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Evaluation of methods to derive pesticide degradation parameters for regulatory modelling

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Abstract Models to simulate the fate of pesticides in the environment are frequently used for risk assessments within the registration process. An adequate description of pesticide degradation in soil is important to provide input for these models. Often, DT50 values (time required for 50% dissipation of the initial concentration) are used as model input, but there is no widely agreed methodology to derive DT50 values from experimental data. DT50 values are often obtained by fitting first-order kinetics to observed degradation patterns. The result depends on the handling of pesticide data (e.g. logarithmic transformation) and initial concentrations (variable or fixed). Kinetics other than first-order may be more suitable to describe the decline of measured concentrations, but the derived DT50 values are then not appropriate as input for many simulation models. Field or laboratory DT50 values can be used for modelling and this has consequences for model parameterisation. Degradation parameters derived from static laboratory experiments may not be applicable to pesticide behaviour under flow conditions in the field. Several methods to simulate the fate of metabolites and to evaluate experimental data are available. The methodology used to derive model input parameters must be consistent with the approach used within the simulation model.

Keywords Pesticide · Degradation · Parameter estimation · Modelling · Regulation

Introduction

Predictions of environmental concentrations of a pesticide in soil, surface water and groundwater are a significant part of the data package submitted for pesticide registration (STET 1995). These predictions often involve

the use of mathematical simulation models, such as PERSIST (Walker and Barnes 1981), PELMO (Jene 1998), PRZM (Carsel et al. 1998), PEARL (Tiktak et al. 2000) and MACRO (Jarvis 1994). One of the most important processes influencing the environmental behaviour of a pesticide is its degradation in soil. Standard laboratory and field dissipation studies are performed within the regulatory process. DT50 values (time required for 50% dissipation of the initial concentration) are derived from these experiments to provide a numerical indication of pesticide persistence in soil. These are then used as input data for the models. A consistent and widely agreed methodology to characterise persistence has not been established. Several methods to derive degradation parameters from experimental data are available, and these may result in different DT50 values. This paper evaluates existing methods and discusses implications for the parameterisation of regulatory simulation models.

Estimation of degradation parameters from laboratory data

Data transformation

Degradation parameters required for modelling can be derived from laboratory studies where the dissipation of a pesticide in soil is investigated under controlled conditions. The decline of concentrations with time is often described according to first-order kinetics (Eq. 1a):

$$\frac{dC}{dt} = -kC \quad (1a)$$

where C is the concentration (mg kg^{-1} soil), t is the time (days) and k is the degradation rate (days^{-1}). The change of pesticide concentration with time (dC/dt) is proportional to the concentration at this time. The integrated form of Eq. 1a gives Eq. 1b:

$$C_{(t)} = C_0 \exp(-kt) \quad (1b)$$

where $C_{(t)}$ is the concentration at time t (mg kg^{-1} soil) and C_0 is the concentration at time 0 (mg kg^{-1} soil). A

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linear relationship is given for the logarithmic form of Eq. 1b with:

$$\ln C_{(t)} = \ln C_0 - kt \quad (2)$$

The time at which the concentration reaches half the initial concentration is referred to as the half-life [$t_{1/2}$; time for 50% degradation of the initial amount of a pesticide (days)]. Substitution into Eq. 2 gives:

$$t_{1/2} = \frac{\ln 2}{k} \quad (3)$$

Under practical conditions, particularly in the field, degradation cannot always be separated from other processes leading to pesticide dissipation. In this case, the term DT50 value is more appropriate and reflects the time for the dissipation of 50% of the initial concentration.

The initial pesticide concentration C_0 and the degradation rate k can be estimated by fitting Eqs. 1a or 1b to experimental data on the decline of pesticide residues in soil. Formerly, this was restricted by the limited availability of appropriate parameter optimisation methods and by extended computing times. To address this problem, the linear form (Eq. 2) was used. C_0 and k in Eq. 2 could then be derived by fitting a straight line to the data. Today, several tools are available which efficiently fit Eqs. 1a or 1b to measured data and estimate those parameters that give the best possible agreement between calculated and observed concentrations. These include ModelMaker (Cherwell Scientific, Oxford, UK), Microsoft Excel Solver (note that the fit of an exponential trendline with Microsoft Excel uses Eq. 2 and not Eq. 1), statistical packages (e.g. SAS, SAS, USA; STATISTICA, StatSoft, Tulsa, USA), and Easyfit (K. Schittkowski, University of Bayreuth, Germany). The use of different tools to fit Eq. 1 to experimental data or of different options within one programme may result in different DT50 values. This can be attributed to differences in the approach used to solve the equation and to discrepancies in statistical criteria to identify “best-fit” parameters.

Both the direct fit of the exponential equation (Eq. 1) to untransformed data and the fit of a straight line to logarithmically transformed concentrations (Eq. 2) are based on first-order kinetics. Nonetheless, these approaches may result in different DT50 values. This is demonstrated in Fig. 1 for two hypothetical datasets. For the first set of concentrations, the logarithmic transformation has only a small impact on the estimated DT50 value relative to an exponential fit. For the second dataset, however, the logarithmic method results in a DT50 value which is twice as long as that obtained by fitting an exponential curve to untransformed data. Logarithmic transformation assigns a larger weight to smaller concentrations (Fig. 1). Today, there are no computational limitations to the direct fit of the exponential equation and this approach is recommended unless experimental evidence suggests otherwise.

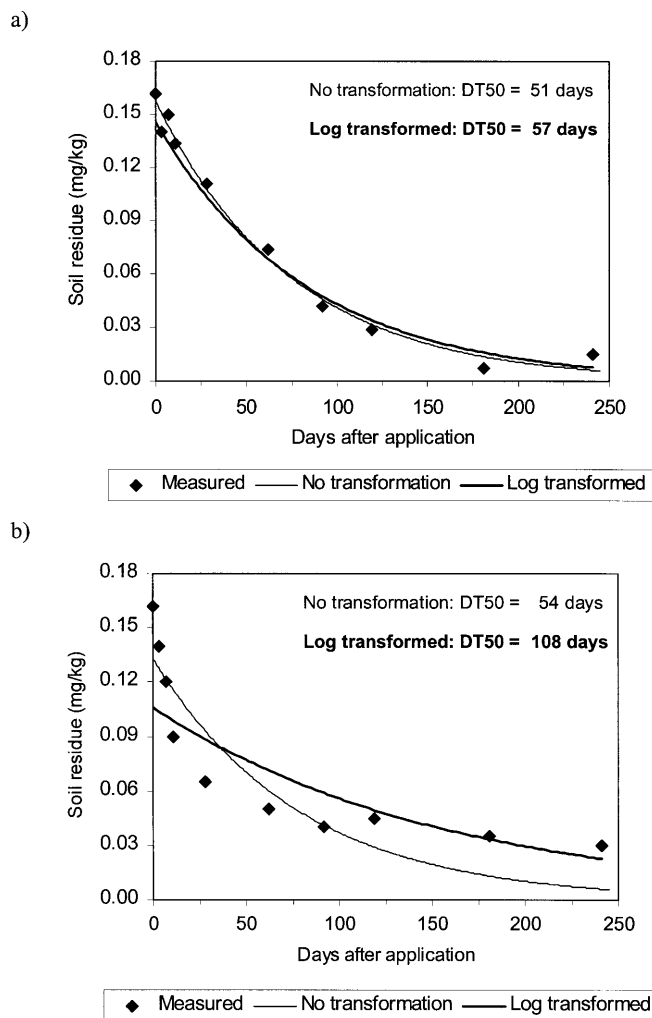


Fig. 1a,b Fit of first-order kinetics to untransformed data (Eqs. 1a, 1b) or to logarithmically transformed concentrations (Eq. 2) for two hypothetical datasets. DT50 Time required for 50% dissipation of the initial concentration

Initial pesticide concentration

The initial concentration of the pesticide in soil was optimised to obtain the best fit to the data in the analyses presented above. It was assumed that the initial concentration is subject to experimental error. Often, however, the initial concentration is fixed to: (1) the concentration measured immediately after application, or (2) the theoretically applied amount. This may have a strong impact on the estimated DT50 value, particularly if deviations from first-order kinetics occur. This is demonstrated for an example dataset in Fig. 2.

Deviation from simple first-order kinetics

Often, degradation does not follow simple first-order kinetics (mono-phasic or one-compartment kinetics), but shows a bi-phasic pattern where soil residues decrease

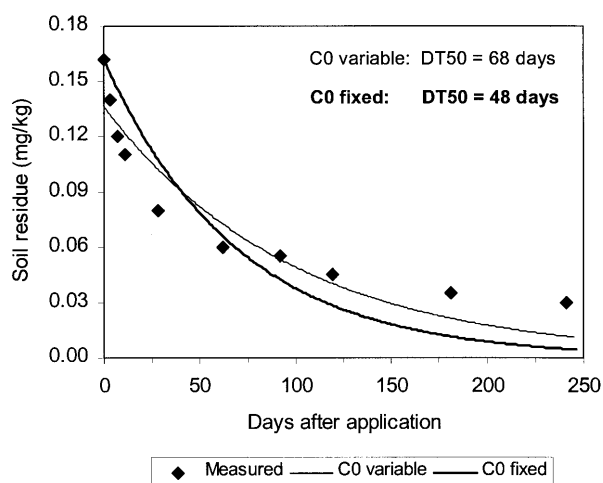


Fig. 2 Pesticide residues in soil fitted by first-order kinetics with variable or fixed initial concentration (C_0)

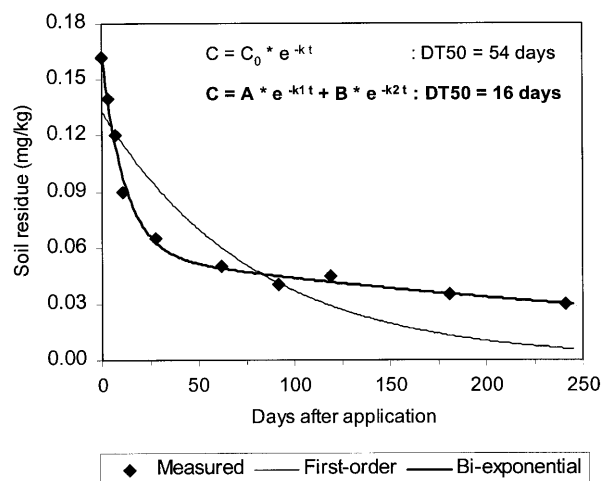


Fig. 3 Pesticide residues in soil fitted by first-order kinetics or a bi-exponential curve, where A (mg kg^{-1} soil) and B (mg kg^{-1} soil) are constants, k_1 (days^{-1}) and k_2 (days^{-1}) are rate constants, and t (days) is time

slowly after an initial rapid decline and persist at a low level until the end of the experimental period. This was the case for the hypothetical data presented in Fig. 1b. The first-order equation is often considered acceptable unless the r^2 value falls below 0.70. The r^2 value for the fit shown in Fig. 1b is 0.81 (untransformed data). The derived DT50 value (54 days) may thus be taken into account in regulatory risk assessments although the visual agreement between observed and simulated data is relatively poor. The decline of residues is under-estimated by simple first-order kinetics early after treatment and over-estimated later in the period (Fig. 1b).

A number of empirical non-linear equations or mechanistic models to describe bi-phasic (or two-compartment) degradation patterns exists. Timme et al. (1986) proposed a computer programme to fit first-order kinetics, 1.5- and second-order kinetics, and a range of root functions to experimental data. In all cases, the data are transformed in order to allow a linear regression analysis. The above discussion on the impacts of such transformations on first-order DT50 values applies equally to the non-linear kinetics proposed by Timme et al. (1986). Several curve-fitting tools and models were compared by Leake et al. (1995) and large differences in estimated DT50 values were found.

Additional approaches to describe the non-linear decline of pesticide residues in soil include bi-exponential kinetics, the hockeystick model, the model proposed by Gustafson and Holden (1990) and the protected compartment model. The bi-exponential curve consists of two exponential terms (Eq. 4).

$$C_{(t)} = A \exp(-k_1 t) + B \exp(-k_2 t) \quad (4)$$

where $C_{(t)}$ is the concentration at time t (mg kg^{-1} soil), A (mg kg^{-1} soil) and B (mg kg^{-1} soil) are constants, k_1 (days^{-1}) and k_2 (days^{-1}) determine the decline of the first

and the second component of the curve, respectively, and t is in days. The bi-exponential curve is compared to mono-phasic first-order kinetics in Fig. 3. If bi-exponential kinetics are used, DT50 values should be estimated with care. Often, DT50 values are derived only from the first term of the equation. This is not appropriate as the degradation pattern is determined by both exponential curves simultaneously. The DT50 value derived from the first component of the bi-exponential curve shown in Fig. 3 is 8 days. This is much shorter than the DT50 value of 16 days which was determined for the complete bi-exponential curve.

It should also be noted that the concept of the DT50 value in the simple first-order equation differs from that in a non-linear model. Only for first-order kinetics is the time for a decrease in pesticide concentration from 100% to 50% the same as the time required for a decline from 50% to 25% of the initial value. DT50 values are often used as input data for simulation models to assess the fate of pesticides. In this case, the approach used to derive degradation parameters from experimental data must be consistent with the methodology used in the simulation model. Most models assume that degradation follows simple first-order kinetics. Parameters estimated using non-linear equations are thus usually inappropriate. This leads to conflicts where degradation data clearly deviate from simple first-order kinetics. Figure 4 shows pesticide concentrations in soil predicted with a simulation model which uses first-order kinetics to describe degradation. Concentrations were simulated using the DT50 values derived by fitting first-order kinetics (54 days) or a bi-exponential curve (16 days) to the data shown in Fig. 3. Much smaller soil residues are simulated on the basis of the bi-exponential DT50 value compared to the first-order DT50 value. This is likely to lead to smaller predicted environmental concentrations in groundwater and surface water. The selection of appro-

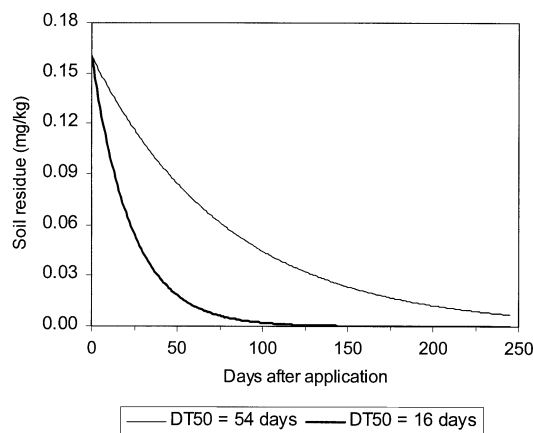


Fig. 4 Pesticide residues in soil predicted by a first-order simulation model using DT50 values which were derived by fitting mono-phasic first-order kinetics (DT50=54 days) or a bi-exponential curve (DT50 value=16 days) to laboratory data

appropriate degradation parameters is important as model outputs are particularly sensitive to these parameters (Dubus et al. 1999).

At present, there is no agreed guidance on how to derive appropriate data for modelling in cases with clear deviation from mono-phasic first-order kinetics. The FOCUS groundwater working group has recently developed standard scenarios to assess the potential for groundwater contamination within pesticide registration at the European level (FOCUS, 2000). Four models can be used to simulate pesticide leaching (PELMO, PRZM, PEARL and MACRO). Version 3.14 of PRZM is the only one of these four models which considers non-first-order degradation. It enables the user to calculate degradation according to mono-phasic first-order kinetics or a bi-phasic model. The inclusion of approaches which deviate from simple first-order kinetics into the remaining models appears desirable.

Field dissipation data

Laboratory DT50 values may not always be appropriate to simulate pesticide persistence in the field. Beulke et al. (2000) evaluated 178 published studies which presented pesticide residues measured in the field and those simulated on the basis of laboratory DT50 values using the persistence model PERSIST (Walker and Barnes 1981) and related approaches. The simulated percentage of the initial pesticide concentration at the time of 50% measured loss was taken as a common criterion for model performance. Of the 178 studies, 28.1% over-estimated the “observed” value (50% loss) by up to a factor of 1.25. An under-estimation by up to a factor of 1.25 was found in only 11.2% of the studies. Simulated values over-estimated those observed by more than a factor of 1.25 in 43.8% of the studies, whereas an under-estimation by more than a factor of 1.25 occurred in only

16.9% of the studies. These results confirm the frequently stated tendency for the model to over-estimate pesticide persistence in the field (Pestemer and Auspurg 1987; Walker and Zimdahl 1981). Discrepancies between simulated and observed data reviewed by Beulke et al. (2000) were partly attributed to difficulties in characterising pesticide behaviour under outdoor conditions using laboratory studies. These arise because of differences in soil conditions between the laboratory and the field, as well as the spatial and temporal variability of degradation.

The use of information from field persistence studies may be an alternative to the use of laboratory data. Often, the time-course of pesticide residues in the field can be approximated by first-order kinetics, but the resulting DT50 value reflects the time to 50% loss of the pesticide due to a number of dissipation processes (e.g. volatilisation, photolysis, uptake by plants or leaching below sampling depth). If these values are used for modelling, sub-routines other than degradation which allow the separate simulation of individual dissipation processes (e.g. volatilisation) must be switched off. An advantage of field DT50 values over laboratory data is that they are determined under conditions specific for the field and thus may closely match the situation which is to be modelled.

Laboratory DT50 values refer to specific temperature and moisture conditions. These values may be corrected within simulation models for actual conditions. In contrast, field DT50 values reflect the variation in degradation over the course of the field study due to fluctuations in soil temperature and moisture. If these values are used as model input, the sub-routines describing temperature and moisture dependence of degradation must be switched off unless detailed temperature/moisture information is available for the period of the field study. Under certain conditions it seems to be acceptable to use mean values for the season (e.g. 16°C air temperature for central Europe).

Coupling degradation with transport processes

In static laboratory experiments, degradation is assessed isolated from transport processes. The true applicability of parameters derived in static systems to flow conditions in the field where degradation and transport occur simultaneously has not been fully established. Estrella et al. (1993) investigated the degradation of 2,4-D in static incubation studies and in column leaching experiments under saturated and unsaturated conditions. Degradation in incubation studies was 3 times faster than that under saturated flow conditions and 14 times faster than in unsaturated column studies. This was partly attributed to differences in aeration and mixing and to the decreasing substrate concentrations in incubation studies compared to a constant influent concentration in the column experiments. Degradation of alachlor occurred more rapidly under transport conditions than in static incubation studies in work by Guo and Wagenet (1999). This was attrib-

uted to non-equilibrium sorption during transport where the time for interaction between the pesticide and soil aggregates may be short and an equilibrium between sorbed and dissolved phases may only rarely be achieved. Sorption is often considered to limit pesticide degradation due to a reduced availability to degrading micro-organisms (Scow 1993).

The applicability of degradation rates derived in isolation of transport processes to complex systems in the field was discussed by Rao et al. (1993). The authors concluded that the linkage between degradation and transport and the influence of non-equilibrium sorption on degradation should be studied more extensively and considered in modelling the fate of chemicals in soil. A combination of analytical modelling techniques with column leaching studies where degradation, sorption and transport are studied simultaneously offers the potential to provide more realistic degradation parameters for use in environmental fate models (Gamerding et al. 1993). However, the mathematical description of these systems is relatively complex and parameters may be difficult to estimate, particularly under flow conditions similar to the field situation. More work is required in this area to establish an experimental and modelling framework which allows robust estimation of realistic model parameters with reasonable effort.

Inverse modelling

Inverse modelling is a technique whereby selected input parameters for a mathematical model are varied many times to optimise the fit between model output and observed behaviour. The method can be used to estimate those degradation parameters that give the best fit between outputs of a pesticide leaching model and experimental data obtained under outdoor conditions (e.g. soil residues, concentrations in leachate from a lysimeter). Tools are available to repeatedly run the model, compare the output to experimental data and modify input parameters until a statistically optimised fit between simulated and observed data is achieved (e.g. Doherty et al. 1994). Gottesbüren (1991) estimated DT50 values at reference temperature and moisture conditions and parameters required to correct degradation for actual conditions from pesticide residues measured in the field. Gottesbüren (1998) discusses the use of pesticide parameters derived by inverse modelling to extrapolate the observed behaviour of a compound in lysimeter studies to a wider range of conditions.

DT50 values provided by inverse modelling are corrected for effects of fluctuations in temperature and moisture conditions and correspond to reference conditions set within the model. These parameters can be used for simulations under different climatic conditions. As with field DT50 values, those derived by inverse modelling are “lumped” parameters incorporating a number of dissipation processes which also depend on the quality of the dataset and the model used to simulate the data.

Results are influenced by the methodology used to derive “best-fit” parameters. Inverse modelling should not be considered as an alternative to experimental laboratory and field studies, but as a complementary approach which helps to characterise the behaviour of a pesticide once released to the environment.

Metabolites

The parent compound is normally of main interest in assessments of the environmental fate of pesticides because metabolites are often less biologically active and occur at smaller concentrations. However, risk assessments are required for metabolites which account at any time for more than 10% of the amount of active substance applied and which exhibit pesticidal, ecotoxicological or toxicological activity. Two main approaches exist to simulate leaching of metabolites to depth. Both are accepted by the FOCUS group although the first method is preferred (FOCUS 2000).

Approach 1

The fate of the parent compound and the metabolite are linked. The models PELMO, PRZM and PEARL allow simulation of the fate of a parent compound and the formation, degradation and leaching to depth of a metabolite in a single model run. The MACRO model can be run successively to simulate the linked fate of the parent and the metabolite.

Approach 2

Alternatively, separate simulations can be performed for the parent and the metabolite with both assumed to be directly applied to the soil. The “application rate” for the metabolite is usually calculated from its maximum accumulation in soil.

Approaches 1 and 2 require different inputs, and the method used to derive degradation parameters for metabolites must be consistent with the methodology used in the simulation model. The most commonly used approaches to derive degradation parameters for metabolites are:

- A. The metabolite is added to the soil, its concentration is determined at intervals and a first-order equation is fitted to the data. The derived degradation rate is suitable for modelling the linked fate of the parent compound and the metabolite in a single or successive model runs (approach 1). The degradation rate for the metabolite needs, however, to be supplemented by information on its formation. Parameters derived following addition of the metabolite to the soil are “true” degradation rates (or half-lives) which do not account for any other processes. Under practical conditions in

the field, the actual dissipation of metabolite concentrations in soil will be slower. This is due to the continued formation of the metabolite from the parent compound. If “true” metabolite degradation rates are used to simulate the fate of the metabolite in a separate model run according to approach 2, actual environmental concentrations of the metabolite may be under-estimated.

B. The parent compound is added to the soil and the concentrations of parent and metabolite are determined at intervals giving actual data on the soil exposure to both.

- First-order kinetics are fitted to the decline of metabolite concentrations from the time of maximum accumulation onwards. This method provides a dissipation rate (or a DT50 value) rather than a “true” degradation rate. It combines the continued formation of the metabolite from the parent compound and metabolite degradation in a single parameter. Degradation of the metabolite is thus under-estimated. Parameters derived using this method are appropriate to simulate metabolite fate in a separate model run (approach 2). Their use in approach 1 is possible, but it should be noted that this is likely to over-estimate the environmental concentrations of the metabolite.

- A kinetic model is fitted to concentrations for the parent compound and the metabolite. This model accounts for the simultaneous degradation of the parent and the formation and degradation of the metabolite. These processes are often described by consecutive first-order kinetics (Fig. 5). Kinetic models give a good representation of the degradation processes that occur in soil. Their use is, however, not recommended

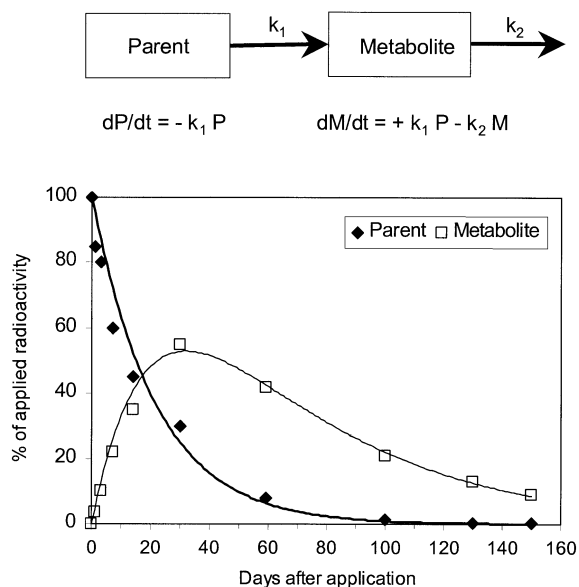


Fig. 5 Kinetic model to describe simultaneously the degradation of a parent compound (P) and the formation and degradation of its metabolite (M) according to consecutive first-order kinetics and fit of the model to a hypothetical dataset

for complex metabolite schemes or where the observed pattern of concentrations does not allow the confident estimation of degradation rates. Degradation rates estimated through the fit of kinetic models are suitable to simulate the fate of a metabolite according to approach 1. Non-linear kinetics may also be applied and these may give a better fit to the data (e.g. Dyson et al. 1999). However, the derived parameters can often not be used as input data for simulation modelling as most models are restricted to the assumption of first-order kinetics.

Conclusions

The method used to derive DT50 values for modelling pesticide degradation from experimental data may have large impacts on the modelling results. Approaches agreed upon amongst members of research organisations, industry and regulators appear desirable to ensure that experimental data are evaluated in a consistent way. A set of rules to support the selection of a scientifically rigorous approach should be established rather than a unique, standard methodology. Particular conflicts arise where degradation of a parent compound and/or its metabolites clearly deviate from simple mono-phasic first-order kinetics because DT50 values estimated on the basis of non-linear approaches are not suitable as input data for most simulation models. Modifications of existing models are required to address this problem.

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