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HIGHLIGHTS

- Uncertainty analysis on the pesticide outputs of STICS-MACRO model was performed
- Climate, agricultural practices, soil and pesticide properties were considered
- Influential factors were climate temporal variability, Kf, hydraulic conductivity
- Small spatial variation in rainfall led to high variation in pesticide concentrations
- The results help to improve environmental management and decision-making processes

ABSTRACT

Modelling of pesticide leaching is paramount to managing the environmental risks associated with the chemical protection of crops, but it involves large uncertainties in relation to climate agricultural practices, soil and pesticide properties. We used Latin Hypercube Sampling to estimate the contribution of these input factors with the STICS-MACRO model in the context of a 400 km^2 catchment in France, and two herbicides applied to maize: bentazone and S-metolachlor. For both herbicides, the most influential input factors on modelling of pesticide leaching were the inter-annual variability of climate, the pesticide adsorption coefficient and the soil boundary hydraulic conductivity, followed by the pesticide degradation half-life and the rainfall spatial variability. This work helps to identify the factors requiring greater accuracy to ensure better pesticide risk assessment and to improve environmental management and decision-making processes by quantifying the probability and reliability of prediction of pesticide concentrations in groundwater with STICS-MACRO.

Keywords:

Uncertainty analysis

Latin hypercube sampling

Meta-model

Pesticide leaching

STICS-MACRO

1. Introduction

Modelling the leaching of pesticides can help prevent and manage groundwater contamination as groundwater protection is a key issue for human health and resources sustainability. However, the prediction of pesticide leaching by process-based models is fraught with considerable uncertainties (Vanderborght et al., 2011). Key sources of uncertainties include (i) primary data (basic physical, chemical and environmental properties either directly fed into a model or used to derive input parameters) because of spatial and temporal variability of environmental variables, sampling procedures in the field and analysis in the laboratory, (ii) procedures to derive some input parameters for lack of experimental data (although the latter are recommended in general): use of first-order kinetics to derive DT50 values, use of pedotransfer functions…, and (iii) modelling (model error i.e.

structural error or model inadequacy, non-inclusion or inappropriate representation of significant processes in the model, modeller subjectivity…) (Dubus et al., 2003a). Understanding the type and degree of uncertainties identified in the assessment helps to characterise the level of risk to the recipients and is, therefore, essential for informed decision-making (EFSA, 2016; Sohrabi et al., 2002).

One of the objectives of sustainable agriculture is to reduce the risks and impacts of pesticide use on the environment by encouraging the development of new cropping systems relying on integrated pest management or low input programmes (Directive 2009/128/EC, 2009; Hossard et al., 2016). Reliable information on the sustainability of each potential new system can be obtained from field experiments. For example, crop residues management and tillage practices were shown to have strong effects on water percolation and pesticide leaching: the presence of a mulch could increase soil water content so water percolation and pesticide leaching, and conventional tillage generally decreases pesticide leaching compared to no-till (Alletto et al., 2010; Lammoglia et al., 2017b). However, there are a wide diversity of possible combinations of crops, agricultural practices (tillage, organic matter management, mulch…), soils, and climates. It is, therefore, time-consuming and expensive to carry out comprehensive *in situ* experiments of each potential new system especially since results are site-specific. Consequently, models such as RZWQM (Malone et al., 2004), STICS-Pest (Queyrel et al., 2016) or STICS-MACRO (Lammoglia et al., 2017a) have been developed as potentially effective and inexpensive tools to assess numerous options and to identify the best cropping systems. The STICS-MACRO model combines the performances of an agro-ecosystem model (STICS, Brisson et al., 1998; Brisson et al., 2009) and of a pesticide fate model (MACRO, Larsbo and Jarvis, 2003). It allows to quantify the environmental impacts of pesticides (i.e. concentrations in soil and water) taking into account the effects of pedoclimatic conditions, agricultural practices, and cropping systems. Compared to RZWQM and STICS-Pest, STICS-MACRO (i) does not need calibration step, (ii) considers non-linear sorption which can be decisive to simulate the fate of pesticides in the environment (Beltman et al., 2008), (iii) allows improvement of the simulation of crop growth that leads to better estimate of crop transpiration therefore of water balance, (iv) allows better estimate of pesticide interception by the crop, so of the amount of pesticide reaching the soil, which is crucial for the prediction of pesticide concentrations in water, (v) allows to consider some agricultural practices such as fertilization, mulch, crop residues management…, and (vi) allows to obtain various environmental outputs such as the dynamic of nitrogen compounds and crop yields (Lammoglia et al., 2017a; Lammoglia et al., 2017b). The ability of STICS-MACRO to accurately predict the crop growth and development, and to predict water and pesticides leaching, has been evaluated through a test of the model and a sensitivity analysis in different agro-pedoclimatic contexts (Lammoglia et al., 2017a; Lammoglia et al., 2017b). The results showed that the performance of the model was acceptable although it depended on the pedoclimatic context (Lammoglia et al., 2017a).

Uncertainty analysis is one of the most important elements in the development and implementation of models (Sohrabi et al., 2002). Uncertainty analysis permits to quantify how the uncertainties of some of the model components (inputs, parameters, equations) translate into uncertainties in model output of interest for the study. A complementary sensitivity analysis allows determining of the relative contribution of the different sources of uncertainty considered (Wallach et al, 2014). There are numerous techniques to propagate uncertainty in models such as differential analysis (e.g. Diaz-Diaz et al., 1999), Monte-Carlo analysis (e.g. Dubus and Brown, 2002), generalised likelihood uncertainty estimation-GLUE (e.g. Beven and Binley, 1992), or fuzzy logic (e.g. Freissinet et al., 1999). Some uncertainty analyses have been done on MACRO (Sohrabi et al., 2002; Steffens et al., 2013; Steffens et al., 2014; Stenemo and Jarvis, 2007). Uncertainties associated to some soil hydraulic and pesticide properties, and pedotransfer functions were shown to cause large variation in simulation results (Sohrabi et al., 2002; Stenemo and Jarvis, 2007). Moreover, the parameter uncertainty can overshadow the effects of model structural error, due to equations, on predicted leaching losses (Steffens et al., 2013). Considering climate uncertainty through several expected future time series of climate data, Steffens et al. (2014) showed that the effect of parameter uncertainty was less important than climate uncertainty. However, the combined effects of uncertainties related to the spatial variability of climate at a small catchment scale, soil hydraulic properties, and pesticides properties on pesticide leaching have never been studied. Among the various climatic variables, rainfall is a key input for all models because it activates flow and mass transport (Chaubey et al., 1999; Lewan et al., 2009). Since rainfall is a driving force behind many kind of pesticide release and subsequent transport mechanisms, ignoring this property of rainfall in the application of models will put a limit on the accuracy of the model results (Chaubey et al., 1999).

Uncertainty analyses performed on the STICS model mainly focused on the effects of climate variability on crop yields (Dumont et al., 2015; Jégo et al., 2015). To the best of our knowledge, no uncertainty analysis considering the other STICS input parameters such as those related to cropping practices has been done.

Therefore, the objectives of this work were (i) to assess the effect of spatial and temporal rainfall variability on STICS-MACRO modelling of pesticide leaching (assessed through local concentrations in the leachate) at a 400 km² catchment scale, (ii) to assess the effect of the uncertainties of rainfall, agricultural practices, and soil and pesticides properties on the modelling of pesticides leaching through an uncertainty analysis of the STICS-

MACRO model, and (iii) to quantify the contribution of each input factor to the uncertainties in simulated pesticide leaching. This work will help to improve environmental management and decision-making processes.

2. Materials and methods

2.1. STICS-MACRO model

MACRO (Larsbo and Jarvis, 2003) is a one-dimensional dual-permeability model of water flow and solute transport in macroporous soil. The water and solute are partitioned into two domains: micropores, where flow and transport occur, represented by the Richards and the convection-dispersion equations, and macropores, where gravity-driven flow occurs. Pesticide sorption is described using the Freundlich isotherm while degradation follows first-order kinetics and depends on soil temperature and moisture content. The representation of crop development is simply based on crops' emergence and harvest dates, maximum leaf area index (LAI), maximum root depth and maximum crop height (as user defined input parameters). No agricultural practices such as mulching or tillage can be considered. Under conventional crop management, the performance of MACRO is known to be good enough to allow acceptable predictions of pesticides leaching (e.g. Marín-Benito et al., 2014).

The STICS crop model (Brisson et al., 1998; Brisson et al., 2009) is a dynamic daily time-step model, which simulates plant growth, water dynamics, and C and N cycles over several growing seasons. STICS describes in details the physical and biological processes occurring in the soil-crop-environment system considering a broad diversity of crop varieties and management practices. STICS predicts many output variables related to the crop production (LAI, crop yield), to the environment (water, carbon, and nitrogen fluxes), and to the evolution of soil water and nitrate contents. STICS has been widely tested for a variety of cropping situations and was shown to be good to predict crop and soil variables, under various agricultural practices (Brisson et al., 2003; Coucheney et al., 2015).

STICS-MACRO results in the combined use of STICS and MACRO in order to simulate crop growth and pesticide fate in complex cropping systems (Fig. 1) (Lammoglia et al., 2017a). Dedicated R packages (R Development Core Team, 2016) were developed to automate the forcing of MACRO inputs with some STICS output variables. The packages allow to sequentially (1) import predefined STICS and MACRO parameterization sets (one for each model), (2) simulate the crop rotation, crop development, water, and nitrogen requirements under agricultural practices such as fertilization or crop residues management with STICS model, (3) extract from STICS output files the estimated potential evapotranspiration, as well as the estimated green and total LAI, the crop height and the maximum root depth (for each time step), (4) convert these to MACRO input file format and adapt

MACRO parameterization, (5) estimate the fraction of the sprayed pesticide intercepted by the crop based on STICS total LAI when the pesticide is sprayed, (6) run the MACRO model with crop shape variables and potential evapotranspiration coming from STICS, and finally (7) import MACRO simulation results into the R environment, i.e. water balance and pesticide concentrations in soils and water as a function of time. The results can either be analyzed and visualized in R or exported in different formats. Internally, the tools use existing command line modes of STICS and MACRO, but do not use the graphical user interfaces of the two models. As indicated above, the performance of STICS-MACRO to simulate the fate of pesticides under different cropping systems was shown to be acceptable although it depended on the pedoclimatic context: the performance of STICS-MACRO was found to be better in a clayey calcic cambisol under average precipitation of 820 mm per year and average annual temperature of 11°C than in stagnic luvisol with 630 mm per year and 13.5 °C (Lammoglia et al., 2017a).

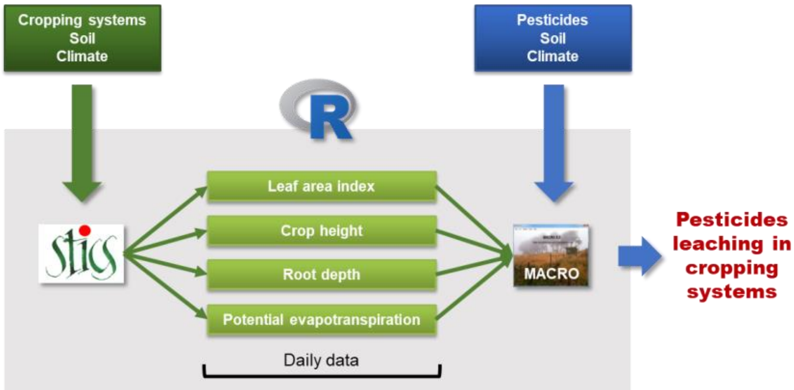

Fig. 1. Combined use of STICS crop model and of MACRO pesticide fate model to simulate pesticides leaching in cropping systems (From Lammoglia et al., 2017a).

2.2. Climate, soil and pesticides characteristics

This work is based on a geographic area corresponding to the catchment of Auzeville which surrounds an experimental site of INRA (Southwest of France; 43°31' N, 1°30' E). The catchment area is defined as a square zone of 400 km^2 (20 km × 20 km) divided into grid cells of 1 km^2 (1 × 1 km), imposed by the resolution of the rainfall data (see 2.2.1). The dominant land use is maize crop production sown from 1st April to 31st May. Maize monoculture has therefore been considered in this study also taking into account it is one of the most cultivated crop in France with a sowing area about 3.11 million ha (grain maize and forage maize) (Agreste, 2016).

2.2.1. Climate

STICS-MACRO requires daily climatic inputs because despite MACRO can be run with hourly rainfall data, STICS cannot. Nevertheless, in MACRO, daily rainfall data are converted internally into hourly rainfall data (Moeys et al., 2012). The daily minimum and maximum air temperature, global solar radiation, relative humidity and wind speed were obtained from the INRA Auzeville meteorological station located close to the catchment (Climatik, 2016). Rainfall data were obtained from Meteo France: they correspond to radar C-band dual polarization data with a spatial resolution of 1 × 1 km and a temporal resolution of 5 minutes. The 5 minutes rainfall data were aggregated to daily values needed as input by the model. The daily meteorological variables used in the study cover the 2007-2013 period.

2.2.2. Soil properties

The loamy-clayey soil of the experimental site of Auzeville was selected as representative of the catchment. The soil textural characteristics such as sand, silt, clay, and organic carbon contents, bulk density and pH were measured (Table 1).

RETC (RETention Curve) (van Genuchten et al., 1991) was used to estimate the soil hydraulic parameters as required in STICS-MACRO such as the water contents at wilting point (*WILT*) and field capacity (*HCCF*), and the water retention parameters (*TPORV*: saturated water content; *XMPOR*: boundary (i.e. between macropores and micropores) water content; *RESID*: residual water content, *KSATMIN*: saturated hydraulic conductivity, and *ALPHA* and *n*: van Genuchten's soil-water retention parameters). The boundary soil water tension (CTEN) and the tortuosity/pore size distribution factor (ZN) were estimated from Beulke et al. (2002) (Table 1). The two soil parameters that were selected for the uncertainty analysis (see 2.4.1), the boundary hydraulic conductivity (*KSM*) and the diffusion pathlength (*ASCALE*), were estimated according to Steffens et al. (2013) and are shown in Table 2.

Table 1

Auzeville catchment reference soil physicochemical and hydraulic characteristics.

Soil characteristic	Depth (cm)			
	0-30	30-60	60-90	90-120
Clay (%)[a]	27.8	32.1	43.0	29.1
Silt (%)[a]	39.7	40.7	42.9	51.6
Sand (%)[a]	32.5	27.2	14.1	19.3
Organic carbon (%)[a]	0.81	0.67	0.33	0.17
pH (water)[a]	6.7	7.9	7.9	8.4
Bulk density (g cm^{-3})[a]	1.4	1.5	1.5	1.5
Soil water content at wilting point – *WILT* (m^3 m^{-3})[a]	0.10	0.12	0.13	0.13
Soil water content at field capacity – *HCCF* (m^3 m^{-3})[a]	0.19	0.18	0.18	0.15
Saturated water content – *TPORV* (m^3 m^{-3})[b]	0.43	0.41	0.44	0.41
Boundary water content – *XMPOR* (m^3 m^{-3})[b]	0.41	0.39	0.41	0.40
Residual water content – *RESID* (m^3 m^{-3})[b]	0.076	0.079	0.090	0.078
Alpha van Genuchten parameter – *ALPHA* (cm^{-1})[b]	0.0097	0.0105	0.0122	0.0079
n van Genuchten parameter – *n* (-)[b]	1.49	1.44	1.37	1.52
Saturated hydraulic conductivity – *KSATMIN* (mm h^{-1})[b]	4.25	2.33	2.13	2.52
Boundary soil water tension – *CTEN* (cm)[c]	25	30	40	25
Tortuosity/pore size distribution factor – *ZN* (-)[c]	4	4	4	4

[a] Measured

[b] Estimated with RETC (RETention Curve) (van Genuchten et al., 1991).

[c] Estimated from Beulke et al. (2002)

Table 2

Nominal and bounds values of the 9 input factors selected for the uncertainty analysis. Their distribution was assumed to be uniform. The nominal value, used for the analysis of the effects of rainfall spatial variation, was defined as a mean value of the range.

Input factors			Bentazone			S-metolachlor		
Symbol	Description	Unit	Lower bound	Nominal value	Upper bound	Lower bound	Nominal value	Upper bound
Kf[a]	Freundlich adsorption coefficient	-	1.20	1.55	1.90	0.30	2.50	4.70
nf[a]	Freundlich exponent	-	1.000	1.005	1.010	1.000	1.005	1.010
DT50[a]	Degradation half-life	days	8.0	55.0	102	7.6	22.6	37.6
dose[b]	Dose of pesticide	g ha^{-1}	750	1071	1392	1500	1711	1921
datepest[b]	Number of days from sowing to pesticide application	days	+30	+55	+80	-5	+12	+30
iplt0[c]	Date of sowing	Julian day	91	121	151	91	121	151
qres[d]	Amount of organic residues added to soil	t ha^{-1}	0	15	30	0	15	30
KSM[e]	Boundary hydraulic conductivity	mm h^{-1}	0.001	1.250	2.500	0.001	1.250	2.500
ASCALE[e]	Effective diffusion pathlength	mm	0.001	150	300	0.001	150	300

[a] From PPDB (2016) and according to the following Freundlich equation: $Qads = Kf \times Ce^{nf}$ where *Qads* (mg kg^{-1}) is amount of adsorbed herbicide in soil at equilibrium concentration, *Ce* (mg l^{-1}) is herbicide equilibrium concentration in supernatant solution, and *Kf* and *nf* are Freundlich empirical adsorption coefficients.

[b] From E-Phy (2016)

[c] From Arvalis (2012)

[d] From Ruget et al. (2002)

[e] From Steffens et al. (2013)

2.2.3. Pesticides

Two herbicides, bentazone and S-metolachlor, were selected because they are among the most used on maize crop for weed control and because they are frequently detected in groundwater (Alletto et al., 2013; Steffens et al., 2013) (Table 2). S-metolachlor is used in pre-emergence and early post-emergence. Bentazone is used in post-emergence; consequently, its interception by the crop canopy during spraying is higher than that of S-metolachlor. Sorption was assumed to be proportional to the soil organic carbon content. Degradation rates in the subsoil were corrected from those in the topsoil according to FOCUS (2000). Following the recommendations for application in France, bentazone and S-metolachlor were considered to be applied on maize at rates ranging from 0.750 to 1.392 kg ha^{-1} and from 1.500 to 1.921 kg ha^{-1}, respectively (Table 2). Bentazone was sprayed from 30 to 80 days after sowing. The earliest S-metolachlor application was done 5 days before the sowing date and the latest was done 30 days after the sowing date (Table 2).

2.3. Assessment of the effects of spatial and temporal variability of rainfall on the modelling of pesticides leaching

To assess the effects of spatial and temporal rainfall variability on the modelling of bentazone and S-metolachlor leaching, STICS-MACRO was run from 2007 to 2013, at every 1 km^2 grid of the 400 km^2 Auzeville catchment. From one grid cell to another, the rainfall time series varied while all other STICS-MACRO parameters were held constant, the uncertain parameters at their nominal values defined as mean values of the range (Table 2). The results were summarized for each year by their mean values over the catchment and their coefficients of variation (CV).

2.4. Uncertainty analysis

Following the assessment of the effects of rainfall variability on the modelling of pesticides leaching, the uncertainty analysis of STICS-MACRO combining uncertainties related to climate, agricultural practices, soil and pesticide properties was performed. To allow, within a reasonable calculation time, the characterization of the spatial variability of rainfall in the uncertainty analysis, four evenly-spaced grid cells were selected among the 400 because they exhibited different ranges of annual rainfall (Fig. 2). Combining the seven rainfall series of the four selected grid cells for every climatic year from 2007 to 2013 led to 28 rainfall series that were used to study the effects of uncertainty related to spatial and temporal rainfall variability.

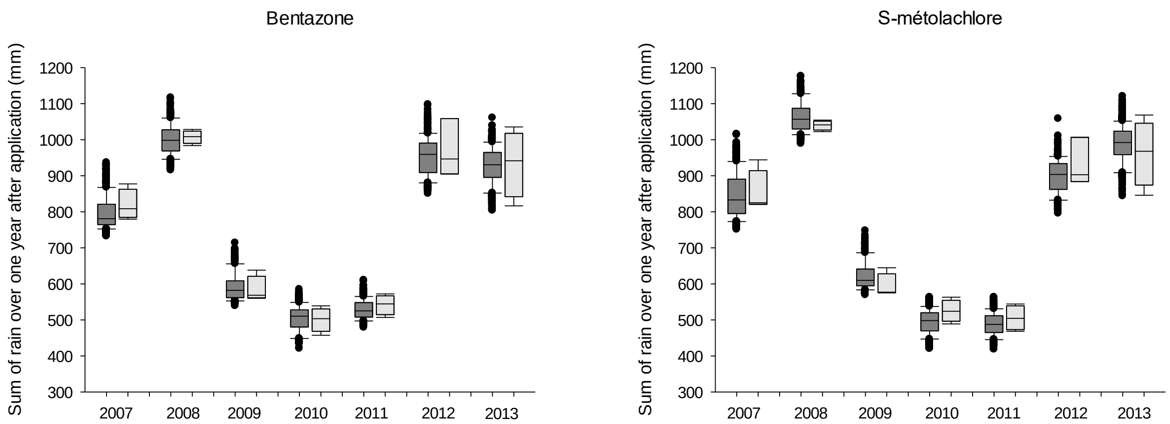

Fig. 2. Distribution of the annual precipitations during the year following pesticide applications in Auzeville catchment from 2007 to 2013. Boxplot for one year represents the variability among the whole 400 positions (■) and among the 4 positions chosen in the 20 km × 20 km area (■) and the 2000 parameters values of the Latin Hypercube Sampling (LHS), including the application date. Each year corresponds to the year the pesticide was applied. The 1-year cumulative period starts at the pesticide application date which is considered as uncertain and influences the sum of precipitation.

2.4.1. Selection of input factors

Based on the results of previous sensitivity and uncertainty analyses carried out with STICS (Ruget et al., 2002; Varella et al., 2010), MACRO (Dubus and Brown, 2002; Dubus et al., 2003b; Larsbo and Jarvis, 2005; Roulier and Jarvis, 2003) and STICS-MACRO (Lammoglia et al., 2017b), seventeen input factors were first considered. These input factors have then been analyzed with the Morris screening method (Morris, 1991) to determine those that had a strong influence on the predictions of bentazone and S-metolachlor leaching. This step avoided spending a large effort to carefully characterize factors that have little impact on the uncertainty of STICS-MACRO outputs.

Among the seventeen input factors, eight of them were found to have low or negligible impact on STICS-MACRO outputs (data not shown). On the contrary, nine input factors were identified as influential (Table 2): the sowing date (*iplt0*), the amount of organic residues added to soil (*qres*), the pesticide application date (*datepest*), the pesticide dose (*dose*), the Freundlich adsorption coefficient (*Kf*), the Freundlich exponent (*nf*), the degradation half-life (*DT50*), the boundary hydraulic conductivity (*KSM*), and the diffusion pathlength (*ASCALE*). The nominal values, the lower and upper bounds of these input factors are presented in Table 2. Their distribution was assumed to be uniform (both for the uncertainty analysis and the sensitivity analysis, see 2.5).

2.4.2. Propagation of the uncertainties of the selected input factors

Monte Carlo methods are often recommended to analyze the propagation of uncertainties through complex environmental models (Helton and Davis, 2003; Wallach et al., 2014). They are probabilistic methods based on the sampling of the output variable space. The deterministic output of the model is computed for the set of sampled inputs according to distribution functions. The model output uncertainty is defined by descriptive statistics such as mean, standard deviation and quantiles, which are computed based on the deterministic set of outputs (Helton and Davis, 2003).

To limit computational cost, we used the Latin Hypercube Sampling (LHS) scheme (McKay et al., 2000) which guarantees that full coverage by stratification over the range of each input variable is represented. First, LHS uniformly divides the range of each input variable into disjoint intervals of equal probability. Then a value from each interval is randomly selected with respect to the specific probability density function in that interval. Finally, one of the random values for each input variable is randomly chosen to form a sampling element. Previous studies have shown that, for a given sample size or number of simulation, LHS can more exhaustively explore model parameter space than simple random sampling (Helton and Davis, 2003; McKay et al., 2000).

When using Monte Carlo method, the sample size has to be carefully determined to obtain reliable results. The more samples are used, the more reliable the statistical inference will be made. On the other hand, an increase in sample size is accompanied by more computational cost which is a major limiting factor with our model. Therefore, the accuracy and the computational cost must be appropriately balanced (Helton and Davis, 2003; McKay et al., 2000). To investigate how the sample size affects the stability of the simulations and to choose the appropriate sample size for the uncertainty analysis, LHS was undertaken with several sample sizes of 100, 500, 1000, 2000 and 5000 for the S-metolachlor case-study. The relationships between the concentrations of S-metolachlor and the different sample sizes were visualized by presenting the 10th quantile, the 90th quantile and the mean annual pesticide concentration (C_{annual}) (Fig. 3a) (see 2.4.3). This relationship has also been plotted with the logarithmic transformation of the C_{annual} of S-metolachlor (Fig. 3b) (this logarithmic transformation procedure is further explained in section 2.5). Following logarithmic transformation, the sample size was found to have little influence on the 10th and 90th quantiles (Fig. 3a and b), and a sample size of 500 seemed adequate. However, without this transformation, Fig. 3a shows that even with a sample size of 5000, the results of C_{annual} were not completely stable. Consequently, in order to keep an acceptable computing cost while minimizing potential sample size effects on the concentrations of S-metolachlor, a sample size of 2000 have been used.

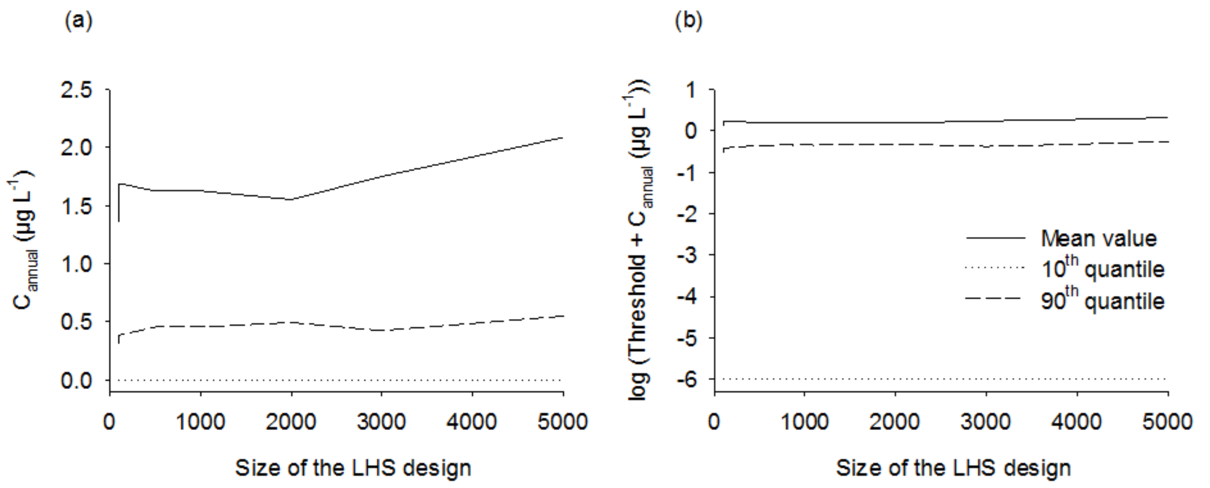

Fig. 3. Effect of the Latin Hypercube Sampling (LHS) size on the mean annual concentration of S-metolachlor (C_{annual}) (a) and on the logarithmic transformation of C_{annual} of S-metolachlor (b).

Using the ranges of variation assigned to the nine input factors (Table 2) and the 28 rainfall series (7 years × 4 positions), the Monte Carlo simulation with LHS was performed by running STICS-MACRO with 2000 as sample size for both bentazone and S-metolachlor. This design resulted in 112 000 simulations (2 pesticides × 2000 samples × 7 years × 4 positions) which needed 25 days calculation (parallel computing on a quad core Xeon® processor at 3.06 GHz).

2.4.3. Outputs

The effects of the uncertainties were assessed on the following two outputs of STICS-MACRO, for each grid cell: (i) the arithmetic mean annual concentration of pesticide leached at 1 m depth C_{annual} (µg L^{-1}), i.e. occurring during one year starting at the pesticide application date, named here as "annual concentration"; (ii) the maximum daily pesticide concentration at 1 m depth over one year period C_{max} (µg L^{-1}), starting at the pesticide application date:

$$C_{annual} = \frac{1}{365} \sum_{n=1}^{365} \frac{M_n}{V_n} \quad (1)$$

$$C_{max} = max \left\{ \frac{M_1}{V_1}, \ldots, \frac{M_{365}}{V_{365}} \right\} \quad (2)$$

where n is the day after the pesticide application date, V_n ($V_1 \ldots V_{365}$) is the volume of percolated water on the day n (on day 1…365) (L), and M_n ($M_1 \ldots M_{365}$) is the mass of leached pesticide on the day n (on day 1…365) (µg).

Then, the arithmetic mean of the C_{annual}, the 10th percentile and the 90th percentile of the distribution for all combinations of the 7 years, 4 spatial positions and 2000 parameters of LHS design were calculated.

Each of the seven selected climatic years was simulated independently from the others to study the effect of climate on pesticide leaching. Consequently, there is no residual amount of pesticide from the previous year in one simulation.

2.5. Sensitivity analysis

Once the uncertainties in STICS-MACRO outputs have been quantified, a sensitivity analysis has to be done to identify the input factors that contribute the most to uncertainties in the outputs. There are several sensitivity analysis methods that can be used and Wallach et al. (2014) recommend to implement several methods and to compare their results.

The 112 000 simulations performed for the uncertainty analysis produced a high number of input-output pairs. Therefore, due to the high computational cost of STICS-MACRO, the sensitivity analysis explored those input-output pairs instead of running again STICS-MACRO with another sampling.

First, the Pearson product moment correlation (PEAR) coefficients were determined for the nine input factors. The PEAR coefficient measures the degree of linear association between the variations of STICS-MACRO output (the C_{annual} was retained for these calculations) and the variation of the studied input factors. A correlation close to +1 or -1 indicates a strong influence of the input factor on pesticide concentrations while a correlation close to zero indicates that the input factor is not influential (Wallach et al., 2014). The PEAR coefficients were determined from the logarithmic transformation of concentrations (see below).

Then, we built and used a meta-model of STICS-MACRO. A meta-model consists in a mathematical function built from a set of simulations of the original model over the domain of variation of the input factor. This approach has already been used in environmental modelling, permitting to apply powerful sensitivity methods (Faivre et al., 2013; Uusitalo, 2015). Linear regression is the most commonly used method for meta-model construction because of its simplicity, however it performs better when the relationship between inputs and outputs is approximately linear (Storlie et al., 2009). Therefore, we built the meta-model on the logarithmic transformation of the outputs to take into account low concentration values of bentazone and S-metolachlor using the linear regression function "*lm*" and the stepwise procedure "*step*" implemented in the R statistical software (R Development Core Team, 2016). We used the log(threshold+X) transformation, where X is C_{annual} or C_{max} of bentazone and S-metolachlor as predicted by STICS-MACRO. The value of the threshold was set to 10^{-6} as a compromise to give weight to low concentrations, but not too much weight to very low values. The nine quantitative input factors presented in Table 2 were considered as quantitative variables, and the seven climatic years (*year*) and the four spatial positions (*pos*) of the selected meteorological data were considered as qualitative input factors. We limited the model to the interactions of order 2. Thus, sensitivity indices were computed using ANOVA method which assesses the main contribution of each input factor to the total variance of the model outputs as well as the interactions between factors (Wallach et al., 2017).

The performance of the meta-model was assessed performing new simulations with STICS-MACRO and with the meta-model with a new and independent LHS sample of size 100. Two statistical indices were calculated to assess this performance, the efficiency (*EF*) and the bias (*B*):

$$EF = 1 - \frac{\sum_{i=1}^{n}(S_i - O_i)^2}{\sum_{i=1}^{n}(O_i - O_m)^2} \qquad (3)$$

$$B = \frac{\sum_{i=1}^{n}(S_i - O_i)}{\sum_{i=1}^{n}(O_i)} \qquad (4)$$

where S_i is the concentrations simulated by the meta-model; O_i is the concentrations simulated by STICS-MACRO; O_m is the mean of the simulations of STICS-MACRO; and n is the number of simulations. *EF* ranges from $-\infty$ to 1, with $EF = 1$ indicating a perfect match between STICS-MACRO and the meta-model. When the bias $B = 0$, it indicates a perfect match; if $B > 0$, it indicates an overestimation by the meta-model, while $B < 0$ indicates an underestimation by the meta-model.

3. Results and Discussion

3.1. Effects of the spatial and temporal variability of rainfall on the modelling of pesticides leaching

The total annual amounts of rainfall on the period of one year after pesticide application were highly variable among the seven years with a mean value (averaged over the 400 km² area) ranging from 504 mm in 2010 to 1000 mm in 2008 for bentazone, and from 488 mm in 2011 to 1062 mm in 2008 for S-metolachlor (Fig. 4, Table 3). These values are different from one pesticide to another because they are considered from the pesticide application date. The coefficients of spatial variation (CV) of annual rainfall ranged from 4.1% in 2008 to 6.9% in 2010 for bentazone, and from 3.9% in 2008 to 7.4% in 2007 for S-metolachlor (Table 3). The largest annual rainfall occurred in 2008 corresponding to the lowest variability over the catchment (CV = 4.1 and 3.9% for bentazone and S-metolachlor, respectively) (Table 3).

Table 3

Mean annual rainfall from 2007 to 2013, and coefficients of variation (CV) over the Auzeville catchment for total mean annual rainfall and mean annual concentrations (C_{annual}) of bentazone and S-metolachlor. Each value is calculated on one year period starting from the pesticide application date.

Pesticide		2007	2008	2009	2010	2011	2012	2013
Bentazone	Mean annual rainfall (mm)	798	1000	592	504	529	953	927
	CV annual rainfall (%)	5.7	4.1	6.4	6.9	4.9	5.6	5.6
	CV C_{annual} (%)	306	98	663	266	544	194	164
S-metolachlor	Mean annual rainfall (mm)	846	1062	622	495	488	898	988
	CV annual rainfall (%)	7.4	3.9	6.2	6.8	6.5	5.2	5.2
	CV C_{annual} (%)	199	68	347	140	207	95	78

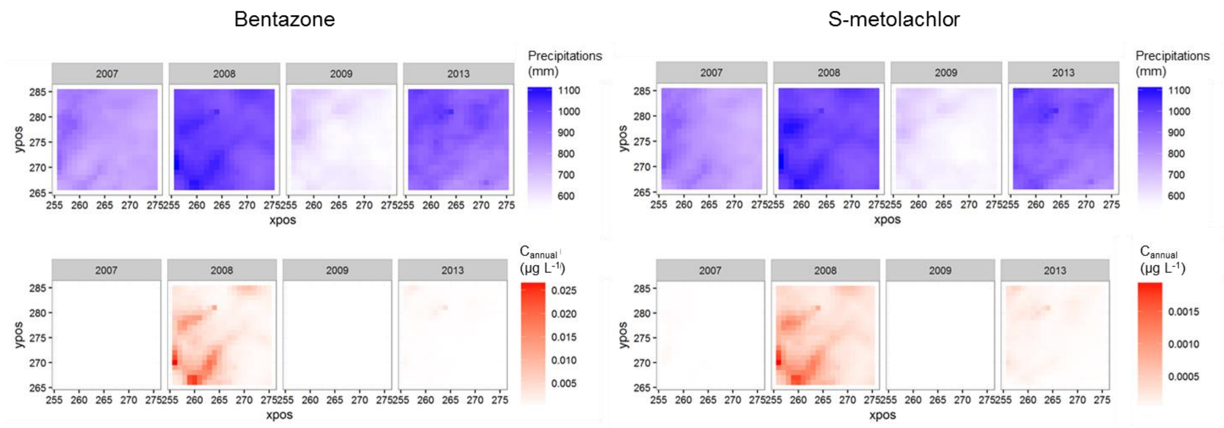

Fig. 4. Spatial variability of annual rainfall (a) and mean annual concentration (b) of bentazone and S-metolachlor for 4 contrasted years (2007, 2008, 2009, 2013) in the Auzeville catchment. *Precipitations*: Total annual amount of rainfall (mm), C_{annual}: Mean annual concentrations of bentazone and S-metolachlor (µg L^{-1}), *xpos* and *ypos*: Spatial positions.

For both bentazone and S-metolachlor, the influence of the spatial and temporal rainfall variabilities was analyzed by running STICS-MACRO at each of the 400 grid cells, from 2007 to 2013, while all other parameters were held constant.

Very large differences were found between the simulated annual concentrations (C_{annual}) of bentazone and S-metolachlor at 1 m depth (Fig. 4). The effects of rainfall uncertainty on the leaching of bentazone and S-metolachlor were also found to be amplified through the STICS-MACRO model. The CV of the C_{annual} of bentazone and S-metolachlor were considerably larger than the corresponding ones for rainfall: from 98 to 663% for bentazone, and from 68 to 347% for S-metolachlor (Table 3). The biggest variations in the C_{annual} of bentazone and S-metolachlor occurred in 2009 when annual rainfalls were low whereas the smallest variations occurred in 2008 when rainfalls were maximal (Table 3). Therefore, assuming a linear transfer of rainfall variability through the STICS-MACRO model would have led to underestimation of the concentrations of bentazone and S-metolachlor.

Bentazone is more mobile and more persistent than S-metolachlor (Table 2) so, as expected, its maximal concentrations C_{max} were higher than those of S-metolachlor (Boesten and van der Linden, 1991) (Fig. 5). In general, the spatial variation of the concentrations of bentazone was also 2 times higher than that of S-metolachlor (Table 3).

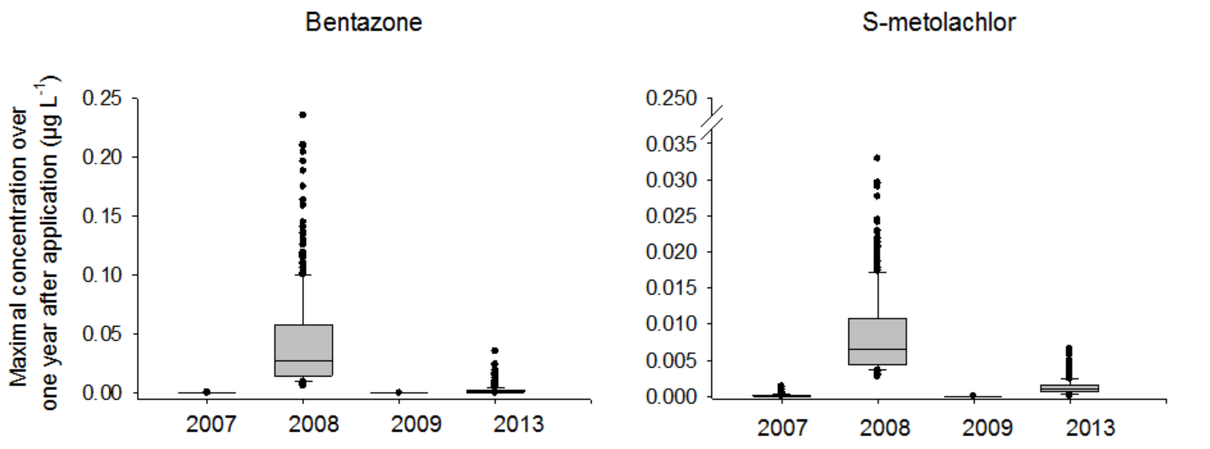

Fig. 5. Maximal concentrations (C_{max}) of bentazone and S-metolachlor simulated at each of the 400 grid cells of the 400 km² Auzeville catchment for four contrasted climatic years.

Finally, a significant positive correlation was found between the annual rainfall amounts and the logarithmic transformation of the concentrations of both bentazone and S-metolachlor at 1 m depth (r^2 = 0.63 and 0.45, respectively), meaning that pesticide leaching increases exponentially with annual rainfall. This is consistent with many results showing that pesticide leaching increases with increasing annual rainfall amounts (e.g. Tiktak et al., 2004).

Overall, this assessment of the influence of rainfall variability on leaching prediction reveals the non-linear effects of annual rainfall on the concentrations of both herbicides, and the importance of taking into account the uncertainties related to spatial and temporal variability of annual rainfall for the estimation of pesticides concentrations in groundwater.

3.2. Uncertainty analysis

The results of the 112 000 simulations led to annual concentration (C_{annual}) at 1 m depth, ranging, over the seven years of simulation, from 0 to 570 µg L^{-1} for bentazone and from 0 to 750 µg L^{-1} for S-metolachlor, while the maximum concentrations (C_{max}) were found to range from 0 to 2.0 10^5 µg L^{-1} for bentazone and from 0 to 2.5 10^5 µg $L^{-1}$for S-metolachlor (any value below the threshold of 10^{-6} has been considered as 0). For the 2007-2013 simulated period, the average C_{annual} of bentazone was 0.287 µg L^{-1} and was lower than that of S-metolachlor of 1.55 µg L^{-1}, and the corresponding median values were 5.5 10^{-7} µg L^{-1} for bentazone and 3.3 10^{-6} µg L^{-1} for S-metolachlor (Table 4). The average C_{max} were high, 16.6 µg L^{-1} for bentazone and 65.2 µg L^{-1} for S-metolachlor, while the median values were lower: 1.0 10^{-5} µg L^{-1} and 5.7 10^{-5} µg L^{-1}, respectively (Table 4).

The logarithmic transformation of concentrations was found to be suitable to represent the distribution of the concentrations of bentazone and S-metolachlor (Fig. 6). It is of importance for meta-model building (see 3.3.2) and it avoids to give too much weight to values less than this threshold and thus to improve the quality of prediction for higher values. The concentrations of both bentazone and S-metolachlor were strongly skewed and did not fit any standard distribution (Fig. 6), among other things because of numerous null or quasi-null concentrations. The results predicted with 80% confidence that the C_{annual} of bentazone would be between 0 and 0.035 µg L^{-1}, and that the C_{annual} of S-metolachlor would be between 0 and 0.414 µg L^{-1} (Table 4). However, the means of the distributions of the C_{annual} of bentazone and S-metolachlor are superior to the 90th percentile (Table 4), reflecting the sensitivity of the arithmetic mean to extreme values (here high concentrations). This result comes from a very non-linear response of the model on the variable of concentration. If the number of low concentrations is 10 times that of high concentrations, then the mean values are greater than the 90th percentile. It emphasizes the difficulty to estimate precisely extreme quantiles and even the simple mean with such models who require high computational time. To go further, it may be interesting to consider the existing correlations within the input factors, but it arises lots of questions on how to qualify these correlations which are poorly documented in the scientific literature and technical databases. Finally, these results mean that there is high probabilities that STICS-

MACRO simulates concentrations lower than the mean of the distribution which will have some consequences on risk assessment because of underestimation of the average leached concentrations of pesticides.

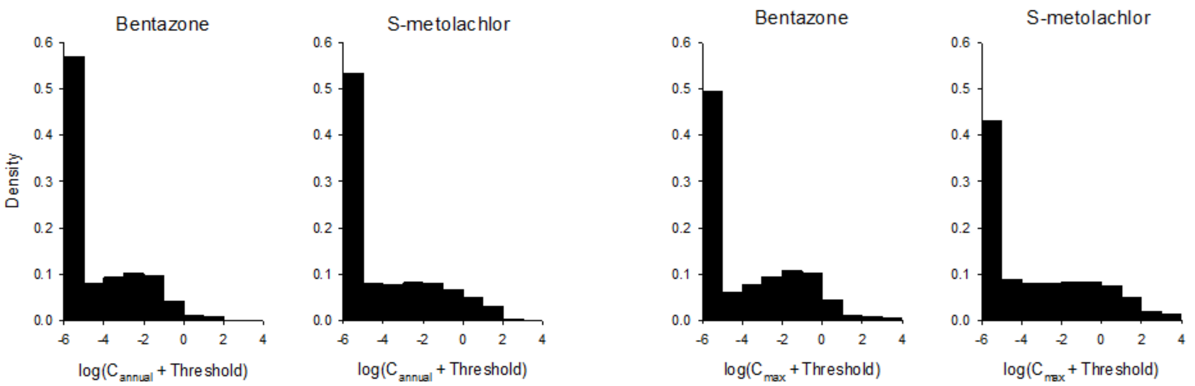

Fig. 6. Distribution of the mean annual concentrations of bentazone and S-metolachlor (C_{annual}) and of maximum daily concentrations of bentazone and S-metolachlor over one year period (C_{max}) for all the combination of the 7 years, the 4 spatial positions and the 2000 parameters of the Latin Hypercube Sampling design. Threshold: 10^{-6} µg L^{-1}.

Table 4

Statistical parameters for mean annual concentrations (C_{annual}) and maximum daily concentrations (C_{max}) of bentazone and S-metolachlor over one year period in the Auzeville catchment. These statistical parameters describe the distribution obtained after running STICS-MACRO during 7 independent years (2007 to 2013), at 4 spatial positions, and sampling size of 2000 with the Latin Hypercube Sampling method. CV: Coefficient of variation; SD: Standard deviation; q10: 10th quantile; q90: 90th quantile.

Pesticide	STICS-MACRO output	Mean (µg L^{-1})	Median (µg L^{-1})	SD (µg L^{-1})	CV (%)	q10 (µg L^{-1})	q90 (µg L^{-1})
Bentazone	C_{annual}	0.287	5.500 10^{-7}	4.270	14.9	2.200 10^{-18}	0.035
	C_{max}	16.6	1.000 10^{-5}	898	54.2	7.470 10^{-17}	0.414
S-metolachlor	C_{annual}	1.550	3.300 10^{-6}	10.8	6.960	5.170 10^{-13}	0.494
	C_{max}	65.2	5.700 10^{-5}	1820	27.8	1.050 10^{-11}	4.920

Finally, it was shown that the predicted annual concentrations of bentazone and S-metolachlor could exceed the regulatory threshold of 0.1 µg L^{-1} at 1 m depth (FOCUS, 2000; Commission Regulation (EU) 546/2011, 2011) in 6% and 15% of the situations, respectively. Considering their maximal concentrations during the first one year following application, bentazone and S-metolachlor could exceed this regulatory threshold in 17% and 24% of the situations, respectively.

3.3. Contribution of the different sources of uncertainty

3.3.1. Correlation-based sensitivity analysis

The PEAR coefficients were calculated to identify the correlations between C_{annual} of pesticides and the 9 input factors, using the 112 000 LHS Monte Carlo simulations. They were computed on the logarithmic values of the concentrations.

The mean values of the PEAR coefficients and the sensitivity ranking were different for bentazone and S-metolachlor, and they varied from one climatic scenario to another (Table 5). For both pesticides, the Freundlich adsorption coefficient *Kf* and the boundary hydraulic conductivity *KSM* were found to be very influential, with a stronger influence of *Kf* for the pre-emergence herbicide S-metolachlor (Table 5). An increase in the values of *Kf* and *KSM* decreased the concentrations of both bentazone and S-metolachlor which is consistent with the findings of Dubus and Brown (2002), and may reflect the fact that the higher *KSM*, the less frequently preferential flow is triggered. However, *KSM* was found more important for the post-emergence herbicide bentazone, though preferential flow and related factors (*KSM*) are known to be more important in determining the leaching of more strongly sorbed pesticides (Dubus and Brown, 2002; Larsson and Jarvis, 2000). A possible explanation might be that a larger *KSM* values induces a relatively faster bulk transport in the soil matrix of mobile compounds such as bentazone. The degradation half-life *DT50* was also influential, and an increase in the values of *DT50* increased the concentrations of both bentazone and S-metolachlor. However, an increase in *DT50* could also lead to a decrease in the concentrations of bentazone, depending on the climatic conditions (Table 5). The influence of the effective diffusion pathlength *ASCALE* on the concentrations of bentazone also seemed to be climate dependant, while this was not observed for S-metolachlor (Table 5).

The other PEAR coefficients were low, but they may show that the crop management factor *qres* (amount of organic residues added to soil) could be more influent than the pesticide application date (*datepest*) and dose (*dose*) (Table 5). For both bentazone and S-metolachlor, an increase in the values of *qres* increased the concentrations, in agreement with the findings of Lammoglia et al. (2017b). Nevertheless, the *qres* and *datepest* factors could have more influence on the concentrations of bentazone than those of S-metolachlor, and their influence could be increased by the climatic conditions. These differences between the ranking of bentazone and S-metolachlor can be explained by the interception of bentazone by the crop canopy as the application date of bentazone was 43 days later than that of S-metolachlor (Table 2). This effect seems to be reinforced with lower annual rainfall.

Table 5

Pearson Product Moment Correlation coefficient (PEAR) between input factors and the mean annual concentration (C_{annual}) averaged over the 28 climate scenarios (Mean) and ordered by decreasing importance for bentazone and S-metolachlor. The ranges of the PEAR coefficients (Range) were obtained amongst climate scenarios. The PEAR values were computed on the logarithmic values of the C_{annual} of bentazone and S-metolachlor for each climate scenarios (7 years × 4 spatial positions).

Bentazone			S-metolachlor		
Input factor (Unit)	Mean	Range	Input factor (Unit)	Mean	Range
KSM (mm h^{-1})	-0.4740	[-0.6770 ; -0.2750]	*Kf* (-)	-0.5670	[-0.7970 ; -0.1830]
Kf (-)	-0.2460	[-0.6000 ; -0.0042]	*KSM* (mm h^{-1})	-0.3530	[-0.4980 ; -0.2520]
DT50 (days)	0.1480	[-0.0217 ; 0.4160]	*DT50* (days)	0.1230	[0.0263 ; 0.2290]
nf (-)	0.0761	[0.0276 ; 0.1330]	*nf* (-)	0.0672	[0.0393 ; 0.0962]
ASCALE (mm)	0.0578	[-0.0040 ; 0.1200]	*ASCALE* (mm)	0.0612	[0.0392 ; 0.1060]
qres (t ha^{-1})	0.0422	[0.0038 ; 0.0653]	*iplt0* (Julian day)	-0.0299	[-0.1970 ; 0.0597]
datepest (days)	-0.0360	[-0.1230 ; 0.0174]	*qres* (t ha^{-1})	0.0272	[0.0100 ; 0.0627]
iplt0 (Julian day)	-0.0119	[-0.1140 ; 0.0419]	*datepest* (days)	-0.0144	[-0.0903 ; 0.0503]
dose (g ha^{-1})	0.0085	[-0.0248 ; 0.0486]	*dose* (g ha^{-1})	-0.0112	[-0.0282 ; 0.0028]

KSM: Boundary hydraulic conductivity; *Kf*: Freundlich adsorption coefficient; *DT50*: Degradation half-life; *nf*: Freundlich exponent; *ASCALE*: Effective diffusion pathlength; *qres*: Amount of organic residues added to soil; *datepest*: Days from sowing to pesticide application; *iplt0*: Sowing date; *dose*: Dose of application.

3.3.2. Quantitative meta-model-based sensitivity analysis

Based on the logarithmic transformations of the predicted concentrations of bentazone and S-metolachlor, a meta-model of STICS-MACRO was built. The quality of the prediction of this meta-model was evaluated on an independent LHS sample of size 100 (Fig. 7). For bentazone, the stepwise procedure selected a model with 129 parameters (instead of 154 parameters with the complete model) and an adjusted r^2 of 0.88. The quality of the prediction was quite satisfying with an efficiency *EF* of 0.66 and a bias *B* of 0.015. For S-metolachlor, the stepwise procedure selected a model with 124 parameters (instead of 154) and an adjusted r^2 of 0.84. The quality of the prediction was also satisfactory with $EF = 0.64$ and $B = -0.008$. For both bentazone and S-metolachlor, the meta-model underestimated the annual concentrations (C_{annual}) for some dry years (for years 2009, 2010, 2011) (Fig. 7, Table 3).

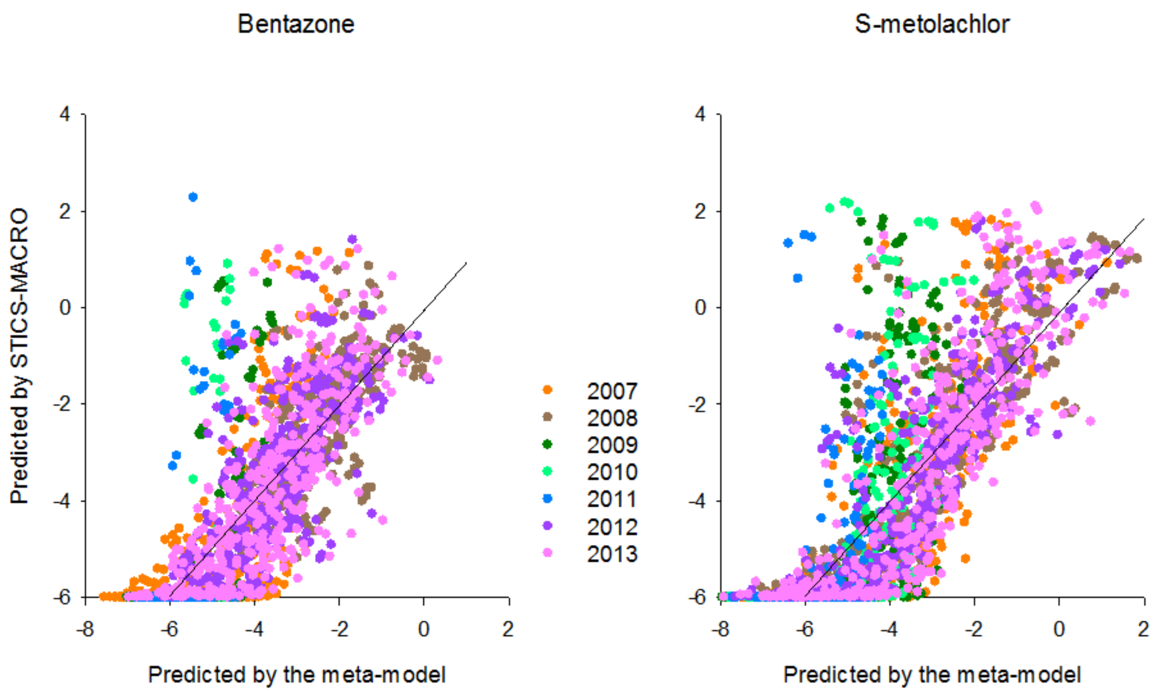

Fig. 7. Comparison of the mean annual concentrations (C_{annual}) (µg L^{-1}) of bentazone and S-metolachlor predicted by STICS-MACRO and its meta-model.

The ANOVA, computed on these meta-models, explained 81% and 80% of the total variability of the concentrations of bentazone and S-metolachlor, respectively (Fig. 8). The total amount of annual rainfall (*year*), the *Kf* and the *KSM* were the three most influencing factors for modelling of the concentrations of both bentazone and S-metolachlor with STICS-MACRO. For the weakly sorbed herbicide bentazone, the annual rainfall (*year*) was the most influential factor, it explained 49% of the total variability of the concentrations of bentazone (Fig. 8). However, the annual rainfall only explained 27% of the total variability of the concentrations of S-metolachlor while the *Kf* explained 34% (Fig. 8). The effects of the *Kf* were less important for the leaching of bentazone (7.3%).

The three most influent factors (*year*, *KSM*, *Kf*) are followed by the *DT50* and the rainfall spatial variability (*pos*) (Fig. 8). The rainfall spatial variability (*pos*) contributed to the variability of the predicted concentrations more than the pesticide properties (*nf*), the crop management properties (*qres*, *iplt0*, *dose*, *datepest*), and the soil property (*ASCALE*). These results agree with those of Steffens et al. (2014) who indicated that uncertainty in model parameters was less important for the prediction of pesticide leaching than climate uncertainty.

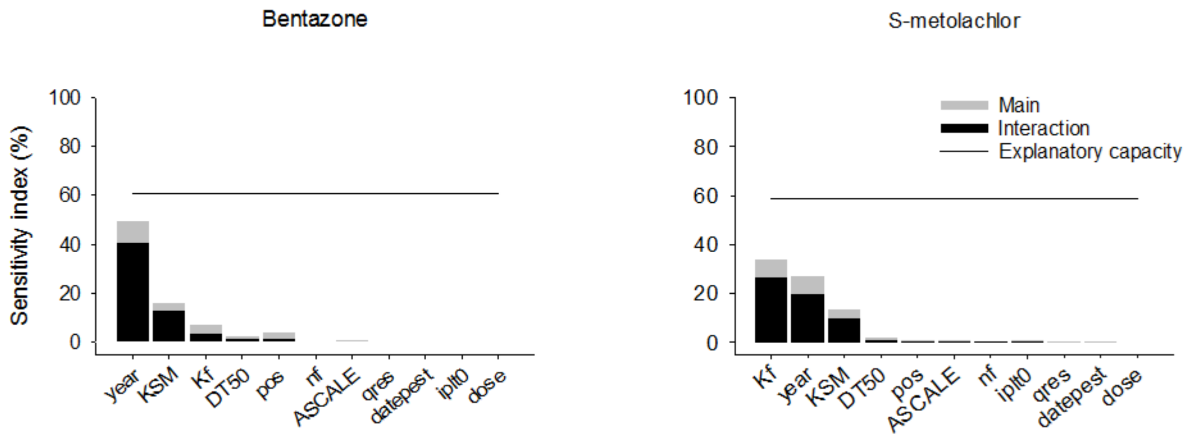

Fig. 8. Main effects and interaction effects on the concentration of bentazone and S-metolachlor calculated for each factor with the ANOVA method based on the meta-model. The horizontal lines represent the explanatory capacity of the meta-model. *year*: Climatic year (7 contrasted years); *KSM*: Boundary hydraulic conductivity (mm h^{-1}); *Kf*: Freundlich adsorption coefficient (-); *DT50*: Degradation half-life (days); *pos*: Spatial position (4 positions); *nf*: Freundlich exponent (-); *ASCALE*: Effective diffusion pathlength (mm); *qres*: Amount of organic residues added to soil (t ha^{-1}); *datepest*: Days from sowing to pesticide application (days); *iplt0*: Crop sowing day (Julian day); *dose*: Dose of pesticide application g ha^{-1}).

The qualitative and quantitative sensitivity analysis methods led to the same conclusions except that, for S-metolachlor, the PEAR coefficient emphasized higher influence of the Freundlich exponent *nf* than of *ASCALE* contrary to the results obtained with the meta-model (Table 5, Fig. 8). In line with the results obtained for the PEAR coefficients (Table 5), the *KSM* had higher influence on the variability of the concentrations of bentazone than of S-metolachlor: 16% and 13%, respectively.

The interactions between the factors were found to be important between annual rainfall (*year*), and pesticide properties (*Kf*) and soil properties (*KSM*) (Fig. 8). The interactions effect were very small for the crop management properties (*qres*, *iplt0*, *dose*, *datepest*) despite previous studies found interaction effects between climate variables, pesticide application scenarios and pesticide use (Steffens et al., 2014; Steffens et al., 2015).

Since the sum of the total effects is high (81% for bentazone and 80% for S-metolachlor), the input factors have major additive effects on the logarithmic values of the concentrations of bentazone and S-metolachlor. This indicates that STICS-MACRO behaved as an additive model with important parameter interactions when the predicted concentrations are logarithmically transformed. However, it is worth remembering that the results of this study only stand in the bounds defined for each input factor and are specific to the soil-crop conditions and the climate characteristics of the catchment assessed.

5. Conclusion

The objective of this work was to study the effects of the uncertainties related to climate, agricultural practices, soil and pesticide properties on the prediction of pesticides leaching with STICS-MACRO. First, the effect of spatial and temporal rainfall variability on mean annual pesticides concentrations was assessed. The interactions between the concentrations of bentazone and S-metolachlor and the annual rainfall were shown to be non-linear, and the variability of the concentrations was higher than that in the annual rainfall amounts (spatial coefficients of variation of annual rainfall ranging from 4 to 7% produced 68 to 663% of variation in the concentrations). These results suggest that the spatial and temporal heterogeneity are paramount when defining representative rainfall data for pesticide leaching prediction. Then, using a Monte Carlo method with Latin Hypercube Sampling, the uncertainties of input factors related to climate, agricultural practices, and soil and pesticide properties were propagated through STICS-MACRO. There was a high probability of predicting concentrations of both bentazone and S-metolachlor lower than the means of their respective distributions because the distributions of their concentrations were strongly skewed and showed mean values superior to the 90^{th} percentile. This has to be considered in risk assessment because of the probable underestimation of the average leached concentrations of pesticides. Even if bentazone is more mobile and persistent than S-metolachlor, there are half less risks that the annual concentrations of bentazone exceed the regulatory threshold of 0.1 µg L^{-1} because of higher interception of bentazone than of S-metolachlor by crop canopy. Then a sensitivity analysis was done based on the Pearson coefficient and on the ANOVA method using a meta-model of STICS-MACRO. The climate temporal variability, the Freundlich adsorption coefficient and the boundary hydraulic conductivity, followed by the degradation half-life and the rainfall spatial variability have been identified by both sensitivity analysis methods as the main input factors involved in the uncertainties in the prediction of the leaching of bentazone and S-metolachlor. The leaching of S-metolachlor used in pre-emergence and early post-emergence was mostly affected by the parameter related to adsorption. Factors related to agricultural practices were most influential on the leaching of the post-emergence pesticide, bentazone. STICS-MACRO also showed non-linear but additive effects on the logarithmic values of the concentrations of bentazone and S-metolachlor. These results depend on the specific soil-crop-climate characteristics considered. Nevertheless, they confirm the strong effects of the uncertainties in climate, pesticide, soil and agricultural practices input factors on the uncertainties in the prediction of pesticides leaching. Extending this uncertainty analysis to other crops, soil types, and different catchment scale will provide additional guidance and information that should be taken into account when using the STICS-MACRO model to predict pesticides leaching in innovative cropping systems. This identification is a valuable indication for model users which may choose to fix little relevant parameters to their nominal values while focusing efforts on measuring the parameters that have shown the strongest impact.

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