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# Performance of a pesticide fate model for predicting multi-year surface runoff contamination in a Mediterranean vineyard

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25 **Abstract**

Characterization of the risk of water contamination by pesticide runoff is an essential issue in the assessment of the environmental impact of pesticide use in agriculture. Models are valuable tools for this purpose. However, the use of pesticide runoff models implies that they can simulate the intra- and interannual variations in runoff contamination with a sufficient accuracy. In this study, we aimed to assess the performance of a modelling approach coupling Richards and convection-dispersion equations with the uniform mixing cell concept and an overland flow routine to predict the between- and within-year variability of the pesticide concentration in runoff water at the outlet of an agricultural field within a Mediterranean context. The model performance was evaluated by calibrating and validating model predictions to observed concentrations of two herbicides, diuron and glyphosate. The temporal structure of the model performance was analysed over 10 and 9 years for diuron and glyphosate, respectively. The results showed a favourable average model performance for runoff pesticide concentration prediction over approximately ten years. However, the annual performance largely varied, suggesting that at least 3 years of data are required to obtain reasonably precise runoff pesticides estimates in terms of the Nash-Sutcliffe efficiency in a Mediterranean climate. Although limited differences in the prediction performance were found between the two compounds, the within-year fluctuation of the predictions was more accurate for glyphosate than for diuron. This is interpreted by ageing effects that affect diuron sorption but not glyphosate sorption. Furthermore, the study results indicated that the parameters critical to precise

estimation depend on the simulation objectives. The main parameter values to be determined include the pesticide half-life time when estimating chronic exposure to pesticide runoff and the sorption coefficient and mixing depth when predicting the maximum observed concentration during a given season.

**Keywords:** Mhydas-Pesticide, Diuron, Glyphosate, Ageing, Calibration, Validation

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## 60 **Highlights**

- Few long term evaluations of pesticide runoff models are available at field scale.
- A model coupling Richards and convection-dispersion with a runoff mixing cell was tested.
- 19-year predictions and observations of herbicides in field runoff compared well.
- Predicted within-year fluctuations were more accurate for glyphosate than for diuron.

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- Estimating accurately model performance requires more than 3 years of evaluation.

## 1. Introduction

Pesticides are widely used in agriculture. Nearly 2 million tons is consumed per year worldwide (Sharma et al., 2019). Their application leads to widespread contamination of different environmental compartments, including surface waters. In France, at least one pesticide compound was measured at 93% of surface water monitoring points in 2021 (Eaufrance, 2023). Runoff is considered a major pathway of surface water contamination [e.g., Wauchope et al. (1995), Louchart et al. (2001) and Reichenberger et al. (2007)], influenced by many factors that vary in space and time (Shipitalo and Owens, 2003; Calvet et al., 2005), such as the type of compound, topography, date and modality of application, climate, soil, and agricultural practices (e.g., tillage). The characterization of the risks of water contamination by pesticide runoff is thus an essential issue in the assessment of the environmental impact of pesticide use in agriculture. In situ monitoring approaches can only be employed in a limited number of situations due to their cost and difficulty of implementation. Mathematical modelling represents a valuable alternative (Ma et al., 2001; Shrestha and Manandhar, 2014) to characterize the risks of contamination under variable conditions. Models can thus be used to assess environmental exposure to pesticides in waters as part of regulatory assessment of the environmental risk resulting from the use of pesticide substances at the European scale (FOCUS, 2001; Boivin and Poulsen, 2017). They can also be employed to assess the risks of contamination of water due to agricultural practices (Zhang and Zhang, 2011, Baffaut et al., 2019, Oh et al., 2021) or to predict the evolution of these risks under changing climatic conditions [e.g., Gagnon et al. (2015)]. In these applications, the variation in the concentration in runoff water has often been simulated over a large number of years to account for climate variability, thereby estimating mean or maximum time-weighted average pesticide concentrations or pesticide mass losses by runoff. This suggests that pesticide runoff

models can simulate the intra- and interannual variations in runoff concentrations and losses with a sufficient accuracy.

100 Pesticide fate and transport models currently applied in pollution risk assessment can be divided broadly into two main categories (Siimes and Kämäri, 2003) according to the description of soil moisture and water transport in soil: (a) capacity models [e.g., the pesticide root zone model (PRZM)—Carsel et al. (1985); Groundwater Loading Effects of Agricultural Management Systems (GLEAMS)—Leonard et al. (1987);  
105 Agricultural Policy/Environmental eXtender (APEX)—Williams et al. (2006); and dynamic agricultural non-point source assessment tool (DANSAT)—Cho et al. (2007)] and (b) models using the Richards' equation [e.g., the root zone water quality model (RZWQM)—Hanson et al. (1998); MACRO—Larsbo et al. (2005); and Pesticide Emission Assessment at Regional and Local scales (PEARL)—Van den Berg et al. (2016)].  
110 Capacity models mainly estimate surface runoff, at a daily time step by applying the empirical Soil Conservation Service (SCS)-curve-number method (e.g., GLEAMS, APEX, and PRZM) whereas Richards based models may estimate surface runoff at sub-daily variable time steps by applying the soil infiltration excess approach (e.g., MACRO, PEARL, and RZWQM) followed by an overland flow description. For simulating pesticide  
115 transport, convection is represented by all models with diffusion whereas hydraulic dispersion is generally only represented by Richards type models (Siimes and Kämäri, 2003). Pesticide losses into surface waters are generally calculated in both model types based on the mixing cell concept, in which rainwater mixes uniformly or variably over a specific depth, and chemical equilibrium is assumed between the water and  
120 solid phases (e.g., GLEAMS, APEX, and DANSAT). Moreover, all models represent sorption and degradation processes in the soil, most often assuming linear or Freundlich partition coefficient and first-order kinetics, respectively.

The accuracy of surface runoff models in the prediction of pesticide transport by runoff has been demonstrated at the laboratory scale and through modelling exercises, but their performance in practical applications, such as at the field scale, is less clear (Young and Fry, 2019). The available plot-scale performance tests aiming to continuously reproduce the temporal dynamics of pesticide runoff contamination under actual rainfall conditions are relatively limited. We identified performance tests of the following models: APEX, DANSAT, GLEAMS, PRZM and RZWQM. These tests are most often based on simulations lasting between one and three cropping seasons (Leonard et al., 1987; Ma et al. 1995; Ghidey et al. 1999; Malone et al. 1999; Connolly et al. 2001; Malone et al. 2004; Miao et al. 2004; Cho and Mostaghimi 2009; Mudgal et al. 2010; Chen et al. 2017; Baffaut et al. 2019). Only Chinkuyu et al. (2005) and Plotkin et al. (2013) performed model evaluations over longer time periods, at 5 and 8 years, respectively. The results shown are remarkably diverse with respect to both the performance criteria used and the performance observed. Concerning the performance criteria adopted, models have been most often evaluated in terms of their ability to reproduce daily exported masses (Ma et al., 1995; Connolly et al., 2001, Chinkuyu et al., 2005; Cho et al., 2009; Mudgal et al., 2010; Chen et al., 2017; Baffaut et al., 2019) or daily concentrations (Ghidey et al., 1999; Malone et al., 1999; Malone et al., 2004; Miao et al., 2004; Chinkuyu et al., 2005). The main performance statistics computed include Pearson's correlation coefficient ( $r$ ) and its related coefficient of determination ( $R^2$ ), Nash-Sutcliffe efficiency (NSE) and percent bias (PBIAS), but only the two latter were recommended by Moriasi et al. (2007) for use in watershed model evaluation. Concerning the performance observed,  $R^2$ , NSE and absolute PBIAS for mass loss predictions varied between 0.001 and 0.99, between -8.74 and 0.96 and between 4 and 98.4%, respectively, whereas  $R^2$  and NSE for concentration predictions varied between 0.001 and 0.94 and between -4.98 and 0.8, respectively (Fig. S1).

According to the performance ratings proposed by Moriasi et al. (2015), the previously  
150 observed performance statistics ranged from unsatisfactory to very good, indicating  
that the accuracy of pesticide runoff models remains highly uncertain even under  
calibration. This applies not only to mass loss predictions but also to concentration  
predictions in surface runoff water, as a worst-case proxy for the concentration in  
surface waters. Surface runoff concentrations are essential to regulatory exposure risk  
155 assessment (FOCUS, 2015). Given the variations in the testing setups, the number of  
model evaluations is insufficient to allow the determination of possible differences in  
performance between the models applied. Indeed, the performance is intrinsically  
variable due to the large range of uncertainty sources in pesticide fate modelling,  
including the modeller's subjectivity [please refer to the review by Dubus et al.  
160 (2003)]. However, we hypothesize that too-short evaluation periods with respect to  
the natural temporal variation in pesticide transfer conditions inhibit comprehensive  
examination of the prediction performance of a given pesticide runoff model, which  
partly explains the high variation in the observed performance statistics.

Thus, the main aim of the present work was to evaluate the performance of a model  
165 coupling Richards' and convection-dispersion equations with the uniform mixing cell  
concept and an overland flow routine to predict the between- and within-year  
variability of the pesticide concentration in runoff in an agricultural plot. Such a model  
is implemented in MHYDAS-Pesticide 1.0, a physically based hydrological model.  
MHYDAS-Pesticide was applied to a Mediterranean vineyard plot where the pesticide  
170 concentrations in surface runoff water were monitored from 1995 to 2014. After  
calibration, the model prediction performance was evaluated by comparison with the  
observed concentrations outside the calibration years of two herbicides, namely  
diuron [N'-(3,4-dichlorophenyl)-N,N-dimethylurea] and glyphosate N-  
(phosphonomethyl)glycin from 1994 to 2014. The specific objectives were (i) to

175 estimate the number of years of data acquisition required to determine the average  
model prediction performance with reasonable accuracy, ii) to identify potential  
patterns of the temporal change in the prediction performance and iii) to analyse the  
influence of model parameters according to the modelling objectives.

## 2. Materials and methods

### 180 2.1. Site description and field measurements

#### 2.1.1. *Field site and studied compounds*

The field site is located in the Roujan experimental catchment (Herault, 60 km west of  
Montpellier, 43°30'N, 3°19'E), which belongs to the Mediterranean Observatory of the  
Rural Environment and Water (Observatoire Méditerranéen de l'Environnement Rural  
185 et de l'Eau or OMERE) observatory (Molénat et al., 2018). The climate is a subhumid  
Mediterranean climate with a prolonged dry season in summer and precipitation, often  
stormy, mainly occurring in spring and autumn. The average annual rainfall over the  
09/1994 to 09/2014 period was 659 mm, which is also marked by high interannual  
variations (from 414 to 1377 mm) and high intra-annual variations (the rainfall from  
190 June to August equals the average rainfall in October, which is the rainiest month). The  
rainfall intensity can be very high (with a maximum intensity over 5 min close to 240  
mm.h<sup>-1</sup>), resulting in dominant Hortonian runoff processes.

The study field is a 1200 m<sup>2</sup> area entirely planted with vines. Its slope varies between  
7% and 15% (Chahinian et al., 2005). The field is hydrologically isolated from its  
195 neighbouring plots via a girdling ditch. The substratum belongs to the Miocene marine  
deposits. The soil is a calcareous cambisol (IUSS-WRB, 2014). The main properties of the  
0-5 cm layer are a bulk density of 1.44 g.cm<sup>-3</sup>, a pH measured in water of 8.5, a soil  
organic carbon content of 1.06%, a CaCO<sub>3</sub> content of 24% and a silty sand texture  
[18.6% clay (0-2 µm), 55.4% silt (2-50 µm) and 26% sand (50-2000 µm)].

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200 The entire surface area of the field was chemically treated with herbicides currently or  
formerly used in viticulture, namely, with diuron, a preemergence herbicide, between  
1995 and 2008, and with glyphosate, a postemergence herbicide, between 2001 and  
2013. Frequently found in surface water monitoring networks, diuron was banned in  
France in 2008. The diuron and glyphosate doses applied, as estimated from farmers'  
205 statements or our measurements prior to spraying, varied between 1 and 2.3 kg.ha<sup>-1</sup>  
and between 2 and 2.7 kg.ha<sup>-1</sup>, respectively [Fig. 1(c)]. Diuron is a moderately  
hydrophobic and moderately water-soluble compound (35.6 mg.L<sup>-1</sup> according to the  
Pesticide Properties DataBase (PPDB) [PPDB, 2022]), while glyphosate is a strongly  
hydrophilic and highly water-soluble compound (100000 mg.L<sup>-1</sup>; PPDB, 2022). The  
210 values of the sorption coefficient ( $K_f$ ) and the Freundlich sorption parameter  $1/n$  range  
respectively from 4.48 to 15.52 L.kg<sup>-1</sup> and 0.67 to 0.89 for diuron, and from 18.1 and  
166.4 L.kg<sup>-1</sup> and 0.54 to 0.78 for glyphosate (PPDB, 2022). Diuron shows a strong  
seasonal increasing trend in sorption (Louchart et al., 2007) due to the ageing  
phenomenon, while glyphosate experiences sorption evolution only within a few days  
215 after application (Padilla and Selim, 2019).

### *2.1.2. Field measurements*

The meteorological and hydrological monitoring protocols are part of the duties of the  
OMERE observatory, which have been presented in detail by Molénat et al. (2018).

#### ● *Meteorological and surface runoff data*

220 The reference crop evapotranspiration (ET<sub>0</sub>) was estimated at hourly time steps  
according to the method proposed by Allen et al. (1998) from standardized  
measurements of the air temperature, relative humidity, global radiation and wind  
speed across the catchment area. The measurements were automatically collected by  
a meteorological station (ENERCO 400 before July 2007 and ENERCO 516i afterwards;

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225 both CIMEL, Paris, France). Rainfall was measured by a tipping bucket rain gauge  
(model 91 SERPE-TESM, Rennes, France) with a 0.5-mm capacity located at the field  
outlet. Runoff was monitored at the field outlet with a Venturi flume (Techniflow,  
Echirolles, France) coupled with a capacitive water level sensor (model CCI, SERPE-  
TESM, Rennes, France), which was also installed at the outlet. Between April 1995 and  
230 March 2014, 863 rainfall events and 638 runoff events were observed [Fig. 1(a) and  
(b)]. A rainfall or runoff event is defined as a period during which rainfall or discharge,  
respectively, can be continuously measured. These events are highly variable in terms  
of i) their duration, ranging from 5 min to 5 days for rainfall and from 5 min to 1.5 days  
for runoff, ii) their peak flow rate, between 0.01 and 44.4 L.s<sup>-1</sup>, and iv) their runoff  
235 volume, between 1.6 and 67000 L. The average runoff coefficient is 0.26 and reaches  
0.4 for rainfall events with a rainfall height larger than 40 mm.

#### ● *Herbicide concentration in runoff*

The diuron concentration in runoff was measured over 11 years between 1995 and  
2000 and then between 2002 and 2009, whereas the glyphosate concentration was  
240 monitored over 9 years between 2002 and 2005 and then between 2008 and 2014.  
Water was sampled via two automatic samplers (Sigma Model 800SL; American  
Sigma, Medina NY) with a capacity of 24 samples of 330 mL, controlled in two distinct  
modes. In one mode, sampling was triggered by water level variations in the Venturi  
flume. In the other mode, samples were collected at regular time intervals of 20 min.  
245 This system makes it possible to record runoff rise, peak and decrease and ensures  
regular sampling throughout the entire runoff duration as much as possible. Until the  
end of 2000, each sample was individually analysed, and then, since 2001, individual  
samples were accumulated in the same container for each runoff event. Samples,  
whether individual or cumulative, were collected within approximately 24 hours of the  
250 end of the sampling period and then stored at less than 4°C before analysis by a

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specialised laboratory. For diuron, concentrations were determined by high performance liquid chromatography (HPLC) separation and diodes bar ultraviolet detection before 2006 and by HPLC and mass spectrometric detection afterwards. For glyphosate, concentrations were determined using derivatization prior to gas chromatography and mass spectrometric detection before 2006 and prior to liquid chromatography and mass spectrometric detection afterwards. Regarding runoff events with several samples, the average runoff concentration was estimated by weighting the concentration measured for each sample by the water volume during the sampling time.

A total of 79 average runoff event concentrations were obtained for glyphosate, and 132 event concentrations were obtained for diuron. The flux-weighted average runoff event concentrations of glyphosate and diuron varied by several orders of magnitude during the monitoring period, namely, between 0.2 and 120  $\mu\text{g.L}^{-1}$  and between 0.1 and 702  $\mu\text{g.L}^{-1}$ , respectively [Fig. 1(d)]. The highest concentration values were observed during the first rainfall events following pesticide application.

## **2.2. Model description**

MHYDAS-Pesticide-1.0 is a fully distributed mechanistic model that can simulate the hydrological fate of a pesticide compound in a heterogeneous cultivated landscape (Crevoisier et al., 2021). In this study, MHYDAS-Pesticide-1.0 was applied at the scale of the agricultural field described in section 2.1.1. A homogeneous field was assumed. A brief description of the numerical representation of the main physico-chemical processes assessed in this study is presented hereafter. A more detailed description of the processes represented by MHYDAS-Pesticide-1.0 is available in Crevoisier et al. (2021).

### *2.2.1. Hydrological processes*

The model simulates the soil water balance, soil infiltration excess and surface runoff propagation. Water movement in soil and infiltration excess are simulated by solving the Richards' equation with the Ross method (Ross, 2003, Crevoisier et al., 2009). Fluxes at the soil surface interface are controlled by a classical atmospheric condition like in other models solving Richards equation (e.g. HYDRUS, Simunek et al. 2013). This boundary condition switches from a Neumann (flux) to a Dirichlet (head) boundary condition when the climatic forcing (rainfall or potential evaporation rate) exceeds the maximum potential soil flux at the soil interface as estimated by Darcy's equation. In case of excess infiltration, ponding is assumed to occur up to a maximum height. The relationships between water content, pressure head and hydraulic conductivity are expressed by the modified Mualem-van Genuchten model (Schaap and Genuchten, 2006). Surface runoff is assumed to correspond to infiltration excess once the maximum ponding height is reached. Then surface runoff is propagated to the outlet of the field by overland flow using the diffuse wave model, a simplification of the Saint-Venant system (1871), which is solved with the Hayami method (Moussa, 1996).

### *2.2.2. Pesticide fate processes*

The main pesticide fate processes simulated involve compound reactive transfer in soil and remobilization and transport by runoff. Vertical transport in soil is represented by convection-dispersion equation. An instantaneous sorption equilibrium relationship is assumed between the liquid- and solid-phase concentrations. In this study, the relationship was represented by a linear model. Compound degradation was represented by first-order kinetics for both the solid and liquid soil phases. The degradation rate was adjusted depending on the soil water content according to Walker's equation (Walker, 1974). To calculate the concentration in runoff, uniform

and instantaneous mixing between runoff and the topsoil mixing cell was considered. The latter can contain several elements of the grid representing the soil profile.

## 2.3. Model performance evaluation

### 305 *2.3.1. Model setup and input parameters*

The soil profile was simulated to a depth of 1.2 m with free drainage as the boundary condition at the profile bottom. The profile was discretized into 39 grid elements whose vertical widths ranged from 0.001 m to 0.1 m (Table S1). Three soil layers were distinguished according to the soil surveyor description. The hydraulic properties  
310 of the two subsoil layers were estimated from measurements stored in the OMERE database (Table S1). The soil hydraulic parameters of the surface layer, namely the hydraulic conductivity ( $K_s$ ) and the ponding height, were estimated by calibration over 5 years and validated on the remaining monitoring years (see details in supplementary materials Text page S5 and Table S2). The pesticide fate parameters,  
315 namely, the sorption coefficient ( $K_D$ ), compound half-life ( $t_{1/2}$ ), exponent of Walker's function ( $b$ ) and thickness of the mixing layer ( $z_{mix}$ ), considered to be calibration parameters and were subject to the investigations described hereafter. The climatic (rainfall and reference evapotranspiration) and agronomic (applied pesticide mass per unit area) forcings were fixed using the data observed in the OMERE observatory  
320 presented in section 2.1. The applied herbicide mass was fully and uniformly incorporated into the 0.001 m top grid element of the discretized soil profile. To fix realistic initial conditions to the simulations, a warm-up period of 18 months of the model was run prior to all simulations. No pesticide application was considered during the warm-up.

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### 2.3.2. Calibration of pesticide fate parameters

#### *Prior sensitivity analysis*

The sensitivity to the pesticide fate parameters ( $K_D$ ,  $t_{1/2}$ ,  $b$ ,  $z_{mix}$ ) was first jointly analysed to determine their respective influence on the model outputs, thereby identifying the most influential parameters for calibration. These parameters were chosen because of their high variability depending on the environmental conditions and the difficulty of transposing laboratory values (e.g.,  $K_D$  and  $t_{1/2}$ ) (Calvet et al., 2005) or the absence of a consensus reference value, e.g.,  $z_{mix}$  (Bruce et al., 1975; Ahuja et al., 1981). In model sensitivity analysis to  $t_{1/2}$  and  $K_D$ , the ranges of the studied values for glyphosate were obtained from the range of values cited by the PPDB (2022), while those for diuron were obtained from measurements in the study field (Baer, 1996 for  $t_{1/2}$  and Louchart and Voltz, 2007 for  $K_D$ ). The chosen ranges of  $z_{mix}$  and  $b$  were the same for both compounds to include most values found in the literature. (e.g., Ahuja et al. (1981) and Bruce et al. (1975) for  $z_{mix}$  and Boesten (1986) for exponent  $b$ ). Table 1 shows the boundaries of the tested values for these two compounds.

Regarding  $t_{1/2}$ ,  $K_D$  and  $b$ , the parameter space was sampled according to a complete and balanced statistical design with a sampling method based on domain tessellation in polygons and sample generation by randomly drawing from each polygon (Faivre et al., 2013). This sampling approach sufficiently covered the parameter space, allowing the execution of analysis of variance (ANOVA). Specifically, for each of the three parameters, the range of variation was divided into 6 levels of equal magnitude, and each level was then combined with all levels of the other parameters. For a given combination of levels of the parameters, the parameter values were determined via a random draw within the levels. Thus, the values of  $t_{1/2}$ ,  $K_D$  and  $b$  varied for each combination of levels. In regard to  $z_{mix}$ , random values could not be drawn in intervals

since a unique grid was adopted to discretize the soil profile to ensure the same resolution of the Richards' equation for all runs. Accordingly, the range of variation in  $z_{\text{mix}}$  was deterministically sampled involving 6 values determined in regular intervals over the logarithmic scale of the  $z_{\text{mix}}$  values. The soil profile discretization was adapted so that all 6 values corresponded to a node of the grid. Parameter space sampling was repeated twice to increase the number of combinations assessed. In total, 2592 simulations were run per compound over 3-year, from March 2002 to March 2005. These 3 years were chosen since observations were available for both diuron and glyphosate and thereby the simulations performed could also be used for subsequent calibration of model parameters. Moreover the duration was set at 3 years in order to include a sufficient number of runoff events.

ANOVA was then conducted to assess the average contribution (main effect or first-order effect) of each model parameter and the contribution of the interactions (interaction effect or higher-order effect than the first-order effect) between the parameters to the overall outcome variance, i.e., the sum of the squared differences between each simulation and the overall mean. Since applications of ANOVA in model sensitivity analysis have been extensively described by many authors (Ginot et al., 2006; Saltelli et al. 2010), we invite the reader to consult these papers for more details. In this application, ANOVA was applied to the simulated log-transformed concentrations of each runoff event during the 3-year period, in order to analyze the influence of parameters at different times after herbicide application. The main effects of the parameters and their second-, third- and fourth-order interaction effects were estimated, with the order corresponding to the number of parameters in the interaction.

#### *Parameter set identification*

For identifying the pesticide fate parameter values that allowed the most accurate simulations, the the simulations run during the sensitivity analysis for the 2002-2005  
380 period were compared with the observed glyphosate and diuron concentrations during the same period. Accordingly, the sampling of the parameter space for parameter identification was thus identical to the sampling done for the sensitivity analysis.

The simulation performance was quantified, as recommended by Moriasi et al. (2015) and Althoff and Rodrigues (2021), using a statistical criterion of  
385 accuracy, namely, NSE, and a correctness criterion, namely, PBIAS. NSE compares the model performance in reproducing the observed values to that of another model comprising a simple average of the observations. The value varies between  $-\infty$  and 1, which is the optimal value, and can be calculated with equation (2):

$$NSE = 1 - \left[ \frac{\sum_{i=1}^n (Y_i^{obs} - Y_i^{simu})^2}{\sum_{i=1}^n (Y_i^{obs} - Y^{mean(obs)})^2} \right] \quad (2)$$

390  $Y_i^{obs}$ : the  $i^{th}$  observation of the studied variable of interest (the original runoff concentration or the log-transformed concentration);

$Y_i^{sim}$ : the  $i^{th}$  simulated value;

$Y^{mean(obs)}$ : the mean of the observed values; and

$n$ : the total number of observed values.

395 PBIAS quantifies the average over- or underestimation of the observations by the simulations. A positive value indicates that the model overpredicts the variable of interest on average, and a negative value indicates that the model underestimates the variable overall [equation (3)]:

$$PBIAS = \left[ \frac{\sum_{i=1}^n (Y_i^{simu} - Y_i^{obs}) \times 100}{\sum_{i=1}^n (Y_i^{obs})} \right] \quad (3)$$

400 These criteria were computed for both the original runoff pesticide concentrations and their log-transformed values. As stressed by Krause et al. (2005), the calculation with log-transformed values reduces the sensitivity of these performance criteria to extreme error values. As a result, given the large range of concentration values and the many low values, criteria based on log-transformed values are sensitive to all  
 405 concentrations, whereas criteria based on concentrations are mostly sensitive to high concentrations occurring soon after application.

No attempt was made to select a unique optimal set of parameter values since, as will be shown in the results section, several sets of parameters could yield a similar and satisfactory fit of the observed data. Among all sampled parameter sets, those  
 410 yielding NSE and PBIAS values over the calibration period (03/2002 to 03/2005) greater than 0.65 and less than 5%, respectively, were selected. According to the performance ratings proposed by Moriasi et al (2015) (Table 2) all parameter combinations satisfying the latter criteria are rated as “very good” in terms of solute concentration simulations. In the case of diuron, only one combination met this  
 415 criterion. Additional simulations were therefore conducted by refining the initial tessellation of the parameter space according by a new grid of values (Table S3) around the only combination identified. This allowed to select, similar to glyphosate, a set of combinations generating a sufficient prediction performance during the calibration period.

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### *2.3.3. Model performance analysis*

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First, the overall performance of the model was assessed by predicting concentrations outside the calibration period with the selected combinations of pesticide parameter values during the calibration approach. To do so, simulations were run continuously  
425 over the entire datasets, i.e. between September 1993 and March 2009 for diuron and between September 2000 and March 2014 for glyphosate, and model performance was computed for the years of data not used for calibration, namely 7 and 6 years for diuron and glyphosate respectively (Table 3). The goodness of fit of the model predictions was quantified using the same criteria as for calibration (see section  
430 2.3.2).

Second, the temporal structure of the model performance was analysed to assess the model's ability to reproduce the inter- and intra-annual variations in the compound concentration in surface runoff water. This analysis was performed with the parameter sets selected after calibration and with all available data records, including the  
435 calibration and validation periods, i.e., 10 and 9 years, respectively, for diuron and glyphosate. To analyse the interannual variability of the prediction performance, the NSE and PBIAS criteria were calculated per year of evaluation. Then, the accuracy of the mean model performance was estimated as a function of the number of evaluation years by computing the theoretical standard error of the sample mean of the annual  
440 NSE and PBIAS values. The theoretical standard error values were computed using the standard deviation value estimated from the sample of evaluation years used in this work, according to the following classical equation [equation (4)]:

$$SE = \frac{\sigma}{\sqrt{n}}$$

445 with  $\sigma = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}}$  (4)

$x_i$  : PBIAS or NSE in year  $i$  calculated with the original or log-transformed concentration values of diuron or glyphosate;

$\bar{x}$  : Mean annual PBIAS or NSE value calculated with the original or log-transformed concentration values of diuron or glyphosate;

450  $\sigma$  : Standard deviation of the annual PBIAS or NSE values estimated from the sample of evaluation years;

$n$  : Number of years used for evaluation; and

$SE$  : Standard error of the estimated mean annual PBIAS or NSE value.

To analyse the intra-annual variability of the prediction performance and accuracy, the  
455 relative error (RE) was estimated for each predicted runoff concentration, according to equation (5):

$$RE = \left( \frac{C^{simu} - C^{obs}}{C^{obs}} \right) \times 100 \quad (5)$$

$C^{simu}$ : Simulated runoff concentration of diuron or glyphosate; and

$C^{obs}$ : Observed runoff concentration of diuron or glyphosate.

460 A time permutation test (Legendre and Legendre, 2012) was then conducted to assess the temporal variation in the median RE of runoff events grouped by two-month intervals following herbicide application. In addition, a Wilcoxon signed-rank test was performed to determine whether the median RE of each two-month interval significantly differed from 0 at the 5% significance level.

## 465 **3. Results**

### **3.1. Sensitivity analysis**

20

The sensitivity of the log-transformed simulated runoff event concentrations to the considered parameters and their interactions was satisfactorily represented by the ANOVA model, which could explain at least 79% of the total variation in the concentrations during all runoff events regardless of the duration after herbicide application (Fig. 2).

However, the main effects of the parameters, as shown in Fig. 2, were very heterogeneous with time after herbicide application. The half-life,  $t_{1/2}$ , was globally the most influential parameter at the annual scale. Its influence increased with increasing time after application, and it explained more than 80% of the variability of the simulated concentrations from 50 days after application. In contrast,  $K_D$  and  $z_{mix}$  were the most influential parameters for runoff events occurring a few days after herbicide application for both diuron and glyphosate. The influence of Walker's exponent was negligible for all simulated events. The main effect of each parameter also varied according to the compound studied, reflecting differences in the influences of the processes driving the fate of each compound. Overall, despite a smaller considered range of  $K_D$  values for diuron than that for glyphosate,  $K_D$  was more influential for diuron than for glyphosate. For a simulated runoff event 30 days after herbicide application,  $K_D$  accounted for nearly 30% of the variability explained by the main effects for diuron, against nearly 14% for glyphosate. Moreover, for diuron  $K_D$ , the influence remained notable up to 100 days, whereas for glyphosate, it remained notable only up to 50 days. For diuron, the main effect of  $K_D$  was always higher than that of  $z_{mix}$  and decreased less rapidly, while for glyphosate, the main effects of  $K_D$  and  $z_{mix}$  were similar for all runoff events. These differences are related with  $K_D$  ranges explored since other parameter ranges are quite similar. It must be noted that the interaction effects eventually imposed a greater influence for glyphosate than for

diuron and exhibited a peak approximately 50 and 180 days after application for glyphosate and diuron, respectively.

These results suggest that the runoff contamination level is mainly controlled by degradation mechanisms except for runoff events occurring shortly after application, during which the sorption mechanism is the most influential.

### 3.2. Identified parameter sets and global model performance

Application of the selection criteria presented in section 2.4.2. allowed us to identify 389 and 16 parameter sets for diuron and glyphosate, respectively, allowing very favourable reproduction of runoff contamination during the calibration period, according to the thresholds set by Moriasi et al. (2015). The ranges of the values for these parameter sets are listed in Table 1. The selected  $K_D$  and  $t_{1/2}$  values differed between the two compounds, while all the selected  $z_{mix}$  values were lower than 1 cm. In line with the compound properties, the selected  $K_D$  values for diuron were significantly lower than those for glyphosate. In contrast, the adjusted half-lives were systematically smaller for diuron than for glyphosate, which ranks differently based on the data in the PPDB. The variability of the  $K_D$  and  $t_{1/2}$  values selected for diuron was smaller than that for glyphosate. This difference was particularly marked for  $K_D$ . The standard deviations of the sets of selected  $K_D$  values were 2.7 and 67.6 L.kg<sup>-1</sup> for diuron and glyphosate, respectively. The variability of the parameter values satisfying the performance criteria could be explained by the positive correlation between  $t_{1/2}$  and  $K_D$  and the negative correlation between  $z_{mix}$  and  $K_D$  (Table 4). Simultaneous calibration of these parameters therefore led to the nonuniqueness issue in model calibration. The correlations between  $K_D$  and  $t_{1/2}$  and between  $z_{mix}$  and  $K_D$  indicate strong compensation effects between these pairs of model parameters in the simulation of the removal of pesticide compounds from the soil by runoff water. The correlation between  $z_{mix}$  and  $K_D$  was much higher for glyphosate than for diuron. This

could be explained by a similar evolution of the sensitivity to  $z_{mix}$  and  $K_D$  for glyphosate but not for diuron, for which the influence of  $z_{mix}$  on the simulated concentrations was more than two times less than that of  $K_D$  from 40 days after application. Thus, as 90% of the runoff events occurred after this time, the vast majority of the runoff concentrations were simulated for diuron at a time when the sensitivity to  $z_{mix}$  was lower than that to  $K_D$ , allowing no compensation.

The values of the performance criteria regarding the simulated concentrations [Fig. 3(a)] for the selected parameter sets were slightly higher for diuron, with an NSE value up to 0.8 versus 0.69 for glyphosate, while the performance levels based on the log-transformed concentrations were higher but equivalent between these compounds, at approximately 0.88. Regarding validation, the overall model performance remained stable or decreased depending on the performance criterion considered and the compound. Concerning the log-transformed concentrations, the model performance was very similar to that during the calibration period and remained high for both compounds [Fig. 3(d)]. The NSE values exceeded 0.77, while the PBIAS values varied between -20% and -8%. In regard to the predicted concentrations over the validation period, the model performance was lower than that during the calibration period, either slightly for glyphosate with a maximum NSE value of 0.74 and a minimum |PBIAS| value of 26% or markedly for diuron with a maximum NSE value of 0.52 and a minimum |PBIAS| value of 45% [Fig. 3(b)].

### **3.3. Between-year variation in the prediction performance**

The interannual variability of the model performance could be high depending on the compound and performance criterion (Fig. 4). It could also be observed that the model performance variability was generally smaller for the log-transformed concentrations than for the original concentrations, except for PBIAS obtained for diuron with

standard deviations of 29.5% and 34.4% for the original and log-transformed concentrations, respectively. For glyphosate, the standard deviations of the annual PBIAS were 18.8% and 15% for the original and log-transformed concentrations, respectively. Concerning the annual NSE, the standard deviations were 0.24 and 0.11 for the original and log-transformed diuron concentrations, respectively, and they were 0.19 and 0.13 for the original and log-transformed glyphosate concentrations, respectively. Thus, the model performance was mostly more variable for diuron than for glyphosate, in particular in regard to the variations in the annual PBIAS values. For diuron, the year 1998 was particularly notable for a high annual |PBIAS| value (69%) and a low NSE value (0.14), based on the mean concentrations.

Fig. 5 shows the evolution of the standard error of the mean annual PBIAS and NSE values as a function of the number of years used for model evaluation. A large number of years of data is required to accurately measure the average model performance in reproducing the interannual variability of the pesticide concentration in runoff. With three years of data used for performance evaluation in reproducing runoff concentrations, the standard errors of the mean annual NSE and PBIAS values reached up to 0.14 and 17%, respectively, which are higher than the ranges of the PBIAS values chosen to define the classes of the simulation performance defined by Moriasi et al. (2015), namely, 10%. To ensure a sufficient estimation accuracy for NSE and PBIAS to categorize the model performance according to the classification of Moriasi, the standard errors should be less than 0.15 and 10% for NSE and PBIAS, respectively. Thus, for example, at least 3 years of data are required to obtain a standard error of the mean annual NSE less than 0.15 for all analysed compounds and variables, and at least 12 years of data are required to obtain a standard error of the mean annual PBIAS less than 10% for all analysed compounds and variables. The number of years of data needed to reach these thresholds varies, however, depending

on the compound considered. For glyphosate, 2 years of data are sufficient to obtain a  
570 standard error of the mean annual NSE less than 0.15, while 4 years of data are  
sufficient to obtain a standard error of the mean annual PBIAS less than 10% for all  
variables analysed.

### **3.4. Within-year variation in the prediction performance**

In general, the intra-annual variability of the runoff concentrations was reproduced  
575 well by the model, even if the performance differed according to the compound, while  
the maximum difference between the predicted and measured concentrations could  
reach up to a factor of 6 (Fig. S2). Fig. 6 shows the distribution of the RE values for  
each 2-month interval after herbicide application. On average, the median RE was low  
for both compounds: it approached -15% and -8% for diuron and glyphosate,  
580 respectively. However, the Wilcoxon test results showed that for diuron and runoff  
events occurring between the 3<sup>rd</sup> and 4<sup>th</sup> months, between the 9<sup>th</sup> and 10<sup>th</sup> months, and  
between the 11<sup>th</sup> and 12<sup>th</sup> months after application, the median RE significantly  
differed from 0 (Table 5). In particular, the diuron concentrations measured between  
the 3<sup>rd</sup> and 4<sup>th</sup> months were overestimated by the model. Furthermore, the  
585 permutation test indicated that the median RE was time dependent for diuron. In  
contrast, for glyphosate, the median RE never significantly differed from 0, and  
accordingly, the permutation test did not indicate a time dependence of the median  
RE for glyphosate.

## **4. Discussion**

590 According to the performance thresholds of Moriasi et al. (2015), the prediction  
performance for the surface runoff pesticide concentration of MHYDAS-Pesticide was  
very good or good on average over the multi-year evaluation period. In regard to the  
available tests of pesticide surface runoff models (Fig. S1), our evaluation results  
25

ranked among the best as compared to the few other tests of field-scale concentration  
595 predictions [e.g., Ghidey et al. (1999); Malone et al. (2004); and Chinkuyu et al.  
(2005)] and the more numerous assessments of mass loss predictions (Mudgal et al.,  
2010; Plotkin et al., 2013; Chen et al., 2017; Baffaut et al., 2019). This result indicates  
that no major temporal prediction bias appeared over almost ten years of runoff  
simulations for either diuron or glyphosate. Moreover, all concentrations were  
600 simulated with the right order of magnitude despite the wide range of the observed  
concentrations. It confirms the capacity of the adopted modelling approach to  
simulate both the between- and within-year variations in the pesticide concentration in  
runoff water, provided calibration was performed satisfactorily over a few years.

Concerning the variation in the between-year prediction performance, it must first be  
605 recognized that in this case study, all observed annual performance values for both  
diuron and glyphosate ranked satisfactory or higher according to the classification of  
Moriassi et al. (2015), apart one year for diuron that exhibited unsatisfactory NSE and  
PBIAS. However, the annual performance still largely varied between individual years.  
The potential sources of variation can be diverse, including sources of environmental  
610 origin, such as variations in climatic conditions or soil surface states (organic matter  
content, soil structure, and soil water content) and sources of experimental origin  
(uncertainties in the applied pesticide amounts and number of observed runoff  
events). Unfortunately, even with ten years of model prediction evaluation, it was  
barely possible to precisely identify and discriminate the variation sources. However,  
615 examination of the contribution of the prediction error of each runoff event to the  
annual NSE and PBIAS values revealed that for many years, one or a few events with  
high concentrations close to application contributed the most (Figs. S3 to S6). This  
explains the slightly better prediction performance criteria for the log-transformed  
concentrations than for the original concentrations. Eventually, the high variation in

620 the performance between individual years suggests that a significant part of the observed variation in the performance in the literature may result from evaluation periods that are too short (Fig. S1). As a rule of thumb, our calculations indicated that at least 3 years of test data are required to obtain estimates of the runoff model performance with a reasonable NSE precision in a Mediterranean climate.

625 Concerning the within-year variations in the prediction errors, they did not significantly differ from zero for glyphosate, while the opposite was observed for diuron for some periods. This difference may be explained by the difference in the sorption and/or degradation behaviour between these two compounds. The assumptions of stable sorption properties and first-order degradation kinetics throughout the pesticide fate  
630 simulation period seemed valid for glyphosate, whereas they must be questioned for diuron. Indeed, the change with time after application of the log-transformed diuron concentrations did not exhibit linear behaviour overall but rather a nonlinear trend including a relatively steep decrease up to 80 days after application and a more moderate decrease thereafter (Fig. 7). Accordingly, a bilinear regression could achieve  
635 a better fit than a simple linear regression (Fig. 7). Hence, after calibration, the RE values of the diuron predictions differed from zero for some periods. To explain this nonlinear behaviour, the first hypothesis is that the degradation rate decreases in summer due to a decrease in the soil water content. However, this hypothesis is not consistent with the sensitivity analysis results, which showed that considering the  
640 effect of the soil water content on the degradation rate generates a negligible influence regardless of the time after application (Fig. 2). The second hypothesis entails a major effect of diuron ageing on the change in diuron sorption in soil notably influencing the concentrations observed in runoff water. Many studies have indeed shown the influence of ageing of various pesticide compounds on  $K_D$  evolution (Laabs  
645 and Amelung, 2005; Regitano et al., 2006; Louchart and Voltz, 2007; Motoki et al.,  
105 27

2016). In particular, it has been determined from soil and water diuron content data acquired at the same study site that the apparent  $K_D$  of diuron increases in two stages, with an initial rapid increase up to 60-90 days after application and a subsequent slower increase (Louchart and Voltz, 2007). The diuron ageing effect could therefore explain the diuron concentration overestimation for events occurring in the third and fourth months after herbicide application and consequently the concentration underestimation after the ninth month after application. In general, the increase in  $K_D$  due to the ageing effect is considered to particularly concern nonionic compounds with a particular affinity for soil organic matter (Motoki et al., 2016), such as diuron. To improve the model performance in simulating diuron concentrations in runoff, the process of the increase in  $K_D$  could be included and assessed in the future. Modelling of  $K_D$  evolution under the ageing effect of compounds has been the subject of increasing interest in recent years, particularly in groundwater contamination assessment (Boesten, 2017; European Commission, 2021). However, in the present case, the expected improvement is limited in view of the admittedly significant but slight differences in the overall prediction performance between diuron and glyphosate.

Finally, the study results also provide hints for the parameterisation of this type of runoff model. First, the sensitivity analysis clearly showed that the parameters that must be precisely estimated depend on the simulation objectives. If the modelling objective is to estimate chronic exposure to pesticides in runoff water over one or several cropping seasons, the main parameter value to be determined is the pesticide half-life time. Half-life time has often been shown as one of the pesticide fate parameters with the greatest influence (Cryer and Havens, 1999; Chinkuyu et al., 2003; Dubus et al., 2003; Luo and Zhang, 2009). However, if the objective is to predict the maximum observed concentrations during a given season, the sorption coefficient,

$K_D$ , and the mixing depth,  $z_{mix}$ , jointly impose a greater influence than  $t_{1/2}$ . Maximum concentrations mainly occur shortly after application before the occurrence of significant degradation. Second, a nonuniqueness phenomenon was observed in parameter selection. The calibrated  $K_D$  and  $z_{mix}$  values were highly correlated and exhibited similar influences on the model outputs. Thus, high indeterminacy existed in the depth of the mixing layer, which in turn allowed us to choose the same mixing depth for the different compounds. These results suggest that there is a nonuniqueness issue in calibration based on the uniform mixing concept. Dubus et al. (2002) already recognized that pesticide fate models are subject to inherent nonuniqueness issues due to the compensation effect between parameters, and they considered it a research priority to identify the data requirements for effective and robust calibration of these models. Here, with only runoff event concentration data, although over several years, calibration of a unique optimal set of parameter values would not have been justified. This also puts into question the data needs for model validation and comparison. For example, Young and Fry (2019), in their field-scale evaluation of models of pesticide uptake into runoff, could not discriminate between the uniform mixing and nonuniform uptake concepts since they both could satisfactorily predict 99 pesticide runoff events observed in different experiments after specific calibration.

## 5. Conclusions

In this study, we aimed to evaluate the prediction performance of MHYDAS-Pesticide-1.0 in the simulation of pesticide concentrations in event runoff water at the field scale. The availability of long-term monitoring data enabled us to estimate the overall model performance and its temporal variation. Several results were obtained. This study first shows that simulations of pesticide concentrations in surface runoff at the field scale

by Richards and convection-dispersion equations coupled with the uniform mixing concept are likely to provide consistent predictions under natural Mediterranean rainfall conditions over a large number of years at the runoff event resolution. It must however be recognized that the satisfactory long-term performance of this model was estimated in rather favourable conditions, namely a single field with a stable topsoil structure and soil management and after a prior calibration of the model parameters over 3 years. The potential sources of variations in model predictions were thus less than all those that were listed by Dubus et al. (2003). Nevertheless, even in this case, there was high variation in the prediction performance among individual years, indicating that to obtain robust estimates of the performance, monitoring data over several climate and application cycles should be adopted in evaluation studies. In this case study, which certainly corresponds to a worst case given the intrinsic variability of the Mediterranean climate, at least 3 annual cycles are advisable. The study results also indicated that the very large within-year variation in the pesticide concentrations in runoff water could be satisfactorily predicted. Differences in the within-year prediction performance were noted between the considered compounds, possibly due to ageing effects on sorption. However, these differences were small, suggesting that, in this case study, the omission of ageing processes in the model was not a major source of prediction uncertainty. Finally, the study provides guidelines concerning pesticide runoff model parameterisation. If the model is applied in predicting the average concentration in runoff water, the compound degradation rate is of paramount influence, whereas if it is applied in predicting peak concentrations known to occur soon after application, the sorption coefficient and the mixing zone depth are the most influential model parameters.

## **CRedit authorship contribution statement**

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**Guillaume Métayer** : Conceptualization, Software, Validation, Formal analysis, Investigation, Writing - Original Draft. **Cécile Dagès** : Conceptualization, Validation, Writing - Review & Editing, Supervision, Funding acquisition. **David Crevoisier** : Validation, Software. **Jean-Stéphane Bailly** : Writing - Review & Editing, Supervision, Funding acquisition. **Marc Voltz** : Conceptualization, Writing - Review & Editing, Supervision, Funding acquisition.

## **Declaration of competing interest**

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

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## **References**

- 745 Ahuja, L.R., Sharpley, A.N., Yamamoto, M., and Menzel, R.G., 1981. The depth of rainfall-runoff-soil interaction as determined by <sup>32</sup>P. *Water Resources Research*, 17, 969-974. <https://doi.org/10.1029/WR017i004p00969>
- Allen, R.G., Pereira, L.S., Raes, D. and Smith, M., 1998. Crop evapotranspiration - guidelines for computing crop water requirements. FAO Irrigation and drainage paper 56. Food and Agriculture Organization, Rome.
- 750
- Althoff, D. and Rodrigues, L.N., 2021. Goodness-of-fit criteria for hydrological models: Model calibration and performance assessment. *Journal of Hydrology*, 600, 126674. <https://doi.org/10.1016/j.jhydrol.2021.126674>
- Baer, U., 1996. Comportement des pesticides dans les sols : Evaluation et simulation de la dissipation au champ. PhD Thesis, INA Paris Grignon.
- 755
- Baffaut, C. , Ghidry, F. , Lerch, R.N., Kitchen, N.R., Sudduth, K.A. and Sadler, E.J., 2019. Long-term simulated runoff and water quality from grain cropping systems on restrictive layer soils. *Agricultural Water Management*, 213, 36-48. <https://doi.org/10.1016/j.agwat.2018.09.032>
- 760
- Boesten, J.J.T.I., 1986. Behaviour of herbicides in soil: simulation and experimental assessment. PhD Thesis, Wageningen Agricultural University. Institute for Pesticide Research, Wageningen.
- Boesten, J.J.T.I. 2017. Effects of aged sorption on pesticide leaching to groundwater simulated with PEARL. *Science of The Total Environment*, 576, 498-507.
- 765 <https://doi.org/10.1016/j.scitotenv.2016.10.099>
- Boivin A. and Poulsen V., 2017. Environmental risk assessment of pesticides: state of the art and prospective improvement from science. *Environmental Science and Pollution Research*, 24, 6889-6894. <https://doi.org/10.1007/s11356-016-8289-2>

- Bruce, R.R., Harper, L.A., Leonard, R.A., Snyder, W.M., Thomas, A.W., 1975. A model  
770 for runoff of pesticides from small upland watersheds. *Journal of Environmental  
Quality*, 4, 541-548. <https://doi.org/10.2134/jeq1975.00472425000400040024x>
- Calvet, R., Barriuso, E., Bedos, C., Benoit, P., Charnay, M. and Coquet, Y., 2005. *Les  
pesticides dans les sols. Conséquences agronomiques et environnementales.*  
France Agricole, Paris.
- 775 Carsel, R.F., Mulkey, L.A., Lorber, M.N. and Baskin, L.B., 1985. The Pesticide Root Zone  
Model (PRZM): A procedure for evaluating pesticide leaching threats to  
groundwater. *Ecological Modelling*, 30, 49-69. [https://doi.org/10.1016/0304-  
3800\(85\)90036-5](https://doi.org/10.1016/0304-3800(85)90036-5)
- Chahinian, N., Moussa, R., Andrieux, P. and Voltz, M., 2005. Comparison of infiltration  
780 models to simulate flood events at the field scale. *Journal of Hydrology*, 306, 191-  
214. <https://doi.org/10.1016/j.jhydrol.2004.09.009>
- Chen, H., Zhang, X., Demars, C. and Zhang, M., 2017. Numerical simulation of  
agricultural sediment and pesticide runoff: RZWQM and PRZM comparison.  
*Hydrological Processes*, 31, 2464-2476. <https://doi.org/10.1002/hyp.11207>
- 785 Chinkuyu, A.J., Meixner, T., Gish, T.J., and Daughtry, C.S., 2003. Sensitivity analysis of  
GLEAMS using multi-objective sensitivity analysis procedure. The American  
Society of Agricultural and Biological Engineers Annual Meeting, Paper number  
032109. <https://doi.org/10.13031/2013.14004>
- Chinkuyu, A., Meixner, T., Gish, T., and Daughtry, C., 2005. Prediction of pesticide  
790 losses in surface runoff from agricultural fields using GLEAMS and RZWQM.  
*Transactions of the American Society of Agricultural and Biological Engineers*. 48,  
585-599. <https://doi.org/10.13031/2013.18333>

- Cho, J. 2007. A comprehensive modeling approach for BMP impact assessment considering surface and groundwater interaction. PhD Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.
- 795
- Cho, J., and Mostaghimi, S., 2009. Evaluating cell-based components of DANSAT for predicting surface and subsurface transport of pesticides. *Biosystems Engineering*, 102, 473–485. <https://doi.org/10.1016/j.biosystemseng.2009.01.007>
- Connolly, R.D., Kennedy, I.R., Silburn, D.M., Simpson, B.W., and Freebairn, D.M., 2001. Simulating Endosulfan Transport in Runoff from Cotton Fields in Australia with the GLEAMS Model. *Journal of Environmental Quality*, 30, 702–713. <https://doi.org/10.2134/jeq2001.303702x>
- 800
- Crevoisier, D., Dagès, C., Fabre, J.C., Roman-Villafane, S. and Voltz, M., 2021. MHYDAS-Pesticides-1.0 : Modélisation Hydrologique Distribuée des AgroSystèmes - Eau et Pesticides. Rapport dans le cadre du projet collaboratif PollDiff Captage 2018-2021 (AAP Readynov FEDER-FSE-Occitanie), INRAE Montpellier, UMR LISAH.
- 805
- Crevoisier, D., Chanzy, A., and Voltz, M., 2009. Evaluation of the Ross fast solution of Richards' equation in unfavourable conditions for standard finite element methods. *Advances in Water Resources*, 32, 936–947. <https://doi.org/10.1016/j.ADVWATRES.2009.03.008>
- 810
- Cryer, S.A., and Havens, P.L., 1999. Regional sensitivity analysis using a fractional factorial method for the USDA model GLEAMS. *Environmental Modelling & Software*, 14, 613-624. [http://dx.doi.org/10.1016/S1364-8152\(99\)00003-1](http://dx.doi.org/10.1016/S1364-8152(99)00003-1)
- Dubus, I.G., Beulke, S., and Brown, C.D., 2002. Calibration of pesticide leaching models: Critical review and guidance for reporting. *Pest Management Science*, 58, 745–758. <https://doi.org/10.1002/ps.526>
- 815

- Dubus, I.G., Brown, C.D., and Beulke, S., 2003. Sensitivity analyses for four pesticide leaching models. *Pest Management Science*, 59, 962-982.  
<https://doi.org/10.1002/ps.723>
- 820 Eaufrance, 2023. Naiades, données sur la qualité des eaux de surface,  
<https://naiades.eaufrance.fr/acces-donnees#/physicochimie>
- European Commission, 2021. Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments. Commission Guidance Document, SANTE/12586/2020 - REV 1.
- 825 Faivre, R., looss, B., Mahevas, S., Makowski, D. and Monod, H., 2013. Analyse de sensibilité et exploration de modèles : Application aux sciences de la nature et de l'environnement. Editions Quae, Versailles.
- FOCUS, 2001. Focus surface water scenarios in the EU evaluation process under 91/414/EEC. Report prepared by the FOCUS Working Group on Surface Water  
830 Scenarios, EC Document Reference SANCO/4802/2001-rev.2 final.
- FOCUS, 2015. Generic guidance for FOCUS surface water Scenarios. Version 1.4. Report prepared by the FOCUS Working Group on Surface Water Scenarios, EC Document Reference SANCO/4802/2001-rev.2 version 1.4.
- Gagnon, P., Sheedy, C., Rousseau, A.N., Bourgeois, G. and Chouinard, G., 2016.  
835 Integrated assessment of climate change impact on surface runoff contamination by pesticides. *Integrated Environmental Assessment Management*, 12, 559-571.  
<https://doi.org/10.1002/ieam.1706>
- Ghidey, F., Alberts, E.E., and Kitchen, N.R., 1999. Evaluation of the Root Zone Water Quality model using field-measured data from the Missouri MSEA. *Agronomy*

- 840 Journal, 91, 183–192.  
<https://doi.org/10.2134/agronj1999.00021962009100020004x>
- Ginot, V., Gaba, S., Beaudouin, R., Aries, F., and Monod, H., 2006. Combined use of local and ANOVA-based global sensitivity analyses for the investigation of a stochastic dynamic model: Application to the case study of an individual-based  
845 model of a fish population. *Ecological Modelling*, 193, 479–491.  
<https://doi.org/10.1016/j.ecolmodel.2005.08.025>
- Hanson, J.D., Ahuja, L.R., Shaffer, M.D., Rojas, K.W., DeCoursey, D.G., Farahani, H., and Johnson, K., 1998. RZWQM: Simulating the effects of management on water quality and crop production. *Agricultural Systems*, 57, 161–195.  
850 [https://doi.org/10.1016/S0308-521X\(98\)00002-X](https://doi.org/10.1016/S0308-521X(98)00002-X)
- IUSS Working Group WRB. 2014. World Reference Base for Soil Resources, 2014. International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome.
- Krause, P., Boyle, D., and Bäse, F., 2005. Comparison of different efficiency criteria for  
855 hydrological model assessment. *Advances in Geosciences*, 5, 89–97.  
<https://doi.org/10.5194/adgeo-5-89-2005>
- Laabs, V., and Amelung, W., 2005. Sorption and aging of corn and soybean pesticides in tropical soils of Brazil. *Journal of Agricultural and Food Chemistry*, 53, 7184–7192. <https://doi.org/10.1021/jf050969c>
- 860 Larsbo, M., Roulier, S., Stenemo, F., Kasteel, and R., Jarvis, N., 2005. An improved dual-permeability model of water flow and solute transport in the vadose zone. *Vadose Zone Journal*, 4, 398–406. <https://doi.org/10.2136/vzj2004.0137>

- Legendre, P. and Legendre, L., 2012. Numerical Ecology (Third English edition). Elsevier, Amsterdam.
- 865 Leonard, R.A., Knisel, W.G., and Still, D.A., 1987. Gleams: Groundwater Loading Effects of Agricultural Management Systems. Transactions of the American Society of Agricultural and Biological Engineers, 30, 1403-1418.  
<https://doi.org/10.13031/2013.30578>
- 870 Louchart, X. and Voltz, M., 2007. Aging effects on the availability of herbicides to runoff transfer. Environmental Science and Technology, 41, 1137-1144.  
<https://doi.org/10.1021/es061186q>
- Louchart, X., Voltz, M., Andrieux, P. and Moussa, R., 2001. Herbicide transport to surface waters at field and watershed scales in a Mediterranean vineyard area. Journal of Environmental Quality, 30, 982-991.  
875 <https://doi.org/10.2134/jeq2001.303982x>
- Luo, Y. and Zhang, M., 2009. Management-oriented sensitivity analysis for pesticide transport in watershed-scale water quality modeling using SWAT. Environmental Pollution, 157, 3370-3378. <https://doi.org/10.1016/j.envpol.2009.06.024>
- 880 Ma, Q.L., Ahuja, L.R., Rojas, K.W., Ferreira, V.F., and Decoursey, D.G., 1995. Measured and RZWQM predicted atrazine dissipation and movement in a field soil. Transactions of the American Society of Agricultural and Biological Engineers, 38, 471-479. <https://doi.org/10.13031/2013.27855>
- 885 Ma, L., Ahuja, L.R., Ascough, J.C., Shaffer, M.J., Rojas, K.W., Malone, R.W., and Cameira, M.R., 2001. Integrating system modeling with field research in agriculture: applications of the root zone water quality model (RZWQM). Advances in Agronomy, 71, 233-292. [https://doi.org/10.1016/s0065-2113\(01\)71016-4](https://doi.org/10.1016/s0065-2113(01)71016-4)

- Malone, R.W., Warner, R.C., Workman, S.R., and Byers, M.E., 1999. Modeling surface and subsurface pesticide transport under three field conditions using PRZM-3 and GLEAMS. Transactions of the American Society of Agricultural and Biological Engineers. 42, 1275-1288. <https://doi.org/10.13031/2013.13292>
- Malone, R.W., Ma, L., Wauchope, R.D., Ahuja, L.R., Rojas, K.W., Ma, Q., Warner, R. and Byers, M., 2004. Modeling hydrology, metribuzin degradation and metribuzin transport in macroporous tilled and no-till silt loam soil using RZWQM. Pest Management Science, 60, 253–266. <https://doi.org/10.1002/ps.738>
- Miao, Z., Vicari, A., Capri, E., Ventura, F., Padovani, L. and Trevisan, M., 2004. Modeling the Effects of Tillage Management Practices on Herbicide Runoff in Northern Italy. Journal of Environmental Quality, 33, 1720–1732. <https://doi.org/10.2134/jeq2004.1720>
- Molénat, J., Raclot, D., Zitouna, R., Andrieux, P., Coulouma, G., Feuerer, D., Grünberger, O., Lamachère, J.-M., Bailly, J.-S., Belotti, J.-L., Ben Azzez, K., Ben Mechlia, N., Ben Younès Louati, M., Biarnès, A., Blanca, Y., Carriere, D., Chaabane, H., Dagès, C., Debabria, A., Dubreuil, A., Fabre, J.C., Fages, D., Floure, C., Garnier, F., Geniez, C., Gomez, C., Hamdi, R., Huttel, O., Jacob, F., Jenhaoui, Z., Lagacherie, P., Le Bissonnais, Y., Louati, R., Louchart, X., Mekki, I., Moussa, R., Negro, S., Pepin, Y., Prevot, L., Samouëlian, A., Seidel, J.L., Trotoux, G., Troiano, S., Vinatier, F., Zante, P., Zrelli, J., Albergel, J. and Voltz, M., 2018. OMERE: a long-term observatory of soil and water resources, in interaction with agricultural and land management in Mediterranean hilly catchments Vadose Zone Journal, 17, 1-18. <https://doi.org/10.2136/vzj2018.04.0086>
- Moriasi, D.N., Arnold, J.G., Van Liew, M.W., Bingner, R.L., Harmel, R.D. and Veith, T.L., 2007. Model evaluation guidelines for systematic quantification of accuracy in

watershed simulations. Transactions of the American Society of Agricultural and Biological Engineers, 50, 885–900. <https://doi.org/10.13031/2013.23153>

915 Moriasi, D.N., Gitau, M.W., Pai, N. and Daggupati, P., 2015. Hydrologic and water quality models: Performance measures and evaluation criteria. Transactions of the American Society of Agricultural and Biological Engineers, 58, 1763–1785. <https://doi.org/10.13031/trans.58.10715>

920 Motoki, Y., Iwafune, T., Seike, N., Inao, K. and Otani, T., 2016. Effect of time-dependent sorption on the dissipation of water-extractable pesticides in soils. Journal of Agricultural and Food Chemistry, 64, 4478–4486. <https://doi.org/10.1021/acs.jafc.6b01028>

Moussa, R., 1996. Analytical Hayami Solution for the diffusive wave flood routing problem with lateral inflow. Hydrological Processes, 10, 1209-1227. [https://doi.org/10.1002/\(SICI\)1099-1085\(199609\)10:9<1209::AID-HYP380>3.0.CO;2-2](https://doi.org/10.1002/(SICI)1099-1085(199609)10:9<1209::AID-HYP380>3.0.CO;2-2)

Mudgal, A., Baffaut, C., Anderson, S.H., Sadler, E.J., and Thompson, A.L., 2010. Apex model assessment of variable landscapes on runoff and dissolved herbicides. Transactions of the American Society of Agricultural and Biological Engineers. 53, 1047-1058. <https://doi.org/10.13031/2013.32595>

930 Oh, J.A., Beltman, W.H., Ter Horst, M.M., Ham, S.N., Park, Y.K., Shin, J.Y. and Kyung, K.S., 2021. Development of surface water exposure scenarios for risk assessment of pesticides in Korea. Science of The Total Environment, 771, 144790, <https://doi.org/10.1016/j.scitotenv.2020.144790>

935 Padilla, J.T. and Selim, H.M., 2019. Time-dependent sorption and desorption of glyphosate in soils: Multi-reaction modeling. Vadose Zone Journal, 18, 1-10. <https://doi.org/10.2136/vzj2018.12.0214>

- Plotkin, S., Wang, X., Potter, T.L., Bosch, D.D., Williams, J.R., Hesketh, E.S. and Bagdon, J.K., 2013. Apex calibration and validation of water and herbicide transport under U.S Southern Atlantic Coastal Plain Conditions. Transactions of the American Society of Agricultural and Biological Engineers. 56, 43-60, 940 <https://doi.org/10.13031/2013.42589>
- PPDB, Pesticide properties database, University of Hertfordshire, 2022. <https://sitem.herts.ac.uk/aeru/ppdb/en/>.
- Regitano, J.B., Koskinen, W.C. and Sadowsky, M.J., 2006. Influence of soil aging on sorption and bioavailability of simazine. Journal of Agricultural and Food Chemistry, 54, 1373-1379. <https://doi.org/10.1021/jf052343s> 945
- Reichenberger, S., Bach, M., Skitschak, A., and Frede, H.G., 2007. Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness; A review. Science of the Total Environment, 384, 1-35. 950 <https://doi.org/10.1016/j.scitotenv.2007.04.046>
- Ross P.J., 2003. Modeling soil water and solute transport – Fast, simplified numerical solutions. Agronomy Journal, 95, 1352-1361. <https://doi.org/10.2134/agronj2003.1352>
- Saint-Venant, B., 1871. Théorie du mouvement non permanent des eaux, avec application aux crues des rivières et à l'introduction des marées dans leurs lits, Comptes rendus de l'Académie des Sciences de Paris, 73, 147-154, 237-240. 955
- Saltelli A., Annoni P., Azzini I., Campolongo F., Ratto M. and Tarantola S., 2010. Variance based sensitivity analysis of model output. Design and estimator for the total sensitivity index. Computer Physics Communications, 181, 259-270. 960 <https://doi.org/10.1016/j.cpc.2009.09.018>

- Schaap, M.G. and van Genuchten, M.T., 2006. A Modified Mualem–van Genuchten formulation for improved description of the hydraulic conductivity near saturation. *Vadose Zone Journal*, 5, 27–34. <https://doi.org/10.2136/vzj2005.0005>
- 965 Sharma, A., Kumar, V., Shahzad, B., Tanveer, M., Sidhu, G.P.S., Handa, N., Kohli, S.K.,  
Yadav, P., Bali, A.S., Parihar, R.D., Dar, O.I., Singh, K., Jasrotia, S., Bakshi, P.,  
Ramakrishnan, M., Kumar, S., Bhardwaj, R., and Thukral, A.K., 2019. Worldwide  
pesticide usage and its impacts on ecosystem. *SN Applied Sciences*, 1, 1446.  
<https://doi.org/10.1007/s42452-019-1485-1>
- 970 Siimes, K. and Kämäri, J., 2003. A review of available pesticide leaching models:  
Selection of models for simulation of herbicide fate in Finnish sugar beet  
cultivation. *Boreal Environment Research*, 8, 31–51.
- 975 Shipitalo, M.J., and Owens, L.B., 2003. Atrazine, deethylatrazine, and  
deisopropylatrazine in surface runoff from conservation tilled watersheds.  
*Environmental Science and Technology*, 37, 944-950 [https://doi.org/doi:  
10.1021/es020870b](https://doi.org/doi:10.1021/es020870b)
- Shrestha, S. and Manandhar, B., 2014. Evaluation of the Root Zone Water Quality  
Model (RZWQM) using field-measured data from the tropical zone, Thailand.  
*Water, Air, and Soil Pollution*, 225, 1958. <https://doi.org/10.1007/s11270-014-1958-1>
- 980 Šimůnek, J., Šejna, M., Saito, H., Sakai, M. and van Genuchten, M. Th., 2013. The  
Hydrus-1D software package for simulating the movement of water, heat, and  
multiple solutes in variably saturated media, Version 4.17, HYDRUS Software  
Series 3. Department of Environmental Sciences, University of California  
Riverside, Riverside, California, USA, pp. 342.
- 985 Van den Berg, F., Tiktak, A., Boesten, J.J.T.I. and Linden, A.M.A. van der, 2016. PEARL  
model for pesticide behaviour and emissions in soil-plant systems. WOt-technical  
41

report, No. 61. Statutory Research Tasks Unit for Nature and the Environment.

<https://edepot.wur.nl/377664>

Walker, A., 1974. A simulation model for prediction of herbicide persistence. *Journal of Environmental Quality*, 3, 396-401.

990 <https://doi.org/10.2134/jeq1974.00472425000300040021x>

Wauchope, R.D., Graney, R.L., Cryer, S., Eadsforth, C., Klein, A. W. and Racke, K.D., 1995. Pesticide runoff: methods and interpretation of field studies. *Pure and Applied Chemistry*, 67, 2089–2108. <https://doi.org/10.1351/pac199567122089>

Williams, J.R., Wang, E., Meinardus, A., Harman, W.L., Siemers, M., and Atwood, J.D., 995 2006. APEX Users Guide. Version 2110. Temple, TX: Texas A&M University, Texas Agricultural Extension Service, Texas Agricultural Experiment Station, Blacklands Research Center.

Young, D.F. and Fry, M.M., 2019. Field-scale evaluation of pesticide uptake into runoff using a mixing cell and a non-uniform uptake model. *Environmental Modelling and Software*, 122, 104055. <https://doi.org/10.1016/j.envsoft.2017.09.007> 1000

Zhang, X. and Zhang, M., 2011. Modeling effectiveness of agricultural BMPs to reduce sediment load and organophosphate pesticides in surface runoff. *Science of the Total Environment*, 409, 1949–1958. <https://doi.org/10.1016/j.scitotenv.2011.02.012>