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PITCH: A model simulating the transfer and retention of pesticides in infiltrating ditches and channel networks for management design purposes

Cécile Dagès¹, Marc Voltz¹, Jean-Stéphane Bailly^{1,2}, David Crevoisier¹, Jeanne Dollinger¹, Christelle

5 Margoum³

1- LISAH, Univ Montpellier, INRAE, Institut Agro, IRD, 2 Place Pierre Viala, 34000, Montpellier, France

2 - AgroParisTech, Paris-Saclay University, Paris, 75005, France

3- RIVERLY, INRAE, CS 20244, 69625, 5 Rue de la Doua, Villeurbanne, 69100 France

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Abstract

Agricultural ditches are frequently included in the panel of landscape elements to be managed to minimize the negative impacts of agriculture on the environment, particularly water contamination.

A new mechanistic model simulating pesticide transfer in ditch networks during flood events was

15 developed for help in designing ditch management. The model considers pesticide sorption

processes to soil, living vegetation and litter and is adapted to heterogeneous and infiltrating tree-

like ditch networks, with a reach resolution. The model was evaluated with pulse tracer experiments

conducted on two vegetated and litter-rich ditches and with two contrasting pesticides, namely,

diuron and diflufenican. It appears necessary to consider exchange of only a small proportion of the

20 water column with the ditch materials to achieve a good reproduction of the chemogram. The model

simulates well the chemogram of diuron and diflufenican during calibration and validation (with

Nash performance criteria values ranging from 0.74 to 0.99). The calibrated thicknesses of the soil

and water layers contributing to the sorption equilibrium were very small. The former was

intermediate between the theoretical transport distance by diffusion and the thicknesses usually

25 considered in mixing models for pesticide remobilization by field runoff. The numerical exploration

of PITCH showed that during flood events, retention in ditches is mainly due to adsorption of the compound by the soil and litter. Retention is thus driven by the corresponding sorption coefficients and by parameters controlling the mass of these sorbents such as ditch width and litter cover. The latter parameters can be modified by management practices. In some cases, infiltration can contribute significantly to pesticide removal from surface water and in return participate in soil and groundwater contamination. Finally, PITCH exhibits a consistent behaviour in predicting pesticide attenuation and is shown to be relevant for evaluating ditch management strategies.

Mechanistic model; Mitigation; Water quality; Mixing layer; Model validation; Sensitivity analysis

1- Introduction

Agricultural ditches are present in many agricultural landscapes and are frequently included in the panel of elements to be managed to minimize the negative impacts of agriculture on the environment, including water contamination and biodiversity erosion (e.g., Dollinger et al., 2015, Herzon and Helenius, 2008). However, few studies and tools are currently available for developing ditch management strategies.

Farmed ditch networks are human-made infrastructures originally designed to control the waterlogging of arable lands and prevent soil erosion by collecting and routing excess shallow groundwater or surface overland flow (Dollinger et al., 2015; Levavasseur et al., 2012). Depending on the depth and fluctuation levels of the water table, the flows in the ditches can be intermittent. This is typically the case in arid and semiarid contexts where shallow permanent water tables are rare and flow in the ditches is often limited to short periods of heavy rainfall that generate overland flows on upstream hillslopes. Infiltration losses in the network can vary greatly between flow events and along a ditch network according to spatial and temporal fluctuations in water table depths, soil water content and soil hydraulic conductivity (e.g., Marofi, 1999). These can be very substantial

and accentuate the intermittence of the flows (Hughes and Sami, 1992; Dagès et al., 2009). In cropped landscapes where overland flow waters collected by ditches may be loaded with pesticides (Louchart et al., 2001; Tang et al., 2012; Voltz and Louchart, 2001), ditch networks can represent a major pathway of rapid pesticide transfer towards surface water or groundwater bodies or both.

55 Moreover, ditches are also reputed to attenuate water contamination due to their buffering capacities (e.g., Dousset et al., 2010, Dollinger et al., 2015, 2016, Dages et al., 2015). Otto et al. (2016) suggested that ditches are the best buffer zones to immediately and locally limit pesticide dispersion from field runoff. As reviewed by Dollinger et al. (2015), the main processes involved in the buffering capacity of ditches include adsorption, degradation, and leaching for infiltrating ditches.

60 Several studies have aimed to elucidate the factors controlling pesticide retention in ditches, mainly for near-permanent flow conditions, by statistical analysis of experimental data (Bundschuh et al., 2016), use of simplified modelling based on fugacity models (Otto et al., 2016, Dollinger et al., 2016) and mechanistic modelling (Adriaanse et al., 2022). The presence of vegetation and litter in ditches was often suggested to improve pesticide retention by increasing both the hydraulic

65 retention time and the sorption capacity of ditches (e.g., Cooper et al., 2004, Dollinger et al., 2015, Bundschuh et al., 2016, Otto et al., 2016). However, these case studies were specific, and the diversity and range of the tested factors do not allow a generic conclusion about the key factors explaining the variability in pesticide retention.

Ditches exhibit great spatial and temporal diversity in their properties and characteristics (geometry,

70 vegetation and litter type and abundance, etc.). Therefore, retention capacity is expected to vary along a network. Considering the spatial and temporal variability in pesticide loads in ditches induced by agricultural practices, the overall mitigation provided by a ditch network is also expected to be highly variable. Thus, management strategies to optimize pesticide mitigation need to be planned at the network scale and relative to the season (Dollinger et al., 2015; Herzon and

75 Helenius, 2008). The design of management strategies is still hampered by the lack of knowledge

about the hierarchy of mechanisms and factors explaining pesticide mitigation capacity (Bundschuh et al., 2016). This could be addressed with mechanistic modelling, but models must properly simulate the transient flows that prevail during floods and the associated pesticide transport. They must also consider the main processes involved in pesticide retention and the properties or factors
80 controlling them. Finally, to assess ecological risk, the models must be able to evaluate both mean and maximal pesticide concentrations (Bundschuh et al., 2016).

There are several modelling approaches to simulate pesticide transfer in ditches, whether they are integrated within catchment hydrological modelling or not. They all assume a well-mixed layer of water overlying a layer of sediment, inducing a homogenous concentration of the water column.
85 They differ mainly in the following three aspects.

First, they have adopted contrasting types of formalisms to calculate the exchange of pesticides between the water column and the soil in a ditch. The most widespread formalism represents exchanges according to a diffusion flow and is implemented in ditch-scale models suitable for surface flows with low velocities and without transmission losses (no infiltration) (e.g., TOXSWA,
90 Adriaanse, 1996) and in watershed hydrological models for higher flow in larger hydrographic networks, such as rivers (e.g., SWAT (Neitsch et al., 2011), Mike-She (DHI, 2020)). Another formalism, similar to fugacity approaches used to calculate retention indicators (e.g., Dollinger et al., 2016, Otto et al., 2016), was adopted in some models, such as SPIDER (Renaud et al., 2008) or PESHMELBA (Rouzies et al., 2019). It is based on the concept of a mixing zone, as already used in
95 many models, such as SWAT or PRZM (Young and Fry, 2014), to simulate pesticide washoff at the field scale by surface runoff. Finally, an empirical relationship developed from a database of transfer in grass strips is used, to our knowledge, only in VSFMOD (Muñoz-Carpena et al., 2010, Philips et al., 2017).

Second, models differ in the consideration of the diversity of materials likely to interact with
100 pesticides. Most models only consider the possibility of sorption onto sediments, whether they are

deposited as a layer below the water column or remain in suspension. To our knowledge, only TOXSWA and VSFMOD consider sorption onto other materials, with explicit consideration of sorption onto macrophytes in TOXSWA and implicit and undifferentiated consideration of material contribution by fitting an overall sorption coefficient for the entire ditch in VSFMOD (Phillips et al., 2017).

Third, models differ in their ability to simulate transient flow along a heterogeneous tree-like ditch network. Several models simulate pesticide transfer at the network scale. Hydrological models, such as SPIDER, Mike-She, and SWAT, can simulate rapid and transient flows that occur during flood events. However, they do not account for ditch diversity, which is considered a shortcoming by Wang et al. (2019) in their review of pesticide fate modelling using SWAT. Thus, these models can only simulate the overall buffering effect of ditches without considering its spatial modulation and can hardly be used to analyse the effect of temporal and spatial arrangement scenarios of management operations likely to control the retention capacity of ditches. TOXSWA can consider nonconfluent and linear networks with a weir at their outlet (Adriaanse and Beltman, 2009). Finally, no model can simulate the transfer of pesticides in infiltrating and heterogeneous ditch networks during flood events with the above detailed specifications. Such situations are often observed in the Mediterranean environment (see, for example, Moussa et al., 2002, Dagès et al., 2009) and lead to water contamination by pesticides (e.g., Louchart et al., 2001).

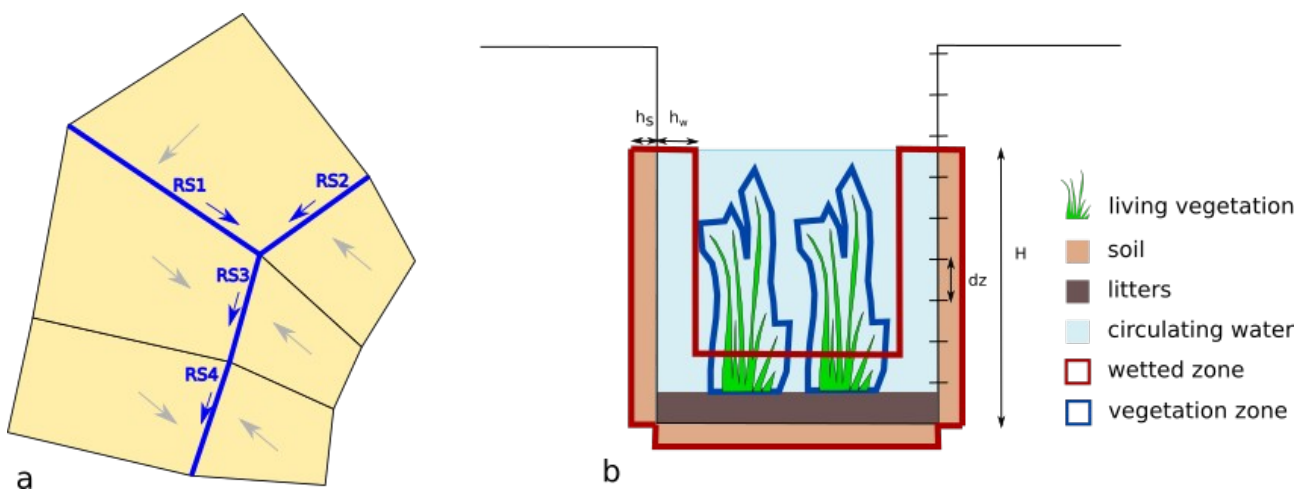
In this paper, we present a new model, PITCH (Pesticides in dITCH networks), that fills this gap. The aims of this study were to i) develop a pesticide transfer model adapted to infiltrating floods and heterogeneous tree-like ditch networks and ii) demonstrate its usefulness for management design purposes. The ditches in the network are described according to topological (position in the network), geometrical (e.g., width, slope) and compositional (e.g., soil type, living vegetation and litter composition) characteristics. The paper describes first the concepts of the model, then evaluates the model against reactive transfer experiments in ditches, and analyses the sensitivity of

its outputs to pesticide and ditch properties and finally discusses its ability to simulate the effect of ditch management on the mitigation of pesticide pollution.

2- PITCH model principles

2.1- Main concepts

130 PITCH was developed to simulate pesticide transport and fate in ditch networks during flood events. Its formalism was kept simple and robust enough to allow easy integration into a hydrological model. Only the most relevant processes at the time scale of a flood event, namely, from a few hours to a few days, were included in the model. Thus, flood water routing and infiltration into ditches and sorption and transport of pesticides are considered, whereas
135 volatilization and degradation are neglected given the small atmosphere–water interface and the usual short duration of flow events. Sorption is assumed to operate on soil but also on living vegetation and on most of the solid materials frequently laying over the ditch bed, such as litter materials.



140 *Figure 1: Ditch representation: (a) Spatial discretization of the network and (b) reach compartments conceptualization. On the left (a), the blue lines mark the network composed of 3 reaches subdivided into four segments, denoted RS1 to RS4. The light yellow polygons correspond to the*

fields. The arrows indicate the flow directions, with the grey arrows indicating the surface flow from the fields to the ditches and the blue arrows indicating the transfer in the ditch network.

145

The ditch network is divided into a serie of connected reach segments (denoted RS), as illustrated with a simple example in Figure 1a. The ditches are hydrologically connected to upstream and downstream RS and possibly to both sides of the adjacent fields. They receive water and dissolved pesticides by surface runoff from the connected fields. The water and pesticides are conveyed to the outlet through the network, which is represented as a single-oriented tree with one to several head RS and a single outlet reach. The water flow routing and pesticide transport are computed at each time step and for each RS, which are treated following the topological order from upstream to the outlet.

To represent exchanges between pesticides in flowing water and in ditch material, three layers are distinguished within the water column (see Figure 1b) with i) a layer interacting with the bank and bottom ditch materials, hereafter called the wetted zone (outlined in red in Figure 1b), ii) another layer interacting with submerged vegetation called the vegetation zone (outlined in dark blue in Figure 1b), and a third layer without interactions (all water flowing out of the first two zones).

Pesticide compounds dissolved in each of these water layers are assumed to be uniformly distributed within the layer and to be at equilibrium with the compounds adsorbed on the materials in contact with this zone. The pesticide concentration of the water infiltrating the ditch bed and banks is assumed to equal the concentration of pesticides in the wetted zone.

In accordance with the resolution of the flow equations detailed in the following sections, the calculations of water and pesticide transfers are performed sequentially by considering first a conservative transfer and then correcting it by subtracting infiltration flows and retention of pesticides. Pesticide concentrations in the water layers are updated assuming that surface transport

between two RS generates perfect mixing throughout the water column. It is assumed that during their transfer within a reach, pesticides that cross the wetted or vegetation zones during the time step are in equilibrium with all the water that stays in that layer and with all the solid phases, namely, soil and litter in the wetted zone and submerged vegetation in the vegetation zone.

2.2. Water flow calculations

For each reach segment and each time step, calculations are performed sequentially in four steps.

First step: calculation of RS inflow

The flow entering the RS during a time step, Q_{inRS} (m^3/s), is calculated as the sum of the flow from the upstream RS (Q_{upRS} , m^3/s), the adjacent field surface runoff (Q_{fields} , m^3/s), and the amount of rainfall (H_{rain} , m) on the RS surface per second.

$$Q_{inRS} = \sum^{upRS} Q_{upRS} + \sum^{connectedfields} Q_{fields} + \frac{H_{rain}LW}{\Delta t} \quad (\text{eq. 1})$$

where L and w are the length and width of the reach (m), respectively, and Δt is the time step (s).

Second step: Calculation of conservative reach outflow if no infiltration occurred across the RS banks and bed

A conservative outflow, Q^{cons} (m^3/s), is calculated using the diffusive wave equation (Eq. 2), assuming no lateral inflow/outflow, as in Moussa et al. (2002).

$$\frac{\partial Q^{cons}}{\partial t} = -C \left(\frac{\partial Q^{cons}}{\partial x} \right) + D \frac{\partial^2 Q^{cons}}{\partial x^2} \quad (\text{eq. 2})$$

where C is the velocity (m/s), D is the diffusivity (m^2/s), and x is the longitudinal distance (m).

This equation is solved using Hayami's analytical solution, considering constant celerity and diffusivity. The outflow is calculated by

$$Q^{cons} = Q_{inRS} * K \quad (\text{eq. 3})$$

where $*$ is the convolution product and K is the Hayami kernel function expressed by

$$190 \quad K = \frac{L}{2(\pi D)^{1/2}} \frac{\exp\left(\frac{CL}{4D}\left(2 - \frac{L}{C\tau} - \frac{C\tau}{L}\right)\right)}{\tau^{3/2}} \quad (\text{eq. 4})$$

where τ (s) is the elapsed time since the flow began.

The Manning-Strickler relations are used to calculate the celerity and diffusivity from the slope and roughness coefficient:

$$C = C_m \frac{\beta}{\beta_m} \frac{n_m}{n} \quad \text{and} \quad D = D_m \frac{\beta}{\beta_m} \frac{n_m}{n} \quad (\text{eq. 5 and 6})$$

195 where C_m and D_m are user parameters corresponding to the mean wave celerity (m/s) and mean wave diffusivity (m²/s), respectively, β is the slope of the reach (m/m), β_m is the mean slope of the ditch network (m/m), n is the roughness coefficient of the reach (s/m^{1/3}), and n_m is the mean roughness coefficient of the ditch network (s/m^{1/3}).

Third step: Calculation of actual infiltration across the RS banks and bed

200 If the outflow Q^{cons} computed in the previous step is not null and if the soil is permeable, infiltration in the reach banks and bed is considered possible. Accordingly, the infiltration flux, q_{inf} (m/s), is computed as a linear function of the saturated hydraulic conductivity K_s (m/s) of the reach banks and bed as

$$q_{inf} = a K_s + b \quad (\text{eq. 7})$$

205 where a (-) and b (m/s) are empirical parameters, whose values are $a = 1.58$ and $b = 1.64e-5$, respectively. The determination of this simple equation for average infiltration along the wetted section of a flooded ditch is detailed in Appendix A.

Infiltration is supposed to occur across the area A_{wz} (m²), which includes the wetted bed and banks of the reach and is computed by

$$210 \quad A_{wz} = (2H + w)L \quad (\text{eq. 8})$$

where H (m) is the wetted height of the banks. The height H is approximated by using the Manning-Strickler relationship with the computed conservative flow and considering that the reach section is rectangular.

Fourth step: Calculation of the actual RS outflow

215 The actual mean outflow, Q (m³/s), during the time step is calculated by subtracting the estimated actual infiltration flow from the conservative mean outflow:

$$Q = Q^P - q_{inf} A_{WZ} \text{ (eq. 9)}$$

2.3. Pesticide fate calculations

220 The simulation of pesticide transfer in an RS is also performed sequentially in four steps.

First step: Calculation of pesticide inflow in the RS

Pesticide input to a reach segment is the sum of pesticide inputs from the upstream portion of the ditch network ($Q_{pest, upRS}$, kg/s) and of adjacent fields ($Q_{pest, fields}$, kg/s) and is expressed as a mass flow ($Q_{pest, inRS}$, kg/s).

225
$$Q_{pest, inRS} = \sum^{upRS} Q_{pest, upRS} + \sum^{connectedfields} Q_{pest, fields} \text{ (eq. 10)}$$

Second step: Calculation of maximum pesticide transport if no retention or lateral losses occur

A conservative transport mass discharge (Q_{pest}^{cons} , kg/s) is calculated using the diffusive wave equation with the same Hayami resolution as that used for water flow, according to equations 3 and 4. The

230 Hayami kernel, K , which is defined for water flow, is also used for pollutant transport.

$$\left\{ \begin{array}{l} \frac{\partial Q_{pest}^{cons}}{\partial t} = -C \left(\frac{\partial Q_{pest}^{cons}}{\partial x} \right) + D \frac{\partial^2 Q_{pest}^{cons}}{\partial x^2} \text{ (eq. 11)} \\ Q_{pest}^{cons} = Q_{pest, inRS} * K \end{array} \right.$$

Third step: Calculation of pesticide sorption at equilibrium

Given the characteristics of the three homogeneous layers (see Figure 1b), the sorption equilibrium is calculated separately in the wetted zone and in the vegetated zone. It is not necessary to consider
 235 the equilibrium in the third zone in the absence, by construction, of sorbing materials.

Hereafter, for each equilibrium zone, we define first the volume of water, masses of sorbing materials involved and the corresponding pesticide masses and then develop the sorption equilibrium equation.

Step 3a: For the wetted zone

240 The materials in contact with the water comprise the soil of the wetted bed and only the submerged portion of the banks and the submerged portion of litter if present. The mass of materials thus depends on the mean maximum wetted bank height H computed during the time step and is estimated by equations 12 and 13 for the soil and litters, respectively.

$$M_{soil} = h_s L (w + 2H) d_{soil} \text{ (eq. 12)}$$

245 where M_{soil} (kg) is the soil mass involved in the wetted zone, h_s (m) is the thickness of the interacting soil layer, and d_{soil} is the bulk density (kg/m³) of the soil.

$$M_{lit} = L \left(\min(H, h_{lit}) w \right) r_{lit} d_{lit} (1 - p_{lit}) \text{ (eq. 13)}$$

where M_{lit} and h_{lit} are the mass (kg), and height (m) of the litter, respectively; r_{lit} is the fraction of the total surface area occupied by the litter (-); and d_{lit} and p_{lit} are the bulk density (kg/m³) and the
 250 porosity (m³/m³) of the litter, respectively.

The volume of water in the wetted zone (V_{wz} , m³) includes (i) the volume of water within the mixing water layer of h_w thickness (m), (ii) the water contained in the litter porosity, (iii) the infiltrated water during the time step, and (iv) the water contained in the soil porosity within the mixing soil layer of h_s thickness. Accordingly, we have

$$255 \quad V_{wz} = L w (h_w + r_{lit} h_{lit} p_{lit}) + 2L h_w (H - h_w) + V_{inf} + h_s L (w + 2H) \theta_s \text{ (eq. 14).}$$

where θ_s (m³/m³) is the soil water content at saturation.

At the end of the time step, the pesticide mass in the wetted zone considered for the equilibrium is the sum of the pesticides crossing the mixing water layer, $P_{WZ, water}$ (kg) during the time step and the pesticides already stored in the soil and litter at the beginning of the time step, P_{soil}^{init} and P_{litter}^{init} (kg),
 260 respectively.

$P_{WZ, water}$ is defined as a fraction of the conservative mass outflow Q_{pest}^{cons} as given by Equation 15:

$$P_{WZ, water} = \frac{Lw h_w + 2 L h_w (H - h_w) + V_{inf}}{Q^{cons}} Q_{pest}^{cons} \quad (\text{eq. 15})$$

The mass of pesticides stored in the soil and contributing to the equilibrium includes the whole stock in the RS bed P_{bed}^{init} and only that in the submerged portion of the banks. For the banks, vertical
 265 heterogeneity of storage according to past water levels is considered, and discrete stocks along the banks, $S_{banks, i}$ (kg), are calculated, assuming uniform behaviour for the right and left banks. Thus, the banks are discretized using a user-defined parameter, Δz (m), corresponding to the vertical spatial resolution (see Figure 1b). Assuming that for the partially wetted cell of the banks, the mass of pesticides in equilibrium is proportional to the degree of wetting of the cell, the mass of
 270 pesticides stored in the soil and contributing to the equilibrium is given by equation 16.

$$P_{soil}^{init} = \sum_{i=0}^{j-1} S_{banks, i}^{init} + S_{banks, j}^{init} \frac{H - (j-1)\Delta z}{\Delta z} + P_{bed}^{init} \quad (\text{eq. 16})$$

With H being the mean conservative water level (m) and therefore the height of the submerged portion of the banks of a reach during the time step, the number of cells contributing to the equilibrium, j , is determined as

$$(j-1)\Delta z < H < j\Delta z \quad (\text{eq. 17})$$

The mass of pesticides stored in the litter and contributing to the equilibrium, P_{lit}^{init} , corresponds to the whole mass stored within the litter layer if the water level is higher than the litter thickness. Otherwise, P_{lit}^{init} is defined according to the same principle as that used for the banks, considering the same vertical discretization, as given by equation 18.

$$280 \quad P_{lit}^{init} = \sum_{i=0}^{j-1} S_{lit,i}^{init} + S_{lit,j}^{init} \frac{H - (j-1)\Delta z}{\Delta z} \quad (\text{eq. 18})$$

Finally, the pesticide concentrations in water, soil and litter within the wetted zone of a reach, $C_{eq,WZ}$, and the final submerged stocks of pesticides (kg) in the soil and litter, respectively P_{soil}^{end} and P_{lit}^{end} , are calculated according to equations 19 to 21, assuming equilibrium and linear sorption. Note that the assumption of equilibrium throughout the wetted zone implies a uniform pesticide content in the submerged portion of the bank. Accordingly, when the water level increases, the stock of the submerged banks is computed as the sum of the stock in the submerged banks at the previous time step and the stock of the newly submerged part of the banks. A fine discretization of the banks height (small Δz) limits the uncertainty in the submerged height of the banks.

$$C_{eq,WZ} = \frac{P_{soil}^{init} + P_{lit}^{init} + P_{WZ,water}}{Kd_{soil} M_{soil} + Kd_{lit} M_{lit} + V_{WZ}} \quad (\text{eq. 19})$$

290 with Kd_{soil} and Kd_{lit} representing the sorption coefficients (L/kg) of the soil and litter, respectively.

$$P_{soil}^{end} = Kd_{soil} C_{eq,WZ} M_{soil} \quad (\text{eq. 20})$$

$$P_{lit}^{end} = Kd_{lit} C_{eq,WZ} M_{lit} \quad (\text{eq. 21})$$

Step 3b: For the vegetation zone

Vegetation is the only sorbing material in contact with water in this zone. The vegetation mass involved is calculated similarly to the calculation of litter mass involved in equation 13. Accordingly, we have:

$$M_{LV} = L \left(\min(H, h_{LV}) w \right) r_{LV} d_{LV} (1 - p_{LV}) \quad (\text{eq. 22})$$

where M_{LV} and h_{LV} are the mass (kg) and height (m) of the living vegetation, respectively; r_{LV} is the fraction of the total surface area occupied by the living vegetation (-); and d_{LV} and p_{LV} are the bulk density (kg/m³) and porosity (m³/m³) of the living vegetation, respectively.

The volume of water (V_{VZ} , m³) involved in the equilibrium in that zone is the water contained in the vegetation porosity below the mean conservative water level (H) during the time step.

$$V_{VZ} = \min(h_{LV}, H) w L r_{LV} p_{LV} \text{ (eq. 23)}$$

The pesticide mass at equilibrium in the vegetation zone is the sum of the pesticide mass, $P_{VZ,water}$ (kg), within V_{VZ} and the pesticide mass stored in the living vegetation at the beginning of the time step, P_{LV}^{init} (kg). The former is calculated proportionally to the volume of water leaving the RS, as shown in equation 24, whereas the latter is computed by adding discrete stocks to account for the variation in the submerged part of the living vegetation with the water level in the reach as for the litter and banks, described by equation 25.

$$P_{VZ,water} = \frac{V_{VZ}}{Q^{cons}} Q_{pest}^{cons} \text{ (eq. 24)}$$

$$P_{LV}^{init} = \sum S_{LV,i}^{init} + S_{LV,j}^{init} \frac{H - (j-1)\Delta z}{\Delta z} \text{ (eq. 25)}$$

The equilibrium concentration $C_{eq,VZ}$ (kg/m³) and new submerged stocks in the vegetation zone P_{LV}^{end} (kg) are calculated according to equations 26 and 27.

$$C_{eq,VZ} = \frac{P_{LV}^{init} + P_{VZ,water}}{Kd_{LV} M_{LV} + V_{VZ}} \text{ (eq. 26)}$$

$$P_{LV}^{end} = Kd_{LV} C_{eq,VZ} M_{LV} \text{ (eq. 27)}$$

with Kd_{LV} representing the sorption coefficient (L/kg) of the living vegetation.

The final stock of pesticides within living vegetation is calculated as the sum of the new submerged stock and the emerged stock.

Fourth step: Calculation of pesticide outflow and pesticide infiltration fluxes

Water is assumed to infiltrate at the concentration of the wetted zone as determined by equation 19, and therefore, the infiltrated mass during a time step, P_{inf} (kg), can be calculated as shown by equation 28.

$$P_{inf} = C_{eq,WZ} q_{inf} A_{WZ} \Delta t \text{ (eq. 28)}$$

Finally, transport is assumed to generate perfect mixing among the three water layers. Thus, the mean concentration of surface water leaving the RS, C_{eq} (kg/m³), and the mass flow rate of pesticides leaving the RS, Q_{pest} (kg/s), are calculated by equations 29 and 30, respectively.

$$C_{eq} = \frac{Q_{pest}^{cons} \Delta t - P_{inf} - P_{soil}^{end} - P_{lit}^{end} - P_{LV}^{end}}{Q^{cons} \Delta t} \quad (\text{eq. 29})$$

$$Q_{pest} = C_{eq} Q \quad (\text{eq. 30})$$

2.4. Computer implementation

PITCH was designed to be inserted into a hydrological model and to be easily extended by adding new processes. It has been implemented in the OpenFLUID v2.1.10¹ platform (Fabre et al., 2020 2010), which allows construction of models by sequentially coupling blocks of code, each of them supporting one of the main functions of the model. The OpenFLUID platform performs the coupling of models via the spatiotemporal exchange of variables. The global structure of the spatial domain is managed using a graph where the nodes are the spatial units (here, SU and RS) and the edges are the relationships between the spatial units (here, hydrological links).

3- Material and Methods

3.1- Evaluation of PITCH with experimental datasets

The ability of PITCH to simulate pesticide transfer was evaluated at the ditch scale with conservative and reactive tracer experiments on two ditches.

3.1.1. Experimental reference datasets

The experiments were performed on two ditches located in western France (Loire Atlantique) in 1999 and 2002. For simplicity, the datasets are hereafter referred to as Ditch B and Ditch A. All experiments, analytical protocols and results are described in detail in Margoum (2003).

¹ SWHID: [swh:1:dir:9526c4ea4c7e87061d10c202bd797908260d034a](https://archive.softwareheritage.org/swh:1:dir:9526c4ea4c7e87061d10c202bd797908260d034a)
<https://archive.softwareheritage.org/swh:1:dir:9526c4ea4c7e87061d10c202bd797908260d034a>

The tracer experiments consisted of the pulse injection of a solution containing two herbicides and a conservative tracer into a ditch with constant flow. Fluxes through the ditch bed and banks, as inferred from the difference between inflow and outflow estimated with a venturi channel or triangular weir, were negligible. The conservative tracer was used to characterize the flow hydrodynamics and to ensure complete solute recovery. The two herbicide compounds, diuron and diflufenican, were among the most widely used herbicides when the experiments were conducted. Diuron and diflufenican differ by their sorption properties in soil, litter and living vegetation, as shown in Supplementary material S1. Therefore, different transport and retention behaviours were expected between the 2 herbicides.

Water was sampled 200 and 100 m downstream from the tracer injection point for Ditch A and Ditch B, respectively, at time steps ranging from 2 to 40 minutes to obtain the variation in solute concentrations in the flowing water. The main characteristics of the two ditches and the two experiments are presented in Table 1. These characteristics were either observed or estimated from literature. Cover rates were estimated visually. The bulk density and porosity values of the litter and living vegetation were taken from Dollinger et al. (2016), who provided measurements on typical ditch vegetation and litter. Ditch B was a smaller, narrower ditch, which was also less covered by litter and living vegetation. The experiments also differed in terms of the injected pesticide concentration, which was an order of magnitude lower for Ditch A than for Ditch B.

365

Table 1: Characteristics of the pulse experiments, PITCH parameters and boundary conditions.

		Ditch A	Ditch B	
Ditch properties corresponding to PITCH input parameters	Length, L (m)	200	100	
	Mean width, w (m)	0.5 ; 0.4 ⁺	0.35	
	Mean slope, β (%)	3	3	
	Manning-Strickler coefficient, n (s/m ^{1/3}) [#]	0.37 ; 0.43 ⁺	0.35	
	Mean living vegetation cover rate, r_{LV} (-)	0.5	0.3	
	Mean litter cover rate, r_{lit} (-)	0.25; 0.4 ⁺	0.3	
	Mean living vegetation height, h_{LV} (m)	0.05	0.1	
	Mean litter thickness, h_{lit} (m)	0.01	0.01	
	Living vegetation porosity, p_{LV} (m ³ /m ³)	0.99	0.99	
	Litter porosity, p_{lit} (m ³ /m ³)	0.97	0.97	
	Living vegetation bulk density, d_{LV} (kg/m ³)	610	610	
	Litter bulk density, d_{lit} (kg/m ³)	380	380	
	Soil bulk density, ρ_{soil} (kg/m ³)	1500	1500	
	Saturated soil water content, Θ_s (kg/m ³)	0.4	0.4	
Flow and pulse characteristics corresponding to PITCH boundary conditions	Ditch discharge (L/s)	2.1	2.5	
	Pulse injection discharge (L/s)	0.16	0.48	
	Pulse duration (s)	600	420	
	Concentrations in the stream at the injection spot (C ₀)	Conservative tracer (mg/L)	196 [*]	230 ^{**}
		DIU (µg/L)	47	548
		DDF (µg/L)	7	101

⁺ The first and second values are related to the section of the ditch prevailing from 0 to 100 m and from 100 to 200, respectively.

^{*} Bromide ^{**} Chloride

[#] Estimated with the Manning Strickler equation, $Q^P = \frac{1}{n} \sqrt{\beta R^{2/3} w L}$, from water level and discharge measurements performed

370 during the experiment (Margoum, 2003), where R is the hydraulic radius of the reach segment (m).

The contrasting properties of the ditches (Table 1) and of the compounds (Table Supplementary material S1) provide a range of maximum normalized downstream concentrations (C_{max}/C_0 from 0.26 to 0.82, see Figure 2) that can be used to test the model under contrasting conditions. Smaller maximum concentration ratios were observed for the compound with the highest sorption coefficient (DFF) and the longest and most litter-rich ditch (Ditch A), which is consistent with other studies (Dollinger et al., 2015).

3.1.2. Evaluation design

The evaluation of PITCH was conducted to mimic as much as possible the application of PITCH in management conditions. We thus chose to parameterize the model with existing data (observed, measured, or from literature and databases) and to limit the calibrated parameters to those that cannot be estimated otherwise. Moreover, the evaluation was performed in a conventional two-step approach using one dataset for calibration and the second dataset for validation. Ditch A was chosen for calibration because it exhibited a greater difference in concentration between inflow and outflow. To focus the evaluation on the reactive transfer model in PITCH, the water transfer part was calibrated for both ditches. This involved the two water transfer parameters that could not be measured, namely, the mean celerity and mean diffusivity (C_m and D_m), that were adjusted using the observed conservative tracer chemograms. Optimal C_m and D_m were determined using the DREAM algorithm (Vrugt et al., 2009) and the dream R package (Guillaume and Andrews, 2011). The ranges of variation in C_m and D_m were set to $[1e-4; 0.1]$ ($m.s^{-1}$) and $[1e-4; 500]$ ($m^2.s^{-1}$), respectively.

Then, the calibration of the unknown thicknesses (h_s and h_w) of the mixing soil and water layers, assumed to be at equilibrium, was performed using the chemograms of the two herbicides in Ditch A. The ditch parameters were fixed to their values in Table 1 whereas the sorption coefficient parameters were fixed to their values in Table S1. The sorption coefficients for litter, living

vegetation, and soil are from Margoum et al. (2006) and Dollinger et al. (2016); they were measured with conventional laboratory batch experiments on soil and litter from Ditch B and on typical ditch plants.

The model was calibrated separately for diuron and diflufenican using the same distribution of parameter values to investigate the possibility that the same parameter values fit well for both compounds. The ranges of h_s and h_w were chosen to cover the range of soil–water layer interaction thickness values reported in the literature. The minimum value of h_s was set to 0.1 mm, which is slightly smaller than the theoretical transport distance (λ) by diffusion of a compound as calculated with the Einstein-Smoluchowsky equation (Calvet et al., 2005, see Appendix B). The maximum value was set to 40 mm, which corresponds to the maximum value that is currently used for soil layers in mixing zones, as reported by Young and Fry (2019). For h_w , the minimum value was set to 0.05 mm, which is the minimum value of the laminar film thickness and the sediment water column interface estimated by Sorensen et al. (2001) in the case of idealized horizontal flow conditions. The maximum value is the contribution of the entire outflow volume leaving the ditch during Δt , which, related to the entire wetted surface of the ditch corresponds to a height of 25 mm. Between these boundaries, 100 values were sampled regularly along a logarithmic scale for h_s and for h_w .

The simulations were performed with a spatial RS discretization of 10 m for the ditch length (L) and 0.1 m for the banks height (Δz) and a time step of 120 s, which is both consistent with the expected mean velocity of the flows and with the spatial and temporal resolution of the experimental data. The simulations were evaluated using three indicators, namely, i) the Nash-Sutcliffe efficiency coefficient calculated from the downstream concentrations, ii) the ratio between the simulated and observed maximum downstream concentrations, and iii) the spread of the chemogram approximated by the lag time between concentration ratios of 0.1 for the increasing and decreasing branches of the chemogram. Then, we selected the pairs of h_s and h_w for each compound that satisfied the criteria described in equation 31.

$$\left\{ \begin{array}{l}
 Nash_k = 1 - \frac{\sum_{i=1}^n (C_i^{obs} - C_i^{sim})^2}{\sum_{i=1}^n (C_i^{obs} - \bar{C}_i^{obs})^2} > 0.65 \\
 Nash_k \geq 0.9 Nash_{max} \\
 0.9 \leq \frac{C_{max}^{sim}}{C_{max}^{obs}} \leq 1.1 \\
 0.8 \leq \frac{S^{sim}}{S^{obs}} \leq 1.2
 \end{array} \right. \quad (eq.31)$$

where C and S are the concentration and the spread, respectively; the superscripts *sim* and *obs* refer to the simulated and observed values, respectively, n is the number of values; and C_{max} and \bar{C} are the maximal and mean concentrations of the observed or simulated chemogram, respectively. $Nash_k$ and $Nash_{max}$ are the Nash-Sutcliffe efficiency coefficient calculated for the simulation with parameter pair values k and the maximum Nash-Sutcliffe efficiency coefficient value obtained for the simulations with all pairs of h_s and h_w for a given compound, respectively.

The two criteria for the Nash-Sutcliffe efficiency coefficient allow for the selection of only the best pairs from those with a very good fit according to Moriasi et al. (2015). The other two criteria allow for the selection of pairs of h_s and h_w that produce a good chemogram shape. Finally, we identified the pairs of h_s and h_w that satisfied equation 31 for both compounds. Validation was performed with the Ditch B experiment using these common pairs of h_s and h_w .

3.2. Numerical evaluation of PITCH behaviour based on a sensitivity analysis

A sensitivity analysis was performed to evaluate both the behaviour of the model and its ability to simulate differences in mitigation according to ditch and compound properties consistent with the wide range of mitigation already observed (Dollinger et al., 2016).

The pulse experimental datasets (section 3.1.1) used to validate the model were not appropriate to
 440 conduct such a numerical analysis since the short pesticide injection pulses were followed by
 complete flushing, leading to a large removal of the injected pesticides. Thus, the sensitivity
 analysis was performed for a ditch subjected to two contrasting flood events selected among those
 monitored at the outlet of a 1200 m² vineyard plot in the Roujan watershed (Hérault, France,
 Louchart et al., 2001, Molénat et al., 2018). The first flood is an intense and long event with high
 445 peak flows, while the second is a small and short event (see Supplementary material S2).
 Concentrations were assumed to be constant during the two events and fixed at different levels for
 the sensitivity analysis (see range of variation in C_{ini} in Table 2).

Simulations were done for a 100-m-long ditch. The calculation time steps and spatial discretization
 were chosen such that i) the infiltration flows are much smaller than conservative flows, which
 450 ensures the validity of approximating water flow height in the ditch from the computed conservative
 flow, and ii) the infiltrated and sorbed pesticide masses always remain lower than the conservative
 mass flows in the ditch from which the former are subtracted at the end of the sequential
 calculations. The mitigation was evaluated using three complementary indicators, namely, mass
 removal of pesticides from surface water $Removal_{surf}$, contamination risk for groundwater $Risk_{GW}$,
 455 and storage of pesticides in the ditch $Storage$. These indicators were computed from the PITCH
 outputs according to equations 32 to 34.

$$Removal_{surf}(\%) = \frac{Mass^{in} - Mass_{surf}^{out}}{Mass^{in}} * 100 = \frac{Mass^{Inf} + Stock^{ditch}}{Mass^{in}} * 100 \text{ (eq. 32)}$$

$$Risk_{GW}(\%) = \frac{Mass^{Inf}}{Mass^{in}} * 100 \text{ (eq. 33)}$$

$$Storage(\%) = \frac{Stock^{ditch}}{Mass^{in}} * 100 \text{ (eq. 34)}$$

460 where $Mass^{in}$ is the mass of pesticides reaching the ditch inlet during the flood (see eq. S3-1);

$Mass_{surf}^{out}$ is the mass of pesticides transported by the ditch outflow (eq. S3-2); $Mass^{Inf}$ is the mass of

pesticides that infiltrated the ditch bed and banks during the flood (eq. S3-37); and $Stock_{ditch}$ is the mass of pesticides still stored in the soil, living vegetation and litter along the ditch at the end of the flood (eq. S3-4).

465 $Removal_{surf}$ corresponds to the percentage of inflowing compounds that did not exit the ditch with outflow, $Risk_{CW}$ corresponds to the percentage of pesticides that infiltrated the ditch bed and banks during the flow event and may therefore contaminate groundwater resources, and $Storage$ is the percentage of the inflowing compounds that are retained in the material at the end of the flow event. This stock may decrease with degradation but may also be remobilized to surface or groundwater
470 during subsequent floods and/or rainfall events.

For a given flood event and ditch length, we evaluated the sensitivity of PITCH to the parameters defining the morphology and composition of the ditch that are likely to vary with management operations (ditch bed width and slope, soil porosity and saturated hydraulic conductivity, and vegetation and litter coverage), to the pesticide concentration in the water entering the ditch, and to
475 the sorption coefficient of the pesticide compound for the ditch material. Note that the roughness coefficient was not included in the sensitivity analysis, as it was estimated from the living vegetation cover rate r_{LV} (Vinatier et al. 2017). Ten parameters were thus selected. Their ranges of variation, displayed in Table 2, were defined by considering physical limits (e.g., coverage rate between 0 and 1), values measured in more than 1000 ditches in France (e.g., width and slope of
480 ditches, Bailly et al., 2015) or values found in the literature (e.g., sorption coefficients from Dollinger et al., 2015). The maximum value of K_s was defined so as to ensure that the flows at the outlet of the ditch remained nonzero during the flood. For parameters covering several orders of magnitude, sampling was performed on a logarithmic scale for a better exploration of their variation range.

485

Table 2: Range of variation in parameter values in the sensitivity analysis

Parameter names	Symbol	Units	Variation range	Variable transformation
Runoff concentration	C_{ini}	$\mu\text{g/L}$	1; 1000	logarithmic
Ditch bed width	w	m	0.25; 1	-
Ditch bed slope	S	m/m	0.001; 0.1	logarithmic
Living vegetation cover rate*	r_{LV}	-	0; 1	-
Litter cover rate**	r_{lit}	-	0; 1	-
Saturated hydraulic conductivity	Ks	m/s	1e-7; 1e-5	logarithmic
Soil moisture at saturation	ths	m^3/m^3	0.2; 0.5	-
Sorption coefficient of soil	Kd_{soil}	L/kg	0.1; 500	logarithmic
Sorption coefficient of living vegetation	Kd_{LV}	L/kg	1; 3000	logarithmic
Sorption coefficient of litter	Kd_{lit}	L/kg	1; 10000	logarithmic

* When $r_{LV} > 0$, the height of vegetation was set to 0.1 m, with a density and porosity as determined by Dollinger et al. (2016), and reported Table S1, leading to biomass of up to 0.18 kg/m^3

** When $r_{lit} > 0$, the height of litter was set to 0.01 m, with a density and porosity as determined by Dollinger et al. (2016), and reported Table S1, leading to biomass of up to 0.11 kg/m^3

To limit the number of simulations, a two-step sensitivity analysis was performed: a first screening analysis was performed to roughly select the most influential parameters among the 10, and then, a
 490 more comprehensive and intensive analysis was performed on these selected parameters. The first step was conducted following a Morris approach, which is considered an effective screening method (e.g., Campolongo et al., 2007, Herman et al., 2013). The description of the experimental design and the results are presented in the Supplementary Material (S4).

For the second step, we chose a Sobol sensitivity approach (Sobol, 2001; Saltelli, 2002) that uses
495 model variance decomposition and assigns the variance in the model output to individual
parameters and their interactions. Sobol defines the first-order index, S_i , which measures the
fraction of the total variance in output caused by parameter i apart from interactions with other
parameters, while the total-order index, ST_i , also includes interactions between i and all other
parameters. These sensitivity indices were approximated here using numerical integration in a
500 Monte Carlo framework as proposed by Martinez (2011) with the Sobol-Martinez function of
sensitivity packages available in R (Iooss et al., 2021). A global sample of the parameter space is
obtained using a regular sequence of 2000 values per parameter (see Table 2 for range and variable
transformation) and 1000 bootstrap replicates, leading to 14000 sets of parameters to be evaluated
by the model.

505

4. Results

4.1. Calibration and validation of PITCH

Conservative transport was well simulated using PITCH by fitting C_m and D_m for both experiments,
as shown in Figure 2 and by the goodness of fit indicators reported for bromide or chloride in Table
510 3. Nash values are greater than 0.97, and relative differences are less than 8% and 20% for
maximum concentration and spread, respectively. The fitted values, also reported in Table 3, are
consistent with the observed average flow velocity and low dispersion of the conservative
chemograms. The adjusted D_m for Ditch A is one order of magnitude higher than that for Ditch B, in
accordance with a higher vegetation cover inducing a more heterogeneous flow.

515

Table 3. Fitted parameter values and goodness-of-fit indicators for calibration (Ditch A) and validation (Ditch B). The ranges of values for h_s and h_w correspond to the minimal and maximal values that satisfy the goodness-of-fit criteria for both compounds, in calibration. The minimum and maximum values of the indicators are given.

	C_m (m/s)	D_m (m ² /s)	h_s (mm)	h_w (mm)		<i>Nash</i>	$\frac{C_{max}^{sim}}{C_{max}^{obs}}$	$\frac{S^{sim}}{S^{obs}}$	
Ditch A	0.063	0.046	0.61	to 0.13	to	Bromide	0.97	0.92	0.81
						Diflufenican	0.74; 0.75	1.04; 1.1	1.07; 1.09
						Diuron	0.93; 0.94	0.95; 1.01	1.12; 1.15
Ditch B	0.086	0.005	0.78	to 0.28		Chloride	0.99	0.99	0.86
						Diflufenican	0.97; 0.97	1.01; 1.03	1.05; 1.05
						Diuron	0.99; 0.99	0.94; 0.95	0.85; 0.88

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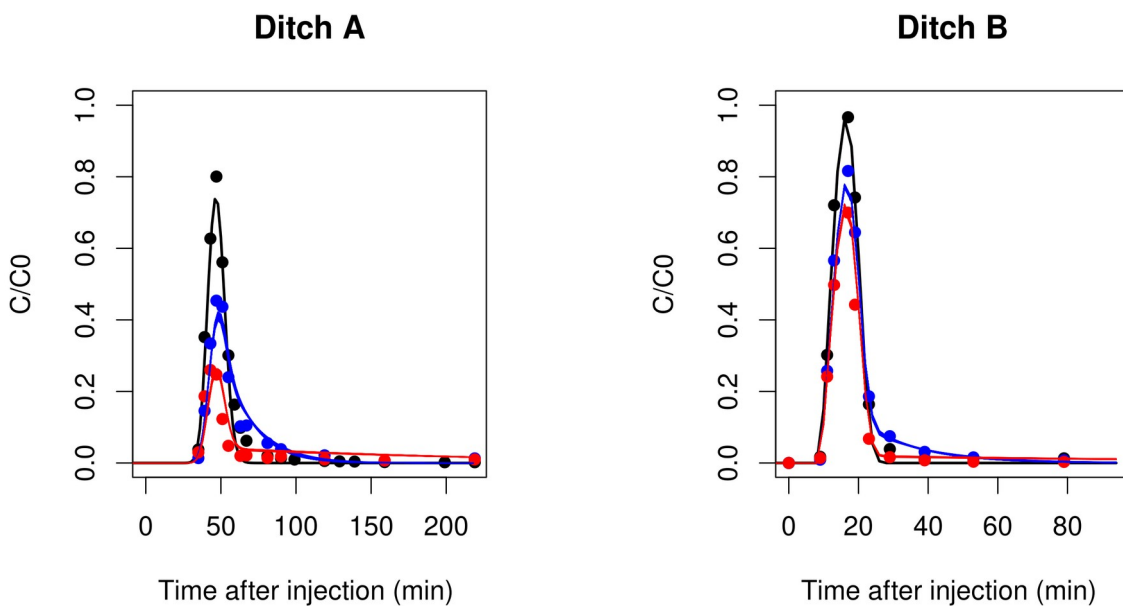


Figure 2: Comparison of observed (dots) and simulated (line) chemograms measured at the ditch outlet for Ditch A (left) and Ditch B (right). The conservative tracer (bromide on the left and chloride on the right) is in

black, diflufenican is in red and diuron is in blue. The red and blue lines show the simulation of the diflufenican and diuron chemograms of all the acceptable pairs of h_s and h_w . Dispersion of the results is low.

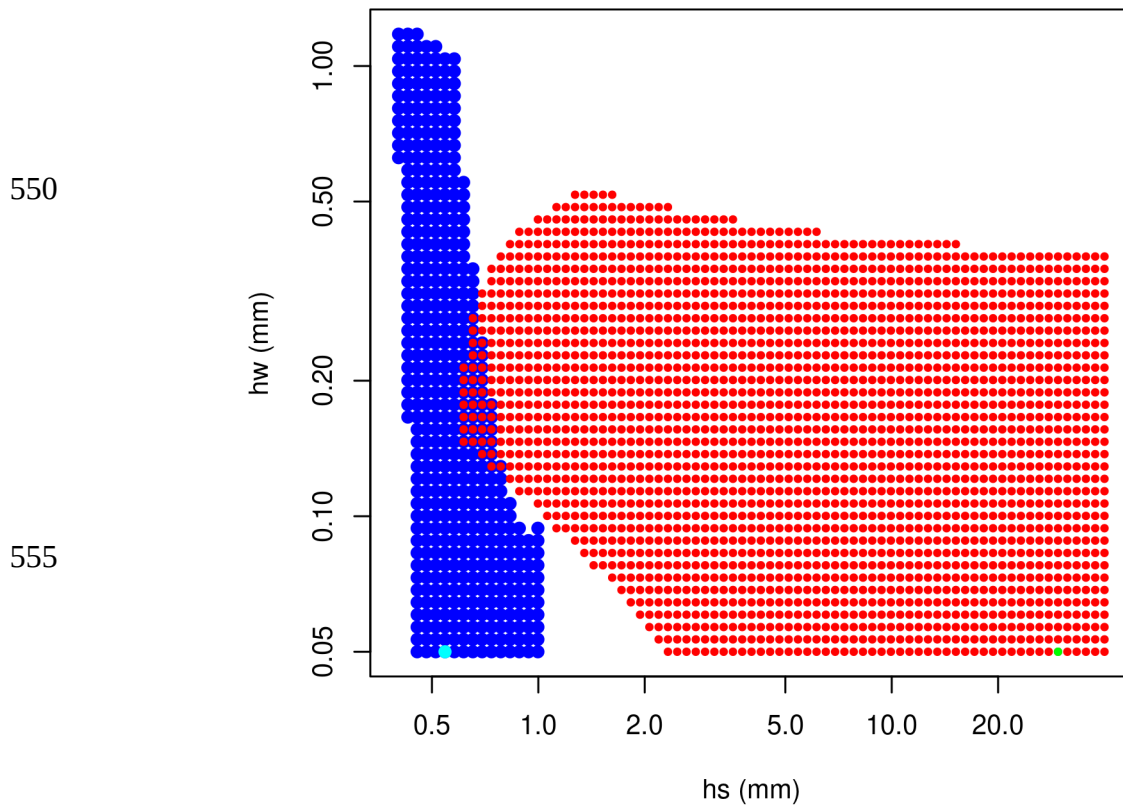
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The exploration of the parameter space for simulating the diflufenican and diuron chemograms for Ditch A shows that several pairs of h_w and h_s values result in simulations that meet acceptable goodness-of-fit criteria (eq. 31) (Fig. 3, Table 3, Supplementary Material S5). For h_w , only values lower than 1.18 mm showed acceptable performances for both compounds. This finding confirms the necessity of considering the water column to be multilayered in the ditch. For h_s , the situation differs depending on the compound. For diflufenican, the acceptable h_s values cover most of the values explored, except for the smallest values below 0.61 mm, whereas for diuron, they are limited to a narrow range between 0.4 and 1 mm. However, as seen in Figure 3, there is a small area of overlap of h_w values between 0.13 and 0.28 mm and of h_s values between 0.61 and 0.78 mm that allow an acceptable fit of the two chemograms in Ditch A. It includes 35 pairs of h_w and h_s values.

The ranges of variation in the goodness of fit indicators calculated for the 35 common pairs of h_s and h_w values are reported in Table 3, and the 35 simulations of diflufenican and diuron chemograms in Ditch A are plotted in Figure 2. Both chemograms are well simulated with respect to the timing and level of peak concentrations for all 35 pairs of h_s and h_w values. The simulated concentrations during flow recession are slightly larger than the measured concentrations, probably due to overestimation of desorption by the model. For diuron, there is a small underestimation of the peak concentration of the same order of magnitude as that for bromide.

The 35 pairs of h_s and h_w values selected for Ditch A also provide a good simulation of the diuron and diflufenican chemograms in Ditch B (Figure 2 and Table 3 for the goodness-of-fit indicators).

545 The Nash values always exceed 0.97, and compound concentration kinetics are well reproduced.



560 *Figure 3: Pairs of h_s and h_w values yielding acceptable goodness-of-fit criteria for diflufenican (in red, with the best pair in green) and for diuron (in blue, with the best pair in cyan). Pairs of h_s and h_w values leading to unacceptable goodness-of-fit criteria are not plotted here.*

565 *4.2. Analysis of the sensitivity of PITCH to the contaminated event characteristics and, to ditch and pesticide properties*

For both flood events, the Morris analysis showed that the simulation of pollution mitigation by the model was mainly sensitive to five parameters out of the ten studied. Two correspond to compound properties, namely, the sorption capacities for the soil and litter materials (Kd_{soil} , Kd_{lit} , respectively), and three correspond to ditch properties that may be affected by management operations, namely, the soil infiltration capacity Ks , the ditch cover rate by litter r_{lit} and the ditch width w (see the results of the Morris analysis in Supplementary Material S4, Figure S4). The other five parameters had

little influence on the model output dispersion. The absence of influence of vegetation parameters, cover rate r_{LV} and sorption coefficient Kd_{LV} can be explained primarily by both the small biomass of living vegetation compared to the soil masses involved in the adsorption process (maximum biomass of 0.183 kg.m⁻³ for living vegetation and a minimum of 1.04 kg.m⁻³ for soil) and the higher maximal sorption coefficient for litter than for living vegetation, despite their similar masses. Additionally, saturated soil water content did not exhibit any influence on any of the three output indicators, which may be related to the fact that the proportion of soil water with respect to the total water volume of the wetted zone is too small to influence the sorption equilibrium. Additionally, the slope, S , which influences the duration of floods, did not appear to be an important parameter, probably because the sensitivity analysis only considered a moderate range of slope values. Finally, the mitigation indicators were not sensitive to the initial mass entering the ditch, controlled here by the initial concentration, C_{ini} . This result can be explained by the linearity of the sorption model used in PITCH. Thus, the equilibrium calculated by PITCH is much more sensitive to factors defining the total effective mass of sorbent involved than to the mass of pesticide at equilibrium or the duration of that equilibrium.

The Sobol indices calculated during the second step of the sensitivity analysis focusing on the 5 parameters identified by Morris as influent were similar for both floods. Thus, only flood 1 indices are plotted in Figure 4 (see Figure S6 for flood 2). Two main elements arise from this sensitivity analysis. The first is that the interactions between parameters, as reflected by the difference between first-order and total indices, were weak to moderate for most of the parameters and for $Removal_{surf}$ and $Storage$. Consequently, the effects of these parameters on the latter two mitigation indicators can be analyzed independently, but their effects on $Risk_{GW}$ cannot. The second is that the variability in the mitigation indicators is more related to the sorption properties of the compounds than to the properties that can be controlled by management, except for $Risk_{GW}$, which is very sensitive to the hydraulic conductivity at saturation. This reflects the impossibility of defining a single generic

management method that can limit water contamination by pesticides, whatever the properties of the involved compounds.

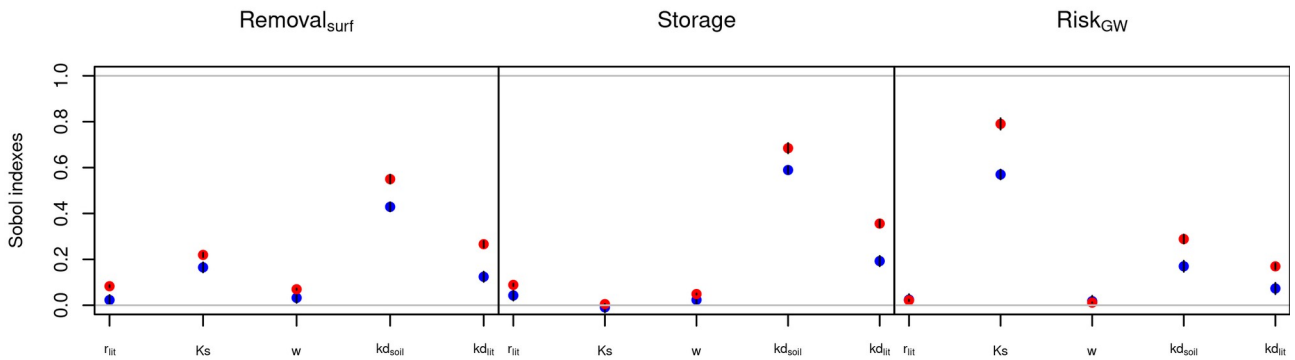


Figure 4: First-order and total Sobol indices (blue and red, respectively) for the three mitigation indicators calculated for flood 1 and for the following parameters: litter cover rate (r_{lit}), saturated soil hydraulic conductivity (K_s), ditch width (w), and the sorption coefficients of the soil (Kd_{soil}) and the litter (Kd_{lit}).

4.3. Factors of variation of mitigation by ditches

The set of simulations was used to explore a very wide range of mitigation rates (Figure 5). Indeed, $Removal_{surf}$ ranged from 3 to 100%, which complies with retention ranges reported in the literature (Dollinger et al., 2015), while $Risk_{GW}$ ranged from nearly 0 to 74%. The variations in the three mitigation indicators relative to those in the 5 most influent parameters were logical, demonstrating the good behavior of the model. Figure 5 also shows that flood intensity impacts the mitigation rate but not the patterns of variation in the indicators. For all parameters and class values, $Storage$ and $Removal_{surf}$ had higher median values and spreads for the small flood (flood 2) than for the large flood (flood 1), whereas $Risk_{GW}$ exhibited lower median values but a larger spread for the small flood than for the large one. This trend may be explained by a greater proportion of the flood volume interacting with the sorbent material due to the low water heights but also a greater proportion of flood water infiltration.

615 The analysis of the histograms specifies the sensitivity expressed by the Sobol indicators for the sorption parameters and reveals the modulation of the mitigation indicators by the parameters potentially affected by management operations. The median values of $Removal_{surf}$ and $Storage$ increase strongly with that of Kd_{soil} and to a lesser extent with Kd_{lit} . Conversely, the median value and dispersion of $Risk_{GW}$ decrease with increasing Kd_{soil} and to a lesser extent with Kd_{lit} . The
620 parameters potentially affected by management also exhibit a marked influence on mitigation indicators. The median $Removal_{surf}$ values increase for flood 1 and flood 2, respectively, by 13 and 24% with changes in the width of the reach w , by 19 and 21% with changes in the hydraulic conductivity at saturation Ks and by 11 and 21 with changes in the litter cover rate, r_{lit} . $Storage$ evolves in a similar fashion as $Removal_{surf}$ in response to changes in r_{lit} and w but is, logically,
625 unaffected by changes in Ks . However, $Risk_{GW}$ evolves only with Ks , going from no risk to a median risk higher than 12% for the highest Ks values and occasionally reaching almost 75%. The increase in the mass of sorbent materials with changes in w and r_{lit} induces changes in the sorption capacities and thus in $Removal_{surf}$ and $Storage$. The increase in the infiltrated volume with Ks logically induces changes in $Risk_{GW}$ but also in $Removal_{surf}$ by limitation of the contaminated water
630 volumes reaching the outlet. It can also be noted that the increase in w does not lead to an increase in the infiltration surface that is sufficient to influence $Risk_{GW}$. At equivalent flow, the widening of the ditch is in fact also associated with a decrease in the water level and in turn a transfer of the infiltration surface from the banks to the ditch bed.

The similarity of the trends of $Removal_{surf}$ and $Storage$ and the overall lower values of the $Risk_{GW}$
635 indicator (3rd quantile less than 10%) show that surface retention is mainly due to adsorption processes, which is generally accepted (Dollinger et al., 2015). However, the $Risk_{GW}$ indicator reaching values occasionally as high as 75% for high Ks values shows that infiltration can contribute significantly to surface removal and, in turn, to soil and groundwater contamination.

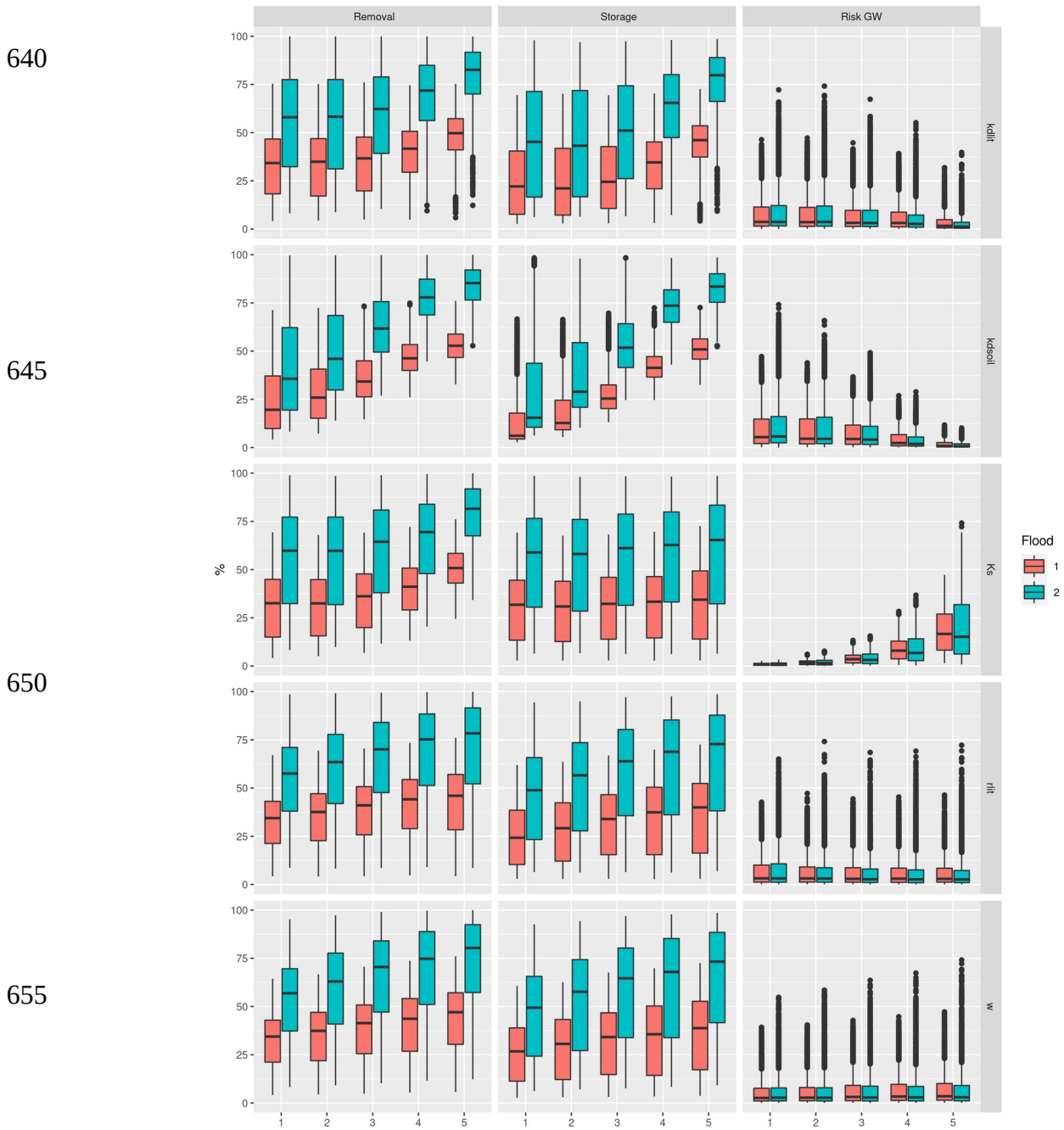


Figure 5: Evolution of the three mitigation indicators (in column) with sensitive physical parameters (in lines) for floods 1 (red) and 2 (green). For each plot, the x-axis marks the 5 parameter classes. Thus,

660 boxplots discriminate the simulation results by classes of parameters. Bounds of the classes are $[1e-3, 3.5e-3, 1.2e-2, 4.2e-2, 1.4e-1, 0.5]$ for Kd_{soil} (m^3/kg); $[1e-3, 6.3e-3, 4.0e-2, 0.25, 1.6, 10]$ for Kd_{lit} (m^3/kg); $[1e-7, 2.5e-7, 6.3e-7, 1.6e-6, 4.0e-6, 1.0e-5]$ for Ks (m/s); $[0, 0.2, 0.4, 0.6, 0.8, 1]$ for r_{lit} (-); and $[0.25, 0.4, 0.55, 0.7, 0.85, 1.0]$ for w (m).

665 5. Discussion

5.1 Ability of PITCH to reproduce pesticide transfer within ditches.

The ability of PITCH to simulate pesticide transfer in ditches during flood events is evidenced by the high values of the goodness-of-fit criteria for both the calibration and validation phases. PITCH
670 was able to simulate the magnitude, spread and lag time of the chemograms of two pesticide compounds with contrasting properties. To our knowledge, this is the first time that a model simulating the fate of pesticides in ditches was evaluated with chemograms measured in flowing ditches and therefore leading to an model evaluation accounting for peak concentrations and mass exports. Moreover, the few simulated cases for which infiltration contributes significantly to surface
675 removal and, reciprocally, to soil and groundwater contamination, demonstrate the interest in simulating infiltration in ditches, as enabled by PITCH, to evaluate mitigation.

Despite the contrasting chemical profiles of the two pesticides, diuron and diflufenican, monitored in the experiments, it was possible to identify several pairs of h_s and h_w values that enable PITCH to reproduce the transfer of both compounds. All pairs are within a very narrow window in the (h_s, h_w)
680 space which allows discussion of the simulation of reactive transfer of pesticides under fast flow conditions.

The first discussion point is the possibility of macroscopically representing the exchanges between water and sorbent materials with a uniform mixing zone concept close to that used to approximate pesticide remobilization by field runoff (Yound and Fryer, 2019). It however implies the assumption
685 that only a small portion of the water column interacts with the sorbent materials. In fact, none of the pairs of h_s and h_w values with h_w taken equal to the whole water column height allowed the model to reproduce the chemograms. In contrast, the calibrated h_w values are very low, between 0.13 and 0.28 mm, which means that less than 2% of the volume of outflowing water was in equilibrium with the ditch bed and banks during a time step. This result is in line with those of

690 Southwick et al. (2003) and Young and Fry (2019), who showed a better reproduction of pesticide export in field runoff considering an incomplete mixing model, i.e., only a fraction of the runoff water interacts with the soil. In the case of field runoff, Young and Fry (2019) found that less than 20% of total runoff interacts with the top 7.5 mm of soil. The second point is the small thickness of the soil mixing layer. Indeed, the adjusted h_s values, between 0.61 and 0.78 mm, are much lower
695 than the 2 cm recommended in some models to calculate the equilibrium in the hydrographic network (Renaud et al., 2008; Rouzies et al., 2019). They are, however, on the same order of magnitude as the one adjusted (1 mm) by Villamizar and Brown (2017) for a watershed-scale application to obtain concentrations at an acceptable order of magnitude. We notice that the thickness of the soil mixing layer is of the same order of magnitude as the theoretical distance
700 covered by a pesticide compound by diffusion over the considered time step (0.3 mm, Appendix B), although the values are higher, despite the use of the equilibrium value K_d . This thickness could reflect faster exchanges than those allowed by diffusion induced by the rapidity of surface flows, similar to those induced by raindrops for runoff (Zhang et al., 1997).

The thickness of soil over which pesticides are likely to be remobilized by field runoff has already
705 been questioned. Indeed, while considering the homogeneity of the mixing zone, Steenhuis and Walter (1980) suggest a dependence on the soil sorption coefficient and define it from site-specific parameters that relate cumulative rainfall and runoff concentrations. Mixing layer thicknesses calculated in this way vary from 0.6 to 10 mm depending on the compound, the soil and the soil surface conditions (e.g., Steenhuis and Walter, 1980; Zhang et al., 1997; Lecomte et al., 2001).
710 Other authors have moved away from the homogeneous mixing zone concept and proposed a decreasing contribution with depth (Ahuja et al., 2000, Young and Fry, 2019). The dependence of the mixing zone thickness on the sorption coefficient could explain the difference in the h_s range of acceptable parameterizations for diuron and diflufenican.

Obtaining an acceptable common parameterization for two compounds and two flow conditions is
715 very encouraging. However, it does not guarantee that it can be generalized to all types of pesticides
or ditches given the limitations discussed above. Moreover, the parametrization was carried out with
the equilibrium sorption coefficients, whereas given the contact times and the rather slow kinetics,
at least for diuron, the equilibrium may not have been reached, as highlighted by Nkedi-Kizza et al.
(2006) and Fernandez-Bayo et al. (2008). Using a multimedia fugacity model that also assumes
720 sorption equilibrium, Otto et al. (2016) interpreted the discrepancy between measured and simulated
concentration reduction in a ditch as a failure to achieve sorption equilibrium. In our case, it is
possible that the adjustment of the two parameters h_s and h_w compensated for the error introduced
by not considering sorption kinetics. The dependence of both the kinetics and the intensity of
adsorption on the stirring conditions and the solid:liquid ratio evidenced from laboratory conditions
725 (Gauillier et al., 2018) suggests that the intensity of exchange between sorbent materials and water
may vary depending on the flow conditions. This reinforces the risk of not being able to easily
generalize the parameterization. However, this risk is common to all transfer models. Therefore, it is
necessary to conduct more experiments with a wider range of compounds and flow conditions to
validate the transfer models more thoroughly. The complementary nature of the three evaluation
730 criteria used in this study highlights the need for detailed chemograms rather than maximum
concentrations for appropriate model parameterization and evaluation (see Supplementary materia
S5).

5.2. Ability of PITCH to assess the effect of ditch management operations on pesticide mitigation

735 An analysis of the model behaviour when predicting pollution mitigation of a ditch provides
insights into both the use of the model and the directions to be explored to improve its pesticide
mitigation potential.

The ability of PITCH to be used to predict the effect of ditch management operations on pesticide pollution mitigation is evidenced first by its validation on experimental datasets in ditches with litter
740 and living vegetation, second by its ability to reproduce the wide range of ditch surface removal reported by Dollinger et al. (2015) due to its sensitivity to key parameters, and third by the facility to parameterize the changes in ditch properties induced by the management operations.

The parameters chosen to describe the ditches can be easily obtained from direct observations or measurements of the ditches (cover rate and thickness or height of litter and live vegetation, ditch
745 width), measured (porosity and vegetation density) in the laboratory with simple protocols (Dollinger et al., 2016) or by photointerpretation (Vinatier et al. 2018). These a priori low-precision estimation methods were sufficient to correctly parameterize PITCH to reproduce the transfers of two molecules with contrasting properties over two ditches with slightly different cover rates. Other model parameters describing the ditch (slope, hydraulic conductivity at saturation) or the molecules
750 (sorption coefficients) are common to other transfer models.

Sensitivity of the model to compounds properties and ditch properties is a prerequisite to predict mitigation change with ditch management operations. The sensitivity analysis shows that this prediction is largely dependent on a good knowledge of the sorption properties of the compounds, with soil and litter sorption coefficients explaining at least 55% of the surface retention and more
755 than 75% considering interactions with the ditch property parameters. The sorption coefficient of living vegetation did not appear to influence the retention indicators calculated with PITCH, whereas it did for TOXSWA (Westein et al., 1998). In contrast, the sorption coefficient on soil largely influenced the retention indicators calculated with PITCH but not those calculated with TOXSWA. These apparent discrepancies can be explained by the different exploration conditions of
760 the two models, particularly the significantly different masses of soil and living vegetation on which the pesticides were likely to sorb. The exploration of PITCH behaviour focused on a Mediterranean-type ditch developed on an undisturbed soil (bulk density of 1500 kg.m^{-3}) with

distinct litter biomass and living vegetation, with the latter varying in a range from 0 to 183 g.m⁻³, as observed in Dollinger et al., (2016). TOXSWA's exploration focused on a Dutch, heavily
765 vegetated (300 g.m⁻³) drainage ditch type with a bed formed by the accumulation of very low-density sediments (80 kg.m⁻³). Finally, the sensitivity analyses of both PITCH and TOXSWA reach similar conclusions regarding the very strong dependence of reactive transfer on the sorption properties of the compounds. As already highlighted in this paper and by Adriaanse et al. (2022), databases of compound properties including the ability of compounds to sorb on a wide range of
770 materials are thus needed to predict mitigation.

Surface retention of pesticides in ditches during flood events has been shown in this study to be sensitive to the mass (at least with w and r_{lit}) and sorptive capacity of the sorbent materials as well as the infiltration capacity of the ditches, which is consistent with the literature. The surface retention was not sensitive to the slope and in turn to the duration of contact between the pesticides
775 and these materials, which was previously identified as a key factor in vegetated treatment systems and ditches (e.g., Stehe et al., 2011, Bundschuh et al., 2016, Otto et al., 2016, Adriaanse et al., 2022). However, those studies analysed the effect on a per compound basis (e.g., Bundschuh et al., 2016), whereas our numerical exploration encompassed a broad spectrum of compounds by considering a wide range of sorption properties. Moreover, the situations explored in this paper
780 correspond to short floods and therefore do not allow for significant variation in hydraulic retention time. The assumption of equilibrium to calculate the sorption exchanges between water and different materials may also lead to an underestimation of the effect of hydraulic retention time on mitigation.

Our study thus highlights that although the sorption properties generally control the order of
785 magnitude of the contamination, management operations can be implemented to modulate it. Finally, further sensitivity analyses specific to the type of flow condition and to the compound need

to be performed to quantify the added retention achievable by ditch management and assess the stability of the hierarchy of influential parameters.

5.3. *Effect of ditch management operations on pesticide mitigation*

790 Despite the above-cited restriction, our simulations show that two types of management levers may improve the mitigation capacity for most compounds. The first type of lever concerns the composition of the ditches and the management practices that regulate this composition. Promoting the emergence of vegetated ditches and controlling the dynamics of vegetation may indeed be favourable to surface removal. Indeed, vegetation destruction practices, such as mowing or burning,
795 increase the mass of litter and in turn improve surface removal, at least for hydrophobic compounds, as already discussed by Dollinger et al. (2016, 2017). Moreover, another positive effect of revegetation would be the increase in soil infiltrability due to the creation of macroposity in connection with root development (e.g., Gould et al. 2016) or with more abundant soil mesofauna in vegetated soils (Herzon and Helenius, 2008). However, increasing infiltrability needs to be carefully
800 considered according to environmental conditions since it is beneficial in limiting the contamination of surface water bodies, but in turn it increases the risk of groundwater contamination. A second type of lever concerns the geometry of the ditch, in particular its width, and should be implemented when the network is created or dredged. The contact surface with the soil, for a given water volume but also potentially the vegetative biomass, increases with width. However, these two levers must
805 be evaluated according to the agricultural context. When they are at the edge of a plot, ditches overlap with the cultivated area, and farmers try to minimize their footprint. Increasing ditch width may therefore not be acceptable by farmers. In the same way, increasing the vegetation density in all or part of a ditch network may be seen, in some contexts like in Mediterranean areas, as contrary to the primary purpose of the ditches, which were built to evacuate floods. Indeed, the increase in
810 roughness due to vegetation increases the risk of overflowing (Dollinger et al., 2017). The

integration of PITCH in a hydrological model would allow to evaluate these controls in terms of both contamination mitigation and flood prevention.

6- Concluding remarks

815 The purpose of this study was to present and evaluate PITCH, a new mechanistic model simulating pesticide transfer in ditch networks at the flood event time scale. Compared to other models, it is adapted to infiltrating ditches and rapid and transient flows and simulates transfers at the tree-like network scale with a reach resolution. PITCH was validated with experimental chemograms of two compounds with contrasting properties, diuron and diflufenican, and for vegetated ditches with
820 litter. None of the parameterizations corresponding to an exchange of the entire water column with the ditch materials yields a good reproduction of the chemogram. The numerical exploration of PITCH demonstrates both its consistent behaviour in predicting pesticide mitigation and its ability for deployment to evaluate ditch management modalities.

The pesticide mitigation potential of ditches is highly variable, ranging from null to extremely high.

825 Favouring wide vegetated ditches and adopting a vegetation control method that enriches the ditch bottom with litter and favours infiltration would improve the mitigation of pesticide pollution, at least for hydrophobic compounds.

PITCH was designed for easy completion. The next steps will be an extension from a flood event model to a continuous model and its integration in a watershed hydrological model. This step
830 requires integrating new processes, such as degradation. To extend its application domain to semiarid contexts where flows are strongly intermittent, it is envisaged to integrate a potential infiltration model that varies according to the initial humidity conditions.

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