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Guidance for inverse modelling using TOXSWA

J.W. Deneer, P.I. Adriaanse, C. van Griethuysen and J.J.T.I. Boesten

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Referaat NL Schatting van afbraaksnelheden van gewasbeschermingsmiddelen in water onder realistische omstandigheden is belangrijk voor het juist schatten van blootstellingsconcentraties in de toelating. Hoewel er gestandaardiseerde testen voor afbraak in water en in water-sediment systemen bestaan, weerspiegelen deze niet de afbraak zoals die onder realistische omstandigheden in het veld optreedt. Dit rapport beschrijft de schatting van afbraaksnelheden in water op basis van data gemeten in cosm studies ontworpen voor bepaling van ecotoxicologische effecten. Resultaten voor metribuzin, linuron en imidacloprid worden besproken. De gevonden afbraaksnelheden waren over het algemeen minder conservatief dan de resultaten uit lagere tiers, er werd meestal snellere afbraak geconstateerd. De voorgestelde methode is bruikbaar voor het schatten van afbraaksnelheden op basis van waterconcentraties gemeten in cosm experimenten, op voorwaarde dat sorptie aan sediment slechts beperkt optreedt. Een van de aanbevelingen behelst uitbreiding van de methode naar verbindingen waarvoor sorptie aan sediment een grotere rol speelt.

Abstract UK Estimation of the degradation rate of plant protection products in water under realistic conditions is important for correct estimation of exposure concentrations for regulatory purposes. Although standardised tests for degradation in water and water-sediment systems exist, these do not reflect degradation under realistic field conditions. This report discusses the estimation of degradation rates of pesticides in water from fate data gathered in cosm studies devised for ecotoxicity testing. Results for metribuzin, linuron and imidacloprid were explored. Results were typically less conservative than those obtained from lower-tier tests, i.e. faster degradation was observed. The proposed method is suitable for estimation of degradation rates from aqueous concentrations measured in cosm experiments, provided that sorption to sediment is limited. Recommendations include extending the method to compounds for which sorption to sediment is more important.

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Summary

The aquatic risk assessment of pesticides requires knowledge about the exposure of aquatic ecosystems in small surface waters. Exposure concentrations are predicted using simulation models, in which the degradation rate in water is an important input parameter. At present, there is no simple standard test to determine the degradation rate in water in a realistic way, as hydrolysis (OECD 111), photolysis (OECD 316), degradation studies in water in the dark (OECD 309) or degradation studies in systems containing both water and sediment (OECD 308) exist, but do not result in aqueous degradation rates representative for realistic conditions for outdoor surface waters.

The estimation procedure described in this report addresses this gap and tries to give guidance on the estimation of degradation rates of pesticides in water from cosm studies. Although such studies are primarily performed for higher-tier ecotoxicological effect assessments, often information on pesticide concentrations in water (and possibly sediment) is gathered, enabling estimation of degradation rates in water under realistic conditions.

The devised procedure for estimation of degradation rates, which uses inverse modelling with the models PEST (version 13.0) and TOXSWA (version 4.4.2), was used for estimation of aqueous degradation rates of metribuzin, linuron and imidacloprid. These compounds were selected because of their limited tendency for sorption to sediments. Both photo-stable (linuron) and photo-sensitive (metribuzin, imidacloprid) compounds were used in evaluation of the method, to test if the proposed method was suitable for both types of compounds.

For each of the compounds, three mesocosm studies were analysed. In all cases, the inverse modelling of aqueous concentrations resulted in satisfactory fits of experimental data, and yielded plausible results for the estimated degradation rates.

The estimated degradation rate constants were typically less conservative than degradation rates estimated from lower-tier data, such as hydrolysis and water-sediment studies.

The method appears suitable for the estimation of degradation rates from aqueous concentrations measured in cosm experiments, provided that sorption to sediment of the compound is relatively limited. The only requirements are that a minimum of five measurements of aqueous concentrations over time are available, and that the depth of the water layer is known. All other parameter values necessary for the calculations, such as properties of the compound, can be acquired relatively easily using sources as identified in the report, or can be estimated using default values, also provided in detail in the report. So, this method results in the estimation of a more realistic degradation rate than the rate found in indoor laboratory studies, that can be used in higher-tier risk assessments for regulatory purposes

It is recommended to extend the procedure to compounds for which sorption to sediment is more important, using data from cosm studies, in which concentrations in both water and sediment have been measured. For experiments with more than a single application, a possible improvement is to not only estimate $C_{t=0}$, i.e. the concentration resulting from the first application, but to treat all concentration increases resulting from applications similarly. Moreover, it is recommended to derive guidance on derivation of a single degradation rate in water in situations where different values are derived from different cosm studies conducted for a compound.

Samenvatting

In de aquatische risicobeoordeling van gewasbeschermingsmiddelen is kennis omtrent blootstellingsconcentraties in klein oppervlaktewater nodig. Dergelijke concentraties worden berekend met modellen, waarbij de afbraaksnelheid van het gewasbeschermingsmiddel in water een belangrijke rol speelt. Er bestaat op dit moment geen gestandaardiseerde test om de afbraaksnelheid onder realistische omstandigheden te bepalen. Informatie omtrent hydrolyse (OECD 111), fotolyse (OECD 316), afbraaksnelheid in water in het donker (OECD 309) of afbraak in systemen die zowel water als sediment bevatten (OECD 308) bestaan weliswaar, maar geven geen informatie omtrent afbraaksnelheden die representatief zijn voor realistische omstandigheden in het veld.

De methodiek die in dit rapport wordt beschreven gaat in op dit manco en geeft richtlijnen voor het schatten van afbraaksnelheden van gewasbeschermingsmiddelen in water in cosm studies. Hoewel dergelijke studies gewoonlijk worden uitgevoerd om de risico's op ecotoxicologische effecten te bestuderen, leveren zij vaak ook informatie omtrent de concentraties van gewasbeschermingsmiddelen in water, en soms in het sediment, waaruit schatting van afbraaksnelheden onder realistische condities mogelijk is.

De ontworpen procedure is gebaseerd op inverse modellering met de modellen PEST (versie 13.0) en TOXSWA (versie 4.4.2) en is gebruikt voor het schatten van afbraaksnelheden in water van metribuzin, linuron en imidacloprid. Deze verbindingen werden geselecteerd vanwege hun beperkte neiging om in sediment te penetreren. Zowel foto-stabiele (linuron) als foto-labele (metribuzin, imidacloprid) verbindingen werden gebruikt om na te gaan of de methode voor dergelijke verbindingen geschikt is.

Voor elk van de verbindingen werden de gegevens van drie mesocosm studies geanalyseerd. In alle gevallen leidde de inverse modellering van de waterconcentraties tot een bevredigende beschrijving van de experimentele gegevens, resulterend in plausibele waarden voor de geschatte snelheidsconstanten.

De geschatte waarden waren doorgaans minder conservatief dan afbraaksnelheden geschat op basis van gegevens uit lagere tiers, zoals gegevens uit hydrolyse studies en gegevens ontleend aan water-sediment studies.

De schattingsmethode lijkt geschikt voor het schatten van afbraaksnelheden op basis van waterconcentraties gemeten in cosm studies, op voorwaarde dat penetratie van de stof in het sediment relatief beperkt is. De enige voorwaarde is dat er tenminste vijf metingen van waterconcentraties beschikbaar zijn, en dat de diepte van de waterlaag bekend is. Alle andere parameter waarden die nodig zijn voor de berekeningen, zoals stofeigenschappen, kunnen relatief eenvoudig worden ontleend aan bronnen die in het rapport worden genoemd, of kunnen worden geschat op basis van standaard waarden die eveneens in het rapport worden gegeven. Dus de beschreven methodiek levert een realistischere waarde op voor de afbraaksnelheid in water dan de waarde gevonden uit experimenten in het laboratorium. Deze realistischere afbraaksnelheid kan gebruikt worden in de hogere tiers van de aquatische risicobeoordeling in de registratieprocedure.

Er wordt aanbevolen om de procedure uit te breiden naar verbindingen waarvoor penetratie in het sediment een grotere rol speelt, waarbij gebruik kan worden gemaakt van gegevens uit studies waar concentraties in zowel water als sediment zijn gemeten. Voor experimenten met meer dan een enkele toediening van de stof is een mogelijke verbetering om niet alleen $C_{t=0}$, de concentratie meteen na de eerste toediening, te schatten maar om de concentratie verhoging(en) na elke toediening op een uniforme wijze te gebruiken. Bovendien wordt aanbevolen om richtlijnen te ontwikkelen hoe om te gaan met situaties waarin meerdere schattingen voor de afbraaksnelheid worden ontleend aan verschillende cosm studies.

1 Introduction

The aquatic risk assessment of pesticides requires the assessment of exposure of aquatic ecosystems in small surface waters adjacent to agricultural fields treated with pesticides. Exposure is predicted using simulation models, in which the degradation rate in water is an important input parameter. The rate of degradation may strongly affect the course of the concentration of the pesticide over time, especially in scenarios with low water flow velocities and/or multiple applications. At present, there is no simple standard test to determine the degradation rate in water in a realistic way. Hydrolysis (OECD 111) and photolysis (OECD 316) studies, degradation studies in the dark (OECD 309) or degradation studies in systems containing both water and sediment (OECD 308) exist, but do not result in degradation rates in the water phase representative of realistic conditions. In view of the importance of model calculations in aquatic risk assessment in registration procedures, it is important to estimate the degradation rate in water of a compound in a realistic way.

Guidance at EU-level for the derivation of DT_{50} values (kinetic endpoints) was developed by the Workgroup on Degradation Kinetics of FOCUS DG SANTE - the FORum for Co-ordination of pesticide fate models and their USe within the European Commission's (EC's) Directorate General for Health and Food Safety (2006). However, the EC guidance provides an estimation of degradation rates in laboratory water-sediment studies and does not address the estimation of degradation rates under more realistic (field) conditions. The estimation procedure described in this report addresses this gap and provides guidance on the estimation of degradation rates in water using data from outdoor cosm studies primarily performed for higher-tier ecotoxicological effect assessments.

Differences with the approach of FOCUS (2006) are as follows:

For surface water, FOCUS (2006) was limited to developing: *'guidance about how to estimate and use the disappearance times (kinetic endpoints) that describe the various aspects of parent and metabolite fate in water-sediment studies'* (FOCUS, 2006). In this report, the emphasis is not on water-sediment studies, but on outdoor cosm studies, performed in the framework of higher-tier ecotoxicological effect assessment.

Secondly, FOCUS (2006) relied on compartmental approaches, rather than more detailed, mechanistic approaches. A distinction was made between two levels: Level P-I for a one-compartmental approach and Level P-II for a two-compartmental approach, combined with several types of kinetics. As an alternative to this approach, FOCUS (2006) suggested to use the TOXic substances in Surface Waters (TOXSWA) model to fit the water-sediment system data. This report only focuses on this alternative approach. Compartmental approaches do not consider processes, such as volatilisation and sorption to aquatic plants, whilst the mechanistic TOXSWA model includes these processes. In outdoor cosms, these processes may play an important role in the disappearance of the compound from the water. Since the aim was to find a generic, broadly-applicable approach, it should be possible to include these processes in the estimation procedure.

In their guidance, FOCUS (2006) made a distinction between two general types of kinetic endpoints: (i) persistence endpoints, used to determine whether various aquatic ecotoxicology studies are needed and (ii) modelling endpoints, needed for calculating Predicted Environmental Concentrations, as part of an aquatic risk assessment. This report focuses on the estimation of the degradation rate in water as a modelling endpoint only.

In the described procedure, degradation rates were estimated by inverse modelling of fate data taken from a cosm study. The procedure used the TOXSWA model coupled to the PEST (Parameter ESTimation) optimisation tool. The procedure is limited to compounds with relatively high water solubilities for which penetration into sediment is negligible. However, future extension of the

procedure will focus on studies and compounds for which penetration into the sediment is more important, with the aim of developing an estimation procedure for degradation rates in water and possibly also in sediment.

More recent guidance on the estimation of $DT_{50, \text{degradation}}$ ($DegT_{50}$) values for surface water was written by Boesten *et al.* (2014). They proposed a stepped approach for the estimation of $DegT_{50, \text{water}}$ values for application in the Dutch surface water scenarios currently under development for use in the pesticide registration procedure in The Netherlands. The procedure described in this report covers the estimation procedure described in the box '*Outdoor studies with algae and possibly macrophytes*' of Chapter 2.10 of Boesten *et al.* (2014). The studies in this box represent the highest (and most realistic) tier of the proposed stepped approach, with lower tiers that include hydrolysis studies, studies with aerobic fresh surface water in the dark or aerobic water-sediment studies in the dark.

Chapter 2 describes the principles of the estimation procedure, including the quality criteria for minimising the differences between simulated and measured concentrations. In Chapter 3, the selection of suitable compounds and cosm studies for testing the estimation procedure is described, whilst Chapter 4 specifies how the cosms must be parameterised for TOXSWA and PEST. In Chapters 5, 6 and 7, the estimation procedure is applied to a number of cosm studies for metribuzin, linuron and imidacloprid, respectively. The estimated degradation rates in cosm water were compared to the corresponding values found in laboratory studies, and provided an assessment of the importance of photolysis, hydrolysis and biodegradation in the overall degradation process. Chapter 8 evaluates if the cosm studies used were suitable for the proposed estimation procedure. Chapter 9 summarises the recommended working procedure to estimate degradation rates in water. Finally, Chapter 10 presents the conclusions and provides some recommendations.

2 Procedure to estimate degradation rates in outdoor stagnant water by inverse modelling with TOXSWA

2.1 Introduction

In regulatory dossiers, the decline rate in water in outdoor cosm studies is sometimes available. However, this rate may be cosm-specific and it encompasses more processes than just degradation. Adriaanse *et al.* (2012) designed a procedure to estimate the degradation rate in water that is suitable for cosm studies with limited data sets, e.g. lacking site-specific sorption coefficients and relevant sediment properties. In this report, this procedure was applied to a number of selected compounds, for which cosm studies were available. However, most of these were performed to evaluate the ecotoxicological effects and, therefore, had limited data sets of the fate of the compound. This report is limited to compounds predominantly present in the water phase, i.e. compounds with a sorption coefficient (K_{oc}) of up to approximately 1,000 L/kg. At a later stage, consideration will be given to compounds that are present both in the water phase and in the sediment. As the compound is mainly present in the water phase, concentrations in the sediment were not considered in the optimisation procedure. Even if concentrations in the sediment were available, which was seldom the case for the selected compounds, only aqueous concentrations were used in the estimation procedures.

2.2 Brief description of the TOXSWA model

The TOXSWA model was selected for the inverse modelling, because it is a process-oriented, deterministic model. It has been used in the pesticide registration procedure of the Netherlands since 1996 and at EU-level since 2003. This carries the advantage that process descriptions in the inverse modelling procedure are fully consistent with process descriptions in the exposure assessments used in registration.

The TOXSWA model describes the behaviour of pesticides in edge-of-field watercourses (Adriaanse, 1997; Adriaanse *et al.*, 2012). It assumes that pesticides can enter the watercourse by various routes, such as spray drift deposition, drain flow or runoff. It models these entries as either instantaneous or distributed over a certain period, and as a point source type or distributed over a certain length of the watercourse.

TOXSWA considers four processes: (i) transport, (ii) degradation, (iii) sorption and (iv) volatilisation. Its simulated watercourse is two-dimensional and consists of a water layer containing suspended solids and macrophytes, and a sediment layer, within which properties (bulk density, porosity and organic matter content) may vary with depth. In the water layer, the pesticide concentration may vary in horizontal direction, x , but is assumed to be uniform within vertical cross-sections. In the sediment, the pesticide concentration varies in the x direction, as well as in the z direction, i.e. with depth.

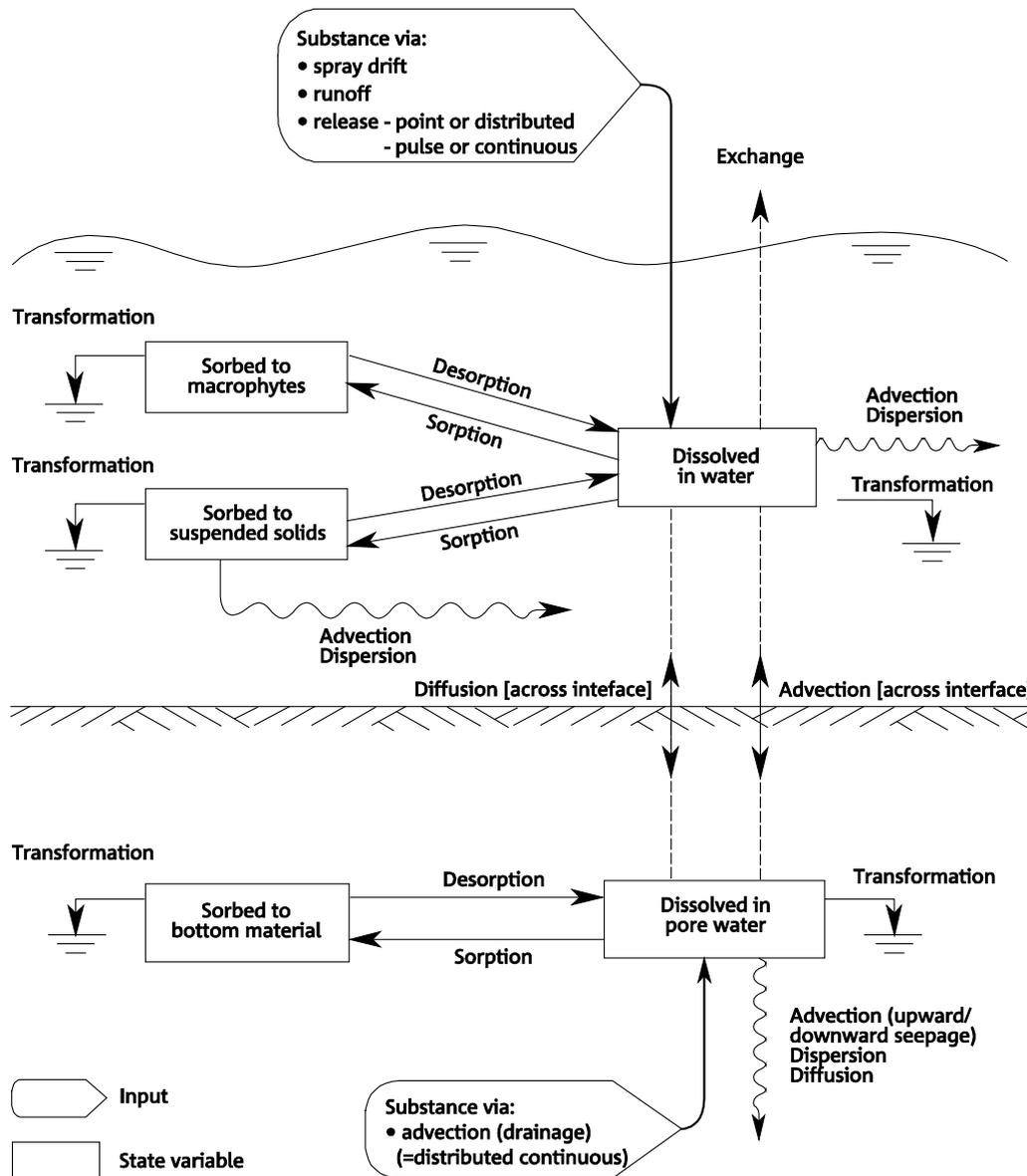


Figure 2.1 Diagram of the processes in TOXSWA for describing the behaviour in watercourses (taken from Adriaanse, 1996).

Figure 2.1 shows the processes included in TOXSWA. In the water layer, pesticides are transported by advection and dispersion, whilst in the sediment, diffusion also occurs. Their degradation rate is dependent upon temperature. Pesticides are sorbed to suspended solids, macrophytes and sediment. They are transported across the water-sediment interface by advection (i.e. upward- or downward seepage) and diffusion. In all the cosm studies, the cosm water was stagnant and there was no seepage into sediment, so both horizontal- and vertical advection and dispersion were zero. A detailed description of the processes in the TOXSWA model, as used for these cosm studies, is provided by Adriaanse *et al.* (2012). The model is based upon two mass conservation equations: one for the water and one for the sediment. These are solved with an explicit central finite difference method. For the numerical solution, the water and sediment are divided into a number of nodes. Since there is no concentration gradient in the horizontal direction in the cosm studies, only one node is used for the water layer. For the sediment, an array of nodes can be defined below the water layer node. The FOCUS default array was used in this study, consisting of a segment size increasing in six steps from 1 mm at the water-sediment interface to 30 mm at 7-10 cm depth. A maximum time frame of 600 s for both water and sediment was used.

2.3 Model optimisation procedure

In this section, the optimisation procedure for estimating the degradation rate in water of the cosm is described. The procedure was based on inverse modelling of the behaviour of the compound in the cosm by TOXSWA.

For each cosm, the TOXSWA model was parameterised as far as possible, i.e. reflecting the conditions in the cosm as much as possible, using all available, relevant, reported parameters. However, for all cosms, the degradation input parameters were unknown, for the water layer, as well as for the sediment, and these parameters had to be estimated. The overall decline rate in the water layer of the cosm was calculated from the measured concentrations. Therefore, a first estimate of the true degradation rate in water was acquired on the basis of the decline rate, taking into account the compound properties, such as saturated vapour pressure and the sorption coefficient. Generally, in the sediment there are no or too few measured concentrations available, and the decline rate is unknown. For the purpose of this study, it was assumed that degradation in sediment is negligible. To implement this assumption in the TOXSWA model, a very high default value for the sediment half-life of 1,000 days was used. This corresponded to the worst case default value given in the guidance of FOCUS (2006) for the estimation of degradation rates in water-sediment studies, and was based on the observation that in water-sediment studies, the degradation rate in sediment is often low. Moreover, as only compounds with a relatively low sorption coefficient were considered in this report (K_{oc} value of below approximately 1,000 L/kg), relatively few mass will enter the sediment and thus, the degradation rate in the sediment is relatively unimportant for the simulation of the compound behaviour in the cosm.

After parameterisation, the TOXSWA model was run and the concentration of the cosm in the water was simulated. To mimic the behaviour of the compound in the cosm as far as possible, two input parameters of TOXSWA had to be optimised: (i) the degradation rate in water - $DegT_{50, water}$, and (ii) the initial concentration in water - c_0 . These two parameters were selected according to the following considerations; Neglecting the behaviour in the sediment, the process parameter $DegT_{50, water}$ is the only remaining process controlling the behaviour in the cosm for compounds with relatively low volatilisation and low sorption (to sediment, suspended solids and macrophytes) (Adriaanse *et al.*, 2012). So, for compounds that are only slightly volatile (saturated vapour pressure at 20-25°C less than 10 mPa; Mensink *et al.*, 1995) with a K_{oc} smaller than 1,000 L/kg, it is justified to optimise only the process parameter $DegT_{50, water}$. The initial pesticide concentration was included in the curve-fitting procedure, in accordance with the general recommendations on data issues of FOCUS (2006) concerning time zero samples. The initial estimate of the aqueous pesticide concentration and/or application(s) were derived from the data reported for the cosm experiment. The optimisation procedure focused on the correspondence between the measured and model-generated concentrations in the water layer of the cosm. It consisted of PEST (Parameter ESTimation; Doherty, 2005), version 13.0 running TOXSWA (FOCUS_TOXSWA_4.4.2 version) many times with parameters, according to Chapter 4.2, plus the compound-specific parameters given in Chapter 5, 6 or 7, but varying $DegT_{50, water}$ and c_0 , whilst minimising the sum of squared differences between model-generated and measured values. The sum is called the objective function ϕ . PEST uses a non-linear estimation technique, the Gauss-Marquardt-Levenberg method, for minimisation of the objective function.

In most cosm studies, the concentrations in the water used in the optimisation procedure correspond to the total concentration in the water layer, i.e. dissolved plus sorbed to suspended solids, because in most cosm studies the water samples were not filtered before analysis. If they were filtered before analysis, the dissolved concentrations were used in the optimisation procedure. As stated earlier, in this report, only concentrations in water were used in the optimisation procedure, even for studies, in which data on concentrations in sediment were available.

The following criteria were used to assess the quality of the optimisation, i.e. the goodness of fit:

- Visual correspondence between the simulated and measured concentrations, as a function of time;
- Visual assessment of the residuals (simulated- minus measured data), as a function of time, in order to reveal patterns of over- or under prediction;
- Chi-Square (χ^2) Test to assess the deviations between simulated and measured values, relative to the uncertainty of the measurements;
- The confidence interval for the estimates of $DegT_{50, water}$ and c_0 ;
- The effect on optimised $DegT_{50, water}$ values using an alternative set of sediment properties.

The first four criteria were derived from FOCUS (2006). FOCUS (2006) was not able to identify a statistical method that provided an objective framework for evaluating the goodness of fit of an individual model and to compare two different models. Therefore, visual assessment, as stated in the first two criteria above, continues to play a major role in evaluating the goodness of fit. This should be used in combination with a χ^2 -Test to compare the goodness of fit of two different kinetics and a t -Test (or confidence intervals) to evaluate the confidence in the parameter estimates.

For the visual assessment of the goodness of fit, measured and optimised data must always be presented graphically. Measured concentrations and the simulated curve should be plotted versus time. A second plot should be made of simulated minus measured data (residuals). In this way, patterns of over- or under prediction may be revealed. For an exact fit, all residuals are zero. If negative and positive residuals are not randomly scattered around zero, systematic deviations may have occurred.

FOCUS (2006) proposed use of the χ^2 -Test as a supplementary tool for assessment of the goodness of fit of an individual model. The χ^2 -Test considers the deviations between observed and predicted values, relative to the uncertainty of the measurements.

$$\chi^2 = \sum \frac{(C-O)^2}{(err/100 \times \bar{O})^2} \quad (2.1)$$

where

C = calculated value

O = observed value

\bar{O} = mean of all observed values (element of scale in error term)

err = measurement error percentage (element of proportionality in error term)

The calculated χ^2 for a specific fit may be compared to tabulated $\chi^2_{m,\alpha}$ values,

where

m = degrees of freedom, i.e. number of measurements (after averaging of replicates) minus number of model parameters that are fitted

α = probability that one may obtain the given or higher χ^2 by chance (FOCUS, 2006).

Tabulated values are given in Table 6-5 of FOCUS (2006). Alternatively, they can be calculated in Excel using the CHINV (α , m) function.

To simplify the test, FOCUS (2006) proposed a pragmatic solution to address the uncertainty of the measurements, and to restrict the computation of χ^2 to using the calculated mean and observed mean values. In this way, the test evaluates the goodness of fit of the model fit and not the variation in replicate values. They stress however, that the true replicate values should be used for the kinetic fit with, in this case, the TOXSWA model.

The χ^2 Significance Test indicates if the hypothesis that there is no relationship between measured and calculated values is valid, i.e. that the model is not appropriate. Often a significance of $\alpha=0.05$ is used, and a value of χ^2 greater than $\chi^2_{m,0.05}$ indicates that the hypothesis is valid and the model is not appropriate. To use the χ^2 -Test, the percent error should be known (see Eq. 2.1). This is often not the case. Therefore, FOCUS (2006) proposes to calculate the minimum error-% of the error term (error-% /100 * mean observed), at which the test is passed with the aid of Eq. (2.2):

$$err = 100 \sqrt{\frac{1}{\chi^2_{tabulated}} \sum \frac{(C-O)^2}{\bar{O}^2}} \quad (2.2)$$

The test is passed if the calculated value of χ^2 is equal or smaller than the standard tabulated value at the 5% significance level and the given degrees of freedom. In this context, the 5% significance level corresponds with the 95th percentile of the χ^2 distribution. Furthermore, a large value of χ^2 means that the deviations are large (see Equation 2.1). Passing the test means that the χ^2 is smaller than the 95th percentile of its distribution. A consequence of this is that a lower significance level leads to a less strict test, which is counterintuitive. E.g. for six degrees of freedom, the tabulated χ^2 is 12.6 for $\alpha = 0.05$ and it is 16.8 for $\alpha = 0.01$ (FOCUS, 2006, p. 91). Therefore, a significance level of 1% would have generated lower *err* values than the chosen level of 5%.

Field data, such as the (mostly outdoor) cosm data in this report, will be inherently more variable than laboratory data generated under controlled conditions. Therefore, for field studies, the error percentages, at which the χ^2 -test is passed will generally be larger than for laboratory studies. FOCUS (2006) suggests that a minimum error-% value of 15% is acceptable for field studies. The minimum error-% to pass the test can be calculated explicitly with Equation 2.2 using the appropriate χ_{tab}^2 values, as well as the observed and predicted values. Appendix 1 gives an example of the calculation of the error-% with the aid of a simple Excel spreadsheet. With the aid of the calculated minimum error-% the results of the optimisation procedure can also be compared for the various cosms.

The uncertainty in the estimated model parameters can also be assessed by performing a *t*-Test or by specifying confidence intervals (FOCUS 2006). This helps to assess whether the optimised parameters, especially the degradation rate, differ significantly from zero at the chosen significance level. PEST generates confidence intervals and, therefore, it was used in this report (at 95% significance) to assess whether the intervals for the *DegT*_{50, water} (and *c*₀) did not include zero, i.e. the parameters differed significantly from zero. The estimation procedure only provided confidence intervals for the estimate of *DegT*_{50, water} and unfortunately, did not provide confidence intervals for the degradation rate constant. The estimation procedure may be adapted in future, if deemed useful, to generate values (and confidence intervals) for the degradation rate constant instead of (or alongside) *DegT*_{50, water}. This was not, however, implemented in the current procedure. Testing if the degradation rate constant significantly differs from zero, i.e. if the perceived degradation contributes significantly to dissipation of the compound, is, therefore, currently not easily accomplished. However, this is mainly of interest in the study of the degradation of metabolites, in which the occurrence (or not) of degradation is often less clearly apparent than for the parent compounds dealt with in the present study.

The correlation coefficient between *c*₀ and *DegT*_{50, water} was calculated by PEST and a standard part of the output given by the fitting procedure. Since a higher value of *c*₀ should result in a faster degradation rate constant, and hence, in a smaller value for *DegT*_{50, water}, the value of the correlation coefficient between *DegT*_{50, water} and *c*₀ should be negative. Checking its value may serve as a very minimal quality check on the correctness of the fitting procedure.

Most papers that have described cosm studies gave little or no properties for the sediment and suspended solids in the cosms (bulk density, organic matter content of sediment and suspended solids, porosity). Default values for use in the optimisations were set at realistic levels. However, to evaluate the extent of the influence of the chosen values, each of the cosms was also optimised using an alternate set of values for the sediment properties (more details are given in Section 4.1).

PEST runs were usually performed for two different sets of initial values of the optimisation parameters to check the uniqueness of their optimised values. If the outcome of the first two runs differed substantially, a third set of initial values was tried. Lower- and upper parameter bounds for *DegT*_{50, water} and *c*₀ were set depending on the concentrations and their observed decrease, based on visual inspection of the concentration data.

3 Selection of example compounds and cosm studies

3.1 Selection of compounds

To enable development and testing of the estimation procedure for the degradation in the water layer of cosms, a number of suitable compounds and cosm studies had to be selected. The cosm studies should be described in sufficient detail to allow inverse modelling with TOXSWA. Ideally, three or more suitable cosm experiments should be available for a compound before it is considered suitable for analysis. This enables studying the effect of external factors (dimensions, environmental parameters etc.) on the degradation under experimental conditions.

Alterra has conducted many indoor- and outdoor cosm experiments over the last decade, resulting in quite detailed data sets, some of which are available in the open domain. Starting with the compounds used in these open domain data sets seemed a logical choice, since there was the certainty that at least one cosm experiment with sufficiently detailed experimental data would be available. Further data sets for these compounds can possibly be retrieved through a literature search.

A list of compounds for which one or more outdoor cosm studies were performed by Alterra in the period 1990 – 2014, was constructed from the list of experiments performed at the experimental station 'Sinderhoeve' (located at Renkum, The Netherlands; for a more detailed description see Drent and Kersting, 1993). Only compounds used in non-GLP experiments were listed. This list was expanded with a number of compounds, for which indoor experiments were performed during that same period (Brock, personal communication). An overview of compounds is given in Table 3.1, together with some data on relevant properties retrieved from the PPDB database, <http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>.

Table 3.1

Overview of compounds for which Alterra has generated cosm data sets in the open domain in the period 1990 – 2014; physico-chemical data taken from the PPDB database.

Compound	DT ₅₀ water/sed. (d)	DT ₅₀ photolysis (d)	Log K _{ow} (-)	K _{oc} ^C (L/kg)	Saturated vapour pressure ^B (mPa)	pK _a (-)
Asulam	71.9	-	0.15	20 ^C	0.0005	1.29
Azoxystrobin	205	8.7	2.5	589	1.1E-07	-
Carbendazim	33.7	22 – 124 ^A	1.48	225 ^C	0.09	4.2
Chlorothalonil	0.1	65	2.94	850	0.076	-
Chlorpyrifos	36.5	29.6	4.7	8151	1.43	-
Fluazinam	3.1	2.5	4.03	16430	7.5	7.34
Imidacloprid	129	0.2	0.57	225 ^C	4.0E-7	-
λ-Cyhalothrin	15.1	40	6.9	283707	0.0002	-
Linuron	46	-	3	739	5.1	-
Lufenuron	112	0.75	5.12	41182 ^C	0.004	10.2
Metamitron	11.1	0.02	0.85	77.7	0.00074	-
Metiram	3.4	0.3	1.76	500000	0.01	-
Metribuzin	50	0.2	1.65	37.9 ^C	0.121	0.99
Metsulfuron-methyl	140	-	-1.7	39.5 ^C	1.1E-7	3.75
Prosulfocarb	214	-	4.48	1693 ^C	0.79	-
Tebuconazole	365	-	3.7	769 ^C	0.0013	5.0
Tolyfluanide	14	-	3.9	-	0.2	-

^A Value at pH 9, stable at pH 5 – 7.

^B Vapour pressure in mPa at 25°C.

^C K_{loc} is used (K_{oc} is not available).

For several of the compounds in Table 3.1, no value for K_{oc} was given in the PPDB database; if K_{oc} is not available, the value for K_{foc} was given, where possible, according to the protocol for selection of physico-chemical properties of Appendix 2, which was also used in Teklu et al (2015). In the protocol, the value of K_{foc} is considered to be less reliable than values for K_{oc} . The use of K_{oc} implies linearity of the sorption isotherm, where K_{foc} allows for non-linear sorption isotherms. However, an important difference between the two parameters, even when the sorption isotherm is linear, is that the unit of K_{foc} depends upon the unit in which the concentration of the pesticide in water and sediment is expressed (and also of the Freundlich exponent of the sorption isotherm). The PPDB database did not mention which concentration units were used in the calculation of K_{foc} , and if consistent units were used for all compounds, so values of K_{foc} are, therefore, considered less reliable.

The possibility of dissociation or protonation of the compound at environmentally-realistic pH values (pH between four and 10), may result in complications in the modelling of the fate of the compound, because the behaviour of the compound in its dissociated- or protonated form differs from the behaviour in its neutral form. Even if the parameters that describe the behaviour of the neutral and charged compound were known, inaccuracies in the value of the pK_a and/or in pH of the water layer would hamper the fate modelling. Compounds, for which FootPrint gave pK_a values of between four and 10 were, therefore, not considered (carbendazim, fluazinam, and tebuconazole).

To be of value in modelling degradation within the water layer, the degradation of a compound should be appreciable within the duration of the cosm test, but should not be so fast that the compound has disappeared within the first few days of the test. For this reason, Table 3.1 provides some data possibly indicative of the compounds' rate of degradation in water. However, DT_{50} values for water-sediment systems reflect the disappearance of the compound from the system as a whole. Therefore, it is difficult to judge the disappearance of the compound solely from the water phase from this parameter only, since the degradation rate in sediment and water may differ substantially. Moreover, water-sediment studies are usually performed in the dark, and thus, do not reflect conditions in outdoor cosms with respect to light conditions. Similarly, laboratory measurements of DT_{50} values for photolysis and hydrolysis are usually performed under conditions that are not typical for outdoor cosms, and are, therefore, not expected to accurately estimate disappearance from the water phase in a cosm. These types of laboratory-derived DT_{50} values, therefore, do not constitute reliable parameters for degradation in water under natural conditions alone. The values for DT_{50} in water-sediment systems and in photolysis studies are given as background information, but are, therefore, not used to select suitable compounds.

3.2 Suitable cosm studies

With the selection criteria above (K_{oc} , pK_a , DT_{50}) applied to the compounds in Table 3.1, 14 compounds remained: asulam, azoxystrobin, chlorothalonil, chlorpyrifos, imidacloprid, lambda-cyhalothrin, linuron, lufenuron, metiram, metribuzin, metsulfuron-methyl, prosulfocarb and tolylfluanide. For these compounds, additional literature was searched in Scopus. The search phrases (in the field 'article title, abstract of key words') used were:

Compound_name AND (meso* OR micro*)

Compound_name AND (mesocosm OR microcosm)

Compound_name AND (fate OR behavi* OR outdoor OR ditch OR pond)

Some information on the studies found is given in Appendix 3.

The studies found were checked for suitability in view of the current purpose, i.e. how much information was provided on:

- Concentrations in the water phase (a minimum of five measurements over time were required);
- Concentrations in sediment (at least three measurements in time were favourable);
- Information on the depth of the aqueous phase (required);
- Information on organic carbon content of sediment (required);
- Information on the presence of aqueous macrophytes (favourable);
- Information on light intensity, temperature and aqueous pH (favourable).

Unfortunately, a great deal of studies found did not give information on the organic carbon/matter content of the sediment used in the study, and were for that reason qualified as unsuitable. Therefore, this requirement was relinquished. This implies that all cosm studies with at least five measured concentrations in water and a measured water depth were qualified as suitable. The number of studies that remained after relaxing the need for information on the organic carbon content of sediment is given in Table 3.2.

Table 3.2

Number of suitable studies found in Scopus.

Compound	Suitable studies in Scopus ^A
Asulam	2
Azoxystrobin	1
Chlorothalonil	2
Chlorpyrifos	11
Imidacloprid	1
λ-Cyhalothrin	5
Linuron	4
Lufenuron	1
Metamitron	3
Metiram	0
Metribuzin	3
Metsulfuron-methyl	2
Prosulfocarb	1
Tolylfluamide	0

^A See text for an explanation of how this number was determined.

Three or more separate suitable microcosm experiments were found for chlorpyrifos, lambda-cyhalothrin, metamitron, metribuzin and linuron only. However, for some of the compounds, confidential descriptions of additional micro- and mesocosm studies may have been used in the course of pesticide authorization. A first inventory by the Dutch Board for the Authorisation of Plant Protection Products and Biocides (Ctgb) of studies mentioned in the EU List of Endpoints resulted in a few additional studies (Table 3.3). Many of the suitable studies found in this way were also described in public literature and were incorporated into Table 3.3. The only notable exceptions were two studies on chlorpyrifos by Van Wijngaarden and Brock (2001, 2002), and two studies on imidacloprid (Heimbach *et al.*, 2001; Ratte and Memmert, 2003) (Table 3.4).

Table 3.3

Additional studies found in the EU List of Endpoints.

Compound	Study	Suitability	Availability of report
Chlorpyrifos	Van Wijngaarden and Brock, 2001 (also described in Van Wijngaarden <i>et al.</i> , 2005)	? ¹	Confidential, also public
	Van Wijngaarden and Brock, 2002 (also described in Van Wijngaarden <i>et al.</i> , 2005)	? ¹	Confidential, also public
Imidacloprid	Heimbach and Hendel, 2001	+	Confidential
	Moring <i>et al.</i> , 1992	- #	Confidential
	Ratte and Memmert, 2003	+	Confidential
Lambda-cyhalothrin	Farmer <i>et al.</i> , 1993 (also described in Farmer <i>et al.</i> , 1995)	-%	Confidential, also public
	Kennedy <i>et al.</i> , 1988	- \$	Confidential
	Brock, 2001 (also described in Van Wijngaarden <i>et al.</i> , 2004)	+	Confidential, also public
Linuron	Brock, 2001 (also described in Van den Brink <i>et al.</i> , 1997)	+	Confidential, also public
Metamitron	Heimbach <i>et al.</i> , 1999 (also described in Brock <i>et al.</i> , 2004)	+	Confidential, also public
Metribuzin	Heimbach <i>et al.</i> , 2000 (also described in Brock <i>et al.</i> , 2004)	+	Confidential, also public

¹ In the open domain paper, no values of measured concentrations are given; it was unclear if the confidential paper study reports measured concentrations.

Only four measurements in water, after the last of four applications, no measurements between applications, not enough overall measurements in water.

% Not enough measurements in water.

\$ Too complex, used a combination of simulated spray drift and simulated run-off for application of test compound (similar to Bennett *et al.*, 2005; see detailed list of references); moreover, the summary in the Draft Assessment Report (2000) did not give values for concentrations measured in water.

3.3 Prioritisation of compounds for inverse modelling

The list of compounds with suitable studies reported in the open domain and confidential studies was merged into a single list without overlaps (Table 3.4). The list ranks the compounds in order of number of suitable studies.

Table 3.4

Compounds with sufficient, but partly confidential, studies available.

Compound	Suitable studies in public literature	Additional suitable confidential studies in EU List	References to confidential studies
Chlorpyrifos	11	2	Van Wijngaarden and Brock (2001) ^a ; Van Wijngaarden and Brock (2002) ^a
Imidacloprid	1	2	Heimbach and Hendel (2001) ^b ; Ratte and Memmert (2003) ^c
Lambda-cyhalothrin	5	-	-
Linuron	3	-	-
Metamitron	3	-	-
Metribuzin	3	-	-

^a Also described in van Wijngaarden *et al.* (2005).

^b Heimbach and Hendel (2001). Fate of imidacloprid SL 200 in outdoor microcosms. Unpublished study. Bayer CropScience AG, Monheim am Rhein, Germany.

^c Ratte, H.T., U. Memmert (2003). Biological effects and fate of imidacloprid SL 200 in outdoor microcosm ponds. Bayer AG, Crop Protection, Leverkusen, Germany. RCC Ltd Study No. 811776.

The primary aim of the analysis above was to select suitable compounds with sufficient suitable cosm studies for the development and testing of a procedure to estimate degradation rates in aqueous (cosm) systems. Therefore, attention was focused on compounds, for which degradation is a major factor in the decline of aqueous concentrations. Compounds, for which decline is mainly governed by volatilisation or sorption to sediment or suspended solids were considered less interesting.

Moreover, many pesticides are prone to photolysis, and the procedure devised for analysis of aqueous degradation rates should be applicable to both types of compounds: stable under the influence of light, and prone to photolysis or other photo-induced degradation. For that reason, it seemed worthwhile to start investigations with a representative of both types of compounds.

This resulted in a high priority for linuron, which is the only compound in Table 3.4 not prone to photolysis.

Metribuzin and imidacloprid are both prone to photolysis, and were considered good candidates for analysis. However, metribuzin was given a higher priority, because of the higher number of studies described in public literature. Although phytopharmaceutical companies are often willing to share confidential information from study reports for research purposes, a substantial amount of time may pass between their consent to provide access and actually having hands-on access to a confidential study. Thus, compounds with sufficient studies described in public literature were given higher priority for practical reasons, favouring metribuzin over imidacloprid.

Although chlorpyrifos is prone to photolysis, this process was expected to be of only minor importance in its dissipation, and chlorpyrifos was, therefore, also given a somewhat lower priority, despite the large number of studies available.

Lambda-cyhalothrin was expected to be strongly sorbed to sediments and suspended solids, and was, therefore, expected to be much more difficult to handle experimentally. The resultant uncertainty in measured concentrations may cause problems in the inverse modelling of aqueous concentrations. For that reason, inverse modelling of this compound was given a lower priority.

Metamitron, the remaining compound in Table 3.4, appears to be very similar to metribuzin in its behaviour, apart from the fact that it undergoes more rapid photolysis.

The preliminary sequence established during an expert meeting held in November 2014 was:

- Metribuzin.
- Linuron.
- Imidacloprid.
- Chlorpyrifos.
- Lambda-cyhalothrin.
- Metramitron.

For imidacloprid, relatively few studies were available in the open domain. The imidacloprid studies by Heimbach and Hendel (2001) and by Ratte and Memmert (2003) were, upon request, kindly provided by Bayer CropScience AG.

In this report, developing and testing an optimisation procedure was limited to consideration of only aqueous concentrations of compounds that were mainly present in the water phase of the cosm. This applied to the three compounds ranked highest in the list above, i.e. metribuzin, linuron and imidacloprid (see Chapters 5, 6 and 7).

Although the optimisation procedure only used aqueous concentrations for parameter estimation, TOXSWA also simulates partitioning between water and sediment. Whether sediment concentrations were estimated correctly or not was not checked by the current optimisation procedure, since a comparison between estimated and experimental sediment concentration was not performed. Failure to correctly simulate partitioning between water and sediment may have consequences for correct estimation of $DegT_{50, water}$, since overestimation of penetration into the sediment may result in compensation for high penetration in TOXSWA through the assumption of slower degradation in the aqueous layer. This issue, and the checks required to identify situations in which penetration into sediment is too high to apply the estimation method, are discussed in more detail in Chapter 8.

4 Analysis of cosm studies

4.1 Introduction

The estimation procedure for the degradation rate in water was based upon the inverse modelling of the cosm study by TOXSWA, coupled to the optimisation tool, PEST.

In brief, the optimisation procedure consists of the following steps:

1. Parameterise the TOXSWA model, as far as possible for the specified cosm, on the basis of the study description;
2. Run the model and compare the simulated concentrations in water to the concentrations measured in the cosm study;
3. Let PEST adjust the TOXSWA input parameters (i) degradation rate in water and (ii) initial concentration, on the basis of the correspondence between simulated and measured concentrations and next, re-run the model;
4. Repeat 3 until a pre-defined stop criterion is met and;
5. Consider whether the quality of the fit is acceptable. If yes, extract the optimised degradation rate in water, $DegT_{50, water}$.

If cosms are comparable, it is often possible to perform steps 1-5 once only by scaling all measured concentration-time profiles from 0 to 1 and comparing these to the (scaled) simulated concentration-time profile (see Section 4.3). Cosms may be considered to be comparable if (i) they can be represented by one set of inputs for the TOXSWA model, which implies that input parameters, such as water depth or temperature of the cosm water, are (approximately) similar, and (ii) the degradation rates of the compound seem to be similar, which can be seen best by plotting the concentrations on a logarithmic scale to see if the slopes are (approximately) similar.

4.2 Parameterisation of cosm studies for PEST-TOXSWA

Each cosm was parameterised for the TOXSWA model. Only two parameters were optimised: $DegT_{50, water}$ and c_0 . All other input parameters were fixed values during the optimisation. Some of the fixed input parameters, such as water depth and temperature, were chosen to reflect the conditions as measured in the cosms. Others were not measured and had to be estimated in another way. Pesticide properties were taken from the Footprint database, including properties that were site-specific, such as the K_{oc} value. A protocol was used to select the most appropriate values from the Footprint database (Appendix 2). All input that was cosm-specific is mentioned in the appendix belonging to the study, e.g. Appendix 4 for metribuzin cosm studies. In addition, compound-specific properties appear in the appendices. Other input parameters, such as sediment properties, were defined in the same way for all cosm studies.

Input parameters that were equal for all cosm simulations include: (i) the concentration of suspended solids and their organic matter content (ii) the sediment properties and the sediment depth, (iii) compound properties, such as molar enthalpies of vaporisation, dissolution and degradation, and the degradation half-life in sediment (Table 4.1).

Table 4.1

Process-related parameter values and their origin, used in all cosm study simulations

Property	Value	Origin
Molar enthalpy of vaporisation (kJ/mole)	95	FOCUS (2001)
Molar enthalpy of dissolution (kJ/mole)	27	FOCUS (2001)
Molar enthalpy of degradation (kJ/mole)	65.4	EFSA (2007)
Degradation half-life in sediment (d)	1000	FOCUS Degradation Kinetics (2006)

TOXSWA uses the degradation half-life in water and sediment at 20°C as input parameters. This is converted to the half-life at the temperature of the water and sediment of the study within TOXSWA. So, the inversely-modelled half-lives do also refer to 20°C. The values for the input parameters of suspended solids and sediment are presented in Table 4.2. An alternate set of values was defined to check the influence of these input values against the estimation of the $DegT_{50, water}$ values. The default set of values was derived from FOCUS (2001) and based on their bulk density and organic matter content, but fulfilled the requirements of Eq. (4.1). The alternate values were derived with the aid of measured data from Adriaanse *et al.* (2015) and also correspond to Eq. (4.1).

Table 4.2

Values of suspended solids and sediment parameters used in TOXSWA for the cosm study simulations

Parameter	Default value	Alternate value
<i>Suspended solids</i>		
Concentration in water (mg/L)	15	15
Organic matter content (%)	9	19
<i>Sediment</i>		
	(0-10 cm)	(0-10 cm)
Bulk density (kg/L)	0.8	0.2
Organic matter content (mass fraction,%)	9	19
Porosity (volume fraction, -)	0.67	0.91
Tortuosity (-)	0.56	0.84
<i>Depth (cm)</i>		
	10	10
<i>Degradation half-life in sediment (d)</i>		
	1000	1000

Equation 4.1 states that the volume fractions of water, organic matter and mineral parts sum up to 1:

$$\varepsilon + \frac{\rho_{sed}}{\rho_{om}} f_{om, sed} + \frac{(1 - f_{om, sed}) \rho_{sed}}{\rho_{min}} = 1 \quad (4.1)$$

where ρ_{om} ($M L^{-3}$) is the phase density of organic matter and ρ_{min} ($M L^{-3}$) is the phase density of mineral matter. Using the values of 1.40 kg L^{-1} for ρ_{om} and 2.65 kg L^{-1} for ρ_{min} , the porosity ε (-) for given values of the sediment bulk density ρ_{sed} ($M L^{-3}$) and the sediment organic matter content $f_{om, sed}$ (-) can be calculated using Equation 4.1.

For the default sediment with $\rho_{sed} = 0.8 \text{ kg.L}^{-1}$ and $f_{om, sed} = 0.09$, $\varepsilon = 0.67$ was obtained, and for the alternate sediment with $\rho_{sed} = 0.2 \text{ kg.L}^{-1}$ and $f_{om, sed} = 0.19$, $\varepsilon = 0.91$ was obtained. The tortuosity was calculated according to the empirical equation (Boudreau, 1996):

$$\lambda = \frac{1}{[1 - \ln(\varepsilon^2)]} \quad (4.2)$$

where λ stands for the tortuosity (-). For the default sediment $\lambda = 0.56$ and for the alternate sediment $\lambda = 0.84$.

Initial estimates of the two parameters to optimise, $DegT_{50, water}$ and c_0 , were derived from each cosm experiment. The degradation rate in water, $DegT_{50, water}$, was loosely based on an estimate of the decline rate in water, whilst the initial concentration, c_0 , was usually set at 1 (scaled value, representing 100% of the initial concentration).

4.3 Scaling of multiple data sets from a single study

In most of the studies used, there were replicates (i.e. physically-separate systems treated at the same concentration) at each treatment level. Whereas some studies report only average concentrations for each treatment level, others report concentrations for each of the replicates separately, thus providing more detailed data.

When data for each replicate are available, analysis can be performed for each of the replicates separately. This provides an estimate of $DegT_{50, water}$ for each of the replicates, which can then be combined by calculating e.g. the geometric mean value.

Alternatively, when combining all available data for a treatment level into a single analysis, a single estimate of $DegT_{50, water}$ can be obtained. Although PEST can handle data from several 'observation groups', each group representing one of the replicates, it operates using a single initial concentration shared by all observation groups. Since initial concentrations at a treatment level may slightly differ between replicates, some form of normalisation of concentrations is required before simultaneous analysis of data sets is possible. This can be achieved by dividing, for each replicate separately, all concentrations of a replicate by the highest aqueous concentration (in mg/L) observed in that replicate. For systems using repeated applications, modelled in TOXSWA through the use of 'loadings', loadings in mg/m² should be scaled by dividing through the same number as well. Thus, aqueous concentrations are normalised to values of 0 – 1 for each replicate in a similar manner, which ensures that aqueous concentrations in the combined data set also range from 0 – 1 (mg/L). An additional advantage of this approach is that, as well as data from multiple systems with similar initial concentrations, data from systems with clearly different initial concentrations can be combined. This should, however, only be done if initial inspection of concentration – time curves indicates that $DegT_{50, water}$ is not dependent on initial aqueous concentration, i.e. similar dissipation rates are observed for the various treatment levels.

Combining systems by scaling is not possible for systems with repeated applications, as usually the loadings of systems will differ - a situation that cannot be accounted for in TOXSWA. Similarly, systems with clearly different water depths or temperatures cannot be simulated by a single TOXSWA run, because only a single value for these parameters can be used in a TOXSWA run.

4.4 Possible effects of scaling concentrations on the outcome of parameter fits

Due to the fact that experimental values contain noise, equally good fits of experimental data can be achieved with different estimates of parameter values. Moreover, results achieved using numerical methods may be affected by the magnitude of values used as input. This mostly depends on the criteria used for assessing whether parameter estimates are sufficiently close to the 'real' parameter values and result in sufficiently close simulation of experimental data to stop adjustment of parameter values and end the running of simulations.

In this respect, PEST can be closely tailored to the user's needs. Default settings use a combination of 'goodness of fit' criteria for judging if a sufficiently accurate parameter estimate has been achieved that may cause the outcome of a parameter estimation to be dependent on the absolute size of the numbers (for details on 'stop' criteria see the PEST manual, section 2.2.29, pages 2.25 – 2.26; Doherty, 2010). PEST has several types of stop criteria, e.g. related to the objective function, to the behaviour of the adjustable parameters or a maximum number of optimisation iterations. In view of

the stop criteria related to the behaviour of the objective function, there is reason to believe that the outcome might depend on the magnitude of numbers used to express aqueous concentrations. Scaling of concentrations, changing the absolute magnitude of input data, may, thus, affect the outcome of parameter estimation.

To investigate the possible effect of the scaling of experimental aqueous concentrations on the resultant $DegT_{50, water}$ estimate, one of the data sets was investigated using both the original, i.e. unscaled, and scaled input data, and comparing the resultant estimates of $DegT_{50, water}$. The results of parameter estimation of these data sets will be discussed, together with the results for other data sets in more detail in the following Chapters. The current text primarily focuses on the effect of scaling of aqueous concentrations on the estimate of $DegT_{50, water}$.

The data set used for the analysis given below was taken from the linuron study by Stephenson and Kane (1984) described in more detail in Chapter 6. Data that referred to a single system were used, neglecting temporarily data for the other systems/enclosures in the study. The original data, together with the result of scaling of the data, are given in Table 4.3, whereas the results of parameter estimation (concentration at time zero and the degradation rate in water, $DegT_{50, water}$, are given in Table 4.4.

Table 4.3

Original-, scaled- and up-scaled concentration data for one of the systems in the Stephenson and Kane (1984) study; scaled data were generated by dividing original data by the maximum concentration (1.2 mg/L), up-scaled data were generated by multiplying unscaled data by 1,000, i.e. changing units from mg/L to µg/L.

Time (days)	Original concentration reported (mg/L)	Scaled concentration (fraction of maximum concentration)	Up-scaled concentration (µg/L)
0	1.2	1.0000	1,200
1	1.0	0.8333	1,000
2	0.96	0.8000	960
4	0.91	0.7583	910
7	0.90	0.7500	900
13	0.82	0.6833	820
23	0.66	0.5500	660

Table 4.4

Estimated $DegT_{50, water}$ values for original, scaled and up-scaled data taken from one of the systems in the Stephenson and Kane (1984) study.

Estimated parameter	Original concentrations	Scaled concentrations	Up-scaled concentrations
Initial concentration c^0	1.09	0.90	1,078
$DegT_{50, water}$	18.55 (6.2 – 30.9)	18.62 (6.2 – 31.0)	16.70 (6.2 – 27.2)
Number of TOXSWA iterations	32	34	22
Sum of squared residuals	2.14 E-2	1.48 E-2	2.38 E-4
Err%	4.77%	4.76%	5.03%

The estimated concentrations at time zero obviously differ widely, which is a direct consequence of the scaling of the numbers. However, the $DegT_{50, water}$ estimated also differs between the three data sets. Going from original to scaled concentrations only resulted in a very slight change in $DegT_{50, water}$ of 18.55 to 18.62 days respectively. However, up-scaling the concentrations by multiplying them with a factor of 1,000 clearly resulted in a somewhat lower value for $DegT_{50, water}$ of 16.7 days. Clearly, the value estimated for $DegT_{50, water}$ is affected by the absolute magnitude of the numbers used as input. The difference between $DegT_{50, water}$ derived for the original and 'adapted' numbers appears to become larger, as the difference between the numbers increases in magnitude, i.e. a larger 'scaling factor' is used.

However, graphical inspection of the simulation reveals that these differences in $DegT_{50, water}$ result in irrelevant changes in the simulation. Figure 4.1 shows the simulated aqueous concentrations calculated for the different values of $DegT_{50, water}$. Obviously, the curves are very similar (and hardly discernible with the naked eye), and none of these curves can be considered superior for describing the experimental values.

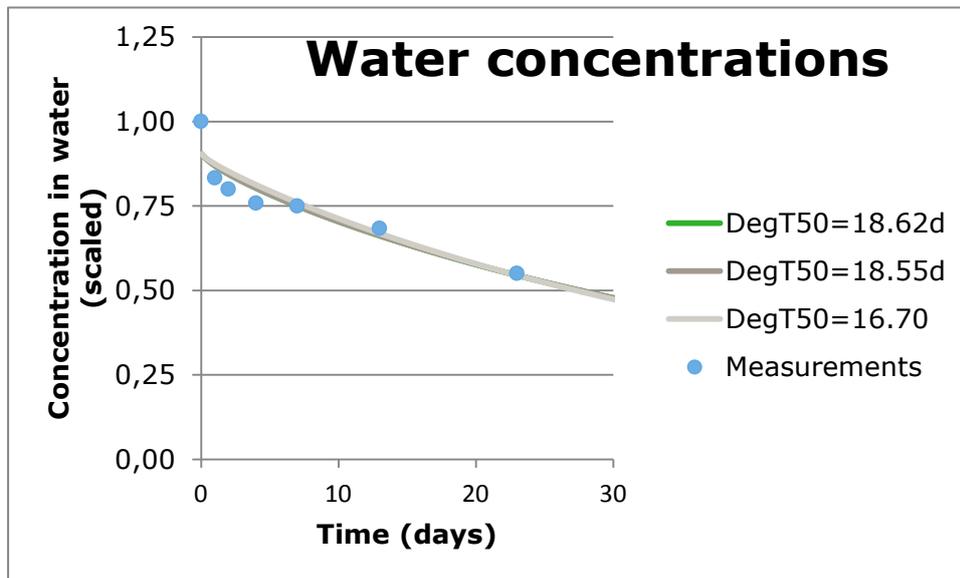


Figure 4.1 Correspondence between measurements and simulated concentrations of linuron using different values of $DegT_{50, water}$ in the Stephenson and Kane (1984) study. The $DegT_{50}$ values shown are for 20°C , whilst the temperature used in the simulations was 11.6°C .

Upon closer inspection of the input parameters, it was realized that the calculated penetration into the sediment calculated by TOXSWA during the course of the simulations may have been different for the unscaled-, scaled- and up-scaled water concentrations. Sorption to sediment and suspended solids was modelled using a Freundlich isotherm. For linuron, a non-linear sorption isotherm with a Freundlich exponent of 0.85 was used.

When the calculations for the three data sets were repeated, consistently using a Freundlich exponent of 1.0 instead of the correct value of 0.85, it was found that the resulting estimates of $DegT_{50, water}$ were much closer: 18.27, 18.28 and 18.25 days for unscaled-, scaled- and up-scaled data, respectively. The variation in $DegT_{50, water}$ of 16.7 – 18.5 days when using different scaling factors, therefore, appears to be the result of a non-linear Freundlich isotherm.

The Freundlich isotherm equation assumes that the K_{om} is specified for a reference concentration of 1 mg/L. Thus, scaling of concentrations may lead to use of the wrong K_{om} . It is recommended to overcome this problem as follows: calculate the geomean of the initial concentrations of the different studies, to give $C_{0,geo}$ (mg/L); then modify the K_{om} in the TOXSWA_cha.txt file using:

$$K_{om,new} = K_{om,org} \left(\frac{C_{ref}}{C_{0,geo}} \right)^{1-N} \quad (4.1)$$

where $K_{om,new}$ is the modified K_{om} , $K_{om,org}$ is the original K_{om} , C_{ref} is the reference concentration of 1 mg/L, and N is the Freundlich exponent (-).

In view of the very small differences found for the Stephenson and Kane (1984) example given above, the literature value of the Freundlich exponent was applied throughout the calculations in this report, without correction for non-linearity, even though scaled concentrations were used.

Figure 4.1 shows that the experimental data span less than one half-life of the test substance. This makes a reliable estimation of $DegT_{50, water}$ difficult. In combination with the relatively large noise in the data, this was responsible for the wide confidence intervals in the estimates of $DegT_{50, water}$ (*more details are given in Chapter 6*). Aqueous concentrations calculated with (slightly) different values of $DegT_{50, water}$ differ more obviously when longer experimental durations are considered. Over the time relevant to this data set (where the last sample was taken on day 23), very large differences in $DegT_{50, water}$ would be required to result in obvious changes in calculated concentrations.

4.5 Weighting of residues for simultaneous use of water and sediment concentrations

For the guidance developed in this report, the optimisation used only the measured aqueous concentrations, even for studies where measurements on concentrations in sediment were available. In the follow-up research, the aim is to derive guidance on the estimation of degradation rates in water for compounds with considerable mass penetration into the sediment, i.e. compounds with K_{oc} values above approximately 1,000 L/kg. In those cases, both aqueous and sediment concentrations will be used simultaneously in the optimisation and, next to the degradation rate in water, parameters determining the penetration into sediment (such as a study-specific K_{oc} , or the sediment properties bulk density or porosity) may also need to be optimised.

When combining aqueous and sediment concentrations in the optimisation, the fact that there may be large numerical differences between concentrations in these compartments, depending on the sorption coefficient of the compound under investigation, must be considered, amongst other factors. To ensure a similar contribution of measured aqueous and sediment concentrations to the estimation, a weighting factor could then be used. The weighting factor would ensure that measurements in water and sediment are given the same importance, irrespective of any differences between their magnitudes. Moreover, the weighting factor would account for any difference in the number of measurements between water and sediment phases. Calculation of the weighting factor is explained in detail in Adriaanse *et al.* (2012).

In the present study, in which only aqueous concentrations were used in the optimisation, no weighting of concentrations was used.

4.6 Consistency of degradation rates between lower- and higher tiers

Boesten *et al.* (2014) proposed guidance on how to proceed if several different $DegT_{50}$ values are available for use in exposure calculations for registration purposes. They devised a hierarchical system for the use of information gathered in different types of studies (hydrolysis- and photolysis studies, and studies that inherently combine various routes of degradation). The stepped approach adheres to the generally-accepted rationale that going from simple to more complex studies should result in more realistic results, giving less conservative estimates of degradation rates.

Their scheme is reproduced in Figure 4.2. The first step is the $DegT_{50}$ that results from hydrolysis. In the second tier, both degradation rate studies with fresh surface water in the dark and photolysis studies in buffered pure water are considered. The three different estimates of $DegT_{50}$ are usually available in registration dossiers, and if available, the data taken from a second-tier study are considered more favourable. The third step results in a $DegT_{50}$ from more sophisticated studies, such as photolysis studies with fresh surface water, indoor- and outdoor studies with algae and possibly

macrophytes. Data generated in this step, if considered reliable, are preferred over data generated in lower tiers, because of increased realism, and are therefore the data-of-choice for estimating exposure concentrations used in registration risk assessment procedures.

Boesten *et al.* (2014) pointed out that there is no guidance on how to standardise data influenced by photolysis to standard irradiation fluxes, which makes data from Boxes 2.4, 2.6, 2.7 and 2.8 very difficult to interpret. Hence, in their guidance, they proposed not to use such data. Comparison between lower and higher tiers is, therefore, limited to data from Boxes 2.2, 2.3, 2.5 and 2.9.

The focus of the present investigation was on data belonging to the third step. This allowed verification of the assumption that more realism will result in less conservative results, i.e. that the $DegT_{50, water}$ estimated from mesocosm data will indicate faster degradation than data from lower tiers, such as hydrolysis- and water/sediment studies. In Sections 5.2, 6.2 and 7.2, which discuss estimates for $DegT_{50, water}$ for metribuzin, linuron and imidacloprid respectively, dissipation data from lower-tier studies and the currently estimated $DegT_{50, water}$ values from higher-tier mesocosm studies are compared.

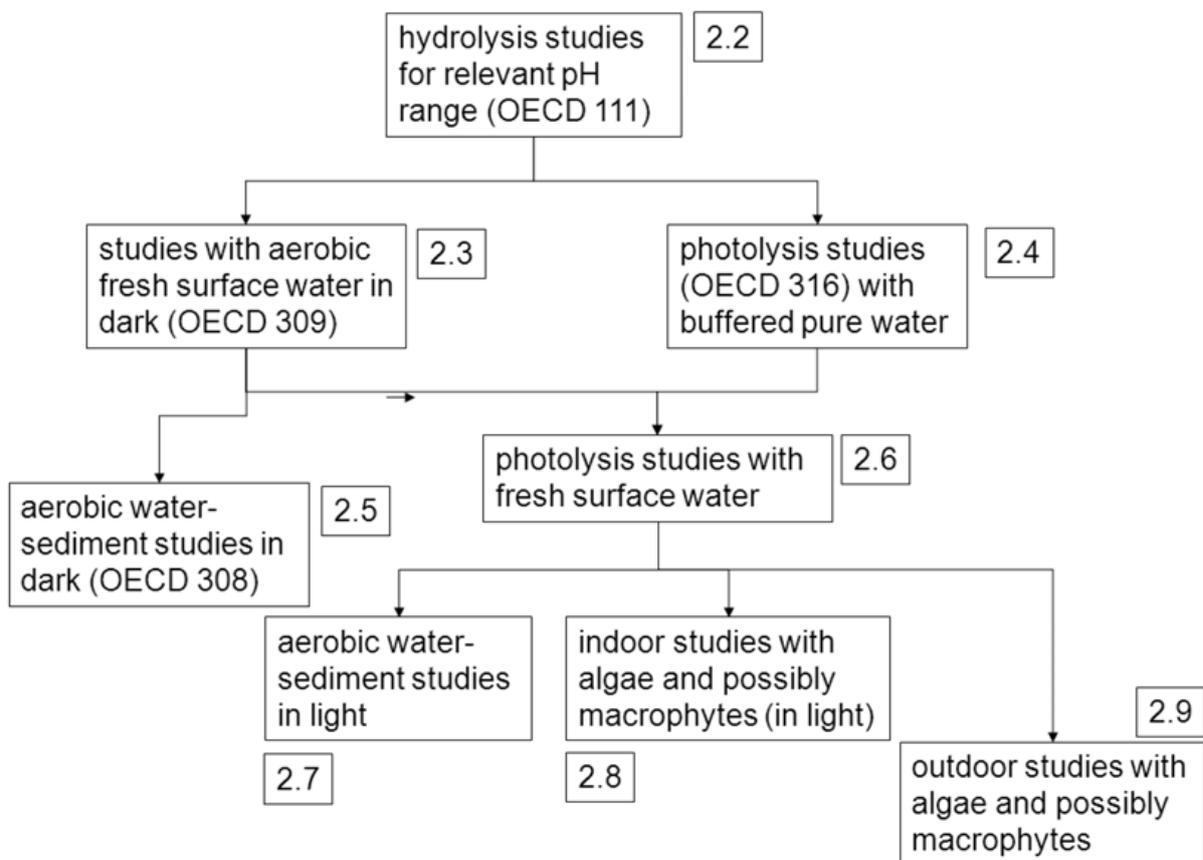


Figure 4.2 Stepped approach for estimating $DegT_{50}$ values for surface water, taken from Boesten *et al.* (2014).

5 Assessment of the degradation rate of metribuzin in cosm water

Three studies were analysed using inverse modelling. The main characteristics of each of the studies are given in Table 5.1.

Table 5.1

Main characteristics for studies involving metribuzin

Data set analysed	Type of cosm	Nominal initial concentration ($\mu\text{g/L}$)	Number of applications	Interval	Number of measurements in water phase	Number of measurements in sediment phase	Water depth (m)	Temperature ($^{\circ}\text{C}$)	pH
Fairchild & Sappington (2002)	Outdoor clay-lined pond	75	1	-	5	-	0.75	19 \pm 4	8.1 \pm 1.2
Arts <i>et al.</i> (2006)	Outdoor ditch	1.6 and 8.2	1	-	5 or 6 per enclosure, 32 in total	-	0.5	17.4	8.45
Brock <i>et al.</i> (2004)	Outdoor enclosures	180	1	-	10 per enclosure	-	0.5	16.55	Variable, 7.3 – 10.5

Fairchild and Sappington

Fairchild and Sappington (2002) described the results of a mesocosm study with metribuzin in ponds located at Columbia, Missouri, U.S.A. Exposure levels were measured only shortly after application of metribuzin on 22nd May (year not given, presumably 2001). Details on measured concentrations are given in Appendix 4. No measurements were performed for concentrations in sediment and in the macrophytes present in the ponds (macrophyte biomass was measured and reported).

The cosm of Fairchild and Sappington (2002) was inversely modelled and the agreement between measured and simulated aqueous concentrations was optimised with the aid of PEST, according to the procedures presented in Chapters 2 and 4. Three optimisations were performed, each with its own initial values of $DegT_{50, water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (1 and 100 d for $DegT_{50, water}$ and 0.1 and 5.0 (scaled) for $c_{t=0}$). Details of the results are given in Appendix 4. Inverse modelling resulted in an estimate for the $DegT_{50, water}$ of 4.0 days with relatively large 95% confidence intervals of 2.1 – 5.9 days. The optimisation passed the χ^2 -Test with an error percentage of 6.4%, which is an acceptable value for field experiments according to FOCUS (2006). Changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) did not affect the estimated value for the $DegT_{50, water}$.

Figure 5.1 presents a satisfactory agreement between scaled optimised and measured water concentrations for one of the optimisations (initial $DegT_{50}$ of five days), whilst Figure 5.2 presents the distribution of the scaled residuals between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

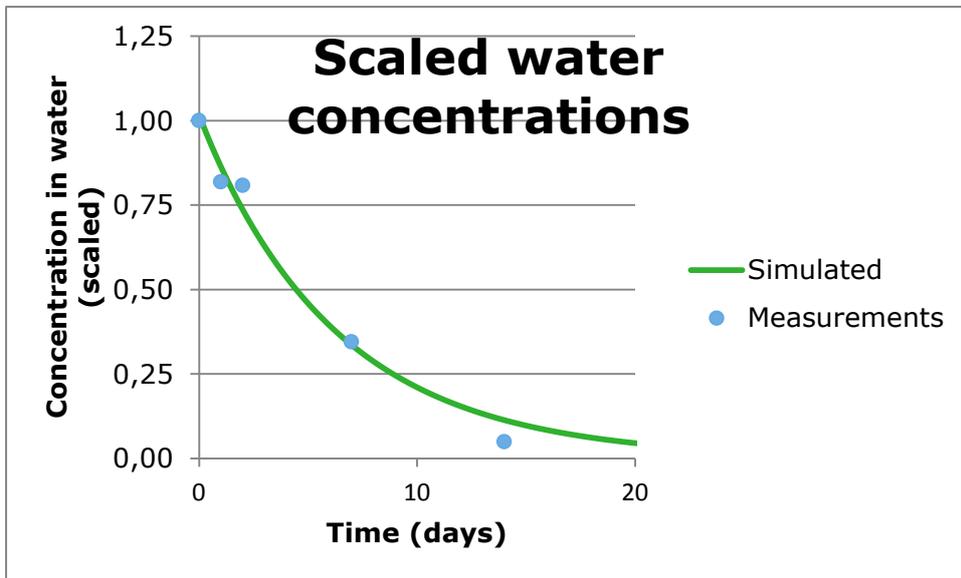


Figure 5.1 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) metribuzin in water as a function of time after first measurement (d) in the cosm of Fairchild & Sappington (2002). Simulated concentration profile obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 5 \text{ d}$ and $c_{t=0, ini} = 1.0$

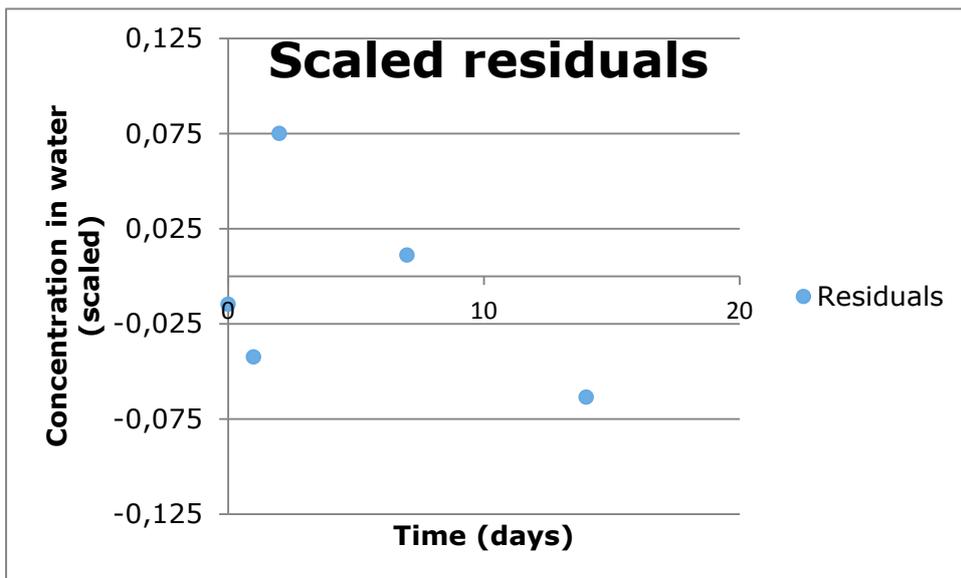


Figure 5.2 Residuals in the total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) metribuzin in water as a function of time after first measurement (d) in the cosm of Fairchild & Sappington (2002). Simulated concentration profile obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 5 \text{ d}$ and $c_{t=0, ini} = 1.0$

Arts et al.

Arts et al. (2006) reported data on the fate of metribuzin in a mesocosm study in outdoor ditches located at Renkum, The Netherlands. Treatment consisted of a single application on 6th May 2002, at three different nominal initial levels, treating three separate ditches at each level. No measurements of metribuzin in sediments were reported, nor was the organic matter content of the sediment given. Details on concentrations measured in the ditches are given in Appendix 4.

The ditches of Arts et al. (2006) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled as described in 4.3) was optimised with the aid of PEST,

according to the procedures presented in Chapters 2 and 4. Various optimisations were performed, each with their own initial values of $DegT_{50, water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (0.1 and 100 d for $DegT_{50, water}$ and 0.01 and 10 (scaled) for $c_{t=0}$). Details of the results are given in Appendix 4. Inverse modelling resulted in an estimate of $DegT_{50, water}$ of 1.05 days with 95% confidence intervals of 0.9 – 1.2 days. The optimisation passed the χ^2 -Test with an error percentage of 8%, which is an acceptable value for field experiments according to FOCUS (2006). Changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) did not affect the estimated value for the $DegT_{50, water}$.

Figure 5.3 presents a satisfactory agreement between scaled optimised and measured water concentrations for all six ditches in one of the optimisation sets (initial $DegT_{50}$ of five days), whilst Figure 5.4 presents the distribution of the scaled residuals between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals are reasonably well-scattered around zero (only after seven days, the simulation seems to be systematically too low), demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

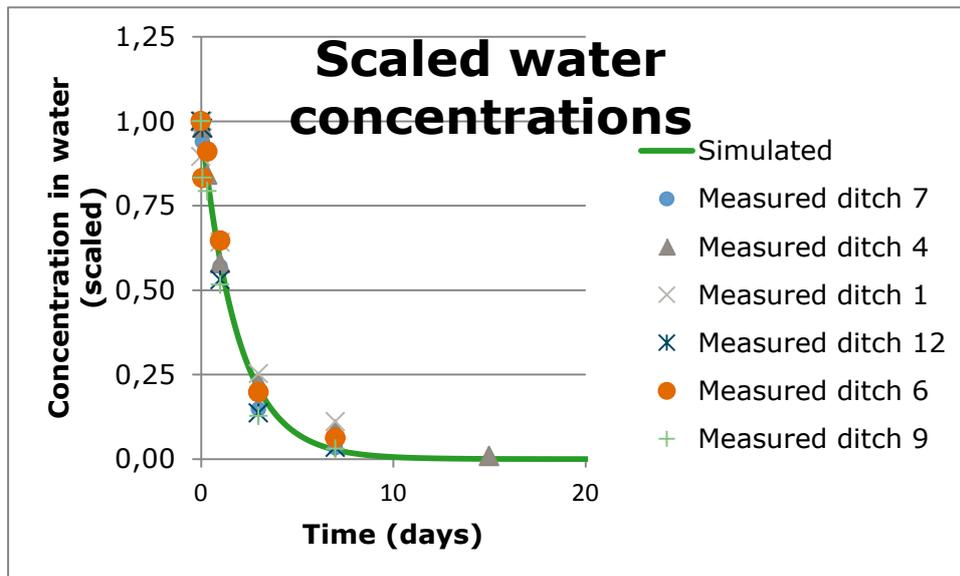


Figure 5.3 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) metribuzin in water as a function of time (d) in the cosms of Arts et al. (2006). Simulated concentration profile obtained by PEST_TOXSWA optimisation for $DegT_{50, ini} = 5$ d and $c_{t=0} = 1.0$.

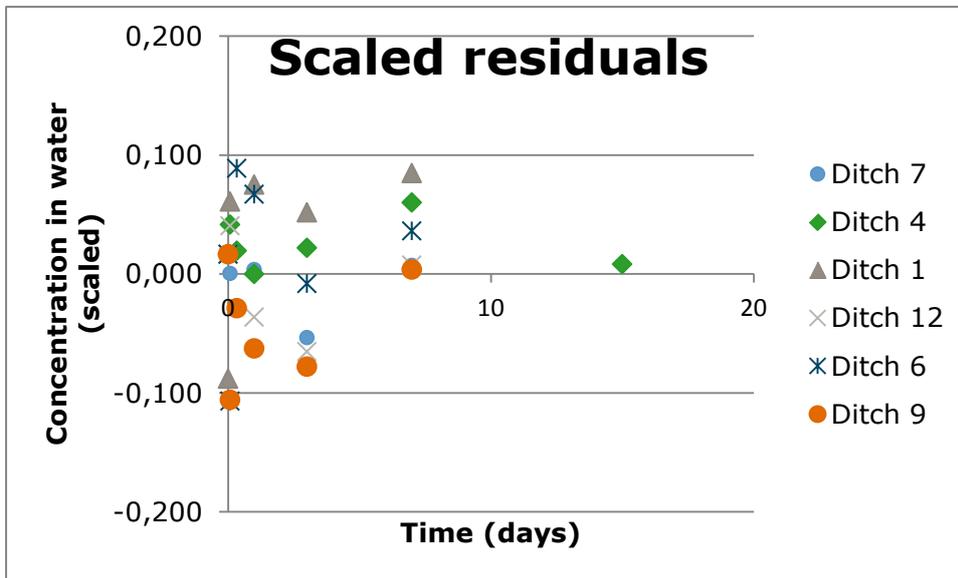


Figure 5.4 Residuals in the total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) metribuzin in water as a function of time (d) in the cosm of Arts *et al.* (2006). Simulated concentration profile obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 5 \text{ d}$ and $c_{t=0} = 1.0$.

Brock *et al.*

The paper by Brock *et al.* (2004) describes fate data for metribuzin in moderately buffered mesotrophic enclosures (polycarbonate, pervious to light, no information on sediment composition is given) in outdoor ditches located at Renkum, The Netherlands. Enclosures were treated at six different exposure levels on May 5, 1999. Water samples were taken nine or 10 times after the application over a 56 days period. More details on the measured concentrations are given in Appendix 4. No analyses in sediment were reported. An initial logarithmic plot of (scaled) concentrations versus time indicated that the dissipation rates in all enclosures were very similar. Assuming that this indicates that the simulated degradation rates were also very similar for all enclosures, it was decided to include only the data for enclosures with the lowest and highest dissipation rates (enclosures 1 and 8, with initial nominal concentrations of 5.6 and 56 $\mu\text{g/L}$, resp.)

The enclosures of Brock *et al.* (2004) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled as described in 4.3) was optimised with PEST, according to the procedures presented in Chapters 2 and 4. Four optimisations were performed, each with their own initial values of $\text{Deg}T_{50, water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (0.1 and 100 d for $\text{Deg}T_{50, water}$ and 0.01 and 10 (scaled) for $c_{t=0}$). Results of the inverse modelling are given in Appendix 4. The modelling resulted in an estimate of $\text{Deg}T_{50, water}$ of 3.1 days with 95% confidence intervals of 2.4 – 3.8 days. An error percentage of 11.6% was observed, which is acceptable for field experiments according to FOCUS (2006). Changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) did not affect the estimated value for the $\text{Deg}T_{50, water}$.

Figure 5.5 presents the agreement between scaled optimised and measured water concentrations for the two enclosures in one of the optimisation sets (initial $\text{Deg}T_{50}$ of five days), whilst Figure 5.6 presents the distribution of the scaled residuals between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals are reasonably well scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model. So, considering all aspects, the optimisation seems satisfactory.

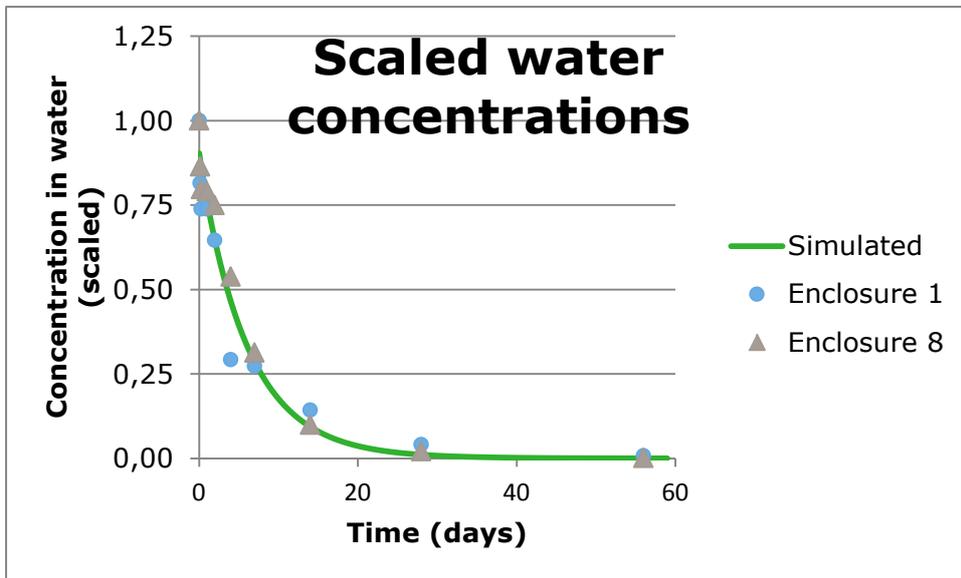


Figure 5.5 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) metribuzin in water as a function of time (d) in the enclosures of Brock et al. (2004). Simulated concentration profile obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 5 \text{ d}$ and $c_{t=0} = 1.0$.

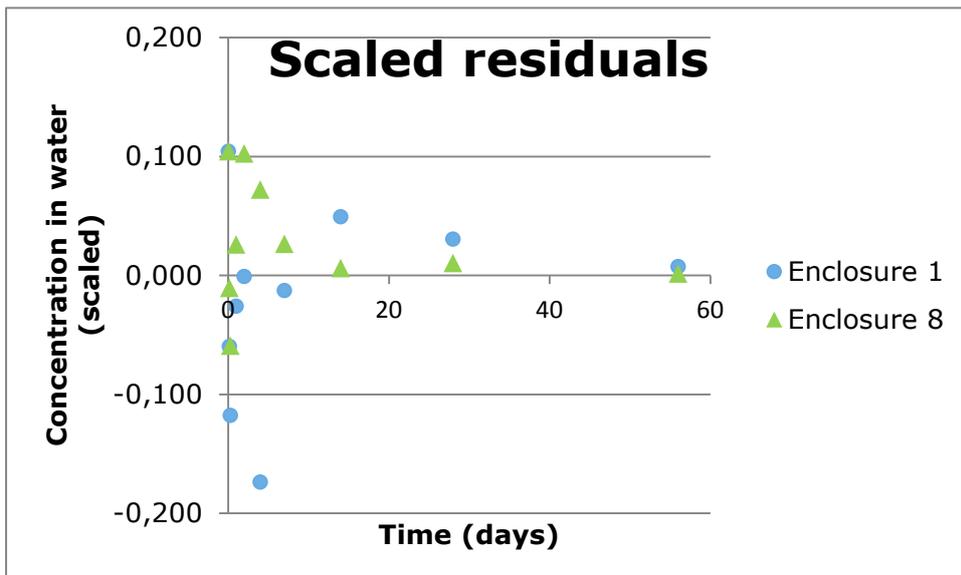


Figure 5.6 Residuals in the total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) metribuzin in water as a function of time (d) in the enclosures of Brock et al. (2004). Simulated concentration profile obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 5 \text{ d}$ and $c_{t=0} = 1.0$.

Overview

An overview of the results of inverse modelling, i.e. the obtained values for $\text{Deg}T_{50}$ in water and the initial concentration $c_{t=0}$, is given in Table 5.2.

Table 5.2

Estimates of $DegT_{50}$ and c_0 plus their 95% confidence intervals and χ^2 errors for metribuzin in water obtained by inverse modelling of the data sets

Data set analysed	$DegT_{50}$ at 20°C ^A (days)	$C_{t=0}$ (-)	Err%
Fairchild and Sappington (2002)	4.04 (2.2 – 5.9)	1.02 (0.86 – 1.18)	6.4%
Arts <i>et al.</i> (2006)	1.05 (0.94 – 1.17)	1.00 (0.96 – 1.03)	8.0%
Brock <i>et al.</i> (2004)	3.11 (2.4 – 3.8)	0.91 (0.85 – 0.97)	11.6%

^A The $DegT_{50, water}$ obtained from experimental data was corrected for temperature, resulting in a value at 20°C, using an Arrhenius type of equation as explained in the text.

The study of Fairchild and Sappington (2002) resulted in a value of $DegT_{50}$ in water of 4.0 days for metribuzin. For the data set of Arts *et al.* (2006) an average value of 1.0 day was found, and the data set of Brock *et al.* (2004) resulted in an intermediate value of $DegT_{50, water}$ of 3.1 days. Changing sediment properties did not affect the estimated values of $DegT_{50, water}$.

Comparison with degradation rates taken from other sources

Table 5.3 gives some data found in several sources on dissipation in water as a result of hydrolysis, photolysis, microbial degradation etc.

Table 5.3

Dissipation half-lives of metribuzin as obtained from different sources.

Process/system	DT ₅₀ (days)	Source
Hydrolysis	Stable over 34 days at pH 4, 7 and 9 (25°C) DT ₅₀ 635 d at pH 9 (25°C)	Annex IIa, point 7.2.1 (taken from Ctg document on Sencor WG)
Hydrolysis	Stable over 34 days at pH 4 – 9 (25°C)	Footprint database
Photolysis	0.18 d, sterile water, sunlight exposure in quartz cell 0.026 d, River Rhine water, Xenon light exposure in quartz cell	Annex IIa, point 7.2.1 (taken from Ctg document on Sencor WG)
Photolysis	0.2 d (pH 7)	Footprint database
Water/sediment	DT ₅₀ water: 41 d DT ₅₀ whole system: 50 d	Annex IIa, point 7.2.1 (taken from Ctg document on Sencor WG)
Water/sediment	DT ₅₀ water: 41 d DT ₅₀ whole system: 50 d	Footprint database

The DT₅₀ values for hydrolysis, photolysis and dissipation in water/sediment systems given in the Footprint database (<http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>) correspond to the values given in Annex IIa, which are reproduced above. They indicate that hydrolysis is relatively unimportant at neutral pH, whereas photolysis in water proceeds relatively fast if the compound is exposed to sunlight or artificial (Xenon) light. Dissipation in water/sediment systems was relatively slow with a DT₅₀ of 41 days in water only. The relatively short DT₅₀ values for photolysis indicate that in natural systems under sunlight, the overall dissipation may occur much faster than observed in water/sediment systems in the dark. Most likely, the overall dissipation in outdoor systems is to a large extent governed by the amount of sunlight to which they are exposed.

For all three cosms studies, for which a $DegT_{50, water}$ was estimated, treatment with metribuzin occurred in May, but the light intensities to which the systems were exposed may have been different. Data to check this assumption are available for the data sets of Brock (May 1999) and Arts (May 2002), using data from the meteorological station 'Haarweg' which is operated by the Faculty for Meteorology of Wageningen University & Research at Wageningen, at some five kilometre distance from the location in Renkum, the Netherlands, where the studies by Brock *et al.* (2004) and Arts *et al.*

(2006) were performed. Unfortunately, these data are lacking for the Fairchild and Sappington (2002) study.

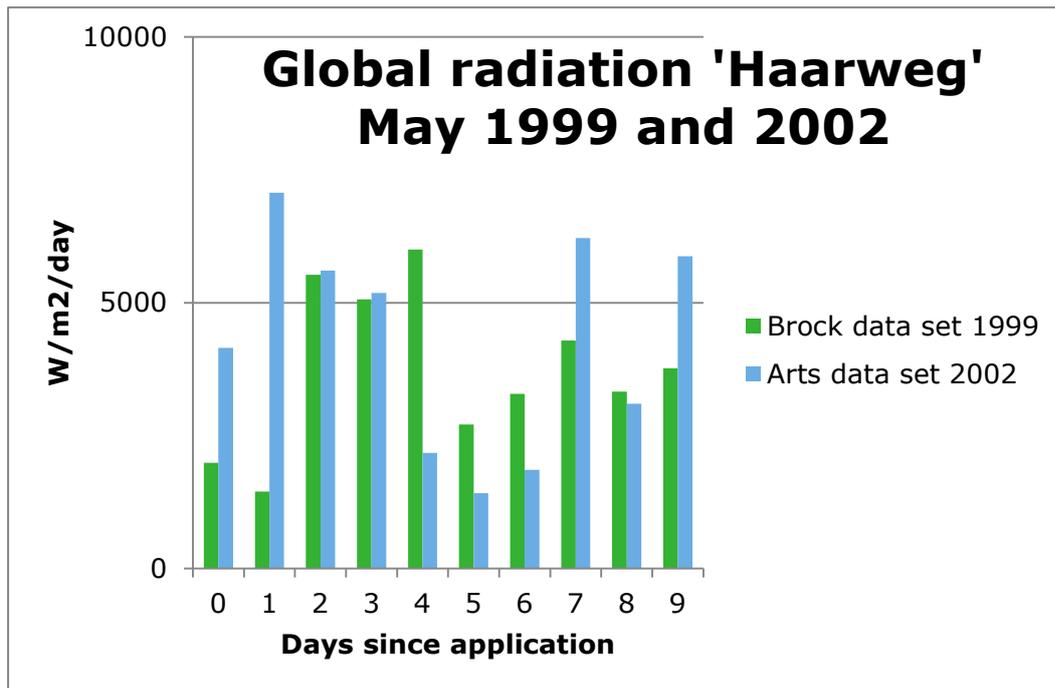


Figure 5.7 Global radiation measured at the meteorological station Haarweg in May of 1999 and 2002, corresponding to the nine-day period after application of metribuzin in the Brock *et al.* (2004) and Arts *et al.* (2006) experiments at the nearby experimental station, Sinderhoeve.

In terms of mass, by far the largest part of the substance was degraded shortly after application, e.g. during the first three half-lives, 87.5% of the substance was already degraded. Hence, a comparison of global radiation rates during the initial phase of the experiment is most useful to explain differences in observed half-lives. Average global radiation rates were 5,610 W/cm² during the first three days (corresponding to three half-lives) of the Arts *et al.* (2006) study, and only 4,000 W/cm² during the first three days (3,940 W/cm² during the first nine days) of the Brock *et al.* (2004) study. Hence, shorter half-life coincided with an approximately 1.4 times higher average global radiation rate in the period immediately after application. Moreover, the study described by Brock *et al.* (2004) used enclosures, which may have resulted in partial blocking of (ultraviolet) sunlight at the water surface, causing systematically lower radiation levels. The study described by Arts *et al.* (2006) was performed in ditches without the use of light-obstructing enclosures. The differences in sunlight between the studies, especially over the first few days after application of the test substance, in combination with the high sensitivity to photolysis of metribuzin, may, therefore, explain to a large extent the differences between estimated $DegT_{50, water}$ of 1 – 3 d for these two studies.

DegT₅₀ values going from lower- to higher tier data

Finally, the consistency of the DegT₅₀ values of the tiered approach, as discussed in Section 4.5, was considered.

Boesten *et al.* (2014) recommended using the longest DT₅₀ in the pH range of 7 – 9.5 for hydrolysis data. This was 635 days at 25°C. Assuming an Arrhenius activation energy of 75 kJ/mol, as proposed by Boesten *et al.* (2014), this corresponds to a DT₅₀ of 1,080 days at 20°C.

Aerobic water-sediment studies indicate a whole-system DT₅₀ of 50 days at 20°C (Table 5.3)

The *DegT_{50, water}* estimated from cosm data was in the range of one to four days at 20°C.

Hence, for the data considered, going from lower- to higher-tier data did indeed result in less conservative estimates for the degradation rate of metribuzin.

6 Assessment of the degradation rate of linuron in cosm water

Three studies were analysed using inverse modelling. The main characteristics of each of the studies are given in Table 6.1.

Table 6.1

Main characteristics for studies involving linuron

Data set analysed	Type of cosm	Nominal initial concentration ($\mu\text{g/L}$)	Number of applications	Interval	Number of measurements in water phase	Number of measurements in sediment phase	Water depth (m)	Temperature ($^{\circ}\text{C}$)	pH
Stephenson and Kane (1984)	Outdoor polyethylene cylinders, three separate systems	1000	1	-	7, 7, 8	-	1	11.6 ^A	7.8 – 9.0
Van den Brink <i>et al.</i> (1997)	Indoor glass aquaria	150 ^B	Several	2 – 3 days	16	-	0.5	19 \pm 2	
Bromilow <i>et al.</i> (2006)	Outdoor stainless-steel tanks	668	1	-	8	8	0.3	9.5	

^A Average temperature in Kent, U.K., in May, taken from web site:

http://www.yr.no/place/United_Kingdom/England/County_of_Kent/statistics.html

^B Systems at five different initial concentrations (nominal 0.5, 5, 15, 50 and 150 $\mu\text{g/L}$) were used in the experiment, only the systems with the highest concentrations were used for analysis of $DegT_{50}$.

Stephenson and Kane

Stephenson and Kane (1984) describe the results of experiments with linuron in three small (1,000 L) enclosures containing macrophytes, macro-invertebrates and zooplankton, in ponds located at Headcorn, Kent, U.K. A single application on 16th May 1979 was used. The initial concentration of linuron was 1 mg/L, and after application, six measurements in water (and none in sediments, for which no organic matter content was given) were reported. Details on the concentrations are given in Appendix 5.

The enclosures of Stephenson and Kane (1984) were inversely modelled and the agreement between measured- and simulated aqueous concentrations (scaled) was optimised with the aid of PEST, according to the procedures presented in Chapters 2 and 4. Four optimisations were performed, each with its own initial values of $DegT_{50, \text{water}}$ and $c_{t=0}$ and specified lower and upper parameter bounds (1 and 200 d for $DegT_{50, \text{water}}$ and 0.1 and 5.0 (scaled) for $c_{t=0}$). Details of the inverse modelling are given in Appendix 5. Optimisation resulted in an estimate of $DegT_{50, \text{water}}$ of 11.1 days with 95% confidence intervals of 8.5 – 13.7 days. The resultant error percentage of 8% was considered an acceptable value, according to FOCUS (2006). Changing the organic matter content of sediment and suspended solids from nine to 19% organic matter (see Chapter 4.1) did not affect the estimated value for the $DegT_{50, \text{water}}$.

Figure 6.1 presents a reasonably good agreement between scaled optimised and measured water concentrations for one of the optimisations (initial $DegT_{50}$ of 10 days), whilst Figure 5.2 presents the distribution of the scaled residual between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals are randomly scattered around zero (although there are some systematic trends for the individual enclosures), demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

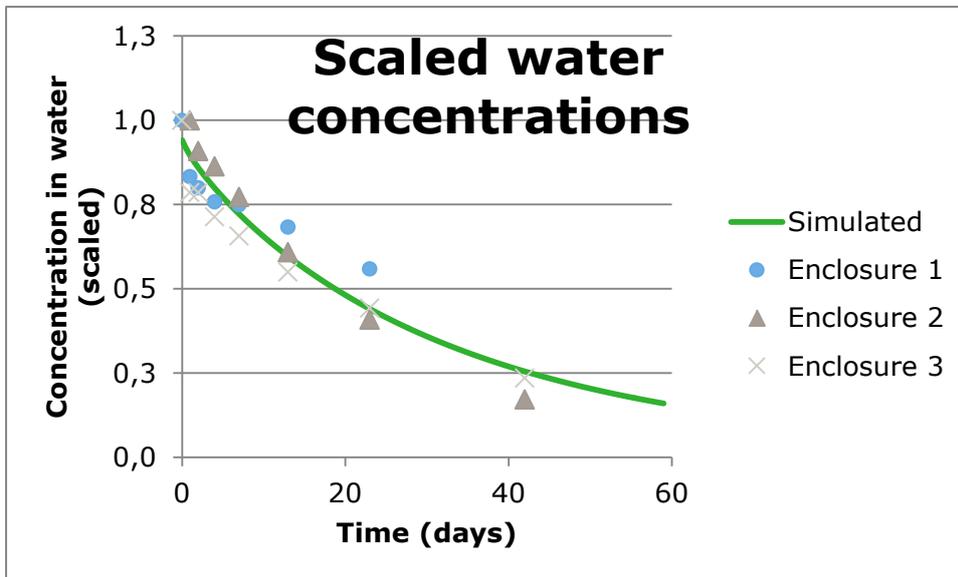


Figure 6.1 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in the study of Stephenson & Kane (1984). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 10$ d and $c_{t=0} = 1.0$.

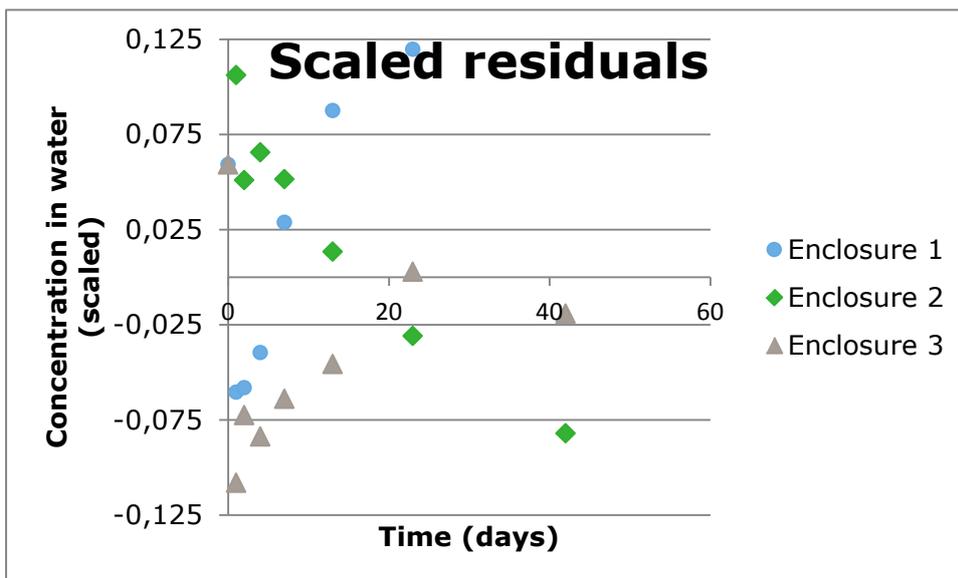


Figure 6.2 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in the study of Stephenson & Kane (1984). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 10$ d and $c_{t=0} = 1.0$.

Van den Brink *et al.*

Van den Brink *et al.* (1997) used indoor microcosms in glass aquaria (600 L water, 50 cm water depth, 10 cm lake sediment) located at Wageningen, The Netherlands, in which the concentration of linuron was kept constant during four weeks, by regularly dosing additional amounts of linuron to the cosms during late February – March 1994. After the initial four weeks, no more linuron was added, and the concentration of linuron was allowed to decline. Detailed information on measured concentrations and the dosings applied are given in Appendix 5. No measurements of concentrations in sediment were performed, and no information on the organic matter content of sediment was given. Results for two cosms (numbers 4 and 8), both with an initial nominal concentration of 50 $\mu\text{g/L}$, were analysed in more detail.

Cosms 4 and 8 of Van den Brink (1997) were each inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of PEST, according to the procedures presented in Chapters 2 and 4. Four optimisations were performed, each with its own initial values of $DegT_{50, water}$ and $C_{t=0}$ and specified lower and upper parameter bounds (1 and 200 d for $DegT_{50, water}$ and 0.1 and 5.0 (scaled) for $C_{t=0}$). The results of optimisations are given in Appendix 5. The inverse modelling resulted in estimates for the $DegT_{50, water}$ of 53.3 d (Cosm 4) and 69.9 d (Cosm 8) with 95% confidence intervals of 45 – 62 d (Cosm 4) and 59–81 d (Cosm 8). The optimisations passed the χ^2 -Test with error percentages of 3.8% (Cosm 4) and 2.9% (Cosm 8), which for field experiments are relatively low values, according to FOCUS (2006). Changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) did slightly affect the estimated values for the $DegT_{50, water}$: 54.7 instead of 53.3 d (Cosm 4) and 72.2 instead of 69.9 d (Cosm 8).

Figures 6.3 and 6.5 present a satisfactory agreement between scaled optimised and measured water concentrations for one of the optimisations of the cosm considered (initial $DegT_{50}$ of 10 days), whilst Figures 6.4 and 6.6 present the distribution of the scaled residuals between model-generated and measured concentrations, as suggested by FOCUS (2006). The graphs show that the residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

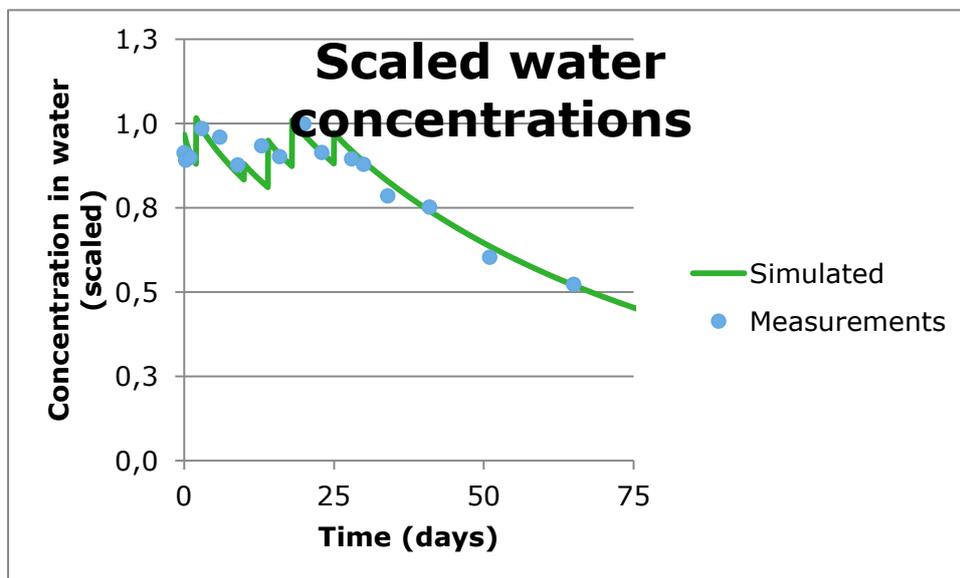


Figure 6.3 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in Cosm 4 of Van den Brink (1997). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $DegT_{50, ini} = 10$ d.

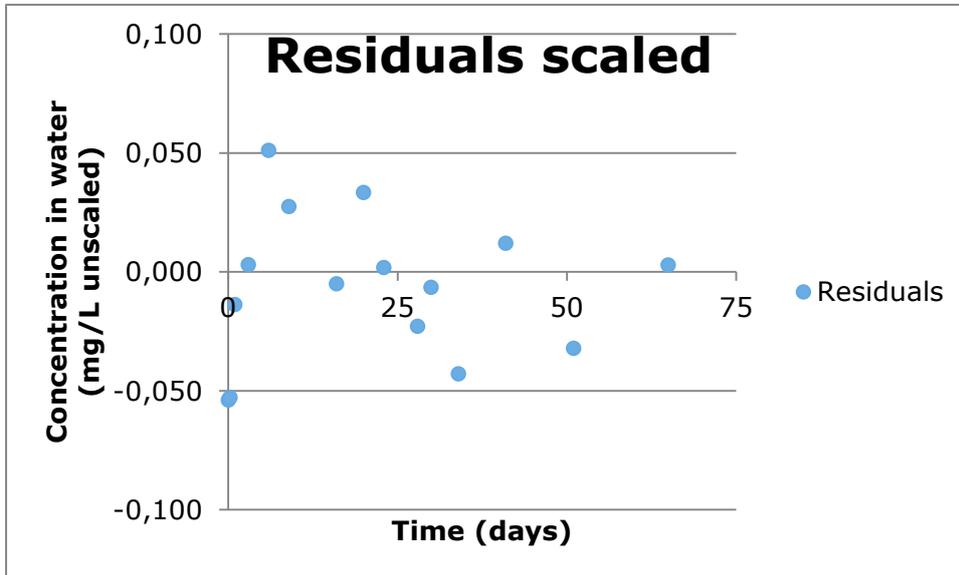


Figure 6.4. Residuals in total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in Cosm 4 of Van den Brink (1997). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50, ini} = 10$ d.

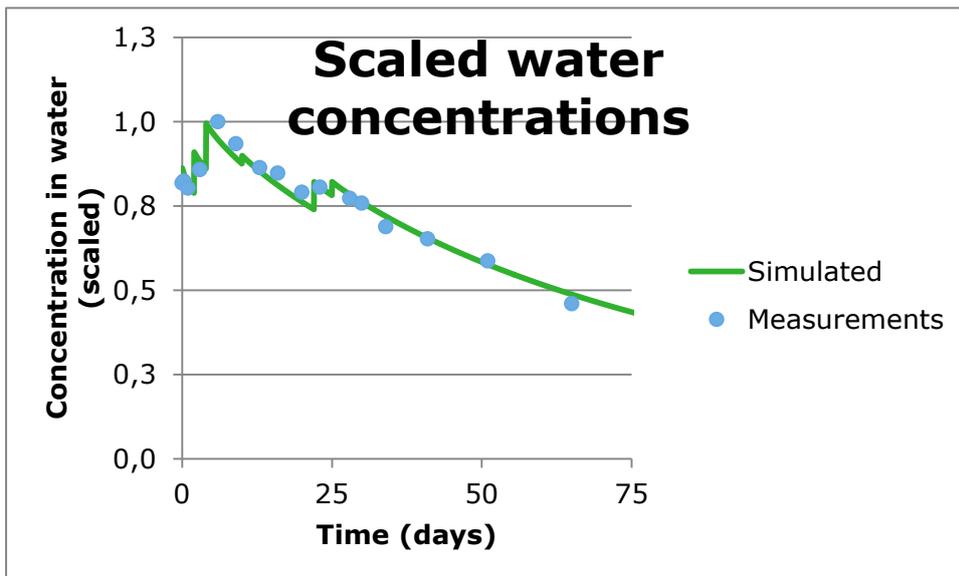


Figure 6.5 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in Cosm 8 of Van den Brink (1997). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50, ini} = 10$ d.

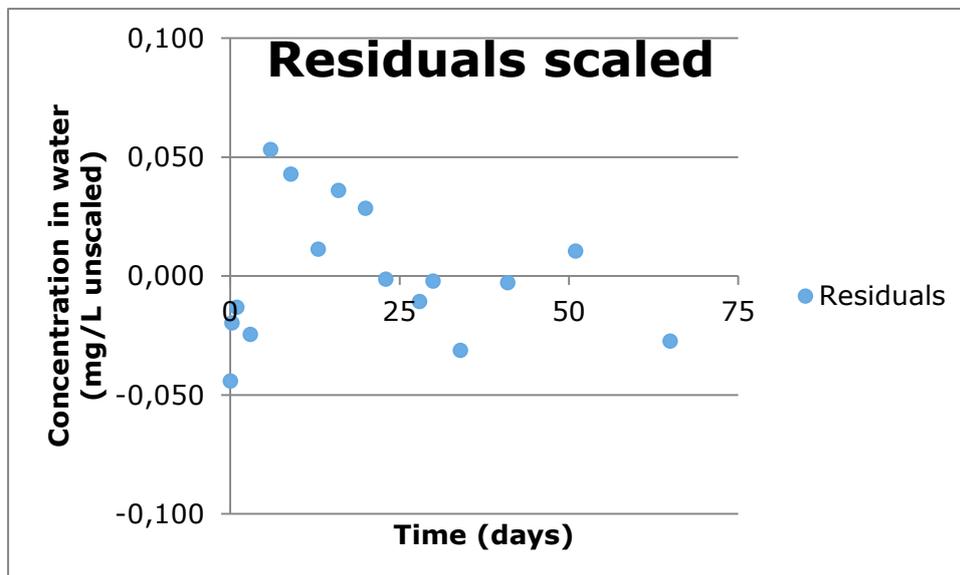


Figure 6.6 Residuals in total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in Cosm 8 of Van den Brink (1997). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 10$ d.

Bromilow et al.

Bromilow et al. (2006) describe the fate of linuron in an experiment that used an initial concentration of 67 $\mu\text{g/L}$ in 300 L outdoor cosms located at Harpenden, Hertfordshire, U.K. Concentrations measured in water, sediment (2.5% organic carbon) and plants were reported. Linuron remained largely in the water phase, to a lesser extent in the sediment and hardly any linuron at all was observed in plant material. Details on measured concentrations are given in Appendix 5. The outdoor study used a single application of linuron, in a rather shallow system (30 cm water depth) at a rather low temperature (application on October 30, 2002), with sediment temperature ranging from 1 - 10°C and average water temperature 4°C above sediment temperature, as stated by the authors.

The tanks of Bromilow et al (2006) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of PEST, according to the procedures presented in Chapters 2 and 4. Three optimisations were performed, each with its own initial values of $\text{Deg}T_{50, water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (1 and 200 d for $\text{Deg}T_{50, water}$ and 0.1 and 5.0 (scaled) for $c_{t=0}$). Inverse modelling resulted in consistent estimates of $\text{Deg}T_{50, water}$ of 25.8 d with a 95% confidence interval of 17.5 - 34.0 d (which is comparatively large). The observed error percentage of 5.1% was considered acceptable, according to FOCUS (2006). Changing the organic matter content of sediment and suspended solids from nine to 19% organic matter (see Chapter 4.1) affected the estimated value for the $\text{Deg}T_{50, water}$ to a negligible extent.

Figure 6.7 presents a good agreement between scaled optimised and measured water concentrations for one of the optimisations (initial $\text{Deg}T_{50}$ of 10 days), whilst Figure 6.8 presents the distribution of the scaled residual between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows a slight trend of increasing residue values with time but the deviations between simulations and measurements are quite small in Figure 6.7 so the fitted $\text{Deg}T_{50, water}$ was considered reliable.

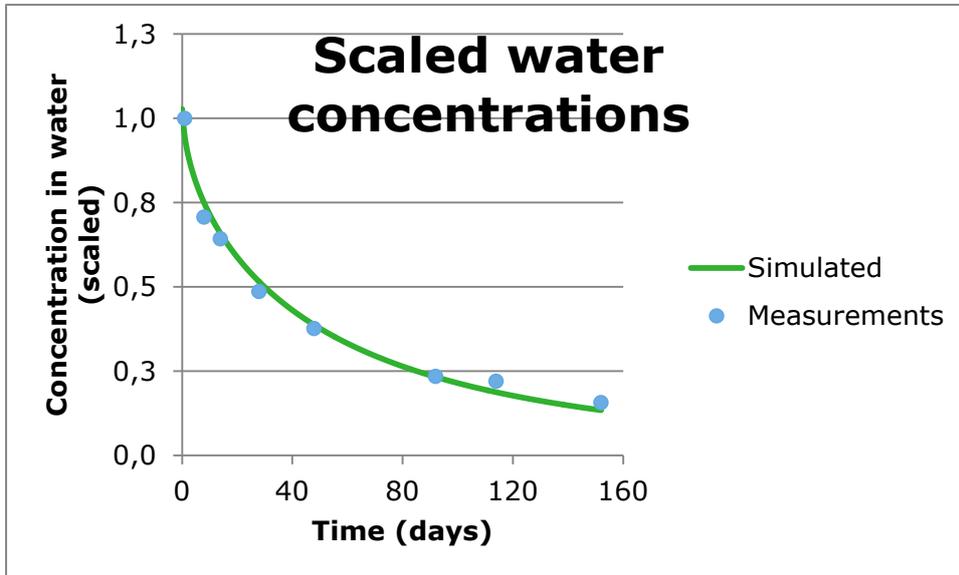


Figure 6.7 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in the cosm of Bromilow (2006). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 10 \text{ d}$

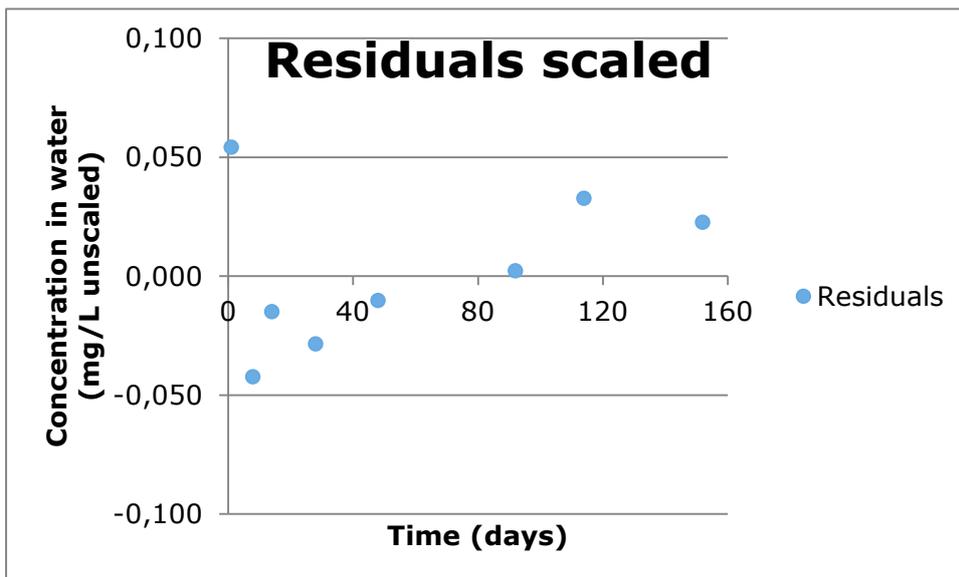


Figure 6.8 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in the cosm of Bromilow (2006). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 10 \text{ d}$

Overview

An overview of the results of inverse modelling, i.e. the obtained values for $\text{Deg}T_{50}$ in water and the initial concentration $c_{t=0}$, are given in Table 6.2.

Table 6.2

Estimates of DegT₅₀ and c₀ plus their 95% confidence intervals for linuron in water obtained by inverse modelling of the data sets.

Data set analysed	DegT ₅₀ at 20°C ^A (days)	C _{t=0} (-)	Err%
Stephenson and Kane (1984)	11.1 (8.5 – 13.7)	0.94 (0.89 – 0.99)	8.0%
Van den Cosm 4	53.3 (44.9 – 61.8)	0.97 (0.93 – 1.01)	3.8%
Brink <i>et al.</i> Cosm 8 (2006)	69.9 (59.2 – 80.5)	0.86 (0.83 – 0.89)	2.9%
Bromilow <i>et al.</i> (2006)	25.8 (17.0 – 34.0)	1.03 (0.96 – 1.10)	5.1%

^A The DegT₅₀ obtained from experimental data is corrected for temperature, resulting in a value at 20°C, using an Arrhenius type of equation, as explained in the text.

For the Stephenson and Kane (1984) data set an overall value of 11.1 days was estimated for DegT₅₀ of all three systems. When analyzing the three different cylinders separately, values for DegT_{50, water} of 18.6, 8.4 and 10.8 days were observed (see Appendix 5); taking the geometric mean of these three values would result in a geomean value of 11.9 days, which is well within the 95%-confidence interval of 8.5 – 13.7 days estimated for the overall value calculated.

Slight differences were observed between the results for Cosms 4 and 8 in the study of Van den Brink *et al.* (1997). On average, a relatively high estimate of the DegT₅₀ of 61 days was estimated.

The study of Bromilow *et al.* (2006) resulted in an intermediate value of DegT₅₀ at 20°C of 26 days.

Changing sediment properties resulted in a slight and non-significant (2 – 3%) increase of the estimated DegT_{50, water} in the studies by van den Brink *et al.* (1997) and Bromilow (2006).

Comparison with degradation rates taken from other sources

Table 6.3 gives some data found in several sources on dissipation in water as a result of hydrolysis, photolysis, microbial degradation etc.

Table 6.3

Dissipation half-life of linuron from different sources

Process / system	DT ₅₀ (days)	Source
Hydrolysis	Stable at pH 5, 7 and 9 (22°C)	Annex IIa, point 7.2.1 (taken from Ctgb document on Linurex 50 SC)
Hydrolysis	DT ₅₀ 1460 d at pH 7 (20°C)	Footprint
Hydrolysis	No hydrolysis during 70 d at any pH	Gatidou and Iatrou (2011)
Photolysis	Stable	Annex IIa, point 7.2.1 (taken from Ctgb document on Linurex 50 SC)
Photolysis	No photolysis at pH 7 and 9; DT ₅₀ approx 70 d at pH 4, enhanced by nitrate	Gatidou and Iatrou (2011)
Photolysis	Rather rapid photolysis in water; Non-quantitative studies in Faure & Boule	Rao and Chu (2009), Rao and Chu (2010), Faure and Boule (1997)
Water/sediment	DT ₅₀ water: 48 d DT ₅₀ whole system: 46 d	Annex IIa, point 7.2.1 (taken from Ctgb document on Linurex 50 SC)

The DT₅₀ values for hydrolysis, photolysis and dissipation in water/sediment systems given in the Footprint database (<http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>) correspond to the values given in Annex IIa, which are reproduced above. They indicate that hydrolysis and photolysis were of hardly any importance. Dissipation in water/sediment systems is relatively slow with a DT₅₀ of 48 days in water only. Since photolysis was not relevant, the overall dissipation in (outdoor) cosms is not expected to be influenced by the amount of irradiation.

For the cosms analyzed in the present study, a $DegT_{50, water}$ was observed ranging from 11 – 70 days. When ranking the studies in order of $DegT_{50, water}$, the system with the highest temperature (Van den Brink *et al.*, 2006) also is the system with the largest $DegT_{50, water}$ indicating that other, as yet unidentified, factors may have a larger influence on degradation than temperature. A possible explanation for the high value of $DegT_{50, water}$ may be lower microbial activity due to the fact that the study by van den Brink *et al.* (2006) was an indoor study, in contrast to the other two studies, which were performed outdoor.

DegT₅₀ values going from lower- to higher-tier data

For hydrolysis data, the longest DT₅₀ in the pH range of 7 – 9.5 was 1,460 d at 20°C.

An aerobic water-sediment study in the dark gave a whole-system DT₅₀ of 46 d and a DT₅₀ for dissipation from water of 48 d at 20°C.

An indoor study with algae and macrophytes generated a $DegT_{50, water}$ at 20°C that ranged from 53 to 70 d.

The $DegT_{50, water}$ at 20°C estimated from two outdoor cosm studies was in the range of 11 – 26 d at 20°C.

Considering the tiered approach of Figure 4.2, the study by van den Brink *et al.* (2006) belongs to the box 'indoor studies with algae and possibly macrophytes' (Box 2.8 in the Figure), and is, according to the scheme, a higher tier than the water-sediment studies in the dark (Box 2.5 in the Figure). The DT₅₀ for dissipation from water of 48 d derived from the water-sediment studies is very probably a lower limit for the $DegT_{50, water}$ (Honti *et al.*, 2015). Thus, we have $DegT_{50, water} > 48$ d from box 2.5 and $DegT_{50, water} = 53-70$ d for Box 2.8. So, no conclusion could be drawn with respect to the consistency of the results for the Boxes 2.5 and 2.8 of the tiered approach.

The indoor study by van den Brink *et al.* (2006) resulted indeed in a higher $DegT_{50, water}$ than the $DegT_{50, water}$ that was found for the outdoor studies (53-70 d versus 11-26 d).

The estimate of the $DegT_{50, water}$ derived from the water-sediment study (i.e. $DegT_{50, water} > 48$ d) is indeed considerably higher than the $DegT_{50, water}$ from the outdoor studies (11-26 d).

Hence, the results obtained for the degradation rate of linuron in the different systems did not indicate inconsistencies in the scheme of Figure 4.2.

7 Assessment of the degradation rate of imidacloprid in cosm water

Three studies were analysed using inverse modelling. The main characteristics of each of the studies are given in Table 7.1.

Table 7.1

Main characteristics for studies involving imidacloprid.

Data set analysed	Type of cosm	Nominal initial concentration (µg/L)	Number of applications	Interval (days)	Number of measurements in water phase	Number of measurements in sediment phase	Water depth (m)	Temperature (°C)	pH
Colombo <i>et al.</i> (2013)	Polypropylene containers in outdoor pond	17.3 ^A	3	7	18	1 ^B	0.11	17°C ^C	
Heimbach and Hendel (2001)	Outdoor: 1 round test pond, 1 rectangular tank	6.0	1	-	8 in pond, 8 in tank	-	Pond 1.0 m; tank 0.3 m	16.7°C ^D	
Ratte and Memmert (2003)	13 round ponds, 1,300 or 1,800 L, 1 m water depth	9.3, 23.5	2	21	14 or 15	Not used	1.0	19.0°C ^E	

^A Systems at six different initial concentrations were used, but only the systems with 17.3 µg/L nominal were monitored sufficiently frequent to be used for analysis.

^B Only a single measurement of the end of the experiment, insufficient data for inverse modelling.

^C Average temperature of night (10°C) and day temperatures (24°C) given in the paper.

^D Average temperature in May (temperature for other months are given as well, but all measurements were in May).

^E Estimated average water temperature over the first 191 days, taken from a graph given in the report.

Colombo *et al.*

Colombo *et al.* (2013) reported the results of experiments in small (20 L water) enclosures with shallow water depth (11 cm) located at Berlin, Germany, and containing sediment, where macrozoobenthos was exposed to imidacloprid. The exposure was implemented as three pulses with weekly intervals, allowing for substantial decrease of concentrations between applications. Applications occurred from late May – June (year not given, probably 2012). Nominal initial concentrations ranged from 0.6 to 40 µg/L. Although exposure concentrations were measured in all of the cosms, the fate of imidacloprid was studied in more detail in cosms with the nominal concentration of 17.3 µg/L, for which a total of 18 measured concentrations in water were reported. Details on measured concentrations are given in Appendix 6. The concentration of imidacloprid in sediment was only measured once, on day 56, at the end of the experiment.

The containers of Colombo *et al.* (2013) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of PEST, according to the procedures presented in Chapters 2 and 4. Three optimisations were performed, each with its own initial values of $DegT_{50, water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (0.1 and 100 d for $DegT_{50, water}$ and 0.1 and 5.0 (scaled) for $c_{t=0}$). Details of the results are given in Appendix 6. The inverse modelling resulted in consistent estimates of $DegT_{50, water}$ of 1.0 days with 95% confidence intervals of 0.77 – 1.25 days. A relatively high error percentage of 19.5% was found, and according to FOCUS (2006), the χ^2 -Test would not be passed. Changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) affected the estimated value for the $DegT_{50, water}$ to a negligible extent.

Figure 7.1 presents the agreement between optimised and measured scaled water concentrations for one of the optimisations (initial DegT₅₀ of 10 days), whilst Figure 7.2 presents the distribution of the scaled residuals between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals show some more under-estimations than over-estimations, but in general, the fit of the model is considered acceptable.

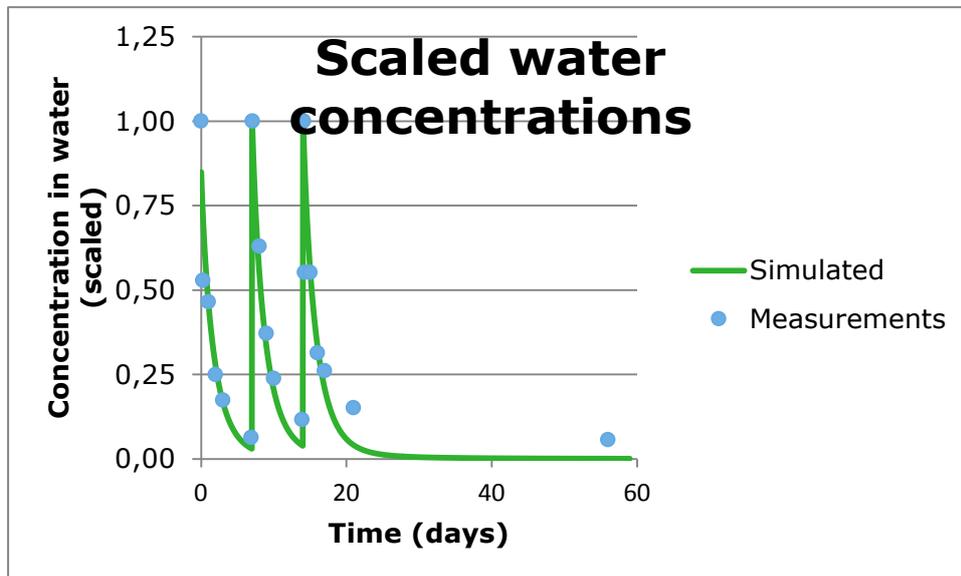


Figure 7.1 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the cosm of Colombo et al (2013). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50, ini} = 10$ d.

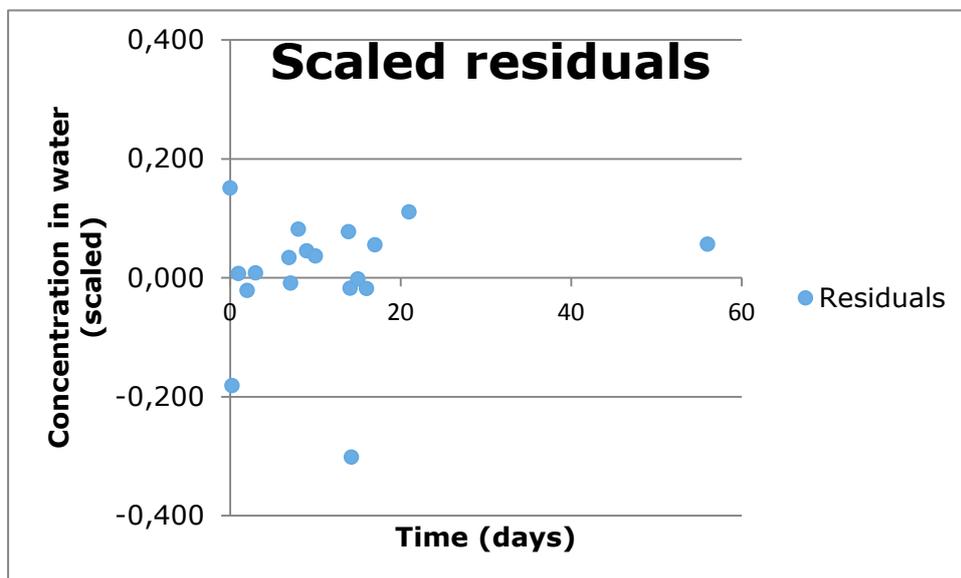


Figure 7.2 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the cosm of Colombo et al (2013). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50, ini} = 10$ d.

Heimbach and Hendel

Heimbach and Hendel (2001) reported results of simultaneous experiments in a small pond (diameter 2.0 m, water depth 1.0 m) and a small rectangular tank (0.6 x 1.8 m, water depth 0.3 m) located at

Monheim, Germany. The exposure for both systems consisted of a single application on 8th May 2000 at a nominal initial concentration of 6.0 µg a.i./L. Details on measured concentrations are given in Appendix 6. The concentration of imidacloprid in sediment was measured eight times over 70 days, but most measurements resulted in values below the limit of quantification. The tank had a much higher coverage with macrophytes (60%) than the pond (approx. 30%) over the first 21 days.

The pond and tank of Heimbach and Hendel (2001) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of PEST, according to the procedures presented in Chapters 2 and 4.

The pond and tank data were analysed separately and also analysed as a single, merged data set. For the merged set, an average water depth of 0.65 m was used (water depth pond: 1.00 m; water depth tank: 0.30 m). Moreover, for the pond data the data were analysed using either all aqueous concentrations in time (eight points in total) or omitting the first measured concentrations (the authors indicated that this first measured concentration was probably low due to insufficient mixing of the aqueous phase during the first few hours after application).

For all cases, three optimisations were performed, each with their own initial values of $DegT_{50, water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (0.1 and 100 d for $DegT_{50, water}$ and 0.1 and 5.0 (scaled) for $c_{t=0}$). Details of the results of inverse modelling are given in Appendix 6. For all cases, changing the organic matter content of sediment and suspended solids from nine to 19% organic matter (see Chapter 4.1) affected the estimated value for the $DegT_{50, water}$ to a negligible extent.

For the pond, using all eight data points in the inverse modelling resulted in a consistent estimate of $DegT_{50, water}$ of 6.9 days with 95% confidence intervals of 3.4 – 10.4 days. The χ^2 -Test was passed with an error percentage of 12.7%, which is an acceptable value, according to FOCUS (2006).

Figure 7.3 presents the agreement between optimised and measured scaled water concentrations for one of the optimisations (initial $DegT_{50}$ of 10 days), it clearly shows that the first measurement seemed to be too low, thus, provoking an unsatisfactory agreement during the first days. Figure 7.4 presents the distribution of the scaled residuals between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that for the first few days the residuals were clearly greater than later on, thus, reflecting the unsatisfactory fit of Figure 7.3.

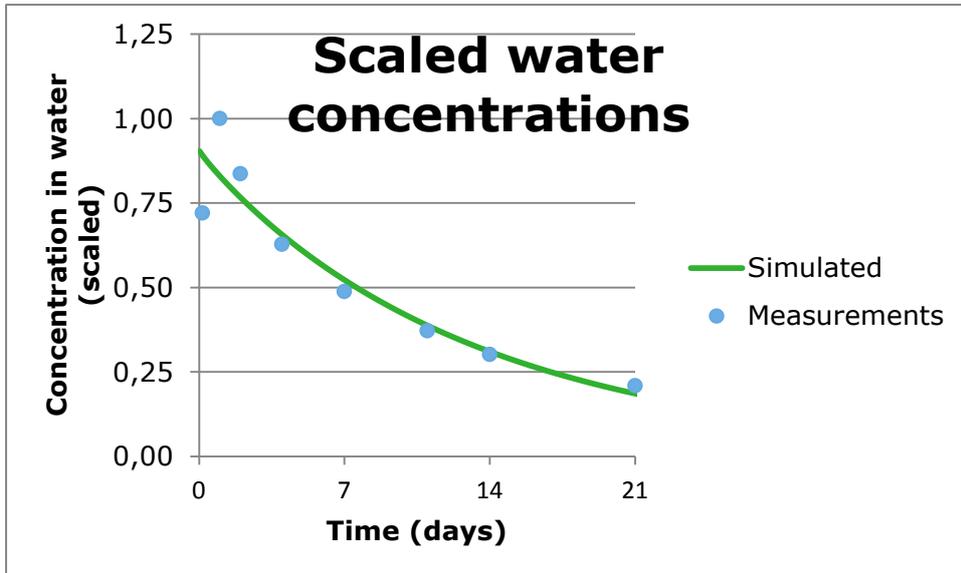


Figure 7.3 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the pond data set of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50, ini} = 10$ d; all data points were included in the calculations.

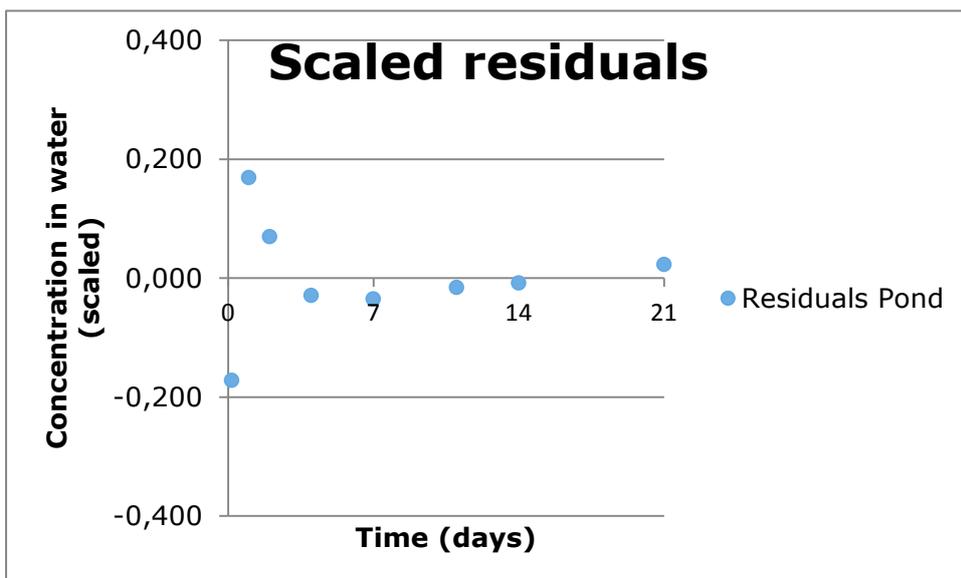


Figure 7.4 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the pond data set of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50, ini} = 10$ d; all data points were included in the calculations.

Omitting the first data point of the pond, because of insufficient mixing resulted in slightly lower value of DegT_{50} : the $\text{DegT}_{50, water}$ was estimated at 5.5 days with 95% confidence intervals of 4.0 – 7.1 days. The χ^2 -Test was passed with an error percentage of 6.9%, which is considerably lower than in the former optimisation with all eight data points.

Figure 7.5 presents the agreement between optimised and measured scaled water concentrations for one of the optimisations (initial DegT_{50} of 10 days), after omitting the first measurement. Compared to Figure 7.3, the agreement clearly improved and was satisfactory. Figure 7.6 presents the distribution of the scaled residuals between model-generated and measured concentrations, as

suggested by FOCUS (2006). The graph now shows that the residuals are neatly randomly scattered around zero (although there seems to be a slight wave-type trend), demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

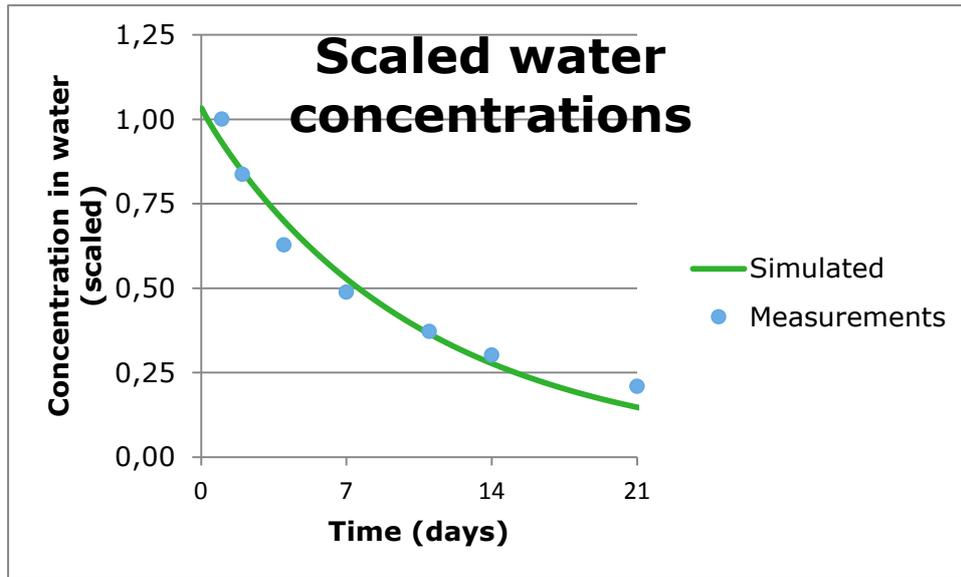


Figure 7.5 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the pond data set of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 10$ d; the first data point was omitted due to insufficient mixing.

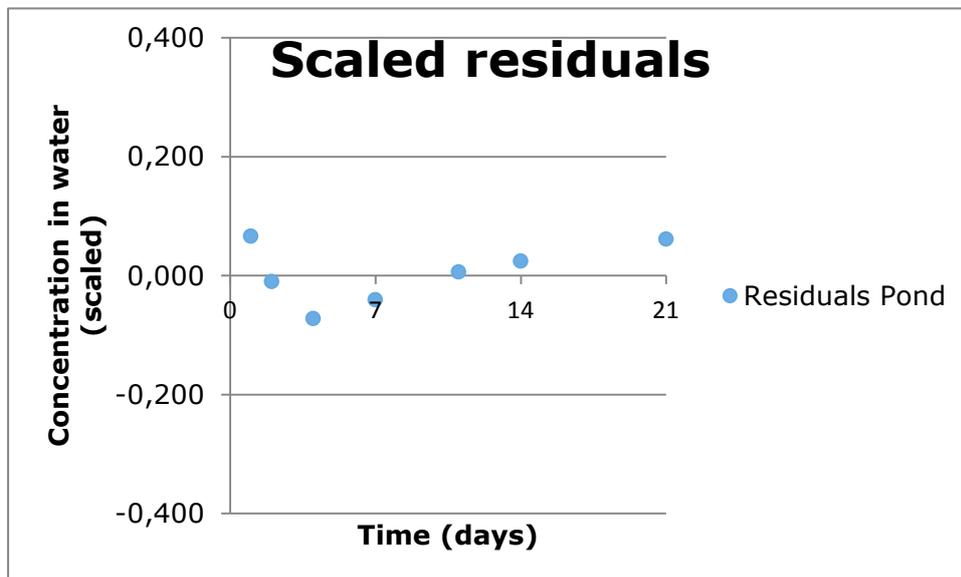


Figure 7.6 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the pond data set of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 10$ d; the first data point was omitted due to insufficient mixing.

For the tank with a water depth of 0.3 m, the inverse modelling resulted in consistent estimates of $\text{Deg}T_{50, water}$ of 4.3 days with 95% confidence intervals of 3.0 – 5.5 days. The χ^2 -Test was passed with an error percentage of 8.3%, which is an acceptable value, according to FOCUS (2006).

Figure 7.7 presents a satisfactory agreement between optimised and measured scaled water concentrations for one of the optimisations (initial $DegT_{50}$ of 10 days). Figure 7.8 presents the distribution of the scaled residuals between model-generated and measured concentrations, as suggested by FOCUS (2006). The residuals as a function of time are not really randomly scattered around zero, but are wave-shaped, indicating that the estimate of the $DegT_{50, water}$ first seems slightly under-predicted and later on, slightly over-predicted, by the single $DegT_{50, water}$ value.

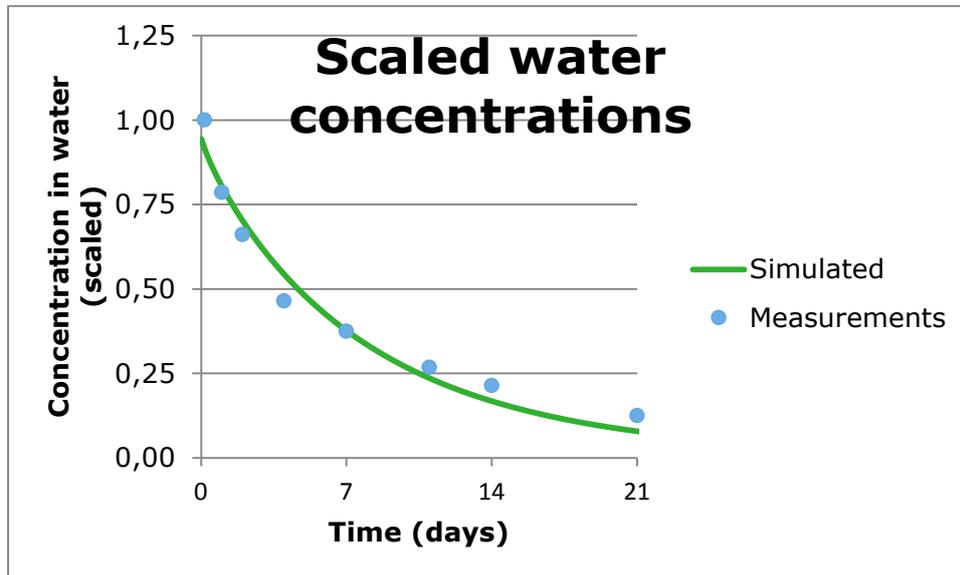


Figure 7.7 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the tank data set of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $DegT_{50, ini} = 10$ d.

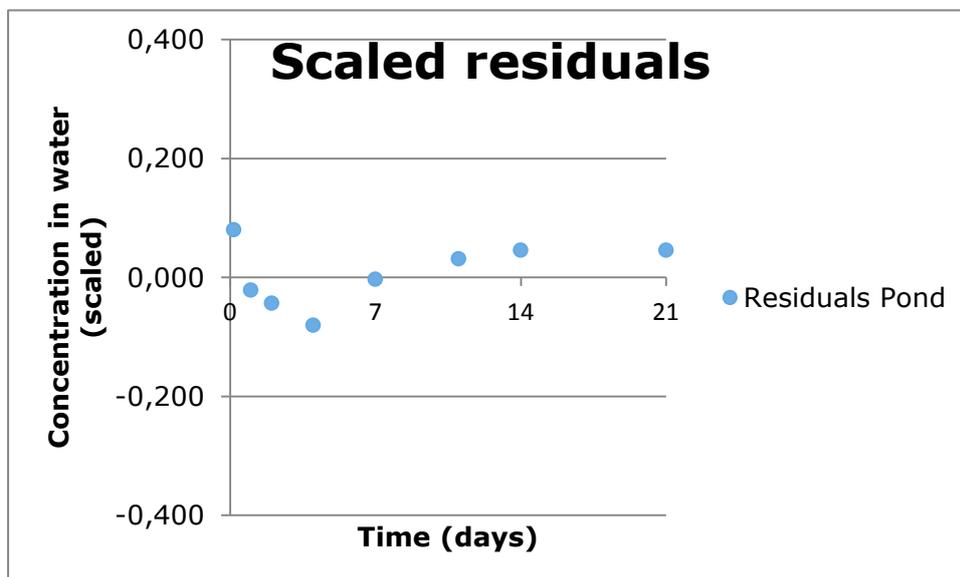


Figure 7.8 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the tank data set of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $DegT_{50, ini} = 10$ d.

For the merged data set of pond and tank (water depth of 0.65 m), inverse modelling resulted in consistent estimates of $DegT_{50, water}$ of 5.5 days with 95% confidence intervals of 3.9 – 7.2 days. The

value of 5.5 d compared quite favourably with the geometric mean of values for the pond (when all data were included: $DegT_{50, water} = 6.88$ days) and the tank ($DegT_{50, water} = 4.26$ days): $DegT_{50, water} = 5.41$ days. The error percentage of 14.4% is an acceptable value, according to FOCUS (2006), and, thus, the χ^2 -Test was passed.

Figure 7.9 presents the agreement between optimised and measured scaled water concentrations for one of the optimisations (initial $DegT_{50}$ of 10 days), after omitting the first measurement. As shown also by the distribution of the scaled residuals in Figure 7.10, with the residuals for the pond lying mainly above and the residuals for the tank mainly below the zero line, the estimated degradation rate appears to be slightly faster than the rate in the pond and it appears slightly slower than the rate in the tank. This corresponds with the statements above with a geometric mean of $DegT_{50, water} = 5.41$ days and values for the pond (when all data are included) of $DegT_{50, water} = 6.88$ days and the tank of $DegT_{50, water} = 4.26$ days.

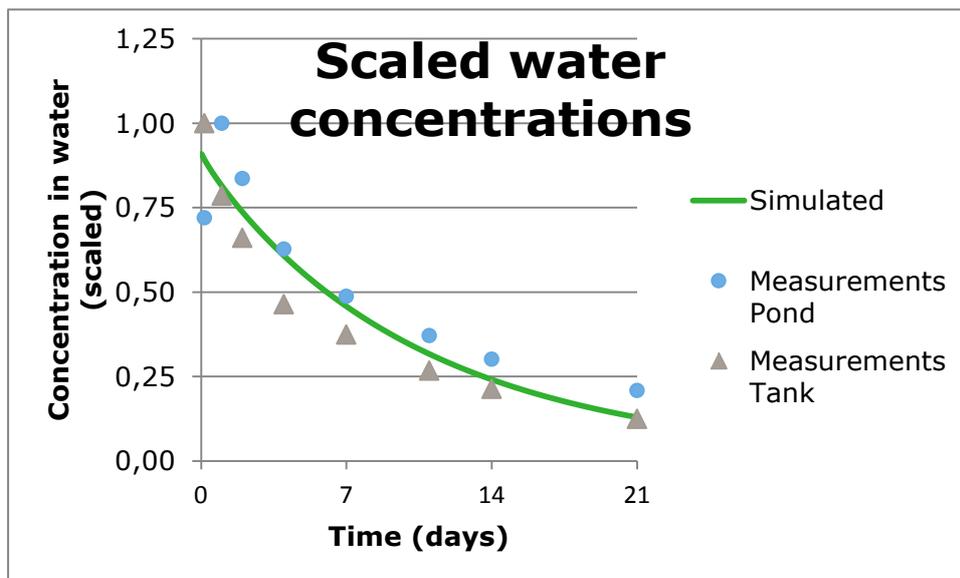


Figure 7.9 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the pond and tank of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $DegT_{50, ini} = 10$ d

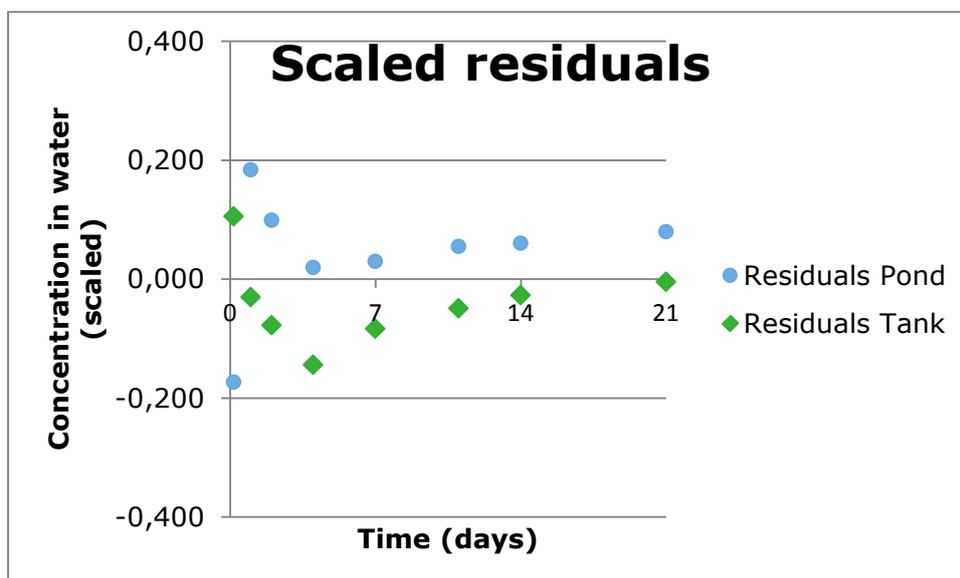


Figure 7.10 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the pond and tank of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 10 \text{ d}$

Ratte and Memmert

Ratte and Memmert (2003) described a study in a collection of 13 outdoor ponds located at Itingen, Switzerland. The test substance was applied twice, on 2nd May and 23rd May 2001. There was no deliberate mixing of the ponds after application and there was no or only slight wind during the applications on both dates. Water samples (14 or 15) were taken on days 0 – 77 or 91 after first application from each of the ponds. Details on measured concentrations and dosages applied are given in Appendix 6. Although the growth of macrophytes was not quantified in the study in detail, the report mentions that floating plants of *Lemna* were removed from the ponds at each sampling date. For this reason, the ponds were considered to have contained only negligible amounts of macrophytes.

The Ponds 7, 13, 2 and 8 of Ratte and Memmert (2003) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of PEST, according to the procedures presented in Chapters 2 and 4.

Estimation of $\text{Deg}T_{50, water}$ was performed for each of the Ponds 7 and 13 (nominal initial concentration 26.5 $\mu\text{g/L}$) and Ponds 2 and 8 (nominal initial concentration 9.3 $\mu\text{g/L}$) separately. Systems could not be merged in the calculations, because of repeated dosing of the test substance causing different 'loadings' to be used for the second application (TOXSWA cannot simultaneously perform calculations with systems needing different 'loadings' on the same day). For each pond, two optimisations were performed, each with its own initial values of $\text{Deg}T_{50, water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (0.1 and 100 d for $\text{Deg}T_{50, water}$ and 0.1 and 5.0 (scaled) for $c_{t=0}$). Details on the results of inverse modelling are given in Appendix 6.

The influence of the change in organic matter content of sediment and suspended solids from nine to 19% organic matter was only considered for Ponds 7 and 2 and it was found that in both cases, the estimated value for the $\text{Deg}T_{50, water}$ was affected to a negligible extent.

For the data of Pond 7, the inverse modelling resulted in an estimate of for the $\text{Deg}T_{50, water}$ of 5.5 days with relatively large 95% confidence intervals of 4.3 – 6.6 days. The optimisation passed the χ^2 -Test with an error percentage of 14.4%, an acceptable value for field experiments according to FOCUS (2006).

Figure 7.11 presents the agreement between scaled optimised and measured water concentrations for one of the optimisations for Pond 7 (initial $\text{Deg}T_{50}$ of 10 days), whilst Figure 7.12 presents the

distribution of the scaled residual between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

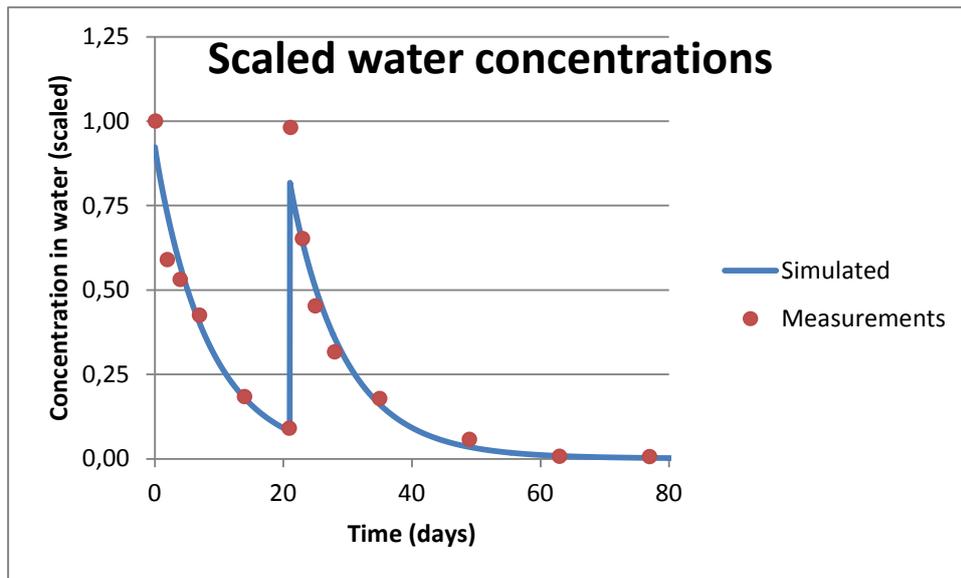


Figure 7.11 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for Pond 7 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 10$ d.

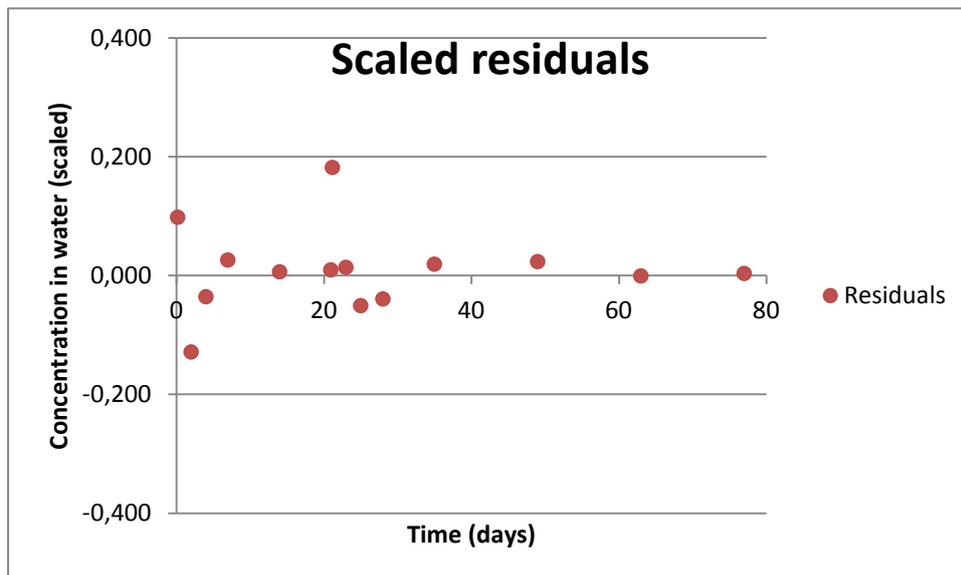


Figure 7.12 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for Pond 7 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 10$ d.

For the data of Pond 13, the inverse modelling resulted in an estimate of the $\text{Deg}T_{50, water}$ of 5.3 days with a 95% confidence intervals of 3.9 – 6.6 days. The observed error percentage of 19.5% is a relatively large value for the χ^2 -Test, even for field experiments according to FOCUS (2006).

Figure 7.13 presents the agreement between scaled optimised and measured water concentrations for one of the optimisations for pond 13 (initial DegT_{50} of 10 days), which is slightly worse than the agreement for pond 7. Figure 7.14 presents the distribution of the scaled residuals between model-generated- and measured concentrations, the residual corresponding to the second loading was clearly the highest one. The other residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

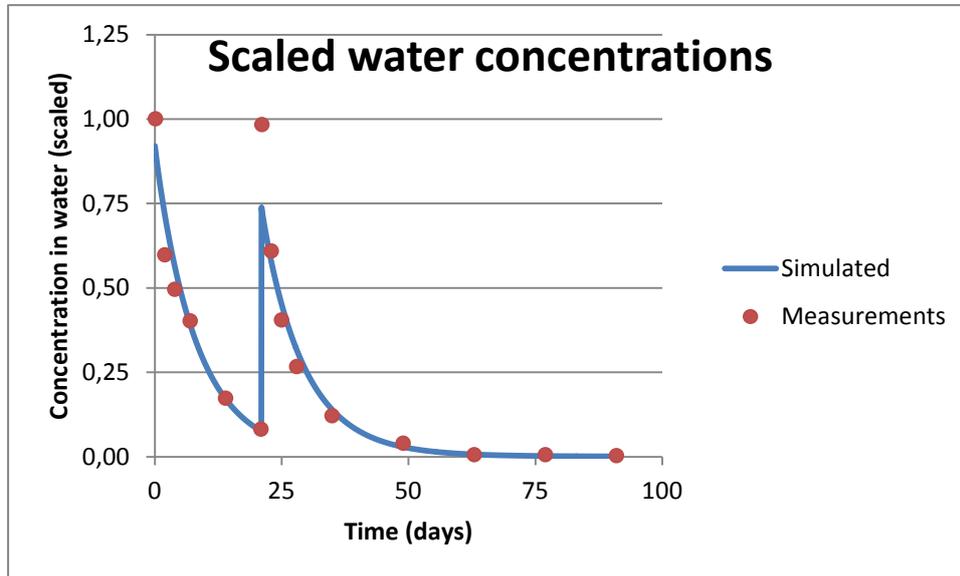


Figure 7.13 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for Pond 13 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50, ini} = 10$ d.

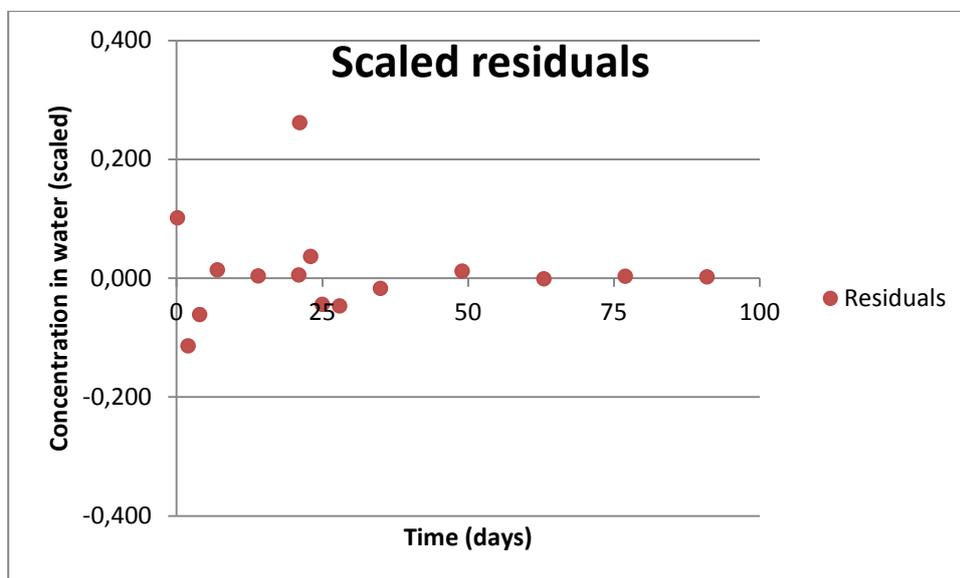


Figure 7.14 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for Pond 13 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50, ini} = 10$ d.

For the data of Pond 2, inverse modelling resulted in an estimate of for the $DegT_{50, water}$ of 5.6 days with a 95% confidence intervals of 4.5 – 6.6 days. The observed error percentage of 13.1% is an acceptable value for field experiments according to FOCUS (2006), so, the optimisation for Pond 2 passed the χ^2 -Test.

Figure 7.15 presents the agreement between scaled optimised and measured water concentrations for one of the optimisations for Pond 2 (initial $DegT_{50}$ of 10 days). Figure 7.16 presents the distribution of the scaled residuals between model-generated and measured concentrations. The residual corresponding to the second loading was again the highest one, whilst the other residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

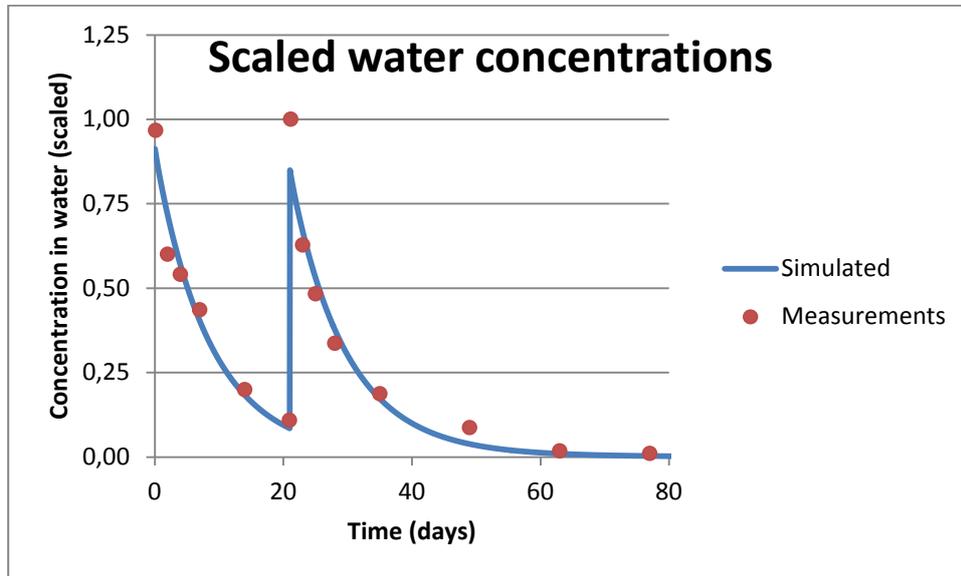


Figure 7.15 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for Pond 2 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $DegT_{50, ini} = 10$ d.

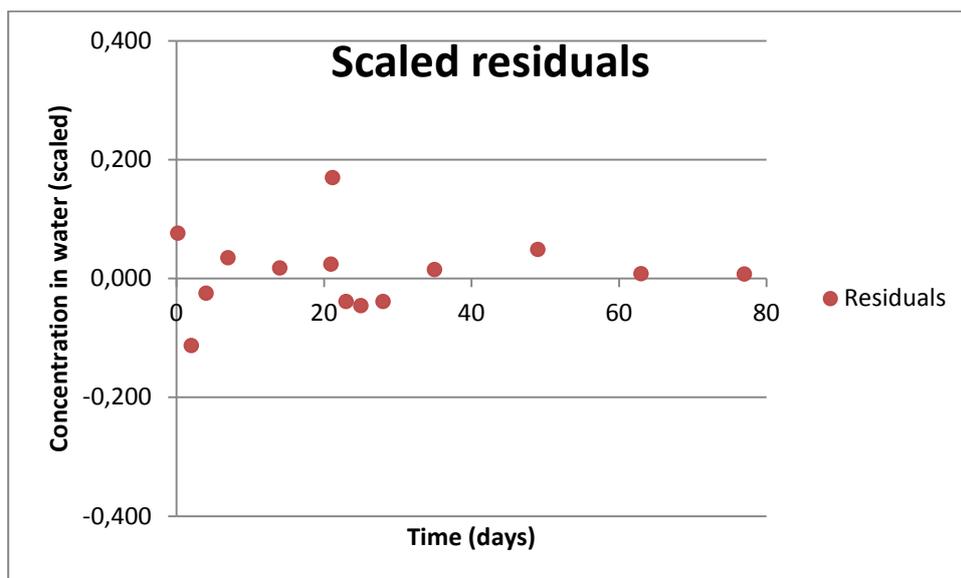


Figure 7.16 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for Pond 2 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $DegT_{50, ini} = 10$ d.

For the data of Pond 8, inverse modelling resulted in an estimate of for the $DegT_{50, water}$ of 5.2 days with relatively large 95% confidence intervals of 4.4 – 6.0 days. The error percentage of 11.4% is an acceptable value for field experiments, according to FOCUS (2006), so the optimisation passed the χ^2 -Test.

Figure 7.17 presents a satisfactory agreement between scaled optimised and measured water concentrations for one of the optimisations for Pond 8 (initial $DegT_{50}$ of 10 days), whilst Figure 7.18 presents the distribution of the scaled residual between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

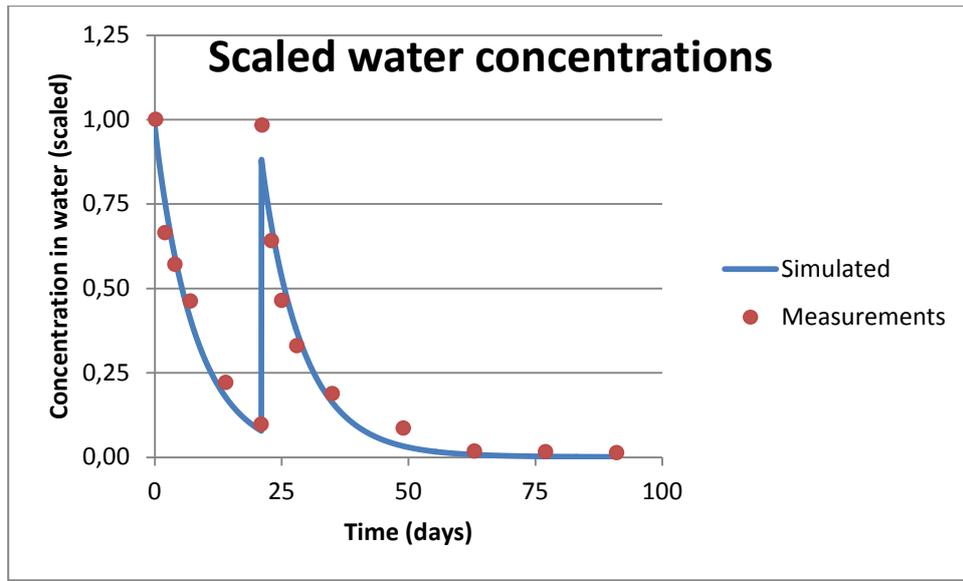


Figure 7.17 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for Pond 8 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $DegT_{50, ini} = 10$ d.

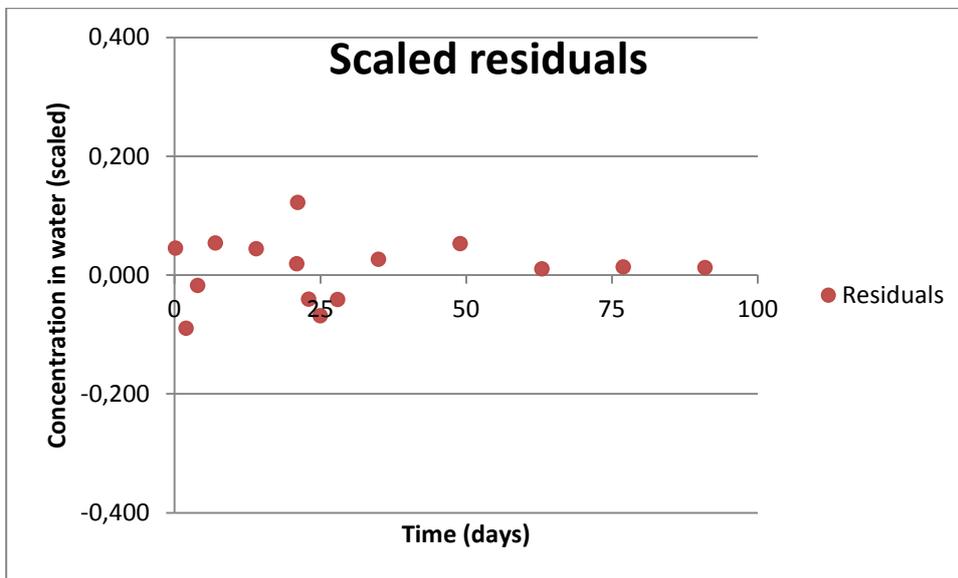


Figure 7.18 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for Pond 8 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50, ini} = 10$ d.

Overview

An overview of the results of inverse modelling, i.e. the obtained values for $\text{Deg}T_{50}$ in water and the initial concentration $c_{t=0}$, are given in Table 7.2.

Table 7.2

Estimates of $\text{Deg}T_{50}$ and c_0 plus their 95% confidence intervals for imidacloprid in water obtained by inverse modelling of the data sets.

Data set analysed		$\text{Deg}T_{50}$ at 20°C ^A (days)	$c_{t=0}$ (-)	Err%
Colombo <i>et al.</i> (2013)		1.01 (0.77 – 1.25)	0.866 (0.70 – 1.03)	19.5%
Heimbach and Hendel (2001)	Pond ^B	5.54 (4.0 – 7.1)	1.036 (0.90 – 1.17)	6.9%
	Tank	4.26 (3.0 – 5.5)	0.949 (0.85 – 1.06)	8.3%
Ratte and Memmert (2003)	Pond 2	5.57 (4.5 – 6.6)	0.916 (0.80 – 1.03)	13.1%
	Pond 7	5.45 (4.3 – 6.6)	0.926 (0.80 – 1.05)	14.4%
	Pond 8	5.22 (4.4 – 6.0)	0.981 (0.89 – 1.08)	11.4%
	Pond 13	5.29 (3.9 – 6.6)	0.923 (0.77 – 1.07)	19.5%

^A The $\text{Deg}T_{50}$ obtained from experimental data was corrected for temperature, resulting in a value at 20°C, using an Arrhenius type of equation, as explained in the text.

^B First measured concentration was omitted, because of insufficient mixing at time of first sampling.

The study of Colombo *et al.* (2013) resulted in a very short $\text{Deg}T_{50}$ in water for imidacloprid of 1.0 days (at 20°C), whereas the study by Heimbach and Hendel (2001) resulted in a geometric mean value of $\text{Deg}T_{50}$ in water at 20°C of 4.9 days. The study by Ratte and Memmert (2003) resulted in a geometric mean value of $\text{Deg}T_{50}$ for 4 ponds of 5.4 days.

Changing sediment properties resulted in negligible changes in the estimated values of $\text{Deg}T_{50, water}$.

Comparison with degradation rates taken from other sources

Table 7.3 gives some data found in several sources on dissipation in water as a result of hydrolysis, photolysis, microbial degradation etc.

Table 7.3

Dissipation half-life of imidacloprid.

Process	DT ₅₀ (days)	Source
Hydrolysis	DT ₅₀ > 1 year at pH 5 and 7; DT ₅₀ 1 year at pH 9 (25°C)	Annex IIa, point 7.2.1 (taken from Ctgb document on Kohinor 700 WG)
Hydrolysis	20.0 d (pH 10.8), 2.85 d (pH 11.8)	Zheng and Liu, 1999
Hydrolysis	Stable at acidic and neutral conditions, increased hydrolysis in alkaline solutions	Liu <i>et al.</i> , 2006
Photolysis	Very confusing results, not given in an understandable way; < 0.12 d in sterile artificial medium	Annex IIa, point 7.2.1 (taken from Ctgb document on Kohinor 700 WG)
Photolysis	Slightly over 3 h, pH 2.8	Banić <i>et al.</i> , 2014
Photolysis	5 – 18 min. (25°C)	Liu <i>et al.</i> , 2006
Photolysis	43 min. a.i., 126 min. formulated product Confidor (temperature not specified)	Wamhoff and Schneider (1999)
Water/sediment	DT ₅₀ water: > 30 d, 14.2 d, 109 d DT ₅₀ whole system: 129 d, 30 d, 150 d	Annex IIa, point 7.2.1 (taken from Ctgb document on Kohinor 700 WG)

The DT₅₀ values for hydrolysis, photolysis and dissipation in water/sediment systems given in the Footprint database (<http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>) were in agreement with the values given in Annex IIa, which are reproduced above. They indicate that hydrolysis is relatively unimportant at neutral pH, whereas photolysis in water proceeds relatively fast, if the compound is exposed to artificial (Xenon) light. Dissipation in water/sediment systems is intermediate, with DT₅₀ values for the whole system ranging from 30 – 150 days, and in water-only ranging from 14 – 109 days. The relatively short DT₅₀ values for photolysis indicate that in natural systems under sunlight, the overall dissipation may occur much faster than observed in water/sediment systems in the dark. Most likely, the overall dissipation in (outdoor) cosms is heavily influenced by the amount of sunlight, to which they are exposed.

For all three cosms studies for which a *DegT_{50, water}* was estimated, treatment with imidacloprid occurred in May, but the light intensities to which the systems were exposed may have been different. The differences in irradiation between the three cosm studies, in combination with the high sensitivity to photolysis of imidacloprid, may be adequate to explain to a large extent the range of estimated *DegT_{50, water}* of 1 – 5.5 d observed.

DegT50 values going from lower- to higher-tier data

For hydrolysis data, the longest DT₅₀ in the pH range of 7 – 9.5 was 1 year at 25°C. Assuming an Arrhenius activation energy of 75 kJ/mole, as proposed by Boesten *et al.* (2014), this corresponds to a DT₅₀ of 620 days at 20°C.

Aerobic water-sediment studies indicate a whole-system DT₅₀ of 30 – 150 days (geometric mean: 83 days) at 20°C.

The *DegT_{50, water}* estimated from cosm data was in the range of 1 – 5.5 days at 20°C. As imidacloprid is not a strongly sorbing compound, it is unlikely that water-sediment studies with a *DegT_{50, water}* of e.g. 5 d would result in whole-system DT₅₀ values of 30 – 150 days.

Hence, for the data considered going from lower- to higher-tier data does indeed result in less conservative estimates for the degradation rate.

8 Applicability of the estimation procedure

The estimation procedure assumes that once other dissipation processes, like sorption to sediment and evaporation, have been accounted for, the remaining decline of the aqueous concentration of the test substance should be due to degradation in the water phase. The three compounds, metribuzin, linuron and imidacloprid were chosen, because it was expected that degradation in the sediment will only play a minor part in the overall dissipation.

Moreover, the current approach is based on the assumption that the partitioning between water and sediment has no effect on the fitted $DegT_{50, water}$. This may, however, not be defensible if the fraction of the mass in the system in the sediment is comparatively large. The fit of the $DegT_{50, water}$ is commonly based on a decline of up to 90% of the initial concentration. Thus, it can be expected that the effects of sediment properties on the fitted $DegT_{50, water}$ is small if the total mass in the sediment is less than 10% of the added mass. If total mass in the sediment exceeds 10% of the mass added to the system, this may result in errors in the estimated value of the degradation rate in water, $DegT_{50, water}$.

Table 8.1 gives the maximum in time of the mass in sediment as a percentage of added mass for each of the systems analysed.

Table 8.1

Maximum concentration of test compound in sediment, given as a percentage of total mass added to the system.

Compound	Study	Organic matter of sediment reported in study (%)	Max percentage of total mass in sediment according to TOXSWA, calculated for an assumed organic matter percentage of 9% (%)
Metribuzin	Fairchild & Sappington (2002)	5.5	1.2
Metribuzin	Arts <i>et al.</i> (2006)	-	1.0
Metribuzin	Brock <i>et al.</i> (2004)	-	1.8
Linuron	Stephenson & Kane (1984)	-	8.1
Linuron	Van den Brink <i>et al.</i> (2006)	-	- [§]
Linuron	Bromilow <i>et al.</i> (2006)	4.3	32.4
Imidacloprid	Colombo <i>et al.</i> (2013)	3.0	- [§]
Imidacloprid	Heimbach & Hendel (2001) [#]	7.05	2.8
Imidacloprid	Ratte and Memmert (2003)	5.9	- [§]

[#] Pond data, first data point omitted.

[§] Calculations using loadings were not performed in the preparation of this table.

Linuron, having the highest K_{oc} of the three compounds tested, was expected to sorb to sediment more than metribuzin and imidacloprid. The maximum percentage penetrated into the sediment, as calculated by TOXSWA (Table 8.1) confirms this assumption. The highest percentage was found for linuron in the study reported by Bromilow *et al.* (2006). Figure 8.1 gives the mass distribution, as calculated with TOXSWA, for linuron in the systems described by Bromilow *et al.* (2006).

After 20 days, 27% of the initial mass was present in the sediment layer, and 57% in the water layer. Thereafter the linuron mass in sediment increased somewhat to a maximum of almost 33% of the initial mass after 74 days, when 27% was present in water. At the end of the study (152 days), 31% of the initial mass was present in the sediment layer and 14% in the water layer.

However, the simulation may have overestimated the importance of transfer of linuron to sediment. The calculations used the default FOCUS value for organic matter (9%), which is a factor of two higher than the actual organic matter content in the sediment of the Bromilow cosms (4.3%). Moreover, Bromilow *et al.* (2006) reported measured concentrations of linuron for the sediment, reproduced in Table 8.2 (taken from Table 5.10 in Appendix 5), which indicate that the maximum amount of linuron penetrated into the sediment remained below 10% of the total mass of linuron added to the system. Uncertainties in the values of K_{om} and porosity used in the TOXSWA calculations may also have contributed to the differences between the estimated and experimental concentrations in the sediment, and may have contributed to overestimation of the importance of the penetration of the sediment.

Table 8.2

Experimental concentrations in water (mg/L) and sediment (mg/kg; 0 – 5 cm layer) as a function of time (d) for the cosm study with linuron by Bromilow et al (2006). Concentrations are given as a percentage of total mass of Linuron added to the system.

Number	Time (days)	Concentration in water (mg/L)	Concentration in sediment (mg/kg)
Data as given in percentage of total mass added			
1	1	91.0%	2.1%
2	8	64.3%	6.9%
3	14	58.6%	8.6%
4	28	44.3%	7.3%
5	48	34.3%	7.3%
6	92	21.4%	8.6%
7	114	20%	4.4%
8	152	14.3%	4.6%

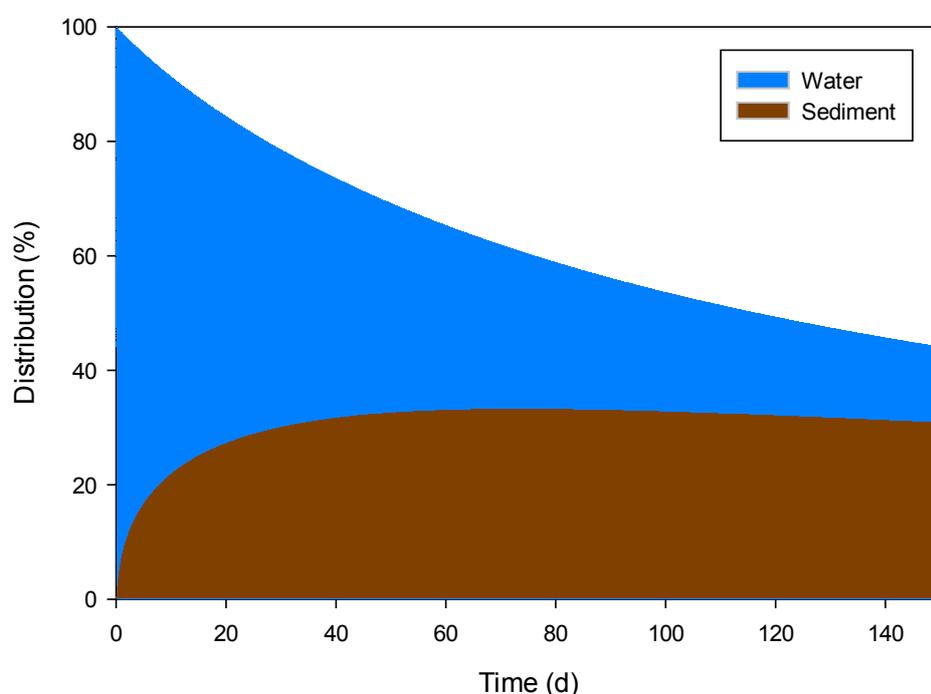


Figure 8.1 *Distribution of total mass of linuron remaining in the system as a function of time between water (dissolved + sorbed to suspended solids) and sediment (dissolved and sorbed to solid phase), as obtained with the fitted $DegT_{50} = 25.8$ d and initial mass of 1.03 mg/L for the cosm of Bromilow et al. (2006). Cumulative percentages are shown.*

Putting effort into estimating a rate constant (or $DegT_{50}$) for the degradation in water only makes sense if this process constitutes a major route of dissipation for the compound. It was expected that if dissipation through sorption into the sediment and through evaporation constitute more important routes than degradation in the water, the uncertainty in estimates of $DegT_{50, water}$ would increase and the estimated value will ultimately be of little value. The calculations performed using TOXSWA explicitly account for sorption to sediment and evaporation, and scrutiny of the detailed results generated by TOXSWA allows us to establish whether the compounds chosen for evaluation do indeed meet the expectation that degradation in water is more important for overall dissipation than the other two routes.

Figures 8.2 – 8.4 compare the contribution of the dissipation through degradation in water, partitioning into sediment and volatilisation for metribuzin, linuron and imidacloprid resp. for the mesocosms studies of Brock *et al.* (2004), Bromilow *et al.* (2006), and Heimbach and Hedel (2001).

For metribuzin, 99.4% of the initial mass is transformed in the simulated cosm study of Brock *et al.* (2004). Figure 9.2 shows that after 30 days 1% of the mass remained in water, with 0.6% of the mass remaining in sediment. Volatilisation of metribuzin was negligible.

For linuron, 50% of the initial linuron mass is transformed in the simulated cosm study of Bromilow (2006). Figure 9.3 shows that at the end of the study (152 days) 13.5% of the initial mass remained in the water layer. Volatilisation accounted for 5.1% of the initial mass at the end of the study. The contribution of sorption of linuron to sediment has been discussed in the previous section. Note that the sediment mass percentage decreases from day 74 onwards due to back diffusion from the sediment to the water layer.

For imidacloprid, 92% of the initial imidacloprid mass is transformed in the simulated cosm study of Heimbach and Hedel (2001). Figure 9.4 shows that at the end of the study 5.9% of the initial mass remained in water, whereas 2.1% remained in sediment. Volatilisation of imidacloprid was negligible.

For all three cosm studies, degradation in water was the major process with regard to dissipation from the water layer, indicating that a correct choice was made in using these three compounds for evaluation of the estimation procedure.

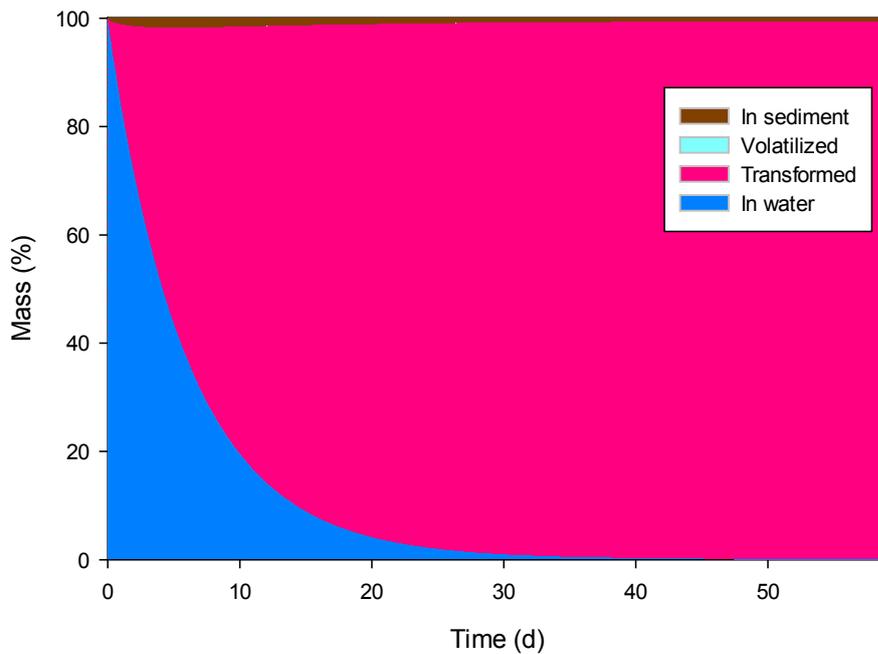


Figure 8.2 Mass balance of total mass of metribuzin as a function of time, given in percentage between remained in water (dissolved + sorbed to suspended solids), transformed, volatilised and remaining in sediment (dissolved and sorbed to solid phase), as obtained with the fitted $DegT_{50} = 3.11$ d and initial mass of 0.91 mg/L for the cosm of Brock et al. (2004). Cumulative percentages are shown.

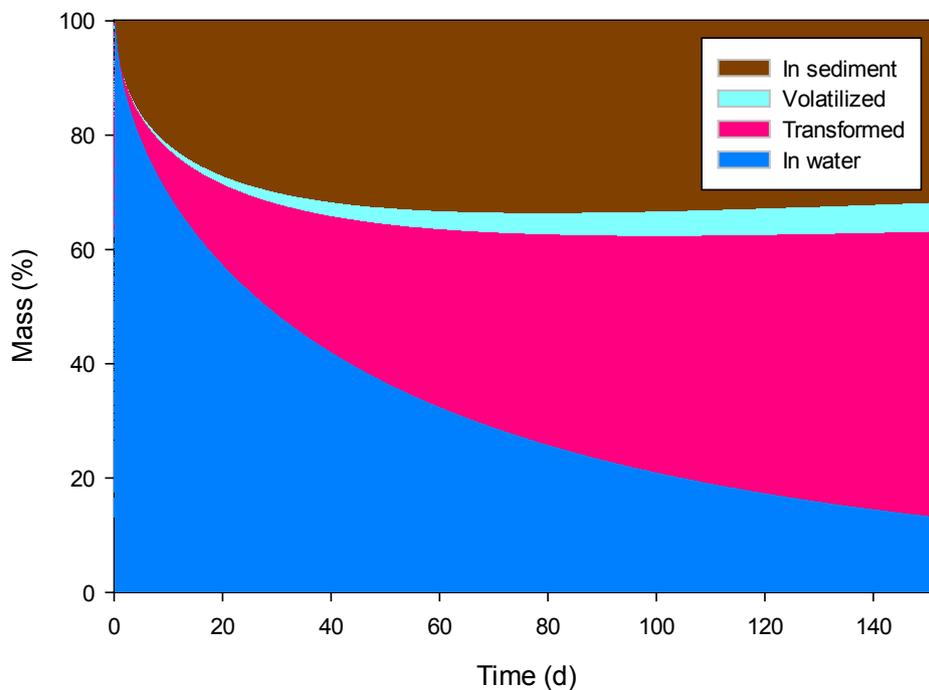


Figure 8.3 Mass balance of total mass of linuron as a function of time given in percentage between remained in water (dissolved + sorbed to suspended solids), transformed, volatilised and remaining in sediment (dissolved and sorbed to solid phase) as obtained with the fitted $DegT_{50} = 25.8$ d and initial mass of 1.03 mg/L for the cosm of Bromilow et al. (2006). Cumulative percentages are shown.

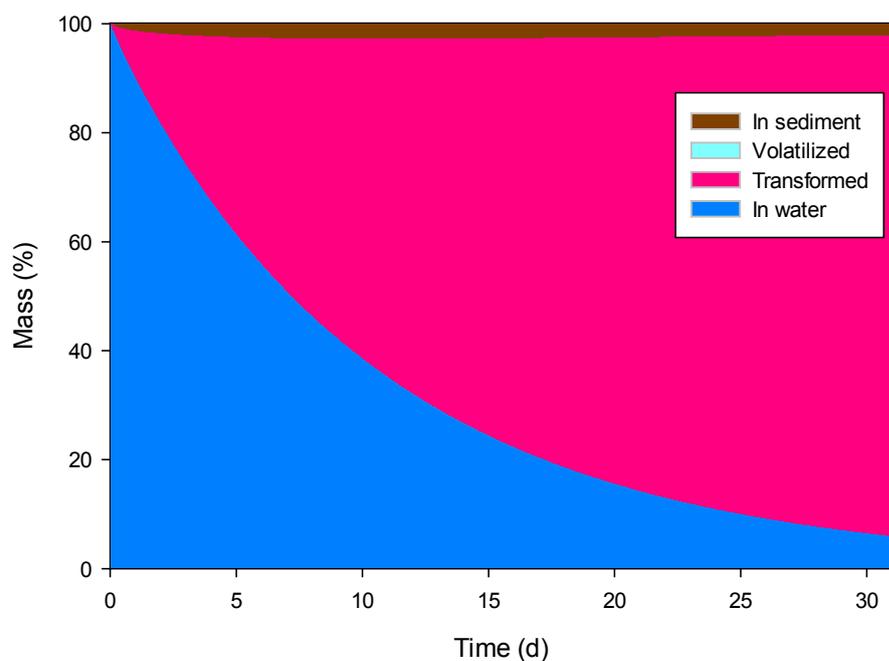


Figure 8.4 Mass balance of total mass of imidacloprid as a function of time given in percentage between remained in water (dissolved + sorbed to suspended solids), transformed, volatilised and remaining in sediment (dissolved and sorbed to solid phase) as obtained with the fitted $DegT_{50} = 5.54$ d and initial mass of 1.036 mg/L for the cosm of Heimbach and Hedel (2001). Cumulative percentages are shown.

The compounds (and experiments) used in this report were selected on the basis of the following considerations:

-
- Availability of sufficiently detailed experimental data;
- Compounds prone to dissociation or protonation at realistic pH values (4 – 10) were excluded;
- Compounds with high tendency to penetrate the sediment were excluded;
- Appreciable degradation of the compound occurs within the duration of the test.

How the estimation procedure deals with data sets that do not meet one or more of these criteria has yet to be established.

9 Automating the optimisation procedure, a 'cook book'

Guidance proposal for estimation of $DegT_{50, water}$ from outdoor mesocosm studies

This guidance can only be used if the data set fulfils the following criteria:

- # concentrations in the water layer are available for at least five sampling times.
- # the depth of the water layer is reported.

If these criteria are fulfilled, the software as described at the end of this section can be used to perform the fit of TOXSWA using PEST. For that purpose three files have to be changed:

```
cosm.met
input_TOXSWA_PEST.txt
TOXSWA_cha.txt.
```

See below for further instructions.

This guidance can be used also if no information is available of the properties of the sediment. The TOXSWA_cha.txt file requires specification of the properties of the sediment as follows:

	Nr	Rho	CntOm	ThetaSat	CofDifRel
165					
166		(kg.m-3)	(kg.kg-1)	(m3.m-3)	(-)
167	1	800.	0.05	0.68	0.57
168	2	800.	0.05	0.68	0.57
169	3	800.	0.05	0.68	0.57
170	4	800.	0.05	0.68	0.57
171	5	800.	0.05	0.68	0.57
172	6	800.	0.05	0.68	0.57

The six lines are for six sediment layers with different thicknesses of the numerical compartments; the thickness of the sediment is 10 cm (the sum of the thicknesses of the six sediment layers); Rho is ρ_{sed} (Equation 4.1), CtnOm is f_{om} (Equation 4.1), ThetaSat is ϵ (Equation 4.1) and CofDifRel is λ (Equation 4.2).

If the organic matter content is not reported, the values shown above are recommended. The f_{om} of 5% is approximately the average of all reported values of the studies in this report. The dry bulk density ρ_{sed} of 800 kg/m³ is based on the default of FOCUS (2001). The porosity $\epsilon = 0.68$ was calculated from f_{om} and ρ_{sed} with Equation 4.1 and the $\lambda = 0.57$ was calculated with Equation 4.2.

If the organic matter content of the sediment is reported, it is recommended to use the measured organic matter content in combination with $\rho_{sed} = 800$ kg/m³. The porosity ϵ and the tortuosity λ then must be calculated with Equations 4.1 and 4.2, respectively.

If concentrations of different studies are combined in one fit by scaling, the consequence is that TOXSWA assumes that the initial concentration in the water is 1 mg/L (whereas it was in reality e.g. 10 µg/L, so 0.01 mg/L). The Freundlich isotherm equation assumes that the K_{om} is specified for a reference concentration of 1 mg/L. Thus, scaling of concentrations may lead to use of the wrong K_{om} . It is recommended to overcome this problem as follows: calculate the geometric mean of the initial concentrations of the different studies, giving $C_{0, geo}$ (mg/L); modify then the K_{om} in the TOXSWA_cha.txt file using:

$$K_{om, new} = K_{om, org} \left(\frac{C_{ref}}{C_{0, geo}} \right)^{1-N} \tag{9.1}$$

where $K_{om,new}$ is the modified K_{om} , $K_{om,org}$ is the original K_{om} , C_{ref} is the reference concentration of 1 mg/L, and N is the Freundlich exponent (-).

If using scaled concentrations, the user should scale loadings (for systems with multiple applications) by dividing the loadings (given in mg/m²) by the same number that was used for scaling concentrations, i.e. divide by the highest aqueous concentration in the system (in mg/L).

The quality of the fit must be checked as follows (based on FOCUS, 2006):

- # compare visually the time course of the measured and fitted concentrations.
- # compare visually the time course of the residuals (i.e., the differences between the measured and fitted concentrations).
- # check whether the χ^2 error is not higher than 15% (higher values than 15% are only acceptable after considering the visual comparison with special intention).
- # check whether the maximum percentage in the sediment is less than 10% (higher values than 10% indicate a strong effect of the sediment on the fitted $DegT_{50,water}$, which is difficult to defend if no measurements of the amount in the sediment are available).

Reporting of the results must include:

- # the two graphs of the time courses of the measured and fitted concentrations and of the residuals.
- # the χ^2 error.
- # the maximum percentage in the sediment in the simulations (together with the measured maximum percentage in the sediment in case the amounts in the sediment were also measured).
- # the estimated initial concentration and $DegT_{50,water}$, together with their 95% confidence intervals.
- # the files input_TOXSWA_PEST.txt, TOXSWA_cha.txt and TOXSWA_PEST_output.txt.

An automated procedure was devised for deriving optimised values for $DegT_{50,water}$ from experimental data taken from mesocosms. The procedure uses PEST and TOXSWA in combination with a set of batch (MS-DOS command) files. The estimation suite of programs requires the user to adapt some of the input files to the experimental data set at hand, using a simple text editor. A full description and user guide of the procedure are given in Appendix 7.

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FOCUS, 2006.

Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. Report of the FOCUS Workgroup on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 434 pp.

10 Conclusions and Recommendations

Plausible results were obtained for all cosm studies selected for estimation of $DegT_{50, water}$ using the designed procedure. Using scaled concentrations enabled the simultaneous analysis of data sets obtained at different treatment levels within the same experiment, provided that preliminary analysis of dissipation data indicated that dissipation, and hence degradation, was not strongly dependent upon treatment level.

Exempt from this were experiments, in which more than a single application of the test compound occurred over the duration of the experiment, which is a shortcoming of the analysis method due to the technical requirements posed by TOXSWA input files. Nevertheless, the data from such experiments could be readily analysed using the devised procedure, although each of the treated systems had to be analysed separately.

A possible improvement for experiments with more than a single application is to not only estimate $C_{t=0}$, i.e. the concentration resulting from the first application, but to treat all applications similarly. At present, the estimation procedure includes variation/estimation of the concentration due to the first application. However, the concentration increases of subsequent applications are calculated by the user and are held constant over the course of estimation of $DegT_{50, water}$. Since the uncertainty in the first and subsequent applications is expected to be similar, it is probably better to treat all applications in a similar fashion. This is, however, not yet part of the current estimation procedure.

If a linear regression on the measured concentrations in water had been simply performed, a true degradation rate, $DegT_{50, water}$, would not have been obtained, but instead, a disappearance rate, $DT_{50, water}$. By using the TOXSWA model, all relevant processes leading to disappearance of the compound from the water layer, i.e. sorption to sediment and volatilisation, are explicitly modelled. Therefore, the estimation procedure described in this report results in a true degradation rate in water.

Most of the results confirm the rationale given by Boesten *et al.* (2014) that going from simple to more complex studies should result in more realistic results, giving less conservative estimates of degradation rates. The only notable exception to this 'rule' was the relatively high $DegT_{50, water}$ observed for linuron in the experiment in indoor cosms described by Van den Brink *et al.* (2006), in which the estimated $DegT_{50, water}$ was slightly higher, i.e. more conservative, than resulted from a lower tier water/sediment study. Thus, the estimated degradation rate constants for outdoor mesocosm are typically less conservative than degradation rates estimated from lower tier data such as hydrolysis and water-sediment studies

In this report, a procedure was developed to estimate the $DegT_{50, water}$ on the basis of measured concentrations in only the water layer of cosm studies. It is strongly recommended to extend the procedure to compounds for which sorption to sediment is more important, using cosm studies in which concentrations in the sediment are also measured. Chlorpyrifos and lambda-cyhalothrin were identified as examples of compounds, for which sufficient suitable cosm studies are available (Chapter 3). For these substances, the procedure will involve a simultaneous optimisation of the correspondence between measured and simulated concentrations in both the water layer and the sediment, and possibly weighting concentrations in water layer and sediment differently, so the procedure will become more complex than the one developed in this study.

In this report, each study was analysed separately, and each study yielded its own estimate of a degradation rate. In some cases, one study yielded several degradation rates, because it was not possible to combine all (scaled) concentration profiles into a single optimisation run, e.g. because systems in the study behaved differently, or had different properties, such as water depth. It is recommended to develop guidance on how a single $DegT_{50, water}$ value can be derived from the various higher-tier degradation rates, found in the cosm studies. This is required as input in surface water scenarios calculations for the aquatic risk assessment in the registration procedure. Boesten *et al.* (2014) propose some initial guidance on how to derive such a single $DegT_{50, water}$ value, e.g. by

distinguishing between compounds that are liable to photo-induced degradation and those where microbial or pH-induced degradation are predominant. For compounds with photo-induced degradation, they have proposed to standardise $DegT_{50, water}$ values obtained from different outdoor cosm studies by calculating them back to a reference global radiation value, comparable to what is done for degradation in soil from field studies with respect to pH and temperature. It is recommended to include this initial guidance in the development of further guidance.

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Annex 1 Example calculation of the minimum error-% at which the χ^2 -test is passed.

1	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Metribuzin Fairchild&Sappington		DegT50,water,fitted = 4.016 d	c0,fitted = 75.065				C-O	(C-O)2		ERR		
2	Time (d)	Observed (ug/L)	Simulated										
3	0	73.8	74.748					0.948	0.898704				
4	1	60.4	63.6314					3.2314	10.44195				
5	2	59.7	54.2881					-5.4119	29.28866				
6	6	25.5	28.8723					3.3723	11.37241				
7	14	3.65	8.2374					4.5874	21.04424				
8													
9	O_ave	44.61							73.04596		6.853326	so, 6.9%	
10	O^2_ave	1990.0521											
11													
12	m = 5-2 = 3												
13													
14	chi^2 tabulated (0.05,3) = 7.815		7.815										
15													
16													
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18													
19													
20													
21													
22													
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25													

Annex 2 Protocol for selecting pesticide properties from the Footprint database (also published by Teklu *et al*, 2014)

For the following pesticide properties in soil and surface water models choices need to be made between the different types of properties in the Footprint database:
(<http://sitem.herts.ac.uk/aeru/ppdb/en/>)

Property in models	Choices in Footprint	
DT50soil	DT50 typical	'Typical values' quoted are those given in the general literature and are often a mean of all studies field and laboratory. This is the value normally used in the regulatory modelling studies and is for aerobic conditions.
	DT50 lab at 20°C	DegT50 values of plant protection products in soil at 20°C obtained from laboratory studies
	DT50 field	DegT50 values of plant protection products in soil obtained from field dissipation studies
Koc	Koc	The linear adsorption coefficient normalised to the organic carbon content of the soil.
	Kfoc	The Freundlich adsorption coefficient normalised to the organic carbon content of the soil.
1/n or N	Freundlich exponent	Freundlich exponent describing the curvature of the Freundlich isotherm.
DT50water	Aqueous hydrolysis pH 5	DT50water for the process of hydrolysis obtained from an aqueous hydrolysis study at pH 5
	Aqueous hydrolysis pH 7	DT50water for the process of hydrolysis obtained from an aqueous hydrolysis study at pH 7
	Aqueous hydrolysis pH 9	DT50water for the process of hydrolysis obtained from an aqueous hydrolysis study at pH 9
	Aqueous photolysis	DT50water for the process of photolysis obtained from an aqueous photolysis study
	Water-sediment DT50	The DT50 of the total water-sediment system obtained from a water-sediment study in the dark (so including processes transformation in water and sediment due to hydrolysis and microbial degradation).

Chosen property from the Footprint database and justification of this choice

Property in models	Chosen property from Footprint	Justification
DT50soil	DT50 lab at 20°C	<p>DT50field values are very likely not determined according the latest EFSA guidance (EFSA, 2010) and therefore not adequate. This EFSA guidance proposes a procedure that ensures that the DegT50 derived from field dissipation studies reflects the degradation rate within in the soil matrix between 1 – 30 cm depth with sufficient accuracy. This procedure aims at diminishing the influence of other loss processes like volatilisation, photochemical degradation runoff etc. which are significant processes in the top millimetres of the soil matrix. Therefore the estimated DegT50 should not be influenced by these loss processes. This can be reached by a proper design of the field study: i.e. by applying irrigation shortly after pesticide application (EFSA advises 10 mm) or by using the proposed method for kinetic evaluation of the field dissipation study for determining the DegT50field. Most field dissipation studies in the dossiers used for the Footprint database are performed before the outcome of the EFSA opinion and it is not very likely that the kinetic evaluations are done according the method advised by EFSA (2010). For the same reason the DT50 typical is not suitable as this is often a mean of all studies both field and laboratory, so based upon inaccurate DegT50field values.</p> <p>EFSA Panel on Plant Protection Products; Guidance for evaluating laboratory and field dissipation studies to obtain DegT50 values of plant protection products in soil. EFSA Journal 2010;8(12):1936 [67 pp.]. doi:10.2903/j.efsa.2010.1936</p>

Koc KOC

KOC is very likely the most reliable parameter. Below an explanation is given why we consider K_{f,oc} data from the Footprint database to be less reliable.

Problems with the use of K_{f,oc} data

The definition of the K_{oc} is based on a linear sorption isotherm:

$$X = m_{oc} K_{oc} C \quad (1)$$

Where X is mass of pesticide sorbed per mass of dry soil (mg kg⁻¹), m_{oc} is mass fraction of organic carbon of the soil (kg kg⁻¹), K_{oc} is the organic-carbon/water distribution coefficient (L kg⁻¹) and C is the mass concentration in the liquid phase (mg L⁻¹).

The definition of the K_{f,oc} is based on the Freundlich isotherm:

$$X = m_{oc} K_{F,oc} C^N \quad (2)$$

Where K_{f,oc} is the Freundlich coefficient for distribution over organic carbon and water (L^N kg⁻¹ mg^{1-N}) and N is the Freundlich exponent (-).

So whereas the unit of K_{oc} depends only on the unit used for the mass of dry soil (kg) and the volume of liquid (L), the unit of K_{f,oc} is also a function of the unit used for the mass of pesticide (mg) and also of N. This has the consequence that the value of K_{f,oc} depends on the unit used for the mass of pesticide. E.g. the K_{f,oc} value obtained by fitting of data with X expressed in mg kg⁻¹ and C expressed in mg L⁻¹ will differ from the K_{f,oc} value obtained by fitting of the same data with X expressed in µg kg⁻¹ and C expressed in µg L⁻¹. Let us consider the following example to illustrate this.

C (mg L ⁻¹)	X (mg kg ⁻¹)
0.001	0.0020
0.01	0.0158
0.1	0.1259
1	1
10	7.4943

These numbers are calculated with Equation 2 using m_{oc} = 0.01, K_{f,oc} = 100 and N = 0.9. So if these values would be fitted back to Equation 1, a K_{oc} value of 100 would have been obtained. Let us now consider a researcher that expresses the same data in µg instead of mg.

C ($\mu\text{g L}^{-1}$)	X ($\mu\text{g kg}^{-1}$)
1	2.0
10	15.8
100	125.9
1000	1000.0
10000	7494.3

Fitting these data to Equation 2 will give a $K_{F,oc}$ value of 200 instead of 100. This can be easily checked by putting the concentrations of the second table in a spreadsheet and calculating X with Equation 2 (using $K_{F,oc} = 199.526$ to get exactly the same result).

Sometimes researchers use also mmol instead of mg (1 mmol is usually about 200 mg). So if a $K_{F,oc}$ value is provided, it is necessary to know in which unit the mass of pesticide is expressed. However, this is not done in the Footprint database. (pers.comm. J.J.T.I. Boesten, WUR)

1/n or N	Freundlich exponent between 0.6 and 1.0	If the average of $1/n > 1$ use a value of 1.0 (see page 28/29 of Boesten <i>et al.</i> , 2011) <i>Boesten, J.J.T.I. , Linden, A.M.A. van der , Beltman, W.H.J. , Pol, J.W. 2011. Leaching of plant protection products and their transformation products : proposals for improving the assessment of leaching to groundwater in the Netherlands. Wageningen : Alterra, 2011 (Alterra-rapport 2264)</i> In case of absence of reliable data use a default value of 0.9. We consider data unreliable if $1/n < 0.6$ (pers. Comm. J.J.T.I. Boesten, WUR) or if $1/n$ is determined using a Kfoc study which is judged less reliable by the Footprint database itself.
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DT50water	Aqueous hydrolysis pH 7 Aqueous hydrolysis pH 9	Estimate the longest DegT50 in the pH range from 7 to 9.5 from the available measurements of hydrolysis experiments and calculate this back to a temperature of 20°C using Eqn. 3 and using the temperature dependencies as measured in the hydrolysis studies to retrieve a value for the Arrhenius activation energy. If these temperature dependencies were not measured, it is recommended to assume an Arrhenius activation energy of 75 kJ/mol (Deneer <i>et al.</i> , 2010). $k(T) = k(T_{ref}) \exp \left[\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]$ (3) where:
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T =	Temperature (K)
Tref =	Reference temperature (K)
k =	Transformation rate (d-1)
E =	Molar Arrhenius activation energy (J mol-1)
R =	Universal gas constant (≈ 8.3144 J mol-1 K-1)

Deneer, J.W., W.H.J. Beltman, P.I. Adriaanse. 2010. Transformation reactions in TOXSWA; transformation reactions of plant protection products in surface water. Wageningen, Alterra. Alterra-report 2074. 94 pp.

Annex 3 Detailed information on studies found in Scopus on some compounds considered suitable for degradation studies in the water phase of cosms

Asulam

Two suitable studies were found, either describing original experimental work or summarizing older work by other authors in a review like manner (see end of section for a list of references).

In the first study (van Wijngaarden *et al.*, 2004) asulam was applied three times to a number of indoor microcosm systems with a water volume of approx. 600 L, containing a 10 cm sediment layer and a 50 cm water layer. Metamitron was applied at 4 different levels, at initial concentrations of 0.63 – 14.7 µg/L and its aqueous concentration was followed in the lowest and highest levels of application. Aqueous concentrations of metamitron are given (in a graph) at 15 different times after its first application over a 56 day time period. Concentrations in sediment are not reported (the paper does not mention measuring concentrations in sediment, nor is the organic matter content of the sediment mentioned). Cover by macrophytes was reported. Data on pH, temperature and dissolved oxygen were measured extensively, and ranges of these parameters as measured over the course of the experiment are provided in the paper.

The second paper (Wendt-Rasch *et al.*, 2004) gives fate data for asulam in outdoor microcosms (concrete tanks containing approx. 500 L of water and a sediment layer). Only the data for the highest (of 4) treatment levels are given (in a graph), at 9 times after treatment (3 times after each of the 3 treatments). Aqueous concentrations are given both for cosms dominated by submerged macrophytes and cosms with a high Lemna coverage, separately. No data on measured concentrations of asulam in sediments is provided, nor are data on the organic carbon content of the sediment given (two different types of sediment were used for the two types of microcosms). Some data on the coverage of the water surface or the proportion of bottom covered with macrophytes is given. Extensive data on temperature, dissolved oxygen and pH of the water are provided.

Catastini, C., M. Sarakha, G. Mailhot (2002).

Asulam in aqueous solutions: fate and removal under solar radiation. *International Journal of Environmental Analytical Chemistry* 82, 591 – 600.

Van Wijngaarden, R.P.A., J.G.M. Cuppen, G.H.P. Arts, S.J.H. Crum, M.W. Van den Hoorn, P.J. Van den Brink, T.C.M. Brock (2004).

Aquatic risk assessment of a realistic exposure to pesticides used in bulb crops: a microcosm study. *Environ. Toxicol. Chem.* 23, 1479 – 1498.

Wendt – Rasch, L., P.J. Van den Brink, S.J.H. Crum, P. Woin (2004).

The effects of a pesticide mixture on aquatic ecosystems differing in trophic status: responses of the macrophyte *Myriophyllum spicatum* and the periphytic algal community. *Ecotoxicol. Environ. Saf.* 57, 383 – 398.

Azoxystrobin

Only a single study (Zafar *et al.*, 2012) reported sufficiently detailed data on the fate of azoxystrobin in a mesocosm study to be of use for the current purpose. Two separate experiments are described, one dealing with a single application of azoxystrobin resulting in an initial concentration of 33 µg/L a.i./L (14 measurements of aqueous concentrations over 42 days), and the other dealing with a four application treatment, each achieving a 16 µg a.i./L with a 10-day interval (25 measurements of

aqueous concentrations over 42 days). Systems contained approx. 1270 L of water (water depth: 0.5 m; diameter: 1.8 m; total depth of the system: 0.8 m; depth of sediment layer: 8 cm; no measurements of azoxystrobin in sediment are described, nor is the organic matter content of the sediment given; detailed description given of the presence of macrophytes; pH, temperature and oxygen content of aqueous phase monitored 6 times after application).

References particular to azoxystrobin

Beketov, M.A., M. Liess (2008).

Potential of 11 pesticides to initiate downstream drift of stream macroinvertebrates. *Arch. Environ. Contam. Toxicol.* 55, 247 – 253.

Bony, S., C. Gillet, A. Bouchez, C. Margoum, A. Devaux (2008).

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Chlorothalonil

Two suitable studies were found, either describing original experimental work or summarizing older work by other authors in a review like manner (see end of section for a list of references).

Arts *et al.* (2006) reported sufficiently detailed data on the fate of chlorothalonil in a mesocosm study to be of possible use for the current purpose. Treatment consisted of four applications with a 1 week interval, at 3 different nominal initial levels (0.96, 4.8 and 24 µg a.i./L). The paper contains sufficient details to warrant numerical analysis of chlorothalonil concentrations. After each application aqueous concentration was measured 5 times before the next application, although measurements after the first application seem to have partly failed. No measurements of chlorothalonil in sediments are reported, nor is the organic matter content of the sediment given.

Kwon *et al.* (2006) describe measurements of the dissipation of chlorothalonil in small water/sediment systems (1.2 cm layer of sediment topped by a 6.4 cm layer of water; two types of sediment with 0.16% and 0.65% organic matter resp.). Concentrations of chlorothalonil both in water and in sediment were measured 7 times after the start of the exposure. Measurements were performed both in dark and in light. Although the dimensions of the systems differ considerably from a 'typical' cosm study, the detail of the concentration measurements makes this paper a possible candidate for analysis of chlorothalonil dissipation in water, especially since concentrations of the most probable main metabolite (4-hydroxy-chlorothalonil) are also reported.

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Chlorpyrifos

A rather large number of studies dealing with mesocosms were found. However, many papers give insufficient details on the analysis of chlorpyrifos in water or studies where no or hardly any chemical analyses have been performed. However, several papers gave sufficiently detailed information for the analysis of degradation in the aqueous compartment of cosms.

Brock *et al.* (1992) describe the fate of chlorpyrifos in indoor cosms containing approx. 50 cm (600 L) water and 10 cm sediment, at two different initial concentrations (5 and 35 µg/L). The authors give details on measured concentrations in water and sediment (2.8% organic matter) at 6 times after application. The results of this experiment have also been described and analysed by van der Kolk and Crum (1993).

Bromilow *et al.* (2006) describe the fate of chlorpyrifos in two different experiments using various different initial concentrations (10, 100 and 250 µg/L). Concentrations measured in water and sediment (2.5% organic carbon) are reported. However, in both experiments the combined measurements in water and sediment one day after addition of chlorpyrifos accounted only for slightly more than half of the added amount of the test substance. In the experiment with intended initial concentrations of 10 and 100 µg/L only 44 – 55% of the chlorpyrifos added was accounted for, whereas in the experiment with an intended initial concentration of 250 µg/L only 61% of the added chlorpyrifos was accounted for. The reason for these low results are not given, and the relatively percentage of mass unaccounted for may hamper adequate analysis of the fate data.

Giddings *et al.* (1997) report a rather detailed set of measurements in water and sediment after simulated spray drift applications resulting in nominal initial concentrations of 0.03 – 3 µg/L (on average 89% of nominal concentrations were found 2 h after application). Fiberglass tanks contained 1.4 m water (11200 L) and approx. 10 cm sediment (1.8 – 3.2% organic content). In the 2 highest application levels 8 (1.0 µg/L) or 9 (3 µg/L) measurements in the aqueous layer and 5 measurements in the sediment were reported. During the course of the study submerged macrophytes developed in the sediment-covered portion of each microcosm.

Hughes *et al.* (1980) describe the concentrations of chlorpyrifos in a single natural and a number of artificial ponds. The strong sorption of chlorpyrifos to polyethylene coating of the artificial systems may have influenced the aqueous concentrations of the pesticide and the results from these artificial systems are therefore considered less reliable. The natural woodland pond was treated with 10 µg/L of chlorpyrifos, and the results of nine measurements of aqueous and sediment concentrations are reported. Organic matter content of the sediment is not given. Dimensions of the natural pond are not explicitly given. Concentrations measured over the first 100 minutes after application of chlorpyrifos indicate inhomogeneous mixing of the water layer. For these reasons this study is considered less suitable for analysis through inverse modelling.

Kale *et al.* (1999) report the fate of radiolabelled (¹⁴C) chlorpyrifos added at an initial concentration of 50 µg/L to a glass water tank containing 20 L sea water and 4 kg of sediment (organic carbon <

0.4%). Samples of water, sediments, clams and algae were collected at 0, 2, 5, 24, 74 h and 12, 15, 30 and 60 days after application of chlorpyrifos. Although the data set is very detailed, the use of radiolabelled material does not allow to distinguish between parent material and degradation products and therefore the data set generated in this study seems less suitable for analysis of the fate of the parent compound in itself.

Knuth and Heinis describe in detail degradation studies of chlorpyrifos in littoral enclosures at initial concentrations of 0.5 – 20 µg/L, reporting 7 – 9 measurements of aqueous concentrations (and 8 measurements of concentrations in sediments, also somewhat describing a depth-differentiation of concentrations within the sediment, which contained 11.6% organic carbon). The enclosures were 5 x 10 m² and had a water depth of 0.6 m. The sediment contained relatively high amounts of organics (). The authors concluded that the slowness of vertical mixing of chlorpyrifos in the water column may have consequences for the concentrations measured in time (the water samples in this paper were taken at mid-depth of the water column, i.e. did not consist of depth-integrated samples).). Concentrations are given in a graph with logarithmic y-axis, and from a detailed analysis of chlorpyrifos concentrations at several depths in the aqueous layer it is concluded that mixing is not complete within the first two hours after application. This study is not used in the inverse modelling because there are large uncertainties in the aqueous concentrations read from logarithmic graphs.

Lopez – Mancisidor *et al.* (2008) describe a study on tanks filled with approx. 6000 L water, containing stainless steel trays filled with sediment (total volume 216 L per tank, organic matter content not given). Chlorpyrifos was applied four times with weekly intervals at nominal concentrations of 0.033, 0.1, 0.33 and 1 µg a.i./L. After the first application concentrations of chlorpyrifos were measured 5 times, after each later application three measurements were performed.

Macalady and Wolfe (1985) describe a study into the sorption and hydrolysis of chlorpyrifos in small water/sediment systems consisting of a few grams of sediment (three types of sediment were used, with 0.48, 1.48 and 2.38% organic carbon) and 25 ml sterile water containing pesticide. Concentrations in sediment and water were determined at 9 times after the addition of pesticide, enabling the calculation of sorption constants and overall (water + sediment) remaining amounts of chlorpyrifos as a function of time. However, after application of chlorpyrifos the systems were continuously shaken and the interaction between the aqueous and sediment phases therefore differed from what would typically occur in a cosm or water/sediment system.

Mazanti *et al.* (2003) describe studies in indoor aquaria (containing no sediment) and outdoor cosms. Ponds were treated with initial concentrations of chlorpyrifos of 0.1 mg/L. Concentrations in sediment were not measured, nor is the organic matter content of sediment given, but the aqueous concentrations of chlorpyrifos were measured at several times after application (5 – 7 times within the first 10 days). Measured concentrations (average values over 4 different ponds) are given in tabular form.

Reimer and Webster (1980) describe a study of loss of chlorpyrifos in pond water. Information on the organic matter content of the sediment is not given. The extraction efficiency of chlorpyrifos (57 ± 3%) makes this study less reliable.

Van Donk *et al.* (1995) investigated the influence of nutrient loading on the effects of chlorpyrifos in cosm experiments. Indoor microcosms contained approx. 385 L water (water depth 50 cm) on top of 10 cm sediment (3% organic matter content). Initial nominal concentrations of chlorpyrifos were 35 µg/L. Eight measurements of aqueous concentrations over the first 100 h after application are reported. Concentrations in sediments were not measured.

Van Wijngaarden (1993) describes and compares the dynamics of chlorpyrifos in three different types of systems (microcosms, approx. 400 L water, water depth 0.5 m, 0.1 cm sediment; artificial ponds, 8000 L water, water depth 0.5 m; experimental ditches, 55000 L water, water depth 0.5 m). Systems were treated with a single doses corresponding to 5 or 35 µg/L, 3 or 30 µg/L and 0.1, 0.7, 5 or 35

µg/L resp. Aqueous concentrations were determined and are given for one of each of the different types of systems in the form of a graph. Organic matter content of the sediments in the various types of systems are not given.

Zafar *et al.*, 2012 reported sufficiently detailed data on the fate of chlorpyrifos in a mesocosm study to be of use for the current purpose. Three separate experiments are described, one dealing with a single application of chlorpyrifos resulting in an initial concentration of 0.9 µg/L a.i./L (8 measurements of aqueous concentrations over 21 days), one dealing with a semi-continuous exposure at 0.1 µg a.i./L, and the other dealing with a three application treatment with a 7-day interval, each resulting in a nominal increase of 0.3 µg a.i./L (19 measurements of aqueous concentrations over 21 days). Systems contained approx. 1270 L of water (water depth: 0.5 m; diameter: 1.8 m; total depth of the system: 0.8 m; depth of sediment layer: 8 cm; no measurements of chlorpyrifos in sediment are described, nor is the organic matter content of the sediment given; detailed description given of the presence of macrophytes; pH, temperature and oxygen content of aqueous phase).

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Imidacloprid

Colombo *et al.* (2013) report the results of experiments in small (20 L water) enclosures located at Berlin, Germany, and containing sediment, where macrozoobenthos was exposed to imidacloprid. The exposure was implemented as three pulses with weekly intervals, with nominal concentrations ranging from 0.6 to 40 µg/L. Applications occurred from late May – June (year not given, probably 2012). Although exposure concentrations were measured in all of the cosms, the fate of imidacloprid was studied in more detail in cosms with the nominal concentration of 17.3 µg/L, resulting in 6 measured concentrations in water after each of the application. The concentration in sediment (3% OM) was only measured on day 56, at the end of the experiment. The authors report the results of detailed analysis of the dissipation rate of imidacloprid in these cosms after each of the pulses.

Daam *et al.* describe the dissipation of imidacloprid from water after application in a rice plot, at an initial concentration (peak) concentration of 52 µg/L. A total of 6 measurements were performed in the water phase after application, but 3 of 6 measurements are indistinguishable from zero and are hence not very useful. Measurements in sediment (OC = 1.55%) were performed at 4 occasions after application, but the outcome of measurements is not reported in the paper.

The report of the study by Heimbach and Hendel (2001) was kindly provided by Bayer CropScience. The report describes results of simultaneous experiments in a small pond (diameter 2.0 m, water depth 1.0 m) and a small rectangular tank (0.6 x 1.8 m, water depth 0.3 m), both located at Monheim, Germany. The exposure for both systems consisted of a single application on May 8, 2000 at a nominal initial concentration of 6.0 µg a.i./L. A total of 11 measurements of aqueous concentrations were performed over a 10-week period in each of the systems, but for both systems only the first 8 measurements during the first 21 days resulted in concentrations above the limit of detection. The concentration of imidacloprid in sediment was measured 8 times over 70 days, but most measurements resulted in values below the limit of quantitation. The tank had a much higher coverage with macrophytes (60%) than the pond (approx. 30%) over the first 21 days. During the first 21 days water temperatures were measured only every 14 days (varying from approx. 13 – 19°C) and only in the morning. Tanks were slightly colder in the morning than ponds, due to their smaller dimensions, but are for the same reason expected to also warm up slightly faster than ponds. For this reason the average air temperature during the first 21 days of the experiment is used as the average temperature during the experiment (16.7°C).

The report of the study by Ratte and Memmert (2003) was kindly provided by Bayer CropScience. The report describes a study in a collection of 13 outdoor ponds located at Itingen, Switzerland (3100 – 3800 L water, approx. 1 m water depth; 10 cm natural sediment containing 3.4% organic carbon; pond diameter 2.0 – 2.2 m) treated at 5 different levels ranging from 0.6 – 23.5 µg a.i./L (two ponds per treatment level, three controls). The test substance was applied twice, on May 02 and May 23, 2001 by applying appropriate amounts of the formulated product Imidacloprid SL 200 through spraying an application solution in water onto the surface of each pond using a hand held spray boom. There was no deliberate mixing of the ponds after application and there was no or only slight wind during the applications on both dates. Water samples were taken on days 0 (3 – 4 h after the first application), 2, 4, 7, 14, 21 (3 – 4 h after the second application), 23, 25, 28, 35, 49, 63, 77, 91, 105 and 119 after first application from each of the ponds. From each pond 6 water samples were taken at different positions, which were pooled into a single sample onto which chemical analysis was applied. Water was not filtrated before analysis, i.e. reported concentrations include material sorbed to suspended solids. Sediment samples were taken on days 0, 7, 14, 21, 28, 35, 49, 63, 77, 91, 105 and 119 after first application from each of the ponds. From each pond sediment samples were collected at 2 positions (depth: 10 cm) and mixed prior to chemical analysis. Chemical analyses were performed only on sediments from ponds with the two highest test levels (9.3 and 23.5 µg imidacloprid/L) and on sediment from control ponds (only samples taken on day 21). Although the growth of macrophytes was not quantified in the study in detail, the report mentions that floating plants of Lemna were removed from the ponds at each sampling date. For this reason the ponds are considered to have contained only negligible amounts of macrophytes. Water temperature and pH in the ponds was measured at approx. 0.5 m below water surface, and was always measured in the morning (8:00 – 9:15 am). Temperature differed only slightly between ponds, and ranged from approx. 10°C on day 6 to approx. 23°C on day 84 after first application of the test substance. Average water temperature over the first 119 days after first application is estimated to have been approx. 19°C, with slightly lower temperatures during the first 49 days and slightly higher average temperatures during the last 70 days. The report gives a detailed summary of daily mean air temperature, precipitation, sunshine and wind strength over the experimental period of May 2 – June 6, 2001. On both days of the applications (May 02 and May 23, 2001) the weather was sunny with few resp. no clouds, and air temperatures are given as 23.3 – 26.1°C and 23.2 – 25.2°C, resp.

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Lambda-cyhalothrin

Arts *et al.* (2006) reported data on the fate of lambda-cyhalothrin in a mesocosm study to be of possible use for the current purpose. Treatment consisted of two applications with four weeks between, at 3 different nominal initial levels (0.12, 0.024 and 0.0048 µg a.i./L). However, aqueous concentrations are reported only at four times after each application in the highest treatment level, whereas for lower concentrations less measurements are reported. No measurements of chlorothalonil in sediments are reported, nor is the organic matter content of the sediment given.

Hand *et al.* (2001) report measurements on the dissipation of lambda-cyhalothrin in indoor aquatic microcosms (10 cm sediment depth, 5.8% organic matter content, 30 cm water depth, 600 L approx.) at an initial concentration of 2.3 µg/L. Aqueous concentrations of lambda-cyhalothrin and a metabolite are reported at 7 times within 96 hours after application. The authors reason that much of the applied pesticide was taken up by and transformed in the macrophytes present.

Roessink *et al.* (2005) describe the effects of different exposure concentrations on biota in pond enclosures. The enclosures with the highest exposure concentrations (0.25 µg/L) were included in a study by Leistra *et al.* (2003) into the effect of macrophyte densities on the fate of lambda-cyhalothrin. The results of chemical analysis were described in more detail by Leistra *et al.* (2003) and were amended by the results of a second experiment, using enclosures in another pond which were also treated with 0.25 µg/L of lambda-cyhalothrin. In both experiments, concentrations of the pesticide were measured in water (seven times after application), plant and sediment samples (both 5 times after application). Concentrations in the aqueous phase are given in graphical format for both experiments, whereas measured concentrations in plants are given in tabular format for the first experiment and in graphical format for the second experiment. Organic matter content of the first

0.01 m top layer of the sediment was measured and was found to be very high (35 and 49% in the first experiment in enclosures in two different ditches, 38% in the second experiment in enclosures in a single ditch). Higher plant densities resulted in a decrease of the fraction of pesticide found in the sediment. The first experiment was part of a more extensive experiment using different exposure concentrations

Wang *et al.* (2007) exposed a small system (10 cm soil, 5 cm water, contained in a glass vessel with a volume of 26 L) simulating a rice paddy water, to an initial aqueous concentration of 10 µg/L. They report the results of 8 measurements of lambda-cyhalothrin in water over a 96-h period, concluding that dissipation of lambda-cyhalothrin occurred according to first-order kinetics. Concentrations in sediment (2.04% organic carbon) were not measured.

The paper by Wendt-Rasch *et al.* (2004) gives fate data for λ-cyhalothrin in outdoor microcosms (concrete tanks containing approx. 500 L of water and a sediment layer). The cosms were treated three times with λ-cyhalothrin at levels of 0.01, 0.025, 0.10 and 0.25 µg/L. Only the concentration data for the highest treatment level are given (in a graph), both for an *Elodea* and a *Lemna* dominated microcosm. Concentrations were measured 10 times after the first treatment. Although the number of measurements between applications is less than the required number of 5 measurements, overall the number of measurements of aqueous concentrations of λ-cyhalothrin are sufficient. Aqueous concentrations are given both for cosms dominated by submerged macrophytes and cosms with a high *Lemna* coverage, separately. No data on measured concentrations of λ-cyhalothrin in sediments is provided, nor are data on the organic carbon content of the sediment given (two different types of sediment were used for the two types of microcosms). Some data on the coverage of the water surface or the proportion of bottom covered with macrophytes is given. Extensive data on temperature, dissolved oxygen and pH of the water are provided.

In the study by van Wijngaarden *et al.* (2004) λ-cyhalothrin was applied five times to a number of indoor microcosm systems with a water volume of approx. 600 L, containing a 10 cm sediment layer and a 50 cm water layer. λ-cyhalothrin was applied at 4 different levels, at initial concentrations of 0.01 – 0.25 µg/L and its aqueous concentration was followed in the lowest and highest levels of application. Aqueous concentrations of λ-cyhalothrin are given (in a graph) at four times after each of the five applications for 36 days post first application. Thus, although the number of measurements after each applications is less than the required 5, the overall number of measurements of aqueous concentrations is sufficient. Concentrations in sediment (nor the organic matter content of the sediment) are not reported (the paper does not mention measuring concentrations in sediment). According to the paper, data on pH, temperature and dissolved oxygen were measured extensively, and ranges of these parameters as measured over the course of the experiment are provided in the paper.

Studies described by Kennedy *et al.* (1988) and Bennett *et al.* (2005) use a combination of simulated spray drift and simulated run-off for application of the test substance, and are therefore considered less suitable. In the study by Bennett *et al.* (2005) sufficiently detailed results of analysis in water, sediment and plants are given. The summary of the study by Kennedy as given in Addendum 3 of the Draft Assessment Report does not explicitly mention the concentrations measured in the aqueous layer and is therefore considered unsuitable

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Linuron

Three studies with sufficiently detailed analyses in water and sediment were found.

Bromilow *et al.* (2006) describe the fate of linuron in an experiment in outdoor cosms located at Harpenden, Hertfordshire, U.K. (location not given in paper, location of affiliation of author used instead) using an initial concentration of 67 µg/L. Concentrations measured in water, sediment (2.5% organic carbon) and plants are reported. Linuron remained largely in the water phase, to a lesser extent in the sediment and hardly any linuron at all was observed in plant material. Dissipation slowed as outdoor temperatures decreased (the initial application was on October 30, 2002). Besides the measurement shortly after application, concentrations were reported at 7 additional times.

Crum *et al.* (1998) provide detailed data of experimental outdoor ditches treated with 4 levels of linuron (0.5, 5, 15 and 50 µg/L). Ditches were kept stagnant during the first week after treatment, during which period 4 measurements in water and sediment are reported, and were subjected to slow water flow starting 1 week after application (5 additional measurements in water and sediment were performed during this period). The organic matter content of the sediment decreased with depth into

sediment, and ranged from 2 – 26% In the highest treatment level more detailed data about stratification of linuron in the aqueous phase and in the sediment are reported. Measurements included concentrations of linuron in macrophytes.

Stephenson and Kane (1984) describe the results of experiments with linuron in three small (1000 L) enclosures in ponds located at Headcorn, Kent, U.K., containing macrophytes, macro-invertebrates and zooplankton. A single application on May 16, 1979 was used. Initial concentration of linuron was 1 mg/L, and after application 6 measurements in water (and none in sediments, for which no organic matter content is given) are reported. The half-life of linuron in the three, similar, ponds were 40, 16 and 24 days.

Van den Brink *et al.* (1997) used indoor microcosms in glass aquaria (600 L water, 50 cm water depth, 10 cm lake sediment) located in Wageningen, The Netherlands, in which the concentration of linuron (5 treatment levels, 0.5, 5, 15, 50 and 150 µg/L) was kept constant during 4 weeks, by regularly dosing additional amounts of linuron to the cosms during half February – March 1994. After the initial 4 weeks no more linuron was doses, and the concentration of linuron was allowed to decline. Six measurements of aqueous concentrations were performed after the initial 4 weeks. No measurements of concentrations in sediment, no information on the organic matter content of sediment.

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Lufenuron

For lufenuron three papers were found, all three of which refer to the same cosm experiment. The papers by Brock *et al.* (2009, 2010) describe in more detail effects on macroinvertebrates in a mesocosm experiment with lufenuron originally described by fate of lufenuron was described by López-Mancisidor *et al.* (2008) who also describe the fate of lufenuron during the experiment. Some of the ditches used were treated over their entire length, whereas some were treated only over part of their length using barriers to divide ditches into treated and non-treated sections. Only the systems treated over their entire length are suitable for analyses of degradation of lufenuron, and in these systems aqueous concentrations were measured seven times in the first 14 days after treatment. Concentrations in sediment were not measured, nor was organic matter content of the sediment.

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Metamitron

Three sufficiently detailed papers were found, both describing cosm studies involving metamitron.

In the first study (van Wijngaarden *et al.*, 2004) metamitron was applied twice to a number of indoor microcosm systems with a water volume of approx. 600 L, containing a 10 cm sediment layer and a 50 cm water layer. Metamitron was applied at 4 different levels, at initial concentrations of 0.55 – 12.6 µg/L and its aqueous concentration was followed in the lowest and highest levels of application. Aqueous concentrations of metamitron are given (in a graph) at 15 different times after its first application over a 56 day time period. Concentrations in sediment (nor the organic matter content of the sediment) are not reported (the paper does not mention measuring concentrations in sediment). According to the paper, data on pH, temperature and dissolved oxygen were measured extensively, and ranges of these parameters as measured over the course of the experiment are provided in the paper.

The second paper (Wendt-Rasch *et al.*, 2004) gives fate data for metamitron in outdoor microcosms (concrete tanks containing approx. 500 L of water and a sediment layer). Only the data for the highest (of 4) treatment levels are given (in a graph), at 5 times after treatment. Aqueous concentrations are given both for cosms dominated by submerged macrophytes and cosms with a high Lemna coverage, separately. No data on measured concentrations of metamitron in sediments is provided, nor are data on the organic carbon content of the sediment given (two different types of sediment were used for the two types of microcosms). Some data on the coverage of the water surface or the proportion of bottom covered with macrophytes is given. Extensive data on temperature, dissolved oxygen and pH of the water are provided.

The third paper by Brock *et al.* (2004) describes fate data for metamitron in moderately buffered mesotrophic enclosures (diameter 1.05 m, height 0.90 m, water depth 0.5 m, no information on sediment composition is given) in outdoor ditches. Enclosures were treated at six different exposure levels (0, 14, 70, 280, 1120, 4480 µg/L) of metamitron. Water samples were 8 times after the application over a 14 days period (nine samples over 28 days for the highest treatment level). Concentrations for the metabolite desamino-metamitron measured in water are also reported. No analyses in sediment are reported.

References particular to metamitron

Brock, T.C.M., S.J.H. Crum, J.W. Deneer, F. Heimbach, R.M.M. Roijackers, J.A. Sinkeldam (2004).

Comparing aquatic risk assessment methods for the photosynthesis-inhibiting herbicides metribuzin and metamitron. *Environ. Poll.* 130, 403 – 426.

Van Wijngaarden, R.P.A., J.G.M. Cuppen, G.H.P. Arts, S.J.H. Crum, M.W. van den Hoorn, P.J. van den Brink, T.C.M. Brink (2004).

Aquatic risk assessment of a realistic exposure to pesticides used in bulb crops: a microcosm study. *Environ. Toxicol. Chem.* 23, 1479 – 1498.

Wendt – Rasch, L., P.J. van den Brink, S.J.H. Crum, P. Woin (2004).

The effects of a pesticide mixture on aquatic ecosystems differing in trophic status: responses of the macrophyte *Myriophyllum spicatum* and the periphytic algal community. *Ecotoxicol. Environ. Saf.* 57, 383 – 398.

Metiram

Only one study (Lin *et al.*, 2012), a mesocosm study in enclosures placed in artificial ditches, was found, but did not meet the criteria with regard to the number of concentration measurements in water. Metiram concentrations were measured 2 h, 17 d and 59 d after the first application of metiram. The authors indicate that measured water concentrations of metiram on day 17 were very low (only 0.04% of the nominal initially applied concentration) and on day 59 these concentrations had fallen below the detection limit. Concentrations in sediment and organic matter content of the sediment are not given. Due to insufficiently detailed knowledge of the aqueous concentration of metiram over time, this study is not usable for the analysis of degradation rates in water as intended in the current report.

References particular to metiram

Lin, R., L. Buijse, M.R. Dimitrov, P. Dohmen, S. Kosol, L. Maltby, I. Roessink, J.A. Sinkeldam, H. Smidt, R.P.A. van Wijngaarden, T.C.M. Brock (2012).

Effects of the fungicide metiram in outdoor freshwater microcosms: responses of invertebrates, primary producers and microbes. *Ecotoxicology* 21, 1550 – 1569.

Metribuzin

Arts *et al.* (2006) reported data on the fate of metribuzin in a mesocosm study in outdoor ditches located at Renkum, The Netherlands. Treatment consisted of a single application in May 2002, at 3 different nominal initial levels (8.2, 1.5 and 0.27 µg a.i./L). Aqueous concentrations are reported at six times in days 0 – 15 after the application in the highest treatment level, whereas for lower concentrations less measurements are reported. No measurements of metribuzin in sediments are reported, nor is the organic matter content of the sediment given.

Fairchild and Sappington (2002) describe results of a mesocosm study with metribuzin in ponds located in Columbia, Missouri U.S.A., with a water volume of approx. 750 m³ (surface area 1000 m², depth 0.75 m) at different exposure levels (0, 9, 19, 38, 75 µg/L). Exposure levels were measured only shortly after application of metribuzin on May 22 (year not given, presumably 2001), using duplicate samples, except for the highest exposure level for which aqueous concentrations were determined at 5 different times during the first week of exposure. No measurements were performed for concentrations in sediment (3.2% organic carbon, taken from a previous study; Fairchild *et al.*, 1992) and in the macrophytes present in the ponds (macrophyte biomass was measured and reported), nor was organic matter content of the sediment reported.

The paper by Brock *et al.* (2004) describes fate data for metribuzin in moderately buffered mesotrophic enclosures (diameter 1.05 m, height 0.90 m, water depth 0.5 m, no information on sediment composition is given) in outdoor ditches located at Renkum, The Netherlands. Enclosures were treated at six different exposure levels (0, 1.8, 5.6, 18, 56 and 180 µg/L) of metribuzin, on May 5, 1999. Water samples were taken 10 times after the application over a 56 days period (9 samples over 56 days for enclosures 5, 9 and 11, with treatment levels of 1.8, 1.8 and 5.5 µg/L resp). No analyses in sediment are reported. An initial logarithmic plot of (scaled) concentrations versus time indicated that the dissipation rates in all enclosures were very similar. Assuming that this indicates that the simulated degradation rates will also be very similar for all enclosures, it was decided to include only the data for enclosures with the lowest and highest dissipation rates (enclosures 1 and 8, with initial nominal concentrations of 5.6 and 56 µg/L, resp. For enclosures 1 and 8 pH ranged from 7.3 – 10.0 and 7.4 – 10.2 resp. Water temperature was measured near the water surface (exact depth not given, presumably 10 cm, the depth at which pH was measured) in the morning, average values over day -8 to day +57 were 16.1°C for enclosure 1 and 17.0°C for enclosure 8. In the calculations an average value of 16.55°C was used.

References particular to metribuzin

Arts, G.H.P., L.L. Buijse – Bogdan, D.M. Belgers, C.H. van Rhenen – Kersten,

R.P.A. van Wijngaarden, I. Roessink, S.J. Maund, P.J. van den Brink, T.C.M. Brock (2006).

Ecological impact in ditch mesocosms of simulated spray drift from a crop protection program for potatoes. *Integrated Environmental Assessment and Management* 2, 105 – 125.

Brock, T.C.M., S.J.H. Crum, J.W. Deneer, F. Heimbach, R.M.M. Roijackers, J.A. Sinkeldam (2004). Comparing aquatic risk assessment methods for the photosynthesis-inhibiting herbicides metribuzin and metamitron. *Environ. Poll.* 130, 403 – 426.

Fairchild, J.F., T.W. La Point, J.L. Zajicek, M.K. Nelson, F.J. Dwyer, P.A. Lovely (1992). Population-, community- and ecosystem-level responses of aquatic mesocosms to pulsed doses of a pyrethroid insecticide. *Environ. Toxicol. Chem.* 11, 115 – 129.

Fairchild, J.F., L.C. Sappington (2002). Fate and effects of the triazinone herbicide metribuzin in experiment pond mesocosms. *Arch. Environ. Contam. Toxicol.* 43, 198 – 202.

Raschke, U., G. Werner, H. Wilde, U. Stottmeister (1998). Photolysis of metribuzin in oxygenated aqueous solutions. *Chemosphere* 36, 1745 – 1758.

Zhong, M.J., Y. Chen, C. Hu (2009). Photochemical fate of metribuzin in aqueous solution under simulated sunlight irradiation. *Acta Scientiae Circumstantiae* 29, 1470 – 1474.

Metsulfuron-methyl

Cessna *et al.* (2006) studied the dissipation of metsulfuron-methyl from farm dugouts (dug holes, containing several hundreds cubic meters of ground water). Initial concentrations of metsulfuron-methyl were 0.9 µg/L, and concentrations in water were measured 12 times over a period of 112 days. Measurements were continued taking monthly samples during ice cover in winter until the end of February, and monthly from May until July when sampling was terminated. Aqueous concentrations reported for the first 112-day period are given in tabular format; concentrations reported for later sampling points are not reported in tabular format but only in a (logarithmic) graph covering the entire 250 day period and may therefore be hard to deduce. Concentrations were not measured in sediment, nor is the organic matter content of the sediment reported.

Wang *et al.* (2011) monitored radio-labelled metsulfuron-methyl in water and sediment (OM 3.05%) of an artificial pond, using both chemical and radio-chemical analysis (allowing the determination of total label and of the parent compound separately). The 'pond' (an outdoor glass aquarium) contained approx. 100 L water, which was treated with an initial concentration of 1 mg/L metsulfuron-methyl. Nine measurements over a 90-day period were reported, both for concentrations in water (label and parent) and in sediment (distinguishing between extractable and bound residue in sediment). The decrease of metsulfuron-methyl concentration in the aqueous phase appeared to be bi-linear, a rapid initial decrease being followed by a somewhat slower decrease after the initial (5 day) period.

References particular to metsulfuron-methyl

Cessna, A.J., D.B. Donald, J. Bailey, M. Waiser, J.V. Headley (2006). Persistence of the sulfonyleurea herbicides thifensulfuron-methyl, ethametsulfuron-methyl and metsulfuron-methyl in farm dugouts (ponds). *J. Environ. Qual.* 35, 2395 – 2401.

Wang, H., F. Yang, G. Liu, Y. Lei, Q. Ye (2011). Monitoring of metsulfuron-methyl and its residues in an artificial pond. *Environ Monit Assess* 174, 597 – 604.

Wendt – Rasch, L., P. Pirzadeh, P. Woin (2003). Effects of metsulfuron-methyl and cypermethrin exposure on freshwater model ecosystems. *Aquat. Toxicol.* 63, 243 – 256.

Prosulfocarb

Two studies were found, one of which (Adriaanse *et al.*, 2013) describes the analysis of concentration data of prosulfocarb in the other study, a mesocosm study giving details of the fate of several pesticides, a.o. prosulfocarb, in a mesocosm study in artificial ditches (Arts *et al.*, 2006). The latter

study gives sufficient detail for the analysis of fate data as intended in the current study, but organic matter content of the sediment is not reported.

References particular to prosulfocarb

Adriaanse, P.I., J.J.T.I. Boesten, S.J.H. Crum (2013).

Estimating biodegradation rates in outdoor stagnant water by inverse modelling with TOXSWA: a case study with prosulfocarb. *Pest Manag Sci* 69, 755 – 767.

Arts, G.H.P., L.L. Buijse – Bogdan, D.M. Belgers, C.H. van Rhenen – Kersten,

R.P.A. van Wijngaarden, I. Roessink, S.J. Maund, P.J. van den Brink, T.C.M. Brock (2006).

Ecological impact in ditch mesocosms of simulated spray drift from a crop protection program for potatoes. *Integrated Environmental Assessment and Management* 2, 105 – 125.

Tolyfluanide

A single study (Ohlauson and Blanck, 2014) was found, describing the evaluation of the effectiveness of 5 antifouling compounds, one of which was tolyfluanide, against marine periphyton in small (300 mL) test systems containing filtered natural seawater, but which did not contain any sediment.

Aqueous concentrations of the test substances were not measured, and only nominal initial concentrations of the test substances were reported. The construction of the test systems, and the lack of concentration measurements obviously renders this study useless for determination of the degradation rate constant of tolyfluanide in water.

Ohlauson, C., H. Blanck (2014).

A comparison of toxicant-induced succession for five antifouling compounds on marine periphyton in SWIFT microcosms. *Biofouling: The journal of bioadhesion and biofilm research* 30, 41 – 50.

Annex 4 Data for three cosm studies with metribuzin

The main characteristics of the studies with metribuzin in the three cosm studies of Fairchild and Sappington (2002), Arts et al (2006) and Brock et al (2004) have been summarized in Table 4.1. The studies have also been briefly described in the main text of Chapter 5.

Table 4.1

Data on cosm studies with metribuzin.

Label in data file	MetrCosm1	MetrCosm2	MetrCosm3
Reference	Fairchild & Sappington (2002)	Arts et al (2006)	Brock et al (2004)
Compound	Metribuzin (technical grade)	Metribuzin	Metribuzin
Type of system	Outdoor clay-lined pond	Outdoor ditch	Polycarbonate enclosures in outdoor ditch, outdoor (ditch, enclosure)
Dimensions system	1000 m ² , 1.5 m depth, 750 m ³ volume	L=40 m, w=1.6-3.3 m, depth=0.5 m, V=55 m ³	Diameter 1.05 m, height 0.9 m, water depth 0.5 m
Side slope (hor/vert)	0	1.7	0
Depth water layer (m)	0.75 m	No measurements, M&M states 'each with a water depth of 0.5 m'	0.5
Depth sediment (cm)	-	25	25
Sediment om%	3.2 oc-5.5 om	-, (sandy loam)	-
Sediment bulk density	-	-	-
Sediment porosity	-	-	-
Macrophytes info	> 80% cov. 40 g/m ² on day - 7, <i>Najas guadalupensis</i> , common water nymph or guppy grass, > 100 g/m ² day 30	Highest treatment: decrease filamentous algae from 40 to 5% coverage	Myrophyllum (up to 75% cover), <i>Sagittaria sagittifolia</i> (<5%) and <i>Elodea nuttallii</i> (<1%) present
pH	Hourly, 8.1 ± 1.2	low conc: 7.3 – 9.7 (8.5 avg); high conc 7.4 – 9.8 (8.4 avg)	10 cm below water surface: 5.6 µg/L: 7.3 – 10.0; 56 µg/L: 7.4 – 10.2
Temperature	Hourly, 19 ± 4°C	low conc: 17.5°C average, high conc: 17.3°C average	Surface (presumably 10 cm below water surface), in the morning: encl. 1 (5.6 ug/L): 16.1°C, encl. 8 (56 ug/L): 17.0°C; average temp of 16.55°C used in calculations average
Light intensity	Day 0 = May 22, turbidity 4.2 ± 2.6 NTU's	-	-
Application number	1	1	1
Application interval	-	-	-
Nominal initial application	75 µg/L	1.6 / 8.2 µg/L	5.6 (encl. 1) and 56 (encl. 8) µg/L. Other concentrations (1.8/18/180 ug/L) used in the study as well, all concentrations in duplicate, but only 2 enclosures included in the analysis

In Chapter 4 the input that was common for all cosm studies has been described. In Table 4.2 below we summarized the input values on the physico-chemical properties of metribuzin and the cosm-specific input, such as e.g. the water depth.

Table 4.2

Parameter values used in the simulations with metribuzin.

Cosm label	MetrCosm1	MetrCosm2	MetrCosm3
Molar mass (g)	214.29		
Saturated vapour pressure (mPa)	0.121 (25°C)		
Solubility (mg/L)	1165 (20°C)		
Kom (estimated) (L/kg)	Kom=22, 1/n=1.08		
pKa	0.99 (strong acid) in our view: weak base)		
Initial $DegT_{50,water}$ (d)	5.0 and 25	1, 15, and 5	5, 25 and 0.1
Water depth (m)	0.75	0.5	0.5
Side slope (hor/vert, -)	0	1,7	0
Temperature (°C)	19 (estimated by us)	17.4	16.55
Measurements in sediment	No	No	No

Table 4.3 presents the measured concentrations in water as a function of time in the cosm study of Fairchild and Sappington (2002). The values have been read from a Figure in the publication and they represent the total concentration in water, as the water was not filtered before extraction.

Table 4.3

Concentrations in water ($\mu\text{g/L}$ and scaled) as a function of time (d) for the cosm study with metribuzin by Fairchild and Sappington (2002).

Number	Time (hours)	Time in TOXSWA	Concentration in water ($\mu\text{g/L}$)	Scaled concentration in water
1	0.25 h	0 days	73.8	1.0000
2	1 d	1	60.4	0.8184
3	2 d	2	59.7	0.8089
4	7 d	7	25.5	0.3455
5	14 d	14	3.65	0.0495

The cosm of Fairchild and Sappington (2002) was inversely modelled and the agreement between measured and simulated aqueous concentrations was optimised with the aid of the PEST, running TOXSWA many times, according to the procedures presented in Chapters 2 and 4. Three optimisations were performed, each with its own initial values of $DegT_{50,water}$ and $c_{t=0}$ and with the same specified lower and upper parameter bounds (1 and 100 d for $DegT_{50,water}$ and 0.1 and 5.0 (scaled) for $c_{t=0}$). Table 4.4 gives estimates of the optimized $DegT_{50,water}$ for each of the three optimisations. It also specifies the optimised $c_{t=0}$ value, the value of the objective function phi (i.e. the sum of squared differences between model-generated and measured aqueous concentrations), the error percentage of the χ^2 -test and the number of times TOXSWA has been run by PEST. Both initial values for $DegT_{50,water}$ of 5 and 25 days resulted in an estimate of for the $DegT_{50,water}$ of 4.0 days with relatively large 95% confidence intervals of 2.1 – 5.9 days. The error percentage of 6.4% is an acceptable value for field experiments according to FOCUS (2006), so the optimisation passed the χ^2 -test. Changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) did not affect the estimated value for the $DegT_{50,water}$.

Table 4.4

Optimisation results for three sets of initial values of $DegT_{50,water}$ and $C_{t=0}$ for the Fairchild and Sappington cosm (2002) with metribuzin.

DegT50 ini (d) and om	$C_{t=0}$, ini, scaled (-)	DegT50, fitted (d)	$C_{t=0}$, fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
5 with 9% om	1.0	4.04 (2.17 – 5.91)	1.02 (0.86 – 1.18)	1.18 E-2	6.4%	34
25 with 9% om	1.0	4.04 (2.16 – 5.92)	1.02 (0.86 – 1.18)	1.18 E-2	6.4%	34
5 with 19% om	1.0	4.05 (2.15 – 5.95)	1.02 (0.86 – 1.18)	1.20 E-2	6.5%	24

Fig 4.1 presents a satisfactory agreement between scaled optimised and measured water concentrations for one optimisation, while Fig 4.2 presents the distribution of the scaled residual between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

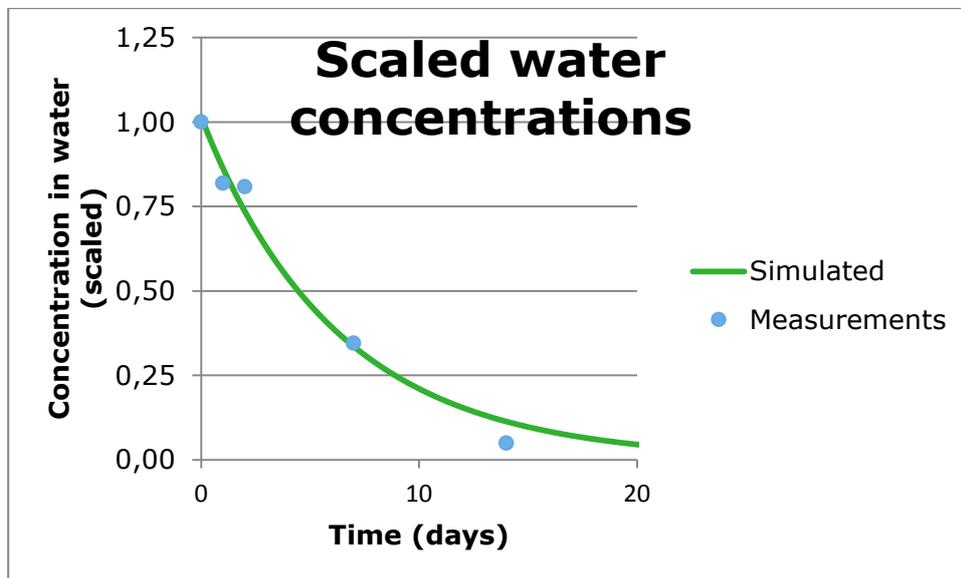


Figure 4.1 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) metribuzin in water as a function of time after first measurement (d) in the cosm of Fairchild & Sappington (2002). Simulated concentration profile obtained by PEST_TOXSWA optimisation for $DegT_{50,ini} = 5$ d and $C_{t=0,ini} = 1.0$

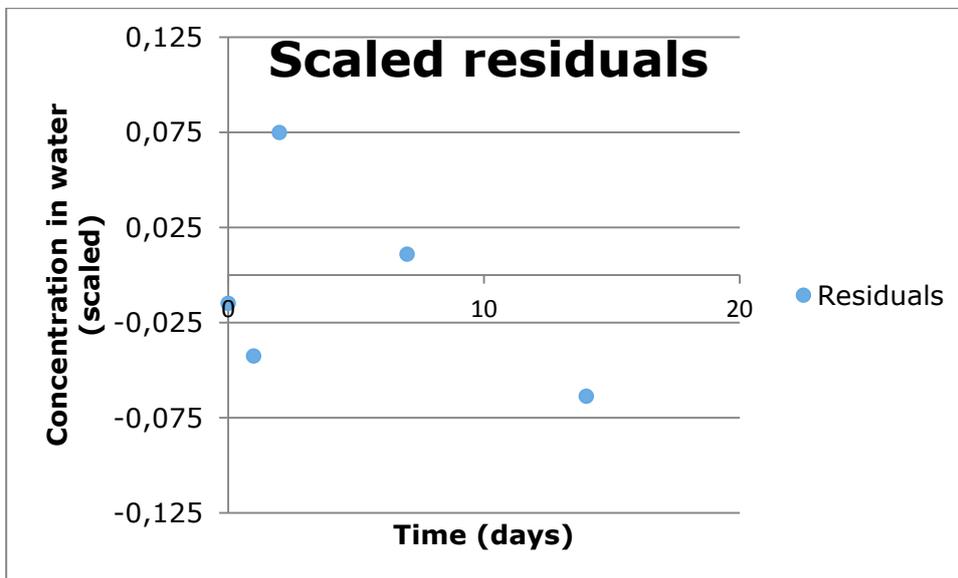


Figure 4.2 Residuals in the total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) metribuzin in water as a function of time after first measurement (d) in the cosm of Fairchild & Sappington (2002). Simulated concentration profile obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50,ini} = 5 \text{ d}$ and $c_{t=0,ini} = 1.0$

Table 4.5 presents the measured concentrations in water as a function of time in the cosm study of Arts et al (2006). The raw data were provided by the author Arts of the publication and they represent the total concentration in water: the water was not filtered, but direct extraction was done using Waters OASIS columns. Two initial nominal concentrations were used in the experiment, corresponding to 1% and 5% spray drift deposition (application rate of 0.35 kg/ha): ditches 1, 7 and 12 were treated with a nominal initial concentration of 1.6 $\mu\text{g/L}$; ditches 4, 6 and 9 were treated with a nominal initial concentration of 8.2 $\mu\text{g/L}$.

Table 4.5

Measured concentrations in water ($\mu\text{g/L}$ and scaled) as a function of time (d) for the ditch study with metribuzin by Arts et al (2006).

Number	Ditch	Time (days)	Concentration in water ($\mu\text{g/L}$)	Scaled concentration in water
1	7	0.00	1.49	1.0000
2	7	0.08	1.40	0.9396
3	7	1	0.85	0.5705
4	7	3	0.22	0.1477
5	7	7	0.05	0.0336
6	4	0.00	7.82	1.0000
7	4	0.08	7.67	0.9808
8	4	0.33	6.58	0.8414
9	4	1	4.53	0.5793
10	4	3	1.78	0.2276
11	4	7	0.68	0.0870
12	4	15	0.07	0.0090
13	1	0.00	1.45	0.8951
14	1	0.08	1.65	1.0000
15	1	1	1.04	0.6420
16	1	3	0.41	0.2531
17	1	7	0.18	0.1111
18	12	0.00	1.47	1.0000
19	12	0.08	1.44	0.9796
20	12	1	0.78	0.5306
21	12	3	0.20	0.1361
22	12	7	0.05	0.0340
23	6	0.00	8.40	1.0000
24	6	0.08	6.99	0.8321
25	6	0.33	7.65	0.9107
26	6	1	5.43	0.6464
27	6	3	1.66	0.1976
28	6	7	0.53	0.0631
29	9	0.00	8.46	1.0000
30	9	0.08	7.05	0.8333
31	9	0.33	6.71	0.7931
32	9	1	4.37	0.5166
33	9	3	1.08	0.1277
34	9	7	0.26	0.0307

The ditches of Arts et al (2006) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of the PEST, running TOXSWA many times, according to the procedures presented in Chapters 2 and 4. Four optimisations were performed, each with its own initial values of $DegT_{50,water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (0.1 and 100 d for $DegT_{50,water}$ and 0.01 and 10 (scaled) for $c_{t=0}$). Table 4.6 gives estimates of the optimized $DegT_{50,water}$ for each of the four optimisations. It also specifies the

optimised $c_{t=0}$ value, the value of the objective function phi (i.e. the sum of squared differences between model-generated and measured aqueous concentrations), the error percentage of the χ^2 -test and the number of times TOXSWA has been run by PEST. Clearly, the run with an initial value of $DegT_{50,water}$ of 25 days results in an unsatisfactory estimation of $DegT_{50,water}$ and $c_{t=0}$, whereas the other initial values of 5 and 0.1 days result in consistent estimates of $DegT_{50,water}$ of 1.05 days with 95% confidence intervals of 0.9 – 1.2 days. The error percentage of 8% is an acceptable value for field experiments according to FOCUS (2006), so the optimisation passed the χ^2 -test. Changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) did not affect the estimated value for the $DegT_{50,water}$.

Table 4.6

Optimisation results for four sets of initial values of $DegT_{50,water}$ and $c_{t=0}$ for the Arts et al ditches (2006) with metribuzin.

DegT50 ini (d) and om (%)	$c_{t=0}$ ini, scaled (-)	DegT50 fitted (d)	$c_{t=0}$ fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
5 d / 9%	1.0	1.05 (0.94 – 1.17)	0.997 (0.96 – 1.03)	9.21 E-2	8.0%	25
25 d / 9%	1.0	9.11 (-37.4 – 55.7)	0.62 (0.48 – 0.79)	3.00	45.7%	21
0.1 d / 9%	1.0	1.05 (0.94 – 1.17)	0.997 (0.96 – 1.03)	9.21 E-2	8.0%	35
5 d / 19%	1.0	1.05 (0.94 – 1.17)	1.00 (0.97 – 1.03)	9.21 E-2	8.0%	24

Fig 4.3 presents a satisfactory agreement between scaled optimised and measured water concentrations for all six ditches in one optimisation set, while Fig 4.4 presents the distribution of the scaled residual between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals are reasonably well scattered around zero (although simulations seem systematically too low after 7 d), demonstrating that there is no clear pattern of under- or over-prediction by the TOXSWA model.

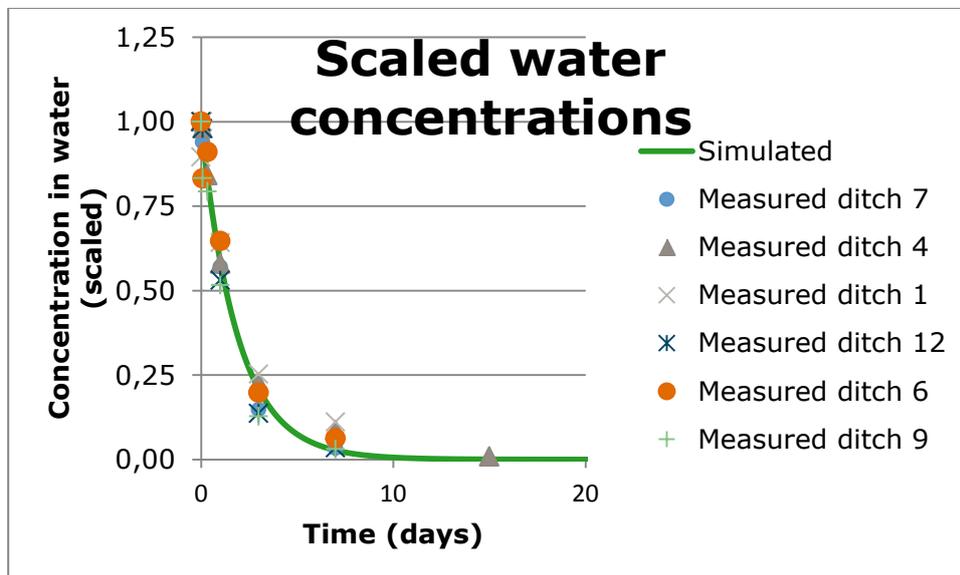


Figure 4.3 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) metribuzin in water as a function of time (d) in the cosms of Arts et al. (2006). Simulated concentration profile obtained by PEST_TOXSWA optimisation for $DegT_{50,ini} = 5$ d and $c_{t=0} = 1.0$.

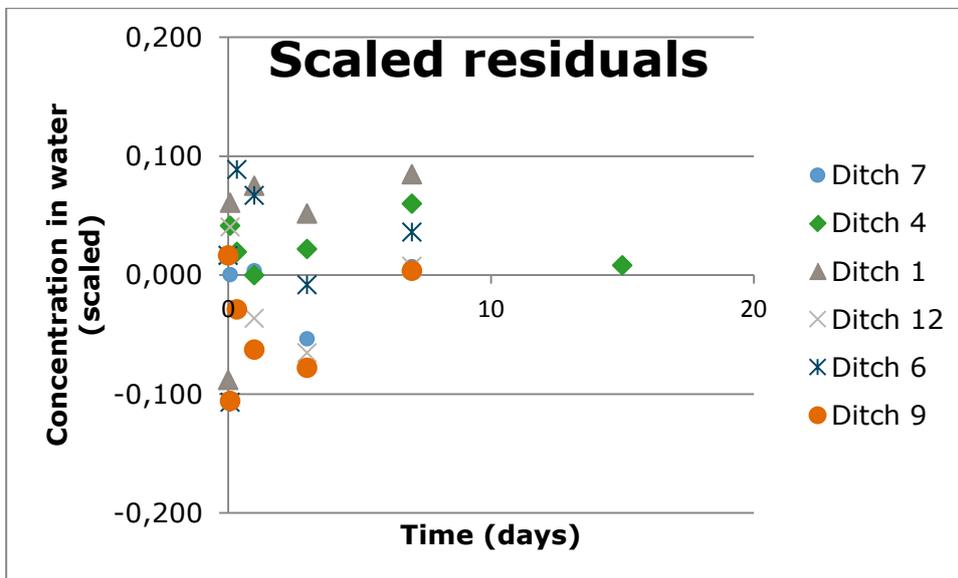


Figure 4.4 Residuals in the total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) metribuzin in water as a function of time (d) in the cosm of Arts et al. (2006). Simulated concentration profile obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,ini} = 5 \text{ d}$ and $c_{t=0} = 1.0$.

Table 4.7 presents the measured concentrations in water as a function of time in the enclosure study of Brock et al (2004). The raw data were provided by the authors of the publication and they represent the total concentration in water: the water was not filtered, but direct extraction was done using Waters OASIS columns. Enclosures were treated at six exposure levels (0, 1.8, 5.6, 18, 56 and 180 $\mu\text{g/L}$), but the optimisation was done for two exposure levels only: enclosures 1 and 8, treated with a nominal initial concentration of 5.6 $\mu\text{g/L}$ and 56 $\mu\text{g/L}$ resp.

Table 4.7

Measured concentrations in water ($\mu\text{g/L}$ and scaled) as a function of time (d) for the ditch study with metribuzin by Brock et al (2004).

Number	Enclosure	Time (days)	Concentration in water ($\mu\text{g/L}$)	Scaled concentration in water
1	1	0.04	6.50	1
2	1	0.17	5.30	0.81538
3	1	0.3	4.80	0.73846
4	1	1	4.80	0.73846
5	1	2	4.20	0.64615
6	1	4	1.90	0.29231
7	1	7	1.78	0.27385
8	1	14	0.93	0.14308
9	1	28	0.27	0.04154
10	1	56	0.05	0.00769
11	8	0.04	59.10	1
12	8	0.17	51.10	0.86464
13	8	0.3	47.10	0.79695
14	8	1	46.70	0.79019
15	8	2	44.30	0.74958
16	8	4	31.80	0.53807
17	8	7	18.50	0.31303
18	8	14	5.90	0.09983
19	8	28	1.25	0.02115
20	8	56	0.10	0.00169

Two optimisations are performed, each with its own initial value of $DegT_{50}$ in water.

The enclosures of Brock et al (2004) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of the PEST, running TOXSWA many times, according to the procedures presented in Chapters 2 and 4. Four optimisations were performed, each with its own initial values of $DegT_{50,water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (0.1 and 100 d for $DegT_{50,water}$ and 0.01 and 10 (scaled) for $c_{t=0}$). Table 4.8 gives estimates of the optimized $DegT_{50,water}$ for each of the four optimisations. It also specifies the optimised $c_{t=0}$ value, the value of the objective function phi (i.e. the sum of squared differences between model-generated and measured aqueous concentrations), the error percentage of the χ^2 -test and the number of times TOXSWA has been run by PEST. Clearly (see e.g. the high phi value and err%), the run with an initial value of $DegT_{50,water}$ of 25 days results in an unsatisfactory estimation of $DegT_{50,water}$ and $c_{t=0}$, whereas the other initial values of 5 and 0.1 days result in consistent estimates of $DegT_{50,water}$ of 3.1 days with 95% confidence intervals of 2.4 – 3.8 days. The error percentage of 11.6% is an acceptable value for field experiments according to FOCUS (2006). Changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) did not affect the estimated value for the $DegT_{50,water}$.

Table 4.8

Optimisation results for four sets of initial values of $DegT_{50,water}$ and $c_{t=0}$ for the Brock et al (2004) enclosures 1 and 8 with metribuzin.

DegT50 ini (d) and om (%)	$c_{t=0}$, ini, scaled (-)	DegT50 fitted (d)	$c_{t=0}$ fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
5 d / 9%	1.0	3.11 (2.4 – 3.8)	0.908 (0.85 – 0.97)	9.45 E-2	11.6%	25
25 d / 9%	1.0	20.3 (0.48 – 40.1)	0.655 (0.51 – 0.80)	1.013	37.9%	23
0.1 d / 9%	1.0	3.11 (2.4 – 3.8)	0.908 (0.85 – 0.97)	9.45 E-2	11.6%	39
5 d / 19%	1.0	3.12 (2.39 – 3.85)	0.910 (0.85 – 0.97)	9.42 E-2	11.6%	25

Fig 4.5 presents the agreement between scaled optimised and measured water concentrations for the two enclosures in one optimisation set, while Fig 4.6 presents the distribution of the scaled residual between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals are reasonably well scattered around zero (although there are some systematic trends for each of the enclosures), demonstrating that there seems to be no clear pattern of under- or over-prediction by the TOXSWA model. So, considering all aspects the optimisation seems satisfactory.

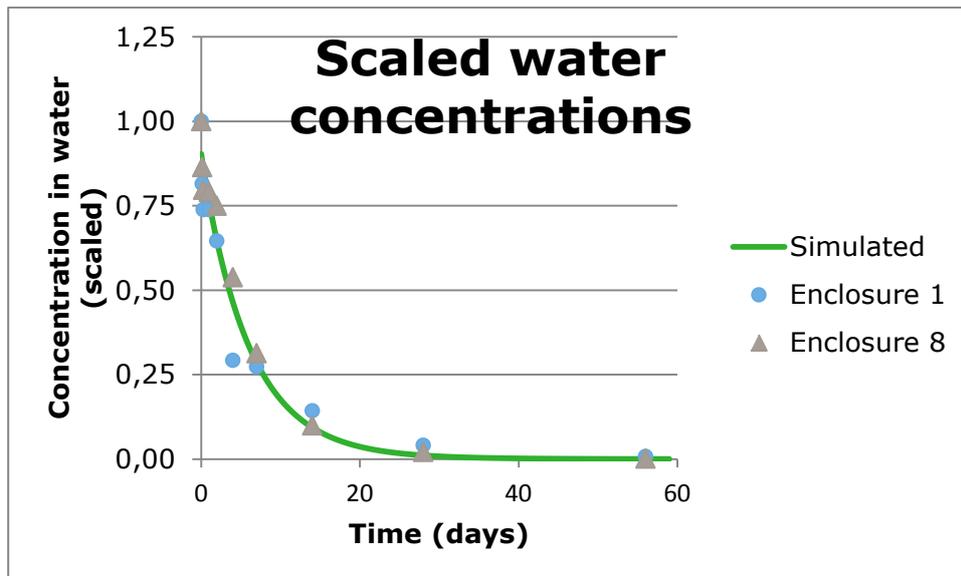


Figure 4.5 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) metribuzin in water as a function of time (d) in the enclosures of Brock et al. (2004). Simulated concentration profile obtained by PEST_TOXSWA optimisation for $DegT_{50,ini} = 5$ d and $c_{t=0} = 1.0$.

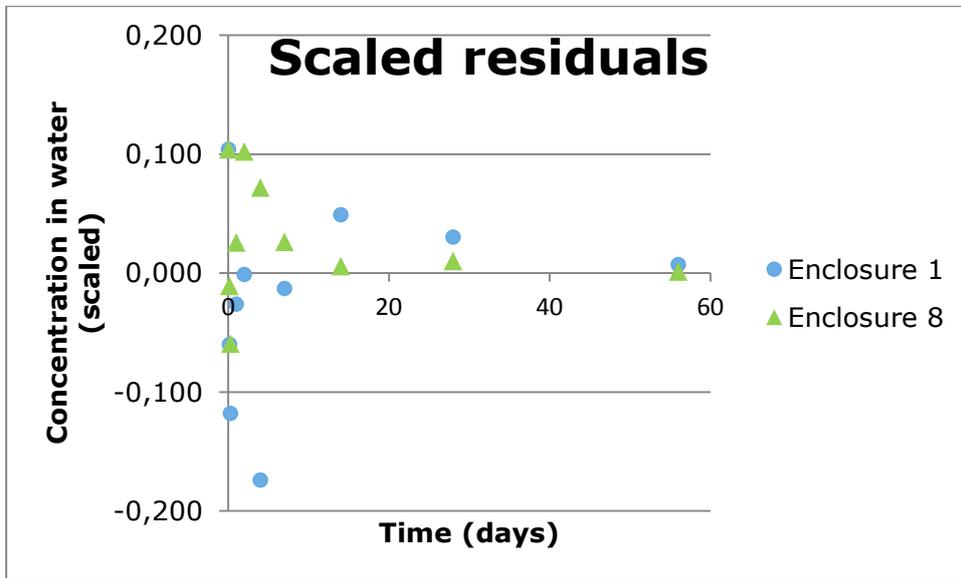


Figure 4.6 Residuals in the total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) metribuzin in water as a function of time (d) in the enclosures of Brock et al. (2004). Simulated concentration profile obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,ini} = 5 \text{ d}$ and $c_{t=0} = 1.0$.

Annex 5 Data for three cosm studies with linuron

The main characteristics of the studies with linuron in the three cosm studies of Stephenson and Kane (1984), Van den Brink et al (1997) and Bromilow et al (2006) have been summarized in Table 5.1. The studies have also been briefly described in the main text of Chapter 6.

Table 5.1

Data on cosm studies with linuron.

Label in data file	LinCosm1	LinCosm2	LinCosm3
Reference	Stephenson and Kane (1984)	Van den Brink et al (1997)	Bromilow et al (2006)
Compound	Linuron (technical grade)	Linuron (Afalon)	Linuron (technical material + surfactant)
Type of system	Polyethylene cylinders, outdoor	Glass aquaria, indoor	Outdoor rectangular stainless steel tanks
Dimensions system	Diam: 115 cm, on average 1020 L of water, depth 1 m	1.1 x 1.1 x 0.7 m, 50 cm water column, 600 L water	100 x 100 x 40 cm; water depth: 30 cm
Side slope (hor/vert)	0	0	0
Depth water layer	1 m, values not measured but taken from Figure giving dimensions of cylinders	50 cm, taken from M&M: '...filled with a 10-cm layer of lake sediment and a 50-cm water column.' No measurements of water depth are reported.	Not measured, taken from M&M: '... and water (30 cm depth) was added'
Depth sediment	Cylinders pushed 5 cm into sediment	10 cm	5 cm
Sediment om%	-	-	2.5% oc --> 4.3% om
Sediment bulk density	-	-	-
Sediment porosity	-	-	-
Macrophytes info	Day 0: none; day 28: considerable quantities	<i>Elodea nuttallii</i> present, treatment related decrease in density	20 x 3 stems of <i>Elodea crisper</i> in each cosm
pH	Over 42 days went from 7.8 to 9	7.5 – 10, lower pH in higher treatments	-
Temperature	Not given, day 0 is May 16, 1979 Temperature from website: 11.6 C average in May http://www.yr.no/place/United_Kingdom/England/County_of_Kent/statistics.html	19 ± 2°C	Sed: 1 – 10°C, water 4°C higher
Light intensity	Not given, day 0 is May 16, 1979	14 h/day, 120 µE/m ² s at water surface	Application in October 2002
Application number	1	9 over first 4 weeks to keep concentration approx. constant	1
Application interval	-	2-3 d	-
Nominal initial application	1.0 mg/L	0.5 / 5 / 15 / 50 / 150 µg/L	668 ug/L

In Chapter 4 the input that was common for all cosm studies has been described. In Table 5.2 below we summarized the input values on the physico-chemical properties of linuron and the cosm-specific input, such as e.g. the water depth.

Table 5.2

Parameter values used in the simulations with linuron.

LinCosm1	LinCosm2	LinCosm3	
Cosm label			
Molar mass (g)	249.09		
Saturated vapour pressure (mPa)	5.1 (25°C)		
Solubility (mg/L)	63.8 (20°C)		
Kom (estimated) (L/kg)	Kom=429.6, 1/n=0.85		
pKa	n.a.		
Initial $DegT_{50,water}$ (d)	10, 100 and 1	10, 100, 1 and 25	10, 100, 1 and 25
Water depth (m)	1.0	0.50	0.30
Side slope (hor/vert, -)	0	0	0
Temperature (°C)	11.6	19.0	9.5°C
Measurements in sediment	No	No	Yes

Table 5.3 presents the measured concentrations in water as a function of time in the cosm study of Stephenson and Kane (1984, Figure 8). The values are given for single cylinders; they represent the total concentration in water, as the water was not filtered before extraction.

Table 5.3

Concentrations in water ($\mu\text{g/L}$ and scaled) as a function of time (d) for the cosm study with linuron by Stephenson and Kane (1984).

Number	Enclosure	Time in TOXSWA (days)	Concentration in water (mg/L)	Scaled concentration
1	1	0	1.2	1.0000
2	1	1	1.0	0.8333
3	1	2	0.96	0.8000
4	1	4	0.91	0.7583
5	1	7	0.90	0.7500
6	1	13	0.82	0.6833
7	1	23	0.66	0.5500
8	2	1	1.10	1.0000
9	2	2	1.0	0.9091
10	2	4	0.95	0.8636
11	2	7	0.85	0.7727
12	2	13	0.67	0.6091
13	2	23	0.45	0.4091
14	2	42	0.19	0.1727
15	3	0	1.4	1.0000
16	3	1	1.1	0.7857
17	3	2	1.1	0.7857
18	3	4	1.0	0.7143
29	3	7	0.92	0.6571
20	3	13	0.77	0.5500
21	3	23	0.62	0.4429
22	3	42	0.33	0.2357

The enclosures of Stephenson and Kane (1984) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of the PEST, running TOXSWA many times, according to the procedures presented in Chapters 2 and 4. Four optimisations were performed, each with its own initial values of $DegT_{50,water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (1 and 200 d for $DegT_{50,water}$ and 0.1 and 5.0 (scaled) for $c_{t=0}$).

Table 5.4 gives estimates of the optimized $DegT_{50,water}$ for each of the four optimisations. It also specifies the optimised $c_{t=0}$ value, the value of the objective function phi (i.e. the sum of squared differences between model-generated and measured aqueous concentrations), the error percentage of the χ^2 -test and the number of times TOXSWA has been run by PEST. Clearly (see e.g. the high phi value and err%), the run with an initial value of $DegT_{50,water}$ of 50 days results in an unsatisfactory estimation of $DegT_{50,water}$ and $c_{t=0}$, whereas the other initial values of 10 and 2 days result in consistent estimates of $DegT_{50,water}$ of 11.1 days with 95% confidence intervals of 8.5 – 13.7 days. The error percentage of 8% is an acceptable value according to FOCUS (2006). Changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) did not affect the estimated value for the $DegT_{50,water}$.

Table 5.4

Optimisation results for four sets of initial values of $DegT_{50,water}$ and $c_{t=0}$ for the Stephenson and Kane (1984) outdoor cylinders with linuron.

DegT50 ini (d)	$c_{t=0,ini}$, scaled (-)	DegT50 fitted (d)	$c_{t=0}$ fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.2	11.09 (8.5 – 13.7)	0.94 (0.89 – 0.99)	9.77 E-2	8.0	21
50	1.2	38.9 (-9.3 – 87.2)	0.82 (0.72 – 0.91)	0.39	16.2	24
2	1.2	11.09 (8.5 – 13.7)	0.94 (0.89 – 0.99)	9.77 E-2	8.0	28
10, 19% om	1.2	11.13 (8.5 – 13.7)	0.94 (0.89 – 0.99)	9.72 E-2	8.0	21

Results of estimation of $DegT_{50,water}$ for each of the cylinders separately, using 10% organic matter content for the sediment, are given in Table 5.5.

Table 5.5

Optimisation results for individual cylinders for the Stephenson and Kane (1984) outdoor cylinders with linuron, assuming 10% organic matter content for each cylinder.

Cylinder	DegT50 fitted (d)	$c_{t=0}$ fitted, scaled (-)	Phi (-)	TOXSWA iterations
1	18.6 (6.2 – 31.0)	0.91 (0.82 – 0.99)	1.48E-2	34
2	8.4 (7.3 – 9.5)	1.05 (1.01 – 1.09)	2.43E-3	27
3	10.8 (6.8 – 14.7)	0.89 (0.81 – 0.97)		21

When analyzing the three different cylinders separately, values for $DegT_{50,water}$ of 18.6, 8.4 and 10.8 days were observed; taking the geometric mean of these three values would result in a geomean value of 11.9 days, which is well within the 95%-confidence interval of 8.5 – 13.7 days estimated for the overall value of 11.1 days in Table 5.4a.

Fig 5.1 presents a reasonably good agreement between scaled optimised and measured water concentrations for one optimisation, while Fig 5.2 presents the distribution of the scaled residual between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

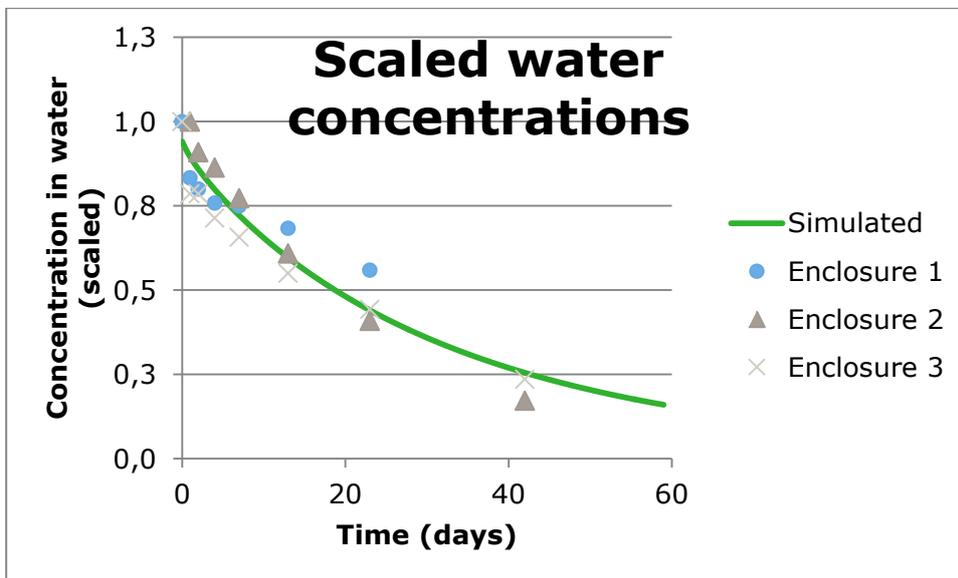


Figure 5.1 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in the study of Stephenson & Kane (1984). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,ini} = 10$ d and $c_{t=0} = 1.0$.

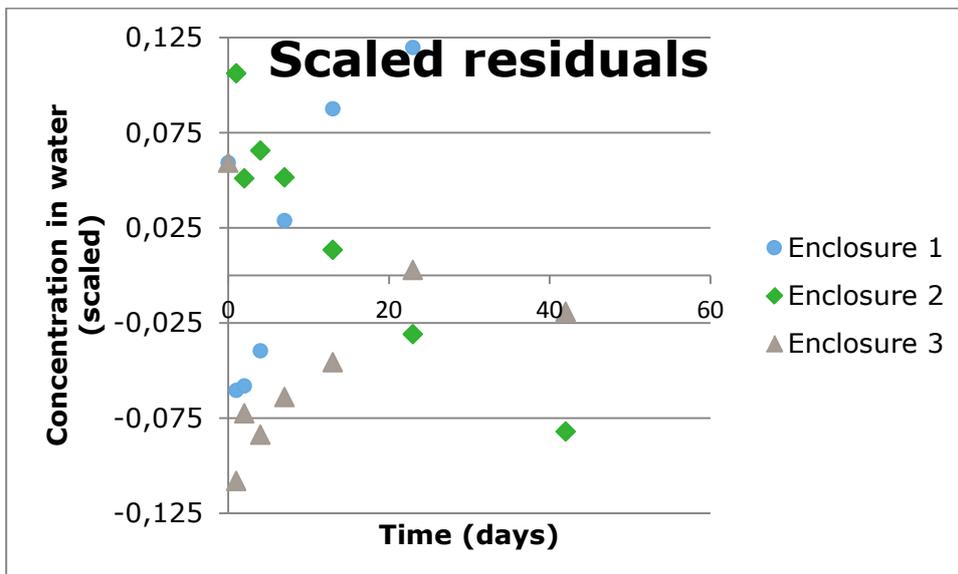


Figure 5.2 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in the study of Stephenson & Kane (1984). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,ini} = 10$ d and $c_{t=0} = 1.0$.

Tables 5.6 and 5.7 presents the measured concentrations in water as a function of time in the cosm study of Van den Brink et al (1997). The values represent the total concentration in water, as the water was not filtered before extraction. The authors have provided a spreadsheet with measured concentrations and loadings (in mg/system) for two separate cosms (cosm 4 and cosm 8). The loadings were converted into loadings/ m^2 by taking into account the dimensions ($1.1 \times 1.1 \text{ m}^2$) of the system. Since TOXSWA cannot handle 2 systems with different loadings at the same time, it was necessary to model concentrations and loadings for individual systems, both exposed at a nominal concentration of $150 \mu\text{g/L}$.

Table 5.6

Concentrations in water (µg/L and scaled) as a function of time (d) for cosm 4 with linuron by Van den Brink et al (1997).

Number	Time in TOXSWA (days)	Concentration in water (µg/L)	Loadings (mg/m ²)	Scaled concentration	Scaled loadings
1	0.06	148.3		0.9137	
2	0.3	144.8		0.8922	
3	1	145.9		0.8990	
	2		11.16		68.76
4	3	160.0		0.9858	
	4		0		0.00
5	6	155.8		0.9600	
	7		0		0.00
6	9	142.5		0.8780	
	10		3.80		23.41
7	13	151.7		0.9347	
	14		11.31		69.69
8	16	146.5		0.9027	
	18		11.17		68.82
9	20	162.3		1.0000	
	22		0		0.00
10	23	148.5		0.9150	
	25		7.51		46.27
11	28	145.3		0.8953	
12	30	142.8		0.8799	
13	34	127.5		0.7856	
14	41	122.1		0.7523	
15	51	98.0		0.6038	
16	65	84.9		0.5231	

Table 5.7

Concentrations in water (µg/L and scaled) as a function of time (d) for cosm 8 with linuron by Van den Brink et al (1997).

Number	Time in TOXSWA (days)	Concentration in water (µg/L)	Loadings (mg/m ²)	Scaled concentrations	Scaled loadings
1	0.06	149.3		0.8185	
2	0.3	150.2		0.8235	
3	1	146.4		0.8026	
	2		11.16		61.184
4	3	156.4		0.8575	
	4		12.40		67.98
5	6	182.4		1.0000	
	7		0		0.00
6	9	170.4		0.9342	
	10		2.23		12.226
7	13	157.5		0.8635	
	14		0		0.00
8	16	154.5		0.8470	
	18		0		0.00
9	20	144.2		0.7906	
	22		7.5		41.12
10	23	146.9		0.8054	
	25		3.70		20.285
11	28	141.0		0.7730	
12	30	138.4		0.7588	
13	34	125.5		0.6880	
14	41	118.9		0.6519	
15	51	107.1		0.5872	
16	65	84.0		0.4602	

The cosms 4 and 8 of Van den Brink (1997) were each inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of the PEST, running TOXSWA many times, according to the procedures presented in Chapters 2 and 4. Four optimisations were performed, each with its own initial values of $DegT_{50,water}$ and $C_{t=0}$ and specified lower and upper parameter bounds (1 and 200 d for $DegT_{50,water}$ and 0.1 and 5.0 (scaled) for $C_{t=0}$). Tables 5.8 and 5.9 give estimates of the optimized $DegT_{50,water}$ for each of the three optimisations. It also specifies the optimised $C_{t=0}$ value, the value of the objective function phi (i.e. the sum of squared differences between model-generated and measured aqueous concentrations), the error percentage of the χ^2 -test and the number of times TOXSWA has been run by PEST. The initial values for $DegT_{50,water}$ of 10 and 100 days resulted in an estimate for the $DegT_{50,water}$ of 53.3 (cosm 4) and 69.9 (cosm 8) days with 95% confidence intervals of 45 – 62 days (cosm 4) and 59-81 days (cosm 8). The error percentage of 3.8% (cosm 4) and 2,9% (cosm 8) are low values, especially for field experiments according to FOCUS (2006), so the optimisations passed the χ^2 -test without doubts. Changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) did slightly affect the estimated values for the $DegT_{50,water}$: 54.7 instead of 53.3 d (cosm 4) and 72.2 instead of 69.9 d (cosms 8).

Table 5.8

Optimisation results for four sets of initial values of $DegT_{50,water}$ and $C_{t=0}$ for the Van den Brink (1997) cosm 4 with linuron.

DegT50 ini (d)	$C_{t=0}$, ini, scaled (-)	DegT50 fitted (d)	$C_{t=0}$, fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.0	53.33 (44.9 – 61.8)	0.97 (0.93 – 1.01)	2.57 E-2	3.8%	34
100	2.0	53.33 (44.9 – 61.8)	0.97 (0.93 – 1.01)	2.57 E-2	3.8%	32
10, 19% om	1.0	54.7 (45.7 – 63.7)	0.97 (0.93 – 1.02)	2.60 E-2	3.9%	36

Table 5.9

Optimisation results for four sets of initial values of $DegT_{50,water}$ and $C_{t=0}$ for the Van den Brink (1997) cosm 8 with linuron.

DegT50 ini (d)	$C_{t=0}$, ini, scaled (-)	DegT50 fitted (d)	$C_{t=0}$, fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.0	69.88 (59.2 – 80.5)	0.86 (0.83 – 0.89)	1.20 E-2	2.9%	35
100	2.0	69.88 (59.2 – 80.5)	0.86 (0.83 – 0.89)	1.20 E-2	2.9%	30
10, 19% om	1.0	72.15 (60.5 – 83.8)	0.87 (0.84 – 0.90)	1.25 E-2	3.0%	35

Fig 5.3 and 5.5 present a satisfactory agreement between scaled optimised and measured water concentrations for one optimisation of the cosm considered, while Fig 5.4 and 5.6 present the distribution of the scaled residuals between model-generated and measured concentrations, as suggested by FOCUS (2006). The graphs show that the residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

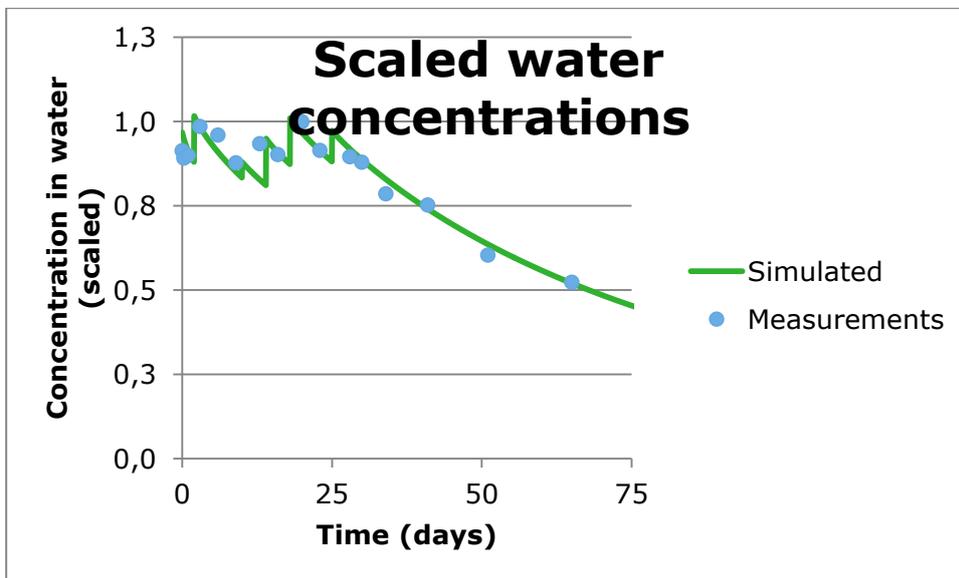


Figure 5.3 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in cosm 4 of Van den Brink (1997). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,\text{ini}} = 10$ d.

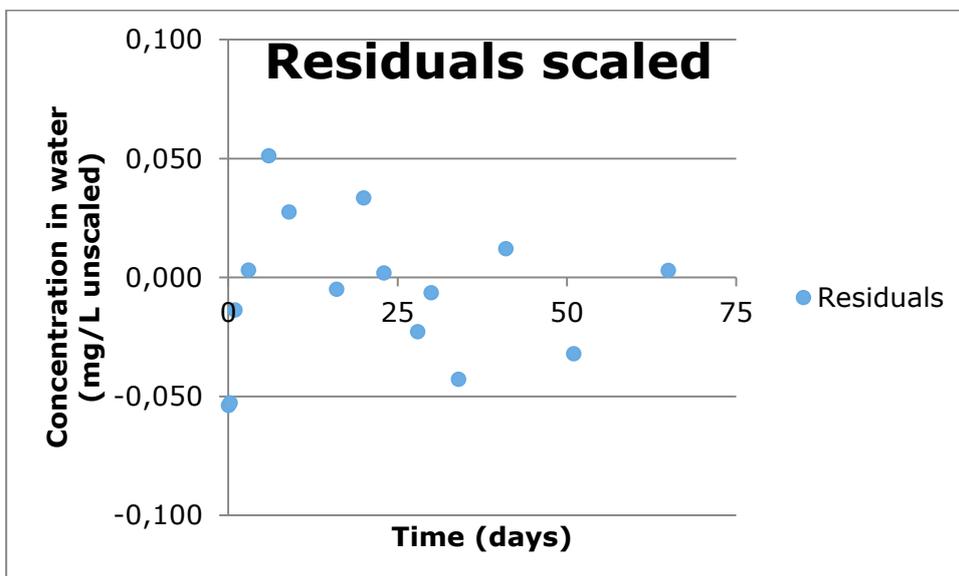


Figure 5.4 Residuals in total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in cosm 4 of Van den Brink (1997). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,\text{ini}} = 10$ d.

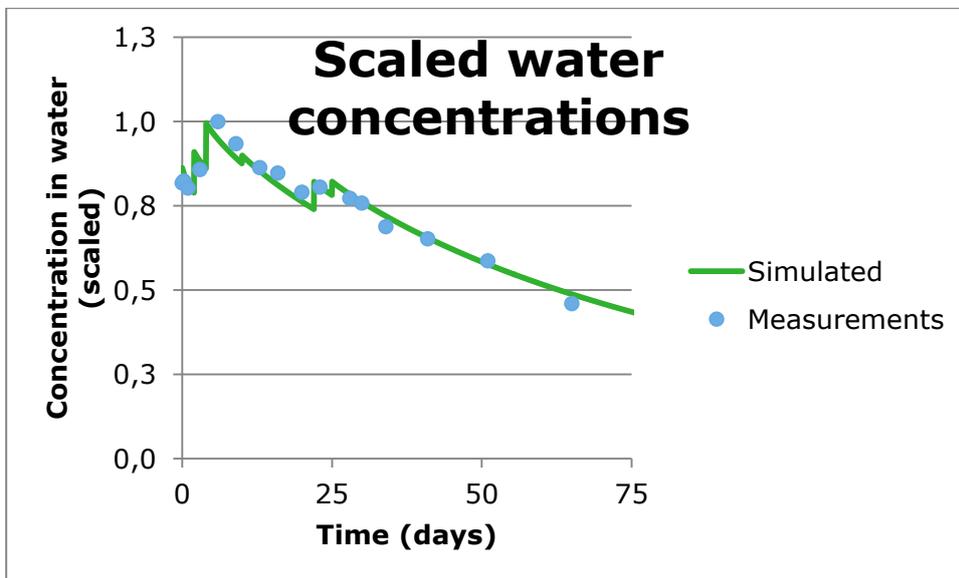


Figure 5.5 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in cosm 8 of Van den Brink (1997). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50,\text{ini}} = 10$ d.

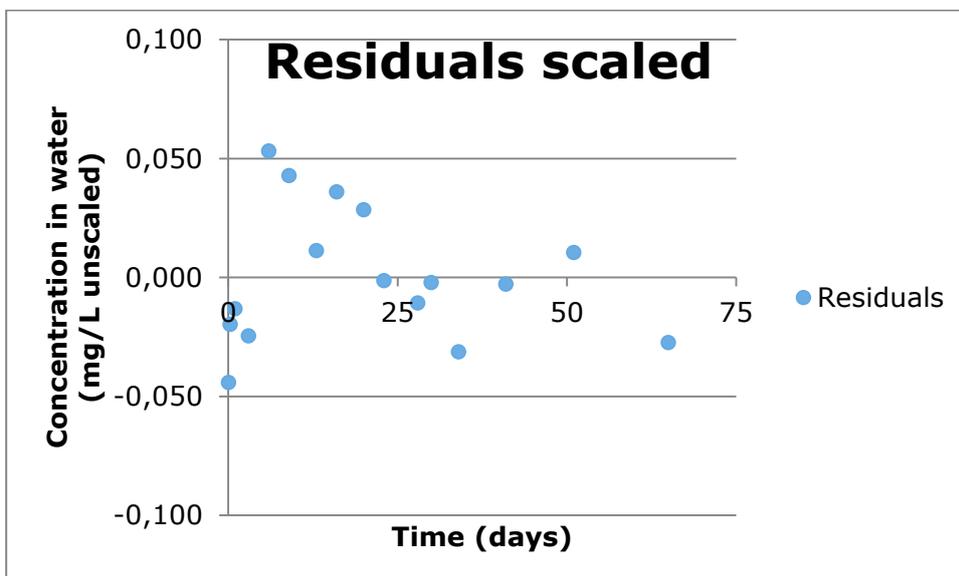


Figure 5.6 Residuals in total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in cosm 8 of Van den Brink (1997). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50,\text{ini}} = 10$ d.

Table 5.10 presents the measured concentrations in water as a function of time in the outdoor cosm of the study of Bromilow et al (2006, Figure 5). The values are given for a single system, tank 8; they represent the total concentration in water, the water was not filtered before extraction, but was directly analysed by the HPLC. In the paper/graph concentrations are reported as percentage of applied mass. These are converted into concentrations on the basis of the calculation given below.

Initial nominal concentration $668 \mu\text{g/L}$, 300 Liters of water. This corresponds to 200.4 mg active added.

Numbers in first 8 lines of data express the mass in the compartment as percentage of total mass initially added. These are converted to concentrations in the second set of data lines, assuming 600 L of water and 5 cm (by 100×100 cm) sediment, corresponding to 50 Liters of sediment, which corresponds to 40 kg of sediment (bulk density = 0.8 kg/L) The third set of numbers represents scaled

concentrations, calculated by dividing all concentrations by the highest concentration observed in water (0.608 mg/L).

Table 5.10

Concentrations in water (mg/L and scaled) and sediment (mg/kg and scaled; 0 – 5 cm layer) as a function of time (d) for the cosm study with linuron by Bromilow et al (2006).

Number	Time (days)	Concentration in water (mg/L)	Concentration in sediment (mg/kg)
Data as given in percentage of total mass added			
1	1	91.0%	2.1%
2	8	64.3%	6.9%
3	14	58.6%	8.6%
4	28	44.3%	7.3%
5	48	34.3%	7.3%
6	92	21.4%	8.6%
7	114	20%	4.4%
8	152	14.3%	4.6%
Data converted to concentrations (see text below)			
1	1	0.608	0.1052
2	8	0.430	0.3465
3	14	0.391	0.4305
4	28	0.296	0.3657
5	48	0.229	0.3657
6	92	0.143	0.4305
7	114	0.134	0.2205
8	152	0.0955	0.2310
Data converted to scaled concentrations			
1	1	1.0000	0.1730
2	8	0.7072	0.5699
3	14	0.6431	0.7081
4	28	0.4868	0.6015
5	48	0.3766	0.6015
6	92	0.2352	0.7081
7	114	0.2204	0.3627
8	152	0.1571	0.3799

The tanks of Bromilow et al (2006) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of the PEST, running TOXSWA many times, according to the procedures presented in Chapters 2 and 4. Three optimisations were performed, each with its own initial values of $DegT_{50,water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (1 and 200 d for $DegT_{50,water}$ and 0.1 and 5.0 (scaled) for $c_{t=0}$). Table 5.11 gives estimates of the optimized $DegT_{50,water}$ for each of the three optimisations. It also specifies the optimised $c_{t=0}$ value, the value of the objective function phi (i.e. the sum of squared differences between model-generated and measured aqueous concentrations), the error percentage of the χ^2 -test and the number of times TOXSWA has been run by PEST. The initial values of 10 and 100 days result in consistent estimates of $DegT_{50,water}$ of 25.8 days with 95% confidence intervals of 17.5 – 34.0 days. The error percentage of 5.1% is an acceptable value according to FOCUS (2006). Changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) affected the estimated value for the $DegT_{50,water}$ to a negligible extent.

Table 5.11

Optimisation results for three sets of initial values of $DegT_{50,water}$ and $C_{t=0}$ for the Bromilow et al (2006) outdoor tank with linuron.

DegT50 ini (d)	$C_{t=0}$ ini, scaled (-)	DegT50 fitted (d)	$C_{t=0}$ fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.0	25.75 (17.5 – 34.0)	1.03 (0.96 – 1.10)	7.5 E-3	5.1%	31
100	1.0	25.75 (17.5 – 34.0)	1.03 (0.96 – 1.10)	7.5 E-3	5.1%	28
10, 19% om	1.0	26.21 (17.5 – 34.9)	1.04 (0.97 – 1.15)	7.5 E-3	5.1%	31

Fig 5.7 presents a good agreement between scaled optimised and measured water concentrations for one optimisation, while Fig 5.8 presents the distribution of the scaled residual between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows a slight trend of increasing residue values with time but the deviations between simulations and measurements are quite small in Figure 6.7 so the fitted $DegT_{50,water}$ is considered reliable.

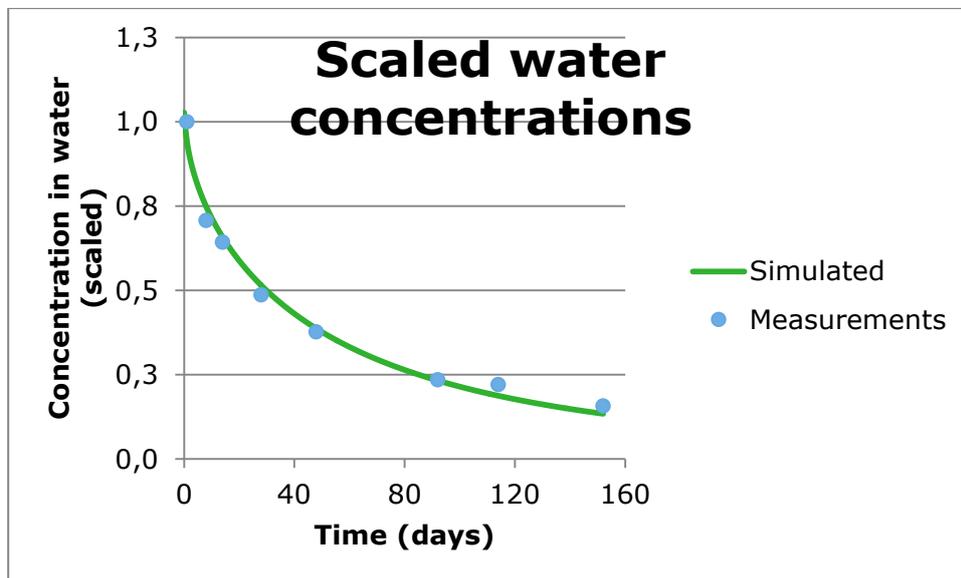


Figure 5.7 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in the cosm of Bromilow (2006). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $DegT_{50,ini} = 10$ d

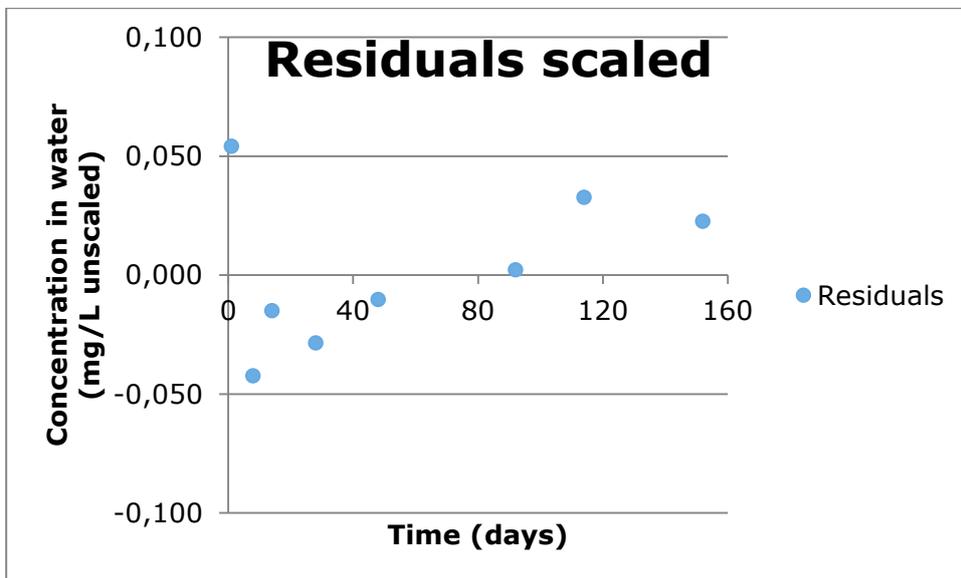


Figure 5.8 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) linuron in water as a function of time (d) in the cosm of Bromilow (2006). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50,\text{ini}} = 10 \text{ d}$

Annex 6 Appendix 6 Data for three cosm studies with imidacloprid

The main characteristics of the studies with imidacloprid in the three cosm studies of Colombo et al (2013), Heimbach and Hendel (2001) and Ratte and Memmert (2003) have been summarized in Table 6.1. The studies have also been briefly described in the main text of Chapter 5.

Table 6.1
Data on cosm studies with imidacloprid

Label in data file	ImiCosm1	ImiCosm2	ImiCosm3
Reference	Colombo <i>et al.</i> (2013)	Heimbach and Hendel (2001)	Ratte and Memmert (2003)
Compound	Imidacloprid (type of material not specified)	Imidacloprid (type of material not specified)	Imidacloprid SL200 formulation, 17.3% w/w imidacloprid
Type of system	Polypropylene containers in outdoor pond	A circular pond and a rectangular tank, both outdoor	13 circular ponds
Dimensions system	45.5 x 30 x 21 cm (20 Liters total volume, 15 L of water, 0.55 cm sediment)	Diameter 2.0 m (water depth 1.0 m) and 0.6 x 1.8 m (water depth 0.3 m)	Water depth 1.0 m, 3100 L (3.1 m ²) or (ponds 11 and 13) 3800 L (3.8 m ²)
Side slope (hor/vert)	0	0	0
Depth water layer	Calculated: 45.5 x 30 cm, 15 Liters of water --> 11.0 cm	Pond 1.0 m, tank 0.3 m (calculations for merged data set used 0.65 m)	All ponds 1.0 m
Depth sediment	0.55 cm	pond: 12 – 15 cm, tank: 12 cm; sediment contained in trays on bottom of pond/tank	10 cm
Sediment om%	3% om silt and clay loam	4.1% oc --> 7.05% om	3.4% oc --> 5.9% om
Sediment bulk density	-	-	-
Sediment porosity	-	-	-
Macrophytes info	None, no turbidity, no colored substances	Pond coverage 30%, tank coverage 60%	<i>Lemna</i> were removed regularly, other macrophytes not mentioned and assumed absent
pH	8-9	7.0 – 8.5, slight increase over time	pH increased from approx. 7.4 on day 0 – 13 to approx. 9.5 (average value on day 35) and then decreased to approx. 7.4 (average value on day 91). Values taken from Figure 91.
Temperature	10 (night) – 24 (day), average value not given	Average air temp in May estimated: 16.7°C	Average water temp days 0 – 191 estimated from graph: 19°C
Light intensity	High levels, UVB 2.35/2.78/2.75 μW/cm ² average after each pulse	No changes in turbidity were observed	Sunny weather on days of application, daily sun hours given
Application number	3	1	2: May 02 and May 23, 2001
Application interval	7 days	-	21 days
Nominal initial application	17.3 μg/L (other conc not monitored often enough)	6.0 μg/L	23.5 and 9.3 μg/L (ponds with initial nominal 3.8, 1.5 and 0.6 ug/L not used for estimation of DegT ₅₀)

In Chapter 4 the input that was common for all cosm studies has been described. In Table 6.2 below we summarized the input values on the physico-chemical properties of imidacloprid and the cosm-specific input, such as e.g. the water depth.

Table 6.2

Parameter values used in the simulations with imidacloprid

Cosm label	ImiCosm1	ImiCosm2	ImiCosm3
Molar mass (g)	255.66		
Saturated vapour pressure (mPa)	4.0 E-7 (25°C)		
Solubility (mg/L)	610 (20°C)		
Kom (estimated) (L/kg)	Kom = 132, 1/n = 0.802		
pKa	n.a.		
Initial $DegT_{50,water}$ (d)	10, 0.5 and 25	10, 0.5 and 25	10, 0.5 and 25
Water depth (m)	0.11	0.65 (average of pond 1.0 and tank 0.30)	1.0
Side slope (hor/vert, -)	0	0	0
Temperature (°C)	17°C (average of 10 and 24)	16.7°C (average air temp in May)	19°C (average water temp over 191 days, estimated from graph)
Measurements in sediment	No, only a single measurement at end of experiment	No, only a single measurement at end of experiment	Yes, but not used in present analysis

Table 6.3 presents the measured concentrations in water as a function of time as well as the loadings and their timings for the outdoor containers in the study of Colombo et al (2013, water concentrations: Figure 1; sediment content: Table 1). Data are given for the 17.3 µg/L treatment level. The values are averages for 7 replicates, values for single systems are not reported; they represent the total concentration in water (incl suspended solids), as the water was not filtered before extraction. At the end of the experiment (56 days after first application) a single measurement of the content of imidacloprid in sediment was performed, resulting in 0.04 µg/kg. Loadings of the second and third application were calculated assuming that the three treatments consisted of dosing with equal values of imidacloprid, which corresponded to 17.3 µg/L (Volume is 15 Liters of water, i.e. 15 * 17.3 µg = 260 µg were dosed. Area of container: 45.5 x 30 cm = 1365 cm²; loading = 260 / 1365 µg/cm² or 1.89 mg/m²).

Table 6.3

Concentrations in water ($\mu\text{g/L}$ and scaled) as a function of time (d) and loadings for the containers with imidacloprid by Colombo et al (2013).

Number	Time in TOXSWA (days)	Concentration in water ($\mu\text{g/L}$)	Scaled concentration in water	Loadings, amount added to system (mg/m^2)	Scaled loadings
1	0	17.2	1.0000		
2	0.25	9.1	0.5291		
3	1	8.0	0.4651		
4	2	4.3	0.2500		
5	3	3.0	0.1744		
6	6.9	1.1	0.06395		
				Load: 08-Jan 1.89 mg/m^2	109.88
7	7.1	17.2	1.0000		
8	8	10.8	0.6297		
9	9	6.4	0.3721		
10	10	4.1	0.2384		
11	13.9	2.0	0.1163		
				Load: 15-Jan 1.89 mg/m^2	109.88
12	14.1	17.2	1.0000		
13	14.25	9.5	0.5523		
14	15	9.5	0.5523		
15	16	5.4	0.3140		
16	17	4.5	0.2616		
17	21	2.6	0.1512		
18	56	0.99	0.05756		

The containers of Colombo et al (2013) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of the PEST, running TOXSWA many times, according to the procedures presented in Chapters 2 and 4. Three optimisations were performed, each with its own initial values of $DegT_{50,water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (0.1 and 100 d for $DegT_{50,water}$ and 0.1 and 5.0 (scaled) for $c_{t=0}$). Table 6.4 gives estimates of the optimized $DegT_{50,water}$ for each of the three optimisations. It also specifies the optimised $c_{t=0}$ value, the value of the objective function phi (i.e. the sum of squared differences between model-generated and measured aqueous concentrations), the error percentage of the χ^2 -test and the number of times TOXSWA has been run by PEST. The initial values of 10 and 100 days result in consistent estimates of $DegT_{50,water}$ of 1.0 days with 95% confidence intervals of 0.77 – 1.25 days. The error percentage of 19.5% is a relatively high value to pass the χ^2 -test according to FOCUS (2006). Changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) affected the estimated value for the $DegT_{50,water}$ to a negligible extent.

Table 6.4

Optimisation results for three sets of initial values of $DegT_{50,water}$ and $c_{t=0}$ for the Colombo et al (2013) containers with imidacloprid

DegT50 ini (d)	$c_{t=0}$, ini, scaled (-)	DegT50 fitted (d)	$c_{t=0}$, fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.0	1.01 (0.77 – 1.25)	0.866 (0.70 – 1.03)	0.184	19.5%	43
100	1.0	1.01 (0.77 – 1.25)	0.866 (0.70 – 1.03)	0.184	19.5%	31
10, 19% om	1.0	1.02 (0.78 – 1.26)	0.873 (0.71 – 1.04)	0.176	19.1%	43

Figure 6.1 presents the agreement between optimised and measured scaled water concentrations for one optimisation, while Figure 6.2 presents the distribution of the scaled residuals between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the

residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

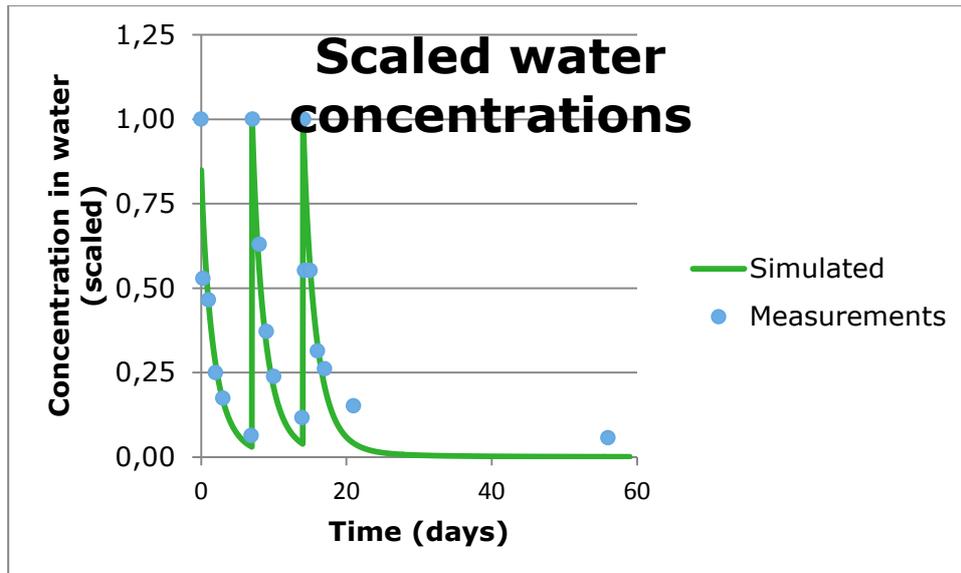


Figure 6.1 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the cosm of Colombo et al (2013). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50,ini} = 10 \text{ d}$

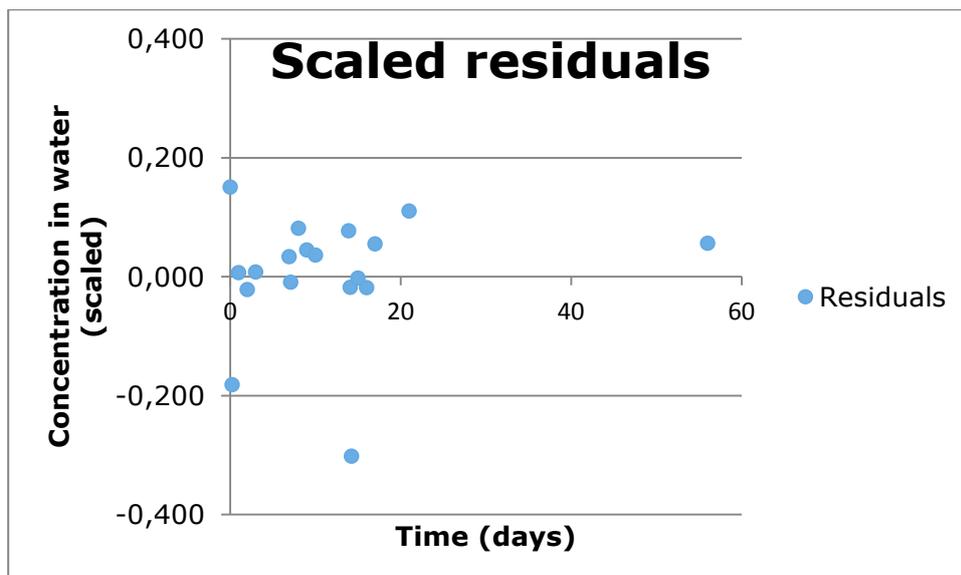


Figure 6.2 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the cosm of Colombo et al (2013). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50,ini} = 10 \text{ d}$

Table 6.5 presents the measured concentrations in water as a function of time in the study of Heimbach and Hendel (2001, water concentrations: Table 11; sediment content: Table 13). No mention is made of filtering the sampled water before extraction, so, the total concentration including suspended solids appears to be measured. Both the pond and the tank were treated at $6.0 \mu\text{g/L}$ nominal initial concentration.

Table 6.5

Concentrations in water ($\mu\text{g/L}$ and scaled) as a function of time (d) and loadings for the containers with imidacloprid by Heimbach and Hendel (2001).

Number	Time in TOXSWA (days)	Concentration in water ($\mu\text{g/L}$)	Scaled concentration
Pond			
1	0.16	3.1	0.7209
2	1	4.3	1.0000
3	2	3.6	0.8372
4	4	2.7	0.6279
5	7	2.1	0.4883
6	11	1.6	0.3721
7	14	1.3	0.3023
8	21	0.9	0.2093
Tank			
9	0.16	5.6	1.0000
10	1	4.4	0.7857
11	2	3.7	0.6607
12	4	2.6	0.4643
13	7	2.1	0.3750
14	11	1.5	0.2679
15	14	1.2	0.2143
16	21	0.7	0.1250

The pond and tank of Heimbach and Hendel (2001) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of the PEST, running TOXSWA many times, according to the procedures presented in Chapters 2 and 4.

The pond and tank data were analysed separately and also analysed as a single, merged data set. For the merged set an average water depth of 0.65 m was used (water depth pond: 1.00 m; water depth tank: 0.30 m). Moreover, for the pond data the data were analysed using either all aqueous concentrations in time (8 points in total) or omitting the first measured concentrations (the authors indicated that this first measured concentration was probably low due to insufficient mixing of the aqueous phase during the first few hours after application).

For all cases three optimisations were performed, each with its own initial values of $DegT_{50,water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (0.1 and 100 d for $DegT_{50,water}$ and 0.1 and 5.0 (scaled) for $c_{t=0}$). Next to estimates of the optimized $DegT_{50,water}$, other results are presented in the tables below: the optimised $c_{t=0}$ value, the value of the objective function phi (i.e. the sum of squared differences between model-generated and measured aqueous concentrations) and the error percentage of the χ^2 -test and the number of times TOXSWA has been run by PEST. For all cases changing the organic matter content of sediment and suspended solids from 9 to 19% organic matter (see Chapter 4.1) affected the estimated value for the $DegT_{50,water}$ to a negligible extent. For the pond and all 8 data points the initial values of 10 and 1 days result in consistent estimates of $DegT_{50,water}$ of 6.9 days with 95% confidence intervals of 3.4 – 10.4 days. The error percentage of 12.7% is an acceptable value according to FOCUS (2006) and thus the χ^2 -test is passed.

Table 6.6

Optimisation results for two sets of initial values of $DegT_{50,water}$ and $C_{t=0}$ for the Heimbach and Hendel (2001) pond with imidacloprid, using all 8 data points

DegT50 ini (d)	$C_{t=0}$ ini, scaled (-)	DegT50 fitted (d)	$C_{t=0}$ fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.0	6.88 (3.37 – 10.39)	0.906 (0.74 – 1.08)	6.58 E-2	12.7%	20
1	1.0	6.89 (3.35 – 10.44)	0.905 (0.73 – 1.07)	6.58 E-2	12.7%	30
10, 19% om	1.0	6.90 (3.36 – 10.44)	0.907 (0.74 – 1.08)	6.57 E-2	12.7%	21

Figure 6.3 presents the agreement between optimised and measured scaled water concentrations for one optimisation, it clearly shows that the first measurement seems to be too low, thus provoking an unsatisfactory agreement during the first days. Figure 6.4 presents the distribution of the scaled residuals between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that for the first few days the residuals are clearly greater than later on, thus reflecting the unsatisfactory fit of Figure 6.3.

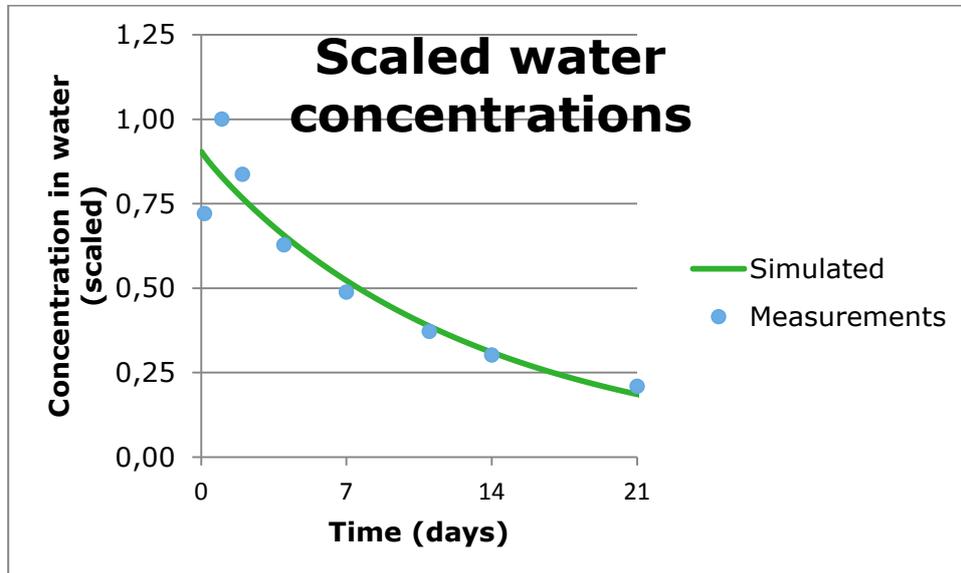


Figure 6.3 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the pond data set of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $DegT_{50,ini} = 10$ d; all data points were included in the calculations.

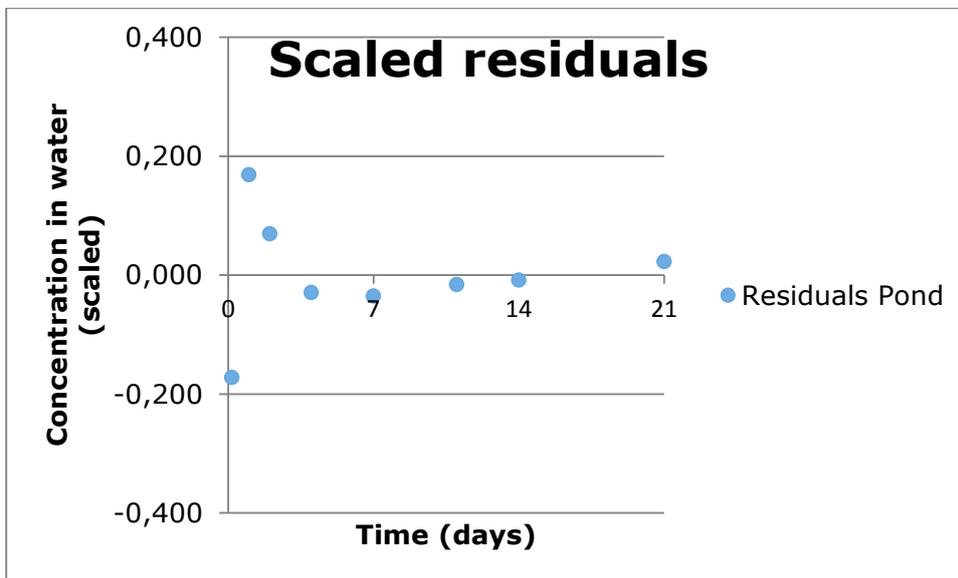


Figure 6.4 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the pond data set of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50,\text{ini}} = 10$ d; all data points were included in the calculations.

Omitting the first data point of the pond because of insufficient mixing, resulted in slightly lower value of DegT_{50} : the $\text{DegT}_{50,\text{water}}$ is estimated at 5.5 days with 95% confidence intervals of 4.0 – 7.1 days. The error percentage of 6.9% is lower than in the former optimisation with all 8 data points and thus the χ^2 -test is passed.

Table 6.7

Optimisation results for two sets of initial values of $\text{DegT}_{50,\text{water}}$ and $c_{t=0}$ for the Heimbach and Hendel (2001) pond with imidacloprid, omitting the first data point because of insufficient mixing

DegT50 ini (d)	$c_{t=0}$ ini, scaled (-)	DegT50 fitted (d)	$c_{t=0}$ fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.0	5.54 (4.00 – 7.08)	1.036 (0.90 – 1.17)	1.57 E-2	6.9%	28
1	1.0	5.54 (4.00 – 7.07)	1.036 (0.90- 1.17)	1.57 E-2	6.9%	45
10, 19% OM	1.0	5.54 (4.00 – 7.09)	1.038 (0.91 – 1.17)	1.56 E-2	6.9%	26

Figure 6.5 presents the agreement between optimised and measured scaled water concentrations for one optimisation, after omitting the first measurement. Compared to Figure 6.3 the agreement clearly improved and is now satisfactory. Figure 6.6 presents the distribution of the scaled residuals between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph now shows that the residuals are neatly randomly scattered around zero (although there seems to be some wave-like trend), demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

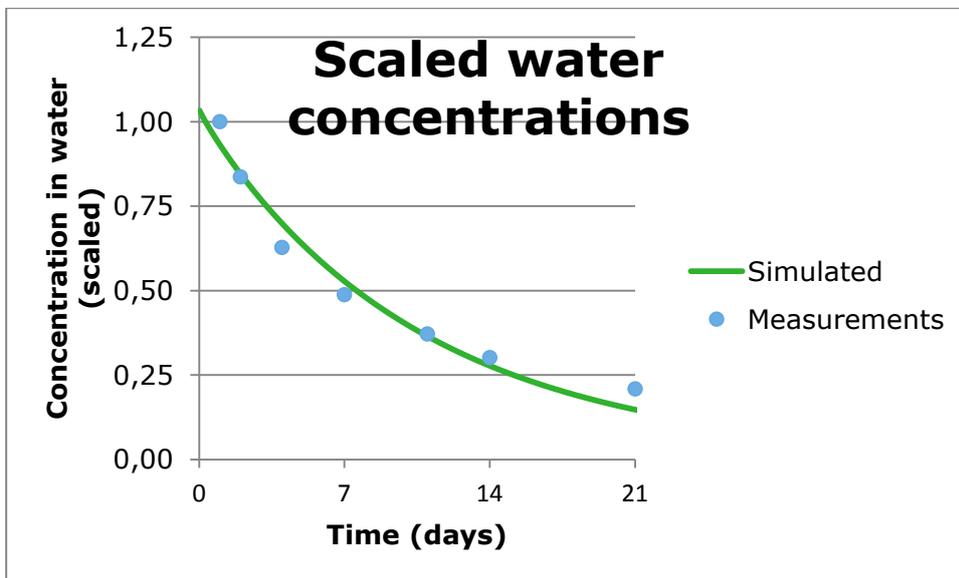


Figure 6.5 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the pond data set of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,\text{ini}} = 10$ d; the first data point was omitted due to insufficient mixing.

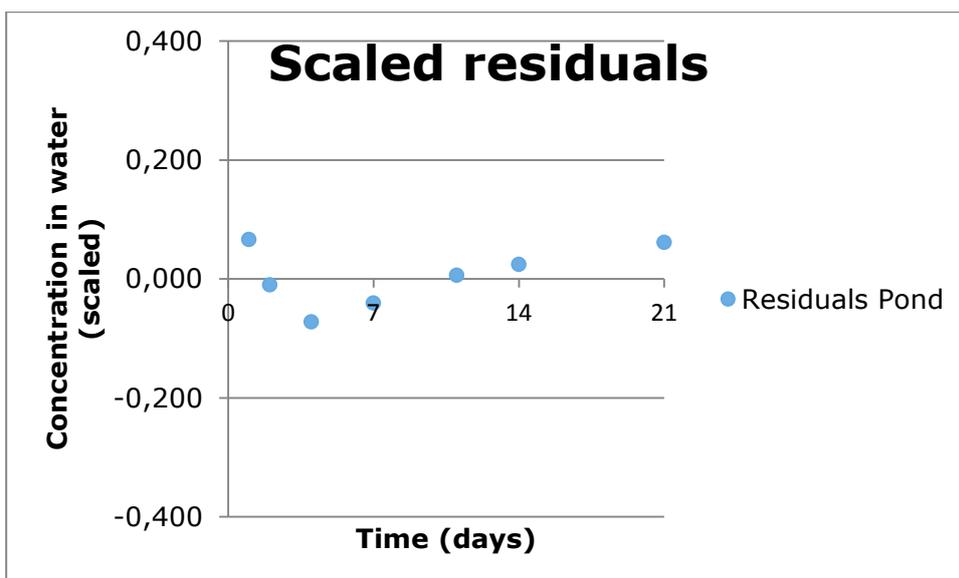


Figure 6.6 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the pond data set of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,\text{ini}} = 10$ d; the first data point was omitted due to insufficient mixing.

For the tank with a water depth of 0.3 m the initial values of 10 and 1 days result in consistent estimates of $\text{Deg}T_{50,\text{water}}$ of 4.3 days with 95% confidence intervals of 3.0 – 5.5 days. The error percentage of 8.3% is an acceptable value according to FOCUS (2006) and thus the χ^2 -test is passed.

Table 6.8

Optimisation results for two sets of initial values of $DegT_{50,water}$ and $C_{t=0}$ for the Heimbach and Hendel (2001) tank with imidacloprid

DegT50 ini (d)	$C_{t=0}$ ini, scaled (-)	DegT50 fitted (d)	$C_{t=0}$ fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.0	4.26 (3.01 – 5.51)	0.949 (0.85 – 1.06)	2.04 E-2	8.3%	29
1	1.0	4.26 (3.01 – 5.51)	0.949 (0.84 – 1.06)	2.04 E-2	8.3%	35
10, 19% OM	1.0	4.27 (3.01 – 5.52)	0.954 (0.85 – 1.06)	2.03 E-2	8.3%	30

Figure 6.7 presents a satisfactory agreement between optimised and measured scaled water concentrations for one optimisation. Figure 6.2 presents the distribution of the scaled residuals between model-generated and measured concentrations, as suggested by FOCUS (2006). The residuals as a function of time are not really randomly scattered around zero, but are wave-shaped, indicating that the estimate of the $DegT_{50,water}$ first seems slightly under-predicted and later on slightly over-predicted by the single $DegT_{50,water}$ value.

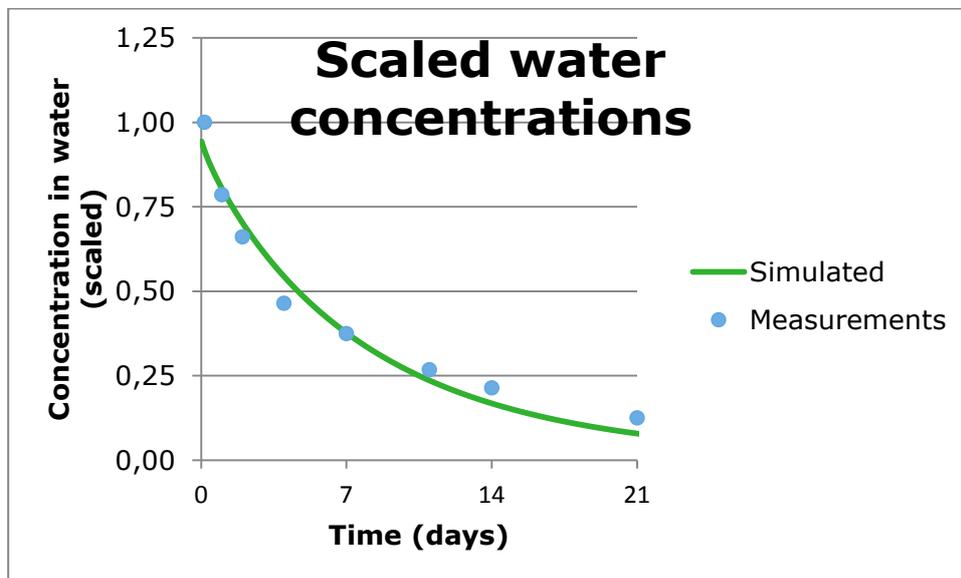


Figure 6.7 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the tank data set of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $DegT_{50,ini} = 10$ d.

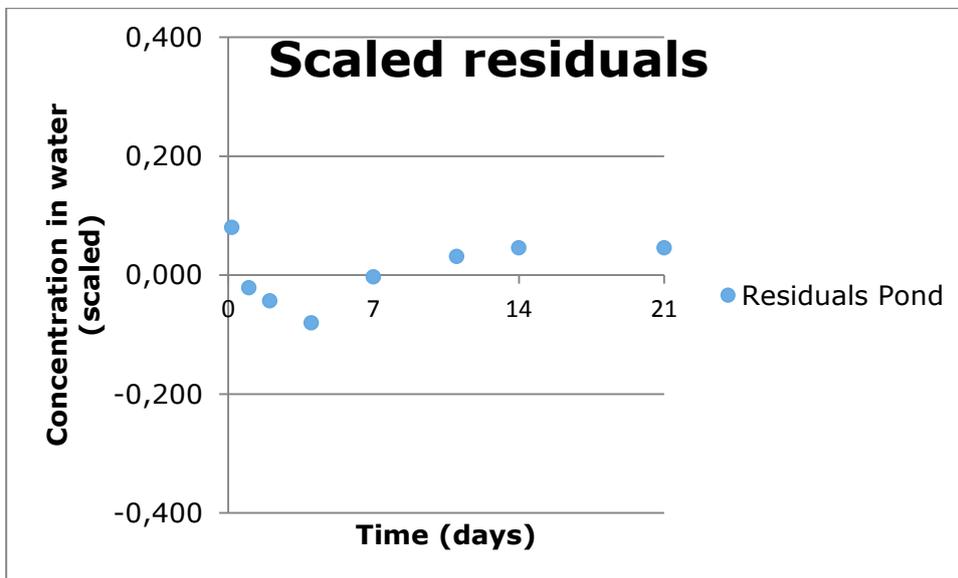


Figure 6.8 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the tank data set of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50,\text{ini}} = 10$ d.

For the merged data set of pond and tank (water depth of 0.65 m) the initial values of 10 and 1 days result in consistent estimates of $\text{DegT}_{50,\text{water}}$ of 5.5 days with 95% confidence intervals of 3.9 – 7.2 days. Clearly, the run with an initial value of $\text{DegT}_{50,\text{water}}$ of 100 days results in an unsatisfactory estimation of $\text{DegT}_{50,\text{water}}$ and $c_{t=0}$ with a much higher sum of squared residuals. The value of 5.5 d compares quite favourably with the geometric mean of values for the pond (when all data are included: $\text{DegT}_{50,\text{water}} = 6.88$ days) and the tank ($\text{DegT}_{50,\text{water}} = 4.26$ days): $\text{DegT}_{50,\text{water}} = 5.41$ days. The error percentage of 14.4% is an acceptable value according to FOCUS (2006) and thus the χ^2 -test is passed.

Table 6.9

Optimisation results for three sets of initial values of $\text{DegT}_{50,\text{water}}$ and $c_{t=0}$ for the Heimbach and Hendel (2001) merged pond and tank data for imidacloprid

DegT50 ini (d)	$c_{t=0}$ ini, scaled (-)	DegT50 fitted (d)	$c_{t=0}$ fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.0	5.54 (3.89 – 7.19)	0.912 (0.80 – 1.02)	0.137	14.4%	32
100	1.0	34.22 (-383 – 452)	0.60 (0.41 – 0.80)	0.761	33.9%	21
1	1.0	5.54 (3.89 – 7.20)	0.912 (0.80 – 1.02)	0.137	14.4%	35
10, 19% om	1.0	5.55 (3.89 – 7.21)	0.914 (0.81 – 1.02)	0.137	14.4%	32

Figure 6.9 presents the agreement between optimised and measured scaled water concentrations for one optimisation, after omitting the first measurement. As shown also by the distribution of the scaled residuals in Figure 6.10 with the residuals for the pond lying mainly above and the residuals for the tank mainly below the zero line, the estimated degradation rate appears to be slightly faster than the rate in the pond and it appears slightly slower than the rate in the tank. This corresponds with the statements above with a geometric mean of $\text{DegT}_{50,\text{water}} = 5.41$ days and values for the pond (when all data are included) of $\text{DegT}_{50,\text{water}} = 6.88$ days and the tank of $\text{DegT}_{50,\text{water}} = 4.26$ days.

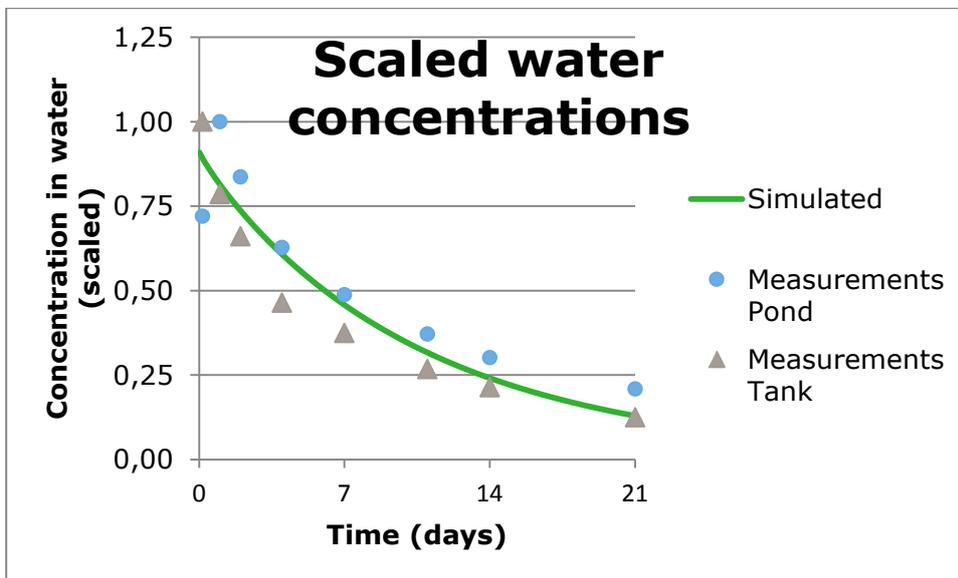


Figure 6.9 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g}\cdot\text{L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the pond and tank of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,ini} = 10$ d

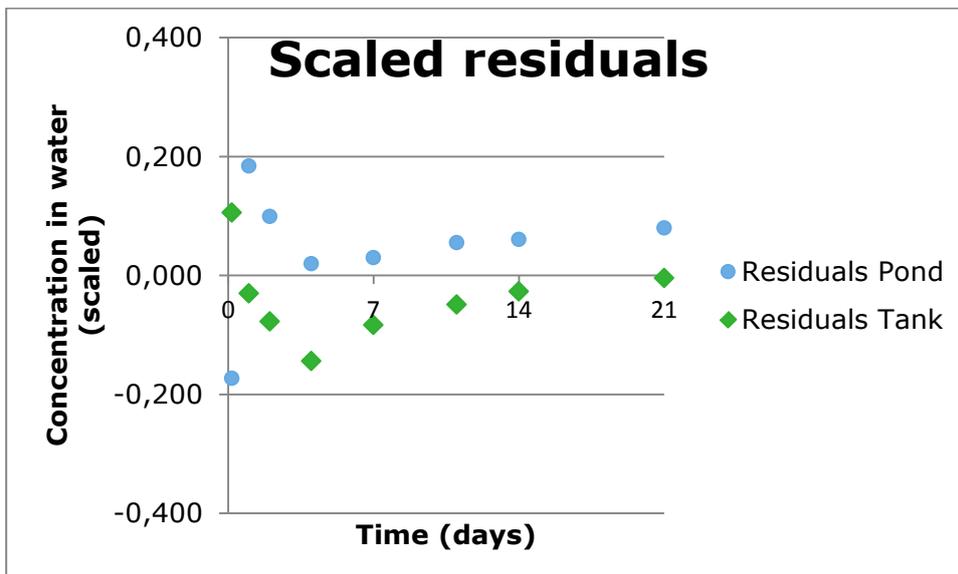


Figure 6.10 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g}\cdot\text{L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) in the pond and tank of Heimbach and Hendel (2001). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,ini} = 10$ d

Tables 6.10 up to 6.14 present the measured concentrations in water as a function of time in the study by Ratte and Memmert (2003). No mention is made of filtering the sampled water before extraction, so, the total concentration including suspended solids appears to be measured. Table 4 in the analytical report accompanying the main body of the study report gives data for aqueous concentrations measured in ponds 13 and 7 (26.5 $\mu\text{g}/\text{L}$ nominal initial), 8 and 2 (9.4 $\mu\text{g}/\text{L}$ nominal initial), 9 and 3 (3.8 $\mu\text{g}/\text{L}$ nominal initial), 10 and 6 (1.5 $\mu\text{g}/\text{L}$ nominal initial), 5 and 11 (0.6 $\mu\text{g}/\text{L}$ nominal initial). For brevity only the systems with the two highest treatment levels, ponds 7, 13, 8 and 2 were used for the estimation of $\text{Deg}T_{50,water}$.

Authors have provided measured concentrations in dosing solutions and the amount of dosing solution applied to each of the systems. These loadings (in mg/system) were converted into loadings/ m^2 by

taking into account the dimensions of the system (water depth of 1 meter, volumes of each of the systems given as 3100 L and therefore an area of 3.1 m², except for ponds 11 and 13 which have a volume of 3800 L and therefore an area of 3.8 m²). Scaled loadings were calculated by dividing the loading (in mg/m²) by the highest aqueous concentration (in mg/L), analogous to the scaling of aqueous concentrations.

Table 6.10

Concentrations in water (µg/L and scaled) as a function of time (d) and loadings for the ponds 13 and 7 with imidacloprid by Ratte and Memmert (2003).

Number	Time in TOXSWA (days)	Pond number	Concentration in water (µg/L)	Scaled concentration
1	0.16	13	35.3	1.0000
2	2	13	21.1	0.5977
3	4	13	17.5	0.4958
4	7	13	14.2	0.4023
5	14	13	6.11	0.1731
6	20.95	13	2.86	0.0810
Loading 22 january 2000: 89.29 mg, 23.50 mg/m ² , scaled: 665.7				
7	21.16	13	34.7	0.9830
8	23	13	21.5	0.6091
9	25	13	14.3	0.4051
10	28	13	9.43	0.2671
11	35	13	4.26	0.1207
12	49	13	1.42	0.0402
13	63	13	0.197	0.0056
14	77	13	0.186	0.0053
15	91	13	0.104	0.0029
16	0.16	7	32.2	1.0000
17	2	7	19.0	0.5901
18	4	7	17.1	0.5311
19	7	7	13.7	0.4255
20	14	7	5.95	0.1848
21	20.95	7	2.93	0.0910
Loading 22 january 2000: 73.79 mg, 23.80 mg/m ² , scaled: 739.13				
22	21.16	7	31.6	0.9814
23	23	7	21.0	0.6522
24	25	7	14.6	0.4534
25	28	7	10.2	0.3168
26	35	7	5.77	0.1792
27	49	7	1.87	0.0581
28	63	7	0.257	0.0080
29	77	7	0.198	0.0062

Table 6.11

Concentrations in water ($\mu\text{g/L}$ and scaled) as a function of time (d) and loadings for the ponds 8 and 2 with imidacloprid by Ratte and Memmert (2003).

Number	Time in TOXSWA (days)	Pond number	Concentration in water ($\mu\text{g/L}$)	Scaled concentration
30	0.16	8	11.8	1.0000
31	2	8	7.84	0.6644
32	4	8	6.74	0.5712
33	7	8	5.46	0.4627
34	14	8	2.61	0.2212
35	20.95	8	1.15	0.0975
Loading 22 january 2000: 29.52 mg, 9.52 mg/m ² , scaled: 806.8				
36	21.16	8	11.6	0.9831
37	23	8	7.56	0.6407
38	25	8	5.48	0.4644
39	28	8	3.89	0.3297
40	35	8	2.22	0.1881
41	49	8	1.01	0.0856
42	63	8	0.212	0.0180
43	77	8	0.191	0.0162
44	91	8	0.159	0.0135
45	0.16	2	12.0	0.9677
46	2	2	7.45	0.6008
47	4	2	6.71	0.5411
48	7	2	5.41	0.4363
49	14	2	2.48	0.2000
50	20.95	2	1.35	0.1089
Loading 22 january 2000: 29.52 mg, 9.52 mg/m ² , scaled: 767.7				
51	21.16	2	12.4	1.0000
52	23	2	7.78	0.6274
53	25	2	5.99	0.4831
54	28	2	4.18	0.3371
55	35	2	2.32	0.1871
56	49	2	1.08	0.0871
57	63	2	0.219	0.0177
58	77	2	0.129	0.0104

Table 6.12

Concentrations in water ($\mu\text{g/L}$ and scaled) as a function of time (d) and loadings for the ponds 9 and 3 with imidacloprid by Ratte and Memmert (2003).

Number	Time in TOXSWA (days)	Pond number	Concentration in water ($\mu\text{g/L}$)	Scaled concentration
59	0.16	9	4.39	1.0000
60	2	9	2.37	0.5399
61	2	9	2.50	0.5695
62	4	9	2.36	0.5376
63	7	9	1.53	0.3485
64	14	9	0.787	0.1793
65	20.95	9	0.512	0.1166
Loading 22 january 2000: 11.93 mg, 3.85 mg/m ² , scaled: 877.0				
66	21.16	9	3.93	0.8952
67	23	9	3.77	0.8588
68	25	9	2.77	0.6310
69	28	9	1.827	0.4162
70	35	9	1.277	0.2909
71	49	9	0.729	0.1661
72	63	9	0.411	0.0936
73	77	9	0.279	0.0636
74	91	9	0.196	0.0447
75	0.16	3	3.89	0.7086
76	2	3	3.00	0.5465
77	4	3	2.68	0.4882
78	7	3	2.18	0.3971
79	14	3	1.159	0.2111
80	20.95	3	0.769	0.1401
Loading 22 january 2000: 11.93 mg, 3.85 mg/m ² , scaled: 701.3				
81	21.16	3	5.49	1.0000
82	23	3	3.63	0.6612
83	25	3	2.73	0.4973
84	28	3	1.99	0.3625
85	35	3	1.214	0.2211
86	49	3	0.548	0.0998
87	63	3	0.333	0.0607
88	77	3	0.219	0.0399
89	91	3	0.142	0.0259

Table 6.13

Concentrations in water ($\mu\text{g/L}$ and scaled) as a function of time (d) and loadings for the ponds 10 and 6 with imidacloprid by Ratte and Memmert (2003).

Number	Time in TOXSWA (days)	Pond number	Concentration in water ($\mu\text{g/L}$)	Scaled concentration
90	0.16	10	1.59	0.9578
91	2	10	0.65	0.3916
92	2	10	0.98	0.5904
93	4	10	0.97	0.5843
94	7	10	0.80	0.4819
95	14	10	0.308	0.1855
96	20.95	10	0.240	0.1446
Loading 22 january 2000: 4.71 mg, 1.52 mg/m ² , scaled: 915.7				
97	21.16	10	1.66	1.0000
98	23	10	1.42	0.8554
99	25	10	0.99	0.5964
100	28	10	0.822	0.4952
101	35	10	0.616	0.3711
102	49	10	0.353	0.2127
103	63	10	0.212	0.1277
104	77	10	0.156	0.0940
105	91	10	0.101	0.0608
106	0.16	6	1.48	0.6637
107	2	6	1.04	0.4664
108	4	6	0.81	0.3632
109	7	6	0.75	0.3363
110	14	6	0.384	0.1722
111	20.95	6	0.226	0.1014
Loading 22 january 2000: 4.71 mg, 1.52 mg/m ² , scaled: 681.6				
112	21.16	6	2.23	1.0000
113	23	6	1.40	0.6278
114	25	6	1.11	0.4978
115	28	6	0.85	0.3812
116	35	6	0.651	0.2919
117	49	6	0.317	0.1422
118	63	6	0.215	0.0964
119	77	6	0.177	0.0794
120	91	6	0.108	0.0484

Table 6.14

Concentrations in water ($\mu\text{g/L}$ and scaled) as a function of time (d) and loadings for the ponds 5 and 11 with imidacloprid by Ratte and Memmert (2003).

Number	Time in TOXSWA (days)	Pond number	Concentration in water ($\mu\text{g/L}$)	Scaled concentration
121	0.16	5	0.69	0.7348
122	2	5	0.446	0.4750
123	4	5	0.309	0.3291
124	7	5	0.286	0.3046
125	14	5	0.149	0.1587
126	20.95	5	< 0.1	
Loading 22 january 2000: 1.88 mg, 0.607 mg/m ² , scaled: 646.4				
127	21.16	5	0.939	1.0000
128	23	5	0.651	0.6933
129	25	5	0.531	0.5655
130	28	5	0.381	0.4058
131	35	5	0.295	0.3142
132	0.16	11	0.65	0.7386
133	2	11	0.401	0.4557
134	4	11	0.286	0.3250
135	7	11	0.257	0.2921
136	14	11	0.165	0.1875
137	20.95	11	< 0.1	
Loading 22 january 2000: 2.28 mg, 0.600 mg/m ² , scaled: 681.8				
138	21.16	11	0.88	1.0000
139	23	11	0.640	0.7273
140	25	11	0.528	0.6000
141	28	11	0.479	0.5443
142	35	11	0.272	0.3091
143	49	11	0.128	0.1455

Assessment of optimized values

The ponds 7, 13, 2 and 8 of Ratte and Memmert (2003) were inversely modelled and the agreement between measured and simulated aqueous concentrations (scaled) was optimised with the aid of the PEST, running TOXSWA many times, according to the procedures presented in Chapters 2 and 4.

Estimation of $DegT_{50,water}$ were performed for each of the ponds 7 and 13 (nominal initial concentration 26.5 $\mu\text{g/L}$) and ponds 2 and 8 (nominal initial concentration 9.3 $\mu\text{g/L}$) separately. Systems could not be merged in the calculations because of repeated dosing of the test substance causing different 'loadings' to be used for the second application (TOXSWA cannot simultaneously perform calculations with systems needing different 'loadings' on the same day). For each pond two optimisations were performed, each with its own initial values of $DegT_{50,water}$ and $c_{t=0}$ and specified lower and upper parameter bounds (0.1 and 100 d for $DegT_{50,water}$ and 0.1 and 5.0 (scaled) for $c_{t=0}$).

Next to estimates of the optimized $DegT_{50,water}$, other results are presented in the tables below: the optimised $c_{t=0}$ value, the value of the objective function phi (i.e. the sum of squared differences between model-generated and measured aqueous concentrations) and the error percentage of the χ^2 -test and the number of times TOXSWA has been run by PEST. We only considered the influence of the change in organic matter content of sediment and suspended solids from 9 to 19% organic matter for the ponds 7 and 2 and found that in both cases the estimated value for the $DegT_{50,water}$ was affected to a negligible extent.

The initial values for $DegT_{50,water}$ of 10 and 1 day resulted in an estimate of for the $DegT_{50,water}$ of 5.5 days with relatively large 95% confidence intervals of 4.3 – 6.6 days (Table 6.15). The error percentage of 14.4% is an acceptable value for field experiments according to FOCUS (2006), so the optimisation passed the χ^2 -test.

Table 6.15

Optimisation results for two sets of initial values of $DegT_{50,water}$ and $C_{t=0}$ for the Ratte and Memmert (2003) pond 7 (26.5 $\mu\text{g/L}$) for imidacloprid

DegT50 ini (d)	$C_{t=0}$ ini, scaled (-)	DegT50 fitted (d)	$C_{t=0}$ fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.0	5.45 (4.3 – 6.6)	0.926 (0.80- 1.05)	6.67 E-2	14.4%	19
1	1.0	5.45 (4.3 – 6.6)	0.926 (0.80- 1.05)	6.67 E-2	14.4%	32
10, 19% om	1.0	5.46 (4.3 – 6.6)	0.927 (0.80 – 1.05)	6.70 E-2	14.4%	20

Fig 6.11 presents the agreement between scaled optimised and measured water concentrations for one optimisation for pond 7, while Fig 6.12 presents the distribution of the scaled residual between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

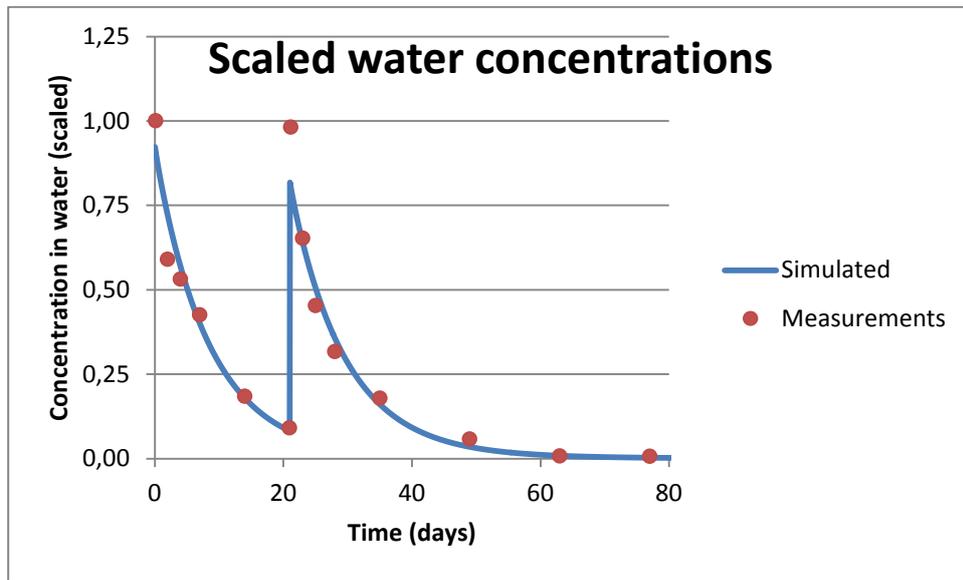


Figure 6.11 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for pond 7 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $DegT_{50,ini} = 10$ d.

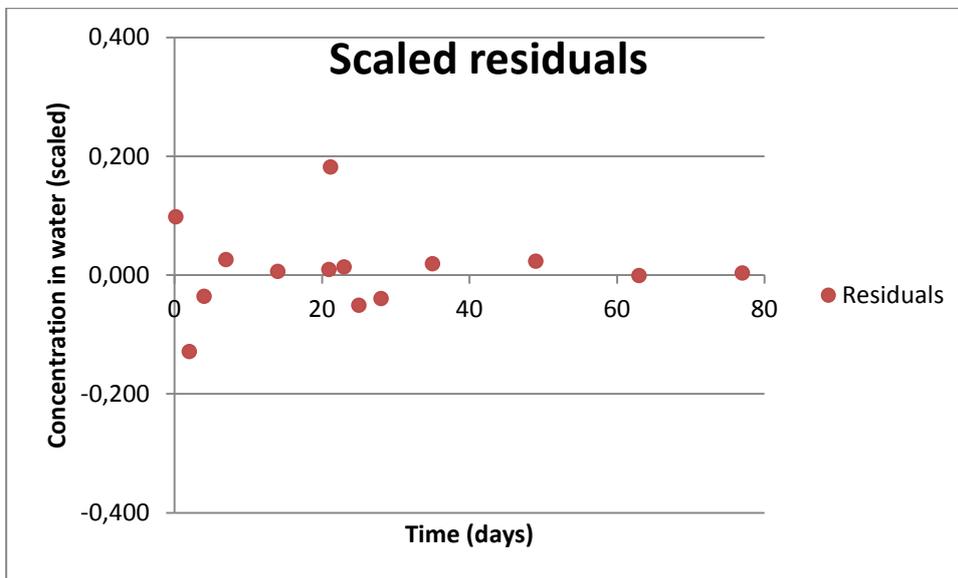


Figure 6.12 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for pond 7 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,\text{ini}} = 10$ d.

The initial values for $\text{Deg}T_{50,\text{water}}$ of 10 and 1 day resulted in an estimate of for the $\text{Deg}T_{50,\text{water}}$ of 5.3 days with a 95% confidence intervals of 3.9 – 6.6 days (Table 6.16). The error percentage of 19.5% is a relatively large value for the χ^2 -test, even for field experiments according to FOCUS (2006).

Table 6.16

Optimisation results for two sets of initial values of $\text{Deg}T_{50,\text{water}}$ and $C_{t=0}$ for the Ratte and Memmert (2003) pond 13 (26.5 $\mu\text{g/L}$) for imidacloprid

$\text{Deg}T_{50}$ ini (d)	$C_{t=0}$ ini, scaled (-)	$\text{Deg}T_{50}$ fitted (d)	$C_{t=0}$ fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.0	5.29 (3.9 – 6.6)	0.923 (0.77 – 1.07)	0.106	19.5%	22
1	1.0	5.28 (3.9 – 6.6)	0.924 (0.77 – 1.07)	0.102	19.5%	34

Fig 6.13 presents the agreement between scaled optimised and measured water concentrations for pond 13, which is slightly worse than the agreement for pond 7. Fig 6.14 presents the distribution of the scaled residual between model-generated and measured concentrations, the residual corresponding to the second loading clearly is the highest one. The other residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

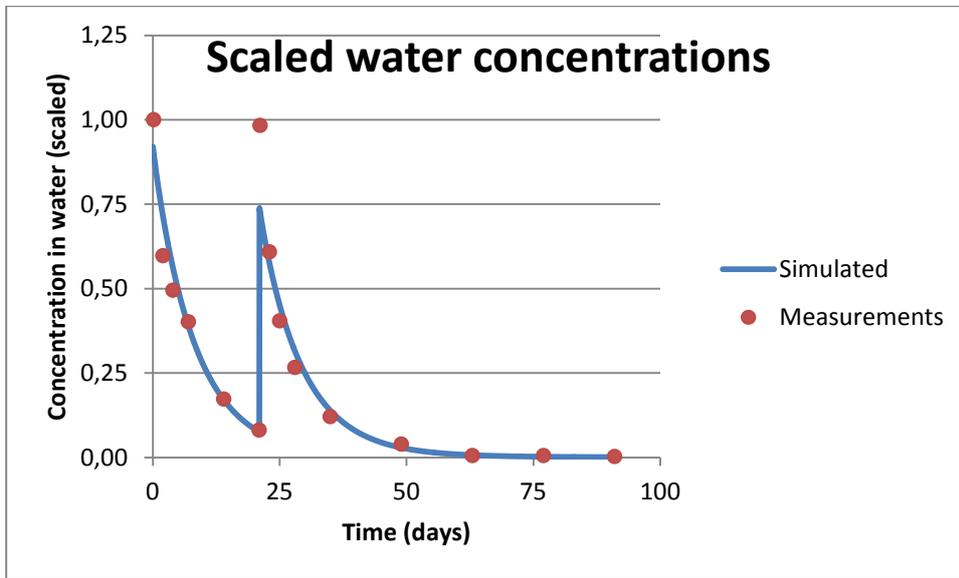


Figure 6.13 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for pond 13 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,\text{ini}} = 10$ d.

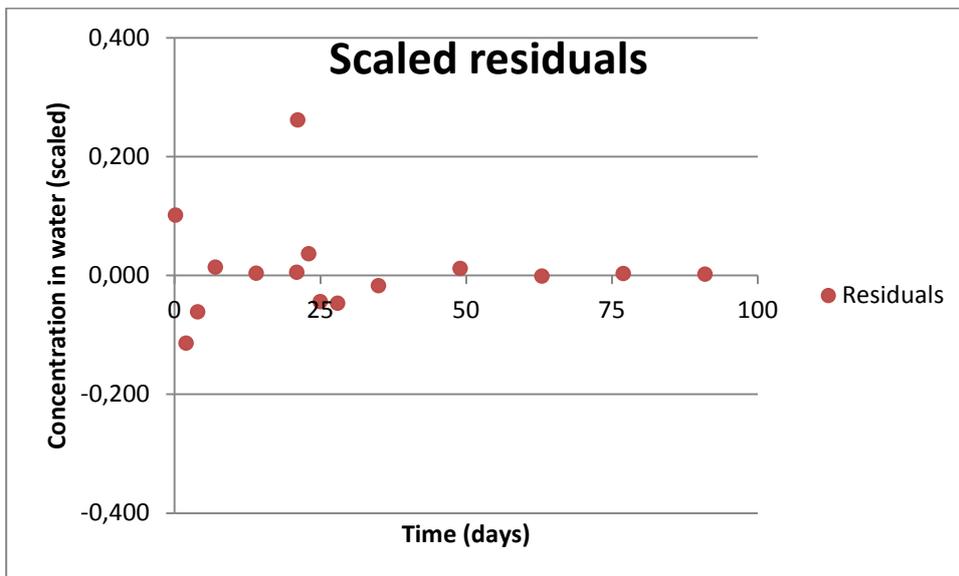


Figure 6.14 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for pond 13 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,\text{ini}} = 10$ d.

The initial values for $\text{Deg}T_{50,\text{water}}$ of 10 and 1 day resulted in an estimate of for the $\text{Deg}T_{50,\text{water}}$ of 5.6 days with a 95% confidence intervals of 4.5 – 6.6 days (Table 6.17). The error percentage of 13.1% is an acceptable value for field experiments according to FOCUS (2006), so the optimisation for pond 2 passed the χ^2 -test.

Table 6.17

Optimisation results for two sets of initial values of $DegT_{50,water}$ and $c_{t=0}$ for the Ratte and Memmert (2003) pond 2 (9.3 $\mu\text{g/L}$) for imidacloprid

DegT50 ini (d)	$c_{t=0}$ ini, scaled (-)	DegT50 fitted (d)	$c_{t=0}$ fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.0	5.57 (4.5 – 6.6)	0.916 (0.80 – 1.03)	5.79 E-2	13.1%	19
1	1.0	5.57 (4.5 – 6.6)	0.916 (0.80 – 1.03)	5.79 E-2	13.1%	30
10, 19% om	1.0	5.58 (4.5 – 6.6)	0.917 (0.80 – 1.03)	5.80 E-2	13.1%	18

The influence of organic matter content on the estimate of DegT50 appears negligible, as was already concluded for the data for pond 7.

Fig 6.15 presents the agreement between scaled optimised and measured water concentrations. Figure 6.16 presents the distribution of the scaled residual between model-generated and measured concentrations. The residual corresponding to the second loading is again the highest one, while the other residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

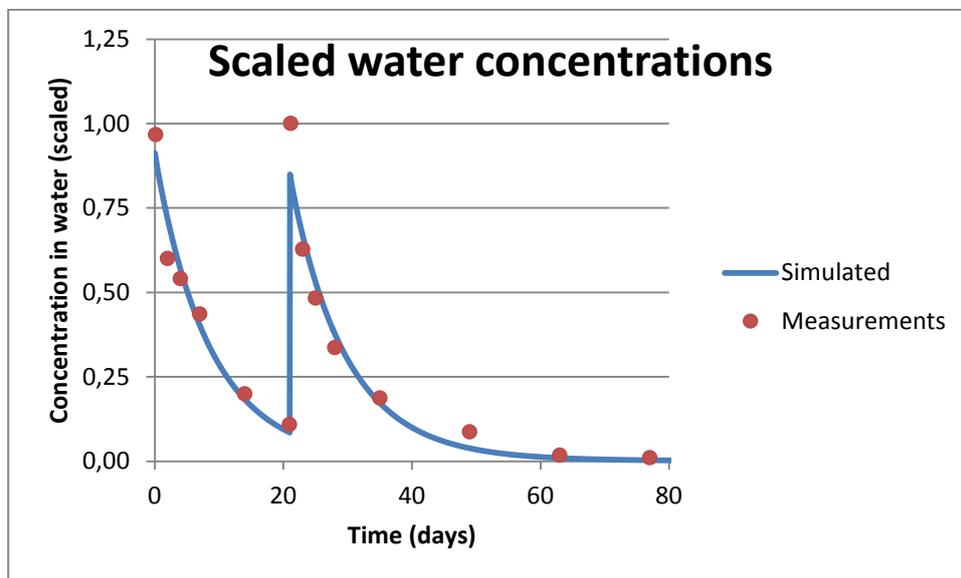


Figure 6.15 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for pond 2 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $DegT_{50,ini} = 10$ d.

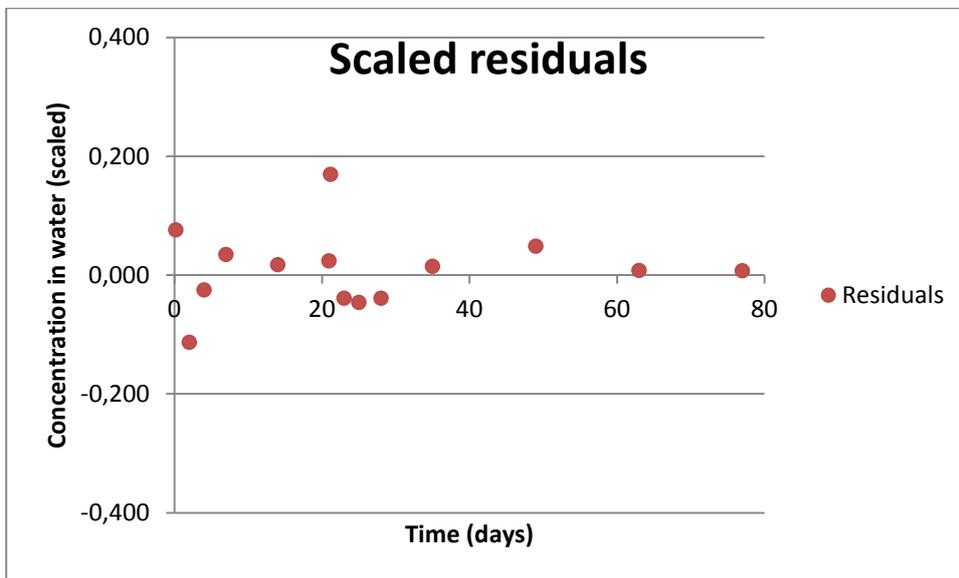


Figure 6.16 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for pond 2 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{DegT}_{50,\text{ini}} = 10$ d.

The initial values for $\text{DegT}_{50,\text{water}}$ of 10 and 1 day resulted in an estimate of for the $\text{DegT}_{50,\text{water}}$ of 5.2 days with relatively large 95% confidence intervals of 4.4 – 6.0 days (Table 6.18). The error percentage of 11.4% is an acceptable value for field experiments according to FOCUS (2006), so the optimisation passed the χ^2 -test.

Table 6.18

Optimisation results for two sets of initial values of $\text{DegT}_{50,\text{water}}$ and $c_{t=0}$ for the Ratte and Memmert (2003) pond 8 ($9.3 \mu\text{g/L}$) for imidacloprid

DegT50 ini (d)	$c_{t=0}$ ini, scaled (-)	DegT50 fitted (d)	$c_{t=0}$ fitted, scaled (-)	Phi (-)	Err%	TOXSWA iterations
10	1.0	5.22 (4.4 – 6.0)	0.981 (0.89 – 1.08)	4.26 E-2	11.4%	26
1	1.0	5.22 (4.4 – 6.0)	0.981 (0.89 – 1.08)	4.26 E-2	11.4%	31

Fig 6.17 presents an satisfactory agreement between scaled optimised and measured water concentrations for one optimisation for pond 8, while Figure 6.18 presents the distribution of the scaled residual between model-generated and measured concentrations, as suggested by FOCUS (2006). The graph shows that the residuals are randomly scattered around zero, demonstrating that there is no pattern of under- or over-prediction by the TOXSWA model.

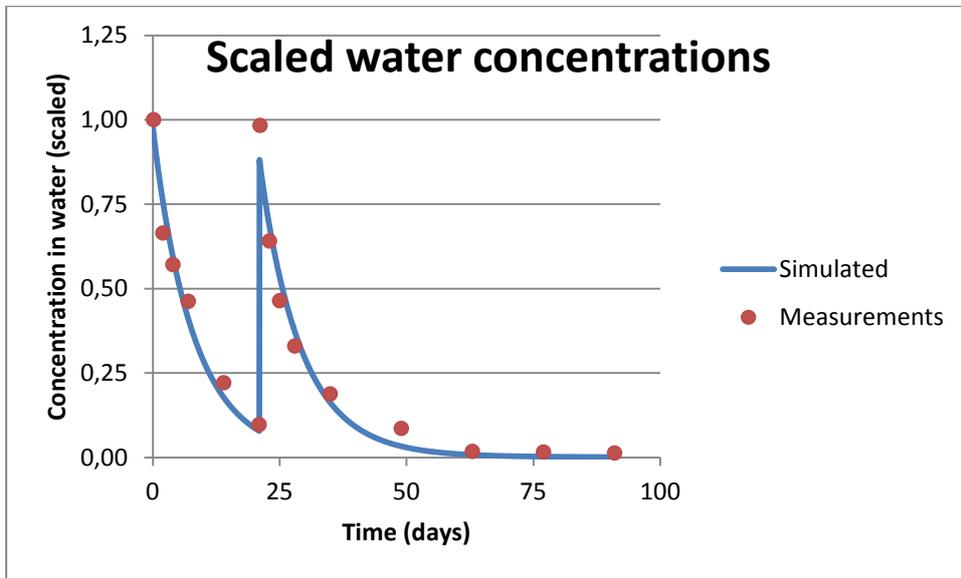


Figure 6.17 Total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for pond 8 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,\text{ini}} = 10$ d.

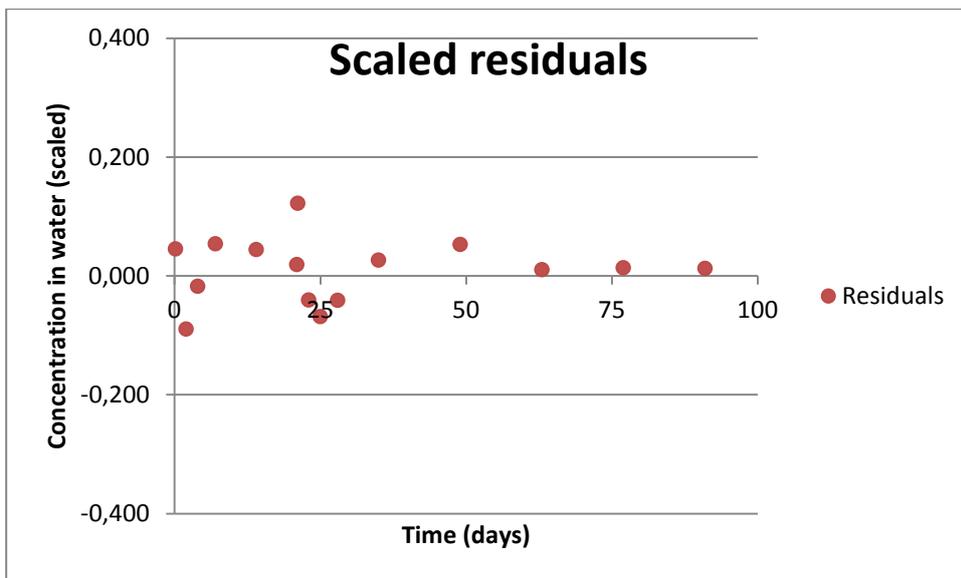


Figure 6.18 Residuals of total concentration (dissolved+ sorbed to suspended solids, $\mu\text{g.L}^{-1}$) imidacloprid in water as a function of time after first measurement (d) for pond 8 in the data set of Ratte and Memmert (2003). Simulated concentration profiles obtained by PEST_TOXSWA optimisation for $\text{Deg}T_{50,\text{ini}} = 10$ d.

Annex 7 Manual for the software for estimation of degradation rates in water ('Cookbook')

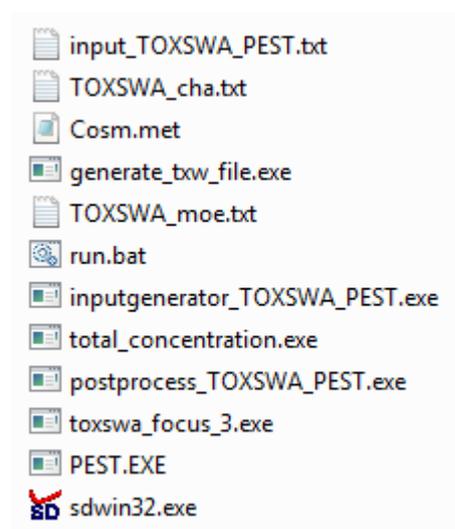
Instruction for running TOXSWA PEST

Jos Boesten, 23 December 2015

1 Overview of the process

Step 1

Install the files as shown in the list below on a local subdirectory:



Step 2

Modify the input files that require action from the user (see Section 3):

the *cosm.met* file containing the meteo data

the *TOXSWA_cha.txt* file which contains the TOXSWA input parameters that have to be specified by the user

the *input_TOXSWA_PEST.txt* file which contains the measured data and initial guesses of the parameters.

Step 3

Run the optimisation by clicking the *run.bat* file which contains:

```
inputgenerator_TOXSWA_PEST  
RUN_PEST.bat
```

Step 4

Inspect the output files:

time_course_TOXSWA.txt contains the simulated time series of the concentrations in terms of time-concentration pairs; e.g.:

```

0.02 0.110947E+01
0.06 0.110667E+01
0.10 0.110392E+01
0.15 0.110122E+01
0.19 0.109857E+01
0.23 0.109597E+01
0.27 0.109341E+01
0.31 0.109089E+01
0.35 0.108843E+01
0.40 0.108601E+01
0.44 0.108363E+01
0.48 0.108129E+01
0.52 0.107899E+01
0.56 0.107672E+01
0.60 0.107449E+01
0.65 0.107227E+01
0.69 0.107011E+01

```

TOXSWA_PEST_output.txt contains the results of the optimisation, e.g.:

TOXSWA OK

concentration includes molecules sorbed to suspended solids

95th percentile of chi2 for 12 degrees of freedom based on 14 data points = 21.026

chi2 error (%) : 1.8

Sum of squared weighted residuals : 0.068795

Total model calls: 24

Parameter	Estimated value	95% percent confidence limits	
		lower limit	upper limit
factor	1.10986	1.03968	1.18003
degt50wl	10.6674	7.66865	13.6662

Sum of squared weighted residuals (ie phi) = 6.87950E-02

Contribution to phi from observation group "group_1" = 4.65474E-02

Contribution to phi from observation group "group_2" = 2.22477E-02

Parameter correlation coefficient matrix

	c_zero_ini	degt50wl
factor	1.000	-0.5988
degt50wl	-0.5988	1.000

echoing of measured data points for graph

nr	time	measured	fitted
1	0.00000	1.20000	1.10947
2	1.00000	1.00000	1.05370
3	2.00000	0.96000	1.01090
4	4.00000	0.91000	0.93845
5	7.00000	0.90000	0.84571
6	12.00000	0.82000	0.71720
7	22.00000	0.66000	0.52379
1	0.00000	1.10000	1.10947
2	1.00000	1.00000	1.05370
3	4.00000	0.95000	0.93845
4	7.00000	0.85000	0.84571

5	12.00000	0.67000	0.71720
6	22.00000	0.45000	0.52379
7	41.00000	0.19000	0.29700

In this file, the parameter 'factor' specifies a multiplication factor: this is the value with which the initial guess of the initial concentration and the additional loadings have to be multiplied to obtain the optimised input parameters.

2. Background information

Description of the files that require no change from the user:

```

--- the executables (exe) perform the different jobs:
# inputgenerator_TOXSWA_PEST generates the required input files for the whole procedure
# generate_twx_file generates a new TOXSWA input file (cosm.twx) after each parameter adjustment
# toxswa_focus_3 performs the TOXSWA calculations
# total_concentration calculates the total concentration in the water if the water samples of the
measured concentrations have not been filtered (so concentration is then sum of concentration in
water plus concentration sorbed at suspended solids)
# sdwin32 extracts data from the TOXSWA output file
# pest performs the PEST optimisation
# postprocess_TOXSWA_PEST processes the PEST and TOXSWA output.

```

--- the *TOXSWA_moe.txt* file is a template of an TOXSWA input file (see Annex 8) which does not need to be changed by the user.

3. Instruction for changing the input files

The *input_TOXSWA_PEST.txt* file contains the initial guesses of the parameters plus the measured data; the file is self-explanatory as follows from the following example:

```

1  0.1  5          factor for concentration and loadings: initial guess -
lower limit - upper limit
80  1  200        DegT50          : initial guess -
lower limit - upper limit
n          water filtered y or n ?
3          number of observation groups
7 7 8          number of observations per group
times and concentrations of the observations
***** group 1
0  1.2
1  1.0
2  0.96
4  0.91
7  0.9
12 0.82
22 0.66
***** group 2
0  1.1
1  1
4  0.95
7  0.85
12 0.67
22 0.45
41 0.19
***** group 3
0  1.4
1  1.1
2  1.1
4  1
7  0.92
12 0.77
22 0.62

```

The file is read line by line by the fortran programme so when generating this input file the sequence of the lines should be exactly as specified above.

The *Cosm.met* describes the course of the monthly temperatures with time as follows:

```
*
* TOXSWA input file
* Filename: C:\SwashProjects\water-sediment\toxswa\MetrCosm1.met
* Linuron, Cosm van Stephenson & Kane
*
* Contents: Input data for TOXSWA concerning temperature
* Date :
*
*-----
*
* temperature in water and sediment per month
2000 1 11.6
2000 2 11.6
2000 3 11.6
2000 4 11.6
2000 5 11.6
2000 6 11.6
2000 7 11.6
2000 8 11.6
2000 9 11.6
2000 10 11.6
2000 11 11.6
2000 12 11.6
! - - - - - o^C : unit
! 0 .... 9999 1 .... 12 4. .... 50 : range
*
*-----END OF FILE-----
```

The file *TOXSWA_cha.txt* (shown below) contains those lines of the TOXSWA input file that need to be changed by the user. The first three positions of each line (except the lines at the end on the initial concentration and the loadings) contain the corresponding line number of the TOXSWA input file (see Appendix A). So e.g. '26' in the first line indicates that this is line 26 of the TOXSWA input file. These numbers should not be changed.

Furthermore the file should not contain empty lines below the last line.

Please note that the TimEnd of 28-Feb-2000 in the first line below has to be consistent with the starting time of 1-Jan-2000 in the *TOXSWA_moe.txt* file in Appendix A. Note that 2000 was a leap year so a TimEnd of e.g. 1 March 2000 corresponds with a simulation period of 61 days.

The last lines of the file contain the additional loadings (so additions of substance later). These lines use a calendar format for the time. The simulations start always on 1-Jan-2000, so the days of the additions have to be transformed into the corresponding date. The format is based on the names of the months in English, so Jan, Feb, Mar, Apr, May, Jun, Jul, Aug, Sep, Oct, Nov, Dec.

Listing of file *TOXSWA_cha.txt*

```
26 20-Mar-2000 TimEnd ! End date of simulation [01-Jan-1900 - 31-Dec-9999]
64 15. ConSus (g.m-3) ! Concentration of suspended solids [1.0 -
100000]
65 0.09 CntOmSusSol (kg.kg-1) ! Mass ratio of organic matter in suspended
solids [0.0 - 1.0]
89 1.00 DepWat (m)
145 ThiHor NumLay
146 (m)
147 0.004 4
148 0.006 3
149 0.01 2
150 0.03 3
```

151	0.02	1			
152	0.03	1			
165	Nr	Rho	CntOm	ThetaSat	CofDifRel
166		(kg.m-3)	(kg.kg-1)	(m3.m-3)	(-)
167	1	800.	0.09	0.6	0.6
168	2	800.	0.09	0.6	0.6
169	3	800.	0.09	0.6	0.6
170	4	800.	0.09	0.6	0.6
171	5	800.	0.09	0.6	0.6
172	6	800.	0.09	0.6	0.6
238	249.09	MolMas_ws	(g.mol-1)	! Molar mass of parent substance [10.0 - 10000]	
241	20.	TemRefTraWat_ws	(C)	! Temperature at which half-life was measured [5.0 - 30]	
244	20.	TemRefTraSed_ws	(C)	! Temperature at which half-life was measured [5.0 - 30]	
247	429.6	KomSed_ws	(L.kg-1)	! Coefficient of equilibrium sorption in sediment [0.0 - 10000000]	
249	0.85	ExpFreSed_ws	(-)	! Freundlich exponent in sediment [0.1 - 2]	
250	429.6	KomSusSol_ws	(L.kg-1)	! Coefficient of equilibrium sorption suspended solids [0.0 - 10000000]	
252	0.85	ExpFreSusSol_ws	(-)	! Freundlich exponent suspended solids [0.1 - 2]	
256	5.1E-3	PreVapRef_ws	(Pa)	! Saturated vapour pressure [0.0 - 200000]	
257	25.	TemRefVap_ws	(C)	! Temperature of reference at which the saturated vapour pressure was measured [0.0 - 40]	
260	63.8	SlbWatRef_ws	(mg.L-1)	! Water solubility [0.001 - 1000000]	
261	20.	TemRefSlb_ws	(C)	! Temperature of reference at which the water solubility was measured [0.0 - 40]	
325	0.05	ThiLayTgt	(m)	! Thickness of the target layer	
1.0		Initial concentration (mg.L-1)			
2-Jan-2000		68.76		Date in calendar format and loading in mg.m-2	
10-Jan-2000		23.41		Date in calendar format and loading in mg.m-2	
14-Jan-2000		69.69		Date in calendar format and loading in mg.m-2	
18-Jan-2000		68.82		Date in calendar format and loading in mg.m-2	
25-Jan-2000		46.27		Date in calendar format and loading in mg.m-2	

Annex 8 Appendix 8 Contents of the Toxswa_moe.txt input file used by the estimation software

```
*-----
* TOXSWA input file
* INPUT FILE for TOXSWA 3 version (f90)
*-----
* This file is intended to be used by expert users.
*
* Contact address:
* -----
* Wim Beltman
* Alterra
* PO BOX 47
* 6700 AA Wageningen
* The Netherlands
* e-mail: wim.beltman@wur.nl
*
* (c) Alterra
*-----
*
* Section 1: Control Section
*-----
*
01-Jan-2000      TimStart      ! Start date of simulation [01-Jan-1900 - 31-Dec-
9999]
28-Feb-2000      TimEnd        ! End date of simulation [01-Jan-1900 - 31-Dec-
9999]
FOCUS           CallingProgram ! Calling program in FOCUS_TOXSWA for EU
authorization
4               CallingProgramVersion ! Version of calling program
4               ModelVersion      ! version number of the model
4               GUIVersion        ! version number of the GUI
2               DBVersion         ! version number of the database
Hourly          OptInp           ! Option for hourly or daily input data (Hourly,
Daily)
OnLine          OptHyd           ! Hydrology simulation option (Only, OnLine, OffLine,
Automatic)
OnLine          OptTem           ! Temperature simulation option (Only, OnLine, OffLine,
Automatic)
600             MaxTimStpWat(s) ! Maximum calculation time step in water layer [0.001 -
3600]
600             MaxTimStpSed(s) ! Maximum calculation time step in sediment [0.001 -
3600]
600.           TimStpHyd (s)    ! Maximum calculation time step for hydrology [0.001 -
3600]
Yes            OptScreen        ! Option to show output on screen (Yes, No)
Calc           OptTimStp       ! Time step substance simulation options (Input, Calc)
*-----
*
* Section 2: Waterbody section
*-----
*
LinCosmlA       Location          ! Name of the location   Paulien: deze 2
gebruikt TOXSWA niet
LinCosmlA       WaterbodyID      ! ID of the water body

* Table WaterBody
* Len           = Length (m) [0.1 - 10000]
* NumSeg        = Number of segments (-) [1 - 1000]
* WidWatSys     = Width of the bottom of water system (m) [0.1 - 100]
* SloSidWatSys  = Side slope of the water system (-) [0.001 - 2]
```

* DepWatDefPer = Water depth defining perimeter for the exchange between water layer and sediment (m) [0 - lowest water depth]

```
table WaterBody
Len          NumSeg      WidWatSys SloSidWatSys DepWatDefPer
(m)          (-)         (m)        (-)          (m)
1.           1           1.0        1.0E-5       0.01
End_table
```

```
15.  Consus (g.m-3)          ! Concentration of suspended solids [1.0 - 100000]
0.09 CntOmSusSol (kg.kg-1 !Mass ratio of organic matter in suspended solids [0.0
- 1.0]
0.   AmaMphWatLay (g.m-2) ! Dry weight of macrophyte biomass per m2 bottom [0.0 -
1000]
```

```
*-----
*
* Section 3: Hydrology: general
*-----
*
```

```
Pond          OptWaterSystemType ! Option for selecting the water system type (Pond,
WaterCourse)
Constant      OptFloWat          ! Option for water flow (Constant, Variable)
```

```
* if: OptWaterSystemType = WaterCourse
Input          OptDis          ! Options are 'Fischer' and 'Input'
```

```
* if: OptDis = Input
0.             CofDisPhsInp (m2.d-1) ! Dispersion coefficient [0. -
100000]
```

```
*-----
*
* Section 3a: Constant water flow
*-----
*
```

```
* if: OptFloWat = Constant
1.00          DepWat (m)
0.            VelWatFlwBas (m.d-1)
```

```
*-----
*
* Section 3b: Variable water flow: pond
*-----
*
```

```
* if: OptFloWat = Variable and OptWaterSystemType = Pond
0.45          AreaSurPndInp (ha)      ! Size of area surrounding the pond
[0.0 - 50.0]
```

```
* if: CallingProgram = FOCUS ! Paulien: gebruikt TOXSWA niet voor water-sed
studie
2.193         QBasPndInp (m3.d-1)     ! Base flow, i.e. inflow into pond [0.001 -
50.0]
1.            HgtCrePnd (m)           ! Height of the weir crest [0.1 - 5.0]
0.5           WidCrePnd (m)          ! Width of the weir crest [0.01 - 10]
```

```
* if: Opt = Runoff
0.06          AreaErsSurPndInp (ha) ! Size of the eroding area around the pond [0.0 -
50.0]
```

```
*-----
*
* Section 3c: Variable water flow: watercourse
*-----
*
```

```
* if: OptFloWat = Variable and OptWaterSystemType = WaterCourse
*representative channel
0.0001        SloBotRepCha (-)      ! Slope bottom representative channel [0.0 -
0.01]
0.4           HgtCreRepCha (m)     ! Height of the weir crest [0.1 - 5.0]
```

```

0.5          WidCreRepCha (m) ! Width of the weir crest [0.01 - 10]

1000.       LenRepCha (m)    ! Length representative channel [10.0 - 2000]
1.          WidBotRepCha (m) ! Width bottom representative channel [0.1 - 10]
1E-005     SloSidRepCha (-) ! Side slope of the representative channel [0.0
- 10]

25.        CofRghRef (-) ! Value of the Manning coefficient for bottom roughness [1.0
- 100]
1.2        CofVelHea (-) ! Energy coefficient resulting from the non-uniform
distribution of flow velocities [1.1 - 1.5]

* if: CallingProgram = NL or FOCUS ! Paulien: gebruikt TOXSWA niet voor water-sed
studie
2.          AreaUpsWatCrsInp (ha) ! Size of the area upstream the representative
channel [0.0 - 10000]
0.66       QBasWatCrsInp (m3.d-1) ! Minimal flow into watercourse [0.0 10000]

2.          AreaUpStrRepCha (ha) ! Size of the area upstream the representative
channel [0.0 - 10000]
1.          QBasRepCha (m3.d-1) ! Minimal flow into watercourse [0.0 - 10000]
*-----
*
* Section 4: Sediment section
*-----
*

FOCUS          SedimentTypeID ! Name of sediment type

* table SedimentProfile
* ThiHor = thickness of horizon [0.0001 - ]
* NumLay = number of layers in horizon [1,]

table SedimentProfile
ThiHor      NumLay
(m)
0.004      4
0.006      3
0.01       2
0.03       3
0.02       1
0.03       1
end_table

Input          OptSedProperties ! Option sediment properties [Input,
Calc]

* table specifying SedimentProperties for each horizon:
* Nr          = number horizon [1,]
* Rho         = bulk density [100 - 2000]
* CntOm       = organic matter mass content [0.1 - 1.0]
* ThetaSat   = saturated water content [0.1 - 0.95]
* CofDifRel  = relative diffusion coefficient [0.0 - 1.0]

table horizon SedimentProperties
Nr          Rho          CntOm          ThetaSat      CofDifRel
           (kg.m-3)    (kg.kg-1)    (m3.m-3)     (-)
1          800.        0.09         0.6           0.6
2          800.        0.09         0.6           0.6
3          800.        0.09         0.6           0.6
4          800.        0.09         0.6           0.6
5          800.        0.09         0.6           0.6
6          800.        0.09         0.6           0.6
end_table

0.          FlwWatSpg (m3.m-2.d-1)

* If: FlwWatSpg not zero
* table horizon DispersionLength
* Nr          = Horizon number []
* LenDisSedLiq = Dispersion length of solute in liquid phase [0.05 - 1.0]

table horizon DispersionLength

```

```

Nr          LenDisSedLiq
           (m)
1           0.015
2           0.015
3           0.015
4           0.015
5           0.015
6           0.015
end_table

* If: OptLoa = PRZM
0.01          ThiLayErs (m)          ! Thickness of sediment layer to which
eroded soil is added [0.0001 - ]
*-----
*
* Section 5: Weather section
*-----
*

Cosm          MeteoStation          ! Name of the *.met file with meteo data

Monthly       OptMetInp          ! Option for hourly or daily input data (Hourly, Daily,
Monthly)

*-----
*
* Section 6: Compound section
*-----
*

ws            SubstanceName          ! Name of parent substance [1 - 6
characters]

table compounds          ! List of substances [1 - 6 characters]
ws
end_table

* Table parent-daughter relationships transformation in water (FraPrtDauWat):
* Column 1: fraction formed from parent into daughter
* Column 2: name of parent
* Column 3: name of daughter

table FraPrtDauWat (mol.mol-1)
end_table

* Table parent-daughter relationships transformation in sediment (FraPrtDauSed):
* Column 1: fraction formed from parent into daughter
* Column 2: name of parent
* Column 3: name of daughter

Table FraPrtDauSed (mol.mol-1)
end_table

* Substance properties for each substance given in table compounds
* Substance code is extension of parameter name
*----- Parent: ws -----

249.09          MolMas_ws (g.mol-1)          ! Molar mass of parent substance [10.0 -
10000]

$ DegT50wl $ DT50WatRef_ws (d)          ! Half-life transformation in water [0.1 -
100000]
20.            TemRefTraWat_ws (C)          ! Temperature at which half-life was measured
[5.0 - 30]
65.4           MolEntTraWat_ws (kJ.mol-1)    ! Molar activation enthalpy of
transformation in water [0.0 - 200]
1000.          DT50SedRef_ws (d)          ! Half-life transformation in sediment [0.1 -
100000]
20.            TemRefTraSed_ws (C)          ! Temperature at which half-life was measured
[5.0 - 30]

```

```

65.4      MolEntTraSed_ws (kJ.mol-1) ! Molar activation enthalpy of
          transformation in sediment [0.0 -
          200]

429.6     KomSed_ws (L.kg-1) ! Coefficient of equilibrium sorption in
          sediment [0.0 - 10000000]
1.        ConLiqRefSed_ws (mg.L-1) ! Reference concentration in liquid
          phase in sediment [0.001 - 100]
0.85     ExpFreSed_ws (-) ! Freundlich exponent in sediment [0.1 - 2]
429.6     KomSusSol_ws (L.kg-1) ! Coefficient of equilibrium sorption
          suspended solids [0.0 - 10000000]
1.        ConLiqRefSusSol_ws (mg.L-1) ! Reference concentration in liquid
          phase suspended solids [0.001 - 100]
0.85     ExpFreSusSol_ws (-) ! Freundlich exponent suspended solids [0.1 -
2]

0.        CofSorMph_ws (L.kg-1) ! Coefficient for linear sorption on
          macrophytes [0.0 - 20000]

5.1E-3    PreVapRef_ws (Pa) ! Saturated vapour pressure [0.0 - 200000]
25.       TemRefVap_ws (C) ! Temperature of reference at which the saturated
          vapour pressure was measured [0.0 - 40]
95.       MolEntVap_ws (kJ.mol-1) ! Molar enthalpy of the vaporization
          process [-200 - 200]

63.8     SlbWatRef_ws (mg.L-1) ! Water solubility [0.001 - 1000000]
20.       TemRefSlb_ws (C) ! Temperature of reference at which the water
          solubility was measured [0.0 - 40]
27.       MolEntSlb_ws (kJ.mol-1) ! Molar enthalpy of the dissolution [-200
- 200]
4.3E-5    CofDifWatRef_ws (m2.d-1) ! Reference diffusion coefficient in
          water [0.0 - 200]

*-----
*
* Section 7: Management section
*-----
*
* Loading options (OptLoa):
* DriftOnly = spray drift only entry route
* PEARL     = drainage calculated by PEARL
* MACRO     = drainage calculated by MACRO
* PRZM      = runoff and erosion calculated by PRZM
* GEM       = point source calculated by GEM

DriftOnly      OptLoa      ! Loading options (DriftOnly, PEARL, MACRO,
PRZM, GEM)

FOCUS_EXAMPLE  ApplicationScheme ! Name of the application scheme

* If: OptLoa = MACRO or OptLoa = PRZM
* Table with path+name of lateral entries files

table Soil substance files
end_table

* If: OptLoa = PEARL or OptLoa = MACRO
100.           WidFldDra (m)      ! Width of field contributing drainage

* If: OptLoa = PRZM
100.           WidFldRnf (m)      ! Width of field contributing runoff
20.           WidFldErs (m)      ! Width of field contributing erosion
0.           RatInfDir (-)       ! Ratio of infiltration water added to
runoff water

* If: CallingProgram = FOCUS and OptWaterSystemType = WaterCourse
Yes           OptUpsInp          ! Switch for upstream catchment treated (Yes, No)
0.           RatAreaUpsApp (-)   ! Ratio of upstream catchment treated [0.0 - 1]
1.           FraMetForUps (-)    ! Fraction primary metabolites formed in water in
upstream catchment

0.0          ConAir (kg.m-3)     ! Concentration of the substance in air

```

0.0 ConWatSpg (g.m-3) ! Concentration in incoming seepage water

* Table initial substance content in sediment (CntSysSedIni)

* Column 1: Depth in sediment (m)

* Column 2: Substance content (mg.kg-1)

table interpolate CntSysSedIni (mg.kg-1)

end_table

*-----

*

* Section 8: Output control

*-----

*

No OptDelOutFiles ! Switch for removing *.out files after run (Yes, No)

FOCUS OptReport ! Options for report type (DutchRegistration, FOCUS)

Yes ExposureReport ! Exposure report (Yes, No)

No PercentileReport ! Percentile report (Yes, No)

DaysFromSta DateFormat ! Date format (DaysFromSta, DaysFrom1900, Years)

e14.6 RealFormat ! Number format of the reals

0.05 ThiLayTgt (m) ! Thickness of the target layer

Hour OptDelTimPrn ! Option to set output time step (Hour, Day, Decade, Month, Year, Automatic, Other)

1 DelTimPrn (d) ! Output time step [0.0 - length simulation

period]

No PrintCumulatives ! Specify whether fluxes should be cumulated over the entire simulation period (Yes, No)

* table HorizontalProfiles: dates are given for which detailed output is wished

* Column 1: dates

table HorizontalProfiles

end_table

* Table output depths (OutputDepths): indicate for which depths the output is selected

* Column 1: Depth

table OutputDepths (m)

end_table

All OptOutputDistances ! Switch output distances (None, All, Table)

* Table output distances (OutputDistances): indicate for which distance the output is selected

* Column 1: Distance

table OutputDistances (m)

end_table

No print_VelWatFlw ! Flow velocity (m/h) [Yes, No]

No print_QBou ! Discharge (m3/h) [Yes, No]

No print_VvrLiqDra ! Drain flow (m/h) [Yes, No]

No print_VvrLiqRnf ! Runoff flow [Yes, No]

No print_FlmDra ! Drain substance flux [Yes, No]

No print_FlmRnf ! Runoff substance flux [Yes, No]

No print_FlmErs ! Erosion substance flux [Yes, No]

Yes print_ConLiqWatLay ! Concentration in water, hour average (g/m3)

[Yes, No]

Yes print_ConSysWatLay ! Total concentration in water (g/m3) [Yes, No]

No print_CntSorMph ! Content sorbed to macrophytes [Yes, No]

Yes print_CntSorSusSol ! Content sorbed suspended solids [Yes, No]

Yes print_ConSysSed ! Total content in sediment [Yes, No]

No print_ConLiqSed ! Concentration in pore water sediment (g/m3)

[Yes, No]

No print_CntSorSed ! Content sorbed to sediment [Yes, No]

No print_DepWat ! Water depth (m) [Yes, No]

No print_DepWatRepCha ! Water depth representative channel [Yes, No]

Yes No]	print_CntSedTgt	! Total content in target layer sediment [Yes,
No	print_ConLiqSedTgt	! Concentration in pore water in target layer sediment [Yes, No]
No No]	print_CntSorSedTgt	! Content sorbed in target layer sediment [Yes,
No	print_ConLiqWatLayCur	! Concentration in water, at end hour (g/m3) [Yes, No]
No	print_AmaWatLay	! Mass in water layer [Yes, No]
No	print_AmaLiqWatLay	! Mass in liquid phase in water layer [Yes, No]
No	print_AmaSorSusSol	! Mass sorbed to suspended solids in water layer [Yes, No]
No [Yes, No]	print_AmaSorMph	! Mass sorbed to macrophytes in water layer
No	print_AmaSed	! Mass in sediment layer [Yes, No]
No No]	print_AmaLiqSed	! Mass in liquid phase in sediment layer [Yes,
No	print_AmaSorSed	! Mass sorbed in sediment layer [Yes, No]
No	print_AmaTraWatLay	! Mass transformed in water layer [Yes, No]
No	print_AmaForWatLay	! Mass formed in water layer [Yes, No]
No	print_AmaVolWatLay	! Mass volatilised in water layer [Yes, No]
No	print_AmaSedInWatLay	! Mass penetrated into sediment from water layer [Yes, No]
No	print_AmaSedOutWatLay	! Mass transferred from sediment into water layer [Yes, No]
No	print_AmaDwnWatLay	! Mass flowed across downstream boundary out of water layer [Yes, No]
No	print_AmaUpsWatLay	! Mass flowed across upstream boundary into water layer [Yes, No]
No No]	print_AmaDrfWatLay	! Mass entered water layer by spray drift [Yes,
No	print_AmaAtmDepWatLay	! Mass entered water layer by atmospheric deposition [Yes, No]
No No]	print_AmaDraWatLay	! Mass entered water layer by drainage [Yes,
No	print_AmaRnoWatLay	! Mass entered water layer by runoff [Yes, No]
No	print_AmaTraSed	! Mass transformed in sediment layer [Yes, No]
No	print_AmaForSed	! Mass formed in sediment layer [Yes, No]
No	print_AmaWatLayInSed	! Mass transferred into water layer from sediment layer [Yes, No]
No	print_AmaWatLayOutSed	! Mass transferred from water layer into sediment layer [Yes, No]
No	print_AmaDwnSed	! Mass leaving sediment layer across lower boundary [Yes, No]
No [Yes, No]	print_AmaErsSed	! Mass entering sediment layer by erosion
No	print_VolErrWatLay	! Volume error in waterbody [Yes, No]
No	print_AmaErrWatLay	! Mass error in mass balance of the waterlayer [Yes, No]
No	print_ConLiqWatLayNLAvg	! Concentration in water, average in evaluation stretch [Yes, No]

*-----
* End of TOXSWA input file
*-----

* Table loadings
* Column 1: Date of application, relevant if OptLoa = DriftOnly, otherwise the
date is a dummy values
* Column 2: Type of loading (-)
* Column 3: Drift deposition (mg.m-2) []
* Column 4: Start of stretch of watercourse loaded by all loading types (m) []
* Column 5: End of stretch of watercourse loaded by all loading types (m) []

table Loadings



Alterra Wageningen UR
P.O. Box 47
6700 AA Wageningen
The Netherlands
T +31 (0)317 48 07 00
www.wageningenUR.nl/en/alterra

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Alterra Wageningen UR is the research institute for our green living environment. We offer a combination of practical and scientific research in a multitude of disciplines related to the green world around us and the sustainable use of our living environment, such as flora and fauna, soil, water, the environment, geo-information and remote sensing, landscape and spatial planning, man and society.

The mission of Wageningen UR (University & Research centre) is 'To explore the potential of nature to improve the quality of life'. Within Wageningen UR, nine specialised research institutes of the DLO Foundation have joined forces with Wageningen University to help answer the most important questions in the domain of healthy food and living environment. With approximately 30 locations, 6,000 members of staff and 9,000 students, Wageningen UR is one of the leading organisations in its domain worldwide. The integral approach to problems and the cooperation between the various disciplines are at the heart of the unique Wageningen Approach.

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