Estimating transformation rates of pesticides, to be used in the TOXSWA model, from water-sediment studies

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Alterra-rapport 023

Alterra, Green World Research, Wageningen, 2002

ABSTRACT

Adriaanse, P.I., J.P.M. Vink, W.W.M. Brouwer, M. Leistra, J.W. Tas, J.B.H.J. Linders & J.W.Pol, 2002. *Estimating transformation rates of pesticides, to be used in the TOXSWA model, from water-sediment studies*. Wageningen, Alterra, Green World Research. Alterra-rapport 023. 130 pp. 21 figs.; 33 tables; 76 refs.

In the Dutch registration procedure the model TOXSWA is used to calculate the exposure of aquatic organisms to the pesticides applied in agriculture. The transformation rates in water and sediment, needed as input for the computations, are not asked directly in the registration procedure. Various test guidelines for water-sediment studies are discussed; they only yield pesticide dissipation rates in water and sediment. Water-sediment studies for three compounds were simulated with TOXSWA to estimate the transformation rates from the measured data. It was found that a detailed interpretation of the experiments and reported data is crucial before the water–sediment studies can be simulated correctly. Using the model, pesticide transformation could be assigned to mainly one of the layers or to both layers. These transformation rates do not depend on system properties like volumes of water and sediment or on the surface area of their interface. The procedure has to be tested for more pesticides and studies. The factors determining microbial transformation of pesticides in aquatic systems were studied; this allows improved characterization of the systems by measurements.

Keywords: aquatic systems, contamination, organic chemicals, registration procedure, test guidelines, watercourses, water quality

ISSN 1566-7197

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Project 359-80592 [Alterra-rapport 023/HM/03-2002]

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Preface

The TOXSWA model for fate of pesticides in surface waters is applied in the Dutch registration procedure since June 1999. The evaluating institutes should be able to derive all necessary input parameters from the submitted dossier data. It was found that all input parameters can be determined from the dossier data in a straightforward way, except the pesticide transformation rates in water body and bottom sediment. Therefore, the Dutch Board of the Authorization of Pesticides (CTB) requested the development of a procedure to estimate pesticide transformation rates on the basis of commonly-submitted dossier data.

In the course of 1998, a working group was set up with representatives from the Dutch Board of the Authorization of Pesticides (CTB), the Plant Protection Service (PD), the Institute for Inland Water Management and Waste Water Treatment (RIZA), the National Institute of Public Health and the Environment (RIVM) and Alterra Green World Research. Up to March 2000, the institutes co-operated in the development of the requested procedure as well as in the assessment of current guidelines on water-sediment studies and in the effect of environmental factors on pesticide transformation. The results of the working group are presented in this report.

On 12 February 1999, a workshop was held at the former DLO Winand Staring Centre to explain how the TOXSWA model can be used in the Dutch registration procedure. A preliminary working method for the derivation of pesticide transformation rates in the compartments of watercourses was presented there. From 1 June 1999 on, the TOXSWA model has been implemented in the Dutch registration procedure, replacing the SLOOT.BOX model. In the present registration procedure a temporary, already existing method is applied to approximate the transformation rates in water and sediment. On 22 February 2000 a second workshop was held at Alterra, where we presented the proposed procedure to derive the transformation rates, together with the design of a ‘decision tree’ explaining when the procedure should be followed. Both subjects are presented in this report. We plan to test the proposed procedure for more studies on pesticides and to elaborate the decision tree further. This may be expected to lead to replacement of the temporary approximation method presently used in the Dutch registration procedure.

The Alterra contribution was performed within the framework of LNV Research Programme 359 ‘Pesticides and the Environment’, financed by the Dutch Ministry of Agriculture, Nature Management and Fisheries.

This report replaces the draft version of the year 2000, in which the identity of the three test compounds could not be disclosed. At our request the three registration applicants kindly consented us to mention the active ingredients in the studies used to develop the procedure for estimating the pesticide transformation rates.

Summary

In the Dutch pesticide registration procedure one of the three environmental criteria deals with the protection of aquatic ecosystems. The computer simulation model TOXSWA is used to estimate the concentrations to which aquatic organisms may be exposed. Transformation rates of pesticides in natural water and in bottom sediment are important input parameters for such a model. Unfortunately, these transformation rates are not required in the registration procedures. Therefore, the present study proposes a method to obtain these transformation rates from water-sediment studies, the main experiment on aquatic fate required in the registration procedures.

Water-sediment studies are carried out with a two-layer system: a water layer which is gently aerated without disturbing the stagnant sediment layer. In the sediment a gradient in oxygen level should exist: from aerobic at the water-sediment interface to anaerobic deeper in the sediment. This reflects the situation in many small surface waters in the Netherlands and elsewhere.

Various test guidelines have been developed for studies on pesticide behaviour in water-sediment systems. We discuss the guidelines of US-EPA (1982), BBA (1990), FAO (1993), SETAC (1995), CTB (1997), US-EPA (1998) and OECD (2000) with respect to their suitablility to yield the desired information. Some guidelines only give a general description of the test. The recent OECD guideline prescribes the most detailed characterization of the experimental procedure and of the elaboration of the results. All tests deliver dissipation rates in water and sediment rather than the transformation rates needed for model simulations.

In water-sediment studies the following processes play a role: (i) volatilization, (ii) sorption to dissolved material and to suspended solids, (iii) diffusion into and out of the sediment, (iv) sorption to the sediment, (v) transformation in the water layer and (vi) transformation in the sediment. We used the TOXSWA model to simulate these processes. By comparing the computed and measured concentrations, it is attempted to estimate the separate pesticide transformation rates in water layer and sediment.

We tested the method for three water-sediment studies, carried out by different laboratories for divergent pesticides. It was found that first of all the experiments have to be checked for errors. In the first study, the pesticide was applied to the water layer at a concentration far above its solubility in water. Consequently, the computations had to be started at a few days after application. In the second study, the concentrations in the sediment layer were calculated incorrectly. In the third study, the sediment layer was extremely loose, possibly due to the slow rotation of the system. A general problem is that the geometry of the system is not specified, which makes it difficult to assess the depths of the water and sediment layers, and the related bulk density of the sediment. Another problem is that transformation kinetics may deviate substantially from first-order kinetics (as assumed in the model).

The transformation of indoxacarb could be assigned to both the water layer and sediment layer. Its rapid dissipation in the water layer is mainly caused by its penetration and strong adsorption in the sediment. Although dicamba is only weakly adsorbed, it was mainly transformed in the sediment layer. Chlorpropham was estimated to be transformed in the water and sediment layers at similar rates. There seems to be no general predominance of transformation in one of the layers.

Based on the experiences with simulating the three studies, an improved procedure is proposed to estimate the pesticide transformation rates. Methods to estimate missing data (in studies according to older guidelines) have to be elaborated further. Ideas were developed for a decision scheme to evaluate for which pesticide the separate transformation rates in water and sediment are critical.

The influence of environmental factors on biotransformation of pesticides in aquatic systems was assessed on the basis of a literature review. Four pesticides were considered, representing different chemical groups. The first important characteristic is the biochemical oxygen demand. The second important group is formed by the nitrogen and phosphorus nutrients (both total-N and total-P concentrations, and concentrations of species). Finally macro and micro nutrients like Ca, Mg and Mn play an important part.

The test guidelines were evaluated with respect to their requirements concerning microbial biomass and microbial viability. Only the BBA and OECD guidelines require microbial biomass measurements at the start and at the end of the test, to check whether microbial activity is maintained. The OECD guideline is the most comprehensive with respect to system characterization; it is the only one that enables adequate evaluation of biotransformation rates and pathways.

1 General introduction

Measurements show that water systems can be contaminated with the pesticides used in agriculture. Emission pathways like spray drift, atmospheric deposition, run-off and discharge of groundwater (e.g via tile drainage) have been studied. Many pesticides present the risk of toxic effects on aquatic organisms, because of their high toxicity. In the pesticide regulation procedures, one of the main aims is to protect the aquatic organisms.

First of all the exposure of aquatic organisms to a pesticide should be assessed. This exposure is the result of both, the load of the aquatic system with pesticide and of the behaviour of the pesticide in the system. The model TOXSWA (TOXic substances in Surface WAters) has been developed to calculate the exposure (Adriaanse, 1996). The result of the model should be compared with the dose-response relationships to make a first assessment of possible toxic effects of the pesticide. Often, the calculated exposure can be compared directly with an established limit value.

Recently, the model TOXSWA was introduced into the pesticide registration procedure in the Netherlands. It was also introduced into USES Version 3.0 (Uniform System for the Evaluation of Substances, RIVM et al, 1999), which deals with environmental contaminants in general. Further, the model is part of the exposure calculation procedure developed by the FOCUS Surface Water Scenarios Working Group, which is submitted to the Working Group on Pesticide Legislation of the European Union.

A computer model needs adequate input data. Sorption of a pesticide to aquatic sediment may have been measured or it can be estimated from its sorption to soils. Other input data can be estimated, e.g. the diffusion coefficients in water and in the pore system of a sediment. It is usually not possible to estimate transformation rates of pesticides under different environmental conditions, so these have to be measured. However, separate transformation rates in natural water and in sediment of water systems are not required in the registration procedures. At present, the main experiment on aquatic fate is the water-sediment study in the laboratory, for which various guidelines have been developed in the course of time.

The question rises whether the separate transformation rates of a pesticide in water layer and sediment layer, as needed for the TOXSWA model, can be derived from the water-sediment studies. Such studies are performed in a two-layer system: a water layer which is gently aerated without disturbing the underlying layer of stagnant sediment. In the two-layer systems different processes are involved in the dissipation of a pesticide from a layer, such as adsorption, diffusion into and out of the sediment, transformation and volatilization. Further the water-sediment systems are heterogeneous, with a mainly aerobic water layer and a largely anaerobic stagnant sediment layer. In the present study it is attempted to simulate the water-sediment

studies with the TOXSWA model in order to derive the separate pesticide transformation rates in the water and sediment layers.

Chapter 2 gives a comparative description of the guidelines developed for water-sediment studies. A possible procedure is described (Chapter 3) for deriving the separate transformation rates of a pesticide in water layer and sediment layer from the measured dissipation rates. The procedure is tried out for three pesticides (Chapter 4) with divergent properties. Based on the experiences, Chapter 5 presents possible improvements in the procedure for estimating the transformation rates. Newer research on the influence of environmental factors on the rate of transformation of pesticides in aquatic systems is discussed in Chapter 6. Finally, Chapter 7 presents the general discussion and the conclusions for the whole study.

2 Suitability of test guidelines on water-sediment studies

2.1 Introduction

The TOXSWA model (Adriaanse, 1996) calculates pesticide concentrations to which aquatic organisms are exposed in a Dutch standard ditch in spring/summer or in autumn. Next to the input data for the environmental scenario, the model requires input data on pesticide behaviour. Major input parameters are the rates of pesticide transformation in the water layer and in the sediment layer of watercourses. Generally, these input parameters are not asked directly in the registration procedures. The data requirements often deal with the dissipation and partitioning of pesticides in water-sediment systems, so the question rises whether the separate transformation rates in water layer and sediment layer can be derived from the results of the water-sediment tests in the laboratory.

In this chapter an overview is given of the guidelines that have been developed for studies on pesticide behaviour in water-sediment systems. The selected guidelines deal with standardised laboratory studies with a stagnant sediment layer, aimed at obtaining a first estimate of pesticide behaviour in aquatic systems. The emphasis is on guidelines a) developed by international organizations and b) used regularly in dossiers for pesticide registration in the Netherlands.

First, the list of the guidelines discussed in this chapter is presented. An outline is given of the way they are used in the Dutch registration procedure. The guidelines are compared with respect to various aspects of the studies. Tables with a comparison of various details on the guidelines for water-sediment studies are given in Appendix 1. The ultimate aim is to evaluate the suitability of the guidelines for providing the separate transformation rates in water layer and sediment layer, needed as input for the TOXSWA model.

2.2 Guidelines considered

The following test guidelines for water-sediment studies are compared with respect to a series of characteristics (see also Table in Appendix 1).

- US-EPA (1982). Pesticide assessment guidelines, Subdivision N, Chemistry, Environmental fate: 162-4. Aerobic aquatic metabolism studies. October 1982. Environmental Protection Agency, Washington DC.
- BBA (1990). Richtlinien für die Prüfung von Pflanzenschutzmitteln im Zulassungsverfahren, Teil IV: 5-1, Abbaubarkeit und Verbleib von Pflanzenschutzmitteln im Wasser/Sediment-System. Dezember 1990. Biologische Bundesanstalt für Land- und Forstwitschaft, Braunschweig.
- FAO (1993). Annex to revised guidelines on environmental criteria for registration of pesticides, revision 3, 28-8-1993. Food and Agricultural Organisation of the United Nations, Rome.

- SETAC (1995). Procedures for assessing the environmental fate and ecotoxicity of pesticides (M.R Lynch, Ed.). March 1995. Society for Ecotoxicology and Chemistry, Brussels.
- CTB (1997). Toelichting op het Aanvraagformulier (Explanation to the Application Form). College voor de Toelating van Bestrijdingsmiddelen (Board of the Authorization of Pesticides). Wageningen.
- US-EPA (1998). Fate, transport and transformation test guidelines. OPPTS 835.3180. Sediment/water microcosm biodegradation test. January 1998. Environmental Protection Agency, Washington DC.
- OECD (2000). Draft proposal for a new guideline: aerobic and anaerobic transformation in aquatic sediment systems. Version of August 2000. Organization for Economic Co-operation and Development, Paris.

The two test guidelines developed by US-EPA, are both relevant for Dutch registration. Many studies in dossiers submitted for pesticide registration in the Netherlands are based on the US-EPA (1982) guideline. It is expected that in the future many studies in Dutch and EU dossiers will be based on the US-EPA (1998) guideline; therefore, this new guideline was included in the comparison as well. Many other studies submitted in the Netherlands are performed according to the German BBA guideline. The FAO guideline is added for reasons of completeness and because it is an internationally accepted guideline. The same holds for the SETAC guideline. The SETAC guideline seems to be identical to that of FAO. The Dutch CTB guideline, which is part of the Explanation to the Application Form, is relevant as well. In these years, the OECD (2000) is active in developing a test guideline. Since the Netherlands participate in the OECD work and because this guideline is considered to become a worldwide harmonized standard, this guideline is included in this study. Other national test guidelines for this type of study exist, e.g. those in the UK and Canada. However, these are not often used for studies submitted for registration in the Netherlands, so such other guidelines are not considered in this comparison.

In the Dutch registration procedure, performance of a proper test, adequate reporting and relevant endpoints are more important than the test guideline used. In practice, all tests performed with test guidelines that meet these criteria are accepted. However, preference is given to international test guidelines, above national guidelines. In some other countries, registration authorities tend to rely more on a specific test guideline.

2.3 Objectives in Dutch registration

In Dutch pesticide registration the water-sediment study is considered to be very important, because many agricultural areas are intersected by field ditches and small canals. Protection of aquatic life is one of the main policy items with respect to the use of pesticides. The study should be performed with a stagnant layer of natural sediment having a layer of the corresponding surface water on top. A gradient in the oxygen level has to be present during the test; the water layer has to be aerobic

(aeration without disturbance of the sediment) and within the sediment layer anaerobic conditions should exist. This reflects the situation in Dutch field ditches. The study should deliver data to enable assessment of the exposure of aquatic life to the pesticide. Relevant endpoints expected from the study are:

- Rate of dissipation of the test substance: the rates in both the water layer and sediment layer, as well as in the whole system are considered to be relevant.
- Transformation pathway: all transformation products in amounts of 10 percent or more of the test substance applied, occurring at any time during the study, are considered to be environmentally relevant. For these transformation products, a separate water-sediment study has to be submitted, unless the required information can be obtained from the study with the parent substance.

It is evident that the tests have to be performed adequately and that complete and transparent reports are submitted. A number of items is checked in the evaluation of the tests for registration; a checklist has been presented by Mensink et al. (1995).

As mentioned, the rate coefficients are used to assess the exposure of aquatic organisms to the pesticide. A predicted environmental concentration in surface water (PEC_{SW}) is used to assess the risk for aquatic life, while a PEC_{SED} is used to assess risks to sediment organisms. To enable this, the test should deliver data for different time points on the amounts/concentrations of individual substances (test substance and transformation products), both in the water layer and the sediment layer.

The dissipation rate coefficients given as endpoints in the water-sediment studies do not characterize the pesticide in an exact way. Dissipation in the water-sediment studies depends not only on pesticide properties, but also on system characteristics like water and sediment volume, size of their interface and sediment properties. Therefore, the TOXSWA simulation model requires separate transformation rates representing pesticide properties only, instead of dissipation rates representing system characteristics as well. On the basis of these transformation rates, exposure concentrations in water and sediment will be calculated in the Dutch registration procedure in the future.

2.4 Applicability of test guidelines

The applicability of test guidelines is discussed, using the following criteria:

a) level of detail
b) system simulated by the test
c) test performance
d) intended endpoints

a) Level of detail

The level of detail of a test guideline deals with the level of guidance given with respect to the objectives, the description of the test system, storage and handling, the way of incubation, sampling, analytics and reporting. Details are necessary to judge the quality of the test, as well as to judge the extent to which the test matches the objectives.

There is a remarkable difference in the level of detail between the guidelines studied. US-EPA refers to Krzeminski et al. (1975a, 1975b) for details on the method, but a look to the papers showed that they do not deal with the type of water-sediment study relevant for our work. Guidelines with a low level of detail are those of FAO and SETAC. The recent US-EPA (1998) guideline is rather detailed, but only with respect to a limited number of items. The guidelines of BBA and CTB have an intermediate level of detail. Without doubt the future OECD (2000) test guideline will have the desired high level of detail.

b) System simulated by the test

All test guidelines, some in a more implicit way, appear to focus on the Dutch objective to have a test system with an aerobic water layer with a gradient to anaerobic conditions deeper in the sediment layer.

c) Test performance

- Labelling. All test guidelines prefer the use of radiolabelled compounds, which facilitates the study of transformation pathways and mass balance.
- Origin of water and sediment. All test guidelines require collection of sediment with associated water from natural systems. OECD (2000) refers to the ISO (1994) guideline ISO/DIS 5667-12 for the way of sampling, while US-EPA (1998) gives guidance at this point too. The depth of the sediment layers to be sampled is described by CTB (upper 2 to 3 cm) and by OECD (2000) (upper 5 to 10 cm). The US-EPA (1998) prescribes taking undisturbed sediment cores to a depth at which still biological activity exists (which can be 40 cm according to the guideline).
- Previous exposure. All test guidelines exclude the use of sediments (with associated water) that have been exposed to the test substance or structural analogues in the previous period. The OECD (2000) test guideline sets this period to 4 years previous to the time of sampling. The US-EPA (1998) and BBA guidelines even require samples to be taken from uncontaminated sites.
- Number of sediments and associated water types. Not stated by any US-EPA guideline; two or more in all other test guidelines.
- Distinction between test systems. The CTB guideline requires a distinction in organic carbon content of the sediments without any further guidance. The OECD (2000) guideline provides guidance on the distinction with respect to organic matter content and texture of the sediment. The BBA guideline adds a third criterium for distinction, namely the microbial biomass, but it gives only limited guidance. Both US-EPA guidelines, as well as those from FAO and SETAC don't have requirements on this item.
- Storage. All test guidelines prefer the use of freshly-sampled water and sediment. If storage is necessary, care has to be taken to maintain the microbial activity. Guidance to do so is given by BBA, US-EPA (1998) and OECD (2000).
- Characterisation in situ. Nothing is stated on characterisation of the water-sediment system in situ in the guidelines of US-EPA (1982) and CTB. FAO and SETAC only state that the temperature in the water has to be measured. BBA, US-EPA (1998) and OECD (2000) require the measurement of different parameters. For more information on this topic, focussed on what is needed based on research by a Dutch institute, see Chapter 6.

- Characterisation in the lab. This characterisation is very important, as it enables a check on the aerobic conditions in the water layer and the anaerobic conditions deeper in the sediment. Little guidance is given by CTB, whereas the guidelines from US-EPA (1982), BBA, FAO, SETAC and OECD (2000) require a rather detailed characterisation. On this topic too, more information is given in Chapter 6.
- Container. The guidelines of US-EPA (1998) and OECD (2000) state that an inert material should be used. The BBA and OECD guidelines require cylindrical containers. This is relevant because the dimensions of the water and sediment layers (including the surface area in between them) should be clear. The thickness of the layers is preferred to be uniform throughout the system; this may not be the case with the OECD guideline which allows the use of centrifuge tubes. Other guidelines don't specify this aspect.
- Ratio sediment to water. Specifications on sediment and water are summarized in Table 2.1. No guidance is given in the US-EPA (1982, 1998) guidelines. BBA, CTB and OECD (2000) guidelines prescribe the thickness of the sediment layer: BBA 2 to 2.5 cm, CTB at least 2 cm and OECD (2000) requires 1 to 2.5 cm. FAO, SETAC, CTB and OECD (2000) guidelines specify the mass percentage of sediment (on dry mass basis) in the system. FAO and SETAC require 10 to 25% sediment, CTB 10% and OECD (2000) 25 to 33%. The sediment layer should be thick enough to reach and maintain anaerobic conditions below a transition top layer. In our opinion, the sediment layer should be at least 2.5 cm thick. The mass ratio sediment : water alone gives incomplete information; the depths of the water and sediment layers are needed, together with the bulk density of the sediment. The higher mass percentages of sediment may not reflect practice in a field ditch; this stresses the importance of obtaining system-independent rate coefficients instead of using simply dissipation rates.

Table 2.1 Specification of quantities with respect to sediment and water in the test guidelines. Mass ratio sediment: water on the basis of dry sediment mass.

Test guideline	*Depth sediment layer (cm)*	*Depth water layer (cm)*	*Mass ratio sediment : water*	*Volumes and masses*
US-EPA (1982)				
US-EPA (1998)	Details to be reported			
BBA (1990)	2 to 2.5	6		500 ml bottles
SETAC (1995) = FAO (1993)			Between 1:4 and 1:10	
CTB (1997)	≥ 2		1:10	
OECD (2000)	1 to 2.5	To be reported	Between 1:3 and 1:4	To be reported

- Measurements during acclimation. Only BBA, US-EPA (1998) and OECD (2000) prescribe these measurements. It is important to ensure that the system has reached or approached equilibrium with respect to oxygen concentration and redox potential before addition of the test substance. It is also important to add the test substance as soon as the system has reached its equilibrium because the biological activity should be maintained. The BBA guideline as well as the OECD (2000) guideline recognised these points.
- Duration of acclimation. Only the BBA, CTB and OECD (2000) guidelines consider this aspect. The OECD (2000) guideline, and to some extent the BBA

guideline too, searches for the balance between equilibration of the system and maintenance of biological activity. The CTB guideline prescribes an acclimation time of 6 to 8 weeks which means that it focusses on equilibration, without paying attention to maintenance of biological activity. In registration practice however, this long acclimation period is no longer required.

- Number of concentrations. All guidelines agree that only one start concentration needs to be used in the test.
- Vehicle. All test guidelines allow the use of a vehicle to add test substances with low solubility in water. However, they limit the use of such a vehicle, either by setting a maximum concentration (BBA, FAO and SETAC) or by stating that adding the vehicle should have no disturbing effect.
- Addition of test substance. The test guidelines all require addition of the substance to the water layer. The OECD (2000) option to apply the pesticide to the sediment is not representative for the field and it does not allow previous acclimation of the system.
- Dose of test substance. With exception of the BBA guideline, all test guidelines state that the dose in the test should reflect levels to be expected from the intended use in the field. The BBA guideline states that the dose should represent overspray into a water layer of 30 cm depth. This means that, with the exception of the rare direct applications to water bodies, the doses will be comparatively high in tests according to the BBA guideline. All test guidelines except the one of BBA, allow for higher concentrations in case of analytical limitations. The guidelines of CTB, US-EPA (1998) and OECD (2000) also point out that the dose should be selected such that there are no adverse effects on microbial activity.
- Temperature. All test guidelines require a constant temperature during the test. Guidelines of BBA, FAO, SETAC and CTB require a temperature of 20 ± 2 °C. This temperature is preferred by the OECD (2000) as well. US-EPA (1982) and OECD (2000) allow any temperature between 18 and 30 °C. The US-EPA (1998) guideline takes a different point of view, as it states that preference is given to a temperature equal to that in the field were the system is taken. The OECD (2000) suggests optional testing at lower temperatures, e.g. 10 °C. In Dutch registration practice various temperatures are acceptable, so between 18 and 30 °C or even lower with a minimum of about 10 °C. Normalisation of rate coefficients to another temperature within this range is considered to be possible.
- Light regime. The CTB guideline requires an 8/16 hr light/dark regime, but registration practice allows the studies to be performed in the dark. All other test guidelines, with the exception of US-EPA (1998), require the study to be performed in the dark. US-EPA (1998) allows for light at an intensity and with a light/dark regime equal to that in the field situation. For use of these studies in a first-tier screening approach, we consider this to be too complicated. The measured effect of light is only valid for specific situations and it is difficult to extrapolate the results to other situations. For easy interpretation, it seems better to perform the study in the dark. The effect of light on transformation in water can be studied in separate photolysis studies.
- Aeration. All test guidelines allow for aeration of the water layer in a way that the sediment is not disturbed. The BBA guideline requires a minimum oxygen concentration in the water of 20% of saturation.

- Replicates. FAO and SETAC guidelines do not require replicates; they state that anomalities will appear by comparison of the results for different time points. In all other test guidelines, two or more replicates are prescribed.
- Sampling times. The BBA guideline is the only guideline in which sampling times are fixed. All other guidelines show flexibility as long as the sampling times allow for adequate evaluation of the dissipation. This implies a higher frequency of sampling in the initial period and a less frequent sampling later on. The OECD (2000) guideline requires at least six sampling times, including zero time.
- Test duration. The BBA guideline does not state anything on this point. Most test guidelines show flexibility in duration based on the test substance. CTB requires at least 90% transformation of the test substance; the same target is mentioned by OECD (2000). FAO, SETAC and OECD (2000) demand that the transformation pathway and the distribution between water and sediment must be clear. All test guidelines have set a maximum to test duration, based on concern about the loss of microbial activity. US-EPA (1982) has set a maximum duration of 30 d, while US-EPA (1998) sets the limit to 60 d. CTB indicates a maximum of 90 d, while FAO, SETAC and OECD (2000) set the maximum duration to 100 d.
- Extraction and analysis. The test has to deliver data on individual substances, including transformation products, in both the water layer and the sediment. All test guidelines, except those of US-EPA (1982) and CTB, require separate analysis of sediment and water. Though not stated in the guideline, this is a requirement of CTB too. FAO, SETAC and OECD (2000) require the extraction and analysis of whole flasks, which excludes sub-sampling. US-EPA (1982) and CTB don't state anything on this topic. According to US-EPA (1998) and OECD (2000) attention has to be paid to adsorption/absorption to test vessels and tubing. Analytics itself is hardly described in the test guidelines; BBA and OECD (2000) use the wording "appropriate analytical techniques". This is reasonable as extraction and analysis depends on the composition and properties of the substances and they are often influenced by the composition of water and sediment.
- Parameters per point in time. According to the FAO and SETAC guidelines, pH and oxygen, both in the water layer, are the only parameters to be measured during incubation. This does not allow for a necessary check on the conditions within the sediment. The BBA guideline prescribes to measure the redox potential within the sediment, while the OECD (2000) requires the pH of the sediment to be measured as well. So, BBA and OECD (2000) guidelines allow for the necessary check on aerobic condition in the water and anaerobic condition in the sediment.
- Identification of metabolites. Though all test guidelines require identification of the most important transformation products, differences exist in the formation thresholds above which identification is obligatory. The guidelines of FAO, SETAC, US-EPA (1998) and OECD (2000) set this threshold at 10% of the amount of test substance applied. CTB states that all products which are not found in soil studies have to be identified. However, this approach is not applied always, since the 10% threshold is valid in the Netherlands as well. The US-EPA (1982) guideline handles the 0.01 mg/kg level, which can deviate considerably from the 10% criterion. In the BBA guideline no threshold is set, since analytical possibilities govern the identification.

- Parameters at termination. BBA and OECD are the only guidelines dealing with measurements at termination. BBA prescribes measurements on oxygen concentration and redox potential which allow for the necessary check on aerobic condition in the water and anaerobic condition in the sediment. Both, BBA and OECD (2000) ask for measurement of the biomass, which gives information on the maintenance of microbial activity. Besides these parameters, OECD (2000) prescribes pH and TOC measurements.
- Mass balance. All test guidelines require mass balances. Different criteria are set to the level of completeness of the mass balances. US-EPA (1998) and CTB require at least 80% of applied radioactivity (AR) to be recovered. FAO and SETAC ask for recovery rates between 90 and 110% AR, and BBA for minimum recoveries of 90% AR. The OECD (2000) guideline sets two threshold values, namely 90-110% for radiolabelled test substances and 70-110% for non-labelled test substances.

d) Intended endpoints

- Rate constants. Table 2.2 summarizes the descriptions of the endpoints in the various test guidelines. Most guidelines are incomplete in specifying the required endpoints and the methods to be used to calculate the endpoints. US-EPA (1982) asks for half-lives, but does not specify this with respect to water, sediment or total system. BBA states the endpoints clearly, but the method of calculation is not clear. FAO and SETAC leave everything open. CTB does not give guidance on how the rates should be characterized or calculated. US-EPA (1982) requires the rate coefficients for disappearance from the water column to be calculated by using first-order kinetics. In the section on reporting, just rate coefficients and half-lives are required. The OECD (2000) is rather complete in specifying endpoints, in defining terms like half-life and DT50 and in presenting methods to be used for the calculations. Even the results of tests according to the OECD (2000) guideline require further elaboration to obtain the separate transformation rates for the water and sediment layers.
- Transformation pathway. All test guideline require the transformation pathway to be given.

Table 2.2 Endpoints of the water-sediment tests as described in the guidelines

Test guideline	*Desired endpoints*	*Calculation method*
US-EPA (1982)	Half-lives	Not stated
US-EPA (1998)	Rate constants for water column Half-life	First-order kinetics
BBA (1990)	DT50, DT90 in water DT50, DT90 in system	Determine order of kinetics
SETAC (1995) = FAO (1993)	Not stated	
CTB (1997)	Rate of transformation of parent and products	Not stated
OECD (2000)	Rate of transformation of parent and products Half-life DT50, DT75, DT90 for water, sediment and total system	Pseudo-first-order kinetics Curve-fitting techniques Compartment models

Endpoints required in the evaluation procedure in the EU are dissipation DT50 and DT90 for the water layer as well as for the sediment layer and the distribution between water and sediment of both the parent substance and its metabolites.

With respect to the characterisation of water-sediment material in the field before taking it to the laboratory, as well as in the laboratory before and during testing, recent research has revealed that other parameters than those commonly recognised are relevant for drawing conclusions on the microbial viability of the test system. These parameters are colony forming units, BOD, Ca^{2+} (water), Mg^{2+} (water), Mn^{2+} (water), N_{tot} (sediment) and P_{tot} (sediment). More information on this topic can be found in Chapter 6.

2.5 Discussion

In the guidelines on the water-sediment studies, the separate transformation rates of the compounds in the water layer and sediment layer are not requested straightforwardly. The endpoints deal with the dissipation of the pesticide in the two layers, which is the result of various processes. The original aim of the guidelines was to get a general picture of persistence of the pesticide in the layers and in the whole system. Further, the tests provide information on the distribution of the substances between the water and sediment layers. A picture is obtained of the products formed from the pesticide and their persistence in water-sediment systems.

The future OECD test guideline will have the desired high level of detail. This will allow judgement of the quality of the tests and of the extent to which the tests meet the objective of simulating field conditions. Further, the OECD guideline provides the best chance that the dimensions of the layers in the test system can be derived from the test reports.

A new guideline like that of OECD (2000) should be more suitable to derive the pesticide transformation rates than its predecessors. The sediment layer should have a minimum thickness (at least 2.5 cm), to allow the existence of a largely anaerobic layer below the aerobic/anaerobic transition. Further, the system should not be centrifuged or filtered before analysis, as this disturbes pesticide distribution between the layers.

The OECD guideline gives a description of the endpoints required, such as the half-lives or DT50's for dissipation of the pesticide in the water and sediment layers. Further, it gives methods to be used to calculate these endpoints. However, even in this new test guideline, the endpoints deal with dissipation of the pesticide and not with transformation in the water and sediment layers, as needed for the TOXSWA model. In its section on reporting, the OECD guideline recognizes that such separate transformation rates are needed. The same is stated in the framework of EU registration. However, no procedure is described to obtain the separate transformation rates.

The pesticide is subjected to a set of simultaneous processes in the water-sediment systems: adsorption, convection, diffusion, volatilization and transformation. The system is heterogeneous, with an aerobic water layer and a mainly anaerobic

sediment layer. A transition layer aerobic/anaerobic is found in the top of the sediment. Further, the distribution of compounds in the system is dynamic: usually mixing in the water layer is fast but penetration into the sediment layer may be slow. If the dissipation from the water layer is comparatively fast, net release from the sediment layer occurs later on.

A computation model seems to be needed to simulate the various simultaneous processes in the water-sediment system and to estimate the separate transformation rates. Then it should be possible to estimate the other processes quite accurately: adsorption, transport in the sediment and volatilization. Requirements are that the water-sediment experiment is set up adequately, and that procedure and results are described in detail. A procedure for deriving the separate transformation rates from water-sediment studies is elaborated in the next chapter. It should show the possibilities and limitations of such a procedure.

3 Procedure for estimating transformation rates in water and sediment

3.1 Introduction

Per 1 June 1999 the TOXSWA model (Adriaanse, 1996) has been implemented in the Dutch pesticide registration procedure. TOXSWA is the acronym of TOXic substances in Surface WAters. The model requires transformation rates for the pesticide in the water and sediment layers as input data. As no specific studies to determine transformation rates in water and sediment are required for pesticide registration, the transformation rates need to be estimated from the results of the water-sediment study.

The aerobic-anaerobic water-sediment study is required in the submission for registration of a pesticide. This study is needed to get insight in the persistence of the compound and its degradation products in shallow surface waters with influence of bottom sediment. In the water-sediment study the decline of the compound is studied in at least two sediments and their associated waters.

In the water-sediment systems the following processes play a role: (i) volatilization, (ii) diffusion into and out of the sediment, (iii) sorption to dissolved organic carbon (DOC) and suspended solids, (iv) sorption to the solid phase of the sediment, (v) transformation in the water layer and (vi) transformation in the sediment. In general the sediment has been sieved before being introduced into the water-sediment system, so we assume that bioturbation does not take place. We also assume that sedimentation and resuspension of solid material can be neglected. Most test protocols prescribe an initial acclimation and sedimentation period before the compound is introduced into the system and an aeration of the system that should not disturb the sediment.

The decline rate of the compound in the entire system covers the processes volatilization and transformation in the water and sediment. The decline rate for the water covers volatilization, diffusion into and out of the sediment, sorption to DOC and suspended solids (depending on the test protocol followed) and transformation in the water. The decline rate for the sediment covers the diffusion out of and into the sediment and the transformation in the sediment. The diffusion rate into the sediment depends strongly on the sorption process in the sediment. Because of the simultaneous processes, we cannot derive in a straightforward way the separate transformation rates in water and sediment from the results of the water-sediment study.

If we quantify all processes for the pesticide and then simulate its behaviour in the water-sediment systems, we obtain concentrations in the water and sediment. These simulated concentrations can be compared with the concentrations measured in the water-sediment system as a function of time. If the transformation rates in the water

and sediment are the only unknown parameters we can attempt to estimate these in such a way that good correspondence between the simulated and measured concentrations is obtained. In this way real transformation rates, and not only decline rates, can be estimated from the results of the water-sediment studies.

The TOXSWA model describes the concentration of a compound as a function of time and distance (or depth) in a water body and its sediment. It includes all processes mentioned to play a role in the water-sediment systems, except the sorption to DOC. Excluding compounds showing very strong sorption (e.g. pyrethroids), sorption to DOC hardly influences the behaviour of a compound in water-sediment systems. Further, the DOC represents only a very small mass of sorbing material. As the TOXSWA model contains all relevant processes we decided to make attempts to use the model for estimating the individual rates of pesticide transformation in the water and sediment layers of the test systems. It should be noted that the main use of TOXSWA in the registration procedure is to calculate the exposure of the organisms in standard watercourses to pesticides.

3.2 Use of TOXSWA

The water-sediment system will be simulated by the TOXSWA model. Below, the input data are described that are needed to run the TOXSWA model for a water-sediment system. Of course, these data should represent the water-sediment system precisely and they should be obtained in a well-defined and unequivocal way.

The TOXSWA model has been developed to describe the fate of pesticides entering ditches (i) by drift or atmospheric deposition, (ii) by surface runoff or (iii) by drainage or leaching through the soil. The simulated watercourse consists of a water layer containing suspended solids and possibly macrophytes, and a sediment layer whose properties (porosity, bulk density and organic matter content) vary with depth. In the water layer, the pesticide concentration is assumed to be constant in the vertical direction, but it varies in the horizontal direction. In the sediment layer, the pesticide concentration is a function of both the horizontal and vertical distances. TOXSWA considers four processes: (i) transport, (ii) transformation, (iii) sorption and (iv) volatilization. In the water layer, pesticides are transported by advection and dispersion; in the sediment layer diffusion is included. The transformation rate covers the combined effects of hydrolysis, photolysis and biodegradation; metabolites are not considered. Sorption to suspended solids and to sediment is described by a linear isotherm. Pesticides are transported across the water-sediment interface by advection (upward or downward seepage) and by diffusion. In the present study TOXSWA is applied to the small water-sediment systems, so no horizontal transport takes place and the pesticide concentration in horizontal direction in both water layer and sediment layer is constant.

All input parameters need to be derived from the description of the water-sediment study and from other studies conducted for the compound. The only exceptions form the transformation rates in the water and in the sediment, which cannot be

derived directly from a water-sediment study. Only the decline rates in the water layer and in the sediment layer are determined in such a study. TOXSWA simulates the water-sediment study using initial estimates for the transformation rates. Next, these rates will be adjusted in such a way that the best possible correspondence between the simulated and measured concentrations in the water as well as in the sediment is obtained. In this way the separate transformation rates will be estimated as they may be needed in the Dutch registration procedure for assessing the hazards to the aquatic ecosystems in the future.

The data required to run the TOXSWA model for the water-sediment system are summarised below. In case they are not mentioned in the report of the water-sediment study nor in the Users Manual of TOXSWA (Beltman and Adriaanse, 1999a) a method to estimate them is proposed.

Physico-chemical and derived properties

Molecular mass of the compound studied ($g.mol^{-1}$)
Saturated vapour pressure (Pa), its temperature of measurement (°C) and its molar enthalpy of vaporisation ($J.mol^{-1}$).
Solubility in water ($g.m^{-3}$), its temperature of measurement (°C) and its molar enthalpy of dissolution ($J.mol^{-1}$).
Coefficients for the exchange of the compound between water and air ($m.d^{-1}$).

Dimensions of the water-sediment system

The water depth and the depth of the sediment layer need to be known to be able to simulate the water-sediment system. Curves for pesticide concentration as a function of time may be expected to differ for systems with a thin or with a thick sediment (or water) layer. Often water-sediment studies only mention the volume of water and the dry mass of the sediment brought into the system. Using the dry bulk density and the porosity of the sediment (see below), the volume of the bottom sediment can be calculated and the ratio between the volumes of water layer and sediment layer is known. When the internal diameter of the test vessels has been reported, the depth of the water and sediment layers can be calculated.

Note that in the TOXSWA model a rectangular water-sediment system has been modelled, while the test vessels used in the standardized water-sediment studies generally are circular. As long as the depths of both layers are correct, TOXSWA will correctly simulate the concentration profiles in the water and sediment layers.

Water layer properties

The water layer in the TOXSWA model contains suspended solids onto which the compound may be sorbed. If the concentration of suspended solids has not been reported, we assume that 15 $mg.l^{-1}$ is present. This concentration is also used in the Dutch standard scenario (Beltman and Adriaanse, 1999b). If the mass fraction of organic matter or organic carbon in the suspended solids has not been reported, we assume that this ratio equals the fraction in the sediment.

Sediment properties

The TOXSWA model simulates the pesticide concentration as a function of depth in the sediment. Sediment composition and structure need to be known, i.e. bulk density, porosity, tortuosity and organic matter content as a function of depth. In general, the sediment has been sieved/homogenised before being introduced into the water-sediment system. Although some differentiation with depth may develop during the sedimentation and acclimation period of the systems, we assume that the sediment is homogeneous in the TOXSWA simulations. More information on the properties of the sediment layer as a function of depth is desirable.

Often the bulk density and the porosity of the sediment are not reported. Sometimes the bulk density is reported for the location of sampling. Using the reported particle size distribution, however, it is possible to estimate the dry bulk density and the porosity of the sediment used. Wösten (1997a and 1997b) describes continuous pedotransfer functions to derive dry bulk densities and the density of the solid phase for soils as a function of the clay and silt fractions, the organic matter content and sometimes the median sand particle size. By using this method, developed for structured soils and not for sediments, the bulk densities may be underestimated and the porosities overestimated. Wösten (pers. communication, 1999) hypothesizes that the bulk densities of structured soils are lower than those of sediments. The bulk density of natural sediments is, on its turn, expected to be smaller than that of sediment that has settled after sieving its components and taking out larger parts of detritus. Evidently, more information on the bulk density and porosity of the sediment layer in water-sediment studies is needed.

The tortuosity factor for diffusion through the liquid phase of the sediment has been given in Beltman and Adriaanse (1999a).

In general the organic carbon content or the organic matter content of the sediment used in the study has been reported. As a rule of thumb the conversion factor of 0.58 is often used to convert the organic matter content into the organic carbon content (or the factor of 1.7 to convert the organic carbon content into the organic matter content). However, recent research (STOWA, 1997) demonstrated that for freshwater sediments the factor of 1.7 is an underestimation and that a factor of 1.97 is a better estimation. This factor is based on linear regression between the total organic carbon (TOC) content and the loss-on-ignition for 38 Dutch freshwater sediments. The regression coefficient was 0.980 and the relative standard deviation 10.1 %. Therefore, we recommend to use this factor of 1.97 to convert the organic carbon content to the organic matter content of the sediment.

Sorption parameters

In the TOXSWA simulation for the water-sediment system, sorption occurs onto the sediment as well as onto the suspended solids. To describe these sorption processes we use the coefficient for distribution between organic matter and water, K_{om}. If reported, the value of K_{om} from the water-sediment study is used. Alternatively, we use the value of K_{om} as determined for the assessment of mobility in soil in the Dutch registration procedure. This adsorption coefficient K_{om} is the average of at

least three K_{om} values determined for different soils representative for Dutch agriculture and ranging in organic matter content from 5 to 150 $g.kg^{-1}$(Brouwer et al., 1994). Generally, the K_{om} values have been estimated at a reference concentration of 1 $mg.l^{-1}$. Most sorption isotherms for soils are not linear and Boesten (1986) recommends to use a Freundlich coefficient *n* of 0.9 as an average for soils. We recommend to apply this value also in the TOXSWA simulations for the water-sediment studies, as we have no better value available. Literature research should be done to find a better founded approximation for sediment sorption isotherms.

Initial estimates of the transformation rates in water and sediment

The decline rates of the compound in the water and in the total system have generally been calculated in the report submitted by the registration applicant. Sometimes the decline rate of the compound in the sediment has also been reported. In case of first-order transformation kinetics the decline rate of the compound in the sediment can be calculated by means of linear regression between the natural logarithm of the concentration in the sediment and time. We recommend to use the decline rate in the total system as initial estimates for the transformation rates in the water layer as well as in the sediment layer. Especially for compounds showing strong sorption, the decline rates in the water layer and sediment layer are strongly influenced by sorption, so they do not reflect the transformation rates of the compound.

Measured concentrations in water and sediment

It is attempted to simulate the measured concentrations of the water-sediment studies by the TOXSWA model. In general, a series of test vessels forms the water-sediment system, each vessel with a (nearly) identical initial concentration of the compound studied. At the selected points in time, complete test vessels are analysed. Amounts of the parent compound are measured as percentages of initial radioactivity. From these data we calculate measured mass concentrations in water and sediment by:

(i) correction for the deviation from the target initial concentration (e.g. measured value of 1.10 $mg.l^{-1}$ instead of the target of 1.00 $mg.l^{-1}$ in the test vessel). Often this correction has already been made by the authors of the study;
(ii) conversion of radioactivity into mass concentration.

The calculations in TOXSWA are made for mass concentrations. The initial mass of the compound is assigned to the water layer, which is the applied volume of water minus the volume penetrated into the dry sediment. The initial concentration corresponds to 100% radioactivity. For each time, the percentages of radioactivity in the water layer can be converted into mass concentrations. The sediment volume equals its dry mass divided by its dry bulk density. For each time, the percentages of radioactivity in the sediment can be converted into mass concentrations in the sediment. Here we assume that the balance of radioactivity has already been checked and approved for the systems studied.

3.3 Discussion

Simulation of the water-sediment experiments with a model like TOXSWA seems to be the only way to obtain separate transformation rates for the pesticide in the water and sediment layers. The principle of the procedure that can be followed is clear. However, some types of problem may arise when applying the procedure to actual water-sediment studies, such as:

- the experimental procedure does not correspond completely to the system simulated by the model;
- the dimensions of experimental system and layers are not stated in explicit way;
- input data for the pesticide are missing;
- the results indicate that one or more processes proceed different from the way described by the model.

Such problems may arise because of the different test guidelines (Chapter 2), especially if they do not ask for experimental details.

In the next chapter, the proposed procedure is tried-out for three pesticides to trace the problems that can be encountered when applying the procedure to actual tests and pesticides.

4 Try-out for three pesticides

4.1 Introduction

In Chapter 3 we proposed a method for estimating the transformation rates of a pesticide in water layer and sediment layer from the results of a water-sediment test. First of all, such a method should be tried-out for some practical cases.

We selected the results of water-sediment studies for three compounds for the try-out. Selection criteria were (i) the water-sediment studies should comply to one of the protocols currently accepted by the Dutch Board of the Authorization of Pesticides, (ii) the compounds should have different sorption strengths and (iii) the water-sediment studies should have been carried out by different laboratories. One study should preferably be carried out by the Dutch TNO Institute. We selected the following three water-sediment studies:

- indoxacarb, studied in 1997, by the laboratory of DuPont Agricultural Products in Wilmington, Delaware, USA.
- dicamba, studied in 1990, by the laboratory of RCC Umweltchemie AG in Itingen, Switzerland and
- chlorpropham, studied in 1992, by the laboratory of the TNO Institute of Environmental Sciences in Delft, the Netherlands.

This try-out should show which practical problems are encountered when trying to use the method. The next question is then whether there are solutions for such problems.

4.2 Indoxacarb

4.2.1 Experiments

Physico-chemical properties

Physico-chemical properties of indoxacarb are given by Priester et al., (1996). The vapour pressure at 20 ^{o}C is 1.3 10 $^{-7}$ mPa (extremely low). The solubility of indoxacarb in water is 15 $\mu g/L$ (pH5 buffer, 20 ^{o}C). The octanol/water distribution coefficient is 41 000 (at 40 ^{o}C).

The half-life of the hydrolysis of indoxacarb in water is > 30 days (pH5), about 30 days (pH7) and about 2 days (pH9) (Tomlin, 1997).

Water-sediment experiment

The rate of transformation of indoxacarb was measured in water-sediment systems (McFetridge and Houben, 1997) taken from:

a) Brandywine River in Delaware County, Pennsylvania (referred to as River);
b) Lums Pond in New Castle County, Delaware, Pennsylvania (referred to as Pond).

A mass of 40 g sediment (dry mass basis) and 160 ml of associated natural water were put in 250 ml PTFE (Teflon) centrifuge bottles. The pre-incubation period was 6 days. Both sediments were of sand texture, with organic matter contents of 1.15% (River) and 0.34% (Pond). The bulk densities were reported to be 1.35 g/cm^3 (River) and 1.46 g/cm ^{3} (Pond). Probably these values apply to the site of collection (not clear). (Compare the pH values mentioned under Source in Tables 3 and 4 with those mentioned in Tables 1 and 2 of McFetridge and Houben, 1997).

DOC concentrations in the water were 2.8 mg/L (River) and 6.7 mg/L (Pond). The concentrations of suspended solids were: 4 mg/L (River) and 44 mg/L (Pond). In the incubation period, the average pH values in the water were 6.1 (River) and 6.4 (Pond). During the incubation, the water layer was aerated. The water layer was aerobic and the sediment layer was moderately anaerobic.

In each of the two incubation series, indoxacarb was radiolabelled at a different position in the molecule. A mass of 160 µg of indoxacarb (in a small volume of acetone) was added to the water. The initial concentration would be about 1000 µg/L, which is far above the water solubility. The systems were incubated in the dark at 20 °C.

At the sampling times in a period of 101 days, the systems were centrifuged to separate water and sediment phases. After this the water layer and the sediment were analysed separately for radioactivity and for indoxacarb.

Concentrations measured in water and sediment layers

The concentrations in water and sediment were calculated by using the percentage of applied radioactivity, measured as a function of time in water and sediment (Tables 9 to 12 of McFetridge and Houben, 1997). The concentration in the water layer equals the fraction of applied radioactivity times 160 µg of added indoxacarb, divided by the volume of the water layer (volume added to the test vessels minus the volume becoming pore water in the sediment). The concentration in the sediment equals the fraction of applied radioactivity times 160 µg of added indoxacarb, divided by the volume of the sediment (i.e. mass of dry sediment added divided by the bulk density). Appendices 2 and 3 present the concentrations for the River and Pond systems, respectively.

Sorption to soils

The adsorption of indoxacarb to four soils was measured by batch equilibration (Priester et al., 1996). Soils: sand, sandy clay loam, loam and silt loam. Range of organic matter contents: 1.0 to 2.4%. A volume of 25 ml solution was shaken with 0.2 to 5.0 g of soil for 1 hour (dark, about 25 °C). The average Freundlich coefficient based on organic carbon, K_{foc}, was 5680 cm^3/g (n = 4; s = 3020 cm^3/g). The average value of the Freundlich exponent was 0.81 (n = 4; s = 0.11). The concentration range in solution after shaking was below 10 µg/L; the Freundlich reference concentration was taken to be 1 µg/L. The average value of the linear-sorption coefficient based on organic carbon, K_{doc}, was 4530 cm^3/g (n = 4; s = 2620 cm^3/g).

In the EU monograph on indoxacarb, a mean K_{oc} value of 1520 l/kg has been used to calculate its mobility in soil. This value is the average of the four Koc values 670,

945, 1780 and 2690 l/kg, that were obtained by calculating the corresponding K_f values at the reference concentration of 1 mg/l normally used. The standard deviation of the average Freundlich coefficient based on organic carbon was 910 l/kg (n=4). The average value of the Freundlich exponent was 0.81 (mentioned only in a background document of the evaluating agency to the EU monograph).

4.2.2 Input data

Below we summarise the input data needed for TOXSWA 1.2 to simulate the water-sediment study of indoxacarb.

The bulk densities of the sediment, probably measured at the site of collection, were 1.35 and 1.46 g/cm^3 for River and Pond sediment, respectively. Before being brought into the test tubes the sediment was not sieved. We assumed the bulk densities in the test tubes during incubation to be 1.40 and 1.50 g/cm^3 for River and Pond sediment, respectively. The densities of the solid phase of the sediments were calculated with the formula of Poelman (Wösten, 1997b) on the basis of the reported particle size distribution; they were 2.64 and 2.66 g/cm^3, respectively. The porosity equals 1 minus the ratio of the bulk density phase of the sediment and the density of its solid phase.

The dimensions of the test vessels were not reported. We assumed the test vessels to have a diameter of 5 cm, into which 40 g dry sediment and 160 ml of associated natural water was brought. Next, the volume of the water layer in the test vessels was calculated as water volume added minus water volume becoming pore water in the sediment. Dividing the volume of the water layer by the cross-sectional area corresponding to the diameter of 5 cm yields the thickness of the water layer.

Sorption of indoxacarb clearly is a non-linear process (n=0.81), so we decided to use the Freundlich-type sorption isotherm description in TOXSWA. Both sets of data mentioned in Table 4.5 (Freundlich coefficient based on organic matter content of 2880 l/kg calculated at a reference concentration of 1 µg/l and 770 l/kg at 1 mg/l) describe the same sorption isotherm and so, we checked that both isotherm descriptions resulted in identical model outcome.

4.2.3 Results for River

For indoxacarb in the River system we ran TOXSWA 1.2 with the input data specified in Tables 4.1 to 4.5. Figure 4.1 shows the results. Initially, the simulated concentrations in the water layer were higher than the measured concentrations, but after about 20 to 25 d the simulated concentrations were lower those measured. The simulated concentration peak in the sediment of nearly 1000 µg/l is low as compared to the measured peaks of 3300 and 2700 µg/l (label 1 and 2, respectively). With both radiolabels in the molecule, similar results were obtained.

A subsequent run with a halved half-life of 5 d in the water layer and a doubled half-life of 20 d in the sediment (and maintaining all other input values) resulted in water layer concentrations somewhat closer to the concentrations measured in the beginning (Fig. 4.2). Correspondence is not very satisfactory, however, as neither the initial rapid drop, nor the sustained concentration levels after about 50 d were simulated well. Again, the simulated concentration peak in the sediment was much lower than the measured concentration peak (about 900 µg/l versus about 3300 µg/l (label 1) and 2700 µg/l (label 2)). Thus, it was not possible to simulate the measured concentration curves by only adapting the half-lives.

4.2.4 Sensitivity analysis for River

As this was our first try-out for a pesticide, we decided to explore the influence of the two input parameters sorption and layer thickness on the simulated concentrations. In the studied water-sediment system the sorption parameter characterising the sediment may differ from the average value found for soils (Priester et al., 1996). The dimensions of the test vessels were not reported, so the real thickness of the layers may differ from that assumed.

We decided to raise the sorption coefficient K_{om} to its average value plus two times its standard deviation (corresponding to a 95 % probability interval). In the new Run Sens1 with the TOXSWA model, a K_{om} of 5940 l/kg was introduced. All other input parameters were as specified in Tables 4.1 to 4.5. Figure 4.3 shows the results. The simulated concentration peak in the sediment rises to about 1250 µg/l, so it is still much lower than the measured concentration peak. The simulated concentrations in the water layer are somewhat lower those shown in Figure 4.1, but they are still higher than the measured concentrations up to 20 d.

As the exact dimensions of the test vessels had not been reported we tried another run (Run Sens2) for wider test vessels (9 cm diameter instead of 5 cm), so with thinner sediment and water layers, the added masses and volumes were maintained. The input data for this run were a K_{om} of 5940 l/kg, a sediment thickness of 4 mm (4 segments of 1 mm) and a water depth of 2.3 cm. All other input data were those of Tables 4.1 to 4.5. The second line in Figure 4.3 presents the results. In this case the simulated concentration peak in the sediment of about 2800 µg/l corresponded well with the measured peaks of about 3300 and 2700 µg/l. On the other hand, the simulated decline in the sediment was too high. In the water layer the simulated concentrations corresponded reasonably well with the measured concentrations.

The third line in Figure 4.3 shows the results of Run Sens3 for a K_{om}-value of 5940 l/kg, a sediment thickness of 4 mm, a water depth of 2.3 cm and transformation half-lives of 10 d and 15 d in the water and sediment layer, respectively. All other input data were those in Tables 4.1 to 4.3 and Table 4.5. The simulated concentrations in the water as well as in the sediment layer corresponded somewhat better to the measured concentrations than those of Run Sens2.

We made these assumptions on sorption parameters and test vessel dimensions only in a preliminary phase to obtain insight on how they influence the simulated concentrations. In the final procedure (Chapter 5) we propose to vary only the individual transformation rates and not other input parameters. All other input parameters need to be estimated in the way described in Section 3.2, unless there are sound, justified reasons to estimate them in a different way.

4.2.5 Results for Pond

For indoxacarb in the Pond system the situation is similar to that in the River system. Main differences in the input data are the organic matter content of the sediment (0.34 % instead of 1.15 %) and the initial estimates for the transformation rates in water and sediment. We ran TOXSWA 1.2 with the input data specified in Tables 4.5 to 4.9. Figure 4.4 shows the results. Up to about 35 d the simulated concentrations in the water layer were higher than the measured concentrations. The simulated concentration peak of about 750 µg/l in the sediment was much too low compared to the measured peaks of about 4000 and 2800 µg/l for Radiolabels 1 and 2, respectively.

Table 4.1. Input data for the water layer, indoxacarb (River)

Water layer
Rectangular (!), vertical cross-section 0.05 m wide (assumption)
Water depth 0.075 m
Water depth defining perimeter for exchange wl-sed 0.001 m
Concentration suspended solids 4 g/m^3 With an organic matter content of 0.0115 kg/kg
No flow, dummy value of 10 m^2/d for longitudinal dispersion coefficient
Initial concentration 1000 µg/l

Table 4.2. Input data for the sediment, indoxacarb (River)

Sediment
Sediment thickness 0.015 m
Bulk density 1400 kg/m^3, constant with depth
Porosity 0.47, constant with depth
Tortuosity 0.45, constant with depth
Organic matter content 0.0115 kg/kg, constant with depth
Initial concentration 0 µg/l

Table 4.3. Input data concerning the simulation, indoxacarb (River)

Simulation
One segment of 0.05 m length in the water layer (assumption)
Segments of 1, 1, 1, 1, 2, 2, 2 and 5 mm corresponding to The total thickness of the sediment
Calculation time step 3600 s
Total time simulated 105 d

Table 4.4. Input data concerning the initial estimates of transformation rates, indoxacarb (River)

Initial estimates for transformation half-lives
Transformation half-life in water 10 d
Transformation half-life in sediment 10 d

Table 4.5. Input data for the compound indoxacarb

Compound
Physico-chemical data:
molecular mass 527.83 g/mol
saturated vapour pressure $1.3*10^{-10}$ Pa at 20 °C
solubility in water $13.6*10^{-6}$ g/l at 20 °C
Sorption:
Kom (soils) 2880 ± 1530 l/kg or 770 ± 460 l/kg, resp.
Freundlich exponent 0.81 or 0.81, resp.
Reference concentration 1 µg/l or 1 mg/l, resp.

Table 4.6. Input data for the water layer, indoxacarb (Pond)

Water layer
Rectangular (!), vertical cross-section 0.05 m wide (assumption)
Water depth 0.076 m
Water depth defining perimeter for exchange wl-sed 0.001 m
Concentration suspended solids 44 g/m^3 With an organic matter content of 0.0034 kg/kg
No flow, dummy value of 10 m^2/d for longitudinal dispersion coefficient
Initial concentration 1000 µg/l

Table 4.7. Input data for the sediment, indoxacarb (Pond)

Sediment
Sediment thickness 0.014 m
Bulk density 1500 kg/m^3, constant with depth
Porosity 0.44 , constant with depth
Tortuosity 0.40 , constant with depth
Organic matter content 0.0034 kg/kg, constant with depth
Initial concentration 0 µg/l

Table 4.8. Input data concerning the simulation, indoxacarb (Pond)

Simulation
One segment of 0.05 m length in the water layer (assumption)
Segments of 1, 1, 1, 1, 2, 2, 2 and 4 mm corresponding to The total thickness of the sediment
Calculation time step 3600 s
Total time simulated 105 d

Table 4.9. Input data concerning the initial estimates of transformation rates, indoxacarb (Pond)

Initial estimates for transformation half-lives
Transformation half-life in water 17 d
Transformation half-life in sediment 17 d

Concentration of pesticide in time

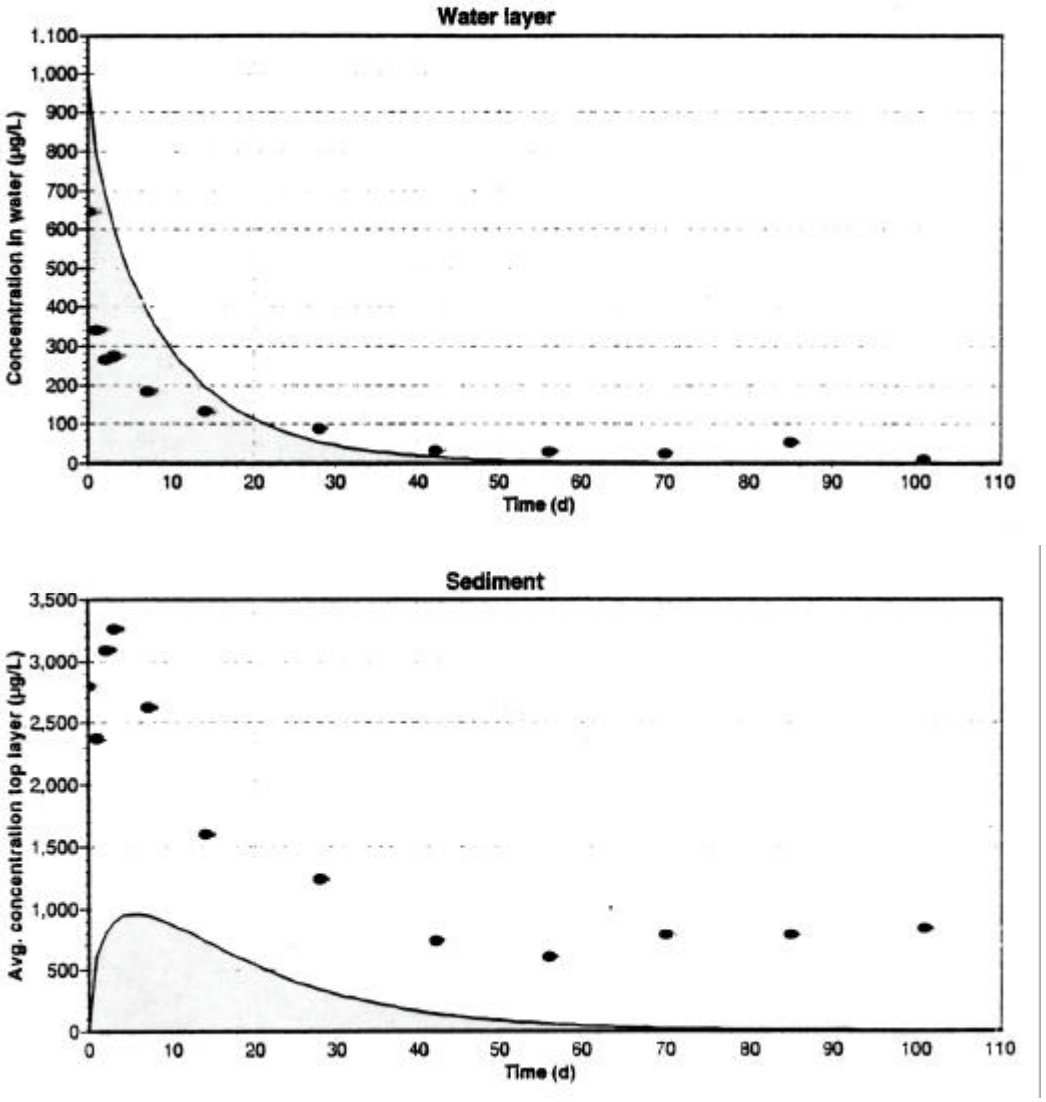


Figure 4.1. Simulated and measured concentrations of indoxacarb as a function of time in water and sediment of the River system ($DT50_{wl}$ = $DT50_{sed}$ = 10 d in TOXSWA input). Points: measured; lines: computed. Radiolabel 1.

Concentration of pesticide in time

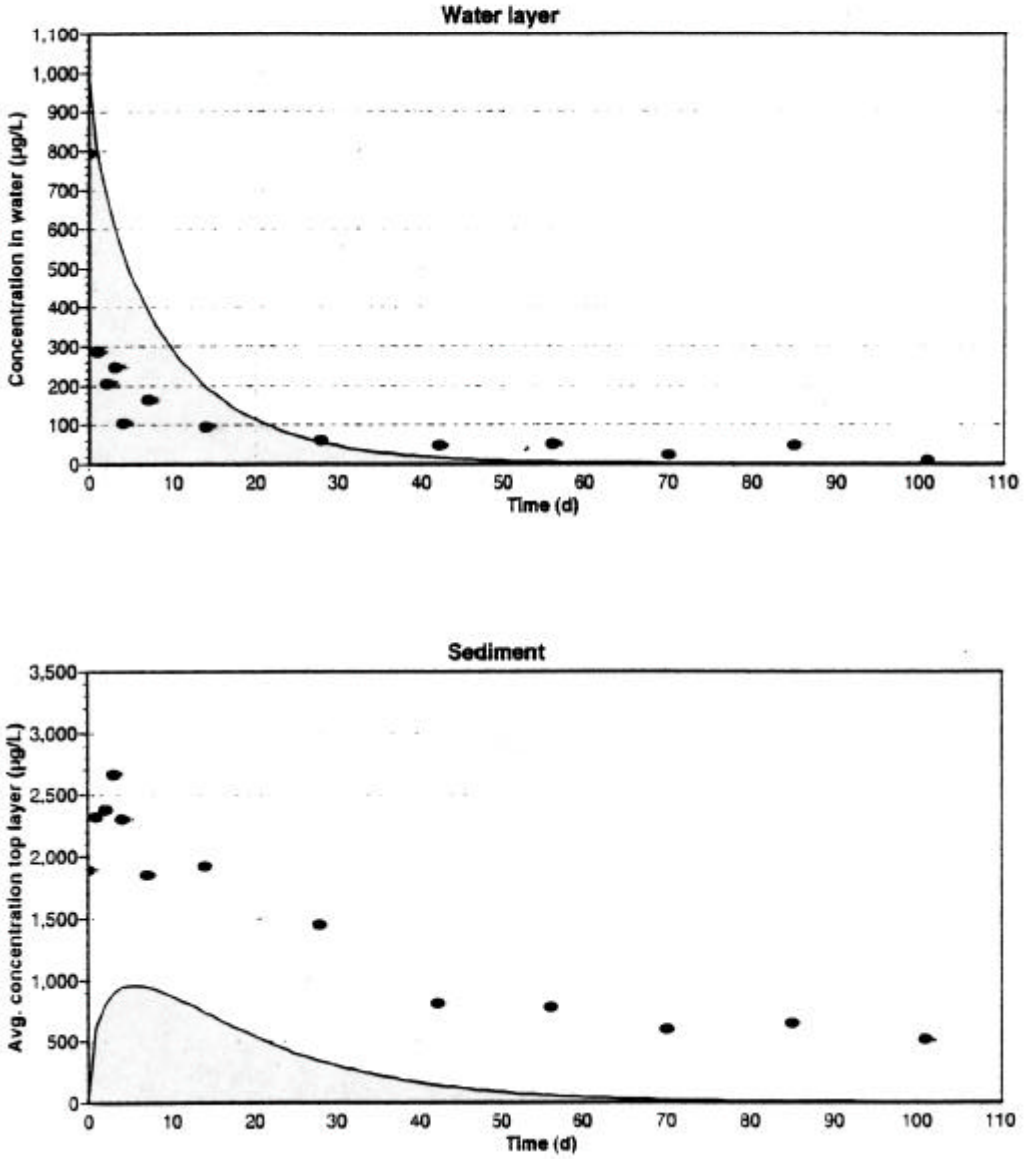


Figure 4.1 (continued). Radiolabel 2.

Concentration of pesticide in time

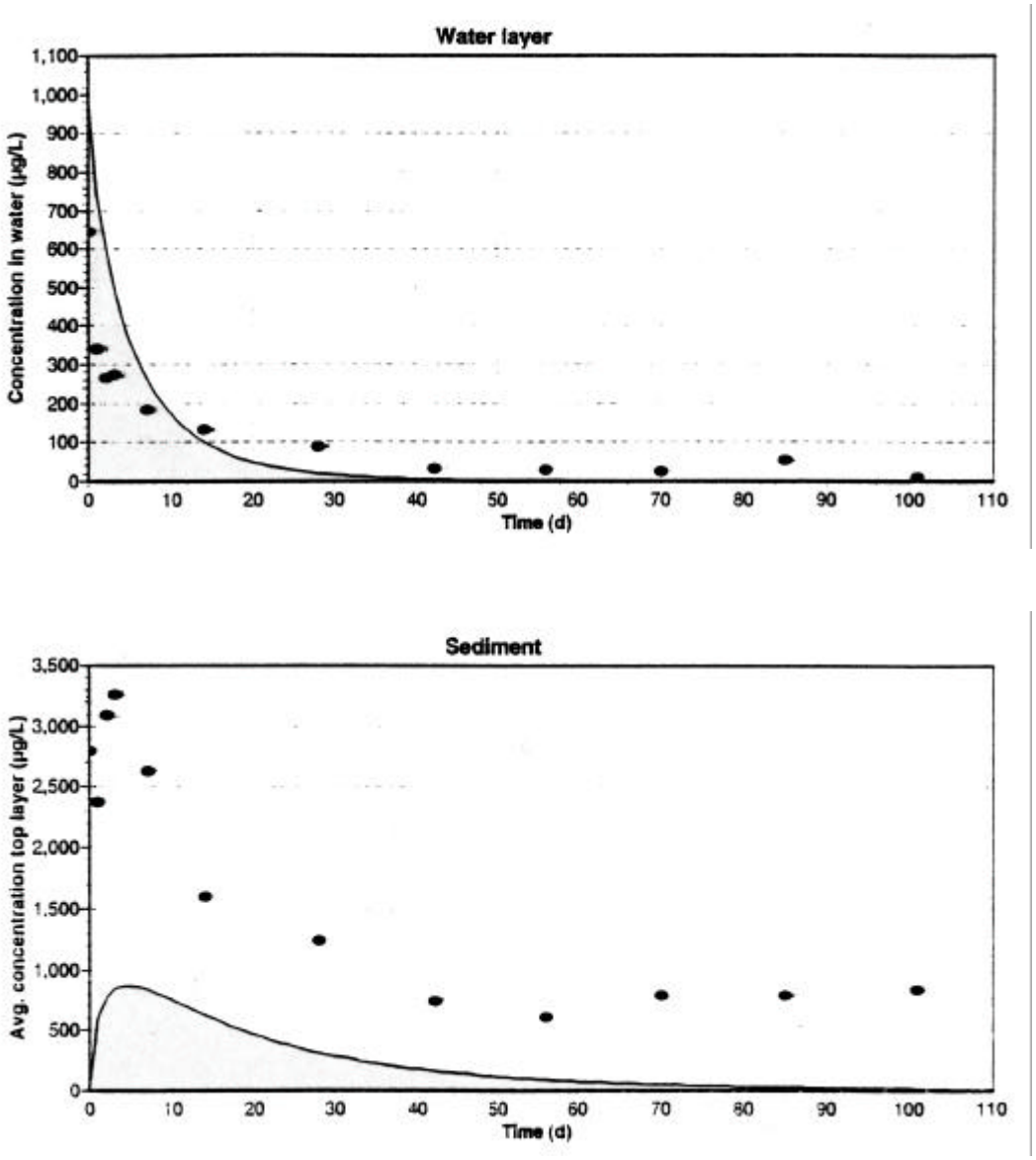


Figure 4.2. Simulated and measured concentrations of indoxacarb as a function of time in water and sediment of the River system ($DT50_{wl}$ = 5 d; $DT50_{sed}$ = 20 d in TOXSWA input). Points: measured; lines: computed. Radiolabel 1.

Concentration of pesticide in time

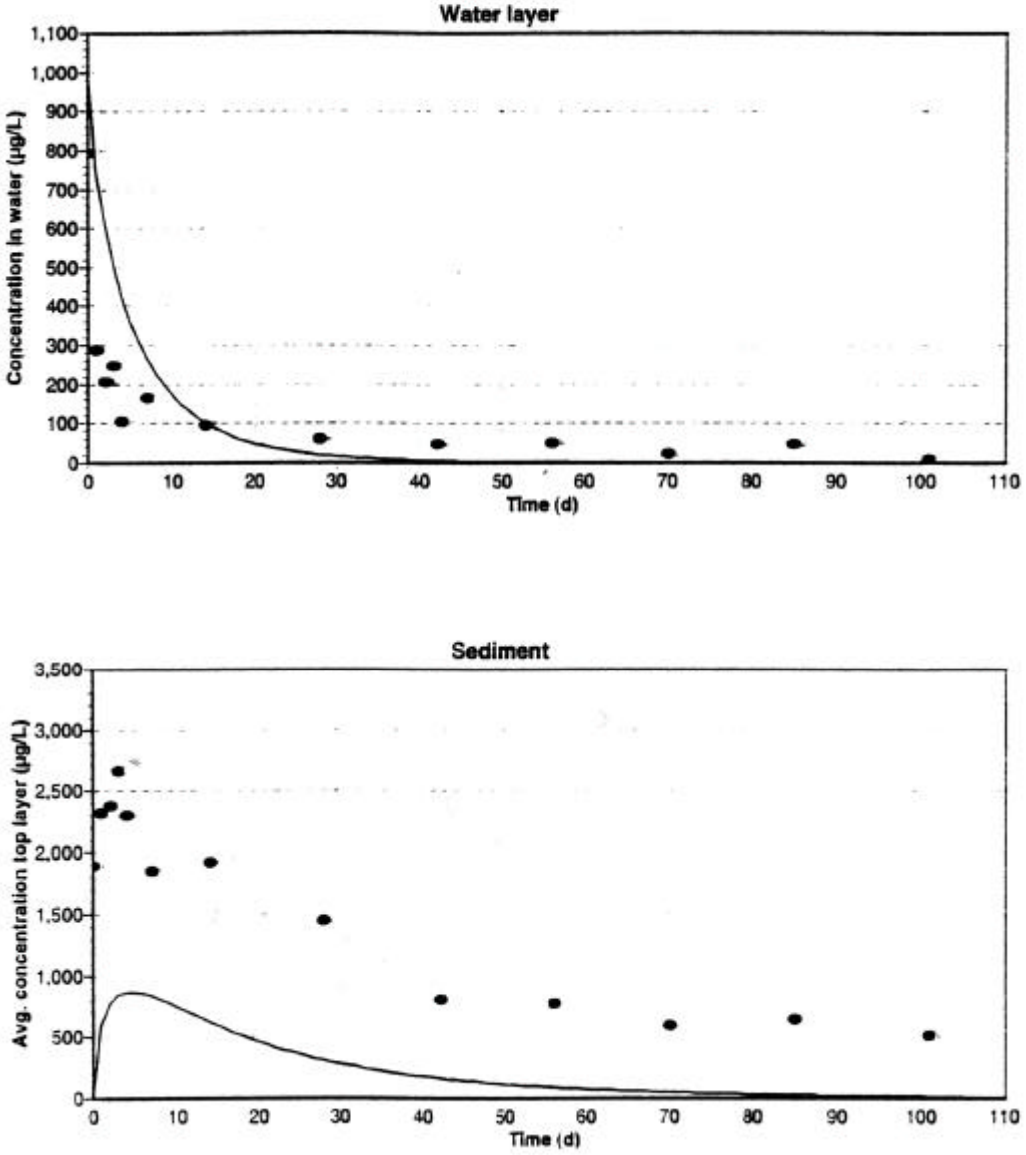


Figure 4.2 (continued). Radiolabel 2.

Concentration of pesticide in time

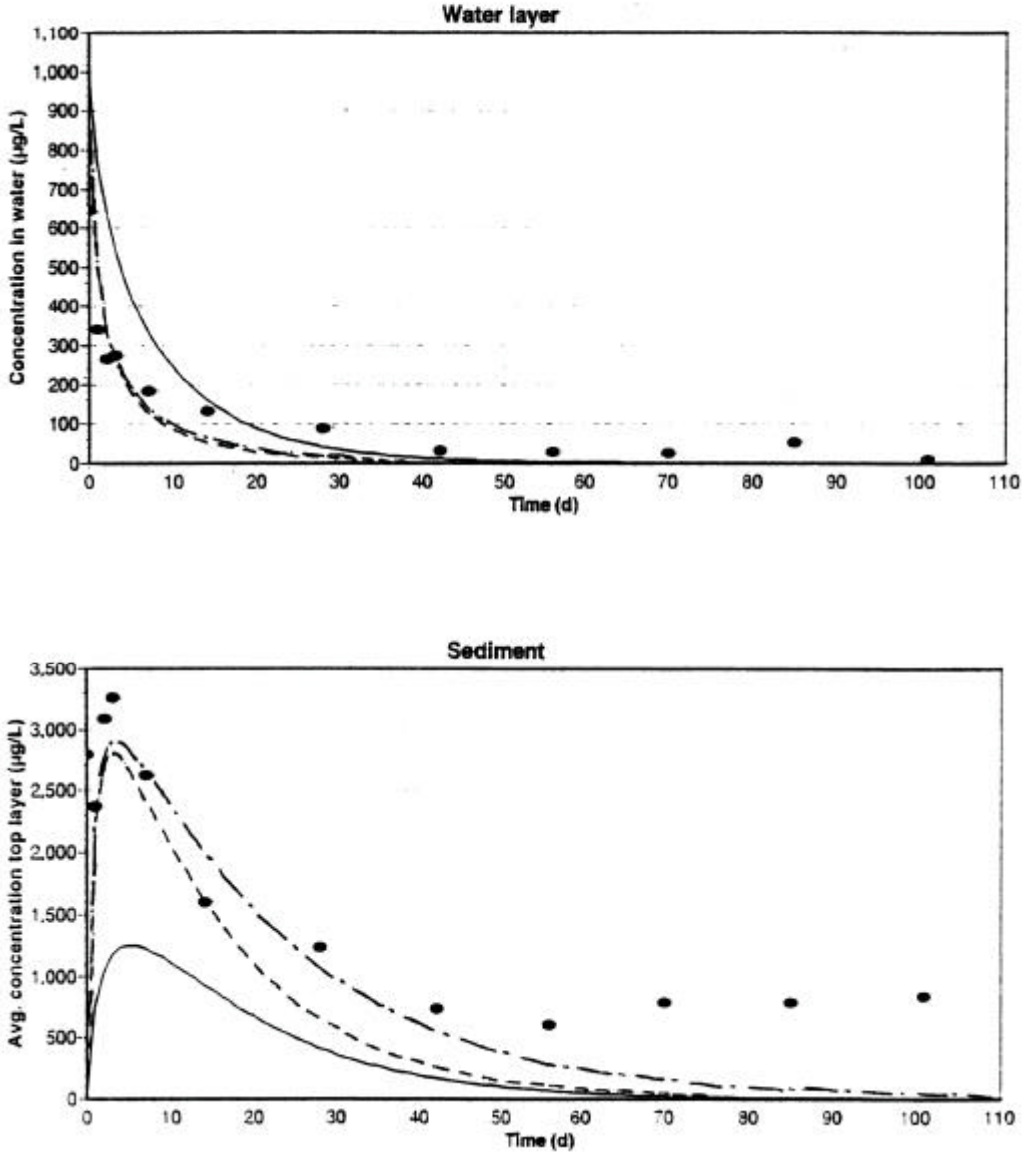
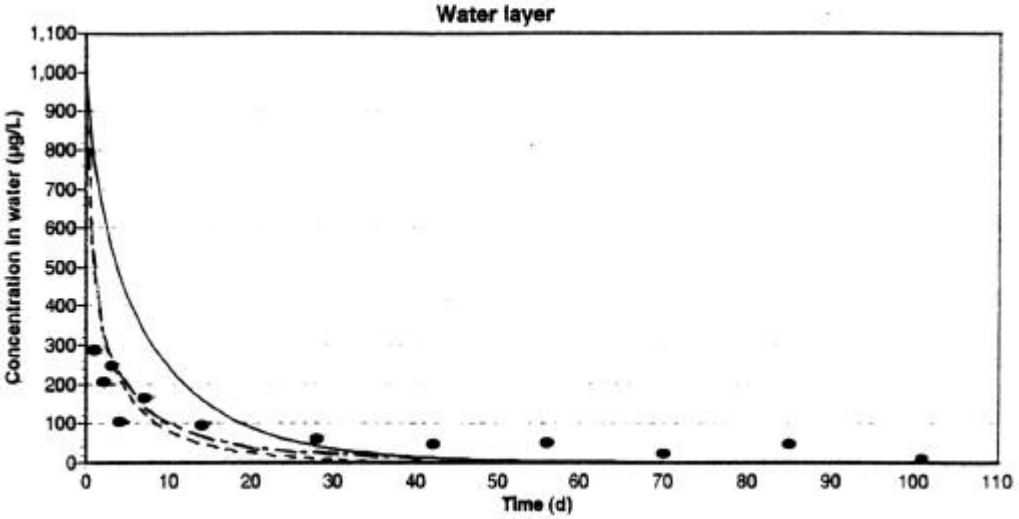


Figure 4.3. Simulated and measured concentrations of indoxacarb as a function of time in water and sediment of the River system. Points: measured (Radiolabel 1); lines: computed. Solid line: Run Sens1; dashed line: Run Sens2; dash-point line: Rund Sens3.

Concentration of pesticide in time



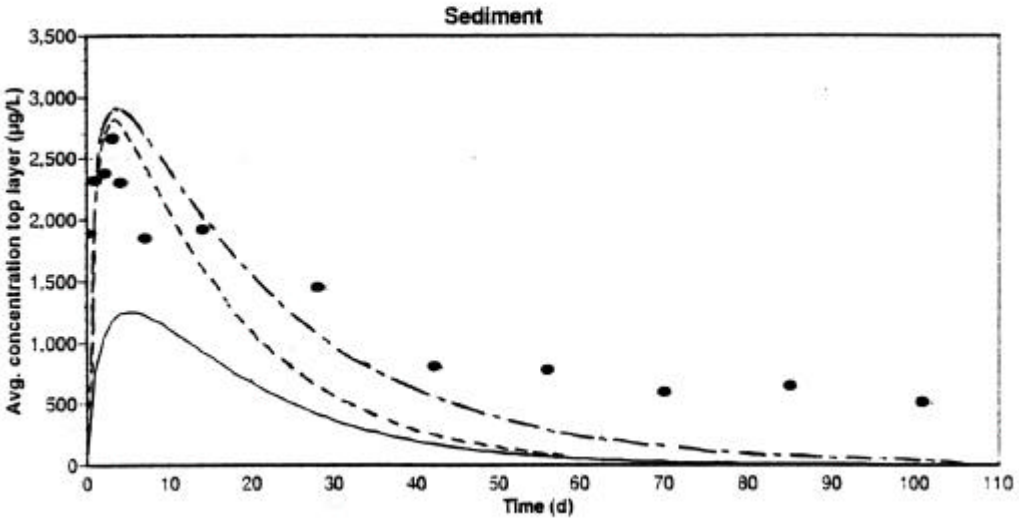


Figure 4.3 (continued). Measurements for Radiolabel 2. Solid line: Run Sens1; dashed line: Run Sens2; dash-point line: Run Sens3.

Concentration of pesticide in time

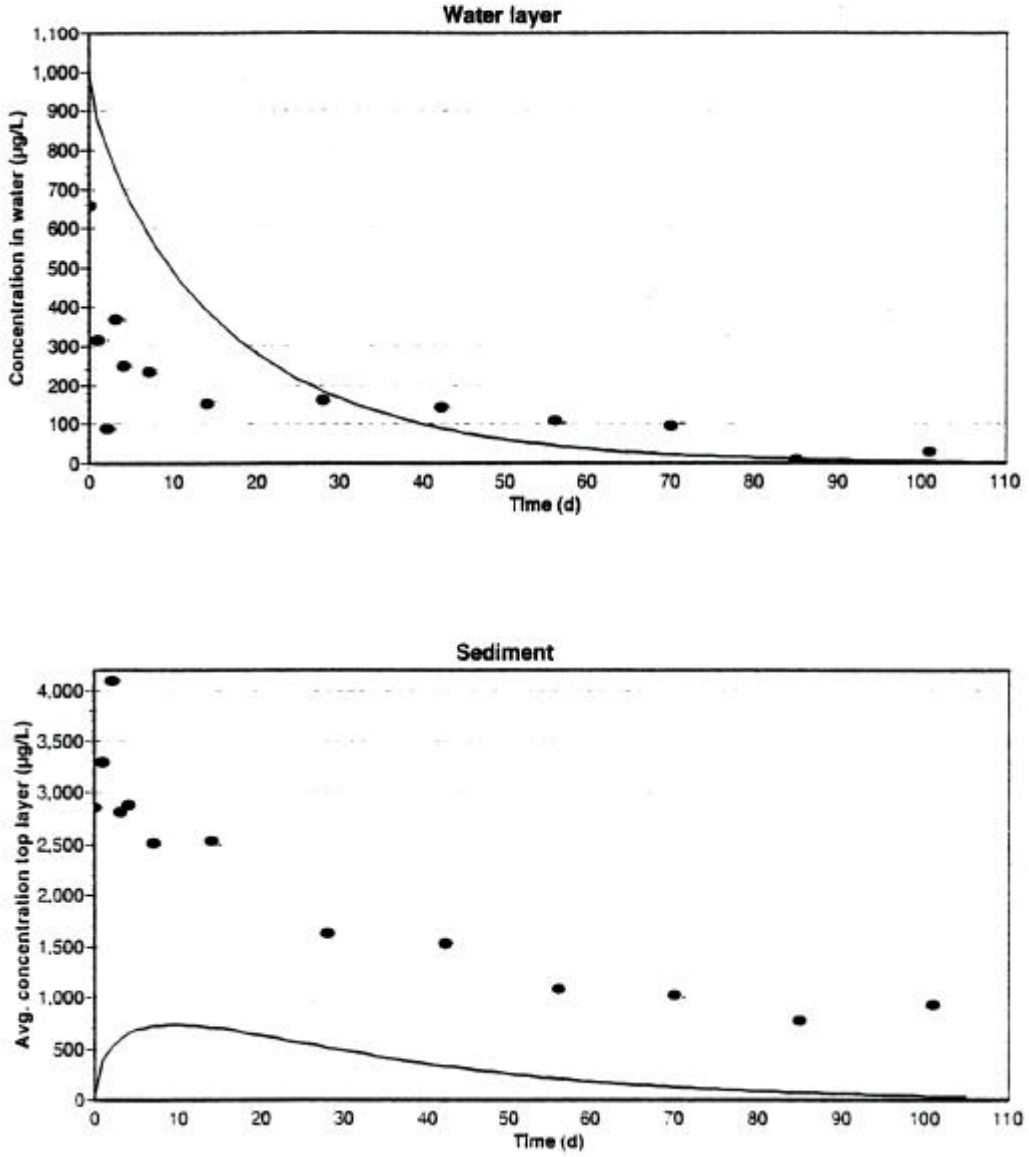


Figure 4.4 Simulated and measured concentrations of indoxacarb as a function of time in water and sediment of the Pond System ($DT50_{wl}$ = $DT50_{sed}$ = 17 d in TOXSWA input). Points: measured; lines: computed. Radiolabel 1.

Concentration of pesticide in time

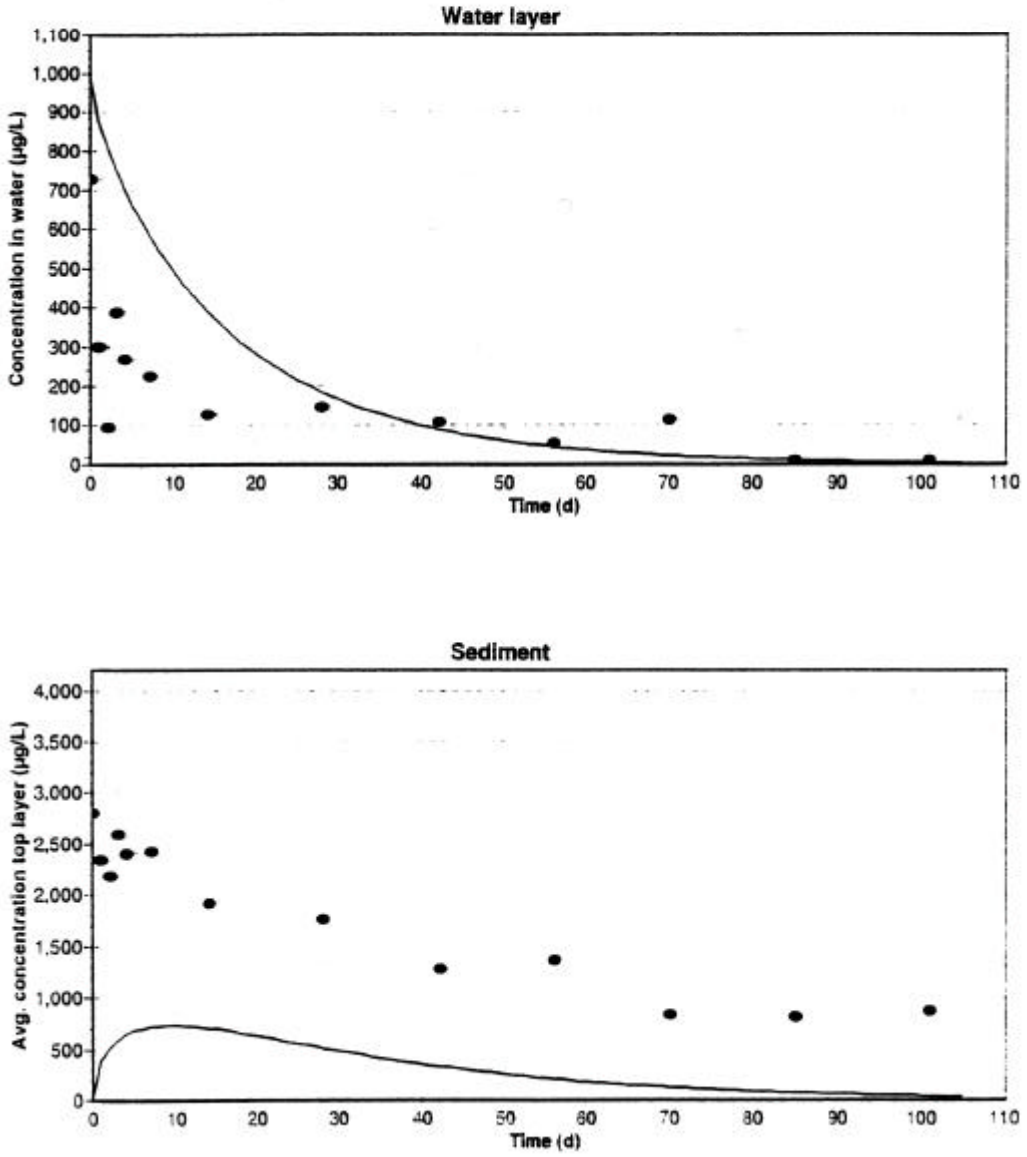


Figure 4.4 (continued). Radiolabel 2.

4.2.6 Sensitivity analysis for Pond

In a sensitvity analysis for indoxacarb in the Pond system, we assumed the test vessels to have a diameter of 9 cm and we increased the K_{om} value. Thus, we decreased the thicknesses of the water and sediment layer. We made Run Sens4 with a K_{om} of 5940 l/kg, a water depth of 2.3 cm and a sediment thickness of 4 mm (4 segments of 1 mm). Figure 4.5 shows that the correspondence between simulated and measured concentrations had improved. Up to about 20 d the simulated concentrations in the water layer were higher than the measured concentrations. The simulated peak concentration in the sediment was about 2300 µg/l. However, correspondence between simulated and measured concentrations was still not satisfactory.

4.2.7 Further results for River

It was not possible to simulate the concentration-time relationships of indoxacarb in the River and Pond systems. As stated already above, the initial concentration in the water phase of the studied systems would be 1000 µg/l, which is far above the water solubility. The measured concentration profiles of indoxacarb in water show a very rapid decline during the first few days. We assume that, soon after being brought into the test vessels, indoxacarb started to crystallize onto suspended matter or DOC and sank to the sediment. This would explain the rapid initial concentration decline in the water phase and the high concentration peaks in the sediment, which could not be simulated as being caused by sorption. The crystals of indoxacarb may redissolve later on, which may partly explain the relatively high, sustained concentration levels after about 50 d. Another part of the explanation may be that the studied substance is a racemic mixture of DPX-KN128 and DPX-KN127. These two enantiomers may not have the same transformation rate, implying that the transformation of the mixture does not meet microbial first-order kinetics. The transformation rates of the two enantiomers have not been measured separately in the water-sediment studies.

Concentration of pesticide in time

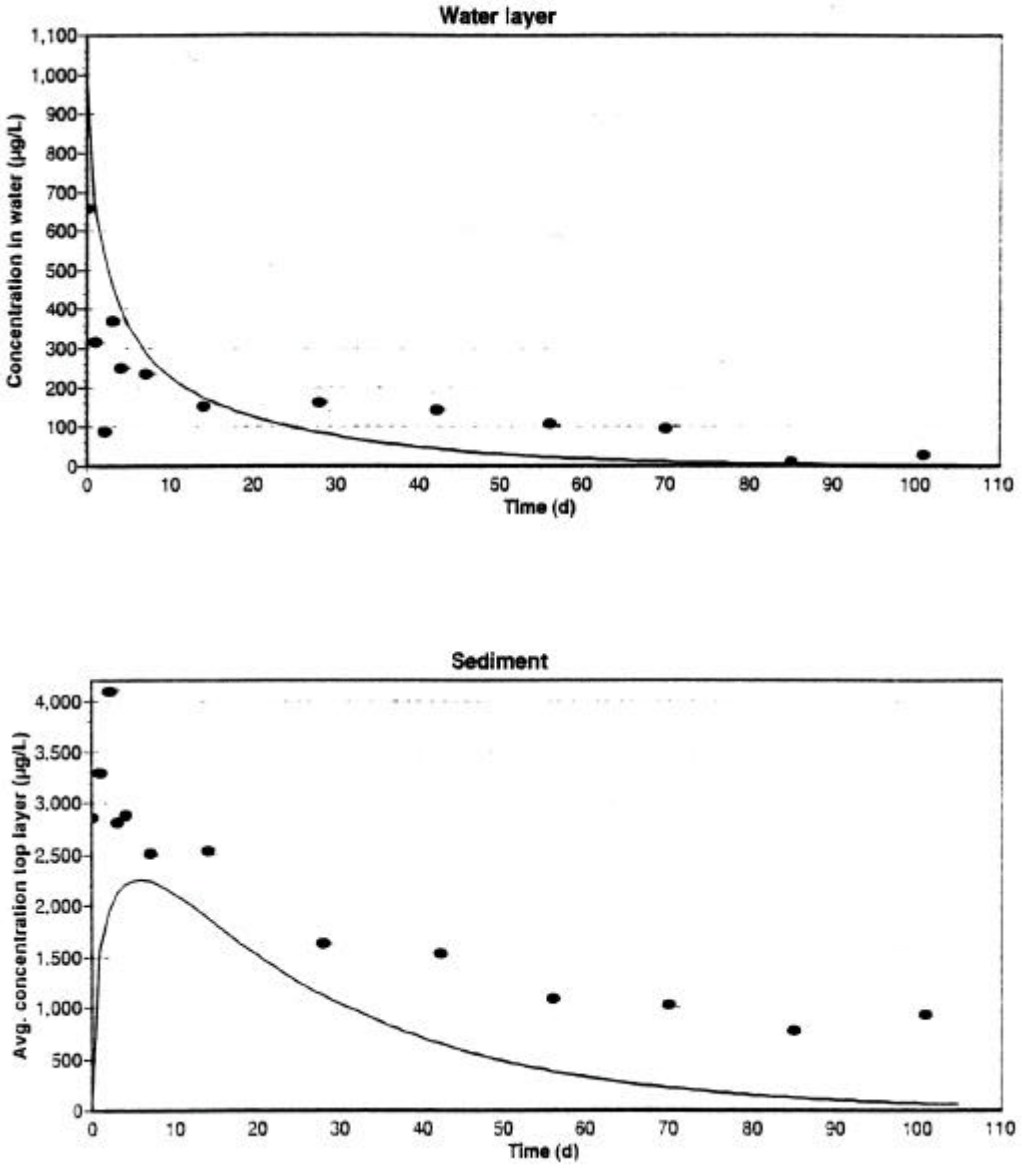


Figure 4.5. Simulated and measured concentrations of indoxacarb as a function of time in water and sediment of the Pond system. Sensitivity Run Sens4. Points: measured; line; computed. Radiolabel 1.

Concentration of pesticide in time

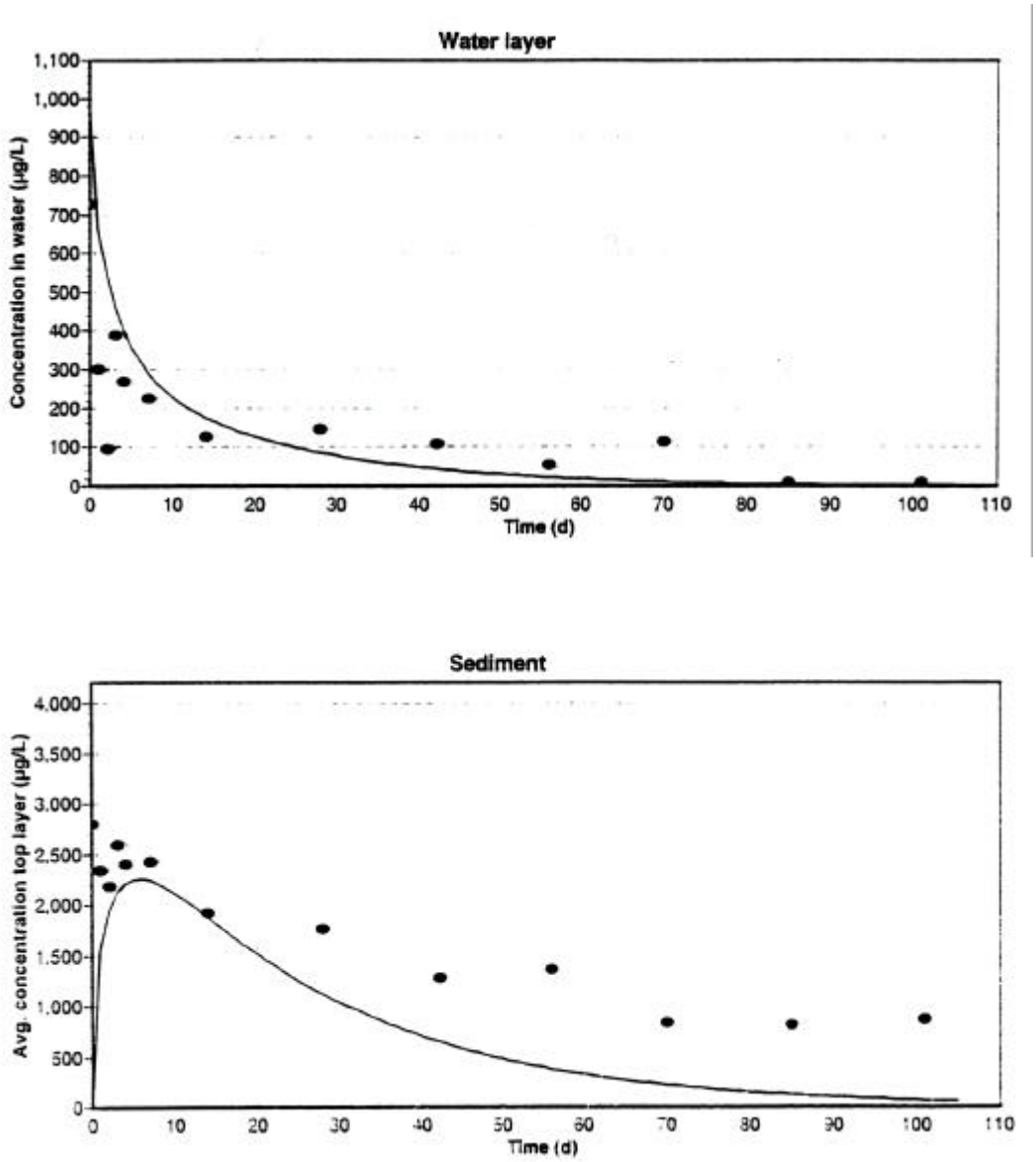


Figure 4.5 (continued). Radiolabel 2.

The TOXSWA model is not able to simulate crystallization and sinking of crystals onto the sediment, so we decided to adapt the simulations. We started at day 3, i.e. after the crystals had sunk to the bottom and the usual processes like sorption, diffusion and transformation had become dominant. Thus, we reran TOXSWA for the River and Pond systems with input as specified in Tables 4.1 to 4.9, except the initial concentrations in water layer and sediment. We now took the concentrations at day 3 as initial concentrations for the simulation runs (Table 4.10). We assumed the mass in the sediment to be uniformly distributed over the 14 and 15 mm depth.

Table 4.10. Initial concentrations of indoxacarb in River and Pond systems for simulations starting 3 d after application

System	Initial concentration (µg/l) in			
	Water		Sediment	
	label 1	label 2	label 1	label 2
River	275	248	3260	2670
Pond	369	388	2810	2590

Figure 4.6 shows the concentration profiles resulting from the adapted run for indoxacarb in the River system. In the water layer the simulated concentrations declined faster than the measured concentrations. The simulated concentration decline in the sediment seemed somewhat too high, compared to the concentrations measured for both labels.

Figure 4.7 shows the results for a run with transformation rates equivalent to half-lives of 15 d in both the water layer and the sediment. Up to 40 to 50 d the simulated concentration profiles corresponded reasonably well with the profiles measured for indoxacarb marked by both, Label 1 and Label 2. After 40 to 50 d measured concentration levels remained comparatively high and decline was not first-order anymore.

It is possible that indoxacarb remained partly bound on suspended matter or DOC, even after having formed crystals that sank to the sediment and after the concentration had declined. This would explain that after 40 or 50 d the concentration of indoxacarb in the water phase was sustained at levels slightly above the solubility and that it did not decrease asymptotically to the *x* axis. Moreover, the crystallized indoxacarb may redissolve, thus sustaining the water concentration. In the sediment too, relatively high concentration levels remained. This may indicate that part of the residue in the sediment was not available for biotransformation.

Thus, for the River system we determined transformation half-lives of 15 d for both the water and the sediment layers. Note that both are higher than the transformation half-life for the overall system. The latter included the effect of crystallization, which made the apparent decline in the water layer faster and was wrongly attributed to transformation.

Concentration of pesticide in time

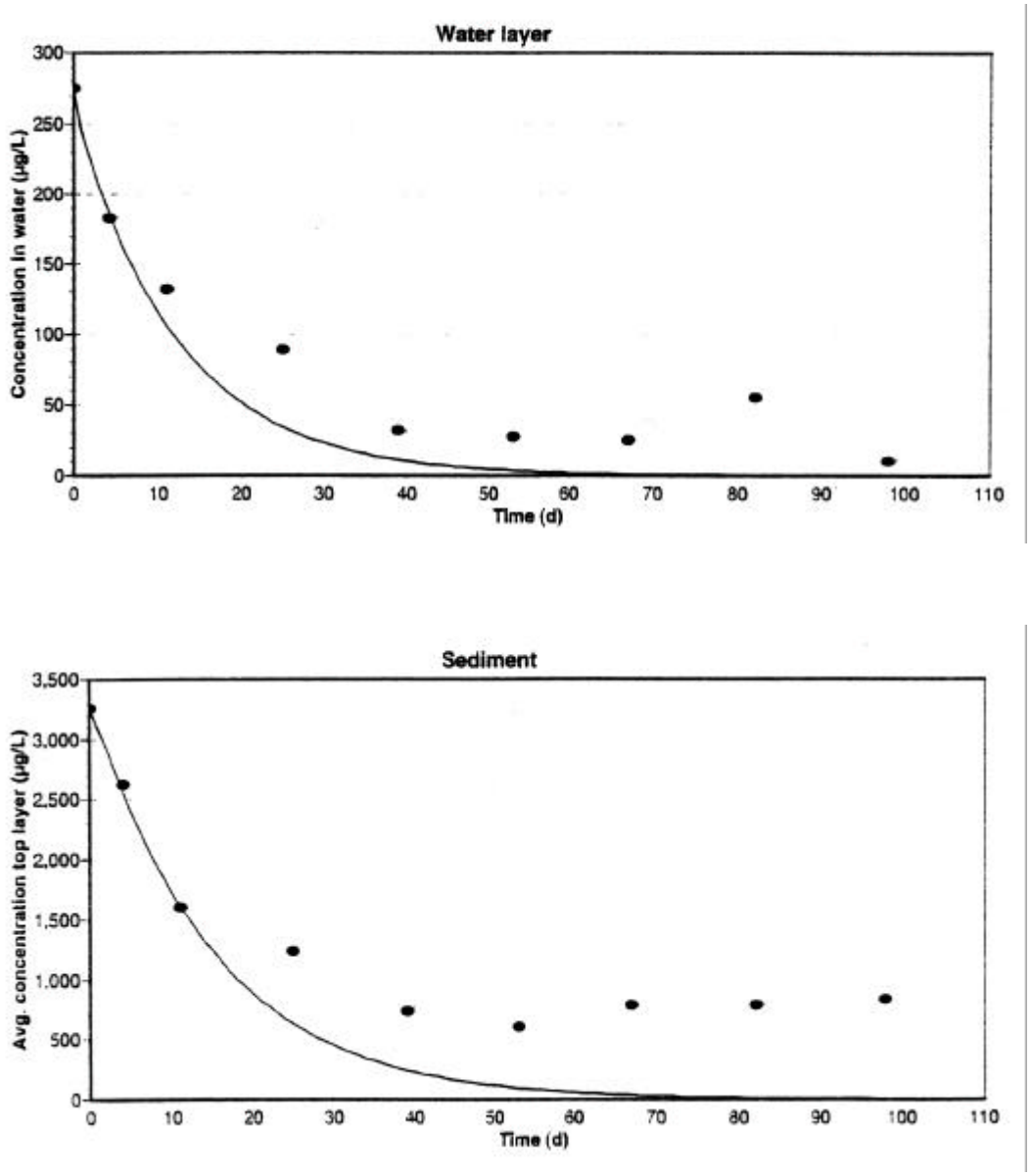


Figure 4.6. Simulated and measured concentrations of indoxacarb as a function of time in water and sediment of the River system, starting 3 d after application ($DT50_{wl}$ = $DT50_{sed}$ = 10 d in TOXSWA input). Points: measured; lines: computed. Radiolabel 1.

Concentration of pesticide in time

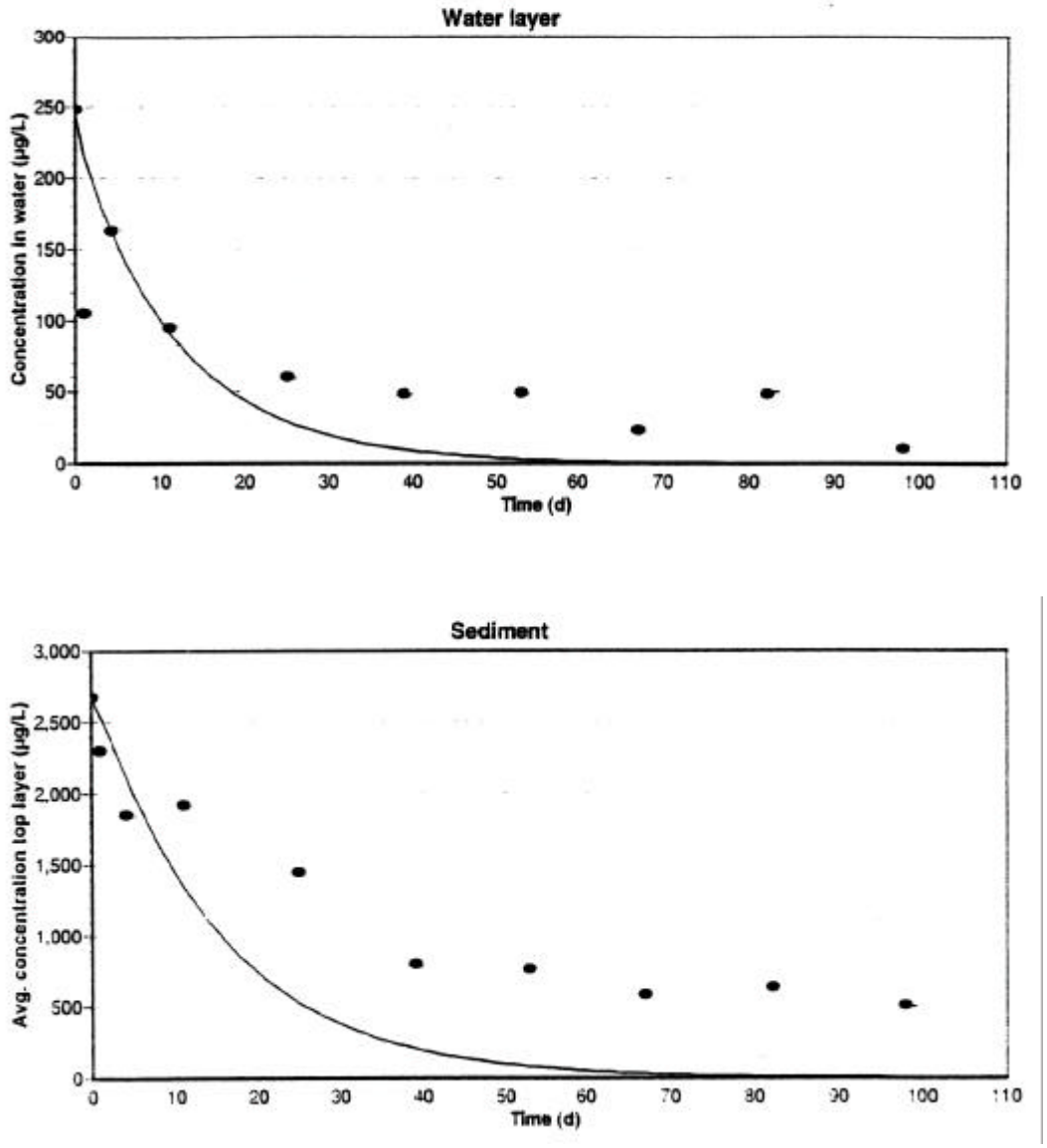


Figure 4.6 (continued). Radiolabel 2.

Concentration of pesticide in time

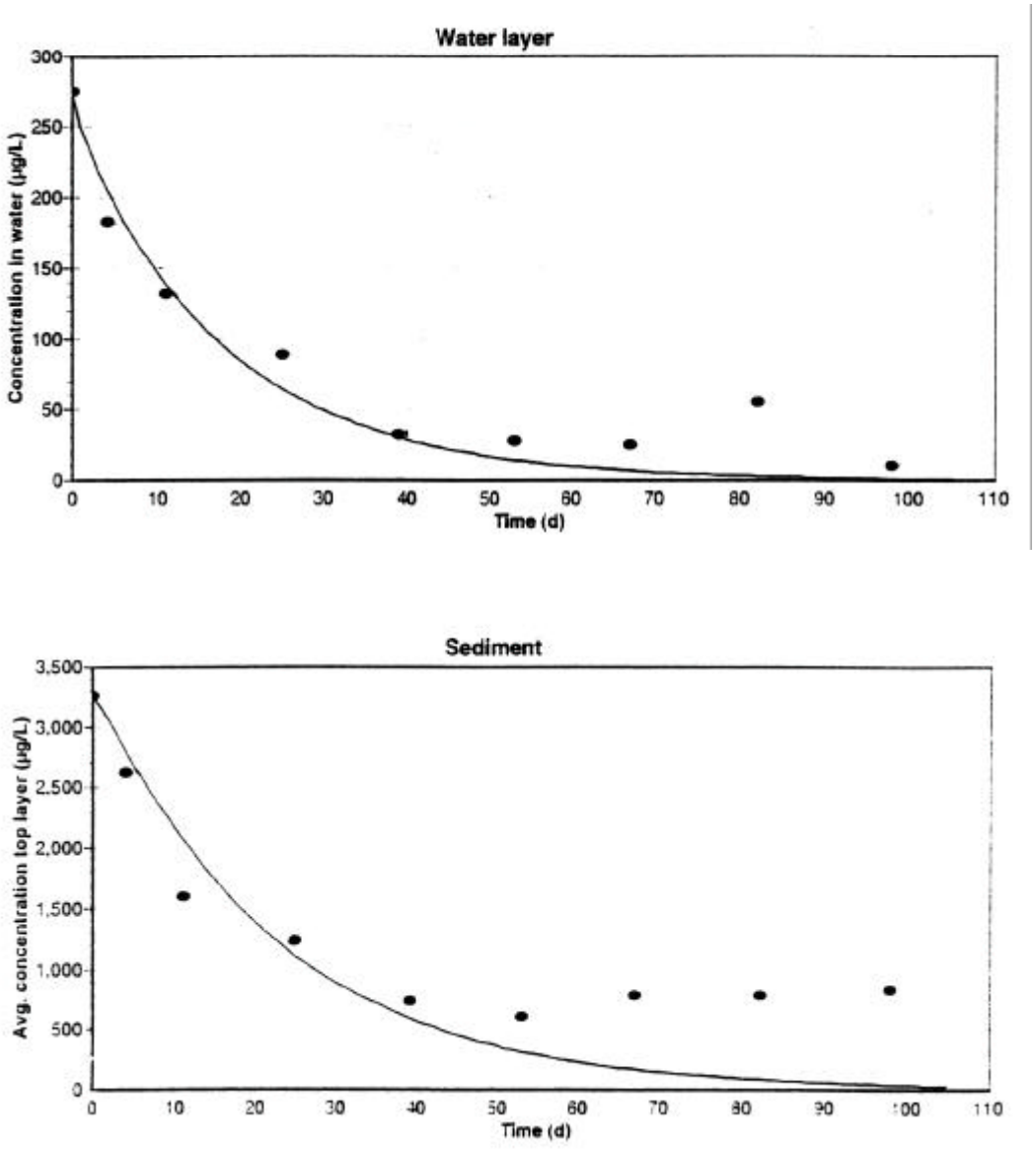


Figure 4.7. Simulated and measured concentrations of indoxacarb as a function of time in water and sediment of the River system, starting 3 d after application ($DT50_{wl}$ = $DT50_{sed}$ = 15 d in TOXSWA input). Points: measured; lines: computed. Radiolabel 1.

Concentration of pesticide in time

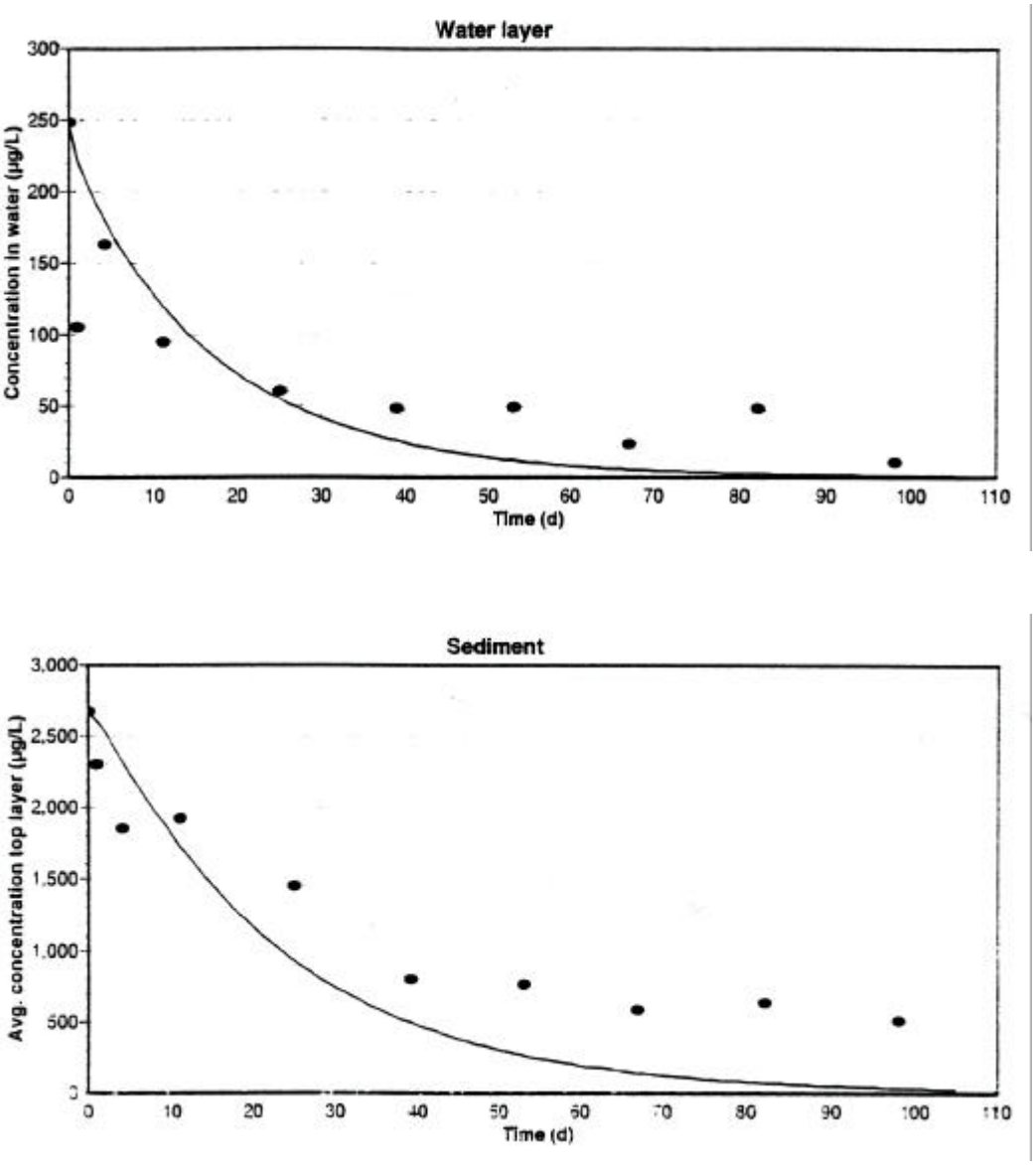


Figure 4.7 (continued). Radiolabel 2.

4.2.8 Further results for Pond

We also reran the TOXSWA model for the Pond system, with input data as specified in Tables 4.5 to 4.9, but starting the simulation 3 d after application. The initial concentrations in this run were those mentioned in Table 4.10. Figure 4.8 shows the results. If we consider especially the period up to 10 to 15 d after treatment, the simulated decline in the water layer was too slow, compared to the measured concentrations. The simulated decline in the sediment was too fast, compared to the measured concentration profile for both radiolabels of indoxacarb..

Using a transformation half-life of 70 d for the sediment and maintaining 17 d for the water layer we obtained Figure 4.9. In the sediment simulated and measured concentrations corresponded well, while in the water layer the simulated transformation was too slow.

We got good correspondence in both sediment and water layer using a transformation half-life of 90 d in the sediment and 10 d in the water layer. Figure 4.10 shows the results. Thus, for the Pond system we estimated the transformation half-life to be 90 d for the sediment and 10 d for the water layer.

Concentration of pesticide in time

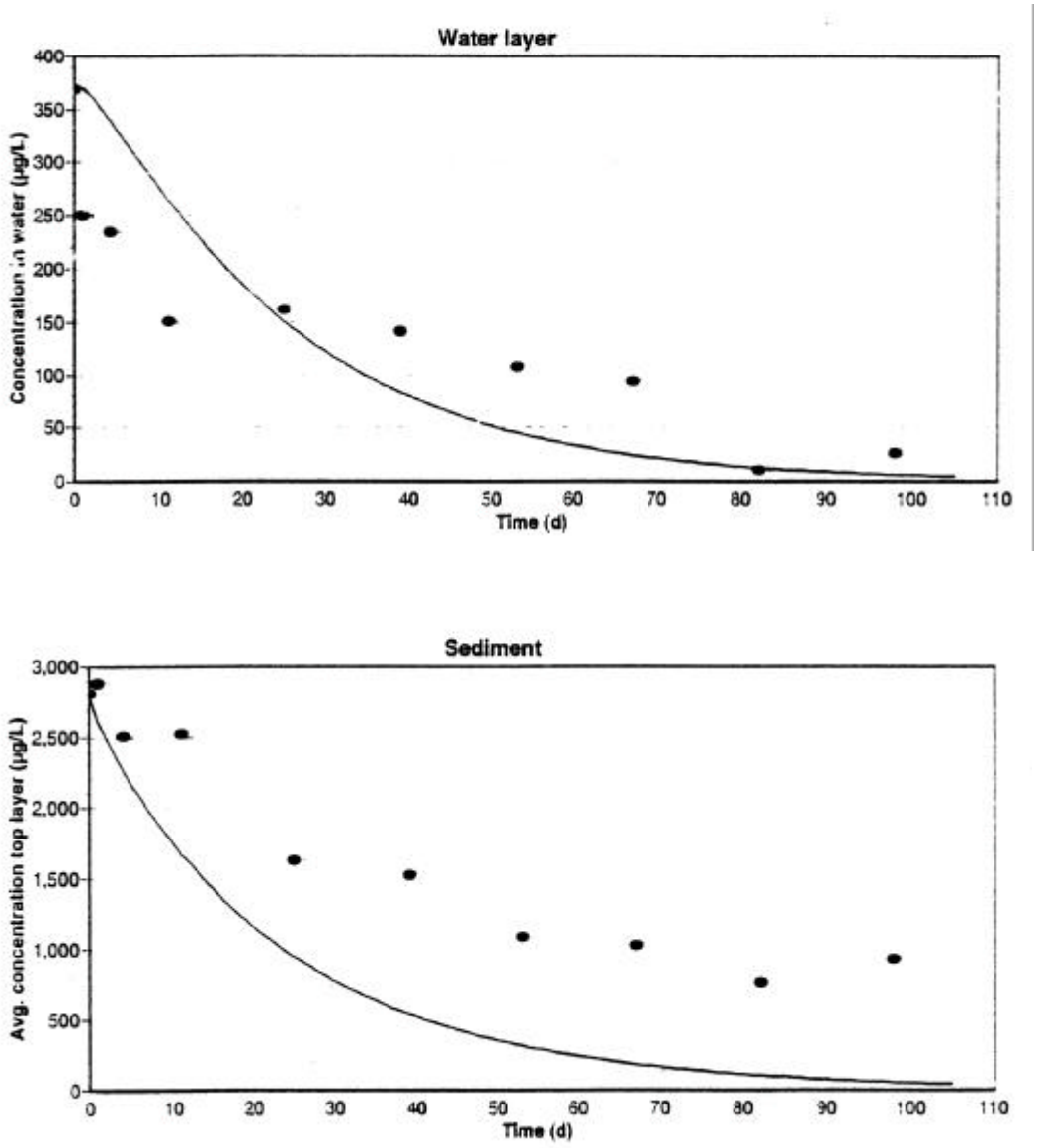
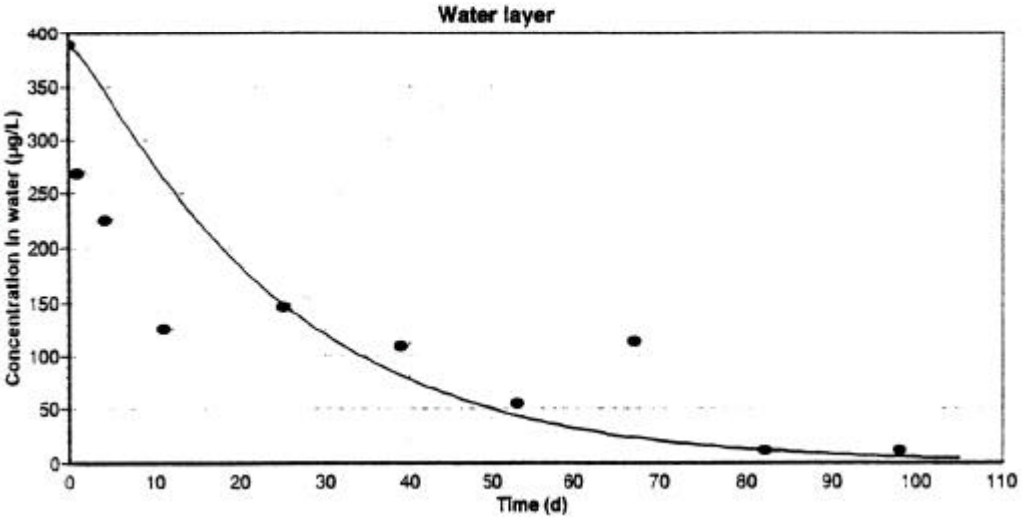


Figure 4.8. Simulated and measured concentrations of indoxacarb as a function of time in water and sediment of the Pond system, starting 3 d after application ($DT50_{wl}$ = $DT50_{sed}$ = 17 d in TOXSWA input). Points : measured; lines : computed. Radiolabel 1.

Concentration of pesticide in time



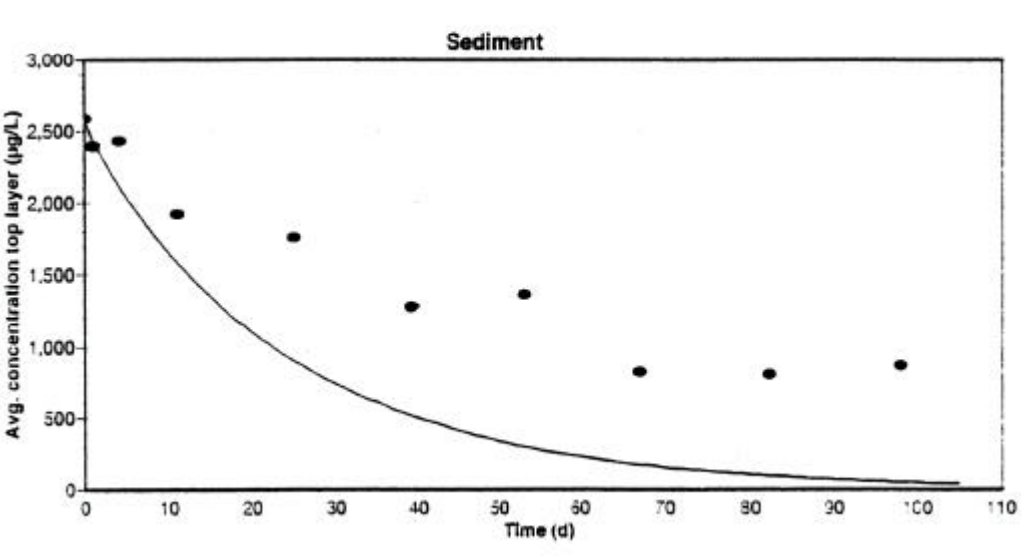


Figure 4.8 (continued). Radiolabel 2.

Concentration of pesticide in time

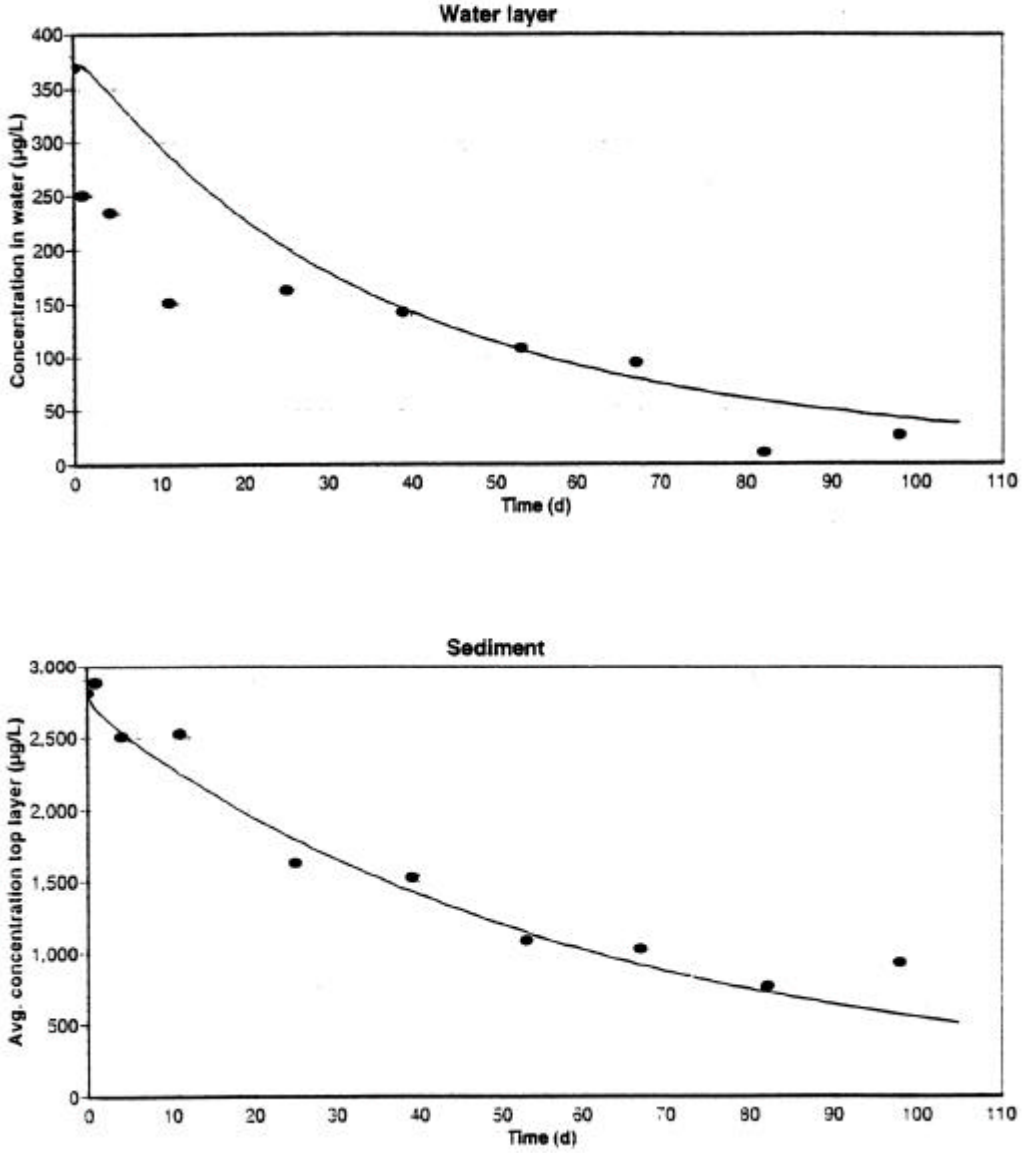


Figure 4.9. Simulated and measured concentrations of indoxacarb as a function of time in water and sediment of the Pond system, starting at 3 d after application ($DT50_{wl}$ = 17 d; $DT50_{sed}$ = 70 d in TOXSWA input). Points : measured; lines : computed. Radiolabel 1.

Concentration of pesticide in time

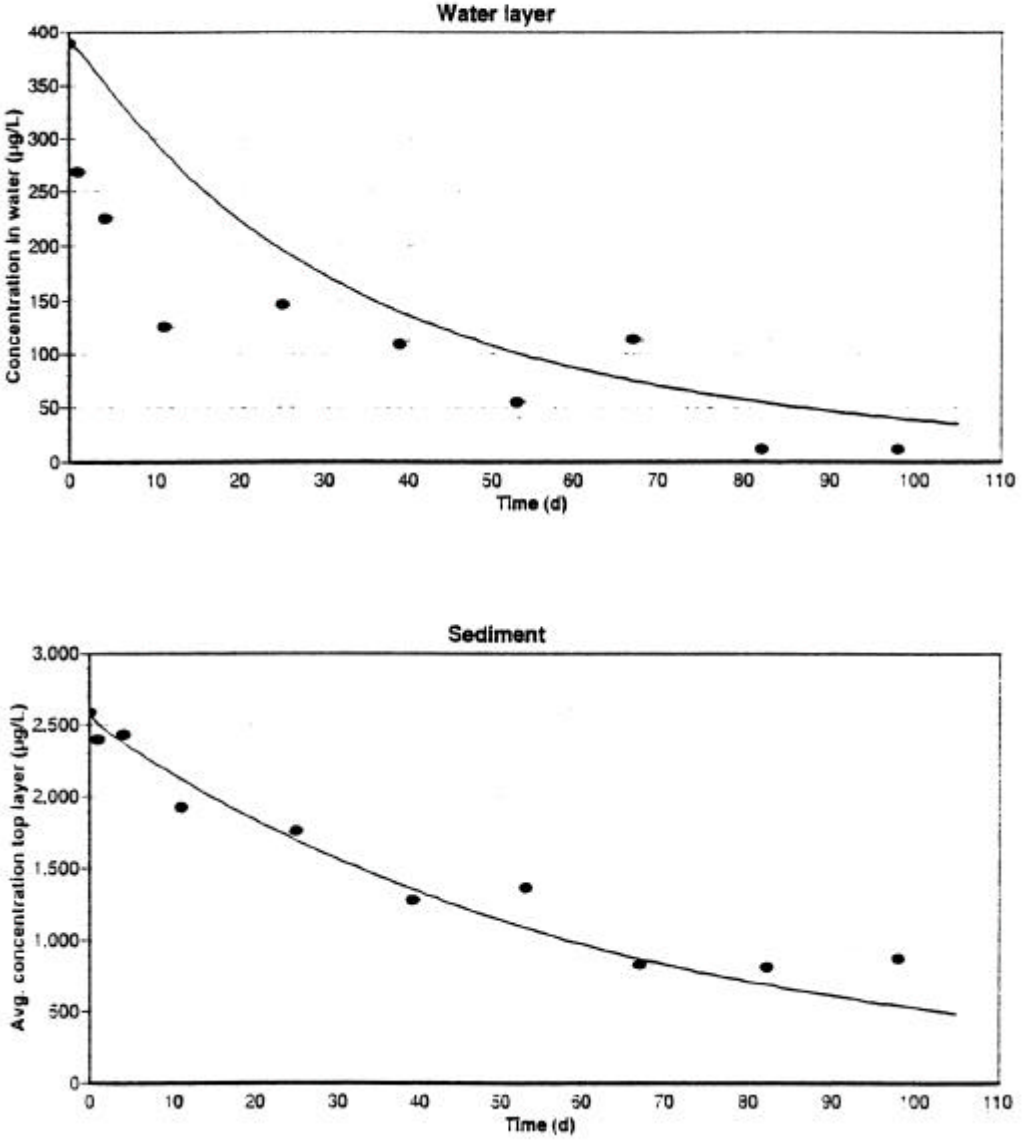


Figure 4.9 (continued). Radiolabel 2.

Concentration of pesticide in time

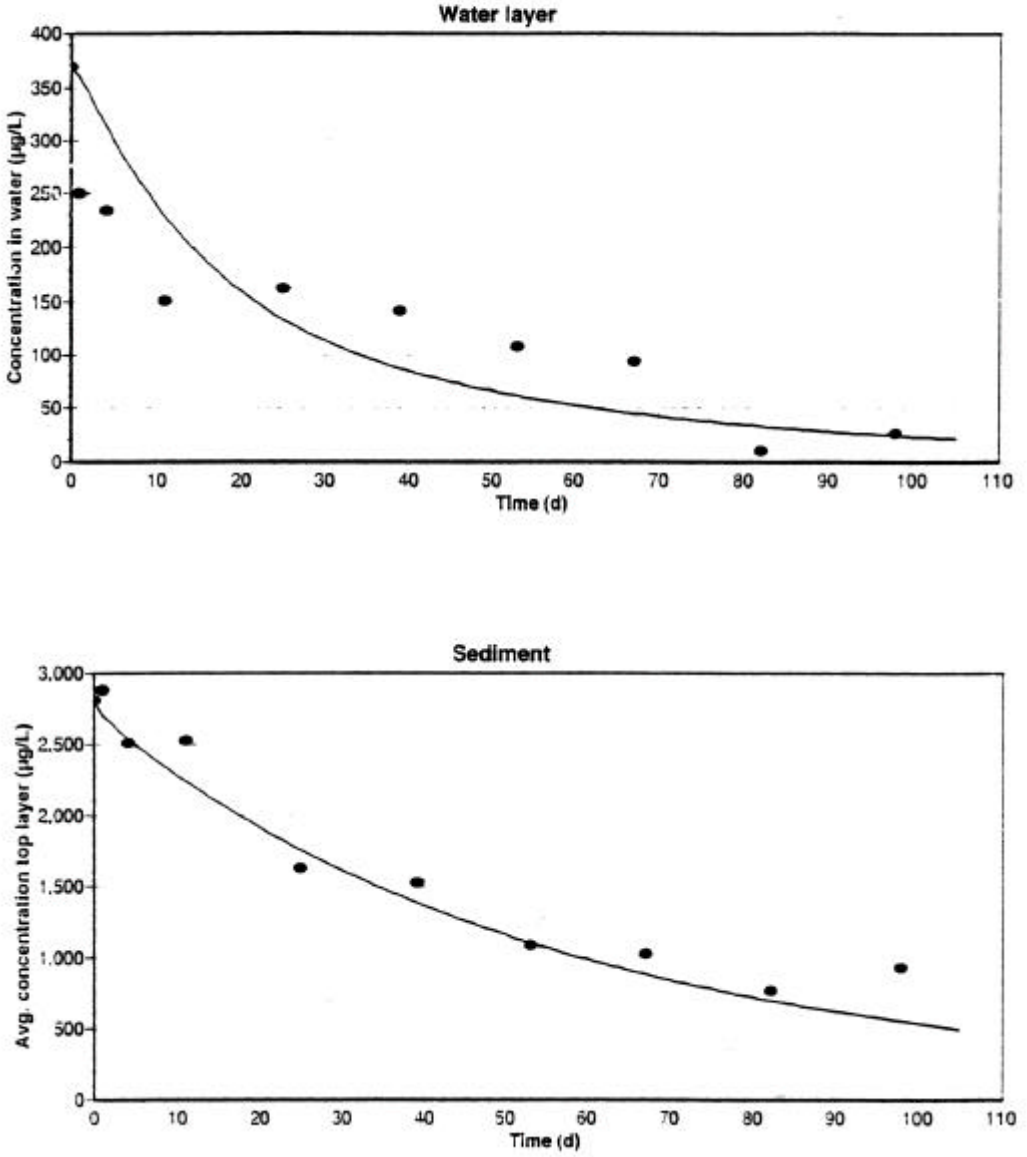


Figure 4.10. Simulated and measured concentrations of indoxacarb as a function of time in water and sediment of the Pond system, starting 3 d after application ($DT50_{wl}$ = 10 d; $DT50_{sed}$ = 90 d in TOXSWA input). Points: measured; lines: computed. Radiolabel 1.

Concentration of pesticide in time

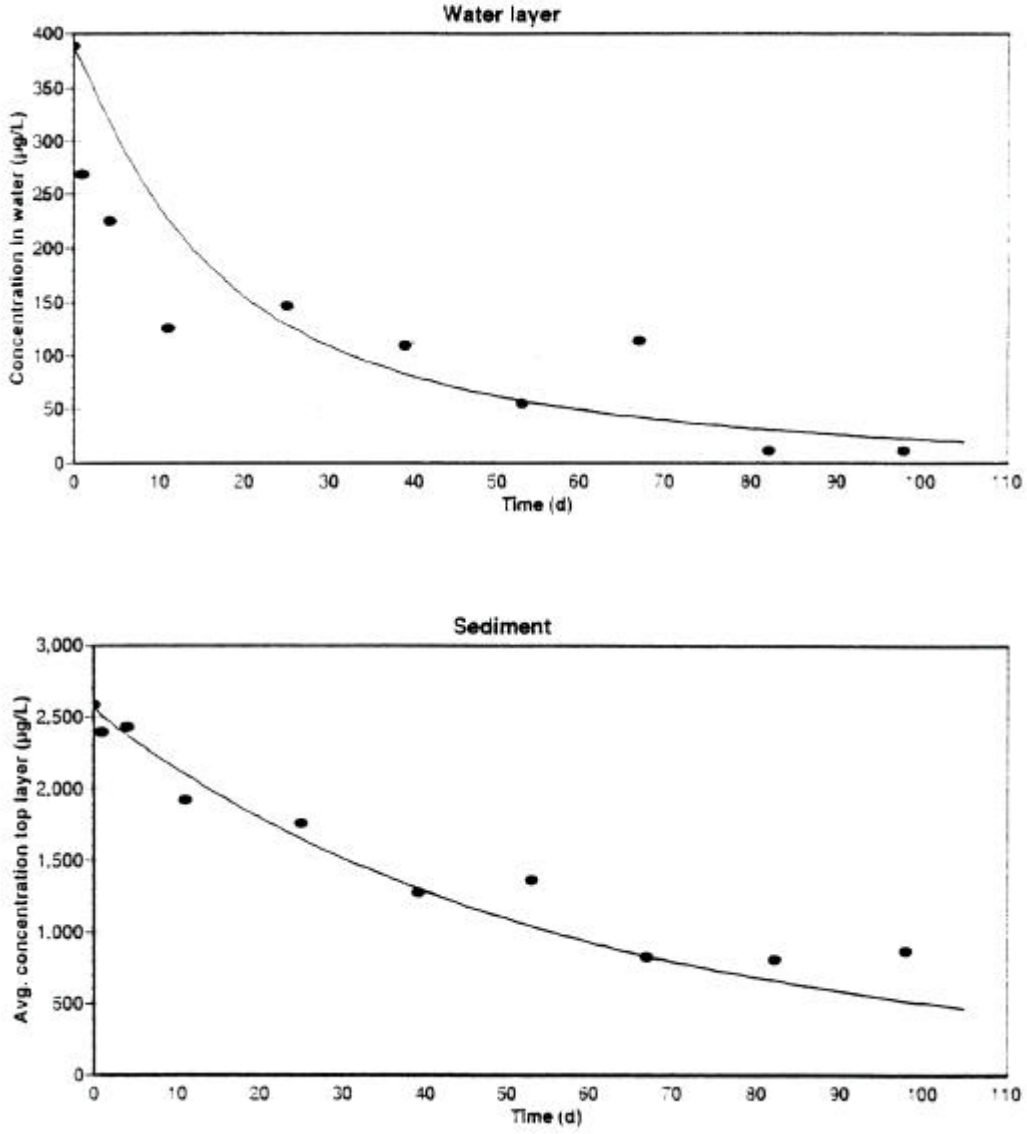


Figure 4.10 (continued). Radiolabel 2.

4.3 Dicamba

4.3.1 Experiments

Physico-chemical properties
The solubility of dicamba in water is 6500 mg/dm^3 (at 25 ^{o}C).

Water-sediment study
In the water-sediment transformation study of Galicia (1990), dicamba was ^{14}C-labelled in the ring. The water and sediment were collected from the Rhine river ('River') and from a pond ('Pond') in Switzerland. The sediment was taken from the top 5 to 10 cm of the bottom layer. Water and associated sediment were sieved before being put into the test vessels. Thereafter, the systems were characterized as follows. Percentages of organic carbon: 0.9% (River) and 1.9% (Pond). Percentages of clay: 7.5% (River) and 20.0% (Pond). A mass of 50 g sediment (on dry mass basis) and a volume of 500 cm^3 water were transferred into a cylindrical glas flask with a horizontal cross-sectional area of 88.2 cm^2.

The initial concentration of dicamba in the water layer was about 1 mg/dm^3. The water-sediment systems were incubated in the dark at 22 ^{o}C. The surface of the water layer was gently stirred. The system was ventilated with an air stream (15 to 30 cm^3/min) over the water surface and the volatiles were trapped. Two flask systems were analysed after each of six incubation periods (up to 90 days).

Before the analyses, sediment and water were separated by centrifugation (is not according to the Dutch protocol). In the River sediment-water systems, there was a lag-phase of about 14 days; after that ^{14}C-dicamba was transformed gradually to 12.4% of the dosage after 90 days. In the Pond systems, ^{14}C-dicamba was transformed gradually to 29.7% of the dosage after 90 days. At each extraction time, less than 7% of the remaining ^{14}C-dicamba was in the sediment layer.

Various transformation products were detected in the systems. Cumulative mineralisation to $^{14}CO_2$ was in the range of 6 to 18 % of the dosage after 90 days. The fraction of sediment-bound residue increased to 40% (River) and 44% (Pond) of the dosage after 90 days. This indicates that the sediment layer was a reactive medium. However, the contribution of the transformation of dicamba itself to the formation of bound residue is not known.

The cumulative volatilization of ^{14}C-labelled organic compounds was measured to be only 0.2% of the dosage after 90 days. Total recovery of radioactivity was almost 100%.

Concentrations measured in water and sediment layers
There is a problem with the concentrations of dicamba in the sediment layer, as calculated by Galicia (1990) and given in Tables 6 and 7 in that report. The values for these concentrations are much lower than can be explained from the percentage of radioactivity present as ^{14}C-dicamba in the sediment layer. Further, the

concentrations of dicamba (weakly adsorbed) in the sediment layer (thin, low content of organic matter) given in Tables 6 and 7 in that report are much lower than expected on the basis of its concentrations in the water layer.

In the Tables 6 and 7 of Galicia (1990), the concentrations in the water and sediment layers are simply added to arrive at the total concentration in the sediment-water system. From this it is inferred that the concentrations in the sediment layer were erroneously expressed on the basis of the volume of water in the systems (500 cm^3). This means that the concentrations of dicamba in the sediment later have to be re-calculated from the corresponding fraction of ^{14}C-radioactivity in this layer.

We recalculated the concentrations of dicamba in the sediment by making estimates for some non-specified quantities. The fraction of radioactivity measured in the sediment times the applied mass of dicamba (i.e. 500 µg in all systems, we assumed) gives its mass measured in the sediment. The volume of the sediment layer has been estimated to be the added dry mass of sediment (50 g) divided by the estimated bulk densities of 1.60 and 1.50 $g.cm^{-3}$ for River and Pond sediment, respectively (see Section 4.3.2). The volumes estimated in this way were 31.25 and 33.33 cm^3 for River and Pond sediment, respectively. As expected from compound and sediment properties, this gives concentrations in the sediment layer that are of the same order of magnitude as the concentrations in the water layer. Appendices 4 and 5 present the correct concentrations for the River and Pond systems, respectively.

Sorption to soils

For soils an average sorption coefficient of 4 $L.kg^{-1}$ ± 4 (n=6) has been used to assess mobility in the Dutch registration procedure (RIVM, 1997). A sorption coefficient of 10 $l.kg^{-1}$ has been reported for a reliable sorption study with sediment (RIVM, 1997). These figures show that dicamba is only weakly adsorbed.

4.3.2 Input data

We determined the bulk densities for the River and Pond systems using the reported particle size distribution. According to the pedotransfer function of Wösten (1997b) for clayey soils we obtained a bulk density of 1550 kg/m^3 for River sediment and 1380 kg/m^3 for Pond sediment. The Van der Sluys pedotransfer functions for river clay A horizon resulted in bulk densities of 1520 and 1440 kg/m^3 for the River and Pond sediments, respectively. In the simulations we took the bulk densities (sediment well-settled after sieving) to be 1600 and 1500 $kg.m^{-3}$ (River and Pond, respectively).

We calculated the porosity of the two sediments by dividing the dry bulk density of the sediment by the density of the solid phase and subtracting the result (i.e. fraction solid phase) from 1. The density of the solid phase was estimated using the reported particle size distribution and the pedotransfer function of Poelman of 1975, compiled for river clays (Wösten, 1997b). We calculated the density of the solid phase to be 2640 kg/m^3 for the River sediment and to be 2630 kg/m^3 for the Pond

sediment. Porosities were calculated to be 40 % and 43 % for River and Pond sediment layers, respectively.

The test vessels had a reported horizontal surface area of 88.2 cm^2. We calculated the thickness of the sediment layer by dividing the dry sediment mass added to the test vessels by its dry bulk density, and next, dividing the resulting sediment volume by the cross-sectional area of 88.2 cm^2. Next, we calculated the water depth in the test vessels from water volume added minus water volume becoming pore water in the sediment (equalling porosity times sediment volume). The remaining water volume was divided by the cross-sectional area of 88.2 cm^2 to obtain the thickness of the water layer.

4.3.3 Results for River

For a linear sorption coefficient K_{om} of 10 $L.kg^{-1}$ and the bulk density of 1.60 $g.cm^{-3}$ (River) we calculated that about 95 % of the added mass of dicamba remained in the 5.5 cm water layer and that only about 5 % entered the 4 mm sediment layer. This implies that the water layer was dominant in the water-sediment study and that it is more important to obtain a good correspondence between the simulated and measured concentrations in the water layer than in the sediment layer in order to simulate the water-sediment system.

Figure 4.11 shows the simulation results for dicamba in the River system. All input is according to Tables 4.11 to 4.15. In the water layer the simulated concentrations were lower than those measured. In the sediment the simulated concentration peak of about 600 $\mu g.l^{-1}$ was lower than the measured peak of about 900 $\mu g.l^{-1}$; after around 30 d correspondence between simulated and measured concentrations was good. The measured peak concentrations were relatively high, because in the water layer there was an initial lag phase of about 14 d, during which hardly any transformation occurred. So, high water concentrations were maintained and in the sediment the concentrations became relatively high.

In Figure 4.12 the transformation half life of dicamba in the water layer was set to 60 d instead of 36 d as used for Figure 4.11. All other input parameters were those in Tables 4.11 to 4.13 and 4.15. For the water layer correspondence between simulated and measured concentrations was better than that in Figure 4.11. The initial lag phase of 14 d without transformation could not be approximated with TOXSWA 1.2, but otherwise correspondence is satisfactory in the water layer. In the sediment the simulated peak rose slightly and simulated decline became slightly slower (compared to Fig. 4.11).

Figure 4.13 shows the results for dicamba when transformation half lives were 60 and 20 d in the water and sediment layer, respectively (all other input according to Tables 4.11 to 4.13 and 4.15). Concentrations in the water layer changed only slightly compared to those in Figure 4.12. In the sediment the simulated concentrations corresponded reasonably to those measured, taking into consideration that during the initial lag phase of 14 d the concentrations in water remained high. Thus, for

dicamba in the River system, we estimated transformation half lives of 60 and 20 d for the water and sediment layers, respectively.

Table 4.11. Input data for the water layer, dicamba (River)

Water layer
Rectangular, vertical cross-section 0.106 m wide (reported inner diameter)
Water depth 0.055 m
Water depth defining perimeter for exchange wl-sed 0.001 m
Concentration suspended solids 15 g/m^3 (assumption) with an organic matter content of 0.018 kg/kg
No flow, dummy value of 10 m^2/d for longitudinal dispersion coefficient
Initial concentration 1031 µg/l

Table 4.12. Input data for the sediment, dicamba (River)

Sediment
Sediment thickness 0.004 m
Bulk density 1600 kg/m^3, constant with depth
Porosity 0.40 , constant with depth
Tortuosity 0.34 , constant with depth
Organic matter content 0.018 kg/kg, constant with depth
Initial concentration 0 µg/l

Table 4.13. Input data concerning the simulation, dicamba (River)

Simulation
One segment of 0.106 m length in the water layer (reported inner diameter)
Segments of 1, 1, 1 and 1 mm corresponding to The total thickness of the sediment layer
Calculation time step 2400 s
Total time simulated 95 d

Table 4.14. Input of initial estimates of the transformation rates, dicamba (River)

Initial estimates for transformation half-lives
Transformation half-life in water 36 d
Transformation half-life in sediment 36 d

Table 4.15. Input data for dicamba

Compound
Physico-chemical data:
Molecular mass 221.0 g/mol
Saturated vapour pressure 4.5*10^{-3} Pa at 25 °C (Tomlin, 1994)
Solubility in water 6.5 g/l at 25 °C
Sorption:
K_{om} (soils) 10 l/kg
Freundlich exponent 0.9

Table 4.16. Input data for the water layer, dicamba (Pond)

Water layer
Rectangular, vertical cross-section 0.106 m wide (reported inner diameter)
Water depth 0.055 m
water depth defining perimeter for exchange wl-sed 0.001 m
Concentration suspended solids 15 g/m^3 (assumption) with an organic matter content of 0.037 kg/kg
No flow, dummy value of 10 m^2/d for longitudinal dispersion coefficient
Initial concentration 965 µg/l

Table 4.17. Input data for the sediment, dicamba (Pond)

Sediment
Sediment thickness 0.004 m
Bulk density 1500 kg/m^3, constant with depth
Porosity 0.43 , constant with depth
Ttortuosity 0.39 , constant with depth
Organic matter content 0.037 kg/kg, constant with depth
Initial concentration 0 µg/l

Table 4.18. Input data concerning the simulation, dicamba (Pond)

Simulation
One segment of 0.106 m length in the water layer (reported inner diameter)
Segments of 1, 1, 1 and 1 mm corresponding to The total thickness of the sediment layer
Calculation time step 2400 s
Total time simulated 95 d

Table 4.19. Input of initial estimates of the transformation rates, dicamba (Pond)

Initial estimates for transformation half-lives
Transformation half-life in water 46 d
Transformation half-life in sediment 46 d

4.3.4 Results for Pond

A first run for dicamba in the Pond system (input according to Tables 4.15 to 4.19) resulted in Figure 4.14. In the water layer simulated concentrations were lower than those measured, while in the sediment the simulated peak concentration of 800 µg.l^{-1} approached the measured peak of about 900 µg.l^{-1}. The simulated decline was slightly slower than the measured decline.

The transformation half lives of dicamba used for the results in Figure 4.15 were 70 and 30 d for the water and sediment layers, respectively (all other input according to Tables 4.14 to 4.18). In the water layer correspondence is good now. In the sediment the simulated decline after about 10 d was still somewhat too slow.

The results in Figure 4.16 were obtained with transformation half lives of 70 and 20 d in the water and sediment layers, respectively (all other input data those of Tables 4.14 to 4.18). Correspondence in the water layer, where more than 90% of the mass of dicamba resided, was still good and the simulated decline corresponded slightly better to the measured decline. than that in Figure 4.15. Thus, for dicamba in the Pond system, we estimated the transformation half-lives to be 70 and 20 d for the water and sediment layer, respectively.

Concentration of pesticide in time

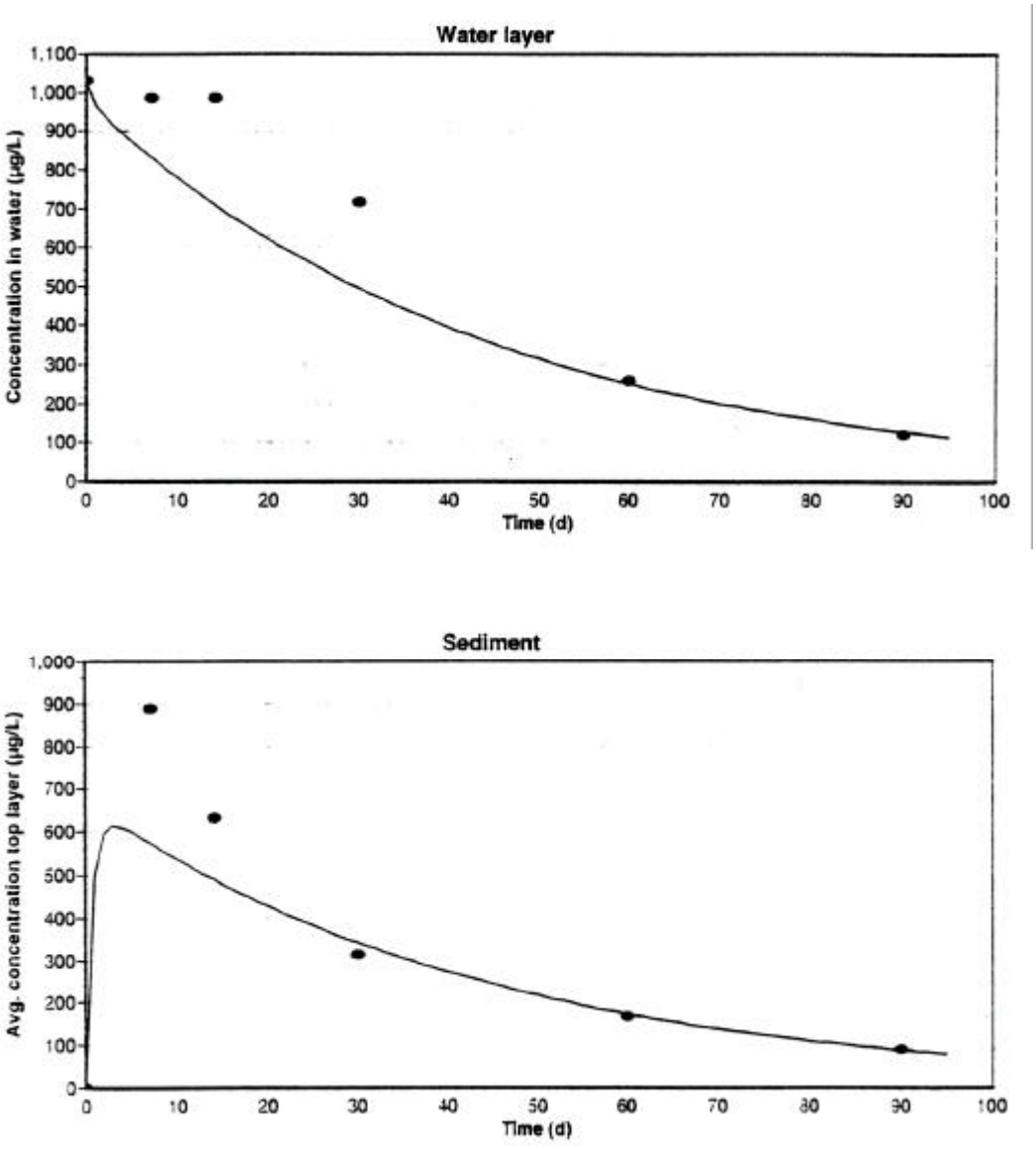


Figure 4.11. Simulated and measured concentrations of dicamba as a function of time in water and sediment of River system ($DT50_{wl}$ = $DT50_{sed}$ = 36 d in TOXSWA input). Points: measured; lines: computed.

Concentration of pesticide in time

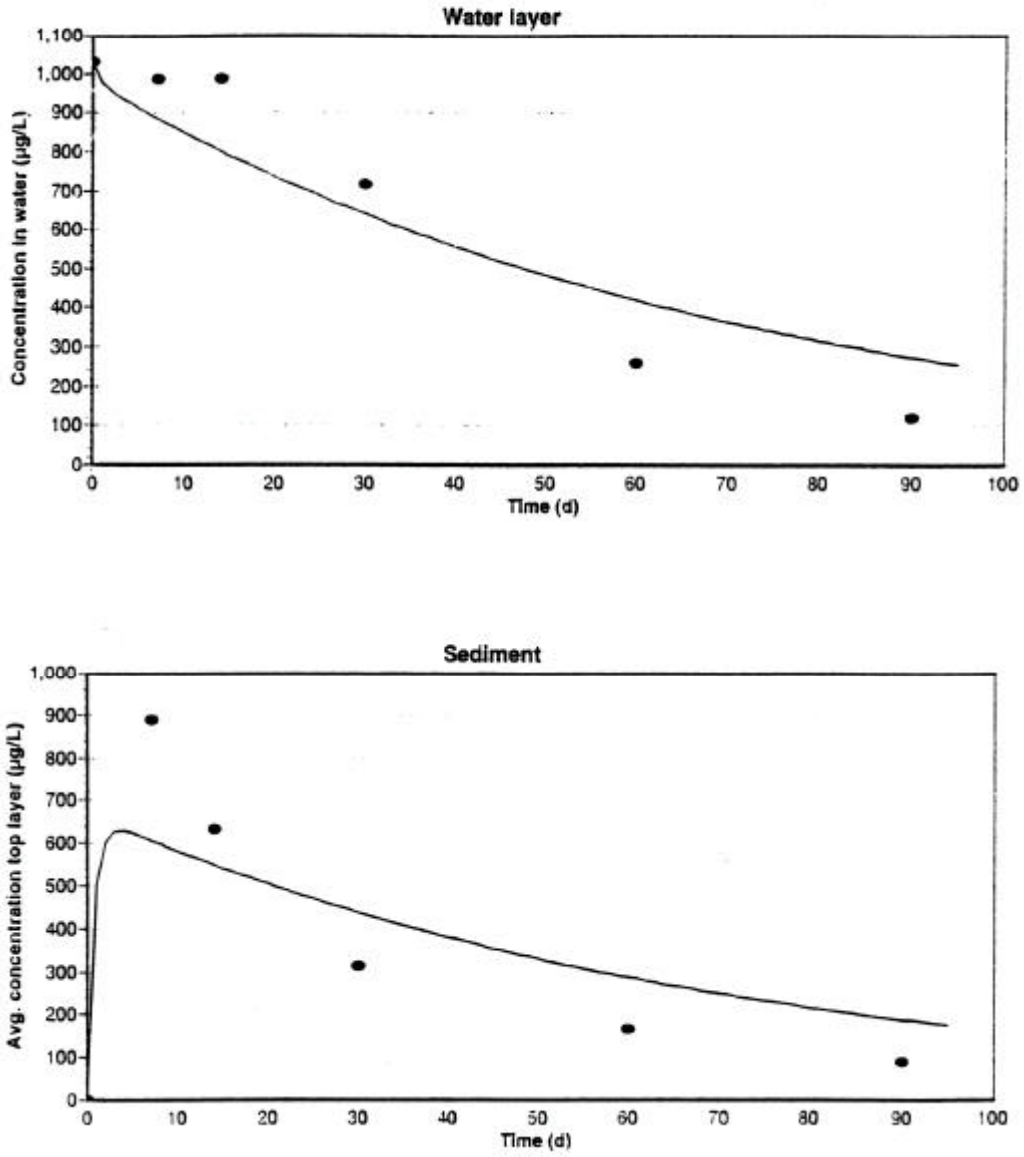


Figure 4.12. Simulated and measured concentrations of dicamba as a function of time in water and sediment of River system ($DT50_{wl}$ = 60 d, $DT50_{sed}$ = 36 d in TOXSWA input). Points: measured; lines: computed.

Concentration of pesticide in time

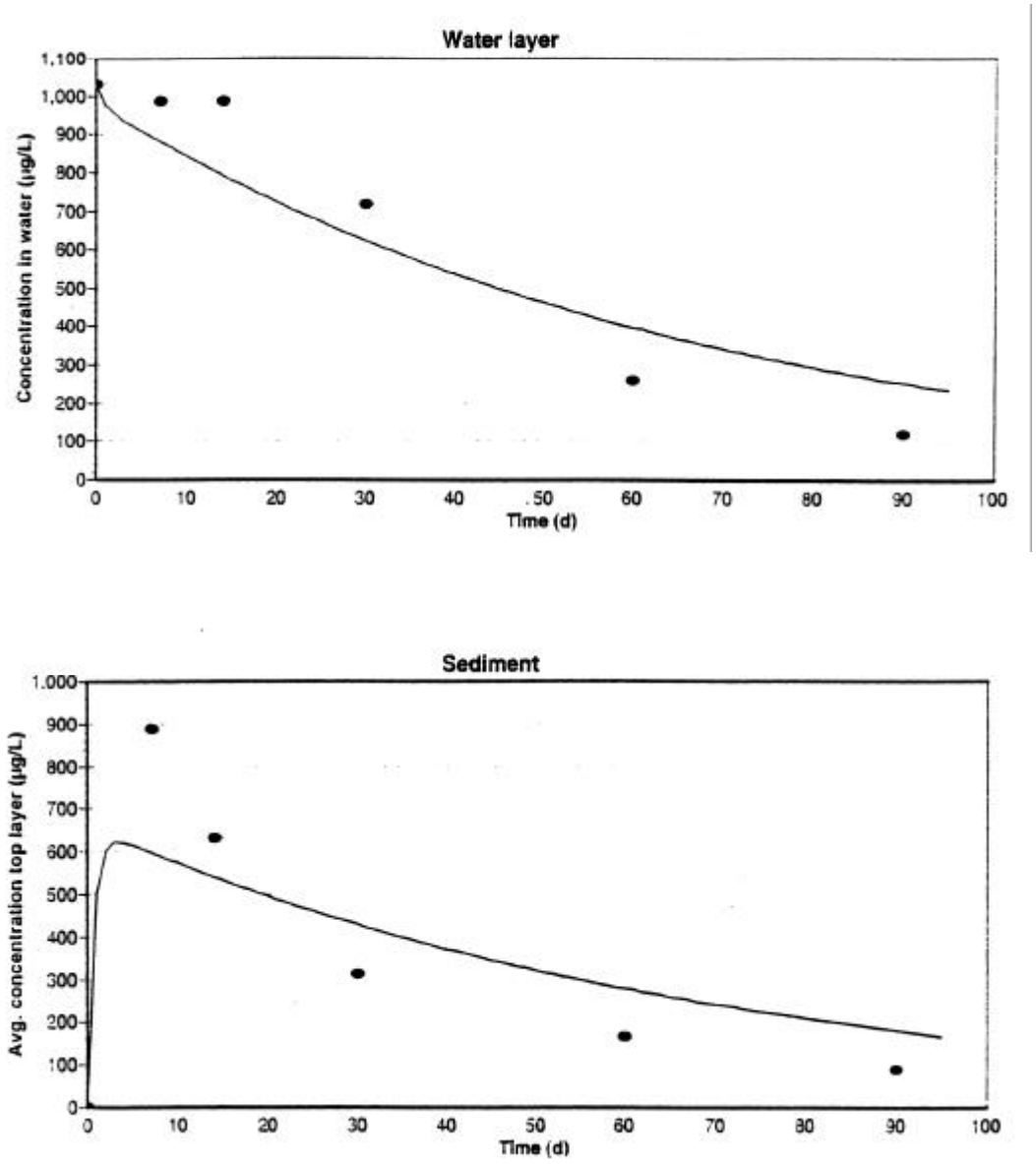


Figure 4.13. Simulated and measured concentrations of dicamba as a function of time in water and sediment of River system ($DT50_{wl}$ = 60 d, $DT50_{sed}$ = 20 d in TOXSWA input). Points: measured; lines: computed.

Concentration of pesticide in time

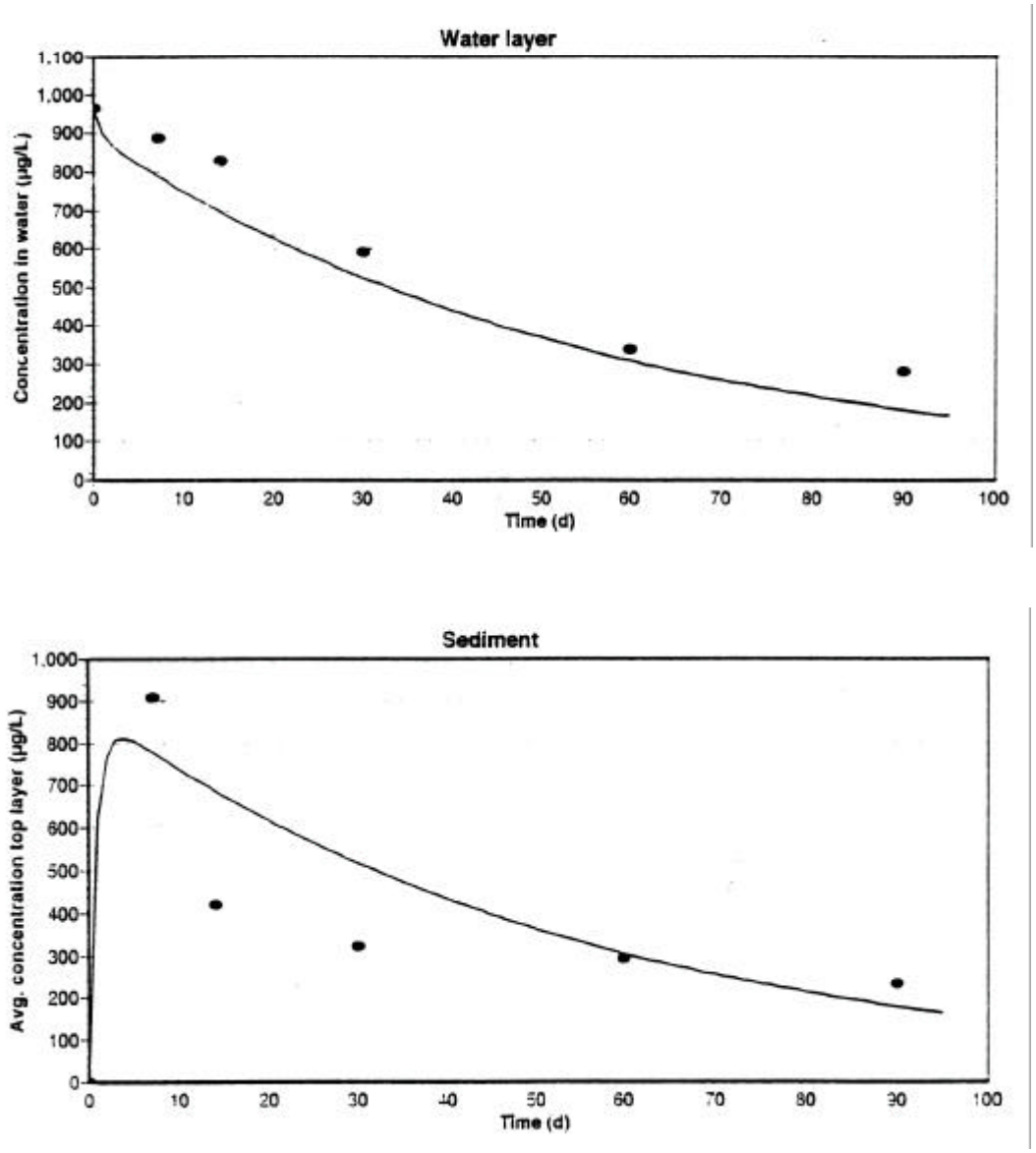


Figure 4.14. Simulated and measured concentrations of dicamba as a function of time in water and sediment of Pond system ($DT50_{wl}$ = $DT50_{sed}$ = 46 d in TOXSWA input). Points: measured; lines: computed.

Concentration of pesticide in time

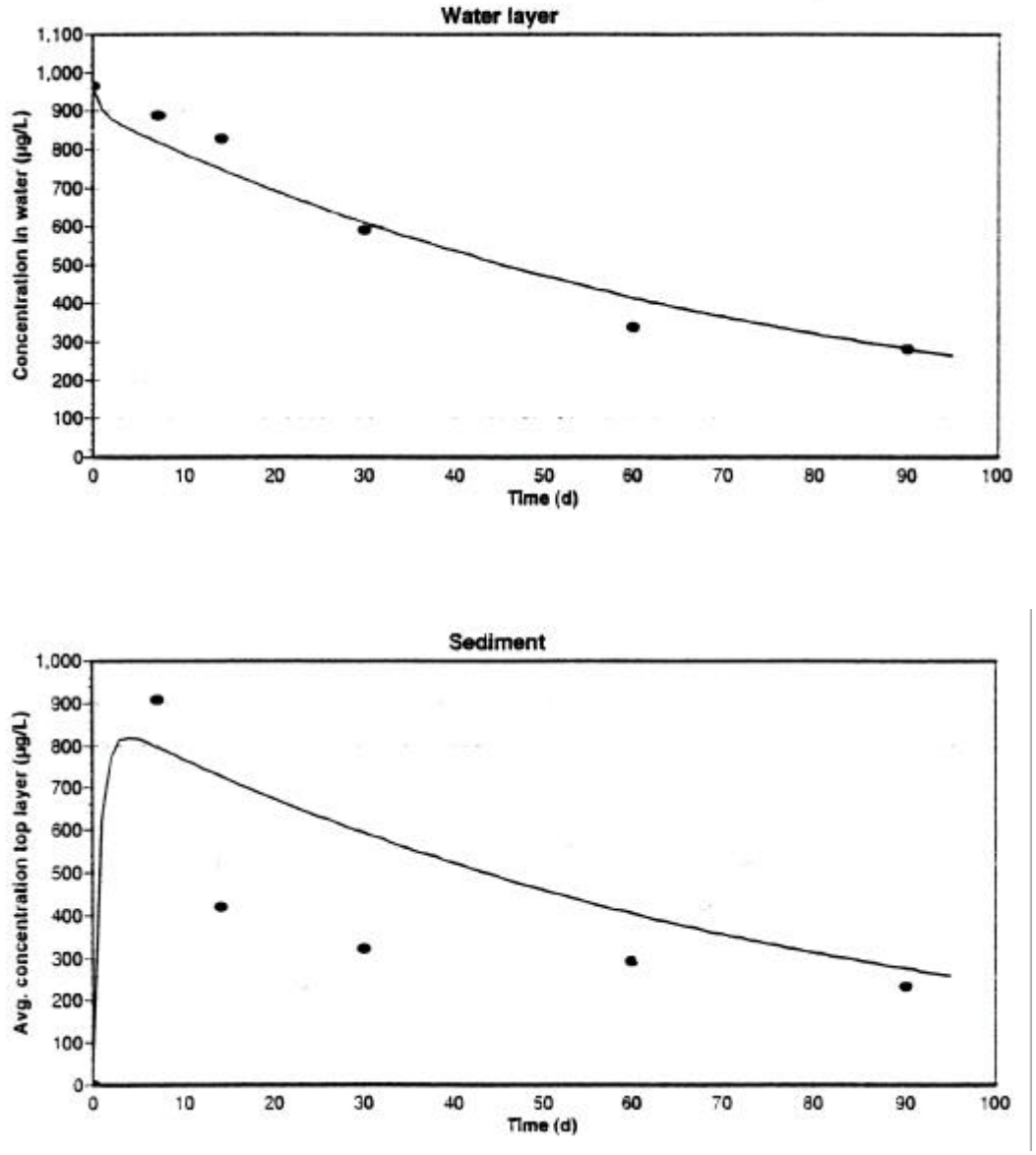


Figure 4.15. Simulated and measured concentrations of dicamba as a function of time in water and sediment of Pond system ($DT50_{wl}$ = 70 d, $DT50_{sed}$ = 30 d in TOXSWA input). Points: measured; lines: computed.

Concentration of pesticide in time

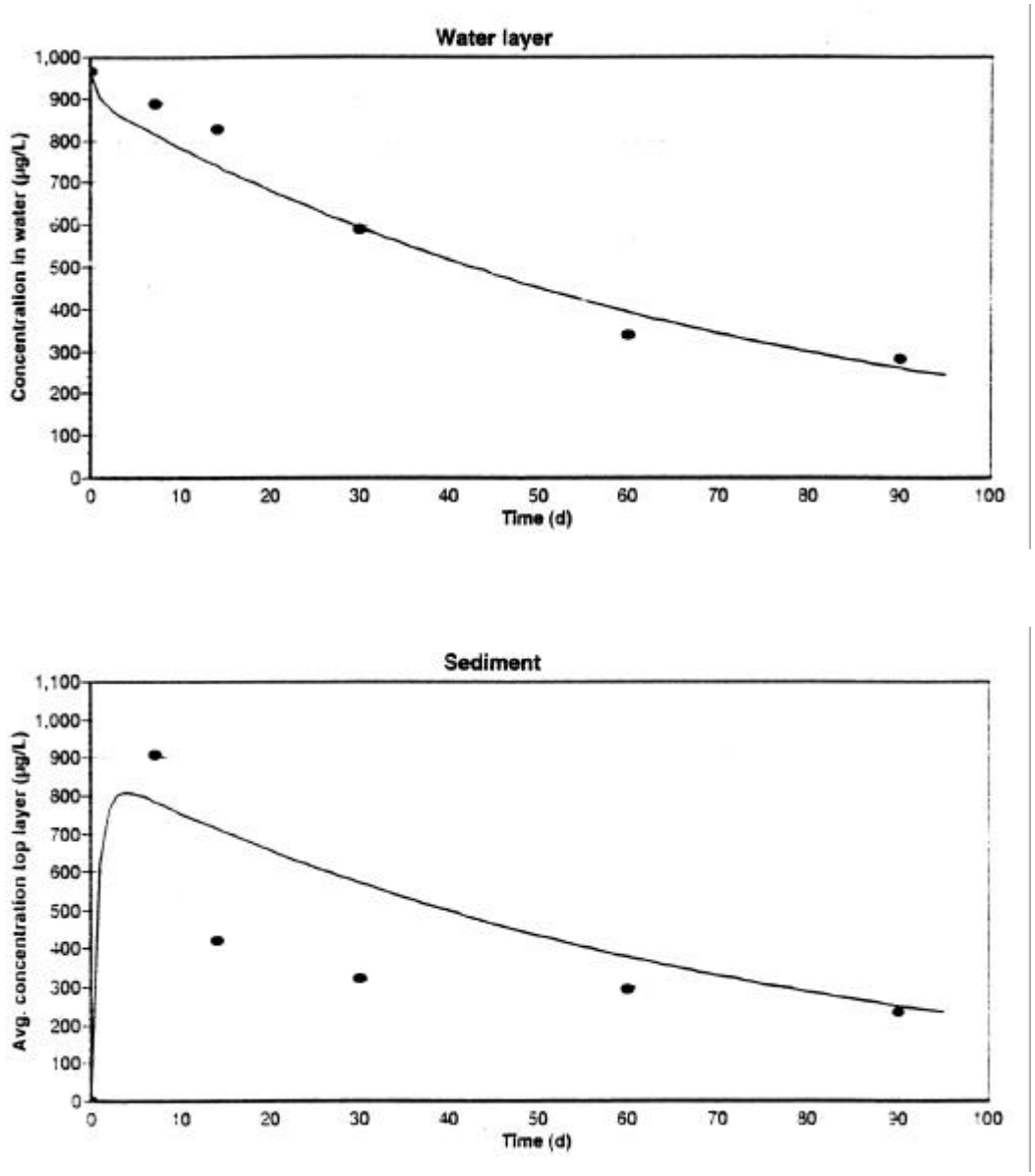


Figure 4.16. Simulated and measured concentrations of dicamba as a function of time in water and sediment of Pond system ($DT50_{wl}$ = 70 d, $DT50_{sed}$ = 20 d in TOXSWA input). Points: measured; lines: computed.

4.4 Chlorpropham

4.4.1 Experiments

Physico-chemical properties
The vapour pressure of chlorpropham is 1.3 mPa at 25 °C (Van de Plassche et al., 1992), so it is slightly volatile. The solubility in water is 89 mg/L (at 25 °C) (Tomlin, 1997).

Water-sediment study
Two water-sediment combinations were collected in the study by Vonk (1992):
a) Ditch 1, a ditch in the Kromme Rijn area, Odijk, Province of Utrecht;
b) Ditch 2, a ditch near the TNO buildings in Zuidpolder, Delft, Province of South-Holland.

The study was set up with 84 g of wet sediment plus 466 ml of ditch water for the Ditch 1 systems; for the Ditch 2 systems these values were 129.5 g plus 420 ml. In this way 10% (m/m) of dry solids in about 500 ml of ditch water was obtained. The biometer flasks had an estimated horizontal area of 95 cm^2. The layer of sediment was about 1.5 cm high; the layer of water was about 4.5 cm high. The organic matter contents of the sediments were 2.0% (Ditch 1) and 11.0% (Ditch 2). The systems were pre-incubated on a orbital shaker (about 60 rpm) in the dark at 20 °C for 18 days.

The nominal concentration of chlorpropham (phenyl-ring-^{14}C-labelled) applied to the water was 3 mg/L. The systems were incubated on the orbital shaker (60 rpm) in the dark at 20 °C for up to 84 days. Although the incubation vessels were shaken orbitally, the sediment layer was not moving and a clear water-sediment interface was visible (Vonk, 1999, pers. comm.). In the incubation period, the average pH in the water was 8.4 (Ditch 1) and 8.3 (Ditch 2).

At some times in the incubation period of 84 days, the water and the sediment were analysed for radioactivity (by LSC) and for chlorpropham (by TLC).

Concentrations measured in water and sediment layers
We calculated the concentrations in water and sediment by using the measurements reported in Tables 5 and 6 (Ditch 1) of Vonk (1992) and in Table 3 (Ditch 2 system, Table 4 was missing). The fraction of radioactivity in the aqueous phase times the initial concentration of 3 $mg.l^{-1}$ resulted in the concentration of chlorpropham in water as a function of time. The radioactivity in the sediment extracts divided by the volume of the sediment layer equals the concentration in the sediment. We averaged the values obtained for Tables 5 and 6 of Vonk (1992), because they refer to the same extracts. Appendices 6 and 7 present the concentrations for the two ditch systems.

Sorption to soils
The average value of K_{om} for sorption of chlorpropham to the organic matter in three soils was calculated to be 200 dm^3/kg (RIVM, 1998).

4.4.2 Input data

The report on chlorpropham did not mention the bulk densities and porosities of the sediment or the dimensions of the incubation vessels. It reported that the water layer was about 4.5 cm high and the sediment layer about 1.5 cm or not higher than 1.5 cm (Fig. 1 of Vonk, 1992). The particle size distribution for both sediments was given in Table C1 of Vonk (1992). We calculated the densities of the solid phase with the pedotransfer functions for clayey soils of Wösten and of Poelman (Wösten, 1997b). After that, the bulk densities and porosities of the layers can be calculated: 0.42 and 0.59 for Ditch 1 and 1.02 and 1.52 $g.cm^{-3}$ for Ditch 2, respectively. We combined these with the reported wet sediment mass plus water volume and the estimated horizontal area of the incubation vessels (95 cm^2, i.e. tubes of 11 cm diameter). The calculated sediment layers were 3 and 5 mm high under water layers of 4.9 and 4.4 cm (Ditch 2 and Ditch 1, respectively). We deduced from these results that the estimated horizontal area of the incubation vessels was correct, but that the bulk densities and porosities were not correct. The division between water volume and dry sediment mass in the added wet sediment seemed correct: 35.3 ml water and 48.7 g dry sediment for the Ditch 1 systems and 76.4 ml water and 53.1 g dry sediment for the Ditch 2 systems. This results in 501.3 ml water and 496.4 ml water in the incubation vessels (Ditch 1 and Ditch 2, respectively), which corresponds to the reported volume of 500 ml water in each vessel.) Therefore, we assumed the calculated masses of dry sediment to be correct. Next, we assumed the 48.7 and 53.1 g sediment (dry mass basis; Ditch 1 and Ditch 2, respectively) to form a 1.5 cm high sediment layer. In this way we calculated the bulk densities to be 0.342 and 0.373 $g.cm^{-3}$ and the porosities to be 0.87 and 0.85 (Ditch 1 and Ditch 2, repectively). These low bulk densities and high porosities imply that the sediment layer was not well settled, but very loose. This may be the result of the orbital shaking at 60 rpm.

We used the sorption coefficient K_{om} of 200 $l.kg^{-1}$ and we assumed the sorption isotherm to be curved and described by a Freundlich coefficient of 0.9, which is the average value for soils (Boesten, 1986). Usually, the reference concentration of the Freundlich equation is taken to be 1 $mg.l^{-1}$.

4.4.3 Results for Ditch 1

Figure 4.17 shows the simulation results for chlorpropham using the input data of the Ditch 1 system, presented in Tables 4.20 to 4.24. For the initial estimates of 28 d for the transformation half-lives in both water and sediment, the simulated concentrations in the water layer were higher than those measured. So the simulated decline was less than measured. In the sediment the maxima of the simulated concentrations were about 2500 $\mu g.l^{-1}$, while the measured concentration peaks were around 6500 $\mu g.l^{-1}$. After around 40 d simulated concentrations were higher than those measured.

Figure 4.18 shows the results for a transformation half-life of 20 d in the water layer; all other input parameters were those in Tables 4.20 to 4.24. Compared to Figure 4.17, correspondence between simulated and measured concentrations of chlorpropham in

water has improved. However, in the sediment the simulated concentration peak hardly changed. Figure 4.18 seems the best fit we can obtain by only changing the input concerning the transformation rates, thus 20 and 28 d are the best estimates for the transformation half-lives for the water and sediment layers, respectively, of the Ditch 1 system.

Table 4.20. Input data for the water layer, chlorpropham (Ditch 1)

Water layer
Rectangular, vertical cross-section 0.11 m wide
Water depth 0.049 m
Water depth defining perimeter for exchange water-sediment 0.001 m
Concentration suspended solids 15 g/m^3 (assumption) With an organic matter content of 0.02 kg/kg
No flow, dummy value of 10 m^2/d for longitudinal dispersion coefficient
Initial concentration 3000 µg/l

Table 4.21. Input data for the sediment, chlorpropham (Ditch 1)

Sediment
Sediment thickness 0.015 m
Bulk density 342 kg/m^3, constant with depth
Porosity 0.87 , constant with depth
Tortuosity 0.87 , constant with depth
Organic matter content 0.02 kg/kg, constant with depth
Initial concentration 0 µg/l

Table 4.22. Input data concerning the simulation, chlorpropham (Ditch 1)

Simulation
One segment of 0.11 m length in the water layer
Segments of 1, 1, 2, 2, 3, 3 and 3 mm corresponding to the total thickness of the sediment layer
Calculation time step 1200 s
Total time simulated 90 d

Table 4.23. Input data of initial estimates of the transformation rates, chlorpropham (Ditch 1)

Initial estimates for transformation half-lives
Transformation half-life in water 28 d (3-5 weeks reported)
Transformation half-life in sediment 28 d (3-5 weeks reported)

Table 4.24. Input data for chlorpropham

Compound
Physico-chemical data:
molecular mass 213.7 g/mol
saturated vapour pressure 1.3*10^{-3} Pa at 25 °C
solubility in water 0.089 g/l at 25 °C
Sorption:
K_{om} (soils) 200 l/kg
Freundlich exponent 0.9

Concentration of pesticide in time

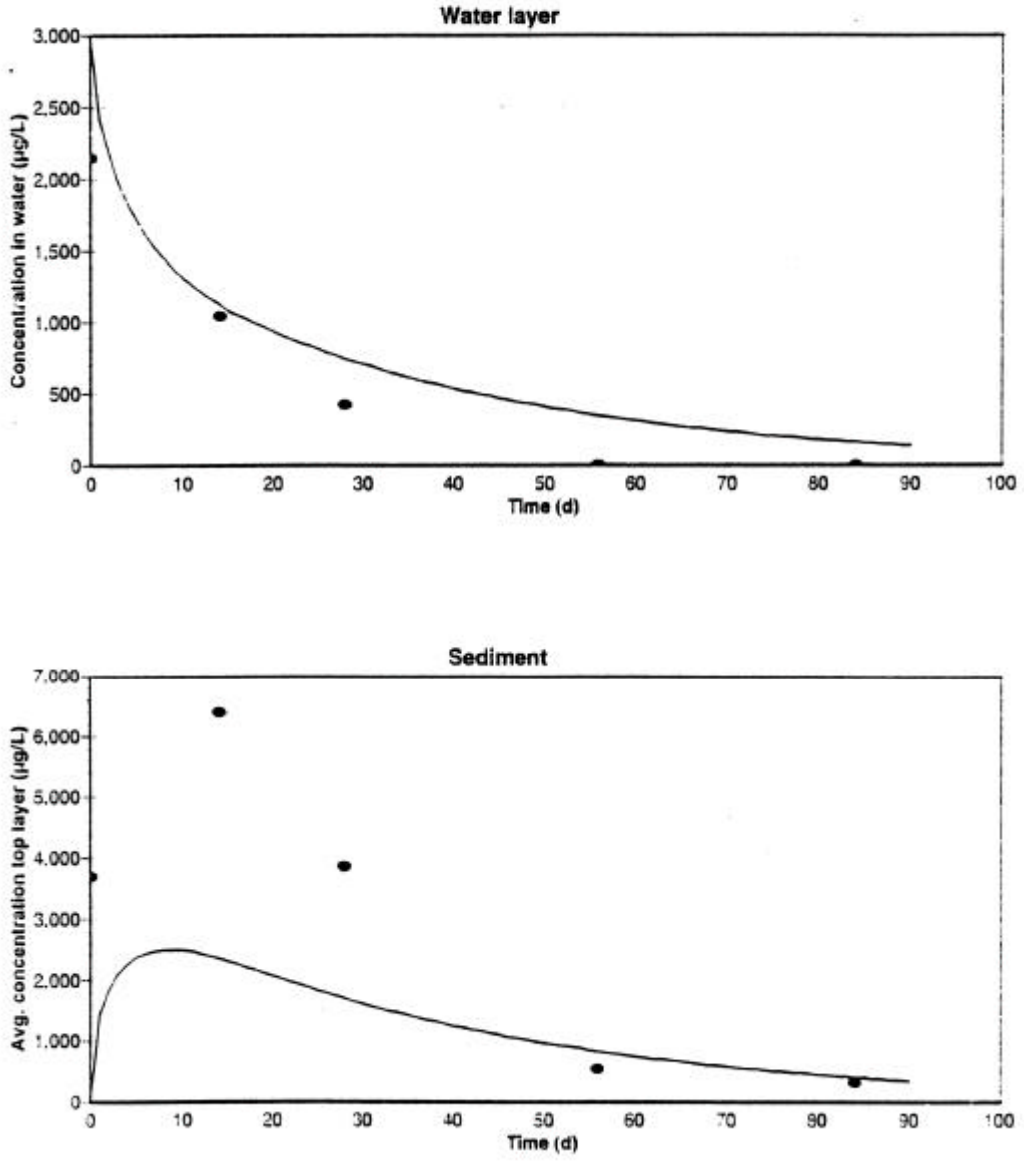


Figure 4.17. Simulated and measured concentrations of chlorpropham as a function of time in water and sediment of Ditch 1 system ($DT50_{wl}$ = $DT50_{sed}$ = 28 d in TOXSWA input). Points: measured; lines: computed.

Concentration of pesticide in time

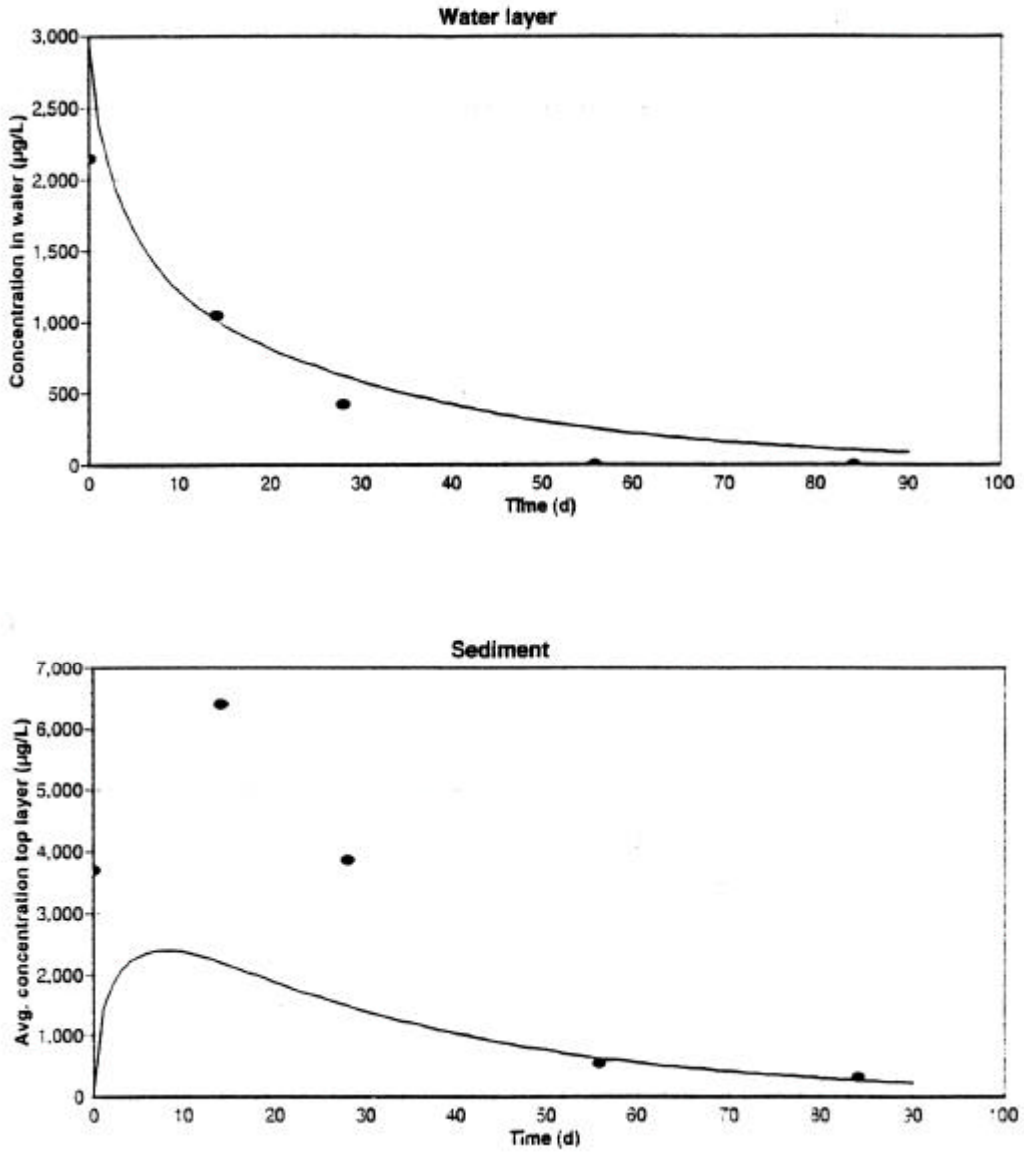


Figure 4.18. Simulated and measured concentrations of chlorpropham as a function of time in water and sediment of Ditch 1 system ($DT50_{wl}$ = 15 d, $DT50_{sed}$ = 28 d in TOXSWA input). Points: measured; lines: computed.

4.4.4 Results for Ditch 2

The situation for chlorpropham in Ditch 2 system is comparable to that for Ditch 1. The initial estimates of 40 d for the transformation half-lives in water and sediment (and all other input according to Tables 4.25 to 4.28) resulted in simulated concentrations in the water layer to be slightly higher than those measured. The simulated peak concentration of about 4000 µg.l^{-1} in the sediment was clearly lower than the measured peak of about 6000 µg.l^{-1} (Fig. 4.19).

Figure 4.20 shows the results for a transformation half-life of 20 d in the water layer and all other input according to Tables 4.25 to 4.28. Correspondence for chlorpropham in the water layer improved, while making the correspondence in the sediment only slightly worse. Thus, for the Ditch 2 system, the best estimates are 20 and 40 d for the transformation half-lives in the water and sediment layers, respectively.

Table 4.25. Input data for the water layer, chlorpropham (Ditch 2)

Water layer
Rectangular, vertical cross-section 0.11 m wide
Water depth 0.044 m
Water depth defining perimeter for exchange water-sediment 0.001 m
Concentration suspended solids 15 g/m^3 (assumption) With an organic matter content of 0.11 kg/kg
No flow, dummy value of 10 m^2/d for longitudinal dispersion coefficient
Initial concentration 3000 µg/l

Table 4.26. Input data for the sediment, chlorpropham (Ditch 2)

Sediment
Sediment thickness 0.015 m
Bulk density 373 kg/m^3, constant with depth
Porosity 0.85 , constant with depth
Tortuosity 0.85 , constant with depth
Organic matter content 0.11 kg/kg, constant with depth
Initial concentration 0 µg/l

Table 4.27. Input data concerning the simulation, chlorpropham (Ditch 2)

Simulation
One segment of 0.11 m length in the water layer
Segments of 1, 1, 2, 2, 3, 3 and 3 mm corresponding to The total thickness of the sediment layer
Calculation time step 3600 s
Total time simulated 90 d

Table 4.28. Input data of initial estimates of the transformation rates, chlorpropham (Ditch 2)

Initial estimates for transformation half-lives
Transformation half-life in water 40 d (5-6 weeks reported)
Transformation half-life in sediment 40 d (5-6 weeks reported)

Concentration of pesticide in time

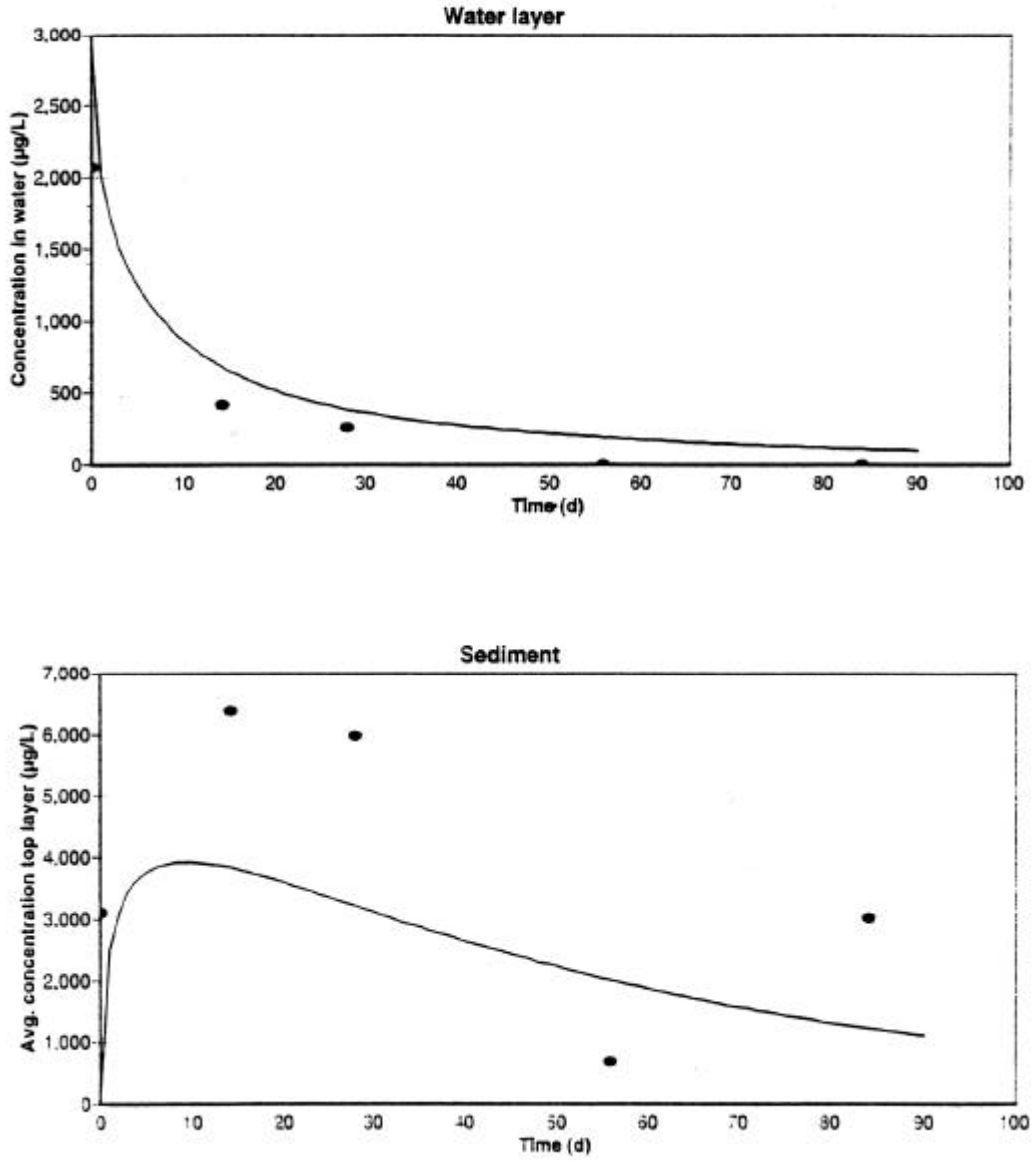


Figure 4.19. Simulated and measured concentrations of chlorpropham as a function of time in water and sediment of Ditch 2 system ($DT50_{wl}$ = $DT50_{sed}$ = 40 d in TOXSWA input). Points: measured; lines: computed.

Concentration of pesticide in time

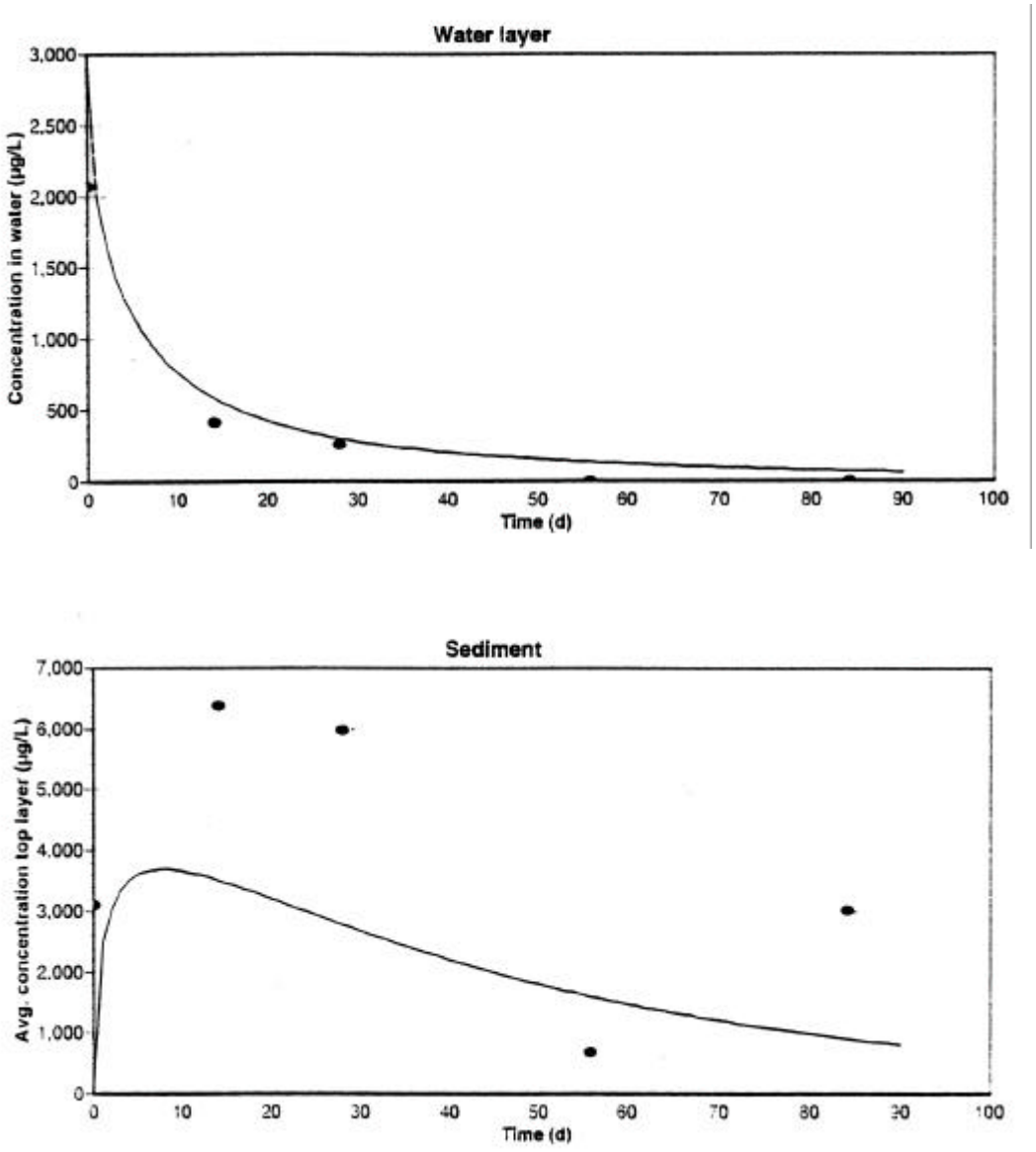


Figure 4.20. Simulated and measured concentrations of chlorpropham as a function of time in water and sediment of Ditch 2 system ($DT50_{wl}$ = 20 d, $DT50_{sed}$ = 40 d in TOXSWA input). Points: measured; lines: computed.

4.5 Discussion

Water-sediment studies were set up for other reasons than for which we use them in this study. Some experimental specifications crucial for our simulations were not measured in a standardised way or they were not measured at all. The dimensions of the water-sediment systems are not always reported. The depths of the water layer and sediment layer should be known for the computations. Further, the dry bulk density of the sediment is needed to estimate diffusion and adsorption in this layer. For making estimates of these essential quantities, various assumptions had to be made. Methods are available to estimate the bulk densities of agricultural soils, but it is uncertain whether these apply to sieved sediment poured into the incubation systems. This lack of details in the reports has an adverse effect on the accuracy of estimating the transformation rates of the pesticide in water and sediment.

The adsorption of the pesticide on the sediment is usually not measured. Therefore, the adsorption has to be estimated on the basis of measurements for soils. In principle, this is possible because the composition of the sediment is characterized. However, it is not known whether adsorption measurements for soils provide good estimates for the adsorption of the pesticide on aquatic sediments. Further, more should be known on the distribution of the organic matter with depth in the sediment. When filling the systems, different sediment fractions may settle at different rates, which results in a stratified sediment layer.

Some elements in the experimental procedures hamper the simulation with the model to obtain the separate transformation rates. In the test for chlorpropham, the system was slowly rotated (orbital shaking). Although there was no large-scale movement of the sediment, some flow of material may have occurred. In some of the water-sediment experiments, the systems were centrifuged before extraction and analysis. This is undesirable, because it may disturbe the system. While compacting the sediment, water flows out; this affects the distribution of pesticide between the two layers.

The first simulations for indoxacarb showed large differences with the measured concentration-time relationships. This could be explained because the calculated initial concentration in the water layer was far above the solubility of indoxacarb in water. In such an experiment additional processes may be expected to occur, e.g. crystallization and sinking onto the sediment, especially in the initial period. When the indoxacarb distribution between water and sediment measured at 3 days after application was taken as initial situation, a much better description was obtained.

The course of the transformation cannot always be described by first-order kinetics. The rate coefficient for indoxacarb in the River sediment was highest in the first month; after that it decreased to a low value. This may be caused by factors like decreasing bioavailability and decreasing microbial activity. Also the fact that indoxacarb is a mixture of two enantiomers with possibly different transformation rates, may contribute. After a distinct decrease in the water layer (first month), low levels of the indoxacarb remained for about 2 months. In the River sediment,

dicamba showed an initial lag phase of about 2 weeks without distinct transformation.

In the report on dicamba there was a problem in the processing of the measured results. The concentrations in the sediment layer were calculated from the radioactivity to be a factor 10 too low. Recalculation of these concentrations was needed.

In the final stage of completion of this report it was realised that wet sediment was brought into the test vessels in the experiments with indoxacarb and dicamba. For indoxacarb this implies that the correct depth of the water layer is 8.2 cm instead of 7.5 cm and 7.6 cm for the River and Pond systems, respectively. For dicamba this means that the correct depth is 5.7 cm instead of 5.5 cm for both systems. We estimate that the calculated transformation rates for the water layer will only change slightly from what is presented in Table 4.29: maximally about 10% for indoxacarb and even less for dicamba.

A detailed analysis of the properties of the sediment used for chlorpropham revealed that the bulk densities could not be estimated using pedotransfer functions, like we did in other cases. Probably, orbital shaking of the systems (60 rpm) caused low bulk densities and high porosities. We deduced the bulk densities to be only about 0.35 to 0.37 g cm^{-3} and the porosities to be about 0.87 to 0.85 for Ditch 1 and Ditch 2, respectively.

Attempts to obtain good correspondence between simulated and measured concentrations in the water layer may make correspondence in the sediment layer worse, and vice versa. If by far most of the pesticide resides in one of the layers, it seems a good choice to concentrate on the correspondence in that layer. However, the rate of pesticide transformation in the other layer is estimated more roughly then.

Table 4.29 gives an overview of the dissipation half-lives presented in the submitted Reports. Besides, it presents the transformation half-lives estimated with TOXSWA for the three pesticides. The transformation half-life of indoxacarb in the water layer is much longer than its dissipation half-life. This is explained by the great effect of adsorption and penetration in the sediment on the dissipation of indoxacarb (strongly adsorbed) in the water layer.

As indoxacarb mainly resides in the sediment, a rather good correspondence of the half-lives for the sediment layer would be expected. However, the differences are a factor 2 to 3 (Table 4.29). A first reason is that it was attempted to get correspondence for both the water layer and the sediment layer. A second reason is that the measured concentration-time relationship deviated from that of first-order kinetics. If more emphasis is put on the initial period, the half-life becomes comparatively short. In the later stages of the incubations, the course of the decline of the concentration levelled-off. More emphasis on the ‘tailing’ in the decline in the River sediment would result in a higher value of the transformation half-life estimated for this layer.

Table 4.29. Half-lives for dissipation in water and sediment layers as calculated in the Reports and half-lifes for transformation estimated by simulating the water-sediment studies with TOXSWA

Compound	Water-sediment system	Dissipation half-life (d) reported			Transformation half-life (d) using TOXSWA	
		total system	water	sediment	water	sediment
Indoxacarb	River	10	2	28	15	15
K_{om}=770 l/kg	Pond	17	2	39	10	90
n=0.81						
Dicamba	River	36	-	-	60	20
K_{om}=10 l/kg	Pond	46	-	-	70	20
n=0.9						
Chlorpropham	Ditch 1	28	-	-	20	28
K_{om}=200 l/kg	Ditch 2	40	-	-	20	40
n=0.9						

The results computed for dicamba (Table 4.29) indicate that the dissipation in the total system can mainly be ascribed to transformation in the sediment layer (shortest half-lives). This is remarkable, as most of the weakly-adsorbed pesticide was present in the water layer.

The transformation half-lives estimated for chlorpropham (moderately adsorbed) in the water and sediment layers are of the same order of magnitude (Table 4.29). Further, they are at the same level as the half-lives for overall dissipation. There is no indication that transformation can be mainly ascribed to one of the two layers.

The results in Table 4.29 indicate that there is no general rule on the predominance of transformation in one of the two layers of the water-sediment system. Other research for the pesticide, e.g. on hydrolysis and on anaerobic transformation in soils, may indicate where most of the transformation can be expected to occur.

Our experience with the three compounds is that estimating transformation half-lives for water and sediment in water-sediment systems is not a straightforward procedure yet. In all three cases experimental peculiarities or even errors required substantial expertise for making good estimates of the transformation half-lives.

In a later stage, the procedure of fitting the simulated concentrations to those measured should be automated. When the preparatory estimates and calculations have been made correctly, the procedure should result in unbiased estimates for the transformation half-lives. However, peculiarities in the experiments, in the processes in water and sediment, and in the reporting may still require that some expertise is used in the fitting procedure.

5 Proposals based on experiences

5.1 Check for suitability of the water-sediment study

First it should be checked whether the water-sediment study is suitable for simulation with the TOXSWA model. The water layer should be well-mixed (as needed for aerobic condition) and the sediment layer should be stagnant. The initial concentration of the pesticide in the water layer should be well below its solubility in water. Pesticide concentrations should have been measured in the layers as present during the incubation. The balance of radioactivity should be satisfactory and it has to be checked whether the mass concentrations were calculated in correct way from the radioactivity fractions. The experiment should meet by far most of the specifications in the OECD (2000) guideline. Some possible actions with respect to the suitability of the experiment are:

a) estimate missing input data;
b) correct errors in data processing;
c) slightly adapt the simulations;
d) reject the experiment for the present purpose.

5.2 Proposed generic procedure

Based on the experiences with the three compounds described in Chapter 4, we propose the following generic procedure to estimate separate transformation rates for the pesticide in the water and sediment layers, using the submitted water-sediment study.

1. Collect the physico-chemical properties of the pesticide, such as molar mass, vapour pressure and solubility in water. Use the most reliable data, e.g. those in Tomlin (1997) or in the company files. Data measured according to international guidelines are preferred.

2. Use the adsorption isotherm measured for the pesticide-sediment combination in the experiment, if available. Otherwise, estimate the adsorption to the sediment on the basis of the adsorption of the pesticide on soils, e.g. by using the difference in organic matter content. Describe pesticide adsorption with the Freundlich equation, using the Freundlich exponent to be 0.9 (Boesten, 1986), unless more specific data are available.

3. Derive depth of the water layer, concentration of suspended solids in water, depth of the sediment layer and bulk density of the sediment layer from the report on the experiment. If not specified, estimate these quantities from the dimension of the vessels, volume of water, mass of sediment and composition of the sediment. For the time being, bulk density can be estimated using continuous pedotransfer functions for structured soils (Wösten, 1997b). Note that more information on

bulk densities of sediments after sieving and pouring them into the incubation vessels is urgently needed. Sandy sediments may show a rather dense packing, but clayey and organic sediments may be comparatively loose. So bulk densities estimated with functions developed for structured soils may be lower, respectively higher, boundary values for the sediment in the incubation vessels. Estimate the porosity in the sediment from the bulk density and the density of the solid phase (Wösten, 1997b).

4. Calculate the mass concentration of the pesticide as a function of time in the water and sediment layers (often measured as percentage of applied radioactivity in the water-sediment study). Make the files (*.DAT) with the measured mass concentrations in both layers to be able to compare simulated and measured concentrations, using the Graphical User Interface of TOXSWA.

5. Take the initial estimates for the transformation rates of the pesticide in the water and sediment layers to be equal to the rate of decline in the whole system.

6. Start the Graphical User Interface of TOXSWA and enter the input data. Include simulation specifications like the number and thickness of computation segments in the sediment, the computation time step and the total simulation time. Consult the User Manual (Beltman & Adriaanse, 1999a) for details.

7. Make a first run with TOXSWA and compare simulated and measured concentrations in the water and sediment layers.

8. Change the estimates for the transformation rates in water and sediment, and run the TOXSWA model another time. Inspect the relation between simulated and measured concentrations.

9. Repeat point 8 until simulated and measured concentrations in the water and sediment layer correspond well. If the major part of pesticide mass resides in one of the two layers of the system, correspondence between simulated and measured concentrations should be best in the layer containing most of the pesticide mass. Show the computed and measured concentrations by making a figure of the results with the TOXSWA user interface.

The procedure described here has been mainly developed on the basis of our experiences with the three selected water-sediment studies. Therefore, the procedure proposed above has a preliminary character; it should now be tried out on other water-sediment studies in order to test its soundness. The procedures to estimate missing data still have to be elaborated in more detail.

5.3 Step by step evaluation of exposure

The derivation of transformation rates from the results of water-sediment studies may take some time and there may be uncertainties. Therefore some ideas have been

developed to speed up the evaluation for non-critical pesticide uses. A stepwise approach could be followed then.

Step 1
When the effect of a single pesticide application on the short-term exposure in the standard ditch is evaluated, the transformation rates in water and sediment do not have an effect. For such pesticide evaluation, the computation with TOXSWA for zero transformation rates is already decisive for the classification 'safe' or 'further evaluation needed'.

Although the transformation rates may set to zero in the first evaluation step, the other processes will be involved in the TOXSWA computation for the standard ditch. These processes are: distribution in the water body, convective transport due to water flow, volatilization, adsorption and penetration into the sediment.

Step 2
There is a chance that for some pesticides the transformation rates in the water and sediment layers are not critical in the evaluation of repeated applications or long-term exposure. Then even the input of zero transformation rates in TOXSWA could lead to an exposure pattern below the limit value in the evaluation. In this case it does not seem to be necessary to have quite accurate estimates of the separate transformation rates. Any transformation rate leads to a lower exposure which is further below the limit value.

Step 3
It seems possible that some pesticide loads are so toxic that the limit values are exceeded, even at very fast transformation. The transformation rates in the water and sediment layers could be set to ten times the rate of dissipation (minus the contribution of volatilization) from the sediment-water systems. Alternatively, a high rate of transformation could be set, corresponding to a very short half-life of e.g. 2 days. If the exposure pattern calculated with TOXSWA then exceeds the limit value, higher-tier evaluation is needed. Then it is not needed to have more accurate estimates of the transformation rates for water and sediment in this first tier. At any more realistic lower transformation rate the exposure will exceed the limit value even more. It should be noted that it is likely that the transformation rates for water and sediment will then be needed in a further evaluation tier.

Step 4
Some pesticides show rather strong adsorption to the sediment. In that case almost all pesticide will be present in the sediment layer of the water-sediment system. The rate of dissipation in the water-sediment system (minus the contribution of volatilization) could then be assigned to the rate of transformation in the sediment layer. Because of the strong adsorption, the rate of dissipation in the water layer is a too high estimate of the rate of transformation in the water layer. If the rate of dissipation in the water layer is introduced into the TOXSWA model (as a first estimate of the transformation rate) and the calculated exposure exceeds the limit

value then evaluation in a further tier is needed. Any more realistic lower rate of transformation in the water layer will lead to an even higher exposure.

Step 5
Another group of pesticides shows only weak adsorption to the sediment. In that case almost all pesticide may be present in the water layer of the water-sediment system. The rate of dissipation from the water-sediment system (minus the contribution of volatilization) could then be assigned to transformation in the water layer. The rate of transformation in the sediment layer could be set to zero, which is an underestimation. If the calculated exposure falls below the limit value, no further evaluation is needed. Introduction of a more realistic higher transformation rate for the sediment layer would lead to an even lower exposure.

Try-out
It is considered to be worthwile to explore the usefulness of such a step by step evaluation, as it could save time in the first evaluation tier. Ultimately, a decision tree could be built from steps like those given above. Only for pesticides for which a quick evaluation is not possible, the more elaborate estimation of the transformation rates in water and sediment using the TOXSWA model would be needed in the first evaluation tier.

5.4 Discussion

It is recommended to investigate whether methods exist to estimate the bulk density and porosity of sediments. By using pedotransfer functions developed for structured soils, sandy-sediment bulk densities may be underestimated and the porosities overestimated. It is recommended to search into literature if and how bulk densities of soils and sediments in standard tests are related and to execute a series of experiments to measure bulk densities for soils and sediments (at their natural site as well as in test vessels, with and without prior sieving) as a function of their particle size distribution.

If the sorption parameters have been determined for the sediment used in the water-sediment study, we use these sorption parameters. If this is not possible, we decided to use the sorption parameters determined for the assessment of mobility in soil in the Dutch registration procedure. Some kind of translation of the adsorption is then needed, e.g. via the organic matter contents. However, if other soil factors play a part in the adsorption, they have to be considered in the translation.

We recommend to carry out a literature research to investigate how the sorption parameters found in studies with soils differ from sorption parameters found in studies with sediments. Often concentration levels are lower in sediment studies and it is not clear whether the average curvature of the sorption isotherm differs from the value of 0.9 generally used for pesticide sorption on soils.

The present study attempts to take the maximum possible benefit from the results of the water-sediment studies. In the next few years, the water-sediment studies will become more and more suitable for simulation with TOXSWA, provided the OECD (2000) guideline is followed. However, for some older studies the attempt may prove to have no succes, because of complicating or missing data. The registration authority should then decide on the next step in the evaluation: ask for a new water-sediment study [according to OECD (2000)] or move to the next tier in the evaluation scheme. That tier may include research with larger model-ecosystems. For such ecosystems too, simulation with the TOXSWA model may provide more quantitative information on the processes. Further, the model can be used to translate the results for model-ecosystems to natural aquatic systems.

6 Influence of environmental factors

6.1 Introduction

The general agreement to include soil properties and soil type characterisation in pesticide behaviour assessments has not yet been implemented in surface water risk assessments. Only relatively few authors (e.g. Bull, 1985; Cook and Hutter, 1981; Feakin *et al.*, 1994; Kuhlman *et al.*, 1995; Lewis *et al.*, 1986; Tett *et al.*, 1994; Vink and Van der Zee, 1997b; Vink *et al.*, 1999; Wolfe *et al.*, 1986) have reported on surface water characteristics and their effect on biotransformation of individual pesticides. Although it may be concluded that the composition of surface waters dictates the overall transformation rate of a specific compound, and the possibilities of the occurrence of metabolites, very little is known yet about the quantitative contribution of individual characteristics and the possible effects in combinations of characteristics.

Quantitative effects that may occur when sediment and water occur simultaneously, such as is prescribed by water-sediment testing protocols for batch experiments, are usually subject to an array of interpretations when the system is not properly or sufficiently characterised. In this chapter, an outline is given of the current knowledge on the relation between relevant surface water characteristics and transformation rates and routes. Suggestions are given to improve characterisation of aqueous systems in such a way that the most probable discriminating (and measurable) variables are taken into account. The main purpose is to give a better foundation to testing protocols.

6.2 Review of literature

There is only partial understanding about the actual mechanisms how pesticides move between the aerobic, terrestrial soil and aquatic environments, and only little progress has been made on predicting biotransformation in the environment. Transformation of the parent pesticide molecule plays a crucial role in processes that determine transport behaviour in soil layers and subsequent emission to the aquatic environment. The impact of conventional and new pesticides on the environment is generally tested with leaching models, using parameters that are derived from and apply to terrestrial conditions (Vink *et al.*, 1997). However, when leached into environments with lower oxygen concentrations, e.g. subsoil, surface waters and saturated sediments, both transformation rates and pathways may change drastically as a result of altered, mostly unfavourable conditions for aerobic micro-organisms. Many publications report on compounds that are highly stable in aqueous systems (Anderson, 1995; Ashley and Leigh, 1963; Boesten *et al.*, 1991; Bromilow *et al.*, 1986; Edwards, 1973; Gerstl *et al.*, 1977; Nicholson, 1986; Reese *et al.*, 1972). The occurrence of generally unstable organochlorine pesticides in fresh water sediments and the accumulation in aquatic organisms have been reported by many authors

(Donald and Syrgiannis, 1995; Goutner *et al.*, 1997; Kenaga, 1980; Stickel, 1968; Tan and Vijayaletchumy, 1994; Zaranyika, 1994).

Models correlating chemical structure with biotransformation potential have been proposed to address the fate of chemicals in the environment (Alexander and Aleem, 1961; Larson, 1984; Paris and Wolfe, 1980; Wolfe et al., 1987). A major weakness in these models is that they do not account for the diversity of environmental factors affecting biotransformation (Davis and Madsen, 1996; Vink et al., 1994; Vink and Van der Zee, 1996). Top layers of sediments in water courses and lakes can become anaerobic during the summer months, allowing the overall transformation to proceed along different pathways (Lehman et al., 1993; Wolfe et al., 1986). Under reduced conditions, some pesticides may undergo partial transformation. Still, only limited information is available on pesticide transformation rates or pathways in low-oxygen environments. Therefore, the influence of transformation in the low-oxygen environments on the overall fate of pesticides has not sufficiently been evaluated.

Next to the potential hazards of ineffective agricultural use, the fate of pesticides in the various environmental compartments is determined by *in-situ* conditions. The significance and relative contribution of individual environmental properties in the overall transformation process has, if studied in any general context, much been debated. It is, for example, generally believed that the dissolved fraction of a compound, as opposed to the sorbed fraction, is much better available to micro-organisms and is therefore metabolised and degraded rapidly. For surface waters however, it has been suggested that sorption may in fact enhance biotransformation by concentrating the target compound (Olmstead and Weber, 1991; Voice *et al.*, 1992), by concentrating nutrients (Tranvik and Jørgensen, 1995), and by providing a large surface area for the attachment of bacteria which are then protected from shear forces by water movement (Shimp and Pfaender, 1987). Biotransformation rates of organic pesticides rely largely on the occurrence and activity of micro-organisms that are able to utilise a specific compound as an energy source to perform their primary functions. In most cases, organic pesticides act as a carbon source, but additional N, P or S which is incorporated in the molecule may be beneficial for the development of a microbial population.

If a compound is present in very small concentrations, it may be insufficient to act as a substrate and hence as an energy source, and decomposition may stop. If it is not completely metabolised as a primary substrate, it may be transformed as a secondary substrate if a chemically simpler or better available carbon source (e.g. dissolved organic carbon, DOC) is present. This phenomenon is known as cometabolism: the compound undergoes microbial transformation without supplying the micro-organisms with sufficient carbon or other nutrients (Alexander, 1981).

The rate at which a compound is transformed in the environment is primarily dictated by the population size of microbial communities in-situ. The actual size of any microbial population is maintained or is stimulated by favourable conditions in the surrounding environment. However, heterogeneity in geochemical, physical and biochemical properties seriously complicates accurate risk evaluations (Hornsby,

1992; Lappin et al., 1985). Vink et al. (1994) developed a model that linked microbial activity and development with time-dependent concentrations of the degrading compound. They were able to produce dynamic, non-linear transformation patterns as dependent on initial concentations and colony forming units (CFU) of micro-organisms.

Transformation rates and pathways that occur over the soil-aqueous transition zone (i.e. aerobic topsoil-subsoil-anaerobic sediment) were tested extensively for four distinctly different pesticides that represent their chemical group (Vink and Van der Zee, 1997a). It was shown that the prevailing redox conditions have a large impact on pesticide transformation rates. Some phenoxy-acetic compounds, which are considered improbable leachers based on their short aerobic half lives, appear to be persistent in low-oxygeneous conditions. The opposite effect was observed for a carbamate, in which chemical catalysis increased transformation rates when redox potentials decreased. It was shown that a temporal but severe period of oxygen inhibition can be survived by the aerobic microbial population. The involved micro-organisms can temporarily decrease their activity and can generally recover, within some days, from a stress period that lasts over three months.

A key issue in pesticide risk assessments is the fact that many compounds are readily transformed into compounds which are toxic to target and non-target organisms throughout the environment. Organophosphate and organosulfur insecticides commonly have initial transformation products with well-established insecticidal activity, often of greater potency than that of the parent compound. A common reaction observed in many sulfide-containing pesticides is oxidation to sulfoxides and sulfones which are usually active on a spectrum of pests similar to the parent compound. The formation of aldicarb sulfoxide and sulfone is an example of this. The simultaneous occurrence of parent compound and oxides may even lead to an increased toxicity. Of much concern is the fact that these toxicologically active transformation products tend to be more mobile than the corresponding parent compound. Thus, there is a risk of underestimating the environmental effects of the active ingredient. It may well be stated that metabolite formation must be considered to be a key issue in pesticide risk evaluations that consider the terrestrial-aquatic emission route.

An attempt to identify the major discriminating variables that determine the fate of pesticides in surface waters was undertaken by Vink and Van der Zee (1997b). A large set of environmental parameters, composed of physico-chemical, bio-chemical and chemical characteristics, was reduced to three major component groups, explaining the majority of variance of transformation rates of four pesticides that were observed in a variety of surface waters. The first component contains variables that promote biorespiratory processes. The second component is a macro/micro-nutrient group. The third component is the phosphorous group. Dissolved oxygen concentrations proved to be non-discriminating. However, the biochemical oxygen demand, which is a measure of biological activity, showed significant relationships. It was shown that small lotic systems such as field ditches have a larger potential to degrade specific compounds than large lentic systems, such as channels and lakes.

This effect is largely attributed to microbial activity and the possibility of a relevant community to develop. This is not restricted to “macro-characteristics” such as suspended solids or organic carbon, but also comprises micro-nutrients which are essential for a bacterial colony to develop.

A specific role of Mg/Mn and phosphorus concentrations in nitrifying surface waters on biotransformation rates was identified. Addition of orthophosphate increased the residence time of dissolved Mn, which may under certain conditions promote biotransformation rates. Also, the redox status of sediments dictates chemical speciation of Mn: solubility is very low in aeobic, and very high under anaeobic conditions.

Redox status may dictate transformation in more ways, sometimes via indirect geochemical or ecological processes. For an s-triazine it was shown that it was virtually persistent in most surface waters, except for a short period that coincides with the nitrification process in which NH_4 dissipates and NO_2 and NO_3 are formed (Vink et al., 1999).

Relationships between essential micro-nutrients and transformation rates of specific pesticides could be derived. These relationships may be used to assess these elements as environmental indicators for potential biotransformation of these compounds, or members of the chemical group, but only in combination with conditions that warrant the development and growth of a degrading population over a longer period of time.

An illustration of the effects of individual properties is given in Figure 6.1. It shows the actual transformation of MCPA in two surface water samples (S1, S2) and in a 1:1 mixture (mix). Sample S2 is considered to be a rapidly degrading medium, whereas the conditions in S1 do not allow equal transformation rates. Mixing evidently results in an increased transformation rate as compared to S1, due to the effect of cancelling out inhibitory effects.

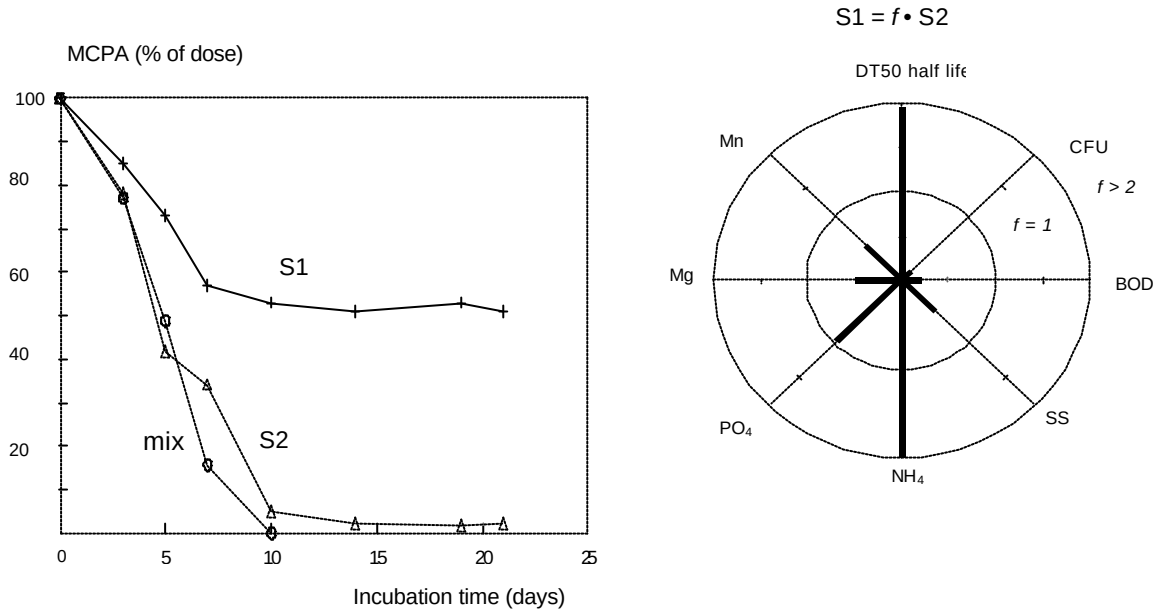


Fig. 6.1. Transformation of MCPA in two surface waters S1 and S2 and a 1:1 mixture (left) dictated by seven discriminating environmental parameters (right).

The individual effects of sample properties may be illustrated with the aid of 'fraction circles', which compare the relative concentrations of environmental properties in two samples. The inner circle (f=1) represents equal values of these properties, which are:

1. CFU = Bacterial Colony Forming Units;
2. BOD = Biochemical Oxygen Demand;
3. SS = Suspended solids, including particulate organic carbon (POC);
4. NH_4 = Ammonium concentration;
5. PO_4 = Orthophosphorus concentration;
6. Mn = Manganese concentration;
7. Mg = Magnesium concentration.

The relationships between these properties were discussed in detail by e.g. Vink and Van der Zee, 1997a, 1997b, Vink et al., 1999 and Weber, 1972. The slower transformation rate observed in S1 as compared to that in S2 may be attributed mainly to the smaller values of CFU, BOD, SS and Mn/Mg concentrations. Ammonium and orthophosphorus concentrations do not impose any limitations on transformation rates in S1. It should be noted that parameter SS is primarily significant for flowing water systems, and is less relevant in batch-type water-sediment studies. In these studies, measurements of dissolved organic carbon (DOC) and the macro nutrient Ca become more important.

The observed behaviour of the studied pesticides is probably not restricted to the individual compound, but may represent analogies for compounds within their chemical group.

6.3 Current requirements for water-sediment testing

Test guidelines for water-sediment studies were presented in Chapter 2, in which a comparison is given for seven guidelines [US-EPA (1982), US-EPA (1998), BBA, FAO, SETAC, CTB and OECD (2000)]. This comparison focuses mainly on the applicability of test guidelines for the purpose of deriving reliable transformation rates for both the water and sediment separately, which is the scope of this report. Characterisation of test materials, either in the field before collection, or in the laboratory prior to, during or at termination of the test, was part of this comparison. Sections 6.1. and 6.2 had the specific aim to look at the characterisation required in different test guidelines from a viewpoint of growth and development of microbial populations, further shortly called microbial viability.
Some of the test guidelines prescribe the direct measurement of microbial biomass (see Table 6.1).

Table 6.1 Comparison of test guidelines with respect to microbial biomass measurements.

Test guideline	Stated about measurements	Method prescribed, recommended or mentioned
US-EPA (1982)	No remarks	-
US-EPA (1998)	Nothing with respect to characterisation of the test system, but the nature of the test guideline is such that microbial activity and its maintenance is important. Also necessary in case solvents are used; to check on adverse effects of the solvent.	Plate counts
BBA (1990)	Prescribed to measure microbial biomass of the sediment: 1. prior to initiation of the test 2. at termination of the test in separate test systems	E.g. Anderson & Domsch (respiration method)
SETAC (1995) = FAO (1993)	No remarks	-
CTB (1997)	No remarks	-
OECD (2000)	Prescribed to measure microbial biomass of the sediment : 1. after collection from the field 2. at the start of the test 3. at termination e.g. in separate test systems Also necessary in case solvents are used; to check on adverse effects of the solvent.	Respiration rate method (Anderson & Domsch) Fumigation-extraction method (ISO-14240-2) Plate counts

From Table 6.1 it becomes clear that the guidelines of US-EPA (1982), FAO, SETAC and CTB do not pay attention to measurements on microbial biomass. US-EPA (1998) is little explicit on measurements of biomass as it is only prescribed to show absence of adverse effects of solvents, while for the rest it might be interpreted only from the nature of the guideline. Only BBA and OECD require microbial biomass measurements at initiation and termination of the test, to check for loss / maintenance of microbial activity during the course of the test.

Table 6.2 provides a compilation of characteristics stated in the seven test guidelines to be measured.

Table 6.2 Parameters to assess microbial viability.

Phase	Characteristic	Test guideline					
		US-EPA 1982	US-EPA 1998	BBA	SETAC= FAO	CTB	OECD
Water	alkalinity		x				x
	bioavailable iron						x
	BOD						x
	Ca^{2+}						x
	conductivity		x				x
	DOC		x	x			
	hardness			x			x
	Mg^{2+}						x
	Mn^{2+}						x
	NO_3^-						x
	NO_3^-/PO_4^{3-}						x
	N_{tot}			x			
	oxygen		x	x	x		x
	pH		x	x	x		x
	PO_4^{3-}						x
	P_{tot}			x			
	redox			x			x
	SO_4^{2-}						x
	temperature		x	x	x		x
	TOC		x	x			x
	total susp. solids		x				x
sediment	carbonate						x
	CEC			x	x		
	clay					x	
	microbial biomass			x			x
	N_{tot}			x			x
	organic carbon			x	x	x	
	particle size distr.			x	x		x
	pH			x	x		x
	P_{tot}			x			x
	redox		x	x			x
	suspended matter			x			
	TOC						x
	water holding cap.						x
System	light intensity		x				
	light period		x				
	redox gradient		x				

From Table 6.2 it becomes clear that, with the exception of the OECD guideline, none of the test guidelines requires the relevant characteristics needed to predict the microbial viability in an adequate way. The test guideline of the BBA calls for N_{tot} and P_{tot} in both the water and the sediment prior to the test and at termination, but this only partly meets the set of parameters to be characterised.

Characterisation has additional perspectives besides prediction of microbial viability, e.g. to enable a check on redox gradient, to explicit its choice when distinct test systems are required, or to enable a check whether representative. The test guideline of US-EPA (1982) gives no arguments for characterisation. The guideline of US-EPA (1998) states that physical/chemical characteristics at the site of collection should be determined. This for reasons of replication of the environmental habitats from which they are derived, and to identify important environmental factors that could potentially affect the rate or extent of biodegradation of a chemical substance. It is recommended that, to the extent that they are applicable, certain physical/chemical characteristics be monitored over the course of the test.

The BBA test guideline gives hardly any arguments on why test systems have to be characterised. The only explicit reason given is the check that the test system is in equilibrium after acclimation, for which the parameters oxygen, pH, E_h are considered to be relevant. FAO and SETAC only state that the test system should be fully characterised without giving any reasons to do so.

The OECD test guideline requires organic carbon and pH of sediments to be measured to ensure that two distinct test systems are used. This scope of characterisation is valid for the CTB (organic carbon and clay contents of the sediments) and also for BBA (N_{tot}, P_{tot}, organic carbon, texture and microbial biomass of the sediment). In addition, other parameters may need to be measured and reported on a case by case basis (e.g. particles, alkalinity, hardness, conductivity, NO_3/PO_4 (ratio and individual values) for water and CEC, water holding capacity, carbonate, N_{tot}, P_{tot} for sediment). Analysis of sediment and water for NO_3, SO_4, bioavailable iron, and possible other electron acceptors may also be useful in assessing redox conditions. To check the equilibrium after acclimation the oxygen content and pH of the water, as well as E_h in both water and sediment are considered to be relevant by the OECD.

6.4 Discussion

It is evident that laboratory water-sediment tests, which are mostly conducted in a batch-type set up, should include system characterisation, and should recognise the changes in these characteristics over the test period. For example, co-precipitation, which is a common phenomenon in heterogeneous solutions, may lead to deficiencies of essential elements that are utilised by pesticide degrading micro-organisms, and therefore affect the interpretation of such experiments.

Characterisation of both water and sediment should include parameters that may provide, in some way, insight in both actual and potential microbial activity. It has been shown that the measurement of the oxygen concentration in water as well as the measurement of redox potential has neither a mechanistic nor a predictive value as far as growth and development of microbial populations are concerned. Furthermore, microbial dynamics are governed by the availability of (macro and micro)nutrients, or at least depend on minimum threshold concentrations. While

measurements on the oxygen concentration in water as well as the measurement of redox potential in both water and sediment are little relevant to predict microbial viability of the test system, these parameters are relevant to check the prerequisites of the test, namely an aerobic layer of water overlying a sediment layer with a gradient in oxygen status.

The OECD testing protocol is the most comprehensive with respect to system characterisation. It provides the only test guideline that fully insists on the necessary parameters to gain this insight and hence provides the tools to interpret and evaluate biotransformation rates and routes adequately.

Shortcomings in other guidelines than that of OECD may partially be covered by:

1. Determining the biochemical oxygen demand (BOD - 5 days) in water, to be carried out at field sampling, start of test and end of test;
2. Including the measurement of N-total and P-total in sediment at field sampling and at the end of the test. Preferably, measurements of N-species (NH_4, NO_x) and P-species ($P_{citr.acid}$, PO_4) are provided, as is proposed in the draft version of the OECD guideline.
3. Determining concentrations of micro/macro nutrients Ca, Mg, Mn in water at start of test and end of test.

Furthermore, it may be desirable to estimate microbial transformation in the sediment and water compartment separately. To do so, it is necessary to know specific (physical) system conditions such as system dimensions, water and sediment layer thickness and density. In this way, specific information is generated on the compound's environmental fate and its transformation products.

7 General discussion and conclusions

Decline rate coefficients given as endpoints in the water-sediment studies do not characterize the pesticide in an exact way. Decline in the water-sediment studies depends not only on pesticide properties, but also on system characteristics like water and sediment volume, surface area of their interface and sediment properties. Transformation rates for water and sediment characterize pesticide properties in a specific environment. Therefore, they are better input parameters than decline rates for models simulating pesticide behaviour in surface waters.

The present test guidelines do not provide data on transformation, since no distinction between the different dissipation processes can be made. However, some guidelines offer better possibilities to derive them from the experimental data than others, depending on the level of detail in which the experiments have been described. Test guidelines used in various countries differ considerably in their level of detail. The BBA and CTB guidelines have an intermediate level of detail, while the future OECD guideline will have a high level of detail. This high level of detail will allow judgement of the quality of the tests and of the extent to which the tests meet the objective of simulating field conditions. Further the OECD guideline provides the best chance that the dimensions of the layers in the test system can be derived from the test report.

In order to represent the situation in small surface waters, the sediment layer should show a gradient from aerobic conditions at the water-sediment interface to anaerobic conditions in deeper layers. Therefore, in our opinion, the sediment layer should be at least 2.5 cm thick. The draft OECD guideline of 2000 does not fulfill this requirement.

The transformation rate of a compound in the environment often depends on the size and nature of microbial populations. However, only the BBA and OECD guidelines require microbial biomass measurements. Various environmental factors may enhance or reduce biotransformation. Important factors are the biochemical oxygen demand, concentration of N-species and P-species as well as of the micro/macro nutrients Mg, Mn and Ca. The measurements have to be made at the start and the end of the test. Adequate description of the aquatic environment is needed in order to be able to evaluate biotransformation rates and routes. The OECD guideline is the most comprehensive guideline in this respect.

The OECD guideline is the only guideline that gives sufficient guidance on the required endpoints and the way to calculate these. It is surprising that the endpoints asked for are transformation rates in water and sediment, while the guideline is set up in such a way that decline and not transformation is measured. The guideline does not describe a procedure to obtain transformation rates.

Possibly, newly-developed guidelines can be made more suitable for deriving the separate transformation rates. Considerable time will be needed to develop the protocol for studying the separate transformation rates in water and sediment, and to introduce them in the registration procedures.

The TOXSWA model is suited for simulating water-sediment experiments, as it describes all relevant processes. However, water-sediment studies were set up for other reasons than for simulating the experiment. Some experimental specifications crucial for our simulations were not measured in a standardized way or they were not measured at all, e.g. thickness of the water and sediment layer, sediment bulk density. Various assumptions had to be made to estimate these essential quantities. This lack of detail in the reports has an adverse effect on the accuracy of estimating the transformation rates of the pesticide in water and sediment. Further, processes may proceed different from the way described by the model, e.g. the compound may crystallize and sink onto the sediment layer. This hampers the estimation of transformation rates as well.

Computations with a model for the water-sediment system requires that the thicknesses of the water layer and sediment layer are known. Further, the mass of solids (on dry mass basis) in the sediment layer should be known. Only if either the sediment layer thickness plus dry mass or the dry bulk density of the sediment is known, the volume fractions of the water phase and solid phase can be estimated. Of course the composition of the sediment is also needed for that. For the derivation of separate transformation rates it is essential that the thicknesses of the layers are requested in the new guidelines, like that of OECD (2000).

The bulk density of the sediment is needed to be able to calculate the sediment layer thickness. Often the bulk density is not specified in the submitted reports. Continuous pedotransfer functions exist to derive dry bulk densities for soils as a function of their composition. However, the packing of sediment poured into the test systems may differ considerably of that of established, structured soils. Therefore, an experiment on the density of the packing when pouring divergent materials into a flask is useful. When pouring sandy material in the system, the packing may be rather dense. However, pouring of clayey or organic material might result in a much looser packing. At the same time it should be studied whether there is segregation of material: larger and denser particles may be expected to settle first. Then the organic matter can be mainly present in the top of the sediment layer.

It is recommeded to study whether adsorption measurements for soils provide good estimates for the adsorption of pesticide on aquatic sediments.

A question is whether it can be said beforehand where the most rapid transformation takes place, in the water layer or in the sediment. In the latter layer, microbial density and activity may be expected to be higher. However, the adsorption of the pesticide may reduce its bioavailability and thus its biotransformation. For various pesticides, the aerobic conditions in the water layer may be favourable, whereas for others the anaerobic conditions in the sediment may favour transformation. Because of the

different factors and compounds it is unlikely that there is a general rule for the relative transformation in water layer and sediment layer.

Results of other research can be helpful in estimating the separate transformation rates of a pesticide in the water and sediment layers. The rate of hydrolysis in water is usually measured. Sometimes even the persistence in 'natural' water is studied. As about half of the sediment volume consists of water, the rate of hydrolysis could be about half the rate in the water layer. For some pesticides, the rate of transformation in anaerobic soils has been measured, which may give an indication of the rate of transformation in anaerobic sediment.

Our experience with the three compounds is that estimating transformation half-lives for water and sediment from water-sediment studies is not a straightforward procedure yet. In all three case experimental pecularities or even errors required substantial expertise for making good estimates of the transformation half-lives.

Considerable differences may exist between the dissipation half-lives reported for the total water-sediment system and the transformation rates for water and sediment estimated by the TOXSWA simulations. Our results show that the interpretation currently used by the CTB has to be revised in the near future. At present, the new procedure presented in this report may be used by experts in critical cases. The exposure concentrations calculated for the Dutch standard ditches using the improved input data may be expected to give a much better description of the concentrations in the field.

Simulation with the TOXSWA model may provide more quantitative information on the processes ocurring in larger model ecosytems. The model can also be used to translate the results for model ecosystems to natural aquatic systems.

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Appendix 1 Comparison of test guidelines in water-sediment studies

Several test guidelines for water/sediment studies were compared with respect to a series of characteristics. These characteristics are listed in the Table. The following test guidelines were compared:

- US-EPA (1982). Pesticide assessment guidelines. Subdivision N, Chemistry, Environmental fate: 162-4 Aerobic aquatic metabolism studies. October 1982. Environmental Protection Agency, Washington DC.
- BBA (1990). Richtlinien für die Prüfung von Pflanzenschutzmitteln im Zulassungsverfahren, Teil IV: 5-1, Abbaubarkeit und Verbleib von Pflanzenschutzmitteln im Wasser/Sediment System. Dezember 1990. Biologische Bundesanstalt für Land- und Forstwirtschaft, Braunschweig.
- FAO (1993). Annex to revised guidelines on environmental criteria for registration of pesticides. Revision 3, 28-8-1993. Food and Agricultural Organisation of the United Nations, Rome.
- SETAC (1995). Procedures for assessing the environmental fate and ecotoxicity of pesticides (M.R. Lynch Ed.). March 1995. Society for Ecotoxicology and Chemistry, Brussels.
- CTB (1997). Toelichting op het aanvraagformulier. College voor de Toelating van Bestrijdingsmiddelen, Wageningen.
- US-EPA (1998). Fate, transport and transformation test guidelines. OPPTS 835.3180 Sediment/water microcosm biodegradation test. January 1998. Environmental Protection Agency, Washington DC.
- OECD (2000). Draft proposal for a new guideline: Aerobic and anaerobic transformation in aquatic sediment systems. Version of August 2000. Organisation for Economic Co-operation and Development, Paris.

Two test guidelines from the US-EPA are available. Both are considered to be relevant. The guideline of 1982 is used for a lot of studies present in Dutch dossiers for pesticide registration. The guideline of 1998 is expected to be used for studies that will be submitted for registration in the Netherlands in the future.

Besides the above-mentioned guidelines others exist, viz. those of Canada and of the UK. These guidelines have not been included in this comparison, because only a few studies in Dutch dossiers are performed according to these guidelines.

The OECD (2000) guideline is still a draft, but it is included in this report because it will be an international standard in the near future, and it has reached a stage that most elements of it will not change drastically anymore.

Empty cells in the Table indicate that these points are not specified within the test guideline.

	US-EPA 1982	*US-EPA 1998*	*SETAC=FAO*	*BBA*	*OECD*	*Netherlands*
Scope of the test guideline						
	Disappearance of parent compound Rates and formation of metabolites	Distribution of test substance between sediment, overlying water, interstitial water and off-gasses		Disappearance of active ingredient Partition behaviour of active ingredient Aerobe-anaerobe transition	Aerobe water column with a gradient to anaerobe conditions deeper in the sediment layer Rate of mineralisation Rate and route of transformation of test substance in water and sediment Distribution of transformation products between water and sediment	Transformation pathway Rates of transformations
Applicability of the test						
					Not for highly volatile test substances	
When required						
	Products intended for aquatic use Aquatic impact after direct discharges of treated water into outdoor aquatic sites			Always, except: when exposure of water bodies can be excluded when active ingredient is readily biodegradable (OECD 301 A-E or EEC guidelines)	always when applied directly to water when it is likely that the test substance will reach the aquatic environment.	Always, except: when contamination of water bodies can be excluded when active ingredient is readily biodegradable (OECD 301 A-E

	US-EPA 1982	*US-EPA 1998*	*SETAC=FAO*	*BBA*	*OECD*	*Netherlands*
Test substance						
Test substance: which?	Each active ingredient in the product	Type of test compound is case dependent	Active ingredient	Principally with the a.i., but: Sometimes with the main metabolite Sometimes with the formulation formulation allowed when applicant shows that it does not influence the results formulation required when it influences the fate of the a.i.	test substances, formulations not preferred	Active ingredients or in case of very fast transformation the primary transformation product Metabolites formed in water/sediment studies in amounts ≥ 10% applied test substance Formulation when it is of influence on the test results
Test-substance: label and purity	Radioisotopic techniques: analytical grade: necessary when material balance is required Non-radioisotopic techniques: at least technical grade Composition test substance, including contaminants and impurities, required	^{14}C-labelled test substances are recommended	Radio-labelled	In general radiolabelled (when the transformation pathway is known, labelling is not obligatory.	Labelled test substance required for studying the pathway and to establish mass balance For other purposes unlabelled test substance is adequate ^{14}C recommended, but other isotopes are allowed label should be positioned in most stable part of the molecule Purity ≥ 95%	

	US-EPA 1982	*US-EPA 1998*	*SETAC=FAO*	*BBA*	*OECD*	*Netherlands*
Type, sampling and storage						
Water + sediment	Representative of that found at an intended use site	Intact benthic sediment and overlying water Collected simultaneously	Natural systems (sediment with associated water) Representative of those likely to be exposed	Natural (sediment with associated water)	sediment with overlying water and sampled at the same time	nothing explicit
Previous exposure of system		To the extent possible, no contamination with test substance, close analogues, pesticides, PCBs, other hazardous chemicals and heavy metals	Not been treated previously with test substance or closely related substance	Of uncontaminated origin	history of contamination (agricultural, industrial and domestic) must be considered substances structurally related to the test substance should not be used in the previous 4 years	Not adapted to the test substance
Number of systems			2 or more (may be necessary)	At least 2	2	At least 2
Required distinction between systems				Sediment: texture, microbial biomass, OC, N_{tot} and P_{tot} OC < 10%	Sediment: OC and texture high OC (2.5-7.5%) and fine texture * low OC (0.5-2.5%) and coar-se texture ** Δ OC $\geq$ 2% Δ fraction <50 µm $\geq$ 20% * fraction <50 µm > 50% ** fraction <50 µm < 50% in particular cases (pKa) pH is relevant	Sediment: OC

	US-EPA 1982	*US-EPA 1998*	*SETAC=FAO*	*BBA*	*OECD*	*Netherlands*
Sampling of sediment		core to the depth of biological activity	not described	not described	ISO/DIS 5667-12 (1994) total upper layer of 5 to 10 cm thickness	from the 2 to 3 cm thick upper ditch sediment layer
Storage		Water: preferably without storage; otherwise at 4 °C Sediment: Structural integrity, including redox gradient and benthic community of the cores should be preserved	Preferably without storage; otherwise under conditions which maintain microbial activity	Sediments: preferably without storage; otherwise at 4 °C (duration not specified)	Freshly sampled water and sediment strongly recommended, else at 4 ± 2 °C for a maximum of 4 weeks free access of air (open containers) sediment and water together and waterlogged (6-10 cm water) in the dark no freezing of drying out allowed	
Characterisation						
In situ		At the site: Light intensity Light period Water: Total suspended solids Oxygen temperature TOC DOC Alkalinity Conductivity pH System: Redox gradient	Water: temperature	Water: Temperature Oxygen (just beneath the water surface and 5 cm above sediment pH redoxpotential	Water: temperature pH Oxygen Sediment: Depth of layer E_h (by means of sensory perception)	

	US-EPA 1982	*US-EPA 1998*	*SETAC=FAO*	*BBA*	*OECD*	*Netherlands*
In the lab		Recommended to ensure functional capability to maintain environmental conditions see at "in situ"; (nothing prescribed)	<u>Water</u>: To be fully characterised: oxygen temperature pH <u>Sediment</u>: CEC particle size distribution OC pH	<u>Water</u>: oxygen redoxpotential pH N_{tot} P_{tot} TOC or DOC Hardness <u>Sediment</u>: Texture OC pH N_{tot} P_{tot} Microbial biomass Dry weight of suspended matter Redox potential CEC	<u>Water</u>: pH E_h TOC oxygen particulate ∇ alkalinity ∇ hardness ∇ conductivity ∇ NO_3^- ∇ PO_4^{3-} ∇ NO_3/PO_4 ∇ <u>sediment</u>: pH E_h particle size distribution TOC CEC ∇ water holding capacity ∇ carbonate ∇ N_{tot} ∇ P_{tot} ∇ <u>sediment + water</u>: NO_3^- ∇ SO_4^{2-} ∇ biological available iron ∇ ∇ on a case by case basis	<u>Sediment</u>: OC Lutum

	US-EPA 1982	*US-EPA 1998*	*SETAC=FAO*	*BBA*	*OECD*	*Netherlands*
Preparation of test systems						
Sieving		none (undisturbed columns)		Water: 0,2 mm Sediment: 2 mm	sediment: 2 mm (wet)	
Container		Either made of inert fluorocarbon plastics (e.g. teflon) and/or glass		Cylindrical	cylindrical glass, unless the test substance does adhere to glass, than an inert material	
Thickness of layers or ratio sediment to water			1:4 to 1:10 (w/w), based on oven dry weight of the sediment	Sediment: 2-2.5 cm Water: circa 6 cm	sediment layer 1- 2.5 cm water : sediment between 3 and 4 : 1	10% sediment (w/w), based on dry weight of the sediment. Sediment: at least 2 cm
Acclimation (pre-incubation)						
Temperature		Test temperature ± 2 °C	20 ± 2 °C	20 ± 2 °C	constant 20 ± 2 °C appropriate; 18 – 30 °C is allowed additional test at 10 °C is optional	
Light regime					in the dark	
Aeration			Yes (stirring the water, gently shaking the flask or bubbling air through the water)	Yes	Yes passing air (not CO_2 free to avoid pH changes) with gentle stirring from above gentle bubbling avoid disturbance of sediment as much as possible	
Movement		Gently	Gently avoid disturbance of sediment	Gently	avoid disturbance of sediment as much as possible	

	US-EPA 1982	*US-EPA 1998*	*SETAC=FAO*	*BBA*	*OECD*	*Netherlands*
Measurements				Oxygen, pH, E_h and phase separation to confirm equilibrium	(see duration): pH, oxygen in water, E_h sediment + water, macroscopic separation of phases	
Duration		In case water has been stored at 4 °C, it should be brought to the test temperature ± 2 °C		until measurable equilibrium based on pH, E_h, oxygen and phase separation	to reach reasonable stability of the system; normally 1-2, maximally 4 weeks	6 to 8 weeks to restore equilibrium and the gradient aerobe to anaerobe
Addition of test substance						
Number of concentrations			One	One	One	One
Vehicle		If water soluble, water, else a water-miscible non-toxic solvent in the minimum amount needed NB: solvent control to be included in the study then (to assess effect on microbial activity)	If water soluble, water, else < 0.1% and water soluble	If water soluble, none, else < 0.1% and water soluble	if water soluble none, else <1% (v/v); vehicle may not have ad-verse effects to the micro-bial activity; use of formulated products is not recommended and is only allowed for poorly water soluble test sub-stances when phase dis-tribution of test substan-ce and metabolites is not affected	If water soluble, water, else an organic solute that does not influence the results too much
Addition of test substance	To the water	Should reflect the release pattern expected in the field	To the water	To the water	To the water	To the water

	US-EPA 1982	*US-EPA 1998*	*SETAC=FAO*	*BBA*	*OECD*	*Netherlands*
Rate of test substance	Sufficient to measure disappearance of parent compound in water and to allow identification of major metabolites in water and sediment	Approximately the expected ambient environmental concentration, taking into account: water solubility analytical possibilities toxic effects on microflora (e.g. from an activated sludge respiration test	aquatic use: maximum recommended dose rate other use: high enough to measure the rate of degradation and to identify degradation products	Label rates with overspray into a waterlayer of 30 cm depth	PPP's applied directly to waterbodies: maximum label dosage else: based on predictions from environmental emissions NB: in case of analytical problems, higher concentrations are justified, as long as it shown that these higher concentrations do not affect the microbial activity	The concentration to be expected in field ditches taking into account: The toxicity to micororganisms and Analytical possibilities
Incubation						
Temperature	constant 18-30 °C	constant recommended: field temperature ± 2 °C, but other may be more appropriate	20 ± 2 °C	20 ± 2 °C	constant 20 ± 2 °C appropriate; 18 – 30 °C is allowed additional test at 10 °C is optional	20 ± 2 °C
Light regime		Light is allowed: light intensity may be at a level that is equivalent to the average light intensity on the sediment surface in the natural system. Photoperiod arbitrary or adjusted to ambient field conditions	Dark	Dark	Dark	Light/dark = 8/16 hr

	US-EPA 1982	*US-EPA 1998*	*SETAC=FAO*	*BBA*	*OECD*	*Netherlands*
Aeration		Allowed (take care of losses due to eg volatiles) No resuspension of the sediment allowed		Oxygen concentration water ≥ 20% saturation Yes, but without disturbance of phase separation	Yes passing air (not CO_2 free to avoid pH changes) with gentle stirring from above gentle bubbling avoid disturbance of sediment as much as possible	Water phase should be aerobe throughout the test
Replicas		≥ 3 and control systems ≥ 2	None	≥ 2	≥ 2	2
Sampling times		Including zerotime Depending on expected disappearance time A few samples within day 1, less frequent later on	6, or at fast transformation less	0, 0.25, 1, 2, 7, 14, 30, 60 and ≥ 100 d	at least 6, including zerotime for hydrophobic sub-stances more frequent sampling in the first days is necessary to obtain the rate of phase distribution	Enough to allow for a clear insight in transformation in time and formation of metabolites
Duration of test	Patterns of decline of test substance and formation and decline of metabolites in water and sediment For maximum of 30 days	Limited to 60 d, unless ….., but than the system has to be monitored for its viability and stability	Until degradation pathway and distribution of parent and metabolites between water and sediment is clear, with a maximum of 100 d	not described	until transformation pathway and water/sediment distribution are established, or when 90% of the test substance is dissipated by transformation and/or volatilization; maximally 100 d	Until 90% of the applied test substance is transformed into CO_2 or other environmentally insignificant metabolites, with a maximum of 3 months

	US-EPA 1982	US-EPA 1998	SETAC=FAO	BBA	OECD	Netherlands
Measurements and analytics						
Extraction and analysis		Separately for water and sediment samples Including washing of test system	Whole flasks Water and sediment separately	Water and sediment separately Appropriate techniques Sediment bound residues to be quantified	whole systems Water and sediment separately Appropriate analytical techniques care should be given to adsorption/ absorption to incubation vessel and tubing	
Parameters per time point		see at characterisation in situ	pH (water) Oxygen (water)	<u>water</u>: Oxygen (water) <u>sediment</u>: microbial biomass <u>water + sediment</u>: E_h pH	<u>water</u>: oxygen BOD # $ Ca, Mg, Mn # $ <u>sediment</u>: pH $N_{tot,}$ P_{tot} $ # microbial biomass * # <u>water + sediment</u>: pH TOC # E_h * respiration method, fumigation method or plate counts # at zerotime and at termination $ in case of characterisation of microbial viability	
Identification of metabolites	Identification residues ≥0.01 mg/l	Each metabolite ≥ 10% applied test substance	Obligatory for metabolites formed in amounts ≥ 10% test substance Attempts for those approaching	yes according to the state of technique	each ≥ 10% AR each <10% AR which shows a continuously increase	Obligatory for those not found in soil studies

	US-EPA 1982	*US-EPA 1998*	*SETAC=FAO*	*BBA*	*OECD*	*Netherlands*
Parameters at termination		see at characterisation in situ		N_{tot}, P_{tot}, oxygen, E_h, microbial biomass (in separarte bottles)	water: pH, TOC, oxygen sediment: pH, TOC, E_h, microbial biomass (in separate bottles)	
Reporting						
mass balance	yes	yes Mass balances (including washings): should account for > 80% of applied test substance	Material Balance per time point: should be approximately between 90 and 110% AR.	Graphs on material balance should be ≥ 10% AR.	mass balance per sampling time as % AR 90-110% AR in case of labelled test substance, otherwise 70-110%	yes
rate constants	half life residue decline curves	Rate constant for loss of test substance from the water column (assuming 1st order kinetics); Mathematical equations to be stated		Estimation of the rate order DT50/DT90 water DT50/DT90 total system	DT50 test substance for both the water and the sediment phase rate constants for formation and transformation of major transformation products	rates for dissipation in water, sediment and total system
Transformation pathway	yes (interpretation of scope of the test)	yes (interpretation of scope of the test)	yes (interpretation of scope of the test)	yes	yes	yes

Remark: The SETAC guideline appears to be identical to the one of FAO.

Endpoints of EU/ECCO
DT50 and DT90 in water column as well as in the whole system
Distribution between water and sediment of active substance as well as metabolites
PEC surface water as well as sediment

Remark: EU data requirements (95/36/EEC) refer to the SETAC guideline.

Appendix 2 Mass concentrations of indoxacarb in River system in water and sediment ($mg.L^{-1}$), based on measured percentages of applied radioactivity (Label 1 and 2)

Table 1 Measured concentration in water layer as a function of time (Label 1)

Sampling time (d)	Concentration (mg/L)
0.0	0.645
1.0	0.342
2.0	0.267
3.0	0.275
7.0	0.183
14.0	0.132
28.0	0.089
42.0	0.032
56.0	0.028
70.0	0.025
85.0	0.055
101.0	0.01

Table 2 Measured total concentration in sediment as a function of time (Label 1)

Sampling time (d)	Concentration (mg/L)
0.0	2.80
1.0	2.37
2.0	3.09
3.0	3.26
7.0	2.63
14.0	1.60
28.0	1.24
42.0	0.73
56.0	0.60
70.0	0.78
85.0	0.78
101.0	0.83

Table 3 Measured concentration in water layer as a function of time (Label 2)

Sampling time (d)	Concentration (mg/L)
0.0	0.792
1.0	0.289
2.0	0.205
3.0	0.248
4.0	0.105
7.0	0.163
14.0	0.095
28.0	0.060
42.0	0.048
56.0	0.049
70.0	0.023
85.0	0.048
101.0	0.01

Table 4 Measured total concentration in sediment as a function of time (Label 2)

Sampling time (d)	Concentration (mg/L)
0.0	1.89
1.0	2.32
2.0	2.38
3.0	2.67
4.0	2.30
7.0	1.85
14.0	1.92
28.0	1.45
42.0	0.80
56.0	0.77
70.0	0.59
85.0	0.64
101.0	0.51

Appendix 3 Mass concentrations of indoxacarb in Pond system in water and sediment (mg.L^{-1}), based on measured percentages of applied radioactivity (Label 1 and 2)

Table 1 Measured concentration in water layer as a function of time (Label 1)

Sampling time (d)	Concentration (mg/L)
0.0	0.658
1.0	0.317
2.0	0.088
3.0	0.369
4.0	0.250
7.0	0.235
14.0	0.151
28.0	0.162
42.0	0.141
56.0	0.108
70.0	0.094
85.0	0.01
101.0	0.027

Table 2 Measured total concentration in sediment as a function of time (Label 1)

Sampling time (d)	Concentration (mg/L)
0.0	2.86
1.0	3.30
2.0	4.09
3.0	2.81
4.0	2.88
7.0	2.51
14.0	2.53
28.0	1.63
42.0	1.53
56.0	1.09
70.0	1.03
85.0	0.77
101.0	0.93

Table 3 Measured concentration in water layer as a function of time (Label 2)

Sampling time (d)	Concentration (mg/L)
0.0	0.728
1.0	0.300
2.0	0.095
3.0	0.388
4.0	0.269
7.0	0.225
14.0	0.125
28.0	0.146
42.0	0.109
56.0	0.055
70.0	0.114
85.0	0.011
101.0	0.011

Table 4 Measured total concentration in sediment as a function of time (Label 2)

Sampling time (d)	Concentration (mg/L)
0.0	2.80
1.0	2.34
2.0	2.19
3.0	2.59
4.0	2.40
7.0	2.43
14.0	1.92
28.0	1.76
42.0	1.28
56.0	1.36
70.0	0.83
85.0	0.81
101.0	0.87

Appendix 4 Mass concentrations of dicamba in River system in water and sediment (mg.L^{-1}), based on measured percentages of applied radioactivity (sediment concentrations, corrected by us)

Table 1 Measured concentration in water layer as a function of time

Sampling time (d)	Concentration (mg/L)
0.0	1.031
7.0	0.985
14.0	0.987
30.0	0.719
60.0	0.258
90.0	0.119

Table 2 Measured total concentration in sediment as a function of time

Sampling time (d)	Concentration (mg/L)
0.0	0.0
7.0	0.888
14.0	0.632
30.0	0.312
60.0	0.168
90.0	0.088

Appendix 5 Mass concentrations of dicamba in Pond system in water and sediment (mg.L^{-1}), based on measured percentages of applied radioactivity (sediment concentrations, corrected by us)

Table 1 Measured concentration in water layer as a function of time

Sampling time (d)	Concentration (mg/L)
0.0	0.965
7.0	0.888
14.0	0.828
30.0	0.590
60.0	0.338
90.0	0.282

Table 2 Measured total concentration in sediment as a function of time

Sampling time (d)	Concentration (mg/L)
0.0	0.0
7.0	0.908
14.0	0.420
30.0	0.323
60.0	0.293
90.0	0.233

Appendix 6 Mass concentrations of chlorpropham in Ditch 1 system in water and sediment ($mg.L^{-1}$), based on measured percentages of applied radioactivity

Table 1 Measured concentration in water layer as a function of time

Sampling time (d)	Concentration (mg/L)
0.0	2.15
14.0	1.04
28.0	0.42
56.0	0.0
84.0	0.0

Table 2 Measured total concentration in sediment as a function of time

Sampling time (d)	Concentration (mg/L)
0.0	3.71
14.0	6.39
28.0	3.87
56.0	0.55
84.0	0.32

Appendix 7 Mass concentrations of chlorpropham in Ditch 2 system in water and sediment ($mg.L^{-1}$), based on measured percentages of applied radioactivity

Table 1 Measured concentration in water layer as a function of time

Sampling time (d)	Concentration (mg/L)
0.0	2.07
14.0	0.41
28.0	0.26
56.0	0.0
84.0	0.0

Table 2 Measured total concentration in sediment as a function of time

Sampling time (d)	Concentration (mg/L)
0.0	3.10
14.0	6.37
28.0	5.98
56.0	0.69
84.0	3.02