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A Markov Chain Monte Carlo technique for parameter estimation and inference in pesticide fate and transport modeling

Julien Boulange*, Hirozumi Watanabe, Shinpei Akai

Tokyo University of Agriculture and Technology, Tokyo, Japan

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ABSTRACT

A Bayesian method involving Markov Chain Monte Carlo (MCMC) technique was implemented into a pesticide fate and transport model to estimate the best input parameter ranges while considering uncertainties included in both the observed pesticide concentrations and in the model.

The methodology used for integrating the MCMC technique into a pollutant fate and transport models was detailed. The uncertainties encompassed in the dissolution rate and in the adsorption coefficient of the herbicide mefenacet were greatly reduced by the MCMC simulations. In addition, an optimal set of input parameters extracted from the MCMC simulations accurately reproduced mefenacet concentrations in paddy water and paddy soil as compared to the original published dataset. Consequently, by simultaneously optimizing multiple parameters of environmental models and conducting uncertainty analysis, MCMC technique exhibits powerful capability for improving the reliability and accuracy of computer models.

The main strengths of the MCMC methodology are: (1) the consideration of uncertainties from both input parameters and observations and (2) the prior distributions of the input parameters which can be reformulate when additional knowledge is available.

1. Introduction

The contamination of water bodies as a result of pesticide used in agricultural fields, including rice paddies, was indicated in the literature (Iwafune et al., 2010). While monitoring is crucial to identify vulnerable areas to prioritize mitigation measures, it is costly and tedious. Simulation models are useful tools that, once validated, can help decision makers. Indeed, providing continuous information through simulation model and forecast assessments is a mandatory step for the registration of pesticide in Europe and in the U.S. (ter Horst et al., 2013). However, a major difficulty in predicting accurate pesticide concentrations arises from the uncertainties incorporated in the input parameters of computer models and in the observed or monitored datasets. A number of factors contribute to the uncertainty of forecasts, including parameter uncertainty, spatial variability, conceptual uncertainty, and boundary uncertainty (Görlitz et al., 2011; Hassan et al., 2009). In addition, since some processes involved in pesticide fate and transport are simplified or ignored by some computer models, the parameters related to such processes cannot be gather through direct measurements in the field, but can only be derived using a calibration procedure (Gallagher and Doherty, 2007; Vrugt et al., 2013). The effects of uncertainty on the predictions of a computer model are usually considered using analytical or numerical tools that spreads the uncertainty's attributes from the inputs to the final outputs of the model. A representative quantification of parameter's uncertainty remains nonetheless a challenge during the calibration and validation phases.

Model performance is typically quantitatively reported using statistical indices, such as the goodness of fit (R^2), which can be maximized by manual or automatic adjustments of the input parameters of the model (Hassan et al., 2009). Most optimization methods are however limited since they do not: (1) estimate the significance of the so-called optimal parameter set and (2) realistically quantify the uncertainty encompassed in the model (Kanso et al., 2006). Thus, it is arguable whether the so-called "optimized" input parameters established during the calibration of a model are appropriate. Indeed, due to non-uniqueness problems, two very different set of input parameters can often produce similar responses of the model (Abbaspour, 2015).

Markov Chain Monte Carlo (MCMC) techniques provide a captivating methodology to conduct the optimization of models while considering uncertainty encompassed in both input parameters and observations. However due their relative complexity, these

* Corresponding author.
E-mail address: boulange.julien@gmail.com (J. Boulange).

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techniques have not yet been demonstrated in a pesticide fate and transport context. Thus, the aim of this research was to implement MCMC techniques to a rice pesticide fate and transport model, the PCPF-1 model. Specific objectives were defined as: (1) implement a MCMC algorithm (Metropolis-Hasting) into the PCPF-1 model, (2) develop the methodology to analyze the outputs of the MCMC simulation, and (3) validate the method by comparing the concentrations of the herbicide mefenacet predicted by the PCPF-1 model using the original validated dataset and the concentrations predicted using the optimized dataset generated through the MCMC output analysis.

2. Materials and method

2.1. PCPF-1 model

The PCPF-1 is a deterministic pesticide fate and transport model used to forecast pesticide concentrations in paddy water (PW) and in 1 cm deep paddy soil layer (PSL) (Watanabe and Takagi, 2000b; Watanabe et al., 2006). The model considers the transport of pesticide with paddy water (through irrigation, percolation, surface runoff and drainage) and the fate of pesticide by computing various degradation, desorption, dilution and dissolution processes. The best management practices for reducing pesticide discharge from paddy fields were identified by analyzing the model forecasts (Phong et al., 2011). The model is currently validated with six herbicides in Japan (Boulange et al., 2015; Takagi et al., 2012; Watanabe and Takagi, 2000a; Watanabe et al., 2006) and is pertinent for rice paddies in Europe (Karpouzas et al., 2006) and in California, USA (Luo et al., 2011). The inputs of the model consist of over 40 parameters which can be categorized into (1) climatic parameter, (2) water balance parameters, (3) soil parameters and (4) pesticides characteristics. A sensitivity and uncertainty analysis of the model stated that the accuracy of the forecasted pesticide concentrations in PW and PSL are extremely dependent on the accuracy of the input parameters (Boulange et al., 2012; Kondo et al., 2012). While improving the accuracy of some input parameters can be achieved with better experimental designs and a re-parametrization of the model, in most instances, the simulations need to be conducted using available data due to cost and time considerations (Malve et al., 2005). Four input parameters were included in the MCMC framework: the pesticide dissolution rate (k_{diss}), the first-order degradation rate of the pesticide in paddy soil (k_{bio}), the desorption rate of the pesticide (k_{des}), and the pesticide partitioning coefficient (k_d). All these parameters were reported to significantly impact the accuracy of the predicted pesticide concentrations (Boulange et al., 2012). A similar approach was adopted by Iizumi et al. (2009) who removed from the optimization process the most robust (certain) parameters even though some of them were empirical.

2.2. Bayesian inference

Bayesian inference prolong the use of probability theory by representing the uncertainty of a system (Malve et al., 2005; Reichert and Omlin, 1997). In a modeling application context, Bayesian inference is applied to estimate the values of θ unknown parameters of a model about which some prior information may be available (Gallagher and Doherty, 2007; Harmon and Challenor, 1997; Qian et al., 2003; Van Oijen et al., 2005). Using Bayesian inference, parameter uncertainty can be realistically implemented as the methodology distinguishes two sources of information for learning about unknown parameters: (1) pre-existing knowledge about parameters of a model, and (2) data collected via experimentation and observation (Bates and Campbell, 2001; Campbell et al., 1999; Hassan et al., 2009).

The prior probability distributions of the θ parameters are then updated to a new, posterior distributions, using the data collected via experimentations and observations (Hartig et al., 2011; Reichert and Omlin, 1997). The updating process is based on Bayes' theorem (Bayes, 1763):

$$P(\theta|d) = \frac{P(\theta)\cdot P(d|\theta)}{\int_{\theta} P(\theta)\cdot P(d|\theta)\cdot d\theta} \propto P(\theta)\cdot P(d|\theta) \quad (1)$$

where $P(\theta|d)$ is the posterior probability density of p model parameters $\theta = (\theta_1, \theta_2 \ldots \theta_p)$ given additional data $d = (d_1, d_2 \ldots d_n)$. $P(\theta)$ is the prior probability density of θ and captures all available knowledge about θ (Campbell et al., 1999; Paulo et al., 2005). $P(d|\theta)$ is the conditional probability density for the measured data d given the parameters θ. It is often referred to as the likelihood function and incorporates the statistical as well as the mechanistic relationships among the predictors and variables (Liu et al., 2008).

Typically, it is difficult to analytically summarize the posterior distributions which limits the practical implementation of Bayesian inference. However, an alternative approach is to use a Markov Chain Monte Carlo (MCMC) algorithm to obtain the numerical summarization of the posterior distribution (Liu et al., 2008). The process of collecting data, and thus acquiring knowledge about θ, is typically reflected in a reduction of uncertainty so that the posterior density will be more concentrated, more informative, than the prior density (Campbell et al., 1999).

2.3. Markov Chain Monte Carlo (MCMC) method

Bayesian inference often produce a posterior probability function that is difficult to compute using conventional numerical methods (Bates and Campbell, 2001). MCMC provides a general methodology of computing the posterior without having to perform integration over it (Harmon and Challenor, 1997; Qian et al., 2003). By generating a large enough sample from the posterior distribution, $P(\theta|d)$, any desired features (expectation value, median or maximum of the distribution) of the posterior distribution may be accurately summarized (Campbell et al., 1999; Chib and Greenberg, 1995; Hassan et al., 2009; Luke, 1994). Monte Carlo Markov Chain sampling methods involve three major steps: (1) formulation of the prior distributions of the selected parameters, (2) specification of the likelihood function, and (3) MCMC sampling to generate the posterior probability distributions of the selected parameters.

The Metropolis-Hastings (M−H) method describes a category of Monte Carlo methods which construct a Markov Chain in steps by randomly sampling from the posterior distribution described by Eq. (1) (Mathé and Novak, 2007; Wang and Chen, 2013). Although the M−H algorithm is not the most efficient Markov Chain sampler, it is extensively used in computer modeling applications due to the simplicity of its implementation, and its generality (Gallagher and Doherty, 2007; Kanso et al., 2006).

In practice, M−H algorithms begin by defining an initial value θ^0, of the model parameters θ. Then, by specifying a proposal density, $P(\theta^*|\theta^{t-1})$, a candidate value θ^* is selected, and the ratio R can be computed (Eq. (2)):

$$R = \frac{P(\theta^*|d)P(\theta^{t-1}|\theta^*)}{P(\theta^{t-1}|d)P(\theta^*|\theta^{t-1})} \quad (2)$$

where $P(\theta^*|d)$ and $P(\theta^{t-1}|d)$ were previously defined as the posterior probability densities of model parameters θ^* and θ^{t-1} given the data d, respectively (see Eq. (1)). The ratio R is compared to a random sample ζ taken from a uniform distribution (0,1). When $R > \zeta$, the candidate value θ^* is accepted as the next value in the sequence ($\theta^t = \theta^*$). In contrast, when $R < \zeta$, the candidate value θ^* is rejected as the next value in the sequence ($\theta^t = \theta^{t-1}$). The sequence

Table 1
Lower and upper limits of the uniform distributions (prior distributions) for the investigated parameters.

Parameters	Units	Lower bound	Upper bound
k_{diss}	day^{-1}	0.12	0.48
k_{bio}	day^{-1}	0.017	0.068
k_{des}	day^{-1}	0.031	0.126
k_d	$L\ kg^{-1}$	12	48

of simulated draws ($\theta^1, \theta^2, \ldots \theta^n$) will converged to a random variable that is distributed accordingly to the posterior distribution of $P(\theta|d)$ (Albert, 2009).

The M–H algorithm used in this study generated candidate values for one parameter at a time and is referred to as single-site M–H algorithm (Bates and Campbell, 2001). To successfully implement the M–H algorithm, the prior, likelihood, and proposal densities must be specified. In addition, the method used to conduct the MCMC output analysis must also be stated (Wu and Chen, 2009).

2.4. Implementation of the M–H algorithm into the PCPF-1 model

2.4.1. Prior density

The prior represents the existing knowledge of the input parameter, before any calibration. The prior distribution can be very complex but is often assumed to be flat (or non-informative) within the admissible parameter range and zero elsewhere (Görlitz et al., 2011; Harmon and Challenor, 1997). In this study, uniform prior distributions were used:

$$P(\theta_i) = \begin{cases} \dfrac{1}{b_i - a_i} & \text{if } a_i \le b_i \\ 0 & \text{else} \end{cases} \quad (3)$$

where a_i and b_i denote the lower and upper limits of θ_i, respectively (Albert, 2009; Korner-Nievergelt et al., 2015a). The characteristics of the prior distribution of the four input parameters included in the MCMC simulations are presented in Table 1. The minimum and maximum of the parameter's ranges were selected by constraining input parameters between M/2 and 2 × M, where M is the parameter value used during the validation of the model (Dubus et al., 2003; Dubus et al., 2002). A major advantage of using prior distributions is that any new knowledge over a parameter can be quickly integrated in the model by reformulating the prior distribution.

2.4.2. Likelihood density

Within an optimization framework, it is necessary to select an objective function which is an indicator of the deviation between a measured and a simulated series (van Griensven and Bauwens, 2003). In this study, the sum of the squares of the residuals (*SSQ*) was used:

$$SSQ1 = \sum_{i=1}^{n_1} (C_{pw-m} - C_{pw-sim})_i^2$$
$$SSQ2 = \sum_{i=1}^{n_2} (C_{s-m} - C_{s-sim})_i^2 \quad (4)$$

where $C_{pw\text{-}sim}$ and $C_{s\text{-}sim}$ are the simulated pesticide concentrations at day i in PW and PSL, respectively. $C_{pw\text{-}m}$ and $C_{s\text{-}m}$ are the corresponding measured pesticide concentrations in PW and PSL, respectively. While several methods are available to aggregate objective functions to a global optimization criterion (van Griensven and Bauwens, 2003), by assuming that the residuals follow a normal distribution, $N(0, \sigma^2)$, a simple method using the variance of the residual can be used (Abbaspour, 2015):

$$\sigma_{SSQ1}^2 = \frac{SSQ1_{\min}}{n_1}$$
$$\sigma_{SSQ2}^2 = \frac{SSQ2_{\min}}{n_2} \quad (5)$$

where $SSQ1_{\min}$ and $SSQ2_{\min}$ are the current minimum sums of the squares of the pesticide concentrations in PW and PSL and n_1 and n_2 are the numbers of observed pesticide concentrations in PW and PSL, respectively. As new candidate parameters are selected, $SSQ1_{\min}$ and $SSQ2_{\min}$ are updated when new minima are reached.

Residue concentrations of pesticide are independent, and therefore can be modeled using a univariate distribution (Paulo et al., 2005). In the most simplistic case, with uncorrelated scalar value measurements, Gaussian distributed residuals with constant variance, σ^2, the likelihood function can be applied (Vrugt et al., 2013). Given that the error in the measured pesticide concentration is additive and normally distributed with zero mean and variance σ, the likelihood takes the form (Hazart et al., 2014):

$$P(\theta|y_{t,obs}) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(y_{t,sim} - y_{t,obs})^2}{2\sigma^2}\right] \quad (6)$$

Combining Eqs. (4), (5), and (6) the likelihood becomes:

$$P(d|\theta) = C1 \cdot \exp\left[-\frac{SSQ1 \cdot n_1}{2 \cdot SSQ1_{\min}}\right] \cdot \exp\left[-\frac{SSQ2 \cdot n_2}{2 \cdot SSQ2_{\min}}\right] \quad (7)$$

where $C1$ is a constant and other parameter were defined above. The sum of the squares of the residuals are weighted using the number of observations divided by the minimum of the squares of the residuals as described by Abbaspour et al. (Abbaspour, 2015). Consequently, the different *SSQ*s are of the same order of magnitude, thereby avoiding the optimization of the compartment where pesticide concentration is the highest. Both compartments will therefore remain significant during the optimization process (van Griensven and Bauwens, 2003).

2.4.3. Proposal density

Different M–H algorithms can be constructed depending on the choice of the proposal density (Albert, 2009). In this study, the candidates of the input parameters were proposed using a symmetrical distribution which is characterized by the property: $P(\theta^{t-1}|\theta^*) = P(\theta^*|\theta^{t-1})$. This type of M–H algorithm is referred to as a random walk M–H (Albert, 2009). Uniform proposal densities $U(\theta^*, \alpha)$ where α is a scale factor (Hazart et al., 2014) were selected as proposal distributions. The current value of an input parameter is set as the mean for the candidate proposal density. All candidate values are therefore contained between −α and α and have equal chances to be selected. While the random walk scheme was reported to give more freedom to explore region of high probability (Bates and Campbell, 2001), the scale factor for the proposal distribution (α) has a great impact on the selection process (Liang et al., 2010). Indeed, small values of scale factor tend to produce proposals to be accepted with large probabilities but result in slow convergence. In contrast, large values of scale factor produce small acceptance rates but faster chain convergence (Liang et al., 2010). Rejection ratios between 20 and 50% were reported to be acceptable, and the scale parameters of each proposal densities were thus accordingly tuned (Hazart et al., 2014).

2.4.4. Implementation of the M–H algorithm into the PCPF-1 model

The implementation of the M–H algorithm into the PCPF-1 model is displayed in Fig. 1. First, an initial value is assigned to

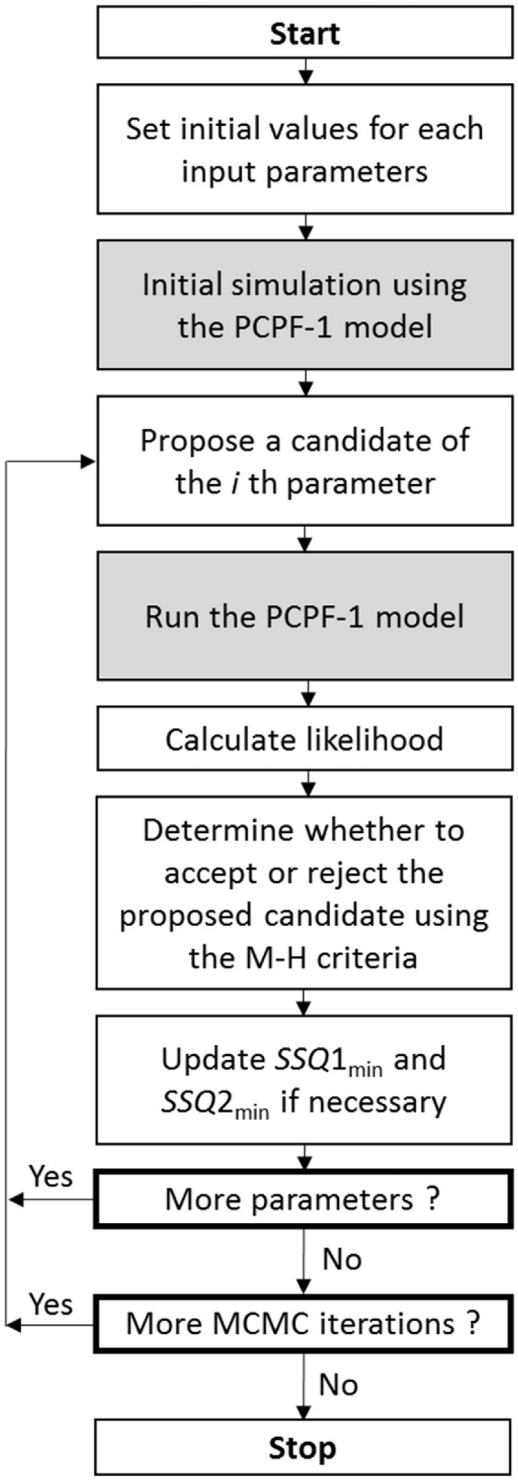

Fig. 1. Implementation of the M–H algorithm into the PCPF-1 model for input parameters estimation.

each of the four input parameters and an initial simulation is generated. Then, using the proposal distribution, a candidate value for one of the four input parameters is selected. The PCPF-1 model is triggered again, using the candidate value. Once the simulation is completed, the likelihood (Eq. (7)) is computed and the proposed candidate value is either accepted or rejected using the M–H criteria (Eq. (2)). This process of generating a candidate, running the PCPF-1 model and accepting or rejecting the candidate is repeated until the specified number of MCMC iterations is reached (Fig. 1).

2.4.5. MCMC output analysis

The distribution of the simulated values at the jth iterate, θ^j, will converge to the posterior distribution as j approaches infinity. Convergence diagnostics determine whether or not it is reasonable to assume that the sample generated by the MCMC simulations is representative of the final equilibrium distribution (Iizumi et al., 2009).

Two different simulations were run for 20,000 iterations using two sets of initial values. The first simulation was performed using initial values equal to the minimum acceptable values of each input parameters. In contrast, for the second simulation, the initial values were set to the maximum acceptable values of each input parameters (Table 1). Hereinafter, these two simulations are referred to as simulation 1 and simulation 2, respectively.

To evaluate the convergence status of the simulations, first, the sample paths of the input parameters were visually checked. Second, the autocorrelation of the chains of the parameters were investigated. Autocorrelation quantifies the degree of similarities between successive values of the same parameter separated by a certain number of iteration called lag (Dzotsi et al., 2015). Third, the method developed by Gelman and Rubin (1992) which requires at least two independent chains (simulations 1 and 2) was applied to assess the convergence of all parameters. Fourth, the method introduced by Geweke (1992) was used to confirm the convergence state of the simulations.

After verifying that the distribution of the simulated values converged to the posterior distribution, the distribution of the input parameters can be used to produce optimum simulations and generate an estimation of the model uncertainty. While all combination of accepted input parameters generate appropriate concentrations of mefenacet in PW and PSL, the "best" parameter set is typically created by computing the median value for each input parameters (Iizumi et al., 2009; Korner-Nievergelt et al., 2015b; Lai, 1997).

3. Results and discussion

3.1. Performances of the MCMC algorithm implemented into the PCPF-1 model

3.1.1. Sample paths

Looking at the sample paths of the parameters (Fig. 2), the initial values of the input parameters only altered the number of iterations required for the chains to converge. The visual inspection of the sample paths did not reveal any non-convergence status as the sample paths of the 2 MCMC simulations (two initial values for each parameter) is consistent for all parameters. In addition, it was observed that the samples of the k_{diss} and k_d parameters are concentrated in the upper region of the parameter ranges (Fig. 2a, d). In contrast, the samples of the k_{bio} and k_{des} parameters are spread over the defined parameter space (Fig. 2b, c). This indicates that, while higher k_{diss} and k_d values may not be realistic regarding the chemical-physical properties of mefenacet, increasing these values may increase the accuracy of the predicted mefenacet concentrations for the given observed mefenacet concentrations. Alternatively, allowing some pesticide characteristic to vary, depending on the physicochemical conditions of the environment (for example kd was reported to vary with temperature for pesticides), could be a good alternative to increasing the parameter's bounds. In the further analysis, the first 5000 values of each chain were discarded (burn-in).

3.1.2. Autocorrelation plots

Rather than using all samples from the chains (Fig. 2), subsets of the chains, every n^{th} data of a chain, can be used (Toft et al., 2007). This process, called thinning, is used to improve the mixing

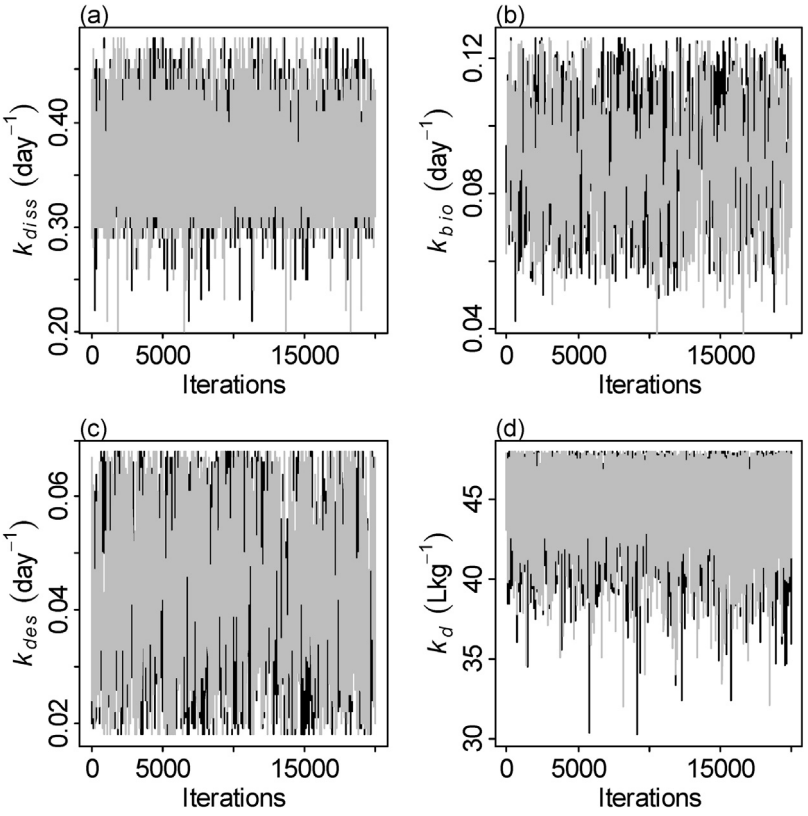

Fig. 2. Sample paths of (**a**) the dissolution rate, (**b**) the first order degradation rate in paddy soil, (**c**) the desorption rate and (**d**) the partitioning coefficient for the MCMC simulations with minimum starting value (in black) and maximum starting values (in grey).

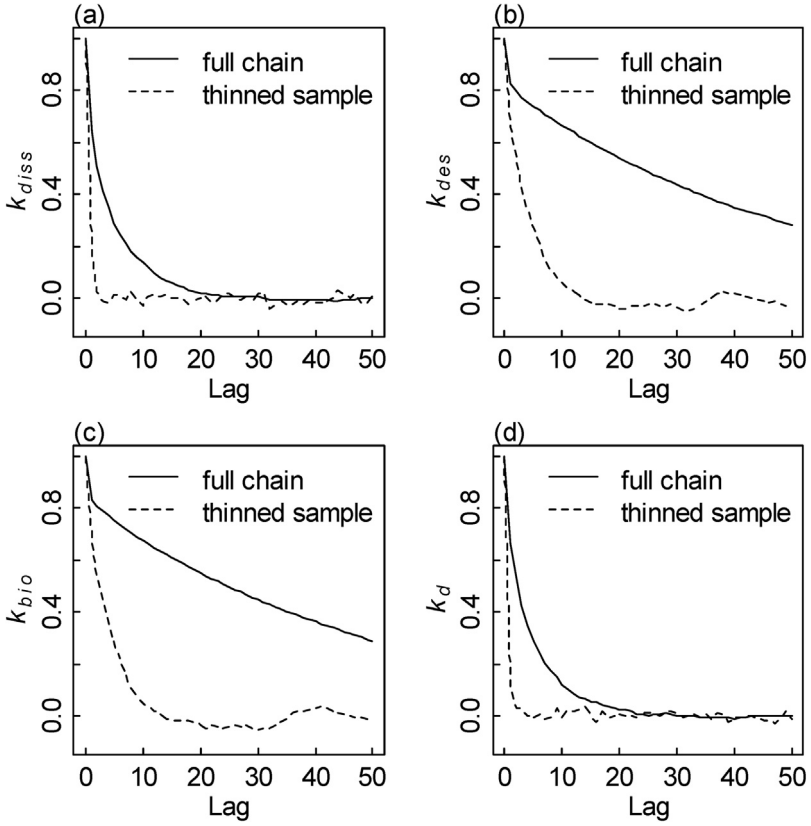

Fig. 3. Autocorrelations of the full and thinned samples (every 10th iterations) for (a) k_{diss}, (b) k_{des}, (c) k_{bio}, and (d) k_d.

Table 2
Convergence diagnostics of the MCMC chains.

Parameters	Gelman-Rubin (1992)	Geweke (1992)	
		Simulation 1	Simulation 2
k_{diss}	$R_C = 1.05$	$Z_n = -0.021$ $Z_\alpha = \pm 1.96$	$Z_n = 0.131$ $Z_\alpha = \pm 1.96$
k_{des}	$R_C = 1.00$	$Z_n = 0.273$ $Z_\alpha = \pm 1.96$	$Z_n = -0.015$ $Z_\alpha = \pm 1.96$
k_{bio}	$R_C = 1.00$	$Z_n = -0.469$ $Z_\alpha = \pm 1.96$	$Z_n = -0.035$ $Z_\alpha = \pm 1.96$
k_d	$R_C = 1.00$	$Z_n = -0.005$ $Z_\alpha = \pm 1.96$	$Z_n = -0.014$ $Z_\alpha = \pm 1.96$

of chains. Good mixing implies that there is very little or ideally no autocorrelation between samples (Toft et al., 2007). The autocorrelation plots (Fig. 3) show the correlation between the samples every *i* iterations (lag) in the chain. The obtained samples in this simulation were thinned every 10 samples from the full chain, then the autocorrelation was recalculated (dotted lines in Fig. 3). In general, the autocorrelation decreased when the number of lag increased. The number of lags required to reach a correlation value of zero have been reported to depend on the skewness of the posterior distribution, with symmetrical posterior distributions reaching a correlation value of zero quicker than highly skewed posterior distributions (Dzotsi et al., 2015). After thinning the samples, using every 10 iterations of the full chain, the mixing of all chains greatly improved (Fig. 3, dotted lines). In the further analysis and discussion, the thinned (every 10 samples) chain for all parameters is used.

3.1.3. Convergence diagnosis methods

The method proposed by Gelman and Rubin (1992) to investigate the convergence state of MCMC chains requires, at least, two independent chains for each parameters. Then, the mean and variance of each chain is compared using a statistic called R_C (El Adlouni et al., 2006). If R_C is close to 1, it can be concluded that the chains have converged. Details regarding the procedure and practical computation of the R_C value can be found in Brooks and Roberts (1998) and El Adlouni et al. (2006). The R_C statistic was computed for all four parameters using two independent chains (simulations 1 and 2) and are reported in Table 2. The convergences of the chains were strongly suggested for all four parameters. Since the method by Gelman and Rubin is not a statistical test, it is difficult to determine if R_C is close enough to 1 (El Adlouni et al., 2006; Gelman and Rubin, 1992). Consequently, an additional convergence diagnosis developed by Geweke (1992) was used. The method is based on testing the equality of location measures for two subsequences of a MCMC chain (El Adlouni et al., 2006). The method was applied to the two chains obtained using minimum and maximum starting values (simulations 1 and 2). The obtained Z_n values and the interval of confidences for the two MCMC simulations are again reported in Table 2. The convergence of the MCMC chains was proved for all parameters since all Z_n values were within the confidence intervals for all parameters and simulations.

3.2. Estimation of the input parameters

Since the chains generated by the MCMC algorithm were indicated as being adequate by the convergence diagnostics, the posterior distributions of the four input parameters were computed using the thinned chains of the two MCMC simulations (Fig. 4). The posterior distributions of k_{bio} and k_{des} were symmetric and characterized by high variances which indicate that the two parameters were generally less influential on the prediction of pesticide concentrations as reported previously (Boulange et al., 2012). In contrast, the posterior distributions of the parameters k_{diss} and k_d are severely skewed (Fig. 3 a, d). The cases of strong asymmetry were reported for parameters that have a strong influence on the ratio *R* (Eq. (2)) of the MCMC (Dzotsi et al., 2015). As uniform priors (Eq. (3)) and a symmetric proposal distribution were used, the ratio *R* depends only upon the likelihood of the data (Eq. (2)).

Table 3
Statistical evaluation of the original and optimized dataset for mefenacet.

	Paddy water (PW)		Paddy soil (PSL)	
	Original dataset	Optimized dataset	Original dataset	Optimized dataset
R^2	0.94	0.88	0.50	0.99
RMSE	0.088	0.12	2.89	0.29

The boxplot of the forecasted four parameters included into the analysis for the 2 MCMC simulations are displayed in Fig. 5. The boxplot of the forecasted input parameters for the two MCMC simulations were similar for all parameters, which strongly indicate that the chains reached convergence. All combinations of input parameters from the reported boxplot produced acceptable (in Eq. (2) sense) simulations. This illustrate the non-uniqueness problem as this combination of input parameter produce very similar results. The uncertainty of each input parameters can also easily be visualized. The MCMC methodology greatly reduced the initial uncertainty of the k_{diss} and k_d parameters that was encompassed in their prior distributions. In contrast, the uncertainty of the k_{bio} and k_{des} parameters was not as greatly reduced. These results are associated with the sensitivity of the input parameters on the predicted mefenacet concentrations and k_d and k_{diss} were indicated as greatly sensitive while k_{des} and k_{bio} only had a minor influence on the predicted mefenacet concentrations. These results are in agreement with previous sensitivity analysis of the PCPF-1 model (Boulange et al., 2012; Kondo et al., 2012). The median values for the k_{diss}, k_{bio}, k_{des}, and k_d were: 0.36 day^{-1}, 0.0455 day^{-1}, 0.087 day^{-1}, and 45.5 L kg^{-1}, respectively. These values are optimized for the given observed mefenacet concentrations.

Deterministic simulations using the original mefenacet dataset and the optimized dataset previously described are displayed in Fig. 6. The daily predicted mefenacet concentrations in paddy soil using the optimized dataset were extremely close to observed data. In contrast, the simulation using the original dataset missed the concentration peak and in general overestimated mefenacet concentrations 5 days after the initial pesticide application. It can be noted that the mefenacet concentration in PW 3 days after the herbicide application was better predicted using the original dataset. This illustrate the difficulty of simultaneously optimizing two compartments which are interacting with each other. In this study, weights were attributed to the PW and PSL compartments (Eq. (7)) to avoid over-calibrating the compartment that possesses more observations and/or higher pesticide concentration. Different weighs can be attributed to favorize a compartment and improve the accuracy of the predicted pesticide concentration at the expense of the other compartment. The statistical evaluations of the predicted pesticide concentrations regarding the observed mefenacet concentrations are reported in Table 3. Since the two compartments, paddy water and paddy soil, are interacting with each other, improving the accuracy of the predictions in one compartment is done at the detriment of the other (Table 3). For example, increasing the k_d of mefenacet increases the amount of mefenacet in PSL but reduces its amount in PW. The use of weights in the likelihood function (Eq. (7)) ensured that despite the differences in observation data points (here identical for PW and PSL) and concentration levels (in general, concentration in PSL > concentration in PW), both compartments were equally considered into

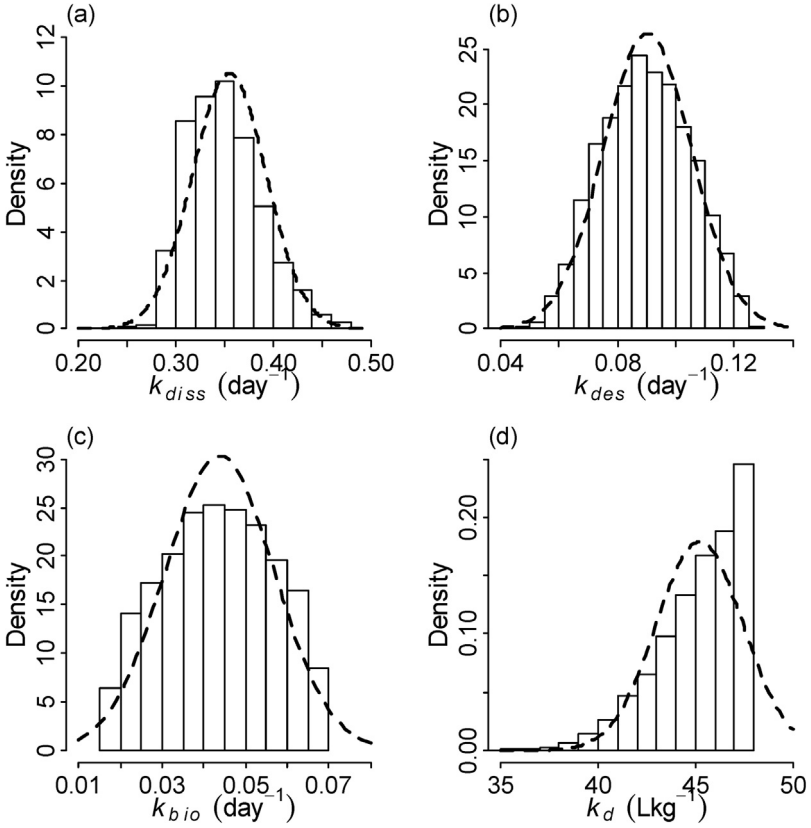

Fig. 4. Posterior distributions of the four input parameters, (a) k_{diss}, (b) k_{bio}, (c) k_{des}, and (d) k_d, using the outputs from the two MCMC simulations.
Note: The dash lines indicate a normal distribution with mean and standard deviation equals to those of the posterior distributions of the input parameters.

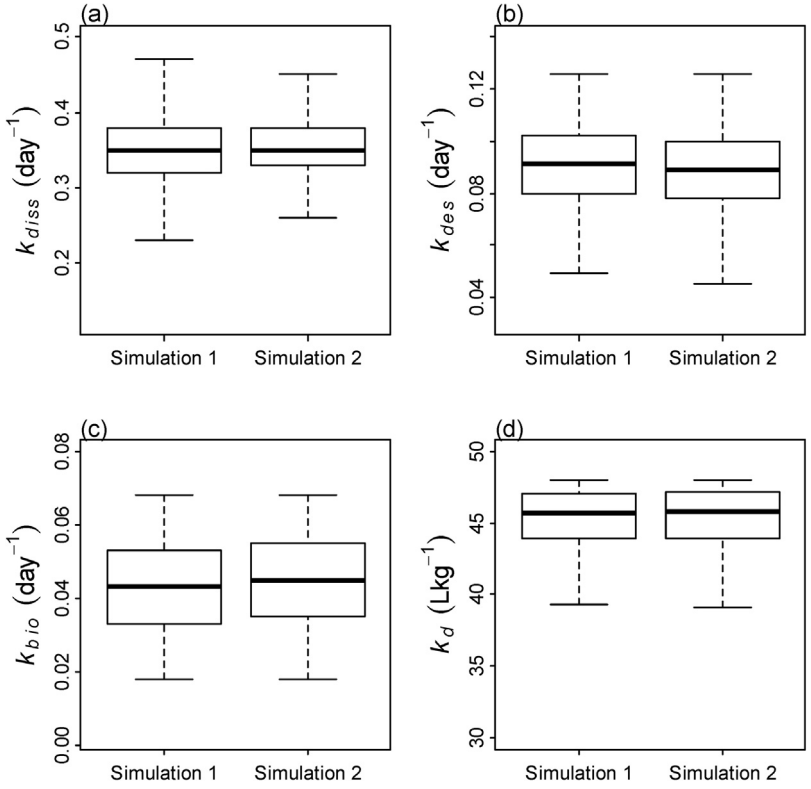

Fig. 5. Boxplot of the forecasted (**a**) k_{diss}, (**b**) k_{bio}, (**c**) k_{des}, and (**d**) k_d input parameters for the simulations using minimum and maximum starting values. The end of the whiskers represents the minimum and maximum of the data.

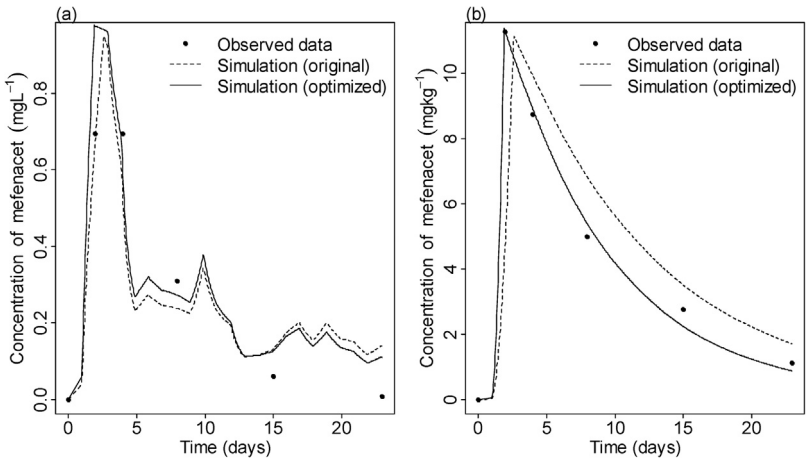

Fig. 6. Observed and predicted concentrations of mefenacet in (**a**) paddy water and (**b**) paddy soil.

the optimization process. Consequently, the accuracies of the predicted mefenacet concentrations in PW and PSL using the optimized dataset were appropriate.

4. Conclusions

A Bayesian approach relying on Markov Chain Monte Carlo (MCMC) technique was applied to (1) optimize multiple parameters of a pesticide fate and transport model (PCPF-1 model) for rice paddy given a set of observed pesticide concentrations and (2) simultaneously quantify the uncertainty of multiple input parameters. The necessary steps for appropriately implementing a Metropolis-Hasting algorithm for a pesticide fate and transport model were demonstrated and consist of defining the prior, likelihood, and proposal densities, and methods for MCMC output analysis.

The analysis of the MCMC output revealed that all chains of the input parameters converged. The posterior distributions of the input parameters better reflect the uncertainty included in the model and in the observed data therefore increasing the accuracy of the predicted pesticide concentrations. Deterministic optimum values of the input parameters were extracted from their respective posterior distribution. The trend of the predicted concentration of the herbicide mefenacet using the optimal input parameters were similar to that of the monitored concentrations and slightly more accurate than the original validation dataset of the model in the PSL. In contrast, in PW for the initial observed mefenacet concentration, the original dataset of the model produced slightly better forecast. This illustrate the trade-off in pesticide forecast accuracy that are necessary when simultaneously and equally optimizing two compartments.

By considering the uncertainty encompassed in the input parameters of the model and in the observed pesticide concentrations, the MCMC methodology increases the reliability and accuracy of the predicted pesticide concentrations and thus the methodology is applicable in pesticide fate and transport context.

For future studies, the single site optimization of the algorithm will be relaxed, in favor of a multi-site optimization scheme, to speed-up the MCMC simulations. In addition, rather than using median values of the posterior distributions, the posterior distributions will be used directly thereby considering the uncertainty included in both observations and the model. Thus, the effectiveness of the best practices in fields to prevent pesticide contamination can also include uncertainty considerations.

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