# Real-time forecasting of pesticide concentrations in soil

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HIGHLIGHTS

- Real-time forecasting of pesticide concentrations in soil was previously impractical.
- New stochastic model developed to account for rainfall variability after application.
- Bayesian methods used to calibrate two reaction parameters for in-field testing.

GRAPHICAL ABSTRACT
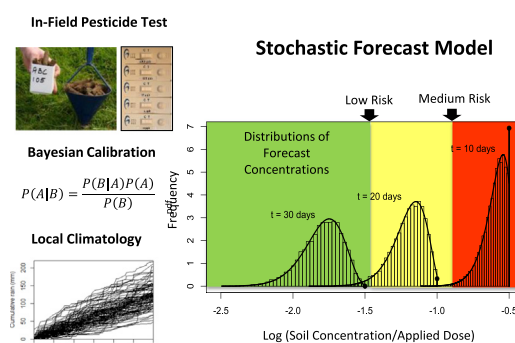
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ABSTRACT

Forecasting pesticide residues in soils in real time is essential for agronomic purposes, to manage phytotoxic effects, and in catchments to manage surface and ground water quality. This has not been possible in the past due to both modelling and measurement constraints. Here, the analytical transient probability distribution (pdf) of pesticide concentrations is derived. The pdf results from the random ways in which rain events occur after pesticide application. First-order degradation kinetics and linear equilibrium sorption are assumed. The analytical pdfs allow understanding of the relative contributions that climate (mean storm depth and mean rainfall event frequency) and chemical (sorption and degradation) properties have on the variability of soil concentrations into the future. We demonstrated the two uncertain reaction parameters can be constrained using Bayesian methods. An approach to a Bayesian informed forecast is then presented. With the use of new rapid tests capable of providing quantitative measurements of soil concentrations in the field, real-time forecasting of future pesticide concentrations now looks possible for the first time. Such an approach offers new means to manage crops, soils and water quality, and may be extended to other classes of pesticides for ecological risk assessment purposes.

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1. Introduction

The time interval between herbicide application and its dissipation to a concentration that is non-toxic to crop growth (withholding period) is a critical factor for agronomic management (e.g. Desaeger

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et al., 2008). Withholding periods are an important consideration in crop rotations, where, for example, a herbicide used to control broadleaf weeds in a wheat crop may have an adverse effect on the following legume crop. In addition, the accumulation of herbicide residues in soil, in which repeat application of the same chemical are more frequent than the time required for complete degradation, can pose both an agronomic and environmental risk. Phytotoxic effects are managed somewhat by pre-registration studies; however, deviations in environmental conditions, soil properties and agronomic practices from the conditions tested at registration can pose a potential risk (FOCUS, 2009). With the advent of inexpensive, easy and rapid measurement methods (Yuan et al., 2011, 2012) there is now the opportunity to develop real-time forecasting tools for practical agronomic and catchment management.

Historically there have been several impediments to real-time forecasts of pesticide concentrations. Numerous models of pesticide fate and transport are available (e.g. Beulke et al., 2001; Tiktak et al., 2004), and while useful in the hands of experts with high quality data (Dann et al., 2006), they are not practical for every-day use. There is significant cost and time required to collect, transport, and then analyze soil samples in an analytical laboratory using advanced methods (e.g. GC–MS, LC-MS). Once the pesticide concentrations have been determined there is the added complexity of the models themselves, their uncertain parameterization, the challenge of calibration and validation and then interpretation (Beulke et al., 2000; Dubus et al., 2003; Dann et al., 2006; Fenner et al., 2013). Finally, once an acceptable model has been developed, there is a need to forecast what the soil residues will likely be in the near future, necessitating an assessment of future weather conditions, a primary factor impacting pesticide retention in soil and subsequent release to streams (Larsbo and Jarvis, 2005; McGrath et al., 2008b). These challenges often push the timeframe from data collection to forecast out to months, if not years. Clearly, this is impractical for forecasting. Ongoing developments in measurement technologies mean that many pesticides can now be rapidly, reliably and cost-effectively measured in the field at environmentally relevant concentrations by non-specialists (Lee and Kennedy, 2001; Kennedy et al., 2013; Gee et al., 2016). To date though modelling efforts have not matched the speed and utility of the measurement technologies.

The persistence of agro-chemicals in soils is largely driven by the nature of rainfall in the period after application (Kladivko et al., 2001; McGrath et al., 2008a). It is well established that the concentration of chemicals, like herbicides, insecticides and fungicides, in surface soils, at the time of significant rain events, is strongly correlated with the concentration observed in drains or rivers immediately afterwards (Ahuja et al., 1981; Kladivko et al., 2001; Nolan et al., 2008). The challenge to forecast pesticide residue levels into the future therefore should incorporate the variability in the way the weather is likely to occur in the weeks and months after pesticide application. Recent approaches have attempted to quantify the role that rainfall variability has in the movement of water and chemicals through soil (McGrath et al., 2008a, 2008b; Botter et al., 2008; Harman et al., 2011; Suweis et al., 2011), from soils to streams (Zanardo et al., 2012; Bertuzzo et al., 2013) or as urban wash-off (Daly et al., 2014). The strength of these stochastic approaches is the transparent understanding of how rainfall variability propagates to retention or solute transport variability.

Table 1
Model parameters used in the mock experiment.

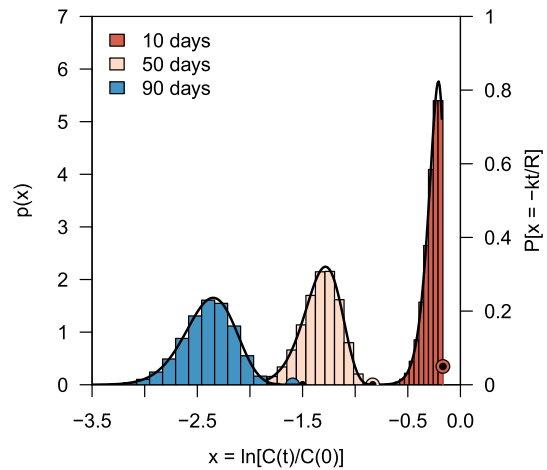| Parameter	Values
k (day^{-1})	0.2
K_{oc} (L kg^{-1})	60
f_{oc} (g/g)	0.01
n (cm^3 cm^{-3})	0.4
z (cm)	5
Standard deviation of ε (−)	0.1

Fig. 1. Transient pdfs, $p_x(x,t)$, of the residual concentration, $x = \ln[C(t)/C(0)]$, at the surface. Numerical results (histograms), derived from 10^9 realizations, are compared to the analytical solutions, Eq. (2) (solid lines). The large circles correspond the largest x value from numerical simulations and its frequency (right axis). The black circles denote the atom of probability from the analytical equations (right axis). Parameters include: $\lambda = 0.3$ day^{-1}; $\gamma = 1$ mm; $n = 0.4$; $z = 25$ mm; $R = 3$; $k = 0.05$ day^{-1}.

Here, an approach, capable of exploiting these new field-based measurement tools, is developed, providing climatological forecasts of pesticide concentrations in soil. The following presents the approach and evaluates its ability to forecast withholding period risk. First a new stochastic model for pesticide persistence in soil is presented. Randomness is considered to arise from variations in the timing and magnitude of rainfall events in the period after pesticide application. The impacts of the climate and reaction parameters are manifest in an analytical solution of the transient probability distribution of pesticide concentrations. This forecast model has, as its basis, a deterministic process-based
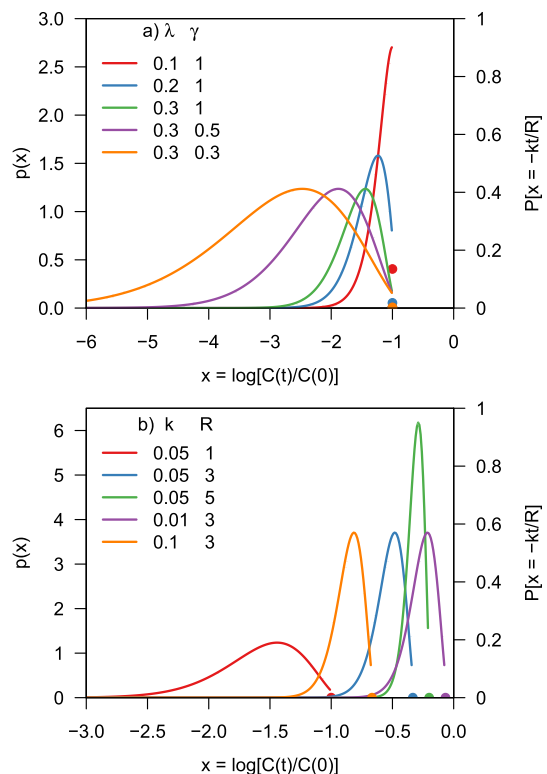

Fig. 2. Dependence of $p_x(x,t)$ on: (a) rainfall properties; and (b) chemical properties. Parameters shown are: (a) $R = 1$, $k = 0.05$ day^{-1}; and (b) $\lambda = 0.3$ day^{-1}, $\gamma = 1$ mm^{-1} and in both (a) and (b) $\theta = 0.4$; $z = 25$ mm; $t = 20$ days; and $x(0) = 0$.

description of pesticide retention in soil. Using observed rainfall in the period since application and field measured concentrations Bayesian calibration of the deterministic model is demonstrated from mock measurements of herbicide concentrations. Finally, updating a forecast, using the newly estimated credible parameter range, is described. Practicalities of risk-based withholding period estimation and managing catchment water quality are then discussed.

2. Theory

2.1. Conceptual basis for modelling

While models are necessarily simplifications of reality, some pesticide persistence models have been developed to the point that their sophistication can account for most known solute fate and transport processes in soils (Beulke et al., 2001). However, the data burden required to calibrate uncertain constitutive relations and to parameterize the many processes leaves these models largely as research tools. Furthermore, such models are mostly deterministic, and to estimate year to year variability Monte Carlo simulations are often run using historical climate data (Nolan et al., 2008). Various approaches have been developed to account for parameter uncertainty, climate variability, and soil heterogeneity, but these are generally computationally expensive, and

time consuming to evaluate. Useful as they are from a research perspective, their complexity tends to make their calibration difficult and uncertain (Dubus et al., 2003).

Reaction and transport parameters are significant sources of variability and uncertainty in modelling pesticide fate (Dubus et al., 2003; Larsbo and Jarvis, 2005; Gassmann et al., 2015). The most sensitive parameters are related to retardation and attenuation processes, which can exhibit significant spatial and temporal variability (Rao and Wagenet, 1985; Müller et al., 2003). While empirical studies help to constrain a priori estimates from the literature the effective value of parameters can change with both the measurement scale and the rate at which processes occur in the field (Vereecken et al., 2011).

A possible solution to these uncertainties is the integration of Bayesian approaches to model development. Bayesian methods are increasingly applied to model calibration. Worrall et al. (1998) were early proponents of the use of Bayesian methods for characterising parameter uncertainty as part of pesticide registration. Both informal and formal Bayesian approaches have been applied to parameter estimation (Larsbo and Jarvis, 2005; Dusek et al., 2015; Boulange et al., 2017) and assessment of model structure (Frey et al., 2011). The Bayesian approach provides a rational methodology to update confidence in model predictions, model parameters, or even the models themselves as new information becomes available.
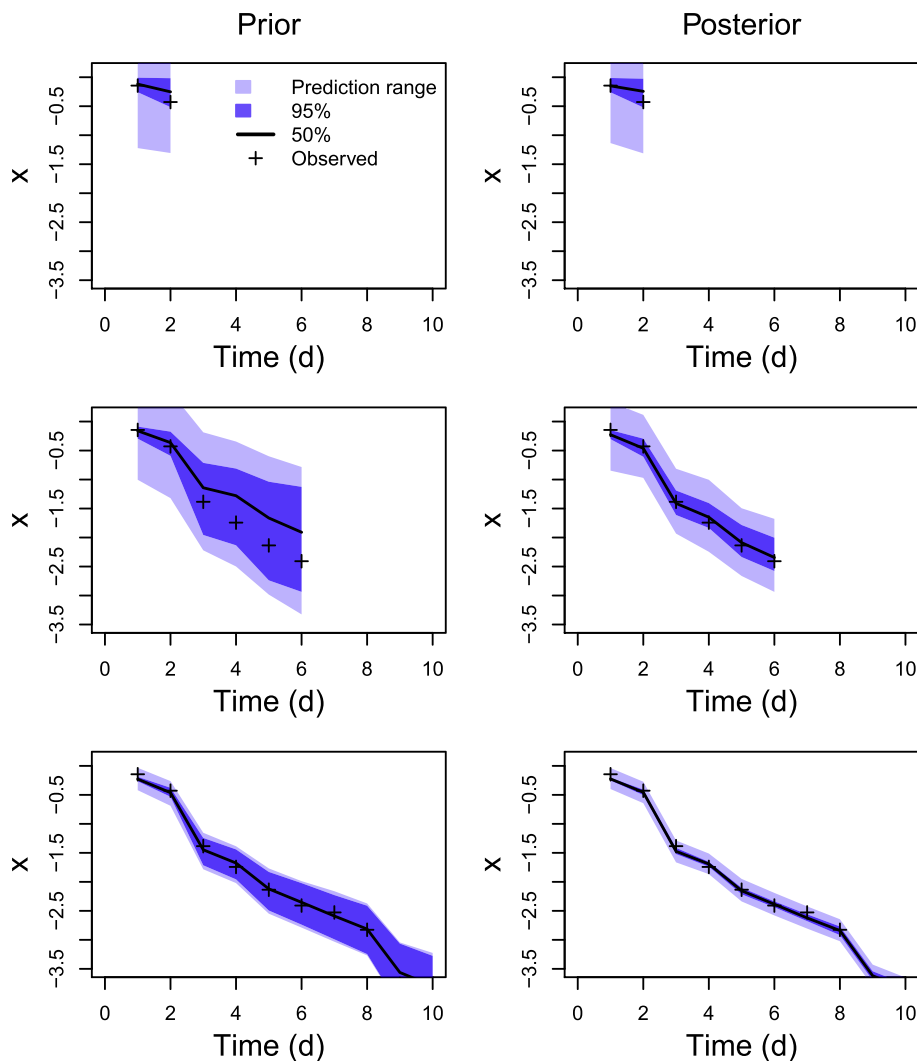

Fig. 3. Sequence of prior and posterior fits of the model to the observed data with mean, 95% confidence interval and range of predictions shown with mock observations from DEzs.

2.2. A stochastic model of pesticide persistence

Forecasting the amount of pesticide remaining in soil at some point into the future requires consideration of the variability of environmental factors that contribute to retention. These environmental factors include temperature, humidity, air pressure and rainfall. For non-volatile chemicals with weak to moderate sorption, rainfall-driven leaching is a primary driver of transport and dissipation (Ahuja et al., 1981; Ahuja and Lehman, 1983). A simple model for the mass balance of a chemical residing near the soil surface, as impacted by rainfall is the following (McGrath, 2008a):

$$nz\,R\frac{dC}{dt} = -k\,nz\,C - J(t)c \qquad (1)$$

where mass balance is considered over a well-mixed layer near the soil surface of depth z (cm) and effective water content n ($cm^3\,cm^{-3}$); the chemical undergoes first order degradation at a rate k (day^{-1}) and linear, instantaneous and reversible sorption is parameterized by the retardation factor R (i.e. $R = 1 + \rho\,K_d/n$) which depends upon the soil dry bulk density, ρ ($g\,cm^{-3}$), water content n, and a linear sorption coefficient, $K_d = K_{oc}\,f_{oc}$ ($cm^3\,g^{-1}$) the product of the organic carbon partitioning coefficient and the fraction organic carbon; J ($cm\,day^{-1}$) denotes the intensity of rain events which flush the chemical from the surface, and t denotes time. The effective water content, n, could be approximated as being close to the field capacity, and while it varies with rainfall its variability during a rain event, is likely to be considerably smaller than the uncertainty in k or R. Botter et al. (2008) coupled a similar stochastic model of soil moisture and nitrogen processes, including uptake and leaching. While approximate and stationary pdfs were derived there, our concern is with pesticide retention which is expected to be highly transient at seasonal time scales.

The possible future sequence of dry spells and rain events can be thought of as a sample from a stochastic process (Rodriguez-Iturbe and Isham, 1987; Daly and Porporato, 2006; Harman et al., 2011). Rain events are assumed to follow a marked Poisson process with a mean rate λ (events/day) resulting in the time between events exponentially distributed with a mean $1/\lambda$. Rainfall depths are assumed here to be exponentially distributed with mean depth $1/\lambda$ (mm/event). Details of the derivation are presented in Appendix A. The resulting equation for the transient probability distribution is:

$$p_X(x,t) = e^{nz\gamma R\left(x-x_0+\frac{kt}{R}\right)-\lambda t}\sqrt{-\frac{\lambda t}{nz\gamma R\left(x-x_0+\frac{kt}{R}\right)}}I_1$$
$$\left(2\sqrt{-nz\gamma R\lambda t\left(x-x_0+\frac{kt}{R}\right)}\right) + e^{-\lambda t}\delta\left(x-x_0+\frac{kt}{R}\right) \qquad (2)$$

where $x = \log[C(t)/C(0)]$. This new contribution provides a climatological forecast of the probable future concentrations in soil. This pdf depends upon the chemical's reaction parameters, k and R, and the climate, through the parameters γ and λ. The impact of these controlling factors will be briefly explored later. Two of the model parameters, γ and λ, can be derived directly from daily rainfall data. The reaction parameters, R and k may vary significantly depending upon the soil mineralogy, soil moisture and soil temperatures and thus are likely to be uncertain, varying across soil types and even within-fields (Rao and Wagenet, 1985; Worrall et al., 1998; Beulke et al., 2000; Wauchope et al., 2002). Bayesian methods will be applied to their estimation.

2.3. Bayesian model calibration

The above stochastic model describes the effect of climate on the variability of future concentrations, assuming the two reaction parameters are known. As discussed above these parameters are uncertain and

spatially variable. With observations of concentrations this parameter variability can be accounted for somewhat by calibrating the deterministic Eq. (2). The following describes the Bayesian methods applied to do this.

Empirical regression methods tend to maximise the conditional probability, $p(D|\theta)$, that the data, D, would be observed given a model, and its parameters, θ. The Bayesian approach on the other hand asks what the conditional probability of the model and its parameters are given the data i.e. $p(\theta|D)$. The relationship between these is given by Bayes formula:

$$p(\theta|D) = \frac{p(D|\theta)p(\theta)}{\int p(D|\theta)p(\theta)d\theta} \qquad (3)$$

where $p(\theta|D)$ is the probability for the parameters conditioned on the data called the posterior distribution, $p(D|\theta)$ is called the likelihood and $p(\theta)$ is the probability distribution of the prior information about the parameters before confronting the model with data (Hartig et al., 2011). Given a set of data, that new information can be used to develop a posterior estimate of model parameters.

The methodological issues in applying Bayesian inference to model parameters are involved and are summarized extensively elsewhere (see for example Thiemann et al., 2001; Vrugt et al., 2009; Hartig et al., 2011). We applied Markov chain Monte Carlo (MCMC) methods to implement Bayes' approach to calibrate Eq. (A2) (Hartig et al., 2017). A range of k and K_{oc}, values for atrazine, as an example, were obtained from the literature (see Supplementary material Table S1). The
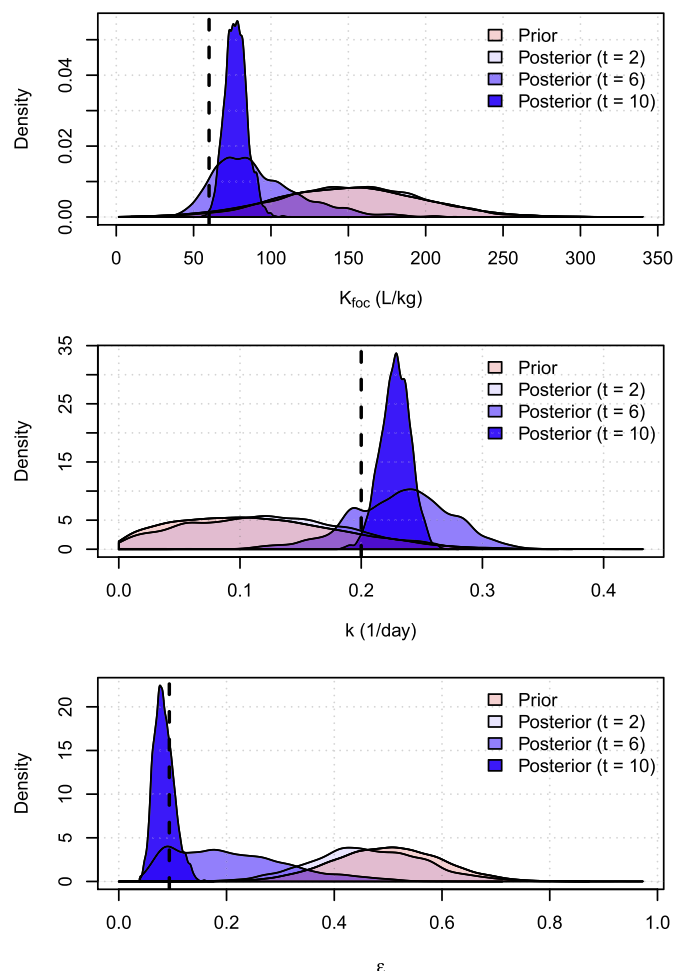

Fig. 4. Sequence of parameter estimates from the initial prior to the posterior distributions at selected times from DEzs. Dashed lines denote the actual model parameters.

mean and variance of these values were used to define truncated normal prior distributions. The truncation ensured draws from prior and posterior distributions return samples of parameters that were non-negative. The standard deviation (ε) of a model error term added to Eq. (A2) was included as a model parameter. This term accounts for measurement variance, model structural errors, and in practice other processes not considered in the model. The log-likelihood used was the sum of logarithms of a normal probability density at values representing the difference between modelled and observed data. While the construction of log-likelihood functions can be quite elaborate, particularly for time series models (e.g. Frey et al., 2011) it was found that this simple log-likelihood function sufficed to help constrain model calibration. It is beyond the scope of this paper to evaluate log-likelihood functions that might perform better, and this is left for future testing on real field data across multiple sites.

Several Markov Chain Monte Carlo (MCMC) samplers were evaluated (Hartig et al., 2017). Those trialed included: the Metropolis Hastings (MH) with prior optimization and delayed rejection (Green and Mira, 2001); Differential Evolution (DE) MCMC (ter Braak, 2006), Differential Evolution with snooker update (DEzs) MCMC (ter Braak and Vrugt, 2008), Differential Evolution Adaptive Metropolis (DREAM) (Vrugt et al., 2009) and finally DREAMzs, with snooker update. Only small differences in the results were found between each and as a result the DEzs sampler was chosen for its consistent ability to approach actual model parameters.

An artificial time series of rainfall was used, together with prescribed model parameters and Eq. (2) (see transformed Eq. (A2)) to model mock herbicide concentration measurements. We further simplified the stochastic model by replacing the degradation term in Eq. (A2), i.e. $-k/R$ with $-k$ and adjusted the transient pdf accordingly. This amounts to assuming the degradation rate is independent of the estimated sorption coefficient, a reasonable assumption in practical cases where it can be difficult to disentangle the effects from dissipation experiments and evidence for little correlation between k and R in spatially heterogeneous fields (Ogram et al., 1985). To these log-transformed measurements Gaussian noise with a standard deviation of 0.1 was added. Table 1 summarizes the model parameter used. Rainfall consisted of 10 mm on day 3, 3 mm on day 5 and 7 mm of day 7. Data collection was assumed to occur daily for a period of 12 days. After every measurement Bayesian calibration was conducted and the results of prior and posterior predictions and parameter estimates determined. Results of this exercise are summarized in Section 3.2.

At each forecast there is a contribution to uncertainty from the reaction parameters. It is possible to include this uncertainty into the forecast model using the Bayesian calibration These pdfs were calculated by averaging the marginal distributions of the forecast concentration over the joint distribution of the uncertain parameters, k and K_{oc} i.e.:

$$p_X(x) = \int_{0^-}^{\infty} \int_{0^-}^{\infty} p_X(x|k, K_{oc}) \, p_{k, K_{oc}}(k, K_{oc}) \, dk \, dK_{oc} \qquad (4)$$
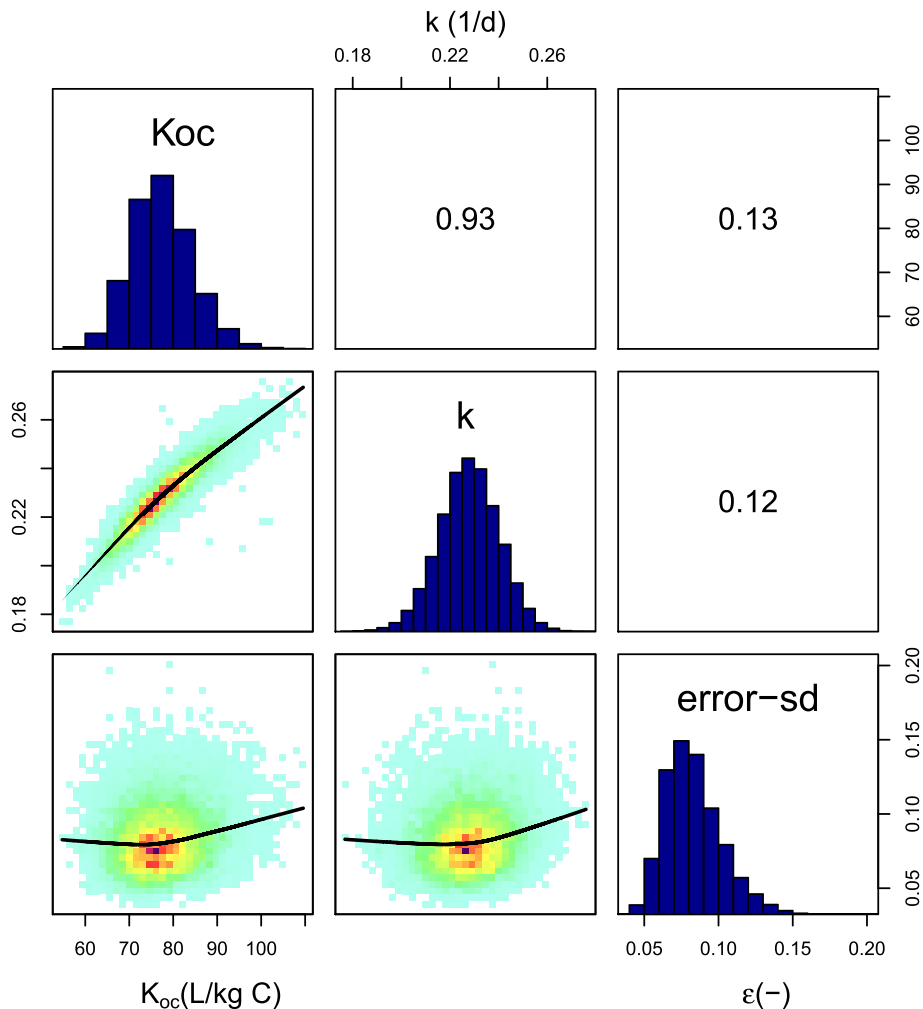

Fig. 5. Final estimates of model parameters and the correlation between parameters by the DEzs algorithm. The colour scale in the correlation plots reflects the density of parameter combinations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In Eq. (4) $p_X(x|k,K_{oc})$ is calculated by Eq. (2), using values of k and K_{oc} sampled from their joint pdf, $p_{k, K_{oc}}(k,K_{oc})$, which is provided by the Bayesian calibration. In practice Eq. (2) was evaluated discretely by calculating $p_X(x)$ over 1000 x values in the range 0 to −20, using jointly sampled values of k and K_{oc}. These were derived from the prior or posterior distributions for 10,000 parameter combinations. The resulting pdf at each x value was then averaged and the pdf rescaled to ensure its discrete integral equaled one. The Bayesian modelling was conducted using the software R and the code is documented in the Supplementary material (R Core Team, 2018).

3. Results

3.1. Climate and chemical controls on the transient residue distribution

The pdf of the residual concentration (Eq. (2)) starts as a discrete, delta distribution (Fig. 1) at $t = 0$. This is the applied concentration. With time a discrete probability remains though shifting to lower concentrations equal to $C(0) \exp(−k\,t)$. The discreteness represents the diminishing probability that no rainfall events have occurred in the time since application. The continuous part of the pdf stems from all the possible ways in which rainfall was likely to have occurred in the period following application. Analytical expressions for the moments of the first passage time to reach threshold concentrations have been previously derived (McGrath et al., 2008b). It was demonstrated that the pdf of concentration tended toward a normal distribution, which can be approximated by those moments. The solution to the pdf here, however, provides a more exact expression for the pdf.

The spread of concentrations and the location of the mode are controlled by a number of factors (Fig. 2). Increasing the rain event frequency increases the variance and lowers the mean log-concentration. Increasing the mean storm depth has a similar effect (Fig. 2a). The degradation rate, k, does not change the shape of the pdf, rather it controls the speed with which the pdf shifts along the x = ln [C(t)/C(0)] axis with time (Fig. 2b). Sorption on the other hand impacts the shape of

the pdf significantly. More strongly sorbing solutes tend to have a narrower pdf at comparable times than those with weaker sorption due to the lessened ability of rainfall to drive leaching losses below the surface.

Given a phytotoxic threshold concentration, the transient pdf can be used to inform an agronomist of the potential risks of crop damage a withholding period of 20 days would be as compared to 30 days, for example. As it is an analytical expression it offers a rapid forecasting tool with very few calibration parameters, i.e. k and R, that can be derived from the soil texture, or other pedotransfer function (i.e. n), or from the measurement or the depth relevant to seeding (i.e. z), and empirically from readily available daily rainfall data. As future rainfall is not known the model uses the known statistics of historical rainfall to quantify the impact of all possible stochastic realizations. Without knowledge of the reaction parameters a priori, estimates of, k and K_d from the literature could be used for predictions. However, when coupled with inexpensive and rapid bioassay measurements that are able to return concentration estimates within minutes, these prior parameter estimates can be refined quickly using Bayesian updating offering the potential for real-time forecast in the field.

3.2. Bayesian model calibration

An example of Bayesian model calibration (BMC) is presented below to demonstrate the potential for just a few concentration measurements to constrain estimates of the model parameters k and K_{oc} as well as the standard deviation of the measurement noise ε (Figs. 3 and 4). When BMC is performed on the first two measurements there is a significant shift in the mode of the estimated k toward the actual value (Fig. 4). There is no change between the prior and posterior for K_{oc} as there is no rainfall in the first two days. However, when the next BMC was conducted on the data up to and including day 6, a 10 mm of rainfall event had occurred on day 3, and a second 3 mm rain event on day 5, giving increases in the rate of atrazine dissipation (Fig. 3). This BMC is then able to provide an update to estimated K_{oc} toward the true value of
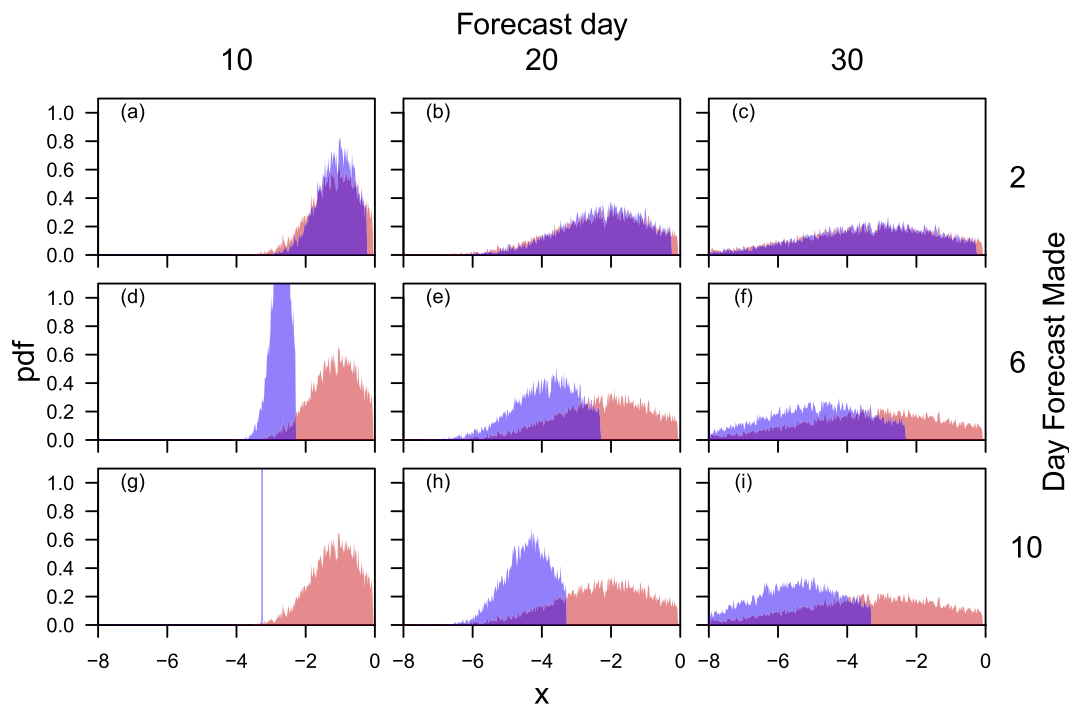

Fig. 6. Changing climatological forecasts for the concentration at 10 d, 20 d and 30 d following application utilising prior and posterior parameter estimates from BMC. Forecasts correspond to (a) The day 10 concentration (x(10)) forecast at day 2 (F(2)) prior (pink) and after (blue) the measurement on day 2; (b) x(20) − F(2); (c) x(30) − F(2); (d) x(10) − F(6); (e) x(20) − F (6); (f) x(30) − F(2); (g) observed value at day 10; (h) x(20) − F(10); (i) x(30) − F(10). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

60 L kg^{-1}. As there is a strong correlation between the two estimates of the parameters (Fig. 5) a bias in over-estimating k leads to a similar bias in underestimating K_{oc} which becomes less severe as more data and more rainfall events enter the data set later (Fig. 4). This correlation may not necessarily hold in soil but is a result of the model structure and the goodness of fit measure (Ogram et al., 1985). The model error also tends toward the value of standard deviation of normally distributed noise we added to the 'measurements'. Based on these results it appears the sorption term is best estimated by sampling just prior to and shortly following rain events.

3.3. Forecasting with BMC

Combining the parameter uncertainty (i.e. the Bayesian calibration) with the variability due to climate (i.e. Eq. (3)) is demonstrated next. Forecasts at days 2, 6 and 10 are made for days 10, 20 and 30 following application. We make forecasts using the prior information only as well as updated forecasts, informed by the measurements (Fig. 6). The spread of the forecasts made on day two after a single measurement do not constrain the predictions much (Fig. 6a–c). However, after some rainfall (days 3 and 5) the forecast made on day 6 for days 20 and 30 after the measurement are considerably constrained as compared those made using the initial uninformed prior (Fig. 6d–e). The modes of these informed distributions are much closer to subsequent predictions made on day 10 for corresponding times (Fig. 6d–i). The initial parameter estimates tended to have slower degradation rates and stronger sorption than the improved estimates provided by the BMC. As a result the forecast concentrations tend to shift to lower concentrations and the uncertainty reduces as new data are collected. A different combination of initial priors may have led to forecast concentrations increasing with additional measurements.

4. Discussion

The stochastic model presented here is the first analytical solution to a transient probability distribution that can be applied to forecast pesticide concentrations in soil. Previous modelling approaches rely on significant computational power; long simulation times of complex models as well as large data requirements and often extensive calibration. This stochastic model can be calculated easily allowing Bayesian model calibration and forecasting to be completed rapidly. With the ability to quantify concentrations in the field the time between measurement and a forecast can be reduced to minutes. Regionalised climate parameters that may vary seasonally, could be easily determined from geo-location services to allow prediction from hand-held devices in the field.

The new stochastic model, which permits an analytical solution, however may need to be adapted to better describe nonlinear dissipation kinetics (FOCUS, 2006). Had the dissipation rate slowed down the model would constantly forecast more rapid dissipation than might actually occur. Nevertheless, the Bayesian calibration would adjust the linear degradation rate as new data becomes available. Providing data from a moving time window may mitigate this effect but would not eliminate it entirely. Simple equations for nonlinear kinetics are common and therefore instead of considering stochastic variations in rainfall, perhaps other factors that are more significant for dissipation in some soils, such as temperature, may be considered (FOCUS, 2006; Daly et al., 2014). These could be easily implemented in a rapid numerical calculation, suitable for Bayesian model selection or model averaging from which a forecast could be made (Johnson and Omland, 2004; Raferty et al., 2005). Analytical expressions for transient pdfs may even be available should the climatic forcing be reasonably approximated by standard noise models (e.g. Daly and Porporato, 2006).

New, rapid and field based measurement methods for many pesticides offer the potential to provide real time forecasting for managing unintended impacts (Pomes et al., 1996; Yuan et al., 2011). The regulation of pesticides in Europe has relied on standardised modelling scenarios to assess exposure and subsequently potential risk to ecological systems and drinking water sources (FOCUS, 2009). Label recommendations for the use of pesticides, developed from field trials and lab experimentation, may not always be appropriate for a specific area. The approach described here provides a means to develop site specific risk measures for water quality and in real-time, permitting more active management of the risks at catchment scales (Bertuzzo et al., 2013).

The presented real-time forecasting approach is a suitable management support tool to optimize pesticide spreading for reaching dual agronomic and environmental goals. There is a potential to further couple the model to output from Soil Moisture Deficit (SMD) models of various drainage classes to estimate risks of off-site migration via surface runoff (Schulte et al., 2005, 2015). We have assumed that, like the Quicktest® for atrazine (Lee and Kennedy, 2001; Kennedy et al., 2013), a field based reader can quantify concentrations under field conditions (Fig. 1). Alternatively, the Bayesian approach might be adjusted to use presence or absence data from simple uncalibrated tests that can target concentration ranges (Trullols et al., 2004).

5. Conclusions

The stochastic approach developed here offers the potential to rapidly forecast withholding or "plant-back" periods for herbicides in real-time, which, to our knowledge, has not yet been possible. With the establishment of phytotoxic thresholds for particular crops the withholding period may now be managed more actively than before. In addition, the approach offers the potential for managing water quality in catchments through monitoring and forecasting residual pesticide concentrations in soil. Ongoing improvements in analytical methodologies, including a growing range of analytes that can be rapidly and inexpensively measured in the field, will likely see increased utility of approaches which can integrate monitoring and modelling efforts.

Competing interests

The authors declare no competing interests.

CRediT authorship contribution statement

Gavan McGrath: Conceptualization, Methodology, Software, Validation, Formal analysis, Writing - original draft, Funding acquisition. **P. Suresh C. Rao:** Writing - review & editing. **Per-Erik Mellander:** Writing - review & editing. **Ivan Kennedy:** Writing - review & editing, Funding acquisition. **Michael Rose:** Project administration, Writing - review & editing, Funding acquisition. **Lukas van Zwieten:** Writing - review & editing, Funding acquisition.

Appendix A

Eq. (1) can be thought of as a stochastic differential equation with multiplicative noise, however given the rain "noise" is of a short duration and intermittent, we can apply the Stratonovic interpretation and

use the normal rules of calculus to transform Eq. (1), via x = log[C/C(0)] into one with just additive noise (Suweis et al., 2011):

$$\frac{dx}{dt} = -\frac{k}{R} - \frac{i(t)}{nz\,R} \qquad (A1)$$

If the rain event duration is short, relative to the time between rain events, then we can instead consider the work done by the event depth, f (mm), and the stochastic equation becomes, after integration:

$$x(t) = x(0) - kt/R - (nz\,R)^{-1} \sum_t f \qquad (A2)$$

where x(0) is the initial log-transformed concentration, $-k/R$ defines a constant drift due to degradation and the last term is a stochastic drift depending upon the cumulative rainfall up till time t. Here we assume rainfall is reasonably described as a compound Poisson process with exponentially distributed times between rainfall events and exponentially distributed rainfall depths (Rodriguez-Iturbe and Isham, 1987). For the same rainfall process Daly and Porporato (2006) derived the pdf for the cumulative rainfall, $F(t) = \sum_t f$ (mm), up until time t as:

$$p_F(F,t) = e^{-F\gamma - \lambda t}\left(\sqrt{\lambda t\gamma/F}\, I_1\left(2\sqrt{\lambda\gamma tF}\right) + \delta(F)\right) \qquad (A3)$$

where, γ is the inverse of the mean storm depth (mm^{-1}), λ is the mean storm arrival rate (day^{-1}), and $I_1(.)$ is the modified Bessel function of the first kind of order 1. The δ denotes the Dirac delta function and thus $\exp(-\lambda t)$ represents the discrete probability that no rainfall occurred in the interval $[0, t)$.

From Eq. (A3) the transient pdf of the concentration, $p_x(x,t)$, can then be derived via a change of variables, i.e.

$$p_X(x,t) = p_F\left(g^{-1}(x,t)\right)\left|\frac{\partial g^{-1}(x)}{\partial x}\right| \qquad (A4)$$

where the function g relates how x depends upon F, which is given by Eq. (A2). The solution is presented as Eq. (2).

Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.01.401.

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