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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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20 **Highlights:**

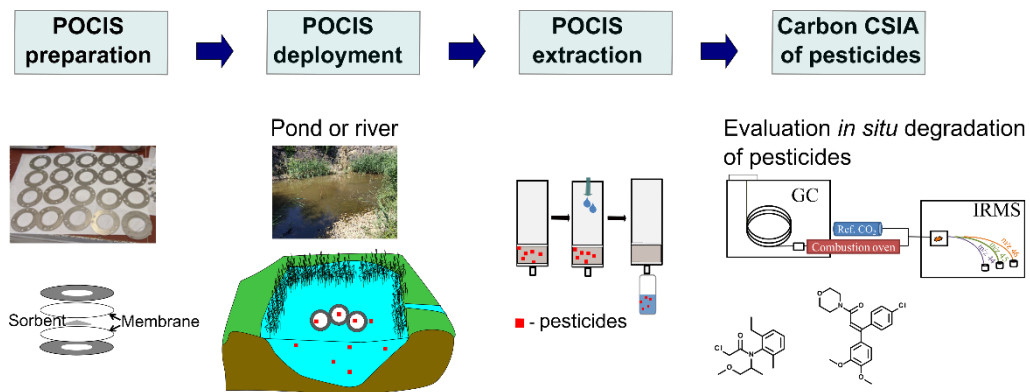
- 21 • POCIS-CSIA approach enables recording $\delta^{13}\text{C}$ of pesticides at ng.L^{-1} range
- 22 • Uptake and extraction from POCIS cause no isotope effect for pesticides
- 23 • $\delta^{13}\text{C}$ values recorded in water confirmed degradation of *S*-metolachlor in soil
- 24 • $\delta^{13}\text{C}$ 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 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 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⁻¹), and runoff events (combined effect of higher concentration 10 µg.L⁻¹ and 14 cm.s⁻¹) on
124 δ¹³C 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⁻¹ 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 cm².

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⁻¹) 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⁻¹), 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⁻¹) 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.

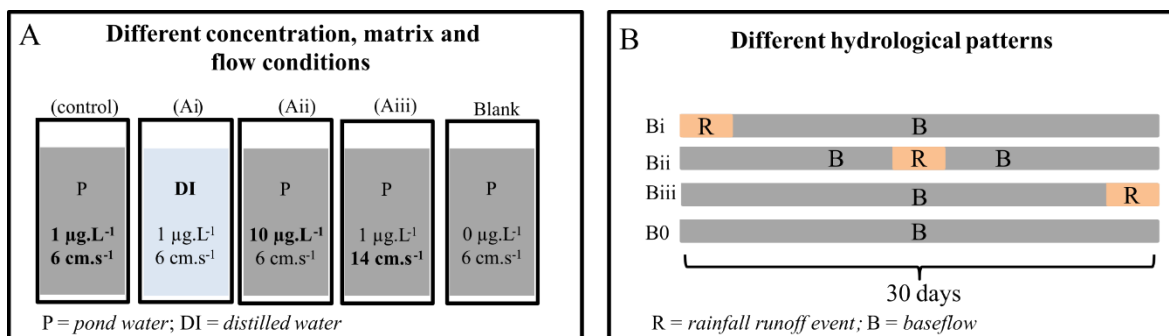
162 To mimic different flow speeds in all laboratory experiments, stirring with a magnetic stir bar
163 was used. The stirring speed (round per minute, rpm) was calculated using the Reynold numbers
164 calculation to reach the targeted flow speed:

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

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, ρ ($\text{g} \cdot \text{cm}^3$) is the density, and μ ($\text{g} \cdot \text{cm} \times \text{min}$
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 19th February 2020 and for Experiment B on 25th May 2020. The pond water was filtered
173 through an 11 μm 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⁻¹ of atrazine, metalaxyl, S-metolachlor,
 182 terbutryn, tebuconazole, and dimethomorph (Z and E isomers) and stirred at 6 cm.s⁻¹ flow speed;
 183 (Ai) a treatment with distilled water (DI) spiked with 1 µg. L⁻¹ of the pesticide mixture and 6
 184 cm.s⁻¹ flow speed; (Aii) a treatment with pond water spiked with 10 µg. L⁻¹ of the pesticide
 185 mixture and 6 cm.s⁻¹ flow speed; and (Aiii) a treatment with pond water spiked with 1 µg. L⁻¹ of
 186 the pesticide mixture and 14 cm.s⁻¹ 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⁻¹ flow speed, and 10 µg. L⁻¹ of five
 189 pesticides (metalaxyl (Ridgold[®] F formulation), terbutryn, tebuconazole, S-metolachlor D-11,
 190 and atrazine); and B – baseflow conditions – 6 cm.s⁻¹ flow speed, and 1 µg. L⁻¹ 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⁻¹) 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 cm.s^{-1} flow speed
198 (350 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 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 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 cm.s^{-1} (750 rpm)
202 (Figure 1A). An unspiked blank treatment with pond water at 6 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 mL) was collected 15 minutes
210 after spiking and at the end of each exposure period for measuring pesticide concentrations and
211 weekly (4 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 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⁻¹ flow,
221 1 µg⁻¹ 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⁻¹ flow, with 10 µg. L⁻¹ 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⁻¹ mixture of metalaxyl
226 (Ridgold[®] F), terbutryn, tebuconazole, *S*-metolachlor D-11, and atrazine.

227 Different initial isotopic composition signatures of metalaxyl (Sigma–Aldrich, δ¹³C = -31.5 ±
228 0.1‰ and Ridgold[®] F, δ¹³C = -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 δ¹³C 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- μm glass filter
244 membranes, and stored at 4 °C until analysis. Grab water samples were preconcentrated using an
245 AutoTrace 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. 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. 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⁻¹ to 1 mg.L⁻¹).

278 **2.7.3. CSIA of pesticides**

279 CSIA measures the ratio of a heavy isotope of an element (e.g., ¹³C) to the light stable isotope
280 (e.g., ¹²C) 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

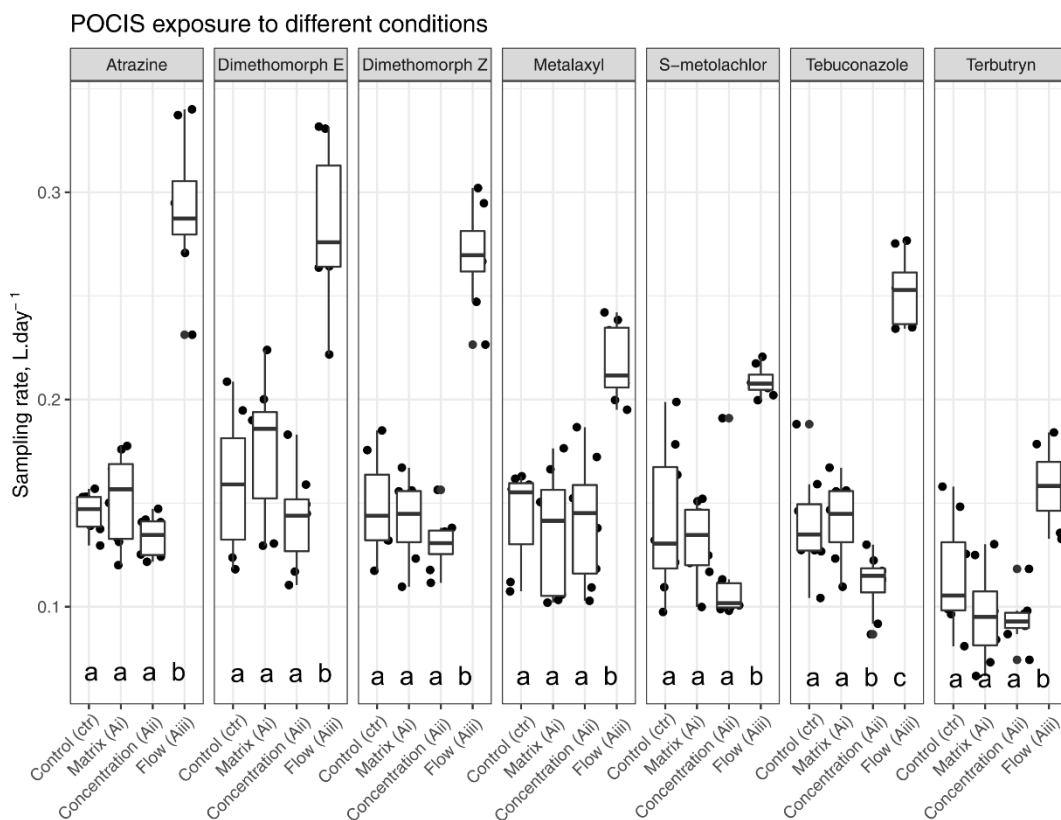
318 $\pm 0.2 \mu\text{g.L}^{-1}$ for the control, matrix (Ai), and flow (Aiii) treatments, and $\pm 1.8 \mu\text{g.L}^{-1}$ for the
319 concentration (Aii) treatment.

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 (~ 10
325 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 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 ± 0.01
333 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 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 L.day^{-1} for the
341 control treatment (6 cm.s^{-1}) and from 0.16 to 0.29 L.day^{-1} for the high flow speed treatment (14
342 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[®]), 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 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 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 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.

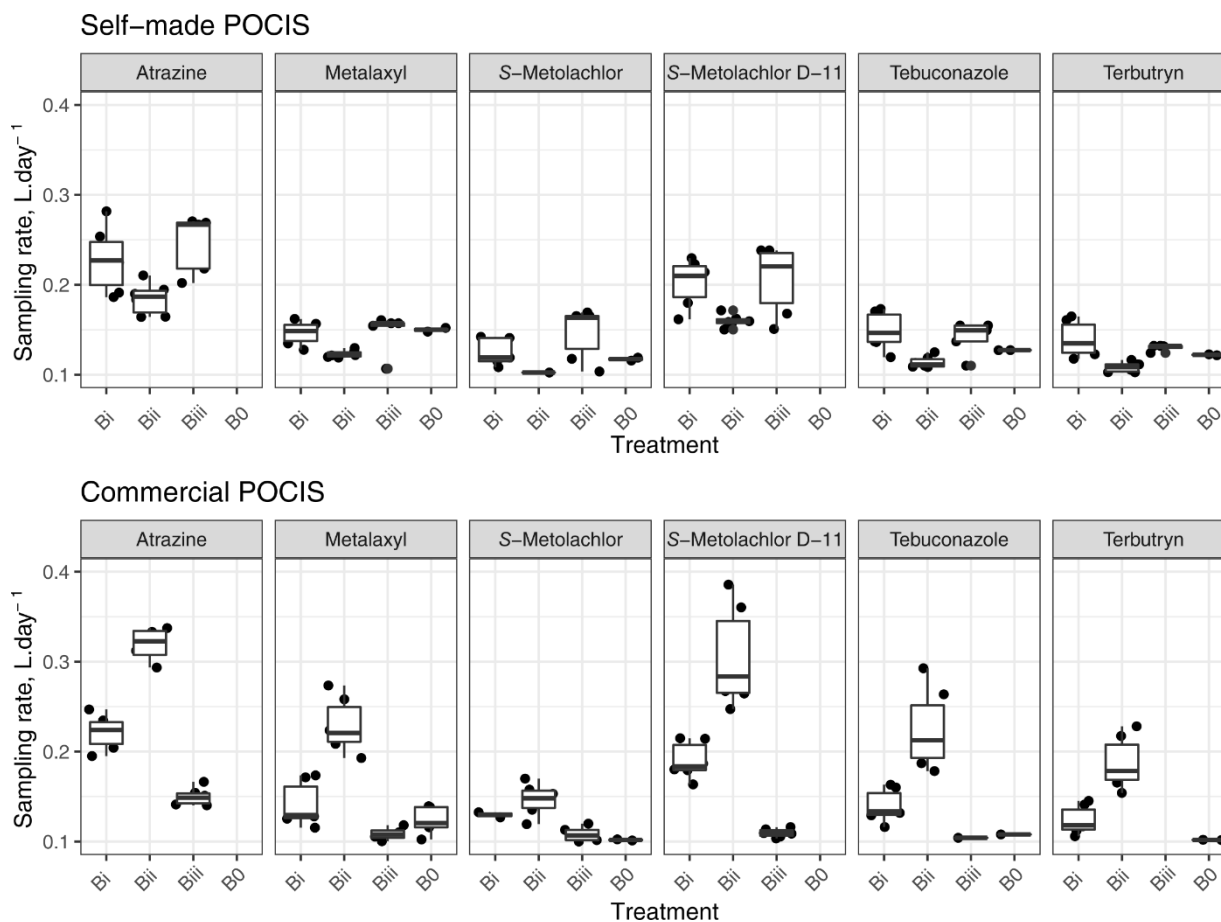


Figure 3. Sampling rates, R_s , in chemical integrative samplers (POCIS) in Experiment B for in-house and commercial POCIS presented in a form of box plots with Runoff Event Bi – on Day 0; Bii – on Day 15; Biii – on Day 30; and B0 - no runoff event. An outlier is defined as a data point that is located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

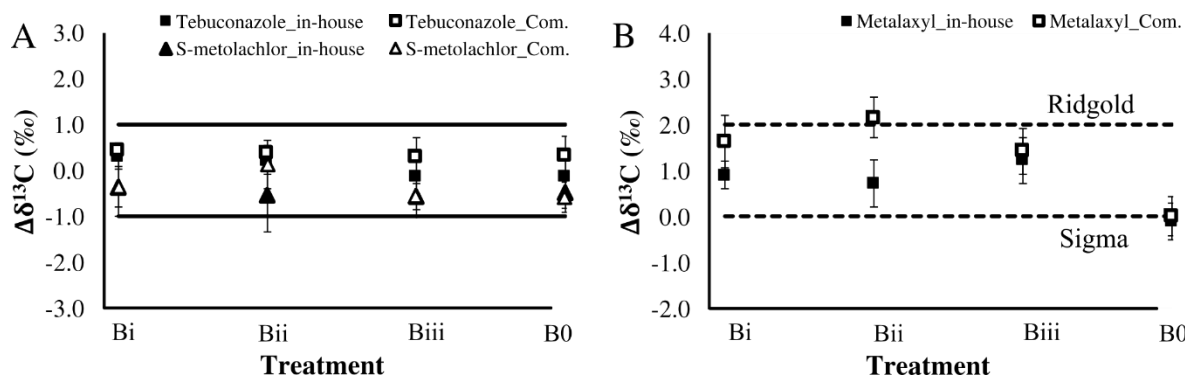
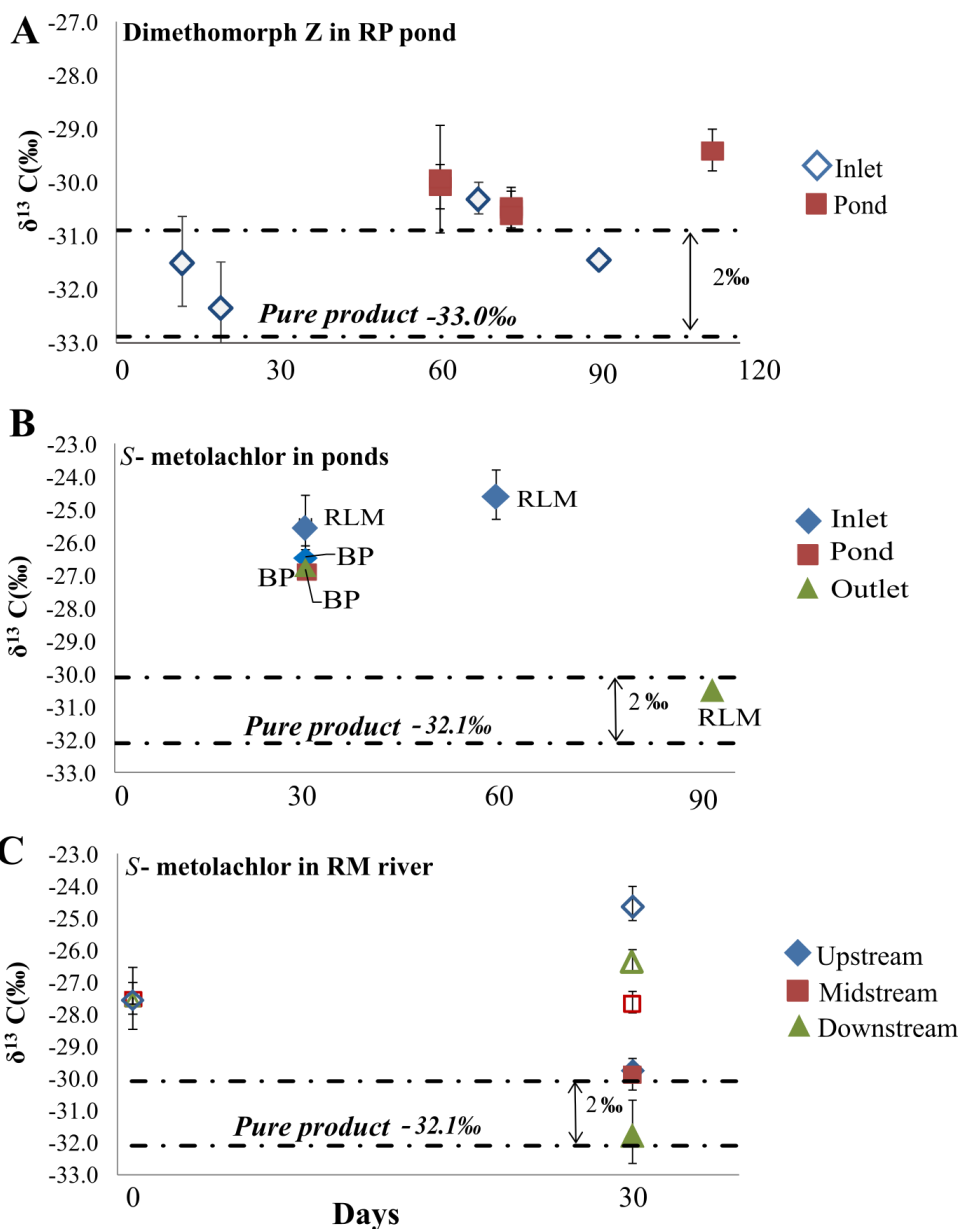


Figure 4. (A) Change in carbon isotope signature ($\Delta\delta^{13}\text{C}$) for pesticide during POCIS uptake in Experiment B. Straight lines represent $\pm 1\%$ from the $\delta^{13}\text{C}$ standard value. (B) Mixing between two standards of metalaxyl. Two dashed lines represent two different standards 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 mg.L^{-1}) compared to its mean concentration (100 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. $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ of the pure product. $\delta^{13}\text{C}$ 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 ϵ_{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}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‰ 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}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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