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Guidance for inverse modelling using TOXSWA

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

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Realistic values for the degradation rates of pesticides in surface water are important for the aquatic risk assessment, that is mandatory before pesticides are admitted authorised. Standardised first-tier laboratory tests exist, but the degradation rates derived from these tests do not reflect the degradation rates in the environment. Outdoor ponds or cosms are often used as a higher-tier risk assessment to evaluate the ecotoxicological effects in a more realistic way. We selected cosms in which pesticide mass had been measured as a function of time in both the water layer (at least 5 times) and the sediment (at least 3 times) and determined the degradation rate in the water layer ($DegT_{50,water}$) by means of inverse modelling the pesticide's behaviour in the cosm with the aid of the TOXSWA model coupled to the optimisation software PEST. The $DegT_{50,water}$ and the initial aqueous concentration were optimised using three or more sets of the often unknown sediment properties (bulk density, organic matter content and porosity). For cosm studies with chlorpyrifos, lambda-cyhalothrin, metsulfuron-methyl and prosulfocarb we obtained satisfactory estimated $DegT_{50,water}$ values, but for a cosm study with linuron we could not satisfactorily estimate the $DegT_{50,water}$. For the four compounds with satisfactory estimated $DegT_{50,water}$ values the obtained values were shorter than the half-lives obtained in the standardised laboratory studies. This implies that under more realistic conditions the aqueous exposure concentration may be lower than the one calculated in the regulatory surface water scenarios using the first-tier degradation rate input, and thus the risks for the aquatic ecosystem may be lower than calculated.

Keywords: pesticide degradation rate in water, outdoor cosm, TOXSWA, inverse modelling, chlorpyrifos, lambda-cyhalothrin, metsulfuron-methyl, prosulfocarb, linuron.

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Contents

| | | |
|----------|--|-----------|
| | Summary | 5 |
| | Samenvatting | 7 |
| 1 | Introduction | 9 |
| 2 | Procedure to estimate $DegT_{50,water}$ in outdoor cosm water by inverse modelling with TOXSWA | 11 |
| | 2.1 Introduction | 11 |
| | 2.2 Brief description of the TOXSWA model | 11 |
| | 2.3 Overview of model optimisation procedure | 13 |
| | 2.4 Procedure for cosms with measurements in water-only or in water and sediment | 17 |
| | 2.5 Uncertainty of estimated $DegT_{50,water}$ when $F_{M,deg-wat} < 50\%$ | 20 |
| 3 | Analysis of cosm studies with measurements in both water and sediment | 22 |
| | 3.1 Introduction | 22 |
| | 3.2 Parameterisation for PEST-TOXSWA for all water-sediment cosm studies | 22 |
| | 3.3 Parameterisation of water-sediment cosms, method 'Water-sediment' | 25 |
| | 3.4 Parameterisation of water-sediment cosms, method 'Water-sediment + o.m. 0-1 cm measured' | 28 |
| | 3.5 Scaling of multiple data sets from a single study | 31 |
| | 3.6 Value of the Freundlich sorption coefficient K_{om} and use of scaled concentrations | 32 |
| | 3.7 Weighting of residues for simultaneous use of water and sediment concentrations | 33 |
| | 3.8 Future improvements of the optimisation procedure | 34 |
| | 3.9 Consistency of degradation rates between lower and higher tiers | 35 |
| 4 | Selection of example compounds and water-sediment cosm studies | 37 |
| | 4.1 Selection of compounds | 37 |
| | 4.2 Evaluation of cosm studies liable to provide measured concentrations in water and sediment | 38 |
| | 4.3 Selected compounds and studies suitable for inverse modelling of water and sediment concentrations | 41 |
| 5 | Assessment of the degradation rate of the selected compounds in cosm water | 44 |
| | 5.1 Chlorpyrifos | 44 |
| | 5.2 Lambda-cyhalothrin | 51 |
| | 5.3 Linuron | 53 |
| | 5.4 Metsulfuron-methyl | 56 |
| | 5.5 Prosulfocarb | 59 |
| | 5.6 Comparison of half-life for decline in water and $DegT_{50,water}$ | 63 |
| | 5.7 Summary | 65 |
| 6 | Overview of guidance to estimate the $DegT_{50,water}$ | 68 |

| | | |
|--------------------|--|------------|
| 7 | Discussion, conclusions and recommendations | 74 |
| 7.1 | Discussion and conclusions | 74 |
| 7.2 | Recommendations | 75 |
| | References | 77 |
| Appendix 1 | Example calculation of the minimum error-% at which the χ^2-test is passed | 79 |
| Appendix 2 | Protocol for selecting pesticide properties from the Pesticides Properties DataBase | 81 |
| Appendix 3 | Inverse modelling with TOXSWA-PEST for two cosm studies with chlorpyrifos | 84 |
| Appendix 4 | Inverse modelling with TOXSWA-PEST for the cosm study with lambda-cyhalothrin | 96 |
| Appendix 5 | Inverse modelling with TOXSWA-PEST for the cosm study with linuron | 102 |
| Appendix 6 | Inverse modelling with TOXSWA-PEST for the cosm study with metsulfuron-methyl | 109 |
| Appendix 7 | Inverse modelling with TOXSWA-PEST for the cosm study with prosulfocarb | 116 |
| Appendix 8 | Instruction to run the software for estimation of $DegT_{50,water}$ | 123 |
| Appendix 9 | The TOXSWA_moe.txt input file used by the estimation software | 141 |
| Appendix 10 | Appendix 10 Format of table presenting the main input and output of the optimisations runs for estimation of $DegT_{50,water}$ | 149 |

Summary

Realistic values for the degradation rates of pesticides in surface water are important for the aquatic risk assessment, that is mandatory before pesticides are admitted on the market. Especially in water bodies with low flow velocities or with multiple spray drift deposition events, exposure concentrations of pesticides are influenced by their degradation rate. Standardised laboratory tests consider photolysis in water (using e.g. Xenon lamp), or hydrolysis at pH 5, 7 and 9, or the decline in water-sediment systems, consisting of approximately 10 cm water on top of a few centimetres sediment. However, the degradation rates found in these tests do not reflect the degradation rates in reality.

Outdoor ponds or cosms are often used as a higher-tier risk assessment to evaluate the ecotoxicological effects in a more realistic way than laboratory tests do. However, guidance to use these outdoor studies for estimating realistic degradation rates is lacking. Therefore, this report intends to present guidance on the estimation of the degradation rate in water for outdoor cosm studies.

To develop the intended guidance we selected cosms with compounds having K_{oc} values ranging between 10 and 30000 L/kg. Studies for five compounds were selected. Pesticide mass had been measured as a function of time in both the water layer (at least 5 times) and the sediment (at least 3 times). We determined the degradation rate in the water layer ($DegT_{50,water}$) by means of inverse modelling the pesticide's behaviour in the cosm with the aid of the TOXSWA model (vs FOCUS_TOXSWA_4.4.2) coupled to the optimisation software PEST (vs 13.0). The $DegT_{50,water}$ and the initial aqueous concentration were optimised using three or more sets of the generally unknown sediment properties (bulk density, organic matter content and porosity). Criteria for the goodness of fit were similar to those of FOCUS Degradation Kinetics (2006), but instead of a maximum χ^2 error of 15% χ^2 errors up to 25% were accepted. So, the goodness of fit criteria included (i) satisfactory visual correspondence between the simulated and measured concentrations in water and in sediment, (ii) satisfactory visual assessment of the residuals (simulated minus measured concentrations) in water and sediment, i.e. no trends, and (iii) the error percentage of the χ^2 -test lower than 25%. For cosm studies with chlorpyrifos, lambda-cyhalothrin, metsulfuron-methyl and prosulfocarb we obtained satisfactory estimated $DegT_{50,water}$ values. However, for the chlorpyrifos study of Giddings et al. (1997) we succeeded for the data set of the highest concentration level (out of three) only, while for metsulfuron-methyl more than ten initial runs plus expert judgement adjustments were needed. For prosulfocarb also expert judgement was needed. For these four compounds the fits were visually acceptable, as well as the trends in the residuals. The χ^2 errors ranged from 7 to 28%. The 95th confidence intervals for the $DegT_{50,water}$ values were wide: they typically ranged within 30 to 170% of the fitted value. For a cosm study with linuron we could not satisfactorily estimate the $DegT_{50,water}$.

Based on our experiences with the optimisation method we developed suggestions for improvement, expanded the method and designed flow charts for it. Recommendations include to test all routes in the flow charts as this has not yet been done.

For the four compounds with successfully optimised $DegT_{50,water}$ values the half-lives were shorter than the half-lives obtained in the standardised laboratory studies on photolysis, hydrolysis and the water-sediment systems. The difference was typically an order of magnitude and at least a factor of two.

Concluding

- # the estimation procedure resulted in sufficiently accurate $DegT_{50,water}$ values for four of the five compounds. So, the procedure seems suitable for use in the authorisation procedure as a higher tier;
- # the $DegT_{50,water}$ values for outdoor cosms were considerably shorter than values for hydrolysis, photolysis and degradation in water-sediment studies. So, they have added value in the tiered exposure assessment and, moreover
- # this implies that under more realistic conditions the aqueous exposure concentration may be lower than the one calculated in the regulatory surface water scenarios using the first-tier degradation rate input, and thus the risks for the aquatic ecosystem may be lower than calculated.

Samenvatting

Voor de aquatische risicobeoordeling van gewasbeschermingsmiddelen is het van belang om over realistische waarden van de afbraaksnelheid in water te beschikken. Dit geldt vooral voor middelen in waterlopen met een lage stroomsnelheid of voor middelen die herhaald worden toegepast. In standaard laboratoriumtesten wordt de afbraaksnelheid onder invloed van licht (fotolyse), pH (hydrolyse) of in water-sediment systemen (met ca 10 cm water boven enkele centimeters sediment) bepaald. De afbraaksnelheden in deze laboratoriumtesten geven echter niet goed de afbraak onder veldomstandigheden weer.

Vijvers of cosms in de buitenlucht worden vaak gebruikt in de zgn. hogere treden van de aquatische risicobeoordeling om de ecotoxicologische effecten op een realistischere manier te kunnen bepalen dan mogelijk is in laboratoriumtesten. Deze studies buiten zouden ook gebruikt kunnen worden om realistische afbraaksnelheden in water te bepalen, maar hiervoor ontbreekt een richtsnoer. Dit rapport heeft de intentie om aan te geven hoe de afbraaksnelheid in water van dergelijke cosm studies in de buitenlucht bepaald kunnen worden.

Allereerst selecteerden we een aantal geschikte studies met middelen die een K_{oc} waarde tussen 10 en 30000 L/kg hadden. Studies met vijf middelen werden geselecteerd. In deze studies was de massa bestrijdingsmiddel gemeten als een functie van de tijd, zowel in de waterlaag (ten minste 5 maal), als in het sediment (tenminste 3 maal). Met behulp van inverse modellering van het gedrag van het middel in de cosm werd vervolgens de afbraaksnelheid ($DegT_{50,water}$) bepaald. Hiervoor werd het model TOXSWA (versie FOCUS_TOXSWA_4.4.2) gekoppeld aan de optimalisatie software PEST (versie 13.0). De $DegT_{50,water}$ en de initiële concentratie in het water werden geoptimaliseerd voor drie of meer sets van de meestal niet gemeten sediment eigenschappen (bulk dichtheid, organische stof gehalte en poriegehalte). Dezelfde criteria voor de 'goodness of fit' werden gehanteerd als die in FOCUS Degradation Kinetics (2006), maar in plaats van maximale χ^2 afwijkingen van 15% werden nu χ^2 afwijkingen tot 25% acceptabel bevonden. Verdere criteria waren (i) bevredigende visuele overeenkomst tussen de gesimuleerde en gemeten concentraties in water en sediment, (ii) bevredigend visueel patroon van de residuen (gesimuleerde minus gemeten concentraties) in water en in sediment, i.e. geen trends, en (iii) afwijkingspercentage in de χ^2 -test kleiner dan 25%. Acceptabele schattingen voor de $DegT_{50,water}$ waarden werden verkregen voor cosms studies met chloorpyrifos, lambda-cyhalothrin, metsulfuron-methyl en prosulfocarb. Maar voor de studie met chloorpyrifos van Giddings et al. (1997) lukte de optimalisatie alleen voor cosms met het hoogste concentratieniveau van de drie, terwijl voor metsulfuron-methyl meer dan tien runs inclusief extra specialistische aanpassingen nodig waren. Ook voor prosulfocarb waren specialistische aanpassingen nodig. Voor de vier genoemde middelen waren de fits visueel acceptabel, evenals de trends in de residuen. De χ^2 afwijkingen besloegen 7 tot 28%. De 95% betrouwbaarheidsintervallen voor de $DegT_{50,water}$ waren breed: kenmerkende bandbreedtes waren 30 tot 170% van de gefitte $DegT_{50,water}$ waarde.

Op basis van onze ervaringen met de optimalisatie methodiek zijn suggesties voor verbetering geformuleerd, is de methodiek uitgebreid en zijn stroomschema's ontwikkeld. Aanbevelingen zijn o.a. om alle routes in de stroomschema's te gaan testen, daar dit nu nog niet is gebeurd.

De vier middelen met succesvol geoptimaliseerde $DegT_{50,water}$ waarden hebben halfwaardetijden voor afbraak die korter zijn dan de halfwaardetijden uit de standaard testen in het laboratorium voor fotolyse, hydrolyse en afbraak in water-sediment systemen. Het verschil was meestal een orde van grootte of op zijn minst een factor twee.

De conclusies zijn:

- de schattingsmethodiek leverde voor vier van de vijf middelen voldoende nauwkeurige $DegT_{50,water}$ waarden op. De ontwikkelde methodiek is daarom geschikt voor gebruik in een hogere trede in de toelatingsprocedure van bestrijdingsmiddelen;
- de $DegT_{50,water}$ waarden voor de cosms in de buitenlucht zijn aanmerkelijk korter dan de halfwaardetijden voor fotolyse, hydrolyse en afbraak in water-sediment studies in het laboratorium. Ze hebben dus een toegevoegde waarde in de getrapte blootstellingsbepaling, en bovendien
- betekent dit dat onder realistische omstandigheden de blootstellingsconcentratie in het water lager kan zijn dan die berekend in de toelatingsscenario's voor oppervlaktewater met de standaard input voor de afbraaksnelheid en dus dat de risico's voor het aquatisch ecosysteem lager kunnen zijn dan berekend.

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 or the peak concentration, 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 surface water in the dark (OECD 309) or degradation studies in systems containing both water and sediment in the dark (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 the aquatic risk assessment in authorisation 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. It is limited to parent compounds.

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 using inverse modelling. This report only focuses on this alternative approach. Compartmental approaches do not consider processes, such as volatilisation and sorption, 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 the guidance of FOCUS Degradation (2006) several types of degradation kinetics are considered. In this report we use the TOXSWA model which has single first-order kinetics for degradation. Therefore, $DegT_{50,water}$ values obtained by the TOXSWA-PEST optimisation procedure cannot be compared to $DegT_{50,water}$ estimates obtained by other kinetics in a straightforward way.

In their guidance, FOCUS (2006) made a distinction between two general types of kinetic endpoints: (i) persistence endpoints, used as trigger 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. The refined estimation of this endpoint, as

presented in this report, may be useful for more refined exposure assessments at EU level. The current repair of the EU FOCUS surface water scenarios by an EFSA Working Group may possibly result in a need for additional higher-tier calculations.

The estimation procedure in this report uses the TOXSWA model coupled to the PEST (Parameter ESTimation) optimisation tool. Degradation rates are estimated by inverse modelling of fate data taken from a cosm study. In the first report on this topic by Deneer et al. (2015), the estimation procedure is limited to compounds with a relatively high water solubility for which penetration into sediment is negligible. In this report the estimation procedure has been extended and it focuses 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. Sorption to macrophytes has not been considered in the estimation procedure. Especially for hydrophobic compounds, this may play a role in the behaviour of the compound in the cosm and thus might influence the $DegT_{50,water}$ estimate. Due to a lack of data it is not easy to parameterise this process and it was not considered in the optimisation procedure.

More recent guidance on the estimation of $DT_{50, degradation}$ ($DegT_{50}$) values for surface water was written by Boesten et al. (2014). They proposed a stepped approach for the estimation of $DegT_{50,water}$ values for application in the Dutch surface water scenarios currently under development for use in the pesticide authorisation 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. The estimate of the degradation in water ($DegT_{50,water}$) in this report represents the overall degradation rate in water and thus it includes photolysis, hydrolysis and microbial degradation.

Chapter 2 describes the principles of the estimation procedure, including the quality criteria for minimising the differences between simulated and measured concentrations. Chapter 3 specifies more in detail how the cosm studies must be parameterised for TOXSWA and PEST, whilst in Chapter 4, the selection of suitable compounds and cosm studies for testing the estimation procedure is described. Note that the estimation procedure was improved on the basis of our experiences with the selected compounds and studies and thus, the final proposed estimation procedure differs at some points of the procedure applied for the selected compounds and studies. Chapter 5 summarizes the results of the estimation procedure when applied to cosm studies for chlorpyrifos, lambda-cyhalothrin, linuron, metsulfuron-methyl and prosulfocarb, respectively. The estimated degradation rates in cosm water are compared to the corresponding values found in laboratory studies, and provide an assessment of the importance of photolysis, hydrolysis and biodegradation in the overall degradation process. Chapter 6 summarises the recommended working procedure by describing the automated optimisation procedure to estimate the degradation rates in water. Finally, Chapter 7 presents the conclusions and provides some recommendations.

2 Procedure to estimate $DegT_{50,water}$ in outdoor cosm 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 studies were performed to evaluate the ecotoxicological effects and, therefore, they had limited data sets of the fate of the compound.

This report builds on the report 'Estimation of degradation rates in cosm water. Guidance for inverse modelling using TOXSWA.' of Deneer et al. (2015). The inverse modelling procedure in their report has been expanded to be applicable not only to cosms with measurements in the water phase only (so-called 'Water-only cosms'), but also to cosms with measurements in both water and sediment (in this report called 'Water-sediment cosms'). In the description of the procedure there is often a distinction between the two types of cosms. However, the extended optimisation procedure has only been applied to water-sediment cosms.

The studies analysed by inverse modelling in this report are limited to compounds that are both present in the water phase and in the sediment, i.e. predominantly compounds with a sorption coefficient (K_{oc}) of approximately 500 L/kg or higher. As the compound is present in water and in sediment both the aqueous and sediment concentrations were considered in the optimisation procedure.

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 authorisation 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 the authorisation procedure.

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 simulates these entries as either instantaneous or distributed entries over a certain period, and as a point source-type or distributed entries 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, whose 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.

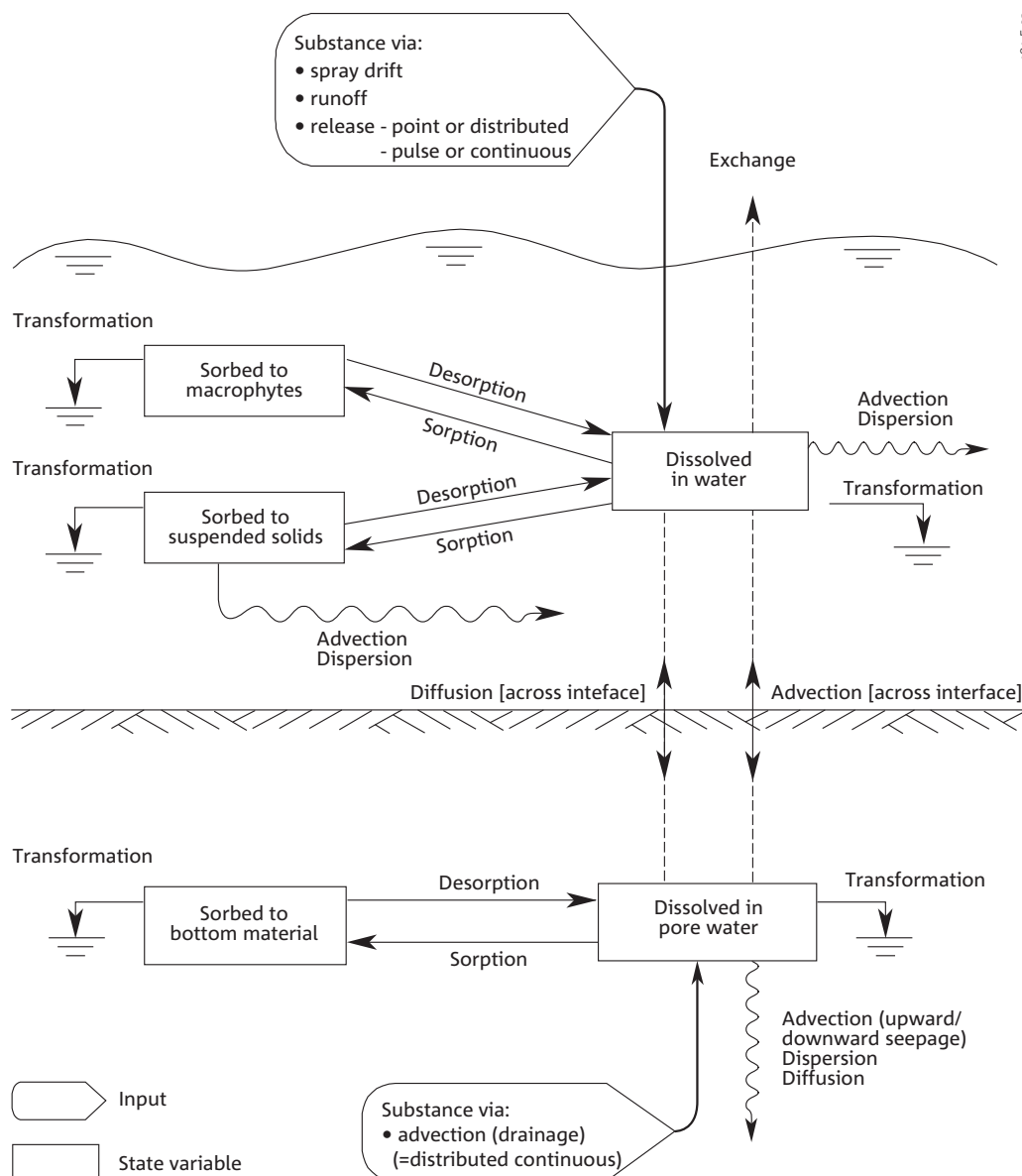


Figure 2.1 Diagram of the processes in TOXSWA for describing the behaviour in watercourses (taken from Adriaanse, 1996).

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. The 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 considered in this report, 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 layer 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 (FOCUS, 2001). A maximum time step of 600 s was used to solve the mass conservation equations numerically, for both water and sediment.

2.3 Overview of 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 well 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 in water. Therefore, a first estimate of the true degradation rate in water was acquired on the basis of the decline rate. This decline rate also reflects the compound properties, such as saturated vapour pressure and the sorption coefficient, that determine the processes of volatilisation and sorption to sediment. Generally, in the sediment there are few measured concentrations available, which often first increase by mass diffusion from the water layer and next decrease by back-diffusion of mass from the sediment into the water layer. So, the decline rate cannot easily be determined from the sediment measurements. For the standard optimisation procedure of this study, it was assumed that degradation in the sediment was negligible. To implement this assumption in TOXSWA a very high default value for the sediment half-life of 1,000 days was used. This corresponded to the worst-case 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. If the standard optimisation procedure could not satisfactorily estimate the $DegT_{50,water}$ a more realistic sediment half-life may be used in the optimisation procedure.

The TOXSWA model is parameterised and run while optimising some input parameters in such a way that the behaviour of the compound in the cosm is mimicked as well as possible. Two types of cosm studies can be distinguished (i) 'water-only studies' in which concentrations measurements have only been done in the water layer and (ii) 'water-sediment studies' in which concentrations in both the water layer and the sediment have been done. Often cosms with only measurements in the water concern compounds with a relatively low sorption coefficient (K_{oc} value of below approximately 500 L/kg) and thus relatively few mass will have entered the sediment. For these cosms we only simulated the behaviour of the pesticide in the water layer (see Deneer et al., 2015). Cosms where measurements in both the water layer and the sediment are available, often concern compounds with a higher sorption coefficient and thus a non-negligible mass has entered the sediment. In this report we focus on this type of studies, but the model optimisation procedure is explained for both types of cosms. For water-sediment cosms the concentrations in both water and sediment are simulated by TOXSWA.

In the water-only cosms 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 - $C_{t=0}$. 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 approximately 500 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.

In the water-sediment cosms one additional input parameter was optimised: (iii) the organic matter content of the sediment. The optimisation was repeated three times using different bulk densities. Adriaanse et al. (2012) demonstrated that the penetration into the sediment is governed by these two parameters defining the organic matter content and the bulk density. We decided not to include the sediment bulk density in the optimisation procedure, but to repeat the optimisation for three different

bulk densities, because optimisation of both the organic matter content and the bulk density resulted in too many degrees of freedom in the optimisation procedure. Often, the organic matter content has not been measured in cosm experiments. If it has been measured it is still optimised, but now within limits representing the uncertainty in the experimentally determined content.

The optimisation procedure uses the correspondence between the measured and model-generated concentrations in the water layer (water-only cosms) or in both the water layer and the sediment (water-sediment cosms). PEST (Parameter ESTimation; Doherty, 2005), version 13.0, is used to run TOXSWA (FOCUS_TOXSWA_4.4.2 version) many times with chosen parameter values, but variable values for $DegT_{50, water}$ and $C_{t=0}$ (water-only cosms) or $DegT_{50, water}$, $C_{t=0}$, and $f_{om, sed}$, the organic matter content of the sediment (water-sediment cosms). PEST uses a non-linear estimation technique, the Gauss-Marquardt-Levenberg method, for minimisation of the objective function ϕ , i.e. the sum of squared differences between model-generated and measured values.

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.

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 in water (water-only cosms) or in water and sediment (water-sediment cosms), 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 prediction 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 $DegT_{50, water}$, $C_{t=0}$ and, if relevant, $f_{om, sed}$;
- For water-only cosms, the effect on optimised $DegT_{50, water}$ values using an alternate 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 the 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 (there were three model parameters in all fits presented in this report)

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 whether 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):

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

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. This value was selected by the FOCUS WG having the estimation of the *DegT*_{50,soil} in mind, a crucial factor for the assessment of leaching of pesticides to the groundwater. For the aim of our study, estimation of *DegT*_{50,water} values we judged that the criterion could be less strict, i.e. a minimum error-% value of 25% is acceptable for outdoor cosm studies. This is based upon the consideration that the direct link of the *DegT*_{50,water} parameter to the regulatory endpoint is less strong than of the *DegT*_{50,soil} parameter: the *DegT*_{50,water} parameter has a significantly smaller effect on the outcome of the aquatic risk assessment (which considers both exposure and ecotoxicological effects) than the *DegT*_{50,soil} has on the leaching assessment.

The minimum error-% to pass the test can be calculated explicitly with Equation 2.2 using the appropriate χ^2_{tab} 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 for water-only cosms as well as the calculation procedure for water-sediments cosms with two groups of observations, one for the water layer and one for the sediment. With the aid of the calculated minimum error-% the results of the optimisation procedure can also be compared for the various cosms. As will be described later, different weights have to be given to these two groups (water and sediment) in the fitting procedure. As described in Appendix 1, these different weights are also given to these two groups in the

calculation of the minimum error-%. If this would not be done, the group with the lowest numbers would hardly contribute to the value of the minimum error-% which is undesirable.

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, these were used in this report (at 95% significance) to assess whether the intervals for the $DegT_{50, water}$ (and $c_{t=0}$ and $f_{om, sed}$) 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, k_{water} . 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 absence) of degradation is often less clearly apparent than for the parent compounds dealt with in the present study.

The correlation coefficients between $c_{t=0}$, $DegT_{50, water}$ and $f_{om, sed}$ were calculated by PEST and given as part of the standard output by the fitting procedure. Since a higher value of $c_{t=0}$ 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 $c_{t=0}$ should be negative. Checking its value may serve as a very minimal quality check on the correctness of the fitting procedure.

In this report, we operationalised the quality criteria for the optimisation procedure, i.e. the goodness of fit, as follows below:

- Visual correspondence between the simulated and measured concentrations in water (water-only cosms) or in water and sediment (water-sediment cosms), as a function of time should be very good, good or at least satisfactory (goodness of visual fit classified as ++=very good, +=good, 0=satisfactory, -=bad, or --=very bad);
- Visual assessment of the residuals (simulated minus measured data), as a function of time should be at least satisfactory (goodness of visual fit classified as +=good, 0=satisfactory or -=bad) and not show trends in over and under prediction;
- Chi-Square (χ^2) test to assess the deviations between simulated and measured values, relative to the uncertainty of the measurements: the error percentage should be lower than 25%. (Note that we decided to accept a higher chi-square error percentage than the 15% recommended by FOCUS (2006).)

In addition the following two points were considered:

- The 95% confidence interval for the estimates of $DegT_{50, water}^1$, $c_{t=0}$ and, if relevant, $f_{om, sed}$ should be reasonable, i.e. the degradation rate constant, k_{water} (d^{-1}) should not include zero, so the $DegT_{50, water}$ should not be extremely high (the estimation procedure only provides $DegT_{50, water}$ values and no k_{water} values). The factor with which the initial concentration and possible loadings should be multiplied should preferably be close to 1 and finally the $f_{om, sed}$ should not fall outside the 0-100% range.
- For water-only cosms: the effect on optimised $DegT_{50, water}$ values using an alternate set of sediment properties should be negligible to small.

Most papers that have described cosm studies gave little or no information on properties for the sediment and suspended solids in the cosms (bulk density, organic matter content of sediment and suspended solids, porosity). Therefore, default values for use in the optimisations were set at realistic levels. However, to evaluate the extent of the influence of the chosen values (water-only cosms) or to improve the robustness of the optimisation procedure (water-sediment cosms), each of the cosms was also optimised using at least one alternate set of values for the sediment properties (more details are given in Section 3.3).

¹ At the beginning of section 2.5 we operationalised this point of a reasonable 95% confidence interval for the estimate of the $DegT_{50, water}$ by introduction of a coefficient of variation, CV value, lower than 25%.

PEST runs were usually performed for a number of different sets of initial values of the optimisation parameters to check the uniqueness of their optimised values. If the outcome of the first sets of runs differed substantially or did not fulfil the quality criteria, more sets of initial values were tried. Lower- and upper parameter bounds for $DegT_{50, water}$ and $C_{t=0}$ were set depending on the concentrations and their observed decrease, based on visual inspection of the concentration data. For $f_{om, sed}$ values the lower limit was set at 2.5% organic matter, representing a realistic low value (OECD, 2002), while the higher limit was set at 50%, a very high value found under realistic conditions in field ditches (Adriaanse et al, 2015). The optimisation procedure is explained into more detail for the various types of cosm in Chapter 3.

2.4 Procedure for cosms with measurements in water-only or in water and sediment

In this section we give an overview of the optimisation procedure for the various cosms, i.e. cosms in which only concentration measurements in the water layer have been done, or cosms in which concentration measurements in both the water layer and the sediment have been done, with or without measuring the organic matter content of the sediment.

First a differentiation is made between cosms in which only water concentrations have been measured and cosms in which sediment concentrations and/or the organic matter content of the sediment have been measured. Next, a general overview of the optimisation procedure to estimate the $DegT_{50, water}$ is presented. This general overview forms the basis for the detailed optimisation procedure described in Chapter 6 for cosms in which concentrations in both the water layer and the sediment have been measured, with or without measurement of the organic matter content of the sediment. How to parameterise the cosms in which sediment concentrations have been measured will be explained in Chapter 3.

So, we distinguish three different types of cosms, depending on the measurements made in the cosms (Figure 2.2). Each cosm has a slightly different approach in its optimisation procedure to obtain the $DegT_{50, water}$. In case A of Figure 2.2 (≥ 5 concentrations in water measured as a function of time, plus water depth measured, no measurements in sediment available) the $DegT_{50, water}$ will be estimated by the method 'Water-only'. This implies that correspondence between simulated and measured concentrations is only optimised for the water layer. In the two other methods, method 'Water-sediment' and 'Water-sediment+ o.m. 0-1 cm measured' correspondence between simulated and measured concentrations is simultaneously optimised for the water layer and the sediment.

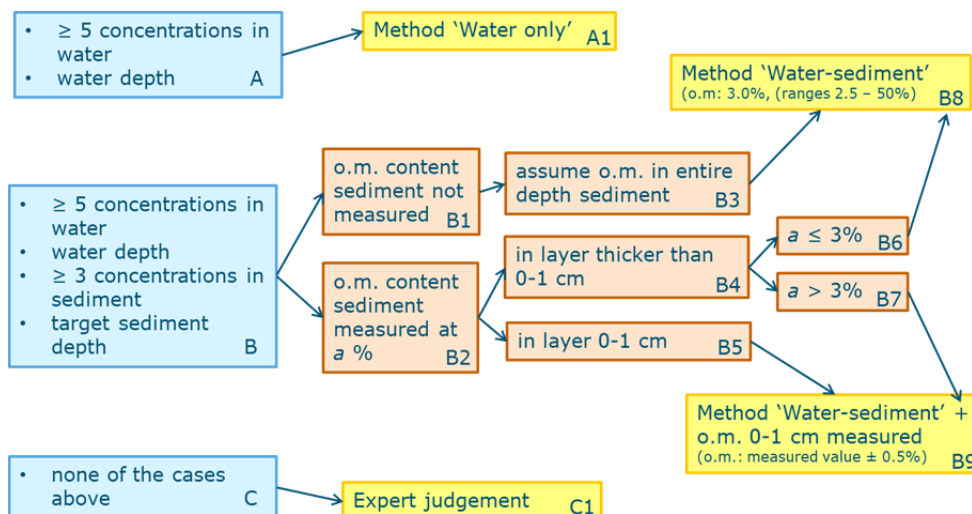


Figure 2.2 Selection of the appropriate optimisation method to estimate the $DegT_{50, water}$, based upon the available measurements in the outdoor cosm study.

Case B applies to situations where ≥ 5 concentrations in water are measured as a function of time, plus the water depth, and ≥ 3 concentrations in sediment are measured as a function of time for a known depth, called target sediment depth in TOXSWA. If in case B the organic matter content of the sediment is not measured (box B1), we assume a realistic low value of 3% for it (box B3) with upper and lower allowed boundary values of 2.5% and 50%. The 2.5% is based upon the average of 0.5-2.5% organic carbon content classified as low organic carbon sediment in the OECD Guideline 308 for water-sediment studies. The average value of 1.5% organic carbon they mention corresponds to $1.724 \times 1.5 \approx 2.5\%$ organic matter content. The realistic low value of 3% o.m. is used for the entire sediment depth in the simulation by the TOXSWA-PEST combination (case B8).

Another possibility for case B is that the organic matter has been measured (box B2), in a sediment layer thicker than the 0-1 cm top layer (box B4). If the o.m. content is lower or equal to 3% for this layer it is very plausible that the 0-1 cm top layer has an o.m. content of at least 3%, as generally the 0-1 cm top layer has a considerably higher o.m. content than deeper layers. However, for the inverse modelling the o.m. content of the 0-1 cm layer is much more important than that of the deeper layers, as very few mass generally penetrates into deeper layers. So the measured o.m. is then considered irrelevant. So, in this case (B6) we end again up in box B8, having an assumed value of 3% o.m. for the entire sediment depth and upper and lower allowed boundary values of 2.5% and 50% in the optimisation by the TOXSWA-PEST combination.

If the organic matter content has been measured in a sediment layer thicker than the 0-1 cm top layer at a value higher than 3% o.m. (box B7), we will use this measured value for the 0-1 cm top layer (box B9), being the best guess available.

A final possibility for case B is that the o.m. content has been measured in the 0-1 cm top layer sediment (box B5). Then the measured value can be used for the entire sediment depth in the simulations by the TOXSWA-PEST combination. The allowed boundary values in the optimisation have been set to the measured value + or - 0.5%² (box B9).

If the measurements in the cosm correspond neither to case A nor to case B it may be possible to estimate the $DegT_{50,water}$ by expert judgement (case C of Figure 2.2).

Note that for the simulations mainly the upper 0-1 cm sediment is important, as very few mass generally penetrates into deeper layers. So, for reasons of simplicity we use the organic matter content of the upper 0-1 cm layer for the entire depth of sediment in the TOXSWA-PEST optimisations.

Ter Horst and Koelmans (2016) estimated $DegT_{50,water}$ from model-generated water-sediment studies by inverse modelling using TOXSWA coupled to PEST, similar to what we did. They demonstrated that the contribution of the degradation to the overall dissipation from the water layer is important for the accuracy in the estimation of the $DegT_{50,water}$. Therefore, they defined the ratio F_M of mass degraded in the water layer divided by the total mass dissipated from the water layer. They demonstrated that the higher the F_M ratio the more accurate the $DegT_{50,water}$, so, in other words: if the contribution of the degradation to the overall dissipation is high, it is possible to estimate the half-life with a higher accuracy, than when the contribution of the degradation to the overall dissipation is low. The trend was observed for all $K_{F,om}$ values studied (1 to 100 000 L/kg) and F_M ratios above approximately 0.2 (Figure S10 of the Supporting Information of Ter Horst and Koelmans, 2016). They expressed accuracy in terms of CV_{pop} , i.e. the ratio of standard deviation of the population of values of $DegT_{50,water}$ divided by the population mean estimated $DegT_{50,water}$ of 25 best fit estimates. Their figure S10 shows that if the ratio F_M exceeds 0.50, the CV_{pop} is lower than 0.1 for most combinations of $K_{F,om}$ (varying from 1 to 100000 L/kg) and 'true' degradation half-lives (varying from 1 to 500 d). (Note that they based their analyses on model-generated water-sediment studies data sets and therefore, the 'true' degradation half-lives were known in water as well as in sediment.)

² Note that in the final guidance in Chapter 6 we propose to use the measured value $\pm 20\%$ instead of the here shown 0.5%.

Based on the findings of Ter Horst and Koelmans (2016) we designed our optimisation procedure also upon the contribution of degradation to the overall dissipation from the water layer, i.e. the ratio of degraded mass in the water and the total dissipated mass from the water (Figure 2.3), but we included the mass volatilised from the water layer in the total mass dissipated from the water layer (Ter Horst and Koelmans (2016) limited their analysis to compounds that did not volatilise). Inspired by Ter Horst and Koelmans (2016) we defined the following entities:

$$F_{M,deg-wat} \equiv \frac{\int M_{deg-wat} dt}{\int M_{diss-wat} dt} = \frac{\int M_{deg-wat} dt}{\int M_{deg-wat} dt + \int M_{vol} dt + \int M_{to-sed} dt} \quad (2.3)$$

and

$$F_{M,vol} \equiv \frac{\int M_{vol} dt}{\int M_{diss-wat} dt} = \frac{\int M_{vol} dt}{\int M_{deg-wat} dt + \int M_{vol} dt + \int M_{to-sed} dt} \quad (2.4)$$

and

$$F_{M,to-sed} \equiv \frac{\int M_{to-sed} dt}{\int M_{diss-wat} dt} = \frac{\int M_{to-sed} dt}{\int M_{deg-wat} dt + \int M_{vol} dt + \int M_{to-sed} dt} \quad (2.5)$$

where $F_{M,deg-wat}$ is the ratio of the mass degraded in the water layer and the overall mass dissipated from the water layer (-), $F_{M,vol}$ is the ratio of the mass volatilised from the water layer and the overall mass dissipated from the water layer (-) and $F_{M,to-sed}$ is the ratio of the mass transported from the water layer into the sediment and the overall mass dissipated from the water layer (-). $M_{diss-wat}$ is the mass rate for the dissipation from the water layer (g/day), $M_{deg-wat}$ is the mass rate of degradation in the water layer (g/day), M_{vol} is the mass rate of volatilisation from the water layer (g/day) and M_{to-sed} is the mass rate of transport from the water layer to the sediment, and t is the time (day). The time integrals in these equations are calculated for the full simulated period.

Similar to Ter Horst and Koelmans (2016) we expressed accuracy in terms of Coefficient of Variation, CV, but we calculated the value of the CV (%) from the output of the PEST model. As PEST specified the 95% confidence interval of the estimated $DegT_{50,water}$ we used this output to calculate the CV as:

$$\begin{aligned} CV &= 100\% \frac{\text{standard deviation}}{\text{mean}} \\ &= 100\% \frac{\text{higher limit} - \text{lower limit of 95\% confidence interval of } DegT_{50,water}}{3.92 * DegT_{50,water}} \end{aligned} \quad (2.6)$$

i.e. 100 times the higher minus lower limit of the 95% confidence interval of the optimised $DegT_{50,water}$ value divided by 3.92 times the optimised $DegT_{50,water}$ value itself. The value 3.92 equals $2 * 1.96$ with 1.96 being the eccentricity of the mean (expressed in standard deviations) for as single-sided probability of exceedance of 2.5% for a normal distribution (see also Figure 2.4, where 1.96 was rounded to 2 in the example calculations of 95% confidence interval).

As stated above Ter Horst and Koelmans (2016) demonstrated that if the ratio F_M exceeds 0.50, the CV_{pop} is lower than 0.1 for most combinations of $K_{F,om}$ and 'true' degradation half-lives. However, the CV value of 10% represents a fairly strict measure. We decided to relax this level of uncertainty in order to use the information of cosm studies as much as possible and to avoid not using the cosm study at all. Therefore we decided that higher CV values may also lead to acceptable optimised $DegT_{50,water}$ values: we propose to accept the optimised $DegT_{50,water}$ value for CV values less than 25%, while for CV values greater than 25% we propose to use the upper limit of the 95% confidence interval of the optimised $DegT_{50,water}$ value as a conservative estimate (Figure 2.3). Based upon the findings of ter Horst and Koelmans (2016) we expect that CV's above 0.1 (10%) only occur for $F_{M,deg-wat}$ smaller than 50%, so therefore the CV criterion of 25% only figures after the $F_{M,deg-wat} < 50\%$ box in Figure 2.3 and not after the upper box with $F_{M,deg-wat} \geq 50\%$.

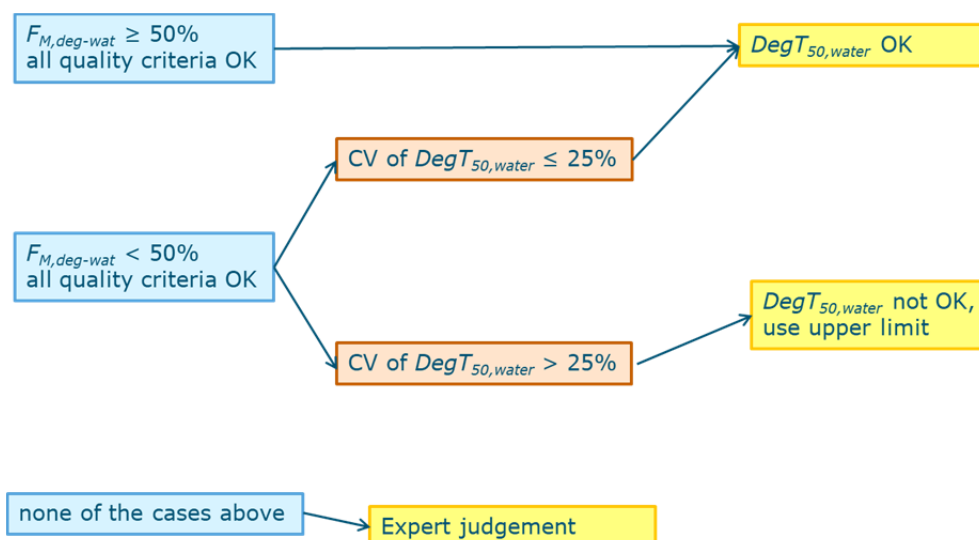


Figure 2.3 Optimisation method for water-only cosms, as well as water-sediment cosms, with or without the organic matter content in the 0-1 cm sediment layer known. For explanation of the mass fraction terms (the F 's) and the coefficient of variation CV, see the text above Figure 2.3. The upper limit refers to the upper limit of the 95% confidence interval of the optimised $DegT_{50,water}$.

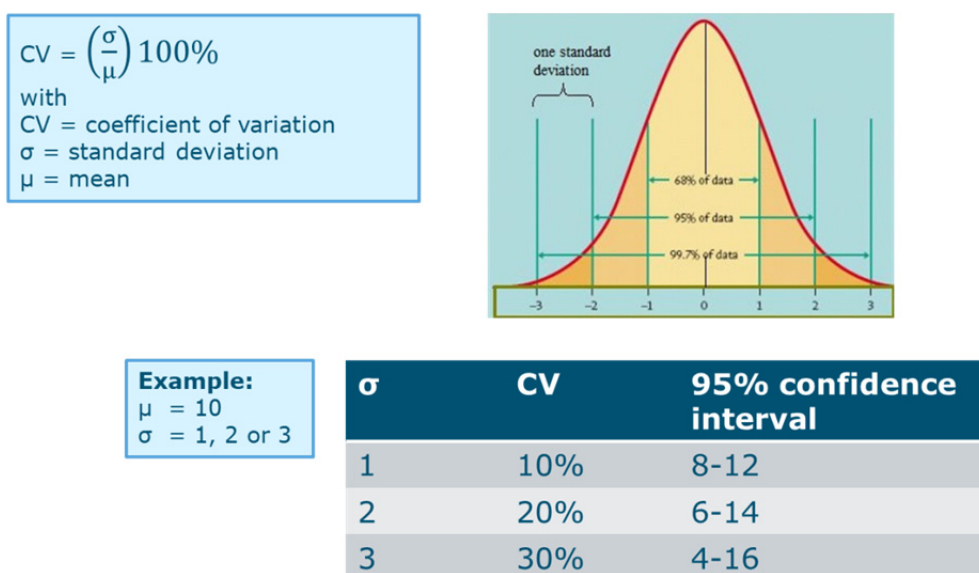


Figure 2.4 Explanation of the size of the CV on the 95% confidence interval for a normal distribution.

2.5 Uncertainty of estimated $DegT_{50,water}$ when $F_{M,deg-wat} < 50\%$

For cases of $F_{M,deg-wat} < 50\%$ we relaxed the CV criterion of Ter Horst and Koelmans (2016) from 0.1 to 0.25 (25%). For these cases only, we therefore want to obtain insight in the uncertainty of the acceptable optimised $DegT_{50,water}$ values (i.e. on the selected optimised $DegT_{50,water}$ value or on its upper limit). We do so by evaluating the effect of the competing dissipation processes of volatilisation and transport to sediment on the selected optimised $DegT_{50,water}$ value. We optimise the $DegT_{50,water}$ for other values of the compound properties P_{sat} and K_{om} (Figure 2.5 and 2.6) and, in these optimisation runs, the $DegT_{50,water}$ is also estimated for values of P_{sat} or K_{om} multiplied by 2 or $\frac{1}{2}$. For 'water-only cosms' we propose to consider three cases: (i) if $F_{M,vol} \geq 2 * F_{M,to-sed}$, so volatilisation is the dominant

competing dissipation process, then consider the influence of the P_{sat} on the optimised $DegT_{50,water}$ (upper pair of pink boxes in Figure 2.5), (ii) if $F_{M,vol} < \frac{1}{2} * F_{M,to-sed}$, so penetration into sediment is the dominant competing dissipation process, then consider the influence of the K_{om} on the optimised $DegT_{50,water}$ (central pair of pink boxes in Figure 2.5) and if none of the conditions of (i) and (ii) apply, then consider the influence of both the P_{sat} and K_{om} on the optimised $DegT_{50,water}$ (lower pair of pink boxes in Figure 2.5). For the water-sediment cosms (Figure 2.6) the uncertainty procedure is simpler than for the water-only cosms (Figure 2.5), because in the water-sediment cosms both degradation in water and transport to sediment have been optimised (by varying $DegT_{50,water}$ and the organic matter content), while in the water-only cosms only degradation in water has been optimised. Therefore, for 'water-sediment cosms' or 'water-sediment + o.m. 0-1 cm measured' cosms we propose only two cases: (i) if $F_{M,vol} \leq F_{M,to-sed}$, so if volatilisation is smaller than the penetration into sediment, then consider the influence of the K_{om} on the optimised $DegT_{50,water}$ (upper pink boxes in Figure 2.6) and (ii) if $F_{M,vol} > F_{M,to-sed}$, so if volatilisation is larger than the penetration into sediment, then consider the influence of the P_{sat} on the optimised $DegT_{50,water}$ (lower pink boxes in Figure 2.6).

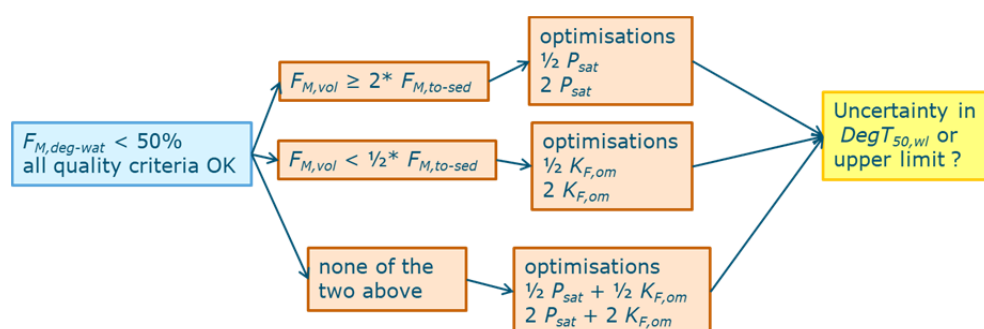


Figure 2.5 Estimation of the uncertainty in the optimised $DegT_{50,water}$ for cosms in which only water concentrations have been measured and which fulfil the two criteria of the most left-hand, blue box.

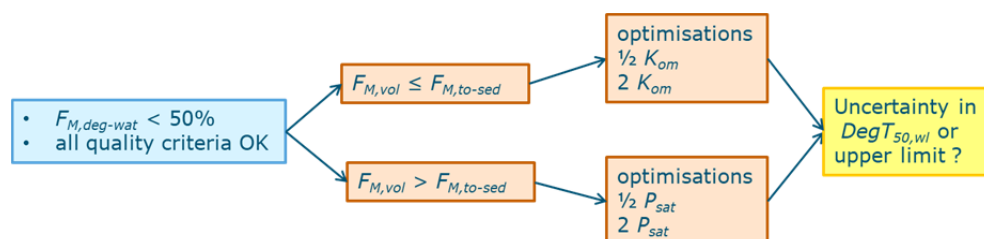


Figure 2.6 Estimation of the uncertainty in the optimised $DegT_{50,water}$ for cosms in which concentrations in the water layer and the sediment have been measured and which fulfil the two criteria of the most left-hand, blue box.

As stated above we decided to relax the level of uncertainty in the estimated $DegT_{50,water}$ from a CV value of 10% to 25%. Whether this is defensible depends on the influence of the $DegT_{50,water}$ on the endpoint of the exposure assessment, e.g. the peak water concentration. Therefore, we recommend to analyse the sensitivity of the target concentration to the estimated value of $DegT_{50,water}$ in the scenarios used for the authorisation procedure, such as the ones of FOCUS or for NL arable or fruit crops in order to be able to judge the expected uncertainty in this concentration.

The parameterisation of the water-sediment systems for the 'Water-sediment' method and the 'Water-sediment + o.m. 0-1 cm measured' method will be described into detail in Chapter 3.

3 Analysis of cosm studies with measurements in both water and sediment

3.1 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. Below we first summarise the procedure for one optimisation run, both for water-only and water-sediment cosms. In the remainder of this chapter we focus on water-sediment cosms only and describe how we performed the estimation procedure for the five compounds of this report.

In brief, one optimisation run by PEST_TOXSWA consists of the following steps:

1. Select the correct optimisation method depending on whether the concentration measurements were done in the water layer only (water-only cosms), or both in the water layer and the sediment (water-sediment cosms) and whether the organic matter content of the sediment was measured (see Chapter 2.4 and Figure 2.2);
2. Parameterise the TOXSWA model, as far as possible for the specified cosm, on the basis of the study description;
3. Run the model and compare the simulated concentrations in water (water-only cosms) or in water and sediment simultaneously (water-sediment cosms) to the concentrations measured in the cosm study;
4. Let PEST adjust the TOXSWA input parameters (i) degradation rate in water, (ii) initial concentration and, for water-sediment cosms (iii) organic matter content of suspended solids and sediment on the basis of the correspondence between simulated and measured concentrations and next, re-run the model;
5. Repeat 3 and 4 until a pre-defined stop criterion is met and
6. Consider whether the quality of the fit is acceptable. If yes, extract the optimised degradation rate in water, $DegT_{50, water}$.

If more than one satisfactory, optimised value of the $DegT_{50, water}$ has been obtained for the same cosm study we recommend to take the geometric mean of the obtained satisfactory values. This follows the guidance of the FOCUS Degradation Kinetics Working group (FOCUS, 2006) for averaging degradation rates or half-lives, because the geometric mean method has the advantage that geomeans of half-lives correspond to the geomeans of degradation rates.

If cosms of the same study are comparable data may be pooled. It is then possible to perform steps 2-6 only once by scaling all measured concentration-time profiles from 0 to 1 and comparing these to the (scaled) simulated concentration-time profile (see Section 3.5). 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 the sediment properties or layer over which the sediment concentrations have been measured (water-sediment cosms) are similar, and (ii) the degradation rates in water of the compound seem to be similar, which can be seen best by plotting the aqueous concentrations on a logarithmic scale to see if the slopes are (approximately) similar.

3.2 Parameterisation for PEST-TOXSWA for all water-sediment cosm studies

Each water-sediment cosm was parameterised for the TOXSWA model. Only three parameters were optimised: $DegT_{50, water}$, $C_{t=0}$ and the organic matter content. 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 Pesticides Properties DataBase. A protocol was used to select the most appropriate values from the Pesticides Properties DataBase (Appendix 2). Although the calculations in this report were performed using data from the Pesticides Properties DataBase, calculations for authorisation purposes should, obviously, be performed using data from the authorisation dossier. All input that was cosm-specific is mentioned in the appendix belonging to the study, e.g. Appendix 3 for chlorpyrifos cosm studies. In addition, compound-specific properties appear in the appendices. Other input parameters were defined in the same way for all cosm studies. How the suspended solids and sediment properties for water-sediment cosms were parameterised is described in detail below and in sections 3.3 and 3.4.

Input parameters that were equal for all water-sediment cosm simulations include: (i) the concentration of suspended solids, and (ii) compound properties, such as molar enthalpies of vaporisation, dissolution and degradation, and the degradation half-life in sediment (Table 3.1).

Table 3.1 *Process-related parameter values and their origin, used in all cosm study simulations.*

| Property | Value | Origin |
|---|-------|---|
| Molar enthalpy of vaporisation (kJ/mol) | 95 | FOCUS (2001) |
| Molar enthalpy of dissolution (kJ/mol) | 27 | FOCUS (2001) |
| Molar enthalpy of degradation (kJ/mol) | 65.4 | EFSA (2007) |
| Degradation half-life in sediment (d) | 1000 | FOCUS Degradation Kinetics (2006) and section 2.3 2 nd paragraph |

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 also refer to 20°C.

The values for the input parameters of suspended solids and sediment for water-sediment cosms are presented in sections 3.3 (Method 'Water-sediment') and 3.4 (Method 'Water-sediment + o.m. 0-1 cm measured'). Both methods make use of a default set and additional sets of suspended solids and sediment properties. The default set of values is presented in Table 3.2, it was derived from FOCUS (2001) and based on their bulk density and organic matter content, but fulfilled the requirements of Eq. (3.1).

Table 3.2 *Values of suspended solids and sediment parameters used in TOXSWA for the cosm study simulations.*

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

Equation 3.1 states that the volume fractions of water, organic matter and mineral parts sum up to 1:

$$\varepsilon + \frac{\rho_{sed}}{\rho_{om}} f_{om, sed} + \frac{(1 - f_{om, sed}) \rho_{sed}}{\rho_{min}} = 1 \quad (3.1)$$

where ρ_{om} (kg L⁻¹) is the phase density of organic matter and ρ_{min} (kg L⁻¹) 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} (kg L⁻¹) and the sediment organic matter content $f_{om, sed}$ (-) can be calculated using Equation (3.1).

For the default sediment with $\rho_{sed} = 0.8$ kg.L⁻¹ and $f_{om, sed} = 0.09$ (Table 3.2), $\varepsilon = 0.67$ was obtained. The tortuosity was calculated according to the empirical equation (Boudreau, 1996):

$$\lambda = \frac{1}{[1 - \ln(\varepsilon^2)]} \quad (3.2)$$

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

The optimisation procedure requires initial estimates. Initial estimates of the two parameters $DegT_{50, water}$ and $C_{t=0}$ 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, $C_{t=0}$, was usually set at 1 (scaled value, representing 100% of the initial concentration). The initial estimate of the $f_{om, sed}$ parameter was based upon the selected set of suspended solids and sediment properties as explained in sections 3.3 and 3.4 for water-sediment cosms.

Minimising the objective function phi and choice of initial values

The inverse modelling procedure attempts to identify the values for the parameters to be fitted that result in the best correspondence between measured and simulated values for the experimental quantities under consideration, i.e. the concentrations of the test compound in water and in sediment.

PEST requires that each of the parameters to be fitted is given an initial value, which is used as the starting point in the comparison between experimental and simulated values. The value is then adjusted by PEST, a new simulation is run, another comparison between experimental and adjusted values is made, parameters are adjusted again, etc. This process is continued until adjusting the parameter values does not result in a better fit anymore.

The 'surface' of the objective function phi used to assess the quality of the fit is bound to contain several minima, and maxima. There may also be some relatively flat parts where changing parameter values hardly has any effect on the quality of the fit. The aim of the estimation procedure is to find the combination of parameter values that results in the 'deepest' minimum in the function surface, further called the 'global minimum'.

There is, however, a chance of hitting a 'local minimum', i.e. the fit does not seem to improve upon slight changes of the parameter values, and a larger change of parameter values is necessary to 'jump out of' the local minimum and continue the search for the true minimum. However, the user has little insight and control over the adjustment of parameter values that PEST uses during optimisation, and there is a distinct risk that PEST ends up in a local minimum.

To circumvent this pitfall, it is common practice to perform the optimisation runs several times, each time using a different combination of initial values for the parameters to be estimated. If the initial values are spaced sufficiently wide, chances that the entire function surface is sampled during at least one of the optimisation runs are greatly improved, and hence the chances of finding the global minimum of the function surface are equally improved, resulting in a much better chance of finding the best combination of parameter values.

For the water-sediment cosms there are three parameters to be fitted by PEST: the $DegT_{50, water}$, the initial concentration in the water, $C_{t=0}$ and the organic matter content of the sediment $f_{om, sed}$. Although

the (often not measured, so unknown) bulk density is a fourth independent parameter, that determines the value of the objective function ϕ , it was not possible to include a fourth parameter in the fitting procedure in view of the often limited number of measurements in the sediment. To circumvent this problem we decided to perform the optimisations for three quite different values of the bulk density, thus enabling PEST to analyse three different parts of the 'surface' of the objective function ϕ . In this way we wanted to decrease the risk of PEST getting stuck in a local minimum.

3.3 Parameterisation of water-sediment cosms, method 'Water-sediment'

Definition of sediment layers in TOXSWA simulations

For reasons of clarity we first define which layers are distinguished in the sediment for the TOXSWA simulations:

The total sediment depth: this is generally set to 10 cm for the cosms, implying that all mass penetrating into the sediment is contained in the sediment subsystem for which TOXSWA simulates the pesticide mass balance. In this report the sediment properties have been kept constant over the entire 0-10 cm sediment in all TOXSWA-PEST optimisations for reasons of simplicity, knowing that the 1-10 cm layer is less important than the upper 0-1 cm which contains the majority of the pesticide mass;

The target sediment layer: this is the sediment layer for which the pesticide concentration (mg/L, or in mg/kg, in the latter case the term content may also be used) has been measured. In order to enable a correct comparison between measured and simulated sediment concentrations, the sediment in the TOXSWA model needs to be parameterised in such a way that the simulated sediment concentrations are given as output for the same sediment layer as the one for which the measurements were done. In TOXSWA this output equals the average pesticide concentration over this so-called 'target sediment layer'

The 0-1 cm top layer: this is the upper first centimetre sediment. This 0-1 cm top layer plays a dominant role in the pesticide behaviour in the sediment.

As explained above the optimisation needs to be repeated several times, starting from different initial values for the optimisation parameters in order to try to find the global minimum of the objective function ϕ and to avoid ending up in local minima of ϕ . As it was not possible to let PEST optimise four independent parameters, we decided to have PEST start at three quite different values of bulk density. To do so, we designed sets of quite different values of bulk densities coupled to different values of organic matter and had PEST starting its optimisations from these different sets of bulk density (fixed value) and organic matter content (initial estimate, to optimise). This procedure is depicted in Figure 3.1 indicating two groups of optimisation rounds: the red ones for the first optimisation round (with three sets of bulk density and organic matter content) and the purple ones for the next round (two sets), if the first round did not result in satisfactory fits.

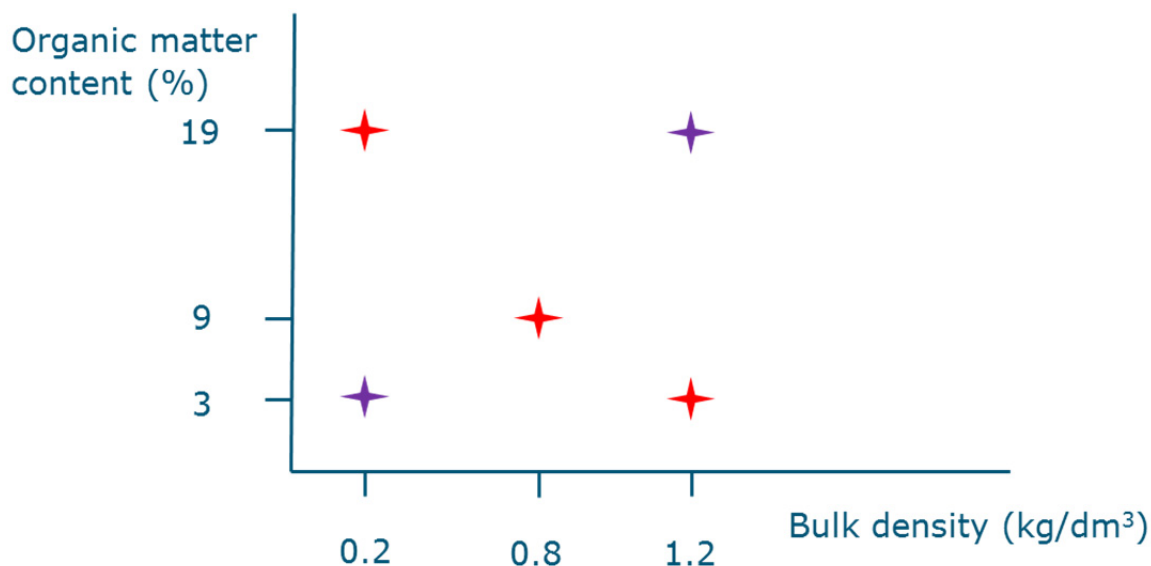


Figure 3.1 Combinations of bulk density (fixed value) and organic matter content (initial value, to optimise) for the sediment of the simulated cosm (red: perform optimisation always, purple: only if needed, see text).

For each of the 3 combinations of bulk density and organic matter content, at least 3 combinations of initial values of $c_{t=0}$ and $DegT_{50,water}$ were used in the optimisations, resulting in at least 9 optimisations overall. If these 9 optimisations yielded three or more satisfactory fits the optimisations are finished and we can calculate the average (geometric mean) $DegT_{50,water}$ from the results of these fits. If these 9 optimisations yielded one or two satisfactory fits (see below for criteria), we continued the optimisations for the purple stars of Figure 3.1 (and not with other combinations of the initial values than the three given in Table 3.4 for $c_{t=0}$ and $DegT_{50,water}$ for the three sets, indicated by the red stars).

So, we then continued the optimisations with one or two other sets of bulk density and organic matter content of the sediment indicated by the purple stars (Figure 3.1). As for the former sets, next to the optimisation of organic matter content, the concentration in water at $t=0$, $c_{t=0}$, and the degradation half-life in water, $DegT_{50,water}$, was optimised and at least 3 combinations of initial values of $c_{t=0}$ and $DegT_{50,water}$ were used in the optimisations.

Table 3.3 specifies the parameter values for the three sets of optimisation for the first optimisation round, indicated by the red stars of Figure 3.1. Table 3.4 specifies the initial values for the first nine optimisation runs, which were always done. If three or more satisfactory fits were obtained from the first nine optimisations (for criteria see above), the optimisation calculations were finished.

Table 3.3 Values for sediment and suspended solids parameters used in TOXSWA for the optimisations. The sediment parameter combinations for bulk density and organic matter content are also shown as red stars in Figure 3.1. Note that the organic matter contents of the suspended solids are equal to those in the sediment.

| Parameter | Default set | Second set | Third set |
|---|-------------|------------|-----------|
| <i>Suspended solids</i> | | | |
| Concentration in water (mg/L) | 15 | 15 | 15 |
| Organic matter content (%) | 9 | 19 | 3 |
| <i>Sediment (0 – 10 cm)</i> | | | |
| Bulk density (kg/L) | 0.8 | 0.2 | 1.2 |
| Organic matter content (mass fraction, %) | 9 | 19 | 3 |
| Degradation half-life in sediment (d) | 1000 | 1000 | 1000 |

Table 3.4 The optimisation parameters with their initial values and lower and upper parameter bounds for the first round of optimisations (red stars in Figure 3.1).

| Parameter | | First set | Second set | Third set |
|--|------------------------|-----------------------|-----------------------------|---------------------------|
| Bulk density (kg/dm ³) | | 0.8 (- ^a) | 0.2 (- ^a) | 1.2 (- ^a) |
| Organic matter content (-) | Initial value | 0.09 | 0.19 | 0.03 |
| | Upper and lower bounds | 0.025-0.50 | 0.025-0.50 | 0.025-0.50 |
| For each of the three sets above perform optimisations, using the three combinations of $c_{t=0}$, scaled and $DegT_{50,water}$ below | | | | |
| $c_{t=0}$, scaled (-) | Initial value | 1 | 1 | 1 |
| | Upper and lower bounds | 0.1-5.0 ^b | 0.1-5.0 ^b | 0.1-5.0 ^b |
| $DegT_{50,water}$ (d) | Initial value | E ^c | (0.1 to 0.5)*E ^c | (2 to 10) *E ^c |
| | Upper and lower bounds | 0.1*E – 100*E | 0.1*E – 100*E | 0.1*E – 100*E |

^a Bulk density was not estimated during inverse modelling, and hence it was given a constant value and lower/upper bounds do not apply.

^b From the nine possible combinations of $c_{t=0}$ and $DegT_{50,water}$ we used the three combinations shown in this table with $c_{t=0}$ is 1.

^c E stands for the decline rate in the water layer, roughly visually estimated by determining the time when half of the initial mass or concentration is present.

Around the used organic matter content of 9, 19 and 3% ranges of 2.5% to 50% were selected, representing respectively a realistic low value and a realistic 'extreme' high value for organic matter for the upper 0-1 cm sediment (Adriaanse et al, 2015). We used the scaled $c_{t=0}$ value of 1 as initial estimate and the realistic, but extreme values of 0.1 and 5 as parameter bounds. The (roughly) estimated value of the dissipation half-life from water was used as initial estimate for the $DegT_{50,water}$ and approximately 0.2-0.1 and 5-10 times this value as its bounds.

So, if the first 9 optimisations (3 sets of bulk density and organic matter content, each combined with three initial values of $DegT_{50,water}$ and a $c_{t=0}$ value of 1) did not result in three or more satisfactory fits, additional optimisations were performed, using the two additional sets of bulk density and organic matter content as presented by the purple stars in Figure 3.1. Their used values for sediment and suspended solids input parameters are specified in Table 3.5. Table 3.6 specifies the initial values for the first three or six additional optimisation runs. As soon as three or more satisfactory fit was obtained (for criteria see section 2.4), the optimisation calculations were finished. As long as only one or two satisfactory fits were achieved, more optimisation runs were done. We first performed the optimisations for the fourth set coupled to the three combinations of initial values for $c_{t=0}$ and $DegT_{50,water}$ specified in Table 3.6 and next, the optimisations for the fifth set coupled to the three combinations of initial values for $c_{t=0}$ and $DegT_{50,water}$ specified in Table 3.6.

If at the end of the nine plus six additional optimisation runs one or two satisfactory fits were obtained, the optimisations were stopped and we are also satisfied with the obtained $DegT_{50,water}$ value (single value or geomean of two values).

If still no satisfactory fit had been found after these nine plus additional 6 optimisations (2 sets times 3 combinations of initial values of $c_{t=0}$ and $DegT_{50,water}$) expert judgement was sought.

As explained in section 2.5 and Figure 2.6, if the acceptable optimised $DegT_{50,water}$ values were obtained for $F_{M,deg-wat} < 50\%$, we suggest to obtain insight in the uncertainty of the optimised $DegT_{50,water}$ values by evaluating the effect of the competing dissipation processes of volatilisation and transport to sediment on the optimised value. To do so, we suggest to re-run the optimisation runs that gave acceptable optimised $DegT_{50,water}$ values, but now with the values for K_{om} or P_{sat} suggested in Figure 2.6.

Table 3.5 Values for sediment and suspended solids parameters used in TOXSWA for the second round of optimisations. The sediment parameter combinations for bulk density and organic matter content are also shown as purple stars in Figure 3.1. Note that the organic matter contents for the suspended solids are equal to those in the sediment.

| Parameter | Fourth set | Fifth set |
|---|------------|-----------|
| <i>Suspended solids</i> | | |
| Concentration in water (mg/L) | 15 | 15 |
| Organic matter content (%) | 3 | 19 |
| <i>Sediment (0 – 10 cm)</i> | | |
| Bulk density (kg/L) | 0.2 | 1.2 |
| Organic matter content (mass fraction, %) | 3 | 19 |
| Degradation half-life in sediment (d) | 1000 | 1000 |

Table 3.6 The optimisation parameters with their initial values and lower and upper parameter bounds for the second round of optimisations (purple stars in Figure 3.1).

| Parameter | | Fourth set | Fifth set | |
|--|------------------------|-----------------------|-----------------------------|--------------------------|
| Bulk density (kg/dm ³) | | 1.2 (- ^a) | 0.2 (- ^a) | |
| Organic matter content (-) | Initial value | 0.19 | 0.03 | |
| | Upper and lower bounds | 0.025-0.50 | 0.025-0.50 | |
| For each of the two sets above perform optimisations, using the three combinations of $c_{t=0}$, scaled and $DegT_{50,water}$ below | | | | |
| $c_{t=0}$, scaled (-) | Initial value | 1 | 1 | 1 |
| | Upper and lower bounds | 0.1-5.0 ^b | 0.1-5.0 ^b | 0.1-5.0 ^b |
| $DegT_{50,water}$ (d) | Initial value | E ^c | (0.1 to 0.5)*E ^c | (2 to 10)*E ^c |
| | Upper and lower bounds | 0.1*E – 100*E | 0.1*E – 100*E | 0.1*E – 100*E |

^a Bulk density was not estimated during inverse modelling, and hence it was given a constant value and lower/upper bounds do not apply.

^b From the nine possible combinations of $c_{t=0}$ and $DegT_{50,water}$ we used the three combinations shown in this table with $c_{t=0}$ is 1.

^c E stands for the decline rate in the water layer, roughly visually estimated by determining the time when half of the initial mass or concentration is present.

3.4 Parameterisation of water-sediment cosms, method 'Water-sediment + o.m. 0-1 cm measured'

The method 'Water-sediment + o.m. 0-1 cm measured' is analogous to the method 'Water-sediment' described above. The difference is that in this cosm the organic matter content of the upper 0-1 cm sediment has been measured and that we use of this additional information. We optimised the measured value of the organic matter content around its measured value, thus taking into consideration the expected uncertainty in its experimentally determined value. In our calculations we used upper and lower bounds of $\pm 0.5\%$ around the measured value in the optimisations, but other values may be chosen. E.g. for four ditches at the experimental station 'De Sinderhoeve' in The Netherlands we found organic matter contents ranging from 3.7 to 5.5% and standard deviations ranging from 2.2 to 3.2% for the 16 measurements per ditch (Crum, pers. comm., 2016). The bulk densities remained fixed at the same three values of 0.8, 0.2 and 1.2 kg/dm³ as before.

Analogous to the method 'Water-sediment' two groups of optimisation rounds have been defined (Figure 3.2): red ones for the first optimisation round and the purple one for the next round, if the first round did not result in sufficiently satisfactory fits.

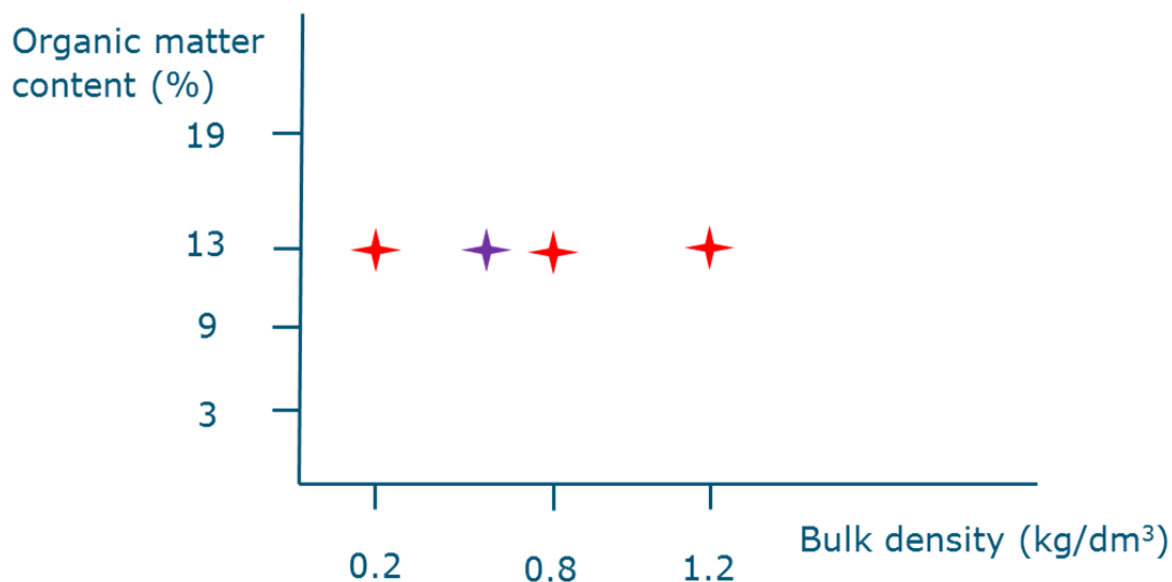


Figure 3.2 Combinations of bulk density (fixed value) and organic matter content (initial measured value, e.g. 13% here, to optimise within limits reflecting measurement uncertainty) for the sediment of the simulated cosm. (red: perform optimisation always, purple: only if needed, see text).

Table 3.7 specifies the parameter values for the three sets of optimisation for the first optimisation round, indicated by the red stars of Figure 3.2. Table 3.8 specifies the initial values for the first nine optimisation runs, which were always done. If three or more satisfactory fits were obtained (for criteria see above), the optimisation calculations were finished. If only one or two satisfactory fits were obtained we continued the optimisations.

Table 3.7 Values for sediment and suspended solids parameters used in TOXSWA for the optimisations. The sediment parameter combinations for bulk density and organic matter content are also shown as red stars in Figure 3.2. Note that the organic matter contents for the suspended solids are equal to those in the sediment.

| Parameter | Default set | Second set | Third set |
|---|-----------------|-----------------|-----------------|
| <i>Suspended solids</i> | | | |
| Concentration in water (mg/L) | 15 | 15 | 15 |
| Organic matter content (%) | mv | mv | mv |
| <i>Sediment (0 – 10 cm)</i> | | | |
| Bulk density (kg/L) | 0.8 | 0.2 | 1.2 |
| Organic matter content (mass fraction, %) | mv ^a | mv ^a | mv ^a |
| Degradation half-life in sediment (d) | 1000 | 1000 | 1000 |

^a Note that the measured value (mv) of the 0-1 cm top layer is used for the entire sediment depth in the TOXSWA simulations.

Table 3.8 The optimisation parameters with their initial values and lower and upper parameter bounds for the first round of optimisations (red stars in Figure 3.2).

| Parameter | | First set | Second set | Third set |
|--|------------------------|-----------------------|-----------------------------|--------------------------|
| Bulk density (kg/dm ³) | | 0.8 (- ^a) | 0.2 (- ^a) | 1.2 (- ^a) |
| Organic matter content (-) | Initial value | mv ^a | mv ^a | mv ^a |
| | Upper and lower bounds | mv-0.005 – mv+0.005 | mv-0.005 – mv+0.005 | mv-0.005 – mv+0.005 |
| For each of the three sets above perform optimisations, using the three combinations of $c_{t=0}$, scaled and $DegT_{50,water}$ below | | | | |
| $c_{t=0}$, scaled (-) | Initial value | 1 | 1 | 1 |
| | Upper and lower bounds | 0.1-5.0 ^b | 0.1-5.0 ^b | 0.1-5.0 ^b |
| $DegT_{50,water}$ (d) | Initial value | E ^c | (0.1 to 0.5)*E ^c | (2 to 10)*E ^c |
| | Upper and lower bounds | 0.1*E – 100*E | 0.1*E – 100*E | 0.1*E – 100*E |

^a The organic matter content has been measured for the 0-1 cm layer, therefore its upper and lower bounds were only $\pm 0.5\%$ around its measured value (mv) to account for uncertainty in its experimentally determined value.

^b From the nine possible combinations of $c_{t=0}$ and $DegT_{50,water}$ we used the three combinations shown in this table with $c_{t=0}$ is 1.

^c E stands for the decline rate in the water layer, roughly visually estimated by determining the time when half of the initial mass or concentration is present.

So, if the total of 9 optimisations (3 sets of bulk density and organic matter content, each combined with 3 combinations of initial values $DegT_{50,water}$ and a $c_{t=0}$ value of 1) did not result in three or more satisfactory fit, additional optimisations were performed, using the additional set of bulk density and organic matter content as presented by the purple star in Figure 3.2. The input parameters for sediment and suspended solids are specified in Table 3.9. Table 3.10 specifies the initial values for these three additional optimisation runs. As soon as three or more satisfactory fits were obtained (for criteria see above), the optimisation calculations were finished and the geomean $DegT_{50,water}$ was calculated. If only one or two satisfactory optimisations were obtained, we also stop the optimisation calculations and are also satisfied with the obtained $DegT_{50,water}$ value (single value or geomean of two values).

If still no satisfactory fit had been found after these additional 3 optimisations expert judgement was sought.

As explained in section 2.5 and Figure 2.6, if the acceptable optimised $DegT_{50,water}$ values were obtained for $F_{M,deg-wat} < 50\%$, we suggest to obtain insight in the uncertainty of the optimised $DegT_{50,water}$ values by evaluating the effect of the competing dissipation processes of volatilisation and transport to sediment on the optimised value. To do so, we suggest to re-run the optimisation runs that gave acceptable optimised $DegT_{50,water}$ values, but now with the values for K_{om} or P_{sat} suggested in Figure 2.6.

Table 3.9 Values for sediment and suspended solids parameters used in TOXSWA for the second round of optimisations. The sediment parameter combinations for bulk density and organic matter content are also shown as a purple star in Figure 3.2. Note that the organic matter contents for the suspended solids are equal to those in the sediment.

| Parameter | Fourth set |
|---|-----------------|
| <i>Suspended solids</i> | |
| Concentration in water (mg/L) | 15 |
| Organic matter content (%) | mv |
| <i>Sediment (0 – 10 cm)</i> | |
| Bulk density (kg/L) | 0.5 |
| Organic matter content (mass fraction, %) | mv ^a |
| Degradation half-life in sediment (d) | 1000 |

^a Note that the measured value (mv) of the 0-1 cm top layer is used for the entire sediment depth in the TOXSWA simulations.

Table 3.10 The optimisation parameters with their initial values and lower and upper parameter bounds for the second round of optimisations (purple star in Figure 3.2).

| Parameter | | Fourth set | | |
|---|------------------------|----------------------|-----------------------------|--------------------------|
| Bulk density (kg/dm ³) | | 0.5 | | |
| Organic matter content (-) | Initial value | mv ^a | | |
| | Upper and lower bounds | mv-0.005 – mv+0.005 | | |
| For the set above perform optimisations, using the three combinations of $c_{t=0}$, scaled and $DegT_{50,water}$ below | | | | |
| $c_{t=0}$, scaled (-) | Initial value | 1 | 1 | 1 |
| | Upper and lower bounds | 0.1-5.0 ^b | 0.1-5.0 ^b | 0.1-5.0 ^b |
| $DegT_{50,water}$ (d) | Initial value | E ^c | (0.1 to 0.5)*E ^c | (2 to 10)*E ^c |
| | Upper and lower bounds | 0.1*E – 100*E | 0.1*E – 100*E | 0.1*E – 100*E |

^a The organic matter content has been measured for the 0-1 cm layer, therefore its upper and lower bounds were only $\pm 0.5\%$ around its measured value (mv) to account for uncertainty in its experimentally determined value.

^b From the nine possible combinations of $c_{t=0}$ and $DegT_{50,water}$ we used the three combinations shown in this table with $c_{t=0}$ is 1.

^c E stands for the decline rate in the water layer, roughly visually estimated by determining the time when half of the initial mass or concentration is present.

3.5 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 (please note that TOXSWA assumes that the scaled concentrations are in 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 scaling should, however, only be applied if initial inspection of concentration – time curves indicates that the $DegT_{50,water}$ is not dependent on initial aqueous concentration, i.e. similar dissipation rates are observed for the various treatment levels.

Also data for the same treatment level from experiments in which concentrations have been measured in both water and sediment can be combined in a single analysis to obtain a single estimate of $DegT_{50,water}$. Again 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, so as well the aqueous as the sediment concentrations are divided by the highest aqueous concentration (in mg/L)

observed in that replicate. Please note that TOXSWA will assume that the scaled sediment concentrations are in g/kg.

Combining systems by scaling is not possible for multiple 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, or different sediment properties or layer over which the sediment concentrations have been measured, cannot be simulated by a single TOXSWA run, because only a single value for these parameters can be used in a TOXSWA run.

We scaled all studies in our calculations in this report. However, we finally recommend not to apply scaling, except when it offers the advantage of being able to combine all available data into a single analysis by PEST. The reason is that scaling always necessitates to consider adjusting the Freundlich sorption coefficient, because the Freundlich isotherm is non-linear (For details: see Chapter 3.6).

3.6 Value of the Freundlich sorption coefficient K_{om} and use of scaled concentrations

Sorption to sediment and suspended solids is described in TOXSWA through a non-linear Freundlich sorption isotherm. As pointed out by Deneer et al. (2015), when dealing with non-linear sorption the use of scaled concentrations requires calculation of an 'adjusted' organic matter partition coefficient (K_{om}). The Freundlich isotherm equation assumes that the K_{om} is specified for a reference concentration of 1 mg/L and therefore scaling of concentrations may result in the use of an erroneous value for K_{om} .

In situations where data sets from multiple cosms are combined, and scaling is necessary to adjust the concentrations in all cosms to a common 0 – 1 range, it is recommended to overcome this problem as follows: calculate the geomean of the (unscaled) initial concentrations of the different studies, to give $C_{t=0, geo}$ (mg/L); then modify the K_{om} in the TOXSWA_cha.txt file using:

$$K_{om,new} = K_{om,org} \left(\frac{C_{ref}}{C_{0,geo}} \right)^{1-N} \quad (3.3)$$

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 the sorption isotherm is linear, i.e. the Freundlich exponent equals 1, $K_{om,new}$ and $K_{om,org}$ have the same value. If scaling is applied to a single data set, the unscaled initial concentration of this data set is used as $C_{t=0, geo}$.

As an example, the initial concentration of chlorothalonil in one of the systems studied by Kwon and Armbrust (2006) was 0.3385 mg/L (systems in the dark, using creek sediment). When using scaled concentrations in the inverse modelling, the original value of K_{om} (1759 L kg^{-1}) was adjusted for severe non-linearity of the sorption isotherm (Freundlich coefficient of 0.64) by calculating an adjusted value for the organic matter partition coefficient. Using Eqn 3.3 resulted in $K_{om,new} = 2598 \text{ L/kg}$.

In the simulations with the scaled concentrations this adjusted value of $K_{om,new}$ equal to 2598 L/kg needs to be used, together with the value of 0.64 for the Freundlich exponent in sediment and in suspended solids.

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

In cosms where concentrations in the water layer as well as in the sediment have been measured it is appropriate to give equal importance to the measurements in the water and sediment layers in the optimisation procedure.

However, there may be large numerical differences between concentrations in these compartments, depending on the sorption coefficient of the compound under investigation, amongst other factors. TOXSWA uses the unit mg/L for the water layer and the unit g/kg³ for the sediment layer so usually the values of concentrations in the sediment are orders of magnitude lower than the values of the concentrations in the water layer. To ensure a similar contribution of measured aqueous and sediment concentrations to the estimation of the $DegT_{50,water}$, a weighting factor could then be used. The weighting factor may ensure that measurements in water and sediment are given the same importance, irrespective of any differences between their magnitudes. Moreover, the weighting factor may account for any difference in the number of measurements between water and sediment compartments. Calculation of the weighting factor is explained in Adriaanse et al. (2012) and detailed here below for our cosm studies. Note that in our optimisation procedure the weight factors are calculated and used as model input in an automated way, so the user does not need to do this himself. (But the user is able to correct the relative weight of the water and sediment compartments with the aid of an additional weight factor, the so-called 'weight multiplication factor for the first group', i.e. water, which by default is set to 1.)

So, concentrations in the water and in the sediment are fitted simultaneously, giving equal weights to the water and the sediment measurement series. Weight factors are calculated using the following equations:

$$W_w = \Phi \frac{1}{c_{w,max} \sqrt{n_w}} \quad (3.4a)$$

$$W_{sed} = \frac{1}{X_{sed,max}^* \sqrt{n_{sed}}} \quad (3.4b)$$

where W_w (L mg⁻¹) and W_{sed} (kg g⁻¹) are weight factors in PEST for measurements in water and in sediment, Φ (-) is the weight multiplication factor for the first group (to give more weight to the measurements in the water if needed), n_w and n_{sed} are the number of measurements in water and in sediment and $c_{w,max}$ (mg L⁻¹) and $X_{sed,max}^*$ (g kg⁻¹) are the maximum measured concentrations in water and in sediment.

Please note that the calculation procedure of the χ^2 -error (see Appendix 1) uses the weight factors of Eqns 3.4a and 3.4b. So if more weight is given to the measurements in the water (by setting $\Phi > 1$), this will also decrease the effect of differences between measured and calculated sediment concentrations on the χ^2 -error.

This allowed the objective function φ to be defined as

$$\varphi = \sum_{i=1}^{n_w} (W_w [c_{w,exp,i} - c_{w,sim,i}])^2 + \sum_{j=1}^{n_{sed}} (W_{sed} [X_{sed,exp,j}^* - X_{sed,sim,j}^*])^2 \quad (3.5)$$

³ Note that in FOCUS_TOXSWA 5.5.3 (TOXSWA source v 3.3.6) the unit has been changed into **mg/kg** for the sediment layer, so the weight factor W_{sed} in PEST needs to be calculated based upon this unit when using the new FOCUS_TOXSWA version 5.5.3.

where $c_{w,exp,i}$ (mg L^{-1}) and $X_{sed,exp,j}^*$ (g kg^{-1}) are the measured concentrations in water and in sediment for measurement number i and j and $c_{w,sim,i}$ (mg L^{-1}) and $X_{sed,sim,j}^*$ (g kg^{-1}) are the simulated concentrations in water and in sediment corresponding to measurement number i and j .

Table 3.11 gives an example of calculated weight factors for the chlorpyrifos cosm study by Brock et al. (1992), using scaled concentrations. The weight factor of 220 for the sediment (compared to the value of 0.354 for the water layer) indicates that the sediment needed to obtain about 1000 times more weight in order to make the correspondence between measured and simulated concentrations in sediment as important as those of the water layer.

Table 3.11 Weight factors used in the optimisation for the chlorpyrifos cosm study by Brock et al. (1992), resulting in equal weights for the water and sediment measurements in the optimisation.

| Weight factor | Value | Remark |
|---------------|---------|--------------------------------------|
| W_w | 0.354 | Using scaled aqueous concentrations |
| W_{sed} | 220.075 | Using scaled sediment concentrations |

The use of weighting ensures equal importance of water and sediment concentrations in the estimation process, regardless of differences in their absolute magnitude or the number of measurements in either compartment. The same applies to the graphic representation of residuals of water and sediment data. Multiplying residuals with their respective weight factor before plotting enables easy comparison of (weighted) water and sediment residuals in a single plot, since they will become comparable in magnitude. This helps observing the presence of possible trends in the residuals, the absence of which is at least as important as their absolute magnitude. This weighting also includes the additional multiplication factor Φ that enables the user to apply extra weight to either the water or sediment measurements.

3.8 Future improvements of the optimisation procedure

DegT_{50,sediment} value

In the current optimisation procedure the $DegT_{50,sediment}$ has been set at 1000 d, i.e. degradation in the sediment is negligible. For some compounds the laboratory water-sediment studies may suggest that this value is not realistic and that the compound does degrade in the sediment, e.g. when for a relatively strongly sorbing compound the majority of the mass has entered the sediment after a couple of days and the overall $DegT_{50}$ of the water-sediment systems is much lower than 1000 d. In this case the overall $DegT_{50}$ value seems a better estimate for the $DegT_{50,sediment}$ than the default value of 1000 d. This may lead to an improved correspondence between simulated and measured values in the sediment (as well as in the water) and thus an improved estimation of $DegT_{50,water}$. However the current software package cannot perform this refinement automatically (the user has to estimate this overall $DegT_{50}$ and enter it in the TOXSWA_moe.txt file himself/herself).

Sediment segmentation for compounds with K_{oc} value above 30000 L/kg

In the current optimisation procedure the standard sediment segmentation (14 segments ranging from 1 mm at the water-sediment interface to 3 cm at 10 cm depth) is used in the numerical solution of TOXSWA. For compounds with a relatively high sorption coefficient a finer segmentation may be needed to obtain an accurate numerical solution. As long as no stable and converging numerical solution for the mass balance equation of the sediment is used, the concentrations in the sediment change with other segmentations, which may affect the water concentrations and thus the estimated $DegT_{50,water}$. This is an undesirable situation: the solution of the mass balance equation should not depend on the selected segment sizes in the numerical solution. In the FOCUS surface water scenarios the so-called 'FOCUS_highKoc sediment segmentation' (27 segments ranging from 0.03 mm at the water-sediment interface to 3 cm at 10 cm depth) is suggested for compounds with K_{oc} values above 30000 L/kg to obtain a stable and converging numerical solution (Beltman et al, 2014, section 4.4.3). However the current software package does not perform this refinement automatically (the user has

to change this in the TOXSWA_moe.txt file himself/herself). Thus, for compounds with K_{oc} values above approximately 30000 L/kg, the accuracy of the estimated $DegT_{50,water}$ may be improved by applying a finer sediment segmentation.

3.9 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 authorisation 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 3.3. 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 authorisation 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 represent increased realistic conditions. However, guidance on how to combine $DegT_{50,water}$ values from different steps for use in the authorisation procedure is beyond the scope of this report.

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 Chapter 5, which discuss estimates for $DegT_{50,water}$ for chlorpyrifos, lambda-cyhalothrin, linuron, metsulfuron-methyl and prosulfocarb; dissipation data from lower-tier studies and the currently estimated $DegT_{50,water}$ values from higher-tier mesocosm studies are compared.

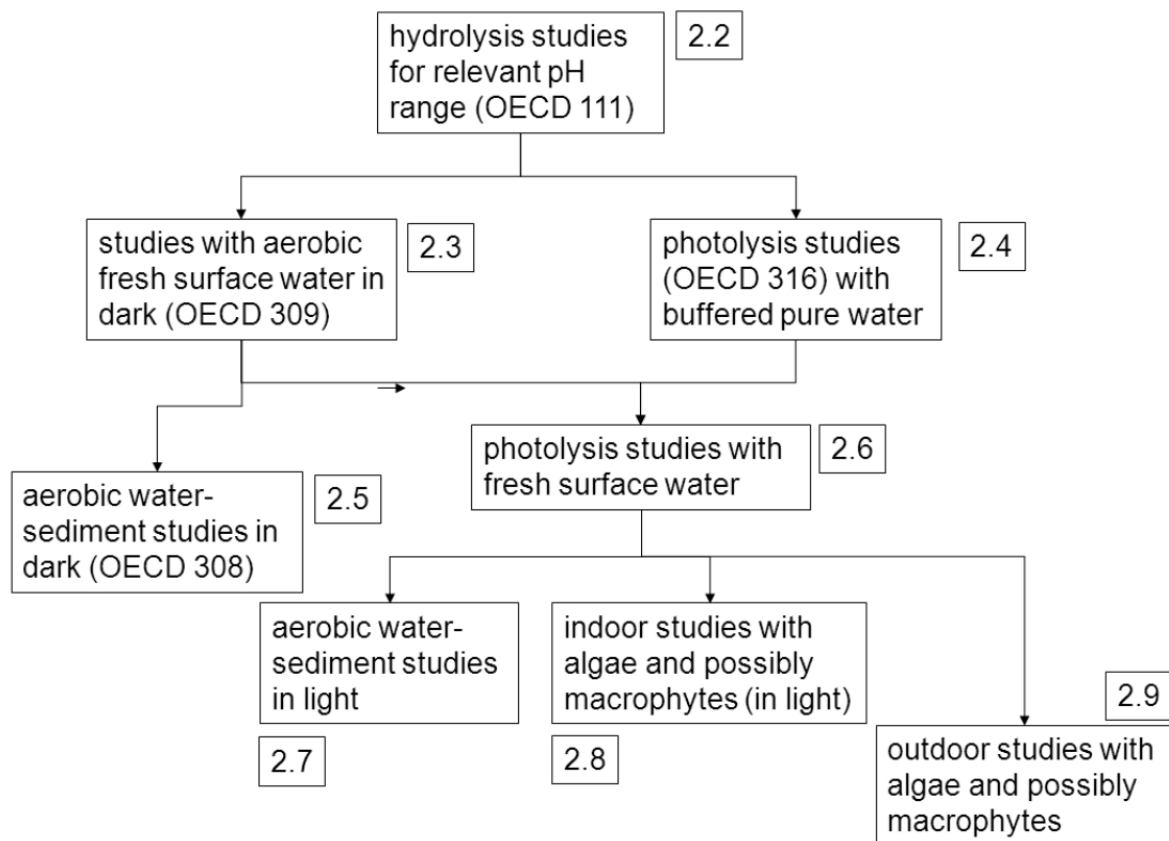


Figure 3.3 Stepped approach for estimating DegT_{50} values for surface water, taken from Boesten et al. (2014).

4 Selection of example compounds and water-sediment cosm studies

4.1 Selection of compounds

In Deneer et al. (2015) a number of example compounds with sufficient available studies were identified for inverse modelling in order to estimate the $DegT_{50,water}$ of the cosm study. These are:

Table 4.1 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 compounds were prioritised for the development and testing of the procedure to estimate degradation rates in cosm systems where only measurements in the water had been done. For the compounds of metribuzin, linuron and imidacloprid Deneer et al. (2015) selected three cosm studies each, in which at least five concentrations in the water layer and the water depth had been measured. The $DegT_{50,water}$ was determined by optimisation as described for the method 'Water-only' (section 2.4).

In the current follow-up study we further develop the estimation method for compounds that penetrate into the sediment of the cosm to a non-negligible extent. Compounds were selected from a list of mesocosm studies for which Alterra had performed one or more (mostly) outdoor studies during the period 1990-2014, expanded with a number of compounds for which indoor experiments were performed during that same period (Deneer et al., 2015). The available Alterra studies were complemented with additional studies available in the open literature. As the currently proposed inverse modelling procedure is intended for use with compounds that sorb to sediment to an appreciable extent, we considered only compounds with a K_{oc} indicative of intermediate to strong sorption to sediments ($K_{oc} \geq 500$ L/kg). This resulted in the compounds azoxystrobin, chlorothalonil, chlorpyrifos, lambda-cyhalothrin, lufenuron and prosulfocarb. We added metsulfuron-methyl which has a K_{oc} of approx. 40 L/kg, because we found a study for this compound in which sediment measurements had been done and we could thus increase the number of suitable studies. The currently proposed inverse modelling analysis requires information on the course over time of concentrations in both water and sediment, as well as water depth.

4.2 Evaluation of cosm studies liable to provide measured concentrations in water and sediment

In order to be suitable for inverse modelling Deneer et al. (2015) stated that at least three concentration measurements in the sediment for a layer of a known depth were needed, in addition to the at least five measurements in water and the water depth measurement. The requirement of information on the organic matter content of the sediment was dropped, as many studies do not specify the organic carbon or organic matter content and too few studies would then classify as suitable for the inverse modelling procedure. Moreover, in this report we focus on outdoor cosms, only the chlorpyrifos study described by Brock et al. (1992) was performed in indoor cosms.

For the selected compounds the previously retrieved papers were checked for the presence of the required additional information on measured concentrations in sediment. Also the overall quality of the experiment and their data was assessed as well as possible from the given information.

Azoxystrobin

The only study found to provide sufficiently detailed data on the fate of azoxystrobin in water was reported by Zafar et al. (2012). However, no measured concentrations of azoxystrobin in sediment are given, and hence the study is not suitable for testing the currently developed procedure which also requires sediment concentrations.

Chlorothalonil

The only study reporting measured concentrations in both the aqueous and the sediment layer is described by Kwon et al. (2006). 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.) is reported. 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. However, the dimensions of the systems differ so considerably from a 'typical' cosm study, that we decided that this study is not suitable for our purpose.

Chlorpyrifos

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). Although this study considers an indoor experiment, this study was considered to be a suitable candidate, as the dimensions of the systems are representative for outdoor water bodies, such as ditches and the quality of the data is good.

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 (depth: 30 cm) and sediment (depth: 5 cm, 2.5% organic carbon) are reported (10 and 100 µg/L: 5 times; 250 µg/L: 8 times). 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. Therefore, we did not analyse this study in this report.

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). During the course of the study submerged macrophytes developed in the sediment-covered portion of each microcosm.

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 and thus this study was suitable for our analysis.

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. Concentrations measured over the first 100 minutes after application of chlorpyrifos indicate inhomogeneous mixing of the water layer and should probably not be considered in the inverse modelling, leaving 5 measurements in water considered usable. A total of 8 measurements in sediment (4 during the first 100 minutes after application) are available. Dimensions of the natural pond, including water depth, are not explicitly given making inverse modelling of the measured concentrations impractical. Therefore, we did not analyse this study in this report.

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 (depth not given, estimated 11 cm) and 4 kg of sediment (depth not given, estimated 1.6 cm; 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 may be less suitable for analysis of the fate of the parent compound. Therefore, we did not analyse this study in this report.

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 concentrations read from logarithmic graphs.

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. Therefore, we did not analyse this study in this report.

Lambda – cyhalothrin

The study described by Bennett et al. (2005) uses a combination of simulated spray drift and simulated run-off for application of the test substance, where run-off entry occurs at a single point upstream. The results are therefore considered less suitable for inverse modelling of concentrations. Sufficiently detailed results of analysis in water, sediment and plants are given.

Hadfield et al. (1993) describe the measurements of residues of lambda-cyhalothrin in ponds (15 x 30 m, depth of each pond varying from 0.15 – 2 m) lined 15 cm layer of clay covered with a 10 cm depth of sandy loam soil (1.1% organic matter). Water depth was 0.35 m. Each pond was treated 18 times (12 'drift' sprays and 6 'run-off' sprays using soil-water slurries) treating 4 sets of

4 cosms each at zero, low, medium and high rates of lambda-cyhalothrin. Although sufficiently detailed results of analysis in water and sediment are given, the use of soil-water slurries to simulate run-off makes the results of the study less suitable for analysis through inverse modelling. Therefore, we did not analyse this study in this report.

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 (water depth: 0.5 m; sediment depth: 0.25 m). In the first (May) experiment, only 3 measurements in water were reported and all measured sediment concentrations were below the limit of quantitation. In the second (August) experiment, typically 7 measurements of aqueous and 5 measurements of sediment concentrations are reported. Organic matter content of the first 0.01 m top layer of the sediment was measured and was found to be very high (38% in the second experiment in August), but lower for a bulk sediment sample taken over an unspecified depth (23% o.m.). Higher plant densities resulted in a decrease of the fraction of pesticide found in the sediment. The study contained sufficiently detailed data to be suitable for the inverse modelling procedure.

Lufenuron

No suitable experiments with lufenuron describing both aqueous and sediment concentrations were available. The paper by López-Mancisidor et al. (2008) describes the fate of lufenuron in a cosm 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. Organic matter content of the sediment was not reported, nor were concentrations in sediment. Therefore the experiment is unsuitable for the inverse modelling of aqueous and sediment concentrations proposed in the present analysis.

Metsulfuron-methyl

Wang et al. (2011) monitored radio-labelled metsulfuron-methyl in water (depth 15 cm) and sediment (depth not given, estimated 2 cm; o.m. 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. Given the number of measurements in water and sediment this study was judged suitable for the inverse modelling procedure.

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 (7 measurements in water, 5 measurements in the upper 5 cm of the sediment layer) for the analysis of fate data as intended in the current study. Water depth was 0.5 m, sediment depth was 0.25 m. Although sediment dry bulk density (1.21 kg/L) and porosity (0.54 L/L) are given for the upper 5 cm, its organic matter content is not reported. Sufficient concentration measurements in water and in sediment are given to be a suitable study for the inverse modelling procedure.

4.3 Selected compounds and studies suitable for inverse modelling of water and sediment concentrations

The review of the papers resulted in a total of five compounds and six studies that were judged to be suitable for the inverse modelling procedure, based upon measured concentrations in both water and sediment. These compounds and studies are: chlorpyrifos of Brock et al. (1992) and Giddings et al. (1997), lambda-cyhalothrin of Leistra et al. (2013), linuron of Bromilow et al. (2006), metsulfuron-methyl of Wang et al. (2011) and prosulfocarb of Arts et al. (2006). For the latter Adriaanse et al. (2013) already determined the $DegT_{50,water}$ by an extensive optimisation procedure, so their half-life value can be compared to the one that we find by our 'Water-sediment' method. Table 4.2 lists the suitable studies and indicates the number of concentration measurements in the water layer and the sediment.

Table 4.2 Table of suitable cosm studies with measurements in water and sediment for inverse modelling.

| Compound | Reference | Number of measurements in water | Number of measurements in sediment |
|--------------------|------------------------|---------------------------------|------------------------------------|
| Chlorpyrifos | Brock et al. (1992) | 8 | 5 |
| Chlorpyrifos | Giddings et al. (1997) | | |
| | Concentration level 3 | 7 | 5 |
| | Concentration level 4 | 8 | 5 |
| | Concentration level 5 | 9 | 5 |
| Lambda-cyhalothrin | Leistra et al. (2003) | 7 | 5, but very crude |
| Linuron | Bromilow et al. (2006) | 8 | 8 |
| Metsulfuron-methyl | Wang et al. (2011) | 8 | 8 |
| Prosulfocarb | Arts et al. (2006) | 7 | 5 |

To give insight into the variety of selected compounds Table 4.3 presents an overview of their most relevant physico-chemical properties, taken from the PPDB database, <http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>.

Table 4.3 Overview of main physico-chemical properties (PPDB database) of the selected compounds.

| Compound | DT ₅₀ water/sed. (d) | DT ₅₀ Photolysis in water (d) | Log K _{ow} (-) | K _{oc} ^B (L/kg) | Saturated vapour pressure ^A (mPa) | pK _a (-) |
|--------------------|---------------------------------|--|-------------------------|-------------------------------------|--|---------------------|
| Chlorpyrifos | 36.5 | 29.6 | 4.7 | 8151 | 1.43 | - |
| λ-Cyhalothrin | 15.1 | 40 | 6.9 | 283707 | 0.0002 | - |
| Linuron | 46 | - | 3 | 739 | 5.1 | - |
| Metsulfuron-methyl | 140 | - | -1.7 | 39.5 ^B | 1.1E-7 | 3.75 |
| Prosulfocarb | 214 | - | 4.48 | 1693 ^B | 0.79 | - |

^A Vapour pressure in mPa at 25°C.

^B K_{foc} is used (K_{oc} is not available).

Table 4.3 demonstrates that the selected five compounds have sorption coefficients K_{oc} above the 500 L/kg, except metsulfuron-methyl, which has a lower sorption coefficient of 39.5 L/kg.

For several of the compounds in Table 4.3, 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. However, as no other values are available, we had to use the K_{foc} values in the optimisations.

The possibility of dissociation or protonation of the compound at environmentally-realistic pH values (pH between 4 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. Luckily, our selected compounds did not include compounds with a pK_a between 4 and 10.

Note that the values of DT_{50} for water-sediment studies and photolysis studies are only given as background information. They do not constitute reliable estimates for degradation in water under natural conditions. DT_{50} values for water-sediment systems reflect the disappearance of the compound from the system as a whole, and as degradation rates in water and sediment may differ substantially, the degradation rate in the water is difficult to quantify. Moreover, water-sediment studies are usually performed in the dark, and thus, do not reflect conditions in outdoor cosms or surface waters with respect to light conditions. Similarly, laboratory measurements of DT_{50} values for photolysis (or hydrolysis) are usually performed under conditions that are not typical for outdoor cosms or surface water and are, therefore, not expected to accurately estimate disappearance from the water phase in a cosm or outdoor water body.

The inverse modelling procedure, as described in Chapters 2 and 3 was developed and tested for the six studies and five compounds of Table 4.2. The analysis and results of each study has been described in Chapter 5 and into more detail in Appendices 3 up to 7 included.

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5 Assessment of the degradation rate of the selected compounds in cosm water

5.1 Chlorpyrifos

Two studies with chlorpyrifos that are suitable for the estimation of the $DegT_{50,water}$ by inverse modelling by TOXSWA-PEST were found in the literature, the study from Brock et al. (1992) and the study of Giddings et al. (1997).

Brock et al. (1992)

Brock et al. (1992) describe the fate of chlorpyrifos in indoor cosms containing approximately 50 cm (600 L) water and 10 cm sediment, at two initial concentration levels of 5 and 35 µg/L. Although the cosms were indoor, we included them in the analysis, as the dimensions of the cosms are representative for outdoor water bodies and the quality of the data were good. The sediment is characterised as sandy loam with an organic matter content of 2.8%. The pH in the cosm water was not measured and the temperature in the room was controlled at 19°C (18-20°C). One application of chlorpyrifos was given. In the cosm with the nominal initial aqueous concentration of 35 µg/L the concentration was measured 8 times in the water and 5 times in the sediment up to 118 d post-application. Maximum chlorpyrifos mass measured in the sediment was 24.9% of the initial mass added to the system on day 8 post-application. Details are given in Appendix 3.

The cosm has been inversely modelled using scaled concentrations. Since the organic matter content of the sediment (upper 10 cm) was given as 2.8%, the OM% was allowed to vary from 2.5 – 50% (Case B8 in Figure 2.2). As the water was not filtered before extraction the measured concentrations needed to be compared to the simulated concentrations of dissolved pesticide mass + mass sorbed onto suspended solids.

Aqueous concentration was allowed to vary from 0.1 – 5 (scaled) with an initial estimate of 1.0, and $DegT_{50,water}$ was allowed to vary from 0.1 – 100 days with an initial estimate of 5, 20 or 1 days, as suggested in Table 3.4. The simulations were performed using three sets of values for initial organic matter content of the sediment of 19% (bulk density 0.2 kg/L), 9% (bulk density 0.8 kg/L) and 3% (bulk density 1.2 kg/L) (Table 3.3). So, a total of nine TOXSWA-PEST optimisations were done.

Satisfactory runs are runs that fulfil the three quality criteria (χ^2 – error below the initially selected 15%⁴, visual correspondence between measured and simulated in water and also in sediment satisfactory and residuals well distributed) and for which the degraded mass in the water phase accounts for at least 50% of total mass dissipated from water layer (Figure 2.3). Three runs with a bulk density of 0.8 kg/L combined with an initial estimate of organic matter content of 9% were satisfactory with χ^2 – errors of 7.6%. Figure 5.1 presents one example of these satisfactory runs with a good visual correspondences between measured and simulated in both water and sediment. Figure 5.2 presents the residuals for the same example, which are well distributed, demonstrating that the optimisation does not show trends. The values for the optimised $DegT_{50,water}$ were 5.92, 5.94 and 5.93 days for the three satisfactory runs. Taking the geometric average of these 3 values results in an estimated value for $DegT_{50,water}$ of 5.93 days for the cosm experiment by Brock et al. (1992).

⁴ N.B. Note that the criterion of χ^2 – error below 15% was set to the less strict value of 25% later in the development of this guidance report. This implies that 8 of the 9 runs now fulfil this new χ^2 – error criterion of 25%. However, the 5 additional runs do not fulfil the criterion of satisfactory visual correspondence between measured and simulated concentrations in water and sediment and thus the $DegT_{50,water}$ geomean value presented above is still correct.

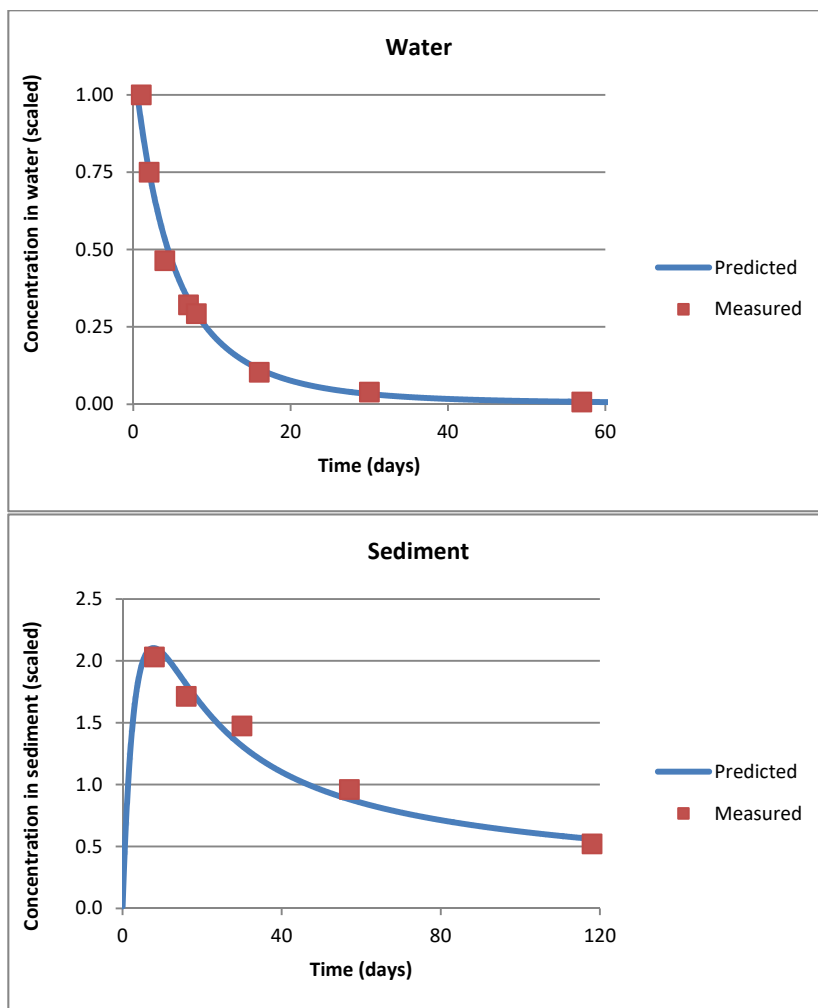


Figure 5.1 Simulated and measured concentrations of chlorpyrifos in water and sediment as a function of time post-application in the study of Brock et al. (1992), cosm with initial concentration of 35 µg/L; data simulated using $DegT_{50,water} = 5.92$ days, an organic matter content of sediment of 5.0% and a simulated initial scaled water concentration of 1.10. The initial values used in the estimation are given as the fourth entry in Table A3.4 of Appendix 3.

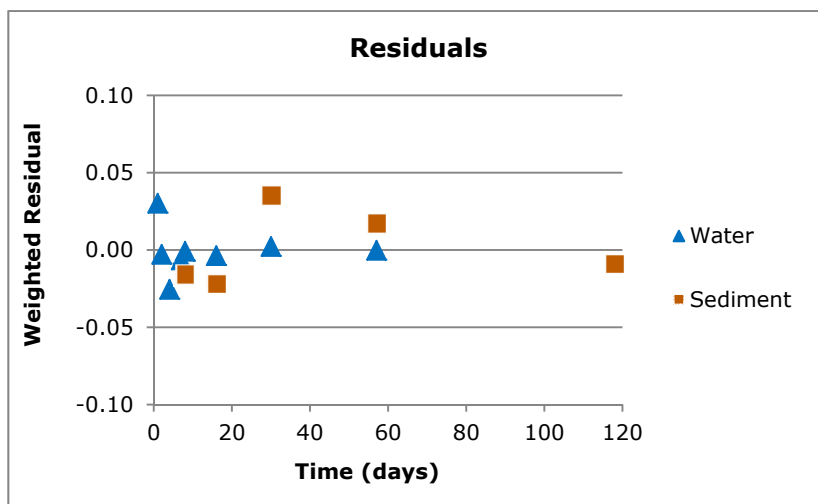


Figure 5.2 Residuals (scaled) of measured minus simulated concentrations, weighted according to Eq. 19, of concentration chlorpyrifos in water and in sediment as a function of time post-application in the study of Brock et al. (1992), cosm with initial concentration of 35 µg/L; data simulated using $DegT_{50,water} = 5.92$ days, an organic matter content of sediment of 5.0% and a simulated initial scaled water concentration of 1.10. The initial values used in the estimation are given as the fourth entry in Table A3.4 of Appendix 3.

Giddings et al. (1997)

Giddings et al. (1997) applied chlorpyrifos at 5 application levels with initial nominal aqueous concentrations ranging from 0.03 to 3 µg/L in fiber glass tanks with a water depth of 1.4 m (11200 L) and approximately 10 cm sediment (2% organic matter content). The cosms were located in Kansas, USA and the experiment was performed in 1991. The pH was not measured in the cosm water and the water temperature was estimated at 27°C in July, 25°C in August, 20.5°C in September and 13°C in October. In the 3 highest application levels 7 (0.3 µg/L), 8 (1.0 µg/L) or 9 (3 µg/L) measurements in the aqueous layer and 5 measurements in the sediment were taken up to 84 days post-application. In view of the sediment contents below detection limit observed at the 2 lower application levels 1 and 2, only the data for the 3 highest levels 3, 4 and 5 have been analysed using inverse modelling. During the course of the study submerged macrophytes developed in the sediment-covered portion of each microcosm. For the level 5 systems, the maximum chlorpyrifos mass in the sediment was calculated at 2.2% on day 10 post-application. (The relatively low mass transfer into the sediment may be due to the fact that only 50% of the bottom of the fiberglass containers were covered with sediment-containing trays combined with a relatively great water depth of 1.4 m.) For more details, see Appendix 3.

The inverse modelling was performed using scaled concentrations. As the water was not filtered before extraction the measured concentrations needed to be compared to the simulated concentrations of dissolved mass + mass sorbed onto suspended solids. Since the organic matter content of the sediment (upper 10 cm) was given as 2.0%, the OM% was allowed to vary from 2.5 – 50% (Case A8 of Figure 2.2). Application was on July 8, and the simulation was therefore allowed to run from July 8 to October 15.

Aqueous concentration was allowed to vary from 0.1 – 5 (scaled) with an initial estimate of 1.0, and $DegT_{50,water}$ was allowed to vary from 0.1 – 100 days with an initial estimate of 2.5, 10 or 0.5 days (Table 3.4). Runs were performed using values for initial organic matter content of the sediment of 19% (bulk density 0.2 kg/L), 9% (bulk density 0.8 kg/L) and 3% (bulk density 1.2 kg/L), as indicated in Figure 3.1 by the red stars.

The initial 9 runs for the 'level 3' cosms did not produce any satisfactory runs with χ^2 -errors below 25%, and for that reason additional runs were performed as indicated in Figure 3.1 (purple stars). These extra runs used bulk density of 0.2 kg/L in combination with an initial organic matter content of 3%, or a bulk density of 1.2 kg/L in combination with an initial organic matter content of 19%. However, even after these 6 extra runs no results with χ^2 -error below 25% were obtained. Figure 5.3 presents an example of an unsatisfactory fit with a χ^2 -error 53.6%. Similarly, the initial 9 runs and additional 6 runs for the 'level 4' cosms did not yield any results with a χ^2 -error below 25%, Figure 5.4 presents a fit having a χ^2 -error of 53.1%.

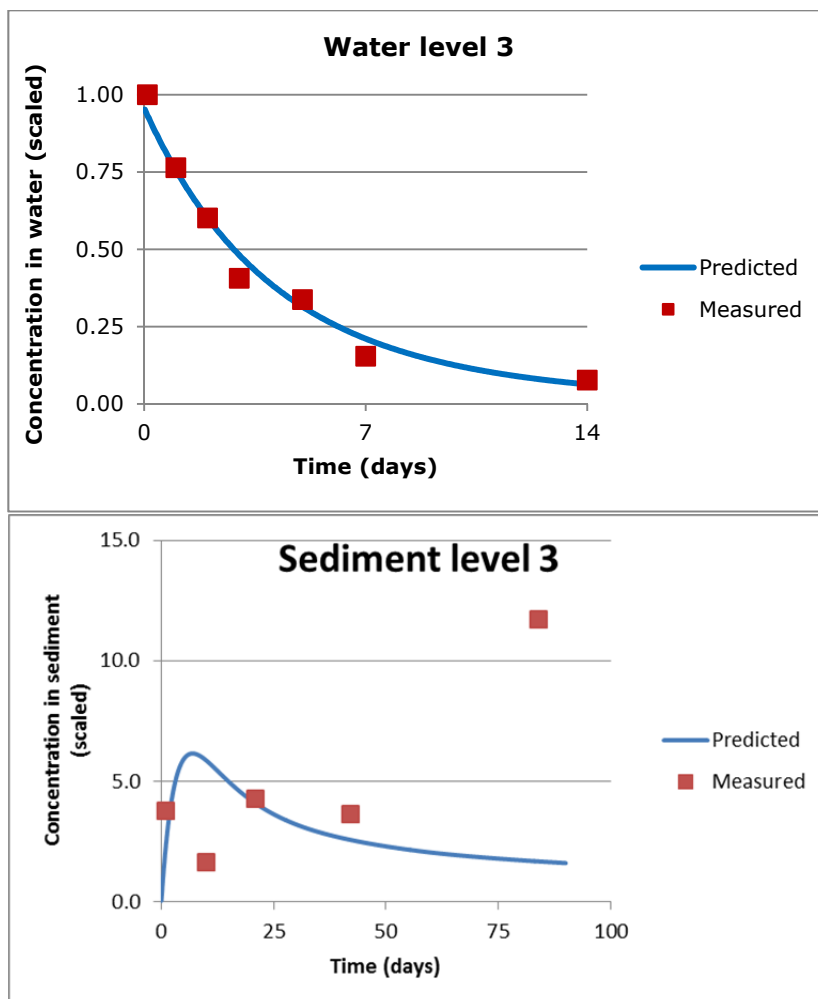


Figure 5.3 Simulated and measured concentrations of chlorpyrifos in water and sediment as a function of time post-application in the study of Giddings et al. (1997); data simulated using $DegT_{50,water} = 7.52$ days, an organic matter content of sediment of 50% and a simulated initial scaled water concentration of 0.89. The initial values used in the estimation are given as the first entry for 'level 3' cosm data in Table A3.6 of Appendix 3).

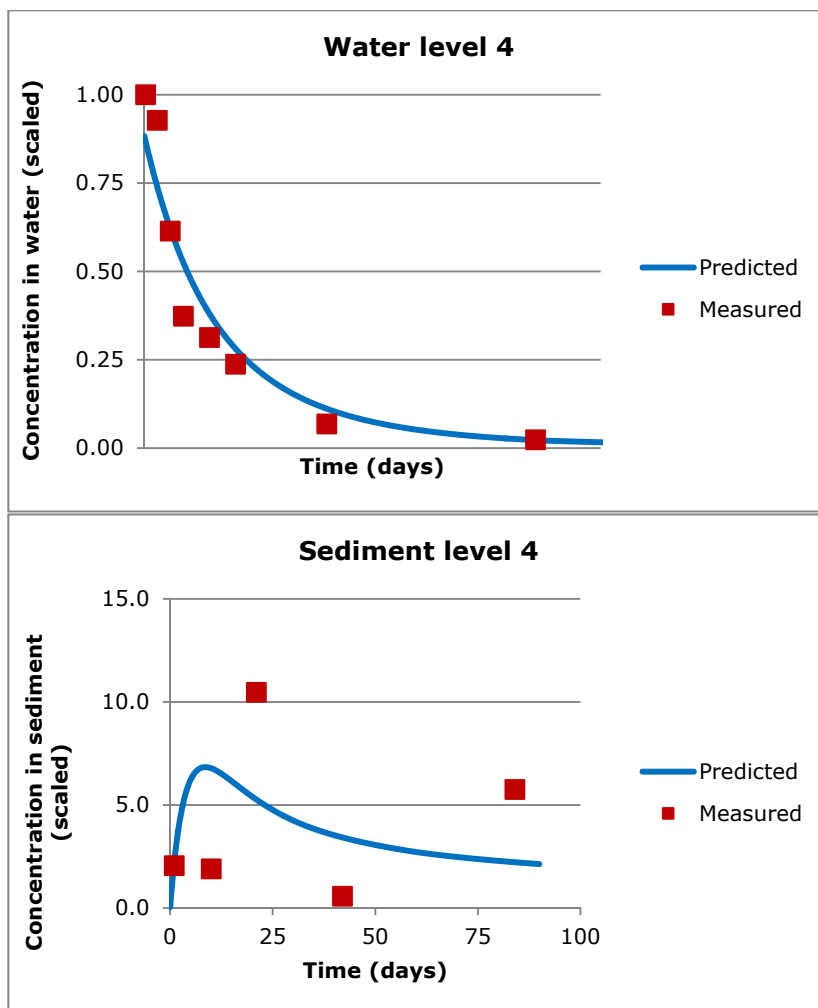


Figure 5.4 Simulated and measured concentrations of chlorpyrifos in water and sediment as a function of time post-application in the study of Giddings et al. (1997); data simulated using $DegT_{50,water} = 11.01$ days, an organic matter content of sediment of 50% and a simulated initial scaled water concentration of 0.83. The initial values used in the estimation are given as the first entry for 'level 4' cosm data in Table A3.6 of Appendix 3).

The failure to fit these 2 data sets is most likely due to the relatively large noise in measured sediment concentrations. In 'level 3' data, the sediment concentration reported for day 84 is by far the largest and outweighs all other sediment concentrations (Figure 5.3). Similarly, for the 'level 4' data set sediment levels reported for 21 and 84 days are higher than levels reported for other days (Figure 5.4). This deviation from expected behaviour possibly resulted in an unsatisfactory fit of the sediment concentrations and prevented the χ^2 -error to fall below 25%.

For the 9 runs performed for the 'level 5' cosms three runs (the first three) resulted in an χ^2 -error of 25.2%. The graph of the fit (Figure 5.5) illustrates that the data are fitted rather well by the estimated values for $DegT_{50,water}$, organic matter content and initial concentration. The residuals are well distributed as well, as shown in Figure 5.6. So, these 3 'level 5' data runs yielding χ^2 - error fulfilling the 25% criterion are reliable. These runs resulted in estimates of $DegT_{50,water}$ of 9.70, 9.71 and 9.72 days resp., yielding a geometric mean $DegT_{50,water}$ for chlorpyrifos of 9.71 days for the experiments of Giddings et al. (1997).

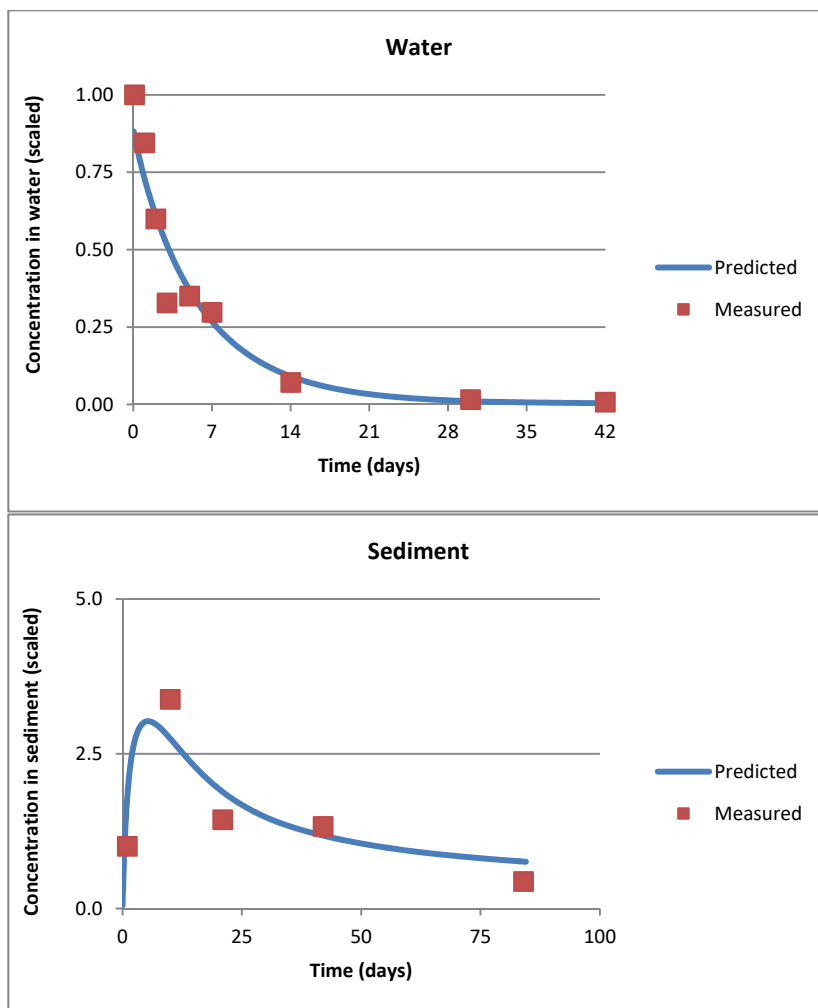


Figure 5.5 Simulated and measured concentrations of chlorpyrifos in water and sediment as a function of time post-application in the study of Giddings et al. (1997); data simulated using $DegT_{50,water} = 9.70$ days, an organic matter content of sediment of 7.0% and a simulated initial scaled water concentration of 0.88. The initial values used in the estimation are given as the first entry for 'level 5' cosm data in Table A3.6 of Appendix 3.

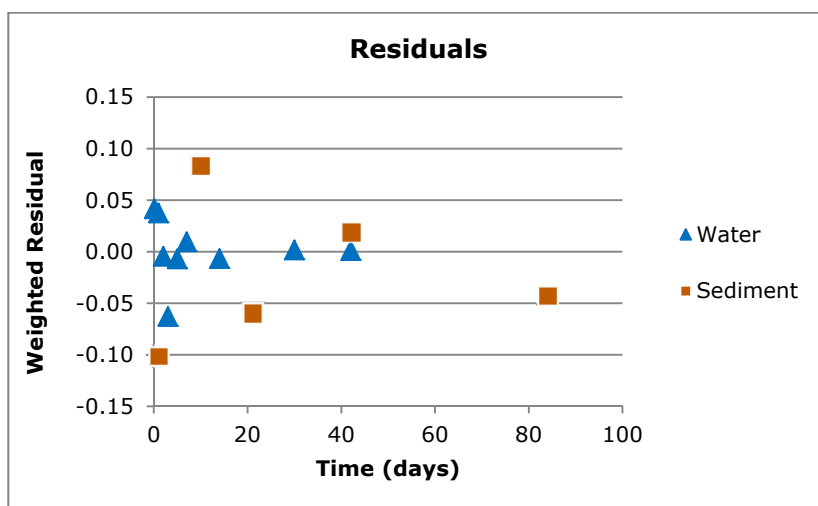


Figure 5.6 Residuals (scaled) of measured minus simulated concentrations weighted according to Eq. 19, of chlorpyrifos in water and sediment as a function of time in the study of Giddings et al. (1997); data simulated using $DegT_{50,water} = 9.70$ days, an organic matter content of sediment of 7.0% and an initial scaled water concentration of 0.88. The initial values used in the estimation are given as the first entry for 'level 5' cosm data in Table A3.6 of Appendix 3.

Comparison with dissipation rates of chlorpyrifos obtained in laboratory tests

The analysis of data taken from the study described by Brock et al. (1992) resulted in an estimate for $DegT_{50,water}$ for chlorpyrifos of 5.93 days, whereas the data taken from Giddings et al. (1997) resulted in a $DegT_{50,water}$ of 9.71 days. TOXSWA reports $DegT_{50,water}$ values at 20°C, i.e. these values are already corrected for temperature differences between the 2 experiments.

Table 5.1 presents half-life values for various dissipation processes, taken from the Pesticides Properties Database (<http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>). The DT_{50} value by hydrolysis equals 25.5 d, the one by photolysis 29.6 d and the overall DT_{50} for the water-sediment system is 36.5 d. These DT_{50} values correspond to degradation half-lives by hydrolysis, photolysis and in water-sediment systems. So, these three DT_{50} values were compared to the optimised $DegT_{50,water}$ values of 5.9 and 9.7 d for the cosm studies of Brock et al. (1992) and Giddings et al. (1997). The optimised $DegT_{50,water}$ values are clearly shorter than the degradation half-lives determined in the laboratory experiments.

Table 5.1 presents also the DT_{50} value for water-only in the water-sediment system. The Pesticide Properties Database describes the water-sediment and water-only DT_{50} s of water-sediment studies as: 'the rate of chemical decomposition in water-sediment systems expressed as DT_{50} s. Data is given for the system as a whole and for the water phase only.' The OECD Guideline 308 (2002) 'Aerobic and anaerobic transformation in aquatic sediment systems', which is often followed to determine degradation in water-sediment systems, states in its article 44 'Information of the rate of dissipation of the test substance in the water and sediment can be obtained through the use of appropriate evaluation tools. These can range from application of pseudo-first order kinetics, empirical curve-fitting techniques which apply graphical or numerical solutions and more complex assessments using, for example, single- or multi-compartment models.' So, both sources do not specify how the DT_{50} water-only has been or should be obtained. However, the OECD Guideline uses the word 'rate of dissipation' and not degradation and as the Pesticide Properties Database contain no specifications we assume that the presented DT_{50} water-only refers to the DT_{50} value obtained by curve-fitting the measurements in the water layer of the water-sediment systems. The observed decline in the water layer is the result of several processes: not only degradation in the water, but also volatilisation to the air and transport by sorption to the sediment. Especially for compounds with sorption coefficients K_{oc} above 500 L/kg transport to sediment may be significant. So, this the decline in water encompasses more processes than only degradation and therefore we do not use this type of half-life in our comparisons between our optimised $DegT_{50,water}$ value and the degradation rates for photolysis, hydrolysis and water-sediment systems (overall system rates). For the compounds of lambda-cyhalothrin, linuron, metsulfuron-methyl and prosulfocarb we did not include the DT_{50} value for water-only of water-sediment studies in the tables on dissipation half-lives of the Pesticides Properties Database.

Table 5.1 Dissipation half-life DT_{50} for chlorpyrifos taken from Pesticides Properties Database.

| Dissipation process | DT_{50} (days) |
|-----------------------------|---------------------|
| Hydrolysis | 25.5 |
| Photolysis | 29.6 |
| Water-sediment (system) | 36.5 |
| Water-sediment (water-only) | 5.5 |

The tiered approach suggested by Boesten et al. (2014), is based on 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. The study by Brock et al. (1992) belongs to the box 'Indoor studies with algae and possibly macrophytes' (Box 2.8 in Figure 3.3), whereas the study by Giddings et al. (1997) belongs to the box 'Outdoor studies with algae and possibly macrophytes' (Box 2.9). Both cosm studies analysed using inverse modelling indeed yield a less conservative estimate for degradation in the water-phase than simple laboratory-derived values for dissipation through hydrolysis, photolysis and dissipation in water-sediment systems. Thus the tiered approach suggested by Boesten et al. (2014) is valid for our estimated $DegT_{50,water}$ values for chlorpyrifos.

5.2 Lambda-cyhalothrin

For lambda-cyhalothrin only one study was found that is suitable for the estimation of the $DegT_{50,water}$ by inverse modelling by TOXSWA_PEST. The study with lambda-cyhalothrin in an outdoor cosm was described by Leistra et al. (2003) and Roessink et al. (2005). The fate data used for inverse modelling were taken from Leistra et al. (2003).

Leistra et al. (2003) studied the effect of macrophyte density on the fate of lambda-cyhalothrin. Transparent polycarbonate enclosures with an internal diameter of 1.05 m, a water depth of 0.5 m (430 L) were placed in outdoor ditches. The 25 cm sediment was loamy with an organic matter content of 38% in the upper cm. The pH was not measured and the temperature was between 11.3 and 23.2 °C (the mean of these two values, 17.25 °C, was used in the simulations). The enclosures received initial nominal aqueous concentrations of 0.25 µg/L and in the experiment in August a sufficient number of measurements was made (typically 7 measurements in the water and 5 in the sediment up to 7 d post-application). As higher plant densities resulted in a decrease of the fraction applied mass found in sediment we selected four systems in which the macrophytes were pruned before application in order to minimise the role of the macrophytes on the inverse modelling. maximum amounts of lambda-cyhalothrin in sediment were reported to be 17% of the initially applied amount (3 days after application) for systems with low macrophyte content, and 12% of the initially applied amount (2, 3 and 7 days after application) for systems with high macrophyte content. Details are given in Appendix 4.

We made nine runs for all four systems with macrophyte densities of 1.1, 1.3, 28 and 45 g/enclosure and three additional runs for a bulk density of 0.6 kg/L for the 1.1 g system (purple star of Figure 3.2, note that the organic matter content in Figure 3.2 has been set at 13% as an example). The inverse modelling was performed using scaled concentrations⁵. As the water was not filtered before extraction the measured concentrations needed to be compared to the simulated concentrations of dissolved mass + mass sorbed onto suspended solids. (For lambda-cyhalothrin a considerable fraction of the mass is sorbed onto the suspended solids, so it is important to make the correct comparison.) Since the organic matter content of the sediment (upper 1 cm) was given as 38%, the OM% was allowed to vary from 37.5 – 38.5%⁶ (Case B9 in Figure 2.2).

Aqueous concentration was allowed to vary from 0.1 – 5 (scaled) with an initial estimate of 1.0, and $DegT_{50,water}$ was allowed to vary from 0.01 – 50 days with an initial estimate of 0.4, 5 or 0.05 days (Table 3.8). Runs were performed using values for bulk density of 0.2 kg/L, 0.8 kg/L and 1.2 kg/L, using an initial organic matter content of 38% (red stars of Figure 3.2).

For all optimisation runs $F_{M,deg-wat}$ was at least 50% of total dissipation (Table A4.4 of Appendix 4), which is a prerequisite for acceptance of the estimated $DegT_{50,water}$. For only 6 of the 39 runs the χ^2 – error was also below 25% (12.7 to 14.4%) and the visual correspondence between measured and simulated concentrations in water and sediment was judged to be not so good but acceptable (see e.g. Figure 5.7), the alternative being not able to use the cosm study at all. The acceptable runs yielded almost exactly the same value for the estimated $DegT_{50,water}$: 0.18, 0.18, 0.19, 0.19, 0.18 and 0.18 days respectively, resulting in an geometric mean value of 0.18 days for the cosm experiment described by Leistra et al. (2003).

Figure 5.7 gives a graphical depiction of the simulated and measured concentrations of the first run for the cosms containing 28 g of macrophytes. As stated above, correspondence between measured and simulated concentrations in the water layer is not so good, but acceptable, while the correspondence in the sediment is acceptable. Figure 5.8 on the residuals confirms that the optimisation for the water layer is not so good, but acceptable, the simulated concentrations underestimating the measured ones.

⁵ As we made separate runs for the four systems differing in macrophyte density scaling had not been necessary here.

⁶ Note that the final guidance is to use upper and lower bounds of \pm of the measured organic carbon content.

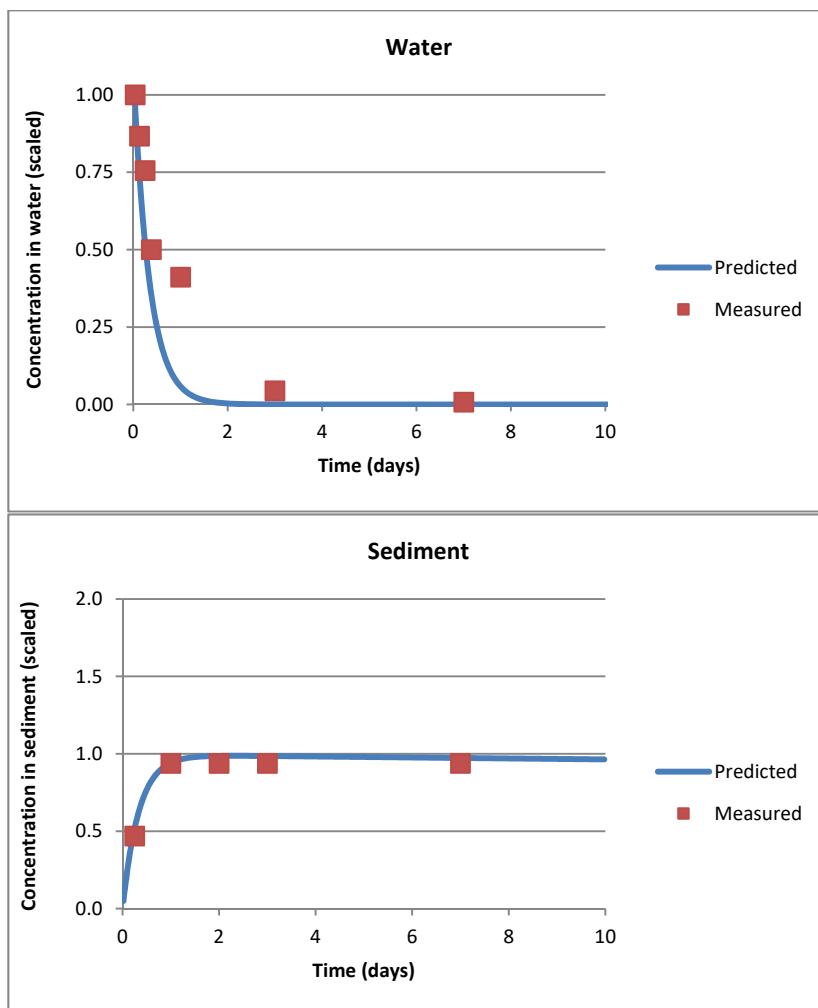


Figure 5.7 Simulated and measured concentrations of lambda-cyhalothrin in water and sediment as a function of time for the lambda-cyhalothrin study of Leistra et al. (2003); data simulated using $DegT_{50,water} = 0.18$ days, an organic matter content of sediment of 38.5% and a simulated initial scaled water concentration of 1.09. The initial values used in the estimation are given as the first entry for cosms with macrophyte density of 28 grams (22nd entry overall in Table A4.4 of Appendix 4).

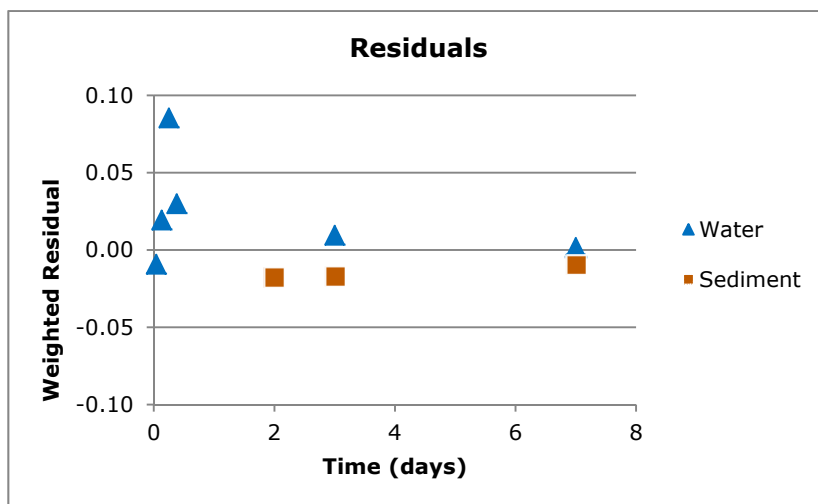


Figure 5.8 Residuals (scaled) of measured minus simulated concentrations, weighted according to Eq. 19, of lambda-cyhalothrin in water and sediment as a function of time post-application for the lambda-cyhalothrin study of Leistra et al. (2003); data simulated using $DegT_{50,water} = 0.18$ days, an organic matter content of sediment of 38.5% and a simulated initial scaled water concentration of 1.09. The initial values used in the estimation are given as the first entry for cosms with macrophyte density of 28 grams (22nd entry overall in Table A4.4 of Appendix 4).

Comparison with dissipation rates of lambda-cyhalothrin obtained in laboratory tests

The analysis of data taken from the study described by Leistra et al. (2003) resulted in an estimate for $DegT_{50,water}$ for lambda-cyhalothrin of 0.18 days at 20°C.

Table 5.2 gives half-life values for various dissipation processes, taken from the Pesticides Properties Database (<http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>). Lambda-cyhalothrin does not undergo hydrolysis, while the DT_{50} by photolysis is 40 d and the overall DT_{50} for the water-sediment system is 15.1 d. These DT_{50} values correspond to degradation half-lives by photolysis and in water-sediment systems. Therefore these three entries in Table 5.2 were compared to the optimised $DegT_{50,water}$ value of 0.18 d for the cosm of Leistra et al. (2003). The optimised $DegT_{50,water}$ value is clearly shorter than the degradation half-lives determined in the laboratory experiments.

Table 5.2 Dissipation half-life DT_{50} for lambda-cyhalothrin taken from Pesticides Properties Database.

| Dissipation process | DT_{50} (days) |
|-------------------------|---------------------|
| Hydrolysis | Stable |
| Photolysis | 40 |
| Water-sediment (system) | 15.1 |

The tiered approach suggested by Boesten et al. (2014), is based on 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. The study by Leistra et al. (2003) belongs to the box 'Outdoor studies with algae and possibly macrophytes' (Box 2.9 in Figure 3.3). The $DegT_{50,water}$ derived from this cosm study, analysed using inverse modelling, indeed yield a less conservative estimate for degradation in the water-phase than simple laboratory-derived values for dissipation through hydrolysis, photolysis and dissipation in water-sediment systems. Thus the tiered approach suggested by Boesten et al. (2014) is valid for our estimated $DegT_{50,water}$ values for lambda-cyhalothrin.

5.3 Linuron

For linuron one study was found that is suitable for the estimation of the $DegT_{50,water}$ by inverse modelling by TOXSWA_PEST. The study with linuron in an outdoor cosm was described by Bromilow et al. (2006).

Bromilow et al. (2006) describe the fate of linuron in outdoor stainless steel tanks in the UK with 30 cm water and 5 cm sediment with an organic matter content of 4.3%. The macrophyte *Elodea crista* was present and the pH was measured at 7.32. As linuron was applied on 30 October 2002, the water temperature was rather low, 9.5°C. Linuron was applied once and in addition to a measurement shortly after application, concentrations were measured in water and sediment 7 more times up to 152 d post-application. Linuron remained largely in the water phase, as can be expected from its relatively low sorption coefficient, K_{oc} of 843 L/kg. Maximum sediment mass was reported to be 8.6% of the mass initially added to the system on days 14 and 92 after application. Details are given in Appendix 5.

The inverse modelling was performed using scaled concentrations⁷. Since the organic matter content of the bulk sediment was given as 4.3%, the OM% was allowed to vary from 3.8 – 4.8% (case B9 of Figure 2.2). As the water was filtered using a 0.45 µm Millipore membrane before analysis through HPLC the measured concentrations needed to be compared to the simulated concentrations of dissolved mass only.

⁷ Note that scaling had not been necessary for this single data set.

Aqueous concentration was allowed to vary from 0.1 – 5 (scaled) with an initial estimate of 1.0, and $DegT_{50,water}$ was allowed to vary from 1 – 100 days with an initial estimate of 30, 75 or 5 days (Table 3.8). Runs were performed using values for bulk density of 0.2, 0.8 and 1.2 kg/L (red stars of Figure 3.2) using an initial estimate of organic matter content of 4.3%. Three additional runs were performed for a bulk density of 0.6 kg/L (purple star of Figure 3.2).

Of the 12 runs only one run seemed satisfactory (χ^2 – error of 22.5% and degradation in the water phase accounting for at least 50% of total dissipation), yielding an estimated $DegT_{50,water}$ value of 7.6 days (ninth entry in Table A5.4 of Appendix 5). However, when we presented the optimisation results in a graph (Figure 5.9) we saw that the correspondence between measured and simulated concentrations in the sediment is relatively good, but the measurements in the water are systematically underestimated and the results of the run are therefore considered unreliable. Therefore, we decided to continue the optimisation procedure, using expert judgement.

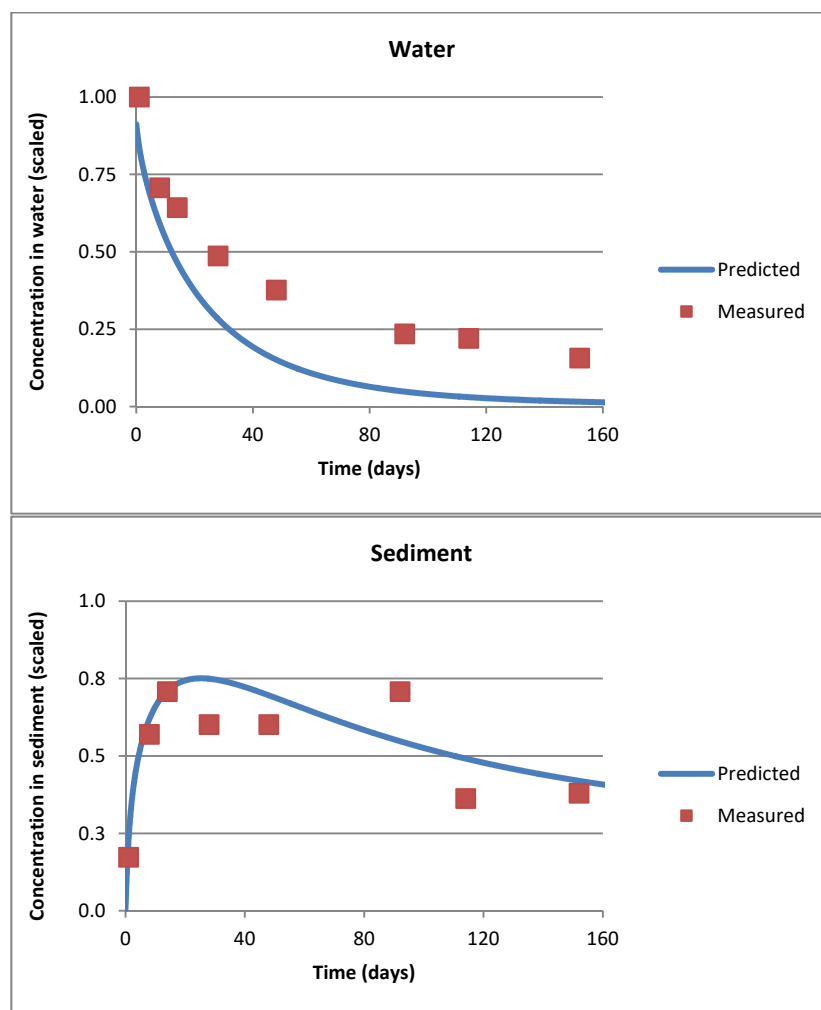


Figure 5.9 Simulated and measured concentrations of linuron in water and sediment as a function of time post-application for Bromilow et al. (2006); data simulated using $DegT_{50,water} = 7.56$ days, an organic matter content of sediment of 3.8% and a simulated initial scaled water concentration of 0.91. The initial values used in the estimation are given as the ninth entry in Table A5.4 of Appendix 5.

For this run (χ^2 – error of 22.5%, $DegT_{50,water}$ estimated as 7.6 days), PEST-TOXSWA estimated that 17% of the mass penetrated into sediment, whereas 88% of the mass in the system was transformed in the water phase (ninth entry in Table A5.4 of Appendix 5). These data were generated using the default 'multiplication factor', i.e. the calculations use equal weights for concentrations measured in water and sediment. In view of the higher importance of degradation in water compared to penetration into sediment, we performed additional calculations using an adjusted weight factor of 5

for the water measurements, reflecting the approximately 5 times higher mass present (and degraded) in the water compared to the sediment. Using the same values for bulk density, organic matter content etc we performed again 12 runs (Table A5.5 of Appendix 5). Although two runs fulfilled the χ^2 – error criterion below 25% (both 22.7%) the visual correspondence between measured and simulated concentrations in both water and sediment is not satisfactory (see e.g. Figure 5.10) and so, their fitted $DegT_{50,water}$ value is not acceptable.

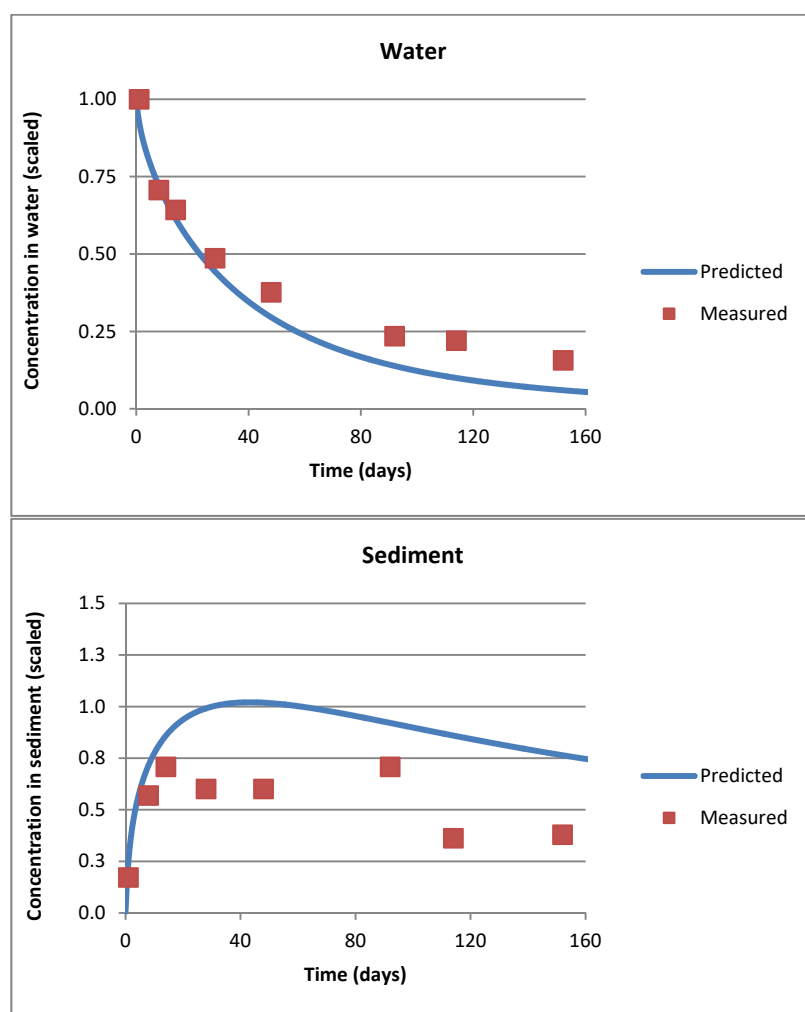


Figure 5.10 Simulated and measured concentrations of linuron in water and sediment as a function of time post-application for Bromilow et al. (2006); data simulated using an additional weight factor of 5 for water measurements, $DegT_{50,water} = 13.25$ days, an organic matter content of sediment of 3.8% and a simulated initial scaled water concentration of 1.00. The initial values used in the estimation are given as the seventh entry in Table A5.5 of Appendix 5.

As can be seen when comparing Figures 5.8 and 5.9 which both represent the fits with best statistics within their sets of simulations, the introduction of an extra weight factor 5 for the water concentrations improves the quality of the fit of water concentrations, but at the same time decreases the quality of the fit of sediment concentrations. Overall, the introduction of a multiplication factor of 5 were judged to not improve the quality of the reverse modelling to a large extent, and the results of the inverse modelling remain unreliable. So, we did not accept the results of the optimisation with the extra weight factor of 5.

However, looking at the graphs it is possible that the results have been negatively influenced by the assumed value of 1000 d for the $DegT_{50,sediment}$. This value may not reflect well the degradation rate for linuron in sediments. The Pesticide Properties DataBase gives a value of 24.1 d for the half-life in the overall water-sediment systems. With a value of 24 d for the $DegT_{50,sediment}$ our optimisation procedure

would possibly give an improved correspondence between measured and simulated concentrations in water and sediment. However, we did not test this within the current project, but the current software does allow to change the default value of 1000 d for another value of the $DegT_{50, \text{sediment}}$ (by making changes in the TOXSWA_moe.txt file). We included this test with a 24 d for the $DegT_{50, \text{sediment}}$ as a recommendation in Chapter 7 and included the use of a more realistic $DegT_{50, \text{sediment}}$ in the Guidance of Chapter 6.

Comparison with dissipation rates of linuron obtained in laboratory tests

The analysis of data taken from the study described by Bromilow et al. (2006) did not result in a reliable estimate for $DegT_{50, \text{water}}$ for linuron. Hence, comparison with other values for dissipation half-lives for dissipation through hydrolysis, photolysis and dissipation in water-sediment systems is not feasible.

5.4 Metsulfuron-methyl

For metsulfuron-methyl one study was found that is suitable for the estimation of the $DegT_{50, \text{water}}$ by inverse modelling by TOXSWA_PEST. The study with metsulfuron-methyl in outdoor glass tanks was described by Wang et al. (2011).

Wang et al. (2011) monitored radio-labelled metsulfuron-methyl in water (depth 15 cm) and sediment (depth not given, estimated 2 cm; organic matter content of 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; initially the system contained 105.5 mg, which corresponds to 1.0 mg/L. 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-phasic, a rapid initial decrease being followed by a somewhat slower decrease after the initial (5-day) period. The pH was not measured during the experiments, but presumably it was above 3.5, i.e. the pKa. An average temperature of 15°C was assumed in the inverse modelling. Maximum concentration in sediment was approximately 14% of the mass initially added to the system (measured on days 45 and 60 after application). This relatively high percentage (in view of its low K_{oc} of 12, PPDB) may in part be caused by the relatively low water depth (0.15 m) in the system. Details are given in Appendix 6.

The inverse modelling was performed using scaled concentrations⁸. Since the organic matter content of the sediment (upper 2 cm) was given as 3.05%, the organic matter % was allowed to vary from 2.55 – 3.55% (Case B9 of Figure 2.2). As water was filtered using a 0.45 µm Millipore membrane before analysis through HPLC the measured concentrations needed to be compared to the simulated concentrations of dissolved pesticide mass only.

Aqueous concentration was allowed to vary from 0.1 – 5 (scaled) with an initial estimate of 1.0, and $DegT_{50, \text{water}}$ was allowed to vary from 0.5 – 50 days with an initial estimate of 5, 20 or 1 days (Table 3.8). Runs were performed using values for bulk density of 0.2, 0.8 and 1.2 kg/L (red stars of Figure 3.2), using an initial organic matter content of 3.05%. Three additional runs were performed for a bulk density of 0.6 kg/L (purple stars of Figure 3.2).

Satisfactory runs (χ^2 – error below 25% and degradation in the water phase accounting for at least 50% of total dissipation) were not obtained for any of the executed runs (Table A6.4 of Appendix 6). Therefore, a second set of calculations was performed, using a multiplication factor for the relative weight of water layer to sediment of 6, approximating the ratio between water degradation (86%) and sediment penetration (14%) found in the first set of calculations. We used the same values for bulk density, organic matter content and initial estimates as in the former set of runs (Table A6.5 of Appendix 6). The introduction of an extra weight factor 6 for the water concentrations clearly improves

⁸ Note that scaling had not been necessary for this single data set.

the quality of the fit of water concentrations, but at the same time clearly decreases the quality of the fit of sediment concentrations. This is clearly shown by Figures 5.10 and 5.11 which both represent the fits with best statistics within their sets of simulations. The value for χ^2 – error is still relatively low, 26.6%. This is due to the fact that a low weight is given to the bad correspondence between measured and simulated concentrations in the sediment compared to the correspondence in the water layer of Figure 5.12. Overall, the introduction of a multiplication factor of 6 improves the quality of the inverse modelling of water concentrations to the extent that results of the inverse modelling are considered sufficiently reliable, the alternative being to neglect entirely the information on metsulfuron-methyl's behaviour of Wang et al. (2011). Figure 5.13 presents the residuals for the run of Figure 5.12. As expected they are well distributed for the water layer, but not for the sediment. As the sediment has received less weight in the optimisation, this does not lead to a rejection of the optimisation results. Six runs have similar χ^2 – errors (runs 4 – 6 with an error of 28.6%, runs 10-12 with an error of 26.6% of Table A6.5 of Appendix 6) and yielded values of $DegT_{50,water}$ close together (6.35, 6.41, 6.47, 6.41, 6.41 and 6.42 days resp.). The geomean value for $DegT_{50,water}$ of these 6 runs is 6.41 days.

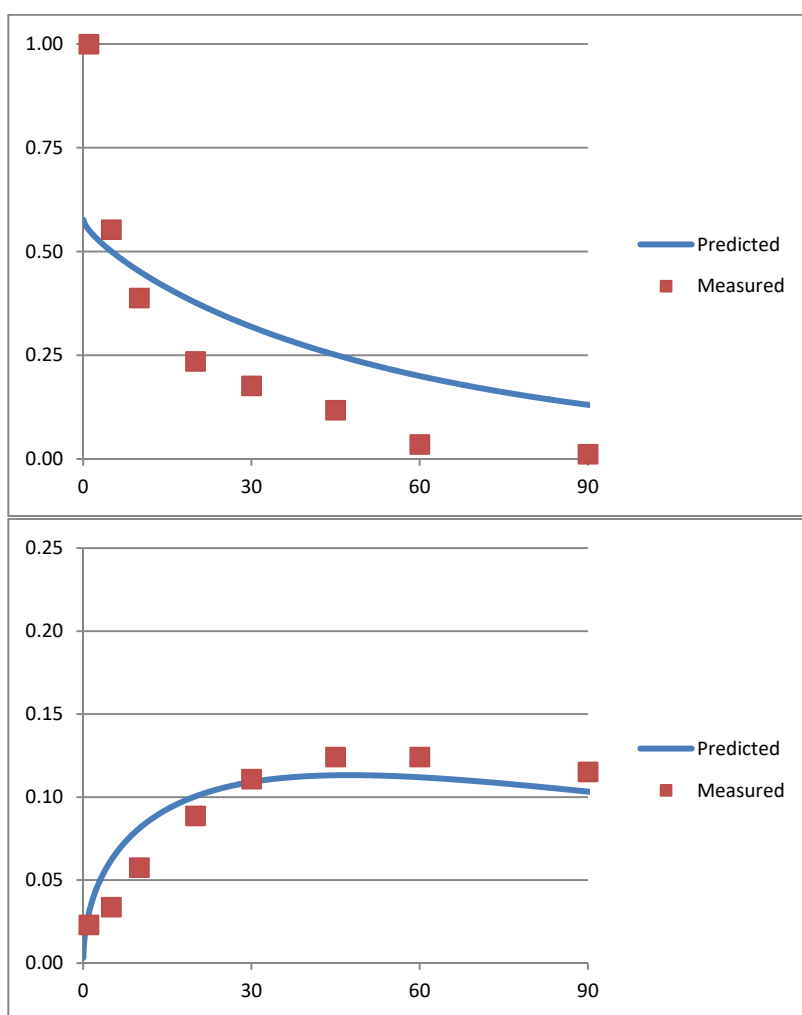


Figure 5.11 Simulated and measured concentrations of metsulfuron-methyl in water and sediment as a function of time post-application in the study of Wang et al. (2011); data simulated using $DegT_{50,water} = 29.5$ days, an organic matter content of sediment of 2.55% and an initial scaled water concentration of 0.58. The initial values used in the estimation are given as the tenth entry in Table A6.4 of Appendix 6.

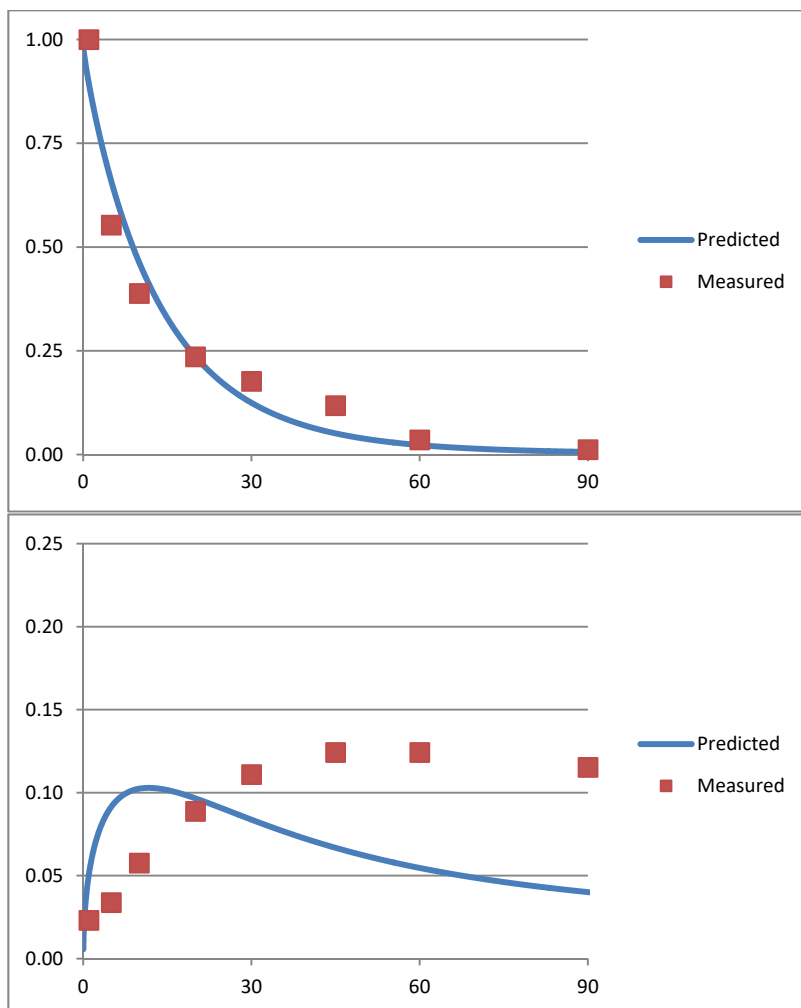


Figure 5.12 Simulated and measured concentrations of metsulfuron-methyl in water and sediment as a function of time post-application in the study of Wang et al. (2011); data simulated using an additional weight factor of 6 for the water measurements, a $\text{Deg}T_{50,\text{water}} = 6.41$ days, an organic matter content of sediment of 3.55% and an initial scaled water concentration of 0.99. The initial values used in the estimation are given as the tenth entry in Table A6.5 of Appendix 6.

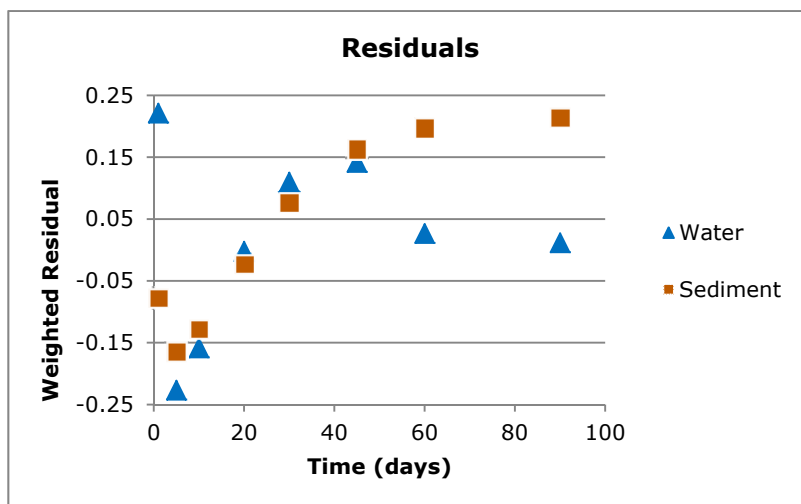


Figure 5.13 Residuals (scaled) of measured minus simulated concentrations, weighted according to Eq. 19, of metsulfuron-methyl in water and sediment as a function of time post-application in the study of Wang et al. (2011); data simulated using an additional weight factor of 6 for the water measurements, a $\text{Deg}T_{50,\text{water}} = 6.41$ days, an organic matter content of sediment of 3.55% and an initial scaled water concentration of 0.99. The initial values used in the estimation are given as the tenth entry in Table A6.5 of Appendix 6.

Comparison with dissipation rates of metsulfuron-methyl obtained in laboratory tests

Table 5.3 gives half-life values for various dissipation processes, taken from the Pesticides Properties Database (<http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>).

Table 5.3 Dissipation half-life DT_{50} for metsulfuron-methyl taken from Pesticides Properties Database.

| Dissipation process | Value DT_{50} (days) |
|-------------------------|----------------------------|
| Hydrolysis | Stable |
| Photolysis | stable for pH 5 and higher |
| Water-sediment (system) | 224.3 |

For the cosms analysed in the present study by Wang et al. (2011), a $DegT_{50,water}$ of 6.41 days at 20°C was observed. Metsulfuron-methyl is stable for hydrolysis as well as for photolysis in water having a pH of 5 and higher, which is mostly the case for outdoor water. The overall system DT_{50} value of 224.3 d is considerably greater than the estimated $DegT_{50,water}$ of 6.41 days of the study of Wang et al. (2011).

The tiered approach suggested by Boesten et al. (2014), is based on 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. The study by Wang et al. (2011) belongs to the box 'Outdoor studies with algae and possibly macrophytes' (Box 2.9). The $DegT_{50,water}$ derived from this cosm study, analysed using inverse modelling, indeed yield a considerably less conservative estimate for degradation in the water-phase than simple laboratory-derived values for dissipation through hydrolysis, photolysis and dissipation in water-sediment systems. Thus, the tiered approach suggested by Boesten et al. (2014) is valid for our estimated $DegT_{50,water}$ value for metsulfuron-methyl.

5.5 Prosulfocarb

For prosulfocarb one study was found that is suitable for the estimation of the $DegT_{50,water}$ by inverse modelling by TOXSWA_PEST. The study in outdoor experimental ditches was described by Arts et al. (2006). Adriaanse et al. (2013) performed an inverse modelling study to determine its $DegT_{50,water}$ by a similar method as the one of this report, but analysed more extensively the simulations and their results. Therefore, we compared the results of our simplified estimation method to the results of their analysis.

Arts et al. (2006) report a mesocosm study giving details of the fate of several pesticides, among others prosulfocarb, in a study in artificial ditches. Water depth was 0.57 m, sediment depth was 0.25 m in ditches of 40 m each. Although sediment dry bulk density (1.21 kg/L) and porosity (0.54 L/L) are given for the upper 5 cm, its organic matter content is not reported. Initially systems contained 4200 mg, which corresponds to 0.075 mg/L in the 56 m³ of water in the ditches. Seven measurements in water and five measurements in the upper 5 cm of the sediment layer were performed up to 28 days post-application. The average water temperature during the experiment was set at 14°C for the simulations and the pH at 8.1. The maximum mass of prosulfocarb in the sediment was 11.0% 3 days after application (Adriaanse et al., 2012). Details are given in Appendix 7.

The inverse modelling was performed using scaled concentrations⁹. Since the organic matter content of the sediment was not given and hence considered unknown, the organic matter % was allowed to vary from 2.5 – 50% (Case B8 of Figure 2.2). As the water was not filtered before analysis through HPLC the measured concentrations needed to be compared to the simulated concentrations of dissolved prosulfocarb mass plus prosulfocarb mass sorbed to suspended solids.

⁹ Note that it was unnecessary to scale this single data set.

Aqueous concentration was allowed to vary from 0.1 – 5 (scaled) with an initial estimate of 1.0, and $DegT_{50,water}$ was allowed to vary from 0.5 – 50 days with an initial estimate of 5, 20 or 1 days (Table 3.4).

Runs were performed using values for bulk density of 0.2, 0.8 and 1.2 kg/L, using an initial organic matter content of 19, 9 and 3% resp. (red stars in Figure 3.1).

A first set of nine simulations was done. Satisfactory runs (χ^2 – error below 25%, satisfactory visual correspondence between measured and simulated concentrations in water and sediment and degradation in the water phase accounting for at least 50% of total dissipation) were not obtained for any of the runs, although 4 of the runs had an χ^2 – error of 18.4% and a similar estimate for $DegT_{50,water}$ of 1.65 days (Table A7.4 of Appendix 7). However, the visual correspondence between measured and simulated concentrations in the cosm water was not satisfactory (see Figure 5.14), so the results were judged to be unreliable.

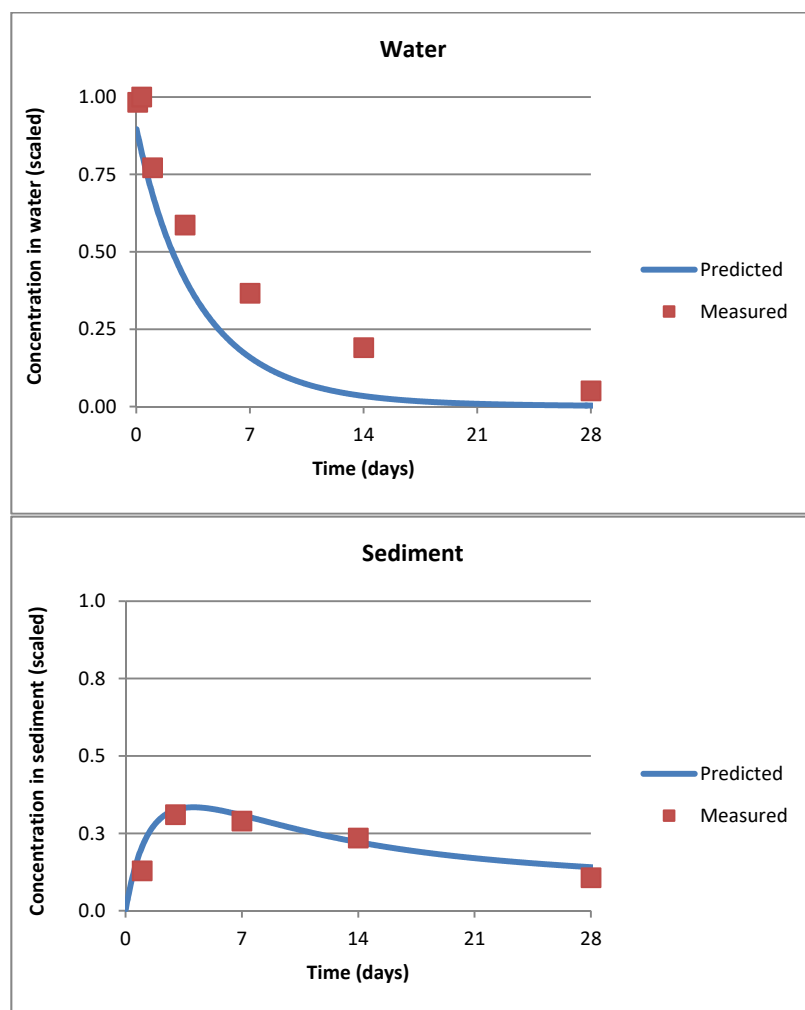


Figure 5.14 Simulated and measured concentrations of prosulfocarb in water and sediment as a function of time post-application for Arts et al. (2006); data simulated using $DegT_{50,water} = 1.65$ days, an organic matter content of sediment of 2.5% and an initial scaled water concentration of 0.90. The initial values used in the estimation are given as the seventh entry in Table A7.4 of Appendix 7.

So, a second set of four simulations was performed, using a multiplication factor of 22 for the correspondence between measured and simulated concentrations in the water layer, approximating the ratio between water degradation (98%) and sediment penetration (4.5%) found in the first set of calculations. The simulations used the same values for bulk density, organic matter content and initial estimates as the ones used in the first set of simulations (Table A7.5 of Appendix 7).

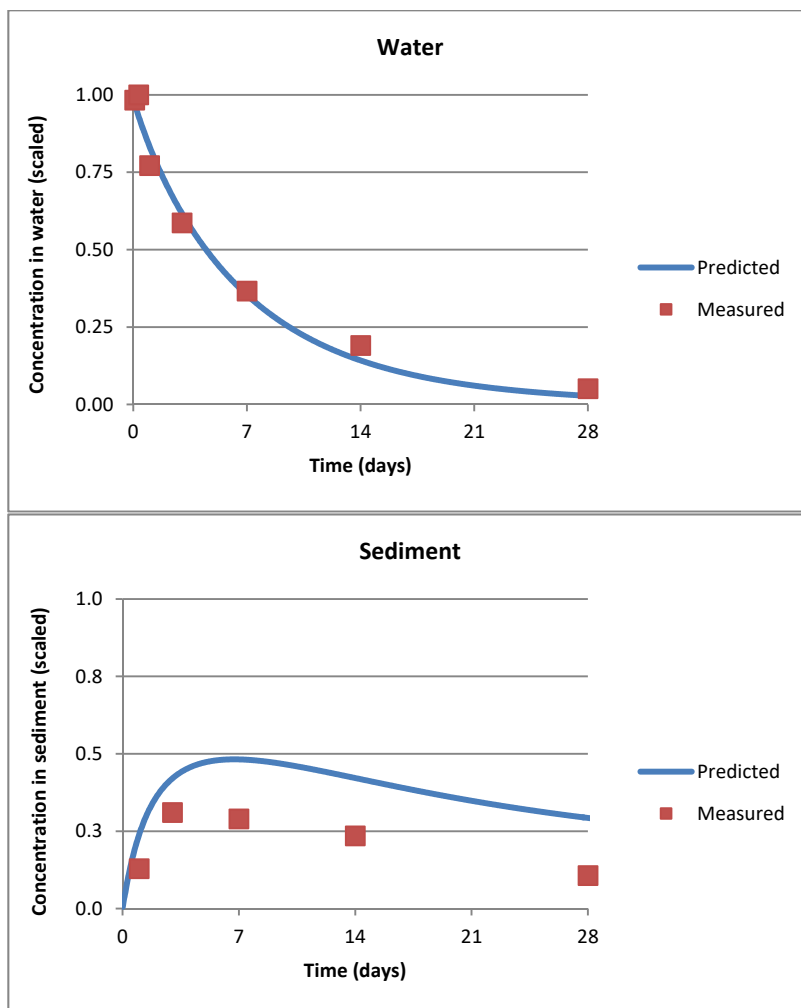


Figure 5.15 Simulated and measured concentrations of prosulfocarb in water and sediment as a function of time post-application of Arts et al. (2006); data simulated using an additional weight factor of 22 for water measurements, $DegT_{50,water} = 2.94$ days, an organic matter content of sediment of 2.5% and an initial scaled water concentration of 0.99. The initial values used in the estimation are given as the seventh entry in Table A7.5 of Appendix 7.

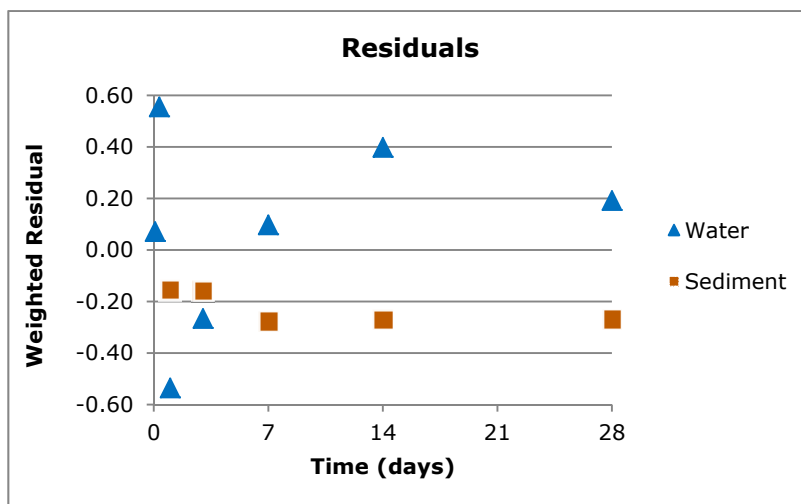


Figure 5.16 Residuals (scaled) of measured minus simulated concentrations, scaled according to Eq. 19, of prosulfocarb in water and sediment as a function of time post-application of Arts et al. (2006); data simulated using an additional weight factor of 22 for water measurements, $DegT_{50,water} = 2.94$ days, an organic matter content of sediment of 2.5% and an initial scaled water concentration of 0.99. The initial values used in the estimation are given as the seventh entry in Table A7.5 of Appendix 7.

As can be seen when comparing Figures 5.13 and 5.14 which both represent the fits with best statistics within their sets of simulations, the introduction of an extra weight factor 22 for the water concentrations clearly improves the quality of the fit of water concentrations, but at the same time clearly decreases the quality of the fit of sediment concentrations. The value for χ^2 – error of the run of Figure 5.15 is still relatively low, 9.0%. This is due to the fact that a low weight is given to the bad correspondence between measured and simulated concentrations in the sediment compared to the correspondence in the water layer of Figure 5.15. Overall, the introduction of a multiplication factor of 22 improves the quality of the inverse modelling of water concentrations to the extent that results of the inverse modelling were reliable. Four runs have similar χ^2 – errors (runs 4 and 6 with an error of 13.2%, and runs 7 and 9 with an error of 9.0%) and yielded values of $DegT_{50,water}$ close together (2.77, 2.76, 2.94 and 2.94 days resp.). The geomean value for the $DegT_{50,water}$ of these 4 runs is 2.85 days.

This value for $DegT_{50,water}$ is clearly different from the value derived from the first set of calculations (1.77 days). This demonstrates that our standard optimisation procedure for the prosulfocarb study was correctly judged to be unreliable, it did indeed not fulfil all quality criteria.

Only by using expert judgement (using a multiplication factor of 22 to increase the relative weight of the correspondence between simulated and measured concentrations in the water layer) we were able to find satisfactory runs and thus satisfactory estimates for the $DegT_{50,water}$. The value of 2.85 days is confirmed by the value of 2.9 days found by Adriaanse et al. (2013) in their inverse modelling exercise for the same cosm study.

Comparison with dissipation rates of prosulfocarb obtained in laboratory tests

The analysis of data taken from the study described by Arts et al. (2006) resulted in an estimate for $DegT_{50,water}$ for prosulfocarb of 2.85 days at 20°C.

Table 5.4 gives half-life values for various dissipation processes, taken from the Pesticides Properties Database (<http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>). Prosulfocarb is stable for hydrolysis and for photolysis. The overall system DT_{50} , dissipation half-life, in water-sediment systems equals 214 days. The three entries in Table 5.4 were compared to the optimised $DegT_{50,water}$ values of 2.85 days for the cosms of Arts et al. (2006). The optimised $DegT_{50,water}$ value is clearly shorter than the degradation half-lives determined in the laboratory experiments.

Table 5.4 Dissipation half-life DT_{50} for prosulfocarb taken from Pesticides Properties Database.

| Dissipation process | Value DT_{50} (days) |
|-------------------------|---------------------------|
| Hydrolysis | Stable |
| Photolysis | Stable |
| Water-sediment (system) | 214 |

The tiered approach suggested by Boesten et al. (2014), is based on 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. The study by Arts et al. (2006) belongs to the box 'Outdoor studies with algae and possibly macrophytes' (Box 2.9). The $DegT_{50,water}$ derived from this cosm study, analysed using inverse modelling, yields a less conservative estimate for dissipation than derived from laboratory studies on hydrolysis and photolysis. It does, however, yield a less conservative estimate for degradation in the water-phase than derived from laboratory studies on dissipation in water-sediment systems. Thus, the tiered approach suggested by Boesten et al. (2014) is valid for our estimated $DegT_{50,water}$ value for prosulfocarb.

5.6 Comparison of half-life for decline in water and $DegT_{50,water}$

In aquatic risk assessment it is common practice to determine overall decline (i.e. dissipation) rates in water of cosms and compare these for the various types of cosms. Decline in water encompasses the processes of volatilisation from the water into the air, transport into (and out of) the sediment and degradation in water. As volatilisation and transport into and out of the sediment depend upon the dimensions of the system, e.g. a cosm with a shallow water layer will lose a higher mass percentage by transport into the sediment than a cosm with a deep water layer, decline rates for cosms with different dimensions cannot be easily compared.

However, degradation rates do not depend on the system dimensions, and therefore they can be used to compare cosms. So we can assess whether the degradation rate depends strongly on the cosm characteristics, such as presence of algae, macrophytes, incoming sunlight, pH etc or not.

As decline rates are still commonly used, especially in ecotoxicological risk assessment, we here evaluate the difference between the half-life for decline and for degradation in water for one example, chlorpyrifos of the study of Brock et al. (1992). We performed a linear regression on the scaled water concentrations as a function of time of Table A3.3 of Appendix 3 according to FOCUS Degradation Kinetics (2006), i.e. an unweighted fit. So, we fitted the individual untransformed data points (so, each having the weight) to the equation:

$$c_t = c_{t=0} e^{-kt} \quad (5.1)$$

with

k = degradation rate in water

We used the FOCUS Degradation Excel spreadsheet FOCUS_DEGKIN v2 (tab 'SFO no reps with fit') and obtained a $c_{t=0}$ of 1.16 (scaled) and a decline rate k of 0.189 d^{-1} , so the DT_{50} equals $\ln 2/k = 3.7 \text{ d}$. The χ^2 error was 9.2% and the visual correspondence between measured and simulated concentrations is presented in Figure 5.17, while the distribution of the residuals is shown in Figure 5.18.

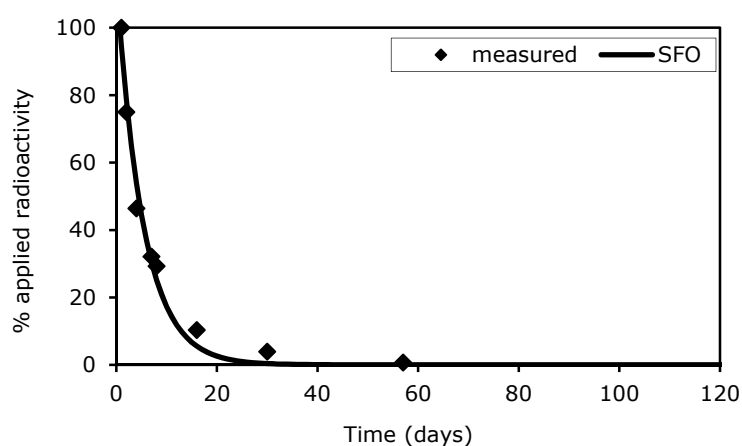


Figure 5.17 Concentration chlorpyrifos in water, measured and simulated by FOCUS_DEGKIN v2 Excel spreadsheet as a function of time post-application for the $35 \mu\text{g/L}$ cosm of Brock et al. (1992) of Appendix 3.

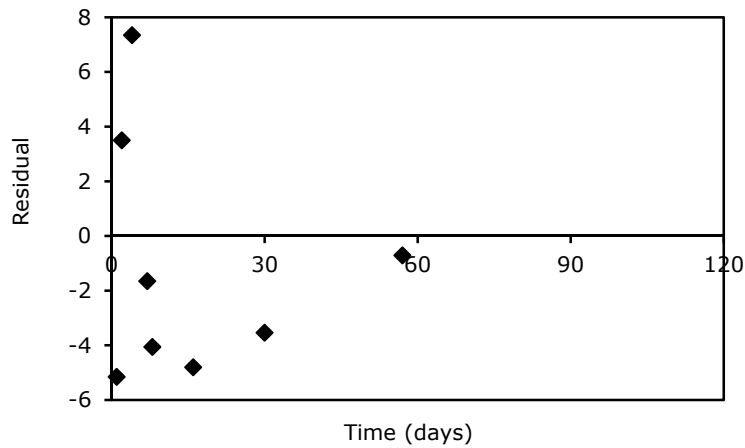


Figure 5.18 Residuals of chlorpyrifos in water as a function of time post-application for the 35 µg/L cosm of Brock et al. (1992) of Appendix 3.

The estimated $DegT_{50,water}$ value obtained by the inverse modelling procedure using PEST-TOXSWA was 5.93 d. So, as expected the half-life for decline in water is smaller than the estimated $DegT_{50,water}$ value obtained by inverse modelling by PEST-TOXSWA for chlorpyrifos (section 5.6), resp. 3.7 vs 5.93 d. By distinguishing between volatilisation, transport to and from the sediment and degradation using TOXSWA, the developed inverse modelling procedure results in a more accurate estimation of the half-life for degradation in the water layer than by the straightforward calculation of the half-life for decline in water, that is commonly used in aquatic risk assessments. Obtaining the real degradation rate is important for use of models that simulate the behaviour of pesticides in surface water, because these types of models often use degradation rates and not decline rates as model input.

N.B. Note that when the fit is done after a logarithmic transformation of the (scaled) water concentration data (Eq. 5.2), another decline rate is obtained.

$$\ln_{c_t} = \ln_{c_{t=0}} - k t \quad (5.2)$$

We now obtained a DT_{50} of 8.1 d (i.e. a value twice as large) with a $c_{t=0}$ of 0.67 (scaled), with a good visual correspondence as presented in Figure 5.19. the reason for this relatively large difference between the two fitted decline rates lies in the logarithmic transformation: by transforming the data the Least Squared Differences method used in the fit attributes as much weight to the low concentrations after 10 to 12 days as to the higher concentrations during the first days post-application, which generally have a higher precision than the later measurements.

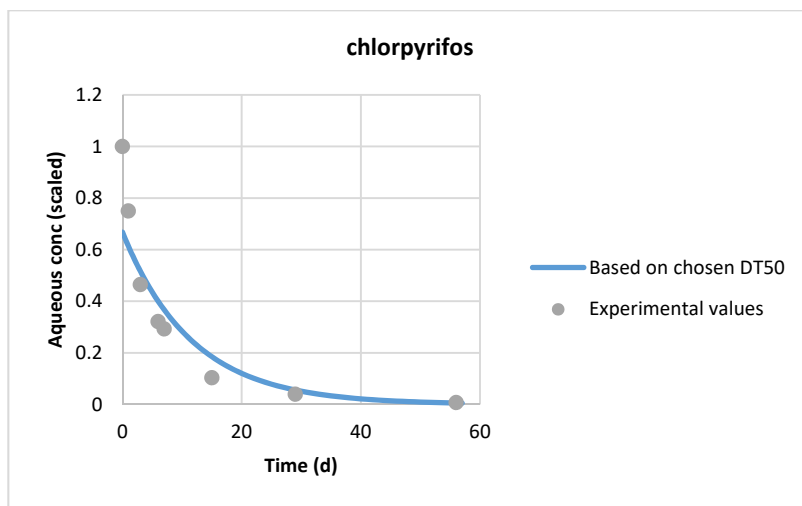


Figure 5.19 Concentration chlorpyrifos in water, measured and fitted to Eq. 5.2 as a function of time post-application for the 35 µg/L cosm of Brock et al. (1992) of Appendix 3.

So,

fitting the decline by weighted or unweighted data has a large impact on the size of the DT_{50} value and

the FOCUS Degradation Kinetics recommended decline rate of 3.7 d is smaller than the optimised $DegT_{50,water}$ value of 5.93 d, which is as expected and in accordance with the modelled processes (i.e. volatilisation, degradation in water and transport to the sediment) in TOXSWA.

5.7 Summary

Table 5.5 gives an overview of the results for the estimated $DegT_{50,water}$ for the five compounds in the six cosm studies. It shows that it was possible to obtain satisfactory results for five of the six studies, i.e. to obtain optimisations fulfilling the three quality criteria of (i) χ^2 – error not exceeding 25%, (ii) visual correspondence between measured and simulated in water and in sediment both satisfactory and (iii) residuals well distributed. However, it was not straightforward to obtain satisfactory optimisation results. For 2 of the 4 available data sets of chlorpyrifos (1 of Brock et al. (1992), 3 of Giddings et al. (1997)) we obtained relatively easy satisfactory optimisations, but for 2 data sets of Giddings et al. (1997) it was impossible. For lambda-cyhalothrin the visual goodness of fit was borderline. For linuron it proved to be impossible to obtain a satisfactory optimisation, while for metsulfuron-methyl and prosulfocarb satisfactory optimisations were obtained after using a multiplication factor giving 6, resp. 22 times more weight to the differences between measured and simulated concentrations in the water layer than those in the sediment.

Table 5.5 Overview of the optimisation results for the $DegT_{50,water}$ for the five compounds in six cosm studies with measurements in water and in sediment.

| | $DegT_{50,water}$ satisfactory ? | χ^2 – error | Visual goodness of fit | $F_{M,deg-wat} \geq 50\%$ | Remark |
|-------------------------|-------------------------------------|------------------|----------------------------|---------------------------|--|
| Chlorpyrifos - Brock | Yes, 5.93 d | 7.6% | Good | Yes, 67.0% | - |
| Chlorpyrifos - Giddings | Yes (but only level 5), 9.71 d | 25.2% | Acceptable | Yes, 81.8% | No acceptable result for level 3 and 4 |
| Lambda-cyhalothrin | Yes, 0.18 d | 12.7-14.4% | Borderline | Yes, 98.1-98.3% | - |
| Linuron | No | 22.5–22.7% | Not acceptable | Yes, 78.2-83.8% | Using weight factor not helpful |
| Metsulfuron-methyl | Yes, 6.41 d | 26.6-28.6% | Acceptable for water layer | Yes, 93.4-94.1% | Weight factor needed |
| Prosulfocarb | Yes, 2.85 d | 9.0-13.2% | Acceptable for water layer | Yes, 93.4-93.5% | Weight factor needed |

Table 5.6 summarises the results of the optimisations into more detail. For each satisfactory, fitted $DegT_{50,water}$ value it specifies the value of the χ^2 – error and the 95% confidence interval expressed as a percentage of the fitted value. The χ^2 – error ranged from 7.6% for the indoor cosm study on chlorpyrifos of Brock et al. (1992) up to 28.6% for some cases of the metsulfuron-methyl cosm study of Wang et al. (2011). The 95% confidence interval expressed as a percentage of the fitted value were relatively wide: it typically ranges from approximately 30 to 170%. The table shows that for metsulfuron-methyl and prosulfocarb 24 initial parameterisations were needed to obtain a number of satisfactory optimisation results. For lambda-cyhalothrin this number was 39, while for linuron 24 initial parameterisations did not result in any satisfactory optimisation. So, often the optimisation procedure is not straightforward and expert judgement is needed to adjust the standard initial parameterisations to obtain successful optimisations, e.g. by introducing a weight factor above 1 for the correspondence between simulated and measured concentrations in the water layer, or possibly by changing the default $DegT_{50,soil}$ for a more realistic lower value.

Table 5.6 Details of the optimisation results for the $DegT_{50,water}$ for the five compounds in six cosm studies with measurements in water and in sediment.

| Compound-study (number of initial parameterisations needed) | Entry in table of Appendix | Value of satisfactory, fitted $DegT_{50,water}$ (d) | χ^2 – error (%) | 95% confidence interval (% of fitted value) |
|--|-------------------------------|---|-------------------------|--|
| Chlorpyrifos Brock – indoor cosms (9) | | | | |
| | 4 | 5.92 | 7.6 | 73-129 |
| | 5 | 5.94 | 7.6 | 71-129 |
| | 6 | 5.93 | 7.6 | 71-129 |
| Chlorpyrifos Giddings | | | | |
| Level 3 (15) | | n.a. | | |
| Level 4 (15) | | n.a. | | |
| Level 5 (9) | 1 | 9.70 | 25.2 | 10-164 |
| | 2 | 9.71 | 25.2 | 36-165 |
| | 3 | 9.72 | 25.2 | 36-164 |
| Lambda-cyhalothrin (39) | | | | |
| | 13 | 0.18 | 13.7 | 50-150 |
| | 15 | 0.18 | 13.7 | 50-150 |
| | 22 | 0.19 | 14.4 | 47-153 |
| | 24 | 0.19 | 14.4 | 47-153 |
| | 31 | 0.18 | 12.7 | 28-178 |
| | 33 | 0.18 | 12.7 | 28-178 |
| Linuron (24) | | | | |
| | | n.a. | | |
| Metsulfuron-methyl (24) | | | | |
| | 16 | 6.35 | 28.6 | 61-139 |
| | 17 | 6.41 | 28.6 | 60-140 |
| | 18 | 6.47 | 28.6 | 60-137 |
| | 22 | 6.41 | 26.6 | 63-137 |
| | 23 | 6.41 | 26.6 | 63-137 |
| | 24 | 6.42 | 26.6 | 63-137 |
| Prosulfocarb (24) | | | | |
| | 19 | 2.77 | 13.2 | 68-132 |
| | 21 | 2.76 | 13.2 | 68-132 |
| | 22 | 2.94 | 9.0 | 78-122 |
| | 24 | 2.94 | 9.0 | 78-122 |

In the five studies with satisfactory optimisations the estimated $DegT_{50,water}$ by the TOXSWA-PEST inverse modelling procedure resulted in shorter degradation half-lives than the half-lives obtained in laboratory studies for hydrolysis, photolysis or in water-sediment studies (Table 5.7). The difference is at least a factor of two, but went up to a half-life of 84 times shorter in the outdoor cosm than in the laboratory for lambda-cyhalothrin.

Boesten et al. (2014) suggested a tiered approach for the determination of $DegT_{50,water}$, in which lower tier values are formed by laboratory tests and the highest tier by outdoor studies with algae and possibly macrophytes (see Chapter 3.9). The fact that all our cosm $DegT_{50,water}$ values are shorter than the half-lives obtained in the laboratory tests of hydrolysis, photolysis and water-sediment systems is in accordance with their tiered approach.

Table 5.7 Comparison of the $DegT_{50,water}$ for the five compounds in six cosm studies with the $DegT_{50}$ values obtained in laboratory tests.

| | Degradation half-life (days) in | | | | |
|-------------------------------|---------------------------------|-----------------|----------------------------|---|--|
| | Outdoor cosm | Laboratory test | | | |
| | Estimated $DegT_{50,water}$ | Hydrolysis | Photolysis | Overall system rate in water-sediment systems | Ratio between shortest $DegT_{50}$ in laboratory and $DegT_{50,water}$ of outdoor cosm |
| Chlorpyrifos – Brock (indoor) | 5.93 | 25.5 | 29.6 | 36.5 | 4.3 (indoor cosm !) |
| Chlorpyrifos – Giddings | 9.71 | 25.5 | 29.6 | 36.5 | 2.6 |
| Lambda-cyhalothrin | 0.18 | stable | 40 | 15.1 | 84 |
| Linuron | n.a.* | | | | n.a. |
| Metsulfuron-methyl | 6.41 | stable | Stable for pH 5 and higher | 224.3 | 35 |
| Prosulfocarb | 2.85 | stable | stable | 214 | 75 |

* n.a. means not available.

6 Overview of guidance to estimate the $DegT_{50,water}$

In this chapter we give an overview of the entire method to estimate the $DegT_{50,water}$ in outdoor cosm water by inverse modelling using TOXSWA and PEST. We here describe all the needed steps and included the most important figures to help the user. For more details the user is referred to the mentioned sections of the main text of this report or to Appendix 8, where a detailed instruction has been described.

Step a

Read the cosm study to get a good overview of the study and apply the flow chart of Figure 6.1 (this is essentially the same figure as Figure 2.2 but in box B9 allowed boundary values of organic matter content in the 0-1 cm layer for the optimisation procedure are 20% instead of 0.5%). In the remainder of this chapter we assume that the following four items have been measured: (i) ≥ 5 concentrations in the water layer, (ii) the water depth and (iii) ≥ 3 concentrations in the sediment as well as (iv) the depth over which the sediment concentrations were measured. This implies that either the optimisation method 'Water-sediment' or the method 'Water-sediment + o.m. 0-1 cm measured' applies, see the boxes B8 or B9 of Figure 6.1.

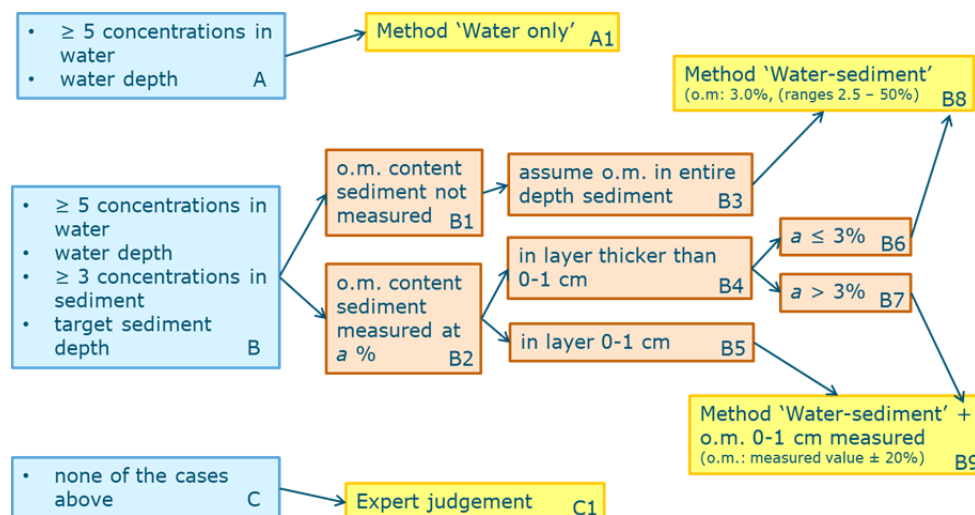


Figure 6.1 Selection of the appropriate optimisation method to estimate the $DegT_{50,water}$ based upon the available measurements in the outdoor cosm study.

Step b

Next, extract the required data from the publications or reports into the following tables, 6.1, 6.2 and 6.3. See section 3.5 for scaling of measured concentrations.

Table 6.1 Measured concentrations in water (mg/L and scaled; ... cm water depth) and sediment (g/kg and scaled; 0 – .. cm sediment layer) as a function of time (d) for the cosm study with (compound and references).

| Number | Time (days) | Concentration in water (mg/L) | Concentration in sediment (g/kg) | Scaled concentration in water (-) | Scaled concentration in sediment (-) |
|-------------------------------------|----------------|-------------------------------|--|-----------------------------------|--------------------------------------|
| Data given as concentrations | | | Data converted to scaled concentrations | | |
| 1 | 0 [#] | .. | | 1.0000 | |
| 2 | 1 | .. | | .. | |
| 3 | .. | | | | |
| 4 | .. | | | | |
| 5 | | | ... | | ... |
| 6 | | | ... | | ... |
| 7 | | | | | |
| 8 | | | | | |
| 9 | | | | | |
| 10 | | | | | |

[#] Mention whether initial concentration has been measured or calculated from dosed amount (i.e. equals the nominal concentration).

Table 6.2 Relevant measurements for the optimisations, other than measured concentrations in water and sediment for the cosm study with (compound and references).

| Cosm label | |
|--|--|
| References | |
| Compound | |
| Type of system | |
| Dimensions system | |
| Side slope (hor/vert) | |
| Number of measurements in water | .. |
| Water depth (m) | .. |
| Water filtered before analysis ? ^a | Yes/No |
| Number of measurements in sediment | .. |
| Sediment layer over which concentrations measured ^b | 0 – .. cm layer |
| Total sediment depth (cm) ^c | 10 |
| Type of sediment | |
| Sediment organic matter measured in layer 0 - x cm? | ...% organic matter in 0-.. cm top layer |
| Sediment bulk density measured ? | Yes/No,kg/dm ³ |
| Sediment porosity measured ? | Yes/No,% |
| Macrophytes info (type, density, e.g. in g/m ²) | |
| pH | |
| Water temperature (°C) | |
| Light intensity (e.g. J/cm ²) | |
| Application number | |
| Application interval (days) | |
| Nominal initial application (mg/L) or loadings (mg/m ²) ^d | |

^a Indicates whether measured concentrations need to be compared to the simulated concentration of dissolved mass in water or to the simulated concentration of dissolved + sorbed to suspended solids in water.

^b Denoted as "thickness of target layer" in the input file *TOXSWA_cha.txt*, corresponds to the depth of sediment for which measured and simulated sediment contents are compared to assess the goodness of fit.

^c Should be at least as thick as 'sediment layer measured' given above; the total sediment depth reflects the thickness and number of horizons defined in *TOXSWA_cha.txt* (default 10 cm).

^d If scaled concentrations are used, loadings should be scaled as well, by dividing the loadings in mg/m² by the same factor used to scale aqueous and sediment concentrations.

Table 6.3 Parameter values used in the simulations for the cosm study with
(compound and references).

| Cosm label | |
|---|--|
| Molar mass (g) | |
| Saturated vapour pressure (mPa) at temperature of | (.. °C) |
| Solubility (mg/L) at temperature of | (.. °C) |
| K_{om} (estimated) (L/kg) ^a | $K_{oc}=....$, so K_{om} (divide K_{oc} by 1.724) =, 1/n=... |
| pK_a | (value or not applicable) |
| Degradation half-life in sediment (d) | 1000 ^b |

^a A scaled coefficient is required when concentrations have been scaled (see section 3.6).

^b Default value, see section 2.3, 2nd paragraph.

Step c

Install the 12 needed files (see Step 2 in Appendix 8) to perform the first optimisation in a subdirectory of your directory CompoundCosm, suggested name: CompoundCosm\opt1a. Parameterise the three input files for the TOXSWA_PEST optimisation, i.e. *cosm.met*, *input_TOXSWA_PEST.txt* and *TOXSWA_cha.txt*, using the data in Tables 6.1, 6.2 and 6.3 plus the data and optimisation parameters of Tables 3.3 and 3.4 for method 'Water-sediment' or Tables 3.7 and 3.8 for method 'Water-sediment + o.m. 0-1 cm measured'). Run the optimisation by first clicking on the *run.bat* file and then clicking on the *RUN_PEST.bat* file.

You will need to repeat this eight times for the first round of nine optimisations (red stars in Figure 3.1 for method 'Water-sediment' or Figure 3.2 for method 'Water-sediment + o.m. 0-1 cm measured'). Therefore, create in total nine subdirectories with suggested names, CompoundCosm\opt1a, CompoundCosm\opt1b, CompoundCosm\opt1c, and CompoundCosm\opt2a, CompoundCosm\opt2b, CompoundCosm\opt2c and CompoundCosm\opt3a CompoundCosm\opt3b, CompoundCosm\opt3c.

After the first optimisation run, copy the content (only the 12 needed files shown in step 2 of Appendix 8) of CompoundCosm\opt1a into CompoundCosm\opt1b and CompoundCosm\opt1c and adjust only the initial values of $C_{t=0}$ and $DegT_{50,water}$ for the two remaining optimisations of this first set of sediment properties (first red star). Run the two remaining optimisations (these 2 runs use the same value for bulk density as the first optimisation run).

For the second and third set of sediment properties of Figure 3.1 or 3.2 copy the content (only the 12 needed files) of CompoundCosm\opt1a into CompoundCosm\opt2a and CompoundCosm\opt3a and adjust the bulk density (both methods) and organic matter content (only method 'Water-sediment'; method 'Water-sediment + o.m. 0-1 cm measured' uses the measured value of organic matter content for the upper cm). Copy the content (only the 12 needed files) of CompoundCosm\opt2a into CompoundCosm\opt2b and CompoundCosm\opt2c and adjust only the initial values of $C_{t=0}$ and $DegT_{50,water}$ for the two remaining optimisations of this second set of sediment properties as suggested in Tables 3.3 and 3.4 or Tables 3.7 and 3.8. Do a similar action with the content of CompoundCosm\opt3a for the third set of sediment properties (third red star of Figure 3.1 or 3.2). Run all six optimisations.

Step d

For each of the nine performed optimisation runs inspect the two output files *time-course_TOXSWA.txt* and *TOXSWA_PEST_output.txt* (see also Step 5 of Appendix 8), go through the flow chart of Figure 6.2 (i.e. Figure 2.3). Evaluate the quality criteria for (1) the goodness of fit, (2) the mass degraded in water, expressed as a percentage of the total mass dissipated from the water layer by degradation, volatilisation or penetration into sediment, $F_{M,deg-wat}$, and (3) the CV, coefficient of variation. The three quality criteria for the goodness of fit are (i) the calculated error percentage of the chi-square test is smaller than 25%, (ii) good visual correspondence of simulated and measured concentrations in water and sediment and (iii) residuals are evenly distributed. Only optimisations that end in the upper yellow box "*DegT_{50,water}* OK" obtain the qualification of being a satisfactory optimisation result for the *DegT_{50,water}*. The results in the central yellow box "*DegT_{50,water}* not OK, use

upper limit" do not immediately qualify as satisfactory optimisation results. These upper limits of the 95% confidence interval of the optimised $DegT_{50,water}$ may be used later in step h below.

Finally, fill in the Table described in Appendix 10, that presents the main input and output of the optimisations runs for estimation of $DegT_{50,water}$. Each run fits into one line of the table. For satisfactory optimisation results make the value found for the $DegT_{50,water}$ bold.

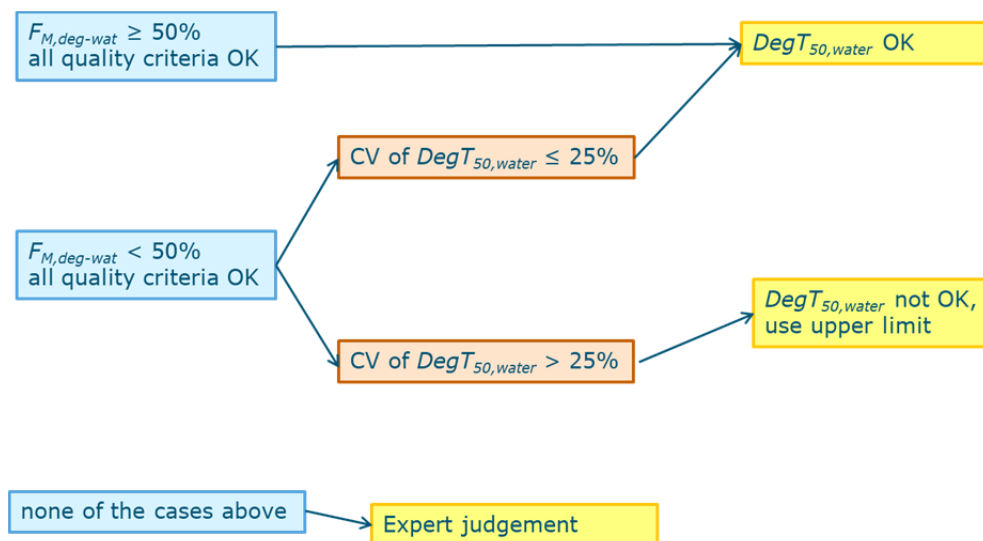


Figure 6.2 Optimisation procedure for water-sediment cosms with or without the organic matter content in the 0-1 cm sediment layer known. For explanation of the mass fraction terms (the F 's) and the coefficient of variation CV, see the text above Figure 2.3 in Chapter 2. The upper limit refers to the upper limit of the 95% confidence interval of the optimised $DegT_{50,water}$.

Step e

If there are three or more satisfactory optimisation results, i.e. runs that result in estimated $DegT_{50,water}$ values that are satisfactory, take the geomean of all satisfactory $DegT_{50,water}$ values (step 9 of Appendix 8). Use this value in the aquatic exposure assessment.

If there are less than three satisfactory optimisation results continue the optimisations for one or two additional sets of sediment properties, as described in step f. (Two additional sets represented by the purple stars of Figure 3.1 for method 'Water-sediment' or one additional set represented by the purple star in Figure 3.2 for method 'Water-sediment + o.m. 0-1 cm measured').

Step f

So, if there are less than three satisfactory optimisation results, repeat step c and d above, but now for one or two remaining combinations of bulk density (both methods) and organic matter content (only method 'Water-sediment'; method 'Water-sediment + o.m. 0-1 cm measured' uses the measured value of organic matter content for the upper cm). Run three or six optimisations for three sets of the initial values of $c_{t=0}$ and $DegT_{50,water}$ as indicated in Tables 3.5 and 3.6 for method 'Water-sediment' or Tables 3.9 and 3.10 for method 'Water-sediment + o.m. 0-1 cm measured'). Do this in three or six sub directories with suggested names CompoundCosm\opt4a into CompoundCosm\opt4b and CompoundCosm\opt4c and CompoundCosm\opt5a into CompoundCosm\opt5b and CompoundCosm\opt5c.

Again for each of the runs, inspect the two output files *time-course_TOXSWA.txt* and *TOXSWA_PEST_output.txt* (see also Step 5 of Appendix 8), go through the flow chart of Figure 6.2 and fill in the Table described in Appendix 10, that presents the main input and output of the optimisations runs for estimation of $DegT_{50,water}$. For satisfactory optimisation results make the value found for the $DegT_{50,water}$ bold.

Step g

Preferably there now are at least three satisfactory optimisation results and the optimisation calculations are finished then. However, if there is only one or two satisfactory optimisation results, we also stop the optimisation calculations and are satisfied with the results. Take the geomean of all satisfactory $DegT_{50,water}$ values (step 9 of Appendix 8) and use this value in the aquatic exposure assessment.

Step h

If there is no satisfactory optimisation result but in a number of cases for which the $F_{Mdeg-wat} < 50\%$ and the CV of the $DegT_{50,water}$ was higher than 25% (i.e. the outcome of Figure 6.2 ended in the central yellow box “ $DegT_{50,water}$ not OK, use upper limit”), then use the values of these upper limits of the 95% confidence interval of the optimised $DegT_{50,water}$ to calculate the geomean of the upper limits and use this value in the aquatic exposure assessment.

Step i

As we relaxed the CV criterion from 10% (Ter Horst and Koelmans, 2016) to 25% for all cases in which the $F_{Mdeg-wat} < 50\%$, evaluate now what is the effect of sorption to sediment or volatilisation (i.e. the two other dissipation processes) on the optimised $DegT_{50,water}$ value or the selected upper limit. To do so, apply the flow chart of Figure 6.3 (i.e. Figure 2.6, for more details, see the text in section 2.5). So, re-run the optimisation runs in which the $F_{Mdeg-wat} < 50\%$ and which results were used earlier to calculate the final geomean $DegT_{50,water}$ for the aquatic risk assessment, but re-run now with the values for K_{om} or P_{sat} suggested in Figure 6.3 and explained into more detail in section 2.5. Note that for each satisfactory optimised $DegT_{50,water}$ value or selected upper limit two additional results will be obtained, namely for each of the two runs (for $\frac{1}{2}$ and 2 times the original P_{sat} or K_{om} value).

Make a new table, listing in the first column all $DegT_{50,water}$ values used to calculate the final geomean obtained in step e, g or h. List in the second column, in the same row as the originally obtained satisfactory optimised $DegT_{50,water}$ value or the selected upper limit, the values obtained after re-running the optimisations according to Figure 6.3. (i.e. the two values in the same box). If no re-running was done, simply repeat the value of the first column in the second column. Now, both columns have not the same number of $DegT_{50,water}$ values. The geomean of all values in the first column is the geomean $DegT_{50,water}$ value proposed for the aquatic risk assessment, obtained earlier in step e, g or h. Compare this geomean to values of the second column, e.g. to the listed, individual values or to a geomean obtained by using the highest, resp. lowest value in each box. Is there a large difference? To judge whether it has been defensible to relax the CV of 10 to 25% we suggest to perform the aquatic risk assessment with e.g. individual or geomean values of the second column and evaluate their effect on the end point of the exposure assessment, e.g. the peak water concentration. (See also the text at the end of section 2.5).

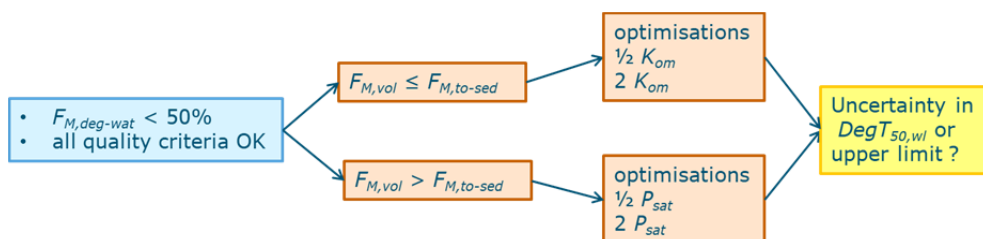


Figure 6.3 Estimation of the uncertainty in the optimised $DegT_{50,water}$ or selected upper limit for cosms in which concentrations in the water layer and the sediment have been measured and which fulfil the two criteria of the most left-hand, blue box.

Step k

If no or less than 3 satisfactory $DegT_{50,water}$ values could be obtained (end of step g) or if less than three $DegT_{50,water}$ could be selected (end of step i) expert judgement need to be sought to see whether it is possible to estimate the $DegT_{50,water}$ in another way. It might be possible to improve the

optimisations, e.g.

by giving the concentration measurements in the water layer more weight than those in the sediment, reflecting the ratio of mass present in the water layer versus the mass in the sediment.

by changing the default value of 1000 d for the $DegT_{50, sediment}$ by a more realistic value, such as the one mentioned in the example on linuron (Appendix 5) with its overall water-sediment $DegT_{50}$ value of 24 d. (In the current software, *TOXSWA_moe.txt* file, it is possible to change the default value of 1000 d of the $DegT_{50, sediment}$ into another value.)

check that the used segmentation of the sediment is sufficiently fine, so using a finer segmentation should not result in other simulated concentration profiles in the sediment. (In the current software, *TOXSWA_moe.txt* file, it is possible to change the default sediment segmentation into another segmentation.)

The use of a more realistic $DegT_{50, sediment}$ value may especially improve the optimisation in cases that the realistic value differs considerably from the default value of 1000 d, as was the case in the linuron example (24 d vs 1000 d).

Note that use of an amended value for $DegT_{50, sediment}$ to improve the fit of water concentrations does not imply that such an amended value may be used in scenario calculations for authorisation purposes, where the default value for $DegT_{50, sediment}$ of 1000 days is typically used.

The cosm studies on linuron, metsulfuron-methyl and prosulfocarb presented in Appendices 5, 6 and 7 provide several examples of optimisations where expert judgement was needed. An extra weight factor was introduced. This weight factor reflects the ratio of the pesticide mass in the water and the mass in the sediment. This ratio is the ratio of the maximum mass in the water and the maximum mass in the sediment during the study and it is approximated by the mass degraded in the water and the mass transported to the sediment (in percentages of the total mass dissipated from the water layer) calculated by TOXSWA for the entire simulation period (minus a possible last incomplete month for which mass balance terms are missing), as indicated in the two last columns of the table in Appendix 10.

Note that the introduction of an extra weight factor led to an improved fit of water concentrations but to a decrease in the quality of the fit of sediment concentrations. Improving the fit of water concentrations was considered to be more important, and an accompanying decrease of the goodness of fit of sediment concentrations was therefore considered acceptable.

7 Discussion, conclusions and recommendations

7.1 Discussion and conclusions

This report shows that it was possible to obtain satisfactory estimated $DegT_{50,water}$ values for four of the five compounds for which cosm studies existed with compound mass present in both the water layer and the sediment: chlorpyrifos, lambda-cyhalothrin, metsulfuron-methyl and prosulfocarb, but not for linuron. However, it was not straightforward to obtain satisfactory optimisation results.

For 2 of the 4 available data sets of chlorpyrifos (1 of Brock et al. (1992), 3 of Giddings et al. (1997)) we obtained relatively easily satisfactory optimisations, but for 2 data sets of Giddings et al. (1997) it was impossible. For lambda-cyhalothrin the visual goodness of fit was borderline. For linuron it proved to be impossible to obtain a satisfactory optimisation, while for metsulfuron-methyl and prosulfocarb satisfactory optimisations were obtained after using a multiplication factor giving 6, resp. 22 times more weight to the differences between measured and simulated concentrations in the water layer than those in the sediment.

As the optimisation procedure repeatedly needed to be adjusted in the course of this research project in order to succeed the optimisation the resulting software may not yet be as user-friendly as possible. Moreover, we recommend to test the developed procedure on a wider range of cases, as well as making it more flexible, e.g. by allowing to change input that is now fixed to default values (see section 7.2).

As expected the half-life for dissipation in water, based upon Single First Order fitting of measured water concentrations, is smaller than the estimated $DegT_{50,water}$ value obtained by inverse modelling by PEST-TOXSWA for chlorpyrifos (section 5.6), resp. 3.7 versus 5.93 d. By distinguishing between volatilisation, transport to and from the sediment and degradation using TOXSWA, the developed inverse modelling procedure results in a more accurate estimation of the half-life for degradation in the water layer than by the straightforward calculation of the half-life for decline in water, that is commonly used in aquatic risk assessments, but does not meet the criteria for application of a degradation endpoint from this kind of studies into environmental modelling.

On the basis of Ter Horst and Koelmans (2016) the uncertainty in the estimated $DegT_{50,water}$ is expected to be small (i.e. coefficient of variation CV smaller than 10%) if $F_{M,deg-wat}$ is more than 50%. If all quality criteria for the goodness of fit are still fulfilled, but $F_{Mdeg-wat}$ is smaller than 50% (and the CV expected to be above 25%) we have proposed to estimate the uncertainty in the estimated $DegT_{50,water}$ by considering the influence of volatilisation and transport to and from the sediment on the estimated $DegT_{50,water}$. In addition PEST mentions the 95% confidence interval of the optimised $DegT_{50,water}$ value.

In addition we highlighted the fact that it is important to establish the impact of the $DegT_{50,water}$ value on the endpoint used in the aquatic risk assessment, e.g. the peak water concentration. E.g. in scenarios used for the authorisation of pesticides with fast moving water the $DegT_{50,water}$ value may have very limited impact on the peak water concentration, in contrary to scenarios with slowly moving water and repeated applications. For details see section 2.5 and the recommendations below.

The estimation procedure resulted in sufficiently accurate $DegT_{50,water}$ values for four of the five compounds. So, the procedure seems suitable for use in the authorisation procedure of pesticides.

For the four compounds with satisfactory optimisations the estimated $DegT_{50,water}$ by the TOXSWA-PEST inverse modelling procedure resulted in shorter degradation half-lives than the half-lives obtained in laboratory studies for hydrolysis or photolysis or the overall dissipation half-life in laboratory water-sediment systems. This means that the $DegT_{50,water}$ values for the outdoor cosms

have added value in the tiered aquatic exposure assessment. This finding is in accordance with the tiered approach suggested by Boesten et al. (2014) for the determination of the $DegT_{50,water}$.

Some limitations of the presented estimation procedure are:

- As the degradation kinetics in TOXSWA are first-order, the estimation procedure with PEST_TOXSWA can only be executed according to single first-order kinetics and not e.g. bi-phasic kinetics;
- The procedure has been developed for cosms with spray drift mimicked exposure, i.e. pesticide mass being directly applied to the water layer. So, cosms with pesticide mass applied to the sediment e.g. by applying slurries containing pesticides, have not been considered;
- The procedure can only be usefully applied to cosms representing relevant and realistic outdoor conditions for degradation in aquatic risk assessment, so, not to e.g. cosms with water layer of a few cm.

7.2 Recommendations

We recommend to test the optimisation procedure described in Chapter 6 for a number of new cosm studies. The reason to do this is that, based upon the experiences with the described cosm studies in this report we changed the criteria for acceptance of the optimised $DegT_{50,water}$ value, i.e. an error percentage of the χ^2 test smaller than 25% is acceptable (while FOCUS Degradation Kinetics (2006) suggested 15%) and a coefficient of variation, CV, of smaller than 25% is acceptable, as shown in Figure 6.2. Moreover, within the framework of this project, we were unable to evaluate the changed optimisation procedure with respect to the uncertainty in the estimated $DegT_{50,water}$ values (Figure 2.5 and 2.6).

We recommend to test the flow chart (Figure 2.3) for the optimisation procedure used in this report for water-sediment cosms only also for the so-called water-only cosms.

We recommend to test all routes of the optimisation procedure for water-only cosms of Figure 6.1, because this has not yet been done in this report.

We recommend to test the suggested procedure to select a maximum $DegT_{50,water}$ value (Figure 6.2, especially the route " $F_{M,deg-wat} < 50\%$ + all quality criteria OK") for water-sediment cosms with or without the organic matter content in the 0-1 cm sediment layer known, because this has not yet been done in this report.

As described in step i of Chapter 6, we recommend to analyse the effect of the uncertainty in the estimated $DegT_{50,water}$ (Figure 6.3) on the endpoint of the exposure assessment, e.g. the peak water concentration. We expect the effect to be higher in watercourses with low flow, so with relatively high hydraulic residence times, than in watercourses with rapid flow. Analogously, we expect the peak concentration in the watercourse to depend more on the degradation rate if the application interval is small, or the application number high, than when application intervals are large and the application number is low.

We suggest to redo the optimisations for the linuron study of Bromilow et al. (2006) now using a $DegT_{50,sediment}$ value of 24.1 d instead of the default 1000 d in the TOXSWA_moe.txt file (see Chapter 5.3). Possibly this would give an improved correspondence between measured and simulated concentrations in water and sediment and thus optimisation runs that would fulfil all quality criteria for the estimation of the $DegT_{50,water}$.

In addition, we recommend to analyse more examples in which the default value of 1000 d for the $DegT_{50,sediment}$ has been replaced by a more realistic value. By introducing a more realistic value for the $DegT_{50,sediment}$ we expect that for certain compounds the optimisation procedure will possibly result in satisfactory estimations of $DegT_{50,water}$ in cases where this would otherwise be not possible.

For compounds with a high sorption capacity (K_{oc} approximately above 500 to 1000 L/kg) sorption to macrophytes, if present, may be important. We therefore recommend to enable the simulation of sorption to macrophytes in the optimisation software in order to be available for expert users.

Finally we recommend to develop a procedure for the authorizing bodies, such as Ctgb how to use the estimated $DegT_{50,water}$ values in the tiered aquatic exposure assessment, considering e.g. required number of estimates or uncertainty.

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

Below the spreadsheet of Figure A1.1 indicates how the minimum error-% is calculated for a simulated cosm study in which only measurements in the water layer were done. The calculated minimum error-% equals 6.9%, which is lower than the tabulated χ^2 -value at the 5% significance level for the 3 degrees of freedom and thus, the χ^2 -test is passed.

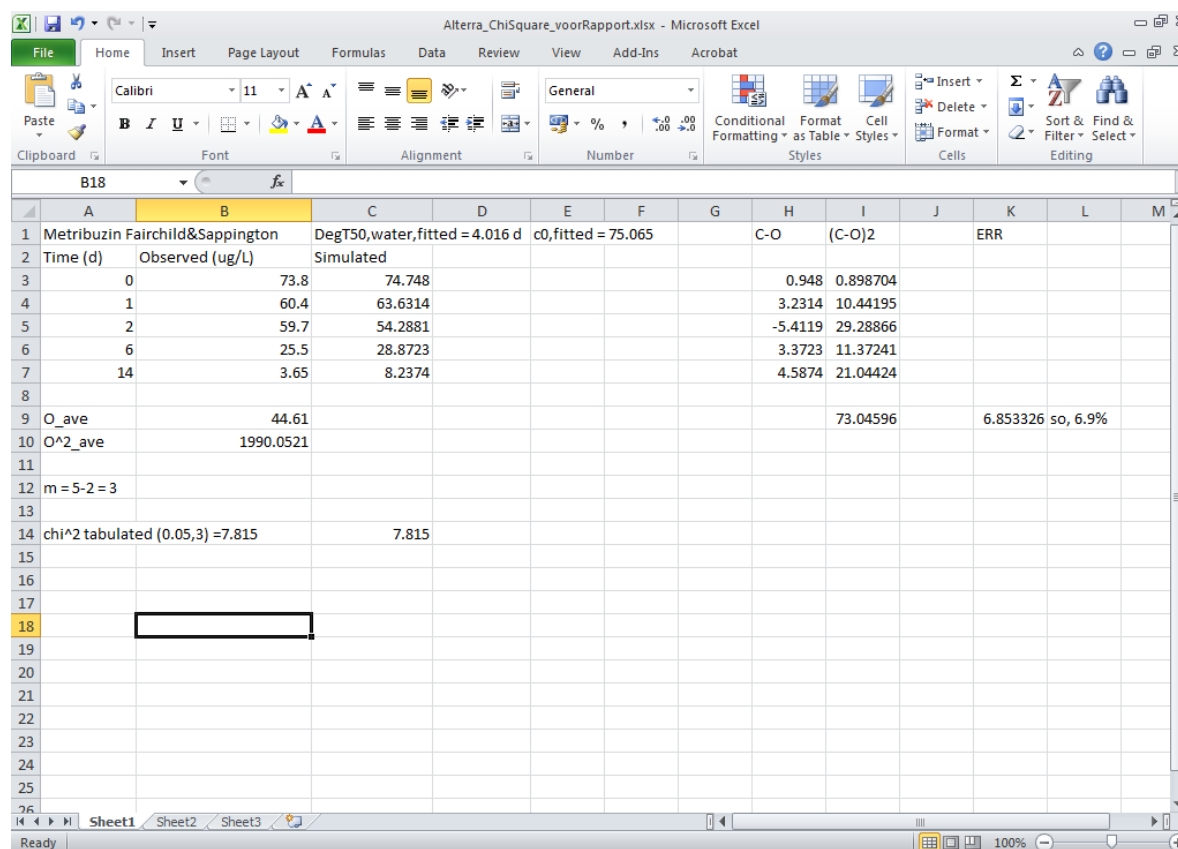


Figure A1.1 Spreadsheet demonstrating the calculation of the χ^2 -test minimum error-% for a cosm with only measurements in the water layer.

For simulated cosm studies with measurements in both water and sediment calculation of the goodness of the fit, i.e. the minimum error-% at which the χ^2 -test is passed, has been done within a post-processing program in Fortran90. This program is called Postprocess_TOXSWA_PEST.f90 and generates a TOXSWA_PEST_output.txt file that contains the following information on the goodness of the fit:

```
(1) 95th percentile of chi2 for 14 degrees of freedom based on 16 data points = 23.685
(2) chi2 error (%) : 11.7
(3) Sum of squared weighted residuals : 23.784925

(4) Sum of squared weighted residuals (ie phi) = 23.78
(5) Contribution to phi from observation group "group_1" = 22.78
(6) Contribution to phi from observation group "group_2" = 1.002
```

Here we explain how this information is generated.

Item (1) is simply the 95th percentile of χ^2 for the degrees of freedom as indicated (so this value can also be obtained from tabulated percentiles of the χ^2 distribution; we use the symbol $\chi^2_{\text{tabulated}}$ for this quantity).

Item (2) is the χ^2 -error (acronym *Err*) as defined by FOCUS (2006) which is calculated as follows:

$$Err = 100 \sqrt{\frac{\varphi}{O_{av}^2 \chi_{tabulated}^2}} \quad (X-1)$$

where O_{av} is the average of the observations and the weighted sum of the squared residuals, φ , is given by:

$$\varphi \equiv \sum_{j=1}^N S_{dd,j} w_j^2 \quad (X-2)$$

where N is the number of groups and w_j is the weight for group j . Note that the group $j = 1, N$ refer to the measurement groups, which mount to 2 for cosm studies with measurements in both water (group 1) and sediment (group 2). $S_{dd,j}$ is given by

$$S_{dd,j} = \sum_{i=1}^{G_j} (C_{m,i} - C_{TOXSWA,i})^2 \quad (X-3)$$

where i is the index for an observation within a group j containing G_j observations, $C_{m,i}$ is the measured value of the observation, $C_{TOXSWA,i}$ is the calculated value for this observation.

The average of the observations, O_{av} , is calculated as:

$$O_{av} = \left(\frac{S_{o,w}}{\sum_{j=1}^N G_j} \right) \quad (X-4)$$

where $S_{o,w}$ is defined as

$$S_{o,w} = \sum_{j=1}^N S_{o,j} w_j \quad (X-5)$$

where $S_{o,j}$ is the sum of the observations of group j :

$$S_{o,j} = \sum_{i=1}^{G_j} C_{m,i} \quad (X-6)$$

The sum of the squared residuals of item (3) is equal to φ .

Items (4), (5) and (6) are not calculated by the Fortran program: this are text strings that are copied from the REC file that is produced by PEST.

Item (4) equals φ and items (5) and (6) are the contributions of each of the N groups to φ as follows from the summation in Eqn X-2.

For those interested in reading the computer program, here the names of the variables in this program are given for convenience:

$$\begin{aligned} \text{sum_dif_dif}(\text{gp}) &= S_{dd,j} \\ \text{sum_obs}(\text{gp}) &= S_{o,j} \\ \text{sum_dif_wei} &= \varphi \\ \text{sum_obs_wei} &= S_{o,w} \\ \text{ave_obs_2} &= O_{av}^2 \end{aligned}$$

Appendix 2 Protocol for selecting pesticide properties from the Pesticides Properties DataBase

This Appendix has also been published by Teklu et al. (2015).

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

| Property in models | Choices in PPDB | |
|--------------------|-------------------------|--|
| 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 Pesticides Properties DataBase and justification of this choice

| Property in models | Chosen property from PPDB | Justification |
|---|---------------------------|---|
| DT50soil | DT50 lab at 20°C | 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 Pesticides Properties 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><i>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</i></p> | | |
| Koc | KOC | KOC is very likely the most reliable parameter. Below an explanation is given why we consider Kfoc data from the Pesticides Properties 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 ($\text{L}^N \text{kg}^{-1} \text{mg}^{1-N}$) 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 $\mu\text{g kg}^{-1}$ and C expressed in $\mu\text{g L}^{-1}$. Let us consider the following example to illustrate this.

| Property in models | Chosen property from PPDB | Justification |
|--------------------|---------------------------|---------------|
|--------------------|---------------------------|---------------|

| 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 2, a $K_{F,oc}$ value of 100 would have been obtained. Let us now consider a researcher that expresses the same data in µg instead of mg.

| C (µg L ⁻¹) | X (µg 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 Pesticides Properties DataBase. (pers.comm. J.J.T.I. Boesten, WUR)

| | | |
|-----------------|---|---|
| 1/n or N | Freundlich exponent between 0.6 and 1.0 | <p>If the average of $1/n > 1$ use a value of 1.0 (see page 28/29 of Boesten <i>et al.</i>, 2011)</p> <p>Boesten, J.J.T.I., Linden, A.M.A. van der, Beltman, W.H.J., Pol, J.W. 2011. <i>Leaching of plant protection products and their transformation products: proposals for improving the assessment of leaching to groundwater in the Netherlands</i>. Wageningen: Alterra, 2011 (Alterra-rapport 2264)</p> <p>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 Pesticides Properties DataBase itself.</p> |
|-----------------|---|---|

| | | |
|------------------|--|---|
| DT50water | Aqueous hydrolysis pH 7 Aqueous hydrolysis pH 9 | <p>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).</p> $k(T) = k(T_{ref}) \exp \left[\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (3)$ <p>where:</p> <p>T = Temperature (K)</p> <p>T_{ref} = Reference temperature (K)</p> <p>k = Transformation rate (d⁻¹)</p> <p>E = Molar Arrhenius activation energy (J mol⁻¹)</p> <p>R = Universal gas constant (≈ 8.3144 J mol⁻¹ K⁻¹)</p> <p>Deneer, J.W., W.H.J. Beltman, P.I. Adriaanse. 2010. <i>Transformation reactions in TOXSWA; transformation reactions of plant protection products in surface water</i>. Wageningen, Alterra. Alterra-report 2074. 94 pp.</p> |
|------------------|--|---|

Appendix 3 Inverse modelling with TOXSWA-PEST for two cosm studies with chlorpyrifos

Two studies with chlorpyrifos that are suitable for the estimation of the $DegT_{50,water}$ by inverse modelling by TOXSWA-PEST were found in literature, the study from Brock et al. (1992) and the study of Giddings et al. (1997). The main characteristics of the studies have been summarized in Table A3.1.

Table A3.1 Data on cosm studies with chlorpyrifos.

| Label in data file | CPF_Cosm1 | CPF_Cosm2 |
|-----------------------------|---|--|
| Reference | Brock et al. (1992) | Giddings et al. (1997) |
| Compound | Dursban 4E formulation, containing 480 g/L chlorpyrifos | Lorsban 4E formulation, 41.32% chlorpyrifos |
| Type of system | Indoor glass aquarium | Outdoor, fiberglass cylinders |
| Dimensions system | LxWxH: 1.1 x 1.1 x 0.7 m | Depth: 1.5 m, diameter: 3.2 m |
| Side slope (hor/vert) | 0 | 0 |
| Depth water layer (m) | 0.5 | 1.4 |
| Depth sediment (cm) | 10 | 10 |
| Sediment om% | Sandy loam, 2.8% OM | 1.8 – 3.2% ('organic content', not clear whether organic matter or organic carbon), 33-50% of bottom covered with sediment |
| Sediment bulk density | Not specified | Not specified |
| Sediment porosity | Not specified | Not specified |
| Macrophytes info | 2 types of systems, either <i>Elodea nuttallii</i> or no macrophytes present; only data from the latter are used since the presence of macrophytes hampered mixing in the water phase | During the study submerged macrophytes developed |
| pH | Not specified | Not specified |
| Temperature | Temp. controlled room, 19 (18 – 20) °C | Not specified, estimated: July: 27°C, August 25°C, September 20.5°C, October 13°C, see text below |
| Light intensity | Indoor, 14 h per day at 140 uE/m s. | Lawrence, Kansas, USA. Application 8 July 1991 |
| Application number | 1 | 1 |
| Application interval | - | - |
| Nominal initial application | 0.035 mg/L | 5 levels, 0.00003 – 0.003 mg/L |

In Table A3.2 below we summarized the input values on the physico-chemical properties of chlorpyrifos, as extracted from the Pesticides Properties Database (PPDB) from the university of Hertfordshire.

Table A3.2 Parameter values used in the simulations with chlorpyrifos.

| Property | Value |
|---------------------------------|---------------------------------|
| Molar mass (g) | 350.89 |
| Saturated vapour pressure (mPa) | 1.43 (25°C) |
| Solubility (mg/L) | 1.05 (20°C) |
| Koc (estimated) (L/kg) | Koc=8151 --> Kom=8151/1.72=4739 |

Brock et al.

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 8 times after application. The results of this experiment have also been described and analysed by van der Kolk and Crum (1993).

Table A3.3 presents the measured concentrations in water and sediment as a function of time in the cosm study of Brock et al. (1992). Nominal initial aqueous concentrations were 35 µg/L. The values have been read from Figure 4 and Tables 1 – 3 in the publication; water was not filtered before extraction.

Table A3.3 Measured concentrations in water at 25 cm depth (mg/L and scaled) and sediment (g/kg and scaled) as a function of time (d) for the cosm study with chlorpyrifos by Brock et al. (1992). Data for indoor 'open' cosms containing no macrophytes, given as averages of two different cosms.

| Number | Time (days) | Concentration in water (mg/L) | Scaled concentration in water | Concentration in sediment (g/kg) | Scaled concentration in sediment |
|--------|-----------------|-------------------------------|-------------------------------|----------------------------------|----------------------------------|
| 1 | 0 | 0.035 [#] | - | - | - |
| 2 | 1 ^{\$} | 0.028 ^{&} | 1.0000 | - | - |
| 3 | 2 | 0.021 ^{&} | 0.7500 | - | - |
| 4 | 4 | 0.013 ^{&} | 0.4643 | - | - |
| 5 | 7 | 0.009 ^{&} | 0.3214 | - | - |
| 6 | 8 | 0.0082 | 0.2929 | 0.0569 E-3 | 2.0321 E-3 |
| 7 | 16 | 0.0029 | 0.1036 | 0.0480 E-3 | 1.7143 E-3 |
| 8 | 30 | 0.0011 | 0.0393 | 0.0413 E-3 | 1.4750 E-3 |
| 9 | 57 | 0.0002 | 0.0071 | 0.0269 E-3 | 0.9607 E-3 |
| 10 | 118 | < 0.00005 | - | 0.0146 E-3 | 0.5214 E-3 |

[#] Initial nominal concentration, not measured but calculated from dosed amount.

^{\$} Concentrations prior to 1 day after application are reported but not used because of apparent incomplete mixing.

[&] Relative large uncertainty in concentrations, because of log-scale used in Figure 4 from which they were read.

On the basis of measured sediment concentrations (in mg/cm³) for 0 – 1, 1 – 2.5 and 2.5 – 10 cm depth given in the paper, the maximum amount of chlorpyrifos in the sediment was calculated to be 24.9% (on day 8 after application) of the mass initially added to the system.

The inverse modelling was performed using scaled concentrations. Since the organic matter content of the sediment (upper 10 cm) was given as 2.8%, the OM% was allowed to vary from 2.5 – 50% (Figure 2.2).

Aqueous concentration was allowed to vary from 0.1 – 5 (scaled) with an initial estimate of 1.0, and *DegT*_{50,water} was allowed to vary from 0.1 – 100 days with an initial estimate of 5, 20 or 1 days, as (approximately) suggested in Table 3.4.

Runs were performed using values for initial organic matter content of the sediment of 19% (bulk density 0.2 kg/L), 9% (bulk density 0.8 kg/L) and 3% (bulk density 1.2 kg/L) (Table 3.3).

Results for the runs are summarised in Table A3.4. Satisfactory runs (χ^2 – error below 15%¹⁰ and degraded mass in the water phase accounting for at least 50% of total mass dissipated from water layer) were obtained with a bulk density of 0.8 kg/L combined with an initial estimate of organic matter content of 9% (runs 4, 5 and 6 in Table A3.4). Graphical results for an inverse modelling run resulting in satisfactory results are given in Figure A5.1, using the data of the fourth run in Table A5.4. The values for $DegT_{50,water}$ estimated in the runs satisfying the quality criteria were 5.92, 5.94 and 5.93 days resp. Taking the geometric average of these 3 values results in an estimated value for $DegT_{50,water}$ of 5.93 days for the cosm experiment by Brock et al. (1992).

¹⁰ N.B. Note that the criterion of χ^2 – error below 15% was set to the less strict value of 25% later in the development of this guidance report. This implies that 8 of the 9 runs now fulfil this new χ^2 – error criterion of 25%. However, the 5 additional runs do not fulfil the criterion of satisfactory visual correspondence between measured and simulated concentrations in water and sediment and thus the $DegT_{50,water}$ geomean value presented above is still correct.

Table A3.4 Results of the initial 9 runs of PEST_TOXSWA inverse modelling ('Method B8' of Figure 2.2) for chlorpyrifos data from Brock et al. (1992) using given initial values for parameters bulk density, organic matter, initial water concentration $C_{t=0}$ and initial $DegT_{50,water}$.

| Input used in optimisation runs | | | | | Results of optimisation runs | | | | | | | | | |
|---------------------------------|--|---|---|------------------------------------|--------------------------------------|---------------------------------------|-------------------------------------|--------------------------------|---------------------------------------|-------------------------------------|--|---|---|--|
| Bulk density (g/L) | Initial organic matter fraction ^A (-) | Initial water concentration ^B (mg/L) | Initial $DegT_{50,water}$ ^C (days) | Estimated $DegT_{50,water}$ (days) | Estimated water concentration (mg/L) | Estimated organic matter fraction (-) | No of runs needed in estimation (-) | Visual goodness of fit (+/0/-) | Sum of squared weighted residuals (-) | Chi-square Error ⁰ % (%) | Percentage of substance volatilised (%) ^D | Percentage of substance penetrated into sediment (%) ^D | Percentage of substance transformed in water (%) ^D | Mass degraded in water, as a percentage of total mass dissipated from water (%) ^E |
| 200 | 0.19 | 1 | 5 | 1.77, -0.16/3.69 | 1.43, 0.45/2.41 | 0.025, -0.72/5.72 | 93 | - / - | 0.0429 | 24.9 | 7.66 | 5.50 | 91.53 | 87.4% ¹¹ |
| 200 | 0.19 | 1 | 20 | 19.0, -2.7/40.6 | 0.33, -0.04/0.71 | 0.025, -0.01/6.04 | 31 | - / - | 0.115 | 40.7 | 43.87 | 12.67 | 48.76 | 46.3% |
| 200 | 0.19 | 1 | 1 | 1.76, -0.13/3.64 | 1.43, 0.44/2.43 | 0.025, -0.01/5.69 | 48 | - / - | 0.0429 | 24.9 | 7.64 | 5.50 | 91.54 | 87.5% |
| 800 | 0.09 | 1 | 5 | 5.92 , 4.32/7.61 | 1.10, 0.98/1.23 | 0.050, 0.033/6.67 | 40 | + / + | 0.00396 | 7.6 | 20.73 | 15.66 | 73.91 | 67.0% |
| 800 | 0.09 | 1 | 20 | 5.94 , 4.22/7.66 | 1.10, 0.98/1.23 | 0.050, 0.033/6.64 | 53 | + / + | 0.00396 | 7.6 | 20.79 | 15.66 | 73.86 | 67.0% |
| 800 | 0.09 | 1 | 1 | 5.93 , 4.22/7.64 | 1.10, 0.98/1.23 | 0.05, 0.033/6.65 | 97 | + / + | 0.00396 | 7.6 | 20.78 | 15.66 | 73.89 | 67.0% |
| 1200 | 0.03 | 1 | 5 | 6.85, 0.96/12.73 | 1.21, 0.87/1.55 | 0.102, -0.05/0.25 | 97 | 0 / - | 0.0265 | 19.6 | 22.49 | 16.66 | 69.60 | 64.0% |
| 1200 | 0.03 | 1 | 20 | 6.98, 0.81/13.14 | 1.21, 0.87/1.54 | 0.101, -0.04/0.24 | 49 | 0 / - | 0.0265 | 19.6 | 22.80 | 16.80 | 69.21 | 63.6% |
| 1200 | 0.03 | 1 | 1 | 6.67, 1.73/11.60 | 1.21, 0.85/1.57 | 0.101, -0.03/0.25 | 104 | - / - | 0.0266 | 19.6 | 22.05 | 16.57 | 70.08 | 64.5% |

^A Range of organic matter content allowed in optimisation runs: 0.025 – 0.50.

^B Range of water concentration allowed in optimisation runs: 0.1 – 5.0.

^C Range of $DegT_{50,water}$ allowed during optimisation runs: 0.1 – 100.

^D Percentages here expressed as percentage of total mass in cosm (i.e. former criterion, now replaced by footnote E) instead as percentages of total mass dissipated from water layer. However, these percentages are not relevant for this cosm study as $F_{M,deg-wat} > 50\%$ (i.e. the last column), see also Figure 2.3.

^E (Mass degraded in water)/(Mass degraded in water + Mass volatilised + Mass penetrated into sediment) * 100%.

¹¹ In this report the numbers in this column have been calculated with the aid of the numbers of the three foregoing columns, e.g. the value of 87.4% has been obtained by dividing 91.53% by (7.66+5.50+91.53=104.69%). Note that the sum of the three foregoing columns exceeds 100% (because mass penetrated into sediment can diffuse back into the water and next, degrade in the water), thus resulting in a value for the mass degraded in water as a % of mass dissipated from water (e.g. 87.4%) being smaller than the mass transformed in water as percentage of the total mass (e.g. 91.53%).

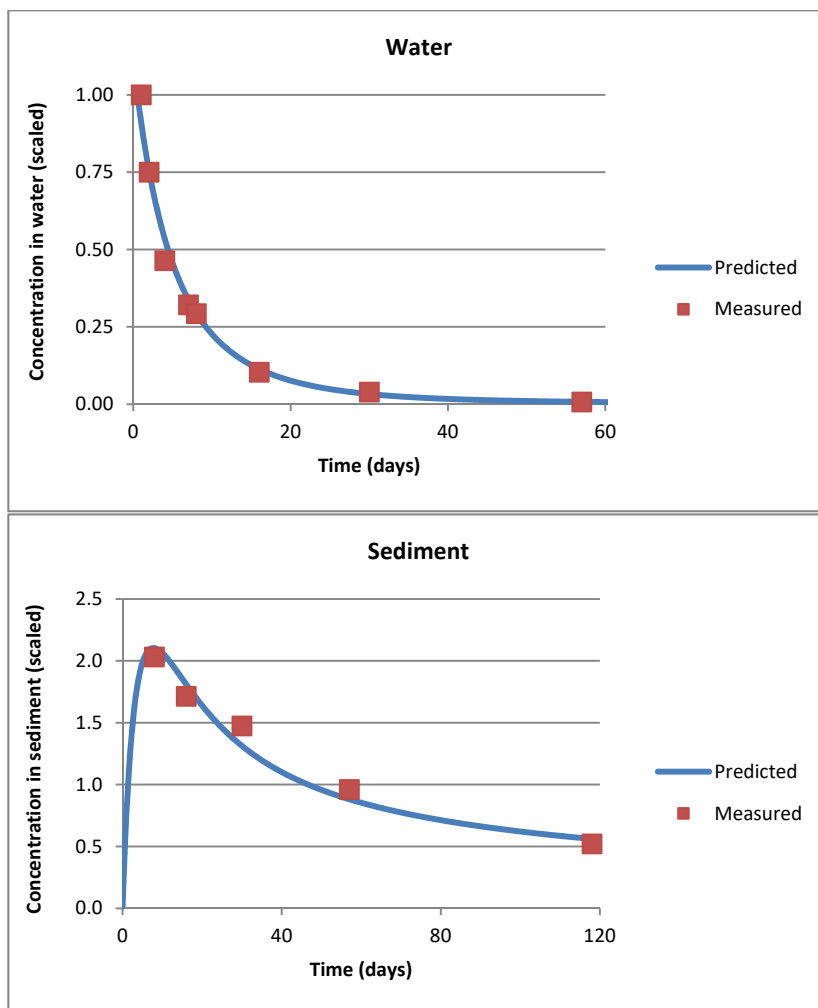


Figure A3.1 Simulated and measured concentrations of chlorpyrifos in water and sediment; data simulated using $DegT_{50,water} = 5.92$ days, an organic matter content of sediment of 5.0% and an initial scaled water concentration of 1.10 (initial values used in the estimation are given as the fourth entry in Table A3.4).

Giddings et al.

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, presumably indicating 2.0% organic matter). In the 3 highest application levels 7 (0.3 µg/L), 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. Giddings et al. (1997) did not report data on the temperature during the exposure period (July 1991 in Kansas, U.S.A.). Average monthly temperatures were estimated on the basis of a graph of historical temperature data collected from 1997 – 2012 at the municipal airport of Lawrence, Kansas (<https://weatherspark.com/averages/30796/Lawrence-Kansas-United-States>). Average monthly temperatures for July (application), August, September and October are given in Table A3.1, temperatures during other months were assumed the same as given for October (but sampling occurred between the beginning of July and the beginning of October, and these temperatures are therefore not relevant for the calculations).

Table A3.5 presents the measured concentrations in water and sediment as a function of time in the cosm study of Giddings et al. (1997). Nominal initial aqueous concentrations were 0.03 – 3 µg/L. The values have been read from Table 1 (water) and Table 5 (sediment) resp. Water was not filtered before extraction. In view of the sediment contents below detection limit observed at level 1 and 2, only the data for level 3, 4 and 5 have been analysed using inverse modelling.

Table A3.5 Measured concentrations in water (mg/L and scaled) and sediment (g/kg and scaled) as a function of time (d) for the cosm study with chlorpyrifos by Giddings et al. (1997). Averages of three replicate cosms.

| Number | Time (days) | Concentration in water (mg/L) | Scaled concentration in water | Concentration in sediment (g/kg) | Scaled concentration in sediment |
|----------------------------|-------------|-------------------------------|-------------------------------|----------------------------------|----------------------------------|
| Level 1 (0.03 µg/L) | | | | | |
| 1 | 0.1 | 0.00003 | | | |
| 2 | 1 | 0.000018 | | 0.00011 E-3 | |
| 3 | 2 | 0.000021 | | | |
| 4 | 3 | 0.000019 | | | |
| 5 | 5 | 0.000007 | | | |
| 6 | 7 | | | | |
| 7 | 10 | | | Below det.limit | |
| 8 | 14 | | | | |
| 9 | 21 | | | 0.00042 E-3 | |
| 10 | 30 | | | | |
| 11 | 42 | | | 0.000275 E-3 | |
| 12 | 84 | | | 0.00095 E-3 | |
| Level 2 (0.1 µg/L) | | | | | |
| 1 | 0.1 | 0.000088 | | | |
| 2 | 1 | 0.000053 | | 0.0001 E-3 | |
| 3 | 2 | 0.000050 | | | |
| 4 | 3 | 0.000040 | | | |
| 5 | 5 | 0.000016 | | | |
| 6 | 7 | 0.000023 | | | |
| 7 | 10 | | | Below det.limit | |
| 8 | 14 | | | | |
| 9 | 21 | | | 0.00083 E-3 | |
| 10 | 30 | | | | |
| 11 | 42 | | | 0.00192 E-3 | |
| 12 | 84 | | | 0.00194 E-3 | |
| Level 3 (0.3 µg/L) | | | | | |
| 1 | 0.1 | 0.000246 | 1.0000 | | |
| 2 | 1 | 0.000188 | 0.7642 | 0.00093 E-3 | 3.7805 E-3 |
| 3 | 2 | 0.000148 | 0.6016 | | |
| 4 | 3 | 0.000100 | 0.4065 | | |
| 5 | 5 | 0.000083 | 0.3374 | | |
| 6 | 7 | 0.000038 | 0.1545 | | |
| 7 | 10 | | | 0.00040 E-3 | 1.6260 E-3 |
| 8 | 14 | 0.000019 | 0.0772 | | |
| 9 | 21 | | | 0.00105 E-3 | 4.2683 E-3 |
| 10 | 30 | | | | |
| 11 | 42 | | | 0.00089 E-3 | 3.6179 E-3 |
| 12 | 84 | | | 0.00288 E-3 | 11.7073 E-3 |
| Level 4 (1.0 µg/L) | | | | | |
| 1 | 0.1 | 0.000830 | 1.0000 | | |
| 2 | 1 | 0.000777 | 0.9277 | 0.00171 E-3 | 2.0602 E-3 |
| 3 | 2 | 0.000510 | 0.6145 | | |
| 4 | 3 | 0.000310 | 0.3735 | | |
| 5 | 5 | 0.000260 | 0.3133 | | |
| 6 | 7 | 0.000197 | 0.2374 | | |
| 7 | 10 | | | 0.00158 E-3 | 1.9036 E-3 |
| 8 | 14 | 0.000057 | 0.0687 | | |
| 9 | 21 | | | 0.00869 E-3 | 10.4698 E-3 |
| 10 | 30 | 0.000020 | 0.0241 | | |
| 11 | 42 | | | 0.00048 E-3 | 0.5783 E-3 |
| 12 | 84 | | | 0.00478 E-3 | 5.7590 E-3 |

| Number | Time (days) | Concentration in water (mg/L) | Scaled concentration in water | Concentration in sediment (g/kg) | Scaled concentration in sediment |
|---------------------------|-------------|-------------------------------|-------------------------------|----------------------------------|----------------------------------|
| Level 5 (3.0 µg/L) | | | | | |
| 1 | 0.1 | 0.002713 | 1.0000 | | |
| 2 | 1 | 0.002293 | 0.8452 | 0.00273 E-3 | 1.0063 E-3 |
| 3 | 2 | 0.001627 | 0.5997 | | |
| 4 | 3 | 0.000890 | 0.3281 | | |
| 5 | 5 | 0.000950 | 0.3502 | | |
| 6 | 7 | 0.000807 | 0.2975 | | |
| 7 | 10 | | | 0.00917 E-3 | 3.3800 E-3 |
| 8 | 14 | 0.000193 | 0.0711 | | |
| 9 | 21 | | | 0.00390 E-3 | 1.4375 E-3 |
| 10 | 30 | 0.000043 | 0.0159 | | |
| 11 | 42 | 0.000020 | 0.000737 | 0.00360 E-3 | 1.3269 E-3 |
| 12 | 84 | | | 0.00119 E-3 | 0.4386 E-3 |

On the basis of measured sediment concentrations given in the paper for the level 5 system, the maximum amount of chlorpyrifos in the sediment was calculated to be 2.2% (on day 10 after application) of the mass initially added to the system. The calculation assumed a bulk density of 0.8 kg/L for the sediment, and a 50% coverage of the bottom of the fiberglass enclosure with sediment containing trays. The relatively low mass transfer into sediment may in part be the result of the use of relatively deep (water depth 1.4 m) enclosures.

The inverse modelling was performed using scaled concentrations. Since the organic matter content of the sediment (upper 10 cm) was given as 2.0%, the OM% was allowed to vary from 2.5 – 50% (Case A8 of Figure 2.2). Application was on July 8, and the simulation was therefore allowed to run from July 8 to October 15.

Aqueous concentration was allowed to vary from 0.1 – 5 (scaled) with an initial estimate of 1.0, and $DegT_{50,water}$ was allowed to vary from 0.1 – 100 days with an initial estimate of 2.5, 10 or 0.5 days (Table 3.4).

Runs were performed using values for initial organic matter content of the sediment of 19% (bulk density 0.2 kg/L), 9% (bulk density 0.8 kg/L) and 3% (bulk density 1.2 kg/L), as indicated in Figure 3.1 by the red stars.

Results for all runs for the 3 data sets are summarised in Table A3.6.

The initial 9 runs for the 'level 3' cosms did not produce any satisfactory runs, and for that reason additional runs were performed as indicated in Figure 3.1 (purple stars). These extra runs used bulk density of 0.2 kg/L in combination with an initial organic matter content of 3%, or a bulk density of 1.2 kg/L in combination with an initial organic matter content of 19% (Figure A3.2 left). However, even after these 6 extra runs no results with χ^2 -error below 25% were obtained. Similarly, the initial 9 runs and additional 6 runs for the 'level 4' cosms did not yield any results with a χ^2 -error below 25% (Figure A3.2 right).

The failure to fit these 2 data sets is most likely due to the relatively large noise in measured sediment concentrations. In 'level 3' data, the sediment concentration reported for day 84 is by far the largest and outweighs all other sediment concentrations. Similarly, for the 'level 4' data set sediment levels reported for 21 and 84 days are higher than levels reported for other days (Figure A3.2 left and right, respectively). This deviation from expected behaviour possibly resulted in an unsatisfactory fit of the sediment concentrations and preventing the χ^2 -error to fall below 25%.

For the 9 runs performed for the 'level 5' cosms three runs (the first three) resulted in an χ^2 -error that fulfilled the 25%-criterion. The graph of the fit (Figure A3.2a, A3.2b) illustrates that the data are fitted rather well by the estimated values for $DegT_{50,water}$, organic matter content and initial concentration. So, these 3 'level 5' data runs yielding χ^2 – error of 25% are reliable. These runs resulted in estimates

of $DegT_{50,water}$ of 9.70, 9.71 and 9.72 days resp., yielding a geometric mean $DegT_{50,water}$ for chlorpyrifos of 9.71 days.

Figure A3.3a depicts a typical example of the results of an inverse modelling run, using the data of the first run for 'level 5' cosms in Table A3.6. The inverse modelling resulted in a fit with a relatively high (but still acceptable) χ^2 – error of 25.2%, and both the aqueous concentrations and the sediment concentrations seem to be fitted relatively well. The results are considered to generate useful results.

Table A3.6 Results of the initial 9 runs plus additional 6 runs of PEST_TOXSWA inverse modelling ('Method B8') for chlorpyrifos data from Giddings et al. (1997) using given initial values for parameters bulk density, organic matter, initial water concentration $C_{t=0}$ and initial $DegT_{50,water}$.

| Input used in optimisation runs | | | | | Results of optimisation runs | | | | | | | | | |
|---------------------------------|--|---|------------------------------------|------------------------------------|---|---------------------------------------|-------------------------------------|--------------------------------|---------------------------------------|-----------------------------------|--|---|---|--|
| Bulk density (g/L) | Initial organic matter fraction ^a (-) | Initial water concentration ^b (mg/L) | Initial $DegT_{50,water}^c$ (days) | Estimated $DegT_{50,water}$ (days) | Estimated init water concentration (mg/L) | Estimated organic matter fraction (-) | No of runs needed in estimation (-) | Visual goodness of fit (+/0/-) | Sum of squared weighted residuals (-) | Chi-square Error ^d (%) | Percentage of substance volatilised (%) ^d | Percentage of substance penetrated into sediment (%) ^d | Percentage of substance transformed in water (%) ^d | Mass degraded in water, as a percentage of total mass dissipated from water (%) ^e |
| Level 3 | | | | | | | | | | | | | | |
| 200 | 0.19 | 1 | 2.5 | 7.52, -7.0/22.0 | 0.89, 0.23/1.55 | 0.50, -1.76/2.76 | 42 | + / 0 | 0.1800 | 55.8 | 10.84 | 10.13 | 88.65 | 80.9% |
| 200 | 0.19 | 1 | 10.0 | 9.16, -11.6/29.9 | 0.86, 0.24/1.48 | 0.40, -1.04/1.85 | 22 | + / 0 | 0.1803 | 55.9 | 12.84 | 10.45 | 85.54 | 78.6% |
| 200 | 0.19 | 1 | 0.5 | 7.48, -6.9/21.8 | 0.90, 0.24/1.55 | 0.50, -1.76/2.76 | 59 | + / 0 | 0.1800 | 55.8 | 10.80 | 10.11 | 88.73 | 80.9% |
| 800 | 0.09 | 1 | 2.5 | 5.18, -4.7/15.1 | 1.05, -0.77/2.87 | 0.43, -10.7/11.6 | 43 | + / - | 0.2375 | 64.1 | 7.78 | 5.22 | 91.83 | 87.6% |
| 800 | 0.09 | 1 | 10.0 | 9.98, -13.0/33.0 | 0.93, 0.17/1.69 | 0.36, -0.91/1.63 | 33 | - / - | 0.2298 | 63.0 | 13.59 | 8.58 | 82.82 | 78.9% |
| 800 | 0.09 | 1 | 0.5 | 8.57, -11.1/28.2 | 0.90, -0.38/2.18 | 0.47, -8.0/8.93 | 112 | - / - | 0.2289 | 62.9 | 11.98 | 7.47 | 85.69 | 81.5% |
| 1200 | 0.03 | 1 | 2.5 | 4.05, -3.48/11.58 | 1.09, 0.04/2.15 | 0.18, -2.38/2.73 | 66 | - / - | 0.2618 | 67.3 | 6.28 | 2.95 | 93.18 | 91.0% |
| 1200 | 0.03 | 1 | 10.0 | 10.01, -15.0/35.1 | 0.98, 0.17/1.79 | 0.12, -0.90/1.14 | 34 | - / - | 0.2607 | 67.2 | 13.91 | 5.78 | 83.21 | 80.9% |
| 1200 | 0.03 | 1 | 0.5 | 3.75, -3.2/10.7 | 1.09, -0.01/2.18 | 0.17, -2.60/2.94 | 65 | - / - | 0.2648 | 67.7 | 5.84 | 2.77 | 93.73 | 91.6% |
| 200 | 0.03 | 1 | 2.5 | 7.54, -7.1/22.2 | 0.89, 0.24/1.55 | 0.50, -1.76/2.76 | 49 | + / 0 | 0.1800 | 55.8 | 10.87 | 10.15 | 88.62 | 80.8% |
| 200 | 0.03 | 1 | 10.0 | 8.77, -11.1/28.7 | 0.86, 0.24/1.48 | 0.44, -1.20/2.07 | 36 | + / 0 | 0.1802 | 55.9 | 12.37 | 10.49 | 86.26 | 79.1% |
| 200 | 0.03 | 1 | 0.5 | 7.54, -7.1/22.2 | 0.89, 0.24/1.55 | 0.50, -1.76/2.76 | 83 | + / 0 | 0.1800 | 55.8 | 10.87 | 10.15 | 88.62 | 80.8% |
| 1200 | 0.19 | 1 | 2.5 | 4.16, -3.6/11.9 | 1.08, 0.037/2.13 | 0.16, -2.22/2.55 | 57 | - / - | 0.2611 | 67.2 | 6.43 | 3.03 | 92.95 | 90.8% |
| 1200 | 0.19 | 1 | 10.0 | 9.90, -15.8/35.6 | 0.92, 0.09/1.74 | 0.18, -1.33/1.68 | 59 | - / - | 0.2551 | 66.5 | 13.73 | 5.76 | 83.28 | 81.0% |
| 1200 | 0.19 | 1 | 0.5 | 4.67, -1.5/10.9 | 1.10, -2.09/4.30 | 0.16, -19.6/19.9 | 63 | + / - | 0.2586 | 66.9 | 7.16 | 3.34 | 91.99 | 89.8% |
| Level 4 | | | | | | | | | | | | | | |
| 200 | 0.19 | 1 | 2.5 | 11.01, -10.1/32.1 | 0.83, 0.31/1.34 | 0.50, -1.34/2.34 | 52 | + / 0 | 0.1407 | 53.1 | 14.82 | 12.18 | 82.72 | 75.4% |
| 200 | 0.19 | 1 | 10.0 | 11.17, -10.8/33.2 | 0.82, 0.31/1.33 | 0.50, -1.35/2.35 | 38 | + / 0 | 0.1406 | 53.1 | 14.99 | 12.25 | 82.74 | 75.2% |
| 200 | 0.19 | 1 | 0.5 | 11.12, -10.6/32.8 | 0.82, 0.31/1.34 | 0.50, -1.35/2.35 | 62 | + / 0 | 0.1406 | 53.1 | 14.95 | 12.24 | 82.55 | 75.2% |
| 800 | 0.09 | 1 | 2.5 | 5.61, -0.23/11.4 | 0.90, -1.10/2.91 | 0.48, -10.3/11.3 | 57 | 0 / - | 0.2388 | 69.3 | 8.34 | 5.42 | 91.24 | 86.9% |
| 800 | 0.09 | 1 | 10.0 | 10.38, -12.9/33.6 | 0.97, -0.05/2.00 | 0.35, -5.36/6.06 | 25 | - / - | 0.2169 | 65.9 | 14.02 | 8.82 | 82.11 | 78.2% |
| 800 | 0.09 | 1 | 0.5 | 3.90, 0.58/7.21 | 1.07, -2.19/4.32 | 0.50, -18.9/19.9 | 39 | - / - | 0.2476 | 70.5 | 6.01 | 3.98 | 94.84 | 90.5% |

| Input used in optimisation runs | | | | | Results of optimisation runs | | | | | | | | | |
|---------------------------------|--|------------------------------------|--|-------------------------------|--------------------------------------|---------------------------------------|-------------------------------------|--------------------------------|---------------------------------------|-----------------------|--|---|---|--|
| Bulk density (g/L) | Initial organic matter fraction ^A (-) | Initial water concentration (mg/L) | Initial DegT _{50,water} ^C (days) | Estimated DegT50,water (days) | Estimated water concentration (mg/L) | Estimated organic matter fraction (-) | No of runs needed in estimation (-) | Visual goodness of fit (+/0/-) | Sum of squared weighted residuals (-) | Chi-square Error% (%) | Percentage of substance volatilised (%) ^D | Percentage of substance penetrated into sediment (%) ^D | Percentage of substance transformed in water (%) ^D | Mass degraded in water, as a percentage of total mass dissipated from water (%) ^E |
| 1200 | 0.03 | 1 | 2.5 | 3.61, -3.1/10.3 | 1.23, 0.21/2.24 | 0.0018, -0.2/0.21 | 32 | - / - | 0.2843 | 75.5 | 5.73 | 0.86 | 94.12 | 93.6% |
| 1200 | 0.03 | 1 | 10.0 | 10.01, -14.2/34.2 | 0.99, 0.19/1.78 | 0.12, -0.73/0.97 | 34 | - / - | 0.2550 | 71.5 | 13.92 | 5.77 | 83.20 | 80.9% |
| 1200 | 0.03 | 1 | 0.5 | 4.38, -3.9/12.7 | 1.14, -1.01/3.29 | 0.20, -11.8/12.2 | 69 | - / - | 0.2615 | 72.5 | 6.75 | 3.08 | 92.68 | 90.4% |
| 200 | 0.03 | 1 | 2.5 | 11.01, -10.1/32.2 | 0.83, 0.31/1.34 | 0.50, -1.34/2.34 | 58 | - / 0 | 0.1406 | 53.1 | 14.83 | 12.18 | 82.72 | 75.4% |
| 200 | 0.03 | 1 | 10.0 | 10.98, -9.9/31.9 | 0.83, 0.31/1.34 | 0.50, -1.33/2.33 | 42 | - / 0 | 0.1407 | 53.1 | 14.79 | 12.16 | 82.78 | 75.4% |
| 200 | 0.03 | 1 | 0.5 | 11.03, -10.2/32.3 | 0.83, 0.31/1.34 | 0.50, -1.35/2.35 | 76 | - / 0 | 0.1407 | 53.1 | 14.84 | 12.19 | 82.70 | 75.4% |
| 1200 | 0.19 | 1 | 2.5 | 5.77, -1.6/13.1 | 0.99, -1.46/3.43 | 0.14, -13.7/14.0 | 73 | 0 / - | 0.2581 | 71.9 | 8.67 | 3.96 | 90.01 | 87.7% |
| 1200 | 0.19 | 1 | 10.0 | 9.95, -15.0/34.9 | 0.94, -0.05/1.94 | 0.15, -4.4/4.7 | 24 | 0 / - | 0.2534 | 71.3 | 13.81 | 5.80 | 83.22 | 80.9% |
| 1200 | 0.19 | 1 | 0.5 | 5.52, -1.2/12.3 | 1.05, -1.50/3.60 | 0.22, -14.3/14.7 | 120 | + / - | 0.2561 | 71.6 | 8.31 | 3.64 | 90.70 | 88.4% |
| Level 5 | | | | | | | | | | | | | | |
| 200 | 0.19 | 1 | 2.5 | 9.70 , 3.50/15.9 | 0.88, 0.65/1.11 | 0.07, -0.002/0.14 | 64 | + / 0 | 0.0303 | 25.2 | 13.77 | 5.08 | 84.75 | 81.8% |
| 200 | 0.19 | 1 | 10.0 | 9.71 , 3.47/16.0 | 0.88, 0.65/1.11 | 0.07, -0.001/0.14 | 26 | + / 0 | 0.0303 | 25.2 | 13.78 | 5.07 | 84.73 | 81.8% |
| 200 | 0.19 | 1 | 0.5 | 9.72 , 3.49/15.9 | 0.88, 0.65/1.11 | 0.07, 0.001/0.14 | 105 | + / 0 | 0.0303 | 25.2 | 13.79 | 5.07 | 84.72 | 81.8% |
| 800 | 0.09 | 1 | 2.5 | 2.64, -2.4/7.7 | 1.02, 0.05/1.98 | 0.36, -0.68/1.40 | 29 | - / - | 0.2245 | 68.7 | 4.19 | 3.01 | 96.74 | 93.1% |
| 800 | 0.09 | 1 | 10.0 | 9.90, -5.0/24.8 | 0.92, 0.44/1.41 | 0.36, 0.07/0.65 | 29 | + / - | 0.1028 | 46.5 | 13.52 | 8.25 | 83.18 | 79.3% |
| 800 | 0.09 | 1 | 0.5 | 3.48, 0.15/6.81 | 1.32, 0.43/2.21 | 0.50, -1.58/2.58 | 41 | - / - | 0.1743 | 60.6 | 5.42 | 3.49 | 95.80 | 91.5% |
| 1200 | 0.03 | 1 | 2.5 | 2.85, -2.7/8.4 | 1.06, -0.13/2.25 | 0.48, -3.56/4.53 | 40 | - / - | 0.2754 | 76.1 | 4.54 | 1.38 | 97.69 | 94.3% |
| 1200 | 0.03 | 1 | 10.0 | 9.98, -10.0/29.9 | 0.97, 0.30/1.64 | 0.12, -0.12/0.36 | 28 | + / - | 0.1877 | 62.9 | 13.89 | 5.58 | 83.39 | 81.1% |
| 1200 | 0.03 | 1 | 0.5 | 3.61, -1.52/8.74 | 1.22, 0.28/2.17 | 0.16, -0.46/0.78 | 83 | - / - | 0.2345 | 70.2 | 5.64 | 2.61 | 94.02 | 91.9% |

^A Range of organic matter content allowed in optimisation runs: 0.025 – 0.50.

^B Range of water concentration allowed in optimisation runs: 0.1 – 5.0.

^C Range of DegT50,water allowed during optimisation runs: 0.1 – 100.

^D Percentages here expressed as percentage of total mass in cosm (i.e. former criterion, now replaced by footnote E) instead as percentages of total mass dissipated from water layer. However, these percentages are not relevant for this cosm study as $F_{M,deg-wat} > 50\%$ (i.e. the last column), see also Figure 2.3.

^E (Mass degraded in water)/(Mass degraded in water + Mass volatilised + Mass penetrated into sediment) * 100%.

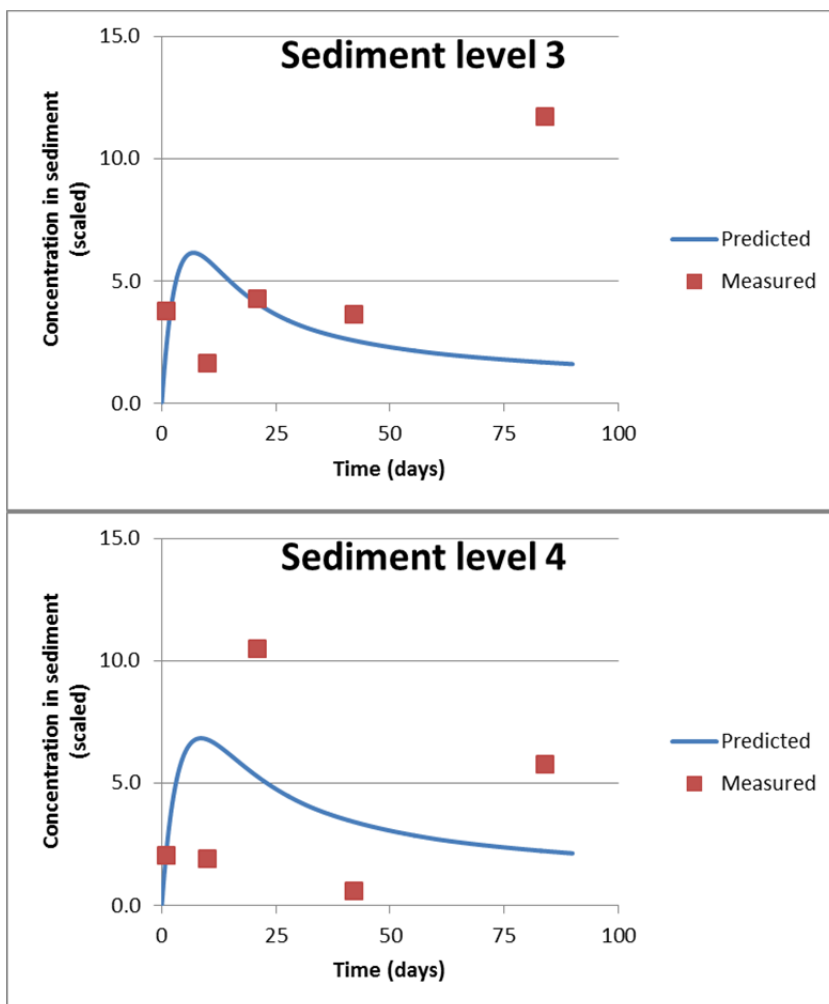


Figure A3.2 Simulated and measured concentrations of chlorpyrifos in water; data simulated using $DegT_{50,water} = 7.52$ and 11.01 days, an organic matter content of sediment of 50 and 50% and an initial scaled water concentration of 0.89 and 0.83 (left hand and right hand graph, respectively) (initial values used in the estimation are given as the first entry for 'level 3 and 4' cosm data in Table A3.6, respectively).

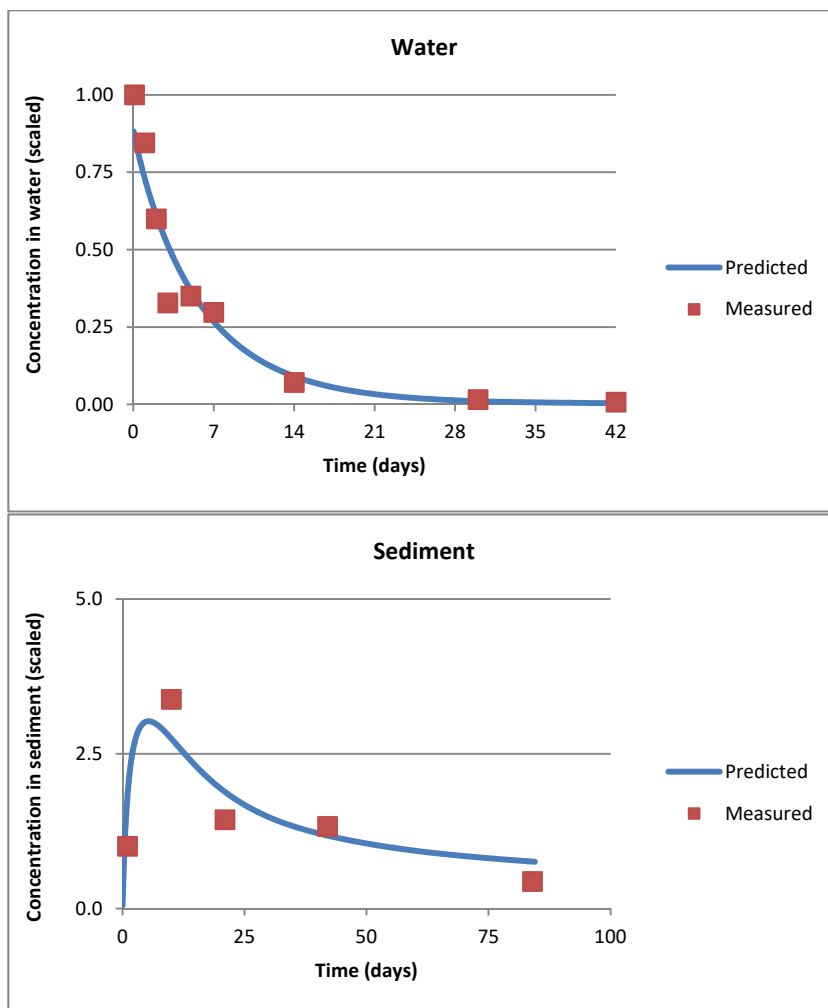


Figure A3.3a Simulated and measured concentrations of chlorpyrifos in water and sediment; data simulated using $\text{DegT}_{50, \text{water}} = 9.70$ days, an organic matter content of sediment of 7.0% and an initial scaled water concentration of 0.88 (initial values used in the estimation are given as the first entry for 'level 5' cosm data in Table A3.6).

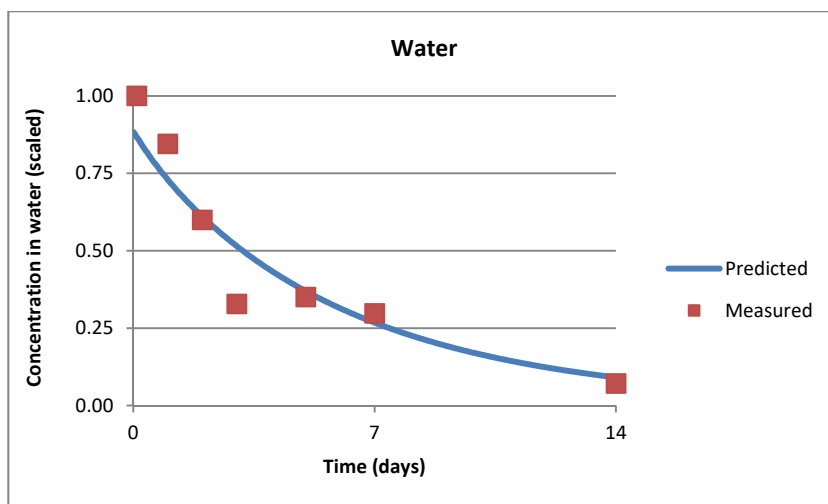


Figure A3.3b Enlarged graph of the water concentrations given in Figure A3.3a, focussing on water concentrations during the first 14 days.

Appendix 4 Inverse modelling with TOXSWA-PEST for the cosm study with lambda-cyhalothrin

For lambda-cyhalothrin only one study was found that is suitable for the estimation of the $DegT_{50,water}$ by inverse modelling by TOXSWA-PEST. The study with lambda-cyhalothrin in an outdoor cosm was described by Leistra et al. (2003) and Roessink et al. (2005) and its main characteristics have been summarized in Table A4.1.

Table A4.1 Data on cosm studies with lambda-cyhalothrin.

| Label in data file | LAMBDA_Cosm1 |
|-----------------------------|--|
| Reference | Leistra et al. (2003), Roessink et al. (2005) |
| Compound | Formulated product: Karate, 100 g/L lambda-cyhalothrin |
| Type of system | Transparent polycarbonate enclosures in outdoor ditches |
| Dimensions system | Internal diameter 1.05 m; height 0.9 m |
| Side slope (hor/vert) | 0 |
| Depth water layer (m) | 430 L, depth 0.5 m |
| Depth sediment (cm) | Loamy, 25 cm; measurements in upper 5 cm |
| Sediment om% | Top 1 cm: 38% OM, averaged over entire depth 23% OM |
| Sediment bulk density | Not specified |
| Sediment porosity | Not specified |
| Macrophytes info | Three different densities of macrophytes: 1 g, 36 g, 90 g dry mass per enclosure |
| pH | Not specified |
| Temperature | 11.3 – 23.2°C |
| Light intensity | Outdoor, applic. 15 August 2000 in Renkum; daily data given in paper (global radiation over 1 week period 1240 – 2020 J cm ⁻²) |
| Application number | 1 |
| Application interval | - |
| Nominal initial application | 0.00025 mg/L |

In Table A4.2 below we summarized the input values on the physico-chemical properties of lambda-cyhalothrin.

Table A4.2 Parameter values used in the simulations with lambda-cyhalothrin.

| Property | Value |
|---------------------------------|---|
| Molar mass (g) | 449.85 |
| Saturated vapour pressure (mPa) | 0.0002 (25°C) |
| Solubility (mg/L) | 0.005 (20°C) |
| Koc (estimated) (L/kg) | Koc=290311; Kom=290311/1.72=168785; adjusted Kom ¹² = 224228 L/kg on basis of geomean conc=2.354E-4 mg/L), 1/n=0.966 |

¹² Later it was found that a Kom of 230353 L/kg was used in the simulations.

Leistra et al.

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 (water depth: 0.5 m; sediment depth: 0.25 m). In the first (May) experiment, only 3 measurements in water were reported and all measured sediment concentrations were below the limit of quantitation. In the second (August) experiment, typically 7 measurements of aqueous and 5 measurements of sediment concentrations are reported. Organic matter content of the first 0.01 m top layer of the sediment was measured and was found to be very high (38% in the second experiment in August), but lower for a bulk sediment sample taken over an unspecified depth (23% OM). Higher plant densities resulted in a decrease of the fraction of pesticide found in the sediment. From the six systems treated we selected the four systems in which macrophytes were pruned prior to the application in order to minimise the role of the macrophytes on the inverse modelling.

Table A4.3 presents the measured concentrations in water and sediment as a function of time in the cosm study of Leistra et al. (2003). Initially systems contained 107.5 µg, which corresponds to 0.00025 mg/L in water and/or $1.76 \cdot 10^{-6}$ g/kg in the upper 5 cm of sediment. The values have been recalculated from values given in Table 5 in the publication, where values were given as percentages of the initial amount present. Water was not filtered before extraction.

Table A4.3 Measured concentrations in water (mg/L and scaled) and sediment (mg/kg and scaled) as a function of time (d) for the cosm study with lambda-cyhalothrin by Leistra et al. (2003). Concentrations are given for systems containing very little or some macrophytes.

| Number | Time (days) | Concentration in water (mg/L) | Scaled concentration in water | Concentration in sediment (g/kg) | Scaled concentration in sediment |
|---------------------------------------|-------------|-------------------------------|-------------------------------|----------------------------------|----------------------------------|
| Dry mass of macrophytes: 1.1 g | | | | | |
| 1 | 0 | 0.000250 [#] | - | - | - |
| 2 | 0.04 | 0.000245 | 1.0000 | - | - |
| 3 | 0.13 | 0.000218 | 0.8898 | - | - |
| 4 | 0.25 | 0.000170 | 0.6939 | 0.1056 E-6 | 0.4310 E-3 |
| 5 | 0.38 | 0.000125 | 0.5102 | - | - |
| 6 | 1.0 | 0.0000975 | 0.3980 | 0.2112 E-6 | 0.8620 E-3 |
| 7 | 2.0 | - | - | 0.2112 E-6 | 0.8620 E-3 |
| 8 | 3.0 | 0.0000825 | 0.03367 | 0.2992 E-6 | 1.2212 E-3 |
| 9 | 7.0 | 0.0000015 | 0.00612 | 0.2112 E-6 | 0.8620 E-3 |
| Dry mass of macrophytes: 1.3 g | | | | | |
| 1 | 0 | 0.000250 [#] | - | - | - |
| 2 | 0.04 | 0.000245 | 1.0000 | - | - |
| 3 | 0.13 | 0.000200 | 0.8163 | - | - |
| 4 | 0.25 | 0.000160 | 0.6531 | 0.1056 E-6 | 0.4302 E-3 |
| 5 | 0.38 | 0.0001025 | 0.4184 | - | - |
| 6 | 1.0 | 0.0001000 | 0.4082 | 0.2112 E-6 | 0.8620 E-3 |
| 7 | 2.0 | - | - | 0.2112 E-6 | 0.8620 E-3 |
| 8 | 3.0 | 0.0000105 | 0.0429 | 0.2112 E-6 | 0.8620 E-3 |
| 9 | 7.0 | 0.00000175 | 0.0071 | 0.2112 E-6 | 0.8620 E-3 |

| Number | Time (days) | Concentration in water (mg/L) | Scaled concentration in water | Concentration in sediment (g/kg) | Scaled concentration in sediment |
|--------------------------------------|-------------|-------------------------------|-------------------------------|----------------------------------|----------------------------------|
| Dry mass of macrophytes: 28 g | | | | | |
| 1 | 0 | 0.000250 [#] | - | - | - |
| 2 | 0.04 | 0.000225 | 1.0000 | - | |
| 3 | 0.13 | 0.000195 | 0.8667 | - | |
| 4 | 0.25 | 0.000170 | 0.7556 | 0.1056 E-6 | 0.4693 E-3 |
| 5 | 0.38 | 0.0001125 | 0.5000 | - | |
| 6 | 1.0 | 0.0000925 | 0.4111 | 0.2112 E-6 | 0.9387 E-3 |
| 7 | 2.0 | - | | 0.2112 E-6 | 0.9387 E-3 |
| 8 | 3.0 | 0.0000100 | 0.0444 | 0.2112 E-6 | 0.9387 E-3 |
| 9 | 7.0 | 0.00000175 | 0.0078 | 0.2112 E-6 | 0.9387 E-3 |
| Dry mass of macrophytes: 45 g | | | | | |
| 1 | 0 | 0.000250 [#] | - | - | - |
| 2 | 0.04 | 0.0002275 | 1.0000 | - | |
| 3 | 0.13 | 0.0001925 | 0.8462 | - | |
| 4 | 0.25 | 0.0001750 | 0.7692 | < 0.1056 E-6 | < 0.4642 E-3 |
| 5 | 0.38 | 0.0001025 | 0.4505 | - | |
| 6 | 1.0 | 0.0000775 | 0.3407 | < 0.1056 E-6 | < 0.4642 E-3 |
| 7 | 2.0 | - | | 0.2112 E-6 | 0.9284 E-3 |
| 8 | 3.0 | 0.00000575 | 0.0253 | 0.2112 E-6 | 0.9284 E-3 |
| 9 | 7.0 | 0.00000100 | 0.0044 | 0.2112 E-6 | 0.9284 E-3 |

Initial nominal concentration, not measured but calculated from dosed amount.

Leistra et al. (2003) report maximum amounts of lambda-cyhalothrin in sediment as 17% of the initially applied amount (3 days after application) for systems with low macrophyte content, and 12% of the initially applied amount (2, 3 and 7 days after application) for systems with high macrophyte content.

The inverse modelling was performed using scaled concentrations. Since the organic matter content of the sediment (upper 1 cm) was given as 38%, the OM% was allowed to vary from 37.5 – 38.5% (Box B9 in Figure 2.2).

Aqueous concentration was allowed to vary from 0.1 – 5 (scaled) with an initial estimate of 1.0, and $DegT_{50,water}$ was allowed to vary from 0.01 – 50 days with an initial estimate of 0.4, 5 or 0.05 days (Table 3.8).

Runs were performed using values for bulk density of 0.2 kg/L, 0.8 kg/L and 1.2 kg/L, using an initial organic matter content of 38% (red stars of Figure 3.2). Three additional runs were performed for a bulk density of 0.6 kg/L (purple stars of Figure 3.2)

Results for the runs are summarised in Table A4.4. The degradation in the water phase always accounted for at least 50% of total dissipation (Figure 2.3), which leads to acceptance of the estimated $DegT_{50,water}$. For a number of runs the χ^2 – error was also below 25%, these are the runs with the $DegT_{50,water}$ values in bold of the data sets with 1.3, 28 and 45 g of macrophytes. Although the visual correspondence between simulated and measured concentrations in the water layer is not so good (see e.g. Figure A4.1) the fits were judged to be acceptable, the alternative being not able to use the cosm study at all. All acceptable runs assumed a bulk density of the sediment of 0.2 kg/L and an initial estimate of $DegT_{50,water}$ of either 0.4 or 0.05 days. These runs yielded almost exactly the same value for the estimated $DegT_{50,water}$: 0.18, 0.18, 0.19, 0.19, 0.18 and 0.18 days resp., resulting in an geometric mean value of 0.18 days. Figure A4.1 gives a graphical depiction of the results of the first run for the cosms containing 28 g of macrophytes.

Table A4.4 Results of the initial and, where necessary: additional, runs of PEST_TOXSWA inverse modelling ('Method B9') for lambda-cyhalothrin data from Leistra et al. (2003) using given initial values for parameters bulk density, organic matter, initial water concentration $C_{t=0}$ and initial $DegT_{50,water}$.

| Input used in optimisation runs | | | | | Results of optimisation runs | | | | | | | | | |
|---------------------------------|--|---|------------------------------------|------------------------------------|---|---------------------------------------|----------------|--------------------------------|---------------------------------------|-----------------------------------|--|---|---|--|
| Bulk density (g/L) | Initial organic matter fraction ^A (-) | Initial water concentration ^B (mg/L) | Initial $DegT_{50,water}^C$ (days) | Estimated $DegT_{50,water}$ (days) | Estimated init water concentration (mg/L) | Estimated organic matter fraction (-) | Value, min/max | Visual goodness of fit (+/0/-) | Sum of squared weighted residuals (-) | Chi-square Error ^D (%) | Percentage of substance volatilised (%) ^D | Percentage of substance penetrated into sediment (%) ^D | Percentage of substance transformed in water (%) ^D | Mass degraded in water, as a percentage of total mass dissipated from water (%) ^E |
| Macrophyte mass 1.1 g | | | | | | | | | | | | | | |
| 200 | 0.38 | 1 | 0.4 | 0.20, 0.07/0.33 | 1.07, 0.72/1.41 | 0.385, 0.09/0.68 | | - / - | 0.0342 | 18.7 | 0.02 | 1.97 | 98.16 | 98.0% |
| 200 | 0.38 | 1 | 5 | 4.38, -3.7/12.5 | 0.16, -0.40/0.73 | 0.385, -0.22/0.99 | | - / - | 0.3901 | 63.1 | 0.25 | 28.04 | 70.97 | 71.5% |
| 200 | 0.38 | 1 | 0.05 | 0.20, 0.07/0.34 | 1.07, 0.72/1.41 | 0.385, 0.09/0.68 | | - / - | 0.0342 | 18.7 | 0.02 | 1.97 | 98.16 | 98.0% |
| 800 | 0.38 | 1 | 0.4 | 1.99, -2.4/6.4 | 0.94, 0.42/1.46 | 0.375, -0.20/0.95 | | - / - | 0.2336 | 48.9 | 0.13 | 7.34 | 92.53 | 92.5% |
| 800 | 0.38 | 1 | 5 | 1.99, -2.4/6.3 | 0.94, 0.42/1.46 | 0.375, -0.20/0.95 | | - / - | 0.2336 | 48.9 | 0.13 | 7.34 | 92.53 | 92.5% |
| 800 | 0.38 | 1 | 0.05 | 1.99, -2.3/6.3 | 0.94, 0.42/1.46 | 0.375, -0.20/0.95 | | - / - | 0.2336 | 48.9 | 0.13 | 7.34 | 92.53 | 92.5% |
| 1200 | 0.38 | 1 | 0.4 | 1.59, -3.6/6.8 | 0.88, 0.13/1.64 | 0.375, -1.3/2.1 | | - / - | 0.4374 | 66.8 | 0.11 | 2.92 | 96.98 | 97.0% |
| 1200 | 0.38 | 1 | 5 | 1.59, -3.6/6.8 | 0.88, 0.13/1.64 | 0.375, -1.3/2.1 | | - / - | 0.4374 | 66.8 | 0.11 | 2.90 | 96.99 | 97.0% |
| 1200 | 0.38 | 1 | 0.05 | 1.61, -3.9/7.1 | 0.88, 0.13/1.63 | 0.375, -1.3/2.0 | | - / - | 0.4374 | 66.8 | 0.11 | 2.95 | 96.96 | 96.9% |
| 600 | 0.38 | 1 | 0.4 | 1.21, -0.42/2.85 | 0.98, 0.59/1.36 | 0.375, -0.03/0.78 | | - / - | 0.1148 | 34.2 | 0.08 | 6.28 | 93.68 | 93.6% |
| 600 | 0.38 | 1 | 5 | 1.21, -0.42/2.85 | 0.98, 0.59/1.36 | 0.375, -0.03/0.78 | | - / - | 0.1148 | 34.2 | 0.08 | 6.28 | 93.70 | 93.6% |
| 600 | 0.38 | 1 | 0.05 | 1.21, -0.42/2.85 | 0.98, 0.59/1.36 | 0.375, -0.03/0.78 | | - / - | 0.1148 | 34.2 | 0.08 | 6.28 | 93.68 | 93.6% |
| Macrophyte mass 1.3 g | | | | | | | | | | | | | | |
| 200 | 0.38 | 1 | 0.4 | 0.18 , 0.09/0.27 | 1.06, 0.77/1.35 | 0.385, 0.16/0.61 | | - / + | 0.0238 | 13.7 | 0.02 | 1.73 | 98.38 | 98.3% |
| 200 | 0.38 | 1 | 5 | 4.53, -2.4/11.4 | 0.14, -0.47/0.75 | 0.385, -0.28/1.05 | | - / - | 0.4516 | 59.8 | 0.14 | 28.63 | 70.36 | 71.0% |
| 200 | 0.38 | 1 | 0.05 | 0.18 , 0.09/0.27 | 1.06, 0.77/1.34 | 0.385, 0.16/0.61 | | - / + | 0.0238 | 13.7 | 0.02 | 1.74 | 98.38 | 98.3% |
| 800 | 0.38 | 1 | 0.4 | 2.23, -2.9/7.4 | 0.95, 0.37/1.54 | 0.375, -0.14/0.89 | | - / - | 0.3177 | 50.1 | 0.15 | 8.16 | 91.67 | 91.7% |
| 800 | 0.38 | 1 | 5 | 2.23, -2.9/7.4 | 0.95, 0.37/1.54 | 0.375, -0.14/0.89 | | - / - | 0.3177 | 50.1 | 0.15 | 8.17 | 91.69 | 91.7% |
| 800 | 0.38 | 1 | 0.05 | 2.23, -2.9/7.4 | 0.95, 0.37/1.54 | 0.375, -0.14/0.89 | | - / - | 0.3177 | 50.1 | 0.15 | 8.16 | 91.67 | 91.7% |
| 1200 | 0.38 | 1 | 0.4 | 3.01, -9.8/15.8 | 0.86, 0.01/1.70 | 0.375, -0.77/1.52 | | - / - | 0.6653 | 72.6 | 0.19 | 5.35 | 94.16 | 94.4% |
| 1200 | 0.38 | 1 | 5 | 3.02, -10.2/16.2 | 0.86, 0.02/1.69 | 0.375, -0.75/1.50 | | - / - | 0.6653 | 72.6 | 0.19 | 5.38 | 94.13 | 94.4% |
| 1200 | 0.38 | 1 | 0.05 | 2.98, -9.7/15.6 | 0.86, 0.01/1.70 | 0.375, -0.76/1.51 | | - / - | 0.6653 | 72.6 | 0.19 | 5.31 | 94.22 | 94.5% |

| Input used in optimisation runs | | | | | Results of optimisation runs | | | | | | | | | |
|---------------------------------|--|---|--|---|--------------------------------------|---------------------------------------|----------------|--------------------------------|---------------------------------------|-----------------------|--|---|---|--|
| Bulk density (g/L) | Initial organic matter fraction ^A (-) | Initial water concentration ^B (mg/L) | Initial DegT _{50,water} ^C (days) | Estimated DegT _{50,water} (days) | Estimated water concentration (mg/L) | Estimated organic matter fraction (-) | Value, min/max | Visual goodness of fit (+/0/-) | Sum of squared weighted residuals (-) | Chi-square Error% (%) | Percentage of substance volatilised (%) ^D | Percentage of substance penetrated into sediment (%) ^D | Percentage of substance transformed in water (%) ^D | Mass degraded in water, as a percentage of total mass dissipated from water (%) ^E |
| Macrophyte mass 28 g | | | | | | | | | | | | | | |
| 200 | 0.38 | 1 | 0.4 | 0.19 , 0.09/0.29 | 1.09, 0.79/1.40 | 0.385, 0.15/0.62 | 30 | - / + | 0.0275 | 14.4 | 0.02 | 1.85 | 98.26 | 98.1% |
| 200 | 0.38 | 1 | 5 | 4.49, -2.8/11.8 | 0.15, -0.47/0.78 | 0.385, -0.28/1.05 | 31 | - / - | 0.4768 | 59.8 | 0.26 | 28.52 | 70.43 | 71.0% |
| 200 | 0.38 | 1 | 0.05 | 0.19 , 0.09/0.29 | 1.09, 0.79/1.39 | 0.385, 0.15/0.62 | 48 | - / + | 0.0275 | 14.4 | 0.02 | 1.85 | 98.26 | 98.1% |
| 800 | 0.38 | 1 | 0.4 | 2.25, -2.9/7.4 | 1.00, 0.40/1.59 | 0.375, -0.15/0.90 | 34 | - / - | 0.3260 | 49.5 | 0.14 | 8.24 | 91.60 | 91.6% |
| 800 | 0.38 | 1 | 5 | 2.25, -2.6/7.1 | 1.00, 0.40/1.59 | 0.375, -0.15/0.90 | 66 | - / - | 0.3260 | 49.5 | 0.14 | 8.24 | 91.58 | 91.6% |
| 800 | 0.38 | 1 | 0.05 | 2.66, -8.0/13.3 | 0.90, 0.05/1.76 | 0.375, -0.85/1.60 | 56 | - / - | 0.6714 | 70.9 | 0.18 | 4.79 | 94.90 | 95.0% |
| 1200 | 0.38 | 1 | 0.4 | 2.66, -7.9/13.2 | 0.90, 0.04/1.76 | 0.375, -0.87/1.62 | 39 | - / - | 0.6713 | 70.9 | 0.18 | 4.76 | 94.93 | 95.1% |
| 1200 | 0.38 | 1 | 5 | 2.66, -8.2/13.6 | 0.90, 0.05/1.76 | 0.375, -0.84/1.59 | 30 | - / - | 0.6714 | 70.9 | 0.18 | 4.79 | 94.92 | 95.0% |
| 1200 | 0.38 | 1 | 0.05 | 2.66, -8.0/13.3 | 0.90, 0.05/1.76 | 0.375, -0.85/1.60 | 56 | - / - | 0.6714 | 70.9 | 0.18 | 4.79 | 94.90 | 95.0% |
| Macrophyte mass 45 g | | | | | | | | | | | | | | |
| 200 | 0.38 | 1 | 0.4 | 0.18 , 0.05/0.32 | 1.10, 0.74/1.46 | 0.385, 0.06/0.71 | 37 | - / + | 0.0210 | 12.7 | 0.02 | 1.78 | 98.35 | 98.2% |
| 200 | 0.38 | 1 | 5 | 4.66, -2.1/11.5 | 0.13, -0.54/0.81 | 0.385, -0.31/1.08 | 31 | - / - | 0.3975 | 54.9 | 0.15 | 29.21 | 69.75 | 70.4% |
| 200 | 0.38 | 1 | 0.05 | 0.18 , 0.05/0.32 | 1.10, 0.74/1.46 | 0.385, 0.06/0.72 | 49 | - / + | 0.0210 | 12.7 | 0.02 | 1.78 | 98.35 | 98.2% |
| 800 | 0.38 | 1 | 0.4 | 2.58, -3.5/8.7 | 0.98, 0.37/1.58 | 0.375, -0.10/0.85 | 38 | - / - | 0.2504 | 43.6 | 0.16 | 9.32 | 90.46 | 90.5% |
| 800 | 0.38 | 1 | 5 | 2.56, -3.4/8.6 | 0.98, 0.37/1.58 | 0.375, -0.11/0.86 | 59 | - / - | 0.2504 | 43.6 | 0.16 | 9.26 | 90.47 | 90.6% |
| 800 | 0.38 | 1 | 0.05 | 2.58, -3.6/8.7 | 0.98, 0.37/1.58 | 0.375, -0.10/0.85 | 68 | - / - | 0.2504 | 43.6 | 0.16 | 9.32 | 90.43 | 90.5% |
| 1200 | 0.38 | 1 | 0.4 | 4.42, -19.1/28.0 | 0.90, -0.09/1.90 | 0.375, -0.66/1.41 | 40 | - / - | 0.7118 | 73.5 | 0.27 | 7.58 | 90.49 | 92.0% |
| 1200 | 0.38 | 1 | 5 | 4.43, -20.6/29.5 | 0.90, -0.09/1.89 | 0.375, -0.63/1.38 | 41 | - / - | 0.7118 | 73.5 | 0.27 | 7.59 | 90.46 | 92.0% |
| 1200 | 0.38 | 1 | 0.05 | 4.42, -20.0/28.9 | 0.90, -0.09/1.90 | 0.375, -0.64/1.39 | 66 | - / - | 0.7118 | 73.5 | 0.27 | 7.58 | 90.47 | 92.0% |

^A Range of organic matter content allowed in optimisation runs: 0.375 – 0.385.

^B Range of water concentration allowed in optimisation runs: 0.1 – 5.0.

^C Range of DegT_{50,water} allowed during optimisation runs: 0.01 – 50.

^D Percentages here expressed as percentage of total mass in cosm (i.e. former criterion, now replaced by footnote E) instead as percentages of total mass dissipated from water layer. However, these percentages are not relevant for this cosm study as $F_{M,deg-wat} > 50\%$ (i.e. the last column), see also Figure 2.3.

^E (Mass degraded in water)/(Mass degraded in water + Mass volatilised + Mass penetrated into sediment) * 100%.

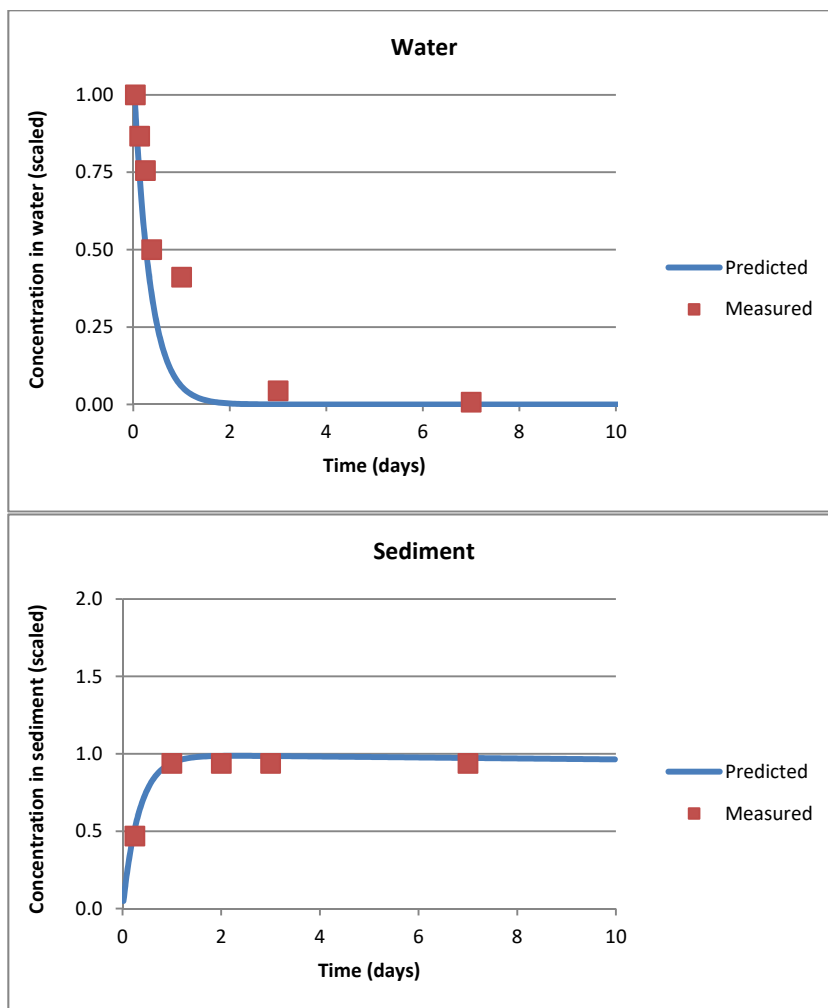


Figure A4.1 Simulated and measured concentrations of lambda-cyhalothrin in water and sediment; data simulated using $DegT_{50,water} = 0.18$ days, an organic matter content of sediment of 38.5% and an initial scaled water concentration of 1.09 (initial values used in the estimation are given as the first entry for cosms with macrophyte density of 28 grams (22nd entry overall in Table A4.4).

Appendix 5 Inverse modelling with TOXSWA-PEST for the cosm study with linuron

For linuron one study was found that is suitable for the estimation of the $DegT_{50,water}$ by inverse modelling by TOXSWA-PEST. The study with linuron in an outdoor cosm was described by Bromilow et al. (2006) and its main characteristics have been summarized in Table A5.1.

Table A5.1 Data on cosm studies with linuron.

| Label in data file | LIN_Cosm1 |
|-----------------------------|---|
| Reference | Bromilow et al. (2006) |
| Compound | Technical material applied with Agral surfactant |
| Type of system | Outdoor stainless steel tanks |
| Dimensions system | 1.0 x 1.0 x 0.40 m |
| Side slope (hor/vert) | 0 |
| Depth water layer (m) | 0.30 |
| Depth sediment (cm) | 5 cm |
| Sediment om% | 2.5% Organic carbon, estimated from this $1.72 \times 2.5 = 4.3\%$ OM |
| Sediment bulk density | Not given, estimated 1.2 kg/dm ³ |
| Sediment porosity | - |
| Macrophytes info | Macrophytes present, 60 stems of <i>Elodea crista</i> per cosm |
| pH | 7.32 |
| Temperature | 9.5°C |
| Light intensity | |
| Application number | 1 |
| Application interval | - |
| Nominal initial application | 0.668 mg/L |

In Table A5.2 below we summarized the input values on the physico-chemical properties of linuron.

Table A5.2 Parameter values used in the simulations with linuron.

| Property | Value |
|---------------------------------|--|
| Molar mass (g) | 249.09 |
| Saturated vapour pressure (mPa) | 0.051 (25°C) |
| Solubility (mg/L) | 63.8 (20°C) |
| Koc (L/kg) | Koc=842.8 --> Kom=842.8/1.72=490.; 1/n=0.87 --> Adjusted Kom=588.5 ¹³ |
| pKa | Not applicable |

Bromilow et al.

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 0.67 mg/L. Concentrations measured in water, sediment

¹³ Value used in the simulations, could not be reproduced by the authors in a final stage of this report.

(2.5% organic carbon, corresponding to approx. 4.3% organic matter) 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. The outdoor study used a single application of linuron, in a rather shallow system (water depth 30 cm) at a rather low temperature (application on October 30, 2002), with sediment temperature ranging from 1 - 10°C, and the authors stating that the average water temperature was 4°C above sediment temperature). An average temperature of 9.5°C was used in the simulations. Besides the measurement shortly after application, concentrations were reported at 7 additional times.

Table A5.3 presents the measured concentrations in water and sediment as a function of time in the cosm study of Bromilow et al. (2006). Originally concentration data were given as percentages of the amount of linuron added to the system. Aqueous and sediment concentrations are read from Figure 2 and Figure 3 resp., and have been recalculated from values in the publication, which were given as percentages of the initial amount present. Water was filtered using a 0.45 µm Millipore membrane before analysis through HPLC.

Table A5.3 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 | Concentration in sediment |
|--|-------------|------------------------|---------------------------|
| 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) | | | |
| | | mg/L | g/kg |
| 1 | 1 | 0.608 | 0.1052E-3 |
| 2 | 8 | 0.430 | 0.3465E-3 |
| 3 | 14 | 0.391 | 0.4305E-3 |
| 4 | 28 | 0.296 | 0.3657E-3 |
| 5 | 48 | 0.229 | 0.3657E-3 |
| 6 | 92 | 0.143 | 0.4305E-3 |
| 7 | 114 | 0.134 | 0.2205E-3 |
| 8 | 152 | 0.0955 | 0.2310E-3 |
| Data converted to scaled concentrations | | | |
| 1 | 1 | 1.0000 | 0.1730E-3 |
| 2 | 8 | 0.7072 | 0.5699E-3 |
| 3 | 14 | 0.6431 | 0.7081E-3 |
| 4 | 28 | 0.4868 | 0.6015E-3 |
| 5 | 48 | 0.3766 | 0.6015E-3 |
| 6 | 92 | 0.2352 | 0.7081E-3 |
| 7 | 114 | 0.2204 | 0.3627E-3 |
| 8 | 152 | 0.1571 | 0.3799E-3 |

The authors report maximum sediment concentrations of 8.6% of the mass initially added to the system on days 14 and 92 after application.

The inverse modelling was performed using scaled concentrations. Since the organic matter content of the bulk sediment was given as 4.3%, the OM% was allowed to vary from 3.8 – 4.8% (Box B9 of Figure 2.2).

Aqueous concentration was allowed to vary from 0.1 – 5 (scaled) with an initial estimate of 1.0, and $DegT_{50,water}$ was allowed to vary from 1 – 100 days with an initial estimate of 30, 75 or 5 days (Table 3.8).

Runs were performed using values for bulk density of 0.2, 0.8 and 1.2 kg/L (red stars of Figure 3.2) using an initial estimate of organic matter content of 4.3%. Three additional runs were performed for a bulk density of 0.6 kg/L (purple stars of Figure 3.2).

Results for the runs are summarised in Table A5.4. Only one satisfactory run (χ^2 – error below 25% and degradation in the water phase accounting for at least 50% of total dissipation) was obtained. Three additional runs, using a bulk density of 0.6 kg/L, initial organic matter content of 4.3%, and initial estimates of $DegT_{50,water}$ of 30, 75 and 5 days were performed (entries 10 – 12 in Table A5.4), but they did not result in additional satisfactory runs. So, of the 12 runs, a single run resulted in a χ^2 – error below 25%, yielding an estimated $DegT_{50,water}$ value of 7.6 days (ninth entry in Table A5.4), and is depicted graphically in Figure A5.1. Although the sediment data in this run are fitted relatively well, the measurements in the water are systematically underestimated and the results of the run are therefore considered unreliable.

For the run with the lowest value for χ^2 – error (22.5%, $DegT_{50,water}$ estimated as 7.6 days), PEST/TOXSWA estimated that 17% of the mass penetrated into sediment, whereas 88% of the mass in the system was transformed in the water phase (Table A5.4, ninth entry). These data were generated using the default ‘multiplication factor’, i.e. the calculations use equal weights for concentrations measured in water and sediment. In view of the higher importance of degradation in water compared to penetration into sediment, it was thought worthwhile to perform calculations using an adjusted weight factor for the water measurements, reflecting the higher importance of compound present (and degraded) in the water. A second set of calculations was performed, using a multiplication factor of 5, which is close to the ratio between water degradation (88%) and sediment penetration (17%) found in the first set of calculations. The results for these calculations, using the same values for bulk density, organic matter content etc., are given in Table A5.5. Although two runs fulfil the χ^2 – error criterion below 25% the visual correspondence between measured and simulated concentrations in both water and sediment is not satisfactory and so, their fitted $DegT_{50,water}$ value is not acceptable.

As can be seen when comparing Figures A5.1 and A5.2 which both represent the fits with best statistics within their sets of simulations, the introduction of an extra weight factor 5 for the water concentrations somewhat improves the quality of the fit of water concentrations, but at the same time decreases the quality of the fit of sediment concentrations. Overall, the introduction of a multiplication factor of 5 does not improve the quality of the reverse modelling to a large extent, and the results of the inverse modelling remain unreliable.

However, looking at the graphs it is possible that the results have been negatively influenced by the assumed value of 1000 d for the $DegT_{50,sediment}$, which may not reflect well the degradation rate for linuron in sediments. The Pesticide Properties DataBase gives a value of 24.1 d for the half-life in the overall water-sediment systems, with a value of 13.0 d for water-only. With a value of 24 d for the $DegT_{50,sediment}$ our optimisation procedure would possibly give an improved correspondence between measured and simulated concentrations in water and sediment. However, the current software does not allow to change the default value of 1000 d for the $DegT_{50,sediment}$, so we were unable to test this now. We did include this suggestion however in Chapter 6 in the recommended optimisation procedure.

Table A5.4 Results of the 9 initial and 3 additional runs of PEST_TOXSWA inverse modelling (Method B9' of Figure 2.2) for linuron data from Bromilow et al. (1992) using given initial values for parameters bulk density, organic matter, initial water concentration $C_{t=0}$ and initial $DegT_{50,water}$.

| Input used in optimisation runs | | | | Results of optimisation runs | | | | | | | | | | |
|---------------------------------|--|---|--|---|---|---|-------------------------------------|--|---------------------------------------|-----------------------|--|---|---|--|
| Bulk density (g/L) | Initial organic matter fraction ^A (-) | Initial water concentration ^B (mg/L) | Initial DegT _{50,water} ^C (days) | Estimated DegT50,water (days) Value, min/max | Estimated init water concentration (mg/L) Value, min/max | Estimated organic matter fraction (-) Value, min/max | No of runs needed in estimation (-) | Visual goodness of fit (+/0/-) Water/sediment | Sum of squared weighted residuals (-) | Chi-square Error% (%) | Percentage of substance volatilised (%) ^D | Percentage of substance penetrated into sediment (%) ^D | Percentage of substance transformed in water (%) ^D | Mass degraded in water, as a percentage of total mass dissipated from water (%) ^E |
| 200 | 0.043 | 1 | 30 | 8.93, -9.2/27.0 | 0.16, -0.11/0.43 | 0.038, -0.16/0.23 | 48 | - / + | 0.2465 | 49.4 | 0.00* | 16.74* | 86.61* | 83.8% |
| 200 | 0.043 | 1 | 75 | 8.90, -8.7/26.5 | 0.16, -0.11/0.43 | 0.038, -0.16/0.23 | 83 | - / + | 0.2465 | 49.4 | 0.00 | 16.70 | 86.64 | 83.8% |
| 200 | 0.043 | 1 | 5 | 8.92, -9.0/26.8 | 0.16, -0.11/0.43 | 0.038, -0.16/0.23 | 47 | - / + | 0.2465 | 49.4 | 0.00 | 16.70 | 86.43 | 83.8% |
| 800 | 0.043 | 1 | 30 | 26.5, 0.69/52.2 | 0.32, -0.09/0.73 | 0.038, -1.44/9.0 | 32 | - / - | 0.2008 | 44.6 | 0.00 | 31.02 | 54.29 | 63.6% |
| 800 | 0.043 | 1 | 75 | 6.51, 1.4/11.7 | 0.63, 0.20/1.06 | 0.038, -0.03/0.10 | 76 | - / + | 0.1154 | 33.8 | 0.00 | 17.27 | 89.14 | 83.8% |
| 800 | 0.043 | 1 | 5 | 6.48, 1.3/11.6 | 0.63, 0.20/1.06 | 0.038, -0.03/0.10 | 45 | - / + | 0.1154 | 33.8 | 0.00 | 17.21 | 89.23 | 83.8% |
| 1200 | 0.043 | 1 | 30 | 25.0, -1.9/51.9 | 0.52, 0.18/0.87 | 0.038, -0.003/7.9 | 34 | - / + | 0.1283 | 35.6 | 0.00 | 28.44 | 57.65 | 67.0% |
| 1200 | 0.043 | 1 | 75 | 26.2, -120, 173 | 0.44, 0.10/0.78 | 0.038, -0.01/8.79 | 32 | - / + | 0.1495 | 38.5 | 0.00 | 29.10 | 55.93 | 65.8% |
| 1200 | 0.043 | 1 | 5 | 7.56, 3.7/11.4 | 0.91, 0.63/1.20 | 0.038, 0.005/7.1 | 58 | - / + | 0.05140 | 22.5 | 0.00 | 17.04 | 88.07 | 83.8% |
| 600 | 0.043 | 1 | 30 | 27.3, 4.5/50.0 | 0.23, -0.20/0.67 | 0.038, -0.02/9.5 | 32 | - / + | 0.2368 | 48.4 | 0.00 | 31.44 | 53.34 | 62.9% |
| 600 | 0.043 | 1 | 75 | 6.47, 0.41/12.5 | 0.47, -0.01/0.95 | 0.038, -0.06/13.4 | 75 | - / + | 0.1553 | 39.2 | 0.00 | 17.22 | 89.13 | 83.8% |
| 600 | 0.043 | 1 | 5 | 6.48, 0.38/12.6 | 0.47, -0.01/0.95 | 0.038, -0.06/0.13 | 60 | - / + | 0.1553 | 39.2 | 0.00 | 17.23 | 89.12 | 83.8% |

* The total percentage of mass volatilised, penetrated into sediment and transformed in water may exceed 100% because of back-diffusion of mass from the sediment into the water, where next, it may be transformed.

^A Range of organic matter content allowed in optimisation runs: 0.038 – 0.048.

^B Range of water concentration allowed in optimisation runs: 0.1 – 5.0.

^C Range of $DegT_{50,water}$ allowed during optimisation runs: 1 – 100.

^D Percentages here expressed as percentage of total mass in cosm (i.e. former criterion, now replaced by footnote E) instead as percentages of total mass dissipated from water layer. However, these percentages are not relevant for this cosm study as $F_{M,deg-wat} > 50\%$ (i.e. the last column), see also Figure 2.3.

^E (Mass degraded in water)/(Mass degraded in water + Mass volatilised + Mass penetrated into sediment) * 100%.

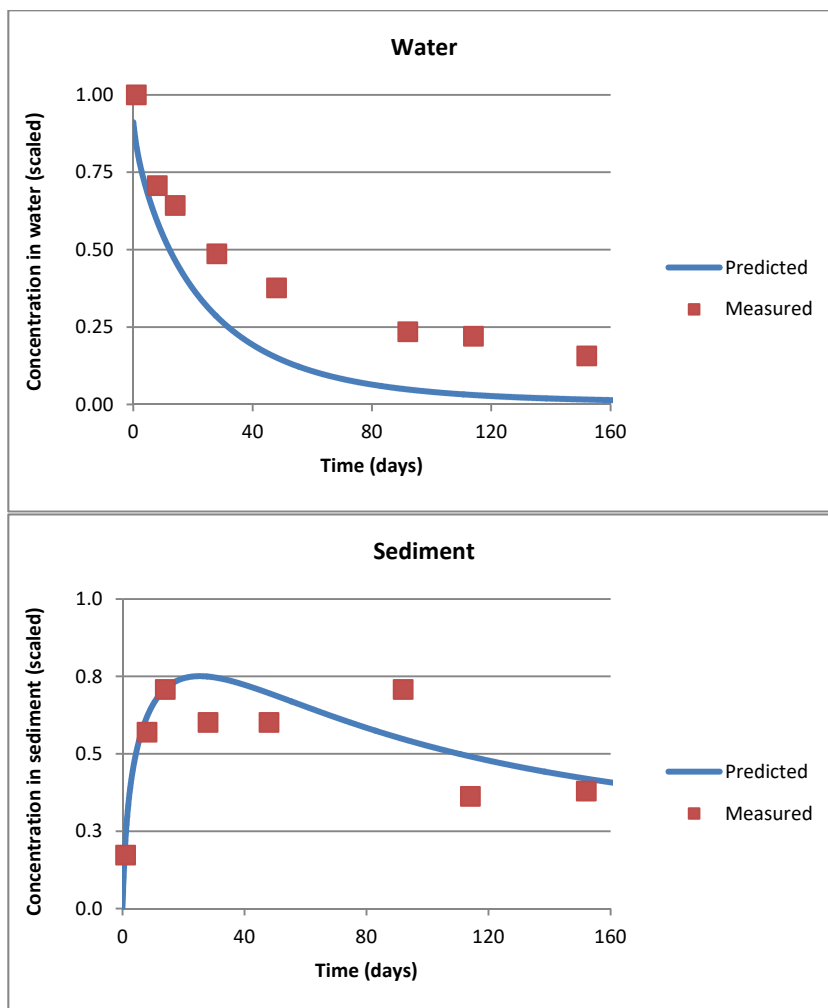


Figure A5.1 Simulated and measured concentrations of linuron in water and sediment; data simulated using $DegT_{50,water} = 7.56$ days, an organic matter content of sediment of 3.8% and an initial scaled water concentration of 0.91 (initial values used in the estimation are given as the ninth entry in Table A5.4).

Table A5.5 Results using a multiplication factor 5 (i.e. using water data with an enhanced weighting factor of 5) for the 9 initial and 3 additional runs of PEST_TOXSWA inverse modelling ('Method B9') for linuron data from Bromilow et al. (1992) using given initial values for parameters bulk density, organic matter, initial water concentration $C_{t=0}$ and initial $DegT_{50,water}$.

| Input used in optimisation runs | | | | | Results of optimisation runs | | | | | | | | | |
|---------------------------------|--|---|---|------------------------------------|--------------------------------------|---------------------------------------|--|--------------------------------|---------------------------------------|-----------------------|--|---|---|--|
| Bulk density (g/L) | Initial organic matter fraction ^A (-) | Initial water concentration ^B (mg/L) | Initial $DegT_{50,water}$ ^C (days) | Estimated $DegT_{50,water}$ (days) | Estimated water concentration (mg/L) | Estimated organic matter fraction (-) | Estimated organic matter fraction Value, min/max | Visual goodness of fit (+/0/-) | Sum of squared weighted residuals (-) | Chi-square Error% (%) | Percentage of substance volatilised (%) ^D | Percentage of substance penetrated into sediment (%) ^D | Percentage of substance transformed in water (%) ^D | Mass degraded in water, as a percentage of total mass dissipated from water (%) ^E |
| 200 | 0.043 | 1 | 30 | 2.53, -2.1/7.1 | 0.72, -0.06/1.49 | 0.038, -0.08/0.15 | 0.038, -0.08/0.15 | - / - | 4.1565 | 78.2 | 0.00* | 8.82* | 96.97* | 91.7% |
| 200 | 0.043 | 1 | 75 | 2.54, -2.1/7.2 | 0.71, -0.06/1.48 | 0.038, -0.08/0.15 | 0.038, -0.08/0.15 | - / - | 4.1564 | 78.2 | 0.00 | 8.83 | 97.01 | 91.7% |
| 200 | 0.043 | 1 | 5 | 2.64, -2.6/7.8 | 0.70, -0.04/1.44 | 0.038, -0.07/0.15 | 0.038, -0.07/0.15 | - / - | 4.1561 | 78.2 | 0.00 | 9.00 | 96.86 | 91.5% |
| 800 | 0.043 | 1 | 30 | 8.26, 1.6/14.9 | 0.99, 0.67/1.30 | 0.038, -0.01/8.2 | 0.038, -0.01/8.2 | - / - | 1.0542 | 39.4 | 0.00 | 18.64 | 85.99 | 82.2% |
| 800 | 0.043 | 1 | 75 | 8.26, 1.6/14.9 | 0.99, 0.67/1.30 | 0.038, -0.01/8.2 | 0.038, -0.01/8.2 | - / - | 1.0542 | 39.4 | 0.00 | 18.64 | 85.99 | 82.2% |
| 800 | 0.043 | 1 | 5 | 8.25, 1.7/14.8 | 0.99, 0.67/1.30 | 0.038, -0.01/8.2 | 0.038, -0.01/8.2 | - / - | 1.0542 | 39.4 | 0.00 | 18.63 | 86.00 | 82.2% |
| 1200 | 0.043 | 1 | 30 | 13.25, 6.8/19.7 | 1.00, 0.83/1.16 | 0.038, 0.01/6.7 | 0.038, 0.01/6.7 | - / - | 0.3524 | 22.7 | 0.03 | 21.43 | 77.10 | 78.2% |
| 1200 | 0.043 | 1 | 75 | 46.93, -67.4/161 | 0.74, 0.54/0.95 | 0.038, 0.01/6.9 | 0.038, 0.01/6.9 | - / - | 0.8399 | 35.2 | 0.05 | 35.09 | 38.69 | 52.4% |
| 1200 | 0.043 | 1 | 5 | 13.24, 6.9/19.6 | 1.00, 0.83/1.17 | 0.038, 0.01/6.9 | 0.038, 0.01/6.9 | - / - | 0.3524 | 22.7 | 0.03 | 21.42 | 77.07 | 78.2% |
| 600 | 0.043 | 1 | 30 | 6.14, -0.07/12.4 | 0.95, 0.53/1.37 | 0.038, -0.02/9.3 | 0.038, -0.02/9.3 | - / - | 1.6779 | 49.7 | 0.00 | 16.26 | 90.19 | 84.7% |
| 600 | 0.043 | 1 | 75 | 20.02, -70/110 | 0.61, 0.28/0.95 | 0.038, -0.04/0.11 | 0.038, -0.04/0.11 | - / - | 2.3662 | 59.1 | 0.00 | 26.86 | 63.97 | 70.4% |
| 600 | 0.043 | 1 | 5 | 6.12, 0.02/12.2 | 0.95, 0.53/1.37 | 0.038, -0.02/9.31 | 0.038, -0.02/9.31 | - / - | 1.6779 | 49.7 | 0.00 | 16.22 | 90.19 | 84.8% |

* The total percentage of mass volatilised, penetrated into sediment and transformed in water may exceed 100% because of back-diffusion of mass from the sediment into the water, where next, it may be transformed.

^A Range of organic matter content allowed in optimisation runs: 0.038 – 0.048.

^B Range of water concentration allowed in optimisation runs: 0.1 – 5.0.

^C Range of $DegT_{50,water}$ allowed during optimisation runs: 1 – 100.

^D Percentages here expressed as percentage of total mass in cosm (i.e. former criterion, now replaced by footnote E) instead as percentages of total mass dissipated from water layer. However, these percentages are not relevant for this cosm study as $F_{M,deg-wat} > 50\%$ (i.e. the last column), see also Figure 2.3.

^E (Mass degraded in water)/(Mass degraded in water + Mass volatilised + Mass penetrated into sediment) * 100%.

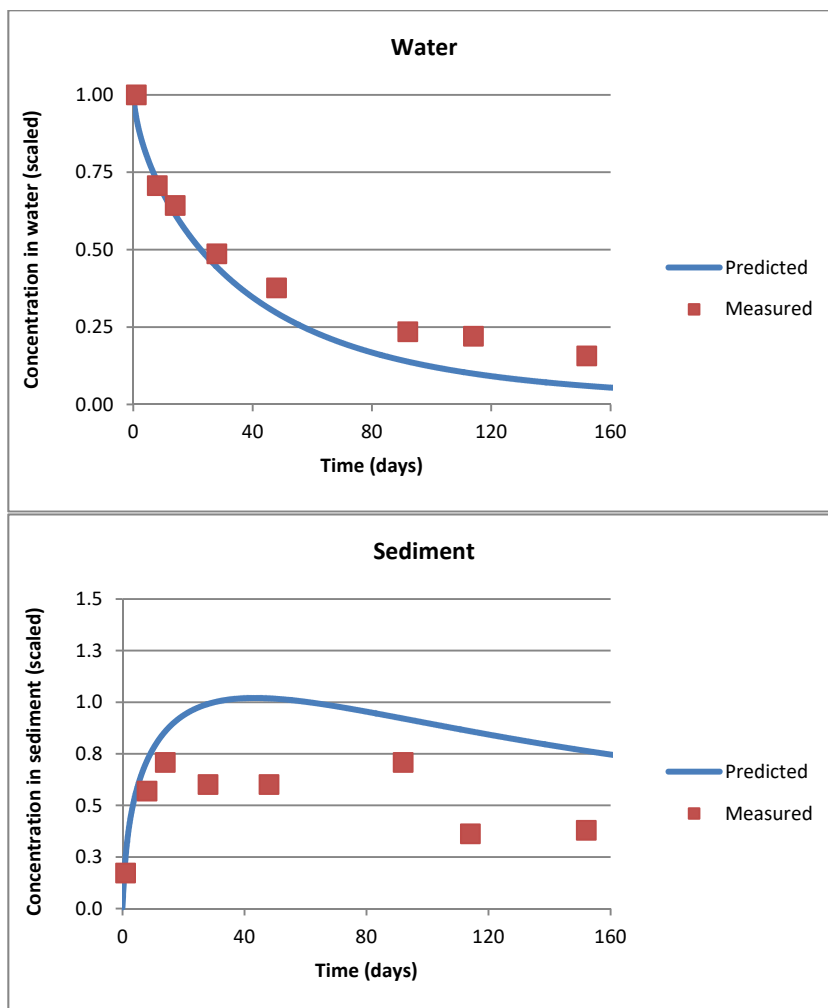


Figure A5.2 Simulated and measured concentrations of linuron in water and sediment; data simulated using an additional weight factor for water measurements, $DegT_{50,water} = 13.25$ days, an organic matter content of sediment of 3.8% and an initial scaled water concentration of 1.00 (initial values used in the estimation are given as the seventh entry in Table A5.5).

Appendix 6 Inverse modelling with TOXSWA-PEST for the cosm study with metsulfuron-methyl

For metsulfuron-methyl one study was found that is suitable for the estimation of the $DegT_{50,water}$ by inverse modelling by TOXSWA-PEST. The study with metsulfuron-methyl in outdoor glass tanks was described by Wang et al. (2011) and its main characteristics have been summarized in Table A6.1.

Table A6.1 Data on cosm studies with metsulfuron-methyl.

| Label in data file | MSM_Cosm1 |
|-----------------------------|---|
| Reference | Wang et al. (2011) |
| Compound | ¹⁴ C-metsulfuron-methyl (96.2%) |
| Type of system | Outdoor glass tanks |
| Dimensions system | 0.95 x 0.70 x 0.45 m |
| Side slope (hor/vert) | 0 |
| Depth water layer (m) | 0.15 |
| Depth sediment (cm) | Estimated: 20 (140 kg) |
| Sediment om% | 3.05% OM |
| Sediment bulk density | Not given, estimated 1.2 kg/dm ³ |
| Sediment porosity | - |
| Macrophytes info | No macrophytes present |
| pH | |
| Temperature | |
| Light intensity | |
| Application number | 1 |
| Application interval | - |
| Nominal initial application | 105.5 mg, which corresponds to 1 mg/L |

In Table A6.2 below we summarized the input values on the physico-chemical properties of metsulfuron-methyl.

Table A6.2 Parameter values used in the simulations with metsulfuron-methyl.

| Property | Value |
|---------------------------------|---|
| Molar mass (g) | 381.36 |
| Saturated vapour pressure (mPa) | $1.4 \cdot 10^{-8}$ (25 °C) |
| Solubility (mg/L) | 2790 (20 °C) |
| Koc (estimated) (L/kg) | Kf=0.77, Kfoc=12.0; 1/n=0.98; Kom assumed 7.0; adjusted Kom 7.3 |
| pKa | 3.75, weak acid |

Wang et al.

Wang et al. (2011) monitored radio-labelled metsulfuron-methyl in water (depth 15 cm) and sediment (depth not given, estimated 2 cm; 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.

For the study by Wang et al. (2011) average temperature during the measurements is not given. No date of application was given and hence it is rather difficult to estimate actual temperatures during the experiments. An average temperature of 15°C was assumed in the reverse modelling.

Table A6.3 presents the measured concentrations in water and sediment as a function of time in the cosm study of Wang et al. (2011). Initially systems contained 105.5 mg, which corresponds to 1.0 mg/L in water and/or 0.754 10⁻³ g/kg in the sediment. Aqueous and sediment concentrations are read from Figure 2 and Figure 3 resp., and have been recalculated from values in the publication, which were given as percentages of the initial amount present. Water was filtered using a 0.45 µm Millipore membrane before analysis through HPLC.

Table A6.3 Measured concentrations in water (mg/L and scaled) and sediment (g/kg and scaled, average of 0 – 15 cm sediment depth) as a function of time (d) for the cosm study with metsulfuron-methyl by Wang et al. (2011). Concentration in water is the concentration of the parent compound only, without metabolite(s), whereas concentration in sediment is the total concentration of parent and metabolites (of extractable residue, i.e. without the separately measured bound residue). Water was filtered prior to HPLC analysis.

| Number | Time (days) | Concentration in water (mg/L) | Scaled concentration in water | Concentration in sediment (g/kg) | Scaled concentration in sediment |
|--------|-------------|-------------------------------|-------------------------------|----------------------------------|----------------------------------|
| 1 | 0 | 1.00 [#] | - | - | - |
| 2 | 1 | 0.85 | 1.0000 | 0.0196 E-3 | 0.02306 E-3 |
| 3 | 5 | 0.47 | 0.5529 | 0.0287 E-3 | 0.03377 E-3 |
| 4 | 10 | 0.33 | 0.3882 | 0.0490 E-3 | 0.05765 E-3 |
| 5 | 20 | 0.20 | 0.2353 | 0.0754 E-3 | 0.08871 E-3 |
| 6 | 30 | 0.15 | 0.1765 | 0.0943 E-3 | 0.1109 E-3 |
| 7 | 45 | 0.10 | 0.1177 | 0.1056 E-3 | 0.1242 E-3 |
| 8 | 60 | 0.03 | 0.0353 | 0.1056 E-3 | 0.1242 E-3 |
| 9 | 90 | 0.01 | 0.0118 | 0.09802 E-3 | 0.1153 E-3 |

[#] Initial nominal concentration, not measured but calculated from dosed amount.

The authors present a graph depicting the concentration of metsulfuron-methyl in sediment (total extractable, i.e. possibly including metabolites) from which it is apparent that the maximum concentration in sediment was approx. 14% of the mass initially added to the system (measured on days 45 and 60 after application). This relatively high percentage may in part be caused by the relatively low water depth (0.15 m) in the systems used.

The inverse modelling was performed using scaled concentrations. Since the organic matter content of the sediment (upper 2 cm) was given as 3.05%, the OM% was allowed to vary from 2.55 – 3.55% (Method B9 of Figure 2.2).

Aqueous concentration was allowed to vary from 0.1 – 5 (scaled) with an initial estimate of 1.0, and $DegT_{50,water}$ was allowed to vary from 0.5 – 50 days with an initial estimate of 5, 20 or 1 days (Table 3.8).

Runs were performed using values for bulk density of 0.2, 0.8 and 1.2 kg/L (red stars of Figure 3.2), using an initial organic matter content of 3.05%. Three additional runs were performed for a bulk density of 0.6 kg/L (purple stars of Figure 3.2).

Results for the runs are summarised in Table A6.4. Satisfactory runs (χ^2 – error below 25% and degradation in the water phase accounting for at least 50% of total dissipation) were not obtained for any of the runs.

A second set of calculations was performed, using a multiplication factor for the relative weight of water layer to sediment of 6¹⁴, approximating the ratio between water degradation (86%) and sediment penetration (14%) found in the best fit of the first set of calculations (χ^2 – error of 27.9%). The results for these calculations, using the same values for bulk density, organic matter content etc., are given in Table A6.5.

As can be seen when comparing Figures A6.1 and A6.2 which both represent the fits with best statistics within their sets of simulations, the introduction of an extra weight factor 6 for the water concentrations clearly improves the quality of the fit of water concentrations, but at the same time clearly decreases the quality of the fit of sediment concentrations. Overall, the introduction of a multiplication factor of 6 improves the quality of the reverse modelling of water concentrations to the extent that results of the inverse modelling are considered reliable. Six runs have similar χ^2 – errors (runs 4 – 6 with an error of 28.6%, runs 10-12 with an error of 26.6% of Table A6.5) and yielded values of $DegT_{50,water}$ close together (6.35, 6.41, 6.47, 6.41, 6.41 and 6.42 days resp.). The average (geomean) value for $DegT_{50,water}$ of these 6 runs is 6.41 days. In this way we are able to use the information captured in the study of Wang et al. (2011) on metsulfuron-methyl, instead of neglecting its information.

¹⁴ The extra weight factor used in the calculations was inadvertently set at 6, although the ratio between the mass transformed in water and penetrated into the sediment actually was approximately 4.5, i.e. 64.44% / 13.92%.

Table A6.4 Results of the initial 9 runs of PEST_TOXSWA inverse modelling ('Method B9' of Figure 2.2) for metsulfuron-methyl data from Wang et al. (2011) using given initial values for parameters bulk density, organic matter, initial water concentration $C_{t=0}$ and initial $DegT_{50, water}^*$

| Input used in optimisation runs | | | | | Results of optimisation runs | | | | | | | | | |
|---------------------------------|--|---|-------------------------------------|-------------------------------------|---|---------------------------------------|-------------------------------------|--------------------------------|---------------------------------------|-----------------------|--|---|---|--|
| Bulk density (g/L) | Initial organic matter fraction ^A (-) | Initial water concentration ^B (mg/L) | Initial $DegT_{50, water}^C$ (days) | Estimated $DegT_{50, water}$ (days) | Estimated init water concentration (mg/L) | Estimated organic matter fraction (-) | No of runs needed in estimation (-) | Visual goodness of fit (+/0/-) | Sum of squared weighted residuals (-) | Chi-square Error% (%) | Percentage of substance volatilised (%) ^D | Percentage of substance penetrated into sediment (%) ^D | Percentage of substance transformed in water (%) ^D | Mass degraded in water, as a percentage of total mass dissipated from water (%) ^E |
| 200 | 0.0305 | 1 | 5 | 48.9, -58/156 | 0.14, -0.15/0.43 | 0.0255, -3.2/3.3 | 75 | - / 0 | 0.1406 | 45.0 | 0.00* | 21.90* | 44.76* | 67.2% |
| 200 | 0.0305 | 1 | 20 | 48.8, -63/161 | 0.14, -0.15/0.43 | 0.0255, -3.3/3.3 | 69 | - / 0 | 0.1406 | 45.0 | 0.00 | 21.90 | 44.76 | 67.2% |
| 200 | 0.0305 | 1 | 1 | 48.9, -64/162 | 0.14, -0.15/0.43 | 0.0255, -3.3/3.3 | 95 | - / 0 | 0.1406 | 45.0 | 0.00 | 21.90 | 44.76 | 67.2% |
| 800 | 0.0305 | 1 | 5 | 30.4, 2.4/58.4 | 0.74, 0.48/1.01 | 0.0355, -0.1/0.2 | 58 | - / - | 0.06793 | 31.3 | 0.00 | 12.67 | 64.23 | 83.5% |
| 800 | 0.0305 | 1 | 20 | 30.4, 2.4/58.3 | 0.75, 0.48/1.01 | 0.0355, -0.1/0.2 | 48 | - / - | 0.06793 | 31.3 | 0.00 | 12.67 | 64.23 | 83.5% |
| 800 | 0.0305 | 1 | 1 | 30.3, 3.0/57.7 | 0.75, 0.48/1.01 | 0.0355, -0.1/0.2 | 69 | - / - | 0.06793 | 31.3 | 0.00 | 12.67 | 64.32 | 83.5% |
| 1200 | 0.0305 | 1 | 5 | 32.1, -19.5/83.8 | 0.90, 0.41/1.39 | 0.0355, -0.1/0.2 | 48 | - / - | 0.2026 | 54.0 | 0.00 | 10.02 | 64.22 | 86.5% |
| 1200 | 0.0305 | 1 | 20 | 32.2, -20.4/84.7 | 0.90, 0.41/1.39 | 0.0355, -0.1/0.2 | 48 | - / - | 0.2026 | 54.0 | 0.00 | 10.02 | 64.22 | 86.5% |
| 1200 | 0.0305 | 1 | 1 | 32.1, -20.1/84.4 | 0.90, 0.41/1.39 | 0.0355, -0.1/0.2 | 67 | - / - | 0.2026 | 54.0 | 0.00 | 10.02 | 64.37 | 86.5% |
| 600 | 0.0305 | 1 | 5 | 29.5, 4.7/54.2 | 0.58, 0.36/0.80 | 0.0255, -0.2/0.2 | 45 | - / - | 0.05408 | 27.9 | 0.00 | 13.92 | 64.44 | 82.2% |
| 600 | 0.0305 | 1 | 20 | 29.4, 4.8/54.0 | 0.58, 0.36/0.80 | 0.0255, -0.2/0.2 | 34 | - / - | 0.05408 | 27.9 | 0.00 | 13.92 | 64.44 | 82.2% |
| 600 | 0.0305 | 1 | 1 | 29.5, 4.6/54.3 | 0.58, 0.36/0.80 | 0.0255, -0.2/0.2 | 80 | - / - | 0.05408 | 27.9 | 0.00 | 13.92 | 64.44 | 82.2% |

* The total percentage of mass volatilised, penetrated into sediment and transformed in water may exceed 100% because of back-diffusion of mass from the sediment into the water, where next, it may be transformed.

^A Range of organic matter content allowed in optimisation runs: 0.0255 – 0.0355.

^B Range of water concentration allowed in optimisation runs: 0.1 – 5.0.

^C Range of $DegT_{50, water}$ allowed during optimisation runs: 0.5 – 50.

^D Percentages here expressed as percentage of total mass in cosm (i.e. former criterion, now replaced by footnote E) instead as percentages of total mass dissipated from water layer. However, these percentages are not relevant for this cosm study as $F_{M, Deg-wat} > 50\%$ (i.e. the last column), see also Figure 2.3.

^E (Mass degraded in water)/(Mass degraded in water + Mass volatilised + Mass penetrated into sediment) * 100%.

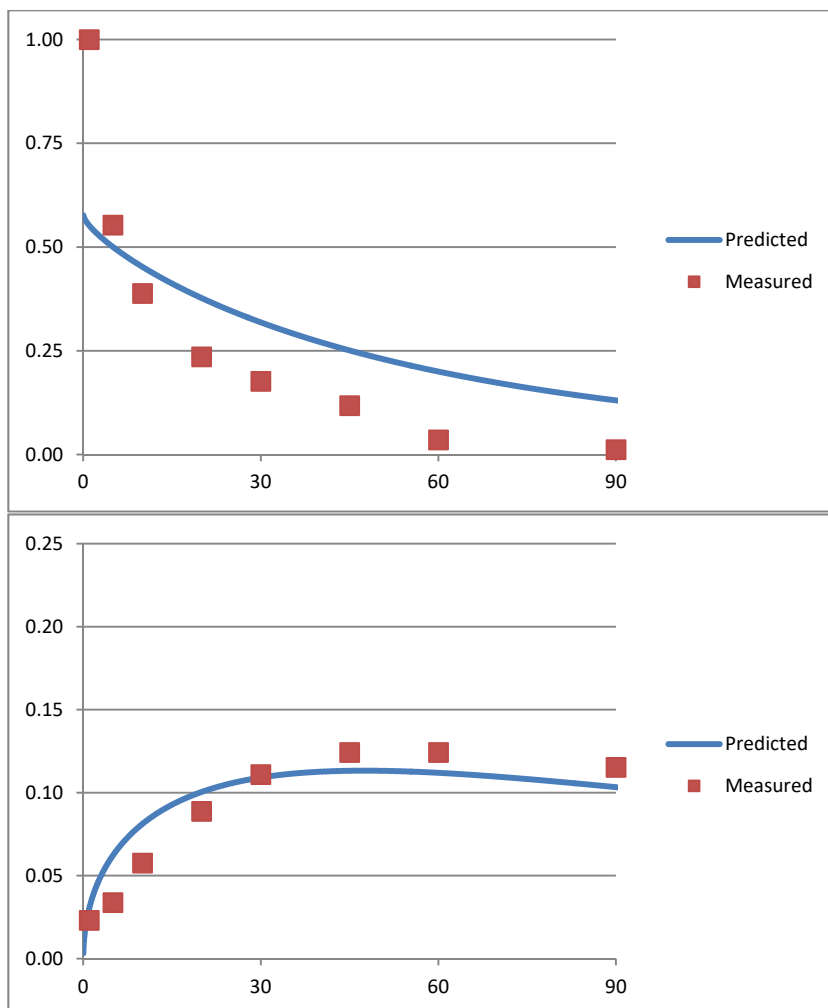


Figure A6.1 Simulated and measured concentrations of metsulfuron-methyl in water and sediment; data simulated using $\text{Deg}T_{50, \text{water}} = 29.5$ days, an organic matter content of sediment of 2.55% and an initial scaled water concentration of 0.58 (initial values used in the estimation are given as the tenth entry in Table A6.4).

Table A6.5 Results using a multiplication factor 6 (i.e. using water data with an enhanced weighting factor of 6) for the initial 9 runs of PEST_TOXSWA inverse modelling ('Method B9') for metsulfuron-methyl data from Wang et al. (2011) using given initial values for parameters bulk density, organic matter, initial water concentration $C_{t=0}$ and initial $DegT_{50,water}$.

| Input used in optimisation runs | | | | Results of optimisation runs | | | | | | | | | | |
|---------------------------------|--|---|--|-------------------------------|--------------------------------------|---------------------------------------|-------------------------------------|--------------------------------|---------------------------------------|-----------------------|--|---|---|--|
| Bulk density (g/L) | Initial organic matter fraction ^A (-) | Initial water concentration ^B (mg/L) | Initial DegT _{50,water} ^C (days) | Estimated DegT50,water (days) | Estimated water concentration (mg/L) | Estimated organic matter fraction (-) | No of runs needed in estimation (-) | Visual goodness of fit (+/0/-) | Sum of squared weighted residuals (-) | Chi-square Error% (%) | Percentage of substance volatilised (%) ^D | Percentage of substance penetrated into sediment (%) ^D | Percentage of substance transformed in water (%) ^D | Mass degraded in water, as a percentage of total mass dissipated from water (%) ^E |
| 200 | 0.0305 | 1 | 5 | 3.48, 0.02/6.95 | 0.89, 0.46/1.33 | 0.0255, -1.0/1.1 | 40 | - / - | 1.7387 | 61.3 | 0.00* | 6.43* | 97.68* | 93.8% |
| 200 | 0.0305 | 1 | 20 | 19.49, 3.4/35.5 | 0.40, 0.07/0.72 | 0.0255, -0.64/0.69 | 33 | - / - | 2.9845 | 80.4 | 0.00 | 14.62 | 75.13 | 83.7% |
| 200 | 0.0305 | 1 | 1 | 3.31, 0.25/6.37 | 0.92, 0.46/1.38 | 0.0255, -1.1/1.1 | 63 | - / - | 1.7375 | 61.3 | 0.00 | 6.32 | 97.75 | 93.9% |
| 800 | 0.0305 | 1 | 5 | 6.35 , 3.87/8.82 | 1.00, 0.81/1.18 | 0.0355, -0.28/0.35 | 48 | + / - | 0.3779 | 28.6 | 0.00 | 5.95 | 96.66 | 94.2% |
| 800 | 0.0305 | 1 | 20 | 6.41 , 3.86/8.97 | 0.99, 0.81/1.18 | 0.0355, -0.28/0.35 | 39 | + / - | 0.3778 | 28.6 | 0.00 | 6.04 | 96.65 | 94.1% |
| 800 | 0.0305 | 1 | 1 | 6.47 , 3.87/8.87 | 1.00, 0.81/1.18 | 0.0355, -0.28/0.35 | 58 | + / - | 0.3778 | 28.6 | 0.00 | 5.96 | 96.59 | 94.2% |
| 1200 | 0.0305 | 1 | 5 | 6.00, 3.28/8.73 | 1.00, 0.78/1.22 | 0.0355, -0.43/0.50 | 47 | + / - | 0.5142 | 33.3 | 0.00 | 4.39 | 97.60 | 95.7% |
| 1200 | 0.0305 | 1 | 20 | 6.06, 3.26/8.86 | 1.00, 0.78/1.22 | 0.0355, -0.42/0.50 | 46 | + / - | 0.5142 | 33.3 | 0.00 | 4.40 | 97.53 | 95.7% |
| 1200 | 0.0305 | 1 | 1 | 5.99, 3.28/8.70 | 1.00, 0.78/1.22 | 0.0355, -0.43/0.50 | 54 | + / - | 0.5142 | 33.3 | 0.00 | 4.39 | 97.61 | 95.7% |
| 600 | 0.0305 | 1 | 5 | 6.41 , 4.06/8.75 | 0.99, 0.82/1.16 | 0.0355, -0.24/0.31 | 39 | + / - | 0.3257 | 26.6 | 0.00 | 6.81 | 96.09 | 93.4% |
| 600 | 0.0305 | 1 | 20 | 6.41 , 4.06/8.75 | 0.99, 0.82/1.16 | 0.0355, -0.24/0.31 | 38 | + / - | 0.3257 | 26.6 | 0.00 | 6.81 | 96.09 | 93.4% |
| 600 | 0.0305 | 1 | 1 | 6.42 , 4.06/8.77 | 0.99, 0.82/1.16 | 0.0355, -0.24/0.31 | 53 | + / - | 0.3257 | 26.6 | 0.00 | 6.81 | 96.09 | 93.4% |

* The total percentage of mass volatilised, penetrated into sediment and transformed in water may exceed 100% because of back-diffusion of mass from the sediment into the water, where next, it may be transformed.

^A Range of organic matter content allowed in optimisation runs: 0.0255 – 0.0355.

^B Range of water concentration allowed in optimisation runs: 0.1 – 5.0.

^C Range of $DegT_{50,water}$ allowed during optimisation runs: 0.5 – 50.

^D Percentages here expressed as percentage of total mass in cosm (i.e. former criterion, now replaced by footnote E) instead as percentages of total mass dissipated from water layer. However, these percentages are not relevant for this cosm study as $F_{M,deg-wat} > 50\%$ (i.e. the last column), see also Figure 2.3.

^E (Mass degraded in water)/(Mass degraded in water + Mass volatilised + Mass penetrated into sediment) * 100%.

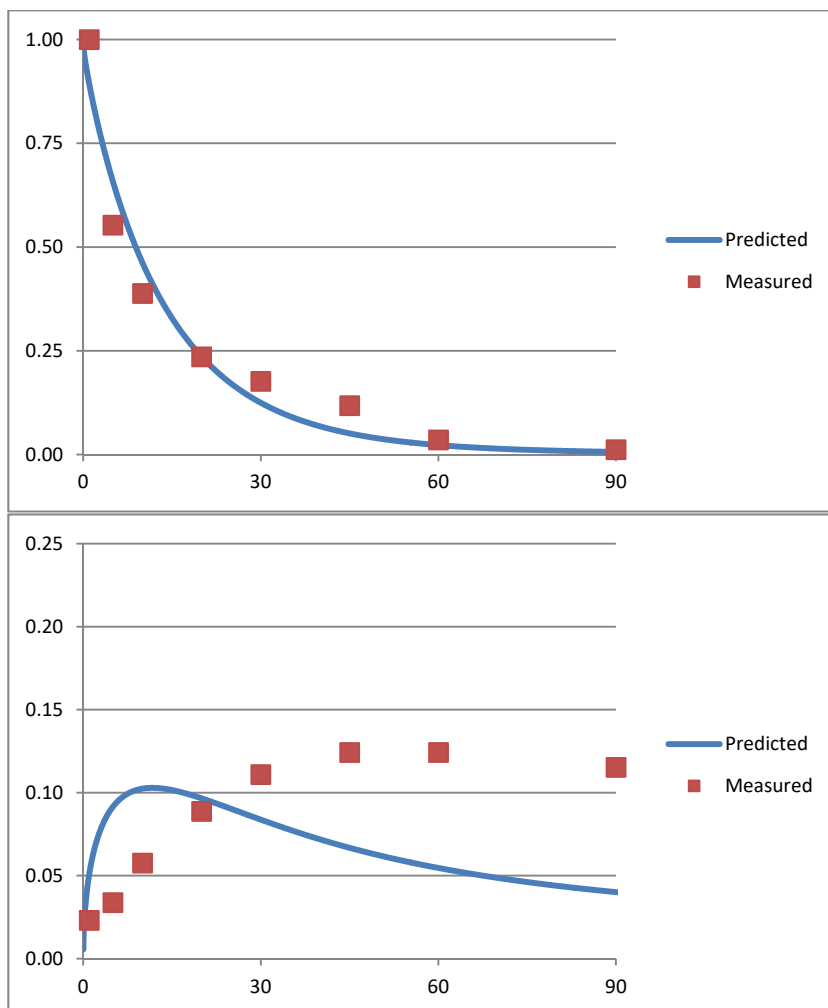


Figure A6.2 Simulated and measured concentrations of metsulfuron-methyl in water and sediment; data simulated using an additional weight factor for water measurements, $DegT_{50,water} = 6.41$ days, an organic matter content of sediment of 3.55% and an initial scaled water concentration of 0.99 (initial values used in the estimation are given as the tenth entry in Table A6.5).

Appendix 7 Inverse modelling with TOXSWA-PEST for the cosm study with prosulfocarb

For prosulfocarb one study was found that is suitable for the estimation of the $DegT_{50,water}$ by inverse modelling by TOXSWA-PEST. The study in outdoor experimental ditches was described by Arts et al. (2006). Its main characteristics have been summarized in Table A7.1. The study has also been briefly described in the main text of Chapter 4.3.

Adriaanse et al. (2013) performed an inverse modelling study to determine its $DegT_{50,water}$ by a similar method as the one of this report, but analysed more extensively the simulations and their results. We will compare the results of our simplified estimation method to the results of their analysis.

Table A7.1 Data on the cosm study with prosulfocarb.

| Label in data file | PSC_Cosm1 |
|-----------------------------|---|
| Reference | Arts et al. (2006) |
| Compound | Boxer, 806 g/L prosulfocarb |
| Type of system | Outdoor ditches, Renkum |
| Dimensions system | LxWxD: 40 x 3.3 x 0.57 m ³ |
| Side slope (hor/vert) | Outdoor ditches, 3/2 (Adriaanse et al, 2013) |
| Depth water layer (m) | 0.57, corresponds to 56 m ³ water |
| Depth sediment (cm) | 25 cm, samples for upper 15 cm |
| Sediment om% | 3% (Adriaanse et al., 2013) |
| Sediment bulk density | Upper 5 cm: 1.21 kg/L |
| Sediment porosity | Upper 5 cm: 0.54 L/L |
| Macrophytes info | Average 94.9 g m ⁻² bottom area |
| pH | June 2002, 7.5 – 8.8 (avg. 8.1) |
| Temperature | June 2002, 11 – 15°C (avg. 14°C) |
| Light intensity | Not specified |
| Application number | 1 |
| Application interval | - |
| Nominal initial application | 3, 15 and 76 µg/L (only data for highest level taken from Adriaanse et al., 2013) |

In Table A7.2 below we summarized the input values on the physico-chemical properties of prosulfocarb.

Table A7.2 Parameter values used in the simulations with prosulfocarb.

| Property | Value |
|---------------------------------|---|
| Molar mass (g) | 251.39 |
| Saturated vapour pressure (mPa) | 0.79 (25°C) |
| Solubility (mg/L) | 13.2 (20°C) |
| Koc (estimated) (L/kg) | Kf=23.1, Kfoc=1693; Kom=1693/1.72=984; Kom adjusted=1091 (on basis of $C_{t=0}$ of 0.0754 mg/L); 1/n=0.96 |
| pKa | Not applicable |

Arts et al.

Arts et al. (2006) report a mesocosm study giving details of the fate of several pesticides, among others prosulfocarb, in a study in artificial ditches. The study gives sufficient detail (7 measurements in water, 5 measurements in the upper 5 cm of the sediment layer) for the analysis of fate data as intended in the current study. Water depth was 0.57 m, sediment depth was 0.25 m. Although sediment dry bulk density (1.21 kg/L) and porosity (0.54 L/L) are given for the upper 5 cm, its organic matter content is not reported.

Table A7.3 presents the measured concentrations in water and sediment as a function of time in the cosm study of Arts et al. (2006). Initially systems contained 4200 mg, which corresponds to 0.075 mg/L in 56 m³ of water and/or 0.2197 10⁻³ g/kg in the 19118 kg of the upper 25 cm of sediment. Aqueous and sediment concentrations are taken from Table 1 in the publication. Water was not filtered before analysis through HPLC.

Table A7.3 Measured concentrations in water (mg/L and scaled) and sediment (g/kg and scaled, average of 0 – 15 cm sediment depth) as a function of time (d) for the cosm study with prosulfocarb by Arts et al. (2006); data taken from Adriaanse et al. (2013). Water was not filtered prior to HPLC analysis.

| Number | Time (days) | Concentration in water (mg/L) | Scaled concentration in water | Concentration in sediment (g/kg) | Scaled concentration in sediment |
|--------|-------------|-------------------------------|-------------------------------|----------------------------------|----------------------------------|
| 1 | 0 | 0.0750 [#] | - | - | - |
| 2 | 0.08 | 0.0754 | 0.9831 | | |
| 3 | 0.33 | 0.0767 | 1.0000 | | |
| 4 | 1 | 0.0592 | 0.7718 | 9.886 E-6 | 128.9 E-6 |
| 5 | 3 | 0.0450 | 0.5867 | 23.81 E-6 | 310.4 E-6 |
| 6 | 7 | 0.0281 | 0.3664 | 22.25 E-6 | 290.1 E-6 |
| 7 | 14 | 0.0146 | 0.1904 | 18.05 E-6 | 235.3 E-6 |
| 8 | 28 | 0.0039 | 0.0509 | 8.200 E-6 | 106.9 E-6 |

[#] Initial nominal concentration, not measured but calculated from dosed amount.

The maximum amount of prosulfocarb in the sediment was 11.0% 3 days after application (taken from Adriaanse et al. 2012).

The inverse modelling was performed using scaled concentrations. Since the organic matter content of the sediment was not given and hence considered unknown, OM% was allowed to vary from 2.5 – 50% (Method B8 of Figure 2.1).

Aqueous concentration was allowed to vary from 0.1 – 5 (scaled) with an initial estimate of 1.0, and $DegT_{50,water}$ was allowed to vary from 0.5 – 50 days with an initial estimate of 5, 20 or 1 days (Table 3.4).

Runs were performed using values for bulk density of 0.2, 0.8 and 1.2 kg/L, using an initial organic matter content of 19, 9 and 3% resp. (red stars in Figure 3.1).

Results for the 9 initial and 6 additional runs are summarised in Table A7.4. Satisfactory runs (χ^2 – error below 25%, satisfactory visual correspondence between measured and simulated concentrations in water and sediment and degradation in the water phase accounting for at least 50% of total dissipation) were not obtained for any of the runs, although 4 of the runs had an χ^2 – error of 18.4% and a similar estimate for $DegT_{50,water}$ of 1.65 days. However, the visual correspondence between measured and simulated concentrations in the cosm water was not satisfactory, so the results were judged to be unreliable.

So, a second set of calculations was performed, using a multiplication factor of 22, approximating the ratio between water degradation (98%) and sediment penetration (4.5%) found in the first set of

calculations for the lowest χ^2 – errors of 18.4%. The results for these calculations, using the same values for bulk density, organic matter content etc., are given in Table A7.5.

As can be seen when comparing Figures A7.1 and A7.2 which both represent the fits with best statistics within their sets of simulations, the introduction of an extra weight factor 22 for the water concentrations clearly improves the quality of the fit of water concentrations, but at the same time clearly decreases the quality of the fit of sediment concentrations. Overall, the introduction of a multiplication factor of 22 improves the quality of the reverse modelling of water concentrations to the extent that results of the inverse modelling are considered reliable. Four runs have similar χ^2 – errors (runs 4 and 6 with an error of 13.2%, and runs 7 and 9 with an error of 9.0%) and yielded values of $DegT_{50,water}$ close together (2.77, 2.76, 2.94 and 2.94 days resp.). The average (geomean) value for $DegT_{50,water}$ of these 4 runs is 2.85 days.

This value for $DegT_{50,water}$ is clearly different from the value derived from the first set of calculations (1.77 days). This demonstrates that our standard optimisation procedure for the prosulfocarb study was correctly judged to be unreliable, (it did indeed not fulfil all quality criteria).

Only by using expert judgement (using a multiplication factor of 22 to increase the relative weight of the correspondence between simulated and measured concentrations in the water layer) we were able to find satisfactory runs and thus satisfactory estimates for the $DegT_{50,water}$. The value of 2.85 days is confirmed by the value of 2.9 days found by Adriaanse et al. (2013) in their inverse modelling exercise for the same cosm study.

Below we compare our expert-adjusted optimisation procedure to the procedure of Adriaanse et al. (2013). Within the scope of this study we were not able to implement the recommendations we do here below.

On the other hand our expert-adjusted optimisation procedure did not result in the best possible fit between measured and simulated concentrations in water and sediment. In their Figure 2 Adriaanse et al. (2013) showed, by forward running of TOXSWA for combinations of organic matter content and bulk density spanning the range of 0-1.0 g/g and 0.2-1.2 kg/L, respectively, that the best fit (lowest phi value) was located in the orange band of organic matter ranging from approximately 0.3 to 0.5 g/g and a bulk density of 0.2 to 0.9 kg/L. As Table A7.4 and A7.5 demonstrate our optimisation procedure did not find these combinations of bulk density and organic matter content (the best fits of Table A7.5 have organic matter contents of 2.5%, i.e. the allowed lower boundary value instead of the organic matter contents of 30% or higher found by Adriaanse et al. (2013)). Apparently our optimisation procedure does not succeed into stepping to the orange band of Figure 2 of Adriaanse et al. (2013). Therefore we would recommend to explore whether our standard optimisation procedure would result in finding these best fits if we would start from initial values of bulk densities and organic matter content that are closer to those in the orange band of Figure 2 of Adriaanse et al. (2013). Note that Adriaanse et al. (2013) did include sorption to macrophytes in their optimisation procedure, which we do not here, so this might also explain that the optimisation procedure might be different.

Note that the cosm of this study with prosulfocarb is an experimental ditch in which macrophytes grow and decay, and organic matter contents of 26% have been measured in these ditches (Crum et al., 1998). In ditches, next to arable fields in the Netherlands and cleaned at least once a year, organic matter contents of 30 to 34% have been measured in their upper centimetre of sediment, coupled to bulk densities of 0.1 to 0.2 kg/L. So, organic matter contents higher than the maximum of 19% we use in our optimisation procedure can happen in reality. Therefore we would recommend to add a combination of initial values of organic matter content and bulk density to the second set of optimisations (the purple stars of Figure 3.1 and 3.2), e.g. a bulk density of 0.2 kg/L coupled to an organic matter content of 40%.

Table A7.4 Results of the 9 initial and 6 additional runs of PEST_TOXSWA inverse modelling (Method B8' of Figure 2.2) for prosulfocarb data from Arts et al. (2006) using given initial values for parameters bulk density, organic matter, initial water concentration $C_{t=0}$ and initial $DegT_{50,water}$.

| Input used in optimisation runs | | | | | Results of optimisation runs | | | | | | | | | |
|---------------------------------|--|---|---|------------------------------------|---|---------------------------------------|-------------------------------------|--------------------------------|---------------------------------------|-----------------------|--|---|---|--|
| Bulk density (g/L) | Initial organic matter fraction ^A (-) | Initial water concentration ^B (mg/L) | Initial $DegT_{50,water}$ ^C (days) | Estimated $DegT_{50,water}$ (days) | Estimated init water concentration (mg/L) | Estimated organic matter fraction (-) | No of runs needed in estimation (-) | Visual goodness of fit (+/0/-) | Sum of squared weighted residuals (-) | Chi-square Error% (%) | Percentage of substance volatilised (%) ^D | Percentage of substance penetrated into sediment (%) ^D | Percentage of substance transformed in water (%) ^D | Mass degraded in water, as a percentage of total mass dissipated from water (%) ^E |
| 200 | 0.19 | 1 | 5 | 1.85, -1.3/5.0 | 0.16, -0.52/0.85 | 0.025, -0.23/0.28 | 49 | - / + | 0.3423 | 56 | 0.37* | 4.02* | 97.69* | 95.7% |
| 200 | 0.19 | 1 | 20 | 19.73, -25.0/64.4 | 0.10, -0.72/0.92 | 0.025, -0.19/0.24 | 33 | - / - | 0.9069 | 92 | 1.40 | 12.00 | 41.20 | 75.5% |
| 200 | 0.19 | 1 | 1 | 1.85, -1.3/5.0 | 0.16, -0.52/0.85 | 0.025, -0.23/0.28 | 44 | - / + | 0.3423 | 56 | 0.37 | 4.02 | 97.69 | 95.7% |
| 800 | 0.09 | 1 | 5 | 4.65, 1.1/8.2 | 0.33, -0.18/0.83 | 0.025, -0.02/6.68 | 32 | - / + | 0.2502 | 48 | 0.73 | 8.02 | 85.92 | 90.8% |
| 800 | 0.09 | 1 | 20 | 15.89, -23.8/55.6 | 0.19, -0.37/0.75 | 0.025, -0.04/8.51 | 34 | - / + | 0.4195 | 62 | 1.37 | 14.03 | 46.84 | 75.3% |
| 800 | 0.09 | 1 | 1 | 1.45, -0.05/2.96 | 0.62, 0.18/1.07 | 0.025, -0.03/7.98 | 41 | - / + | 0.1351 | 35 | 0.26 | 4.62 | 97.88 | 95.3% |
| 1200 | 0.03 | 1 | 5 | 1.65, 0.65/2.64 | 0.90, 0.67/1.13 | 0.025, -0.002/5.2 | 34 | - / + | 0.03654 | 18.4 | 0.29 | 4.57 | 97.65 | 95.3% |
| 1200 | 0.03 | 1 | 20 | 14.31, -25.0/53.6 | 0.32, -0.18/0.82 | 0.025, -0.02/7.0 | 33 | - / - | 0.3373 | 56 | 1.32 | 12.66 | 50.76 | 78.4% |
| 1200 | 0.03 | 1 | 1 | 1.65, 0.67/2.63 | 0.90, 0.67/1.13 | 0.025, -0.002/5.1 | 36 | - / + | 0.03654 | 18.4 | 0.29 | 4.57 | 96.63 | 95.3% |
| 200 | 0.03 | 1 | 5 | 1.85, -1.31/5.01 | 0.16, -0.52/0.85 | 0.025, -0.23/0.28 | 52 | - / + | 0.3423 | 56 | 0.37 | 4.02 | 97.56 | 95.7% |
| 200 | 0.03 | 1 | 20 | 1.85, -1.30/5.00 | 0.16, -0.52/0.85 | 0.025, -0.23/0.28 | 91 | - / + | 0.3423 | 56 | 0.37 | 4.02 | 97.69 | 95.7% |
| 200 | 0.03 | 1 | 1 | 1.85, -1.24/4.93 | 0.16, -0.52/0.85 | 0.025, -0.23/0.28 | 62 | - / + | 0.3423 | 56 | 0.37 | 4.02 | 97.59 | 95.7% |
| 1200 | 0.19 | 1 | 5 | 1.65, 0.66/2.63 | 0.90, 0.67/1.13 | 0.025, -0.001/5.1 | 38 | - / + | 0.0365 | 18.4 | 0.29 | 4.57 | 97.63 | 95.3% |
| 1200 | 0.19 | 1 | 20 | 19.9, -42.8/82.6 | 0.25, -0.07/0.57 | 0.025, -0.40/0.45 | 27 | - / - | 0.3836 | 60 | 1.44 | 14.41 | 40.19 | 71.7% |
| 1200 | 0.19 | 1 | 1 | 1.65, 0.67/2.62 | 0.90, 0.67/1.13 | 0.025, -0.001/5.1 | 62 | - / + | 0.03635 | 18.4 | 0.29 | 4.57 | 97.63 | 95.3% |

* The total percentage of mass volatilised, penetrated into sediment and transformed in water may exceed 100% because of back-diffusion of mass from the sediment into the water, where next, it may be transformed.

^A Range of organic matter content allowed in optimisation runs: 0.025 – 0.50.

^B Range of water concentration allowed in optimisation runs: 0.1 – 50.

^C Range of $DegT_{50,water}$ allowed during optimisation runs: 0.5 – 50.

^D Percentages here expressed as percentage of total mass in cosm (i.e. former criterion, now replaced by footnote E) instead as percentages of total mass dissipated from water layer. However, these percentages are not relevant for this cosm study as $F_{M,deg-wat} > 50\%$ (i.e. the last column), see also Figure 2.3.

^E (Mass degraded in water)/(Mass degraded in water + Mass volatilised + Mass penetrated into sediment) * 100%.

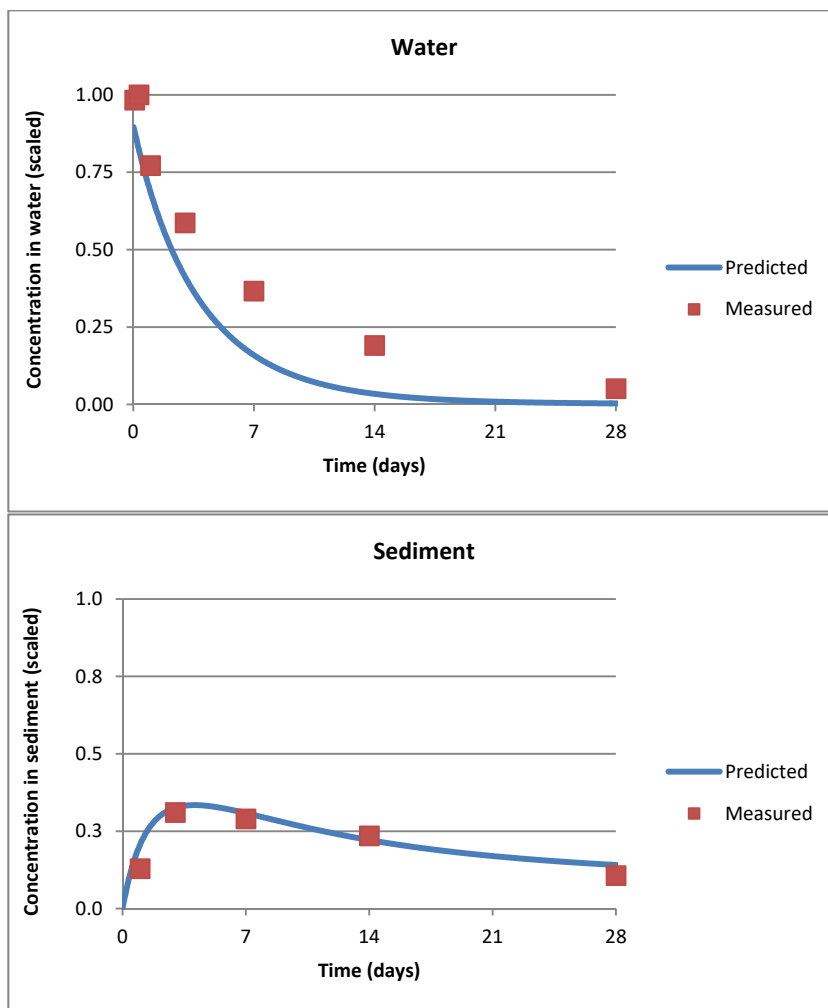


Figure A7.1 Simulated and measured concentrations of prosulfocarb in water and sediment; data simulated using $\text{Deg}T_{50, \text{water}} = 1.65$ days, an organic matter content of sediment of 2.5% and an initial scaled water concentration of 0.90 (initial values used in the estimation are given as the seventh entry in Table A7.4).

Table A7.5 Results using a multiplication factor of 22 (i.e. using water data with an enhanced weighting factor of 22) for the runs of PEST_TOXSWA inverse modelling ('Method B8' of Figure 2.1) for prosulfocarb data from Arts et al. (2006) using given initial values for parameters bulk density, organic matter, initial water concentration $C_{t=0}$ and initial $DegT_{50, water}$.

| Input used in optimisation runs | | | | Results of optimisation runs | | | | | | | | | | |
|---------------------------------|--|---|--|-------------------------------|---|---------------------------------------|-------------------------------------|--------------------------------|---------------------------------------|-----------------------|--|---|---|--|
| Bulk density (g/L) | Initial organic matter fraction ^A (-) | Initial water concentration ^B (mg/L) | Initial DegT _{50,water} ^C (days) | Estimated DegT50,water (days) | Estimated init water concentration (mg/L) | Estimated organic matter fraction (-) | No of runs needed in estimation (-) | Visual goodness of fit (+/0/-) | Sum of squared weighted residuals (-) | Chi-square Error% (%) | Percentage of substance volatilised (%) ^D | Percentage of substance penetrated into sediment (%) ^D | Percentage of substance transformed in water (%) ^D | Mass degraded in water, as a percentage of total mass dissipated from water ^E |
| 200 | 0.19 | 1 | 5 | 1.58, 0.18/2.98 | 0.99, 0.71/1.28 | 0.025, -0.03/7.7 | 30 | - / - | 19.23 | 37 | 0.28* | 3.62* | 98.15* | 96.2% |
| 200 | 0.19 | 1 | 20 | 1.58, 0.18/2.98 | 0.99, 0.71/1.28 | 0.025, -0.03/7.7 | 37 | - / - | 19.23 | 37 | 0.28 | 3.62 | 98.15 | 96.2% |
| 200 | 0.19 | 1 | 1 | 1.58, 0.19/2.96 | 0.99, 0.71/1.28 | 0.025, -0.03/7.7 | 39 | - / - | 19.23 | 37 | 0.28 | 3.62 | 98.15 | 96.2% |
| 800 | 0.09 | 1 | 5 | 2.77 , 1.88/3.65 | 0.99, 0.90/1.08 | 0.025, -0.01/5.8 | 36 | + / - | 2.405 | 13.2 | 0.46 | 6.20 | 94.39 | 93.4% |
| 800 | 0.09 | 1 | 20 | 14.09, -21.9/50.1 | 0.73, 0.49/0.98 | 0.025, -0.11/0.16 | 29 | - / - | 24.81 | 42 | 1.29 | 13.04 | 50.96 | 78.1% |
| 800 | 0.09 | 1 | 1 | 2.76 , 1.88/3.65 | 0.99, 0.90/1.08 | 0.025, -0.01/5.83 | 41 | + / - | 2.405 | 13.2 | 0.46 | 6.20 | 94.41 | 93.4% |
| 1200 | 0.03 | 1 | 5 | 2.94 , 2.28/3.60 | 0.99, 0.92/1.05 | 0.025, -0.01/6.16 | 26 | + / - | 1.145 | 9.0 | 0.49 | 6.03 | 93.95 | 93.5% |
| 1200 | 0.03 | 1 | 20 | 9.74, -18.1/37.5 | 0.74, 0.55/0.94 | 0.04, -0.04/0.12 | 28 | - / - | 16.04 | 34 | 1.08 | 12.76 | 62.67 | 81.9% |
| 1200 | 0.03 | 1 | 1 | 2.94 , 2.28/3.60 | 0.99, 0.92/1.05 | 0.025, -0.01/6.17 | 37 | + / - | 1.145 | 9.0 | 0.49 | 6.03 | 93.97 | 93.5% |

* The total percentage of mass volatilised, penetrated into sediment and transformed in water may exceed 100% because of back-diffusion of mass from the sediment into the water, where next: it may be transformed.

^A Range of organic matter content allowed in optimisation runs: 0.025 – 0.50.

^B Range of water concentration allowed in optimisation runs: 0.1 – 5.0.

^C Range of $DegT_{50, water}$ allowed during optimisation runs: 0.5 – 50.

^D Percentages here expressed as percentage of total mass in cosm (i.e. former criterion, now replaced by footnote E) instead as percentages of total mass dissipated from water layer. However, these percentages are not relevant for this cosm study as $F_{M, deg-wat} > 50\%$ (i.e. the last column), see also Figure 2.3.

^E (Mass degraded in water)/(Mass degraded in water + Mass volatilised + Mass penetrated into sediment) * 100%.

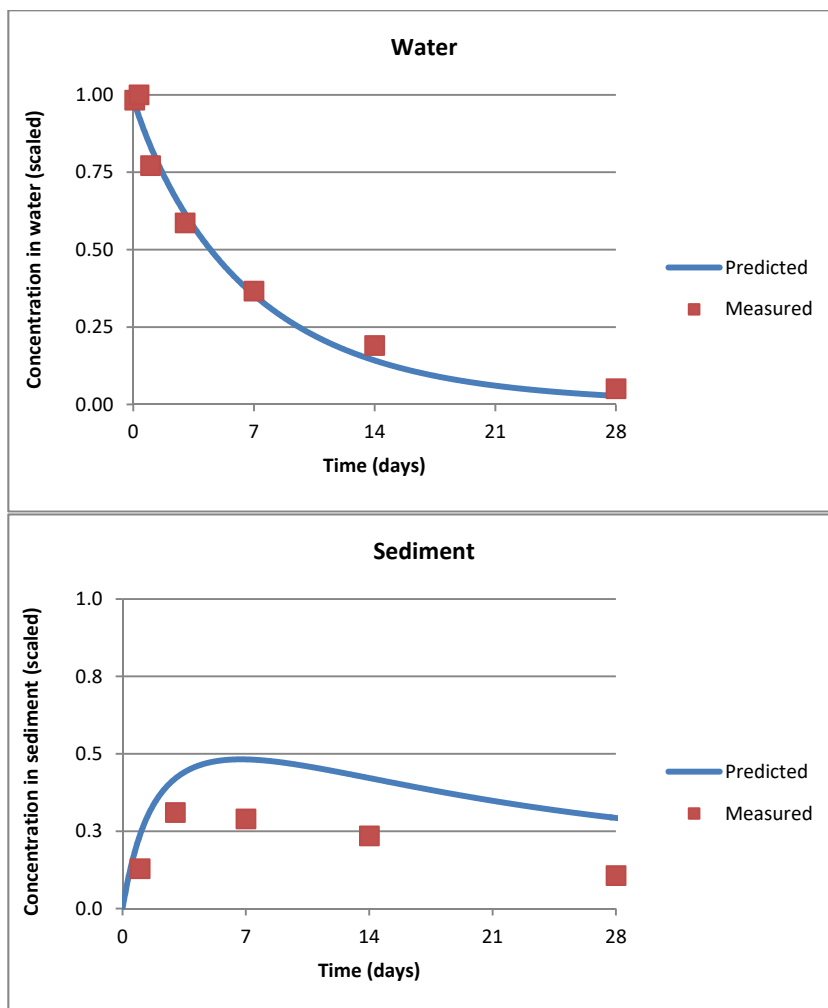


Figure A7.2 Simulated and measured concentrations of prosulfocarb in water and sediment; data simulated using an additional weight factor for water measurements, $DegT_{50,water} = 2.94$ days, an organic matter content of sediment of 2.5% and an initial scaled water concentration of 0.99 (initial values used in the estimation are given as the seventh entry in Table A7.5).

Appendix 8 Instruction to run the software for estimation of $DegT_{50,water}$

This appendix presents a detailed instruction on how to parameterise and run the software needed to estimate the $DegT_{50,water}$. The software consists of the seven files presented in step 2 below and are available upon request to one of the authors.

This appendix focuses on water-sediment cosm studies, i.e. cosm studies in which concentrations of pesticides have been measured in both the water layer and sediment of the cosm. Figure A8.1 presents a flow chart that indicates which procedure should be selected to estimate the $DegT_{50,water}$ for the cosm study. The water-only method has been described in Deneer et al. (2015). In this appendix we describe the two methods: the 'Water-sediment' method and a special case of this, the 'Water-sediment + o.m. 0-1 cm measured' method.

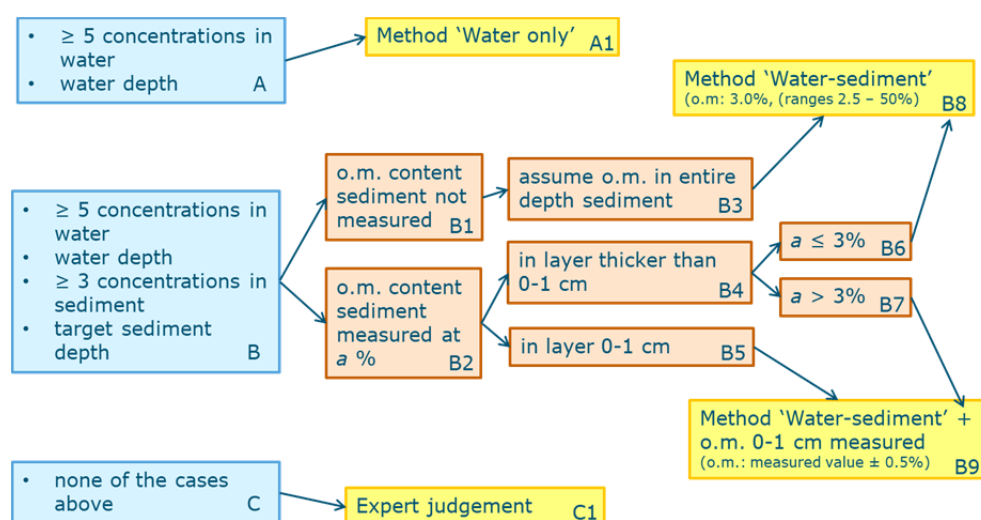


Figure A8.1 Flow chart when to select which estimation method for the $DegT_{50,water}$, based on the measured data available in the cosm study.

1. Overview of the 'Water-sediment' method

The method is demonstrated using data from a mesocosm experiment for chlorpyrifos (Brock et al., 1992). Details on the input files used for the chlorpyrifos example are given in sections 3 and 4 of this appendix.

Section 6 explains the method 'Water-sediment + o.m. 0-1 cm measured'.

Step 1- Summary of method

We propose to perform three sets of optimisation according to step 2 up to and including step 7 for each combination of bulk density and organic matter content of the sediment, that is indicated by the red stars (Figure A8.2). Each set (i.e. combination of bulk density and organic matter content of the sediment) will be run trice for the following suggested initial values: (i) $c_{t=0}$, scaled = 1 and $DegT_{50,water} = E$, (ii) $c_{t=0}$, scaled = 1 and $DegT_{50,water} \approx 0.2E$ and (iii) $c_{t=0}$, scaled = 1 and $DegT_{50,water} \approx 2E$ (with E denoting the estimated decline rate in the water layer). This results in 9 runs. In these runs the concentration in water at $t=0$, $c_{t=0}$, and the degradation half-life in water, $DegT_{50,water}$, will be optimised, next to the optimisation of organic matter content of the sediment layer.

For each of the 3 sets (i.e. combinations of bulk density and organic matter content), at least 3 combinations of initial values of $C_{t=0}$ and $DegT_{50,water}$ should be used in the optimisations, resulting in

at least 9 optimisations overall. If these 9 optimisations yield at least 3 satisfactory runs (for criteria, see section 2.3 plus Figure 2.3 of the main text), then proceed to step 9, i.e. calculate the average (geometric mean) $DegT_{50,water}$ from the results of these 3 runs. If less than 3 satisfactory runs are achieved, more combinations of $C_{t=0}$ and $DegT_{50,water}$ could be used in principle. We suggest to continue with the other optimisation sets indicated by the purple stars (see here below).

If less than three satisfactory runs have been obtained by the combinations indicated by the red stars of Figure A8.2, one or two other sets of optimisation should be performed, using other combinations of bulk density and organic matter content of the sediment indicated by the purple stars (Figure A8.2). As for the former sets, each set (i.e. combination of bulk density and organic matter content of the sediment) will be run three times for the following initial values: (i) $C_{t=0}$, scaled = 1 and $DegT_{50,water} = E$, (ii) $C_{t=0}$, scaled = 1 and $DegT_{50,water} \approx 0.2E$ and (iii) $C_{t=0}$, scaled = 1 and $DegT_{50,water} \approx 2E$ (with E being the estimated decline rate in the water layer).

If at least one satisfactory run (for criteria, see section 2.3 plus Figure 2.3 of the main text) has been obtained, proceed to step 9, i.e. calculate the average (geometric mean) $DegT_{50,water}$ from the results of the satisfactory runs.

If no satisfactory runs can be obtained expert judgement should be sought.

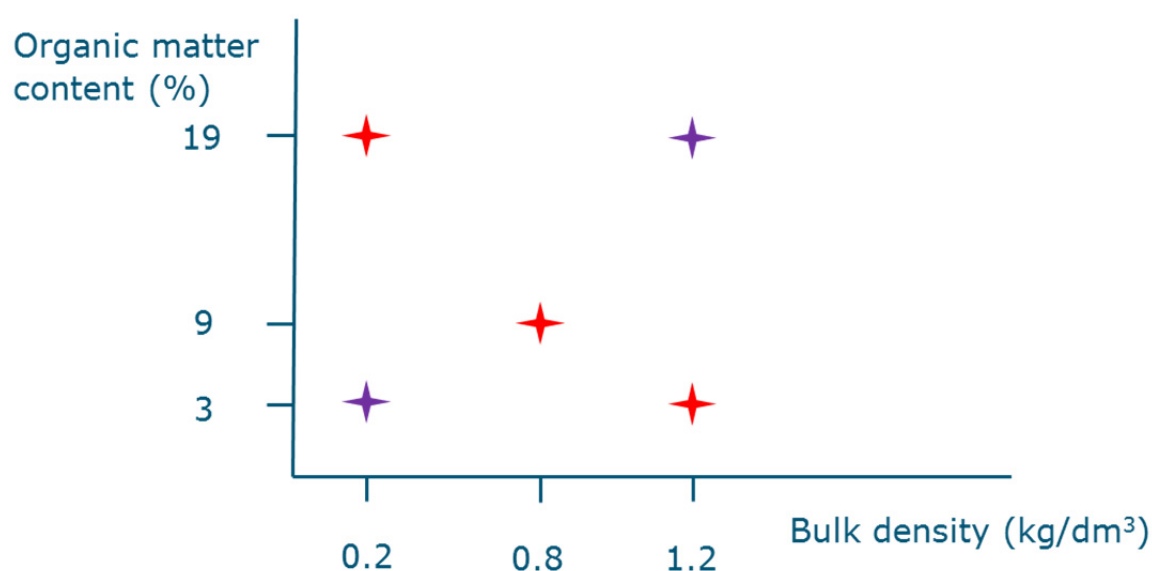


Figure A8.2 Combinations of bulk density (fixed value) and organic matter content (initial value, to optimise) for the 10 cm sediment of the simulated cosm (red: perform optimisation always, purple: see text).

Step 2

Install the files as shown in the list below on a local subdirectory (suggested name \CompoundCosm\opt1a\)

| Name | Date modified | Type | Size |
|------------------------------------|------------------|--------------------|----------|
| autom_PEST_TOXSWA_via_loadings.exe | 15/03/2017 17:54 | Application | 1,084 KB |
| Cosm.met | 23/12/2015 15:11 | MET File | 1 KB |
| generate_tbw_file.exe | 13/04/2017 17:17 | Application | 1,069 KB |
| input_TOXSWA_PEST.txt | 19/03/2017 11:07 | Text file | 1 KB |
| PEST.EXE | 13/09/2010 23:46 | Application | 1,301 KB |
| postprocess_TOXSWA_PEST.exe | 02/08/2017 12:12 | Application | 1,160 KB |
| run.bat | 22/12/2015 15:05 | Windows Batch File | 1 KB |
| sdwin32.exe | 16/05/2000 16:35 | Application | 38 KB |
| total_concentration.exe | 14/03/2017 22:30 | Application | 1,019 KB |
| TOXSWA_cha.txt | 07/04/2017 16:43 | Text file | 2 KB |
| toxswa_focus_3.exe | 14/03/2017 15:22 | Application | 3,116 KB |
| TOXSWA_moe.txt | 23/12/2015 11:50 | Text file | 21 KB |

These files represent:

- # three input files to be changed by the user, (i) *cosm.met*, (ii) *TOXSWA_cha.txt* and (iii) *input_TOXSWA_PEST.txt*
- # plus one input file changed by PEST for each run (the *TOXSWA_moe.txt*, i.e. the TOXSWA mother input file)
- # one bat file to run the programs, *run.bat* and
- # seven .exe files to run PEST, TOXSWA and pre-process and post-process their input and output.

Two output files (not present in a freshly prepared subdirectory, and hence not shown) are produced: (i) *time-course_TOXSWA.txt* and (ii) *TOXSWA_PEST_output.txt*. Several other intermediate files are used and produced by the software, most of which are deleted at the end of runs.

For more information on these files see the sections 2 (Background information) and 3 (Example data) below.

Step 3

Modify the input files that require action from the user (see section 3 and 4 below for details using the Brock – chlorpyrifos example):

- # 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 4

Run the optimisation by first clicking the *run.bat* file which contains *inputgenerator_TOXSWA_PEST.exe*. Once this run has finished, a batch file *RUN_PEST.bat* file has been created and is present in the subdirectory. Click *RUN_PEST.bat* to start the simulations and wait until the message indicating the end of runs is shown on the screen.

```

End of program

D:\DATA C:\Jos runpakket augustus_2017\Runs voor rapport screendumps etc\Chlorpyrifos Brock runs voor Appendix
set -o edwin.dat

Recording run statistics .....

See file fit_toxswa.rec for full run details.
See file fit_toxswa.sen for parameter sensitivities.
See file fit_toxswa.seo for observation sensitivities.
See file fit_toxswa.res for residuals.

D:\DATA C:\Jos runpakket augustus_2017\Runs voor rapport screendumps etc\Chlorpyrifos Brock runs voor Appendix
Press any key to continue . . .

```

Step 5

Inspect the output files that are created in the same directory:

- # *time-course_TOXSWA.txt* contains the simulated time series of the concentrations in terms of time-concentration pairs, these should be used to construct a graphical representation of the results of the

optimisation and the measured concentrations in water and in sediment to assess their visual correspondence, e.g.:

| | | | |
|---------|--------------|---------|--------------|
| 0.021 | 0.141700E+01 | 0.021 | 0.164662E-03 |
| 0.062 | 0.138693E+01 | 0.062 | 0.528574E-03 |
| 0.104 | 0.135823E+01 | 0.104 | 0.847086E-03 |
| 0.146 | 0.133076E+01 | 0.146 | 0.112725E-02 |
| 0.187 | 0.130437E+01 | 0.187 | 0.137487E-02 |
| 0.229 | 0.127896E+01 | 0.229 | 0.159477E-02 |
| 0.271 | 0.125442E+01 | 0.271 | 0.179094E-02 |
| 0.312 | 0.123068E+01 | 0.312 | 0.196669E-02 |
| 0.354 | 0.120768E+01 | 0.354 | 0.212481E-02 |
| 0.396 | 0.118535E+01 | 0.396 | 0.226761E-02 |
| 0.437 | 0.116364E+01 | 0.437 | 0.239705E-02 |
| 0.479 | 0.114252E+01 | 0.479 | 0.251476E-02 |
| | | | |
| 120.812 | 0.116922E-03 | 120.812 | 0.478490E-03 |
| 120.854 | 0.116854E-03 | 120.854 | 0.478378E-03 |
| 120.896 | 0.116786E-03 | 120.896 | 0.478266E-03 |
| 120.937 | 0.116719E-03 | 120.937 | 0.478155E-03 |
| 120.979 | 0.116651E-03 | 120.979 | 0.478044E-03 |

The first and third columns contain time (days), the second and fourth column contain the concentrations in water (mg/L) and sediment (g/kg) resp. calculated for those times. Columns are separated by at least a single space character. The data can be separated with the Excel function "Text to columns".

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

TOXSWA OK

concentration includes molecules sorbed to suspended solids

chi2 error (%) : 24.9

Sum of squared weighted residuals : 0.042956

Total model calls: 109

explanation of fitted parameters

factor is the multiplication factor for the initial concentration and the loadings so the fitted initial concentration and loadings equal those specified in the TOXSWA_cha.txt file multiplied with this factor

degt50wl is the fitted degt50 of the water layer (d)

contom is the fitted organic matter content (kg/kg)

| Parameter | Estimated value | 95% percent confidence limits | |
|-----------|-----------------|-------------------------------|-------------|
| | | lower limit | upper limit |
| factor | 1.43518 | 0.447806 | 2.42256 |
| degt50wl | 1.75858 | -0.169954 | 3.68712 |
| contom | 2.500000E-02 | -7.143289E-03 | 5.714329E-0 |

CV (%) of degt50wl: 56.0

Sum of squared weighted residuals (ie phi) = 4.2961E-02
Contribution to phi from observation group "group_1" = 2.0533E-02
Contribution to phi from observation group "group_2" = 2.2428E-02

Parameter correlation coefficient matrix ----->

| | factor | degt50wl | contom |
|----------|---------|----------|---------|
| factor | 1.000 | -0.8721 | 0.4155 |
| degt50wl | -0.8721 | 1.000 | -0.7788 |
| contom | 0.4155 | -0.7788 | 1.000 |

echoing of measured data points for graph

| nr | time | measured | fitted | weight |
|----|--------|-------------|-------------|---------|
| 1 | 1.00 | 1.000000000 | 0.924585998 | 0.354 |
| 2 | 2.00 | 0.750000000 | 0.618614972 | 0.354 |
| 3 | 4.00 | 0.464300007 | 0.288067997 | 0.354 |
| 4 | 7.00 | 0.321399987 | 0.098249301 | 0.354 |
| 5 | 8.00 | 0.292899996 | 0.069964200 | 0.354 |
| 6 | 16.00 | 0.103600003 | 0.007503610 | 0.354 |
| 7 | 30.00 | 0.039299998 | 0.001348700 | 0.354 |
| 8 | 57.00 | 0.007100000 | 0.000407326 | 0.354 |
| 1 | 8.00 | 0.002032100 | 0.002556320 | 220.075 |
| 2 | 16.00 | 0.001714300 | 0.001628720 | 220.075 |
| 3 | 30.00 | 0.001475000 | 0.001101970 | 220.075 |
| 4 | 57.00 | 0.000960700 | 0.000759324 | 220.075 |
| 5 | 118.00 | 0.000521400 | 0.000486196 | 220.075 |

weight multiplication factor for first group : 1.000

analysis of output for optimised parameters

(in case of scaled concentrations the specified masses are based on the assumption that the scaled concentrations are interpreted in TOXSWA as having the unit of mg/L)

maximum concentration in sediment (ug/kg) : 3830.90
maximum concentration in water (ug/L) : 1404.20
depth of water layer (m) : 0.50
thickness of target sediment layer (m) : 0.05
dry bulk density of sediment layer (kg/m3): 200.00
maximum mass in sediment (mg/m2) : 38.31
maximum mass in water (mg/m2) : 702.10

maximum mass in sediment as percentage of maximum mass in water : 5.46
(based on simulated concentrations)

Percentages transformation, volatilisation or penetration into sediment

N.B. Mass balance does not include incomplete last month (e.g. if simulation runs up to 15 June the mass balance runs up to 31 May).

Percentages expressed as percentages of total mass dissipated from the water layer, i.e. the sum of the masses (i) transformed in water, (ii) penetrated into sediment and (iii) volatilised from water:

| | | | |
|-------------|--------------------------------|---|-------|
| F_M,deg-wat | : transformed in water layer | : | 87.45 |
| F_M,t-sed | : penetrated into sediment | : | 5.25 |
| F_M,vol | : volatilised from water layer | : | 7.29 |

In this file, there are three fitted parameters: 'factor', DegT50wl (the degradation half-life in the water layer) and contom (the organic matter content of the sediment). This implies that 'factor' is also a fitted parameter, 'factor' specifies a multiplication factor: the value with which the initial guess of the initial concentration and the additional loadings have to be multiplied to obtain the true fitted values of parameters $C_{t=0,water}$ and the concentration additions.

In this file approximate percentages of total mass are listed, for the amounts transformed in the water layer, volatilised from the water layer into the air and penetrated into sediment (i.e. without calculating the back-diffusion). These percentages are approximate because they are based upon the monthly mass balances as reported in the *.sum file, which does not report the mass balances for the last month, when it is an incomplete month.

Note that these percentages represent the mass fractions $F_{M,deg-wat}$, $F_{M,vol}$ and $F_{M,to-sed}$ of section 2.4, expressed as percentages.

With the aid of both output files the user should make the two graphs (one for the water layer and one for the sediment) in which the simulated concentrations as a function of time are compared to the measured concentrations (e.g. Figure A8.3), as well as the two graphs in which the residuals are plotted as a function of time. Next the user should copy relevant information into the output table summarising the main input and output of each optimisation, which allows for a systematic check on all quality criteria as well as for the flow chart of Figure 2.3. An example of the output table is presented in Section 5 below, Table A8.7.

Step 6

Fill in the output tables (see section 5, Table A8.7). A run is classified as being satisfactory if all checks were satisfactory: (A) the optimisation results should fulfil the three quality criteria of (i) simultaneous visual correspondence of simulated vs measured concentrations in water and sediment is satisfactory, (ii) residuals are well distributed and (iii) the calculated error percentage of the chi-square test is smaller than 25%. (B) the simulated $F_{M,deg-water}$, i.e. the percentage of mass degraded in the water layer, should be above 50% or, if the simulated $F_{M,deg-water}$ is smaller than 50%, the CV of the $DegT_{50,water}$ should be smaller or equal to 25% (Figure 2.3). If both A and B are fulfilled, the obtained $DegT_{50,water}$ is satisfactory. If the CV of the $DegT_{50,water}$ is greater than 25%, the estimated $DegT_{50,water}$ value is judged to be not reliable and, only if no satisfactory results have been obtained at the end of Step 9, we suggest to use the upper limit of its estimated value as a conservative estimate for the $DegT_{50,water}$ (Figure 2.3).

If all checks are satisfactory, highlight the $DegT_{50,water}$ value obtained for this optimisation.

Step 7

Repeat steps 2 – 6 for two other pairs of initial estimates of the $c_{t=0}$ and $DegT_{50,water}$ in local subdirectories (suggested names of \CompoundCosm\opt1b and \CompoundCosm\opt1c).

Step 8

Repeat step 2 up to and including step 7 included for the second and third combination of bulk density and organic matter content of the sediment, indicated by the red stars (Figure A2). Perform the optimisations in separate subdirectories (suggested names of \CompoundCosm\opt2a, \opt2b and \opt2c, and \CompoundCosm\opt3a, \opt3b and \opt3c).

If less than 3 satisfactory runs have been achieved, continue with one or two other sets of optimisation, indicated by the purple stars (Figure A8.2). So, repeat step 2 up to and including step 7

included for one or two other combinations of bulk density and organic matter content of the sediment. Perform the optimisations in separate subdirectories (suggested names of \CompoundCosm\opt4a, \opt4b and \opt4c, and \CompoundCosm\opt5a, \opt5b and \opt5c).

Step 9

Determine the geometric mean of all satisfactory $DegT_{50,water}$ values (i.e. the highlighted values of the obtained $DegT_{50,water}$). Preferably at least 3 satisfactory $DegT_{50,water}$ values are needed, but only 1 or 2 values are also judged to be acceptable. Use the geomean value in the aquatic risk assessment. As said above in Step 1, ideally at least three satisfactory runs with estimated $DegT_{50,water}$ should have been obtained in the optimisation procedure. However, in several cases less than three satisfactory runs have been obtained and expert judgement was needed to assess whether runs with estimated $DegT_{50,water}$ were judged acceptable or not.

2. Background information

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

--- the seven executables (.exe) that perform the different jobs:

autom_PEST_TOXSWA_via_loadings.exe generates the required input files for the whole procedure.

generate_twx_file.exe generates a new TOXSWA input file (*cosm.twx*) after each parameter adjustment

toxswa_focus_3.exe performs the TOXSWA calculations

total_concentration.exe 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.exe extracts data from the TOXSWA output file

PEST.exe performs the PEST optimisation

postprocess_TOXSWA_PEST processes the PEST and TOXSWA output.

--- the input file *TOXSWA_moe.txt* is a template of a TOXSWA input file (see Appendix 9) which is adjusted automatically by PEST before each new run and should not be changed by the user. The only exception is when expert judgement is used to change e.g. the degradation rate in the sediment or the sediment segmentation, as stated in step h of Chapter 6.

--- the bat file *run.bat* file takes care that the optimisation, including pre-processing, all simulations and post-processing, is performed correctly

--- the two output files *time-course_TOXSWA.txt* and *TOXSWA_PEST_output.txt* file present the output of the optimisation (see Step 5 above).

There are three input files (see Step 3) that do need to be adapted by the user: *cosm.met* (meteo data), *input_TOXSWA_PEST.txt* (measured data and initial guesses of the parameters) and *TOXSWA_cha.txt* (TOXSWA input specified by the user). These are explained in the next section, Section 3.

3. Instruction for changing the input files

The input file *Cosm.met*

The *Cosm.met* describes the course of the monthly temperatures with time as follows below. We suggest to change the relevant items in the header as well as the 12 temperatures to the ones in the studied cosm.

```
*
* TOXSWA input file
* Filename:
* Chlorpyrifos, Cosm Brock et al. (1992)
* Temperature of temp controlled room: 19oC
* Contents: Input data for TOXSWA concerning temperature
* Date :
```

```

*
*
*-----
* temperature in water and sediment per month
2000 1 19.0
2000 2 19.0
2000 3 19.0
2000 4 19.0
2000 5 19.0
2000 6 19.0
2000 7 19.0
2000 8 19.0
2000 9 19.0
2000 10 19.0
2000 11 19.0
2000 12 19.0
! - - o^C : unit
! 0 .... 9999 1 .... 12 4. .... 50 : range
*
*-----END OF FILE-----

```

The file *input_TOXSWA_PEST.txt*

The *input_TOXSWA_PEST.txt* file contains the initial guesses of the optimisation parameters $C_{t=0}$, $DegT_{50,water}$ and OM, the organic matter content of the sediment plus the measured data; the file is self-explanatory as follows from the example below. Data in 'group 1' contains the (possibly scaled) water concentrations, whereas data in 'group 2' contains the (possibly scaled) sediment concentrations. Please note that the last line contains the value for bulk density (ρ), specified in units of g/L. We suggest to change all data to data relevant for the studied cosm.

```

1.0 0.1 5      Concentration: initial guess - lower limit - upper limit
5.0 0.1 100    DegT50      : initial guess - lower limit - upper limit
0.19 0.025 0.50 OM        : initial guess - lower limit - upper limit
n          water filtered y or n ?
2          number of observation groups
8 5        number of observations per group
1.0        multiplication factor for weights for group 1
times and concentrations of the observations
***** group 1 *** water concentrations
1.00 1.0000
2.00 0.7500
4.00 0.4643
7.00 0.3214
8.00 0.2929
16.0 0.1036
30.0 0.0393
57.0 0.0071
***** group 2 *** sediment concentrations
8.0 2.0321E-3
16.0 1.7143E-3
30.0 1.4750E-3
57.0 0.9607E-3
118.0 0.5214E-3
*****
200. rho

```

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.

The input file *TOXSWA_cha.txt*

The file *TOXSWA_cha.txt* contains 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 if there are, the loadings) contain the corresponding line number of the TOXSWA input file, *cosm.txw* (prepared according to the format of the *TOXSWA_moe.txt* file of Appendix 9). So e.g. '26' in the first line indicates that this is line 26 of the TOXSWA input file, *cosm.txw*. These numbers should not be changed.

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

Please note that the TimStart and TimEnd in the first 2 lines should be consistent with the duration of the sampling period, for which measured concentrations are specified in input_TOXSWA_PEST.txt. Note that 2000 was a leap year so a TimEnd of e.g. 1 March 2000 corresponds to a simulation period of 61 days.

The last lines of the file may contain the additional loadings (additions of substance after the initial day of application). These lines use a calendar format for the time. The simulations always start on 1-Jan-2000, assuming this date as the day of application, and the days of the additional loadings have to be transformed into the corresponding date. The format is based on the abbreviated names of the months in English: Jan, Feb, Mar, Apr, May, Jun, Jul, Aug, Sep, Oct, Nov, Dec. In the data set used in this chlorpyrifos example, no loadings were required, but for completeness of how to deal with this is given as an example in the text below.

```
25 01-Jan-2000      TimStart      ! Start date of simulation [01-Jan-1900 - 31-Dec-9999]
26 30-Apr-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]
89 0.50             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
238 350.89          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 4739            KomSed_ws (L.kg-1) ! Coefficient of equilibrium sorption in sediment [0.0 - 10000000]
249 1.00            ExpFreSed_ws (-) ! Freundlich exponent in sediment [0.1 - 2]
250 4739            KomSusSol_ws (L.kg-1) ! Coefficient of equilibrium sorption suspended solids [0.0 - 10000000]
252 1.00            ExpFreSusSol_ws (-) ! Freundlich exponent suspended solids [0.1 - 2]
256 1.43E-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 1.05            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)
```

Note that the initial concentration given in the last line of this file is being replaced by PEST as soon as the optimisation runs start, so the first TOXSWA run is done with the initial guessed value for the initial (possibly scaled) concentration and the next TOXSWA runs are done with values determined by PEST after analysing the differences in simulated and measured concentrations of the foregoing run. The user should however leave the default value (1.0 mg/L) as it is. If there would have been additional loadings after $t=0$ then the following type of lines should have been created:

| | | |
|-------------|-------|---|
| 02-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 |

Finally below we give some explanations on the definition of the sediment layer, as this is not self-explanatory.

Depth of the sediment layer in the file *TOXSWA_cha.txt*

With regard to sediment depth a requirement is that the depth given ('thickness of the target layer', corresponding to the depth for which experimental sediment concentrations are reported) must be exactly equal to one of the segment depths given in the TOXSWA input file. Standard horizon depths are given in *TOXSWA_cha.txt* as

| | | |
|-----|--------|--------|
| 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 |

This sequence of input lines describes a first sediment horizon of 4 mm, consisting of 4 segments of 1 mm each, a second horizon of 6 mm, consisting of 3 segments of 2 mm each, a third horizon of 1 cm, consisting of 2 segments of 5 mm each, etc. The sediment depth is specified (in meters) in *TOXSWA_cha.txt*:

325 0.05 ThiLayTgt (m) ! Thickness of the target layer in this example: 5 cm

and should correspond to one of the segment depths given, i.e. 1, 2, 3, 4, 6, 8, 10, 15, 20, 30, 40, 50, 70 or 100 mm. If the actual target layer depth of the sediment is above 10 cm, the user should either adjust the lines in *TOXSWA_cha.txt* to enable this larger depth, or alternatively set 10 cm as the depth of the target layer. Specification of sediment depths in between the default segment depths will result in error messages and abortion of the calculations. Where necessary, the user should adjust the thickness of segments in the input file such that the desired and specified target layer depth of the sediment corresponds to one of the segment depths. As an example, the sediment depth in the chlorothalonil study by Kwon and Armbrust (2006) is given in the paper as 12 mm, i.e. a target layer depth of 12 mm. This depth is in between the standard segment depths of 10 and 15 mm, and is therefore only possible through adjusting the segment depths used by TOXSWA. The input file *TOXSWA_cha.txt* would have to be changed such that the desired depth of the target layer of 12 mm coincides with the depth of the second horizon, e.g. by adding a fourth segment to the second horizon and changing the last segment into 2.8 cm (instead of 3 cm) to maintain the total depth of 10 cm:

| | | |
|-----|--------|--|
| 145 | ThiHor | NumLay |
| 146 | (m) | |
| 147 | 0.004 | 4 |
| 148 | 0.008 | 4 |
| 149 | 0.01 | 2 |
| 150 | 0.03 | 3 |
| 151 | 0.02 | 1 |
| 152 | 0.028 | 1 |
| 325 | 0.012 | ThiLayTgt (m) ! Thickness of the target layer |

4. Example data used in the calculations for chlorpyrifos on the basis of mesocosm data taken from Brock et al. (1992).

This section provides a detailed example of input taken from a published mesocosm study (Brock et al., 1992) providing sufficient experimental detail to enable calculation of a $DegT_{50,water}$ for the compound under consideration (the insecticide chlorpyrifos). Both the input data as well as the output generated by the optimisation software are discussed in detail.

Measurements in the cosm

Tables A8.1 and A8.2 summarize the main measurements of the compound-cosm study on which the input of the optimisations is based. Data are given for indoor cosms containing no macrophytes, values given are averages of data for 2 different cosms (denoted as cosms 6 and 9 in the original publication). Although the cosms were indoor, their size is such (600 L and water depth of 50 cm) that they are judged to represent sufficiently well chlorpyrifos behaviour in outdoor small surface waters.

Table A8.1 Measured concentrations in water (mg/L and scaled; 50 cm depth) and sediment (mg/kg and scaled; 0 – 5 cm layer) as a function of time (d) for the cosm study with chlorpyrifos by Brock et al. (1992).

| Number | Time (days) | Concentration in water (mg/L) | Concentration in sediment (g/kg) |
|--|----------------|-------------------------------|----------------------------------|
| Data given as concentrations | | | |
| 1 | 0 | 0.035 [#] | |
| 2 | 1 [§] | 0.028 ^{&} | |
| 3 | 2 | 0.021 ^{&} | |
| 4 | 4 | 0.013 ^{&} | |
| 5 | 7 | 0.009 ^{&} | |
| 6 | 8 | 0.0082 | 0.0569 E-3 |
| 7 | 16 | 0.0029 | 0.0480 E-3 |
| 8 | 30 | 0.0011 | 0.0413 E-3 |
| 9 | 57 | 0.0002 | 0.0269 E-3 |
| 10 | 118 | < 0.00005 | 0.0146 E-3 |
| Data converted to scaled concentrations | | | |
| 1 | 0 | - | - |
| 2 | 1 | 1.0000 | |
| 3 | 2 | 0.7500 | |
| 4 | 4 | 0.4643 | |
| 5 | 7 | 0.3214 | |
| 6 | 8 | 0.2929 | 2.0321 E-3 |
| 7 | 16 | 0.1036 | 1.7143 E-3 |
| 8 | 30 | 0.0393 | 1.4750 E-3 |
| 9 | 57 | 0.0071 | 0.9607 E-3 |
| 10 | 118 | | 0.5214 E-3 |

[#] Initial nominal concentration, not measured but calculated from dosed amount.

[§] Concentrations prior to 1 day after application are reported but not used because of apparent incomplete mixing.

[&] Relative large uncertainty in concentrations, because of log-scale used in Figure 4 from which they were read.

Table A8.2 Relevant measurements for the optimisations, other than measured concentrations in water and sediment for the cosm study with chlorpyrifos by Brock et al. (1992).

| Cosm label | CpfCosm1 |
|--|---|
| Water depth (m) | 0.50 |
| Water temperature (°C) | 19.0 |
| Measurements in sediment | Yes (5) |
| Sediment layer measured ^a | 0 – 5 cm layer |
| Total sediment depth (cm) ^b | 10 |
| Sediment organic matter measured in layer 0- x cm? | 2.8% organic matter in 0-5 cm top layer |
| Sediment bulk density measured ? | No |
| Sediment porosity measured ? | No |
| Degradation half-life in sediment (d) | 1000 |

^a Denoted as “thickness of target layer” in the input file *TOXSWA_cha.txt*, corresponds to the depth of sediment for which measured and simulated sediment contents are compared to assess the goodness of fit.

^b Should be at least as thick as ‘sediment layer measured’ given above; the total sediment depth reflects the thickness and number of horizons defined in *TOXSWA_cha.txt* (default 10 cm).

Other input, including adjustment of sorption parameters

Table A8.3 gives an overview of other input needed for the TOXSWA model, whose values are fixed during the optimisations. With exception of the ‘side slope’ which relates to the geometry of the mesocosm systems, these parameters describe the physico-chemical properties of the substance of importance for the calculations in TOXSWA. Note that it may be necessary to adjust the organic matter partition coefficient, K_{om} and $1/n$ value, due to the use of scaled concentrations for non-linear sorption to suspended solids or sediment. How to do this is explained in section 3.6 of this report, including a worked-out example. For the study/compound under consideration (chlorpyrifos) a value of $1/n = 1.000$ was retrieved, and adjustment of the organic matter partition coefficient is not necessary.

Table A8.3 Parameter values used in the simulations for the cosm study with chlorpyrifos by Brock et al. (1992).

| Cosm label | CpfCosm1 |
|---------------------------------|--|
| Molar mass (g) | 350.89 |
| Saturated vapour pressure (mPa) | 1.43 (25°C) |
| Solubility (mg/L) | 1.05 (20°C) |
| Kom (estimated) (L/kg) | Koc=8151, Kom calculated: 4728, $1/n=1.00$ |
| pKa | Not applicable |

Calculation of weight factors for water and sediment data

Concentrations in the water and in the sediment are fitted simultaneously. Using the standard settings, equal weight is given to the water and the sediment measurement series. These weight factors are calculated by the optimisation software, and need not be calculated by the user. The weight factors used in the calculation are part of the output of the optimisation, and can be found in the ‘TOXSWA_PEST_output.txt’ file in the ‘echoing of measured data points for graph’ section under the heading ‘weight’.

The calculation of the weight factors is explained in Section 3.7 of the main text of this report. Although the software uses these weight factors automatically, the user is able to attribute more weight to either the water or the sediment measurements. The input file ‘input_TOXSWA_PEST.txt’ contains a line annotated as ‘multiplication factor for weights for group 1’, which specifies the ‘extra’ weight factor for water measurements and as default contains the value 1. The user may change this value, attributing more (value > 1) or less (value < 1) weight to water measurements (which are typically given in group 1). How this is done is explained in step k of Chapter 6.

Table A8.4 summarizes the calculated weight factors for water and sediment used in the optimisation of the example data set of Brock et al. (1992), where equal weights were attributed to water and sediment measurements.

Table A8.4 Weight factors used in the optimisation for the chlorpyrifos cosm study by Brock et al. (1992), resulting in equal weights for the water and sediment measurements in the optimisation.

| Weight factor | Value | Remark |
|---------------|---------|--------------------------------------|
| W_w | 0.354 | Using scaled aqueous concentrations |
| W_{sed} | 220.075 | Using scaled sediment concentrations |

Estimation of initial values of optimisation parameters

Finally Table A8.5 presents the input values that vary between optimisations as indicated in Steps 3 – 8 described in Section 2.

Table A8.5 Suggested values for sediment and suspended solids parameters used in TOXSWA for the optimisations. The sediment parameter combinations for bulk density and organic matter content are also shown in Figure A8.2. Note that the parameter values for the suspended solids are equal to the corresponding parameters in the sediment.

| Parameter | Default value | Alternate value | Third set |
|---|---|-----------------|-----------|
| <i>Suspended solids</i> | | | |
| Concentration in water (mg/L) | 15 | 15 | 15 |
| Organic matter content (%) | 9 | 19 | 3 |
| <i>Sediment (0 – 10 cm)</i> | | | |
| Bulk density (kg/L) | 0.8 | 0.2 | 1.2 |
| Organic matter content (mass fraction, %) | 9 | 19 | 3 |
| Porosity (volume fraction, -) | Calculated by the software using Eqns 3.1 and 3.2 | | |
| Tortuosity (-) | | | |

As explained at the end of Section 3.2 of the main text of this report TOXSWA_PEST runs were made for three different sets of values of the parameters bulk density and organic matter content in order to obtain the unique, lowest value and not a local minimum value of the objective function ϕ in the optimisation process. To do so, we fixed the bulk density value at three widely different values, while the organic matter content is allowed to be varied by PEST. Also $c_{t=0}$ and $DegT_{50,water}$ are varied by PEST. It is suggested to obtain the initial value for the $DegT_{50,water}$ by estimating it as well as possible from the measured decline in the water and next, take a slightly lower and a slightly higher value. We suggest to define upper and lower boundary values of the three optimisation parameters, $c_{t=0}$, $DegT_{50,water}$ and organic matter content such that they may vary widely. An example is presented in Table A8.6.

Table A8.6 The optimisation parameters with their initial values and lower and upper parameter bounds for the example of the chlorpyrifos cosm study by Brock et al. (1992).

| Parameter | Initial value | Lower boundary | Upper boundary |
|---|---------------------|----------------|----------------|
| Bulk density (kg/dm ³) | 0.8, 0.2, and 1.2 | - ^a | - ^a |
| Organic matter content (-) (sediment+suspended solids) | 0.09, 0.19 and 0.03 | 0.025 | 0.50 |
| $C_{t=0}$, scaled (-) | 1 | 0.1 | 5.0 |
| $DegT_{50}$ (d) | 5, 1, 10 | $0.1 * E^b$ | $100 * E^b$ |

^a Bulk density is not estimated during inverse modelling, and hence it is given a constant value and lower/upper limit do not apply.

^b E denotes the initial estimate established e.g. from dissipation in water-sediment.

5. Overview of output tables

Table A8.7 summarizes the main optimisation results and highlights the obtained $DegT_{50,water}$ values for which all checks were satisfactory: (A) the optimisation results should fulfil the three quality criteria of (i) simultaneous visual correspondence of simulated vs measured concentrations in water and sediment is satisfactory, (ii) residuals are well distributed and (iii) the calculated error percentage of the chi-square test is smaller than 15%. (B) Check also whether the simulated $F_{M,deg-water}$, i.e. the percentage of mass degraded in the water layer is above 50% or, if the simulated $F_{M,deg-water}$ is smaller than 50%, whether the CV of the $DegT_{50,water}$ is smaller or equal to 25% (see Figure 2.3). If both A and B are fulfilled, the obtained $DegT_{50,water}$ is satisfactory.

Satisfactory runs with a Chi-square error% of less than 25% and good visual distribution of fitted data and residuals were only obtained with optimisations using initial values for bulk density of 0.8 kg/L and initial organic matter contents of 9% (highlighted in **bold** in Table A8.7). Values for $DegT_{50,water}$ obtained during these satisfactory runs were 5.94, 5.94 and 5.95 days resp.

Sufficient (≥ 3) satisfactory runs were achieved using the initial combinations of bulk density and organic matter, and additional runs are therefore not necessary. How to deal with situations yielding insufficient satisfactory runs is explained in Chapter 6 (steps e – k).

The geometric average value of the 3 satisfactory results for $DegT_{50,water}$ (5.94, 5.94 and 5.95 days) results in an estimate of $DegT_{50,water}$ for chlorpyrifos of 5.94 days.

Figure A8.3 gives a typical example of comparison between measured and simulated concentrations in water and sediment obtained for the estimated values given as the second entry in Table A8.7 (bulk density 0.8 kg/L, estimated $DegT_{50,water}$ of 5.94 days, estimated organic matter fraction of 0.049).

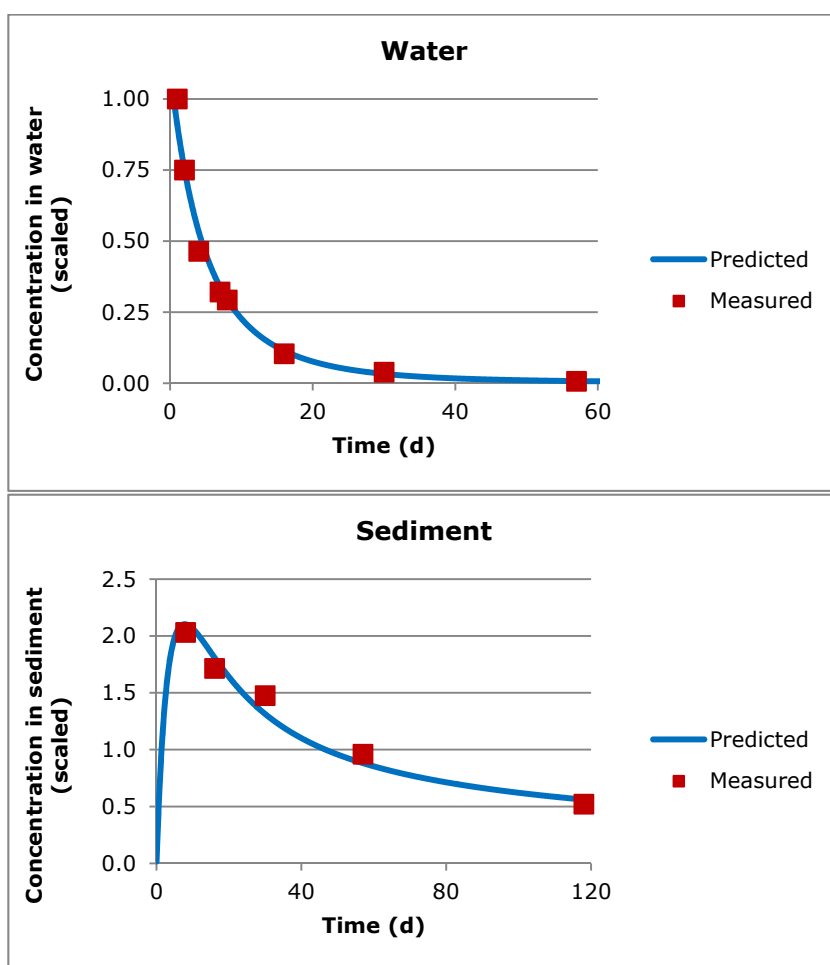


Figure A8.3 Simulated and measured concentrations in water and sediment for the data taken from the cosm experiment for chlorpyrifos reported by Brock et al. (1992). Results of simulation using bulk density 0.8 kg/L, estimated $DegT_{50,water}$ of 5.94 days and an estimated organic matter fraction of 0.049.

Table A8.7 Results of the initial 9 runs of PEST_TOXSWA inverse modelling ('Water-sediment') using chosen initial values for parameters bulk density, organic matter, initial water concentration $C_{t=0}$ and initial $DegT_{50,water}$.

| Input used in optimisation runs | | | | Results of optimisation runs | | | | | | | | | | | | | |
|---------------------------------|--|---|--|-------------------------------|--|---------------------------------------|----------------|-------------------------------------|--------------------------------|--|---------------------------------------|-----------------------------------|--------|---|---|--|--|
| Bulk density (g/L) | Initial organic matter fraction ^A (-) | Initial water concentration ^B (- if scaled, or mg/L) | Initial DegT _{50,water} ^C (days) | Estimated DegT50,water (days) | Estimated initial water concentration (- if scaled, or mg/L) | Estimated organic matter fraction (-) | Value, min/max | No of runs needed in estimation (-) | Visual goodness of fit (+/0/-) | Visual distribution of residuals (+/0/-) | Sum of squared weighted residuals (-) | Chi-square Error ^D (%) | CV (%) | Leave open if CV ≤ 25% Fill in if CV>25%: K_{om} or P_{sat} value equal to ½, 1 or 2 K_{om} or P_{sat} (Figure 2.6) | Mass volatilised as percentage of mass dissipated from water layer (%) ^D | Mass penetrated into sediment as percentage of mass dissipated from water layer (%) ^D | Mass transformed in water as percentage of mass dissipated from water layer (%) ^D |
| 800 | 0.09 | 1 | 5 | 5.94, 4.23/7.65 | 1.11, 0.98/1.24 | 0.049, 0.033/6.57 | 40 | + / + | + | 0.003987 | 7.6 | 14.7 | 18.85 | 14.17 | 66.98 | | |
| 800 | 0.09 | 1 | 1 | 5.94, 4.23/7.65 | 1.11, 0.98/1.24 | 0.049, 0.033/6.57 | 97 | + / + | + | 0.003987 | 7.6 | 14.7 | 18.85 | 14.17 | 66.98 | | |
| 800 | 0.09 | 1 | 50 | 5.95, 4.22/7.69 | 1.11, 0.98/1.24 | 0.049, 0.033/6.55 | 65 | + / + | + | 0.003987 | 7.6 | 14.8 | 18.90 | 14.16 | 66.94 | | |
| 200 | 0.19 | 1 | 5 | 1.76, -0.17/3.69 | 1.44, 0.45/2.42 | 0.025, -0.01/5.71 | 109 | - / - | - | 0.042956 | 24.9 | 56.0 | 1 | 7.29 | 5.25 | 87.45 | |
| 200 | 0.19 | 1 | 1 | 1.75, -0.14/3.65 | 1.44, 0.44/2.44 | 0.025, -0.01/5.69 | 47 | - / - | - | 0.042956 | 24.9 | 55.1 | 1 | 7.28 | 5.24 | 87.48 | |
| 200 | 0.19 | 1 | 50 | 43.3, -53.6/140 | 0.27, -0.11/0.65 | 0.025, -0.02/6.60 | 29 | - / - | - | 0.147253 | 46.1 | 114.2 | 1 | 57.56 | 14.39 | 28.05 | |
| 1200 | 0.03 | 1 | 5 | 5.26, 1.08/9.45 | 1.35, 0.94/1.76 | 0.12, -0.06/0.31 | 31 | + / - | - | 0.027965 | 20.1 | 40.6 | 1 | 17.16 | 13.72 | 69.12 | |
| 1200 | 0.03 | 1 | 1 | 6.89, 0.56/13.2 | 1.22, 0.88/1.57 | 0.10, -0.03/0.23 | 186 | 0 / = | - | 0.025816 | 19.3 | 46.8 | 1 | 20.78 | 15.31 | 63.91 | |
| 1200 | 0.03 | 1 | 50 | 6.90, 0.92/12.87 | 1.22, 0.87/1.57 | 0.10, -0.04/0.24 | 69 | + / - | - | 0.025784 | 19.3 | 44.2 | 1 | 20.80 | 15.35 | 63.85 | |

^A Range of organic matter content allowed in optimisation runs: 0.025 – 0.50.

^B Range of initial water concentration allowed in optimisation runs: 0.1 – 5.0 if scaled, or $C_{t=0}$ * (0.1 – 5.0) if mg/L.

^C Range of $DegT_{50,water}$ allowed during optimisation runs: 0.1 – 100 days.

^D Mass expressed as percentage of (Mass degraded in water + Mass volatilised + Mass penetrated into sediment).

6. Overview of the method 'water-sediment + o.m. 0-1 cm measured'

The method is similar to the method 'Water-sediment' described above except that only the bulk density has three different values, whereas the initial organic matter content is kept constant and equal to the experimental value established for the upper 1 cm of sediment. Consequently, Figure A8.4 replaces Figure A8.2: (i) three values for bulk density (0.2, 0.8 and 1.2 kg/L) are combined with a single value for the organic matter content established for the 0-1 cm layer, and (ii) the upper and lower parameter bounds of the organic matter content should be close to the measured value and represent e.g. the expected uncertainty in the measurement of the organic matter content of this layer (in the example used organic matter content is allowed to vary $\pm 0.5\%$ around the experimentally determined value of 4.0%).

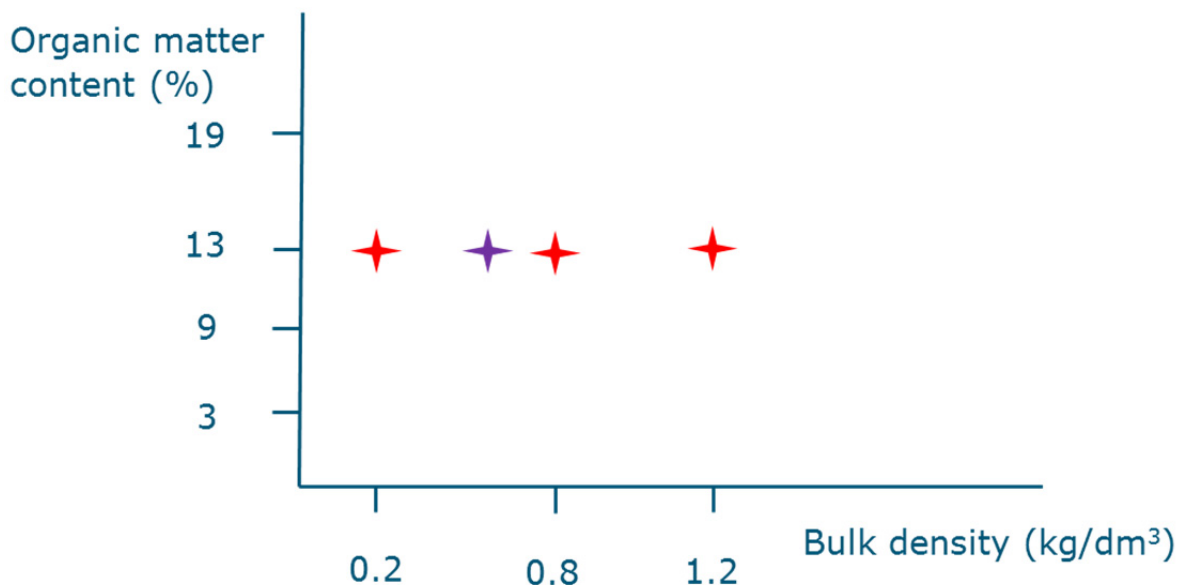


Figure A8.4 Combinations of bulk density (fixed value) and organic matter content (initial measured value, to optimise within limits reflecting measurement uncertainty) assumed for the 10 cm sediment of the simulated cosm, when the organic matter content for the 0-1 cm sediment layer has been measured, e.g. to be 13% in this example graph (red: perform optimisation always, purple: see text).

Input files for the method 'Water-sediment + o.m. 0-1 cm measured' are identical to the input files that would be used in the method 'Water-sediment' example, with the only exception that the value and allowed range of organic matter content should be in line with experimentally established value of this parameter for the upper 1 cm of sediment. All other parameters to be optimised ($C_{t=0}$, $DegT_{50,water}$) and parameters like thickness of the target layer are identical to values used in the method 'Water-sediment'.

In the example mesocosm data for chlorpyrifos (Brock et al., 1992) the organic matter content of the upper 1 cm of the sediment layer was reported as $4.1 \pm 2.8\%$ (ditch 6) and $3.9 \pm 3.2\%$ (ditch 9) (Brock, personal communication), yielding an average value of $4.0 \pm 3.0\%$. This means that for this example data set optimisations were performed with bulk densities of 0.2, 0.8 and 1.2 kg/L, using a constant initial organic matter content of 0.040 which for the sake of optimisation was allowed to vary $\pm 20\%$ of the average measured value, i.e. from 0.032 – 0.048. For initial aqueous concentrations and initial $DegT_{50,water}$ the same values as used in the previously described method 'Water-sediment' were used. The combinations of bulk density, initial aqueous concentration and initial $DegT_{50,water}$ used in the simulations are given in Table A8.8.

Table A8.8 Results of the initial 9 runs of PEST_TOXSWA inverse modelling ('Water-sediment + o.m. 0-1 cm measured') using chosen initial values for parameters bulk density, organic matter, initial water concentration $C_{t=0}$ and initial $DegT_{50,water}$.

| Input used in optimisation runs | | | | Results of optimisation runs | | | | | | | | | | | | |
|---------------------------------|--|---|--|-------------------------------|--|---------------------------------------|---------------------------------|--------------------------------|--|---------------------------------------|-----------------------|--------|--|---|--|--|
| Bulk density (g/L) | Initial organic matter fraction ^A (-) | Initial water concentration ^B (- if scaled, or mg/L) | Initial DegT _{50,water} ^C (days) | Estimated DegT50,water (days) | Estimated initial water concentration (- if scaled, or mg/L) | Estimated organic matter fraction (-) | No of runs needed in estimation | Visual goodness of fit (+/0/-) | Visual distribution of residuals (+/0/-) | Sum of squared weighted residuals (-) | Chi-square Error% (%) | CV (%) | Leave open if CV ≤ 25% Fill in if CV>25%: <i>K_{om}</i> or <i>P_{sat}</i> value equal ½, 1 or 2 | Mass volatilised as percentage of mass dissipated from water layer (%) ^D | Mass penetrated into sediment as percentage of mass dissipated from water layer (%) ^D | Mass transformed in water as percentage of mass dissipated from water layer (%) ^D |
| 800 | 0.04 | 1 | 5 | 6.04, 4.30/7.78 | 1.11, 0.98/1.24 | 0.048, 0.032/6.38 | 37 | + / + | + | 0.003999 | 7.6 | 14.7 | | 19.12 | 14.12 | 66.76 |
| 800 | 0.04 | 1 | 1 | 6.04, 4.30/7.78 | 1.11, 0.98/1.24 | 0.048, 0.032/6.38 | 42 | + / + | + | 0.003999 | 7.6 | 14.7 | | 19.12 | 14.12 | 66.75 |
| 800 | 0.04 | 1 | 50 | 6.04, 4.30/7.78 | 1.11, 0.98/1.24 | 0.048, 0.032/6.38 | 57 | + / + | + | 0.003999 | 7.6 | 14.7 | | 19.12 | 14.12 | 66.75 |
| 200 | 0.04 | 1 | 5 | 1.44, -0.34/3.22 | 1.56, 0.25/2.87 | 0.032, -0.011/7.51 | 87 | - / - | - | 0.050166 | 26.9 | 62.9 | 1 | 6.06 | 5.37 | 88.57 |
| 200 | 0.04 | 1 | 1 | 1.44, -0.31/3.20 | 1.56, 0.24/2.88 | 0.032, -0.011/7.49 | 34 | - / - | - | 0.050166 | 26.9 | 61.9 | 1 | 6.06 | 5.37 | 88.57 |
| 200 | 0.04 | 1 | 50 | 44.05, -34.4/122.5 | 0.24, -0.16/0.64 | 0.032, -0.016/7.99 | 29 | - / - | - | 0.15962 | 48.0 | 90.9 | 1 | 56.82 | 15.90 | 27.28 |
| 1200 | 0.04 | 1 | 5 | 11.02, -1.45/23.5 | 1.14, 0.80/1.48 | 0.048, -0.013/0.11 | 45 | - / - | - | 0.038134 | 23.5 | 57.7 | 1 | 28.87 | 15.82 | 55.31 |
| 1200 | 0.04 | 1 | 1 | 11.03, -1.70/23.8 | 1.14, 0.81/1.48 | 0.048, -0.013/0.11 | 86 | - / - | - | 0.038134 | 23.5 | 58.9 | 1 | 28.91 | 15.82 | 55.28 |
| 1200 | 0.04 | 1 | 50 | 11.03, -1.74/23.8 | 1.14, 0.81/1.48 | 0.048, -0.013/0.11 | 32 | - / - | 0 | 0.038134 | 23.5 | 59.1 | 1 | 28.91 | 15.82 | 55.28 |

^A Range of organic matter content allowed in optimisation runs: 0.032 – 0.048.

^B Range of initial water concentration allowed in optimisation runs: 0.1 – 5.0 if scaled, or $C_{t=0}$ * (0.1 – 5.0) if mg/L.

^C Range of $DegT_{50,water}$ allowed during optimisation runs: 0.1 – 100 days.

^D Mass expressed as percentage of (Mass degraded in water + Mass volatilised + Mass penetrated into sediment).

Satisfactory runs (with a Chi-square error% of less than 25%) were only obtained with optimisations using initial values for bulk density of 0.8 kg/L (highlighted in **bold** in Table A8.8). Values for $DegT_{50,water}$ obtained during these satisfactory runs were 6.04 days for all three runs. Hence the geometric mean over these values results in a geomean value of 6.04 days, which is quite close to the value of 5.94 days obtained when allowing a wider range of organic matter content in the optimisation ('Water-sediment').

Sufficient (≥ 3) satisfactory runs were achieved using the initial combinations of bulk density and organic matter, and additional runs are therefore not necessary. How to deal with situations yielding insufficient satisfactory runs is explained in Chapter 6 (steps e – k) of the water-sediment method, where several suggestions for additional optimisations by using expert judgement are given.

Appendix 9 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
*-----
*

LinCosm1A        Location      ! Name of the location Paulien: deze 2 gebruikt TOXSWA niet
LinCosm1A        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 (m) | NumSeg (-) | WidWatSys (m) | SloSidWatSys (-) | DepWatDefPer (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: de volgende input 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: de volgende input 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 | print_CntSedTgt | ! Total content in target layer sediment [Yes, No] |
| No | print_ConLiqSedTgt | ! Concentration in pore water in target layer sediment [Yes, No] |
| No | print_CntSorSedTgt | ! Content sorbed in target layer sediment [Yes, No] |
| 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 | print_AmaSorMph | ! Mass sorbed to macrophytes in water layer [Yes, No] |
| No | print_AmaSed | ! Mass in sediment layer [Yes, No] |
| No | print_AmaLiqSed | ! Mass in liquid phase in sediment layer [Yes, No] |
| 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 | print_AmaDrfWatLay | ! Mass entered water layer by spray drift [Yes, No] |
| No | print_AmaAtmDepWatLay | ! Mass entered water layer by atmospheric deposition [Yes, No] |
| No | print_AmaDraWatLay | ! Mass entered water layer by drainage [Yes, No] |
| 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 | print_AmaErsSed | ! Mass entering sediment layer by erosion [Yes, No] |
| No | print_VolErrWatLay | ! Volume error in waterbody [Yes, No] |
| No | print_AmaErrWatLay | ! Mass error in mass balance of the waterlayer [Yes, No] |
| No | print_ConLigWatLayNLAvg | ! 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

Appendix 10 Format of table presenting the main input and output of the optimisations runs for estimation of $DegT_{50,water}$

[illegible]

^A Range of organic matter content allowed in optimisation runs: 0.025 – 0.50.

^a Range of initial water concentration allowed in optimisation runs: 0.1–5.0 if scaled, or $C_{i=0}^*$ (0.1–5.0) if mg/L.

c Range of $DegT_{50, water}$ allowed during optimisation runs: 0.1 – 100 days.

^d Mass expressed as percentage of (Mass degraded in water + Mass volatilised + Mass penetrated into sediment).
(range of 2.9–30/water) and another column (penetration) (range of 1.0–0.07).

Wageningen Environmental Research
P.O. Box 47
6700 AA Wageningen
The Netherlands
T +31 (0)317 48 07 00
www.wur.nl/environmental-research

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The mission of Wageningen University and Research is "To explore the potential of nature to improve the quality of life". Under the banner Wageningen University & Research, Wageningen University and the specialised research institutes of the Wageningen Research Foundation have joined forces in contributing to finding solutions to important questions in the domain of healthy food and living environment. With its roughly 30 branches, 5,000 employees and 10,000 students, Wageningen University & Research is one of the leading organisations in its domain. The unique Wageningen approach lies in its integrated approach to issues and the collaboration between different disciplines.



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of nature to
improve the
quality of life



Wageningen Environmental Research
P.O. Box 47
6700 AB Wageningen
The Netherlands
T +31 (0) 317 48 07 00
www.wur.eu/environmental-research

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