Constraining topsoil pesticide degradation in a conceptual distributed catchment model with compound-specific isotope analysis (CSIA)

Sylvain Payraudeau[1], Pablo Alvarez-Zaldivar[1], Paul van Dijk[2], Gwenaël Imfeld[1]

[1]Institut Terre et Environnement de Strasbourg, Université de Strasbourg, CNRS/ENGEES, ITES UMR 7063, Strasbourg, 67084, France

[2]Chambre Régionale d'Agriculture Grand Est, Espace Européen de l'Entreprise, 2 rue de Rome CS 30022 Schiltigheim, 67013 France

Correspondence to: Sylvain Payraudeau (sylvain.payraudeau@engees.unistra.fr)

Abstract. Predicting pesticide dissipation at the catchment scale using hydrological models is challenging due to limited field data distinguishing degradative from non-degradative processes. This limitation hampers the calibration of key parameters such as biodegradation and volatilization half-lives (DT_{50}), and the carbon-water partition coefficient (K_{oc}), often leading to equifinality and reducing confidence in predictions of pesticide persistence in topsoil and transport from agricultural field to catchment outlets. This study examines the use of pesticide Compound-Specific Isotope Analysis (CSIA) data to improve model predictions of pesticide persistence in topsoil and off-site transport at the catchment scale. The study was conducted in a 47-ha crop catchment using the pre-emergence herbicide S-metolachlor. A new conceptual distributed hydrological model, PIBEACH, was developed to simulate daily pesticide dissipation in soils and its transport to surface waters. The model integrates changes in the carbon isotopic signatures ($\delta^{13}C$) of S-metolachlor during degradation to constrain key parameters and reduce equifinality. Model and parameter uncertainties were estimated using the Generalized Likelihood Uncertainty Estimation (GLUE) method. Incorporating $\delta^{13}C$ data and S-metolachlor concentrations from topsoil samples reduced uncertainty in the degradation half-life by more than half and improved six key metrics related to pesticide persistence and transport. The results highlighted that moderate, targeted sampling effort can identify degradation hot-spots and hot-moments in agricultural soil when stable isotope fractionation is integrated into the model. Overall, integrating CSIA data into PiBEACH model significantly enhances the reliability of pesticide degradation predictions at the catchment scale. In addition, PiBEACH, which accounts for spatial and seasonal variations in topsoil pesticide concentrations, enables coupling with distributed, event-based hydrological models such as OpenLISEM OLP to capture intra-event pesticide transport dynamics more accurately.

1 Introduction

Ongoing intensive use of pesticides can lead to accumulation of pesticides and their transformation products in agricultural soils, and pesticide off-site transport for decades. Pesticides on agricultural soil can be mobilized and transported off-site towards aquatic ecosystems during rainfall-runoff events, thereby threatening drinking water supply as well as ecosystem and human health (Vorosmarty et al., 2010; Fenner et al., 2013; Stone et al., 2014; Weisner et al., 2021). While pressure on aquatic ecosystems is increasing, the contribution of each pesticide dissipation processes in soil driving to a mass decrease and

pesticide off-site transport toward the catchment outlet remains difficult to evaluate and predict accurately. In this context, reliable and validated hydrological models that predict pesticide dissipation and off-site transport have the potential to address fundamental questions, such as the relationship between hydro-climatic factors and pesticide dissipation processes with

35 respects to the transfer risks of pesticides on the catchment scale. The contribution of degradative processes, including both biotic or abiotic degradation, as well as non-degradative pesticide dissipation processes, including sorption, leaching, volatilization and off-site transport, must be quantified for this purpose in models (Larsbo and Jarvis, 2005; Steffens et al., 2015; Gassmann, 2021). The accurate and sufficiently precise prediction of pesticide dissipation and off-site transport on the agricultural catchment scale raises, however, two fundamental limits. First, the complexity of reactive transport models has

40 increased over the last decade while field datasets available to calibrate and validate such models remain scarce (Medici et al., 2012; Ammann et al., 2020). In addition, existing models frequently fail to accurately quantify the contribution of concomitant pesticide dissipation processes for accurate estimation of off-site pesticide transport (Gassmann et al., 2021).

Model prediction of pesticide dissipation and off-site transport towards aquatic ecosystems generally suffers from field data

45 limitations to constrain model parameters by calibration. Conceptual and physically-based hydrological models account for many dissipation and transport phenomena, each of which generally accounts for several physico-chemical processes and described by several parameters obtained in reference laboratory experiments (Gatel et al., 2020; Gassmann, 2021). Linking pesticide dissipation parameters obtained under laboratory conditions with field processes is however difficult, because the extent and the range of values for a given parameter may differ under laboratory and field conditions (Malone et al., 2004;

50 Köhne et al., 2009). As a result, parameter calibration is often required to fit observations. For instance, pesticide half-life (DT_{50}) in soil, i.e., the time required for 50 % dissipation of the parent compound in soil, is typically derived under laboratory conditions (Lewis et al., 2016). However, when extrapolated to field conditions, other process-controlling parameters, including soil moisture, temperature, K_{OC}, organic carbon content and porosity distribution, affect pesticide concentrations (Dubus et al., 2003). As a result, DT_{50} values obtained from literature typically span up to one order of magnitude (Lewis et

55 al., 2016; Wang et al., 2018). Pesticide half-life is thus generally considered as a lumped calibration parameter in reactive transport models (Dubus et al., 2002), merging both degradative and non-degradative pesticide dissipation processes across different soil components and redox conditions (Honti and Fenner, 2015). As a result, reducing uncertainty in DT_{50} values remains challenging at the catchment scale, despite being crucial for improving the predictive accuracy of pesticide transport models that can serve water quality management.

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Pesticide concentrations in topsoil and at the catchment outlet are currently the most accessible information for modelling pesticide reactive transport at the catchment scale (Wendell et al., 2024). In the best of cases, calibration is carried out based on concentrations of both parent and main transformation products in soil, runoff or aquifer (Gassmann, 2021), which improved model prediction (Sidoli et al., 2016; Lefrancq et al., 2018). Transformation products, however, are typically numerous, several

65 of them are unknown and possibly further degraded, which may lead to incomplete and uncertain mass balance accounts. As

a result, pesticide and transformation product concentration data often provide limited insight into distinguishing degradative from non-degradative dissipation processes in catchments (Fenner et al., 2013). Consequently, existing models struggle to differentiate between competing dissipation processes and to quantify their respective contributions.

70 Evaluating pesticide dissipation processes in field is essential as degradation is the only process that reduces the total pesticide load in environmental compartments. While degradation limits long-term pesticide accumulation, it may also produce unknown and potentially toxic transformation products that can be transported to surface and groundwater. In this context, pesticide compound specific isotope analysis (CSIA) offers an alternative approach, as it infers degradation independently of concentration data and transformation product identification, relying instead on changes in stable isotope ratios (Elsner and
75 Imfeld, 2016; Hofstetter et al., 2024). During pesticide degradation, lighter isotopes (e.g., ^{12}C) typically react slightly faster than heavier ones (e.g., ^{13}C), producing a kinetic isotope effect. This effect creates a distinct isotopic signature, reflected in changes in the isotope ratios of degrading molecules (Elsner, 2010). The stable isotope fractionation (ε_{lab}, e.g., for carbon) can be determined through closed-system microcosm experiments and applied under specific conditions to quantify pesticide degradation under field conditions (Alvarez-Zaldivar et al., 2018). In contrast, non-destructive processes like dispersion and
80 sorption are not expected to induce significant isotope fractionation under agricultural field conditions (Eckert et al., 2013; van Breukelen and Prommer, 2008; van Breukelen and Rolle, 2012; Kopinke et al., 2017). Hence, incorporating pesticide CSIA data into hydrological models can reduce uncertainties in pesticide dissipation processes by distinguishing between degradative and non-degradative processes, as well as transformation pathways. Such uncertainties may arise from compensatory effects among overlapping dissipation processes, as previously demonstrated for legacy contaminants in aquifers (Hunkeler et al.,
85 2008; Blázquez-Pallí et al., 2019; Thouement et al., 2019; Antelmi et al., 2021; Prieto-Espinoza et al., 2021) and wetlands (Alvarez-Zaldivar et al., 2016).

More recently, CSIA data in a parsimonious have been integrated into a lumped transport model using travel-time distributions, improving the interpretation of pesticide transport at the catchment scale (Lutz et al., 2017). However, lumped models primarily
90 capture aggregate hydrological behaviour and do not account for spatial variability in parameters such as soil moisture or temperature (Fatichi et al., 2016). This limits their ability to represent landscape heterogeneity, including variations in crops and pesticide applications, thereby hindering the identification of contaminant sources and degradation hot spots (Grundmann et al., 2007). In contrast, distributed conceptual and physically-based models explicitly represent spatially distributed hydro-climatic dynamics regulating hydrological processes, such as runoff and infiltration. Yet, pesticide CSIA data have not been
95 integrated into the calibration and validation of such models due to the lack of suitable field datasets. Moreover, the limited availability of information on the initial isotopic composition of commercial pesticide formulations has constrained the broader application of CSIA. This limitation has recently been addressed by ISOTOPEST, a database compiling the isotopic signatures of commercial formulations to support the use of CSIA in pesticide studies (Masbou et al., 2024).

This study aimed to evaluate the benefits of using both topsoil pesticide concentrations and CSIA data for calibrating a distributed hydrological model to quantify pesticide dissipation and off-site pesticide transport at the catchment scale. The study relied on a unique field dataset comprising weekly measurements of S-metolachlor concentrations and carbon isotope ratios ($\delta^{13}C$) in soil and runoff from a 47-hectare agricultural headwater catchment located in Alsace, France (Alvarez-Zaldivar et al., 2018). To capture hydro-climatic effects on pesticide degradation, drawing upon previous work by Boesten and Vanderlinden (1991), Schroll et al. (2006) and Gassmann (2021), we adapted the Bridge Event Continuous Hydrological (BEACH) distributed conceptual model, originally developed for soil water dynamics (Lefrancq et al., 2017; Alvarez-Zaldivar et al., 2018; Lefrancq et al., 2018). This adaptation led to the development of PiBEACH (Pesticide isotope BEACH), extending the lumped isotope modeling approach of Lutz et al. (2017) into a spatially distributed framework. Model calibration was performed using the Generalized Likelihood Uncertainty Estimation (GLUE) approach with a using Monte-Carlo method. This allowed us to evaluate how the inclusion of CSIA data improved model predictions and parameter identifiability, particularly in representing pesticide degradation across heterogeneous catchment conditions.

2 Material and Methods

2.1 Field site

The dataset, including concentrations and carbon isotope signatures ($\delta^{13}C$) of S-metolachlor in soil, was collected from March 19th (day 0) to July 12th (day 115), 2016 from the 47-ha Alteckendorf headwater catchment (Bas-Rhin, France; 48 47 19.56 N; 7 35 2.27 E) (Alvarez-Zaldivar et al., 2018; Lefrancq et al., 2018) (Fig. 1).

Daily temperature and potential evapotranspiration were obtained from the MétéoFrance station in Waltenheim-sur-Zorn,
located 7 km southwest of the study site. Daily rainfall was measured using a tipping bucket rain gauge (Précis Mécanique®,
125 Fig. 1). Detailed climate and hydrological data are provided in Table S1. The catchment is predominantly arable land, with
corn (18 %), sugar beet (70 %) and wheat (3 %) as the main crops in 2016. A subsurface tile drainage system, of unknown
spatial extent, is present at a depth of 0.8 m depth. Water is collected via ditches and discharged through a 50 cm diameter
pipe at the catchment outlet (Fig. 1). Soils are classified as Haplic Cambisol Calcaric Siltic and Cambisol Eutric Siltic on
hillsides (north and south), and Cambisol Colluvic Eutric Siltic in the central valley. Soil analysis from 48 topsoil samples (0-
130 20 cm) and six 2 m depth profiles showed low spatial variability across the catchment (Lefrancq et al., 2018). Texture was
consistent with clay (30.8 ± 3.9 %), silt (61.0 ± 4.5 %), and sand (8.5 ± 4.2 %). Soil composition included $CaCO_3$ (1.1 ± 1.6
%), organic matter (2.2 ± 0.3 %), total soluble phosphorus (0.11 ± 0.04 g kg^{-1}), and cation exchange capacity (CEC: 15.5 ± 1.3
cmol kg^{-1}). Soil pH averaged 6.7 ± 0.8 (n = 30). A compacted plough layer was observed between 20 and 30 cm depth. In
2016, S-metolachlor was applied to corn and sugar beet plots in three applications: March 20-25, April 13-14 and May 25-31.
135 These plots covered 88 % of the catchment area. Application dates, doses and formulation were obtained for each plot from
farmer surveys, providing spatially distributed data for modelling. In total, 20.2 kg, 5.9 kg, and 14.0 kg of S-metolachlor were
applied to the North, Valley, and South transects, respectively (Table S2).

2.2 Soil and water sampling and outlet discharge measurements

140 Topsoils (0-1 cm) were collected from individual plots and upstream-downstream transects across the catchment (Fig. 1 and
S1; Alvarez-Zaldivar et al., 2018). Thirteen marked plots were sampled before S-metolachlor application and on days 1, 50,
and 100 after application. In addition, weekly weighted composite samples were taken along the north, valley, and south
transects (green dots in Fig. 1) from March 19 (day 0) to July 12 (day 115). All soil samples were analysed for S-metolachlor
concentration and carbon isotope composition ($\delta^{13}C$) using CSIA. Volumetric topsoil water content (m³ $_{water}$ m^{-3} $_{soil}$) was
145 derived from gravimetric measurements after drying at 110°C following NF ISO 1146 (Lefrancq et al., 2018). This calculation
incorporated seasonal variations of topsoil bulk density, as predicted by PiBEACH and described in the Supplement, Section
7.2.

Runoff discharge at the catchment outlet was measured using a Doppler flowmeter (2150 Isco) with 3% accuracy and a 2 min
150 resolution. Automatic, refrigerated continuous flow proportional sampling was performed using an Isco Avalanche

autosampler equipped with twelve 330 mL bottles. Samples were collected at fixed weekly discharge volumes from 50 to 150 m^3, capturing the increasing baseflow discharges from April to June 2016 (Alvarez-Zaldivar et al., 2018). To obtain sufficient S-metolachlor for quantification and CSIA, samples were combined weekly into composite samples based on hydrograph phase (base-flow, rising limb, and falling limb), resulting in one to four samples per week with volumes ≥ 990 mL (Alvarez-Zaldivar et al., 2018). Piezometric monitoring of the shallow aquifer was not possible due to the absence of observation wells on the study site.

2.3 S-metolachlor quantification and $\delta^{13}C$ analysis

To separate dissolved and particulate phases of S-metolachlor, river samples were filtered through 0.7 µm glass fibre filters. Extraction of S-metolachor from soil and water samples was performed using an AutoTrace 280 Solid Phase Extraction (SPE) system (Dionex) with SolEx C18 cartridges (Dionex ®), as previously described (Alvarez-Zaldivar et al., 2018; Gilevska et al., 2022b). Quantification was carried out using chromatography–mass spectrometry (GC-MS, ISQ™, Thermo Fisher Scientific). Quantification limits were 0.01 µg L^{-1} for water and 0.001 µg g^{-1} (dry weight) for soil and suspended matter, with a total analytical uncertainty of 8 % and 16 %, respectively. Carbon isotope ratios ($\delta^{13}C$) of S-metolachlor in soil and water were analysed using a GC-C-IRMS, comprising a TRACE™ Ultra gas chromatograph (ThermoFisher Scientific) coupled to a Delta V plus isotope ratio mass spectrometer via a GC IsoLink/ Conflow IV interface (Alvarez-Zaldivar et al., 2018; Gilevska et al., 2022b; see also Section 5, Supplement). The reproducibility of triplicate $\delta^{13}C$ measurements was ≤0.2‰ (1σ). A minimum peak amplitude of 300 mV, corresponding to approximately 10 ng of carbon injected on column, was required for accurate isotope analysis.

2.4 PiBEACH model description

170 *PiBEACH development.* The Pesticide-isotopes BEACH model (PiBEACH) was developed in Python based on the conceptual Bridge Event Continuous Hydrological (BEACH) model (Sheikh et al., 2009). BEACH was chosen for its demonstrated ability to simulate daily topsoil moisture and catchment discharge with high accuracy (Nash-Sutcliffe efficiency of 0.79) in a 42 ha catchment (Sheikh et al., 2009) with loess soils and crops similar to those observed in the study catchment. BEACH is a grid-based model that simulates spatially distributed soil water content and catchment outlet discharge by accounting for key

175 hydrological processes, including evaporation, plant transpiration, percolation, deep percolation, lateral flow and runoff (Sheikh et al., 2009). At the cell scale, daily vertical water fluxes are computed across soil layers, followed by lateral fluxes upstream to downstream. Surface flow direction is derived from the digital elevation model using flow-accumulation functions, without employing a numerical scheme (Sheikh et al., 2009).

The model is driven by daily meteorological records (rainfall, air temperature and potential evaporation), soil physical

180 properties (saturated hydraulic conductivity, bulk density, porosity, both for the plow layer and a deeper soil layer), and crop-specific agronomical parameters. PiBEACH extends BEACH by incorporating experimental knowledge of hydrological and pesticide transport processes observed in the Alteckendorf catchment (Lefrancq et al., 2017; Lutz et al., 2017; Alvarez-Zaldivar et al., 2018; Lange et al., 2018; Lefrancq et al., 2018). It translates the perceptual model developed by field researchers into a conceptual framework, following the approach of Ammann et al. (2020).

185 Key modifications in PiBEACH include: (i) a topsoil mixing layer, assuming that pesticide transport is controlled by a mixing layer from 0.25 to 2 cm below the soil surface, in which rainfall, soil solution and runoff are assumed to mix instantaneously (McGrath et al., 2008), and deeper soil layers to capture groundwater contributions to discharge, (ii) daily simulation of topsoil temperature (Neitsch et al., 2011), (iii) daily dynamic topsoil hydraulic properties that reflect crop-specific agronomical practices (Lefrancq et al., 2018), (iv) first-order pesticides degradation and linear sorption/desorption, and (v) pesticide carbon

190 stable isotopic fractionation and transport of bulk heavy and light carbon in the pesticide molecule (e.g., ^{13}C and ^{12}C) (Lutz et al., 2017; Alvarez-Zaldivar et al., 2018). PiBEACH requires spatially explicit inputs of pesticide application dates and quantities for each plot.

Comparison of PiBEACH with physically-based models. The finite difference or finite volume method is typically used to

195 simulate agricultural catchment hydrology in 3D physically-based models, e.g., Hydrogeosphere (De Schepper et al., 2015) or CATHY (Gatel et al., 2020). However, modelling pesticide reactive transport including pesticide sorption-desorption and degradation on the catchment scale remains challenging. This is because the numerical dispersion (Gatel et al., 2020) is generally of the same order of magnitude as pesticide export coefficient (i.e., the ratio of the mass transported at the outlet to the applied mass at the catchment scale), i.e., from 1‰ to 1% of the applied amount of pesticides. The numerical dispersion

200 issues can be mitigated, though this leads to longer computation times in both 2D (Lutz et al., 2013) and 3D (Gatel et al., 2020) models. PiBEACH simulates water and pesticide fluxes on a daily time step, tracking flow from upstream to downstream along

branches of the drainage network using flow-accumulation grid-based functions (Sheikh et al., 2009). While it avoids numerical issues by not employing differential equations and associated numerical schemes, this approach also limits its ability to predict fast flow dynamics, i.e., runoff genesis and preferential water flow. This network can be extracted from a LIDAR digital elevation model (Lefrancq et al., 2017). A vertical mass balance is computed using the sum of discharges and pesticides masses of the upstream grid cells as lateral inputs for the downstream grid cells (section 6 of the SI and equation 2). The daily resolution of PiBEACH reduced by one to two orders of magnitude lower the computation time compared to 2D or 3D models for catchments of similar size (Gatel et al., 2020). The limitations associated with this conceptual approach are discussed in the next section.

PiBEACH description and sub-model components. To account for landscape features affecting pesticide off-site transport, such as grass strips or roads, the Alteckendorf catchment was modelled using a 2×2 m raster resolution. The vertical soil profile was divided into five successive layers from the topsoil to the groundwater (Fig. 2): (i) a surface mixing layer (z_0: 0-1 cm) (McGrath et al., 2008), (ii) a plow layer observed in the field (z_1: 1-30 cm), (iii) a drainage layer controlled by tile drains, as observed in the Alteckendorf catchment (z_2: 30-80 cm), (iv) a variably saturated layer groundwater layer (z_3), and (v) a permanently saturated groundwater layer (z_4). The combined groundwater depths ($z_3 + z_4$) varied spatially and seasonally across the catchment, with a maximum observed depth of 23.2 m, consistent with recharge dynamics in monitored hillslopes (Molenat et al., 2005). The partitioning between z_3 and z_4 was defined as a calibration parameter z_f , such that: $z_3 + z_4 = 23.2$ m; $z_3 = 23.2 \times z_f$; $z_4 = 23.2 \times (1 - z_f)$ (Table S3 in Supplement).

The hydrological balance follows the formulation of Sheikh et al., (2009), with process-specific implementations detailed in Section 6 of the Supplement. For each grid cell i and soil depth Z (mm), the daily change in volumetric soil water content (θ, m³ m⁻³) is calculated using:

$$Z\Delta\theta_i = R_i - RO_i + \Delta LF_i - Ea_i - Ta_i - P_i$$

(1)

where daily rainfall (R), runoff (RO) (calculated for z_0), net cell lateral inflow-outflow (ΔLF), actual evaporation (Ea), actual transpiration (Ta) and percolation (P) were expressed in mm H₂O d⁻¹. Evaporation (Ea) affects layers z_0 to z_3, while transpiration (Ta) depends on plant root depth following crop-specific development stages (see sections 6.5 and 6.6 in the Supplement). Lateral flow (ΔLF) and percolation (P) are calculated from upstream to downstream cells for layers z_0 to z_3 (Manfreda et al., 2005). Percolation across the saturated layer z_4 is routed to the outlet as a global linear reservoir (Manfreda et al., 2005).
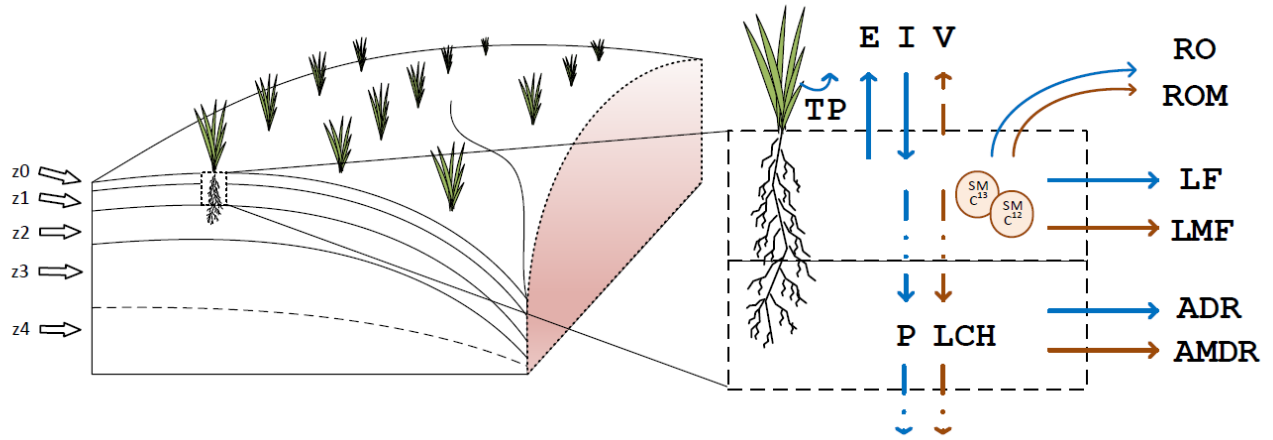
Figure 2: Conceptual representation of the five-layer spatially distributed hydrological and reactive transport model PiBEACH. Hydrological processes include evaporation (E), transpiration (TP), percolation (P), volatilization (V), runoff (RO), lateral flow (LF), and artificial drainage (ADR). Pesticide mass transfer processes include volatilization (V), runoff mass (ROM), lateral mass flow (LMF), leaching (LCH), mass transfer via artificial drainage (AMDR), and degradation with isotope fractionation (SM ^{13}C and SM ^{12}C).

The agronomical sub-model of PiBEACH (Lefrancq et al., 2017) (see Supplement, Section 7) simulates seasonal variation of in topsoil soil hydraulic properties, improving the hydrological balance of the headwater catchment (Lefrancq et al., 2017). The pesticide dissipation sub-model of PiBEACH represents the key processes governing pesticide reactive transport at the catchment scale (Fig. 2). The pesticide mass (M, g) balance for each cell i and each layer is expressed as:

$$\frac{dM_i}{dt} = A_i - ROM_i + \Delta LMF_i - V_i - LCH_i - DEG_i \qquad (2)$$

where M is the pesticide mass (g), A is the applied mass (g d^{-1}), ROM is mass lost via runoff (z_0 only), ΔLMF is lateral mass flow (z_0–z_3), V is volatilization (z_0), LCH is leaching (z_0–z_3), and DEG is degradation (z_0–z_4).

Pesticide partitioning into dissolved, sorbed and gaseous phases follows Leistra et al., (2001) (see Supplement Section 8). Partition into the dissolved and adsorbed phases was determined by linear sorption, considering the organic carbon-water partition coefficient K_{OC} (mL g^{-1}) normalized by the fraction of organic carbon f_{OC} (kg kg^{-1}) in soil, where the pesticide dissociation coefficient (K_d, mL g^{-1}) was given by $K_d = K_{OC} \times f_{OC}$. Partition into the gas phase was obtained from the dimensionless Henry constant, $K_H^{cc} = 9.55 \ 10^{-5}$ for S-Metolachlor (Feigenbrugel et al., 2004). General pesticide mass flux J (µg d^{-1}) for each model cell is computed as:

$$J = q_{x,y} \times C_{aq} \qquad (3)$$

where $q_{x,y}$ is the water flux vector (mm d^{-1}) inthe lateral (x) and vertical (z) direction and C_{aq} is the dissolved S-metolachlor concentration in the aqueous phase (µg mm^{-1}). In the topsoil layer (z_0), runoff and volatilization are included:

$$J_{zo} = q_{x,y} + c_{aq}\left(ROe^{-\beta_{RO}D_{zo}} + \frac{1}{r_a + r_s}\right) \tag{4}$$

where RO is runoff (mm), β_{RO} is a calibration constant ($1 \geq \beta_{RO} \geq 0$) and D_{z0} (mm) is the mixing layer depth (Ahuja and Lehman, 1983). Volatilization was limited to the first 5 days after application (Gish et al., 2011), (Prueger et al., 2005), and follows (Leistra et al., 2001), with fluxes across topsoil controlled by air transport resistance, r_a, (d m^{-1}) and diffusion resistance, r_s (d m^{-1}) (Leistra et al., 2001) (see sub-section 8.2 of the Supplement).

Biodegradation occurs only in bioavailable fractions of adsorbed (ads) and aqueous (aq) phases (Thullner et al., 2013). A similar stable isotope fractionation associated with degradation was then considered for the bioavailable fractions, including the adsorbed (Eq. 5, second term) and the aqueous (Eq. 6) phases. The bioavailable fraction was controlled kinetically by an ageing rate k_{age} (d^{-1}) on the adsorbed fraction (Schwarzenbach, 2003). Due to the physicochemical properties of S-metolachlor, abiotic degradation processes such as photolysis, and their associated isotope fractionation, were excluded from the model. While non-destructive processes like dispersion and sorption may induce isotope fractionation under conditions of strong sorption behavior, transient diffusion, or repeated sorption–desorption cycles (Eckert et al., 2013; van Breukelen and Prommer, 2008; van Breukelen and Rolle, 2012; Kopinke et al., 2017), these effects were considered negligible. Given the rapid biodegradation of S-metolachlor in soil and the limited impact of sorption-induced fractionation in surface agro-ecosystems, only biodegradation was included in the model. Since not significant alteration of the isotope composition of pollutants was expected during sorption and ageing (Schmidt et al., 2004; Droz et al., 2021), the ratios of light to heavy isotopologues did not significantly vary during sorption and ageing processes (Eq. 5, first term). Altogether, representing pesticide mass (M) as separate light (l) and heavy (h) isotopologues, the change in aqueous and adsorbed phases is expressed as:

$$\frac{dM_{ads}}{dt} = -k_{age}\left(M_{ads}^l + M_{ads}^h\right) - k_{deg}\left(M_{ads}^l + \alpha M_{ads}^h\right) \tag{5}$$

$$\frac{dM_{aq}}{dt} = -k_{deg}\left(M_{aq}^l + \alpha M_{aq}^h\right) \tag{6}$$

where $k_{deg} = \ln(2) / DT_{50}$ and DT_{50} (days) was the observed degradation half-life in soil. Stable isotope fractionation associated with S-metolachlor degradation in soil was considered through the carbon fractionation factor (α_C), expressed as $\alpha_C = \varepsilon_C/1000 + 1$, where ε_C (‰) was the carbon stable isotope fractionation value of the targeted pesticide retrieved from a degradation reference experiment. Degradation rates for S-metolachlor freshly sorbed in the organic fraction of soil was assumed to be equal to degradation rates in the dissolved phase (Wu et al., 2011; Long et al., 2014). The reduction of bioavailability of the aged fraction of S-metolachlor as a function of the increasing fraction of irreversible sorbed S-metolachlor over time (Sander et al., 2006; Arias-Estevez et al., 2008; Torabi et al., 2020) was taken into account with the rate k_{irs} (d^{-1}) of irreversible sorption for the aged S-metolachlor mass (M_{age}, g):

$$\frac{dM_{age}}{dt} = -k_{irs}\left(M_{age}^l + M_{age}^h\right) \tag{7}$$

Decrease in M_{age} due to abiotic degradation (Xu et al., 2018) was not included, since it was unlikely to be significant under abiotic conditions in the studied aerobic soil (Torabi et al., 2020), even after 200 days of incubation (Alvarez-Zaldivar et al., 2018).

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Pesticide degradation rates generally decline with soil depth due to reduced microbial activity (Cruz et al., 2008; Lutz et al., 2017) and increased sorption (Arias-Estevez et al., 2008) in deeper layer. However, the absence of concentration and CSIA data for S-metolachlor in subsoil prevented direct quantification of depth-dependence degradation. Following the approach used in advanced pesticide fate models such as MACRO (Garratt et al., 2003), the degradation rate (k_{deg}) in PiBEACH was

295   modelled as a function of soil hydro-climatic conditions, such as soil temperature and water content. A dynamic degradation rate ($k_{Dynamic}$, d^{-1}) was calculated daily on soil temperature (F_T) and water content (F_θ):

$$k_{Dynamic} = k_{Ref} \times F_T \times F_\theta \tag{8}$$

where k_{ref} (d^{-1}) was the degradation rate constant from degradation half-life (days) at reference conditions ($k_{Ref} = \ln(2) / DT_{50,Ref}$).

300   A dynamic half-time $DT_{50,Dynamic}$ was derived to be compared to $DT_{50,Ref}$ ($DT_{50, Dynamic} = \ln(2) / k_{Dynamic}$).

For soil temperature dependence, the modified Arrhenius equation for low temperatures was considered (Boesten and Vanderlinden, 1991; Larsbo and Jarvis, 2003):

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$$F_T = \begin{cases} 0, & if, T_C \leq 0 \\ \frac{T_{K,Obs} - 273.15}{5} exp\left(\frac{E_a}{R}\left(\frac{1}{T_{K,Ref}} - \frac{1}{T_{K,Obs}}\right)\right), & if, 0 < T_C \leq 5 \\ exp\left(\frac{E_a}{R}\left(\frac{1}{T_{K,Ref}} - \frac{1}{T_{K,Obs}}\right)\right), & if\ T_C > 5 \end{cases} \tag{9}$$

where T_K and T_C were soil temperatures in Kelvin and Celsius, respectively and $T_{K,Ref}$ was the reference temperature at 293.15 K. E_a was the S-metolachlor activation energy (23.91 10^3 J mol^{-1}) (Jaikaew et al., 2017) and R was the gas constant (8.314 J mol^{-1} K^{-1}). This modified Arrhenius equation was validated against DT_{50} values derived from microcosm degradation experiments with S-metolachlor conducted at 20 and 30°C (Section 9 of SI, Figure S4).

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Influence of water content followed Walker, (1974) and Larsbo and Jarvis (2003):

$$F_\theta = min\left(1.0, \left(\frac{\theta_t}{\theta_{Ref}}\right)^{\beta_\theta}\right) \tag{10}$$

where β_θ was a calibration constant and θ_{Ref} the reference water content, which was set at 0.2 m^3 m^{-3}. Note that F_θ was slightly modified from Walker (1974), as microcosm experiments for S-metolachlor did not show an increase in degradation rates with increases in moisture contents (Figure S4). Between March and July, topsoil temperatures increased, creating a stronger

vertical temperature gradient and leading to reduced degradation activity at greater depths. In July, for instance, DT_{50} values were estimated at 25 days in the topsoil (Fig. 3C) and 34 days at 2 m depth (data not shown), consistent with predictions from the lumped model developed by Lutz et al. (2017) for this catchment. While the model accounts for degradation as a function of depth, soil temperature, and moisture (Lutz et al., 2017), it captures only general trends. Microbial activity remains highly uncertain and difficult to quantify across soil depth and spatial scales.

2.5 Model limitations

Although PiBEACH was primarily developed to simulate pesticides dissipation in topsoil, four aspects of its desing may limit its application for predicting pesticide dynamics at the outlet of the headwater catchment. First, PiBEACH operates on a daily time step and is not suited to capture rapid flow dynamics, such as runoff generation and event-scale hydrological dynamics (Sheikh et al., 2009). Consequently, S-metolachlor concentrations and corresponding $\delta^{13}C$ values measured at the catchment outlet were not included in the model calibration objective function. This limitation could be addressed by coupling PiBEACH with a distributed event-based model, such as the Limburg Soil Erosion Model (OpenLISEM) (Baartman et al., 2012), which recently integrated a pesticide module (OLP) (Commelin et al., 2024). Second, PiBEACH uses a conceptual linear reservoir to represent shallow aquifer dynamics and does not explicitly simulate the effects of transit time distribution on pesticide release from groundwater to surface water (Hrachowitz et al., 2016). While incorporating transit time distribution into lumped reactive transport model has shown promise (Lutz et al., 2017), applying such approach in distributed model remains challenging, as demonstrated for nitrate (Kaandorp et al., 2021).

In addition, pesticide leaching across soil layers was considered without distinguishing matrix and preferential flows. Macropores can also play a significant role on pesticide breakthrough in the vadose zone (Urbina et al., 2020). However, the explicit integration of macropore at the catchment scale necessitates advanced in situ measurements (Weiler, 2017), and a combination of geostatistical methods, pedotransfer functions or meta-models, i.e., simplified statistical models built with 1D soil reactive transport models such as MACRO (Lindahl et al. 2008).

PiBEACH integrates the main catchment compartments, including soil layers, vegetation and crops, and major processes controlling pesticide fate. However, plant uptake of S-metolachlor was not included, as it is likely negligible. No correlation was found between residual S-metolachlor in the topsoil and the growth of the sugar beet and corn (Lefrancq et al., 2018). Additionally, pesticides wash off on plants was not considered in PiBEACH as S-metolachlor is a pre-emergent herbicide applied on bare soil.

Considering degradation in reactive transport models as a lumped process with only one half-life parameter is a strong simplification which may alter the predictability of degradation in models. However, this limitation is shared among existing pesticide transport models (Leistra et al., 2001; Lindahl et al, 2008; Lutz et al., 2017; Gatel et al.,2020). The implementation of soil temperature and moisture dependence for pesticide degradation, as proposed in this study, may strengthen the description of degradation within the catchment and across the hydrological or growing season (Gassmann 2021). Nonetheless,

soil temperature and moisture are also forcing variables of the soil microbial activity, and thus of biodegradation, which remains extremely difficult to characterize and conceptualize with respect to pesticide transformation (Imfeld and Vuilleumier,

350   2012; Bongiorno, 2020; Höhener et al., 2022) for implementation in reactive models at the catchment scale.

2.6 Model uncertainty assessment

The GLUE and formal Bayesian methods are commonly used methods to quantify the uncertainty of hydrological models and provide distributions of parameters and water discharges. Bayesian methods are more convenient to calculate the uncertainty interval of one-step ahead forecasting with a formal or exact likelihood function (Jin et al., 2010). In contrast, the GLUE

355   method integrates a true calibration process in which both inputs and model structural errors contribute to uncertainties of the model outputs (Beven et al., 2007). The GLUE method was thus adopted in our study to calibrate PiBEACH and retrieve output uncertainties. Rather than seeking an optimal model solution, the GLUE approach recognizes that more than one model structure or parameter set may lead to acceptable model results, i.e. equifinality (Beven and Binley, 1992). The GLUE method involved a sampling method of PiBEACH parameters, an objective function incorporating observed dataset (i.e., topsoil S-

360   metolachlor concentration only, then combined to S-metolachlor $\delta^{13}C$), a threshold of this objective function to select behavioural parameter sets, and the calculation of posterior probability distributions for parameters and uncertainties associated to the outputs of PiBEACH.

For the sampling method of parameters, PiBEACH required the calibration of 43 parameters (Table S3 in the Supplement).

365   The range, i.e. min-max values, of these parameters were defined based either on literature or field data collected in 2012 and 2016 (Lefrancq et al., 2017 and 2018; Alvarez-Zaldivar et al., 2018). These parameters were assumed to be *a priori* uniformly distributed within these min and max values (Table S3 in the Supplement). To reduce the number of runs required by the GLUE method, three steps were successively applied. First, a pre-sensitivity global analysis based on the Morris method (Morris, 1991; Herman and Usher, 2017) was conducted (section 10 of the Supplement) to select the most sensitive parameters.

370   Although the Morris method yields a qualitative indication of relative parameter importance, it is efficient compared to other sensitivity approaches (Gan et al., 2014) that screen for sensitive parameters (Herman et al., 2013). The Morris method allowed to reduce the PiBEACH parameter number from 43 to 25 (Table S3 in the Supplement). Second, a Latin-Hypercube sampling (Herman and Usher, 2017) was used to reduce the numbers of runs (n = 2500) to cover the parameter space for the 25 parameters. To further reduce the computation time, the GLUE assessment focused on the growing period (March 19th to July

375   12th, 2016), where pesticide degradation and exports are of most significance. Initial hydrological state was estimated from a spin-up period of one full hydrological year (Oct. 1st, 2015 - Sept. 30th, 2016) and hydrological parameters calibrated against observed discharge at the catchment outlet (March 19th and July 12th, 2016) using particle swarm optimization (Bratton et al., 2007).

380   For the second step of the GLUE method, the KGE (Gupta et al., 2009) metric was adopted as the objective function to maximize during calibration. Goodness of fit between simulations and observations are given relative to a maximum efficiency of 1 and given by:

$$KGE = 1 - \sqrt{(r-1)^2 + (\alpha_{KGE} - 1)^2 + (\beta_{KGE} - 1)^2} \qquad (11)$$

385

where r was a linear correlation coefficient, $\alpha_{KGE} = s_I / s_0$, and $\beta_{KGE} = \mu_i / \mu_0$, where σ and μ represent the standard deviation and mean of simulated (i) and observed (o) values, respectively.

The KGE metric was selected to provide equal weight across correlation, bias and variability measures. KGE metric is also an
390   improved measure of model performance compared to other metrics, such as the mean squared error and the Nash-Sutcliffe efficiency, which favour parameter values and underestimate variance of the model results (Gupta et al., 2009). Three KGE metrics were calculated with (i) KGE_{SM} with weekly topsoil S-metolachlor concentration, (ii) KGE_δ with weekly topsoil $\delta^{13}C$ and (iii) KGE_Q with daily discharge at the outlet. The KGE metrics were successively built to assess the benefit of CSIA by incorporating topsoil S-metolachlor concentration only or in combination with topsoil S-metolachlor $\delta^{13}C$ observations, and
395   the minimal topsoil S-metolachlor concentration and $\delta^{13}C$ sampling effort to reduce the uncertainties of PiBEACH outputs. For the latter, KGE metric incorporates topsoil S-metolachlor concentration and $\delta^{13}C$ from (i) individual plot observations (13 black dots, Fig. 1), (ii) aggregated plot observation along three transects across the catchment (North, Valley and South transect, Fig. 1) and (iii) transect composite soil (green dots, Fig. 1).

400   The threshold to retain acceptable model results runs (out of 2500 simulation runs) for topsoil S-metolachlor degradation and transport was set to $KGE_{SM} >0.5$ and $KGE_Q >0.5$. An additional isotope data constraint of $KGE_\delta >0.8$ was then consider to evaluate the benefit of CSIA during the calibration process. We hypothesized that the uncertainty of degradation extent controlled by $DT_{50,Ref}$ (Eq. 8) should be reduced considering CSIA, resulting in a smaller standard deviation of $DT_{50\,Ref}$.

405   Distributions of the acceptable parameter sets, including $KGE_{SM} >0.5$ and $KGE_Q >0.5$ and $KGE_\delta >0.8$, with the 25 most sensitive parameters were extracted for the fifth and last step of GLUE. The PiBEACH outputs were then reported as an ensemble and with the 95 % confidence interval obtained from the acceptable parameter sets. Calibrating 25 parameters is challenging and justifies the extensive dataset collected across the catchment and throughout the growing season. This unique dataset included the use of isotopic signatures and comprises a total of 103 topsoil samples analyzed for S-metolachlor
410   concentration and $\delta^{13}C$, 115 daily discharge measurements, and 51 river outlet samples with S-metolachlor concentration.

In the final step of the GLUE procedure, the distributions of the 25 most sensitive parameters were extracted from the subset of acceptable parameter sets, defined by $KGE_{SM} > 0.5$ and $KGE_Q > 0.5$ and $KGE_\delta > 0.8$. PiBEACH outputs were then expressed as an ensemble and with the 95 % confidence intervals based on these parameter sets.

2.7 Metrics of pesticide persistence and transport risks

415   Six metrics were derived from PiBEACH outputs to assess S-metolachlor persistence and transport risk at the catchment scale. Expressed as percentages of the applied mass, these metrics included: (1) S-metolachlor degradation, (2) the remaining bioavailable mass of S-metolachlor (BAM) in the topsoil (i.e., dissolved and reversibly sorbed S-metolachlor), (3) S-metolachlor export to the catchment outlet via runoff and drainage, (4) off-site transport of S-metolachlor through leaching, (5) the remaining mass of irreversibly sorbed S-metolachlor (i.e., aged S-metolachlor), and (6) S-metolachlor volatilization,

420   from the first application on March 19 (day 0) to July 12, 2016 (day 115). The first three metrics were also derived from field observations to evaluate the predictive accuracy of PiBEACH. Observed BAM in the topsoil was estimated through spatial extrapolation of weekly soil samples. The observed S-metolachlor degradation was estimated using the mean $\delta^{13}C$ derived from the same spatial extrapolation, combined with the enrichment factor (ε) obtained from microcosm lab-scale experiments using soil from Alteckendorf. Export to the outlet was calculated by integrating continuous discharge measurements with sub-

425   weekly river S-metolachlor concentrations. The remaining three metrics, leaching, volatilization, and aging, could not be estimated from field data due to limitations of the catchment-scale sampling campaign and were therefore not computed from observations.

3 Results and discussion

3.1 Topsoil hydro-climatic dynamics and effect on S-metolachlor degradation rates

430   Topsoil (z_0) water contents showed substantial variability, consistent with weekly field measurements (Fig. 3A) and previous application of the BEACH model in catchments with similar soils, crops and conditions (Sheikh et al., 2009). Simulated discharges at the catchment outlet closely matched observations (Fig. 3B), with a maximum Kling-Gupta Efficiency (KGE_Q) of 0.75, demonstrating the model's ability to capture prevailing hydrological dynamics. However, PiBEACH slightly overestimated runoff generation, a known limitation related to the underlying assumptions of the SCS-CN method (Section

435   6.2 in the Supplement), and the use of a daily time step, which does not resolve sub-daily rainfall intensity. Hydro-climatic variability drove changes in the simulated degradation rates ($k_{Dynamic}$) and associated half-times ($DT_{50,Dynamic}$) of S-metolachlor over time (Fig. 3C). Low S-metolachlor degradation rates during the first 10 days ($DT_{50} = 46 \pm 17$ d) coincided with cold (7.1 $\pm$ 1.7 °C) and dry period (7.4 mm of rainfall) (Fig. 3A). In contrast, increasing degradation rates ($DT_{50} = 22 \pm 2$ d) between 50 to 120 days following the first application of S-metolachlor were associated with warmer conditions (16.9 $\pm$ 3.6 T°C).

440   Simulated S-metolachlor concentrations (Fig. 3D) and carbon isotope ratios (Fig. 3E) in topsoil aligned with weekly field observations, confirming the model's ability to reproduce both concentration dynamics and isotopic trends.
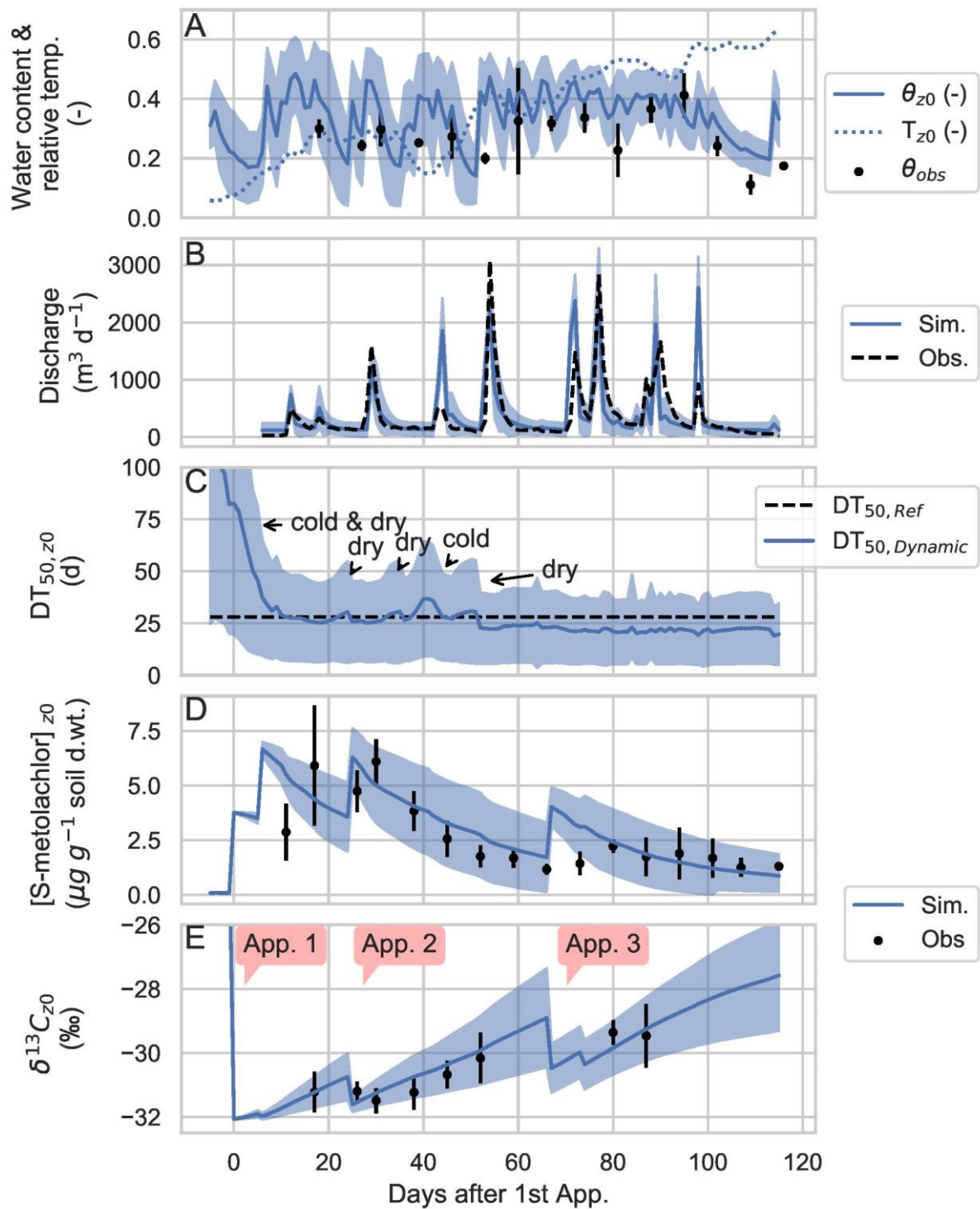
Figure 3: Predicted water content (m^3 m^{-3}) and relative topsoil temperatures ($T_{z0}/T_{air,\ max}$; with $T_{air,\ max} = 27°C$) in the topsoil layer (z_0: 0-1cm) from March 14 (day -5, before first application) and July 12 (day 115). Shaded area indicates the 95 % confidence intervals (CI). Weekly observed water content (θ_{obs}) in topsoil is also shown (A), with error bars reflecting uncertainties in soil bulk density (used for gravimetric-to-volumetric conversion) and the standard error of gravimetric water content measurements. (B) Simulated and observed daily outlet discharge at the catchment scale, with the shaded area representing 95 % CI of the model ensemble. (C) Simulated mean dynamic degradation half-life ($DT_{50,\ Dynamic}$) of S-metolachlor in the topsoil (z_0), 95 % CI and the reference half-life ($DT_{50,\ Ref}$) shown for comparison. (D) Simulated and observed S-metolachlor concentrations composite topsoil transects (z_0), with error bars showing the standard deviation of measured values. (E) Simulated and observed $\delta^{13}C$ values of S-metolachlor in topsoil, with error bars showing the standard deviation. Application periods are marked as App. 1 (days 0 and 6), App. 2 (day 25), and App. 3 (days 67 and 74).

Out of 2500 simulation runs generated using Latin Hypercube sampling, 672 were deemed acceptable based on hydrological and concentration performance criteria (KGE_Q >0.5 and KGE_{SM} >0.5). Applying an additional constraint based on isotope data (KGE_δ >0.8) further reduced the ensemble to 244 simulations. Thus, only 36% of the acceptable runs also provided a reliable prediction of S-metolachlor degradation. In contrast, the remaining 64% accurately simulated hydrology and soil concentrations but showed poorer performance in reproducing degradation dynamics, as indicated by a wider range of $DT_{50,Ref}$ values (Fig. 4). These results highlighted the added value of including CSIA data during model calibration to constrain degradation parameters more effectively.

3.2 Uncertainty reduction through incorporation of CSIA data

The benefit of incorporating both topsoil pesticide concentrations and CSIA data during model calibration was assessed by comparing two calibration approaches: one using only S-metolachlor concentrations (NIC: no isotope constraint), and the other using both concentrations and associated CSIA data (WIC: with isotope constraint). For the composite transect soil (Fig. 4), the mean $DT_{50,Ref}$ values (μ; Eq. 8) were similar between NIC and WIC calibrations. However, the standard deviation of $DT_{50,Ref}$ was twice as large for NIC, indicating significantly higher uncertainty. This demonstrates that including CSIA data in the calibration phase substantially improved the constraint on S-metolachlor degradation estimates.
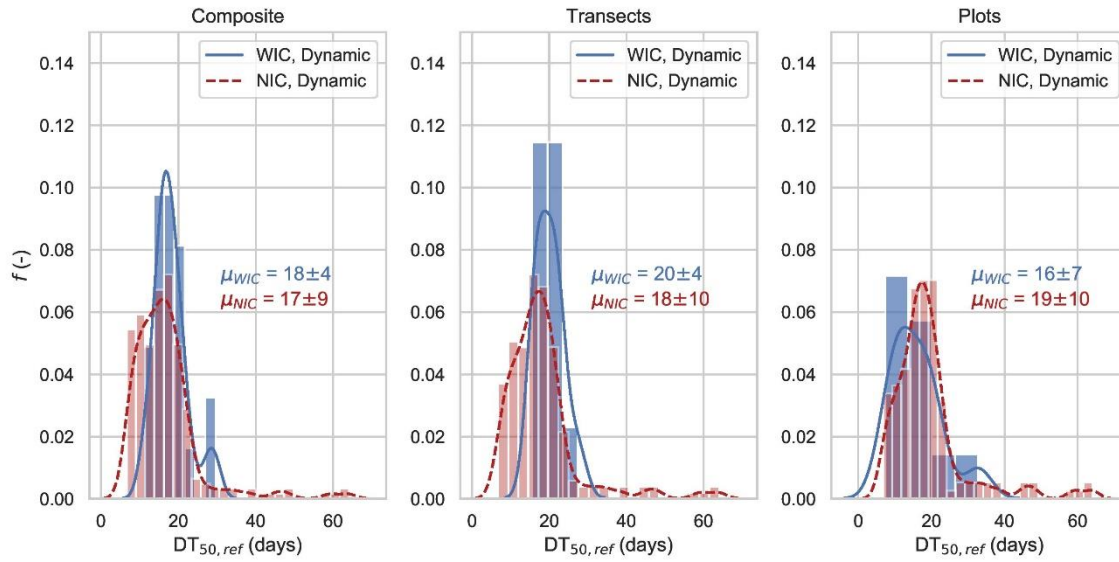
Figure 4: Distribution of calibrated DT_{50} values for 2,500 runs, shown for models without isotope constraints (NIC, $n = 672$) and with isotope constraints (WIC, $n = 244$), across three sampling resolutions: composite transect, transect and plot-scale soils. NIC simulations were selected based on $KGE_{SM} > 0.5$ and $KGE_Q > 0.5$, while WIC simulation also included $KGE_\delta > 0.8$. Mean $DT_{50,Ref}$ distributions are indicated by solid (WIC) and dotted (NIC) lines, and standard deviations are reported as $\mu \pm SD$.

Reducing uncertainty in pesticide degradation estimates in soil is essential, as degradation half-lives can vary by one order of magnitude depending on the compound (Wang et al., 2018), largely affected by hydro-climatic and soil conditions. In this study, the WIC calibration yielded mean $DT_{50,Ref}$ below 20 days, with low standard deviations (SD <7 days; Fig. 4), indicating that aerobic degradation of S-metolachlor, typically reported between 14 and 21 days (Lewis et al., 2016), was the dominant process in Alteckendorf topsoil. In contrast, anaerobic degradation, characterized by longer half-lives ($DT_{50} = 23 - 62$ days; Seybold et al., 2001; Long et al., 2014), appeared to play a limited role.

The mean calibrated $DT_{50,Ref}$ values for transect composite soil, individual transects across the catchment, and plot resolutions differed by less than four days (Fig. 4). However, standard deviations reflecting uncertainty, were approximately 50% lower when isotopic constraints (WIC) were applied, compared to calibrations without isotopic constraints (NIC), for both transect composite and transect-scale data. At the plot scale, uncertainty remained unchanged. These results indicated that increasing resolution (plots > transects > transect composite samples) did not significantly improve model calibration in this catchment. Therefore, pooling transect samples into a single composite soil sample was sufficient for CSIA-based calibration, while also reducing sampling and analytical efforts. This approach may reliably capture variations in pesticide degradation at the catchment scale.

490 Integration of CSIA data into PiBEACH yielded an isotope fractionation factor of $\varepsilon C = -2.7 \pm 0.6$ ‰ for S-metolachlor degradation in topsoil, exceeding previously reported values (Alvarez-Zaldivar et al., 2018: -1.5 ± 0.5 ‰; Lutz et al., 2017: -1.3 ± 0.5 ‰). This discrepancy likely reflects differences in environmental conditions, microbial activity, and transformation pathways, though it remains within the model ensemble's uncertainty range. Compared to laboratory-derived estimates, the stronger fractionation observed suggests either alternative degradation pathways or the influence of distinct microbial consortia

495 at the catchment scale, relative to laboratory conditions. These findings underscore the importance of site-specific calibration in CSIA applications and highlight the value of model ensemble approaches in capturing the range of degradation processes in heterogeneous agro-ecosystems. While previously reported εC values may slightly overestimate degradation in some field settings, ensemble modelling with integrated CSIA data provides a more robust, field-relevant assessment of pesticide transformation.

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3.3 Metrics of pesticide persistence and transport risks

Six metrics were derived from PiBEACH outputs to evaluate S-metolachlor persistence in soil and its transport risk via leaching and runoff from topsoil across the catchment. Each metric was expressed as a percentage of applied S-metolachlor and included: (i) S-metolachlor degradation (Fig. 5A), (ii) remaining bioavailable mass of S-metolachlor (BAM) in topsoil

505 (i.e. dissolved and reversibly-sorbed S-metolachlor; Fig. 5B), (iii) remaining mass of irreversibly sorbed S-metolachlor (aged; Fig. 5E), (iv) off-site transport of S-metolachlor by leaching (Fig. 5D), (v) S-metolachlor volatilization (Fig. 5F), and (vi) S-metolachlor export to the catchment outlet by runoff and drainage (Fig. 5C). All metrics were calculated from the first application on March 19 (day 0) to July 12, 2016 (day 115). For two metrics, degradation and remaining mass in topsoil, PiBEACH closely matched observations (Fig. 5A, 5B and section 4 of the Supplement). The modelled degradation extent (72

510 $\pm 13\%$) was consistent with the value derived from $\delta^{13}C$ measurements on composite transect soil and the Rayleigh equation ($68 \pm 1\%$) on day 87, corresponding to the last quantifiable soil isotope measurement (Fig. 5A). The remaining bioavailable mass (BAM) was estimated from measured concentrations and transect areas (Fig. 1, Fig. S1). The extrapolated remaining BAM from transect composite soil was $12 \pm 8\%$, which fell within the modelled range at day 115 ($18 \pm 3\%$). S-metolachlor export to the outlet was slightly overestimated by the model ($2 \pm 6\%$) compared to observations ($0.5 \pm 0.1\%$) for the same

515 period, though still within the model's uncertainty range. It is important to note that observed export estimates were based solely on the dissolved phase, as particulate-bound S-metolachlor (> 0.7 µm) remained below quantification limits in all river samples. The S-metolachlor export metric depends on PiBEACH ability to simulate daily discharge. Although PiBEACH was originally designed to initialize sub-hourly, event-based distributed models like Openlisem-OLP (Commelin et al., 2024), it also accurately reproduced daily discharge dynamics (Fig. 3B), consistent with prior applications in similar catchments (Sheikh

520 et al., 2009). Finally, S-metolachlor volatilization predicted was below (<1 %) during the first 120 h after application, in line

with the low vapor pressure of S-metolachlor (= 1.7 mPa, Lewis et al., 2016). However, volatilization rates ranging from 5 to 63 % of the applied mass has been reported under variable meteorological conditions (Gish et al., 2011).

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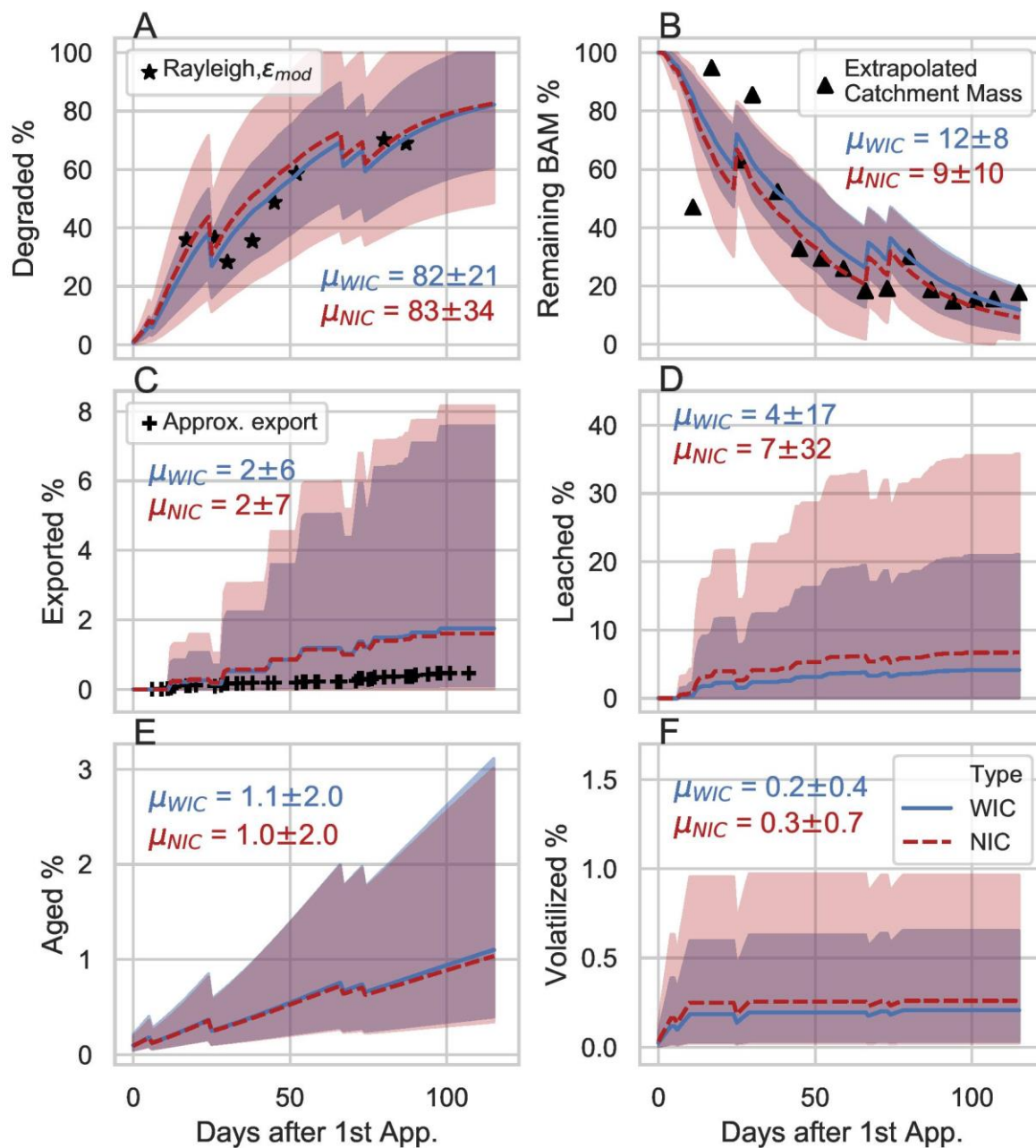
Figure 5: Pesticide dissipation processes and corresponding ensemble mean from a total of 672 simulations without isotope constraints (NIC, dotted line) and 244 simulations with isotope constraints (WIC, solid line). The 95% confidence intervals (CIs) are shown in red for NIC and blue for WIC. All metrics are expressed as percentages of the applied cumulative S-metolachlor mass across the catchment, starting

from the first application on March 19, 2016. Final dissipation values (μ_{WCI} and $\mu_{NIC} \pm 95\%$ CI) are reported for day 115. Black markers indicate estimates derived from catchment-scale mass balances based on farmer surveys (Supplement, Sections S3 and S4).

535   The six pesticide transport metrics confirmed that incorporating CSIA data reduced the uncertainty of degradation estimates and other dissipation processes simulated by the PiBEACH model. Comparison of 95 % confidence intervals for showed that, by the end of the season (day 115), uncertainty was reduced by half in the WIC ensemble (with CSIA data) compared to the NIC ensemble (without CSIA data). Although the mean S-metolachlor degradation was similar for both dynamic DT_{50} models at the end of the season (i.e., $\Delta\mu = 1\%$), the uncertainty around degradation extent was 60% higher in the NIC ensemble. The

540 higher uncertainty propagated to other processes; for example, both mean and uncertainties of S-metolachlor leaching were twice as high in the NIC simulations compared to WIC.

This modelling framework, applied to the same compound and catchment as in Lutz et al. (2017), provides insights into the benefits and limitations of using $\delta^{13}C$ data from soil and river samples to constrain reactive transport models. The lumped model by Lutz et al. (2017) focuses on $\delta^{13}C$ values at the catchment outlet, providing an integrated signature of degradation

545 processes across the catchment. In contrast, PiBEACH allowed evaluation of the added value of topsoil $\delta^{13}C$ data for constraining degradation kinetics. Model predictions for three components of the S-metolachlor mass balance, degraded mass, remaining mass in topsoil, and export at the outlet, were validated against observations. Due to limitations in representing rapid surface off-site transport associated with runoff and erosion, PiBEACH did not incorporate $\delta^{13}C$ data from river into the calibration. However, future coupling of PiBEACH with an event-based model like OpenLISEM-OLP could enable

550 simultaneous integration of both topsoil and river $\delta^{13}C$ datasets, improving constraints on degradation and enhancing simulation of fast-flow transport during high-intensity rainfall-runoff events.

In summary, $\delta^{13}C$ data from both soil and river samples can enhance model calibration by constraining degradation processes along different transport pathways. Lumped models (e.g., Lutz et al., 2017) and distributed models like PiBEACH each offer complementary perspectives on pesticide dynamics. However, only a distributed model can account for spatial heterogeneity

555 across the catchment and support management decisions. PiBEACH also provides spatially explicit outputs on pesticide concentrations, hydraulic properties, and topsoil moisture as critical inputs for initializing distributed event-based models. A large portion of the outlet data, i.e. discharge for calibration (as part of the KGE objective function), and discharge and S-metolachlor concentrations for evaluating export, was used to assess model performance. Nevertheless, due to limitations of PiBEACH's conceptual structure and daily resolution, the comparison between observed and simulated reactive transport was

560 limited, unlike previous lumped approaches (Lutz et al., 2017). The forthcoming PiBEACH–OpenLISEM-OLP modelling effort will explore the added value of incorporating observed S-metolachlor concentrations and isotopic signatures at the outlet into the calibration process.

This study demonstrates that even a moderate sampling effort, including weekly CSIA measurements from composite topsoil samples across the catchment, can effectively identify hot spots and hot moments of pesticide degradation at the catchment scale. In PiBEACH, degradation is primarily driven by soil temperature and moisture, which exhibits clear seasonal and vertical gradients. As a result, degradation hotspots were consistently located in the topsoil. In contrast, soil moisture, although more spatial variable than temperature, played a secondary role. No significant spatial differences in DT_{50} were observed among plots treated with S-metolachlor over the growing season. The limited predicted spatial variation in DT_{50} across the catchment does not diminish the value of PiBEACH's distributed nature, particularly when considering its future integration with distributed event-based models such as OpenLISEM-OLP. This coupling remains essential for simulating surface transport during rainfall events and refining predictions of pesticide fate under dynamic hydrological conditions.

As the field of pesticide CSIA evolves, through multi-element CSIA applications (Torrentó et al., 2021; Höhener et al., 2022) and the development of passive sampling techniques (Gilevska et al., 2022a), the ability to evaluate dissipation processes and distinguish between competing pathways (Elsner and Imfeld, 2016; Hofstetter et al., 2024) will enhance assessments of pesticide degradation in agricultural soils and enable more robust catchment-scale modelling.

3 Conclusion

This study addresses the gap between the increasing complexity of reactive transport models and the limited availability of field data for their calibration and validation. Although the representation of interactions between hydro-climatic conditions, biogeochemical processes, and degradation dynamics has improved significantly in recent decades, it remains oversimplified in many 2D catchment models (Lutz et al., 2013) or is not explicitly defined (DeMars et al., 2018). Incorporating more detailed physical and biological representations of degradation catchments increases model complexity and uncertainty, making it essential to acquire additional data to constrain parameter ranges and reduce equifinality. Our findings suggest that using only topsoil pesticide concentrations and discharge measurements is insufficient to effectively constrain reactive transport models at the catchment scale. We demonstrated that incorporating complementary data, such as pesticide CSIA data (Fenner et al., 2013, Elsner and Imfeld, 2016; Hofstetter et al., 2024), can help differentiate between degradative and non-degradative processes contributing to observed concentration declines. In many cases, carbon isotope data ($\delta^{13}C$) alone may be adequate to provide evidence of in situ degradation, thereby supporting pesticide mass balance closure and model validation at the catchment scale. Looking ahead, multi-element CSIA has the potential to further elucidate competing degradation pathways (Höhener et al., 2022). To improve model accuracy, future research should also consider the dynamics of microbial functional diversity, biomass, and biodegradation potential (Konig et al., 2018).

Our results highlight the potential of topsoil CSIA data to inform pesticide management strategies by providing more reliable estimates of degradation and transport processes at the headwater catchment scale. Given the strong effect of hydro-climatic factors on pesticide degradation and transport, especially under changing rainfall and temperature regimes driven by climate

change (Barrios et al., 2020), it is essential to account for these dynamics is pesticide fate assessments. Furthermore, risk metrics for pesticide risk assessment often require probabilistic approaches, including confidence intervals (CI) (Lutz et al., 2013). Therefore, to support decision-making and ecotoxicological assessments, hydrological models should systematically incorporate uncertainty frameworks to capture the full range of parameter values affecting pesticide transfer risks.

4 Code availability

The codes developed for this study are available from the corresponding author upon request.

5 Data availability

The data produced for this study are available from the corresponding author upon request.

6 Author contributions

PAZ performed conceptualization, data curation, formal analysis, investigation and writing. PVD developed the agronomical module, produced associated results, and performed writing. SP and GI performed conceptualization, funding acquisition, project administration, supervision and writing – review & editing.

7 Supplement

The supplement related to this article includes a summary of hydro-climatic conditions, detailed catchment and sampling descriptions, farmer survey results, $\delta^{13}C$ analysis and detailed model descriptions and is available in assets section.

8 Competing interests

The authors declare that they have no conflict of interest.

9 Acknowledgements

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