reichenberger et al., 2007;  
76 Taghavi et al., 2010). Overall, the interplay of biological (e.g., microbial degradation, plant  
77 transformation), chemical (e.g., hydrolysis, photolysis), and physical (e.g., sorption, dispersion)  
78 processes in aquatic systems may favor pesticide dissipation or storage in surface waters

79 (McKnight et al., 2015; Passeport et al., 2011a, 2011b). Aquatic systems, such as ponds,  
80 wetlands, and streams may thus limit pesticide inputs into freshwater, although little is known  
81 about the *in situ* processes of pesticide dissipation in environmental compartments.

82 To estimate pesticide dissipation in surface waters, especially in ponds and wetland systems, a  
83 mass balance of the pesticides and their transformation products in different compartments is  
84 typically used (Chaumet et al., 2021). However, based on concentration data, it is not possible to  
85 assess the contribution of both degradative (i.e., biotic or abiotic degradation) and non-  
86 degradative (i.e., dilution, sorption) processes driving pesticide dissipation in surface waters, as  
87 both types of processes lead to a concentration decrease. In contrast, compound-specific isotope  
88 analysis (CSIA) allows teasing apart dissipation processes, as it is directly correlated to  
89 degradation (Hunkeler et al., 2008; Meckenstock et al., 1999). Due to the slower reaction rate of  
90 bonds containing heavier isotopes, changes in  $\delta^{13}\text{C}$  of the pollutant can be directly linked to  
91 degradation by a Rayleigh relationship (Urey, 1947). CSIA was first and widely applied to  
92 examine the degradation of highly concentrated industrial chemicals in aquifers (Hunkeler et al.,  
93 2008). CSIA applications to micropollutants in surface waters, including pesticides and  
94 pharmaceuticals, are currently constrained due to lower environmental concentrations of non-  
95 point pollution (Elsner and Imfeld, 2016). This issue can be partly overcome by collecting,  
96 processing, and extracting large water volumes to apply CSIA to micropollutants (Schreglmann  
97 et al., 2013; Torrentó et al., 2019). However, this may lead to a large matrix effect due to the  
98 limited extraction selectivity of classical extraction methods (Elsner and Imfeld, 2016),  
99 underscoring a need for alternative sampling strategies.

100 In surface water, pesticide concentrations are typically monitored by grab sampling and  
101 automated sampling, providing a snapshot of the concentrations (Rabiet et al., 2010). However,  
102 episodic events with pesticide concentration peaks associated with acute ecotoxicological risks  
103 may be overlooked (Polard et al., 2011). In this context, the passive sampling technique has been  
104 widely used to integrate mean concentrations of organic pollutants over extended sampling  
105 periods (<56 days) (Alvarez et al., 2004; Bernard et al., 2018a) and to preconcentrate  
106 micropollutants, allowing their detection in surface waters, even in trace concentration (11–68  
107  $\text{pg.L}^{-1}$ ) (Harman et al., 2008). Polar organic chemical integrative sampling (POCIS)  
108 (Vermeirssen et al., 2012) is one of the most common passive sampling techniques used to  
109 record and preconcentrate organic compounds in water phase. The effect of pesticide  
110 concentrations on POCIS sampling rates, flow speeds, and water matrices with different  
111 dissolved organic carbon (DOC) concentrations has been evaluated in several studies (Dalton et  
112 al., 2014; Gallé et al., 2020; Mazzella et al., 2007; Miège et al., 2012). To date, POCIS and CSIA  
113 have not been combined to evaluate micropollutant degradation in surface waters over extended  
114 periods.

115 In this study, we coupled POCIS and CSIA to investigate pesticide degradation in surface waters.  
116 A series of laboratory experiments were designed to evaluate the ability of POCIS to concentrate  
117 and accurately record carbon isotope signatures ( $\delta^{13}\text{C}$ ) of selected herbicides, i.e., atrazine,  
118 terbutryn, *S*-metolachlor, and fungicides, i.e., metalaxyl, dimethomorph, and tebuconazole. The  
119 selected pesticides cover a wide range of frequently detected herbicides and fungicides that are  
120 potentially toxic to a broad range of organisms (Fang et al., 2019; Grégoire et al., 2010; Zubrod  
121 et al., 2019). We evaluated the effect of the matrices (distilled water (DI) and pond water with  
122 high DOC concentrations), pesticide concentrations (1–10  $\mu\text{g.L}^{-1}$ ), flow speed conditions (6–14

123 cm.s<sup>-1</sup>), and runoff events (combined effect of higher concentration 10 µg.L<sup>-1</sup> and 14 cm.s<sup>-1</sup>) on  
124 δ<sup>13</sup>C values of selected pesticides for commercial and in-house (cost-effective) POCIS.  
125 Following validation in the laboratory, field deployments served as a benchmark to assess the  
126 potential of POCIS for a broad CSIA application of pesticides in agricultural catchments. POCIS  
127 was deployed in three artificial flow-through and off-stream ponds, characterized by different  
128 sizes, DOC concentrations, vegetation covers, types of surrounding agriculture, and pesticide  
129 inputs, in different French regions. POCIS was also deployed in a river tributary in an  
130 agricultural catchment.

## 131 **2. Materials and methods**

### 132 **2.1. Chemicals**

133 Solvents (dichloromethane (DCM), acetonitrile (ACN), ethyl acetate (EtOAc), and methanol  
134 (MeOH)) were HPLC grade purity (>99.9%) and purchased from Sigma–Aldrich. Analytical  
135 standards (purity >98%) of atrazine, metalaxyl, *S*-metolachlor, *S*-metolachlor D-11, terbutryn,  
136 tebuconazole, and dimethomorph (*Z* and *E* isomers) were purchased from Sigma–Aldrich,  
137 PESTANAL. Metalaxyl, dimethomorph, and *S*-metolachlor from commercially available  
138 formulations and their isotope signatures used in the study are listed in Table S1. Pesticide stock  
139 solutions were prepared in ACN at 1 g. L<sup>-1</sup> and stored at -18 °C. An intermediate solution in DI  
140 water for spiking during laboratory experiments was prepared according to pesticide solubilities.

### 141 **2.2. POCIS preparation**

142 Commercial POCIS was purchased from AFFINISEP. Empty solid-phase extraction (SPE)  
143 cartridges were purchased from AFFINISEP or Thermo Scientific. In-house POCIS was



144 prepared using 250 mg of HyperSep™ Retain (Thermo Scientific) sorbent (equivalent to Oasis  
145 HLB sorbent (Waters)). The sorbent was placed between two microporous polyethersulfone  
146 (PES) membranes (0.1 µm pore size, 90 mm, outside diameter, Pall Corporation) and fixed  
147 tightly with two stainless steel rings (90 mm, outside diameter) and three screws (Figure S1).  
148 The surface areas of the in-house and commercial POCIS membranes were identical, i.e., 45.8  
149 cm<sup>2</sup>.

### 150 2.3. Calculation of sampling rates

151 Ficks law describes POCIS uptake of a pollutant, assuming a linear uptake of dissolved  
152 chemicals on the POCIS sorbent (Alvarez et al., 2004; Vrana et al., 2005). The duration of the  
153 linear uptake phase depends on external parameters (concentration, flow speed, etc.), and sorbent  
154 and compound physicochemical characteristics. In the uptake phase, the sampling rate ( $R_s$ )  
155 (L.day<sup>-1</sup>) is estimated with Equation 1:

$$R_s = \frac{N_{POCIS}}{C_w \times t} \quad \text{Equation 1}$$

156 where  $t$  is the exposure time (day),  $C_w$  is the time-weighted average concentration (µg. L<sup>-1</sup>), and  
157  $N_{POCIS}$  is a pollutant amount in POCIS (µg), which is molecule-dependent and influenced by  
158 environmental conditions.  $N_{POCIS}$  (µg) and sorbent mass ( $M_{POCIS}$ ) (g) define the pollutant  
159 concentration ( $C_{POCIS}$ ) (µg.g<sup>-1</sup>) in POCIS:

$$C_{POCIS} = \frac{N_{POCIS}}{M_{POCIS}} \quad \text{Equation 2}$$

160 The uptake phase is followed by an equilibrium partitioning phase with constant compound  
161 concentrations until the sorption capacity is reached.

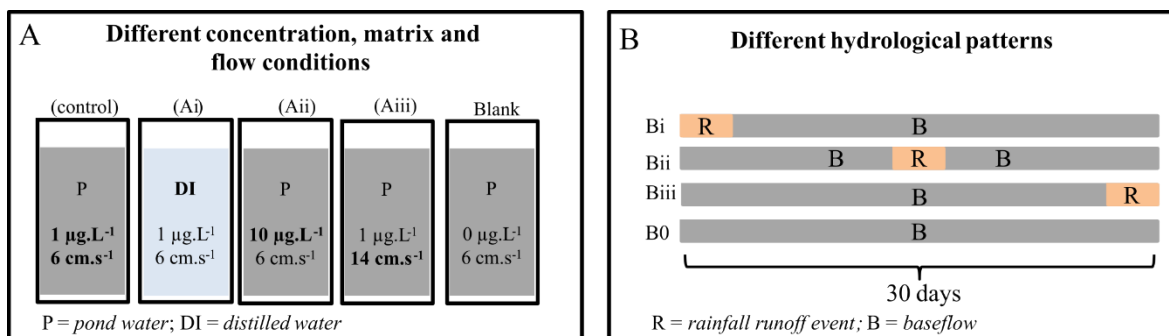
162 To mimic different flow speeds in all laboratory experiments, stirring with a magnetic stir bar  
163 was used. The stirring speed (round per minute, rpm) was calculated using the Reynold numbers  
164 calculation to reach the targeted flow speed:

$$\text{rpm} = \frac{v \times L \times \mu}{u \times D^2 \times \rho} \times 60 \quad \text{Equation 3}$$

165 where  $L$  (m) is the diameter of the beaker,  $u$  ( $\text{m}^2 \cdot \text{s}^{-1}$ ) is the kinematic velocity,  $v$  ( $\text{m} \cdot \text{s}^{-1}$ ) is the  
166 flow speed,  $D$  (cm) is the length of the stirring bar,  $\rho$  ( $\text{g} \cdot \text{cm}^3$ ) is the density, and  $\mu$  ( $\text{g} \cdot \text{cm} \times \text{min}$   
167  $^{-1}$ ) is the dynamic velocity.

#### 168 **2.4. Experimental setup**

169 Two experiments, A and B, were set up to evaluate the sampling rates ( $R_s$ ) and associated carbon  
170 isotope fractionation ( $\Delta\delta^{13}\text{C}$ ) of selected pesticides for commercial and in-house POCIS. The  
171 water (~300 L) for Experiment A was collected from a stormwater pond in Rouffach (France) on  
172 19<sup>th</sup> February 2020 and for Experiment B on 25<sup>th</sup> May 2020. The pond water was filtered  
173 through an 11  $\mu\text{m}$  paper filter (Whatman®) to remove organic and inorganic particles and kept in  
174 the dark at 4°C. The physicochemical properties of the pond water are described in the  
175 Supporting Information (SI) (Table S6). Both experiments were set up under static renewal  
176 calibration, i.e., a closed system with a renewal of the pesticide solution at certain interval times  
177 (Figure 1).



178

179 Figure 1. Pesticide uptake experiments coupling polar organic chemical integrative samplers  
 180 (POCIS) and compound-specific isotope analysis (CSIA). (A) Experiment A included a control  
 181 treatment (control) with pond water spiked with 1 µg. L<sup>-1</sup> of atrazine, metalaxyl, S-metolachlor,  
 182 terbutryn, tebuconazole, and dimethomorph (Z and E isomers) and stirred at 6 cm.s<sup>-1</sup> flow speed;  
 183 (Ai) a treatment with distilled water (DI) spiked with 1 µg. L<sup>-1</sup> of the pesticide mixture and 6  
 184 cm.s<sup>-1</sup> flow speed; (Aii) a treatment with pond water spiked with 10 µg. L<sup>-1</sup> of the pesticide  
 185 mixture and 6 cm.s<sup>-1</sup> flow speed; and (Aiii) a treatment with pond water spiked with 1 µg. L<sup>-1</sup> of  
 186 the pesticide mixture and 14 cm.s<sup>-1</sup> flow speed, and a blank treatment without the addition of  
 187 pesticides. (B) Experiment B simulates different hydrological patterns Bi, Bii, Biii, and B0 with  
 188 two alternating conditions: R-runoff conditions – 14 cm.s<sup>-1</sup> flow speed, and 10 µg. L<sup>-1</sup> of five  
 189 pesticides (metalaxyl (Ridgold<sup>®</sup> F formulation), terbutryn, tebuconazole, S-metolachlor D-11,  
 190 and atrazine); and B – baseflow conditions – 6 cm.s<sup>-1</sup> flow speed, and 1 µg. L<sup>-1</sup> of four pesticides  
 191 (metalaxyl (Sigma–Aldrich standard), terbutryn, tebuconazole, and S-metolachlor).

192 *Experiment A* (Figure 1A) evaluated the effect of (i) matrices (distilled (DI) and pond water (P)),  
 193 (ii) pesticide concentrations, and (iii) flow speeds (6 and 14 cm.s<sup>-1</sup>) representative of baseflow  
 194 and runoff event conditions within the stormwater pond. Experiment A consisted of five 5 L  
 195 tanks containing eight commercial POCISs each (Figure 1A). A control treatment (Figure 1A-

196 control) with pond water was spiked with  $1 \mu\text{g. L}^{-1}$  of atrazine, metalaxyl, *S*-metolachlor,  
197 terbutryn, tebuconazole, and dimethomorph (*Z* and *E* isomers) and stirred at  $6 \text{ cm.s}^{-1}$  flow speed  
198 ( $350 \text{ rpm}$ ). Four treatments were compared to the control and were set up (Ai) with distilled  
199 water (DI) spiked with  $1 \mu\text{g. L}^{-1}$  of the pesticide mixture at  $6 \text{ cm.s}^{-1}$  (Figure 1A); (Aii) with pond  
200 water (Rouffach (France)) spiked with  $10 \mu\text{g. L}^{-1}$  of the pesticide mixture at  $6 \text{ cm.s}^{-1}$  (Figure 1A);  
201 and (Aiii) with pond water spiked with  $1 \mu\text{g. L}^{-1}$  of the pesticide mixture at  $14 \text{ cm.s}^{-1}$  ( $750 \text{ rpm}$ )  
202 (Figure 1A). An unspiked blank treatment with pond water at  $6 \text{ cm.s}^{-1}$  evaluated the background  
203 pesticide concentration on POCIS from the pond water and cross-contamination during the  
204 experiment (Figure 1A). Tanks were maintained at laboratory temperature ( $20 \pm 1 \text{ }^\circ\text{C}$ ) and  
205 covered with aluminium foil to prevent photodegradation and algal development. Water was  
206 changed in each tank after a day to determine the decrease in concentration. Following this  
207 assessment, the water was changed in each tank every 3-4 days, ensuring a constant pesticide  
208 concentration during the experiment (Table S2). Duplicate POCIS samples were collected from  
209 each treatment on Days 5, 10, 20, and 30. In parallel, water ( $100 \text{ mL}$ ) was collected 15 minutes  
210 after spiking and at the end of each exposure period for measuring pesticide concentrations and  
211 weekly ( $4 \text{ L}$ ) for CSIA of pesticides.

212 *Experiment B* examined the influence of the alternation of hydrological patterns, i.e., base flow  
213 and runoff events, with consecutive high flow speed and pesticide concentrations and low flow  
214 speed and pesticide concentrations, on the pesticide uptake capacity of both commercial and in-  
215 house (homemade) POCIS to reduce operation costs (Figure 1B). Higher pesticide concentration  
216 during runoff events mimicked transient pesticide peaks occurring after rainfall and lasting up to  
217 several hours in agricultural catchments. Three commercial and three in-house POCISs for each  
218 hydrological pattern were immersed consecutively in  $5 \text{ L}$  tanks during runoff conditions and in

219 24 L tanks during baseflow conditions. Four treatments, each lasting 30 days, were conducted in  
220 parallel under baseflow conditions, i.e., low flow and low pesticide concentration (6 cm.s<sup>-1</sup> flow,  
221 1 µg<sup>-1</sup> mixture of metalaxyl (Sigma–Aldrich), terbutryn, tebuconazole, and *S*-metolachlor)  
222 (Figure 1B). Treatment B0 served as a control with permanent baseflow conditions. Treatments  
223 Bi, Bii, and Biii involved a 24-h simulated runoff event (14 cm.s<sup>-1</sup> flow, with 10 µg. L<sup>-1</sup> of each  
224 pesticide in the mixture) on Day 1 (treatment Bi), Day 15 (treatment Bii), or Day 30 (treatment  
225 Biii). During the simulated runoff event, water was spiked with 10 µg. L<sup>-1</sup> mixture of metalaxyl  
226 (Ridgold<sup>®</sup> F), terbutryn, tebuconazole, *S*-metolachlor D-11, and atrazine.

227 Different initial isotopic composition signatures of metalaxyl (Sigma–Aldrich, δ<sup>13</sup>C = -31.5 ±  
228 0.1‰ and Ridgold<sup>®</sup> F, δ<sup>13</sup>C = -29.5 ± 0.3‰) (Table S1) in the runoff and baseflow tanks were  
229 used to evaluate the effect of a runoff event on the δ<sup>13</sup>C of metalaxyl. To compare the uptake  
230 during the experiment, *S*-metolachlor D-11 was spiked in the runoff tanks to match the molecular  
231 structure of *S*-metolachlor in the baseflow tank. A fresh pesticide mixture in pond water was  
232 prepared every 6 days in the baseflow tank to maintain the pesticide concentration during the  
233 experiment. The pesticide mixture in the runoff tanks was freshly prepared before each POCIS  
234 immersion. All POCIS were collected after 30 days of immersion. Water (100 mL) was collected  
235 before and after each period of POCIS immersion for analysis of pesticide concentrations.

## 236 **2.5.Deployment of POCIS in surface waters**

237 POCIS were deployed in triplicate for 1 to 3 consecutive periods of 28 days in two flow-through  
238 ponds (Rouffach Pond (RP), Bassioué Pond (BP)), in the off-stream pond (Rampillon Pond  
239 (RLP), and one river (Rupt de Mad (RM) with constant high-flow and lower DOC than in the

240 ponds. A detailed comparison between ponds and river with pictures of deployment positions of  
241 POCIS and water phycochemical properties can be found in SI (Table S6, and S7, section S2.1).

## 242 **2.6.Pesticide extraction from POCIS and water samples**

243 Water samples were transported in coolers, immediately filtered through 0.45- $\mu\text{m}$  glass filter  
244 membranes, and stored at 4 °C until analysis. Grab water samples were preconcentrated using an  
245 AutroTrace 280 SPE system (Dionex® 160) with SolEx C18 cartridges (1 g, Dionex®) (Elsayed  
246 et al., 2014). Briefly, extraction cartridges were washed with ethanol (5 mL), rinsed with ACN (5  
247 mL), conditioned with deionized water (10 mL), loaded with the samples (10 mL.  $\text{min}^{-1}$ ), and  
248 dried under nitrogen flux for 10 min. The target molecules were eluted with 5 mL of EtOAc  
249 followed by 5 mL of ACN. Extracts were evaporated to dryness under a gentle stream of  
250 nitrogen and reconstituted in 0.5 mL of ACN prior to concentration analysis and CSIA.

251 POCISs were transported on ice to the laboratory and generally extracted within 15 h after  
252 collection or frozen at -18 °C before extraction. Each POCIS was placed into a separate plastic  
253 bag to protect the membrane from damage and prevent drying. Each POCIS was carefully  
254 opened to transfer the sorbent into an empty solid-phase extraction (SPE) cartridge and covered  
255 from both sides by HDPE frits (AFFINISEP or Thermo Scientific). Samples were eluted using  
256 the SPE procedure (Lissalde et al., 2011). Briefly, cartridges were dried under a gentle stream of  
257 nitrogen for 20 min. This prolonged drying allowed removing all the water from the sorbent  
258 taken up from POCIS, while enabling the transfer of wet sorbent. Pesticides were then eluted (5  
259 mL.  $\text{min}^{-1}$ ) with successive 3 mL volumes of 100% MeOH and MeOH:EtOAc, 75:25 (v/v).  
260 Extracts were evaporated up to dryness under a gentle stream of nitrogen and reconstituted in 0.5  
261 mL of ACN. For some samples, an additional preconcentration step (up to 10 times) by solvent

262 evaporation under nitrogen enabled CSIA measurements. After extraction, the POCIS sorbent  
263 was dried and weighed to determine  $M_{POCIS}$  (Equation 2).

## 264 **2.7. Chemical analysis**

### 265 **2.7.1. Hydrochemistry**

266 Conductivity, pH, dissolved oxygen concentration and redox conditions were directly measured  
267 in the ponds and river water using WTW multi 350i sensors (Rouffach and Rupt de mad) or  
268 AquaTROLL (Bassioué Pond). The hydrochemical composition of the water was analysed by  
269 ionic chromatography (IC) and inductively coupled plasma atomic emission spectroscopy using  
270 ISO laboratory procedures (Table S7), as described elsewhere (Lucas et al., 2010).

### 271 **2.7.2. Pesticide quantification**

272 Pesticides were analysed with a gas chromatograph (GC, Trace 1300, ThermoFisher Scientific)  
273 coupled to a mass spectrometer (MS, ISQ™, ThermoFisher Scientific). Chromatographic  
274 separation was performed with a TG-5MS column (30 m × 0.25 mm ID, 0.25 μm film  
275 thickness). *S*-metolachlor D-11 or atrazine D-5 were systematically used as internal standards.  
276 Additional parameters are described in SI (Table S1). All samples were diluted to be within the  
277 linear range (100 μg.L<sup>-1</sup> to 1 mg.L<sup>-1</sup>).

### 278 **2.7.3. CSIA of pesticides**

279 CSIA measures the ratio of a heavy isotope of an element (e.g., <sup>13</sup>C) to the light stable isotope  
280 (e.g., <sup>12</sup>C) for individual compounds. All isotopic measurements are reported in delta notation :

$$\delta^{13}\text{C} = \left[ \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{sample}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{standard}}} - 1 \right] \quad \text{Equation 4}$$

281 where  $\delta^{13}\text{C}$  is the isotopic value (‰),  $\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{sample}}$  is the ratio of heavy to light isotopes in the  
282 sample, and  $\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{standard}}$  is the ratio of heavy to light isotopes in the standard on an  
283 international isotopic scale. Carbon isotope signatures ( $\delta^{13}\text{C}$ ) of pesticides were measured using  
284 a GC-C-IRMS system consisting of a TRACE™ Ultra Gas Chromatograph (ThermoFisher  
285 Scientific) coupled via a GC IsoLink/Conflow IV interface to an isotope ratio mass spectrometer  
286 (DeltaVplus, ThermoFisher Scientific). Chromatographic separation was performed on a TG-  
287 5MS column (60 m × 0.25 mm ID, 0.25 μm film thickness). Samples were injected in  
288 split/splitless modes, depending on pesticide concentration, with an injection volume of 2 μL and  
289 injector temperature of 250 °C. Samples were injected in triplicate, and  $\delta^{13}\text{C}$  values are reported  
290 as the arithmetic mean. A laboratory standard of benzene, toluene, ethylbenzene, and xylene  
291 (BTEX) standard mix was injected at the beginning of each session to check the conversion  
292 performance of the instrument.  $\delta^{13}\text{C}$  of pesticide standards were calibrated relative to Vienna  
293 Pee Dee Belemnite (VPDB) scale with EA-IRMS (Flash EA IsoLink™ CN IRMS, Thermo  
294 Fisher Scientific) using a two- point calibration with international reference materials AIEA600,  
295 USGS40, and USGS41. Standard injections with known isotopic signatures of atrazine,  
296 metalaxyl, S-metolachlor, terbutryn, tebuconazole, and dimethomorph (Z and E isomers) (Table  
297 S1) were injected every six samples to ensure the accuracy of the measurements. The  
298 reproducibility of  $\delta^{13}\text{C}$  measurements ranged from ± 0.4 ‰ to ± 0.6 ‰.



299 Carbon isotope fractionation ( $\Delta\delta^{13}\text{C}$ ) <1 ‰ for pesticide standards before and after uptake and  
300 extraction from POCIS was considered not significant in all laboratory experiments based on the  
301 reproducibility of measured pesticides (Sherwood Lollar et al., 2007).

302 The extent of biodegradation (B) (%) was calculated using isotope fractionation values  $\varepsilon_{bulk,C}$   
303 according to Equation 5.

$$B = \left( 1 - \left( \frac{\delta^{13}\text{C}(t) + 1}{\delta^{13}\text{C}_0 + 1} \right)^{\frac{1}{\varepsilon_{bulk,C}}} \right) \times 100 \quad \text{Equation 5}$$

#### 304 **2.7.4. Statistical analysis**

305  $R_s$  values were compared among treatments using the Kolmogorov–Smirnov test of normality.  
306 Depending on data normality, data were compared using one-way ANOVA, followed by Tukey's  
307 HSD tests for multiple comparisons, or by Kruskal–Wallis tests followed by the Wilcoxon–  
308 Mann–Whitney post hoc tests, at  $\alpha=0.05$ . All tests were performed with R (Version R\_4.1.0; R  
309 Core Team, 2020) using the packages tidyverse, readxl, gridExtra, ggpubr, plotrix. A linear  
310 regression model without forcing through zero was used to evaluate the uptake linearity.

### 311 **3. Results and Discussion**

#### 312 **3.1. Laboratory experiment A: Effect of the matrix, pesticide concentration, and flow** 313 **speed on POCIS rates ( $R_s$ ) and $\delta^{13}\text{C}$**

314 *Effect on sampling rates ( $R_s$ ).* No pesticides were detected in the blank treatment, confirming  
315 pesticide concentrations below the detection limit in the pond water and excluding cross-  
316 contamination during the experiment, preparation, and extraction (Figure 1A). Pesticide  
317 concentrations remained constant (Table S2) in all treatments (Fig. 1A), with a mean variation of

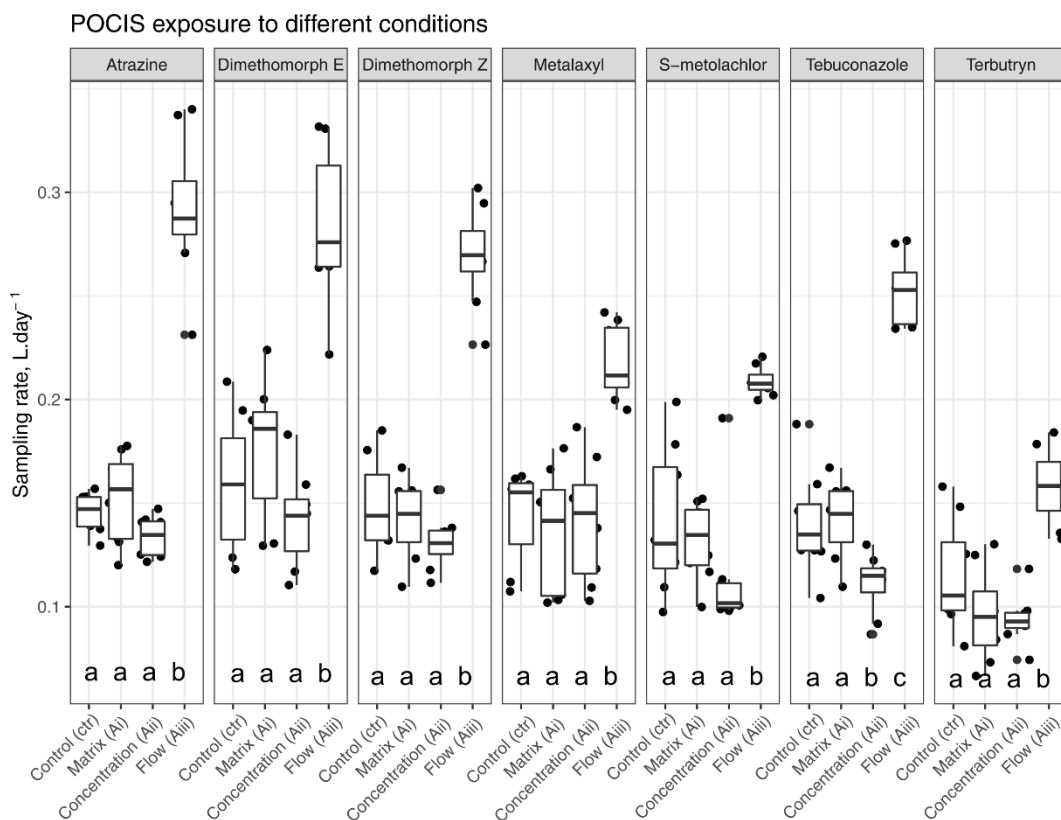
318  $\pm 0.2 \mu\text{g.L}^{-1}$  for the control, matrix (Ai), and flow (Aiii) treatments, and  $\pm 1.8 \mu\text{g.L}^{-1}$  for the  
319 concentration (Aii) treatment.

320 Pesticide uptake by POCIS was gradual and linear in all treatments over the 30 days of  
321 immersion (Table S3, Figure S2), enabling estimation of  $R_S$  with Equation 1 (Figure 2). Overall,  
322  $R_S$  values were in the range generally determined for POCIS in both laboratory and field  
323 experiments (Table S4). The  $R_S$  values did not differ significantly ( $p > 0.05$ ) in the control  
324 treatment with pond water and treatment with distilled water (Figure 2 (Ai)). Hence, DOC ( $\sim 10$   
325  $\text{mg.L}^{-1}$ ) did not affect  $R_S$  values, as only approximately 1% of pesticides were bound to DOC  
326 (data not shown), in agreement with previous results (Charlestra et al., 2012), but contrasting  
327 with another study with DOC concentrations of up to  $10 \text{ mg.L}^{-1}$  (Gourlay et al., 2005). This  
328 suggests that the type of organic carbon affects the capacity of passive samplers to take up  
329 pesticides (Gourlay et al., 2005).

330 The pesticide concentration generally did not affect  $R_S$  values (Figure 2 (Aii)), in agreement with  
331 previous studies (Bernard et al., 2018b; Mazzella et al., 2008; R. B. Taylor et al., 2020).  
332 However, tebuconazole exhibited slight but significantly ( $p < 0.05$ ) lower  $R_S$  values ( $0.11 \pm 0.01$   
333  $\text{L.day}^{-1}$ ) at a high concentration ( $10 \mu\text{g.L}^{-1}$ ) compared to the control treatment ( $0.14 \pm 0.02 \text{ L.day}^{-1}$ ),  
334 which may be due to competition between pesticides during POCIS uptake. The sorption of  
335 nonionic pesticides onto Oasis-like sorbents is primarily explained by apolar interactions  
336 (Harman et al., 2008). However, interactions with the PES membrane, especially for neutral  
337 compounds, as well as competitive sorption related to the matrix, have also been reported to  
338 influence  $R_S$  values (A. C. Taylor et al., 2020; Vermeirssen et al., 2012).

339 In contrast, a higher flow speed (Figure 2 (Aiii),  $14 \text{ cm.s}^{-1}$ ) significantly ( $p < 0.05$ ) increased  $R_s$   
340 for all pesticides. The mean  $R_s$  values for all pesticides ranged from 0.12 to  $0.17 \text{ L.day}^{-1}$  for the  
341 control treatment ( $6 \text{ cm.s}^{-1}$ ) and from 0.16 to  $0.29 \text{ L.day}^{-1}$  for the high flow speed treatment ( $14$   
342  $\text{cm.s}^{-1}$ ). Our results are in line with previous studies, indicating that  $R_s$  values increase with  
343 higher flow velocity due to thinning out of the water boundary layer (Alvarez et al., 2004; Gallé  
344 et al., 2020; Mazzella et al., 2008).

345 It is worth noting that the terbutryn  $R_s$  was significantly lower ( $p < 0.05$ ) than the  $R_s$  of the other  
346 pesticides in all treatments (Figure 2). Although Oasis HLB-like resins can be used for pesticides  
347 with  $\log K_{ow}$  from 0 to 4, the uptake of compounds with high  $\log K_{ow}$ , such as terbutryn ( $\log K_{ow}$   
348 = 3.7), remains low (Ibrahim et al., 2013). In contrast,  $R_s$  of tebuconazole ( $\log K_{ow} = 3.7$ ) had  
349 similar  $R_s$  to the more polar pesticides but was also sensitive to concentration changes.  
350 Tebuconazole may have a lower affinity for sorbing on PES membranes than terbutryn and/or a  
351 higher affinity for sorbing on Oasis HLB-like resins (octanol/water coefficient,  $\log K_{OC \text{ tebuconazole}}$   
352 = 3.2 and  $\log K_{OC \text{ terbutryn}} = 2.8$ ; (European Centre for Ecotoxicology and Toxicology of  
353 Chemicals, 2021)). Overall, these results suggest that  $\log K_{ow}$  alone cannot predict  $R_s$  values,  
354 similarly to other passive samples (e.g. Chemcatcher<sup>®</sup>), and water solubility and molecular  
355 weight of compounds are also useful parameters in predicting the uptake (Ahrens et al., 2015).



356

357 Figure 2. Sampling rates ( $R_s$ ) for pesticide uptake by polar organic chemical integrative samplers  
 358 (POCIS) for A-control (P,  $1 \mu g \cdot L^{-1}$  of the pesticide mixture at  $6 cm \cdot s^{-1}$ ), (Ai) matrix (DI,  $1 \mu g \cdot L^{-1}$   
 359  $1$  of the pesticide mixture at  $6 cm \cdot s^{-1}$ ), (Aii) concentrations (P,  $10 \mu g \cdot L^{-1}$  of the pesticide mixture  
 360 at  $6 cm \cdot s^{-1}$ ), and (Aiii) flow (P,  $1 \mu g \cdot L^{-1}$  of the pesticide mixture at  $14 cm \cdot s^{-1}$ ) treatments  
 361 presented in the form of box plots (McGill et al., 1978). The same letter (a, b, c) for each  
 362 chemical denotes similar ( $p < 0.05$ )  $R_s$  values among experiments. DI- distilled water, P-Rouffach  
 363 pond water. An outlier is defined as a data point that is located outside the whiskers of the box  
 364 plot.

365 *Effect of POCIS uptake on carbon isotope signature ( $\delta^{13}C$ ).* The  $\delta^{13}C$  values of pesticides in  
 366 water collected did not change ( $\Delta\delta^{13}C < 1\%$ ) over time (Figure S3). This indicates that water  
 367 exchange and spiking did not affect pesticide  $\delta^{13}C$  in the tanks over 30 days. Pesticide uptake in

368 POCIS and subsequent extraction did not result in significant isotope fractionation ( $\Delta\delta^{13}\text{C}<1\%$ )  
369 for all pesticides and treatments (Figure S4). However, matrix effects with peak coelution  
370 occurred during GC-IRMS measurements of atrazine, metalaxyl, and terbutryn extracted from  
371 POCIS collected from both control and flow treatments after 10 days of immersion (Figure S5).  
372 Nevertheless, coelutions became negligible for longer immersion times (Days 20 and 30) as  
373 pesticide concentrations increased relative to baseline levels (Figure S5). This underscores the  
374 capacity of POCIS to preconcentrate pesticides faster than pond organic matter, provided that the  
375 deployment time is sufficient. The pesticide/baseline ratio may increase in media with lower  
376 matrix interferences, e.g., stream, thereby lowering the limit for reliable CSIA from POCIS.  
377 Based on the measured  $R_s$  values, an average pesticide concentration in water of 100-200  $\text{ng.L}^{-1}$   
378 during 30 days of exposure was sufficient for reliable carbon CSIA of tebuconazole, *S*-  
379 metolachlor, and dimethomorph Z and E. Reliable carbon CSIA for atrazine, metalaxyl, and  
380 terbutryn would typically require higher concentrations (300-600  $\text{ng.L}^{-1}$ ). Hence, POCIS appears  
381 relevant in moderately (concentration  $>100 \text{ ng.L}^{-1}$ ) contaminated surface waters. In particular,  
382 POCIS can provide accurate pesticide CSIA during hydrological events following applications  
383 when pesticide concentrations increase in surface waters.

### 384 **3.2. Laboratory experiment B: Effect of transient high flow conditions and high pesticide** 385 **concentrations on POCIS rates ( $R_s$ ) and $\delta^{13}\text{C}$**

386 *Effect on sampling rates ( $R_s$ ).* Pesticide concentrations remained constant in all treatments, with  
387 an average variation of  $\pm 0.39 \mu\text{g. L}^{-1}$  for the baseflow and  $\pm 1.4 \mu\text{g. L}^{-1}$  under high flow and high  
388 pesticide concentration, respectively (Table S5). Overall, a short simulated runoff event within a  
389 one-month exposure period significantly increased pesticide uptake by POCIS, except in the

390 treatment with a simulated runoff event on Day 30 and with commercial POCIS. This is  
391 consistent with Experiment A, showing that a higher flow speed ( $14 \text{ cm.s}^{-1}$ ) significantly  
392 ( $p < 0.05$ ) increased pesticide uptake, with higher concentrations ( $10 \mu\text{g.L}^{-1}$ ), resulting in higher  
393  $R_s$  values.

394 Cumulative  $R_s$  values did not differ significantly ( $p < 0.05$ ) between commercial and in-house  
395 POCIS under changing flow conditions (Figure 3), confirming similar compositions of sorbents  
396 in both samplers. However,  $R_s$  values differed significantly between the in-house and  
397 commercial POCIS under high flow conditions for treatments Bii and Biii, with highest p-values  
398 of 0.003 and 0.047 respectively. The in-house POCIS similarly recorded the simulated pesticide  
399 runoff events on Day 0 (treatment Bi), Day 15 (treatment Bii), and Day 30 (treatment Biii).  
400 Hence, in-house POCIS could capture a runoff event even after 30 days of exposure under  
401 baseflow conditions. However,  $R_s$  values for all pesticides varied among treatments Bi, Bii, and  
402 Biii with commercial POCIS (Figure 3;  $p < 0.05$ ). The lower  $R_s$  observed in treatment Biii  
403 suggest that commercial POCIS may not capture a runoff event occurring after a long (29 days)  
404 period under base flow conditions, likely due to limited uptake capacity. Darker membranes  
405 (Figure S6) and sorbent material (data not shown) at the end of the experiment also suggest  
406 higher DOC accumulation in commercial than in-house-built POCIS. In previous studies, POCIS  
407 could capture short peaks of pesticides (Bernard et al., 2018a; Mazzella et al., 2008, 2007) in  
408 experiments with distilled or tap water, and with shorter (9, 14, and 21 days) exposure times than  
409 in our experiment. Overall, our results highlight that the ability of POCIS to record short periods  
410 of pesticide exposure during runoff events should be systematically tested and account for the  
411 effect of the environmental matrix.

412 It is also worth noting that the positioning of POCIS in the tank and inhomogeneous flow during  
413 stirring may have led to higher variabilities in  $R_s$  values in treatment Biii with in-house POCIS  
414 and treatment Bii with commercial POCIS. This was particularly pronounced for atrazine and *S*-  
415 metolachlor-D11, which were present only in the tank under high flow conditions. This suggests  
416 that stirring in static experiments with renewal calibration to evaluate POCIS uptake may not  
417 systematically reproduce homogeneous flow and uptake. In turn, this may increase the  
418 uncertainty associated with  $R_s$  values during short exposure to pesticide during runoff events.

419 Altogether, POCIS preferentially captures short runoff events with higher pesticide  
420 concentrations. This supports the idea that POCIS may be used in surface waters to integrate  
421 baseflow conditions while capturing runoff events with high pesticide concentrations.

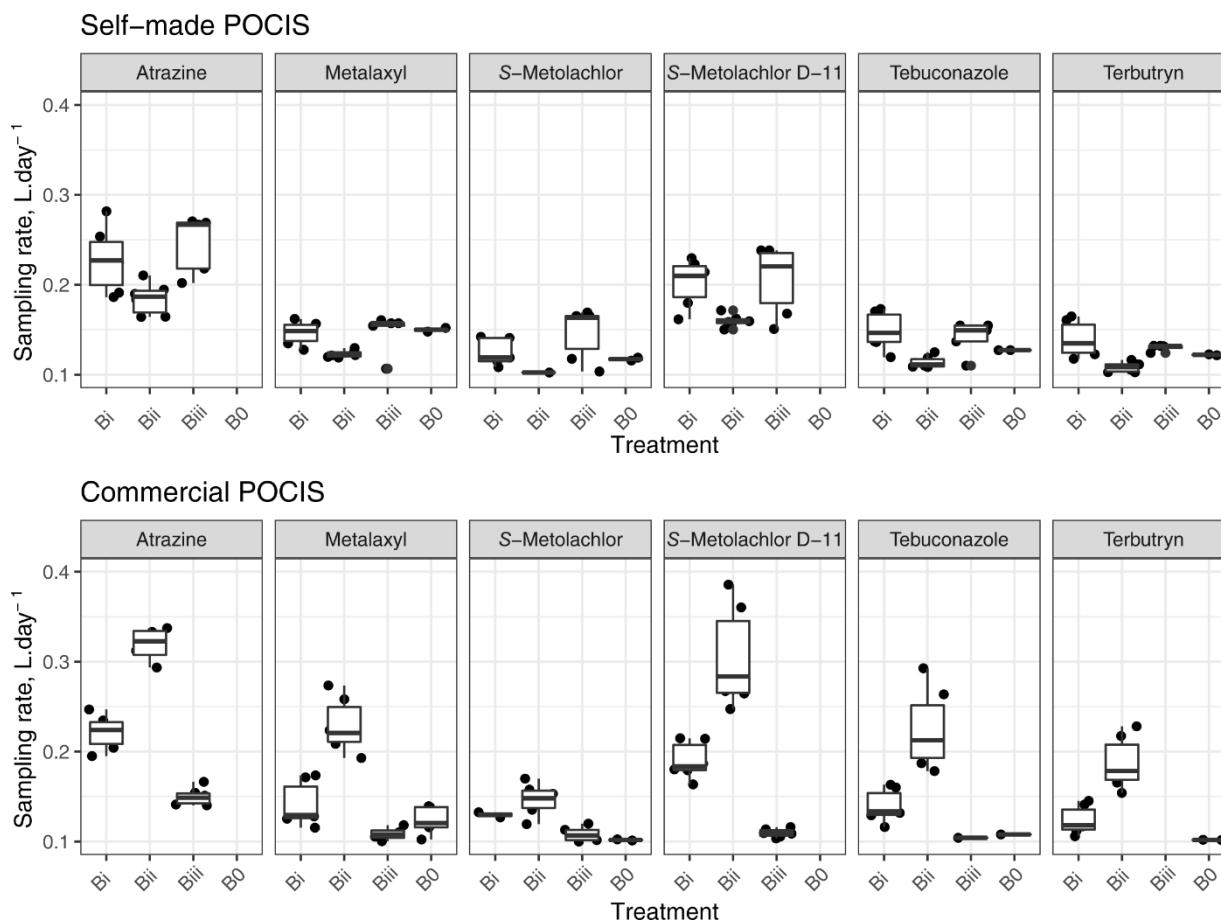


Figure 3. Sampling rates,  $R_s$ , in chemical integrative samplers (POCIS) in Experiment B for in-house and commercial POCIS presented in a form of box plots with Runoff Event Bi – on Day 0; Bii – on Day 15; Biii – on Day 30; and B0 - no runoff event. An outlier is defined as a data point that is located outside the whiskers of the box plot.

422 *Effect of POCIS uptake on carbon isotope signatures of pesticides ( $\delta^{13}C$ ).* Overall, POCIS  
 423 accurately recorded the  $\delta^{13}C$  of pesticides in treatments under varying hydrological patterns.  
 424 Pesticide concentrations were sufficient for CSIA of metalaxyl, terbutryn, *S*-metolachlor and  
 425 tebuconazole. The concentrations of atrazine and *S*-metolachlor D-11 under high flow conditions  
 426 were below the detection limit for carbon CSIA due to the short exposure time (24 h) limiting  
 427 POCIS uptake. Pesticide CSIA was not feasible for terbutryn due to a strong matrix effect,



428 suggesting different pond water matrix in Experiments A and B. It is therefore recommended to  
429 collect large volumes of water to identify possible peak coelution with the target analytes before  
430 deploying POCIS in the field.

431 The  $\delta^{13}\text{C}$  values of tebuconazole and *S*-metolachlor in in-house and commercial POCIS did not  
432 change after 30 days of exposure (Figure 4 A). The different initial  $\delta^{13}\text{C}$  values of metalaxyl in  
433 the baseflow and runoff tanks were used to estimate the contribution of a runoff event to the  
434 overall pesticide uptake based on the  $\delta^{13}\text{C}$  of metalaxyl in POCIS. As expected, the  $\delta^{13}\text{C}$  of  
435 metalaxyl in POCIS (Figure 4 B) was close to the  $\delta^{13}\text{C}$  of the Sigma–Aldrich standard in the  
436 treatment without runoff (B0), and between the  $\delta^{13}\text{C}$  values of the two standards (Sigma–Aldrich  
437 and Ridgold<sup>®</sup> F, Table S1) in treatments Bi, Bii, and Biii. The  $\delta^{13}\text{C}$  values of metalaxyl in  
438 commercial and in-house-built POCIS were similar ( $\Delta\delta^{13}\text{C}<1\%$ ), except in treatment Bii  
439 ( $\Delta\delta^{13}\text{C}>1\%$ ), where the  $\delta^{13}\text{C}$  value for commercial POCIS was similar to that of Ridgold<sup>®</sup> F.  
440 This is consistent with the higher  $R_s$  for commercial POCIS in treatment Bii (Figure 3).

441 These results indicate that a runoff event carrying a pesticide with a different  $\delta^{13}\text{C}$  than that of  
442 baseflow conditions may affect the  $\delta^{13}\text{C}$  of pesticides in POCIS deployed in surface water. If  
443 pesticide degradation occurs in the agricultural soil (Alvarez-Zaldivar et al., 2018) before the  
444 pesticide runoff enters into surface water, the  $\delta^{13}\text{C}$  of pesticides in POCIS would reflect pesticide  
445 degradation in both the soil and surface water. Under baseflow conditions, the  $\delta^{13}\text{C}$  of pesticides  
446 in POCIS may only reflect significant pesticide degradation in surface water. Overall, results of  
447 the laboratory experiments under both static and dynamic flow conditions validate the use of  
448 POCIS for accurate integrative CSIA of pesticides in surface water.

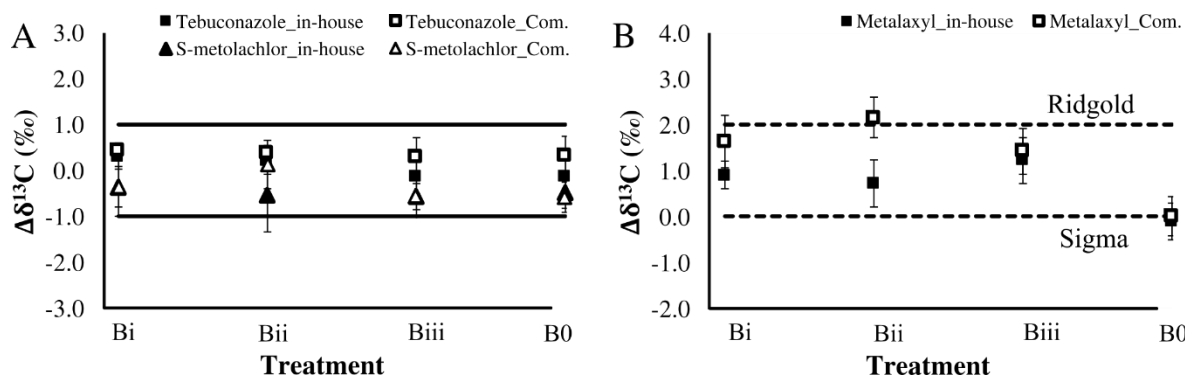
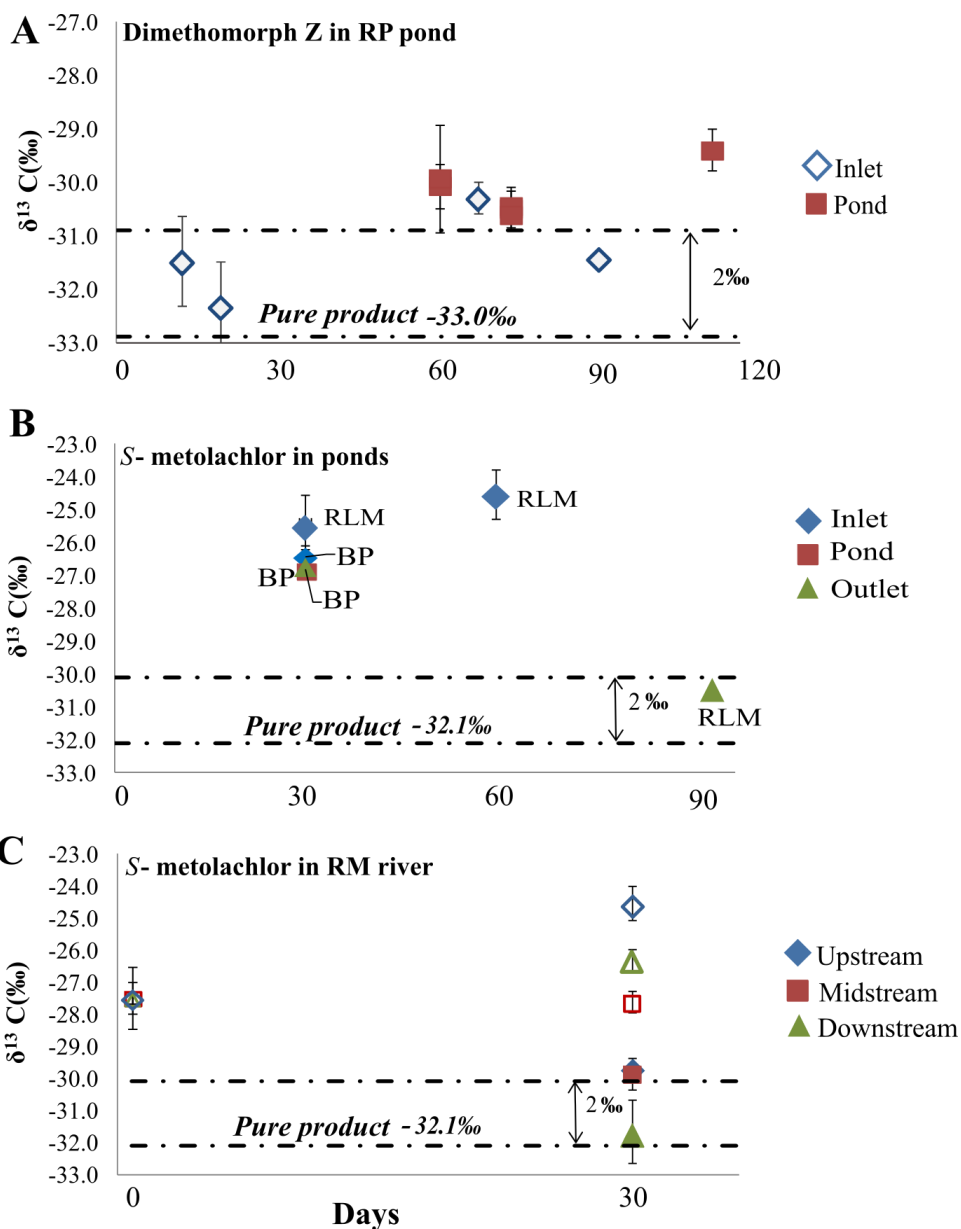


Figure 4. (A) Change in carbon isotope signature ( $\Delta\delta^{13}\text{C}$ ) for pesticide during POCIS uptake in Experiment B. Straight lines represent  $\pm 1\%$  from the  $\delta^{13}\text{C}$  standard value. (B) Mixing between two standards of metalaxyl. Two dashed lines represent two different standards of metalaxyl.

### 449 3.3. POCIS-CSIA approach to evaluate pesticide degradation in ponds and river water

450 Several pesticides were detected in water samples and POCIS from three ponds and river (Table  
 451 S8). The widely used fungicide dimethomorph (isomer Z) could be preconcentrated in POCIS  
 452 extracts, i.e., 20,000-fold (to reach  $5 \text{ mg.L}^{-1}$ ) compared to its mean concentration ( $100 \text{ ng.L}^{-1}$ ) in  
 453 water of the RP pond, enabling carbon CSIA. CSIA was also possible for *S*-metolachlor in  
 454 POCIS collected from RPL and BP ponds and RM river (Figure 5). It is also worth noting that  
 455 the limit for carbon CSIA of *S*-metolachlor was nearly five times lower in the RM river samples  
 456 than in the pond samples with higher DOC content.

457 The  $\delta^{13}\text{C}$  value of commercial formulations ( $-33.0 \pm 0.3\%$  for dimethomorph E and Z and  
 458  $\delta^{13}\text{C} = -32.1 \pm 0.3 \%$  for *S*-metolachlor; Table S1) were used as the source signature (Equation 5,  
 459  $\delta^{13}\text{C}_0$ ) and compared with  $\delta^{13}\text{C}$  of dimethomorph and *S*-metolachlor in POCIS and water grab  
 460 samples. The threshold of  $\Delta\delta^{13}\text{C} > 2 \%$  was defined as a significant carbon isotope effect due to  
 461 pesticide transformation (Figure 5) (Hunkeler et al., 2008).



462

463 Figure 5.  $\delta^{13}C$  of pesticides in polar organic chemical integrative samplers (POCIS) (filled

464 symbols) and water samples (empty symbols) deployed at the inlet or upstream (diamonds), pond

465 or midstream (square), outlet or downstream (triangle) for (A) dimethomorph Z in stormwater

466 RP pond in Rouffach; (B) S-metolachlor in BP pond in Aurade and in RLP pond in Rampillon;

467 and (C) S-metolachlor in RM Rupt de Mad stream. The dashed-dotted line represents the 2 ‰

468 range for  $\delta^{13}C$  of the pure product.  $\delta^{13}C$  of pesticides in POCIS are the results of 30 days

469 exposure time \*- represents possible pesticide application periods. The error bars for water  
470 samples represent the measurement reproducibility (n=3).

471 *Dimethomorph in RP pond.* In POCIS deployed in the RP,  $\Delta\delta^{13}\text{C}$  up to 3.6 ‰ of dimethomorph  
472 Z in water compared with GRIP TOP® (Figure 5A) indicated degradation in the pond or in the  
473 vineyard soil. However,  $\delta^{13}\text{C}$  values of dimethomorph Z in water at the pond inlet were similar  
474 to those of the GRIP TOP® formulation ( $\Delta\delta^{13}\text{C}<2\text{‰}$ ), except on day 68. This suggests that  
475 degradation mainly occurred in the RP pond, while vineyard soil may not be the primary  
476 compartment for dimethomorph Z degradation. Furthermore, a  $\Delta\delta^{13}\text{C}$  for dimethomorph Z was  
477 observed between POCIS from day 112 and water at the pond inlet from day 90 (no rain event  
478 between these days). This supports further the idea that dimethomorph Z mainly degraded in the  
479 pond. Biodegradation in the sediments and photodegradation on the surface of water are the main  
480 putative transformation processes affecting dimethomorph Z in the RP pond (Avetta et al., 2014;  
481 Zhang et al., 2020). Provided that  $\epsilon_{\text{C}}$  will be derived in reference laboratory experiments,  
482 degradation of dimetomorph Z may be quantified.

483 *S-metolachlor in ponds.* Similar  $\delta^{13}\text{C}$  values ( $-26.6 \pm 0.3\text{‰}$ ; n=9) for S-metolachlor measured in  
484 POCIS in the three sampling points in BP pond suggested limited degradation in the pond  
485 (Figure 5B). However, these  $\delta^{13}\text{C}$  values were 5.6 ‰ ( $\Delta\delta^{13}\text{C}$ ) higher compared to the  $\delta^{13}\text{C}$  of S-  
486 metolachlor in commercial formulations, indicating significant S-metolachlor biodegradation in  
487 the agricultural soil hydrologically connected to the BP pond. Biodegradation (Equation 5) for S-  
488 metolachlor in soil ranged from 92 to 99%, using an average  $\epsilon_{\text{C}} = -1.8 \pm 0.5$  retrieved from soil  
489 biodegradation studies (Table S9). Similarly, significant isotope fractionation ( $\Delta\delta^{13}\text{C} = 7.1 \text{‰}$ )  
490 for S-metolachlor between pond inlet water in RPL pond and commercial formulations suggested

491 *S*-metolachlor biodegradation (estimated from 96 to 99 %) in the agricultural soil (Figure 5B). In  
492 RPL pond, *S*-metolachlor from POCIS collected on day 90 had a  $\delta^{13}\text{C}$  value similar to that of *S*-  
493 metolachlor in commercial formulations ( $\Delta\delta^{13}\text{C}<2\text{‰}$ ). This suggests that POCIS could capture  
494 the late winter application of *S*-metolachlor. Hence, POCIS deployed before and after pesticide  
495 application allowed to integrate fast change in  $\delta^{13}\text{C}$ , which mirrored either degradation in soil or  
496 fresh application of *S*-metolachlor.

497 Overall, the results from BP and RLP ponds support the idea that biodegradation of *S*-  
498 metolachlor in agricultural soil is the prevailing process responsible for carbon isotope  
499 fractionation (Alvarez-Zaldivar et al., 2018; Pérez-Rodríguez et al., 2021; Rose et al., 2018).  
500 Similar  $\Delta\delta^{13}\text{C}$  of about 5 ‰ for *S*-metolachlor were observed in leachates from vegetated forest  
501 soil (Pérez-Rodríguez et al., 2021) and *in situ* in the agricultural catchment (Alvarez-Zaldivar et  
502 al., 2018).

503 *S-metolachlor in the RM river.* *S*-metolachlor CSIA was carried out from grab samples and  
504 POCIS in RM river, allowing comparison of both sampling approaches. Grab samples collected  
505 on day 0 had consistent values of  $-27.5 \pm 0.6\text{‰}$  at all sites (Figure 5C), yielding estimates of *S*-  
506 metolachlor degradation from 86 to 92%. Comparatively, *S*-metolachlor in the grab samples on  
507 day 30 was isotopically enriched in  $^{13}\text{C}$  throughout the flow path ( $\Delta\delta^{13}\text{C}=3\text{‰}$ ). In contrast,  $\delta^{13}\text{C}$   
508 values of *S*-metolachlor in POCIS collected on day 30 were similar ( $-29.8\text{‰}$  for upstream and  
509 downstream points) along the flowpath. The  $\delta^{13}\text{C}$  values of *S*-metolachlor in POCIS deployed in  
510 the midstream and commercial formulations were similar ( $\Delta\delta^{13}\text{C}<2\text{‰}$ ). Hence, runoff of fresh  
511 *S*-metolachlor depleted in  $^{13}\text{C}$  could be recorded by the POCIS samplers, especially in the  
512 midstream sampling site, but not by the grab samples. This suggests nearby *S*-metolachlor

513 application or lower degradation capacity in the soil of the midstream area of the catchment. In  
514 comparison to POCIS, the isotope data obtained from grab samples provided more sensitive but  
515 punctual information on *in situ* degradation in surface water.

#### 516 **4. Conclusions**

517 The POCIS-CSIA approach holds potential for reliable assessment of  $\delta^{13}\text{C}$  for widespread and  
518 commonly detected pesticides at environmental concentrations in surface waters. Our results  
519 show that coupling carbon CSIA and POCIS is feasible for *S*-metolachlor and dimethomorph in  
520 surface waters and can help evaluate pesticide degradation. In-house POCIS is a cost-effective  
521 and time-efficient approach compared to processing large volumes of water that can be  
522 customized with different POCIS designs, membranes, and sorbent, depending on the target  
523 pollutants. When isotope fractionation values for specific pesticide degradation process have  
524 been determined under representative conditions in laboratory experiments, pesticide degradation  
525 may be estimated in surface waters without additional information on pesticide concentrations or  
526 transformation products. However, the feasibility of POCIS application for CSIA depends on  
527 pesticide concentrations, the degradation extent, and the corresponding isotope fractionation.  
528 Significant degradation was required to measure isotope fractionation ( $\Delta\delta^{13}\text{C} > 2\text{‰}$ ) for *S*-  
529 metolachlor and dimethomorph due to their large number of carbon atoms and subsequent  
530 dilution effect. Here, multielement CSIA with chlorine CSIA, if a bond with chlorine atom is  
531 broken during degradation, shows promise for tracing pesticide behavior *in situ* (Torrentó et al.,  
532 2021). Additionally, coelution with the surface water matrix may severely limit isotope  
533 measurements and should be systematically verified before applying the POCIS-CSIA approach.  
534 Whenever possible, one or several clean-up strategies, depending on the complexity of the

535 matrix, should be used. For instance, molecularly imprinted polymers (MIP) together with  
536 POCIS may help preconcentrate the target pesticide while limiting the matrix effect (Berho et al.,  
537 2020, 2017). Overall, we anticipate that this study may pave the way for a widespread  
538 application of the POCIS-CSIA approach to evaluate the contribution of degradation to the  
539 overall dissipation of a variety of micropollutants in waters.

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543 **Declaration of competing interest**

544 The authors declare that they have no known competing financial interests or personal  
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551 **Appendix A.** Supplementary data

552 **Literature**

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