Evaluating pesticide degradation in artificial wetlands with compound-specific isotope analysis: a case study with the fungicide dimethomorph

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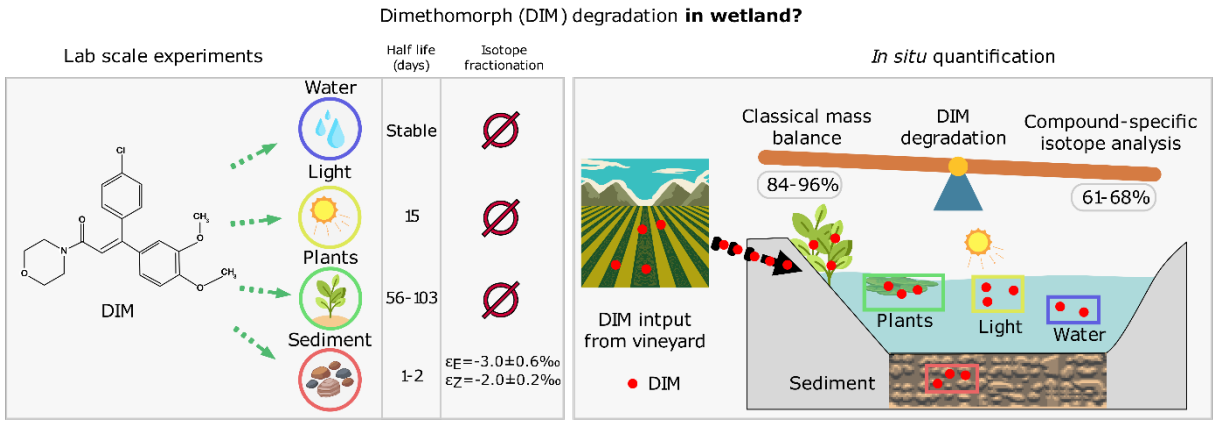

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Abstract

Pesticide degradation in wetland systems intercepting agricultural runoff is often overlooked and mixed with other dissipation processes when estimated based on pesticide concentrations alone. This study focused on the potential of compound-specific isotope analysis (CSIA) to estimate pesticide degradation in a stormwater wetland receiving pesticide runoff from a vineyard catchment. The fungicide dimethomorph (DIM), with diastereoisomers E and Z, was the prevalent pesticide in the runoff entering the wetland from June to September 2020. DIM Z, the most commonly detected isomer, exhibited a significant change ($\Delta^{13}C$>3 ‰) in its carbon isotopic composition in the wetland water compared to the runoff and commercial formulation, indicating degradation. Laboratory DIM degradation assays, including photodegradation and biodegradation in oxic wetland water with and without aquatic plants and in anoxic sediments, indicated that DIM degradation mainly occurred in the wetland sediments. The rapid degradation (E:$t_{1/2}$ = 1.2 ± 0.6, Z: $t_{1/2}$ = 1.5 ± 0.8 days) of DIM in the wetland sediment led to significant carbon isotopic fractionation ($\varepsilon_{DIM\text{-}E}$ = −3.0 ± 0.6 ‰, $\varepsilon_{DIM\text{-}Z}$ = −2.0 ± 0.2 ‰). In contrast, no significant isotope fractionation occurred during DIM photodegradation, despite the rapid isomerization of the

E isomer to the Z isomer and a half-life of 15.3 ± 2.2 days for both isomers. DIM degradation was slow (E: $t_{1/2}$ = 56-62 days, Z: $t_{1/2}$ = 82-103 days) in oxic water with plants, while DIM persisted (120 days) in water without plants. DIM CSIA was thus used to evaluate the *in situ* biodegradation of DIM Z in the wetland. The DIM Z degradation estimates based on a classical concentration mass balance (86-94%) were slightly higher than those from the isotopic mass balance (61-68%). This study highlights the potential of CSIA to conservatively evaluate pesticide degradation in wetland systems, offering a reliable alternative to classical labor-intensive mass balance approaches.

1. Introduction

Pesticide runoff from agricultural catchments poses serious environmental risks to downstream ecosystems (Tang et al., 2021). Nonetheless, pesticide use may increase in the coming decades as a result of climate change, pest prevalence, introduction of invasive species, and pesticide resistance (Koli et al., 2019). Although the reduction or elimination of pesticide use remains the best option to limit impacts on human and ecosystem health, ponds and constructed wetlands at catchment outlets can partially intercept surface runoff events and protect surface waters from pesticide pollution (Maillard et al., 2011). In fact, artificial wetlands offer a variety of biogeochemical conditions across wetland compartments (i.e., water, sediments, plants, suspended solids), driving the dissipation of organic pollutants from agricultural catchments (Imfeld et al., 2021). Pesticide dissipation, i.e., the apparent decrease in pesticide concentrations in wetlands, is the result of several dissipation processes, including sorption to sediments, plant uptake, and biotic and abiotic degradation. Only pesticide degradation can lead to the complete mineralization of pesticides, although intermediate and potentially toxic transformation products (TPs) may be

formed. However, the contribution of pesticide degradation to the overall dissipation in stormwater wetlands receiving pesticide runoff from agricultural catchments remains mostly unknown since dissipation processes co-occur and may vary over time.

The efficiency of wetland systems in removing pesticides is generally estimated based on a work-intensive, often uncertain, and costly mass balance comparing inlet and outlet fluxes of pesticides. A major drawback of this black-box approach is that processes contributing to overall pesticide dissipation, including degradation and sorption, remain elusive (Grégoire et al., 2009) and depend on the physicochemical properties of the pesticide. Therefore, the underlying hypothesis of this study is that better quantification of processes contributing to pesticide dissipation in wetland compartments can facilitate the evaluation of the potential of wetland systems to degrade pesticides and to form transformation products (TPs).

In contrast to mass balance approaches based on concentration analysis, compound-specific isotope analysis (CSIA) may help differentiate degradative (i.e., involving molecular bond cleavage) or nondegradative processes leading to a decrease in the concentration of a specific contaminant molecule. CSIA is used to measure the ratio of a heavy isotope of an element (^{H}E) to the light stable isotope (^{L}E) in an individual compound (Urey, 1947). During reactions, chemical bonds containing exclusively light isotopes (e.g., ^{12}C) are cleaved at slightly faster rates than those containing heavier isotopes (e.g., ^{13}C). This may lead to a change in the isotope ratio in the remaining, nondegraded contaminant fraction. Combined with concentration analysis, pesticide CSIA can provide multiple lines of evidence for pesticide transformation in wetlands and allow for the quantification of the extent of degradation when corresponding isotope fractionation values (ε) are known. Only a few studies have investigated pesticide degradation in surface water using CSIA

(Alvarez-Zaldivar et al., 2018; Gilevska et al., 2022a; Masbou et al., 2022; Schreglmann et al., 2013; Suchana et al., 2022), and reference studies on pesticide CSIA in wetland systems are currently limited (Chen et al., 2022) .

In this context, the purpose of this study is to determine the contribution of pesticide degradation to overall pesticide dissipation in a stormwater wetland collecting pesticide runoff from a vineyard catchment. In previous studies, a mass balance approach based on concentration data enabled the quantification of pesticide partitioning, distribution, and dissipation in the compartments of a stormwater wetland (Grégoire et al., 2010; Maillard et al., 2011). Although these studies underscored that the stormwater wetland acted as a pesticide sink, with dissipation depending on pesticide properties and involved compartments, direct proof and reliable estimates of pesticide degradation are currently missing. Dimethomorph (DIM), a morpholine fungicide, prevailed in pesticide runoff entering the wetland and in the wetland over the studied period. DIM was thus used as a model compound to examine pesticide degradation using CSIA. DIM is a racemic compound, i.e., composed of equal proportions of the diastereoisomers E and Z, with isomer Z exhibiting fungicidal activity by inhibiting ergosterol synthesis (Avetta et al., 2014). Laboratory experiments were set up to retrieve reference isotope and isomer (IF(Z)) fractionation values for photodegradation and biodegradation in wetland compartments (i.e., water, sediments, and plants), allowing for the quantification of degradation of DIM Z, the most commonly detected isomer, using CSIA. A comparison of the mass balances based on field DIM Z concentration and stable isotope data to evaluate pesticide degradation in the stormwater wetland underscored the potential of pesticide CSIA to improve the evaluation of the natural attenuation of pesticides in wetland systems.

2. Material and Methods

2.1. Study wetland

The stormwater wetland (47°57′9 N, 07°17′3 E) was located at the outlet of a 42.7 ha vineyard catchment area in Alsace (eastern France). In 2020, conventional vineyards, with applications of synthetic pesticides, covered 50% (14.5 ha) of the vineyard area of the catchment, involving more than 30 wine growers. The characteristics of the vineyard catchment and the stormwater wetland have been detailed previously (Duplay et al., 2014; Grégoire et al., 2010; Imfeld et al., 2020; Maillard et al., 2011). Six fungicides (DIM Z and E, cyprodinil, metalaxyl, pyrimethanil, tebuconazole, tetraconazole) and four herbicides (pendimethalin, *S*-metolachlor, atrazine, terbuthylazine) were selected in this study based on the aforementioned studies and their compatibility for CSIA. Volatility was a key criterion for applying CSIA, ensuring that the compounds could be analyzed by gas chromatography with high precision and accuracy for CSIA. Briefly, the study wetland (319 m^2) consisted of a forebay (215 m^2) and a 0.6 m deep gravel filter containing a maximum volume of 62 m^3 to increase the hydraulic retention time and dissipation efficiency (Figure S1) (Maillard and Imfeld, 2014). The wetland has a maximum storage capacity of 1108 m^3. Six piezometers of 0.6m depth were located in the gravel filter. The sediment was partly (75%) excavated from the forebay area in February 2020 to increase the water storage capacity and reduce flood risk. As a result, water stagnated in the forebay, with water depths ranging from 0.25 m to 0.40 m from June to September 2020, corresponding to a dead water volume of 63 m^3 upstream of the outflow pipes. The vegetation, i.e., *Phragmites australis* (common reed), *Lemna minor* (common duckweed), *Typha Latifolia* (common cattail), coverage increased from approximately 50% of the forebay in April up to 100% from the end of July until September 2020.

2.2. Sampling

Water. From June 2nd to September 28th, water samples (300 mL) were collected at the wetland inlet every 3 m^3 using an automatic flow proportional sampler (6712FR ISCO Teledyne automatic sampler with a maximum capacity of 24 L, Lincoln, NE, USA). In parallel, four grab water subsamples (2.5 L) were collected weekly with a beaker using a telescopic pole from four representative spots in the wetland forebay. The subsamples were then pooled into a weekly composite sample. Water was additionally sampled monthly from the piezometers in the gravel filter (2 L per piezometer, a total of 12 L) after a 2-minute purge.

Water samples were successively filtered at 11 µm through grade one cellulose (Whatman 1001-047) and 0.45 µm cellulose acetate membrane filters and stored at 4 °C until further analysis. The hydrochemical composition (Supplementary material (SI), Table S1) of water samples was determined by ion chromatography (IC) and inductively coupled plasma atomic emission spectroscopy (ICP–AES) using standard analytical procedures (NF/ISO) (Lucas et al., 2010). Conductivity, temperature, and pH were directly measured in the wetland water using WTW multi 350i sensors (WTW, Weilheim, Germany). Total suspended solids (TSS) were obtained from the inlet, forebay, and piezometer water samples by passing the water through 0.45 µm filters and weighing the mass of the suspended solids after drying.

Polar Organic Chemical Integrative Samplers (POCIS). POCIS were used to obtain integrative isotope signatures of pesticides in the forebay area over time in water samples and to compare the integrative signatures with punctual isotope signatures from grab samples. POCIS were deployed in triplicate in the stormwater wetland forebay area over three consecutive periods of 28 days, from June 30th to September 22nd. The POCIS were transported on ice to the laboratory and extracted within 15 h after collection or frozen at –20 °C before extraction (Gilevska et al., 2022a). Briefly, each POCIS was opened to transfer the sorbent to an SPE cartridge, which was

153 then covered by HDPE frits. The samples were eluted using the SPE procedure, with cartridges
154 dried for 20 minutes with N_2 nitrogen and eluted with successive 3 mL volumes of MeOH and
155 MeOH:EtOAc (Lissalde et al., 2011). The extracts were evaporated and reconstituted in ACN.

156 *Sediment.* The top (0-10 cm) forebay sediments were sampled with a stainless-steel shovel
157 that was cleaned with ultrapure water and ethanol and wiped between collections. Sediment
158 samples were sieved through a 2-mm mesh and stored at 4 °C before analysis in tightly closed glass
159 bottles. The physicochemical characteristics of the sieved sediment samples (Table S2) were
160 measured using standard analytical procedures (NF/ISO) (Lucas et al., 2010).

161 *Vegetation.* Common reeds, common duckweed, and common cattail individuals (n_{total}=20)
162 were sampled monthly from June to September from the wetland forebay and separated into roots
163 and aerial parts (except for duckweed). Plant roots and aerial parts were washed by shaking the
164 roots for 10 min in ultrapure water. The water was replaced several times until the sediment was
165 entirely separated from the roots (Barillot et al., 2013). A 0.9% NaCl solution was then used twice
166 to rinse the plant material to remove rhizosphere sediments. The plant material was homogenized
167 with a hand blender (Bosch MSM66110) and frozen at –20 °C until further use.

168 **2.3. Pesticide extraction**

169 The pesticide extraction method for water samples (inlet runoff, forebay, piezometer and
170 from DIM degradation assays) was adapted from USA EPA method 525.2, and extraction was
171 carried out using an AutoTrace 280 solid-phase extraction (SPE) system (Dionex®, CA, USA)
172 (Elsayed et al., 2014). The pesticides obtained from the sediment, soil, or plants were extracted
173 using a solid-liquid extraction protocol (modified ultrasonic-assisted extraction) described

previously (Gilevska et al., 2022b). The POCIS were handled and extracted separately using SPE (Gilevska et al., 2022a).

2.4. DIM degradation assays

Since DIM prevailed in pesticide runoff entering the wetland and in the wetland over the studied period (60% of the total mass of the ten targeted pesticides), DIM was used as a model compound to examine pesticide degradation in the wetland. Pseudo first-order kinetics were assumed in all degradation experiments (SI, Section S2).

2.4.1. DIM photodegradation

DIM direct and indirect (i.e., with nitrate and dissolved organic carbon) photodegradation in an aqueous solution was performed under constant simulated sunlight (Q-Sun Xe 1 chamber) with 0.68 W/m^2 at 340 nm. The direct photodegradation of DIM takes place through direct interaction with light, while indirect photodegradation typically involves reactive intermediates or products formed during a photochemical reaction during DIM degradation. The light intensity corresponded to the Solar Maximum condition, i.e., global noon sunlight at normal incidence on the summer solstice. The irradiance time was later normalized according to 5.21 peak sun hours per day in June in France (Honsberg and Bowden, 2019). The aqueous solution was prepared to mimic the wetland hydrochemical conditions (Table S1) with nitrate (2 mg/L sodium nitrate salts), 10 mM phosphate buffer ($Na_2HPO_4 \cdot 7H_2O$ 1.084 g/NaH_2PO_4O 408 mg), Suwanee River fulvic acid (20 mg/L - carbon content ~53%) and DIM (0.5 mg/L). Duplicate samples were extracted on Days 1, 2, 3, 4, 5, 7, and 8. Controls were kept in the dark at 60 °C (mimicking Q-Sun Xe 1 chamber temperature) and were extracted on Days 1, 4, 6, and 8. In parallel, an experiment with 0.5 mg/L DIM in distilled water was set up to account for direct photolysis (i.e., DIM transformation as a

consequence of DIM light absorption), and samples were extracted on Days 1, 4, and 8. Considering the low (0.001 mPa) vapour pressure of DIM, no significant DIM volatilization was expected, and any volatilization was accounted for in the dark control experiment. Degradation kinetics were expressed as the sum of Z and E isomers due to the possible isomerization of E into Z upon irradiation (Avetta et al., 2014).

2.4.2. DIM degradation in wetland water

DIM dissipation was investigated in well-homogenized, oxic wetland water microcosms consisting of 60 mL vials filled with 40 mL of water spiked with DIM (0.5 mg/L) and crimped with PTFE caps (Interchim®). A Rotilabo® PTFE syringe filter (0.2 μm) mounted on a syringe tip was used to maintain oxic conditions while avoiding contamination (Torabi et al., 2020). Duplicate microcosms were incubated in the dark at room temperature (20 ± 1 °C) and maintained under constant shaking (orbital shaker, 80 rpm). Duplicate controls were prepared with autoclaved wetland water following the same procedure as above. Four blanks were prepared with DI water without DIM to account for the background matrix of the wetland water samples. Samples were collected on Days 1, 5, 10, 15, 30, and 120. The controls were sampled on Days 1, 30, and 120, and the blanks were sampled on Days 1 and 120.

2.4.3. DIM degradation in wetland water with common duckweed

Common duckweed collected from the stormwater wetland was used to examine DIM degradation in the presence of plants. Our experiment focused on the combined effect of DIM degradation within the plant and by the root microbiome while accounting for DIM uptake by the plants by following temporal changes of DIM concentrations within the plant. A total of 50 microcosms were set up in 40 mL beakers, including six treatments. The effect of common

duckweed on DIM degradation was examined in microcosms with autoclaved and nonautoclaved wetland water. In parallel, DIM degradation in the absence of plants but with reduced natural light exposure to mimic plant coverage in the wetland was examined in dark (D) and semidark (SD) microcosms. The semidark and dark light control microcosms were wrapped in aluminium foil from the top, with the semidark having five holes (Ø: 2 mm) on the top cap. In parallel, six blanks with DI water (processional blank, PB) and four microcosms with nonspiked wetland water and plant material (background blank, BB) were set up. All beakers were wrapped with pierced transparent foil to limit evaporation and covered with aluminium foil up to the water level. The microcosms with common duckweed and autoclaved and nonautoclaved wetland water were sampled on Days 1, 7, 15, 20, 27, 37, and 45. The control (D and SD) and blank (PB, BB) samples were collected on Days 1, 15, 27, and 45.

2.4.4. DIM degradation in wetland sediment

DIM degradation was evaluated in anoxic (Maillard and Imfeld, 2014) (Table S1) wetland sediment. The sieved sediment was spiked with an aqueous DIM solution (20 μg/g, racemic mixture of Z and E isomers), thoroughly homogenized, and 20 g (wet weight) of sediment was distributed into twenty-one 40 mL glass vials. The procedure was repeated using autoclaved (autoclaved three cycles, 120°C, 20 min) sediment as an abiotic control. Six additional background controls that consisted of 20 g of sediment were spiked with DI water only without DIM. The vials were capped with blue butyl rubber stoppers and incubated under a N_2 atmosphere. Nonsterile and sterile (autoclaved) triplicate vials were collected on Days 0, 5, 6, 7, 8, and 10 and extracted as described above.

2.5. Chemical analysis

2.5.1. Pesticide quantification and isomer analysis

DIM and other pesticides were quantified with a gas chromatograph (GC, Trace 1300, Thermo Fisher Scientific) coupled to a mass spectrometer (MS, ISQ™, Thermo Fisher Scientific) (Masbou et al., 2018). Chromatographic separation was performed with a TG–5MS column (30 m × 0.25 mm ID, 0.25 µm film thicknesses). The mass spectrometry and GC parameters are provided in SI, Section S3.

Changes in the E/Z ratios of DIM were calculated with the isomer fractionation IF(Z) (Equation S3) (Masbou et al., 2022), with IF(Z) = 0.5 and IF(Z)>0.5 featuring a racemic mixture and enrichment in DIM Z, respectively.

2.5.2. DIM CSIA

The concentrations of DIM Z in the wetland water throughout the sampling campaign ($\bar{X}$ ± σ: 306 ± 534 ng/L) were sufficient for carbon CSIA, whereas DIM E concentrations ($\bar{X}$ ± σ: 93 ± 148 ng/L) were insufficient. The carbon stable isotope values ($\delta^{13}C$) of DIM Z were measured using a GC-C-IRMS system consisting of a TRACE™ Ultra gas chromatograph (ThermoFisher Scientific) coupled via a GC IsoLink/Conflow IV interface to an isotope ratio mass spectrometer (DeltaVplus, ThermoFisher Scientific) (Masbou et al., 2022). To ensure measurement accuracy, standard injections with known isotopic compositions of DIM (Z and E isomers), characterized by elemental analyzer IRMS, were performed every six samples. The reproducibility of $\delta^{13}C$ measurements was ± 0.4 ‰ (n≥3). The total uncertainty in carbon isotopic measurements, including precision, accuracy, and reproducibility, was ± 0.6 ‰ (n= ≥3). All isotopic measurements are reported in delta notation (Coplen, 2011) relative to an international isotopic scale (Vienna Pee Dee Belemnite).

Isotope fractionation values (ε_E), that relate a change in $\delta^H E$ to the extent of degradation, were derived from the Rayleigh equation without forcing the regression line through the origin (Scott et al., 2004):

$$\ln\left(\frac{\delta^H E\ (t)+1}{\delta^H E_0+1}\right) = \varepsilon_E \times \ln\left(\frac{c(t)}{c_0}\right) \qquad \text{Equation 1}$$

where $\delta^H E_0$ and $\delta^H E(t)$ represent the isotope signatures at time 0 and t of degradation, respectively, whereas $c(t)/c_0$ is the fraction of remaining pesticide at time t.

The extent of biodegradation B, expressed in % (Hunkeler et al., 2008) was calculated using the ε_E value determined in this study, according to Equation 2. A large (>60%) biodegradation extent is typically required to observe significant ($\Delta(^{13}C)$ >2 ‰) carbon isotope fractionation in large molecules like DIM, as the magnitude of fractionation decreases with increasing carbon number.

$$B = \left(1-\left(\frac{\delta^H E\ (t)+1}{\delta^H E_0+1}\right)^{\frac{1}{\varepsilon_E}}\right)\times 100 \qquad \text{Equation 2}$$

2.6. Mass balance calculations

2.6.1. Hydrological mass balance

A simple hydrological model of the wetland provided the filling-emptying dynamics and the water volumes of the forebay and gravel compartments of the wetland during the study period

(SI, Section S4). The model included water discharge at the wetland inlet from the upstream catchment, direct rainfall, evapotranspiration, and outflow.

2.6.2. Pesticide mass balance from concentration data

The pesticide mass stored in the wetland (*Mx*) on a weekly basis or over different periods, depending on the hydrological functioning of the wetland, was calculated with Equation 3:

$$M_x = \sum^4 M_{dissolved} + M_{TSS} + M_{plant} + M_{sediment} \quad \text{Equation 3}$$

where four pools of pesticide mass (mg) are considered: the dissolved phase $(M_{dissolved})$ and a total suspended solid (M_{TSS}) in water stored in the wetland, the uptaken mass in plants (M_{plant}), and the sorbed mass in wetland sediments $(M_{sediment})$ (Table S3).

The weekly mass load of pesticides at the wetland inlet, considering the pesticide mass in both the dissolved and the suspended solid phases in inlet samples, was calculated with Equation 4:

$$M_{inlet,x} = M_{dissolved\_inlet} + M_{Tss\_inlet} \quad \text{Equation 4}$$

The extent of pesticide degradation during periods without outflowing water was calculated with Equation 5:

$$Degradation\ (\%) = \frac{M_x}{M_{x-1} + \sum M_{inlet,x}} \times 100 \quad \text{Equation 5}$$

where (M_x) is the pesticide mass stored in the current week, (M_{x-1}) is the pesticide mass stored in the previous week or beginning of the period, and ($\sum M_{inlet,x}$) is the sum of all the mass loads from the inlet during the evaluated period.

Assumptions for the mass balance, including plant density, weight and coverage, and sediment depth, are provided in Table S3.

2.6.3. Isotope mass balance

The isotope mass balance was calculated on a weekly basis or for a defined period, i.e. wet or dry periods when entering runoff or stored volume did or did not generate outflow, respectively. To estimate DIM Z degradation in the wetland, two different calculations were used, depending on the presence or absence of DIM Z runoff at the inlet. Equation 2 was used to quantify DIM Z degradation in a period without an incoming runoff. Here, $\delta^{13}C_x$ measured at week x in the forebay was used as $({}^{H}E_{(t)})$, while $\delta^{13}C_{x-1}$ measured at the beginning of the period was used as $(\delta^{H}E_{0})$.

When runoff entered the wetland, the extent of DIM Z degradation was calculated using Equation 2 with the $(\delta^{13}C_x)$ value of DIM Z measured in week x in the forebay as $({}^{H}E_{(t)})$ and $(\delta^{H}E_{0})$ calculated with Equation 6:

$$\delta^{H}E_{(0)} = \frac{(\mathrm{M}_{x-1} \times \delta^{13}C_{x-1} + \mathrm{M}_{x,inlet} \times \delta^{13}C_{x,inlet})}{(\mathrm{M}_{x-1} + \mathrm{M}_{inlet,x})} \quad \text{Equation 6}$$

where (M_{x-1}) is the mass stored in the forebay the week before, $(M_{x,inlet})$ is the DIM Z load at the inlet in week x, and $(\delta^{13}C_{x-1})$ and $(\delta^{13}C_{x,inlet})$ are the respective isotopic compositions.

2.6.4. Estimation of uncertainties

The uncertainties associated with pesticide loads (Equation 4) and degradation estimates (Equations 2, 5, and 6) were calculated via error propagation by accounting for errors associated with (i) the terms of the hydrological mass balance (Section 2.6.1), including the water depth measurement in the inlet venturi channel (range ± 2 mm compared to the recorded water depth), (ii) the topographical/elevation data for the forebay, stone barrier, and sediment zone water volume (range: ± 5 cm), and (iii) the total analytical errors associated with DIM quantification and CSIA.

3. Results and discussion

3.1. Hydrological dynamics and DIM load entering the wetland

From June 2nd to September 28th, 1059 m^3 of surface runoff from the upstream vineyard catchment entered the wetland, while direct rainfall on the wetland contributed 83 m^3. Outflow and evapotranspiration reached 928 m^3 and 254 m^3, respectively. The simulated water volume in the wetland varied from 9 to 184 m^3. The sampling campaign was divided into two periods based on hydrological dynamics. Two periods from June 30th to August 1st and from August 11th to September 28 were defined as "dry" as entering runoff or stored volume did not generate outflow. During the dry periods, the wetland was considered a half-closed system, i.e., without outflow and with evapotranspiration only. In contrast, during the wet periods with outflow, the wetland behaved as an open system.

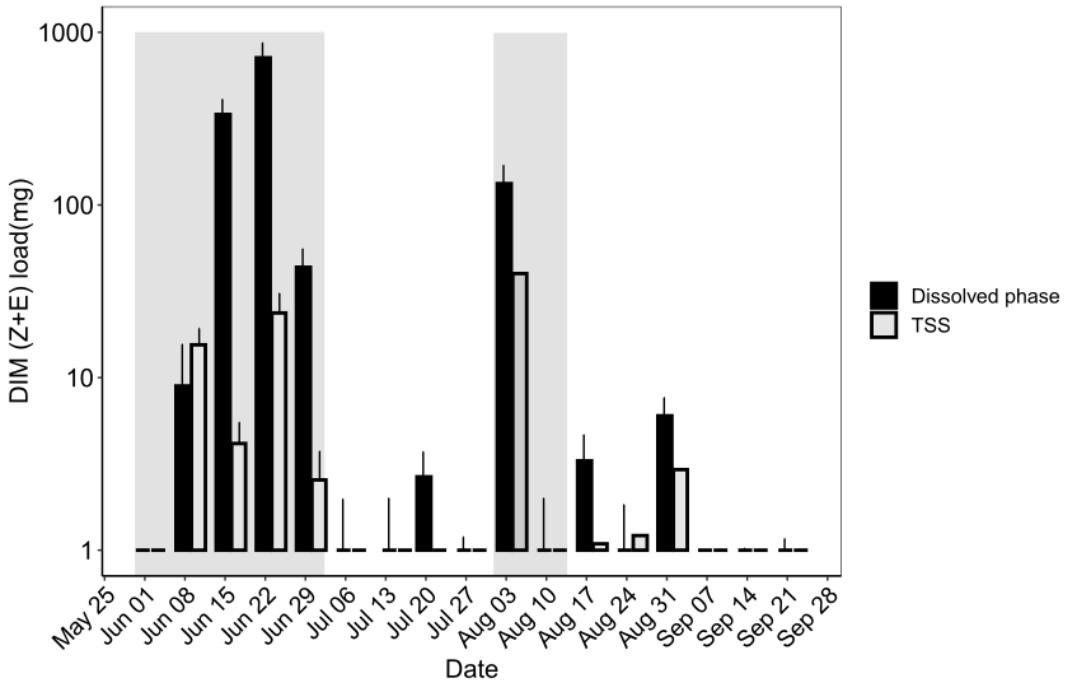


Figure 1. Load of DIM (Z+E) in dissolved and total suspended solids (TSS) phases of runoff entering the stormwater wetland (Rouffach, France). The shaded area corresponds to wet periods

with outflow. The error bars associated with the DIM loads correspond to the propagated error (Section 2.6.4)

The DIM loads (Equation 4) from the upstream catchment and entering into the wetland were 100 times higher during wet than during dry periods, with the highest occurrence and loads of DIM observed in the dissolved phase (Figure 1). Other pesticides detected during the study are presented in Section S6. Strong storm events mobilized significant amounts of TSS and associated DIM from the vineyard plots. For instance, a single intense storm event on August 2nd (peak flow velocity at inlet: 91 L/s) mobilized a DIM load associated with TSS (46 ± 9 mg) that was equivalent to the total DIM load in June (40 ± 7 mg) (Figure 1). The loads of DIM Z in the dissolved phase (952 ± 175 mg) and total suspended solids (TSS) (200 ± 29 mg) were three times higher than loads of DIM E (Table S4).

The concentrations of DIM found in the runoff samples varied from below the detectable limit (1 ng/L) up to 2.2 µg/L in the dissolved phase. Based on the toxic unit (TU) (Inostroza et al., 2018) and a toxicity database (Olker et al., 2022), these concentrations may cause adverse chronic effects in fish (TU>1) but not in algae (TU<1). This underscores the importance of intercepting DIM surface runoff from the vineyard catchment to prevent downstream impacts.

3.2. DIM degradation assays

DIM degradation assays were conducted to evaluate DIM degradation in the wetland compartments and to retrieve isotope fractionation values to establish the isotope mass balance using CSIA data. The assays emphasized significantly different kinetics and isotope fractionation values for DIM photodegradation in water and DIM degradation in oxic water with and without plants (Common duckweed) and in anoxic sediments (Table 1).

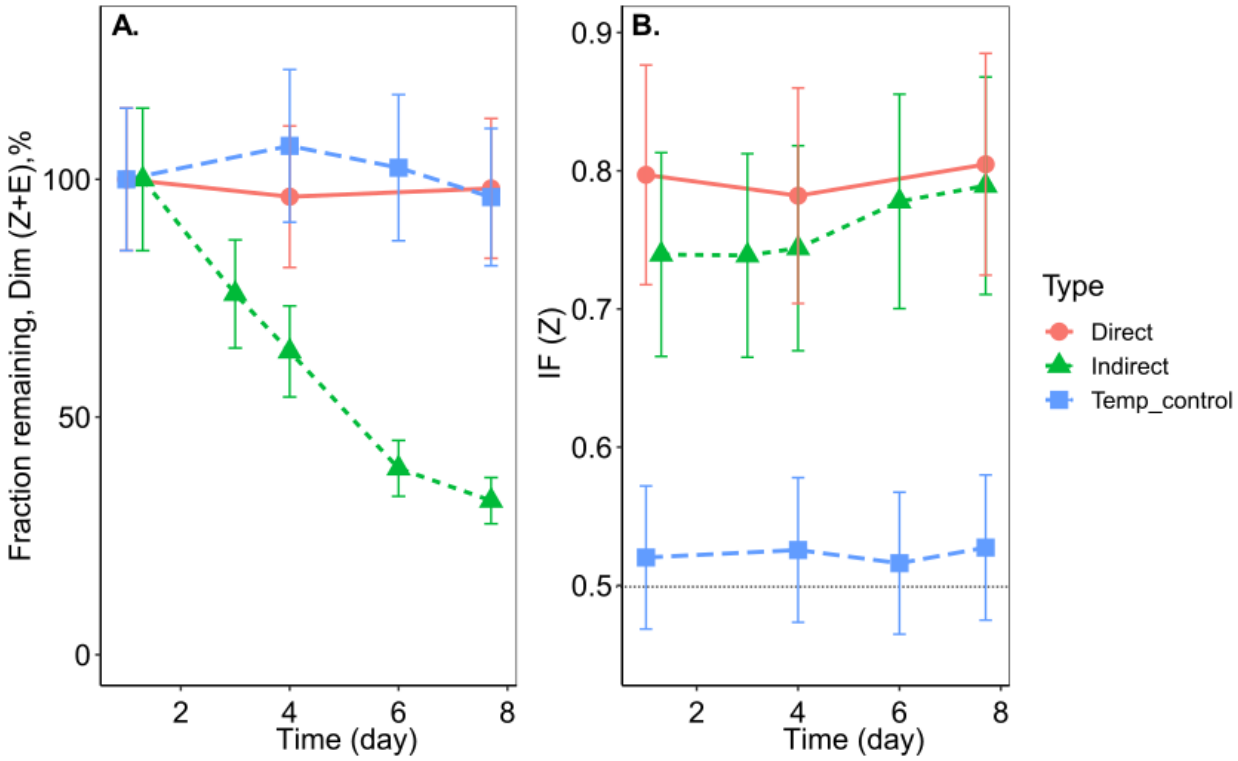
Table 1. Results of DIM E and Z laboratory degradation assays. The duration of laboratory assays varied among the experiments and conditions. n.s. means within the uncertainty range.

Experiment	Condition	Degradation (%)	Isotope fractionation (ε) (‰)	Inversion between isomers	Half-life ($t_{1/2}$) (d)
Photodegradation (indirect)	oxic	75 (sum E+Z)	n.s.	E isomer into Z	15.3 ± 2.2 for sum E+Z
Biodegradation, water	oxic	n.s.	n.s.	n.s.	-
Biodegradation, water, and plant	oxic	45 (E), 30 (Z)	n.s.	n.s.	56-62 (E) and 82-103 (Z)
Biodegradation sediment	anoxic	96 (E) and 96 (Z)	−3.0 ± 0.6 (E) −2.0 ± 0.2 (Z)	n.s.	1.2 ± 0.6 (E) and 1.5 ± 0.8 (Z)

3.2.1. DIM direct and indirect photodegradation

DIM underwent rapid (<24 h) inversion from the E to Z isomer (IF(Z) – 0.8) in indirect photodegradation experiments with synthetic wetland water and in direct photodegradation experiments (Figure 2) as already observed previously (Avetta et al., 2014). In contrast, IF(Z) concentration did not vary significantly in the dark control experiment, confirming that light exposure caused the inversion from the E to Z isomer of DIM. Up to 75% DIM (Z+E) was degraded within 8 days under laboratory conditions, corresponding to a half-life of 15.3 ± 2.2 days under field conditions, i.e., 5.21 peak sun hours per day.

No carbon isotope fractionation was observed for both isomers during photodegradation (Figure S5) since radical formation likely occurred irrespective of the presence of heavy and light isotopes (Rosario-Ortiz and Canonica, 2016). The reaction may proceed by radical addition to the double bond of DIM, resulting in the formation of an alkyl radical. Since the radical may be formed at the (R1R2C=) carbon or the (=CH(CO) carbon, the reaction would mainly produce 4-chlorophenyl-3,4-dimethoxyphenyl methanone (CPMPM) or N-formyl morpholine, respectively (Al Rashidi et al., 2013; Avetta et al., 2014). CPMPM was detected in photodegradation experiment samples but only in trace amounts (data not shown). Similar to anoxic biodegradation (Section 3.2.3), a mono-demethylated transformation product was also detected, but in small quantities (<3% of the initial DIM amount). Therefore, the DIM transformation pathway during photodegradation could not be elucidated, likely due to the further degradation of unknown DIM transformation products.



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378 **Figure 2**. Fraction remaining (%) of DIM (Z and E isomers) (A) and isomeric ratio IF(Z) of DIM
379 (B) during direct and indirect photodegradation experiments and in dark control experiments. The
380 dotted black line in panel B represents the IF(Z) ratio of a standard.

381 **3.2.2. DIM degradation in wetland water with and without plants**

382 In the oxic biodegradation experiments, DIM Z and DIM E did not degrade for 120 days in
383 the wetland water without duckweed (Figure S6). However, DIM Z and DIM E showed moderate
384 degradation in experiments with duckweeds in both autoclaved and nonautoclaved wetland water
385 (Figure S7A). In contrast, DIM was not significantly ($p \geq 0.36$) degraded in the corresponding
386 control experiments (Figure S7B), indicating that moderate and slow DIM degradation was
387 associated with the presence of duckweeds.

The degradation of DIM in experiments involving duckweeds was driven either by the plant itself or its associated microbiome. To accurately assess DIM mass in the microcosm, the calculations accounted for DIM concentrations in the plant to include DIM plant uptake and sorption. The half-lives of DIM Z (from 82 and 103 days) were longer than those of DIM E (from 56 and 62 days) in both experiments with wetland water and plants and with autoclaved wetland water and plants (Table 1). This suggests the preferential degradation of DIM E, although shorter half-lives (from 2.1 to 3.7 days in potato plants) for DIM degradation in plants have been previously reported (Chen et al., 2018; Yang et al., 2022). However, DIM analysis indicated no carbon stable isotope fractionation, either because only a minor (<45%) degradation of DIM was observed after 45 days (Figure S8) or due to the absence of isotope fractionation during plant-associated biodegradation. Overall, these results revealed that plant degradation associated with duckweeds may not be a prevailing dissipation process for DIM in stormwater wetlands.

3.2.3. DIM degradation in the wetland sediment

The dissipation half-lives of DIM E and Z in the wetland sediment were 1.2 ± 0.6 and 1.5 ± 0.8 days, respectively, which were one and two orders of magnitude higher than in photodegradation and degradation in water with duckweeds, respectively. DIM concentrations did not significantly change in the abiotic controls, excluding significant DIM abiotic degradation. These half-lives are consistent with the reported half-lives of DIM (EFSA, 2006; Masbou et al., 2022), indicating slower degradation of the Z isomer in aerobic and field studies.

Stable isotope fractionation observed for both DIM Z and E confirmed the occurrence of *in situ* biodegradation in the sediment. The ε_C values were −2.0 ± 0.2‰ and −3.0 ± 0.6‰ for DIM Z and E, respectively (Figure S9). Variations of ε_C between geometric isomers (DIM Z and E) can be

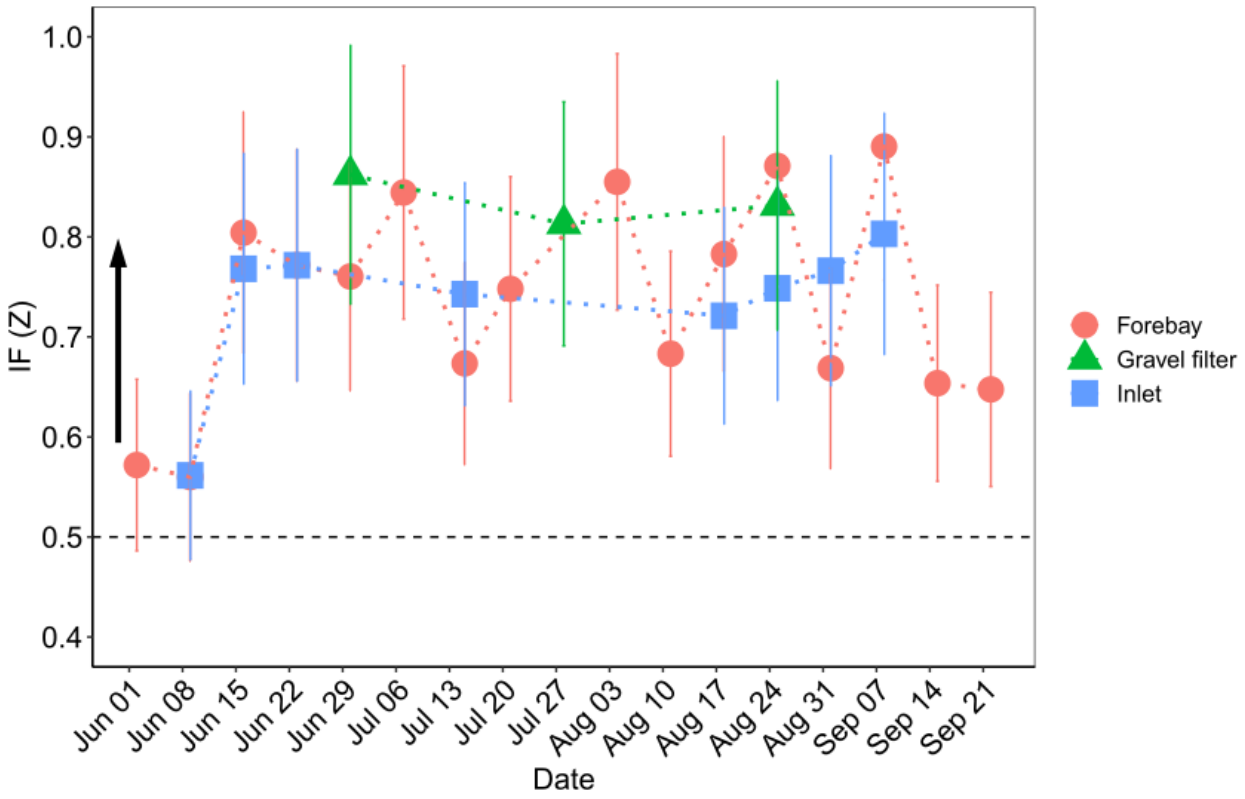
attributed to differences in their electronic structures and steric effects, as observed during the anaerobic degradation of compounds like *cis*- and *trans*-1, 2-dichloroethene (Hunkeler et al., 2002). This is the first report of isotope fractionation during DIM degradation under anoxic conditions. Close but lower isotopic fractionation values ($\varepsilon_{DIM\text{-}(Z)} = -1.6 \pm 0.2‰$ and $\varepsilon_{DIM\text{-}(E)} = -1.5 \pm 0.2‰$) were recently reported for degradation in oxic vineyard soils (Masbou et al., 2023). Under oxic conditions, DIM degradation by the strain *Bacillus cereus WL08* has been proposed to start with the oxidative cleavage of the carbon double bond (Zhang et al., 2020). Under anoxic conditions, DIM degradation to mono-demethylated products (EFSA, 2006) which, have also been detected in wetland sediments (data not shown), was reported. Although microorganisms capable of degrading DIM under anoxic conditions are not known and were not examined in this study, it is worth noting that different bacteria associated with the Firmicutes phylum, which were abundant in the sediments (Figure S10), have been shown to possess the ability to O-demethylate organic compounds (Levy-Booth et al., 2021). DIM degradation to mono-demethylated products would imply C-O bond cleavage, with a maximum value of the kinetic isotope effect of ~1.061 based on the semiclassical Streitwieser limit (Elsner, 2010). This is consistent with the apparent kinetic isotope effect (AKIE) values for C-O oxygen bond cleavage for isomer Z (1.044 ± 0.004) and isomer E (1.064 ± 0.012) (SI, Section S5).

3.3. Isomer fractionation of DIM in the stormwater wetland

The degradation experiments demonstrated that the degradation potential of DIM isomers largely varied among wetland compartments. Moreover, DIM E degrades faster than DIM Z, although sunlight exposure converts it quickly into DIM Z. Hence, the IF(Z) (isomeric ratio) was used to examine DIM transformation in the stormwater wetland.

At the beginning of the study (June 2nd), the IF(Z) ratio of DIM entering in the wetland was close to 0.5 (Figure 3), corresponding to the isomeric ratio of DIM in the commercial formulations (GRIP TOP®) applied in the vineyard between the end of May to the end of June (Masbou et al., 2022). From the 16th of June onwards, the IF(Z) of DIM in runoff entering the wetland gradually increased to 0.83 (IF(Z)>0.5 featuring enrichment in DIM Z). Such an increase in IF(Z) over time was also observed in the vineyard soil and the runoff water, which may reflect DIM biodegradation in soil and/or via light exposure (Masbou et al., 2022).

The IF(Z) in the wetland forebay reached 0.8 on the 16th of June and then fluctuated from 0.65 to 0.90 throughout the study period (Figure 3). Several co-occurring processes, including biodegradation, photodegradation, mixing, and desorption from sediments, may have affected the DIM isomeric ratios in the wetland. However, vegetation fully covered the wetland by the end of July, which likely limited the effect of light on isomerization. This, along with the rapid degradation of DIM in the wetland sediment, supports the idea that higher IF(Z) ratios in the water of the forebay and the gravel filter indicate DIM biodegradation in the wetland sediment. The subsequent section extends the analysis from isomeric ratios to the exploration of the isotopic ratios of DIM Z in the wetland.



448

449 **Figure 3**. Isomer fraction IF(Z) of DIM in the water of the inlet (blue squares), forebay (red circles),
450 and gravel filter (green triangles) area of the stormwater wetland (Rouffach, France). The dashed
451 line represents the IF(Z) of the applied formulation. An arrow indicates preferential E degradation
452 from June onwards. The error associated with IF(Z) represents the analytical uncertainties of
453 isomer measurements (n >3).

454 **3.4. Carbon stable isotope fractionation of DIM Z in the stormwater wetland**

455 The DIM Z isotope signatures ($\delta^{13}C$) in the wetland grab water samples were measured
456 with a high preconcentration factor (×20,000-fold) down to DIM Z concentrations of 88 ng/L. The
457 POCIS were also used to measure DIM Z $\delta^{13}C$ after 30 days of deployment in the wetland forebay.
458 While POCIS measurements represent an integrative $\delta^{13}C$ value over 30 days, punctual $\delta^{13}C$ values
459 were retrieved from the grab water samples from the wetland (Gilevska et al., 2022a).

460 The source signature in this study was the stable isotope composition ($\delta^{13}C$) of the
461 commercially applied formulation in the Rouffach catchment (GRIP TOP®; $\delta^{13}C = -33.0 \pm 0.3‰$),
462 which was compared to the $\delta^{13}C$ values from the POCIS and grab water samples. The changes in
463 the $\delta^{13}C$ of DIM Z in the wetland were attributed to DIM biodegradation in the sediment (Table 1).
464 Indeed, photo- and plant-associated degradation did not cause significant isotope fractionation in
465 laboratory experiments, while abiotic degradation in control microcosms was insignificant. A
466 threshold of $\Delta(^{13}C)>2$ ‰ was used to determine significant carbon isotope fractionation caused by
467 DIM transformation (Figure 6) (Hunkeler et al., 2008). A significant isotope fractionation
468 ($\Delta(^{13}C)>2‰$) corresponded to more than 60% DIM Z anaerobic sediment degradation, accounting
469 for the error in the fractionation factor value (Equation 1).

470 The similarity of $\delta^{13}C$ values of DIM Z in the runoff water entering the wetland and GRIP
471 TOP® formulation (Figure 4), except on August 18th, suggested that the extent of DIM Z
472 degradation in the vineyard soil was generally too small to be detected using CSIA. While DIM
473 degradation in the soil may prevail in specific areas, it is likely that the cumulative runoff primarily
474 consists of undegraded DIM exported from vineyard plots. These findings differ from those of
475 (Masbou et al., 2022), who reported significant degradation of DIM Z in the vineyard soil of the
476 upstream catchment in 2016 and 2017. This difference could be explained by the interannual
477 variability in environmental conditions affecting DIM degradation in soil, such as rainfall,
478 temperature, soil properties, and agricultural practices.

479 Overall, the grab samples provided punctual information on *in situ* degradation in the
480 wetland whereas POCIS samples were affected by fresh inputs of undegraded DIM in the runoff
481 entering the wetland (Figure 4). The grab samples were more able to capture DIM Z isotopic
482 signatures in the wetland, with $\delta^{13}C$ values of DIM Z showing significant enrichment in ^{13}C (2.0≥

$\delta^{13}C \leq 5.1‰$) compared to those of GRIP TOP®. The difference in the $\delta^{13}C$ values between the inlet and forebay samples ($\Delta(^{13}C)$ of 3.0‰, Figure 4) over time also confirmed the *in situ* biodegradation of DIM Z.

Based on laboratory experiments, it was expected that rapid DIM biodegradation mainly occurred in the wetland sediment. Microorganisms associated with DIM biodegradation were likely more abundant in sediments than in the water column, explaining the very low concentrations of DIM in the sediments, which limited DIM CSIA. In contrast, light penetration (first 10 cm of water column) in natural waters (Mathon et al., 2019) is generally limited, and DIM photodegradation only contributed to DIM degradation in June, when the wetland was not covered by duckweeds (Figure S2).

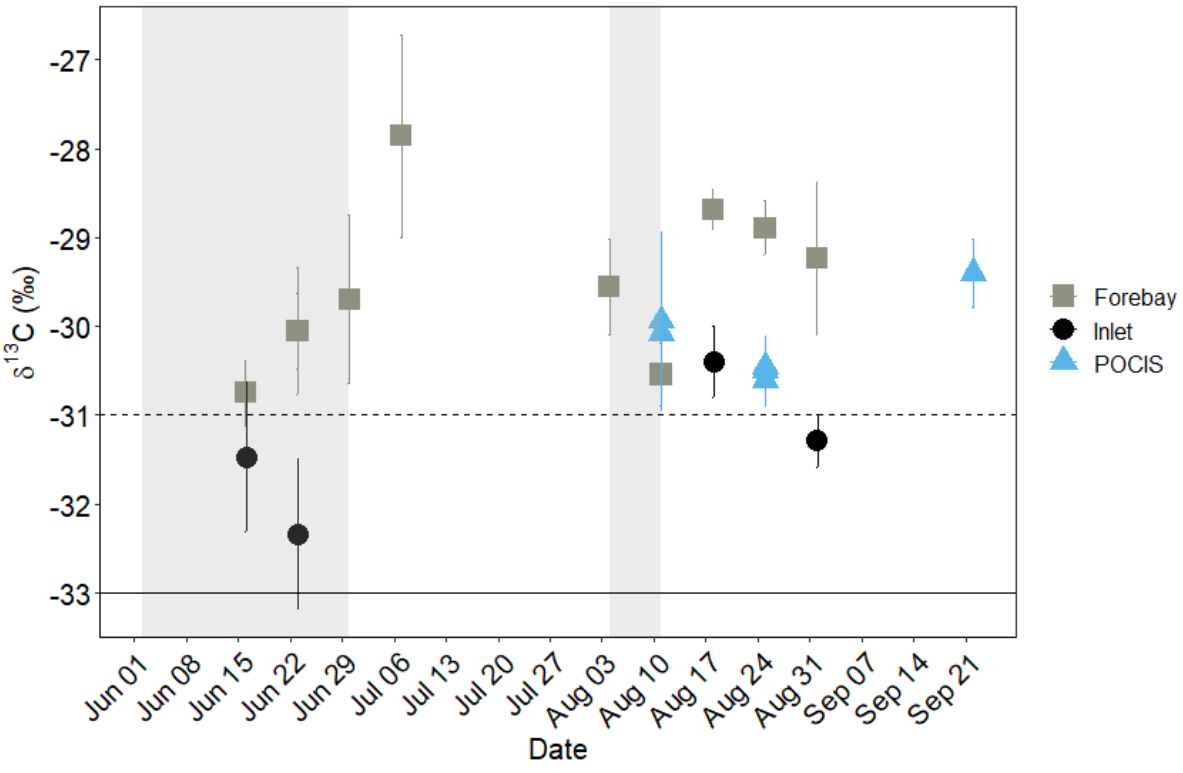


Figure 4. $\delta^{13}C$ values of DIM Z from grab water samples at the inlet (black circle), and forebay (grey squares) areas of the stormwater wetland (Rouffach, France) and from POCIS (blue triangle). The dashed line represents the 2‰ range from the carbon isotope value of the pure product (GRIP TOP®, −33.0‰) represented by the solid line. The shaded area corresponds to wet periods, with water outflow from the wetland. The error bar represents the reproducibility of the measurements (n≥3).

3.5. Quantitative estimates of DIM Z biodegradation in the wetland

A concentration-based mass balance was used to quantify the extent of dissipation and degradation of all detected pesticides in the stormwater wetland (SI, Section S7). Mass balances based on DIM Z concentrations (Equation 5) and stable isotope data (Equation 2 and 6) provided similar estimates for the extent of DIM Z degradation and indicated significant (>46 ± 20%) DIM Z degradation over the study period (Table 2). Interestingly, the extent of DIM Z degradation during the two dry periods was similar, despite their different durations (Table 2). The agreement between both mass balance approaches is remarkable considering their different conceptual and methodological basis. This confirms the validity of using CSIA for evaluating the contribution of pesticide degradation in wetland systems.

513 **Table 2**. Degradation estimates of DIM Z in the stormwater wetland (Rouffach, France) for the
514 wet and dry periods using the classical (Equation 5) and isotope mass balance approaches
515 (Equations 2 and 6). n.a.: not applicable due to a lack of outflow monitoring.

Period	Degradation extent (%)	
	Classical mass balance	Isotope mass balance
Wet period (June 2nd - June 30th)	n.a.	71 ± 18
Dry period (June 30th– August 1st)	94 ± 22	61± 26
Wet period (August 1st– August 11th)	n.a.	46 ± 20
Dry period (August 11th– September 22nd)	86 ± 18	68 ± 17

516

517 In the classical mass balance approach, the accuracy of pesticide degradation estimates
518 largely depends on the physicochemical properties of the compound and the consideration of
519 processes and compartments assumed to be involved in pesticide degradation. For instance, DIM
520 degradation could be estimated with this approach, since DIM is not volatile (Lewis et al., 2006)
521 and its sorption or uptake in plants and sediments was accounted for in our study. However,
522 extensive field and laboratory work is required to account for all processes and compartments
523 potentially involved in pesticide degradation and their dynamics.

524 It is also noteworthy that degradation based on concentration mass balance was estimated
525 by assuming that the pesticide detection limits were similar across wetland compartments.
526 However, the detection limits for pesticides in the dissolved phase were >1000-fold lower than
527 those in the sediment, plant, or TSS samples since large (up to 12 L) water volumes were processed
528 (Gilevska et al., 2022b). Such differences in detection limits among wetland compartments can
529 lead to a severe overestimation of pesticide dissipation, which may explain the higher estimates of

DIM Z degradation in the stormwater wetland using the classical mass balance approach. In addition, the estimation of pesticide concentrations in the TSS from the wetland runoff may be inaccurate due to the variability in the TSS concentration (32 to 378 mg/L) in runoff entering the wetland. This variability can lead to the collection of small and poorly representative amounts of TSS during periods of low or moderate runoff, which can further bias the actual pesticide loads measured in the TSS.

In this context, the main advantage of estimating pesticide biodegradation using CSIA is that it relates changes in the isotopic composition of the target pesticide to its degradation, which is typically not influenced by nondegradative processes, such as sorption or volatilization (Hunkeler et al., 2008). This may result in more accurate and reliable estimates of biodegradation. However, systematic and lab-intensive reference degradation experiments are required to retrieve isotope fractionation values, if they do not already exist, and to identify transformation pathways. In the case of DIM Z, carbon stable isotope analysis (CSIA) primarily indicated biodegradation in the wetland sediment, with no observed isotopic fractionation during DIM photodegradation. This suggests that relying solely on isotope data for estimating DIM Z degradation in wetlands may underestimate its extent if non-fractionating degradative processes play a significant role, thus rendering such degradation estimates conservative. When the estimation of DIM Z degradation extent is extended to both isomers of DIM using the isotope approach, it reinforces a more cautious perspective. This is because laboratory experiments have shown that DIM E, the second isomer, is more degradable compared to DIM Z.

The isotope mass balance approach was also advantageous in estimating DIM Z degradation during wet periods (Table 2). In fact, isotope fractionation can be directly related to degradation, and thus, a closed hydrological mass balance with inlet and outlet sampling is not needed. Notably,

553 DIM Z degradation during the second wet period was lower than that during the first wet period. It
554 can be hypothesized that the high input loads of DIM Z into the wetland during the intense storm
555 event on August 2nd reduced the DIM Z residence and reaction time in the wetland and thus the
556 extent of biodegradation (46 ± 20%, Table 2). Hence, pesticide dissipation, including
557 biodegradation, in stormwater wetlands receiving runoff from agricultural catchments may largely
558 vary depending on the runoff regime.

559 **3. Conclusion**

560 The contribution of pesticide degradation in wetlands intercepting agricultural runoff is often
561 overlooked and confounded with other dissipation processes when quantified based on pesticide
562 concentrations alone. This study confirms the potential of wetland systems for pesticide dissipation
563 and the crucial role of wetland sediments in pesticide degradation. It also highlights the variability
564 of pesticide removal in stormwater wetlands, depending on hydro-climatic dynamic. The CSIA
565 approach enabled to evaluate DIM Z degradation in a stormwater wetland, showing its
566 complementarity with traditional concentration-based methods. Estimates of DIM Z degradation
567 using concentration and CSIA data in the stormwater wetland were similar, which validated the
568 CSIA approach. The laboratory degradation assays identified wetland sediments as the primary
569 compartment controlling DIM degradation, emphasizing the need to evaluate co-occurring
570 processes to understand pesticide dissipation in wetland systems. Additionally, the DIM isomer
571 ratio (Z and E) was a sensitive proxy for the occurrence and intensity of DIM degradation.
572 Altogether, this study highlights the relevance of combining multiple lines of evidence, including
573 field surveys and laboratory experiments, and using concentration-, isotope- and isomer-based
574 approaches, to evaluate and quantify pesticide transformation in wetland systems. Future research
575 may benefit from monitoring transformation products during pesticide degradation to distinguish

incomplete and complete mineralization, and from multi-element CSIA to offer further insights into pesticide degradation pathways in wetlands.

Author contribution statement

Tetyana Gilevska: Conceptualization, Investigation, Writing - Original Draft. **Sylvain Payraudeau:** Conceptualization, Data Curation, Writing - Review & Editing. **Gwenaël Imfeld:** Conceptualization, Writing - Review & Editing, Project Management, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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