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Acceptability of inversely-modelled parameters for non-equilibrium sorption of pesticides in soil

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ABSTRACT

Simulation of the increase of sorption in time is one of the options in higher tiers of pesticide regulatory leaching assessments to obtain more realistic leaching estimates. Therefore, accurate estimates of non-equilibrium sorption parameters are required as input for the pesticide leaching scenarios. Usually, non-equilibrium sorption is described with a two-site equilibrium/non-equilibrium model in which the non-equilibrium sorption is described with two parameters (*i.e.* the desorption rate coefficient of the non-equilibrium site and the Freundlich sorption coefficient of this site). Estimates of these parameters can be obtained with inverse modelling techniques. At the moment, there is little understanding about whether the confidence intervals provided by inverse modelling can be used as measure of the likely accuracy (*i.e.* how close the estimated value is to the true value) of these estimates. We set up a semi-global inverse modelling exercise for a large number of parameter sets (*i.e.* different pesticides) using simulated datasets. Inverse modelling of non-equilibrium parameters demonstrated decreasing accuracy of the estimates for decreasing values of the non-equilibrium sorption parameters and the equilibrium sorption coefficient. Furthermore, we found a relationship between the accuracy of a parameter estimate and its CV (coefficient of variation) provided by the inverse modelling technique. Using this relationship we calculated the likelihood of rightly or wrongly accepting or rejecting a parameter estimate as a function of this CV. We recommend to use this likelihood as the basis of communication with decision makers on how to decide on accepting or rejecting parameter estimates.

1. Introduction

Contamination of groundwater due to pesticide use on agricultural crops is considered to be a threat for safe drinking water. Therefore, assessing the risk of pesticide leaching to groundwater is part of the authorisation procedure in the EU and the USA. For that purpose pesticide fate models are used as a first step in the EU (FOCUS, 2000). These models describe the most important processes to simulate pesticide leaching and are based on chromatographic transport. One of the key processes in these models is the sorption of pesticides to soil (*e.g.* Boesten and Van der Linden, 1991).

In the first tier of regulatory leaching assessments it is usually assumed that pesticide sorption is instantaneous (FOCUS, 2000). This implies that sorption coefficients are constant in time (equilibrium sorption). However, it also has been recognised for some time that sorption increases with increasing time of interaction with soil, *i.e.* non-equilibrium sorption (Walker and Jurado-Exposito, 1998; Cox and Walker, 1999; Walker et al., 2005; Wauchope et al., 2002) and thus consequently influence pesticide movement through soil and leaching to groundwater considerably (Walker, 1987; Boesten, 1991; Boesten and Van der Linden, 2001; Streck et al., 1995). Sorption is a very rapid process in the first days after application and slows down over time. To accurately describe sorption over the whole time scale multi-site models are needed. These multi-site models assume several types of non-equilibrium sites reacting at different rates, hence requiring a large number of input parameters. Two-site models are preferred for regulatory pesticide fate modelling because they provide a reasonable balance between the complexity of the model and the experimental effort required to determine model parameters. A drawback of a two-site model is that it cannot simulate a diffusive sorption process over several time scales. Only either the initial rapid increase in sorption of the first hours and days or the more gradual increase of sorption

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over time can be described adequately. Chromatographic transport of pesticides through soil takes place on a time scale of days to months. Therefore, a two-site model that is able to describe the increase of sorption from a few days after application onwards was considered suitable for establishing non-equilibrium sorption parameters for regulatory fate modelling. Such a model assumes that the equilibrium sorption sites are at equilibrium in the first few days after application.

The pesticide leaching model PEARL (Leistra et al., 2001), which is used in EU pesticide registration, contains a two-site model where sorption at the first site is an equilibrium process described by a Freundlich isotherm and sorption at the second site is a non-equilibrium process described with a pseudo first-order sorption rate equation. The pesticide content sorbed to the second site is not subject to transformation. The same two-site model is implemented in the PEARLNEQ software (Boesten and Ter Horst, 2012) which is particularly designed to estimate non-equilibrium sorption parameters with an inverse modelling technique and using long-term sorption experiments. For this purpose, the optimisation package PEST (Doherty, 2005) is incorporated in PEARLNEQ. An important advantage of PEST is that it can easily be linked to any stand-alone modelling software with ASCII-based input and output (Finsterle and Zhang, 2011). In case of the PEARLNEQ model five parameters need to be estimated simultaneously using a limited number of measurements. Applying inverse modelling to derive accurate non-equilibrium sorption parameters is challenging and is therefore only performed at higher tiers of regulatory leaching assessments. The purpose of higher tiers is to give more realistic leaching estimates to demonstrate that a potential risk identified in a lower tier does not exist in reality. Consequently, higher tiers have to be scientifically sound and non-equilibrium sorption parameters need therefore to be accurate enough. However, there is at this moment little understanding of the factors that determine the accuracy of the estimated non-equilibrium parameters (*i.e.* how close the estimated value is to the true value) identified by inverse modelling.

Inverse modelling techniques such as PEST provide the user with confidence intervals of the parameter estimates. A straightforward solution to our problem would be (i) to estimate the non-equilibrium sorption parameters from the long-term sorption experiments, (ii) to calculate the confidence intervals and (iii) then use the confidence limits for a worst-case simulation. However, this is in regulatory practise not a good solution because many risk managers wish higher tiers to be as close to reality as possible which may be incompatible with a simulation based on worst-case parameters. So a more subtle approach is necessary.

Moreover, confidence intervals calculated by local inverse modelling algorithms such as those implemented in PEST (*i.e.* the gradient-based Gauss–Levenberg–Marquardt algorithm) may be inaccurate for a nonlinear model like PEARLNEQ. The Gauss–Levenberg–Marquardt algorithm provides individual linear confidence intervals (FOCUS, 2006). "Individual" means that the confidence interval of a particular parameter estimate has a specified probability of including the true value, regardless of whether confidence intervals of other parameter estimates include their true value (Hill and Tiedeman, 2007). "Linear" means that the confidence intervals are based on a Student's *t* distribution with degrees. PEST calculates confidence intervals using a t-value from a Student's *t* test with degrees of freedom based upon the number of measurements and number of parameters estimated. To truly represent uncertainty at the given significance level in this way parameter estimates should be t-distributed. This requirement is often not met and the linear, individual 95% confidence intervals might therefore not be accurate. For nonlinear models like PEARLNEQ, nonlinear confidence intervals are usually more accurate than linear intervals (Hill and Tiedeman, 2007). Nonlinear confidence intervals can be calculated by for instance using the methods of Vecchia and Cooley (1987). Results of Monte Carlo analyses can approximate nonlinear confidence intervals as well (Hill and Tiedeman, 2007). Calculating nonlinear confidence intervals or using Monte Carlo based modelling techniques such as MCMC (Markov Chain Monte Carlo) might therefore be preferred.

Another drawback of local inverse modelling algorithms is that the estimated parameter values may be less accurate because finding the global minimum in the objective function depends on the starting values specified by the user (Dubus et al., 2004; Sorooshian and Gupta, 1995). In this respect, MCMC might too perform better as it is a global inverse modelling technique aiming at finding the global minimum of the object function. The MCMC optimisation algorithm can be seen as a random walk in the parameter domain guided by a decision algorithm (for instance Metropolis et al., 1953). MCMC is thus not confined to uphill or downhill moves in the parameter space and therefore less influenced by the presence of local minima of the object function (Mosegaard and Tarantola, 1995). MCMC is increasingly being used in environmental modelling (Gallagher and Doherty, 2007; Gottschalk et al., 2010; Dotto et al., 2011). However, we choose the PEST model and its local inverse modelling technique because it was our objective to build upon the existing practise of pesticide regulatory fate modelling.

Our study aims at addressing the problem of deciding on acceptability of inversely modelled parameters which is a fundamental issue when these parameters are further used as input into sophisticated risk assessment procedures (which will often be the case for environmental problems). We consider as a case kinetic pesticide-sorption parameters used to assess pesticide leaching to groundwater, but the proposed methodology is likely to be applicable also in other sectors. We propose the following procedure: (i) specify the required accuracy of a parameter in terms of the maximum acceptable deviation from its true value based on the risk assessment procedure (this deviation is a given in our study and will be fixed at 25%), (ii) generate a large number of datasets for known parameter values, representing possible experimental datasets from laboratory studies (the datasets are created for known parameter values, so that the parameter values resulting from parameter optimisations can be compared to the 'true' values) (iii) fit the process model to the data, (iv) plot the deviation from the true parameter value against some measure of the confidence limits as generated by the inverse modelling tool (the coefficient of variation in our study), (v) derive from this plot the likelihood of wrongly or rightly accepting or rejecting a certain parameter value if judgement would be made based on the confidence limits generated by the inverse modelling, (vi) decide on acceptance of a parameter value based on this likelihood using criteria agreed with decision makers (*e.g.* <5% probability for wrongly accepting a parameter value). Communication with decision makers in terms of this likelihood will improve the understanding between scientists and decision makers and thus contribute to better decisions. Assessment of the level of the maximum acceptable deviation from the true value in the overall risk assessment procedure is beyond the scope of our study; this deviation may *e.g.* depend on the margin of safety in the decision making procedure.

2. Material and methods

2.1. Experimental procedure for long-term sorption experiments

The normal procedure for long-term sorption experiments is as follows. Moist soil is weighted into glass jars. Then an aqueous solution containing the pesticide is added and the soil is mixed. After given time intervals, two jars are sampled. The soil in the first jar is extracted with organic solvent to derive the total mass of pesticide