National Institute
for Public Health
and the Environment

**Report 601712002/2008**

A.M.A. van der Linden et al.

# Evaluation of the 2006 proposal for risk assessment of persistence of plant protection products in soil

ctgb ALTERRA

rivm ALTERRA ctgb

RIVM Report 601712002/2008

# Evaluation of the 2006 proposal for risk assessment of persistence of plant protection products in soil

AMA van der Linden, RIVM
JJTI Boesten, Alterra
TCM Brock, Alterra
GMA van Eekelen, CTB
MMS ter Horst, Alterra
FMW de Jong, RIVM
MHMM Montforts, RIVM
JW Pol, CTB

Contact:
AMA van der Linden
RIVM
Ton.van.der.Linden@rivm.nl

This investigation has been performed by order and for the account of the Netherlands Ministry of Housing, Spatial Planning and the Environment within the framework of project M/601712 'Consultancy on pesticides and Biocides'. The Alterra contribution has been performed by order and for the account of the Netherlands Ministry of Agriculture, Nature and Food Quality within the framework of research programme BO-06-010 'Risk assessment methodology for pesticide registration'. The contribution of Ctgb has been performed for the account of both ministries.

ISBN: 978-90-6960-197-7

# Abstract

**Evaluation of the 2006 proposal for risk assessment of persistence of plant protection products in soil**

This report describes the evaluation of the 2006 proposal for the risk assessment of persistence of plant protection products in soil. The proposal considered three protection goals and proposed tiered assessment and decision schemes for each protection goal. The three schemes appeared to be consistent, both internally and with each other. It was found that both pore water concentrations and total content have to be considered in the soil risk assessment.

The evaluation has been performed for five substances with all available information from both registration dossiers and open literature. Nevertheless, insufficient information was available to evaluate all aspects of the proposal. In practice this means that pesticide industry has to provide additional information for many dossiers. Furthermore, it was found that existing information often needs to be re-interpreted and a need for standardisation of evaluation of terrestrial (semi-)field experiments was observed. The proposal would require specific expertise and investments of evaluating authorities as well as stakeholders.

To better understand fate and effects of persistent substances, it is recommended to investigate the behaviour of substances in the field over longer periods, to perform exposure concentration measurements while performing ecotoxicological tests, to develop protocols for testing effects on fungi, and to gain the necessary experience on the conduct and interpretation of (semi-)field studies with respect to the relation between exposure and effects of plant protection products.

Key words:
decision tree, ecotoxicological effects, persistence in soil, pesticides, protection goals

# Rapport in het kort

**Evaluatie van het voorstel uit 2006 voor de risicobeoordeling van persistentie van gewasbeschermingsmiddelen in de bodem**

Dit rapport evalueert het voorstel uit 2006 voor de beoordeling van milieurisico's van gewasbeschermingsmiddelen die lang in de bodem aanwezig blijven. Dit voorstel beschreef drie beschermdoelen en stelde getrapte beoordelingssystemen (beslisbomen) voor. De uitkomsten van deze beoordelingssystemen bleken consistent. De optie uit het voorstel om de risico's niet alleen te beoordelen op basis van het totaalgehalte in de bodem maar ook op de concentraties in het bodemvocht moet worden verplicht.

De evaluatie is uitgevoerd met alle beschikbare gegevens uit toelatingsdossiers en openbare literatuur van vijf stoffen. De gegevens bleken voor verschillende onderdelen van de beslisbomen niet toereikend, waardoor fabrikanten aanvullende gegevens zullen moeten leveren voor veel toelatingsdossiers. Ook moeten beschikbare studies meestal opnieuw worden geïnterpreteerd om de benodigde gegevens voor de nieuwe beoordeling af te leiden. Een goede beoordeling vereist daarom specifieke expertise van zowel aanvragers als beoordelende instanties.

Om gedrag en effecten van persistente stoffen beter te kunnen begrijpen, wordt eveneens aanbevolen het gedrag in het veld over langere duur te onderzoeken, de concentraties in testsystemen te meten, testen met bodemschimmels te ontwikkelen, en ervaring op te doen met (semi-)veldstudies naar de relatie tussen blootstelling en effecten.

Trefwoorden:
beschermdoelen, beslisboom, bestrijdingsmiddelen, ecotoxicologische effecten, persistentie in de bodemporiewater

# Contents

# 1 Introduction

## 1.1 Remit

The Ministries of VROM and LNV decided in 2006 that the proposal for the risk assessment for persistence in soil as described by Van der Linden et al. (2006) should be evaluated by applying it to a number of relevant plant protection products (PPPs).

The ministries decided also that the exposure part of the proposal should be made fully operational; implying that the necessary scenarios and software for the different exposure tiers had to be developed and also that a calculation procedure and software had to be developed for exposure assessment in ecotoxicological experiments.

The ministries decided that the evaluation should be carried out via a phased procedure. Initially the proposal should be evaluated using the dossier data of three PPPs. After that, the need for evaluating with more PPPs should be discussed with the ministries and agrochemical industry.

The following selection criteria for the first three PPPs were set:
1. different mode of actions;
2. dossiers with more than average information on soil ecotoxicology;
3. part of the PPPs should have a half-life ($DT_{50}$) longer than 180 days and part should have a half-life between 30 and 180 days;
4. PPPs should include a soil disinfectant;
5. PPPs should not be all from the same company.

Based on the above criteria, the first three plant protection products considered were paraquat (Syngenta, herbicide, $DT_{50}$ in the order of 10 years), quinoxyfen (Dow Chemical Company, fungicide, $DT_{50}$ in the order of 1 year), and chlorpyrifos (Bayer Crop Sciences, insecticide, $DT_{50}$ of a few months). So selection criterion four was ignored. Interim results for these PPPs were reported in January 2007 and then the ministries and agrochemical industry agreed that it would be meaningful to perform additionally an evaluation of the pesticide carbendazim (not longer registered as a PPP, fungicide, half-life of about 6 months). Carbendazim was selected because much soil ecotoxicological information for carbendazim is available in the literature.

The intention of the evaluation procedure was to assess all possible aspects of the proposed exposure and effect flow charts. As a consequence, the risk assessment procedure was applied going through all tiers of these flow charts as much as possible (so also going to higher tiers if it was already concluded in a lower tier that there was no risk).

Additionally, the ministries of VROM and LNV requested to estimate the extra costs that notifiers would need to make as a result of applying the procedure proposed by Van der Linden et al. (2006). This estimation is reported elsewhere.
In view of the limited experience with field studies on effects on the terrestrial ecosystem, the ministries requested that the risk assessment procedures of such studies should be documented as carefully as

possible (if possible including recommendations for improvements for these risk assessment procedures).

## 1.2 Approach

As stated in section 1.1 the purpose of this study is to evaluate the functioning of the decision trees for the assessment of the persistency of plant protection products in soil. The evaluation was carried out by going through the decision schemes for a total of five substances, four active substances and one metabolite. For each of the substances all proposed schemes were considered, whether or not the scheme was triggered. In more detail, the work included:

1. evaluation of dossier and open literature information with respect to soil fate and soil ecotoxicological aspects of each substance;
2. (re-)interpretation of original experiments, if necessary, taking into account recent guidelines;
3. evaluation of the schemes using the soil fate and soil ecotoxicological values obtained under 1) and 2).

The evaluation under three included whether the fundamental principles of tiered assessments are obeyed.

## 1.3 Overview decision trees

Report 601506008 (Van der Linden et al., 2006) gives three decision schemes for the evaluation of persistence of plant protection products in soil. The schemes and their coherence are reproduced here for easy reference. Abbreviations are explained in the Glossary (Appendix 1).

| **protection goal** | **time window** | **trigger** | | |
|---|---|---|---|---|
| | | **$DT_{50}$ > 30 days** | **$DT_{50}$ > 90 days** | **$DT_{50}$ > 180 days** |
| Functional Redundancy Principle (FRP) | cropping season | testing according to FRP (Figure 1.2) | testing according to FRP (Figure 1.2) | testing according to FRP (Figure 1.2) |
| | | | **AND** | **AND** |
| Community Recovery Principle (CRP) | two years post last application | | testing according to CRP (Figure 1.3) | testing according to CRP (Figure 1.3) |
| | | | | **AND** |
| Ecological Threshold Principle (ETP) | seven years post last application | | | testing according to ETP (Figure 1.4) |

Figure 1.1 Relation between the trigger value for 50% dissipation time ($DT_{50}$) of the plant protection product and the testing procedures in line with the three protection goals

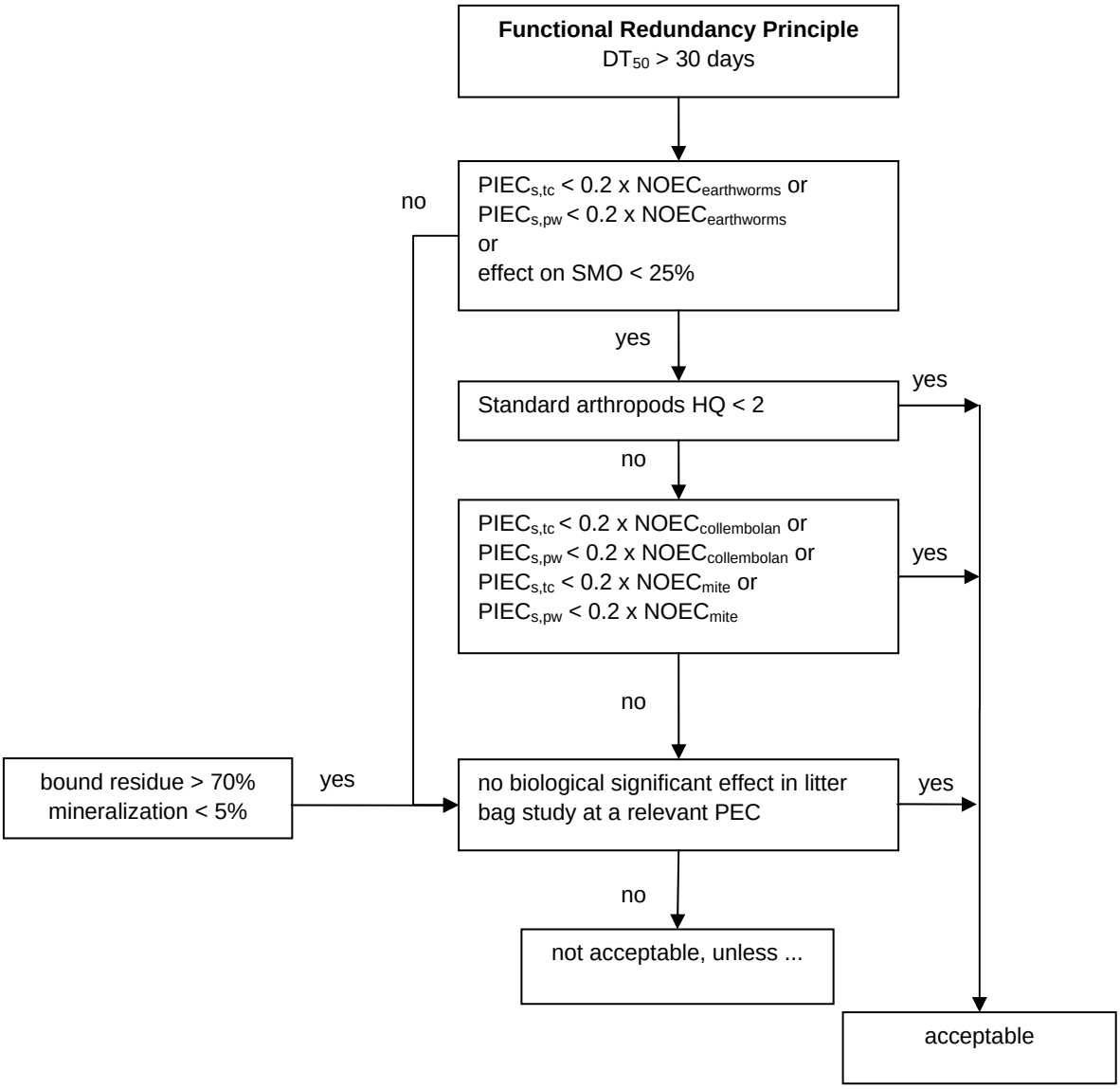



Figure 1.2 Decision tree for in-crop effect assessment in line with the Functional Redundancy Principle (largely based on EU Guidance Document Terrestrial Ecotoxicology)

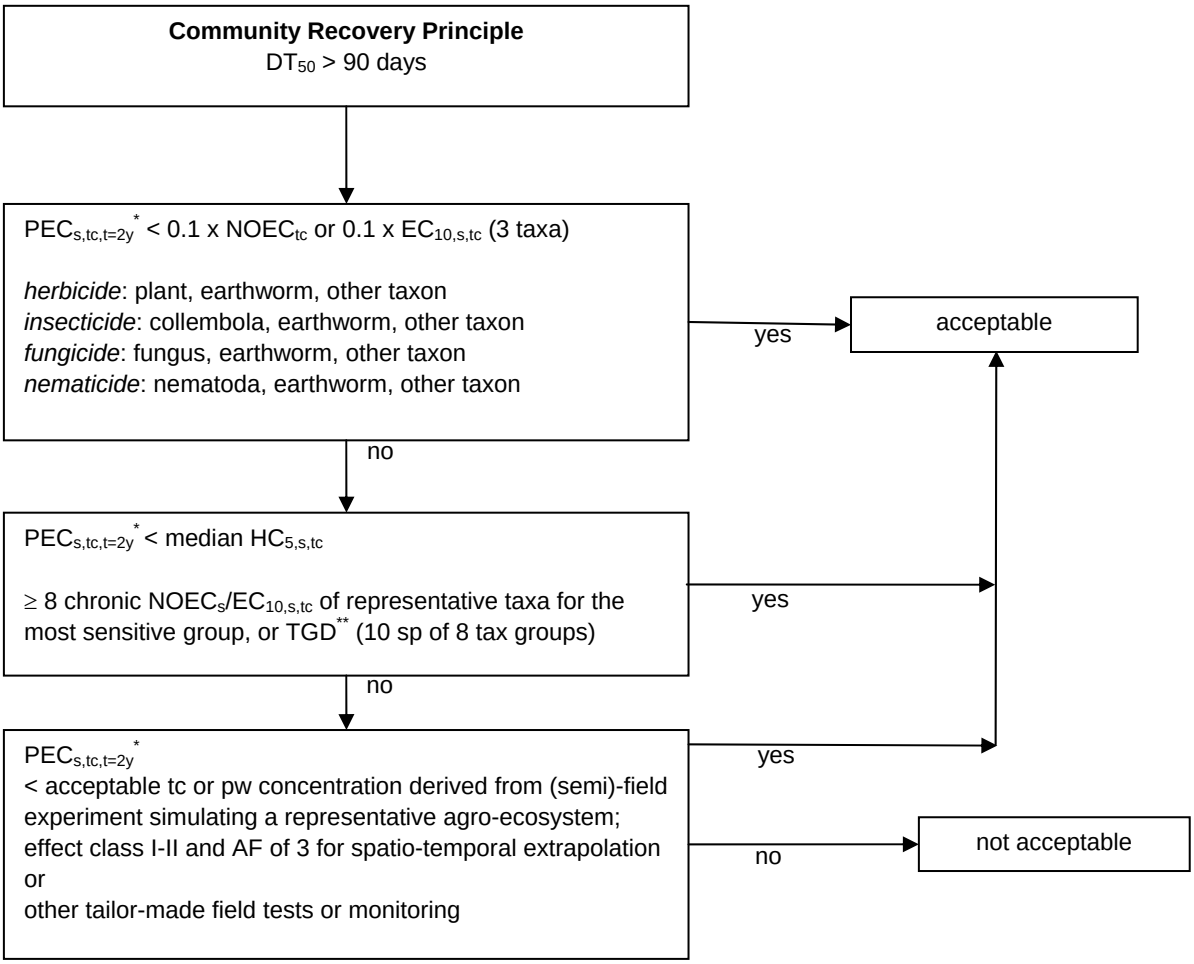



Figure 1.3 Decision tree for in-crop (in the year post the year of last application) effect assessment in line with the Community Recovery Principle

* The use of PEC is in conformity with the present approach; when more data are available, such as the time to effect, a $PEC_{TWA}$ can be used as well. Instead of total content, pore water concentration can be used (see Van der Linden et al., 2006).

** Species sensitivity distribution (SSD method, see Aldenberg and Jaworska, 2000). If a clear sensitive group exists, meaning at least an order of magnitude difference in sensitivity compared to other groups, data for 8 taxa from the most sensitive group can be taken, in conformity with the procedure for the aquatic environment (Campbell et al., 1999). Alternatively, in case of general biocidal activity, the TGD approach can be taken (TGD, 2003). A minimum of 10 NOECs for at least 8 taxonomic groups should be taken. In the TGD an assessment factor of 5 – 1 is applied, to be fully justified on a case-by-case basis (for soil discussion is going on about different trophic levels, the use of functional endpoints (micro-organisms) etcetera).

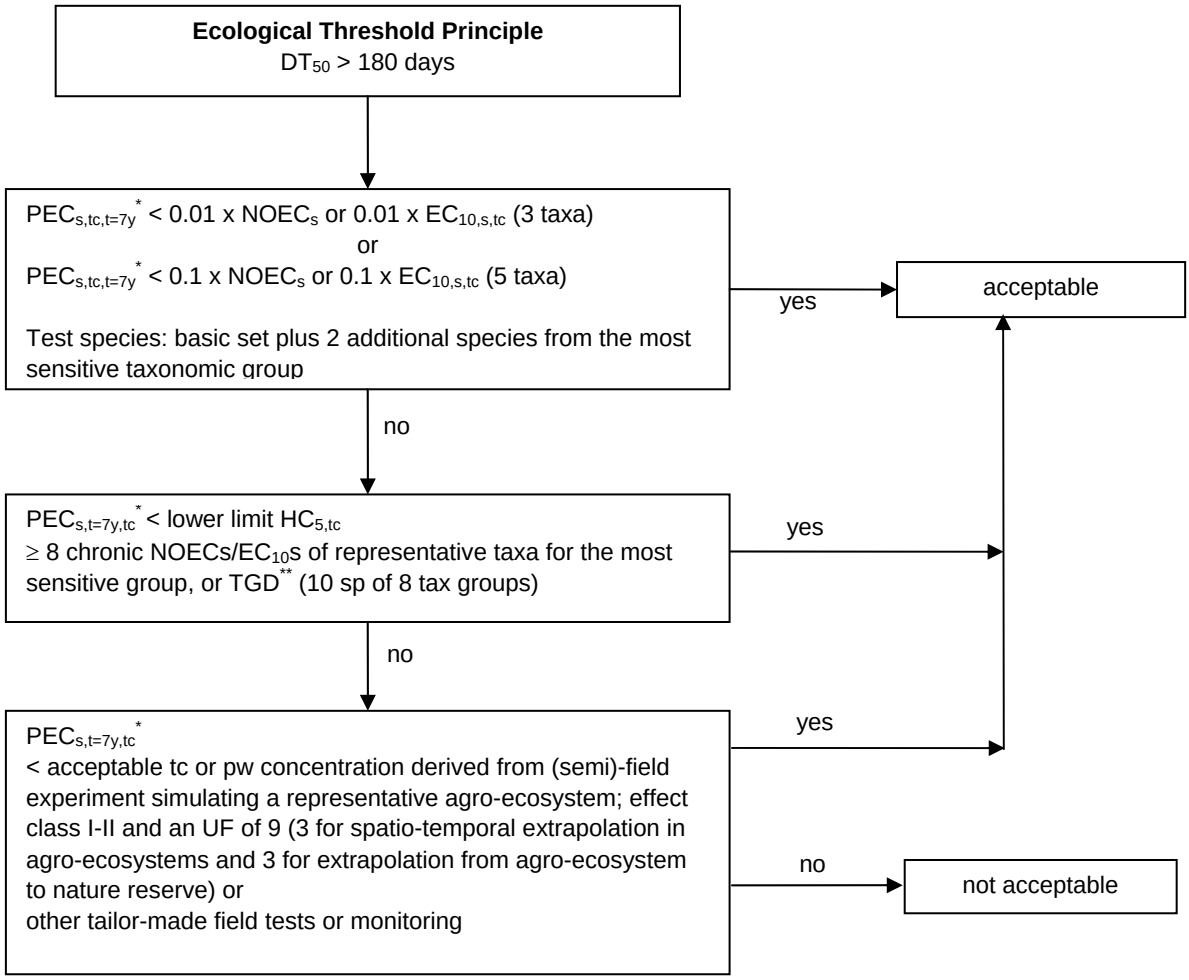



Figure 1.4 Decision tree for in-crop (7 years post last application) effect assessment in line with the Ecological Threshold Principle

* The use of PEC is in conformity with the present approach; when more data are available, such as the time to effect, a $PEC_{TWA}$ can be used as well. Instead of total content, pore water concentration can be used (see Van der Linden et al., 2006).

** Species sensitivity distribution (SSD method, see Aldenberg and Jaworska, 2000). If a clear sensitive group exists, meaning at least an order of magnitude difference in sensitivity compared to other groups, data for 8 taxa from the most sensitive group can be taken, in conformity with the procedure for the aquatic environment (Campbell et al., 1999). Alternatively, in case of general biocidal activity, the TGD approach can be taken (TGD, 2003). A minimum of 10 NOECs for at least 8 taxonomic groups should be taken. In the TGD an assessment factor of 5 – 1 is applied, to be fully justified on a case-by-case basis (for soil discussion is going on about different trophic levels, the use of functional endpoints (micro-organisms) etcetera).

## 1.4 Reading guidance

The evaluation of the assessment method for persistence of plant protection products was carried out by studying five substances in detail, four active substances and one metabolite. This report gives the results of the evaluation study. The study revealed that some changes to the methodology would be appropriate. RIVM report 601712003 (Van der Linden et al., 2008) gives the revised methodology and supersedes RIVM report 601506008 (Van der Linden et al., 2006).

This report is organised as follows. This chapter gives the remit of the working group and the proposed evaluation method. Chapters 2 – 6 give the results of the evaluation of the individual substances. Details of specific aspects of these evaluations can be found in the appendices. Chapter 7 gives the overall conclusions of the evaluation project and some recommendations.

Unless stated otherwise in this report, application rates and concentrations concern the substance under investigation.

# 2 Carbendazim

## 2.1 Overview of selected carbendazim uses

Carbendazim controls a wide range of fungal pathogens on cereals, fruits, cotton, tobacco, turf, ornamentals and vegetables. The agricultural use of carbendazim selected for this risk assessment is an application in Brussels sprouts of 0.5 kg $ha^{-1}$ twice per season in August - September. The minimal interval between two applications is ten days according to the Draft Assessment Report (DAR). Both applications are at growth stage BBCH[2] 49 (other Brassica vegetables, see Appendix 2).

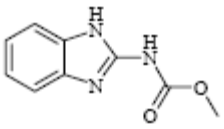
Table 2.1 Selected carbendazim uses

| substance | crop | formulation | frequency | dose | BBCH | interception |
|---|---|---|---|---|---|---|
| carbendazim | Brussels sprouts | Brabant Carbendazim Flowable | 2 (15 August, 1 September) | 0.5 kg $ha^{-1}$ | 49 | 60% |

## 2.2 Relevant fate parameters of carbendazim

### 2.2.1 Physico-chemical properties of carbendazim

Table 2.2 Basic data of carbendazim

| | |
|---|---|
| ISO name | CARBENDAZIM |
| IUPAC | methyl benzimidazol-2-ylcarbamate |
| CAS | 10605-21-7 |
| Purity | 980 g $kg^{-1}$ |
| Molecular formula | C9H9N3O2 |
| Structure |  |

Molecular mass, vapour pressure and solubility in water (Table 2.2) are taken from the List of End points (SANCO 5032/VI/98 final version of 5 January 2007) of carbendazim.

[2] The abbreviation **BBCH** derives from **B**iologische **B**undesanstalt, Bundessortenamt and **CH**emical industry. The BBCH-scale is a system for a uniform coding of phonologically similar growth stages of all mono- and dicotyledonous plant species.

The List of End points (SANCO 5032/VI/98 final version of 5 January 2007) asserts stronger adsorption at low pH and a $pK_a$ of 4.2. In order to estimate parameters for the pH-dependent sorption relationship, as many sorption studies as possible were gathered from the EU monograph and open literature. Reliability of each measurement in each study was checked using the P-criterion (Boesten, 1990), rendering seven reliable studies. The reliable results from these seven studies were used to fit the relation between pH and the sorption constant $K_{OM}$ (see Appendix A2.1). A $K_{OM,acid}$ of 2073 $dm^3\ kg^{-1}$ and a $K_{OM,base}$ of 201.9 $dm^3\ kg^{-1}$ were fitted for the protonated (acid) and the neutral molecule (base) respectively. The default value of 0.9 is taken for the Freundlich exponent.

Concerning half-lives in soil, both laboratory degradation studies and field dissipation studies are available. The monograph did not provide reliable half-lives for degradation ($DegT_{50,lab}$) from laboratory experiments. A study was considered not reliable if:

- the storage time of the soil before analysis was not specified;
- the used dose was not specified;
- the soil moisture content at which the $DegT_{50}$ is measured was not specified;
- the used dose was > 11 mg $kg^{-1}$ (advised annual dose is 0.45 mg $kg^{-1}$).

The only reliable value was found in Matser and Leistra (2000). A $DegT_{50,lab}$ of 141 days was measured (moisture content: 0.22 g $g^{-1}$) for a soil sample from Droevendaal (Wageningen, the Netherlands). Normalization to pF2 (field capacity) is not necessary for the Droevendaal sample because the moisture content in the soil is high enough. Relevant fate parameters of carbendazim used in Tier 1 and/or Tier 3 calculations are given in Table 2.3.

Table 2.3 Relevant fate parameters of carbendazim

| **parameter** | **value + unit** | **source** |
|---|---|---|
| molecular mass | 191.21 g $mol^{-1}$ | List of End points<br>SANCO 5032/VI/98 final version of 5 January 2007 |
| vapour pressure | 9.0 E-3 Pa (20 °C) | |
| solubility in water | 8 mg $dm^{-3}$ (20 °C) | Tomlin CDS. 2003. |
| $K_{OM,acid}$<br>$K_{OM,base}$ | 2073 $dm^3\ kg^{-1}$ (20 °C)<br>201.9 $dm^3\ kg^{-1}$ (20 °C) | see Appendix A2.1 |
| $pK_a$ | 4.2 | |
| Freundlich exponent (1/n) | 0.90 (-) | default value |
| $DegT_{50,lab}$ | 141.0 d (pF2, 20°C)<br>310.2 d (pF2, 10°C) | Matser and Leistra (2000) |
| $DegT_{50,field}$ | - | |

### 2.2.2 Assessment of (semi-)field dissipation studies of carbendazim

Details of the assessment of the field dissipation studies of carbendazim are given in Appendix 2.

Assessment of the field dissipation studies did not result in a reliable estimate of the $DegT_{50,field}$. Therefore the result of the available laboratory study is used for the calculation of exposure levels and for comparison with the $DegT_{50}$ trigger values of the FRP, CRP and ETP. The $DegT_{50,lab}$ value of 141 days (20 °C, pF2; Matser and Leistra, 2000) will be used for the calculation of exposure levels. The

$DegT_{50,lab}$ value of 310.2 days (10 °C, pF2; Matser and Leistra, 2000) is used for comparison with the $DT_{50}$ trigger values of the FRP, CRP and ETP.

For indoor terrestrial model ecosystems dissipation $DT_{50}$ values in soil (soil temperature 10 – 14 °C) in the range of 28.7 – 93.3 days (geometric mean value 49.5 days; n = 8) are reported, while in corresponding outdoor field validation experiments $DT_{50}$ values in similar soils (soil temperatures not reported) in the range of 21.7 – 65.8 days (geometric mean value 40.8 days; n = 4) are mentioned (Jones et al., 2004). However, these values refer to dissipation while $DegT_{50}$ values are needed. A more detailed assessment of these field studies and semi-field studies is not possible since the underlying data, which are needed to calculate a $DegT_{50}$, were not published by Jones et al. (2004).

## 2.3 Trigger values carbendazim

The $DegT_{50,lab}$ value of 310.2 days (10 °C, pF2; Matser and Leistra, 2000) is used for comparison with the $DegT_{50}$ trigger values of the FRP, CRP and ETP. This $DegT_{50}$ triggers the procedure in line with the FRP (trigger value $DegT_{50}$ > 30 d). The risk assessment procedures in line with the CRP ($DegT_{50}$ > 90 d) and the ETP ($DegT_{50}$ > 180 d) are triggered as well.

## 2.4 Input for exposure calculations

**$PEC_s$**

The concentration of carbendazim in soil and/or pore water is needed to assess the risk for soil organisms of persistent substances according to the community recovery principle (CRP) and the ecological threshold principle (ETP). The $PEC_s$ for spray applications is calculated for the upper 5 cm of soil.

***Tier 1***

Input for the first tier exposure calculation is the actual worst-case application rate of 0.5 kg $ha^{-1}$ for each of the two doses given per season. It is assumed that there is no interception by the crop, no tillage and the soil dry bulk density is 1000 kg $m^{-3}$. The calculation is independent of the crop and the time of application. For metabolites all available data concerning substance properties are regarded. The following input data are used for the calculation:

**Tier 1 input for carbendazim**

Active substance:
Worst case $DegT_{50,lab}$ for degradation in soil (20°C): 141 days (based on one laboratory study)
$K_{OM,acid}$: 2073 $dm^3$ $kg^{-1}$ (used for calculating total content)
$K_{OM,base}$: 201.9 $dm^3$ $kg^{-1}$ (used for calculating pore water concentration)
Molecular weight: 191.21 g $mol^{-1}$

Other parameters: standard settings of Tier 1 calculation programme

***GeoPEARL***

In the third tier (no second tier developed), the concentration of carbendazim in soil and/or pore water in the potential area of use is evaluated using the spatially distributed model GeoPEARL 3.3.3. Input variables are the actual worst-case application scheme 0.5 kg $ha^{-1}$ for each of the two applications given per season to the crop Brussels sprouts (in GeoPEARL represented by the crop 'vegetables') and an interception value of 60% (40% to the soil), appropriate for the crop at growth stage BBCH 49. Tillage is included in the calculations.

The date of the yearly first application is 15 August and the date of the yearly second application is 1 September (realistic worst case scheme for this application). The following input data are used for the calculation:

**GeoPEARL input for carbendazim**

Active substance:

worst case $DegT_{50,lab}$ for degradation in soil (20°C)*: 141 days ($DegT_{50,lab}$ used, because a $DegT_{50,field}$ is lacking)

$K_{OM,acid}$: 2073 $dm^3$ $kg^{-1}$

$K_{OM,base}$: 201.9 $dm^3$ $kg^{-1}$

1/n: 0.9

pKa: 4.2

Non-equilibrium sorption is assumed:

Desorption rate coefficient: 0.01 $d^{-1}$ (default)

Factor relating non-equilibrium and equilibrium sorption, CofFreNeq and CofFreEql: 0.5 (-, default)

Saturated vapour pressure: 9.0E-3 Pa (20 °C)

Solubility in water: 8 mg $dm^{-3}$ (20 °C)

Molecular weight: 191.2 g $mol^{-1}$

Crop: vegetables

Number of plots (minimum 250): 250

Other parameters: standard settings of GeoPEARL 3.3.3

* Only one reliable $DegT_{50,lab}$ available.

## 2.5 Ecotoxicological endpoints of carbendazim

### 2.5.1 Ecotoxicological endpoints in line with the FRP

In the decision tree for in-crop effect assessment in line with the FRP it is first checked if the predicted exposure concentration of the substance leads to toxic effects on earthworms or soil micro-organisms ($PIEC_{s,tc} < 0.2 * NOEC_{earthworms}$ or effects on SMO < 25%). Application of 0.5 kg $ha^{-1}$ (2 times) results in a third-tier $PIEC_{s,tc}$ value of 0.876 mg $kg^{-1}$ (see Table 2.13). In the EU dossier (3 May 2004) the selected 56-d $NOEC_{repro}$ for earthworms is 1.0 mg $kg^{-1}$ (*Eisenia fetida*; Lührs 2001a in EU dossier; see Table 2.4). The $PIEC_{s,tc}$ of 0.876 mg $kg^{-1}$ is larger than $0.2 * NOEC_{earthworms}$, so that effects on soil functions such as organic matter mineralization cannot be excluded.

In the list of endpoints of the EU dossier it is reported that at exposure concentrations as high as

1.5 kg ha$^{-1}$ (= 3 mg kg$^{-1}$ in the upper 5 cm of the soil; $\rho_b$ = 1000 kg m$^{-3}$) no substantial effects on microbial nitrogen and carbon mineralization can be observed (Carbendazim DAR list of endpoints; Appendix II, 3. Ecotoxicology, 30 September 2004).

According to the FRP decision scheme a litter bag study is required, since the criterion $PIEC_{s,tc} < 0.2 * NOEC_{earthworms}$ is not met. However, in the EU dossier a litter bag study with carbendazim in accordance with the EPFES Guidance Document (Römbke et al., 2003) is not available. In Addendum 6 to the Monograph (section B.8.7; DOC 15032/ECCO/BVL/03) results of a litter bag study with the fungicide benomyl are reported (nominal benomyl test concentrations 150, 300 and 750 g ha$^{-1}$). The main metabolite of benomyl is carbendazim, which is formed rapidly. The litter bags filled with hay (5.0 g dry weight) were exposed on the soil surface during benomyl application and after one hour horizontally buried at a depth of 2 - 5 cm. Initially, small (up to 18% difference relative to controls) and short-term effects on hay decomposition were demonstrated at the benomyl treatment levels of 300 and 750 g ha$^{-1}$. 193 days after application, statistically significant differences in remaining hay litter between treatments and controls could not be demonstrated anymore. If it is assumed that benomyl is completely transformed into carbendazim these data suggest that the difference in litter mass loss between controls and soils treated once with carbendazim up to 494 g ha$^{-1}$ (= 0.99 mg kg$^{-1}$ in the upper 5 cm of the soil; $\rho_b$ = 1000 kg m$^{-3}$) will be less than 10% after 12 months. In that case the risk is considered to be low according to the EPFES Guidance Document (Römbke et al., 2003).

The effects of carbendazim on microbial nitrogen and carbon mineralization and the results of the benomyl litter bag study reported in the EU dossier are more or less in accordance with observed effects of carbendazim on functional endpoints in terrestrial model ecosystems and field soils as reported in the open literature for four different European sites, viz., Amsterdam (the Netherlands), Bangor (UK), Coimbra (Portugal) and Flörsheim (Germany) (Knacker et al., 2004; Förster et al., 2004; Sousa et al., 2004; Van Gestel et al., 2004). Förster et al. (2004) studied the effects of carbendazim application on organic matter (cellulose filter paper) decomposition in soils in indoor terrestrial model ecosystems (TMEs) and in corresponding soils in the field at Flörsheim (Germany). According to Förster et al. (2004) the carbendazim-induced effects on organic matter decomposition in the TMEs and in the field were comparable and followed a clear dose-response relationship. After eight weeks of incubation the differences in weight loss of the cellulose filter paper were most pronounced. The calculated $EC_{50}$ values for organic matter decomposition after eight weeks were 9.5 and 7.1 kg ha$^{-1}$ for the grassland TMEs and the grassland field, respectively. The larger impact of the same treatment level in the field compared to the TMEs was attributed to lower moisture levels in the field. The data presented by Förster et al. (2004) suggest that statistically different treatment-related effects on weight loss of cellulose paper do not occur at levels up to 1.08 kg ha$^{-1}$ (2.16 mg kg$^{-1}$; upper 5 cm; $\rho_b$ = 1000 kg m$^{-3}$).

Overall, it can be concluded from the data presented above that effects of two applications of 0.5 kg ha$^{-1}$ (third tier $PIEC_{s,tc}$ of 0.876 mg kg$^{-1}$) on litter breakdown in soils cannot be excluded but most probably will be relatively small and short-term. In addition, in the TMEs and field plots mentioned above it was also demonstrated by Van Gestel et al. (2004) that dosages as high as 87.5 kg ha$^{-1}$ (175 mg kg$^{-1}$; upper 5 cm; $\rho_b$ = 1000 kg m$^{-3}$) did not have a significant impact on soil nutrient cycling. Furthermore, in the same test systems Sousa et al. (2004) studied the impact of carbendazim application on substrate induced respiration (mg $CO_2$/g dry soil /h), dehydrogenase activity (mg triphenylformazan/g dry soil/h), phosphatase activity (mg para-nitrophenol/g dry soil /h) and thymidine incorporation (pmol[$^3$H]thymidine/g dry soil /h). For the endpoints related to microbial activities clear dose-response relationships often could not be observed. More or less consistent NOECs of 1.08 - 3.24 kg ha$^{-1}$

(= 2.16 – 6.48 mg $kg^{-1}$) could be calculated for some test systems (but not at all locations) for dehydrogenase activity and phosphatase activity. These observations suggest that effects of two applications of 0.5 kg $ha^{-1}$ (= third tier $PIEC_{s,tc}$ of 0.876 mg $kg^{-1}$) on microbial activity and nutrient cycling in soils will be negligible.

## 2.5.2 Ecotoxicological endpoints in line with the CRP and ETP

### Chronic laboratory toxicity tests with soil organisms

In Table 2.4 the chronic laboratory toxicity data reported for soil organisms in the EU dossier (in italics) and open literature are reported. The majority of toxicity data reported in Table 2.4 comprise chronic NOEC values for Enchytraeidae (potworms) and Lumbricidae (earthworms). In addition, a chronic toxicity value is available for the arthropod *Folsomia candida* and the plant *Lactuca sativa*. Among the soil invertebrates tested worms appear to be the most sensitive.

Table 2.4 Chronic laboratory toxicity data for soil dwelling organisms and carbendazim as reported in the EU dossier (italics) and open literature. In bold the toxicity value used in the dossier to perform the long-term risk assessment.

| species | formulation | OM (%) | pH | duration (d) | endpoint | value (mg $kg^{-1}$) | value# (µg $dm^{-3}$) | reference |
|---|---|---|---|---|---|---|---|---|
| *Enchytraeus albidus* (Enchytraeidae) | Derosal | 10 | 5.5* | 42 | $EC_{10}$ repro | 0.4 | 3.5* | Römbke, 2003 |
| *Eisenia andrei* (Lumbricidae) | Derosal | 10 | 6 | 21 | NOEC repro | 0.6 | 7.2 | Van Gestel et al., 1992 |
| *Eisenia fetida* (Lumbricidae) | Derosal | ? | 5.5* | 28 | NOEC repro | 0.6 | 5.2* | Römbke, 2003 |
| ***Eisenia fetida* (Lumbricidae)** | ***Derosal*** | ***10*** | 5.5* | ***56*** | ***NOEC repro*** | ***1.00*** | ***8.6**** | ***Lührs, 2001a*** |
| *Eisenia fetida (Lumbricidae)* | *Derosal* | *10* | 5.5* | *56* | *NOEC repro* | *1.03* | *8.9** | *Lührs, 2001b* |
| *Eisenia fetida (Lumbricidae)* | *Derosal* | *10* | 5.5* | *56* | *NOEC repro* | *1.20* | *10.4** | *Lührs, 2002/2003* |
| *Eisenia fetida* (Lumbricidae) | | 10 | 7.5 | 28 | NOEC repro | 2.2 | 33.7 | Vonk et al., 1986 |
| *Folsomia candida (Arthropod)* | *technical* | *10* | 5.5* | *28* | *NOEC repro* | *320* | *2762.7** | *Heusel, 1993 (in ECCO, 1997)* |
| *Lactuca sativa* (Rooted plant) | | 1.4 | 7.5 | 14 | NOEC | 46 | 704.1 | Vonk et al., 1986 |

# Pore water concentration estimated from total soil content

* No information on soil properties: OECD guideline 222 defaults (OM: 10%, volumetric moisture content: 0.5) used to calculated pore water concentration, $K_{OM,pH5.5}$: 1153.3 $dm^3$ $kg^{-1}$. A volumetric moisture content of 0.5 was used for all calculations.

Too few chronic toxicity data are available to apply the SSD approach to assess the risks for potworms and earthworms (NOEC values for three species only) or soil organisms (NOEC values for four taxonomic groups only). Although carbendazim is a fungicide, reliable chronic laboratory toxicity data for soil fungi are not available.

### Acute laboratory toxicity tests with soil organisms

Table 2.5 gives the acute laboratory toxicity data reported for soil organisms in the EU dossier (italics) and open literature. Again, the majority of toxicity data reported in Table 2.5 comprise values for

worms (Lumbricidae and Enchytraeidae). In addition, additional acute toxicity values are available for the arthropods *Trigoniulum corallinus* (Diplopoda) and *Circoniscus ornatus* (Isopoda). Again, among the soil invertebrates tested, worms appear to be the most sensitive. In the EU dossier and open literature reliable acute laboratory toxicity data for soil fungi and carbendazim could not be found.

Table 2.5 Acute carbendazim laboratory toxicity data for soil dwelling organisms as reported in the EU dossier (italics) and open literature

| species | formulation | OM % | days | endpoint | value mg kg$^{-1}$ | reference |
|---|---|---|---|---|---|---|
| **Lumbricidae** | | | | | | |
| *Eisenia andrei* | Derosal | 10 | 21 | $LC_{50}$ | 5.7 | Van Gestel et al., 1992 |
| *Eisenia fetida* | | ? | 28 | | 6 | Römbke, 2003 |
| | *technical* | *10* | *14*<br>*28* | | *5.4*<br>*3.9* | *Vonk et al., 1986* |
| | *36% SC* | *10* | *14* | | *64* | *Heusel, 1991* |
| *Pontoscolex corethurus* | Derosal | 3.5 | 14 | | 48.2 | Garcia, 2004 |
| **Enchytraeidae** | | | | | | |
| *Enchytraeus albidus* | Derosal | 10 | 28 | $LC_{50}$ | 6 | Römbke, 2003 |
| *Enchytraeus coronatus* | | 10 | 21 | $EC_{50}$ (RI) | 14.1 | Arrate et al., 2002 |
| *Fridericia ratzeli* | | ? | 28 | $LC_{50}$ | 3.3 | Frampton et al., 2006 |
| **Arthropods** | | | | | | |
| *Trigoniulus corallinus* (Diplopoda) | Derosal | 3.5 | 14 | $LC_{50}$ | 503.5 | Garcia, 2004 |
| *Circoniscus ornatus* (Isopoda) | | 3.5 | 14 | $LC_{50}$ | 1000 | |

**Field and semi-field tests**

Several ecotoxicological (semi-)field tests are reported for carbendazim in a special issue of the scientific journal Ecotoxicology (see Knacker et al., 2004). The reported (semi-)field tests comprise studies in indoor Terrestrial Model Ecosystems (TMEs) and corresponding outdoor field plots representative for four different European sites, viz. Amsterdam (the Netherlands), Bangor (UK), Coimbra (Portugal) and Flörsheim (Germany). We considered these (semi-)field experiments appropriate to use in the risk
assessment procedure on basis of the following criteria:

1. the test systems represented a relevant soil community;
2. the experimental set-up of the experiments was adequately described;
3. the exposure regime in the test systems was well-enough characterized (although a detailed evaluation needs the basic data that underly the scientific publications);
4. the investigated endpoints, particularly Enchytraeidae and Lumbricidae, are reported to be sensitive to the fungicide carbendazim (although structural aspects of soil fungi were not investigated);
5. it was possible to evaluate the observed effects statistically and ecologically (univariate and multivariate techniques).

Summaries of the consistent ecological threshold levels for carbendazim on structural measurement endpoints in the TMEs and the field plots are reported in Table 2.6 and Table 2.7, respectively. The structural measurement endpoints investigated in the TMEs and field plots mainly concerned soil

invertebrates. Treatment-related effects on soil microorganisms were only investigated from a functional point of view (microbial activity like nutrient cycling and carbon mineralization; see section 2.5.1).

For a proper effect and risk assessment the (semi-)field threshold levels in kg $ha^{-1}$ in Table 2.6 and Table 2.7 are recalculated to obtain higher tier NOEC or LOEC values for the soil invertebrate community in terms of total concentration or pore water concentration in the upper 5 cm of soil. A FORTRAN program was developed to calculate concentrations in ecotoxicological studies (Appendix 8 in Van der Linden et al., 2008). This program is used to calculate the concentrations in the upper 5 cm of the soil. Data on soil properties needed by the program for calculating the concentrations are found in Knacker et al. (2004) and Jones et al. (2004) and presented in Table 2.8.

Table 2.6 Observed ecological threshold levels (expressed in terms of A: dose applied, B: total concent, C: pore water concentration in the upper 5 cm of soil) for carbendazim on structural invertebrate measurement endpoints in Terrestrial Model Ecosystems

| location | NOEC most sensitive structural endpoint for different soil invertebrate groups | | | | most sensitive structural endpoint in test system | |
|---|---|---|---|---|---|---|
| | **nematodes** (Moser et al., 2004a) | **arthropods** (Koolhaas et al., 2004) | **potworms** (Moser et al., 2004b) | **earthworms** (Römbke et al., 2004) | **Effect class I NOEC** | **Effect class II LOEC** |
| **A** expressed in terms of dose applied (kg $ha^{-1}$) | | | | | | |
| **Amsterdam** | 1.08 | 0.36 – 2.16 | 2.16 | 2.16 | 0.36 (Collembola - community) | 1.08 (Collembola -community) |
| **Bangor** | 29.2 | 0.36 – 2.16 | 2.16 | 2.16 | 0.36 (Acari; community) | 1.08 (Acari; community) |
| **Coimbra** | 1.08 (increase !) | | 2.16 * | 1.08 | 1.08 (earthworm biomass; Nematoda - plant parasites) | > 1.08 ? (earthworm biomass; Nematoda - plant parasites) |
| **Flörsheim** | 29.2 | | <0.36 | 1.08 | <0.36 (abundance of potworms) | 0.36 (abundance of potworms) |
| **B** expressed in terms of total content in the upper 5 cm of the soil (mg $kg^{-1}$) | | | | | | |
| **Amsterdam** | 1.73 | 0.57 – 3.46 | 3.46 | 3.46 | 0.57 (Collembola - community) | 1.73 (Collembola - community) |
| **Bangor** | 43.58 | 0.54 – 3.22 | 3.22 | 3.22 | 0.54 (Acari; community) | 1.61 (Acari; community) |
| **Coimbra** | 2.06 (increase !) | | 4.11 * | 2.06 | 2.06 (earthworm biomass; Nematoda - plant parasites) | > 2.06 ? (earthworm biomass; Nematoda - plant parasites) |
| **Flörsheim** | 58.40 | | <0.72 | 2.16 | <0.72 (abundance of potworms) | 0.72 (abundance of potworms) |
| **C** expressed in terms of pore water concentrations in the upper 5 cm of the soil (mg $kg^{-1}$) | | | | | | |
| **Amsterdam** | 17.7 | 5.9 – 35.4 | 35.4 | 35.4 | 5.9 (Collembola - community) | 17.7 (Collembola - community) |
| **Bangor** | 770.1 | 9.5 – 57.0 | 57.0 | 57.0 | 9.5 (Acari; community) | 28.5 (Acari; community) |
| **Coimbra** | 82.8 (increase !) | | 165.5* | 82.8 | 82.8 (earthworm biomass; Nematoda - plant parasites) | > 82.8 ? (earthworm biomass; Nematoda - plant parasites) |
| **Flörsheim** | 807.8 | | <10.0 | 29.9 | < 10.0 (abundance of potworms) | 10.0 (abundance of potworms) |

* an observed trend of a treatment-related response that is not statistically different

? an Effect class II concentration cannot easily be derived since treatment-related effects on relevant endpoints were studied at the end of the TME experiment only

Table 2.7 Observed ecological threshold levels for carbendazim on structural invertebrate measurement endpoints in field plot studies performed in Amsterdam, Bangor, Coimbra and Flörsheim

| location | NOEC most sensitive structural endpoint for different soil invertebrate groups | | | | most sensitive structural endpoint in test system | |
|---|---|---|---|---|---|---|
| | **nematodes** (Moser et al., 2004 a) | **arthropods** (Koolhaas et al., 2004) | **potworms** (Moser et al., 2004 b) | **earthworms** (Römbke et al., 2004) | **Effect class I NOEC** | **Effect class II LOEC** |
| **A** expressed in terms of dosa applied (kg $ha^{-1}$) | | | | | | |
| **Amsterdam** | 0.36 | >87.5 | 9.72 | 3.24 | 0.36 (Nematoda – omnivores) | > 0.36 ? (Nematoda – omnivores) |
| **Bangor** | 1.08 | | >87.5 | 9.72 | 1.08 (Nematoda – omnivores) | > 1.08 ? (Nematoda – omnivores) |
| **Coimbra** | 3.24 * | | >87.5 | 1.08 * | 1.08 * (abundance earthworms) | > 3.24 * ? (maturity index – Nematoda) |
| **Flörsheim** | 9.72 | | 9.72 | 3.24 | 3.24 (biomass earthworms) | > 3.24 ? (biomass earthworms) |
| **B** expressed in terms of total content in the upper 5 cm of the soil (mg $kg^{-1}$) | | | | | | |
| **Amsterdam** | 0.58 | >140.0 | 15.5 | 5.2 | 0.58 (Nematoda – omnivores) | > 0.58 ? (Nematoda – omnivores) |
| **Bangor** | 1.6 | | >130.6 | 14.5 | 1.6 (Nematoda – omnivores) | > 1.6 ? (Nematoda – omnivores) |
| **Coimbra** | 6.2 * | | >166.7 | 2.1* | 2.1* (abundance earthworms) | >6.2* ? (maturity index – Nematoda) |
| **Flörsheim** | 19.4 | | 19.4 | 6.5 | 6.5 (biomass earthworms) | > 6.5 ? (biomass earthworms) |
| **C** expressed in terms of pore water concentrations in the upper 5 cm of the soil (mg $kg^{-1}$) | | | | | | |
| **Amsterdam** | 5.9 | > 1434.8 | 159.4 | 53.1 | 5.9 (Nematoda – omnivores) | > 5.9 ? (Nematoda – omnivores) |
| **Bangor** | 28.5 | | > 2307.6 | 256.3 | 28.5 (Nematoda – omnivores) | > 28.5 ? (Nematoda – omnivores) |
| **Coimbra** | 248.3* | | > 6707.6 | 82.8* | 82.8* (abundance earthworms) | > 248.3* ? (maturity index – Nematoda) |
| **Flörsheim** | 268.9 | | 268.9 | 89.6 | 89.6 (biomass earthworms) | > 185.2 ? (biomass earthworms) |

* an observed trend of a treatment-related response that is not statistically different

? an Effect class II concentration cannot easily be derived since treatment-related effects on the relevant measurement endpoint were studied at the end of the field plot experiment only (16 weeks post treatment)

It can be concluded from Table 2.6 that in the indoor Terrestrial Model Ecosystems arthropods (Collembola, Acari) and earthworms/potworms were among the most sensitive measurement endpoints. Unfortunately, arthropod endpoints were only studied for the Amsterdam and Bangor sites. Overall, differences in Effect class I-II values between sites were relatively small. It can be concluded from Table 2.7 that in the outdoor field plots earthworms and Nematoda were among the most sensitive measurement endpoints. Differences in Effect class I values between sites were relatively large. The Amsterdam field plot revealed the lowest Effect class I NOEC, particularly for pore water.

Table 2.8 Properties of Amsterdam, Bangor, Coimbra and Flörsheim soils needed for calculating total contents and pore water concentrations

| soil property | unit | Amsterdam | Bangor | Coimbra | Flörsheim |
|---|---|---|---|---|---|
| soil type | | sandy loam | loam | sandy loam | silty clay loam |
| $\rho^{\#}$ (0-5 cm layer) | kg $m^{-3}$ | 1250 | 1340 | 1050 | 1000 |
| OM | % | 4.5 | 6.1 | 3.4 | 5.2 |
| WHC | % | 37.3 | 70.0 | 75.0 | 93.9 |
| porosity | % | 52.8 | 49.4 | 60.4 | 62.3 |
| pH | - | 4.8-5.1 | 5.8-6.6 | 6.4-7.1 | 5.3 – 5.9 |
| irrigation | mm $week^{-1}$ | 15.2 | 21.0 | 18.9 | 12.5 |
| moisture content | - | 0.1969 | 0.3458 | 0.453 | 0.594 |

$^{\#}$ dry bulk density

The moisture contents of the soils are calculated from the WHC and the porosity, assuming a density of 2650 kg $m^{-3}$ for the solids. Field capacity (pF2) is assumed for every locaction because the soils are irrigated weekly (see Table 2.8). Moisture contents calculated for Flörsheim, a silty clay loam soil situated in a river basin (river Main, Germany), and Amsterdam comply quite well with literature data for such soils (Figure 3.12 in Koorevaar, 1983). Evaluation of the calculated moisture contents at Bangor and Coimbra is not possible as more general data on pF curves of soils for these locations are not available. However, the calculated moisture contents at field capacity are considered acceptable.

From a regulatory point of view realistic worst-case concentrations should be calculated. The pore water concentration depends strongly on the value of the sorption coefficient. A higher sorption coefficient gives a lower pore water concentration, consequently worst-case estimates of the test concentrations. The sorption coefficient of carbendazim is pH dependent and the pH differs per location (see Table 2.8; Knacker et al., 2004). Using the fitted relation between $K_{OM}$ and pH and the uncertainty in this relation (Appendix 2, Figure A2.2) and the lower boundary of the pH range, the $K_{OM}$ per location is calculated (Table 2.9). A conservative estimate of the $K_{OM}$ is obtained using the upper boundaries of the 95% confidence intervals of both $K_{mol}$ and $K_{anion}$, the fitted value for the surface acidity effect (PSH) and the known $pK_a$ and relative molar mass (RM, see also Appendix 2, Figure A2.2).

Table 2.9 Sorption coefficients and dissipation half-lives for Amsterdam, Bangor, Coimbra and Flörsheim soils needed for calculating exposure concentrations

| | pH (lower boundary) | $K_{OM}$ ($dm^{-3}$ $kg^{-1}$) (higher boundary) | TME ring test mean $DT_{50}$ (d) | field plot study mean $DT_{50}$ (d) |
|---|---|---|---|---|
| Amsterdam | 4.8 | 2163.9 | 97.3 | 65.8 |
| Bangor | 5.8 | 922.1 | 32.2 | 32.2 |
| Coimbra | 6.4 | 717.7 | 39.2 | 21.7 |
| Flörsheim | 5.3 | 1378.9 | 63.7 | 60.2 |

$DT_{50}$ values are needed for the calculations of TWA concentrations and PEC's at times > 0 days. As $DT_{50}$ values are determined in both the TMEs and the field plot studies it was decided to use these $DT_{50}$ values (Table 2.9).

Since in chronic standard toxicity tests and in the Flörsheim TMEs potworms are the most sensitive organisms, and the duration of the lower-tier test with potworms is 42 days, $TWA_{42}$ concentrations are calculated as well. The calculated concentrations are shown in Table 2.10.

Table 2.10 Calculated carbendazim exposure concentrations in the upper 5 cm soil layer of the Terrestrial Model Ecosystems

| type of exposure concentration | at time (d) | Amsterdam | | Bangor | | Coimbra | | Flörsheim | |
|---|---|---|---|---|---|---|---|---|---|
| | | Effect class I NOEC | Effect class II LOEC | Effect class I NOEC | Effect class II LOEC | Effect class I NOEC | Effect class II LOEC | Effect class I NOEC | Effect class II LOEC |
| PEC total content (mg $kg^{-1}$) | 0 | 0.57 | 1.73 | 0.54 | 1.6 | 2.1 | >2.1 ? | <0.72 | 0.72 |
| PEC pore water (µg $dm^{-3)}$ | 0 | 5.9 | 17.7 | 9.5 | 28.5 | 82.8 | >82.8 ? | <10.0 | 10.0 |
| PEC total content (mg $kg^{-1}$) | 42 | 0.43 | 1.3 | 0.22 | 0.65 | 0.98 | >0.98 ? | <0.46 | 0.46 |
| PEC pore water (µg $dm^{-3)}$ | 42 | 4.4 | 13.1 | 3.8 | 11.5 | 39.4 | >39.4 ? | <6.3 | 6.3 |
| $PEC_{TWA42}$ total content (mg $kg^{-1}$) | | 0.50 | 1.5 | 0.35 | 1.1 | 1.45 | >1.45 ? | <0.58 | 0.58 |
| $PEC_{TWA42}$ pore water (µg $dm^{-3}$) | | 5.1 | 15.3 | 6.2 | 18.7 | 58.4 | >58.4 ? | <8.0 | 8.0 |

* an observed trend of a treatment-related response that is not statistically different

? an Effect class II concentration that cannot easily be derived since treatment-related effects on the relevant measurement endpoint were studied at the end of the field plot experiment only (16 weeks post treatment)

Table 2.11 and Table 2.12 provide the threshold levels for the most sensitive measurement endpoint in each test system based on estimated concentrations on day 42 and the time weighted average concentrations over 42 days ($TWA_{42}$). For the TWA calculations a 42 days time window was adopted since in the first-tier tests with standard test organisms *Enchytraeus albidus* was the most sensitive soil dwelling invertebrate. Standard tests with this potworm take 42 days.

Table 2.11 Calculated carbendazim exposure concentrations in the upper 5 cm soil layer in field plots.

| type of exposure concentration | at time (d) | Amsterdam | | Bangor | | Coimbra | | Flörsheim | |
|---|---|---|---|---|---|---|---|---|---|
| | | Effect class I NOEC | Effect class II LOEC | Effect class I NOEC | Effect class II LOEC | Effect class I NOEC | Effect class II LOEC | Effect class I NOEC | Effect class II LOEC |
| PEC total content (mg $kg^{-1}$) | 0 | 0.58 | >0.58 ? | 1.6 | >1.6 ? | 2.1* | >6.2* ? | 6.5 | >6.5 ? |
| PEC pore water (µg $dm^{-3)}$ | 0 | 5.9 | >5.9 ? | 28.5 | >28.5 ? | 82.8* | >248.3* ? | 89.6 | >89.6 ? |
| PEC total content (mg $kg^{-1}$) | 42 | 0.37 | >0.37 ? | 0.65 | >0.65 ? | 0.54* | >1.6* ? | 4.0 | >4.0 ? |
| PEC pore water (µg $dm^{-3)}$ | 42 | 3.8 | >3.8 ? | 11.5 | >11.5 ? | 21.6* | >64.9* ? | 55.3 | >55.3 ? |
| $PEC_{TWA42}$ total content (mg $kg^{-1}$) | | 0.47 | >0.47 ? | 1.1 | >1.1 ? | 1.1* | >3.4* ? | 5.1 | >5.1 ? |
| $PEC_{TWA42}$ pore water (µg $dm^{-3)}$ | | 4.8 | >4.8 ? | 18.7 | >18.7 ? | 45.6* | >136.7* ? | 71.1 | >71.1 ? |

* an observed trend of a treatment-related response that is not statistically different

? an Effect class II concentration that cannot easily be derived since treatment-related effects on the relevant measurement endpoint were studied at the end of the field plot experiment only (16 weeks post treatment)

Table 2.12 presents a summary of the Effect class I and II threshold concentrations in the TMEs and field plots that will be used in the Tier 3 risk assessment. In this table the lowest values reported for the four TMEs and for the four field plots are given, as well as the geometric mean values for all the TMEs and field plot sites. In calculating these geometric means ‘larger than’ and ‘smaller than’ values were not used. Overall it can be concluded that the lowest Effect class I NOECs are remarkably similar between the TMEs and field plots. However, the geometric mean Effect class I NOECs are approximately a factor two higher for the field plots when compared with the TMEs. In the TMEs the difference between Effect class I NOECs and Effect class II LOEC’s is relatively small.

Although carbendazim is a fungicide, hardly any information is available on the impact of carbendazim on densities of soil fungi and/or the composition of the fungal community in soils. In the EU dossiers of carbendazim no relevant information could be found on this topic.

Table 2.12 Lowest and geometric mean calculated exposure concentrations in the upper 5 cm soil layer of the four TMEs (see Table 2.10) and field plot studies (see Table 2.11)

| | | Terrestrial Model Ecosystems | | | | field plots | | | |
|---|---|---|---|---|---|---|---|---|---|
| **type of exposure concentration** | **at time (d)** | **lowest value** | | **geometric mean value** | | **lowest value** | | **geometric mean value** | |
| | | **Effect class I NOEC** | **Effect class II LOEC** | **Effect class I NOEC** | **Effect class II LOEC** | **Effect class I NOEC** | **Effect class II LOEC** | **Effect class I NOEC** | **Effect class II LOEC** |
| PEC total content (mg $kg^{-1}$) | 0 | 0.54 | 0.72 | 0.86 | 1.26 | 0.58 | - | 1.89 | - |
| PEC pore water (µg $dm^{-3)}$ | 0 | 5.90 | 10.00 | 16.68 | 17.15 | 5.90 | - | 33.42 | - |
| PEC total content (mg $kg^{-1}$) | 42 | 0.22 | 0.46 | 0.45 | 0.73 | 0.37 | - | 0.85 | - |
| PEC pore water (µg $dm^{-3)}$ | 42 | 4.40 | 6.30 | 8.70 | 9.83 | 3.80 | - | 14.98 | - |
| $PEC_{TWA42}$ total content (mg $kg^{-1}$) | | <0.58 | 0.58 | 0.63 | 0.98 | 0.47 | - | 1.31 | - |
| $PEC_{TWA42}$ pore water (µg $dm^{-3)}$ | | 5.10 | 8.00 | 12.27 | 12.96 | 4.80 | - | 23.23 | - |

- indicates that a geometric mean Effect class II concentration cannot be derived since it mainly concerned 'larger than' values

In the open literature it is reported that carbendazim at soil exposure concentrations of 0.5 mg $kg^{-1}$ (test duration 4 days) significantly inhibits $^{32}P$ transport and succinate dehydrogenase activity in external hyphae of arbuscular mycorrhiza species (*Glomus intraradices, Glomus claroideum, Glomus invermaium*) in symbiosis with pea (*Pisum sativum*), while hyphal length densities of these mycorrhiza species are hardly affected at this exposure level (Kling and Jakobsen, 1997). In a follow-up study, Schweiger and Jakobsen (1998) demonstrated that the threshold level of carbendazim on P uptake by arbuscular mycorrhiza species associated with pea is approximately 0.006 mg $kg^{-1}$ soil (test duration post treatment 6 days). The impact of this effect on micorrhizal P-uptake for the fitness of the host plant was not investigated, although it was suggested that arbuscular mycorrhizal fungi enhance plant growth by increasing the phosphorous supply to plants. These experiments mainly provide insight in treatment related effects on the physiological performance of mycorrhiza. The possible concentration-response relationship between carbendazim and the structural characteristics of the mycorrhiza community remains to be investigated.

In the open literature it is reported that in clay soil samples from the botanical garden of the Assiut University (Egypt), treated with 0.75 – 6.07 mg $kg^{-1}$, statistically significant effects on counts of some common fungal species occurred (Abdel-Fattah et al., 1982). At the lowest treatment level (0.75 mg $kg^{-1}$, estimated nominal pore water concentration 134.7 µg $dm^{-3}$) the most pronounced effects were observed 5 days post carbendazim application for total counts of fungal species and *Aspergillus fumigatus* (reduction relative to controls > 50 %), while 10 and 20 days post-treatment statistically significant effects could not be demonstrated anymore. However, 40 days post treatment a statistically significant reduction of approximately 20% in total counts of fungal species could be demonstrated again in the 0.75 mg $kg^{-1}$ treatment. At treatment levels of 3.03 and 6.07 mg $kg^{-1}$ a significant but partial

reduction in counts of *Aspergillus* and total fungal species was also observed at the end of the experiment (80 days post treatment). Although statistically significant reductions in counts were demonstrated for several low abundance species on one or a few sampling days (for example *Aspergillus niger*, *Humicola grisea*, *Fusarium solani*) in soil samples treated with 0.75 mg $kg^{-1}$, their numbers in control soil samples were so low (< 10 per mg) that it is hard to interpret the ecological impact of carbendazim on the densities of these species (Abdel-Fattah et al., 1982). Overall it can be concluded from this experiment that in the soil tested a concentration of 0.75 mg $kg^{-1}$ (134.7 µg $dm^{-3}$ (pH 7.4, OM 0.8%)) resulted in a short-term and partial reduction in counts of common fungal species (Effect class II-III).

## 2.6 CRP effect assessment

On basis of the single species laboratory toxicity tests with soil organisms (Table 2.4 and Table 2.5) it appears that information on the effect of carbendazim on structural measurement endpoints of fungi is lacking, despite the fact that the test substance is a fungicide. Of the soil organism tested worms (Lumbricidae; Enchytraeidae) appear to be more sensitive than arthropods and plants. The semi-field tests (Table 2.6 and Table 2.7) reveal that also Nematoda and the soil arthropod community may comprise sensitive measurement endpoints. The fact that the arthropod community (Collembola, Acari) in some of the indoor TMEs was relatively sensitive might be explained by possible effects via the fungal community. Several soil Collembola and Acari are reported to feed on soil fungi (Koolhaas et al., 2004). Treatment-related effects of carbendazim on structural endpoints of soil fungi were not investigated in the (semi)field experiments summarised in Table 2.6 and Table 2.7. Some literature data, however, reveal that carbendazim at concentrations as low as 0.01 mg $kg^{-1}$ may affect the physiological performance of mycorrhiza species (Schweiger and Jakobsen, 1998), while a concentration as low as 0.75 mg $kg^{-1}$ (134.7 µg $dm^{-3}$ (pH 7.4, OM 0.8%)) resulted in a short-term and partial reduction in counts of common fungal species (Effect class II-III) in soil samples (Abdel-Fattah et al., 1982). Since this Effect class II-III pore water concentration for soil fungi is more than a factor of 10 higher than the lowest reported Effect class I-II pore water concentration (t = 0) given in Table 2.12, we assume that the lowest Effect class I-II thresholds as reported in Table 2.12 for soil invertebrates can be used in the higher-tier risk assessment.

### 2.6.1 First tier (standard test species approach)

In case of a fungicide the CRP decision tree requires chronic NOEC/$EC_{10}$ values for at least a fungus, an earthworm and another taxon. In the EU dosssiers nor in the open literature chronic NOEC/$EC_{10}$ values derived from laboratory toxicity tests for a fungus could be found (Table 2.4 and Table 2.5). Consequently, a first tier effect assessment according to the proposed CRP decision tree (to derive a $RAC_{CRP}$) could not be performed.

### 2.6.2 Second tier (SSD approach)

According to the CRP decision tree the SSD approach cannot be used since less than eight chronic NOEC values are available for different taxonomic groups (assuming that carbendazim has a biocidal toxic mode-of-action) or for the most sensitive taxonomic group (assuming that Lumbricidae and Enchytraeidae are the representative sensitive taxa; or at least as sensitive as fungi). Also the available acute toxicity data are not sufficient to construct an acute SSD, at least when applying the criteria mentioned above.

### 2.6.3 Third tier (Model ecosystem approach)

From Table 2.12 it can be concluded that a nominal treatment level of 0.58 – 0.72 mg $kg^{-1}$ can be considered as an overall threshold level for effects on soil invertebrates in the indoor TMEs and outdoor field plots. These values correspond with $TWA_{42}$ concentrations of 0.47 - 0.58 mg $kg^{-1}$ and peak and $TWA_{42}$ pore water concentrations of 5.90 – 10.00 µg $dm^{-3}$ and 4.80 - 8.00 µg $dm^{-3}$, respectively. Strictly speaking this threshold level cannot directly be used in the effect assessment of carbendazim since treatment-related effects on the structure of the fungal community in the semi-field tests were not investigated. Abdel-Fattah et al. (1982), however, reported that a pore water concentration of 134.7 µg $dm^{-3}$ resulted in short-term and partial reductions in counts of common fungal species (Effect class II-III) in soil samples. Since effects of a carbendazim pore water concentration of 134.7 µg $dm^{-3}$ on counts of fungal species in soil samples were relatively small and short-term, we decided to use the lowest Effect class I-II threshold levels for invertebrates as derived from the TMEs and field plots in the effect assessment. In addition, in these TMEs and field plots effects on microbial activity and nutrient cycling were much less sensitive than structural responses of soil invertebrates (see section 2.5.2).

To derive the $RAC_{CRP,s,tc}$ spatio-temporal extrapolation has to be considered when evaluating threshold concentrations of semi-field tests. If only one valid (semi-)field test is available an AF of 3 has to be applied according to the decision scheme. For carbendazim several (semi-)field tests are available so that it seems fair to use an AF of 1 for spatio-temporal extrapolation when the lowest Effect class I-II threshold value is used. When selecting the lowest Effect class I-II thresholds from the four TMEs and the four field plots the nominal $RAC_{CRP,s,tc}$ becomes 0.58 - 0.72 mg $kg^{-1}$ and the $RAC_{CRP,s,TWA42,tc}$ 0.47 - 0.58 mg $kg^{-1}$. These values correspond with a third-tier nominal $RAC_{CRP,s,pw}$ of 5.90 - 10.00 µg $dm^{-3}$ and a $RAC_{CRP,s,TWA42,pw}$ of 4.80 - 8.00 µg $dm^{-3}$.

## 2.7 ETP effect assessment

### 2.7.1 First tier (standard test species approach)

A first tier $RAC_{ETP,s,tc}$ can be derived by applying an AF of 10 to the estimated first-tier $RAC_{CRP,s,tc}$. Since a $RAC_{CRP}$ could not be derived, because of lack of basic data, a $RAC_{ETP}$ also cannot be derived.

### 2.7.2 Second tier (SSD approach)

According to the ETP decision tree the SSD approach cannot be used since less than eight chronic NOEC values are available for different taxonomic groups (assuming that carbendazim has a biocidal toxic mode-of-action) or for the most sensitive taxonomic group (assuming that Lumbricidae and Enchytraeidae are the representative sensitive taxa; or at least as sensitive as fungi).

### 2.7.3 Third tier (Model ecosystem approach)

A third tier $RAC_{ETP,s,tc}$ can be derived by applying an AF of 3 to the derived third tier $RAC_{CRP,s,tc}$, resulting in a value of 0.19 - 0.24 mg $kg^{-1}$. These values correspond with third-tier $RAC_{ETP,s,pw}$ values of 1.97 - 3.33 µg $dm^{-3}$. In addition, the estimated third-tier $RAC_{ETP,s,TWA42,tc}$ and $RAC_{ETP,s,TWA42,pw}$ values are 0.16 - 0.19 mg $kg^{-1}$ and 1.60 - 2.67 µg $dm^{-3}$, respectively.

## 2.8 Carbendazim persistency risk assessment

### 2.8.1 Functional Redundancy Principle

Table 2.13 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) in line with the Functional Redundancy Principle (FRP)

| | **$PIEC_{s,tc}$** | **$PIEC_{s,pw}$** | **$PEC^{\#}_{s,tc,TWA42}$** | **$PEC^{\#}_{s,pw,TWA42}$** | **$RAC_{FRP\ s,tc}$** | **$RAC_{FRP\ s,pw}$** | **$RAC^{\#}_{FRP\ s,tc,TWA42}$** | **$RAC^{\#}_{FRP\ s,pw,TWA42}$** |
|---|---|---|---|---|---|---|---|---|
| | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) |
| Tier 1 | 5.9 | 950 | 5.7 | 910 | * | * | * | * |
| Tier 2 | - | - | - | - | 0.99** | | | |
| Tier 3 | 0.88 | 100 | 0.83 | 70 | | | | |

* Litter bag study according to EPFES Guidance Document not available

# TWA period of 42 days chosen because of the duration of the tests with potworms

Within the year of application a third tier $PIEC_s$ of 0.88 mg $kg^{-1}$ and 100 µg $dm^{-3}$ was calculated for total content and pore water, respectively (Table 2.13). The Tier 3 PIECs are 10 – 15 % of the Tier 1 PIECs, indicating a potential screening function. A litter bag study is required irrespective of the reference temperature of the $DegT_{50}$, both the $DegT_{50}$ (10°C, pF2) value of 310.2 days and the $DegT_{50}$ (20°C, pF2) value of 141 days trigger a litter bag study. However, in the EU dossier a litter bag study with carbendazim that is in accordance with the EPFES Guidance Document (Römbke et al., 2003) is not available. From additional data (see section 2.5.2) it was concluded at a peak concentration level of 0.99 mg $kg^{-1}$ effects on litter breakdown cannot be excluded but most probably will be relatively small and short-term. These additional data suggest that risks in accordance with the FRP are acceptable, based on the $PIEC_{s,tc}$ value.

### 2.8.2 Community Recovery Principle

Table 2.14 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) in line with the Community Recovery Principle (CRP)

| | **$PEC_{s,tc,t=2y}$** | **$PEC_{s,pw,t=2y}$** | **$PEC^{\#}_{s,tc,t=2y,TWA42}$** | **$PEC^{\#}_{s,pw,t=2y,TWA42}$** | **$RAC_{CRP\ s,tc}$** | **$RAC_{CRP\ s,pw}$** | **$RAC^{\#}_{CRP\ s,tc,TWA42}$** | **$RAC^{\#}_{CRP\ s,pw,TWA42}$** |
|---|---|---|---|---|---|---|---|---|
| | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) |
| Tier 1 | 2.7 | 230 | 2.6 | 230 | | | | |
| Tier 2 | - | - | | | | | | |
| Tier 3 | 0.11 | 3.4 | 0.11 | 3.2 | 0.58 – 0.72 | 5.90 – 10.0 | 0.47 – 0.58 | 4.80 – 8.00 |

# TWA period of 42 days chosen because of the duration of the tests with potworms

Two years post last application third tier $PEC_s$ values are calculated to be 0.11 mg $kg^{-1}$ and 3.4 µg $dm^{-3}$ for total content and pore water, respectively. Tier 3 PEC's are 1 – 5% of Tier 1 PEC's. These third tier $PEC_s$ values are lower than the calculated third tier $RAC_{CRP}$ values reported in Table 2.14.

Consequently, the CRP decision tree indicates acceptable risks for momentary and TWA values, for both total contents and pore water concentrations.

### 2.8.3 Ecological Threshold Principle

Table 2.15 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) in line with the Ecological Threshold Principle (ETP).

| | **PEC** $_{s,tc,t=7y}$ | **PEC** $_{s,pw,t=7y}$ | **PEC**$^{\#}$ $_{s,tc,t=7y,TWA42}$ | **PEC**$^{\#}$ $_{s,pw,t=7y,TWA42}$ | **RAC**$_{ETP}$ $_{s,tc}$ | **RAC**$_{ETP}$ $_{s,pw}$ | **RAC**$_{ETP}^{\#}$ $_{s,tc,TWA42}$ | **RAC**$_{ETP}^{\#}$ $_{s,pw,TWA42}$ |
|---|---|---|---|---|---|---|---|---|
| | (mg kg$^{-1}$) | (µg dm$^{-3}$) | (mg kg$^{-1}$) | (µg dm$^{-3}$) | (mg kg$^{-1}$) | (µg dm$^{-3}$) | (mg kg$^{-1}$) | (µg dm$^{-3}$) |
| Tier 1 | 0.38 | 7.2 | 0.37 | 6.9 | | | | |
| Tier 2 | - | - | | | | | | |
| Tier 3 | 8.3E-3 | 0.11 | 8.2E-3 | 0.11 | 0.19 – 0.24 | 2.0 – 3.3 | 0.16 – 0.19 | 1.6 – 2.7 |

$^{\#}$ TWA period of 42 days chosen because of the duration of the tests with potworms

Seven years post last application third tier $PEC_s$ values are calculated to be 0.0083 mg kg$^{-1}$ and 0.11 µg dm$^{-3}$ for total content and pore water, respectively. These values are about 1 – 2% of the Tier 1 $PEC_s$values. The third tier $PEC_s$ values are lower than the calculated third tier $RAC_{ETP}$ values reported in Table 2.15. Consequently, the ETP decision tree indicates acceptable risks, for momentary and TWA values, for both total contents and pore water concentrations.

## 2.9 Discussion points for risk assessment

After the evaluation of the soil transformation studies, both laboratory and field, insufficient $DegT_{50}$ values remained for a proper risk evaluation. The registration procedure requires at least four transformation rate values.

Adequate tests that studied the sensitivity of soil fungi were not available. This is expected since toxicity data for soil fungi currently are not required in the European risk assessment procedure for non-target soil organisms. As carbendazim is a fungicide, it is expected that soil fungi might be sensitive. However, fungi are a very diverse group and therefore, with the current state of knowlegde, it is difficult to make a general statement to their response to fungicidal pesticides. The presence of tests with soil fungi is strongly recommended to underpin the risk evalution.

The responses of soil dwelling organisms in laboratory single species tests and (semi-)field experiments revealed that, although potworms (Enchytraeidae) comprised the most sensitive species, also other taxonomic groups of worms may be sensitive. In aquatic studies performed with carbendazim also worms were among the most sensitive species (Cuppen et al., 2000; Van den Brink et al., 2000; Van Wijngaarden et al., 1998). The decision to use the results of the field experiments is based on the expert judgement that the experience with the aquatic data can be extrapolated to the soil environment. In-crop effects on micro-organisms were observed in soil communities, but recovery of function is reported to be rapid (Van den Brink et al., 2007).

The PEC/RAC ratios based on pore water concentrations are slightly higher than the ratios based on total contents, for both CRP and FRP.

The data presented in this evaluation do not indicate inconsistencies within decision trees (different tiers) or between decision trees (for CRP and ERP). However, the lack of laboratory toxicity data for additional soil species did not allow to evaluate the SSD approach.

# 3 Chlorpyrifos

## 3.1 Overview of selected chlorpyrifos uses

Chlorpyrifos is an organophosphate insecticide that is used to control insect pests by disrupting the nervous system of insects. In the EU, application in vineyards is considered as safe use. The advised dose is 0.245 kg $ha^{-1}$ for this treatment. In the Netherlands a granular application of chlorpyrifos is used in tree nurseries and chlorpyrifos is used as seed treatment of cabbage (advised dose 4.8 g $ha^{-1}$). We performed a GeoPEARL calculation for the application in vineyards only since the advised dose for this treatment is highest. The application is at growth stage BBCH 53, 55 or 57 (before flowering).

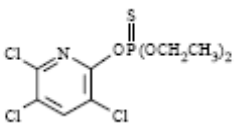
Table 3.1 Selected chlorpyrifos uses

| **substance** | **crop** | **formulation** | **frequency** | **dose** | **BBCH** | **interception** |
|---|---|---|---|---|---|---|
| chlorpyrifos | grape vine | EC | 1 (1 May) | 0.245 kg $ha^{-1}$ | 53, 55 or 57 | 0% (application type: to the soil surface) |

## 3.2 Relevant fate parameters of chlorpyrifos

### 3.2.1 Physico-chemical properties of chlorpyrifos

Table 3.2 Basic data of chlorpyrifos

| | |
|---|---|
| ISO name | CHLORPYRIFOS |
| IUPAC | O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate |
| CAS | 2921-88-2 |
| Purity | 970 g $kg^{-1}$ |
| Molecular formula | $C_9H_{11}Cl_3NO_3PS$ |
| Structure |  |

Molecular mass, vapour pressure and solubility in water are taken from the List of End points (SANCO/3059/99 – rev. 1.5 3, June 2005 of chlorpyrifos).

The mean $K_{OC}$ of five soils (5501 $dm^3$ $kg^{-1}$ at 20 ± 1 °C) given in the monograph (Damon and Heim, 2001) is taken. For GeoPEARL calculations $K_{OM}$ values are needed instead of $K_{OC}$ values. The conversion factor of 1.724 (FOCUS, 2000) is used to calculate $K_{OM}$ from $K_{OC}$. From the same study the mean Freundlich exponent of the same five soils is taken as input for fate calculations.

Concerning half-lives in soil, both laboratory degradation studies and field dissipation studies are available. A laboratory degradation study using four soils is described in the monograph (Annex B Chapter 8, December 2002). The measured $DegT_{50}$ values are normalized to pF2 (field capacity) by multiplying the measured $DegT_{50}$ values with a correction factor (Walker, 1974). The procedure for calculating the correction factor is as follows:

- The laboratory degradation study is undertaken at 40% maximum water holding capacity ($WHC_{max}$). The moisture content under study conditions is calculated by multiplying the $WHC_{max}$ with 0.4.
- Using the water content at pF2 from different soil textures given in Table 5.2 of FOCUS (2000) as reference moisture content the correction factor according to Eq.3.1 is calculated (see Table 3.3a).

$$f = \left( \theta / \theta_{ref} \right)^{0.7} \qquad \text{Eq.3.1}$$

where:

| | |
|---|---|
| f | soil moisture correction factor |
| θ | moisture content under study conditions |
| $\theta_{ref}$ | reference moisture content at pF2 from reference soil texture (Table 5.2 in FOCUS, 2000) |

For each soil, the measured $DegT_{50}$ from the laboratory degradation study is multiplied by the correction factor in order to normalize the $DegT_{50}$ to pF2. Next normalized $DegT_{50}$ values at 10°C are calculated from normalized $DegT_{50}$ at 20°C with Eq.3.2 (see Table 3.3b):

$$DegT_{50,10°C} = DegT_{50,20°C} \; Q_{10}^{((T_{act} - T_{ref})/10)} \qquad \text{Eq.3.2}$$

where:

| | |
|---|---|
| $DegT_{50,10°C}$ | half-life at 10°C ($T_{act}$), (d) |
| $DegT_{50,20°C}$ | half-life at 20°C ($T_{ref}$), (d) |
| $Q_{10}$ | factor accounting for the mean activation energy for pesticide degradation in the soil (default 2.2, FOCUS, 2000) |
| $T_{act}$ | actual temperature (10°C) |
| $T_{ref}$ | reference temperature (20°C) |

Table 3.3a Normalization of $DegT_{50}$'s to reference moisture conditions

| soil | soil texture | WHCmax measured (% w/w) | moisture content under study conditions (% w/w) | reference moisture content at pF2 (%) | correction factor (-) |
|---|---|---|---|---|---|
| Marcham | sandy clay loam | 45.6 | 18.24 | 22 | 0.877 |
| Charentilly | silty clay loam | 44.3 | 17.72 | 30 | 0.692 |
| Cuckney | sandy clay loam | 34.9 | 13.96 | 22 | 0.727 |
| Thessaloniki | sandy silt loam | 43.4 | 17.36 | 19* | 0.939 |

* sandy silt loam is not given in Table 5.2 FOCUS (2000): the value of sandy loam is used
*study is undertaken at 40 % $WHC_{max}$*

Table 3.3b Normalization of $DegT_{50}$'s to reference moisture and temperature conditions

| soil | soil texture | $DegT_{50}$ measured | $DegT_{50}$ normalized to pF2 (20°C) | $DegT_{50}$ normalized to pF2 (10°C) |
|---|---|---|---|---|
| | | (d) | (d) | (d) |
| Marcham | sandy clay loam | 43 | 37.7 | 83.0 |
| Charentilly | silty clay loam | 95 | 65.7 | 144.6 |
| Cuckney | sandy clay loam | 111 | 80.7 | 177.6 |
| Thessaloniki | sandy silt loam | 46 | 43.2 | 95.0 |
| arithmetic mean of $DegT_{50}$'s | | | 56.8 | 125.0 |
| geometric mean of $DegT_{50}$'s | | | 54.2 | 119.3 |

In case of chlorpyrifos field dissipation studies are available. Field results are preferred over laboratory results because they are determined under conditions specific for the intended use of a pesticide in an agricultural field and thus closely match the situation which is to be modelled (FOCUS, 2006). Assessment of the field dissipation studies is therefore necessary. The assessment of the field dissipation studies of chlorpyrifos is described in Appendix 3.

Information on fractions transformed is given in Monograph Annex B Chapter 8, December 2002, p 8-10 and Monograph Chapter 7, 1999, p. 614. Table 3.4 gives the maximum percentages transformed to the metabolite trichlorpyridinol (TCP) found in different studies. For calculations with GeoPEARL the average of the maximum percentages transformed to the metabolite (TCP) of the different studies is taken as an approximation for the formation fraction of TCP from chlorpyrifos.

Table 3.4 Maximum TCP contents in chlorpyrifos transformation studies

| soil | maximum TCP content (molar% of applied chlorpyrifos) | source |
|---|---|---|
| sandy clay loam, Marcham, UK | 38.6 | Monograph Annex B, Chapter 8, December, 2002, p. 8 |
| silty clay loam Charentilly, France | 5.5 | |
| sand, Cuckney, UK | 6.5 | |
| sandy silt loam, Thessaloniki, Greece | 50.0 | |
| clay loam, Chehalis | 29.7 | Monograph, Chapter 7, 1999, p. 614 |
| silt loam, Sultan | 34.4 | |

Table 3.5 gives relevant fate parameters of chlorpyrifos used in risk assessment exposure calculations.

Table 3.5 Relevant fate parameters of chlorpyrifos

| parameter | value + unit | source |
|---|---|---|
| molecular mass | 350.6 g $mol^{-1}$ | List of End points SANCO/3059/99 – rev. 1.5 3, June, 2005 |
| vapour pressure | 1.43 E-3 Pa (20 °C) | |
| solubility in water | 1.05 mg $dm^{-3}$ (20 °C) | |
| $K_{OM}$ | 3190.8 $dm^3$ $kg^{-1}$ (20 ± 1 °C) | Damon and Heim, 2001; Monograph chapter 8, p 36/37, December, 2002 |
| Freundlich exponent (1/n) | 0.91 (-) | Monograph Annex B, Chapter 8, December, 2002 |
| $DegT_{50,lab}$ | arithmetic mean: 56.8 d (pF2, 20°C)<br>geometric mean: 54.2 d (pF2, 20°C)<br>arithmetic mean: 125.0 d (pF2, 10°C)<br>geometric mean: 119.3 d (pF2, 10°C) | Monograph Annex B, Chapter 8, December, 2002 |
| $DegT_{50,field}$ | arithmetic mean: 17.4 d (pF2, 20°C)<br>geometric mean: 15.5 d (pF2, 20°C)<br>arithmetic mean: 38.3 (pF2, 10°C)<br>geometric mean: 34.1 (pF2, 10°C) | Monograph Chapter 7, 1999<br>Monograph Annex B, Chapter 8, December, 2002<br><br>Re-evaluation: Appendix 3 of this report |
| Formation fraction TCP from chlorpyrifos | 0.2745 (-) | Monograph Chapter 7, 1999<br>Monograph Annex B, Chapter 8, December, 2002 |

### 3.2.2 Assessment of field dissipation studies of chlorpyrifos

Appendix 3 gives details of the assessment of the field dissipation studies of chlorpyrifos. It shows that the $DegT_{50,field}$ values derived from the field studies are considerably different from the $DegT_{50,lab}$. Degradation in the field is faster than degradation in the laboratory. Therefore the geometric mean of the $DegT_{50,field}$ values (15.5 days (20 °C, pF2)) will be used for the calculation of exposure levels in the risk assessment.

## 3.3 Trigger values chlorpyrifos

The $DegT_{50,field}$ of chlorpyrifos is considerably different from the $DegT_{50,lab}$. Degradation in the field is faster than degradation in the laboratory. The $DegT_{50,field}$ values are preferred because these reflect practice better. The Ministries of LNV and VROM have chosen for $DT_{50}$ trigger values that are related to a temperature of 10 °C and pF2 as reference conditions (Van der Linden et al., 2006). The geometric mean of the $DegT_{50,field}$ values (34.1 days (10 °C, pF2)) will be used for comparison with the $DT_{50}$ trigger values of the FRP, CRP and ETP.

For chlorpyrifos the $DegT_{50}$ values based on field data overrule the $DegT_{50}$ values based on laboratory data. The calculated $DegT_{50}$ (20°C, pF2) and $DegT_{50}$ (10°C, pF2) values on basis of field studies are 15.5 and 34.1 days, respectively. If the $DegT_{50}$ (10°C, pF2) value is used, only a risk assessment in line with the Functional Redundancy Principle (FRP) is triggered (trigger value $DT_{50}$ > 30 d). However, if the existing procedure as described in the EU Guidance Document on Terrestrial Ecotoxicology is followed, the $DegT_{50}$ (20°C, pF2) has to be used to assess whether a litter bag study has to be performed or not. The calculated field $DegT_{50}$ (20°C, pF2) does not trigger a risk assessment in line with the FRP.

To study the consistency of the proposed decision trees the effect assessments for all protection goals will be performed, despite the fact that the field $DegT_{50}$ (20°C, pF2) calculated for chlorpyrifos does not trigger a risk assessment in line with the FRP, and the field $DegT_{50}$ (10°C, pF2) value does not trigger risk assessments in line with the Community Recovery Principle (CRP) nor isk assessment in line with the Ecological Threshold Principle (ETP).

## 3.4 Input for exposure calculations

**$PEC_s$**

The concentrations of chlorpyrifos and its metabolite TCP in soil and/or pore water are needed to assess the risk for soil organisms of persistent substances according to the community recovery principle (CRP) and the ecological threshold principle (ETP). The $PEC_s$ for spray applications is calculated for the upper 5 cm of soil.

**Tier 1**

Input variables are the actual worst-case application rate of 0.245 kg $ha^{-1}$ and the assumption of no interception and no tillage using a soil bulk density of 1000 kg $m^{-3}$. The calculation is independent of the crop and the time of application. For metabolites all available data concerning substance properties are regarded. The following input data are used for the calculation:

**Tier 1 input for chlorpyrifos and TCP**

**Active substance**:
Geometric mean $DegT_{50,lab}$ for degradation in soil (20°C): 54.2 d
Mean $K_{OM}$ (pH-independent): 3190.8 $dm^3\ kg^{-1}$
Molecular weight: 350.6 g $mol^{-1}$

**Metabolite:**
Geometric mean $DT_{50,lab}$ for degradation in soil (20°C): 21.1 d
$K_{OM,acid}$: 1190.8 $dm^3\ kg^{-1}$ (used for calculating total content)
$K_{OM,base}$: 63.7 $dm^3\ kg^{-1}$ (used for calculating pore water concentration)
Molecular weight: 198.4 g $mol^{-1}$
Formation fraction metabolite: 0.2745

Other parameters: standard settings of Tier 1 calculation programme

**GeoPEARL**

In the third tier (no second tier developed), concentrations of chlorpyrifos and its metabolite in soil and/or pore water in potential area of use is evaluated using the spatially distributed model GeoPEARL 3.3.3.
Input variables are the actual worst-case application scheme 0.245 kg $ha^{-1}$, the crop vines (in GeoPearl represented by the crop "fruit culture") and a worst case assumption for interception: pesticide applied to the soil surface. Tillage is included in the calculations. Date of yearly application is 1 May. For metabolites all available data concerning substance properties are regarded. The following input data are used for the calculation:

**GeoPEARL input for chlorpyrifos and TCP**

**Active substance**:
Geometric mean $DegT_{50,field}$ for degradation in soil (20°C): 15.5 d
Mean $K_{OM}$ (pH-independent): 3190.8 $dm^3\ kg^{-1}$
1/n: 0.91
Saturated vapour pressure: 1.43 E-3 Pa (20 °C)
Solubility in water: 1.05 mg $dm^{-3}$ (20 °C)
Molecular weight: 350.6 g $mol^{-1}$
Formation fraction metabolite TCP: 0.2745 (-)

**Metabolite:**
Worst case $DT_{50,field}$ for degradation in soil (20°C): 111 d
$K_{OM,acid}$: 1190.8 $dm^3\ kg^{-1}$
$K_{OM,base}$: 63.7 $dm^3\ kg^{-1}$
1/n: 0.90 (-)
$pK_a$: 4.55 (-)
Saturated vapour pressure: 1.64E-7 Pa (25°C)

Solubility in water: 220 mg $dm^{-3}$ (20°C)
Molecular weight: 198.4 g $mol^{-1}$

**For both substances:**
Non-equilibrium sorption is assumed:
Desorption rate coefficient: 0.01 $d^{-1}$ (default)
Factor relating CofFreNeq and CofFreEql: 0.5 (-, default)

Crop: fruit culture
Number of plots (minimum 250): 250

Other parameters: standard settings of GeoPEARL 3.3.3

## 3.5 Ecotoxicological endpoints of chlorpyrifos

### 3.5.1 Ecotoxicological endpoints in line with the FRP

In the decision tree for in-crop effect assessment in line with the FRP, that is largely based on the EU Guidance Document on Terrestrial Ecotoxicology, it is first checked if the predicted exposure concentration of the substance leads to toxic effects on earthworms or soil micro-organisms ($PIEC_{s,tc} < 0.2*NOEC_{earthworms}$ or effects on SMO < 25%). Application of chlorpyrifos at a rate of 245 g $ha^{-1}$ will result in a $PIEC_{s,tc}$ value of 0.425 mg $kg^{-1}$. The selected 56-d $NOEC_{repro}$ for earthworms is 12.7 mg $kg^{-1}$ (*Eisenia fetida*; Hayward, 2002 in EU dossier; see Table 3.6). On basis of this toxicity value the $PIEC_{s,tc} < 0.2*NOEC_{earthworms}$. In addition, in the EU dossier no significant effects on soil microorganisms are reported at 4.8 kg $ha^{-1}$, indicating that at a $PIEC_{s,tc}$ value of 0.425 mg $kg^{-1}$ (equivalent to 245 g $ha^{-1}$) no effects on soil micro-organisms are expected.

If the predicted exposure of the substance ($PIEC_{s,tc}$) is not toxic to earthworms or soil micro-organisms, as is demonstrated above for chlorpyrifos, it is checked whether the substance is toxic to non-target arthropods (*Standard arthropods HQ < 2*). The HQ approach is currently validated for *Typhlodromus pyri* and *Aphidius rhopalosiphi* only. However, relevant standard toxicity data for these species are not reported in the DAR list of endpoints. Consequently, it cannot be excluded that the predicted exposure concentration of chlorpyrifos is harmful to these non-target arthropods.

Table 3.6 Laboratory toxicity tests reported for earthworms in EU dossier for chlorpyrifos (italics) and open literature. Note that the EU dossier sometimes wrongly cites data from the literature. Here the correct values are reported. The toxicity value used in the EU dossier to perform the long-term risk assessment for earthworms is given in bold.

| Species | Formulation | OM % | Days | Endpoint | Value mg $kg^{-1}$ | Value µg $dm^{-3}$ | Reference |
|---|---|---|---|---|---|---|---|
| *Eisenia fetida* | *Tech.* | *10* | *14* | $LC_{50}$ | *1077* | *2328.4* | *Ma and Bodt, 1993* |
| *Eisenia fetida* | *Dursban 5G* | *10* | *14* | $LC_{50}$ | *209.9* | *453.8** | *Rodgers et al. 1994 OECD 207* |
| *Eisenia fetida* | *480* g $dm^{-3}$ *EC* | *10* | *14* | $LC_{50}$ | *152* | *328.6** | *Candolfi, 1996 OECD 207* |
| *Eisenia fetida* | *Dursban 480* | *10* | *14* | $LC_{50}$ | *137* | *396.2** | *Johnson, 1993 OECD 207* |
| *Eisenia fetida* | *active substance* | *10* | *14* | *NOEC (mortality)* | *486* | *1050.7* | *Ma and Bodt, 1993* |
| ***Eisenia fetida*** | ***Dursban 480 EC*** | ***10 ?*** | ***56*** | ***NOEC (repro)*** | ***12.7*** | ***27.5**** | ***Hayward 2002 (ISO 11268-2)*** |
| *Eisenia veneta* | *Technical* | *10* | *14* | $LC_{50}$ | *1174* | *2538.1* | *Ma and Bodt, 1993* |
| *Eisenia veneta* | *Technical* | *10* | *14* | *NOEC (mortality)* | *875* | *1891.7* | *Ma and Bodt, 1993* |
| Eisenia veneta | Technical | 3.7 | 14 | NOEC (repro) | 49 | 285.7** | Ma and Bodt, 1993 (field soil) |
| Aporrectodea caliginosa | Technical | 3.78 | 14 | $LC_{50}$ | 69 | 394.5 | Booth, 2000 OECD 207 |
| *Aporrectodea caliginosa* | *Technical* | *10* | *14* | $LC_{50}$ | *755* | *1632.2* | *Ma and Bodt, 1993* |
| *Aporrectodea caliginosa* | *Technical* | *10* | *14* | *NOEC (mortality)* | *486* | *1050.7* | *Ma and Bodt, 1993* |
| *Aporrectodea longa* | *Technical* | *10* | *14* | $LC_{50}$ | *778* | *1682.0* | *Ma and Bodt, 1993* |
| *Aporrectodea longa* | *Technical* | *10* | *14* | *NOEC (mortality)* | *486* | *1050.7* | *Ma and Bodt, 1993* |
| *Lumbriculus rubellus* | *Technical* | *10* | *14* | $LC_{50}$ | *129* | *278.9* | *Ma and Bodt, 1993* |
| Lumbriculus rubellus | Technical | 3.7 | 14 | $LC_{50}$ | 262 | 1527.8** | Ma and Bodt, 1993 |
| *Lumbriculus rubellus* | *Technical* | *10* | *14* | *NOEC (mortality)* | *83* | *179.4* | *Ma and Bodt, 1993* |
| Lumbriculus rubellus | Technical | 3.7 | 14 | NOEC (mortality) | 150 | 874.7** | Ma and Bodt, 1993 |
| Lumbriculus rubellus | Technical | 3.7 | 14 | NOEC (repro) | 4.6 | 26.8** | Ma and Bodt, 1993 |
| *Lumbriculus terrestris* | *Technical* | *10* | *14* | $LC_{50}$ | *458* | *990.1* | *Ma and Bodt, 1993* |
| *Lumbriculus terrestris* | *Technical* | *10* | *14* | *NOEC* | *270* | *583.7* | *Ma and Bodt, 1993* |

* No information on soil properties available. Default values used to calculated pore water concentration (OM 10%, moisture content: 0.5 $dm^3$ $dm^{-3}$; guideline OECD 222)

** the artificial soil is replaced with a natural sandy soil (Kooyenburg). It is not specified whether the moisture content of this soil is kept at the same value as the artificial soil, but it is assumed that this is the case (moisture content: 0.55 $dm^3$ $dm^{-3}$).

For the calculation of all pore water concentrations in Table 3.6 the maximum $K_{OM}$ of 4620.07 $dm^3$ $kg^{-1}$ reported in the dossier is used (recommended in Van der Linden et al., 2006, pag. 68).

A litter bag study is required if also the criteria $PIEC_{s,tc} < 0.2*NOEC_{collembola}$ or $PIEC_{s,tc} < 0.2*NOEC_{mite}$ are not met. The dossier gives no NOEC data for soil dwelling Collembola and the soil mite *Hypoaspis aculeifer*. In the open literature a 28-d NOEC of 0.065 mg $kg^{-1}$ (recalculated value of 0.059 mg $kg^{-1}$) is reported for *Folsomia candida* (see Table 3.8 and Table 3.9), indicating that the $PIEC_{s,tc} > 0.2*NOEC_{collembola}$. Consequently a litter bag study is required.

According to the dossier, a litter bag study is not available. Within the context of the existing procedure as described in the EU Guidance Document for Terrestrial Ecotoxicology this is not unexpected, since the $DegT_{50}$ (20°C,pF2) of 15.5 days does not trigger the effect assessment in line with the FRP.

## 3.5.2 Ecotoxicological endpoints in line with the CRP and ETP

**Laboratory toxicity tests with earthworms**

In the EU dossier the reported toxicity data on soil organisms predominantly comprise earthworms. In Table 3.6 the laboratory toxicity data reported for earthworms in the EU dossier (italics) and open literature are reported. Only one 56-d chronic $NOEC_{repro}$ value is reported for *Eisenia fetida*. This value is also used in the EU dossier. The majority of toxicity data reported in Table 3.7 comprise acute $LC_{50}$ values for six different species. As already discussed by Jänsch et al. (2006), sufficient acute toxicity data only are available to apply the SSD approach to assess the risks for earthworms. According to Jänsch et al. (2006), the median $HC_5$ value based on $LC_{50}$ values for six different species of earthworms is 124.8 mg $kg^{-1}$ and its lower limit is 25.8 mg $kg^{-1}$. Even this lower limit value is more than two orders of magnitude higher than the $LC_{50}$ for the soil arthropod *Folsomia candida* (see below), indicating that earthworms do not comprise the sensitive taxonomic group for chlorpyrifos.

**Laboratory toxicity tests with soil-dwelling arthropods**

In the EU dossier no toxicity data for soil dwelling arthropods are reported. In the open literature $LC_{50}$ values and a NOEC value for the Collembola *Folsomia candida* were found (Table 3.7). Detailed examination of the lowest toxicity value (NOEC = 0.065 mg $kg^{-1}$) provided by Herbert et al. (2004) reveals that the reported toxicity values are based on nominal treatment levels and that the test substance was added to the soil five days before the test animals were introduced. For this reason we recalculated the expected exposure concentration in the *Folsomia candida* laboratory toxicity test performed by Herbert et al. (2004). The recalculated values are reported in Table 3.8. The calculated soil exposure concentrations on t = 0 (the day that test animals were introduced in the test systems) resulted in a NOEC of 0.0593 mg $kg^{-1}$ for the total soil and 0.128 µg $dm^{-3}$ for pore water. On basis of the TWA concentrations for the exposure duration of the toxicity test (28 d) the corresponding NOECs were 0.0463 mg $kg^{-1}$ and 0.1002 µg $dm^{-3}$, respectively.

Table 3.7 Laboratory toxicity data for soil dwelling arthropods as reported in the open literature

| species | 'formulation | OM % | duration (d) | endpoint | value (mg $kg^{-1}$) | reference |
|---|---|---|---|---|---|---|
| *Folsomia candida* | Technical | 10 ? | 35 | $LC_{50}$ | 0.24 (0.20 – 0.28) | Crommentuijn et al., 1995 (OECD 207) |
| *Folsomia candida* | Technical ? | 10 % peat | 28 | $LC_{50}$<br>NOEC | 0.18 – 0.28<br>0.065 | Herbert et al., 2004 (ISO 1999) |

Table 3.8a Recalculated 35-d $LC_{50}$ values for Folsomia candida and chlorpyrifos after Crommentuijn et al. (1995), see Table 3.7

| | values based on t = 0 concentrations | values based on $TWA_{35}$ concentrations |
|---|---|---|
| **total content soil** | 0.24 mg $kg^{-1}$ | 0.117 mg $kg^{-1}$ |
| **pore water** | 0.1589 µg $dm^{-3}$ | 0.383 µg $dm^{-3}$ |

Table 3.8b Recalculated 28-d NOEC values for Folsomia candida and chlorpyrifos after Herbert et al. (2004), see Table 3.7

| | values based on t = 0 concentrations | values based on $TWA_{28}$ concentrations |
|---|---|---|
| **total content soil** | 0.0593 mg $kg^{-1}$ | 0.0463 mg $kg^{-1}$ |
| **pore water** | 0.128 µg $dm^{-3}$ | 0.1002 µg $dm^{-3}$ |

**Laboratory toxicity tests with soil algae and rooted plants**

In the EU dossier no toxicity data for soil algae and rooted terrestrial vascular plants are reported. For soil algae the review paper of Barron and Woodburn (1995) reports 5-d $EC_{50}$ values in the range of 6000 - 41700 µg $dm^{-3}$. The lowest consistent NOEC for these algae (100 µg $dm^{-3}$) is reported for *Chlorococcum minitum* (Nikolenko and Amirkhanov, 1993).

Aben et al. (1992) report 10-d EC50 values of 26 - 75 mg $kg^{-1}$ in tests studying the germination and emergence of the mustard species *Arabidopsis thaliana* in three different types of soil. Lockly and Laiche (1990) evaluated the phytotoxicity (reduction in root and non-root biomass) of chlorpyrifos in standard potting medium to foliage and woody landscape plants. Of the 39 cultivars tested with granular chlorpyrifos mixed with soil, concentrations of 25.2 mg $kg^{-1}$ soil did not affect any cultivar (see also Barron and Woodburn, 1995).

**Laboratory toxicity tests with other soil dwelling taxa**

For soil-dwelling invertebrates other than earthworms and Collembola no single species toxicity data are available in the EU dossier. In addition, in the review papers of Frampton et al. (2006) and Jänsch et al. (2006) no toxicity data of soil invertebrates that do not belong to earthworms or Collembola are reported. Aben et al. (1992) reported 48-h $LC_{50}$ values for the nematode *Globodera rostochiencsis* in the range of 1.1 – 1.6 µg $dm^{-3}$ in soil pore water and 1.1 – 2.9 mg $kg^{-1}$ soil in tests with three different soil types.

**Semi-field tests**

In the DAR list of endpoints no semi-field studies focussing on soil-dwelling invertebrates are reported from which an appropriate NOEC for the soil community can be derived. Study J78 (Brown, 1993) describes the effects of Dursban on predatory epigeal arthropods in grassland and not on soil-dwelling arthropods.

In the open literature a nice overview of the effects of chlorpyrifos on soil invertebrates in model ecosystems and field studies is presented by Jänsch et al. (2006). However, on basis of available higher tier tests a NOEC for soil dwelling invertebrates could not be derived. The best LOEC estimate was

≤ 0.64 mg $kg^{-1}$ (based on the peak concentration) or ≤ 0.57 mg $kg^{-1}$ (based on TWA28 concentrations). This LOEC comprises slight short-term to pronounced effects on Collembola.

## 3.6 CRP effect assessment

On basis of the toxic mode-of-action of chlorpyrifos, laboratory toxicity tests with soil organisms and results of (semi)field tests it appears that terrestrial arthropods are the most sensitive taxonomic group. For the basic set of standard test species only for earthworms a 56-d chronic NOEC value is reported in the EU dossier. However, the open literature provides additional long-term toxicity data for plants (the soil alga *Chroococcum minutum* and vascular plants) and for the soil arthropod *Folsomia candida* that can be used for the derivation of a Regulatory Acceptable Concentration (RAC) (see summary Table 3.9).

Table 3.9 Summary of relevant long-term toxicity data for soil organisms reported in the EU dossier and the open literature. For more detailed information see the text. Note that the reported total soil concents are not corrected for OM content of the test soil.

| | **long-term NOEC** | | | |
|---|---|---|---|---|
| | **total soil (mg $kg^{-1}$)** | | **pore water (µg $dm^{-3}$)** | |
| | t = 0 | $TWA_{28}$ | t = 0 | $TWA_{28}$ |
| *Eisenia fetida* (earthworm) | 12.7 | 9.9 | 27.3 | 21.5 |
| *Chroococcum minutum* (alga) | | | 100 | |
| Vascular plants | (25.2) | | | |
| *Folsomia candida* (arthropod) | 0.059 | 0.0463 | 0.128 | 0.1002 |

**First tier (standard test species approach)**
When taking into account the open literature data as well, NOEC data are available for at least one representive of earthworms, plants and arthropods. The Regulatory Acceptable Concentrations ($RAC_{CRP}$) that can be derived are based on the available NOECs re-calculated for *Folsomia candida*, which is the most sensitive species mentioned. The application of an AF of 10 to the *Folsomia* NOEC values results in $RAC_{CRP}$ values of 0.0059 mg $kg^{-1}$ (based on the t = 0 concentration in total soil of the toxicity test), 0.00463 mg $kg^{-1}$ (based on $TWA_{28}$ concentration in total soil), 0.0128 µg $dm^{-3}$ (based on the t = 0 concentration in pore water) and 0.01002 µg $dm^{-3}$ (based on the $TWA_{28}$ concentration in pore water), respectively.

**Second tier (SSD approach)**
Assuming that arthropods are the most sensitive taxa an appropriate median $HC_5$ value cannot be derived, because only one chronic NOEC value is available for typical soil arthropods. Also the TGD approach cannot be applied because insufficient chronic NOEC data (< 10) are reported for an insufficient number of taxonomic groups (< 8).

**Third tier (model ecosystem approach)**
An overall LOEC for sensitive endpoints of ≤ 0.64 mg $kg^{-1}$ (PIEC) is reported by Jänsch et al. (2006). This LOEC was derived from two different semi-field studies. In one of these studies this LOEC comprised effects of small magnitude (≤ 30%) and short duration (< 100 d) on soil-dwelling

Collembola. In the second study this LOEC concerned a pronounced effect in a short-term study (recovery not adequately studied). The reported LOEC value corresponds with a $TWA_{28}$ concentration of 0.57 mg $kg^{-1}$. Strictly speaking a third-tier $RAC_{CRP}$ cannot be derived because the highest concentration studied in the semi-field test at least resulted in short-term effects on Collembola. Application of an Uncertainty Factor (UF) of 3 will at least result in a third-tier $RAC_{CRP}$ of < 0.21 mg $kg^{-1}$ (PIEC) and < 0.19 mg $kg^{-1}$ ($TWA_{28}$).

## 3.7 ETP effect assessment

The application of an AF of 100 to the *Folsomia* NOEC values results in $RAC_{ETP}$ values of 0.00059 mg $kg^{-1}$ (based on the t = 0 concentration in total soil of the toxicity test), 0.000463 mg $kg^{-1}$ (based on the $TWA_{28}$ concentration in total soil), 0.00128 µg $dm^{-3}$ (based on the t = 0 concentration in pore water of toxicity test) and 0.001002 µg $dm^{-3}$ (based on $TWA_{28}$ concentration in pore water), respectively.

**Second tier (SSD approach)**
Assuming that arthropods are the most sensitive taxa an appropriate lower limit $HC_5$ value cannot be derived, because only one chronic NOEC value is available for typical soil arthropods. Also the TGD approach cannot be applied because insufficient chronic NOEC data (< 10) are reported for an insufficient number of taxonomic groups (< 8).

**Third tier (model ecosystem approach)**
This higher tier approach is not possible because of the lowest concentration tested resulted in effects (see CRP). Application of an Uncertainty Factor (UF) of 9 to the observed LOEC of the semi-field study will at least result in a third-tier $RAC_{ETP}$ of < 0.07 mg $kg^{-1}$ (PIEC) and < 0.06 mg $kg^{-1}$ ($TWA_{28}$).

## 3.8 Chlorpyrifos persistency risk assessment

### 3.8.1 Functional Redundancy Principle

Table 3.10 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) in line with the Functional Redundancy Principle (FRP)

| | **$PIEC_{s,tc}$** | **$PIEC_{s,pw}$** | **$PEC^{\#}_{s,tc,TWA28}$** | **$PEC^{\#}_{s,pw,TWA28}$** | **$RAC_{FRP\ s,tc}$** | **$RAC_{FRP\ s,pw}$** | **$RAC^{\#}_{FRP\ s,tc,TWA28}$** | **$RAC^{\#}_{FRP\ s,pw,TWA28}$** |
|---|---|---|---|---|---|---|---|---|
| | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) |
| Tier 1 | 0.76 | 9.8 | 0.72 | 8.7 | * | * | * | * |
| Tier 2 | - | - | - | - | | | | |
| Tier 3 | 0.43 | 2.9 | 0.35 | 1.9 | | | | |

* litter bag study not available
# TWA of 28 days chosen because majority of chronic toxicity data are for this period

Within the year of application third tier $PIEC_s$ of 0.43 mg $kg^{-1}$ and 2.9 µg $dm^{-3}$ were calculated for total content and pore water, respectively. These values are about 50% respectively 25% of the Tier 1 values for total content and pore water. When using the $DegT_{50}$ (10°C, pF2) trigger value of 34.1 days a litter

bag study is required but not provided. Consequently, a proper risk assessment in line with the FRP cannot be performed. Within the context of the existing procedure as described in the EU Guidance Document for Terrestrial Ecotoxicology this is not unexpected, since the $DegT_{50}$ (20°C, pF2) of 15.5 days does not trigger the effect assessment in line with the FRP.

### 3.8.2 Community Recovery Principle

Table 3.11 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) in line with the Community Recovery Principle (CRP)

| | **$PEC_{s,tc,t=2y}$** | **$PEC_{s,pw,t=2y}$** | **$PEC^{\#}_{s,tc,t=2y,TWA28}$** | **$PEC^{\#}_{s,pw,t=2y,TWA28}$** | **$RAC_{CRP,s,tc}$** | **$RAC_{CRP,s,pw}$** | **$RAC^{\#}_{CRP,s,tc,TWA28}$** | **$RAC^{\#}_{CRP,s,pw,TWA28}$** |
|---|---|---|---|---|---|---|---|---|
| | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) |
| Tier 1 | 0.11 | 0.9 | 0.11 | 0.8 | 0.0059 | 0.0128 | 0.0049 | 0.0105 |
| Tier 2 | - | - | | | | | | |
| Tier 3 | 8.5E-4 | 1.7E-3 | 7.6E-4 | 1.2E-3 | < 0.21 | | < 0.19 | |

# TWA of 28 days chosen because majority of chronic toxicity data are for this period

Two years post last application third tier $PEC_s$ values are calculated to be 8.5 $10^{-4}$ mg $kg^{-1}$ for total content and 1.7 $10^{-3}$ µg $dm^{-3}$ for pore water. These third tier $PEC_s$ values are less than 1% of the Tier 1 $PEC_s$ values and substantially lower than the first tier $RAC_{CRP}$ values reported in Table 3.11. Consequently, the CRP decision tree indicates no risk, for momentary and TWA values, for both total contents and pore water concentrations. The PEC/RAC values for pore water assessments are slightly lower than those for total content assessments.

### 3.8.3 Ecological Threshold Principle

Table 3.12 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) in line with the Ecological Threshold Principle (ETP)

| | **$PEC_{s,tc,t=7y}$** | **$PEC_{s,pw,t=7y}$** | **$PEC^{\#}_{s,tc,t=7y,TWA28}$** | **$PEC^{\#}_{s,pw,t=7y,TWA28}$** | **$RAC_{ETP,s,tc}$** | **$RAC_{ETP,s,pw}$** | **$RAC^{\#}_{ETP,s,tc,TWA28}$** | **$RAC^{\#}_{ETP,s,pw,TWA28}$** |
|---|---|---|---|---|---|---|---|---|
| | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) |
| Tier 1 | 0.001 | <0.05 | 0.001 | <0.05 | 0.00059 | 0.00128 | 0.00049 | 0.00105 |
| Tier 2 | - | - | | | | | | |
| Tier 3 | <1E-7 | <1E-4 | <1E-7 | <1E-4 | < 0.07 | | < 0.06 | |

# TWA of 28 days chosen because majority of chronic toxicity data are for this period

Seven years post last application third tier $PEC_s$ values are calculated to be <1E-7 mg $kg^{-1}$ and <1E-4 µg $dm^{-3}$ for total content and pore water, respectively. These third tier $PEC_s$ values are less than 1% of their corresponding Tier 1 values and substantially lower than the first tier $RAC_{ETP}$ values reported in Table 3.12. Consequently, the ETP decision tree indicates no risk, for momentary and TWA values, for both total contents and pore water concentrations.

## 3.9 Discussion points for risk assessment

The calculated field $DegT_{50}$ (20° C, pF2) for chlorpyrifos of 15.5 days does not trigger the performance of a litter bag study nor long-term toxicity tests with soil arthropods, at least when following the current risk assessment procedure as described in the EU Guidance Document on Terrestrial Ecotoxicology. Consequently it seems logical that these data are not provided in the EU dossier. Therefore, the consistency of the FRP, CRP and ERP decision trees could only be checked by using data published in the open literature.

The published chronic toxicity data for soil dwelling organisms revealed that the collembolan *Folsomia candida* was the most sensitive soil-dwelling species tested in the laboratory. The long-term sensitivity of this species was more than two orders of magnitude higher than that of earthworms and plants. Also in semi-field tests Collembola were the most sensitive taxa that showed a treatment-related decline after chlorpyrifos application. The observation that arthropods are the most sensitive taxa is in line with the numerous toxicity data available for aquatic species and the specific toxic mode-of-action of chlorpyrifos (see for example Barron and Woodburn, 1995).

The data presented above illustrate that the results of the CRP and ERP risk assessment procedures are not in conflict with the $DegT_{50}$ trigger values of the proposed decision trees. In addition, these results do not indicate inconsistencies within decision trees (different tiers) or between decision trees (for CRP and ERP). However, the lack of laboratory toxicity data for additional soil (arthropod) species did not allow to evaluate the SSD approach. Furthermore, in the available semi-field tests relatively high chlorpyrifos concentrations were tested and the lowest concentration tested already caused treatment-related effects.

# 4 Paraquat

## 4.1 Overview of selected paraquat uses

The use of paraquat selected for this risk assessment is an application of 1.1 kg $ha^{-1}$ around 1 May in potatoes. In Dutch areas where starch potatoes are grown, potatoes may be grown every two years. Therefore the exposure assessment was based on the assumption that this application takes place every two years.

Table 4.1 Selected paraquat uses

| substance | crop | formulation | frequency | dose | BBCH | interception |
|---|---|---|---|---|---|---|
| paraquat | potatoes | SL | 1 (every 2 years, 1 May) | 1.1 kg $ha^{-1}$ | 9 | 0% (application type: to the soil surface) |

## 4.2 Relevant fate parameters of paraquat

### 4.2.1 Physico-chemical properties of paraquat

Table 4.2 Identity and seleced physico-chemical properties of paraquat

| | |
|---|---|
| ISO name | PARAQUAT |
| IUPAC | 1,1'-dimethyl-4,4'-bipyridinium |
| CAS | 4685-14-7 |
| Purity | >95% |
| Molecular formula | $C_{12}H_{14}N_2$ |
| Molar mass | 186.26 |
| Structure |  |
| solubility water | 620 g $dm^{-3}$ (20 °C) |
| vapour pressure | $<10^{-8}$ kPa (25 °C) |

The EU monograph reports that no measurable degradation was observed in a laboratory study with a sandy loam soil after 180 days of incubation. However, two long-term field studies carried out in the UK indicate a half-life due to degradation ranging from 5 to 20 years in soil. The accuracy of the estimated half-lives was in general low. The monograph reports additionally one long-term USA field

study which resulted in estimated half-lives ranging from 0.5 to 310 years. The accuracy of these values was reported to be low due to scatter in the residue levels and the monograph states that a more reliable estimate of the $DT_{50}$ is considered to be in the order of 10 to 20 years. Based on this information, it was assumed for the Dutch exposure assessment that the half-life in soil is 20 years at 10°C and at field capacity.

The EU monograph showed also evidence of photodegradation on plant surfaces, indicating losses due to photochemical degradation of 42 - 46% over a period of three weeks. However, we ignore losses due to photodegradation in the exposure assessment because spraying before potato emergence is unlikely to lead to a significant percentage of plant interception.

Dyson et al. (1994) reported sorption measurements of paraquat to soils performed by shaking 10 g of soil with 250 mL of water containing at least six different levels of fortification. Shaking time was 16 h. The supernatant was bioassayed using wheat seeds. The fortification level equivalent to a root length reduction of 50% was deduced from the dose-response curve. The sorption coefficient $K_D$ was calculated as $X / C$ where $X$ is mass of paraquat sorbed per mass of dry soil and $C$ is the concentration of paraquat in the water. The value of $C$ was assumed to be 0.01 mg $dm^{-3}$ based on other bioassays with wheat seeds. Dyson et al. (1994) summarized sorption studies from a number of EU countries but we restrict ourselves to the data collected for Dutch soils because these are most relevant for the Dutch risk assessment procedure. Figure 4.1 shows that the sorption coefficient was correlated to the clay content and that the sorption of paraquat is extremely high. Figure 4.2 zooms in on the results for the low clay contents and shows that there is considerable scatter in the relationship between $K_D$ and these clay contents.

First tier calculations were based on a half-life of 20 years at a reference temperature of 10 °C and a worst-case $K_D$ value of 2000 $dm^3\ kg^{-1}$. This is the lowest sorption coefficient of 37 Dutch soils including many sands with low clay contents as reported by Dyson et al., 1994 (see Figure 4.1 and Figure 4.2). Long-term sorption was not included in the Tier-1 exposure assessment because the sorption mechanism of paraquat is different from the mechanism of most other pesticides and because no measurements of long-term sorption of paraquat are available.

The Tier 3 calculations with GeoPEARL were also based on a half-life of 20 years at 10 °C and field capacity. The Arrhenius activation energy was assumed to be 54 kJ $mol^{-1}$ (default GeoPEARL). The GeoPEARL model includes an option for a sorption coefficient that is linearly proportional to the clay content:

$$K_D = a + b\, f_{clay} \qquad \text{Eq.4.1}$$

where

a intercept, ($m^3\ kg^{-1}$)

b slope, ($m^3\ kg^{-1}$)

$f_{clay}$ mass fraction of clay of the soil, ($kg\ kg^{-1}$).

However, GeoPEARL accepts only positive values of a and b. The measurements in Figure 4.1 imply that it will be difficult to obtain a good description of the data by Eq.4.1 if the intercept (a) cannot be negative. Therefore the regression was based on the sorption coefficients measured for clay contents below 10% as shown in Figure 4.2. This resulted in a = 2.7 $m^3\ kg^{-1}$ and b = 59.1 $m^3\ kg^{-1}$. Long-term

sorption was not included in the Tier 3 calculations because the sorption mechanism of paraquat is different from the sorption mechanism of most other pesticides.

In absence of data, the Freundlich exponent was assumed to be 0.9, which is the default value used in the Dutch leaching assessment. Information in open literature confirms that paraquat isotherms are not linear corresponding to Freundlich exponents less than 1 (Riley et al., 1976).

In the GeoPEARL simulations, the sorption of paraquat to soil is described with the following sorption isotherm equation:

$$X_{EQ} = K_{F,EQ}\, c_{L,R} \left( \frac{c_L}{c_{L,R}} \right)^N \qquad \text{Eq.4.2}$$

$c_L$ concentration in the liquid phase, (mg $dm^{-3}$)
$c_{L,R}$ reference concentration in the liquid phase, (mg $dm^{-3}$)
$X_{EQ}$ content sorbed at equilibrium sites, (mg $kg^{-1}$)
$K_{F,EQ}$ equilibrium Freundlich sorption coefficient, ($dm^3$ $kg^{-1}$)
N Freundlich exponent, (-).

As described before the $K_D$ values measured by Dyson et al. (1994) were based on a concentration in the liquid phase of 0.01 mg $dm^{-3}$. To ensure consistency with this approach, the reference concentration in the liquid phase was set to 0.01 mg $dm^{-3}$ (which is different from the conventional value of 1 mg $dm^{-3}$).

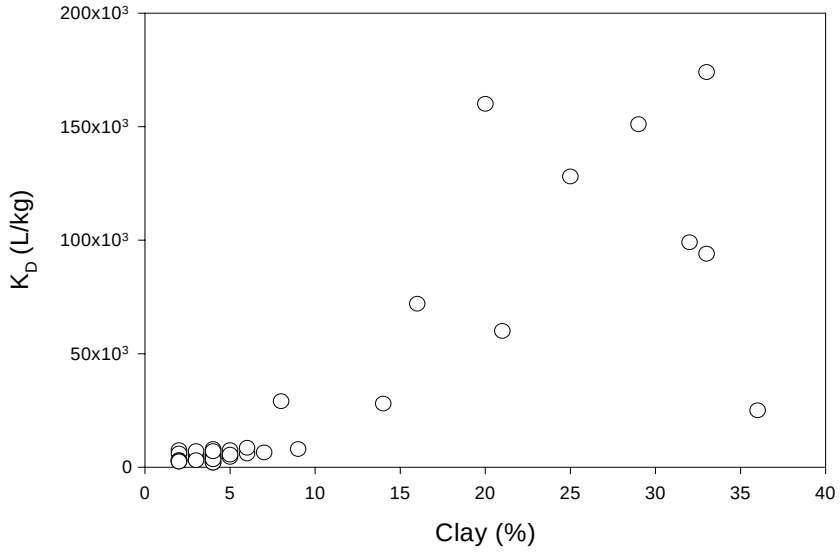



Figure 4.1 Sorption coefficients of paraquat as measured by Dyson et al. (1994) for a range of Dutch soils as a function of the mass fraction of clay of the soils

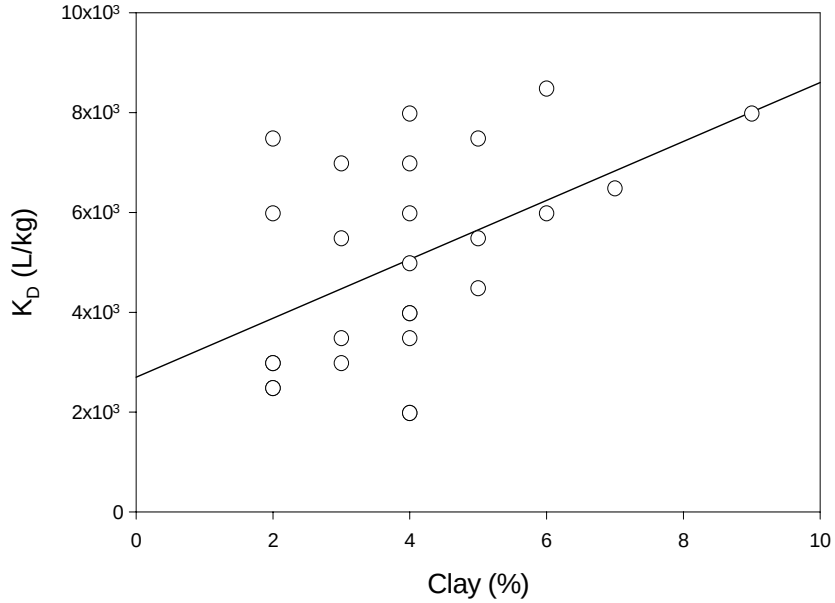



Figure 4.2 Sorption coefficients of paraquat as measured by Dyson et al. (1994) for Dutch soils with clay contents below 10% as a function of the mass fraction of clay of the soils. The points are measurements; the straight line is the result of linear regression analysis using Eq.4.1. One $K_D$ value of about 25000 $dm^3$ $kg^{-1}$ at a clay content of about 8% was not included in the graph because it was considered to be an outlier (see Figure 4.1).

## 4.3 Trigger values paraquat

The Ministries of LNV and VROM have chosen for $DT_{50}$ trigger values that are related to a temperature of 10 °C and pF2 as reference conditions (Van der Linden et al., 2006). The estimated half-life for these conditions was 20 years, so paraquat triggers the FRP, CRP and ETP protection goals.

## 4.4 Input for paraquat exposure calculations

**PECs**

The concentration of paraquat in soil and/or pore water is needed to assess the risk for soil organisms of persistent substances according to the community recovery principle (CRP) and the ecological threshold principle (ETP). The $PEC_s$ for spray applications is calculated for the upper 5 cm of soil.

***Tier 1***

Input variables are the actual worst-case application rate 1.1 kg $ha^{-1}$ per season and the assumption of no interception and no tillage using a soil bulk density of 1000 kg $m^{-3}$. The calculation is independent of the crop and the time of application. The following input data are used for the calculation:

**Tier 1 input for paraquat**

Active substance:
Geometric mean $DegT_{50}$ for degradation in soil (10°C): 20 years

*sorption dependent on fraction clay in soil:*
$K_D$: 2000 $dm^3$ $kg^{-1}$ (for paraquat a pseudo-$K_{OM}$ is used see section 4.2)
Molecular weight: 186.3 g $mol^{-1}$

Other parameters: standard settings of Tier 1 calculation programme

***GeoPEARL***

In the third tier (no second tier developed), concentration of paraquat in soil and/or pore water in the potential area of use is evaluated using the spatially distributed model GeoPEARL 3.3.3. Input variables are the actual worst-case application scheme 1.1 kg $ha^{-1}$ to the crop potatoes and an interception value appropriate to the crop of 0% (pre-emergent). Tillage is included in the calculations. Date of biennial application is 1 May (realistic worst case scheme for this application). For metabolites all available data concerning substance properties are regarded. The following input data are used for the calculation:

**GeoPEARL input for paraquat**

Active substance:
Best guess $DegT_{50,field}$ for degradation in soil (10°C): 20 years (see section 4.2)

The sorption of paraquat is dependent on the clay content of the soil. The following sorption equation is used in GeoPEARL: $K_D = 2700 + 59100 * f_{clay}$
1/n: 0.9
Saturated vapour pressure: <1E-5 Pa (25 °C)
Solubility in water: 620 g $dm^{-3}$ (20 °C)
Molecular weight: 186.3 g $mol^{-1}$

Non-equilibrium sorption is assumed not to occur.

Crop: potatoes
Number of plots (minimum 250): 250

Other parameters: standard settings of GeoPEARL 3.3.3

## 4.5 Ecotoxicological endpoints of paraquat

**Laboratory toxicity data**
Table 4.3 summarises the laboratory data, available from the registration and open literature.

Table 4.3 Paraquat laboratory toxicity data for terrestrial species

| Species | formulation | OM [%] | Duration [d] | Param | Endpoint | Value mg kg$^{-1}$ | Value µg dm$^{-3}$ | Source |
|---|---|---|---|---|---|---|---|---|
| **soil micro-organisms** | | | | | | | | |
| soil micro-organisms | SL, 100 g dm$^{-3}$ | ? | 28 | nitrogen mineralization | NOEC | ≥ 4 | | DAR |
| | | ? | 28 | carbon mineralization | NOEC | ≥ 4 | | |
| ***Humicola fuscoatra*** | 'commercial formulations' | **agar** | **?** | **growth** | **NOEC** | **120 mg dm$^{-3}$ in agar** | **500** *[3] | (Tan and Chua, 1986) in DAR |
| soil fungi, *Tricoderma*, *Gliocladium virens* | | agar | ? | growth | NOEC | 12000 mg dm$^{-3}$ in agar | 50E3 *[3] | |
| soil fungi and bacteria | gramoxone | ? | 14 | | NOEC | 0.115 mg cm$^{-2}$ | *[5] | DAR |
| Rhizobium species | paraquat | agar | | tolerance | NOEC | 50 | 200 | Roslycky, 1985 |
| *Rhizobium meliloti* | gramoxone | YMB | | growth | NOEC | 6 mg dm$^{-3}$ YMB | *[4] | Flores and Barbachano 1992 |
| *Curvularia lunata*, *Paecilomyces variotti* | gramoxone | agar | 7 | growth | NOEC | < 50 mg dm$^{-3}$ in agar | < 200 | Hamzah et al., 1988 |
| **earthworms** | | | | | | | | |
| *Eisenia fetida* | SL formulation | 10 | 14 | mortality | $LC_{50}$ | >1000 | | DAR |
| | gramoxone | 10 | 14 | | $LC_{50}$ | >1000 | | |
| | ? | 10 | 14 | | $LC_{50}$ | > 200 | | |
| | ? | 10 | 14 | | $LC_{50}$ | >3200 | | |
| | SL formulation | 10 | 14 | weight | NOEC | <1000 | | |
| | gramoxone | 10 | 14 | mortality | $LC_{50}$ | >1656 | | (Hooftman and Heugens, 2006) |
| | gramoxone | 10 | 14 | weight | NOEC | 102.4 | 20 *[2] | |
| *Lumbricus terrestris*[a] | ? | 10 | 14 | | $LC_{50}$ | >1000 | | DAR |
| | ? | 10 | 14 | | $LC_{50}$ | >1000 | | |
| *Apporectodea caliginosa*[a] | ? | 10 | 14 | | $LC_{50}$ | > 580 | | |
| *Eisenia andrei* | a.s. | **10** | **21/56** | **juv./worm/week** | **$EC_{10}$** | **207** *[1] | **35** *[2] | (Van Gestel et al., 1992) |
| | | 10 | 21 | coc./worm/week | $EC_{10}$ | 298 *[1] | 49 *[2] | |
| | | 10 | 21 | growth | NOEC | ≥ 1000 | | |
| **plants** | | | | | | | | |
| *Trifolium subterraneum* | ? | ? | 18 w | | NOEC | > 10 | | Eberbach and Douglas, 1991 |
| *Oryza sativa* | a.s. | solution | 6 | root biomass | NOEC | | 50 | (Wang, 1994) |
| **Triticum spp.** | | | 14 | | $EC_{50}$ | | 48 *[1] | Hebden and Riley, 1987 |
| | | | **14** | | $EC_{10}$ | | **1** *[1] | |
| *Lactuca sativa* | | 5.64 | 21 | | $EC_{10}$ | 8.5 | 2 *[6] | (Denier van der Gon et al., 1991) |

*[1] recalculated from original data using a log-logistic model
*[2] calculated (see Appendix 5)
*[3] recalculated assuming agar = OM and K = 10.000 dm$^3$ kg$^{-1}$
*[4] not calculated because of unknown OM content
*[5] details for calculating pore water concentration not available
*[6] calculated based on 1.6% lutum and K = 3646 dm$^3$ kg$^{-1}$
Bold values used for risk assessment (see section 4.6)

### Selection of endpoints

In this part the selection of the endpoints from Table 4.3 that can be used for risk assessment is substantiated. Some endpoints (nitrogen en carbon mineralization, litter bag study) are needed for the FRP only. Other endpoints are needed for the first tier of the CRP and ETP.

***Soil Micro Organisms***

The standard laboratory tests with nitrogen and carbon mineralization did not show effects within the range tested. Therefore no NOEC could be derived, but the results indicate a NOEC > 4 mg $kg^{-1}$. In one test described in the DAR with soil fungi, the application was on the soil surface. Since paraquat has a very strong binding capacity to soil particles, the exposure of soil organisms could not be quantified as concentration in soil or pore water. In studies of (Tan and Chua, 1986), Hamzah et al. (1988) and Roslycky (1984) NOECs for soil fungi in agar were derived. Because these tests were performed in agar, they can be seen as indicative for pore water content only. The pore water concentration is calculated as follows:

Total content = solution volume * concentration + OM * content. For agar the OM content is estimated to be 25 g $dm^{-3}$, and a K value of 10.000 $dm^3$ $kg^{-1}$ is used (see Appendix 5). In the study of Roslycky (1984) effects were described as visual observation of growth. Since this parameter is not quantified, the results are considered less reliable and therefore the results are not used for risk assessment.

***Earthworms***

For earthworms no chronic toxicity data according to OECD guidelines was available. The data show that paraquat has a low acute toxicity, and mortality did not occur at very high dosages. Sublethal parameters, however, appear to be more sensitive. Semi chronic data (21 days) are found in Van Gestel et al. (1992) for *Eisenia andrei*. Recalculation of the $EC_{10}$ for the most sensitive endpoint (juveniles/worm/week), using a log-logistic model, yields an $EC_{10}$ value of 207 mg $kg^{-1}$. Although the duration of the exposure is shorter (3 weeks compared to 8 weeks) in the test of Van Gestel than in the standard earthworm reproduction test, reproduction endpoints are studied. Therefore, for the purpose of evaluation of the persistence decision tree, the value of 207 mg $kg^{-1}$ soil is taken as endpoint for earthworms.

Based on Figure 4.1 and the fact that kaolinite in general has a relatively small sorption capacity, a sorption coefficient of 6000 $dm^3$ $kg^{-1}$ is taken as a realistic estimate (see Appendix 5). The concentration in pore water at the $EC_{10}$ for *Eisenia andrei* therefore is estimated to be [207 mg $kg^{-1}$] / [6000 $dm^3$ $kg^{-1}$] = 0.0345 mg $dm^{-3}$ = 34.5 µg $dm^{-3}$.

***Plants***

The available laboratory data in the EU dossier concern experiments with direct exposure of the plants. Since gramoxone is a contact herbicide the effects of direct spraying cannot be separated from potential effect via the soil. Therefore the laboratory data in the dossier for plants cannot be used for risk assessment of plants exposed via soil.

Apart from these standard laboratory tests, a number of so called Strong Adsorption Capacity – Wheat Bioassay (SAC-WB) tests with *Triticum* are available. The SAC-WB is defined as the concentration of adsorbed paraquat when the concentration of paraquat in the equilibrium soil solution is sufficient to reduce the length of 14 day old wheat roots by 50%. This concentration is approximately 10 µg $dm^{-3}$ ((Dyson et al., 1994)). Hebden and Riley (1987) describe the development of this bioassay. From these data the $EC_{10}$ for root elongation was recalculated, using a log-logistic model, resulting in a lowest $EC_{10}$ value for dry weight of the wheat seedling of 1.0 µg $dm^{-3}$. Wang (1994) reports a NOEC for rice seed emergence of 50 µg $dm^{-3}$; this means that the value for dry weight of *Triticum* is protective for rice seed emergence.

The results of the SAC-WB tests show that a wide range of concentrations, 24 - 1740 mg $kg^{-1}$ expressed as dry weight content, result in 50% reduction of root length. In an adapted method RIVM (Denier van der Gon et al., 1991) tested *Lactuca sativa* plants, and looked at the $ED_{25}$ values for growth of above ground parts. From this data for the most sensitive soil an $EC_{50}$ value of 18.0 mg $kg^{-1}$ and an $EC_{10}$ value of about 8.5 mg $kg^{-1}$ was derived, using a log-logistic model. Taking into account the different clay contents of the different soils used, the $EC_{10}$ is 2.2 µg $dm^{-3}$. This again means that the value for the weed seedlings of 1.0 µg $dm^{-3}$ is protective.

Eberbach and Douglas (1991, open literature) reported a NOEC on root and shoot weight of > 10 mg $kg^{-1}$. For other endpoints reported in this paper were not used for risk assessment, because the effects were unclear and not significant.

Table 4.4 Overview of selected endpoints

| **Taxonomic group** | **NOEC/$EC_{10}$** (mg $kg^{-1}_{dw}$) | **NOEC/$EC_{10}$** (µg $dm^{-3}$) |
|---|---|---|
| Plants | | |
| *Triticum spp.* | | 1 |
| Earthworms | | |
| *Eisenia andrei* | 207 | 35 |
| Soil fungi | | |
| *Humicola fuscoatra* | | 500 |

**(Semi) field data**
The available semi-field data for paraquat from the dossier are given in Table 4.5.

Table 4.5 Field data for terrestrial species and paraquat

| Species | Substance | OM (%) | Duration (y) | Parameter | Endpoint | Value | NOEC or $EC_{10}$ ($\mu g\ dm^{-3}$) | Source |
|---|---|---|---|---|---|---|---|---|
| plants | | | | | | | | |
| crop species | gramoxone | 1.2-26.4 | 6 | yield | NOEC | 78 mg $kg^{-1}$ *** | 12 | Lane and Bouman, 2000 in DAR |
| natural vegetation | gramoxone | 1.9 | 21 | species composition and abundance | recovery after 15 year | 112 kg $ha^{-1}$ 20-80 mg $kg^{-1}$ | 1 – 0. 3 | Wilkinson et al., 1993a in DAR |
| Annelida | | | | | | | | |
| earthworms | ? | ? | 1 | | NOEC (50% effect) | 1.2 kg $ha^{-1}$ | | Edwards, 1985 in DAR |
| earthworms | ?<br>? | ?<br>? | 1<br>6<br><br>1 | earthworm numbers | NOEC<br>NOEC<br><br>NOEC | 90 kg $ha^{-1}$*<br>198 kg $ha^{-1}$ *(recovery)<br>33 kg $ha^{-1}$** | | Edwards, 1980 in DAR |
| soil organisms | | | | | | | | |
| litter bags | ? | | 0.3 | | LOEC | 0.19% (dipping) | | Hendrix and Parmelee, 1985 in DAR |
| soil fungi | paraquat dichloride | | 7 | | NOEC | 198 kg $ha^{-1}$ | 10 | Drew and Davies, 1980 in DAR |

* incorporated in soil to 150 mm
** incorporated in soil to 25 mm
*** for the soil resulting in the highest concentration in pore water, measured value 6 years after application

**Semi-field tests with earthworms**
Earthworm field data indicate that no long term effects on field populations are to be expected. A relatively high dosage of 90 kg $ha^{-1}$ (incorporated to a depth of 150 mm) did not show long term effects; dosages of 198 and 720 kg $ha^{-1}$ showed effects one year after application. The 720 kg $ha^{-1}$ treatment showed effects six years after treatment. In the same study dosages of 15, 33 and 120 kg $ha^{-1}$ were applied, but incorporated to 25 mm. Here effects were found one year after application in the 120 kg $ha^{-1}$ treatment. The conclusions are based on the summary in the DAR. Given the date (1980 and 1985) of the field studies, it is expected that the studies are not conducted according to present requirements. It is therefore in questionable whether the results can be used for risk assessment.

In another long-term field experiment (Wilkinson and Edwards, 1993) the results of the assessment of the earthworm community was not deemed suitable for use in risk assessment.

**Semi-field tests with rooted plants**
Long term field studies in the Netherlands ((Lane et al., 1992; Lane and Bouwman, 2000); see Appendix 6) show that at SAC-WB values of 41% and lower no effects on yield parameters were found

in the period 1 - 9 year after application. From these studies a NOEC of 119% of the SAC-WB can be derived for the situation 6 - 7 years after the last application. This concentration is equivalent to a pore water concentration of 1.19 * 10 µg $dm^{-3}$ = 12 µg $dm^{-3}$.

Long term fields studies in the UK (Wilkinson et al. 1993a, see Appendix 6) show that the application of 112 kg $ha^{-1}$ results in clear effects up to 5 years, but full recovery is found 15 years after treatment. A treatment of 1700 kg $ha^{-1}$ results in differences in species composition, biomass and nutrient uptake 10 - 14 years after application. Below the SAC-WB no effects were found. Above the SAC-WB effects did occur of which some recovered. Measurements in the soil in the 112 kg $ha^{-1}$ treatment showed that the concentration in the different soil layers varied from 20 – 80 mg $kg^{-1}$ 15 - 25 years after application, depending on depth (0 - 2.5 cm, 2.5 - 5 cm and 5 - 10 cm). Since the soil had a clay content of 17%, corresponding pore water concentrations were estimated to be of 0.3 - 1 µg $dm^{-3}$ (using Figure 4.1, K = 59466 $dm^3$ $kg^{-1}$).

**Semi-field tests with soil micro-organisms**
A field study in which 90, 198 and 720 kg $ha^{-1}$ paraquat was incorporated to a depth of 150 mm showed no statistical significant effects in the highest treatment, seven years after treatment for carbon or nitrogen mineralization. The same study showed “minor” statistically significant differences in the number of soil fungi in the 702 kg $ha^{-1}$ treatment. According to the authors this next lower treatment (198 kg $ha^{-1}$) is equivalent to 110% of the SAC-WB, which is approximately 10 µg $dm^{-3}$.

The field studies of Wilkinson et al., 1993 and Cole & Wilkinson, 1985, mentioned in the DAR are not deemed reliable (see Appendix 6). Therefore these data cannot be used for risk assessment.

In the litter bag study (Hendrix and Parmelee, 1985), see Appendix 6, the litter bags containing dried *Sorghum halepense* leaves were dipped in paraquat solutions with 0.19% and 1.9% and then dried and placed in a grass stand. Effects on decomposition were found in both concentrations. The test, however, does not fulfil the current requirements for litter bag tests.

### 4.5.1 Ecotoxicological endpoints in line with the FRP

For the FRP it is first checked whether the substance is toxic for earthworms or soil micro-organisms ($PIEC_{s,pw}$ < 0.2 * $NOEC_{earthworms}$ or effects on SMO < 25%). As stated above the endpoint chosen for earthworms is 34.5 µg dm-3. This means that the Tier 1 PIEC value (14.3 µg dm-3) > 0.2*$NOEC_{earthworms}$, but the Tier 3 PIEC value (1.9 µg dm-3) is not. According to the FRP scheme, tests with standard arthropods are required, but not available. Also a reliable litter bag study is absent. This means that for the FRP the first tier is not passed. However, according to an EFSA opinion (SCP/PARAQ/002-Final) of January 2002 the data provided are sufficient to show that no effects will occur on soil dwelling organisms. Therefore, these studies and this opinion could be used as a substitute for the standard arthropods in the scheme for the FRP, resulting in "acceptable" as outcome of the FRP decision tree. The litter bag study described in A6.1 cannot be used for risk assessment and therefore not be used to underpin the conclusion.

### 4.5.2 Ecotoxicological endpoints in line with the CRP and ETP

**First tier**
For the first tier of the CRP laboratory data are available for plants, earthworms and fungi. From the data (see Table 4.3) it is clear that the differences in sensitivity between plants and earthworms, expressed in concentration in pore water are limited. For soil micro organisms, the highest

concentrations did not result in an effect. The $RAC_{CRP}$ in the first tier of the CRP is based on the lowest NOEC for plants and is 0.1 x 1 µg $dm^{-3}$ = 0.1 µg $dm^{-3}$. For the ETP an extra factor of 10 is used and the $RAC_{ETP}$ is 0.01 µg $dm^{-3}$.

**Second tier**
The second tier ($HC_5$) cannot be tested because of the absence of data.

**Third tier**
For the third tier, long term field studies are available (see Appendix 6). From the first tier the results indicate that plants are the most sensitive group. Therefore a higher tier study should address effects on plants.

**CRP**
From the available reliable field studies it can also be concluded that plants are the most sensitive group.

The field studies in the Netherlands ((Lane et al., 1992; Lane and Bouwman, 2000)) focus on yield parameters of crop species. These studies clearly show that the crop is not affected (six years post application) up to 119 % of the SAC-WB (= 1.19 * 10 µg $dm^{-3}$ = 11.9 µg $dm^{-3}$). However, the studies concern a limited number of (crop) species. In order to use this result for agro-ecosystems, an extrapolation factor of 10 is used to cope with the intra species variation between plants. An extra safety factor of 3 is not deemed necessary since data are available for three agro-ecosystems. As a result the $RAC_{CRP}$ based on this field study would be 1.2 µg $dm^{-3}$.

The long term field study in the UK (Wilkinson et al., 1993a, see Appendix 6), indicated a NOEC range of 0.3 – 1 µg $dm^{-3}$. According to the decision scheme an extrapolation of 3 should be applied, resulting in a $RAC_{CRP}$ of 0.1 – 0.3 µg $dm^{-3}$. Since these values are in the same order of magnitude as the RAC based on the laboratory data, it is proposed to use the $RAC_{CRP}$ based on the laboratory data.

**ETP**
For the field studies in the Netherlands an extrapolation factor of 3 is used to cope with the variation in natural vegetations, and the $RAC_{ETP}$ would be 1.3 µg $dm^{-3}$; for the UK study the RAC would be 0.03 - 0.1 µg $dm^{-3}$. Given the uncertainties concerning the exposure at different depths and the limited difference with the laboratory based RAC (0.01 µg $dm^{-3}$) it is proposed to use the latter value as $RAC_{ETP}$.

## 4.6 Paraquat persistence risk assessment

### 4.6.1 Functional Redundancy Principle

Table 4.6 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) in line with the Functional Redundancy Principle (FRP)

| | **$PIEC_{s,tc}$** | **$PIEC_{s,pw}$** | **$PEC^{\#}_{s,tc,TWA28}$** | **$PEC^{\#}_{s,pw,TWA28}$** | **$RAC_{FRP\ s,tc}$** | **$RAC_{FRP\ s,pw}$** | **$RAC^{\#}_{FRP\ s,tc,TWA28}$** | **$RAC^{\#}_{FRP\ s,pw,TWA28}$** |
|---|---|---|---|---|---|---|---|---|
| | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) |
| Tier 1 | 29 | 14 | 29 | 14 | * | * | * | 6.9 |
| Tier 2 | - | - | - | - | | | | |
| Tier 3 | 10 | 1.9 | 10 | 1.9 | | | | $ |

* no reliable litter bag study available

# the time period of 28 days for the TWA is chosen arbitrarily

$ acceptable according to EFSA opinion

Third tier $PEC_s$ values for total content and pore water are 33% respectively 15% of their corresponding Tier 1 values. The third tier $PEC_{s,pw,TWA28}$ fulfills the corresponding first tier RAC. Since no risk for non-target arthropods is indicated according to EFSA, the requirements for passing the FRP are fulfilled.

### 4.6.2 Community Recovery Principle

Table 4.7 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) in line with the Community Recovery Principle (CRP)

| | **$PEC_{s,tc,t=2y}$** | **$PEC_{s,pw,t=2y}$** | **$PEC_{s,tc,t=2y,TWA28}$** | **$PEC_{s,pw,t=2y,TWA28}$** | **$RAC_{CRP\ s,tc}$** | **$RAC_{CRP\ s,pw}$** | **$RAC_{CRP\ s,tc,TWA28}$** | **$RAC_{CRP\ s,pw,TWA28}$** |
|---|---|---|---|---|---|---|---|---|
| | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) |
| Tier 1 | 27 | 13 | 27 | 13 | | 0.1 | | 0.1 |
| Tier 2 | - | - | | | | | | |
| Tier 3 | 7.5 | 1.3 | 7.5 | 1.3 | | 0.1 | | |

# the time period of 28 days for the TWA is chosen arbitrarily

Two years post last application the values for the $PEC_{s,pw}$ and $PEC_{s,pw,TWA28}$ are 13 µg $dm^{-3}$ in the first tier and 1.3 µg $dm^{-3}$ in the third tier. Third tier $PEC_s$ values for total content and pore water are 28% respectively 10% of their corresponding Tier 1 values. The third tier pore water $PEC_s$ values are above the $RAC_{CRP}$ value for both the momentary and TWA concentration indicating that it is not demonstrated that no risk exists for paraquat with respect to the CRP. For paraquat, pore water concentrations are used for the risk assessment, because for this substance ample evidence exists that effects on plants are asserted via the soil solution (Riley et al., 1976).

### 4.6.3 Ecological Threshold Principle

Table 4.8 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) in line with the Ecological Threshold Principle (ETP)

| | **PEC** $_{s,tc,t=7y}$ | **PEC** $_{s,pw,t=7y}$ | **PEC** $_{s,tc,t=7y,TWA28}$ | **PEC** $_{s,pw,t=7y,TWA28}$ | **$RAC_{ETP}$** $_{s,tc}$ | **$RAC_{ETP}$** $_{s,pw}$ | **$RAC_{ETP}$** $_{s,tc,TWA28}$ | **$RAC_{ETP}$** $_{s,pw,TWA28}$ |
|---|---|---|---|---|---|---|---|---|
| | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) |
| Tier 1 | 23 | 12 | 23 | 12 | | 0.01 | | 0.01 |
| Tier 2 | - | - | | | | | | |
| Tier 3 | 6.3 | 1.1 | 6.3 | 1.1 | | 0.01 | | |

[#] the time period of 28 days for the TWA is chosen arbitrarily

Seven years post last application the values for the $PEC_{s,pw}$ and $PEC_{s,pw,TWA28}$ are 12 µg $dm^{-3}$ in the first tier and 1.1 µg $dm^{-3}$ in the third tier. Third tier $PEC_s$ values for total content and pore water are 27% respectively 10% of their corresponding Tier 1 values. The third tier $PEC_{s,pw}$ values, both momentary and TWA, are higher than the $RAC_{ETP}$ so that it is not demonstrated that no risk exists for paraquat with respect to the ETP. For paraquat, pore water concentrations are used for the risk assessment, because for this substance ample evidence exists that effects on plants are asserted via the soil solution (Riley et al., 1976).

## 4.7 Discussion points for risk assessment

**Ecotox**
Although a lot of references were found in the public available literature, only a few references appeared useful for risk assessment in the end. One of the reasons is that the (semi)-field studies in from the open literature often were conducted with one dose only, or that paraquat was applied in combination with other pesticides. Therefore the studies could not be used to derive an endpoint like an $EC_{10}$ or a NOEC. Therefore a lot of studies, that appeared useful based on the title, could not be used after further evaluation of the publication, due to the lack of a dose response design.

Paraquat is acceptable according to the FRP decision tree, but not according to the CRP and the ETP decision trees. The main reason is that in the FRP decision tree toxicity for plants is not taken into account, in contrast to the CRP and the ETP decision trees. In the case of a herbicide, this means that organisms (plants), assumed to be sensitive to the particular compound, are not included in the FRP, resulting in passing of this protection goal.

Riley et al. (1976) have shown that effects of paraquat on plants are controlled by the pore water concentration and not by the total content. In addition Boesten (1993) calculated from measurements of Riley et al. (1976) that the bioavailability of paraquat to plants was reduced by a factor of about 100000 due to adsorption to the solid phase in soil. Therefore it is scientifically not meaningful to perform the CRP and ETP effect assessment on the basis of the total content.

# 5 Quinoxyfen

## 5.1 Overview of selected quinoxyfen uses

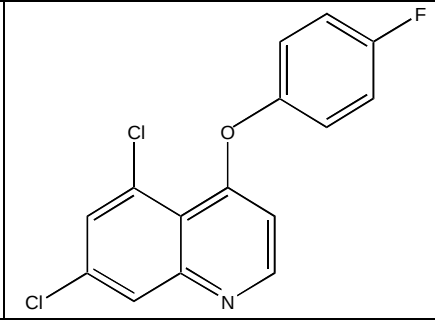
The applicant has requested that a maximum individual rate of 250 g $ha^{-1}$ be considered with a maximum total use rate of 400 g $ha^{-1}$. For the evaluation, quinoxifen is applied on cereals in spring at 250 g $ha^{-1}$ and summer at 150 g $ha^{-1}$. The first application is at growth stage BBCH 30 – 35 and the second at growth stage BBCH 50.

Table 5.1 Selected quinoxyfen uses

| substance | crop | formulation | frequency | dose | BBCH | interception |
|---|---|---|---|---|---|---|
| quinoxyfen | cereals | SC | 1 spring | 0.250 kg $ha^{-1}$ | 30 – 35 | 50% |
| | | | 1 summer | 0.150 kg $ha^{-1}$ | 50 | 90% |

## 5.2 Relevant fate parameters of quinoxyfen

Table 5.2 Identity of quinoxyfen

| | |
|---|---|
| Iso name | Quinoxyfen |
| IUPAC | 5,7-dichlor-4-chinolyl 4-fluorfenyl ether |
| CAS | 124495-18-7 |
| Purity | 970 g $kg^{-1}$ |
| Formula | $C_{15}H_8Cl_2FNO$ |
| Molar mass | 308.14 |
| Structure |  |



Quinoxyfen is solid with a melting point of 106 – 107.5 °C. The vapour pressure is low (1.2E-5 Pa at 20 °C. The solubility in water is low and slightly dependent on the pH: pH5 0.13 mg $dm^{-3}$, pH7 0.05 mg $dm^{-3}$. The octanol/water partitioning coefficient (log $K_{OW}$) is 4.66. Hydrolysis in water may occur at low pH ($DT_{50}$ = 7 days at 50 °C), but at higher pH quinoxyfen is stable.
The $pK_a$ of quinoxyfen is 3.56 (reaction $Hquinoxyfen^+ > H^+$ + quinoxyfen)

**Transformation quinoxyfen**
$DegT_{50,lab}$ (20 °C): 224 – 508 d, average 359 days (DAR)
$DegT_{50,lab}$ (10 °C): 874 days (Q10 > 3) (DAR)
$DegT_{50,lab,anaerobic}$ (20 °C): 289 days (DAR)
Photolysis in water was observed.

Based on available field studies the $DegT_{50,field}$ is 232 days (see Appendix 8). Four out of seven field trials on the dissipation resulted in acceptable $DegT_{50,field}$ values. These values were derived after reinterpretation of the field studies. The reinterpretation included day length normalization and fitting reaction kinetics to the normalized data (FOCUS 2006). According to the procedure, a DFOP (double first order parallel kinetics) model was considered to fit the data best; see Appendix 8 for details. Approximately 55% of applied quinoxyfen dissipated from the soils by fast initial processes (probably including volatilization and photodegradation). Approximately 45% was assigned to the slower dissipating phase, assumed to be soil transformation processes. The geometrical half-life of this phase was 232 days.

**Sorption quinoxyfen**
$K_{OM}$: 10600 – 16800 $dm^3\ kg^{-1}$ (non-GLP: 1240 – 20000), average 12460 $dm^3\ kg^{-1}$ (DAR). There are too few data to fit a Kom – pH relationship. The Freundlich exponent 1/n = 0.99 (range 0.97 – 1) (DAR).

**Metabolites**
One metabolite has been observed in soil experiments with quinoxyfen: 3-hydroxyquinoxyfen. Another metabolite, 5,7-dichloro-4-hydroxyquinoline, is mentioned in the DAR, but it is not reported to be formed in the soil environment. Appendix I of EU dossier states that 3-hydroxyquinoxyfen is not expected to be a significant metabolite, because the metabolite is formed only in significant amounts under anaerobic conditions. However, the metabolite was found in one soil with a formation fraction of 0.27 and was found in the top layer of the soil in all field accumulation experiments. Further information on this metabolite is lacking, so no persistency risk assessment could be performed.

## 5.3 Trigger values for different protection goals

The mean $DegT_{50,lab}$ of 359 days at 20 °C triggers the FRP, CRP and ETP. The geometric mean $DegT_{50,field}$ of 232 days at 20 °C, equal to 510 days at 10 °C, also triggers all decision trees.

## 5.4 Input for quinoxyfen exposure calculations

**$PEC_s$**
The concentration of quinoxyfen in soil and/or pore water is needed to assess the risk for soil organisms of persistent substances according to the community recovery principle (CRP) and the ecological threshold principle (ETP). The $PEC_{soil}$ for spray applications is calculated for the upper 5 cm of soil.

**Tier 1**
Input variables are the actual worst-case application rate 0.400 kg $ha^{-1}$ and the assumption of no interception and no tillage using a soil bulk density of 1000 kg $m^{-3}$. The calculation is independent of the crop and the time of application. The activation energy for the dependency of transformation on

temperature is taken to be 54 kJ $mol^{-1}$ (default value of GeoPEARL). The following input data are used for the calculation:

**Tier 1 input for quinoxyfen:**

Active substance:
Geometric mean $DegT_{50,field}$ for degradation in soil (20 °C): 232 d
Mean $K_{OM}$ (pH-independent): 12460 $dm^3$ $kg^{-1}$
Molecular weight: 308.14 g $mol^{-1}$

Other parameters: standard settings of Tier 1 calculation programme

### GeoPEARL

In the third tier (no second tier developed), concentrations of quinoxyfen in soil and/or pore water in potential area of use is evaluated using the spatially distributed model GeoPEARL 3.3.3. Input variables are the actual worst-case application scheme of 0.250 kg $ha^{-1}$ at growth stage BBCH 30 and 0.150 kg $ha^{-1}$ at growth stage 50, the crop cereals and a appropriate assumption for interception: 50, respectively 90% interception (FOCUS, 2000). In the GeoPEARL input file the application rates are defined as 125 g, respectively 15 g applied to the soil surface. Tillage is included in the calculations.

Dates of yearly applications are 5 May and 26 May. For the calculations it is assumed that fast transformation and dissipation processes at the soil surface do not occur. Microclimatic conditions at the soil surface in a wheat crop at growth stages BBCH 30 respectively 50 will differ considerably from the microclimatic conditions in the field trials, in which applications were at earlier growth stages. The following input data are used for the calculations:

**GeoPEARL input for quinoxyfen**

Geometric mean $DegT_{50,field}$ for degradation in soil (20 °C): 232 days
$pK_a$: 3.56 (reaction: $Hquinoxyfen^+ > H^+$ + quinoxyfen) (not used in sorption calculations because of insufficient data to fit the relation)
1/n: 0.99

Saturated vapour pressure: 1.2 E-5 Pa (20 °C)
Solubility in water: 0.05 mg $dm^{-3}$ (20 °C)
Molecular weight: 308.14 g $mol^{-1}$

Non-equilibrium sorption is assumed:
Desorption rate coefficient: 0.01 $d^{-1}$ (default)
Factor relating CofFreNeq and CofFreEql: 0.5 (-, default)

Crop: cereals
Number of plots (minimum 250): 250

Other parameters: standard settings of GeoPEARL 3.3.3

## 5.5 Ecotoxicological endpoints of quinoxyfen

The effect assessment is based on the DAR List of Endpoints, including all available addenda plus the SCP opinion. A literature search conducted in 2006 revealed no other relevant information. The available laboratory data for plants, invertebrates and micro-organisms are given in the table below.

Table 5.3 Toxicity data for terrestrial species

| species | formulation | OM (%) | duration (d) | endpoint | value |
|---|---|---|---|---|---|
| earthworms | | | | | |
| *Eisenia fetida* | EF-1186[1] | 10 | 56 | NOEC | ≥ 4 $dm^3$ $ha^{-1}$ |
| *Eisenia fetida* | technical | 10 | 14 | $LC_{50}$ | > 923 mg $kg^{-1}$ |
| *Eisenia fetida* | technical | 10 | 28 | | |
| plants | | | | | |
| *Hordeum vulgare* | EF-1186 | ? | ? | NOEL | 4 mg $kg^{-1}$ |
| *Brassica napus* | EF-1186 | ? | ? | NOEL | 4 mg $kg^{-1}$ |
| *Cucumis sativus* | EF-12951[2] | ? | 19 | NOEL | 0.016 kg $ha^{-1}$ |
| microbial processes | | | | | |
| microorganisms | EF-1186 | 1.7 | 28 | NOEC | ≥ 53 mg $kg^{-1}$ |
| microorganisms | EF-1186 | 5 | 28 | NOEC | ≥ 53 mg $kg^{-1}$ |
| microorganisms | EF-1186 | 1.7 | 28 | NOEC | ≥ 53 mg $kg^{-1}$ |
| microorganisms | EF-1186 | 5 | 28 | NOEC | ≥ 53 mg $kg^{-1}$ |

1: 500 g $dm^{-3}$ SC
2: Quintec, 25% w/v SC

Data on the toxicity of quinoxyfen as 'EF-1295' to *Typhlodromus pyri* were submitted. This formulation indicated that there was 20.6% mortality and 93.3% reduction in 'beneficial capacity' when treated at the equivalent of 100 g $ha^{-1}$ in 2000 $dm^3$ water. In a subsequent study using the same formulation there was 37.3 - 55.2% mortality and a corresponding reduction in 'beneficial capacity' of 100%.

Additional non-standard leaf tests with effects on (leaf) fungi (typically no effects except for species related to pest species) are not really suitable to derive soil concentrations. Extra data on plants and insects corroborate the available data from standardised testing.

Several different sets of data to assess the likely affects of quinoxyfen on soil organisms and organic matter breakdown are available: laboratory tests on surface dwelling arthropods, laboratory tests on earthworms and plants, laboratory tests on soil micro flora and field tests involving the monitoring of soil invertebrates and the decomposition of buried leaves (litter bags).

### 5.5.1 Ecotoxicological endpoints in line with the FRP

In the decision tree for in-crop effect assessment in line with the FRP, that is largely based on the EU Guidance Document on Terrestrial Ecotoxicology, it is first checked if the predicted exposure concentration of the substance leads to toxic effects on earthworms or soil micro-organisms ($PIEC_{st}$ < $0.2*NOEC_{earthworms}$ *or effects on SMO < 25%*).

Data have been submitted that indicate that there was no statistically significant effect on microbial respiration in two soil types at concentrations of 0.53 to 5.3 mg $kg^{-1}$ soil.

For comparison of the $PEC_{s,tc}$ with the earthworm toxicity, a 56-days NOEL of 2 kg $ha^{-1}$ is available. Assuming the same distribution within the soil of the experiment as within the soil of the exposure calculation; the NOEC is 4.0 mg $kg^{-1}$ (assuming a $\rho_b$ of 1000 kg $m^{-3}$). The $PEC_{s,tc,TWA56}$ amounts to 3.55 mg $kg^{-1}$ ($PEC_{s,pw,TWA56}$ is 9 µg $dm^{-3}$), based on $DegT_{50,field}$. Hence the PEC is > 0.2*NOEC.

The available studies indicate that quinoxyfen is toxic to *Typhlodromus pyri*. No data for the standard parasitic wasp were available. Further data that lead to an HQ estimate for *Typhlodromus pyri* are not available; it is however likely that under the field dosage of 150 - 250 g $ha^{-1}$ the HQ for this species is > 2. In the monograph this species was however not further assessed, since *Poecilus cupreus* and *Episyrphus balteatus* were considered more relevant species.

For the following step no data for collembolans and mites are available.

A litter bag study was however available.
A first litter bag study was considered flawed by the SCP. A new second study involved realistic worst case exposure and appropriate substrate, environmental conditions and statistics. The plots were in a cereal field, and were sprayed with 400 g $ha^{-1}$. Then after three days litter bags were placed horizontally in shallow holes and plots and bags were over sprayed with 150 - 400 g $ha^{-1}$. Next the bags were covered with soil to 6 cm depth. Soil concentrations were measured. The results confirmed that quinoxyfen was present in the soil in the treated plots at concentrations from 0.220 mg $kg^{-1}$ to 0.594 mg $kg^{-1}$ compared with < 0.001 mg $kg^{-1}$ in the control plots (recoveries ranged from 74% to 95%). The mean concentrations of quinoxyfen found for each treatment increased with increasing application rate. There were no to only slight effects (max. 3% difference) at the highest test rate. However, a clear and statistically significant effect was observed with the positive control (carbendazim).

### 5.5.2 Effect endpoints in line with the CRP and ETP

**Laboratory toxicity tests**

All available information is presented in the previous section.

**Semi-field tests**

Field data have been delivered on mesofauna. It should be noted that concentrations have not been verified and that applications were made to grass. It is to be expected that mostly epigeic mesofauna has been exposed, and the method of sampling also monitors epigeic fauna. The experiment is thus not informative for the exclusion of possible effects of in-soil presence of quinoxyfen to in-soil ecosystems.

A field study was conducted from March 1994 - November 1996 at a farm in Devon, UK. Although the intended use of quinoxyfen is in wheat and barley, experimental plots on this farm consisted of grazing pasture, as they provide greater invertebrate diversity.

Quinoxyfen was applied to 3 plots in the spring at 250 g $ha^{-1}$ and summer at 150 g $ha^{-1}$, while 3 plots received a toxic reference (hostathion; active substance triazophos). Three control plots were left untreated, and the same treatments were allocated to the same plots throughout the study. Arthropods were collected by pitfall traps which were left open for 1 week periods at various times through the study. Similarly, earthworms were sampled by applying formalin within two quadrants per plot at various times through the study period. In brief, the data on arthropods exhibited high variance and seasonality typical of field trials. The majority of taxa (carabid beetles, staphylinid beetles, linypiid spiders, soil mites) were not consistently affected by quinoxyfen. However, lycosid spiders (*Pardosa* sp.) and collembola (superfamily Entomobryoidea) were reduced in treated plots compared to controls, possibly as a result of indirect rather than direct effects. Entomobryoidea were the most abundant prey species found in the pitfall traps in all three years and they tended to show an approximate decrease of 20 - 60% in population size in the one to two months following exposure to quinoxyfen, before recovering to control levels. These organisms are largely fungivores and are common in leaf litter, and therefore they may play some role in organic matter decomposition. There was no indication of adverse effects of quinoxyfen on earthworms, since they appeared at approximately equal mean abundance in treated and control plots over each of the three study years.

The SCP opinion on the mesofauna study is as follows: ‘Given the complex picture of results and the problems for the evaluation (partly as a consequence of the study design), the Committee is of the opinion that the available studies on quinoxyfen and the field study in particular do not convincingly demonstrate acceptable impact on the environment. Those effects which occurred do raise concern, considering the persistence of quinoxyfen and the intended use in large-scale crops which are grown in short crop rotation in many EU countries.’ (SCP, 2001).

As a result of a treatment of 250 g $ha^{-1}$ in spring and 150 g $ha^{-1}$ in summer on grass, impact on epigeic mesofauna is demonstrated; it has not been demonstrated that unacceptable effects are absent. Given the size of the effects and the recovery period the results can be classified as a class III effect (recovery within 8 weeks). It should be noted that the study focused on mesofauna only; but picking up indirect effects that may relate to the food chain for collembolans.

## 5.6 CRP effect assessment

**First tier (standard test species approach)**
For the comparison of the $PEC_{s,tc,t=2y}$ data on fungi, earthworms, and another taxon are needed. For earthworms only a 56-days NOEL of 2 kg $ha^{-1}$ is available. Assuming the same distribution within the soil of the experiment as within the soil of the exposure calculation; the NOEC is 2.67 mg $kg^{-1}$.

For plants two NOECs at 4 mg $kg^{-1}$ are available, and one NOEL at 16 g $ha^{-1}$ (equivalent to 0.021 mg $kg^{-1}$ following the reasoning for earthworms). Soil properties are unknown; endpoints could be the highest concentrations tested.

For soil fungi no data are available. Additional non-standard leaf tests with effects on (leaf) fungi (typically no effects except for species related to pest species) are not really suitable to derive soil concentrations. Extra data on plants and insects corroborate the available data from standardized testing.

**Second tier (SSD approach)**
There are too few data to test the CRP Tier 2.

**Third tier (Model ecosystem approach)**
Field data have been delivered on mesofauna. It should be noted that concentrations have not been verified and that applications were made to grass. It is to be expected that mostly epigeic mesofauna has been exposed, and the method of sampling also monitors epigeic fauna. The experiment is thus not informative for the exclusion of possible effects of in-soil presence of quinoxyfen to in-soil ecosystems.

As a result of a treatment of 250 g $ha^{-1}$ in spring and 150 g $ha^{-1}$ in summer on grass, impact on epigeic mesofauna is demonstrated; it has not been demonstrated that unacceptable effects are absent. Given the size of the effects and the recovery period the results can be classified as a Class III effect (recovery within 8 weeks). It should be noted that the study focused on mesofauna only; but picking up indirect effects that may relate to the food chain for collembolans.

## 5.7 ETP effect assessment

**First tier (standard test species approach)**
For the comparison of the $PEC_{s,t=7y,tc}$ data on fungi, earthworms and another taxon are needed. For earthworms only a 56-days NOEL of 2 kg $ha^{-1}$ is available. Assuming the same distribution within the soil of the experiment as within the soil of the exposure calculation, the NOEC is 2.67 mg $kg^{-1}$.

For plants two NOECs at 4 mg $kg^{-1}$ are available and one NOEL at 16 g $ha^{-1}$ (equivalent to 0.021 mg $kg^{-1}$ following the reasoning for earthworms). Soil properties are unknown; endpoints could be the highest concentrations tested.

For soil fungi no data are available. Additional non-standard leaf tests with effects on (leaf) fungi (typically no effects except for species related to pest species) are not really suitable to derive soil concentrations. Extra data on plants and insects corroborate the available data from standardized testing.

**Second tier (SSD approach)**
There are too few data to test the ETP Tier 2.

**Third tier (model ecosystem approach)**
Field data have been delivered on mesofauna. It should be noted that concentrations have not been verified and that applications were made to grass. It is to be expected that mostly epigeic mesofauna has been exposed, and the method of sampling also monitors epigeic fauna. The experiment is thus not informative for the exclusion of possible effects of in-soil presence of quinoxyfen to in-soil ecosystems. As a result of a treatment of 250 g $ha^{-1}$ in spring and 150 g $ha^{-1}$ in summer on grass, impact on epigeic mesofauna is demonstrated; it has not been demonstrated that unacceptable effects are absent. Given the size of the effects and the recovery period the results can be classified as a class III effect (recovery within 8 weeks). It should be noted that the study focused on mesofauna only; but picking up indirect effects that may relate to the food chain for collembolans.

## 5.8 Quinoxyfen persistence risk assessment

The assessment concerns two substances: quinoxyfen and the metabolite 3-hydroxyquinoxyfen. No data on the metabolite 3-hydroxyquinoxifen are available; the risk assessment cannot be completed. For quinoxyfen, the results of the three decision trees are summarised below.

### 5.8.1 Functional Redundancy Principle

It concerns the use of quinoxyfen at a dosage of 250 g $ha^{-1}$ in spring followed by 150 g $ha^{-1}$ in summer. Based on the Tier 3 $PIEC_{s,tc}$ and the Tier 1 $RAC_{FRP,s,tc}$ the FRP has been satisfied. The Tier 3 $PIEC_{s,tc}$ is approximately 17% of the Tier 1 $PIEC_{s,tc}$. The Tier 3 $PIEC_{s,pw}$ is approximately 5% of the Tier 1 $PIEC_{s,pw}$.

Table 5.4 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) in line with the Functional Redundancy Principle (FRP)

| | **$PIEC_{s,tc}$** | **$PIEC_{s,pw}$** | **$PEC^{\#}_{s,tc,TWA28}$** | **$PEC^{\#}_{s,pw,TWA28}$** | **$RAC_{FRP,s,tc}$** | **$RAC_{FRP,s,pw}$** | **$RAC^{\#}_{FRP,s,tc,TWA28}$** | **$RAC^{\#}_{FRP,s,pw,TWA28}$** |
|---|---|---|---|---|---|---|---|---|
| | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) |
| Tier 1 | 3.6 | 9.7 | 3. 6 | 9.3 | 1.5* | | | |
| Tier 2 | - | - | - | - | | | | |
| Tier 3 | 0.615 | 0.44 | 0.606 | 0.43 | | | | |

* litter bag study with appropriate dosing (150 - 400 g $ha^{-1}$)
\# duration of TWA period chosen arbitrarily; no tox data to choose from

### 5.8.2 Community Recovery Principle

An assessment according to CRP was triggered by quinoxyfen. The calculated Tier 3 $PEC_{s,tc,t=2y}$ is approximately 7% of the Tier 1 $PIEC_{s,tc,t=2y}$. The calculated Tier 3 $PEC_{s,pw,t=2y}$ is approximately 2% of the Tier 1 $PIEC_{s,pw,t=2y}$. Since no $RAC_{CRP}$ could be derived, the risk assessment cannot be completed.

Table 5.5 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) in line with the Community Recovery Principle (CRP)

| | **PEC** $_{s,tc,t=2y}$ | **PEC** $_{s,pw,t=2y}$ | **PEC**$^{\#}$ $_{s,tc,t=2y,TWA28}$ | **PEC**$^{\#}$ $_{s,pw,t=2y,TWA28}$ | **RAC**$_{CRP}$ $_{s,tc}$ | **RAC**$_{CRP}$ $_{s,pw}$ | **RAC**$_{CRP}^{\#}$ $_{s,tc,TWA28}$ | **RAC**$_{CRP}^{\#}$ $_{s,pw,TWA28}$ |
|---|---|---|---|---|---|---|---|---|
| | (mg kg$^{-1}$) | (µg dm$^{-3}$) | (mg kg$^{-1}$) | (µg dm$^{-3}$) | (mg kg$^{-1}$) | (µg dm$^{-3}$) | (mg kg$^{-1}$) | (µg dm$^{-3}$) |
| Tier 1 | 2.2 | 5.1 | 2.2 | 5.0 | | | | |
| Tier 2 | - | - | | | | | | |
| Tier 3 | 0.16 | 0.069 | 0.15 | 0.068 | | | | |

$^{\#}$ duration of TWA period chosen arbitrarily; no tox data to choose from

### 5.8.3 Ecological Threshold Principle

An assessment according to FRP was triggered by quinoxyfen. The calculated Tier 3 $PEC_{s,tc,t=7y}$ is approximately 6% of the Tier 3 $PIEC_{s,tc,t=7y}$. The calculated Tier 3 $PEC_{s,pw,t=7y}$ is approximately 3% of the Tier 3 $PIEC_{s,pw,t=7y}$. Since no $RAC_{CRP}$ could be derived, the risk assessment cannot be completed.

Table 5.6 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) in line with the Ecological Threshold Principle (ETP)

| | **PEC** $_{s,tc,t=7y}$ | **PEC** $_{s,pw,t=7y}$ | **PEC**$^{\#}$ $_{s,tc,t=7y,TWA28}$ | **PEC**$^{\#}$ $_{s,pw,t=7y,TWA28}$ | **RAC**$_{ETP}$ $_{s,tc}$ | **RAC**$_{ETP}$ $_{s,pw}$ | **RAC**$_{ETP}^{\#}$ $_{s,tc,TWA28}$ | **RAC**$_{ETP}^{\#}$ $_{s,pw,TWA28}$ |
|---|---|---|---|---|---|---|---|---|
| | (mg kg$^{-1}$) | (µg dm$^{-3}$) | (mg kg$^{-1}$) | (µg dm$^{-3}$) | (mg kg$^{-1}$) | (µg dm$^{-3}$) | (mg kg$^{-1}$) | (µg dm$^{-3}$) |
| Tier 1 | 0.66 | 1.5 | 0.65 | 1.5 | | | | |
| Tier 2 | - | - | | | | | | |
| Tier 3 | 0.042 | 0.015 | 0.041 | 0.015 | | | | |

$^{\#}$ duration of TWA period chosen arbitrarily; no tox data to choose from

## 5.9 Discussion points for risk assessment

The evaluation of quinoxyfen revealed some aspects of risk assessment that have not been addressed in the proposal.

- Re-evaluation of the field soil degradation studies according to the FOCUS procedures was needed and a two-phase degradation pattern was used to derive the true $DegT_{50}$ in soil. This concerned then agreement on the criteria to find the appropriate fitting procedure (DFOP), and the appropriate phase for setting the $DegT_{50}$.
- The studies showed that the metabolite 3-hydroxyquinoxyfen was present in all field soils, and showed a maximum formation percentage of 27%, thus satisfying all criteria for assessment under the Directive 91/414/EEC. However, since no data have been supplied for this metabolite, because in the evaluation process these facts have not been addressed, no further assessment could be made.
- The ecotoxicological database for this fungicide was not according to the Annex II & III data requirements; since data for relevant arthropod species were not available.
- Some relevant studies had been performed by overspraying of the soil surface, which renders the result for the persistency assessment less useful. The most sensitive taxa (fungi) have not been tested. This hampered the assessment, and also made the conversion of total content to pore water content difficult. In view of the lack of data, no test results have been recalculated to pore water concentrations.

- The litter bag test satisfied all requirements, but the field test was not useful for persistency risk assessment. The field test focused on the epigeal soil mesofauna, and showed class III effects as a result of the application. For persistency risk assessment, the absence of effects of in-soil residues should have been demonstrated. It has been considered to apply extra safety factors on the field test result to bridge the shortcomings. After consideration of the lack of scientific basis to derive the proper assessment factor, accounting for 1) extrapolation from Class III effects to Class I effects, 2) extrapolation from epigeal to in-soil organisms and 3) extrapolation from agricultural soils to pristine soils, it was decided that it was not appropriate to use an assessment factor.
- The persistency risk assessment for quinoxyfen could therefore not be completed.

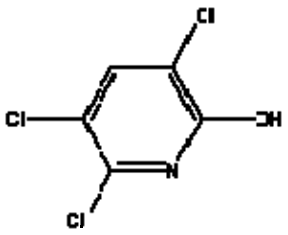
# 6 TCP (metabolite of chlorpyrifos)

## 6.1 Relevant fate parameters of TCP

### 6.1.1 Physico-chemical properties of TCP

Molecular mass, vapour pressure and solubility in water are taken from an evaluation report of the RIVM (RIVM rapport 08413A01, Verschoor, 2001).

Table 6.1 Identification of TCP

| | |
|---|---|
| IUPAC | 3,5,6-trichloro-2-pyridinol |
| CAS | 6515-38-4 |
| Formula | $C_5H_2Cl_3NO$ |
| Molar mass | 308,14 |
| Structure |  |

The list of end points specifies $K_{OC}$ values in the range of 67.2 $dm^3\ kg^{-1}$ to 315 $dm^3\ kg^{-1}$ and states that the $K_{OC}$ is not pH dependent. However, the evaluation report of the RIVM (RIVM rapport 08413A01, Verschoor, 2001) gives a pKa value of 4.55 indicating that the $K_{OC}$ might be pH dependent and that the $K_{OC}$ values given in the list of end point may not be reliable. TCP contains an OH group, which may dissociate and thus TCP may be very mobile in soils with a high pH (see Table 6.2). The presumed pH dependency of the $K_{OC}$ of TCP was analysed, but the fit was not very good. However as no better data were available, the fit was used in calculations with GeoPEARL. The conversion factor of 1.724 (FOCUS, 2000) is used to calculate $K_{OM}$ from $K_{OC.}$ The Freundlich exponent was not specified and therefore the default FOCUS value of 0.9 is used (FOCUS, 2000).

Concerning half-lives in soil, both laboratory degradation studies and field dissipation studies are available. A laboratory degradation study using four soils is described in the monograph (Annex B Chapter 8 December, 2002). The measured $DegT_{50}$ values are normalized to pF2 (field capacity) by multiplying the measured $DegT_{50}$ values by a correction factor. The procedure for calculating the correction factor is described in section 3.2.1 of this report. Normalized $DegT_{50}$ values are given in Table 6.3.

In the case of TCP field dissipation studies are available. Field results are preferred over laboratory results because they are determined under conditions specific for the intended use of a pesticide in an agricultural field and thus closely match the situation which is to be modelled (FOCUS, 2006). Assessment of the field dissipation studies is therefore necessary. Only one of the three available field studies is assessed. The assessment of this field dissipation study of TCP is described in Appendix 9. The result is a $DegT_{50}$ at 20°C of 111 days. This value is confirmed by visual inspection of the graphs of the other field dissipation studies of TCP.

A $DegT_{50,field}$ of about 100 days does not correspond to the results of the laboratory studies (Table 6.2). Two laboratory studies give $DegT_{50}$ values of around 60 days and two studies give $DegT_{50}$ values of around 10 days. This is an exceptional case, where the substance degrades faster in a laboratory study than in the field for two out of four experiments. This is probably due to adapted micro-organisms in the soil (Monograph chapter 7, page 628). Considering the assumed pH dependent sorption, availability of the substance might be an issue. However this is not confirmed by the laboratory studies. One would expect more degradation at higher pH values (low $K_{OM}$ at high pH, so more substance available at high pH), but Table 6.3 shows faster degradation at low pH values.

Table 6.2 gives relevant fate parameters of TCP used in Tier 1 and/or Tier 3 calculations.

Table 6.2 Relevant fate parameters of TCP

| parameter | value + unit | source |
|---|---|---|
| molar mass | 198.4 g $mol^{-1}$ | RIVM rapport 08413A01 Verschoor, 2001 |
| vapour pressure | 1.64 E-7 Pa (at 25 °C) | |
| solubility in water | 220 mg $dm^{-3}$ (at 20 °C) | |
| $K_{OM}$ | results of the fit:<br>$K_{OM,acid}$ = 1190.8 $dm^3$ $kg^{-1}$<br>$K_{OM,base}$ = 63.7 $dm^3$ $kg^{-1}$<br>$pK_a$ = 4.55 | re-evaluation and conversion of $K_{OC}$ to $K_{OM}$: see Appendix 9 |
| Freundlich exponent (1/n) | 0.9 (-) | default FOCUS value (FOCUS, 2000) |
| $DegT_{50,lab}$ | arithmetic mean: 32.7 d (pF2, 20°C)<br>geometric: 21.1 d (pF2, 20°C)<br>arithmetic mean: 71.9 d (pF2, 10°C)<br>geometric mean: 46.5 d (pF2, 10°C) | Monograph Annex B Chapter 8 December, 2002 |
| $DegT_{50,field}$ | 111 d (pF2, 20°C) | re-evaluation: see Appendix 9 |

Table 6.3 Normalization of $DegT_{50}$'s to reference moisture conditions and temperature

| soil | soil texture | pH | $DegT_{50,lab}$ measured | $DegT_{50,lab}$ normalized to pF2 (20°C) | $DegT_{50,lab}$ normalized to pF2 (10°C) |
|---|---|---|---|---|---|
| | | | (d) | (d) | (d) |
| Marcham | sandy clay loam | 7.7 | 67 | 58.8 | 129.3 |
| Charentilly | silty clay loam | 6.1 | 10 | 6.9 | 15.2 |
| Cuckney | sandy clay loam | 6.0 | 12 | 8.7 | 19.2 |
| Thessaloniki | sandy silt loam | 7.9 | 60 | 56.3 | 123.9 |
| | arithmetic mean $DegT_{50,lab}$ | | | 32.7 | 71.9 |
| | geometric mean $DegT_{50,lab}$ | | | 21.1 | 46.5 |

### 6.1.2 Assessment of field dissipation studies of TCP

Details of the assessment of the field dissipation studies of TCP are given in Appendix 9. A $DegT_{50,field}$ at 20°C of 111 days was found whereas the geometric mean of the $DegT_{50,lab}$ is 21.1 days (pF2, 20°C).

Two laboratory studies give $DegT_{50}$ values of around 60 days and two studies give $DegT_{50}$ values of around 10 days. This exceptional case, where the substance degrades faster in a laboratory study than in the field is probably due to adapted micro-organisms in the soil.

The $DegT_{50,field}$ value of 111 days (20 °C, pF2) will be used for the calculation of exposure levels. Using the correction factor calculated according to Eq.3.2, the $DegT_{50,field}$ value of 222 days (10 °C, pF2) will be used for comparison with the $DegT_{50}$ trigger values of the FRP, CRP and ETP.

## 6.2 Trigger values TCP

The Ministries of LNV and VROM have chosen for $DT_{50}$ trigger values that are related to a temperature of 10 °C and pF2 as reference conditions (Van der Linden et al., 2006). The $DegT_{50,field}$ value of 222 days (10 °C, pF2) will be used for comparison with the $DegT_{50}$ trigger values of the FRP, CRP and ETP.

## 6.3 Input for TCP exposure calculations

TCP is a metabolite of chlorpyrifos. Exposure concentrations of parent and metabolite are calculated at the same time, using one input file. The input for the calculations is given in section 3.4.

## 6.4 Ecotoxicological endpoints of TCP

### 6.4.1 Ecotoxicological endpoints in line with the FRP, CRP and ETP

In the DAR list of endpoints (chlorpyrifos, SANCO/3059/99 – rev.1.5, 3 June, 2005) the following ecotoxicological data for soil organisms concerning the metabolite TCP are presented:

- 14-d $LC_{50}$ earthworm of 9.8 mg $kg^{-1}$;

- 56-d NOEC earthworm of 4.6 mg $kg^{-1}$ ≈ 38.5 µg $dm^{-3}$ (pore water concentration based on OECD guideline 222 and $K_{OM,acid}$).

Since other information is not provided and additional data could not be found in the open literature, a proper effect assessment of TCP in line with the FRP, CRP and ETP cannot be performed.

## 6.5 TCP persistency risk assessment

### 6.5.1 Functional Redundancy Principle

Table 6.4 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) of TCP in line with the Functional Redundancy Principle (FRP)

| | **PIEC $_{s,tc}$** | **PIEC $_{s,pw}$** | **PEC$^{\#}$ $_{s,tc,TWA28}$** | **PEC$^{\#}$ $_{s,pw,TWA28}$** | **$RAC_{FRP}$ $_{s,tc}$** | **$RAC_{FRP}$ $_{s,pw}$** | **$RAC_{FRP}^{\#}$ $_{s,tc,TWA28}$** | **$RAC_{FRP}^{\#}$ $_{s,pw,TWA28}$** |
|---|---|---|---|---|---|---|---|---|
| | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) |
| Tier 1 | 0.032 | 16 | 0.032 | 16 | * | * | * | * |
| Tier 2 | - | - | - | - | | | | |
| Tier 3 | 0.075 | 12 | 0.074 | 9.6 | | | | |

* litter bag study not available

# duration of TWA period chosen arbitrarily; no tox data to choose from

An assessment according to FRP was triggered by TCP. The calculated Tier 3 $PIEC_{s,tc}$ is higher than the Tier 1 $PIEC_{s,tc}$. Also the Tier 3 $PEC_{s,tc,TWA28}$ is higher than the Tier 1 values. This is due to the exceptional situation in which the $DegT_{50,field}$ was found to be higher than the $DegT_{50,lab}$. Since no $RAC_{FRP}$ could be derived, the risk assessment cannot be completed.

### 6.5.2 Community Recovery Principle

Table 6.5 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) of TCP in line with the Community Recovery Principle (CRP)

| | **PEC $_{s,tc,t=2y}$** | **PEC $_{s,pw,t=2y}$** | **PEC$^{\#}$ $_{s,tc,t=2y,TWA28}$** | **PEC$^{\#}$ $_{s,pw,t=2y,TWA28}$** | **$RAC_{CRP}$ $_{s,tc}$** | **$RAC_{CRP}$ $_{s,pw}$** | **$RAC_{CRP}^{\#}$ $_{s,tc,TWA28}$** | **$RAC_{CRP}^{\#}$ $_{s,pw,TWA28}$** |
|---|---|---|---|---|---|---|---|---|
| | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) | (mg $kg^{-1}$) | (µg $dm^{-3}$) |
| Tier 1 | 0.01 | 1.1 | 0.009 | 1.0 | * | * | * | * |
| Tier 2 | - | - | | | | | | |
| Tier 3 | 0.011 | 0.42 | 0.011 | 0.40 | | | | |

* sufficient toxicity data for relevant soil organisms not available

# duration of TWA period chosen arbitrarily; no tox data to choose from

Although less pronounced than in the FRP case (see section 6.5.1), Tier 3 $PEC_{tc}$ values are higher than the Tier 1 values due to the $DegT_{50,field}$ value being higher than the $DegT_{50,lab}$ value. Since no $RAC_{CRP}$ could be derived, the risk assessment cannot be completed.

### 6.5.3 Ecological Threshold Principle

Table 6.6 Predicted Environmental Concentrations (PEC) and Regulatory Acceptable Concentrations (RAC) of TCP in line with the Ecological Threshold Principle (ETP)

| | **PEC** $_{s,tc,t=7y}$ | **PEC** $_{s,pw,t=7y}$ | **PEC**$^{\#}$ $_{s,tc,t=7y,TWA28}$ | **PEC**$^{\#}$ $_{s,pw,t=7y,TWA28}$ | **RAC**$_{ETP}$ $_{s,tc}$ | **RAC**$_{ETP}$ $_{s,pw}$ | **RAC**$_{ETP}^{\#}$ $_{s,tc,TWA28}$ | **RAC**$_{ETP}^{\#}$ $_{s,pw,TWA28}$ |
|---|---|---|---|---|---|---|---|---|
| | (mg kg$^{-1}$) | (µg dm$^{-3}$) | (mg kg$^{-1}$) | (µg dm$^{-3}$) | (mg kg$^{-1}$) | (µg dm$^{-3}$) | (mg kg$^{-1}$) | (µg dm$^{-3}$) |
| Tier 1 | <5E-4 | <0.05 | <5E-4 | <0.05 | * | * | * | * |
| Tier 2 | - | - | | | | | | |
| Tier 3 | 1.6E-4 | 3.6E-3 | 1.5E-4 | 3.4E-3 | | | | |

* sufficient toxicity data for relevant soil organisms not available

$^{\#}$ duration of TWA period chosen arbitrarily; no tox data to choose from

Calculated Tier 1 and Tier 3 $PEC_s$ values cannot really be compared, because values of the first tier calculations are below the minimum output values of the Tier 1 calculation programme. Since no $RAC_{ETP}$ could be derived, the risk assessment cannot be completed.

## 6.6 Discussion points for risk assessment

A proper risk assessment according to Van der Linden et al. (2006) cannot be performed for TCP due to the lack of toxicity data for relevant soil organisms.

Tier 1 exposure calculations do not seem to be conservative enough in the case of TCP. However, input parameters on $DegT_{50}$ differ in an exceptional way from each other. For chlorpyrifos the $DegT_{50,field}$ is smaller than the $DegT_{50,lab}$, which occurs regularly. For TCP the $DegT_{50}$ values differ the other way around, which occurs seldom. In the Tier 1 model TCP is formed more slowly, but transformed faster than in the GeoPEARL model. This results in lower total contents in the Tier 1 model. If the value of 111 days for the $DegT_{50}$ is used in the Tier 1 model, the results are again conservative compared to the GeoPEARL results (data not shown).

# 7 Discussion, conclusions and recommendations

**Remit**
The ministries of LNV and VROM asked the workgroup to evaluate the proposed procedure for the assessment of persistence of plant protection products in soil (Van der Linden et al., 2006). The procedure was evaluated using dossier and open literature information on five substances.

**Availability of data**
In the proposed risk assessment procedure specific data are necessary as input for the decision trees. Data according to these, sometimes new, data requirements are not yet available in the EU dossiers. For that reason it was decided to also use open literature data to evaluate the decision trees for the five selected substances. In principle, however, the data used should become part of the EU dossiers and subject to the required aspects of quality assurance.

Although substances were selected with a supposed high number of ecotoxicological data, the evaluation of the proposed assessment procedure is rather limited. The number of relevant ecotoxicological studies was rather low. Furthermore, many studies, especially older studies, do not meet the current requirements on methodology, interpretation and reporting.

Advanced interpretation of field degradation studies, as recommended by FOCUS (2006) proved useful to derive adequate degradation coefficients for the substances.

**Total content and pore water concentration**
Assessments for carbendazim based on pore water concentrations resulted in higher PEC/RAC ratios than assessments based on total contents. For chlorpyrifos the opposite was found. Unless on basis of the ERC a clear choice between pore water and total content can be made, it is recommended to perform always both assessments and base the decision on the lowest ratio and to change the assessment schemes accordingly. For the other substances this could not be tested.

**Decision power of the risk assessment schemes**
The evaluation of existing dossiers for the selected pesticides indicates that first and higher tier ecotoxicological studies needed for the proposed risk assessment procedure may be lacking for a relatively large number of pesticides, even when open literature is considered. In the absence of data, the proposed procedure recommends conservative approaches. As a consequence it is likely that introduction of this approach in near future in the Netherlands will lead to the situation that for a considerable fraction of the pesticides submitted to the Ctgb the conclusion will be 'risk cannot be excluded, additional data are required’.

**Consistency between the decision trees**
Calculated exposure concentrations, both total contents and pore water concentrations, declined in the order FRP > CRP > ETP. The FRP decision tree does not include tests with plant species and may therefore be inconsistent with CRP and FRP for herbicides. Although no examples of non-consistency were observed for CRP and ETP (see Table 7.1), the number of tests is too small to draw definite conclusions on whether the schemes are consistent overall. This is due to lack of ecotox data, particularly with respect to the SSD approach.

Table 7.1 Summary of results of risk assessment for both the Community Recovery and Ecological Threshold Principles based on the ERC's 'pore water' and total content. Symbols indicate whether (✓) or not (✗) it was possible to conclude to 'acceptable risk' using information from this tier. A ✗ in the exposure assessment indicates that it was impossible to find an acceptable risk even with the highest available tier from the effect assessment. Similarly a ✗ in the effect assessment indicates that it was impossible to find an acceptable risk even with the highest available tier from the exposure assessment. A ✓ in the exposure assesment indicates that it was possible to find an acceptable risk with the corresponding tier (that is ✓) of the effect assessments. A ✓ in the effect assessment indicates that it was possible to find an acceptable risk with the corresponding Tier 2 of the exposure assessment. Grey circles indicate that the tier could not be applied due to lacking data; for paraquat assessments based on total content are possible but are considered not relevant (indicated as "NR") as justified in section 4.7.

| | exposure assessment | | effect assessment | | |
|---|---|---|---|---|---|
| | Tier 1 | Tier 3 | Tier 1 | Tier 2 | Tier 3 |
| Community Recovery Principle based on **pore water** | | | | | |
| carbendazim | ✗ | ✓ | ● | ● | ✓ |
| chlorpyrifos | ✗ | ✓ | ✓ | ● | ● |
| TCP | ✗ | ✗ | ● | ● | ● |
| paraquat | ✗ | ✗ | ✗ | ● | ✗ |
| quinoxyfen | ✗ | ✗ | ● | ● | ● |
| Community Recovery Principle based on **total content** | | | | | |
| carbendazim | ✗ | ✓ | ● | ● | ✓ |
| chlorpyrifos | ✗ | ✓ | ✓ | ● | ● |
| TCP | ✗ | ✗ | ● | ● | ● |
| paraquat | NR | NR | NR | ● | NR |
| quinoxyfen | ✗ | ✗ | ● | ● | ● |
| Ecological Threshold Principle based on **pore water** | | | | | |
| carbendazim | ✗ | ✓ | ● | ● | ✓ |
| chlorpyrifos | ✗ | ✓ | ✓ | ● | ● |
| TCP | ✗ | ✗ | ● | ● | ● |
| paraquat | ✗ | ✗ | ✗ | ● | ✗ |
| quinoxyfen | ✗ | ✗ | ● | ● | ● |
| Ecological Threshold Principle based on **total content** | | | | | |
| carbendazim | ✗ | ✓ | ● | ● | ✓ |
| chlorpyrifos | ✗ | ✓ | ✓ | ● | ● |
| TCP | ✗ | ✗ | ● | ● | ● |
| paraquat | NR | NR | NR | ● | NR |
| quinoxyfen | ✗ | ✗ | ● | ● | ● |

**Consistency within the decision trees**

Van der Linden et al. (2006) prescribe an exposure flow chart with three tiers. The first tier is a simple calculation procedure, the second tier consists of a number of PEARL scenarios and the third tier consists of calculations with the GeoPEARL model. The workgroup discovered that development of the PEARL scenarios for the second tier would become too complicated because of the large number of possible endpoints. Development of a tier is only meaningfull if it has enough added value in the risk assessment. The workgroup decided that this was not the case for this second tier (considering that the higher tier of GeoPEARL calculations has shown to be relatively easy for the Dutch groundwater risk assessment). Therefore nowhere in the report Tier 2 fate results are reported. As a consequence the workgroup decided to eliminate this second tier of the exposure flow chart in the proposal for the risk assessment procedure.

Exposure estimates for both pore water concentrations and total contents obtained with GeoPEARL are lower than obtained with the Tier 1 model. The differences depend on the sorption and transformation parameters of the substances. For the CRP and ETP decision trees, differences can be in the order of one to several orders of magnitude.

Derived Regulatory Acceptable Concentrations in Tier 3 were always higher than those derived in Tier 1, when they could be compared. Tier 1 in the ecotox decision trees was therefore sufficiently conservative with respect to Tier 3 for FRP, CRP and ETP. Assessment factors, when applicable, seem to be chosen correctly. Due to lack of data, Tier 2 RAC values (based on SSD) could not be derived and no conclusions can be drawn on the consistency and whether also Tier 2 is sufficiently conservative with respect to Tier 3. Due to the relatively small number of substances considered in the evaluation exercise, no conclusion can be drawn on the screening function of the decision trees.

**Screening action of the Tiers in the decision trees**

Calculated Tier 1 $PEC_s$ values were consistently higher than corresponding Tier 3 values, in all decision schemes. The differences are dependent on substance properties and range from a factor of 3 (paraquat total content, FRP scheme) to over a factor of 1000 (chlorpyrifos, ETP scheme). TCP is left out of this consideration because of the fact that $DegT_{50,field}$ of TCP being higher than the $DegT_{50,lab}$ is exceptional. The factors indicate potential screening, but it could not be tested whether this screening function of the first exposure tier would fulfil the requirements. This is due to the low number of substances tested so far. The first tier being sufficiently conservative is however much more important than the screening function. For none of the substances a decision could be taken on basis of first Tier exposure calculations.

Whether the screening action is OK, too low or too high for the ecotox part cannot be concluded from this evaluation. This is due to insufficient data for deriving ecotoxicological end points. The second tier of the ecotoxicological schemes could not be tested at all, because no SSDs could be constructed.

It is remarkable that for most of the substances in the evaluation, the FRP could not be tested because of incompleteness of the dossier. In some cases laboratory data were lacking, in other cases reliable litter bag studies were not available. Partly this could be solved by gathering information from open literature.

**Increasing work load for risk assessment agencies**
It is necessary to define the exposure in the ecotox studies in a consistent and transparent way, both for laboratory studies and field studies. A problem is that in most laboratory and field studies the concentration in soil or pore water is not measured or estimated. In the risk assessment procedure, exposure in ecotox studies has to be evaluated along with the toxicological aspects. Existing studies may need to be reinterpreted and reevaluated for both aspects. This requires additional skills of the assessors and may bring additional work for the risk assessment agencies.

**Short cuts**
The principle of a tiered approach allows to jump over tiers and to combine a higher tier on the exposure side with a lower tier on the ecotox site and vice versa. It is expected that higher tier exposure modelling will be performed before it is decided to perform higher tier ecotox experiments. This approach will be cheaper, at least if field degradation experiments are available from the dossier. For the selected active ingredients, there were no signs of error due to taking short cuts. The case of the metabolite TCP revealed that parameter selection should be done with care.

**Additional or higher safety factors**
Validation of the extrapolation factor for field studies was hardly possible. In general too few reliable or useful field studies could be found to validate this point. Based on estimated exposure, the Effect class I–II concentrations derived from the four TMEs with carbendazim (Table 2.10) revealed that the difference between the lowest and highest threshold concentration is smaller than a factor of 4 for total soil concentrations and approximately a factor of 10 for pore water concentrations. In the field plots this variability in Effect class I concentrations was higher (Table 2.11). Although the data presented suggest that the assessment factor of three for spatio-temporal extrapolation is not adequate, we conclude that the available data can not be used to adjust this factor because the true exposure response relationship is unknown.

**Needs for future research in the exposure assessment of persistent plant protection products for soil organisms**
The Dutch persistence risk assessment focusses on remaining contents and pore water concentrations in the top layer at two or seven years after the last application. The exposure assessment is based on calculations with the PEARL model. There are about 200 field tests available in literature on testing of remaining amounts in top soil using models with concepts similar to the PEARL model (Beulke et al., 2000). However most of these tests considered periods not longer than the first four months after application. Field tests for periods of many years are very scarce and field tests for periods of seven years are to the best of our knowledge not available. This implies that the risk assessment is based on procedures for extrapolating in time that have not yet been tested for the range of agricultural soils and weather conditions in the Netherlands. It is therefore recommended to conduct research on long-term field behaviour of persistent pesticides in the top layer of soil to increase the validation status of the PEARL model for simulating such very old residues. This research does not necessarily need to last for seven years but could perhaps be based on studying aged residues of pesticides in soils from experimental farms with known pesticide application history.

The results of the first tier calculating model are straightforward for parent substances when non-equilibrium sorption is switched off and sorption is not dependent on soil pH. When non-equilibrium sorption is taken into account and / or when sorption is dependent on pH and / or when

metabolites are involved, a number of calculations have to be performed and the selection of conservative exposure estimates is rather complex. It is recommended that a user friendly software tool is developed and that the selection is performed automatically.

**Needs for future research in the effect assessment of persistent plant protection products for soil organisms**

***Exposure assessment in soil ecotoxicological tests***

The current procedure for the effect assessment of plant protection products for soil organisms is to base the NOEC and $EC_x$ estimates on the nominal concentration applied and mixed through the soil. In the proposed decision schemes, however, not only the nominal exposure concentrations for the total system are required to derive toxicity values, but also pore water concentrations and time-weighted average (TWA) concentrations for the total soil content and the pore water. Because pore water concentrations and TWA concentrations usually are not assessed in current lower and higher tier soil tests we used models and realistic worst-case assumptions to estimate these pore water and TWA concentrations. An important research need is to develop technical guidance for a cost-effective measurement of ecotoxicologically relevant concentrations (total content; pore water; etc). Another research need is to investigate for soil organisms of different trophic/taxonomic groups what constitutes the ecotoxicologically relevant concentration (ERC). Within this context it might be worthwhile to develop refined toxicity tests with standard test species by using standard and or non-standard soils, with measurements of both total content and pore water concentrations.

***Standard and additional laboratory toxicity tests***

This evaluation revealed that the available laboratory toxicity tests with soil organisms usually are limited to a few taxonomic groups (for example Lumbricidae; Enchytraeidae; crop plants). An important research need is to develop a standardised test for soil fungi that can be used in the risk assessment for fungicides.

We noticed that the SSD approach could not be applied for the substances we selected because of lack of data. An important research need is to perform, for a few test substances that differ in toxic mode-of-action, laboratory tests with a wide array of soil species to allow the scientific underpinning of the proposed SSD procedures. These procedures are the TGD approach (SSD constructed with chronic NOEC/$EC_{10}$ values of at least ten taxa from eight different taxonomic groups) and the HARAP approach (SSD constructed with chronic NOEC/$EC_{10}$ values of at least eight toxicity data from the sensitive taxonomic group(s)). Ideally, with these selected substances also semi-field tests should be performed to evaluate the predictive value of the $HC_5$ estimates derived from these SSDs. Another research item is to investigate whether it is possible to use SSDs constructed with acute toxicity data (cheaper and easier to conduct for a wider array of soil species) to derive long-term Regulatory Acceptable Concentrations (RACs), for example by applying an AF of ten.

***Terrestrial semi-field experiments***

The principle of a tiered approach is that higher tier data may overrule lower tier data. In a normal procedure, however, lower tier data would be available and these data serve to focus the design of higher tier studies. When lower tier data are lacking, a higher tier study cannot ignore the question of the potentially sensitive endpoints (taxonomic groups) that have to be studied. This problem might be solved by means of including a broad scale of measurement endpoints (for different taxonomic groups) in the higher tier study.

To date terrestrial semi-field experiments with persistent plant protection products to study treatment-related responses in a regression design are relatively scarce and predominantly have been performed using soils of agro-ecosystems. An important research question is whether the results can be extrapolated in space and time, and which AF should be applied if only one valid semi-field experiment is available. In this context an important research need is to perform several semi-field tests in different soil types/geographical areas with a selected number of substances that differ in toxic mode-of-action (for example an insecticide, a herbicide, a nematicide and a fungicide). Nice examples of such a research are the semi-field tests performed with carbendazim which are described in Chapter 2. Comparable studies with herbicides, nematicides and insecticides are lacking.

We assumed in our report that the soil communities of off-crop sites (for example in nature reserves) are more sensitive than the soil communities of agro-ecosystems. Whether the AF of three that we proposed to extrapolate results from agro-ecosystems to off-crop areas is adequate needs to be underpinned. A database on life-cycle characteristics and ecology of typical soil organisms should be developed to guide the number and frequency of samplings to assess effects and recovery from effects. In addition, technical guidance should be developed on aspects of statistics (including power analysis) to evaluate the treatment-related responses observed.

***Overall***

Since the selected substances only partly allowed to evaluate the proposed decision trees, and more data-rich substances most probably are not yet available to assess the risks of persistent plant protection products in greater detail, the most important research need is to perform comparative studies with a few selected substances differing in toxic mode-of-action that address all tiers of our decision trees. A problem is that knowledge concerning the habitat of species (which soil layer) is not readily available.

As a general recommendation the design of field studies needs to be improved:

- a regression design is needed to derive concentration – response relationships;
- exposure concentration need to determined;
- besides univariate statistics application of multivariate techniques is required to evaluate ecological responses in semi-field studies;
- tests with a limited number of species is only useful when it is known that these are the most sensitive species.

**Suggested changes to the proposal**

Risk assessment according to the FRP was included in the proposal for the overall persistence risk assessment. The method was copied from the procedures followed in the European risk assessment. As the methods at the European level are under discussion and possible conflicting trigger values are used according to political choices, it was decided to propose to leave FRP risk assessment at the European level only and exclude it from the system.

For reasons of consistency and deriving sufficiently conservative exposure estimates, it was decided to make some changes in the parameterisation of the first tier exposure model. We decided to use $DegT_{50}$ values from higher tier experiments (if available) and to do calculations for both equilibrium and non-equilibrium sorption. We decided not to correct the $DegT_{50}$ values for the non-equilibrium sorption process unless this correction can be adequately derived from the experiments.

In the ETP risk assessment in the first tier an option was included to derive a RAC value from five toxicity values and applying a safety factor of 10. For reasons of consistency with the CRP risk assessment, it is recommended to drop this option and keep only the option of deriving a RAC on the basis of toxicity data for three species and applying a safety factor of 100. The option of deriving a RAC value from five toxicity values and applying a safety factor of 10 could not be tested due to lack of data.

The evaluation exercise comprised a small (five) number of substances. Despite the fact that these substances in the past have been considered to pose some persistency risk, the availability of reliable fate and ecotox data is limited. As far as could be tested, the exercise did reveal only a few inconsistencies in the proposed decision schemes. A few changes are suggested in order to improve the consistency between the CRP and ETP decision schemes. The new procedure will be described in a companion report (Van der Linden et al., 2008).

# References


Aben WJW, Houx NWH, Leistra M. 1992. Toxicity of pentachlorophenol and chlorpyrifos in soil and in solution to a nematode and a plant species. Report 59, DLO Winand Staring Centre, Wageningen, the Netherlands.

Abdel-Fattah HM, Abdel-Kader MIA, Hamida S. 1982. Effects of Bavistin, Cotoran and Curacron on Egyptian soil fungi. Mycopathologia 80:101-106.

Afzal M, Ghannoum MA, Hanssan RAH, Dhami MSI. 1990. Variation in growth and fatty acid contents of Trichoderma viride induced by herbicides. FASEB (FEDERATION OF AMERICAN SOCIETIES FOR EXPERIMENTAL BIOLOGY) JOURNAL 4(3).

Aharonson N, Kafkafi U. 1975a. Adsorption of Benzimidazole Fungicides on Montmorillonite and Kaolinite Clay. Journal of Agric. Food Chem. 23 (3), 434–437.

Aharonson N, Kafkafi U. 1975b. Adsorption, Mobility and Persistence of Thiabendazole and Methyl-2-Benzimidazolecarbamate in Soils. Journal of Agric. Food Chem. 23 (4), 720–724.

Aldenberg T, Jaworska J. 2000. Uncertainty of hazardous concentrations and fraction affected for normal species sensitivity distributions. Ecotoxicol. Environ. Saf. 46: 1–18.

Arrate JA, Rodriguez P, Martinez-Madrid M. 2002. Effects of three chemicals on the survival and reproduction of the oligochaete worm *Enchytraeus coronatus* in chronic toxicity tests. Pedobiologia 46: 136-149.

Barron MG, Woodburn KB. 1995. Ecotoxicology of chlorpyrifos. Reviews of Environmental Contamination and Toxicology 144:1-93.

Beelen P van, Fleuren-Kemila AK.1993. Toxic effects of pentachlorophenol and other pollutants on the mineralization of acetate in several soils. Ecotoxicol. Environ. Saf. 26(1): 10-17.

Beulke S, Dubus IG, Brown CD, Gottesbüren B. 2000. Simulation of pesticide persistence in the field on the basis of laboratory data – a review. Journal of Environmental Quality 29: 1371-1379.

Boesten JJTI. 1990. Influence of solid/liquid ratio on the experimental error of sorption coefficients in pesticide/soil systems. Pestic. Sci. 30, 31-41.

Boesten JJTI. 1993. Bioavailability of organic chemicals in soil related to their concentration in the liquid phase: a review. The Science of the Total Environment, Supplement 1993, 397-407.

Bolt GH (1976) Transport and accumulation of soluble soil components. In: Bolt GH, Bruggenwert MGM (eds). Soil chemistry. A: basic elements. Elsevier, Amsterdam, p. 126-140.

Booth LH, Hodge S, O'Halloran K. 2000. Use of cholinesterase in *Aporrectodea caliginosa* (Oligochaeta; Lumbricidae) to detect organophosphate contamination: Comparison of laboratory tests, mesocosms, and field studies. Environ Toxicol Chem 19:417-422.

Brink PJ van den, J Hattink, F Bransen, Donk E van, TCM Brock. 2000. Impact of a chronic application of the fungicide carbendazim in freshwater microcosms. II. Responses of zooplankton and primary producers. Aquatic Toxicology 48:251-264.

Brink P J van den, Maltby L, Wendt-Rasch L, Heimbach F, Peeters F (eds). 2007. New Improvements in the Aquatic Ecological Risk Assessment of Fungicidal Pesticides and Biocides. SETAC PRESS, Publication of the Society of Environmental Toxicology and Chemistry, Pensacola/Brussels.

Campbell PJ, Arnold DJS, Brock TCM, Grandy NJ, Heger W, Heimbach F, Maund SJ, Streloke M. 1999. Guidance document on higher-tier aquatic risk assessment for pesticides (HARAP). SETAC-Europe Publication.

Crommentuijn T, Stab JA, Doornekamp A, Estoppey O, Gestel CAM van. 1995. Comparitive ecotoxicity of cadmium, chlorpyrifos and triphenyltin hydroxide for four clones of the parthenogenetic collembolan *Folsomia candida* in an artificial soil. Functional Ecology 9: 734-742.

Cuppen JGM, Brink PJ van den, Camps E, Uil KF, Brock TCM. 2000. Impact of a chronic application of the fungicide carbendazim in freshwater microcosms. I. Fate of carbendazim and responses of macroinvertebrates and community metabolism. Aquatic Toxicology 48: 233-250.

Damon A, Heim L. 2001. Adsorption and desorption of 14C-chlorpyrifos to five European soils, (K116), 46259, GH-C 5325 [00390] GLP (Confidential).

Day SR, Rudel H. 1993. The persistence of chlorpyrifos in air and its evaporation behaviour from soil and leaf surfaces following application of Dursban 480 (EF 1042) – Germany 1992. GHE-P-2966 (K60) GLP (Confidential).

Denier van der Gon HAC, Berg S van den, Linden AMA van der, 1991. Een onderzoek naar de beschikbaarheid van paraquat in vijf kwetsbare Nederlandse bodemtypen. RIVM, Bilthoven, the Netherlands, rapport 725801004 (in Dutch).

Dios Cancela G, Romero Taboada E, Sancenz-Rasero F. 1992. Carbendazim adsorption on montmorillionite, peat and soils. Journal of Soil Science, 43, 99-111.

Dirven- van Breemen EM, Gestel CAM van, Pol JJC van der, Straalen NM van, Baerselman R.1991. Toxiciteit van Paraquat voor Enkele Bodemorganismen (Toxicity of Paraquat for Some Soil Microorganisms). RIVM, Bilthoven, the Netherlands, rapport 710301003 (in Dutch).

Drew and Davies. 1980. In: Paraquat: draft assessment report (monograph) on the evaluation of paraquat in the context of the Council Directive 91/414/EEC and Regulation 3600/92, prepared by the United Kingdom, September 1996 (Volumes 1 to 3).

Dyson JS, Ferguson RE, Lane MCG. 1994. Paraquat: adsorption and desorption properties in temperate soils. Zeneca report TMJ3225B, Zeneca Agrochemicals, Jealott's Hill Research Station, Bracknell UK.

Eberbach PL, Douglas LA, 1991. Effect of herbicide residues in a sandy loam on the growth, nodulation and nitrogenase activity (acetylene/ethylene) of *Trifolium subterraneum*. Plant Soil. 131(1): 67-76.

ECCO. 1997. European Commission Peer Review Programme. Carbendazim. Braunschweig, Germany.

Edwards. 1980. In: Paraquat: draft assessment report (monograph) on the evaluation of paraquat in the context of the Council Directive 91/414/EEC and Regulation 3600/92, prepared by the United Kingdom, September 1996 (Volumes 1 to 3).

Edwards. 1985. In: Paraquat: draft assessment report (monograph) on the evaluation of paraquat in the context of the Council Directive 91/414/EEC and Regulation 3600/92, prepared by the United Kingdom, September 1996 (Volumes 1 to 3).

Edwards CA, Bohlen PJ. 1992. The effects of toxic chemicals on earthworms. In: Ware GW (Ed.). Reviews of Environmental Contamination and Toxicology, Vol. 125, 23 - 99.

EFSA, 2005. Opinion of the Scientific Panel on Plant Health, Plant Protection Products and their Residues on a request from EFSA related to the default Q10 value used to describe the temperature effect on transformation rates of pesticides in soil. The EFSA Journal 322: 1-40.

Fischer E. 1989. Effects of atrazine and paraquat-containing herbicides on *Eisenia foetida* (Annelida Oligochaeta). Zool. Anz. 223(5-6): 291-300.

Flores M, Barbachano M. 1992. Effects of herbicides Gramoxone, diuron and Tota-col on growth and nodulation of three strains of *Rhizobium meliloti*. Sci. Total Environ. 123-1242: 49-60. ISSN: 0048-9697.

FOCUS. 2000. FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater Scenarios Workgroup, EC document Sanco/321/2000 rev. 2, 197 pp. Available at http://arno.ei.jrc.it/focus

FOCUS. 2006. Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. Report of the FOCUS Work Group on Degradation Kinetics. EC Document Reference Sanco/10058/2005, version 2.0, June 2006.

Förster B, Gestel CAM van, Koolhaas JE, Nentwig G, Rodrigues JML, Sousa JP, Jones SE, Knacker T. 2004. Ring-testing and field-validation of a terrestrial model ecosystem (TME) – An instrument for testing potentially harmful substances: Effects of carbendazim on organic matter breakdown and soil fauna feeding. Ectoxicology 13: 129 – 141.

Frampton GF, Jänsch S, Scott-Fordsmans JJ, Römbke J, Van den Brink PJ. 2006. Effects of pesticides on soil invertebrates in laboratory studies: A review and analysis using species sensitivity distributions. Environ Toxicol Chem. 25: 2480–2489.

Garcia M. 2004. Effects of pesticides on soil fauna: Development of ecotoxicological test methods for tropical regions. Ecology and Development Series 19. Cuvillier Verlag, Göttingen, Germany.

Gestel CAM van. 1992. The influence of soil characteristics on the toxicity of chemicals for earthworms: A review. In: Greig-Smith PW, Becker H, Edwards PJ, Heimbach F (eds). Ecotoxicology of Earthworms. Intercept Press, Andover, p 44–54.

Gestel CAM van, Dirven-Van Breemen EM, Baerselman R, Emans HJB, Janssen JAM, Postuma R, Vliet PJM van. 1992. Comparison of sublethal and lethal criteria for nine different chemicals in standardized toxicity tests using the earthworm *Eisenia andrei*. Ecotoxicol. Environ. Saf. 23: 206–220.

Gestel CAM van, Koolhaas JE, Schallnass H-J, Rodrigues JML, Jones SE. 2004. Ring-testing and field-validation of a terrestrial model ecosystem (TME) – An instrument for testing potentially harmful substances: Effects of carbendazim on nutrient cycling. Ecotoxicology 13: 119–128.

Gianfreda L, Sannino F, Ortega N, Nannipieri P. Activity of free and immobilized urease in soil: effects of pesticides. Soil Biol. Biochem. 1994; 26(6): 777-84.

Görlitz G, Klöckner Ch. 1985. Translation of document No. A31451: Hoe 017411, adsorption/desorption in the soil/water system. Hoechst Actiengesellschaft.

Hamzah A, Sahid I, Tahir WHWM. 1988. The effect of paraquat on the growth of some fungi isolated from a peat soil. MALAYSIAN APPLIED BIOLOGY 17(2); 85-90.

Havens PL, Kieatiwong S, Shepler K. 2002. The photochemical degradation of chlorpyrifos on soil by natural sunlight. GH-C 2867 (K59) GLP. Confidential.

Hayward JC. 2002. Effects of DURSBAN 480 EC on reproduction and growth of the earthworm *Eisenia fetida* (J113), CEMR-1719, GHE-T-1165.

Hebden JMC, Riley D, 1987. Paraquat and Diquat: Bioassay with wheat seedlings and its application for determining the Strong Adsorption Capacities (SAC-WB) of soils.

Helweg A. 1977. Degradation and Adsorption of Carbendazim and 2-Aminobenzimidazole in Soil. Pestic. Sci. 8, 71-78

Hendrix PF, Parmelee RW, 1985. Decomposition, nutrient loss and microarthropod densities in herbicide-treated grass litter in a geargia piedmont agroecosystem. Soil Biol. Biochem. 17, 421 – 428.

Herbert IN, Svendsen C, Hankard PK, Spurgeon DJ. 2004. Comparison of instantaneous rate of population increase and critical-effect estimates in *Folsomia candida* exposed to four toxicants. Ecotoxicology and Environmental Safety 57: 175–183.

Heusel R. 1991. Carbendazim: water miscible suspension concentrate; 360 g/l (HOE 017411 00 SC32 A209) Effect to *Eisenia fetida* (earthworm) in a 14 day artificial soil test (method OECD). CE91/073. ARW95-00092.

Heusel R. 1993. Carbendazim – substance, technical (Hoe 017411 00 ZD99 0010). Effect to *Folsomia candida* (springtails) in a 28 day reproduction test in artificial soil (method OECD/ISO – drafts). CE92/037. ARW96-00055.

Hooftman RN, Heugens EHW. 2006. Gramoxone (paraquat-dichloride). TNO, Zeist. CTB-2005-019-MIL-NL.

ISO11268-2. 1998. Soil Quality – Effects of pollutants on earthworms (*Eisenia fetida*). Part 2: Determination of effects on reproduction, No.11268-2. ISO, Geneva.

ISO 11267. 1999. Soil quality - Inhibition of reproduction of Collembola (Folsomia candida) by soil pollutants.

Jänsch S, Frampton GF, Römbke J, Van den Brink PJ, Scott-Fordsmans JJ. 2006. Effects of pesticides on soil invertebrates in model ecosystem and field studies: A review and comparison with laboratory toxicity data. Environ Toxicol Chem. 25:2490–2501.

Jones SE, Williams DJ, Holliman PJ, Taylor N, Baumann J, Förster B, Gestel CAM van, Rodrigues JML. 2004. Ring-testing and field-validation of a terrestrial model ecosystem (TME) – An instrument for testing potentially harmful substances: Fate of the model chemical carbendazim. Ecotoxicology 13: 29–2.

Khan S, Khan NN. 1986. Adsorption and interactions of Methyl 2-Benzimidazolecarbamate (MBC) with illites. Clay Research 5 (2), 82–87.

Kling M, Jakobsen I. 1997. Direct application of carbendazim and propiconazole at field rates to the external mycelium of three arbuscular mycorrhizal fungi species: effects on $^{32}P$ transport and succinate dehydrogenase activity. Mycorrhiza 7:33-37.

Knacker T, Gestel CAM van, Jones SE, Soares AMVM, Schallnass H-J, Förster B, Edwards CA. 2004. Ring-testing and field-validation of a terrestrial model ecosystem (TME) – An instrument for testing potentially harmful substances: Conceptual approach and study design. Ecotoxicology 13: 9 – 27.

Koolhaas JE, Gestel CAM van, Römbke J, Soares AMVM, Jones SE. 2004. Ring-testing and field-validation of a terrestrial model ecosystem (TME) – An instrument for testing potentially harmful substances: Effects of carbendazim on soil microarthropod communities. Ecotoxicology 13: 75 – 88.

Koorevaar P, Menelik G, Dirksen D. 1983. Elements of Soil Physics. Elsevier, Amsterdam.

Krebs B, Baedelt H. 1990a. Untersuchung des Abbaus im Boden unter Freilandbedingungen. A42435 ! DEU88F10641. BOD95-00447 (in German).

Krebs B, Baedelt H. 1990b. Untersuchung des Abbaus im Boden unter Freilandbedingungen. A42436 ! DEU88F10631. BOD95-00448 (in German).

Krebs B, Baedelt H. 1990c. Untersuchung des Abbaus im Boden unter Freilandbedingungen. A42438 ! DEU88F10611. BOD95-00450 (in German).

Lane MCG, Bouwman JJ, Bewick DW. 1992. Paraquat. Long-term high rate trials in the Netherlands (1986-1991). Final Report. ICI Agrochemicals, Bracknell Berkshire, UK. RJ11868.

Lane MCG, Bouwman JJ. 2000. Paraquat. Long-term high rate trials in the Netherlands III; Paraquat residues in soil and effect on crops 1992-1996. Zeneca Agrochemicals, Bracknell Berkshire, UK. TMJ4345B.

Leistra M, Linden AMA van der, Boesten JJTI, Tiktak A, Berg F. van den. 2001a. PEARL model for pesticide behaviour and emissions in soil-plant systems. Description of processes. Wageningen, Alterra, report 013.

Leistra M, Matser AM, Ende JE van den. 2001b. Absorptie, omzettingssnelheid en transport van carbendazim in twee bloembollengronden. Wageningen, Alterra Green World research, rapport 218 (in Dutch).

Lewis FJ. 1993. Paraquat: Long-Term Ecological Trial at Jealott's Hill, UK, 1964-90. 3. Effect on soil microflora and their activities. ICI Agrochemicals, Bracknell Berkshire UK. TMJ3054B.

Linden AMA van der, Boesten JJTI, Brock TCM, Eekelen GMA van, Jong FMW de, Leistra M, Montforts MHMM, Pol JW. 2006. Persistence of plant protection products in soil. A proposal for risk assessment. Bilthoven, RIVM, report 601506008. ISBN 90-6960-140-0

Linden AMA van der, Boesten JJTI, Brock TCM, Eekelen GMA van, Horst MMS ter, Jong FMW de, Montforts MHMM, Pol JW. 2008. Revised proposal for the risk assessment of persistence of plant protection products in soil. Bilthoven, RIVM, report 601712003.

Lockley TC, Laiche AJ. 1990. Relative phytotoxicity of chlorpyrifos in a standard potting medium to foliage and woody landscape plants. Miss. Agric. For. Exp. Stn. Tech. Bull. 15:1-4.

Lührs U. 2001a. Effects of derosal SC360 on reproduction and growth of earthworms, *Eisenia fetida* (Savigny 1826), in artificial soil. BAY 9801022 GLP, confidential, ARW2003-100.

Lührs U. 2001b. Carbendazim/ flusilazole (DPX-N7872) SE (1:2): Effects on reproduction and growth of the earthworm, *Eisenia fetida* (Savigny 1826), in artificial soil. BAY 10111022 GLP, confidential, ARW2002-121.

Lührs U. 2002. Effects of Derosal SC 360 on reproduction and growth of earthworms, *Eisenia fetida,* in artificial soils. BAY 12621022 GLP, confidential, ARW2003-99.

Lührs U. 2003. Effects of Derosal SC 360 on reproduction and growth of earthworms, *Eisenia fetida*, in artificial soil. BAY 15071022 GLP, confidential, ARW2003-102.

Ma W, Bodt J. 1993. Differences in toxicity of the insecticide chlorpyrifos to six species of earthworms (Oligochaeta, Lumbricidae) in standardized soil tests. Bull. Environ. Contam. Toxicol. 50: 864-870.

Matser AM, Leistra M. 2000. Bioavialability of the fungicides carbendazim and iprodione in soil, alone and in mixtures. Wageningen, Alterra Green World research, rapport 156 (in Dutch).

Mikolasch B, Schäfer D. 2006. Kinetic Evaluation with MATLAB. Introduction to the Use of KINGUI, Version 1.1. Bayer CropScience AG

Moser T, Schallnass H-J, Jones SE, Gestel CAM van, Koolhaas JE, Rodrigues JML, Römbke J. 2004a. Ring-testing and field-validation of a terrestrial model ecosystem (TME) – An instrument for testing potentially harmful substances: Effects of carbendazim on nematodes. Ecotoxicology 13: 61–74.

Moser T, Gestel CAM van, Jones SE, Koolhaas JE, Rodrigues JML, Römbke J. 2004b. Ring-testing and field-validation of a terrestrial model ecosystem (TME) – An instrument for testing potentially harmful substances: Effects of carbendazim on enchytraeids. Ecotoxicology 13: 89–103.

Nicholls PH, Evans AA. 1991a. Sorption of Ionisable Organic compounds by Field Soils. Part 1: Acids. Pest. Sci. 33, 319–330.

Nicholls PH, Evans AA. 1991b. Sorption of Ionisable Organic compounds by Field Soils. Part 2: Cations, Bases and Zwitterions. Pest. Sci. 33, 331–345.

Nikolenko AG, Amirkhanov DV. 1993. Comparative hazardousness of various types of insecticides to soil algae. Eurasian Soil Sci 25:103-110.

OECD 207. 1984. Guideline for testing chemicals 207. Earthworm acute toxicity test. Adopted: 4 April 1984.

OECD 222. 2004. Guideline for testing chemicals 222; Earthworm Reproduction Test (*Eisenia fetida*/ *Eisenia Andrei*). Adopted 13 April 2004.

Ortiz A, Burriel J, Cantarino H. 1995. Paraquat toxicity in protozoans. European Journal of Protistology 31(4).

Patil SG, Deshpande PB. 1985. Adsorption of Carbendazim (MBC) by soils and clay minerals. Madras Agric. J. 72 (1), 16-21.

Riley, D, Wilkinson W, Tucker BV. 1976. Biological unavailability of bound paraquat residues in soil. In: Bound and conjugated pesticide residues (Eds: Kaufman DD et al.). ACS Symposium Series 29: 301-353.

Römbke J. 2003. Ecotoxicological tests with enchytraeids: A review. Pedobiologia 47: 607-616.

Römbke J, Heimbach F, Hoy S, Kula C, Scott-Fordsmand J, Sousa P, Stephenson G, Weeks J (eds). 2003. Effects of plant protection products on functional endpoints in soil (EPFES). SETAC, Pensacola, FL, USA.

Römbke J, Gestel CAM van, Jones SE, Koolhaas JE, Rodrigues JML, Moser T. 2004. Ring-testing and field-validation of a terrestrial model ecosystem (TME) – An instrumnet for testing potentially harmful substances: Effects of carbendazim on earthworms. Ecotoxicology 13: 89–103.

Roslycky EB. 1985. Sensitivity and adaptation of selected rhizobia and agrobacteria to paraquat. Can. J. Soil Sci. 65(3):555-62.

Schweiger PF, Jakobsen I. 1998. Dose-response relationships between four pesticides and phosphorous uptake by hyphae of arbuscular mycorrhizas. Soil Biol. Biochem. 30: 1415–1422.

SCP. 2001. Opinion of the Scientific Committee on Plants regarding the evaluation of quinoxyfen in the context of council directive 91/414/EEC concerning the placing of plant protection products on the market. SCP/QUINOX/002-Final 22 March 2001.

Smit AAMFR, Berg F van den, Leistra M. 1997. Estimation method for the volatilization of pesticides from fallow soil. Wageningen, DLO Winand Staring Centre, Environmenal Planning Bureau series 4.

Sousa JP, Rodrigues JML, Loureiro S, Soares AMVM, Jones SE, Förster B, Gestel CAM van. 2004. Ring-testing and field-validation of a terrestrial model ecosystem (TME) – An instrument for testing potentially harmful substances: Effects of carbendazim on soil microbial parameters. Ecotoxicology 13: 43–60.

Süss A, Pritzl E. 1977. Sorption, Abbau und Pflanzenverfügbarkeit von Carbendazim. Zeitschrift für Pflanzenkrankheiten und Pflanzenschutz. 83 (6), 352-362 (in German).

Tan TK, Chua LH.1986. The response of four soil fungi to paraquat treatment. Cryptogamie, Mycol. 7, 311-317.

TGD. 2003. Technical Guidance Document on Risk Assessment, Part II: Environmental Risk Assessment. In support of: Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances, Commision Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. European Chemicals Bureau, European Commission Joint Research Centre, EUR 20418 EN/2.

Tomlin CDS. 2003. The pesticide manual. A world compendium. British Crop Protection Council, Alton, Hampshire, UK.

Vonk JW, Adema DMM, Barug D. 1986. Comparison of the effects of several chemicals on microorganisms, higher plants and earthworms. In: Assink JW, Brink JW van den. (Eds). Contaminated Soil. Dordrecht, the Netherlands: Kluwer Academic Publishers, pp. 191–202.

Walia S, Dureja P, Mukerjee SK .1988. New photodegradation products of chlorpyrifos and their detection on glass, soil and leaf surfaces. Arch. Environ. Contam. Toxicol. 17:183-188.

Walker A. 1974. A simulation model for prediction of herbicide persistence. J. Environ. Qual. 3:396-401.

Wang W. 1994. Rice seed toxicity tests for organic and inorganic substances. Environmental Monitoring and Assessment 29(2): 101-107.

Weber JB, Perry PW, Upchurch RP. 1965. The influence of temperature and time on the adsorption of paraquat, diquat, 2,4-D and prometon by clays, charcoal, and an anion-exchange resin. Soil Science of America Proceedings 29: 678-688.

Wilkinson W, Edwards PJ. 1993. Paraquat: Long-Term Ecological Trial at Jealott's Hill, UK, 1964-90. 5. Effect on earthworms (Lumbricidae) and pot worms (Enchytraeidae), and residues in earthworms and slugs. ICI Agrochemicals, Bracknell Berkshire UK. TMJ3056B.

Wilkinson W, Cole JFH, Everett CJ, Riley D. 1993a. Paraquat: Long-Term Ecological Trial at Jealott's Hill UK, 1964-90. 1. Description of the trial and abservations on vegetation. ICI Agrochemicals, Bracknell Berkshire UK. TMJ3052B.

Wilkinson W, Cole JFH, Gough HJ. 1993b. Paraquat: Long-Term Ecological Trial at Jealott's Hill UK, 1964-90. 4. Effect on soil microarthropods. ICI Agrochemicals, Bracknell Berkshire UK. TMJ3053B.

Wijngaarden RPA van, Crum S J H, Decraene K, Hattink J, Kammen A van. 1998. Toxicicity of Derosal (active ingredient Carbendazim) to aquatic invertebrates. Chemosphere 37: 673–683

Yackovich PR, Miller JH, McCall PJ. 1985. Photodegradation of chlorpyrifos on commerce soil surface. GH-C-1699R (K33).

# Appendix 1 Glossary

**AF** Assessment Factor
**BBCH** Numerical code for crop growth stages as described by the German **B**iologischen Bundesamt, the German **B**undessortenamt and the German **CH**emical Industry (Industieverband Agrar)
**CEC** cation exchange capacity
**CRP** Community Recovery Principle
**Ctgb** College voor de toelating van gewasbeschermingsmiddelen en biociden. Board for the Authorisation of Plant Protection Products and Biocides
**DAA** Days After Application
**DAR** Draft Assessment Report
**$DegT_{50}$** Degradation half-life
**DFOP** Double First Order Parallel kinetics
**$DT_{50}$** dissipation half-life
**EC** 1) in ecotox: effect concentration, 2) in formulations: emulsifiable concentrate
**ECCO** European Community Co-Ordination
**ED** Effect dose
**EFSA** European Food Safety Authority
**EPFES** see Römbke et al. (2003)
**ERC** ecotoxicologically relevant concentration
**ETP** Ecological Treshold Principle
**EU** European Union
**FOCUS** FOrum for the Co-ordination of pesticide fate models and their Use
**FRP** Functional Redundancy Principle
**$HC_x$** Hazardous Concentration, x indicates the percentile
**HQ** Hazard Quotient
**$K_D$** sorption distribution coefficient
**$K_{OC}$** Freundlich organic carbon sorption coefficient
**$K_{OM}$** Freundlich organic matter sorption coefficient
**$K_{OM,acid}$** Freundlich organic matter sorption coefficient for acidic species
**$K_{OM,base}$** Freundlich organic matter sorption coefficient for basic species
**LNV** Ministry of Agriculture, Nature and Food Quality
**LSD** Least Squares Difference
**LOD** Limit Of Detection
**LOEC** Lowest Observed Effect Concentration
**LOQ** Limit Of Quantification
**ND** Not Detected
**NOEC** No Observed Effect Concentration
**NOEL** No Observed Effect Level
**OECD** Organisation for Economic Coordination and development
**OM** Organic Matter
**PEC** Predicted Environmental Concentration
**PIEC** Predicted Initial Environmental Concentration
**RAC** Regulatory Acceptable Concentration
**RH** Relative Humidity

**SAC** strong adsorption capacity – **-WB** wheat bioassay
**SANCO** Health and Consumer Protection Directorate General of the European Union
**SCP** Scientific Committee on Plants
**Screening function of a tier** balance between probabilities that risk is acceptable or not acceptable when this tier is applied
**SL** soluable concentrate
**SMO** Soil Micro-Organism
**SSD** Species Sensitivity Distribution
**TCP** trichlorpyridinol, metabolite of chlorpyrifos
**TGD** Technical Guidance Document
**TME** Terrestrial Model Ecosystem
**$TWA_{xx}$** Time Weighted Average, xx indicates the averaging period in days
**UF** Uncertainty Factor
**VROM** Ministry of Housing, Spatial Planning and the Environment
**WHC** Water Holding Capacity
**ρ** soil dry bulk density

# Appendix 2 Details of carbendazim exposure evaluations

## A2.1 Assessment of sorption studies of carbendazim

$K_{OM}$ values are needed for the assessment of exposure. $K_{OM}$ or $K_{OC}$ values from laboratory studies were available from the monograph and open literature. Reliability of the results of each study was checked using the P-criterion (Boesten, 1990). If the dimensionless P-value is above 0.3 the study is considered reliable. No other quality criteria were used to verify the reliability of a $K_{OM}/K_{OC}$ value. An overview of results from the studies is given in Table A2.1. The study of Aharonson and KafKafi (1975b) given in the monograph was not used because sorption coefficients were not determined. The study of Helweg (1977) was also not suitable because sorption was not measured. Furthermore two other studies given in the monograph (Aharonson and KafKafi, 1975a; Khan and Khan, 1986) were not useful because only sorption to clay minerals was measured. Using the reliable results (P >0.3) from the studies a relation between $K_{OM}$ and pH can be found (Figure A2.1). The increase of the $K_{OM}$ values around pH 4 is consistent with the surface acidity effect.

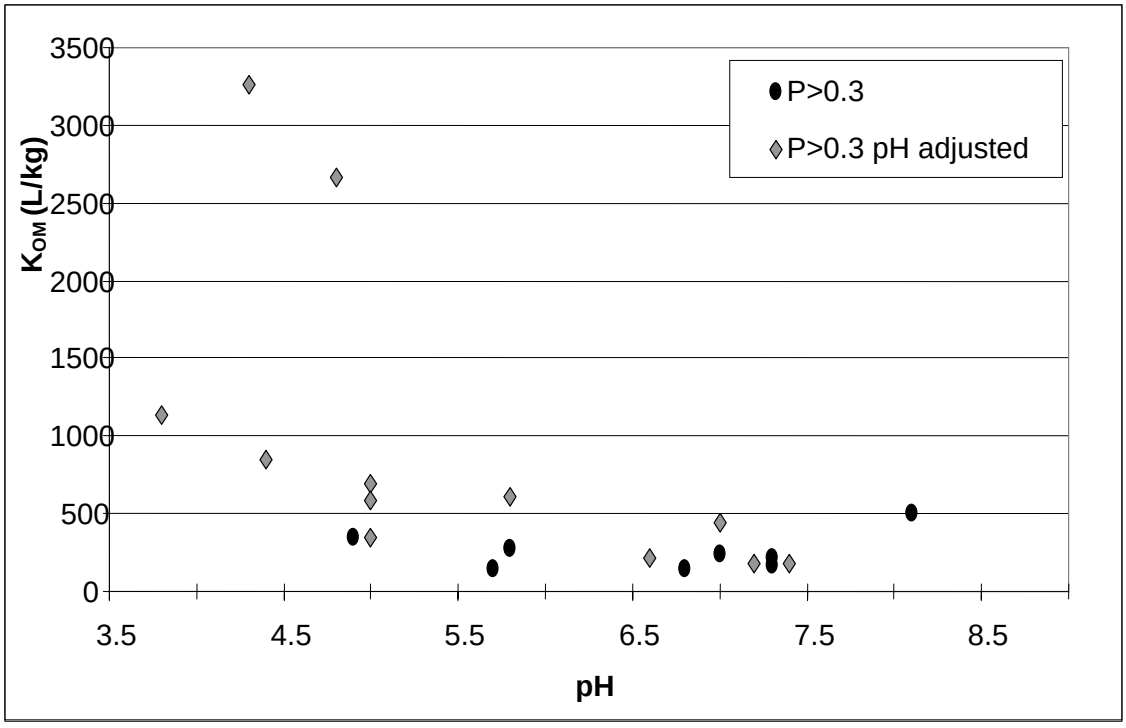



Figure A2.1 pH versus $K_{OM}$; reliable results (P >0.3) from sorption studies with carbendazim

The program GraphPad PRISM 4 was used to fit the relation between $K_{OM}$ and pH (see Figure A2.2 and Figure A2.3). Although the 95% confidence intervals of the fitted values are wide and the $R^2$ is low, these results are the best ones available and used for the PEC calculations.

Table A2.1 Results of six different sorption studies with carbendazim

| Study | pH | $K_{OC}$ ( $dm^3$ $kg^{-1}$) | $K_{OM}$ ( $dm^3$ $kg^{-1}$) | P | Temp (°C) | Details | pH measurement* |
|---|---|---|---|---|---|---|---|
| Görlitz and Klöckner, 1986 | 6.8 | 246 | 143 | > 0.3 | 22 | | ? |
| Leistra et al., 2001b (Lisse) | 7.3 | 374 | 217 | > 0.3 | 10 | | molar KCL # |
| Leistra et al., 2001b (St Maartensbrug) | 7 | 412 | 239 | > 0.3 | 10 | | molar KCL # |
| Matser and Leistra, 2000 (Speyer 2.2) | 5.7 | 252 | 146 | > 0.3 | 20 | | molar KCL # |
| Patil and Deshpande, 1985 | 5.8 | 483 | 280 | > 0.3 | ? | | ? |
| Patil and Deshpande, 1985 | 8.1 | 869 | 504 | > 0.3 | ? | | ? |
| Patil and Deshpande, 1985 | 5 | 1196 | 694 | > 0.3 | ? | adjusted pH | ? |
| Patil and Deshpande, 1985 | 5 | 592 | 343 | > 0.3 | ? | adjusted pH | ? |
| Patil and Deshpande, 1985 | 5 | 1005 | 583 | > 0.3 | ? | adjusted pH | ? |
| Patil and Deshpande, 1985 | 7 | 762 | 442 | > 0.3 | ? | adjusted pH | ? |
| Süss and Pritzel, 1977 | 4.9 | 590 | 342 | > 0.3 | 30 | | ? |
| Süss and Pritzel, 1977 | 7.3 | 292 | 169 | > 0.3 | 30 | | ? |
| Nicholls and Evans, 1991a (R) | 3.8 | 1960 | 1137 | > 0.3 | 18 | adjusted pH | ? |
| Nicholls and Evans, 1991a (R) | 4.4 | 1470 | 853 | > 0.3 | 18 | adjusted pH | ? |
| Nicholls and Evans, 1991a (R) | 6.6 | 367 | 213 | > 0.3 | 18 | adjusted pH | ? |
| Nicholls and Evans, 1991a (R) | 7.2 | 306 | 178 | > 0.3 | 18 | adjusted pH | ? |
| Nicholls and Evans, 1991b (W) | 4.3 | 5625 | 3263 | > 0.3 | 18 | adjusted pH | ? |
| Nicholls and Evans, 1991b (W) | 4.8 | 4583 | 2659 | > 0.3 | 18 | adjusted pH | ? |
| Nicholls and Evans, 1991b (W) | 5.8 | 1042 | 604 | > 0.3 | 18 | adjusted pH | ? |
| Nicholls and Evans, 1991b (W) | 7.4 | 313 | 181 | > 0.3 | 18 | adjusted pH | ? |
| Görlitz and Klöckner, 1986 | 5.2 | 200 | 116 | < 0.3 | 22 | | ? |
| Görlitz and Klöckner, 1986 | 7 | 230 | 133 | < 0.3 | 22 | | ? |
| Dios Cancela et al., 1992 (P-8) | 8.1 | 227 | 132 | < 0.3 | 30 | | water |
| Dios Cancela et al., 1992 (P-9) | 7.1 | 593 | 344 | < 0.3 | 30 | | water |
| Dios Cancela et al., 1992 (P-10) | 8.4 | 494 | 286 | < 0.3 | 30 | | water |
| Dios Cancela et al., 1992 (P-11) | 8.2 | 393 | 228 | < 0.3 | 30 | | water |
| Dios Cancela et al., 1992 (P-12) | 8.4 | 338 | 196 | < 0.3 | 30 | | water |
| Dios Cancela et al., 1992 (M-106) | 7.45 | 292 | 169 | < 0.3 | 30 | | water |
| Dios Cancela et al., 1992 (M-130) | 7.87 | 299 | 173 | < 0.3 | 30 | | water |
| Dios Cancela et al., 1992 (M-272) | 7.74 | 541 | 314 | < 0.3 | 30 | | water |

* because pH measurement procedures were usually not clear, pH values as provided by the authors were used without correction

# personal communication M Leistra

? not reported

**Results of GraphPad PRISM 4**
Fitformula:
Y=(Kmol + Kanion RM (10^(X-pka-pSH)))/(1+RM 10^(X-pka-pSH))

Y = apparent sorption constant
X = pH
Kmol = H-carbendazim$^{+}$
Kanion = carbendazim.
RM = relative molar mass
pKa = acid dissociation constant
pSH = parameter accounting for surface acidity

Best-fit values

| | |
|---|---|
| KMOL | 2073 |
| KANION | 201.9 |
| RM | 0.9948 |
| PKA | 4.200 |
| PSH | 0.6104 |

Std. Error

| | |
|---|---|
| KMOL | 743.8 |
| KANION | 208.6 |
| PSH | 0.4858 |

95% Confidence Intervals

| | |
|---|---|
| KMOL | 503.3 to 3642 |
| KANION | -238.3 to 642.1 |
| PSH | -0.4147 to 1.636 |

Goodness of Fit

| | |
|---|---|
| Degrees of Freedom | 17 |
| $R^2$ | 0.4476 |
| Absolute Sum of Squares | 7.3316e+006 |
| Sy.x | 656.7 |

Constraints
RM = 0.9948
PKA = 4.200

Data

| | |
|---|---|
| Number of X values | 20 |
| Number of Y replicates | 1 |

Figure A2.2 GraphPad Prism fit for the dependency of sorption of carbendazim on soil pH

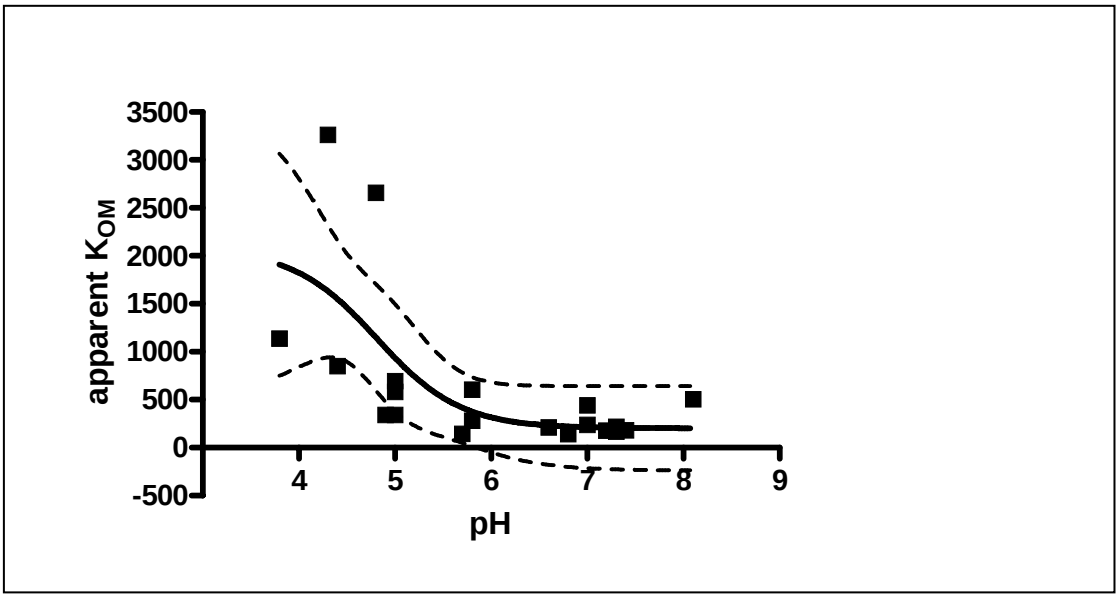



Figure A2.3 Fit and confidence limits for the pH dependent sorption of carbendazim

## A2.2 Assessment of field dissipation studies of carbendazim

**Introduction**

$DegT_{50}$ values are needed for both the assessment of trigger values and exposure. $DegT_{50}$ values are calculated to compare with $DegT_{50}$ trigger values of the FRP, CTP and ETP (Van der Linden et al., 2006). Tier 2 and Tier 3 in the estimation of the exposure levels for use in assessment schemes need $DegT_{50}$ values as input in the model PEARL (Tier 2) and GeoPEARL (Tier 3). Only one $DegT_{50}$ value from a laboratory study (Matser and Leistra, 2000) was found to be reliable. Additional information from field dissipation studies was available. Field results are preferred over laboratory results because they are determined under conditions specific for the intended use of a pesticide in an agricultural field and thus closely match the situation which is to be modelled (FOCUS, 2006). The results from the additional field dissipation studies may lead to a different value for both the comparison with trigger values and the input for the calculation of exposure concentrations if this $DegT_{50,field}$ is statistically significant different from the $DegT_{50,lab}$.

Three field dissipation studies from Germany on sandy soils were available (Krebs and Baedelt, 1990a; Krebs and Baedelt, 1990b; Krebs and Baedelt, 1990c). A fourth study, specified in the monograph as Krebs and Baedelt H. 1990. Untersuchung des Abbaus im Boden unter Freilandbedingungen. BOD95-00449 was not available to the authors of this report.

FOCUS (2006) recommends normalizing the field dissipation data to reference conditions (temperature and moisture conditions) to allow widespread use. Furthermore it should be evaluated whether the field studies results are appropriate for calculation of the $DegT_{50}$. A critical assessment of the significance of other dissipation processes (for example photodegradation, volatilisation) is therefore necessary.

**Material and methods**

***Study design***

The design of the three field studies is generally the same. Bare soil plots (two about 6.5 * 10 m, one about 2 * 25 m) were treated with a formulation containing carbendazim. Soil cores were taken from the 0 – 20 cm layer at various time intervals. Each core was split into horizons and replicate horizons were bulked into one sample, so no replicate samples were available. The samples were analysed for carbendazim. No samples were taken below 20 cm depth. The notifier did not find this necessary due to the presumed low leaching capacity of carbendazim. Every study showed satisfying recoveries.

Table A2.2 Field studies with carbendazim

| study | location | soil type | reference |
|---|---|---|---|
| BOD95-00447 | Frankfurth-Schwanheim (Germany) | silty sand | Krebs, Baedelt, 1990a |
| BOD95-00448 | Gersthofen (Germany) | sandy silty loam | Krebs, Baedelt, 1990b |
| BOD95-00450 | Stelle, Kreis Hamburg (Germany) | silty sand | Krebs, Baedelt, 1990c |

***Assessment of possible dissipation processes.***

In order to determine a $DegT_{50}$ it is essential that the decline in the field is only the result of degradation. Critical evaluation of possible dissipation processes is therefore necessary. Processes which may attribute to the dissipation of carbendazim are photodegradation, volatilization and wind erosion. The List of Endpoints gives information on volatilization from both bare soil and plants are negligible. Additionally cumulative volatilization from bare soil was estimated at 21 days after application with an empirical relation described by Smit et al. (1997). The used formulas are described below.

$$CV_{normal\text{-}moist} = 71.9 + 11.6 \log(100\ FP_{gas});\ 6.33E\text{-}9 < FP_{gas} \leq 1 \qquad \text{Eq. A2.1}$$

Where:

CV cumulative volatilization, (% of dosage active ingredient)

$FP_{gas}$ fraction of pesticide in the gas phase, (-)

Eq.A2.1 is an empirical relation found for the cumulative volatilization from soils under normal to moist field conditions during 21 days after application.

$$FP_{gas} = \theta_{gas}/Q \qquad \text{Eq. A2.2}$$

Where:

Q the capacity factor, (-)

$\theta_{gas}$ volume fraction of gas, ($m^3$ gas $m^{-3}$ soil); assumed to be 0.2

$$Q = \theta_{gas} + \theta_{liquid}\ K_{l/g} + \rho_{soil}\ K_{l/g}\ K_{s/l} \qquad \text{Eq. A2.3}$$

Where:

| | |
|---|---|
| $\theta_{liquid}$ | volume fraction of moisture, ($m^3$ liquid $m^{-3}$ soil); assumed to be 0.2 |
| $K_{l/g}$ | liquid-gas partitioning coefficient, (kg $m^{-3}$ liquid )/(kg $m^{-3}$ gas) |
| $\rho_{soil}$ | dry bulk density of the soil, (kg solid $m^{-3}$ soil); assumed to be 1250 kg $m^{-3}$ |
| $K_{s/l}$ | solid-liquid partitioning coefficient, (kg $kg^{-1}$ solid)/(kg $m^{-3}$ liquid) |

$$K_{s/l} = f_{OM} K_{OM} \qquad \text{Eq. A2.4}$$

Where:

| | |
|---|---|
| $f_{OM}$ | fraction organic matter, (-); assumed to be 0.01 |
| $K_{OM}$ | sorption coefficient to organic matter, ($m^3$ $kg^{-1}$) |

$$K_{l/g} = 1/K_H \qquad \text{Eq. A2.5}$$

Where:

| | |
|---|---|
| $K_H$ | Henry coefficient (-) |

$$K_H = P\ M/\ O\ c \qquad \text{Eq. A2.6}$$

Where:

| | |
|---|---|
| P | vapour pressure (Pa = N $m^{-2}$) |
| M | molar mass (g $mol^{-1}$): 350.6 g $mol^{-1}$ for carbendazim |
| O | solubility in water (g $m^{-3}$): 1.05 g $m^{-3}$ for carbendazim |
| c | constant: 2430 (J $mol^{-1}$ = Nm $mol^{-1}$) |

In one of the three studies a relatively small plot (about 2 m wide) was used. Although information about the wind direction is not available the possibility of wind erosion can not be ignored. However, in case of precipitation shortly after application, transporting the substance deeper into the soil, wind erosion is not very likely to occur. This concept also applies to volatilization and photodegradation. Therefore an analysis was made of the precipitation amounts in the period after application.

**Evaluation of the field dissipation studies**

***Assessment of measurements***

Per residue it was checked whether other dissipation processes than degradation were also responsible for the decline. If there was any doubt about the dissipation not being exclusively attributable to degradation in soil, the measurement was not taken into account for derivation of the $DegT_{50}$.

FOCUS (2006) recommends the number of data points not to be smaller than five. Furthermore the pattern of decline should be clearly established (FOCUS, 2006). The method for handling of measurements below the limit of quantification (LOQ) or the limit of detection (LOD) is described in FOCUS (2006) and used. Most important procedures are:

- all values between LOD and LOQ are set tot the actual measured value. If the actual measured concentration has not been reported, use 0.5·(LOQ + LOD);
- measurements with smaller values than the LOD (0.01 mg $kg^{-1}$) are set to 0.5·LOD (FOCUS, 2006);

- cut off the curve after the pesticide has largely dissipated. All samples after the first non-detect (< LOD) should be omitted unless positive detections above LOQ are made later in the experiment (FOCUS, 2006).

***Normalization to reference conditions***

FOCUS (2006) advises to normalize field dissipation half-lives to reference temperature and reference moisture conditions. Measurements of moisture content were not given. In such a case FOCUS (2006) advises to calculate the moisture contents with the PEARL model. However this was impossible because there was not enough information available to run the model for these studies. It is therefore not possible to normalize the measurements to reference moisture conditions. It is thus assumed that all field dissipation studies were carried out under reference moisture conditions (pF2). This a conservative approach, because the soil was probably dryer in the field, causing slower degradation. Normalization to reference temperature is possible. We used the time-step normalization approach suggested by FOCUS (2006) using the average air temperature as reference soil temperature. Note however that only the first month daily temperatures were given. For the other days, the average month temperature was used.

The idea of the time-step normalization is the reduction of increase of day lengths depending on soil temperature and moisture by means of correction factors. The procedure for normalization to reference soil temperature only is described below.

Calculation of the correction factor $f_{Temp}$:

$$f_{Temp} = Q_{10}^{(Tact-Tref)/10} \quad \text{for } T_{act} > 0\ °C \qquad \text{Eq. A2.7}$$
$$f_{Temp} = 0 \quad \text{for } T_{act} \leq 0\ °C$$

Where:

| | |
|---|---|
| $f_{Temp}$ | correction factor for soil temperature, (-) |
| $Q_{10}$ | 2.2 (FOCUS, 2000), (-) |
| $T_{act}$ | actual soil temperature, (°C) |
| $T_{ref}$ | reference soil temperature, (°C); for example 10 °C |

Calculation of the normalized day length:

$$D_{Norm} = f_{Temp} \qquad \text{Eq. A2.8}$$

Where:

| | |
|---|---|
| $D_{norm}$ | normalized day length, (d) |

The normalized day lengths ($D_{Norm}$) are summed up, resulting in 'normalized days' after application (FOCUS, 2006).

***Calculation of the $DegT_{50}$***

There are several options for calculation of the $DegT_{50}$ values from the field studies. The one most preferred is simulation of the field studies with the PEARL model (Leistra et al., 2001a) and inverse

modelling of the $DegT_{50soil}$. However, not enough data were available to model the studies with PEARL. So more simple approaches were chosen:

1 Single First Order (SFO) kinetics, fitting the initial amount of the chemical and the rate constant.
2 Double First Order in Parallel (DFOP) kinetics, fitting 4 parameters of this bi-exponential model.

More information about these two models can be found in FOCUS (2006). The program KinGUI (Mikolasch and Schäfer, 2006) is used for the fitting of the parameters. It was not considered meaningful to apply First-Order Multi-Compartment (FOMC) kinetics. Note that this is also not necessary based on FOCUS (2006), because this FOCUS guidance applies only to laboratory experiments, not to field experiments.

**Results and discussion**

***Assessment of possible dissipation processes***

The List of Endpoints states that losses due to volatilisation from both bare soil and plants are negligible. Additionally volatilisation from bare soil was estimated to be about 29% at 21 days after application with an empirical relation described by Smit et al. (1997) assuming a value of 1250 kg $m^{-3}$ for the bulk density and a value of 0.2 for both the volume fractions of gas and moisture in soil.

Analysis of precipitation after application of carbendazim shows that for only field study (BOD95-00447) precipitation occurred several days after application. In these days photodegradation, volatilization and wind erosion might take place (this is also the study with the 2m wide plot). The observed decline in residues in these days can not only be attributed to degradation.

Table A2.3 Precipitation during the field experiments shortly after application of carbendazim; day of application is day 0

| study | rain showers after application |
|---|---|
| BOD95-00447 | day 3: 4 mm, day 6: 0.5 mm, day 7: 7.5 mm, day 8: 1.5 mm, day 9: 3.9 mm |
| BOD95-00448 | day 0: 19.7 mm, day 1: 23.1 mm, day 2: 10.2 mm. |
| BOD95-00450 | day 0: 5 mm, day 1: 4 mm, day 2 - 4: 3mm |

***Evaluation of the field dissipation studies***

For each field dissipation study the decline in residues was analysed for involved dissipation processes. If there was any doubt about the dissipation not being exclusively attributed to degradation in soil the measurement was not taken in to account for derivation of the $DegT_{50}$. Studies were analysed for the number of measurements left and the decline pattern. If less than 5 measurements were left or if the decline pattern was not satisfying the study was rejected. Table A2.4 gives a summary of which measurements were excluded and which studies were rejected.

Table A2.4 Summary of measurements to exclude or studies to reject

| study | excluded measurements | reason |
|---|---|---|
| BOD95-00447 | study is rejected | measured residues are too close to the detection limit |
| BOD95-00448 | none | |
| BOD95-00450 | none | |

Figure A2.4 and Figure A2.5 show graphs of the carbendazim residues, including the residues at t = 0 calculated from the dose (using a dry bulk density of 1250 kg $m^{-3}$) and the precipitation for the studies not rejected. If the residue at t = 0 calculated from the dose is much larger than the residue measured at t = 0 then this indicates the involvement of other dissipation processes than degradation at the start of the study. The study BOD95-00447 was rejected. Measured residues were too close to the limit of detection. Therefore this study is considered not suitable for kinetic evaluation.

***Normalization to reference conditions***

Day lengths are normalized to 20 °C so the estimated $DegT_{50,field}$ can be compared with the $DegT_{50,lab}$ which are measured at 20 °C (see Figure A2.6 and Figure A2.7).

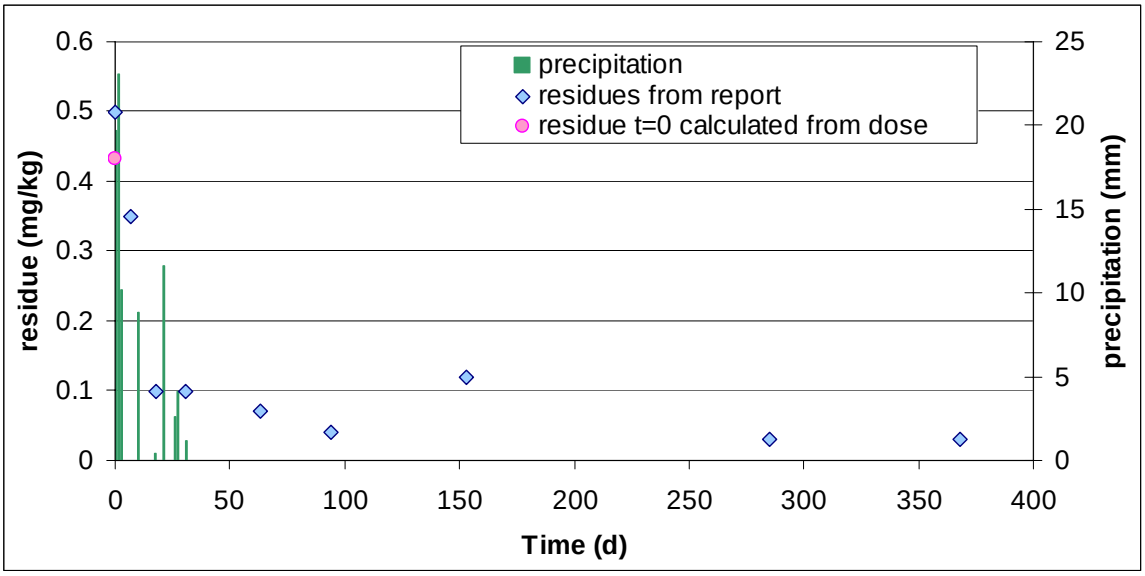



Figure A2.4 Measured residues of carbendazim in soil and measured precipitation[3] of study BOD95-00448

[3] Note that precipitation was only measured in the first 30 days of the study

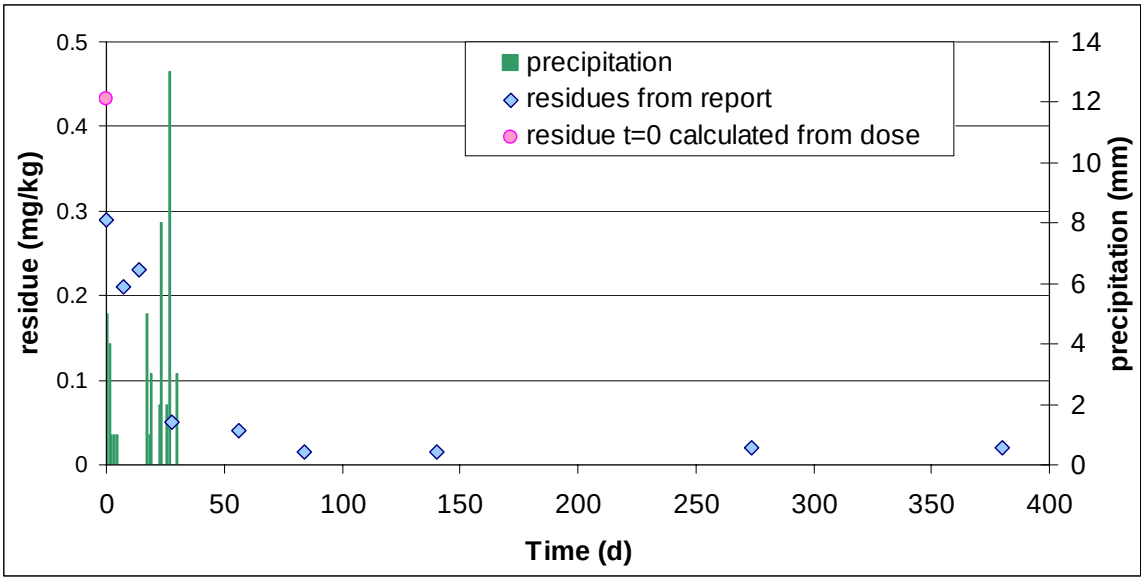



Figure A2.5 Measured residues of carbendazim in soil and measured precipitation[3] of study BOD95-00450

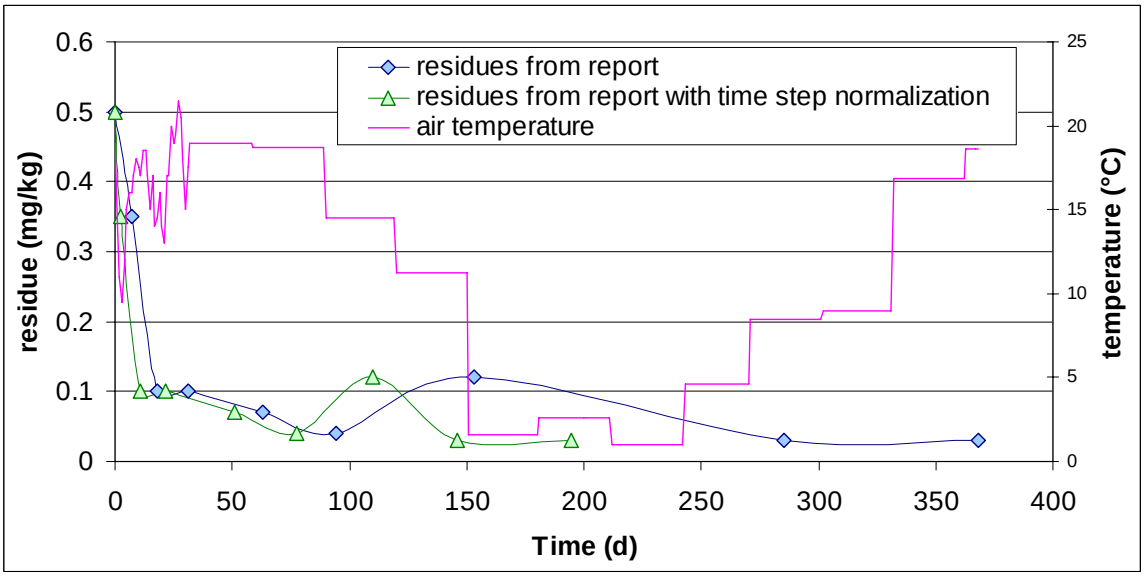



Figure A2.6 Measured residues versus time (diamonds) and versus normalized time (triangles) and measured air temperature[1] of study BOD95-00448

[1] Air temperature measured daily in the first month of the study, thereafter monthly averages temperatures are used

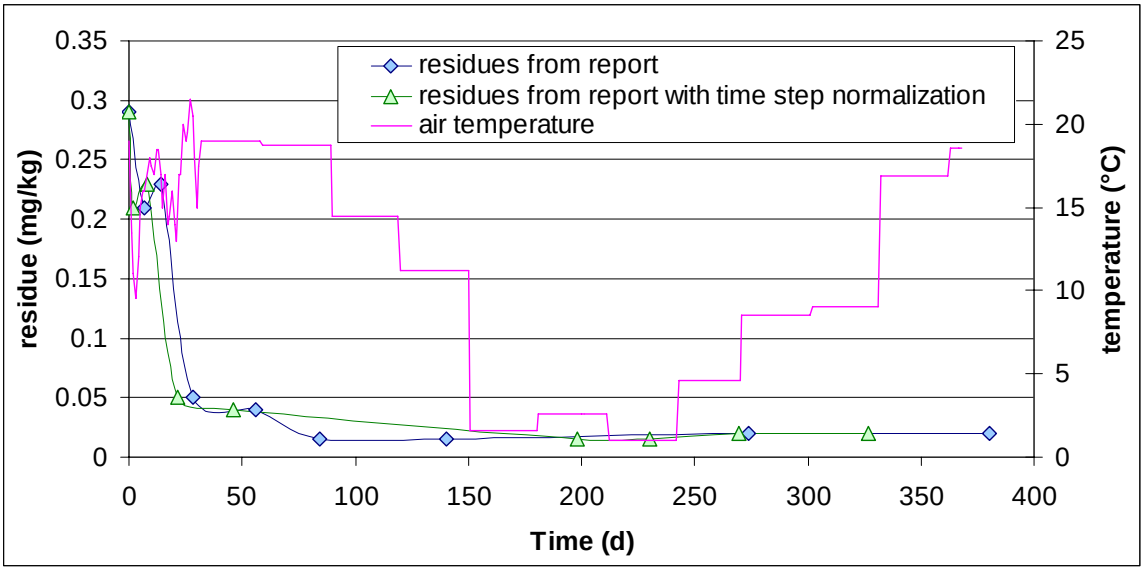



Figure A2.7 Measured residues versus time (diamonds) and versus normalized time (triangles) and measured air temperature[1] of study BOD95-00450

***Calculation of the DegT$_{50}$***

DegT$_{50,field}$ values are fitted with the program KinGUI (Mikolasch and Schäfer, 2006). Results of the fits to normalized data sets are shown in Figure A2.8 - Figure A2.11. Fits are done using two different degradation models: SFO and DFOP.

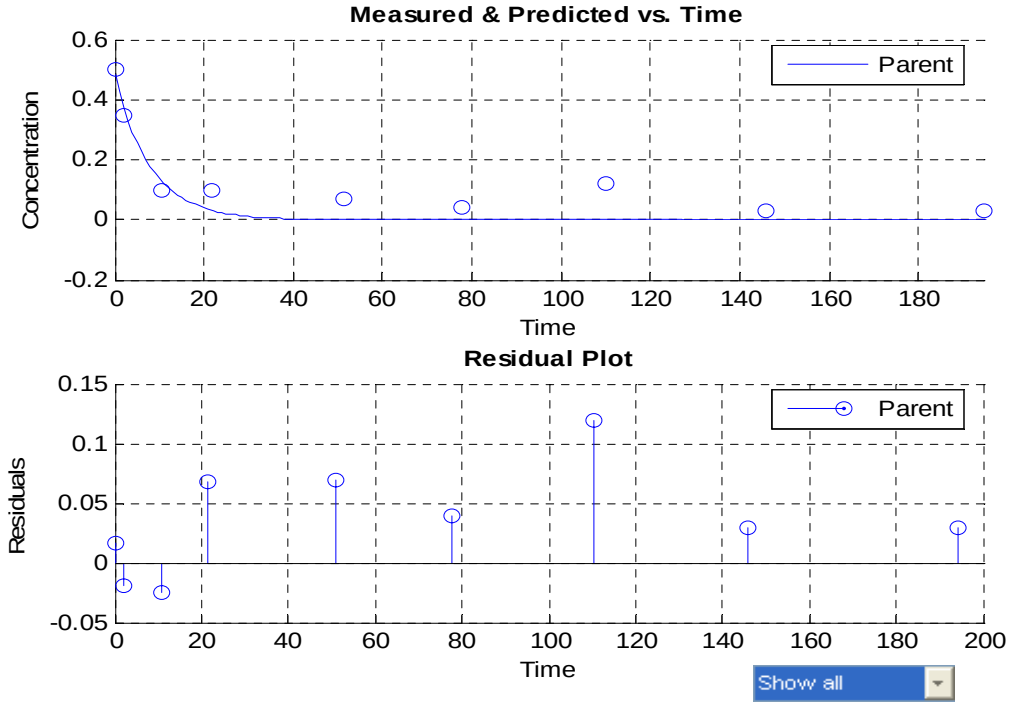



Figure A2.8 SFO fit of study BOD95-00448

Table A2.5 Fitted parameters for study BOD95-00448

| | initial value | estimated value | SD | prob > t |
|---|---|---|---|---|
| SFO | | | | |
| parent_k | 0.126 | 0.13 | 0.042 | 0.01 |
| parent_$M_0$ | 0.48 | 0.48 | 0.056 | |
| DFOP | | | | |
| parent_$k_1$ | 0.24 | 0.24 | 0.077 | 0.013 |
| parent_$k_2$ | 0.004 | 0.0041 | 0.0041 | 0.18 |
| parent_g | 0.82 | 0.82 | 0.066 | 3.0e-5 |
| parent_$M_0$ | 0.48 | 0.50 | 0.033 | |

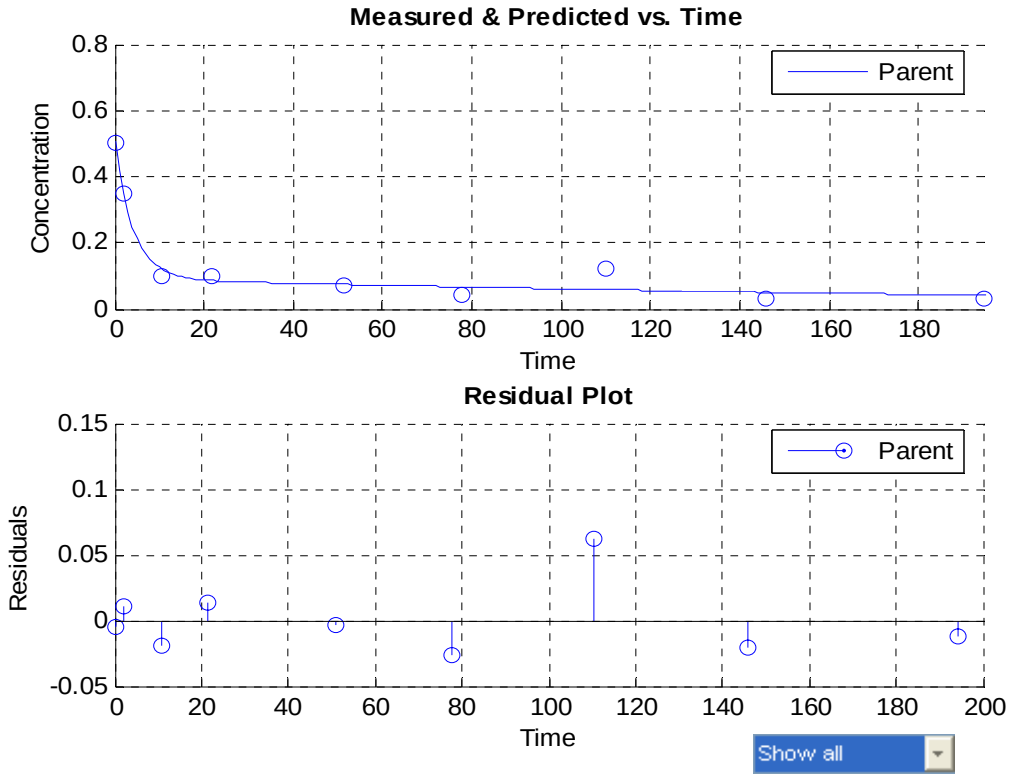



Figure A2.9 DFOP fit of study BOD95-00448

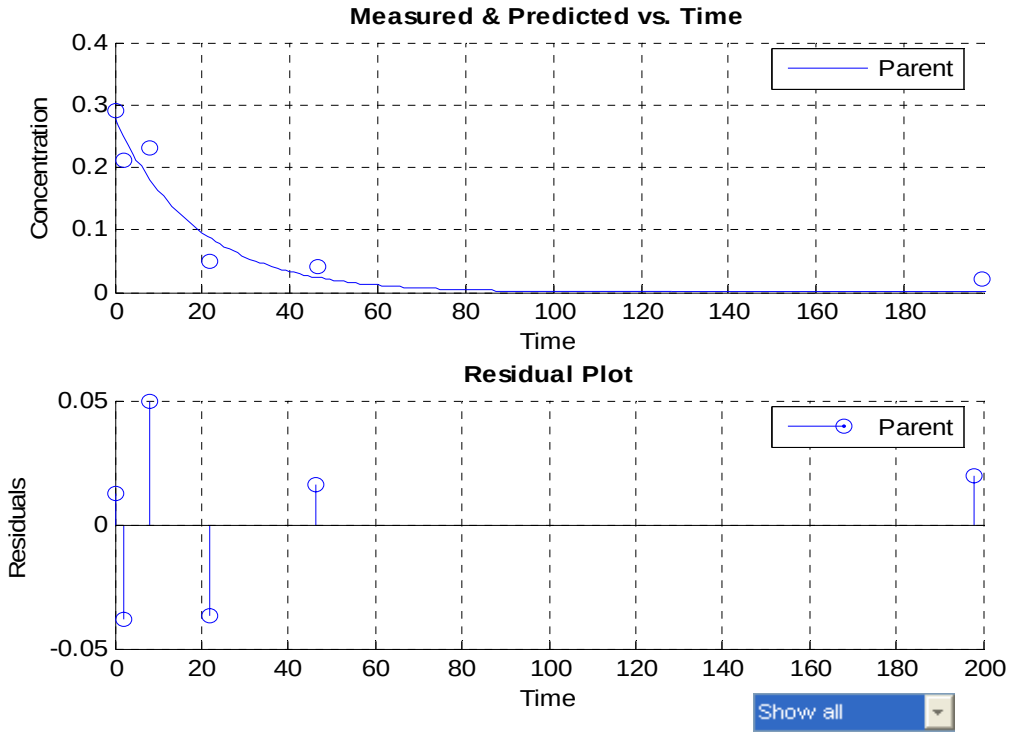



Figure A2.10 SFO fit of study BOD95-00450

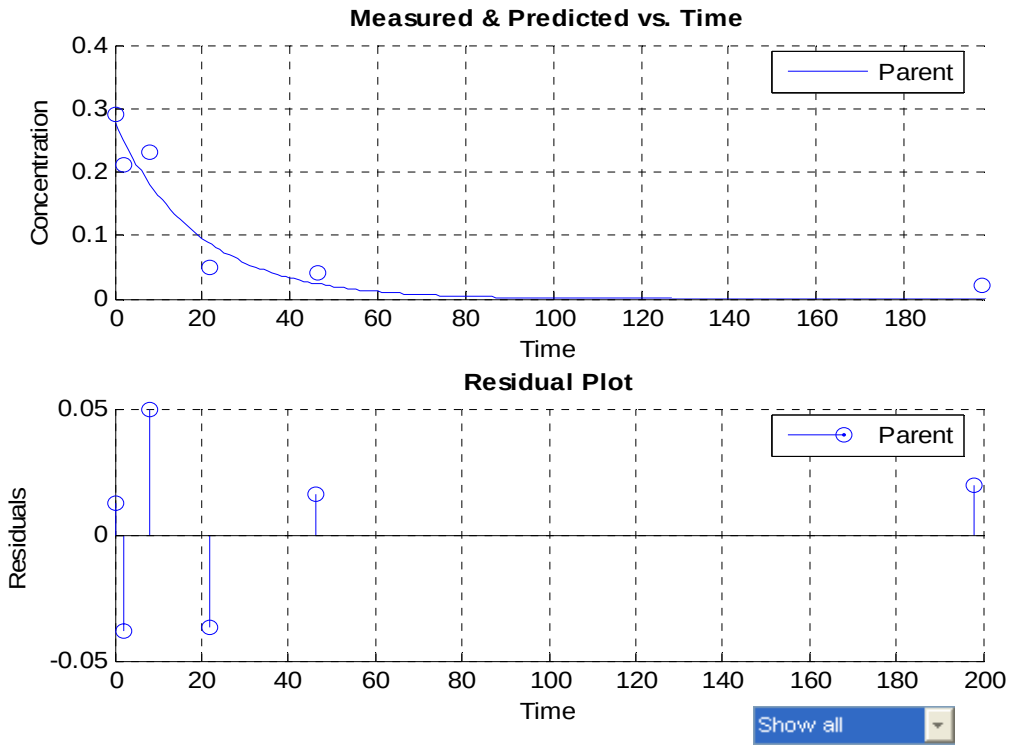



Figure A2.11 DFOP fit of study BOD95-00450

Table A2.6 Fitted parameters for study BOD95-00450

| | initial value | estimated value | SD | prob > t |
|---|---|---|---|---|
| SFO | | | | |
| parent_k | 0.015 | 0.053 | 0.017 | 0.018 |
| parent_$M_0$ | 0.25 | 0.28 | 0.03 | |
| DFOP | | | | |
| parent_$k_1$ | 0.05 | 0.053 | > 1000 | 0.5 |
| parent_$k_2$ | 0.05 | 0.053 | > 1000 | 0.5 |
| parent_g | 0.2 | 0.25 | > 1000 | 0.5 |
| parent_$M_0$ | 0.28 | 0.28 | 0.049 | |

$Chi^2$ values (see Table A2.7) are in all cases larger than 15 (FOCUS, 2006 p. 115: "No further action is required and the half-life can be used for modelling if the fit is visually acceptable and passes the $chi^2$-test at an error level of 15% or less"). Except for the SFO fits, not every fitted parameter value in each test is reliable (t-test). Both methods result in about the same value for the $DegT_{50}$. Table A2.7 shows the estimated $DegT_{50,field}$ values of the two field dissipation studies.

Table A2.7 Estimated $DegT_{50,field}$ values for carbendazim (measurements normalized to 20 °C)

| study | kinetics | $DegT_{50,I}$ (d) | $DegT_{50,II}$ (d) | g | $Chi^2$ | t-test < 0.05 (for each fitted parameter) |
|---|---|---|---|---|---|---|
| BOD95-00448 | SFO | 5.5 | | | 30.3 | Yes |
| | DFOP | 2.9 | 169.1 | 0.82 | 15.4 | No |
| | | | | | | |
| BOD95-00450 | SFO | 13.0 | | | 18.2 | Yes |
| | DFOP | 13.0 | 13.0 | 0.75 | 22.9 | No |

$_I$ and $_{II}$ denote the compartment considered in the kinetics model

Field persistence studies are higher tier studies that may overrule laboratory studies. After applying quality criteria, only two studies were left. Study BOD95-00448 has nine measuring points up to about 190 days and shows clear biphasic behaviour with the fast phase ending after about 10 d. Study BOD95-00450 has six measuring points with only a few measuring points for times longer than 20 days. We interpret the fast decline in study BOD95-00448 as rapid loss processes at the soil surface, so not as degradation in the soil. The $DegT_{50,II}$ in Table A2.7 of 169 days is consistent with the $DegT_{50lab}$ of 141 days of Matser and Leistra (2000). Figure A2.11 indicates that in study BOD95-00450 the rate slows down after 20 days but the number of measuring points is too small to reliably estimate the $DegT_{50}$ of the slow phase. Thus study BOD95-00450 has no added value. So the $DegT_{50,lab}$ of 141 days of Matser and Leistra (2000) is used for calculating exposure concentrations, because the field persistence studies did not demonstrate convincingly that the degradation rate in field soil is faster than expected from this $DegT_{50,lab}$.

# Appendix 3 Details of chlorpyrifos exposure evaluations

## A3.1 Assessment of field dissipation studies of chlorpyrifos

**Introduction**

$DegT_{50}$ values are needed for both the assessment of trigger values and exposure. $DegT_{50}$ values are calculated to compare with $DegT_{50}$ trigger values of the FRP, CTP and ETP (Van der Linden et al., 2006). Tier 2 and Tier 3 in the estimation of the exposure levels for use in assessment schemes need $DegT_{50}$ values as input in the model PEARL (Tier 2) and GeoPEARL (Tier 3). $DegT_{50}$ values from laboratory studies were available from the monograph (chapter 8, annex B, Dec 2002). Additional information from field dissipation studies was available. Field results are preferred over laboratory results because they are determined under conditions specific for the intended use of a pesticide in an agricultural field and thus closely match the situation which is to be modelled (FOCUS, 2006). The results from the additional field dissipation studies may lead to a new $DegT_{50}$ value for comparison with the trigger values and the input parameter for the calculation of exposure concentrations if this $DegT_{50,field}$ is statistically significant different from the $DegT_{50,lab}$.

Eight field dissipation studies (representing different areas and soils in Europe) were available. FOCUS (2006) recommends normalizing the field dissipation data to reference conditions (temperature and moisture conditions) to allow widespread use. Furthermore it should be evaluated whether the field study results are appropriate for calculation of the $DegT_{50}$. A critical assessment of the significance of other dissipation processes (for example photodegradation, volatilization) is therefore necessary.

**Material and methods**

***Study design***

The design of the eight field studies is generally the same. Bare soil plots (about 3 x 30 m) were treated with a formulation containing chlorpyrifos. Soil cores were taken at various time intervals. Each core was split into horizons and replicate horizons were bulked into one sample, so no replicate samples were available. The samples were analysed for chlorpyrifos and its metabolite pyridinol (TCP). No residues of chlorpyrifos were detected below 10 cm. Every study showed satisfying recoveries.

***Assessment of possible dissipation processes***

See section A2.2

**Evaluation of the field dissipation studies**

In all eight studies relatively small plots (about 3 m wide) were used. Although information about the wind direction is not available the possibility of wind erosion can not be ignored. However, in case of precipitation shortly after application, transporting the substance deeper into the soil, wind erosion is not very likely to occur. This concept also applies to volatilization and photodegradation. Therefore an analysis was made of the precipitation amounts in the period after application.

***Assessment of measurements***

See section A2.2

***Normalization to reference conditions***

FOCUS (2006) advises to normalize field dissipation half-lives to reference temperature and reference moisture conditions. Measurements of moisture content were not given. In such a case FOCUS (2006) advises to calculate the moisture contents with the PEARL model. However this was impossible because there was not enough information available to run the model for these studies. It is therefore not possible to normalize the measurements with respect to reference moisture conditions. It is thus assumed that all field dissipation studies were carried out under reference moisture conditions (pF2). This a conservative approach, because the soil was probably dryer in the field, causing slower degradation. Normalization to reference temperature is possible. The time-step normalization approach suggested by FOCUS (2006) was applied using either measured soil temperatures (Thessaloniki) or average air temperatures (all other dissipation studies). See section A2.2 for details on the method.

***Calculation of the $DegT_{50,field}$***

There are two options for calculation of the $DegT_{50}$ values from the field studies. The one most preferred is simulation of the field studies with the PEARL model (Leistra et al., 2001) and inverse modelling of the $DegT_{50}$. However there were not enough data available to model the studies with PEARL. So a more simple approach was chosen: fitting the initial amount of the chemical and the rate constant to the normalized measurements assuming Single First Order (SFO) kinetics:

$$M = M_0 e^{-kt} \qquad \text{Eq. A3.1}$$

Where:

| | |
|---|---|
| M | total amount of chemical present at time t, (mg $kg^{-1}$) |
| $M_0$ | total amount of chemical present at time t = 0, (mg $kg^{-1}$) |
| k | degradation rate constant, ($d^{-1}$) |
| t | time, (d) |

Fitting of $M_0$ and k is done with the Solver option in Microsoft Excel ®.

**Results and discussion**

***Assessment of possible dissipation processes***

The monograph summarises studies on soil photolysis of chorpyrifos. From the first two studies (Havens et al. (1992) and Yackovich et al. (1985)) it is concluded that chlorpyrifos degraded rapidly in both light and dark. Hardly any difference in degradation rates between the light and the dark situations was detected. The summary of the third study (Walia et al. (1988)) is somewhat unclear, but it suggests that soil photolysis of chlorpyrifos might be possible.

The list of endpoints of chlorpyrifos gives an estimation of volatilization from soil of 22 - 26% in 24 hours (wind tunnel experiment of Day and Rudel (1993)). Additionally, cumulative volatilization from bare soil was estimated to be about 25.4% at 21 days after application, using an empirical relation as described by Smit et al. (1997) and assuming a value of 1250 kg $m^{-3}$ for the dry bulk density and 0.2 for both the volume fractions of gas and moisture in soil.

Analysis of the precipitation after application of chlorpyrifos showed that especially for the field studies at Tranent (Scotland) and Tarragona (Spain) the first rain shower occurred several days after

application. In these days photodegradation, volatilization and wind erosion might have taken place. The observed decline in residues in these days cannot only be attributed to degradation.

Table A3.1 Information on precipitation of the field dissipation studies for chlorpyrifos; day of application: t = 0 d

| name soil/location | rain showers after application |
|---|---|
| Adelshausen (Germany) | day 1: 15 mm, day 2: 1 mm, day 3: 4 mm |
| Grebin (Germany) | day 0 - 6: 2.6, day 7 - 13: 3 mm |
| Herford (Germany) | day 0: 5.6 mm, day 1: 7.9 mm, day 2: 8.8 mm |
| Lauter (Germany) | day 0: 1 mm, day 6: 3 mm, day 7: 5 mm day 8: 5 mm |
| Tranent (Scotland) | day 9: 0.6 mm, day 13: 2.8 mm, day 14: 0.8 mm, day 15: 19 mm |
| Charentilly (France) | day 2: 2.4 mm, day 4: 1.2 mm, day 7: 1.6 mm, day 10 1.2 mm |
| Thessaloniki (Greece) | day 1: 4 mm, day 2: 24.6 mm, day 3: 17 mm |
| Tarragona (Spain) | day 5: 0.8 mm, day 6: 42.4 mm, day 7: 0.2 mm |

***Evaluation of the field dissipation studies***

For each field dissipation study the decline in residues was analysed for contributions of various dissipation processes. If there was any doubt about the dissipation not being exclusively attributable to degradation in soil, the measurement was not taken into account for derivation of the $DegT_{50}$. Studies were analysed for the number of measurements left. If less than five measurements were left, the study was rejected. Table A3.2 gives a summary of which measurements were excluded and which studies were rejected.

Table A3.2 Summary of measurements to exclude or studies to reject

| study | excluded measurements | reason |
|---|---|---|
| Adelshausen (Germany) | t = 0 d | other dissipation processes involved |
| Grebin (Germany) | none | |
| Herford (Germany) | none | |
| Lauter (Germany) | t = 0 d | other dissipation processes involved |
| Tranent (Scotland) | t = 0 d, t = 3 d and t = 7 d; study is rejected | other dissipation processes involved |
| Charentilly (France) | t = 0 d | other dissipation processes involved |
| Thessaloniki (Greece) | t = 0 d | other dissipation processes involved |
| Tarragona (Spain) | t = 0 d and t = 3 d; study is rejected | other dissipation processes involved |

Figure A3.1 - Figure A3.8 show graphs of the residues, including the residues at t = 0 calculated from the dose (using a dry bulk density of 1250 kg $m^{-3}$), and the precipitation for the studies. If the residues at t = 0 calculated from the dose are much higher than the residues measured at t = 0 then this indicates possible involvement of other dissipation processes than degradation at the start of the study. For this reason most measurements on t = 0 were excluded from the kinetic evaluation. The studies from both Tranent and Tarragona were rejected. Several measurements at the beginning of the study were

excluded leaving only measurements with values close to the limit of detection. Therefore these studies were considered not suitable for kinetic evaluation.

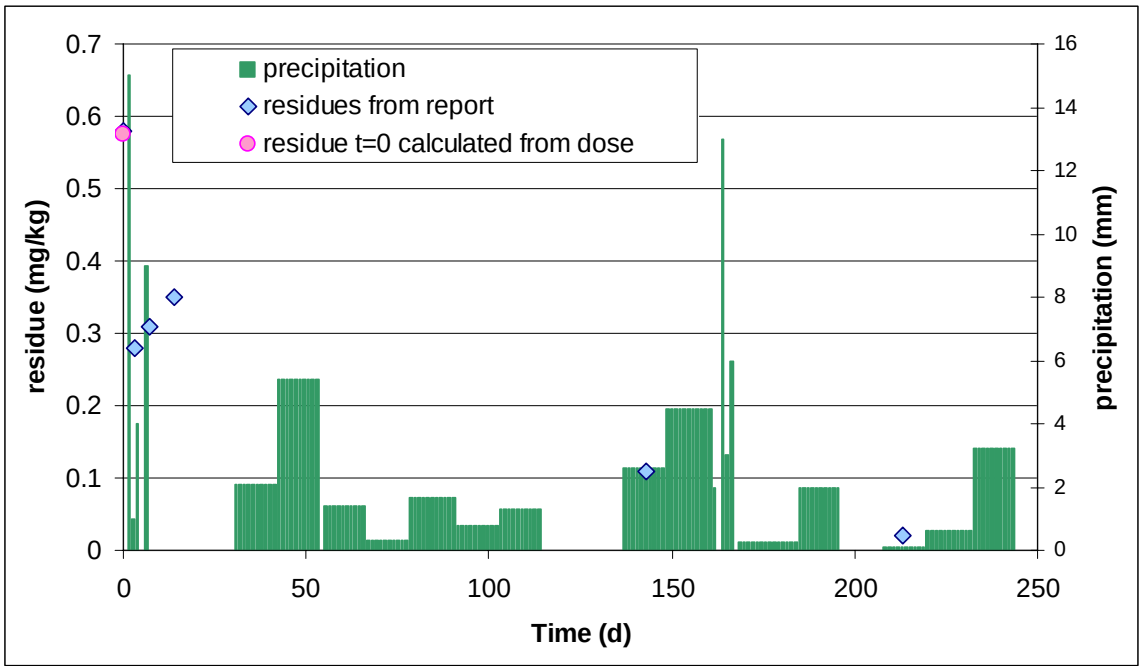
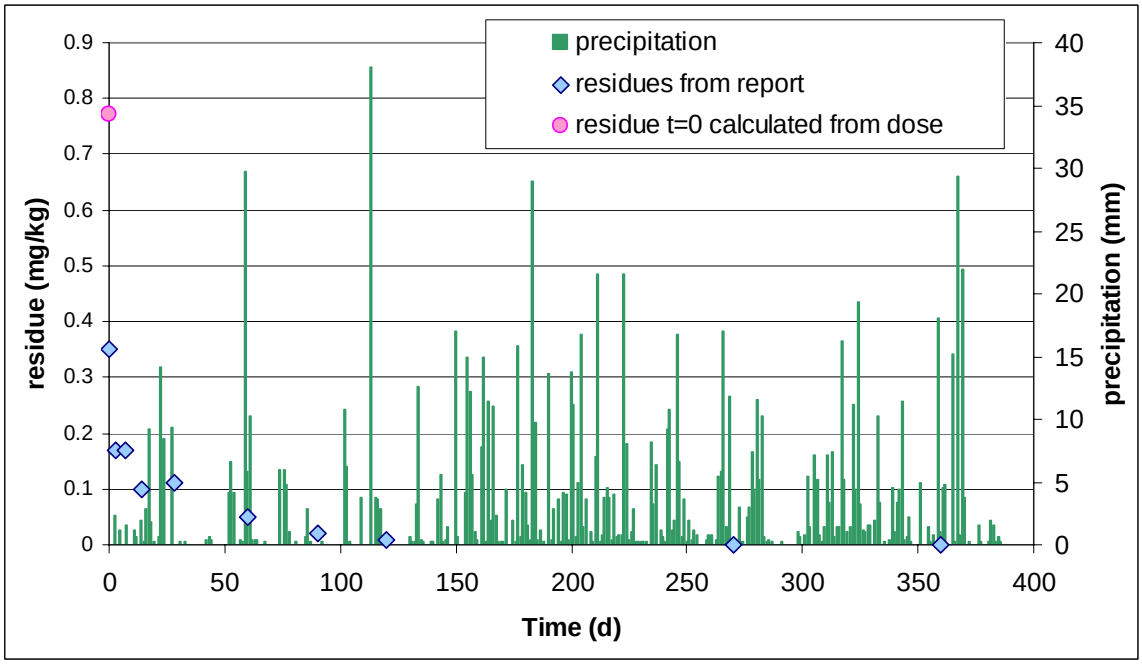



Figure A3.1 Measured residues of chlorpyrifos in soil and precipitation[4] at location Adelshausen




[4] Precipitation was measured periodically. So the precipitation during the period is spread over the days.

Figure A3.2 Measured residues of chlorpyrifos in soil and precipitation at location Charentilly

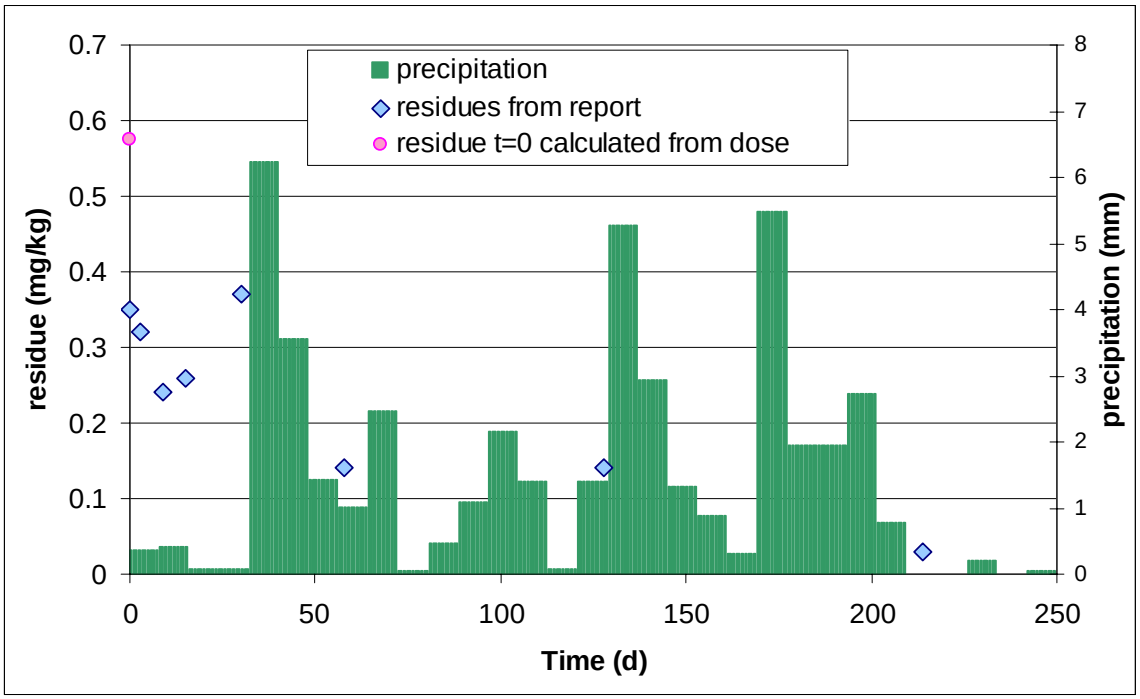



Figure A3.3 Measured residues of chlorpyrifos in soil and precipitation[4] at location Grebin

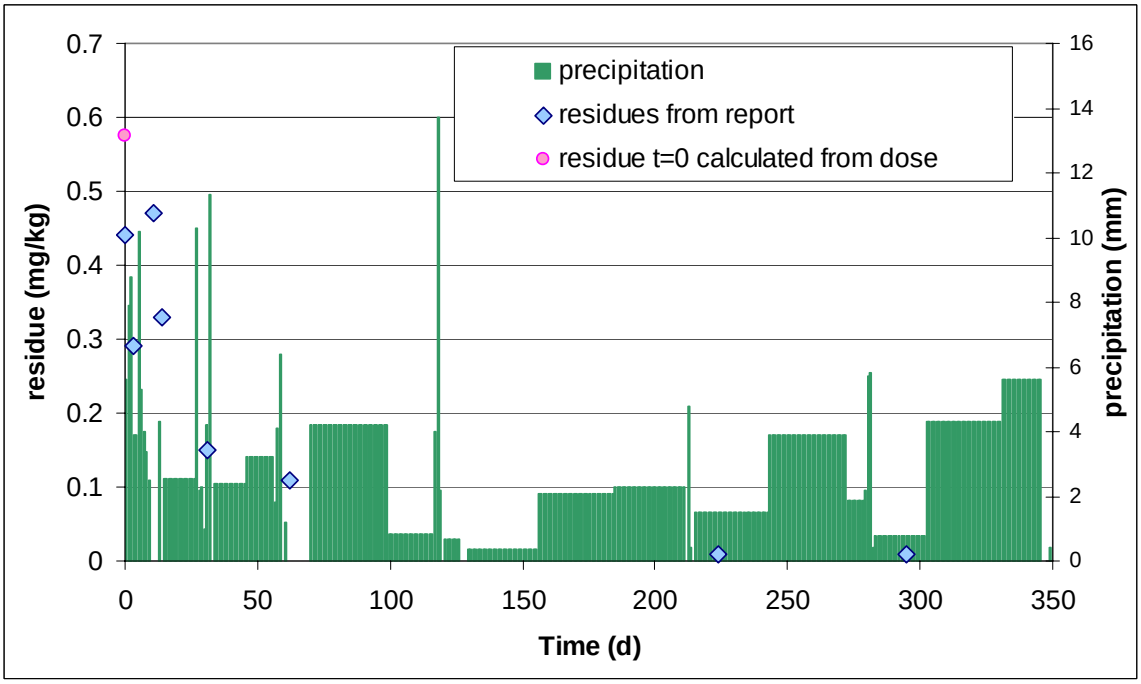



Figure A3.4 Measured residues of chlorpyrifos in soil and precipitation[4] at location Herford

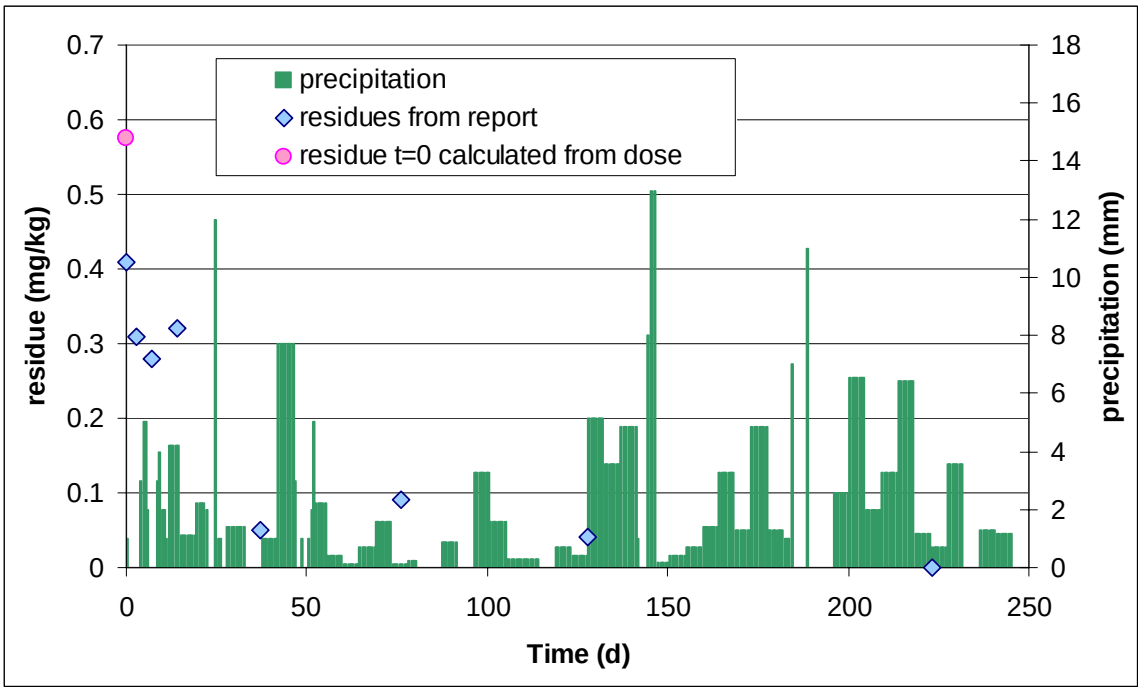



Figure A3.5 Measured residues of chlorpyrifos in soil and precipitation[4] at location Lauter

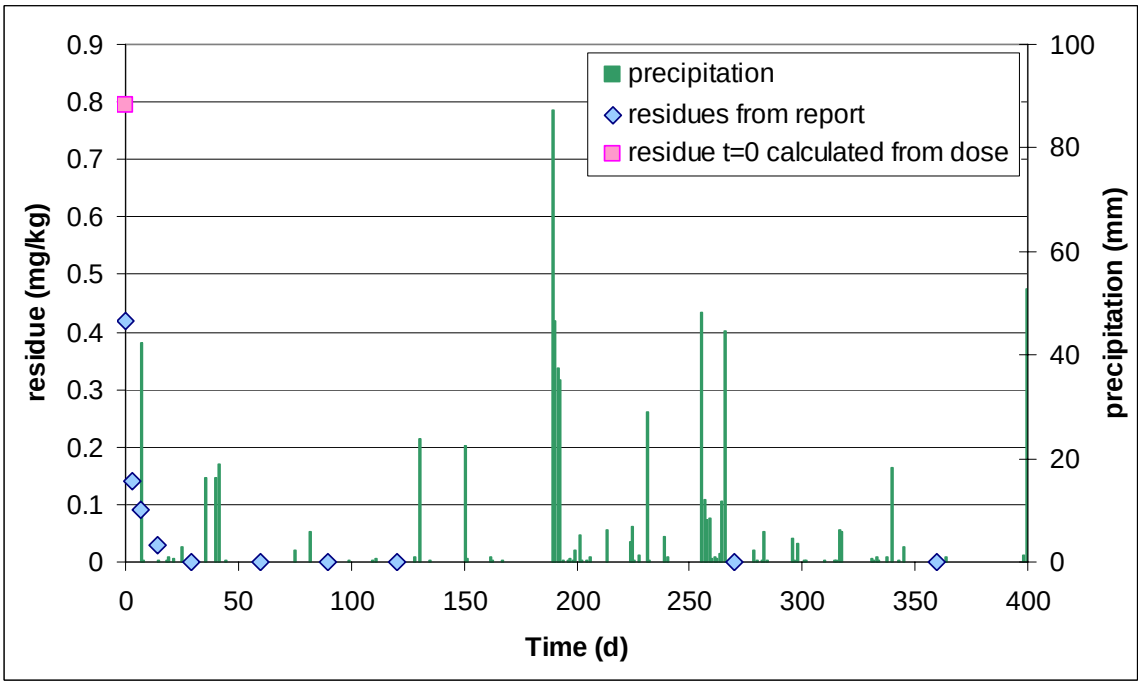



Figure A3.6 Measured residues of chlorpyrifos in soil and precipitation at location Tarragona

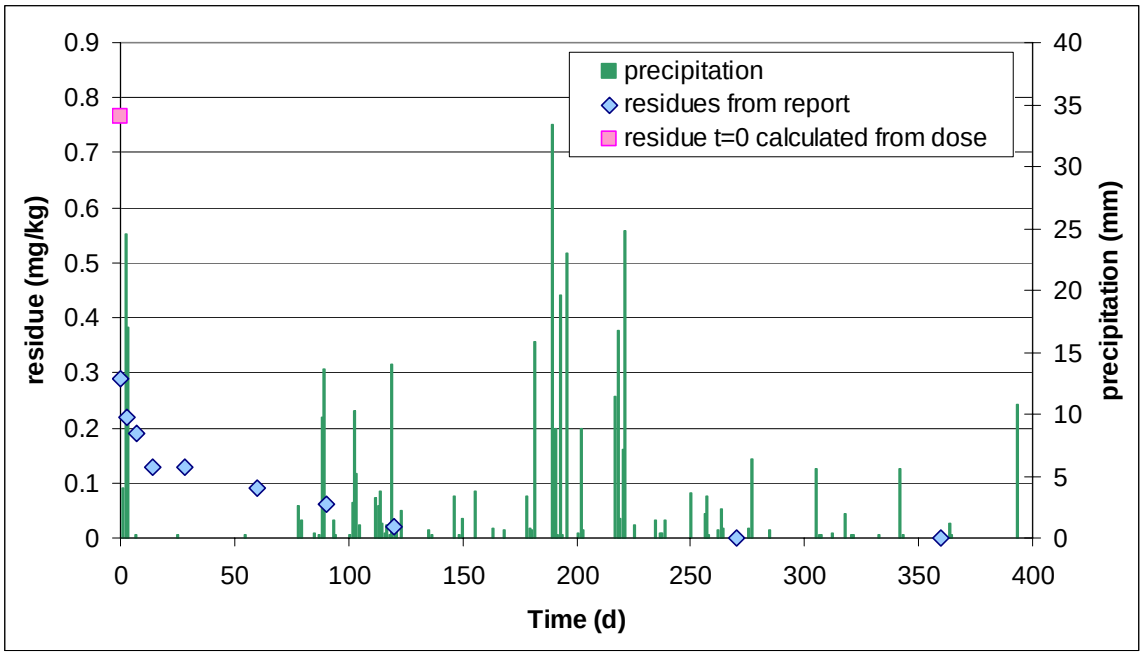



Figure A3.7 Measured residues of chlorpyrifos in soil and precipitation at location Thessaloniki

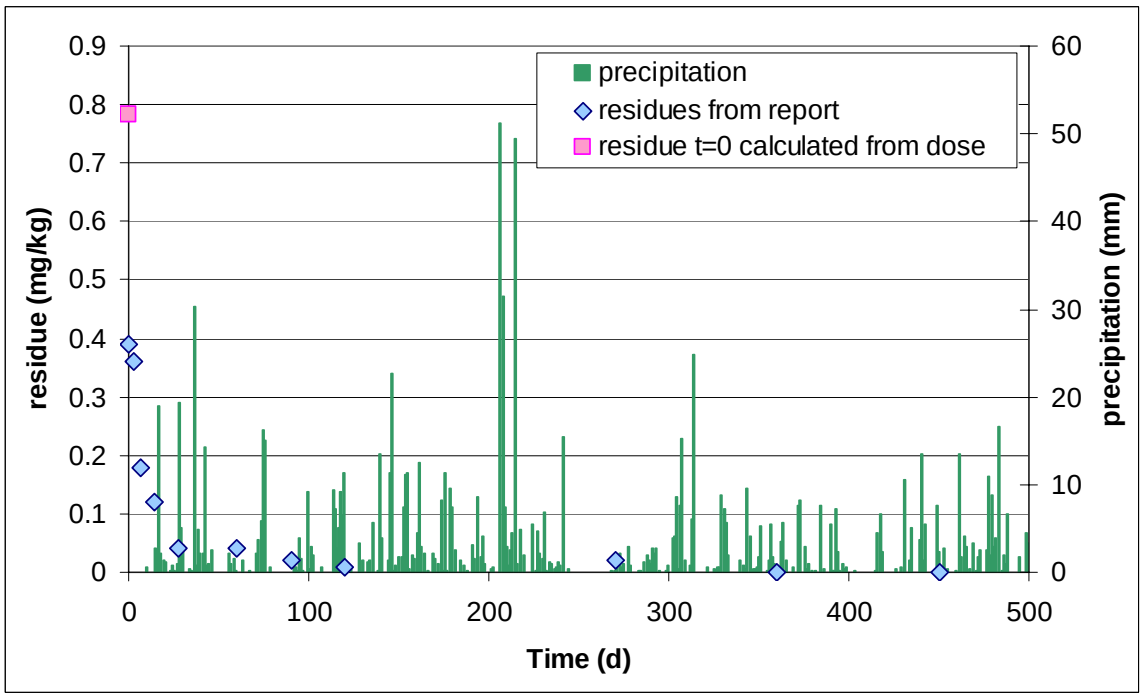



Figure A3.8 Measured residues of chlorpyrifos in soil and precipitation at location Trenant

***Normalization to reference conditions***

Day lengths are normalized to 20 °C so that the estimated $DegT_{50,field}$ refers to that temperature and can be compared with the $DegT_{50,lab}$. Figure A3.9 - Figure A3.14 show the normalized dissipation curves of the studies remaining after the examination for dissipation processes other than degradation. The measured soil or air temperatures were generally lower than the reference temperature of 20 °C. Overall, the time-step normalization method led to smaller interval periods between the measurements. This resulted in new patterns of decline of the residues.

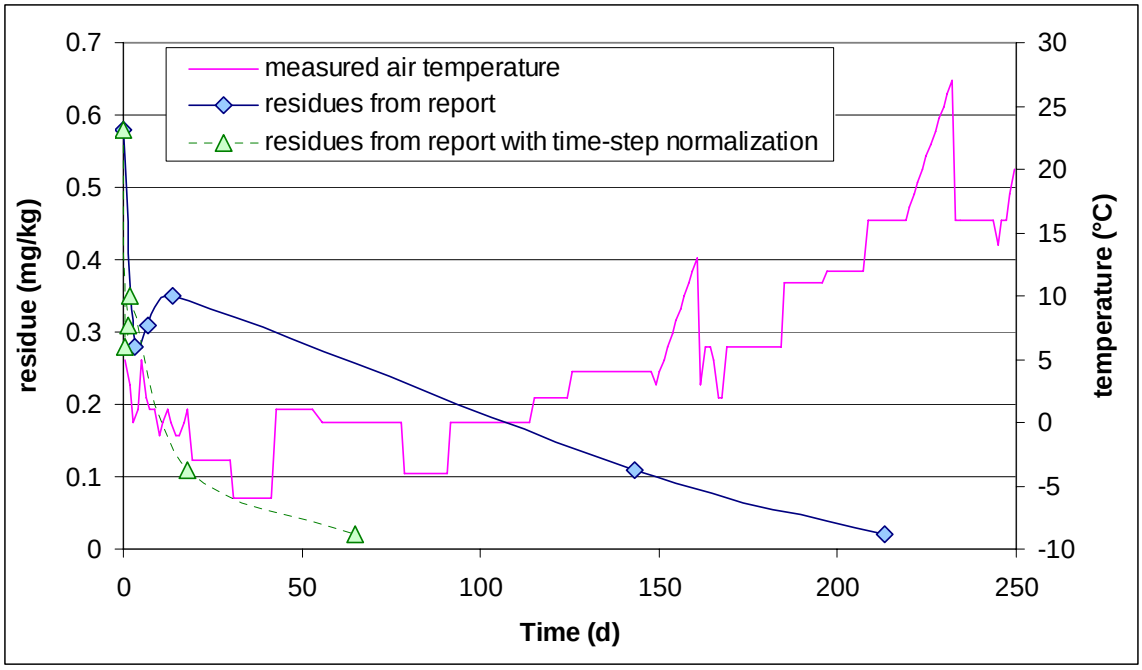



Figure A3.9 Measured residues versus time (diamonds) and versus normalized time (triangles) and measured air temperature at location Adelshausen

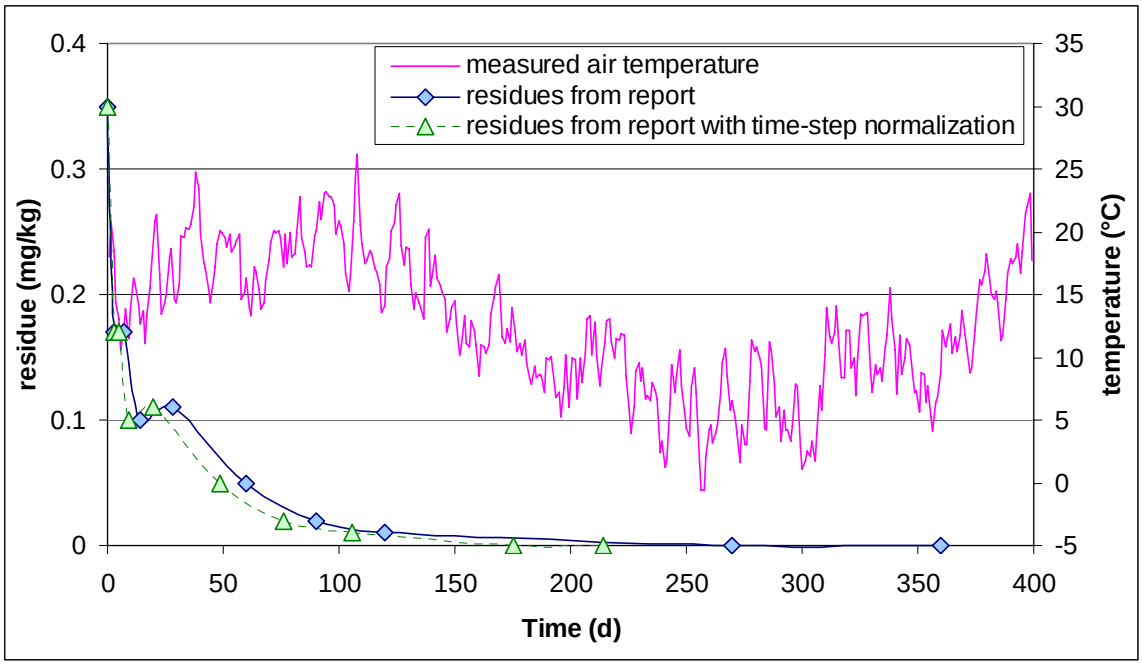



Figure A3.10 Measured residues versus time (diamonds) and versus normalized time (triangles) and measured air temperature at location Charentilly

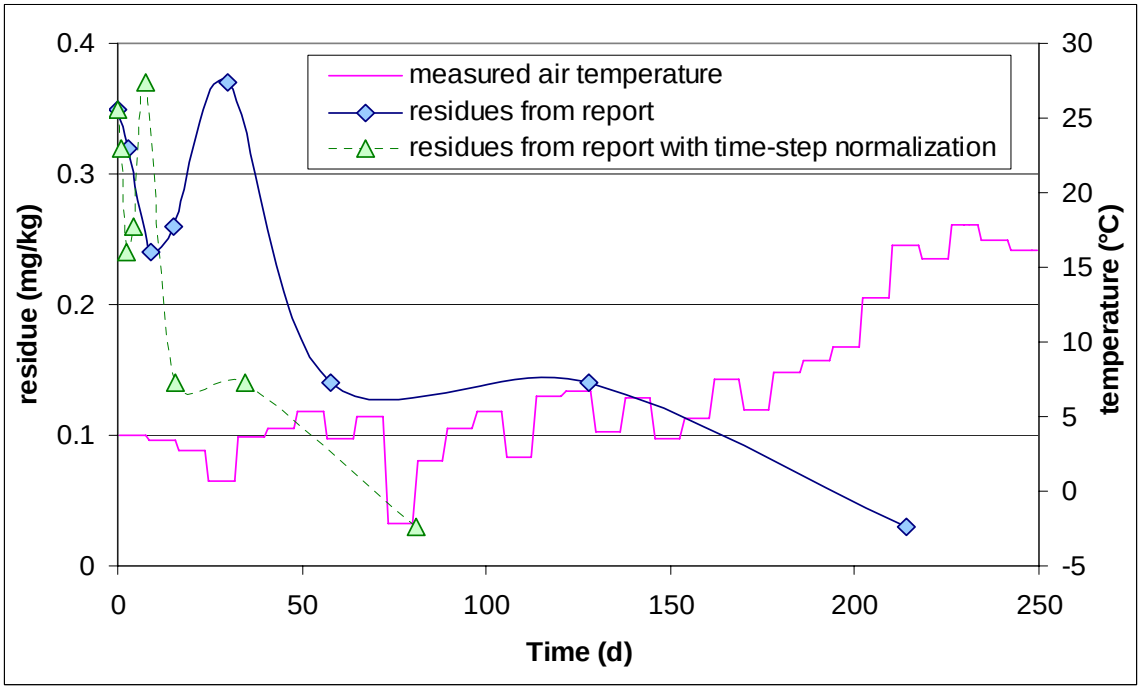



Figure A3.11 Measured residues versus time (diamonds) and versus normalized time (triangles) and measured air temperature[5] at location Grebin

[5] Daily air temperatures were not given, periodical averages are used

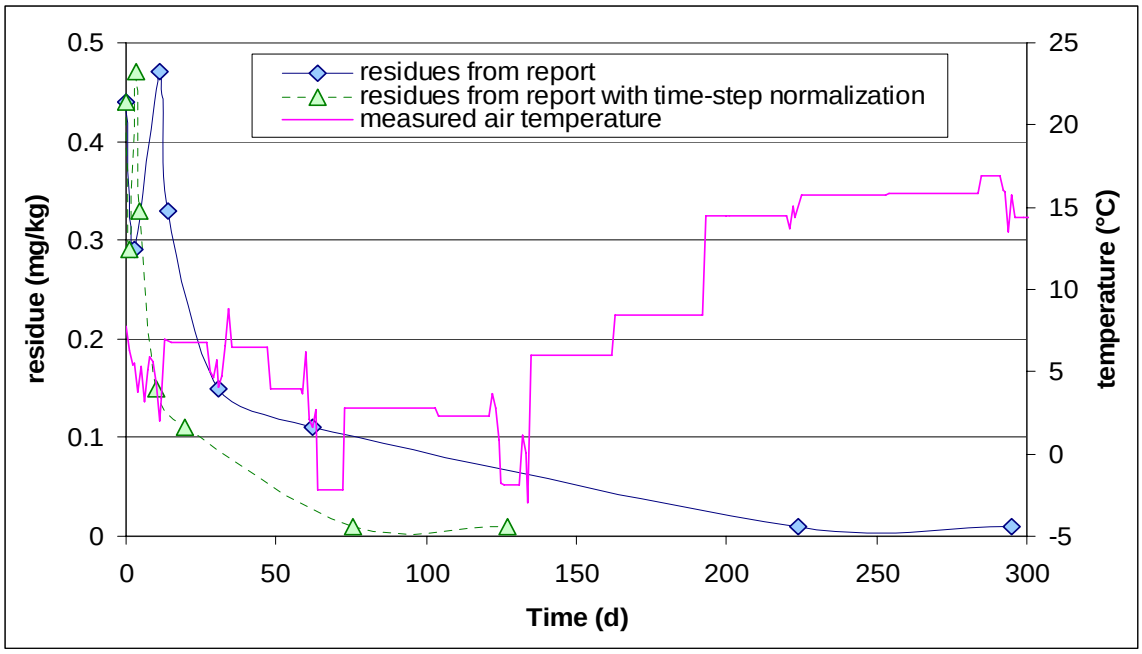



Figure A3.12 Measured residues versus time (diamonds) and versus normalized time (triangles) and measured air temperature[5] at location Herford

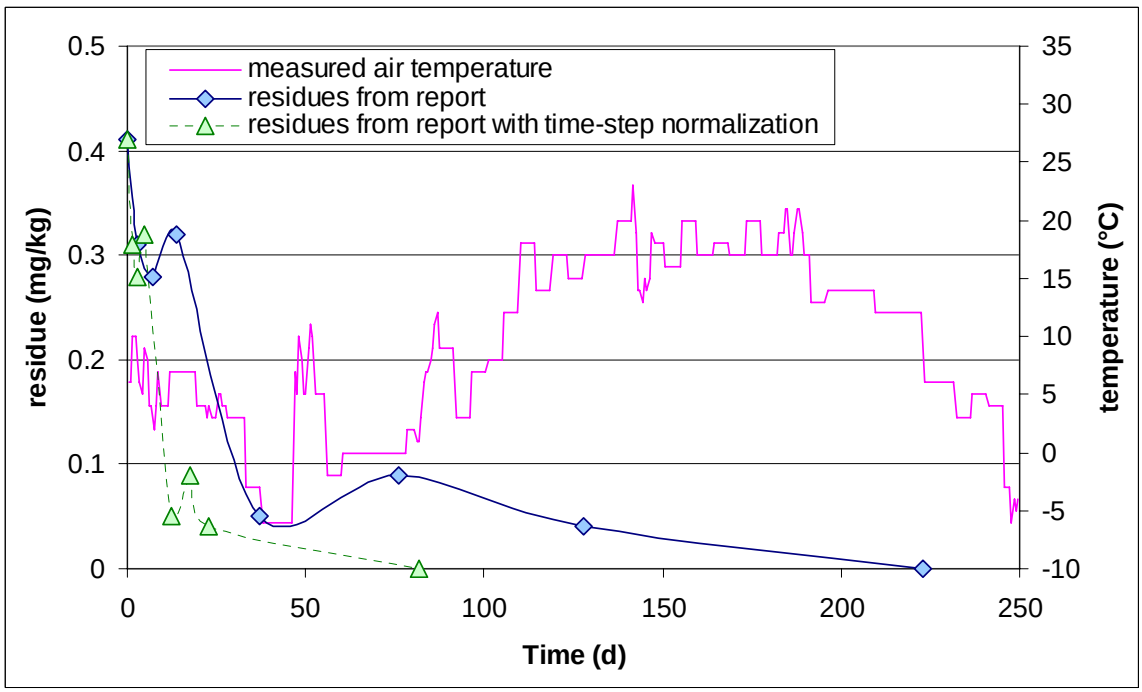



Figure A3.13 Measured residues versus time (diamonds) and versus normalized time (triangles) and measured air temperature[5] at location Lauter

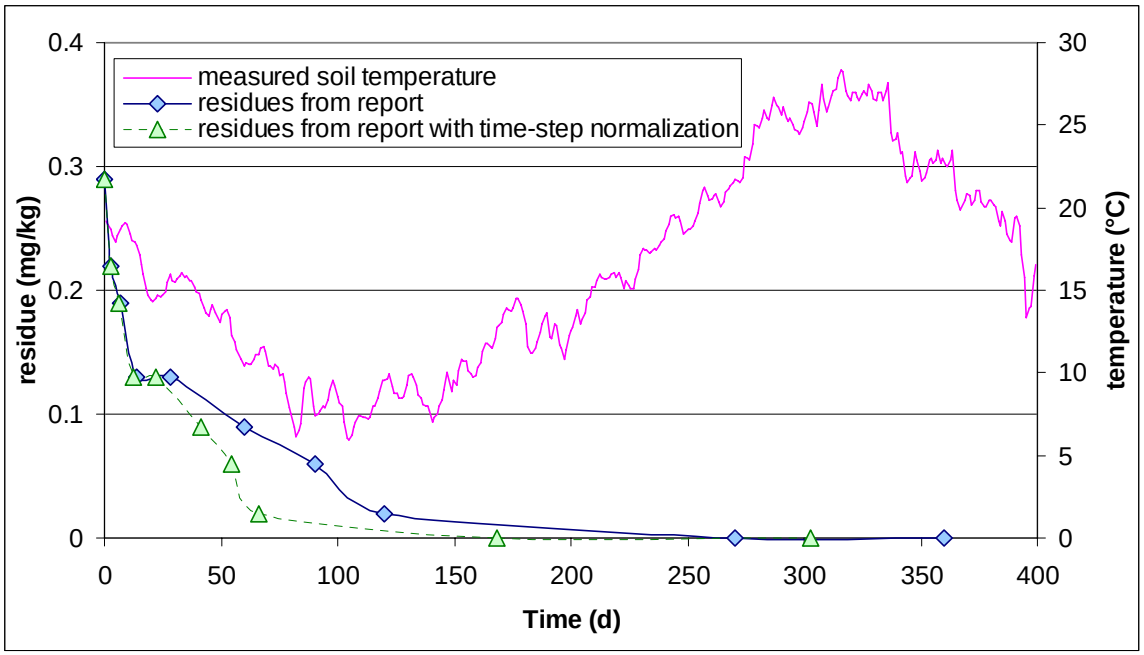



Figure A3.14 Measured residues versus time (diamonds) and versus normalized time (triangles) and soil temperature at location Thessaloniki

**Calculation of the $DegT_{50}$**

For the accepted field dissipation studies, single first order (SFO) fits were satisfactory (see Figure A3.15 - Figure A3.20. Visually the fits are suitable, residuals are low and evenly spread and the error levels of the $chi^2$-test are in the range of 10 – 25% (see also Table A3.3). Table A3.4 shows the estimated $DegT_{50,field}$ values of the accepted field dissipation studies.

Table A3.3 Results and statistics of the SFO fits for chlorpyrifos

| Location | parameter | estimated value | SD | $Chi^2$ | t-test <0.05 | Prob > t |
|---|---|---|---|---|---|---|
| Adelshausen | parent_k | 0.056 | 0.018 | 11.1 | Y | 0.0278 |
| | parent_$M_0$ | 0.32 | 0.024 | | Y | |
| Charentilly | parent_k | 0.028 | 0.0058 | 14.7 | Y | 0.0014 |
| | parent_$M_0$ | 0.18 | 0.011 | | Y | |
| Grebin | parent_k | 0.029 | 0.011 | 18.2 | Y | 0.0221 |
| | parent_$M_0$ | 0.32 | 0.033 | | Y | |
| Herford | parent_k | 0.069 | 0.026 | 22.7 | Y | 0.0198 |
| | parent_$M_0$ | 0.43 | 0.051 | | Y | |
| Lauter | parent_k | 0.097 | 0.030 | 19.9 | Y | 0.0166 |
| | parent_$M_0$ | 0.38 | 0.042 | | Y | |
| Thessaloniki | parent_k | 0.027 | 0.0039 | 11.3 | Y | 2.1E-4 |
| | parent_$M_0$ | 0.22 | 0.012 | | Y | |

Table A3.4 Estimated $DegT_{50,field}$ values (measurements normalized to 20 °C)

| **field dissipation study** | **$DegT_{50,field}$ (d)** |
|---|---|
| Adelshausen | 12.5 |
| Charentilly | 24.7 |
| Grebin | 24.3 |
| Herford | 10.1 |
| Lauter | 7.1 |
| Thessaloniki | 25.8 |

Table A3.5 shows a comparison between the arithmetic mean $DegT_{50}$ values of the field and the laboratory studies and the geometric mean $DegT_{50}$ values of the field and the laboratory studies. The $DegT_{50,field}$ is statistically significantly different from the $DegT_{50,lab}$. Degradation in the field is faster than degradation in the laboratory. In such a case field results are preferred over laboratory results (FOCUS, 2006). So the results from the additional field dissipation studies led to a new $DegT_{50}$ for the calculation of exposure concentrations. Van der Linden et al. (2006) recommend using the geometric mean $DegT_{50}$ for calculation of exposure levels.

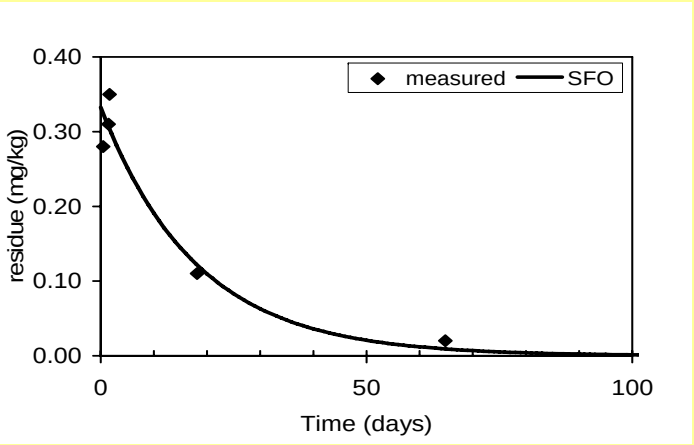
**FOCUS_DEGKIN v1**

**Parameter optimisation for SFO kinetics with Excel Solver Add-In**
**Visual assessment and chi2-test**
**For datasets without replicates, optimisation of two parameters (M0 and k)**
1. Enter measured data
2. Enter starting values in cell F19 and F20
3. Optimise parameters (Tools Solver, minimise target cell E23 by changing cells F19 and F20)
**Change number of parameters if M0 is fixed in optimisation!**

User input, all other cells calculated or automated
Optimise using Solver

**Name of dataset:** Adelshausen

| No | Time | Observed | Calculated | SFO parameters and endpoints | | | |
|---|---|---|---|---|---|---|---|
| 1 | 0.48531 | 0.28 | 0.32 | **M0** | 0.33 | **DT50** | 12.5 |
| 2 | 1.48079 | 0.31 | 0.31 | **k** | 0.05549 | **DT90** | 41.5 |
| 3 | 1.70435 | 0.35 | 0.30 | | | | |
| 4 | 18.1248 | 0.11 | 0.12 | | | | |
| 5 | 64.8166 | 0.02 | 0.01 | **0.004** | **Residual Sum of Squares** | | |
| 6 | | | | | | | |
| 7 | | | | | | | |
| 8 | | | | | | | |
| 9 | | | | | | | |
| 10 | | | | | | | |
| 11 | | | | **Error level Chi2 test** | 11.1 | | |
| 12 | | | | | | | |
| 13 | | | | 0.004 | **Residual Sum of Squares** | | |
| 14 | | | | 5 | **Number of observations** | | |
| 15 | | | | 2 | **Number of parameters** | | |
| 16 | | | | 0.2 | **Average of observed** | | |
| 17 | | | | 0.02 | **Scaled Error** | | |
| 18 | | | | 7.815 | **Chi2 calculated** | | |
| 19 | | | | 7.815 | **Chi2 Table** | | |
| 20 | | | | | | | |
| 21 | | | | | | | |
| 22 | | | | | | | |
| 23 | | | | | | | |



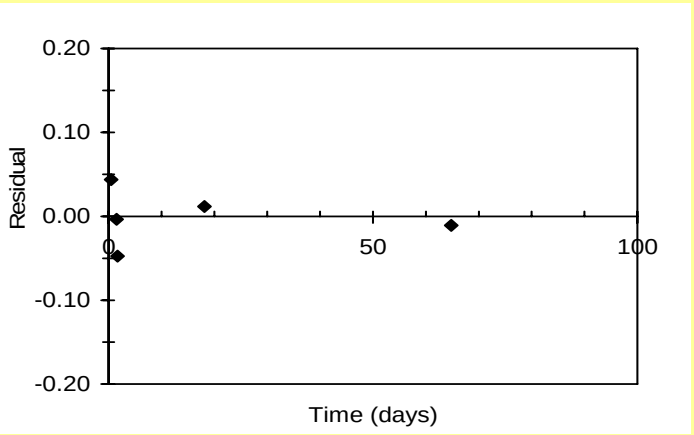




Figure A3.15 Parameter and goodness-of-fit estimation for the Adelshousen experiment

**FOCUS_DEGKIN v1**

**Parameter optimisation for SFO kinetics with Excel Solver Add-In**
**Visual assessment and chi2-test**
**For datasets without replicates, optimisation of two parameters (M0 and k)**
1. Enter measured data
2. Enter starting values in cell F19 and F20
3. Optimise parameters (Tools Solver, minimise target cell E23 by changing cells F19 and F20)
**Change number of parameters if M0 is fixed in optimisation!**

User input, all other cells calculated or automated
Optimise using Solver

**Name of dataset:** **Charentilly**

| No | Time | Observed | Calculated |
|---|---|---|---|
| 1 | 2.59 | 0.17 | 0.16 |
| 2 | 4.80 | 0.17 | 0.15 |
| 3 | 9.19 | 0.10 | 0.14 |
| 4 | 19.67 | 0.11 | 0.10 |
| 5 | 48.44 | 0.05 | 0.05 |
| 6 | 76.34 | 0.02 | 0.02 |
| 7 | 105.41 | 0.01 | 0.01 |
| 8 | 175.34 | 0.005 | 0.00 |
| 9 | | | |
| 10 | | | |
| 11 | | | |
| 12 | | | |
| 13 | | | |
| 14 | | | |
| 15 | | | |
| 16 | | | |
| 17 | | | |
| 18 | | | |
| 19 | | | |
| 20 | | | |
| 21 | | | |
| 22 | | | |
| 23 | | | |

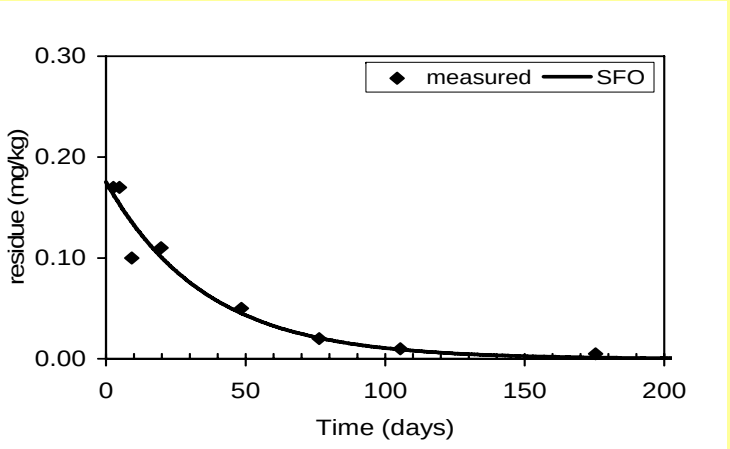
**SFO parameters and endpoints**

| | | | |
|---|---|---|---|
| **M0** | 0.18 | **DT50** | 24.7 |
| **k** | 0.02801 | **DT90** | 82.2 |

**0.002** **Residual Sum of Squares**

**Error level Chi2 test** 14.7

| | |
|---|---|
| 0.002 | **Residual Sum of Squares** |
| 8 | **Number of observations** |
| 2 | **Number of parameters** |
| 0.1 | **Average of observed** |
| 0.01 | **Scaled Error** |
| 12.592 | **Chi2 calculated** |
| 12.592 | **Chi2 Table** |



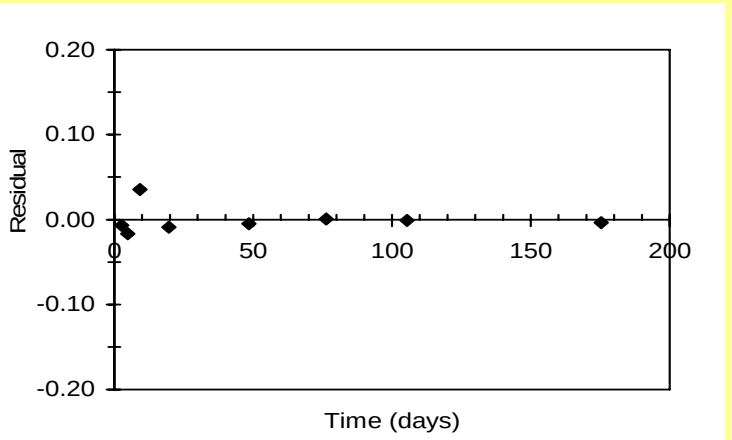




Figure A3.16 Parameter and goodness-of-fit estimation for the Charentilly experiment

**FOCUS_DEGKIN v1**

**Parameter optimisation for SFO kinetics with Excel Solver Add-In**
**Visual assessment and chi2-test**
**For datasets without replicates, optimisation of two parameters (M0 and k)**
1. Enter measured data
2. Enter starting values in cell F19 and F20
3. Optimise parameters (Tools Solver, minimise target cell E23 by changing cells F19 and F20)
**Change number of parameters if M0 is fixed in optimisation!**

User input, all other cells calculated or automated
Optimise using Solver

**Name of dataset:** Grebin

| No | Time | Observed | Calculated |
|---|---|---|---|
| 1 | 0.00 | 0.35 | 0.32 |
| 2 | 0.83 | 0.32 | 0.32 |
| 3 | 2.47 | 0.24 | 0.30 |
| 4 | 4.06 | 0.26 | 0.29 |
| 5 | 7.69 | 0.37 | 0.26 |
| 6 | 15.83 | 0.14 | 0.21 |
| 7 | 34.69 | 0.14 | 0.12 |
| 8 | 80.74 | 0.03 | 0.03 |
| 9 | | | |
| 10 | | | |
| 11 | | | |
| 12 | | | |
| 13 | | | |
| 14 | | | |
| 15 | | | |
| 16 | | | |
| 17 | | | |
| 18 | | | |
| 19 | | | |
| 20 | | | |
| 21 | | | |
| 22 | | | |
| 23 | | | |

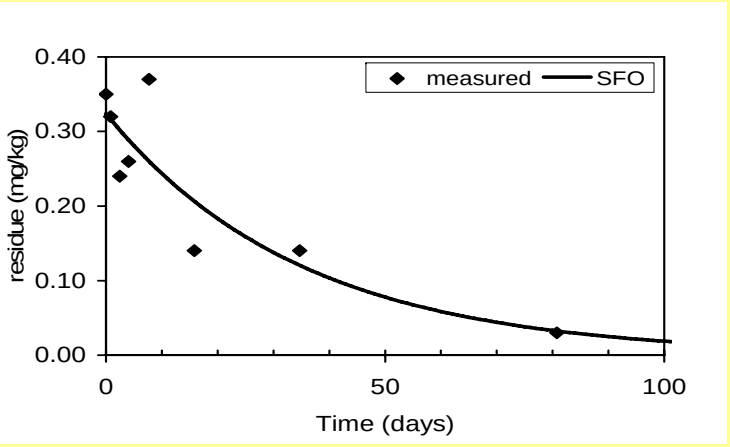
**SFO parameters and endpoints**

| | | | |
|---|---|---|---|
| **M0** | 0.32 | **DT50** | 24.3 |
| **k** | 0.02848 | **DT90** | 80.8 |

**0.022** **Residual Sum of Squares**

**Error level Chi2 test** 18.2

| | |
|---|---|
| 0.022 | **Residual Sum of Squares** |
| 8 | **Number of observations** |
| 2 | **Number of parameters** |
| 0.2 | **Average of observed** |
| 0.04 | **Scaled Error** |
| 12.592 | **Chi2 calculated** |
| 12.592 | **Chi2 Table** |



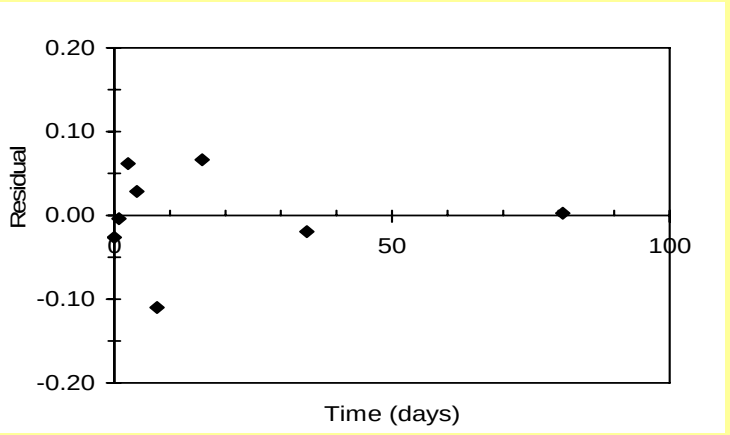




Figure A3.17 Parameter and goodness-of-fit estimation for the Grebin experiment

**FOCUS_DEGKIN v1**

**Parameter optimisation for SFO kinetics with Excel Solver Add-In**
**Visual assessment and chi2-test**
**For datasets without replicates, optimisation of two parameters (M0 and k)**
1. Enter measured data
2. Enter starting values in cell F19 and F20
3. Optimise parameters (Tools Solver, minimise target cell E23 by changing cells F19 and F20)
**Change number of parameters if M0 is fixed in optimisation!**

User input, all other cells calculated or automated
Optimise using Solver

**Name of dataset:** **Herford**

| No | Time | Observed | Calculated |
|---|---|---|---|
| 1 | 0.00 | 0.44 | 0.43 |
| 2 | 0.97 | 0.29 | 0.40 |
| 3 | 3.32 | 0.47 | 0.34 |
| 4 | 4.31 | 0.33 | 0.32 |
| 5 | 10.11 | 0.15 | 0.21 |
| 6 | 19.86 | 0.11 | 0.11 |
| 7 | 75.82 | 0.01 | 0.00 |
| 8 | 126.99 | 0.01 | 0.00 |
| 9 | | | |
| 10 | | | |
| 11 | | | |
| 12 | | | |
| 13 | | | |
| 14 | | | |
| 15 | | | |
| 16 | | | |
| 17 | | | |
| 18 | | | |
| 19 | | | |
| 20 | | | |
| 21 | | | |
| 22 | | | |
| 23 | | | |

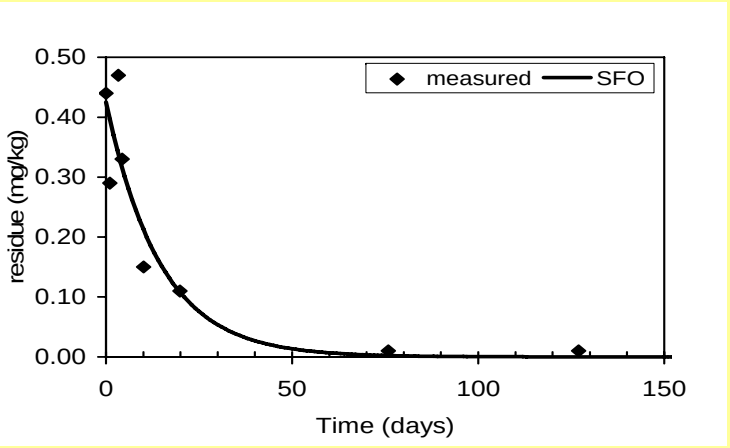
**SFO parameters and endpoints**

| | | | |
|---|---|---|---|
| **M0** | 0.43 | **DT50** | 10.1 |
| **k** | 0.06897 | **DT90** | 33.4 |

**0.033** **Residual Sum of Squares**

**Error level Chi2 test** 22.7

| | |
|---|---|
| 0.033 | **Residual Sum of Squares** |
| 8 | **Number of observations** |
| 2 | **Number of parameters** |
| 0.2 | **Average of observed** |
| 0.05 | **Scaled Error** |
| 12.592 | **Chi2 calculated** |
| 12.592 | **Chi2 Table** |



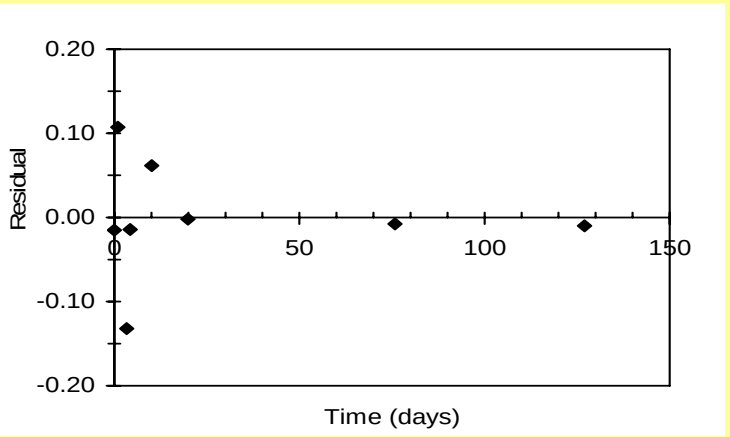




Figure A3.18 Parameter and goodness-of-fit estimation for the Herford experiment

**FOCUS_DEGKIN v1**

**Parameter optimisation for SFO kinetics with Excel Solver Add-In**
**Visual assessment and chi2-test**
**For datasets without replicates, optimisation of two parameters (M0 and k)**
1. Enter measured data
2. Enter starting values in cell F19 and F20
3. Optimise parameters (Tools Solver, minimise target cell E23 by changing cells F19 and F20)
**Change number of parameters if M0 is fixed in optimisation!**

User input, all other cells calculated or automated
Optimise using Solver

**Name of dataset:** **Lauter**

| No | Time | Observed | Calculated |
|---|---|---|---|
| 1 | 1.24 | 0.31 | 0.34 |
| 2 | 2.69 | 0.28 | 0.29 |
| 3 | 4.81 | 0.32 | 0.24 |
| 4 | 12.17 | 0.05 | 0.12 |
| 5 | 17.52 | 0.09 | 0.07 |
| 6 | 22.73 | 0.04 | 0.04 |
| 7 | | | |
| 8 | | | |
| 9 | | | |
| 10 | | | |
| 11 | | | |
| 12 | | | |
| 13 | | | |
| 14 | | | |
| 15 | | | |
| 16 | | | |
| 17 | | | |
| 18 | | | |
| 19 | | | |
| 20 | | | |
| 21 | | | |
| 22 | | | |
| 23 | | | |

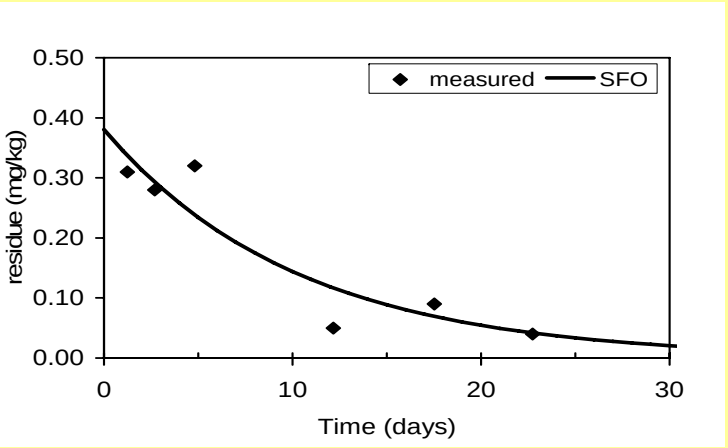
**SFO parameters and endpoints**

| | | | |
|---|---|---|---|
| **M0** | 0.38 | **DT50** | 7.1 |
| **k** | 0.09702 | **DT90** | 23.7 |

**0.012** **Residual Sum of Squares**

**Error level Chi2 test** 19.9

| | |
|---|---|
| 0.012 | **Residual Sum of Squares** |
| 6 | **Number of observations** |
| 2 | **Number of parameters** |
| 0.2 | **Average of observed** |
| 0.04 | **Scaled Error** |
| 9.488 | **Chi2 calculated** |
| 9.488 | **Chi2 Table** |



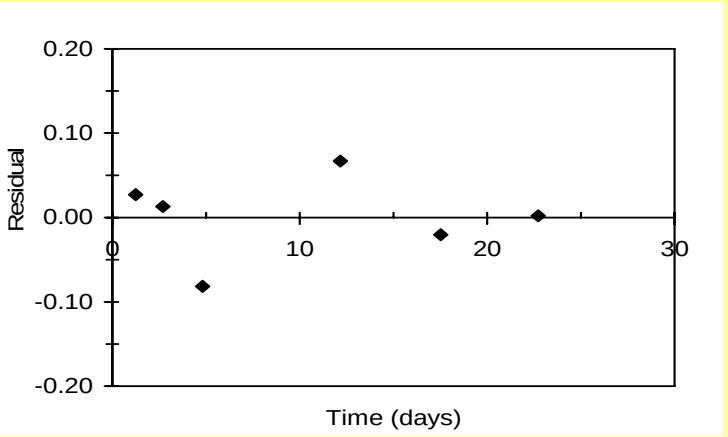




Figure A3.19 Parameter and goodness-of-fit estimation for the Lauter experiment

**FOCUS_DEGKIN v1**

**Parameter optimisation for SFO kinetics with Excel Solver Add-In**
**Visual assessment and chi2-test**
**For datasets without replicates, optimisation of two parameters (M0 and k)**
1. Enter measured data
2. Enter starting values in cell F19 and F20
3. Optimise parameters (Tools Solver, minimise target cell E23 by changing cells F19 and F20)
**Change number of parameters if M0 is fixed in optimisation!**

User input, all other cells calculated or automated
Optimise using Solver

**Name of dataset:** **Thessaloniki**

| No | Time | Observed | Calculated |
|---|---|---|---|
| 1 | 2.70 | 0.22 | 0.21 |
| 2 | 6.24 | 0.19 | 0.19 |
| 3 | 12.31 | 0.13 | 0.16 |
| 4 | 21.85 | 0.13 | 0.12 |
| 5 | 41.46 | 0.09 | 0.07 |
| 6 | 54.42 | 0.06 | 0.05 |
| 7 | 66.13 | 0.02 | 0.04 |
| 8 | 168.48 | 0.005 | 0.00 |
| 9 | | | |
| 10 | | | |
| 11 | | | |
| 12 | | | |
| 13 | | | |
| 14 | | | |
| 15 | | | |
| 16 | | | |
| 17 | | | |
| 18 | | | |
| 19 | | | |
| 20 | | | |
| 21 | | | |
| 22 | | | |
| 23 | | | |

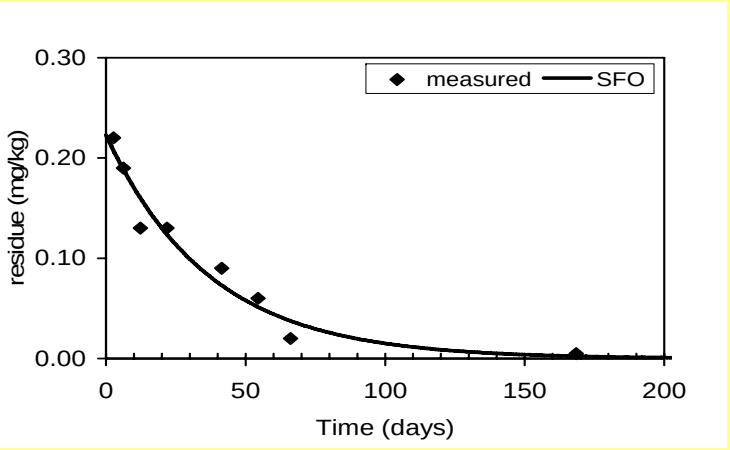
**SFO parameters and endpoints**

| | | | |
|---|---|---|---|
| **M0** | 0.22 | **DT50** | 25.8 |
| **k** | 0.02692 | **DT90** | 85.5 |

**0.002** **Residual Sum of Squares**

**Error level Chi2 test** 11.3

| | |
|---|---|
| 0.002 | **Residual Sum of Squares** |
| 8 | **Number of observations** |
| 2 | **Number of parameters** |
| 0.1 | **Average of observed** |
| 0.01 | **Scaled Error** |
| 12.592 | **Chi2 calculated** |
| 12.592 | **Chi2 Table** |



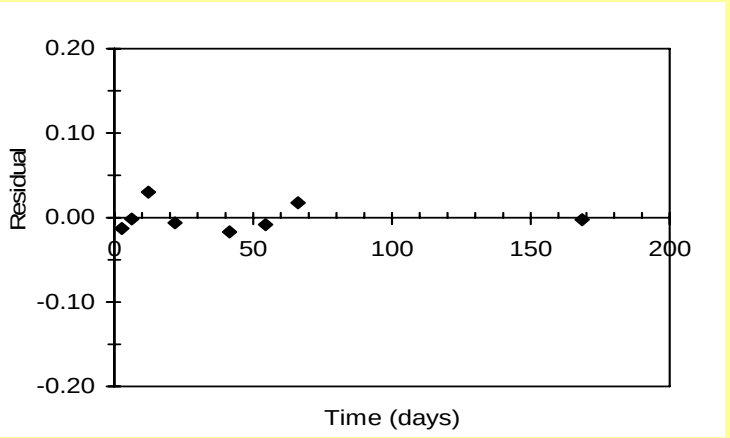




Figure A3.20 Parameter and goodness-of-fit estimation for the Thessaloniki experiment

Table A3.5 Average $DegT_{50}$ values estimated from laboratory and field experiments

| | **$DegT_{50}$ (d; 20 °C, pF2)** | |
|---|---|---|
| | **laboratory** | **field** |
| arithmetic mean | 56.8 | 17.4 |
| geometric mean | 54.2 | 15.5 |

Furthermore the geometric mean $DegT_{50,field}$ can be used to compare with the $DT_{50}$ trigger values of the FRP, CRP and ETP (Van der Linden et al., 2006). The Ministries of LNV and VROM have chosen for $DT_{50}$ trigger values that refer to a temperature of 10 °C and pF2 as reference conditions (Van der Linden et al., 2006). So the $DT_{50}$ trigger values of the FRP, CRP and ETP need to be compared with the geometric mean $DegT_{50}$ at a temperature of 10 °C and pF2. The geometric mean $DegT_{50}$ (10 °C, pF2) is calculated to be 34.1 days.

**Conclusion**

It is shown that the $DegT_{50,field}$ is considerably different from the $DegT_{50,lab}$. Degradation in the field is faster than degradation in the laboratory. Therefore the geometric mean of 15.5 days (20 °C, pF2) of the $DegT_{50,field}$ values will be used for the calculation of exposure levels.

The geometric mean of 34.1 days of the $DegT_{50}$ values (10 °C, pF2) will be used for comparison with the $DegT_{50}$ trigger values of the FRP, CRP and ETP.

# Appendix 4 Exposure concentrations in chlorpyrifos toxicity tests

Herbert et al. (2004) used six nominal treatment levels. The NOEC was found to be 0.065 µg $g^{-1}$ ($4^{th}$ treatment level). Because the test substance was added to the soil five days before the test animals were introduced, the expected exposure concentrations were recalculated. The calculation procedure is described below.

The predicted exposure concentration (PEC) at time t is calculated according equation A4.1:

$$TSC_t = TSC_I \, e^{-kt} \qquad \text{Eq.A4.1}$$

where:

| | |
|---|---|
| $TSC_t$ | test system exposure concentration at time t, (µg $g^{-1}$ or µg $dm^{-3}$ ) |
| $TSC_I$ | test system exposure concentration at time t = 0, (µg $g^{-1}$ or µg $dm^{-3}$ ) |
| k | degradation rate, ($d^{-1}$) |
| t | time, (d) |

$$k = \ln 2 / DegT_{50} \qquad \text{Eq.A4.2}$$

where:

| | |
|---|---|
| $DegT_{50}$ | half-life, (d) |

Both soil and pore water concentrations are needed for the test systems. Equation A4.3 is used to calculate pore water concentrations from total soil contents (given).

$$m = (w + K) \, C_l \qquad \text{Eq.A4.3}$$

where:

| | |
|---|---|
| m | total test system concent, (µg $g^{-1}$ ) |
| $C_l$ | test system concentration in pore water, (µg $dm^{-3}$) |
| K | sorption coefficient, ($dm^3$ $g^{-1}$) |
| w | moisture content in soil, (g $g^{-1}$) |

$$K = K_{OM} \, OM \qquad \text{Eq.A4.4}$$

where:

| | |
|---|---|
| $K_{OM}$ | coefficient of sorption on soil organic matter, ($dm^3$ $g^{-1}$) |
| OM | mass fraction of organic matter in soil, (g $g^{-1}$) |

The time weighted average concentrations ($TSC_{TWA}$) are calculated according to equation A4.5:

$$TSC_{TWAt} = TSC_I \, (1 - e^{-kt})/kt \qquad \text{Eq.A4.5}$$

where:
$TSC_{TWAt}$ time weighted average concentration over t days, (µg $g^{-1}$ or µg $dm^{-3}$)

Van der Linden et al. (2006) recommends to assume non-equilibrium sorption and to use the maximum of the $K_{OM}$ values and the minimum of the $DegT_{50}$ values reported. The maximum reported $K_{OM}$ value in the study of Damon and Heim (2001, monograph chapter 8) is 4620 $dm^3$ $kg^{-1}$. The minimum $DegT_{50,lab}$ reported in the monograph chapter 8 is 37.7 days (20 °C, pF2). Non-equilibrium sorption was regarded to be too complicated to take into account, because it would require recalculation of the $DegT_{50}$. Herbert et al. (2004) note that the moisture content of the medium was maintained at 35% (dry weight). Furthermore the test medium consisted of 70% quartz sand, 20% kaolinite clay and 10% peat (Herbert et al., 2004). From this information we assumed the mass fraction of organic matter in the medium to be 0.1. Table A4.2 give the results of the calculations.

Table A4.1 Momentary and time weighted average test system concents of chlorpyrifos in soil

| | | | ***nominal treatment level 4*** | |
|---|---|---|---|---|
| | **time after application of chlorpyrifos** (d) | ***time after introduction test animals*** *(d)* | **$TSC_{tc,t}$ at time t=t** (µg $g^{-1}$) | **$TSC_{tc,TWAxx}$ over xx days** (µg $g^{-1}$) |
| $TSC_{I,tc}$ | 0 | *-5* | 0.065 | |
| | 5 | *0* | 0.059291 | |
| | 6 | *1* | 5.82E-02 | 5.87E-02 |
| | 8 | *3* | 5.61E-02 | 5.77E-02 |
| | 12 | *7* | 5.21E-02 | 5.56E-02 |
| | 19 | *14* | 4.58E-02 | 5.23E-02 |
| | 33 | *28* | 3.54E-02 | 4.63E-02 |

Table A4.2 Momentary and time weighted average test system concentrations of chlorpyrifos in pore water

| | | | ***nominal treatment level 4*** | |
|---|---|---|---|---|
| | **time after application of chlorpyrifos** (d) | ***time after introduction test animals*** *(d)* | **$TSC_{pw,t=t}$ at time t** (µg $dm^{-3}$) | **$TSC_{pw,TWAxx}$ over xx days** (µg $dm^{-3}$) |
| $TSC_{I,pw}$ | 0 | *-5* | 1.41E-01 | |
| | 5 | *0* | 1.28E-01 | |
| | 6 | *1* | 1.26E-01 | 1.27E-01 |
| | 8 | *3* | 1.21E-01 | 1.25E-01 |
| | 12 | *7* | 1.13E-01 | 1.20E-01 |
| | 19 | *14* | 9.91E-02 | 1.13E-01 |
| | 33 | *28* | 7.66E-02 | 1.00E-01 |

# Appendix 5 Estimation of pore water concentrations of paraquat in artificial soil

Van Gestel et al. (1992) used an artificial soil to investigate the toxicity of paraquat to earthworms. In first instance, the sorption coefficient for this artificial soil was estimated conservatively to be 100000 $dm^3\ kg^{-1}$. However, it appeared that then earthworms would be almost equally sensitive as plants, which seemed not realistic. Therefore it was attempted to estimate the sorption coefficient using more realistic assumptions, but still conservative. The artificial soil consisted of 10% peat and 20% kaolinite. It is assumed that the sorption coefficient of the artificial soil can be described with:

$$K = m_{peat} K_{peat} + m_{kao} K_{kao} \qquad \text{Eq.A5.1}$$

where $K$ is the sorption coefficient ($dm^3\ kg^{-1}$) of paraquat to artificial soil, $m_{peat}$ is the mass fraction (-) of peat of the soil (that is 0.1), $K_{peat}$ is the sorption coefficient ($dm^3\ kg^{-1}$) of the peat, $m_{kao}$ is the mass fraction (-) of kaolinite of the soil (that is 0.2), and $K_{kao}$ is the sorption coefficient ($dm^3\ kg^{-1}$) of the kaolinite.

The next step was to estimate the sorption coefficients of peat and kaolinite. Weber et al. (1965) measured sorption of paraquat to the clay minerals montmorillonite and kaolinite. No accurate sorption coefficients could be derived from their kaolinite isotherm because their lowest concentration of paraquat in the liquid phase was 0.05 mmol $dm^{-3}$, so about 10 mg $dm^{-3}$. At that concentration the slope of the sorption isotherm of paraquat was about 4000 $dm^3\ kg^{-1}$. In view of the shape of the isotherm measured by Weber et al. (1965) the kaolinite sorption coefficient of paraquat ($K_{kao}$) is expected to be considerably higher at a concentration in the liquid phase of about 10 μg $dm^{-3}$. So we had to estimate $K_{kao}$ more accurately. Weber et al. (1965) found also that the maximum contents of paraquat sorbed to montmorillonite and to kaolinite were almost exactly equal to the cation exchange capacities of the clays (montmorillonite 850 meq $kg^{-1}$, kaolinite 50 meq $kg^{-1}$). Based on this it was assumed that the sorption coefficient of paraquat of kaolinite at a concentration in the liquid phase of about 10 μg $dm^{-3}$ can be estimated from the sorption coefficient of soils with a CEC of 50 meq $kg^{-1}$.

Figure A5.1 shows the relationship between SAC and the CEC for soils from the Netherlands, Italy, Denmark and UK; the data for the soils from Germany were not included because the CEC values of a number of these soils seemed to be too low and because almost all studied German soils had organic matter contents above 5%. Figure A5.1 shows that a SAC of 500 mg $kg^{-1}$ is an upper limit for a CEC of 100 meq $kg^{-1}$. Assuming a CEC of kaolinite of 50 meq $kg^{-1}$, gives a SAC for kaolinite of 250 mg $kg^{-1}$ which corresponds with a sorption coefficient of 25000 $dm^3\ kg^{-1}$ for kaolinite ($K_{kao}$) at a concentration in the liquid phase of 10 μg $dm^{-3}$. This value of $K_{kao}$ is indeed considerably higher than the value of 4000 $dm^3\ kg^{-1}$ derived from Weber et al. (1965).

Dyson et al. (1994) reported SAC values of hundreds of soils. Eleven of these soils were peats. Their average SAC value was 101 mg $kg^{-1}$ and their range was from 25 to 340 mg $kg^{-1}$. Organic matter contents of these soils ranged from 50 to 90% so for part of the soils there may have been a significant contribution from mineral soil parts. For example the SAC of 340 mg $kg^{-1}$ was found for a soil with 59% organic matter. The SAC values for the three soils with the highest organic matter content ranged

from 45 to 75 mg $kg^{-1}$. In view of this a SAC value of 100 mg $kg^{-1}$ for a soil consisting of 100% peat seems a defensible realistic worst case assumption, so $K_{peat}$ was set at 10000 $dm^3$ $kg^{-1}$.

Using $K_{peat}$ = 10000 $dm^3$ $kg^{-1}$ and $K_{kao}$ = 25000 $dm^3$ $kg^{-1}$ results in an upper limit of the paraquat sorption coefficient of the artificial soil of 6000 $dm^3$ $kg^{-1}$. So this more refined approach decreases the estimated paraquat sorption coefficient from 100000 $dm^3$ $kg^{-1}$ to 6000 $dm^3$ $kg^{-1}$.

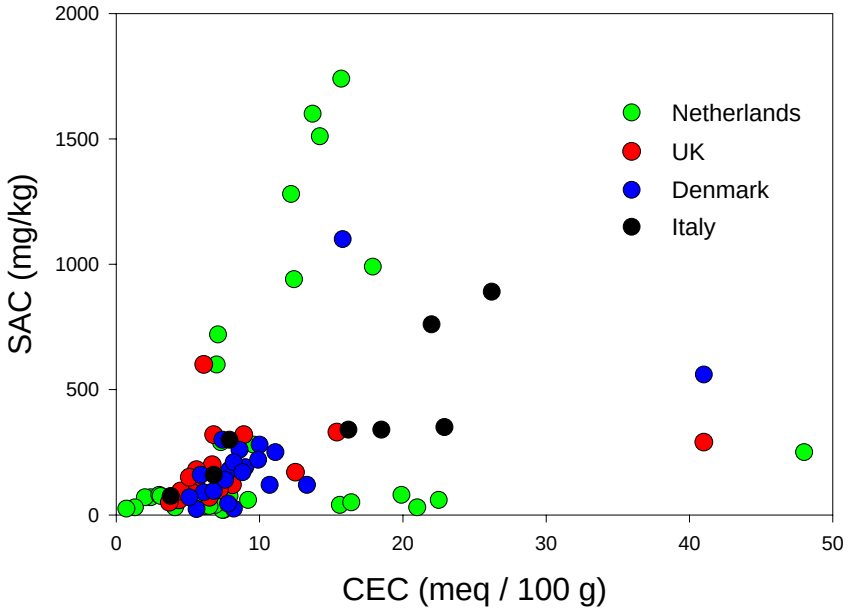



Figure A5.1 The relationship between SAC and the CEC as reported by Dyson et al. (1994) for soils from the Netherlands, UK, Denmark and Italy as indicated

# Appendix 6 Details of paraquat effect evaluations

## A6.1 Litter bag study in Georgia: July-November 1982

**Reference**
(Hendrix and Parmelee, 1985)

**Description**
In the litter bag study the litter bags contained dried *Sorghum halepense* leaves and consisted of 3 g oven dried leaves (40 ºC) in 15 $cm^2$ fiberglass windowscreen litter bags with 1.0 mm mesh. Fifteen litter bags per treatment were dipped during 30 s in paraquat solutions of 0.19% and 1.9% and distilled water as a control, and than dried for 24 h at 20 ºC. The soil of the site is a well-drained sandy clay loam, with a mowed Johnson grass stand. The litter bags were placed in this grass stand. Three bags per treatment were sampled at 29, 49, 70, 91 and 112 days post application. After sampling micro-arthropods were extracted and dry weight of the remaining biomass was determined, as well as several chemical properties, such as ash, Ca, K, Mg, P and total N.

**Results**
The 1.9% treatment showed a significant lower decomposition from day 49 and the 0.19% treatment from day 70 till the end of the experiment (day 112). Nutrient concentrations were significantly lower in the treated litter bags. Micro-arthropod density was affected at the 1.9% treatment level. Overall arthropods density was higher, caused by prostigmatid mites, while number of mesostigmatid mites was (not significantly) lower.

**Remarks**
The test does not fulfil current requirements for litter bag studies. Therefore the test results cannot be used for risk assessment.

## A6.2 Long term field studies in the Netherlands: 1986-1996

**References**
(Lane et al., 1992; Lane and Bouwman, 2000)

**Description**
In the Netherlands three long term field trials were conducted with paraquat. In these field trials paraquat was applied in a single treatment at rates equivalent to 0, 15, 30, 60 and 120% of the previously determined SAC-WB value. Paraquat was applied as gramoxone, in October - November 1986. The substance was applied with watering cans. On two locations the soil was rotovated to 15 cm and on one location to 35 cm to facilitate incorporation of the substance to the desired depth.

On the different locations different crops were grown in the years following application: spring wheat, starch potatoes, spring barley, ware potatoes, sugar beet, tulips, crocus and daffodil. Measured effect parameters: visual damage and various yield parameters. Three locations were studied: A, B and C, with different soils and different SAC-WB values of 65, 300 and 80 mg $kg^{-1}$ respectively.

**Results**
The results show clear effects on yield parameters at the two highest application rates (see Table A6.1).

Table A6.1 Effects of paraquat treatment on yield parameters; SAC-WB is expressed as % of the previous determined value

| site | dose applied # | nominal SAC-WB | measured SAC-WB | | measured paraquat | 87 | 88 | 89 | 90 | 91 | 93 | 94 | 95 | 96 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | kg ha$^{-1}$ | % | 1 y p.a. | 6 y p.a. | mg kg$^{-1}$ 6 y p.a. | % of control yield | | | | | | | | |
| A | 19 | 15 | 18 | 21 | 14 | 103 | 100 | 100 | 100 | 100 | 104 | 100 | 129 | 100 |
| | 38 | 30 | 39 | 39 | 26 | 100 | 106 | 106 | 104 | 101 | 100 | 97 | 117 | 101 |
| | 76 | 60 | 70 | 72 | 47 | 81* | 89 | 102 | 96 | 133 | 99 | 106 | 152 | 97 |
| | 152 | 120 | 130 | 119 | 78 | 0* | 0* | 96 | 26* | 130 | 93 | 103 | 146 | 102 |
| B | 102 | 15 | 11 | 11 | 34 | 101 | 106 | 88 | 98 | 97 | 98 | 94* | 100 | 93 |
| | 202 | 30 | 23 | 17 | 50 | 101 | 105 | 100 | 100 | 99 | 101 | 100 | 108 | 101 |
| | 406 | 60 | 38 | 34 | 103 | 97 | 103 | 91 | 109 | 98 | 105 | 98 | 100 | 100 |
| | 810 | 120 | 93 | 74 | 221 | 37* | 85* | 64* | 87 | 76* | 100 | 96* | 103 | 95 |
| C | 64 | 15 | 25 | 20 | 16 | n.e. | 102 | 101 | 104 | 101 | 99 | n.e. | n.e. | n.e. |
| | 126 | 30 | 41 | 37 | 30 | n.e. | 98 | 98 | 104 | 102 | 98 | n.e. | n.e. | n.e. |
| | 252 | 60 | 92 | 73 | 58 | n.e. | 85* | 81* | 106 | 102 | 95 | n.e. | n.e. | n.e. |
| | 504 | 120 | 180 | 113 | 91 | n.e. | 40* | 33* | 100 | 101 | 91 | n.e. | n.e. | n.e. |

# applied as gramoxone (paraquat contents: 200 g dm$^{-3}$)
n.e. not estimated
p.a. post application
* statistically significantly different from control

From the study results it can be concluded that effects on yield parameters are found up to five years post last application. Two years after application, effects were found at 92% and more of the SAC-WB, and not at 41% and lower. Ten years after application no significant effects were found in any of the treatments. The initial dosages were reached using artificial exposure. This means that the short term availability of paraquat in soil will be unrealistic for a situation with long term exposure, and therefore the effects longer after application are most realistic. However, the concentrations in soil were measured only at one and six years after application, and therefore this exposure is taken and compared to the effects seven years after application (since effects were not measured six years after application). From the results it is concluded that at concentration levels up to 119 % of the SAC-WB no effects were found.

## A6.3 Long-term ecological trial at Jealott's Hill, UK, 1964-1990

**Management of site, effects on vegetation**

**Reference**
(Wilkinson et al., 1993a)

**Description**
Field plots were treated with paraquat to determine the effects on vegetation, residues in the soil, effects on soil micro-flora (see Appendix A6.4) and micro-arthropods (see Appendix A6.5) and effects on and residues in earthworms (see Appendix A6.6).

***Site location and description***

The test field was located at Jealott's Hill Research Station, Berkshire, UK. Soil type: sandy loam, pH 5.8, OM 1.9%, CEC 100 mmol $kg^{-1}$. The Strong Adsorption Capacity of the soil was determined to be 800 (or more recent: 670 mg $kg^{-1}$), using a wheat bioassay (with 50% reduction in root length of wheat seedlings as the effect parameter).

***Test design and application***

Before the trial the plots (in 1960 sawn with spring barley, undersown with grass) were used as ley for silage and grazing. Before the start of the trial in 1964 the ley was terminated by a paraquat (gramoxone W) treatment of 1.12 kg $ha^{-1}$ and the plots were rotovated, leaving a bare soil for the treatment. A randomised block design was made, with two replications per treatment, one series of 15 plots per block, of which 9 were used for this experiment. The experiment can be divided into 3 experiments:

A October 1964. 0 kg $ha^{-1}$, 2.24 kg $ha^{-1}$ and 112 kg $ha^{-1}$ (+ 2.24 kg $ha^{-1}$ before reseeding in May 1976), single spray on previously rotovated soil, followed by rotovation.

B 0 kg $ha^{-1}$, 260 kg $ha^{-1}$ (118 sprayings between October 1964 and December 1973) and 565 kg $ha^{-1}$ (5 sprayings between October 1964 and July 1969) kg $ha^{-1}$. Soil was left undisturbed except for direct drilling.

C 1 kg $ha^{-1}$, 561 kg $ha^{-1}$ (May 1971) and 1700 kg $ha^{-1}$ (August 1971). Single applications followed by rotovation (incorporation to a depth of 10 cm).

All applications were sprayed formulations, except the 1700 kg $ha^{-1}$ treatment, where the unformulated paraquat concentrate was applied from a watering can with a dribble bar.

***Management and cropping***

In the 1964 series (A and B series) the plots were sawn with rye-grass on 6 November. The plots with the 112 kg $ha^{-1}$ treatment had to be reseeded in 1965, since the original sowing failed. Only superficial hand drilling was used and no further cultivation took place. In the 260 kg $ha^{-1}$ treatment two reseedings took place in September 1967 and April 1968. No reseeding took place during the 118 repeated treatments, and in 1973 the vegetation was left to regenerate naturally. On the 565 kg $ha^{-1}$ plot several attempts were made to establish a vegetation cover and one quarter of the plots were cultivated up to 15 cm. Then in 1972 the last additional seeding took place. In the 1971 series (C series) the control and the 561 kg $ha^{-1}$ treatment were sown with rye-grass after treatment, but the 1700 kg $ha^{-1}$ treated plots were left to regenerate naturally, since residue levels were supposed to be phytotoxic. No further cultivation or reseeding took place. Mowing and cutting took place on an irregular basis, mainly when access for sampling was required. During the yield study (1981-1985) mowing was confined to just after yield samples had been taken.

***Assessments***

Vegetation assessments were brief comments after the 1964 spraying, full floral survey in 1979, and %cover estimates in 1981-1985. The floral survey was done using a point quadrat survey, along 10 points at 10 cm intervals, on 8 positions in each plot. A visual estimate of overall frequency on the plots was also made. The cover estimates were done in May 1981, June 1983 and May 1985 by taking three 60 x 60 $cm^2$ square plots, with minimum estimates of 5% cover. In 1981, 1983 and 1985 in spring and autumn the yield of the vegetation was estimated by taking 3 squares of 60 x 60 $cm^2$ from each plot. Dry and wet weights were determined, as was the nutrient content.

***Statistics***

The point quadrate survey and the cover assessments were square root transformed and analysed using ANOVA. When the ANOVA was significant, a pair wise comparison using a two-sample t-test was done, comparing treatments with control. The yield and nutrient data were treated in the same way without transformation. Another seven plots were added to the analyses to improve the estimation of between-plot error, but otherwise excluded from the report.

## Results

***Visual estimates of the 1964 series***

A-series. No differences were seen between the control and the 2.24 kg $ha^{-1}$ treatment. In the 112 kg $ha^{-1}$ treatment, the rye-grass sawn after treatment did not survive. Also germination of the reseeding after six months after application was not good, but the cover developed soon, including mayweed and clover. Three years after application the plots were dominated by clover (85% in block I and 35% in block II), and paraquat (2.24 kg $ha^{-1}$) was applied and the plots were reseeded. Visible differences remained present for 2 years after reseeding (5 years after first treatment).

B-series. In the 260 kg $ha^{-1}$ plot the first 11 sprayings (2.24 kg $ha^{-1}$, 1964-1969) were irregular, to be in line with other plots and resulted in large differences with the control. From September 1969 until December 1973 the plots were sprayed every two weeks, which resulted in a vegetation consisting mainly of moss. On the 565 kg $ha^{-1}$ plot the original seeding did not survive after the first spraying (112 kg $ha^{-1}$ paraquat). Also the reseeding in May next year developed poorly. In September/October the plots were lush and green. The next spraying (July 1966) removed all vegetations. The grass vegetation recovered by October, but died during winter. Next spring the remaining vegetation was killed with a low dose of paraquat and plots were reseeded. The third spraying, in August, killed all vegetation, leaving primarily moss as vegetation. After the fifth spraying, in July 1969, the plot was reseeded, with very little success in November; also reseedings in April and October 1970 were unsuccessful. Then a quarter of the plots was dug, and on these parts the grass established well. On the other parts several further attempts (till 1972) were needed in order to establish a grass vegetation.

***Floral survey 1979***

The results of the floral survey show that 15 years after treatment in 1964 no significant differences were found, but that 8 years after treatment in 1971 with 1700 kg $ha^{-1}$ paraquat significant differences with the control were present.

***Cover estimates in 1981-1985***
The results show that 17 - 21 years after application no significant differences in vegetation cover are found for the plots treated with 2.24 and 114 kg ha$^{-1}$. In the 260 and 565 kg ha$^{-1}$ plots, significant differences were found for one species (*Dactylis glomerata*), but the cover of this species was generally low in all plots. In 1983 no differences were found for this plots and the control, and in 1985 in the 565 kg ha$^{-1}$ plot differences were found for three species (lower cover for *Lolium perenne* and *Dactylis glomerata*, higher cover for *Poa trivialis*). In the 1700 kg ha$^{-1}$ plots, treated in 1971, clear differences were found between treatment and control on all three assessment dates. These plots were dominated by *Festuca rubra*, while the untreated control was dominated by *Holcus lanatus*. In the 561 kg ha$^{-1}$ treated plot (1971) only on the first assessment date (May 1981) a significant difference with the control was seen (due to a high cover of *Poa trivialis*).

***Yield estimates 1981-1985.***
The yield of the vegetation, corrected for 85% dry matter did show a significant difference between treated and control plots for the 1700 kg ha$^{-1}$ treatment only in October 1985.

**Conclusions of the authors**
The authors conclude that soil residues below the soil's SAC-WB value have no effect on plant growth or nutrient uptake. For the plots with applications above the SAC it is concluded that the responses differed due to the combination of herbicidal effect, soil conditions, natural seed distribution, plant succession and competition. It is discussed that the large number of variables renders it difficult to attribute the effect to the amount of paraquat applied. Twenty-five years after application an equilibration in the plots treated in 1964 is (almost) seen. In the 1971 treated plots this equilibrium is not established yet, 15 years after application.

**Remarks**
From the results of the study it is clear that all applications have clear short term effects on vegetation. For the differences on the longer term, it is difficult to distinguish between direct toxic effects of the substance and indirect effects as a result of the (large) differences in the vegetation shortly after application. In the case of the 1964 treatments the substance was applied to the soil surface, leading to discussion about the concentration in the soil top layer. In the 1971 treatment the substance was mixed through the top 10 cm soil. The result that the application of 112 kg ha$^{-1}$ result in clear effects up to 5 years, but full recovery after 15 years can be used for risk assessment. The result that effects of the 1700 kg ha$^{-1}$ result in differences in species composition, biomass and nutrient uptake 10 – 14 years after application can also be used for risk assessment.

## A6.4 Effects on soil micro-organisms and their activities

**Reference**
(Lewis, 1993)

**Description**
Microbial content and activity were determined in samples taken from a field site that had been treated with paraquat according to different application schemes (see above). For this effect parameter only the single spray plots sprayed in 1964 and 1971 (A and C series) were used. In 1978 soil samples were taken from five positions within the plots; the samples were mixed and sieved (2 mm). Samples were

put into vessels, moistened to 40% of the WHC and incubated for one week at 20 ± 1 °C to stabilise the soil.

***Microbial tests***
Microbial content. Microbial content was determined by ATP-assay and total counts using microscopy.
Microbial degradation of carbon substrates. Microbial degradation of soil organic matter, glucose and plant material was estimated.
Nitrification and ammonification. Nitrification in ammonium sulphate amended soil and ammonification of lucerne meal were determined.
Enzyme activity. Phosphatase and dehydrogenase actitivity were determined.

***Calculations and statistics***
Results were analysed by ANOVA, with data from this trial and a parallel diquat trial combined to improve the estimate of the between-plot error in the analysis. Results are thus from a pooled analysis according to a randomised block design.

**Results**

***Microbial content***
No significant differences between plots were found for ATP-content, total propagules, algae, bacteria and actinomycetes and *L. starkeyi*. Numbers of fungi in the treated 1964 plots (2.24 and 114 kg $ha^{-1}$, not incorporated) were significantly higher than in the control, no difference was found for the incorporated plots. Since no significant effects on ATP were found, the authors conclude that the differences found may not be of ecological importance.

***Microbial degradation of carbon substrates***
No treatment related effects were found.

***Nitrification and ammonification***
In the soils amended with lucerne meal, nitrate formation in the 1700 kg $ha^{-1}$ treatment was significantly higher after 0, 52 and 66 days, as was ammonium (52 and 66 days). This indicates a stimulation of ammonification. In soils amended with ammonium sulphate, ammonium was higher in the 1700 kg $ha^{-1}$ treatment after 14, 21 and 28 days and nitrate was higher after 0 and 7 days.

***Enzyme activity***
No significant differences between treatments were observed and no clear trends were present.

**Remarks**
The tests do not meet the current quality requirements, because only single samples were used for most parameters. N-turnover was tested in duplicate, but individual values are not shown. At least triplicate measurements are needed for a proper statistical evaluation of the variation within each test. The results cannot be used for risk assessment.

## A6.5 Arthropod field study

**Reference**
(Wilkinson et al., 1993b)

**Description**
The effects of paraquat on soil micro-arthropods were assessed on the field site at Jealott's Hill (see A6.3). Series A and B plots: Microarthropods were randomly sampled in October 1964 as pre-treatment and December 1964 (2.5 months after treatment). Sampling was continued each October/ November and April until October 1968. Thereafter three samplings took place in December 1969, November 1970 and May 1979. Series C plots were sampled in January 1971 (eight months before application) and in May 1979. Additional plots, not forming part of the paraquat experiment, were also sampled to improve statistical power. Among these were plots C11 and C12, which were to be part in the series C study.

Series A pre-treatment sampling was performed taking 30 random samples over the whole site, the first post-treatment sampling consisted of two 15-cm cores per plot (Series A). From the third sampling (April 1965) onwards, three samples per plot were taken, each of which consisted of four bulked cores. Soil was stored at -15 °C until processing.

Arthropods were extracted from the soil by washing, flotation and differential wetting techniques, collected, counted and identified. At the beginning of the trial only the major groups were recorded, identification became more detailed later on, but reporting is restricted to major groups.

***Calculations and statistics***
For the 10 major taxonomic groups selected during 1964 – 1979, counts were expressed in hundreds per $m^2$. Counts were then log+1-transformed. A two-way ANOVA for a randomised block design was performed using all treatments, for each taxon and sampling date. The resulting estimate of error variance was used to compute the 5% and 1% Least Square Difference (LSD) to compare treatments with control. Data treated with another herbicide were included to improve the estimation of variability.

**Results**
A few significant differences were found in the series A study, but no consequent dose related effects were found. The same was found for the 561 and 1700 kg $ha^{-1}$ trials (C series), although this is based on one post treatment sampling only.

The repeated exposure on plots B resulted in large effects on several groups of soil micro-arthropods. In 1979 no significant differences were found any more. Therefore, and combined with the findings in the other plots it is concluded that the effects found are indirect effects, as result of the severe effects on vegetation in the plots B.

**Remarks**
For the 1971 trial (series C), only one post-treatment sampling was performed after eight years. Results cannot be used for risk assessment. Pre-sampling for series A was done randomly over the site, it can thus not be checked whether differences between treatments and control were already present before treatment. Despite this, the data do not suggest a direct effect of paraquat as most taxa do not show a

consistent dose related trend as result of a single dose and the effects of a repeated dose recover, when vegetation is re-established.

## A6.6 Effects on earthworms

**Reference**
(Wilkinson and Edwards, 1993)

**Description**
The effects of paraquat on earthworms were assessed on the field site at Jealott's Hill, UK, described above. Earthworms were sampled using formalin extraction of 60 x 60 $cm^2$ areas on 13 October 1965 (one year after application; single samples, two plots per treatment), on 31 October – 2 November 1966 (two years after treatment; single samples, two plots per treatment) and on 1-3 May 1979 (15 years after treatment; three samples) on the plots treated in 1964 and on 1 - 3 May 1979 (8 years after application, three samples, two plots per treatment) on the plots treated in 1971. Worms were weighed, identified and counted.

In 1965 and 1966 residues in earthworms were measured. In 1965, the samples from each block were bulked into single samples per treatment, in 1966 each block was analysed separately. In May 1965 extra samples for residue analyses were taken in the 112 kg $ha^{-1}$ plot and the control plot. Paraquat was applied to the whole site at the rate of 1.12 kg $ha^{-1}$ before the trial was set up in 1964 and 1971.

As extra part (PhD research) enchytraeid sampling was included. Samples from series A and B plots were taken in April 1967 and additionally from series B plots in August 1967, September 1967 and January 1968. Five samples were taken on each occasion form each plot, and handled separately.

***Statistical evaluation***
Data were analysed by ANOVA of log-transformed counts and untransformed weight data. Data from ten extra fields with different cultivation patterns were added, resulting in 12 treatment/cultivation combinations, in a randomized block design.

**Results**
The results do not indicate clear treatment related effects for the series A and C plots. Series B plots showed significant differences, which might indicate indirect effects. Paraquat concentrations show that paraquat residues are found 5, 12 and 24 months after application, and that the levels decline with time. The enchytraeid worms showed effect in the repeated treatment. Since the vegetation was affected as well in these plots, it is not possible to determine whether these effects are direct or indirect.

**Remarks**
The study does not meet the present requirements. Among others, sampling frequency was too low, weather data are not presented, no positive control was included and not all raw data are presented. Furthermore, only one sub sample was taken per plot on the first two sampling dates. Given the low number of replicates and the lack of pre-treatment samples, it is also not clear whether the earthworm populations were homogeneously distributed over the plots. The results cannot be used for risk assessment.

# Appendix 7 Details of the paraquat literature search

A literature search was done in Toxline for the period 1985-2001 and in current contents for the period 2001-januari 2007.

For the selection of paraquat data from the open literature the following search profile was used:

1 terms in journal title: (agric* or weed* or zool* or plant* or crop* or pest* or pedobio* or ecolog* or geobios* or biol* or biochem* or toxic* or ecotoxic* or environ* or pollut* or soil* or chemosphere or phytol*)
2 terms in title: (effect* or impact* or bioassay* or toxic* or ecotoxic* or mortalit* or sensitiv* or phytotox* or assessment* or reproduct* or lethal* or field or response* or growth or terrestr*)
3 paraquat* or 4685-14-7 or 4685147

The combination of 1, 2 and 3 resulted in 1511 hits.
To exclude a too large number of human or aquatic studies, a number of words in the title were excluded:

4 Exclude: (liver* or drug* or aquatic* or poison* or daphnia* or fish* or resisten* or aremia or rat or mice)

Running the above profile resulted in 778 hits. After removal of double hits and papers that clearly concerned human or aquatic aspects, 394 references remained. A further selection (based on title and/or abstract) rendered 71 titles. It was not clear from each title whether the paper would be suitable for assessing the effects of paraquat on soil organisms. After a further selection 11 references remained (see Table A7.1). These were studied in detail to derive endpoints.

Table A7.1 Papers remaining after selection from the literature search

| **Literature used to derive an endpoint: 11 references** |
|---|
| Afzal M; Ghannoum M A; Hanssan R A H and Dhami, M S I. Variation in growth and fatty acid contents of Trichoderma viride induced by herbicides. FASEB (FEDERATION OF AMERICAN SOCIETIES FOR EXPERIMENTAL BIOLOGY) JOURNAL 4(3). 1990 Apr 1-1990 Apr 1; A663. 74th Annual Meeting of the Federation of American Societies for Experimental Biology Part I. CODEN: FAJOEC. **Endpoints may be derived, however only abstract available (no endpoint to be derived from abstract).** |
| Dirven-van Breemen E M; Van Gestel CAM; Van der Pol JJC; van Straalen NM, and Baerselman R. Toxiciteit van Paraquat voor Enkele Bodemorganismen (Toxicity of Paraquat for Some Soil Microorganisms). Govt Reports Announcements & Index (GRA&I), Issue 17, 1991. NTIS/PB91-194548, Available Only in the U.S., Canada and Mexico. All Others Refer to National Institute of Public Health and Environmental Protection, P.O. Box 1, 3720 BA Bilthoven, The Netherlands., 21p. NTIS Prices: PC A03/MF A01. 1990. **Data for soil microorganisms derived in accordance with van Beelen et al. Data for earthworms are the same as reported in van Gestel et al. In the test with *Porcellio* non dose related mortality occurred, so no reliable endpoint can be derived. *Orchesella cincta* and *Platynorthrus peltifer* were exposed via food. These organisms live on the soil surface. Exposure via food could be translated to soil; in the past these data have been used, assuming that the food consist of 100% organic matter. No effects were seen at the highest concentration of 1000 mg $kg^{-1}$ food.** |
| Eberbach P L and Douglas L A. Effect of herbicide residues in a sandy loam on the growth, nodulation and nitrogenase activity (acetylene/ethylene) of Trifolium subterraneum. Plant Soil. 1991; 131(1):67-76. CODEN: PLSOA2; ISSN: 0032-079X. **Effects of residues in soil (150 d) on *Trifolium subterraneam* were studied. No effects of paraquat were seen, so that a > value will be found as an endpoint. Publication with soil data ordered.** |
| Edwards C A and Bohlen P J. The effects of toxic chemicals on earthworms. Ware, G. W. (Ed.). Reviews of Environmental Contamination and Toxicology, Vol. 125. Ix+186p. 23-99. Springer-Verlag New York, Inc.: New York, New York, USA; Berlin, Germany. Illus. Maps. 1992. CODEN: RCTOE4. **Based on literature it is concluded that 5 field studies (dose 11.4-200 kg $ha^{-1}$) and 4 laboratory studies (64-2000 mg $kg^{-1}$) show that paraquat is nontoxic to earthworms.** |
| Fischer Erno. Effects of atrazine and paraquat-containing herbicides on *Eisenia foetida* (Annelida Oligochaeta). Zool. Anz. 1989; 223(5-6):291-300. CODEN: ZOANA6; ISSN: 0044-5231. **Chronic endpoints for *Eisenia foetida* derived, however expressed as wet weight.** |
| Flores M and Barbachano M. Effects of herbicides Gramoxone, diuron and Tota-col on growth and nodulation of three strains of *Rhizobium meliloti*. Sci. Total Environ. 1992; 123-124249-60. CODEN: STENDL; ISSN: 0048-9697. **Endpoint in culture medium extracting.** |
| Gianfreda L; Sannino F; Ortega N and Nannipieri, P. Activity of free and immobilized urease in soil: effects of pesticides. Soil Biol Biochem 1994; 26(6):777-84. CODEN: SBIOAH; ISSN: 0038-0717. **Effects on enzyme systems.** |
| Ortiz A; Burriel J and Cantarino H. Paraquat toxicity in protozoans. European Journal of Protistology 31(4). 1995 Jul 21-1995 Jul 26; 452. Second European Congress of Protistology and Eighth European Conference on Ciliate Biology Clermont-Ferrand; ISSN: 0932-4739. **Protozoa in solution; endpoints derived.** |
| Van Beelen P and Fleuren Kemila A K. Toxic effects of pentachlorophenol and other pollutants on the mineralization of acetate in several soils. Ecotoxicol. Environ. Saf. 1993; 26(1):10-17. CODEN: EESADV; ISSN: 0147-6513. **Endpoint (no-effect at highest dose tested) extracted.** |
| Van Gestel C A M; Dirven-Van Breemen E M; Baerselman R; Emans H J B; Janssen J A M; Postuma R, and Van Vliet P J M. Comparison of sublethal and lethal criteria for nine different chemicals in standardized toxicity tests using the earthworm Eisenia andrei. Ecotoxicol. Environ. Saf. 1992; 23(2):206-20. CODEN: EESADV; ISSN: 0147-6513. **Endpoint (NOEC) extracted.** |
| Wang W. Rice seed toxicity tests for organic and inorganic substances. Environmental Monitoring and Assessment 29(2); 101-107. 1994; ISSN: 0167-6369. **Acute emergence test (root dry weight). Test solution. An $EC_{10}$ could be derived, and used as indicative when no chronic data are available.** |

Table A7.2 Ecotoxicological endpoints for paraquat derived from open literature

| Species Process activity | species properties | soil type | pH | OM (%) | clay (%) | Temp (°C) | exp. time | criterion | test endpoint | result test soil (mg $kg^{-1}$) | note | reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Trifolium subterraneum* | seedlings | sandy loam | | | | 26 | 18w | root weight | NOEC | >10 | a | Eberbach, Douglas,1991 |
| | | | | | | | 18w | shoot weight | NOEC | >10 | a | |
| | | | | | | | 18w | nodulation | NOEC | <2 | a | Eberbach, Douglas,1992 |
| | | | | | | | 9w | nitrogenase | NOEC | <2 | a | Eberbach, Douglas,1993 |
| | | | | | | | 12w | | NOEC | >10 | a | |
| | | | | | | | 15w | | NOEC | >10 | a | |
| *Oryza sativa* | seeds | solution | | | | 25 | 144h | dry root biomass | NOEC | 0.05 mg $dm^{-3}$ | | Wang, 1994 |
| *Stentor coeruleus* | protozoa | | | | | 20 | 1h | | LD50 | 3.5 mg $dm^{-3}$ | | Ortiz et al., () |
| | protozoa | | | | | 20 | 10d | | NOEC | <0.16 mg $dm^{-3}$ | | |
| urease | | clay | 7,5 | 3,74 | 48 | 37 | 1h | activity | EC11 | 43 | | Gianfreda et al., 1994 |
| | | | 7,5 | 3,6 | 48 | 38 | | | EC6 | 43 | | Gianfreda et al., 1995 |
| | | | 7,6 | 3,4 | 47 | 39 | | | EC5 | 43 | | Gianfreda et al., 1996 |
| | | | 7,6 | 3,7 | 39 | 40 | | | EC5 | 43 | | Gianfreda et al., 1997 |
| | | | 7,6 | 3,6 | 39 | 41 | | | EC5 | 43 | | Gianfreda et al., 1998 |
| | | sandy loam | 6,6 | 5,3 | 16 | 42 | | | EC6 | 43 | | Gianfreda et al., 1999 |
| | | clay | 5,5 | 4,4 | 12 | 43 | | | EC17 | 43 | | Gianfreda et al., 2000 |
| Soil Microflora | | | 4.8 | 5.2* | 2.5 | 10 | | acetate mineralisation | NOEC | >=1700 | | Van Beelen and Fleuren-Kemila, 1993 |
| | | sandy soil | 5.7-6.1 | <0.1* | 0.5 | 10 | | | NOEC | >=1700 | | |
| | | Dune | 4.4 | 0.5-0.6* | 0.4-0.5 | 10 | | | NOEC | >=1700 | | |
| | | sand | 3,8 | 0,5 | 0,5 | 10 | | | NOEC | >=1000 | | Dirven et al., 1990 |
| Soil fungi: *Gliocladium virens, Trichoderma hamatum, Trichoderma koningii, Humicola fuscoatra* | | agar | | | | 28 | | Growth and sporulation | | | | (Tan and Chua, 1986) |
| *Rhizobium meliloti* | | Culture medium, (Yeast Mannitol Broth) | | | | 28 | 7 d | growth | NOEC | 6 mg $dm^{-3}$ | b | Flores and Barbachano, 1992 |
| *Medicago sativa* | | Thornton medium | | | | 20-25 | 35-40 | nodulation | NOEC | <2 mg $dm^{-3}$ | b | |
| *Eisenia andrei* 8.5-15.5 weeks, 170-582 mg | | artificial soil | 6.0 ±0.5 | 10% peat | 20 | 20±5 | 3 w | growth | NOEC | 450 | c | Van Gestel et al.,1992 |
| | | | | | | | | reproduction (cocoon production) | NOEC | 200 (n.s.)-450 | c | |
| | | | | | | | | | NOEC | 298 | c,d | |
| | | | | | | | | reproduction (juveniles) | NOEC | 450 | c | |
| *Eisenia andrei* 5-6 weeks, 198 ± 31 mg | | peaty soil and horse manure | 7.54-7.64 | | | 19-22 | 6 w | survival | $EC_{10}$ | 177 | d | Fischer, 1989 |
| | | | | | | | 6 w | growth | $EC_{10}$ | 123 | d | |
| | | | | | | | 8 w | cocoon production | $EC_{10}$ | 183 | d | |

Notes a: dosed soils aged for 120 days outside, b: statistics unclear, c: cow dung added, d: mg $kg^{-1}$ wet weight, moisture content appr. 60%; values recalculated from original data using a log logistic model, *OC

# Appendix 8 Details of quinoxyfen exposure evaluations

This appendix summarizes field experiments performed with quinoxyfen in several European countries. The description of the field accumulation studies (sections A6.1 – A6.3) was insufficient to derive transformation rates for quinoxyfen and its 3-hydroxy-metabolite. The field dissipation studies (sections A8.4 - A8.10) were re-evaluated with respect to the transformation of quinoxyfen in soil. The re-evaluation included time-step correction based on measured temperatures in the field according to the method described in FOCUS (2006) and in Appendix 2 of this report. First-order and biphasic transformation constants were obtained using the software tools Berkeley Madonna (version 8.0.1) and KinGui (version 1.1) (Mikolasch and Schäfer, 2006). Section A8.11 gives an overview of the obtained transformation constants for the seven field dissipation studies.

## A8.1 Marcham, UK

**Description**

Location Marcham field station, Oxfordshire, UK. Sandy clay loam (26/21/52), pH 7.1, OC 1.6%, CEC 240 mmol $kg^{-1}$, plot 33 * 3 $m^2$. Six applications 1993 bare soil, 400 g $ha^{-1}$, 1994 – 1998 250 + 150 g $ha^{-1}$ boom sprayer, winter wheat BBCH 32 - 45 and BBCH 49 - 57 (1996 single application approximately one month too late 400 g $ha^{-1}$ on partly cut wheat, BBCH 79 before cutting (due to incorrect labelling)) Sampling depth 0 – max 60 cm. Biomass-C 244 - 399 mg $kg^{-1}$.

**Results**

Quinoxyfen was recovered in the 0 – 20 cm layer (twice below LOQ in the 20 - 30 cm layer). Figure A8.1 gives the residues (g $ha^{-1}$) of quinoxyfen and its 3-OH-metabolites in soil, assuming a dry bulk density of 1500 kg $m^{-3}$. The 3-hydroxy-metabolite was found in the 0 – 10 cm layer (and below LOQ in 10 – 20 and 20 - 30 cm layers).

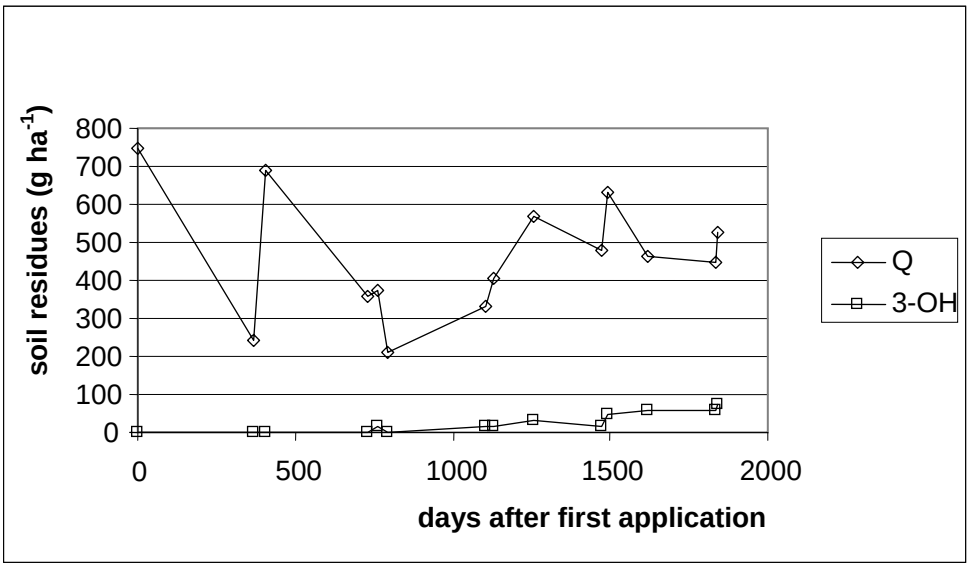



Figure A8.1 Residues of quinoxyfen (Q) and its 3-OH-metabolite (3OH) in Marcham soil

**Conclusion**
There is no indication of accumulation of quinoxyfen; a sort of plateau was reached at the end of the study. The 3-OH-metabolite increases towards the end of the study. Information on climate parameters is insufficient to derive dissipation / transformation parameters from the study.

**Reference**
Koshab A, Gambie A. Residues of quinoxyfen and its 3-hydroxy metabolite in soil following five annual applications of EF-1186, UK – interim report – year 5. Dow Agrosciences, report GHE-P-7338.

## A8.2 München, Germany

**Description**
Location München. Loamy silt (13/67/20), pH 7.5, OC 4.2%, CEC 239 mmol $kg^{-1}$, bare soil, plot 29 * 2.5 $m^2$. Five applications: 1993 bare soil, 400 g $ha^{-1}$, 1994 – 1997 425, 400, 400, 400 g $ha^{-1}$, boom sprayer, winter wheat at stage BBCH 32 and BBCH 49 (approx. 250 + 150 g $ha^{-1}$). Sampling depth 0 - 45 cm. Biomass 425 - 1140 mg $kg^{-1}$ (control 180 – 1143 mg $kg^{-1}$).

**Results**
Quinoxyfen was recovered in the 0 – 30 cm layer. Figure A8.2 gives the residues (g $ha^{-1}$) of quinoxyfen and its 3-OH-metabolites in soil, assuming a dry bulk density of 1500 kg $m^{-3}$. There was a possibly mislabeling of layers 1 and 2 in May 1996, but this does not influence the results presented here. The 3-hydroxy-metabolite was found also in the 0 – 30 cm layer and detected once below LOQ in the 30 - 40 cm layer.

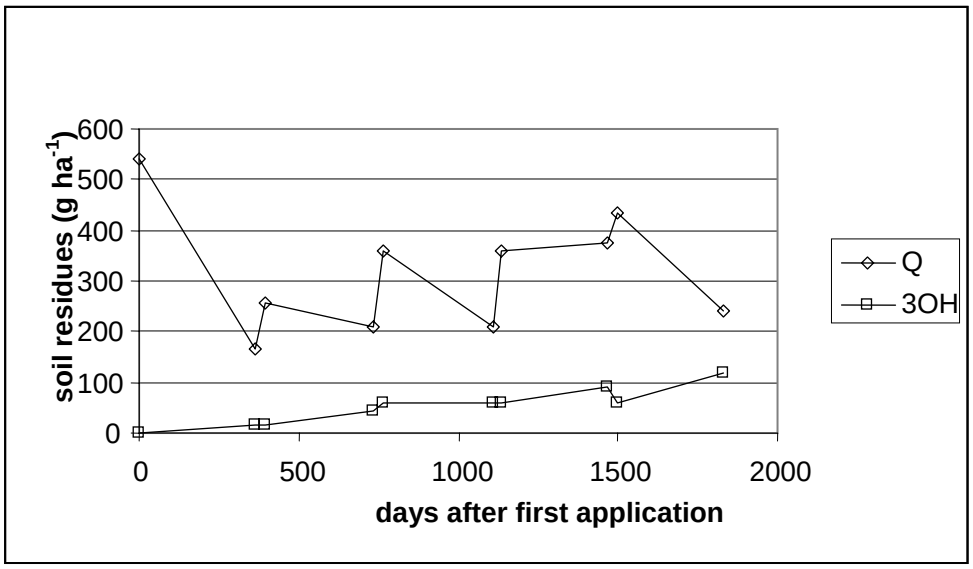



Figure A8.2 Residues of quinoxyfen (Q) and its 3-OH-metabolite (3OH) in München soil

**Conclusion**
There is no indication of accumulation of quinoxyfen; a sort of plateau was reached at the end of the study. The 3-OH-metabolite increases towards the end of the study. Information on climate parameters is insufficient to derive dissipation / transformation parameters from the study.

**Reference**
Koshab A, Gambie A. Residues of quinoxyfen and its 3-hydroxy-metabolite in soil following five annual applications of EF-1186, Germany. Dow Agrosciences, report GHE-P-7337.

## A8.3 St Martin des Champs, Ile-de-France

**Description**
Location St Martin des Champs, Ile-de-France. Sandy clay loam (16/65/19), pH 6.6, OC 2.1%, CEC 111 mmol $kg^{-1}$, bare soil, plot 33 * 3 $m^2$. Five applications 1993 bare soil, 400 g $ha^{-1}$, 1994 – 1997 415, 375, 415, 405 g $ha^{-1}$ boom sprayer, winter wheat BBCH 32 - 33 and BBCH 49 - 55, approximately 250 + 150 g $ha^{-1}$. Sampling depth 0 – 25 later 0 – 50 cm. Biomass-C 117 – 191 mg $kg^{-1}$.

**Results**
Quinoxyfen was recovered in the 0 – 30 cm layer and detected once in the 30-40 cm layer. Figure A8.3 gives the residues (g $ha^{-1}$) of quinoxyfen and its 3-OH-metabolite in soil, assuming a dry bulk density of 1500 kg $m^{-3}$. The 3-hydroxy metabolite was found also in the 0 – 30 cm layer.

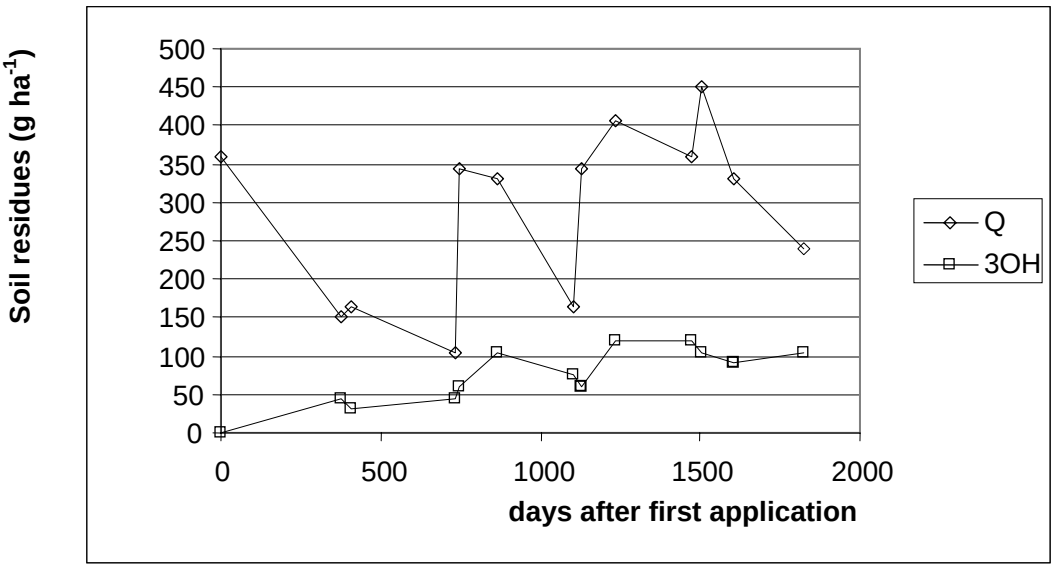



Figure A8.3 Residues of quinoxyfen (Q) and its 3-OH-metabolite (3OH) in St Martin des Champs soil

**Conclusion**
There is no indication of accumulation of quinoxyfen; a sort of plateau was reached at the end of the study. The 3-OH-metabolite increases towards the end of the study. Information on climate parameters is insufficient to derive dissipation / transformation parameters from the study.

**Reference**

Koshab A, Gambie A. Residues of quinoxyfen and its 3-hydroxy metabolite in soil following five annual applications of EF-1186, northern France. Dow Agrosciences, report GHE-P-7336.

## A8.4 Ismaning, Oberbayern, Germany

**Description**

Location Ismaning Oberbayern. Loamy silt (11/68/21), pH 7.5, OC 4.65%, CEC 233 mmol $kg^{-1}$, plot 29.5 * 2.5 $m^2$. Application 5 May 1993, 400 g $ha^{-1}$, backpack sprayer, bare soil. Air temperature 14 °C, soil temperature (10 cm) 12 °C, wind 2 – 3 m/s, RH 60 at time of application. Weather data München Flughafen. In report: daily for 15 days, thereafter mostly per decade or month. Rain DAA1 1mm, DAA7 4 mm. DAA2 – DAA7: 11 – 13 h sunshine. Average temperature during experiment 11 °C, total rain 1418 mm (79 mm per month). Sampling depth 0 - 30, 0 – 45 cm. Biomass-C: 919 – 1095 mg $kg^{-1}$ control, 987 – 1108 mg $kg^{-1}$ treated.

**Results**

The recovery at DAA0 was120%.

Residues: quantifiable residues only in 0 – 10 cm layer, trace amounts of quinoxyfen in 2nd layer. A first order fit (Berkeley Madonna) using all data points resulted in a $DT_{50}$ of 202 days. Very uncertain. The report states 374 days (result from linear regression after logtransformation). Accounting for temperature deviating from 20 °C, a corrected first-order $DT_{50}$ is 100 days. 3-hydroxy-metabolite at maximum at end of experiment, no 3-hydroxy-metabolite in 2nd layer. According to FOCUS (2006) an analysis for biphasic behaviour was performed. Figure A8.4 and Table A8.1 give the results for the DFOP fit.

Table A8.1 Ismaning fit statistics

| | initial value | estimated value | SD | prob > t |
|---|---|---|---|---|
| SFO | | | | |
| parent_k | 0.01 | 0.007 | 0.0021 | 0.0058 |
| parent_$M_0$ | 0.3 | 0.28 | 0.031 | |
| DFOP | | | | |
| parent_$k_1$ | 0 | 0.026 | 0.023 | 0.15 |
| parent_$k_2$ | 0 | 3.0E-10 | 0.0048 | 0.50 |
| parent_g[#] | 0 | 0.71 | 0.32 | 0.20 |
| parent_$M_0$ | 100 | 0.31 | 0.036 | |

[#] The two compartments were switched by the KinGui software, so actually 1-g was given as the result. The statistics refer to 1-g.

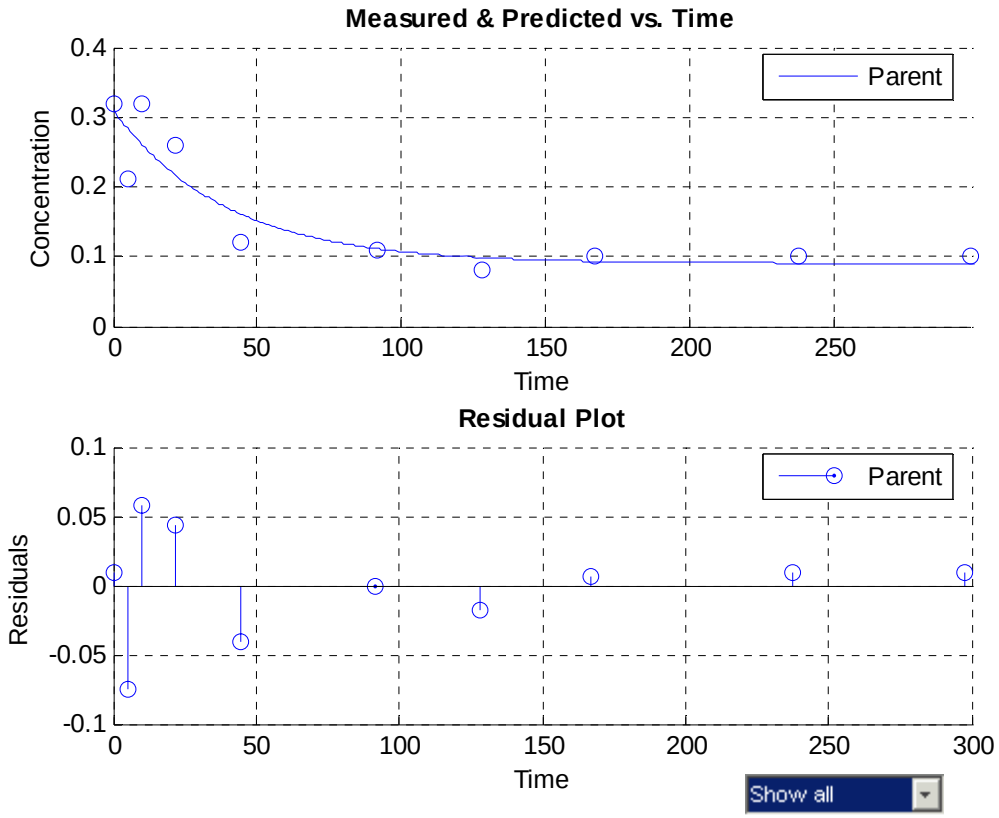



Figure A8.4 DFOP fit for Ismaning soil, after time step normalization assuming a Q10 of 2.2

**Conclusion**

According to the DFOP analysis, a non-significant transformation in the slow phase takes place. The uncertainty in this parameter is very high and therefore this result is not reliable. The result is not included in the calculation of the geometric mean of all field studies.

**Reference**

Gambie A. The dissipation of XDE-795 and its 3-hydroxy metabolite in soil at intervals following application of EF-1186, Germany – 1993. Dow Agrosciences, report GHE-P-5135.

## A8.5 St Nicholas-de-la-Grave, Midi Pyrenees, France

**Description**

Location St Nicholas-de-la-Grave, Midi Pyrenees, France.
Clay loam (//), pH 6.1, OC 1.6%, CEC 101 mmol $kg^{-1}$, bare soil, plot 33 * 3 $m^2$. Application 31 March 1993, 400 g $ha^{-1}$, boom sprayer, spring barley BBCH 21. Air temperature 17.6 °C, soil temperature (10 cm) 11.5 °C, wind 5 - 10 m $s^{-1}$, RH 43 at time of application. Weather data location? Weather data daily for 15 days, thereafter mostly per decade or month. Rain DAA1 1mm, DAA7 4 mm. DAA2 – DAA7: 11 – 13 h sunshine. Average temperature during experiment 11 °C, total rain 1418 mm (79 mm per month). Sampling depth 0 – 25 (first two sampling days), 0 – 50 cm later sampling days. Biomass-C 57 mg $kg^{-1}$ (control), 29 - 63 mg $kg^{-1}$ (treated).

**Results**

Recovery DAA0 67%. First order fit (Berkeley Madonna): 186 days (all data points), reasonable fit (report states 251 days from regression line after log transformation). Assuming a Q10 of 2.2, the corrected half-life is 135.3 days. Maximum content of 3-hydroxy-metabolite is 0.03 mg $kg^{-1}$ in 0–10 cm layer. Figure A8.5 gives the results for a DFOP fit and Table A8.2 gives statistical measures.

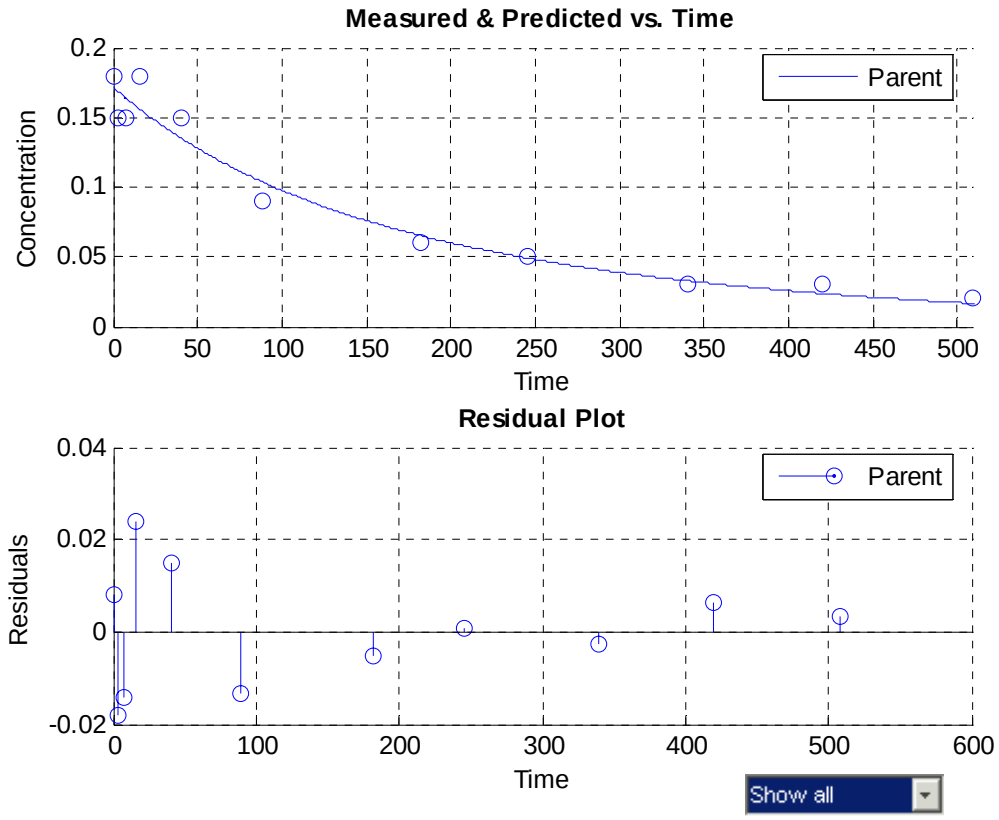



Figure A8.5 DFOP fit for St Nicholas-de-la-Grave soil, after time step normalization assuming a Q10 of 2.2

Table A8.2 St Nicholas-de-la-Grave fit statistics

| | initial value | estimated value | SD | prob > t |
|---|---|---|---|---|
| SFO | | | | |
| parent_k | 0.01 | 0.0051 | 6.3E-4 | 9.9E-6 |
| parent_$M_0$ | 0.2 | 0.17 | 0.007 | |
| DFOP | | | | |
| parent_$k_1$ | 0 | 0.011 | 0.043 | 0.40 |
| parent_$k_2$ | 0 | 0.0039 | 0.0062 | 0.27 |
| parent_g[#] | 0 | 0.33 | 2.0 | 0.37 |
| parent_$M_0$ | 100 | 0.17 | 0.0097 | |

[#] The two compartments were switched by the KinGui software, so actually 1-g was given as the result. The statistics refer to 1-g.

**Conclusion**
Conclusion: study result is not very reliable, but value can be used. Visually and according to the $Chi^2$-error% the fit is quite good.

**Reference**
Gambie A, Long T. The dissipation of XDE-795 and its 3-hydroxy metabolite in soil at intervals following a single application of EF-1186, southern France – 1993. Dow Agrosciences, report GHE-P-5136.

## A8.6 Warlus, France

**Description**
Location Warlus, Nord Pas de Calais, France. Silty clay loam (21/60/19), pH 7.9, OC 2.8%, CEC 251 mmol $kg^{-1}$, barley, plot 33 * 3 $m^2$. Application 19 April 1993, 400 g $ha^{-1}$, boom sprayer, spring barley BBCH11-13. Air temperature 11 °C, soil temperature (10 cm) 8.6 °C, wind 0 - 5 m $s^{-1}$, RH 74 at time of application. Weather data location? Weather data daily for 15 days, thereafter per decade, rain 0.6 - 1.8 mm $d^{-1}$ first week after treatment. Average temperature during experiment 12.2 °C, total rain 1348 mm (69.5 mm per month). Sampling depth 0 - 50 cm. Biomass-C 264 - 276 mg $kg^{-1}$ (control), 308 – 382 mg $kg^{-1}$ (treated).

**Results**
Recovery DAA0 282%.
First order fit (Berkeley Madonna): 17.2 days (all data points), bad fit (report states 235 days from regression line after log transformation). Excluding data for DAA0 and DAA7, the first order fit (Berkeley Madonna) is 299 days. Assuming a Q10 of 2.2 the corrected half-life is 165 days. The 3-hydroxy metabolite was not detected. Figure A8.6 gives the results for a DFOP fit, while Table A8.3 gives statistical measures.

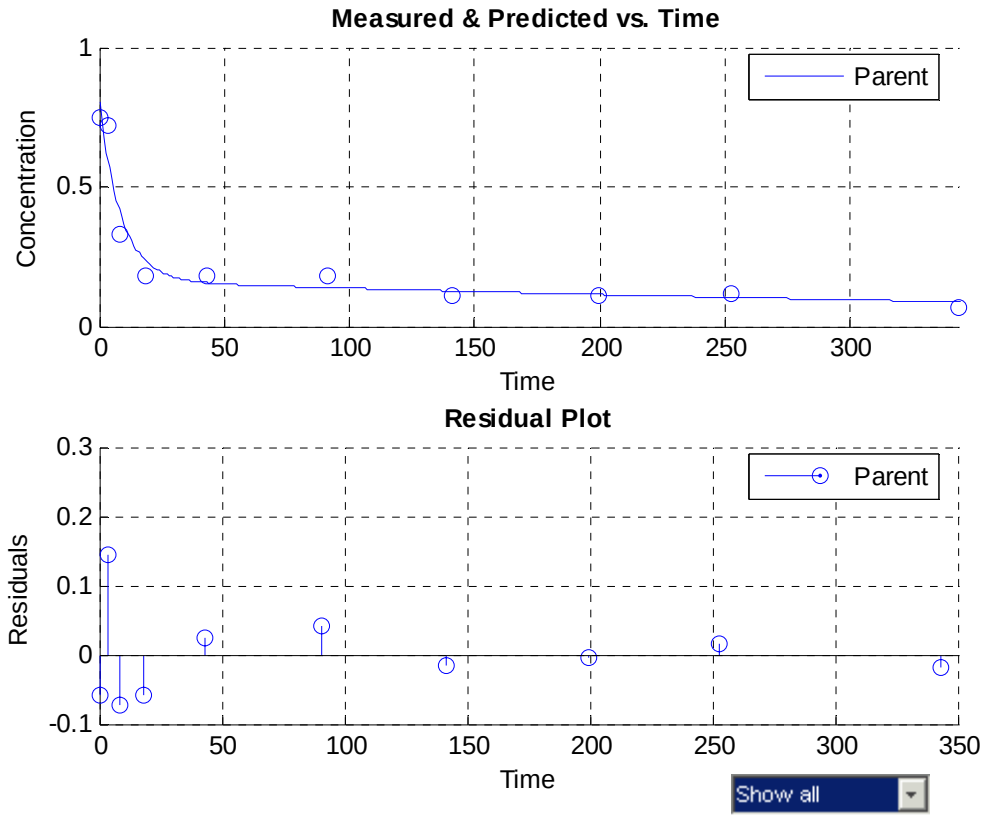



Figure A8.6 DFOP fit for Warlus soil, after time step normalization assuming a Q10 of 2.2

Table A8.3 Warlus fit statistics

| | initial value | estimated value | SD | prob > t |
|---|---|---|---|---|
| SFO | | | | |
| parent_k | 0.01 | 0.069 | 0.024 | 0.011 |
| parent_$M_0$ | 0.7 | 0.078 | 0.11 | |
| DFOP | | | | |
| parent_$k_1$ | 0 | 0.11 | 0.041 | 0.016 |
| parent_$k_2$ | 0 | 0.0018 | 0.0028 | 0.27 |
| parent_g[#] | 0 | 0.80 | 0.097 | 0.040 |
| parent_$M_0$ | 100 | 0.81 | 0.073 | |

[#] The two compartments were switched by the KinGui software, so actually 1-g was given as the result. The statistics refer to 1-g.

**Conclusion**

Low reliability due to extreme recovery immediately after application. Values not to be used.

**Reference**

Gambie A. The dissipation of XDE-795 and its 3-hydroxy metabolite in soil at intervals following a single application of EF-1186, northern France – 1993. Dow Agrosciences, report GHE-P-5137.

## A8.7 Laubach, Germany

**Description**

Location Laubach, Hessen, Germany. Loamy silt (15/81/4), pH 5.9, OC 1.2%, CEC 197 mmol $kg^{-1}$, barley, plot 35 * 2.5 $m^2$. Application 5 May 1994, 400 g $ha^{-1}$, bicycle sprayer, bare soil. Air temperature 15 °C, soil temperature (10 cm) 10 °C, wind 1 - 2 m $s^{-1}$, RH 83 at time of application. Weather data location Giessen. Daily to weekly (few data gaps), rain 1 mm DAA0 and 4 mm following 6 days. Average temperature during experiment 12.2 °C, total rain 1348 mm (69.5 mm per month). Sampling depth 0 - 45 cm. Biomass-C 199 - 227 mg $kg^{-1}$.

**Results**

Recovery DAA0 64%. Quinoxyfen was recovered from the first layer. Contents in the second layer were ND - <0.01 mg $kg^{-1}$. First order fit (Berkeley Madonna): 287d (all data points), (report states 359 days from regression line after log transformation). Assuming a Q10 of 2.2, the first order fit gives a corrected half-life of 164 days. The 3-hydroxy metabolite content was 0.01 mg $kg^{-1}$ at DAA551, not detected until DAA123 and <0.01 mg $kg^{-1}$ at other dates. Figure A8.7 gives the results for a DFOP fit and Table A8.3 gives statistical details.

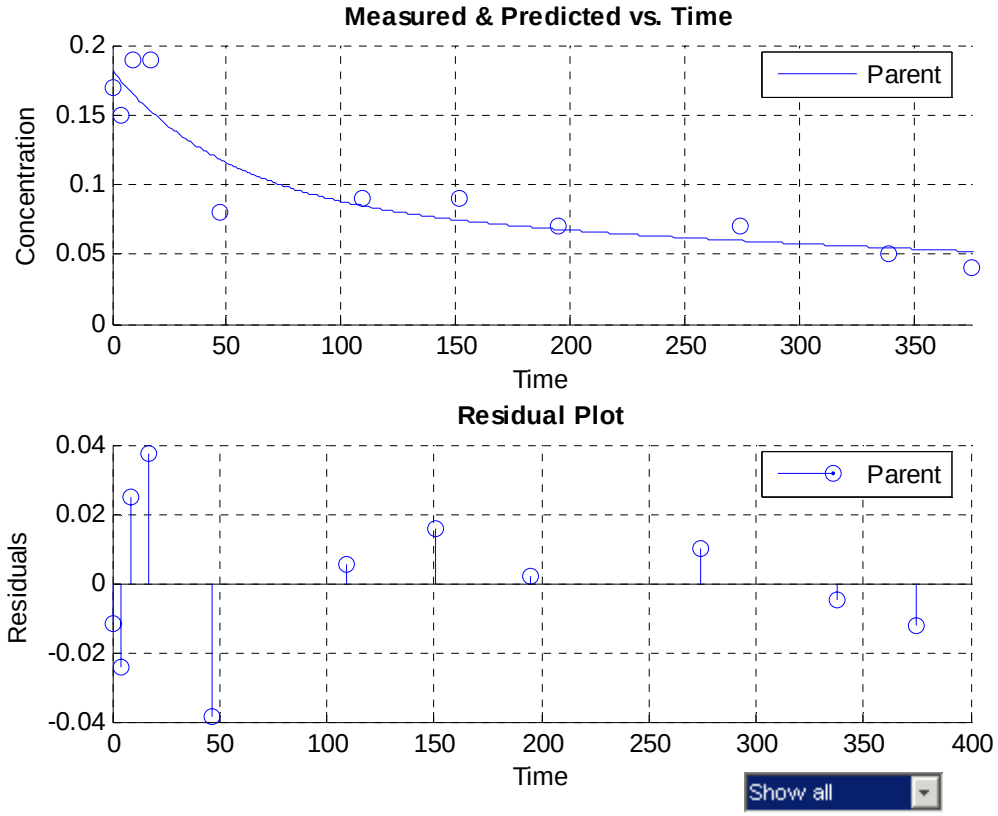



Figure A8.7 DFOP fit for Laubach soil, after time step normalization assuming a Q10 of 2.2

Table A8.4 Laubach fit statistics

| | initial value | estimated value | SD | prob > t |
|---|---|---|---|---|
| SFO | | | | |
| parent_k | 0.01 | 0.0042 | 9.1E-4 | 6.3E-4 |
| parent_$M_0$ | 0.2 | 0.17 | 0.013 | |
| DFOP | | | | |
| parent_$k_1$ | 0 | 0.020 | 0.027 | 0.24 |
| parent_$k_2$ | 0 | 0.0013 | 0.0032 | 0.35 |
| parent_g[#] | 0 | 0.53 | 0.43 | 0.16 |
| parent_$M_0$ | 100 | 0.18 | 0.018 | |

[#] The two compartments were switched by the KinGui software, so actually 1-g was given as the result. The statistics refer to 1-g.

**Conclusion**

The study result is not very reliable, but the results can be used for further analysis. Visually the fit is quite good and the $Chi^2$-error% is just slightly above the value of 15%.

**Reference**

Gambie A. The dissipation of quinoxyfen and its 3-hydroxy metabolite in soil at intervals following a single application of EF-1186, Germany – 1994. Dow Agrosciences, report GHE-P-5439.

## A8.8 Crimplesham, UK

**Description**

Location Crimplesham, Norfolk, UK. Sand (7/7/86), pH 6.4, OC 1.0%, CEC 83 mmol $kg^{-1}$, spring barley, plot 45 * 3 $m^2$. Application 10 May 1994, 400 g $ha^{-1}$, sprayer, spring barley BBCH15-22. Air temperature 16.5 °C, soil temperature (10 cm) 16 °C, wind 5 – 8 mph, RH 51 at time of application. Weather data location Crimplesham. Daily weather data (given for year 1994 only; data for 1995 and 1996 in other report but not available for now), rain 1.6 mm at DAA0 (possibly before spraying) and 7.4 mm at DAA5. Average temperature during experiment 12.5 °C, total rain 333.2 mm (May - December 1994, 44.4 mm per month). Sampling depth 0 - 50 cm. Biomass-C 138 - 189 mg $kg^{-1}$.

**Results**

Recovery DAA0 41%. Quinoxyfen was found in the first two layers, <0.01 in 20 – 30 cm layer at DAA120. First order fit (Berkeley Madonna): 497d (all data points), (report states 589 days from regression line after log transformation). Assuming a Q10 of 2.2, the first order fit for the corrected half-life is 186 days for the period DAA0 – DAA226. The 3-hydroxy-metabolite content was 0.01 mg $kg^{-1}$ at DAA361, detected at DAA498 and DAA553, 0.01 mg $kg^{-1}$ at DAA 729. Figure A8.8 gives the results for a DFOP fit and Table A8.5 gives statistical details.

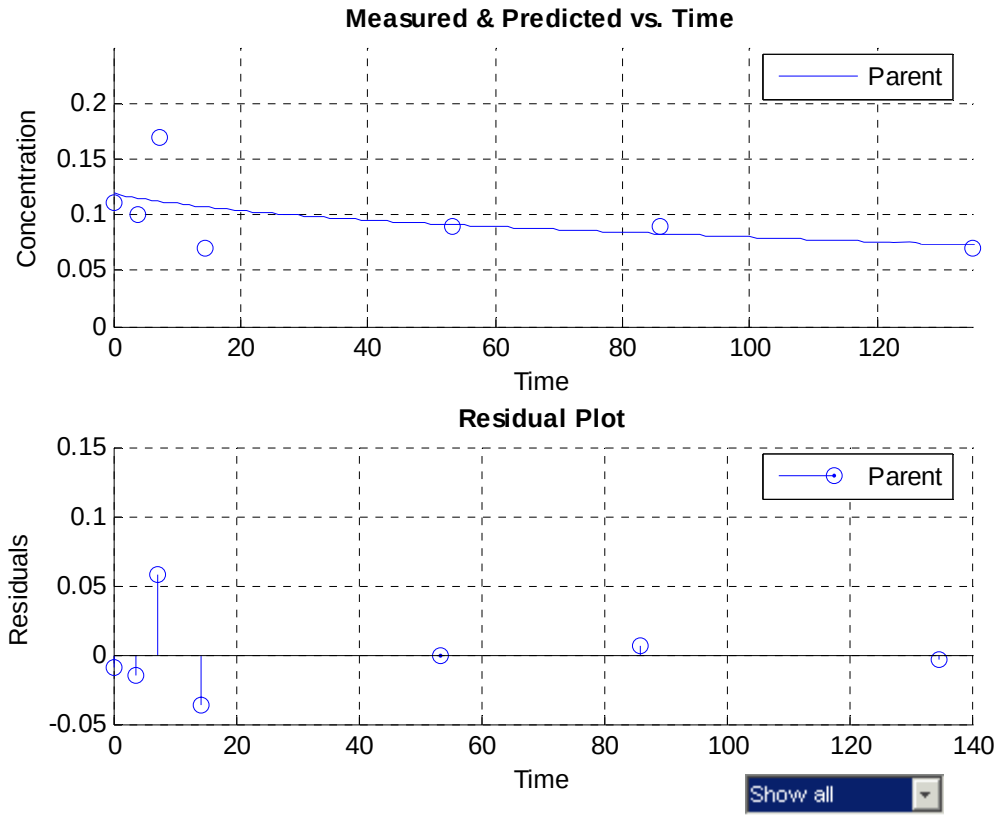



Figure A8.8 DFOP fit for Crimplesham soil, after time step normalization assuming a Q10 of 2.2

Table A8.5 Crimplesham fit statistics

| | initial value | estimated value | SD | prob > t |
|---|---|---|---|---|
| SFO | | | | |
| parent_k | 0.01 | 0.0037 | 0.0031 | 0.14 |
| parent_$M_0$ | 0.15 | 0.12 | 0.017 | |
| DFOP | | | | |
| parent_$k_1$ | 0 | 0.053 | 0.74 | 0.47 |
| parent_$k_2$ | 0 | 0.0026 | 0.013 | 0.43 |
| parent_g[#] | 0 | 0.87 | 1.18 | 0.26 |
| parent_$M_0$ | 100 | 0.12 | 0.036 | |

[#] The two compartments were switched by the KinGui software, so actually 1-g was given as the result. The statistics refer to 1-g.

**Conclusion**

The study result is not reliable, due to too low recovery and the incomplete weather data. Furthermore, the results of the DFOP fit are very uncertain and the $Chi^2$-error% indicates a bad fit.

**Reference**

Gambie A. The dissipation of quinoxyfen and its 3-hydroxy metabolite in soil at intervals following a single application of EF-1186, UK – 1994. Dow Agrosciences, report GHE-P-5440.

## A8.9 Nimes, France

**Description**

Location Nimes, France. Silty clay loam (37/46/17), pH 8, OC 2.1%, CEC 216 mmol $kg^{-1}$, spring barley, plot 46 * 3 $m^2$. Application 20 April 1994, 400 g $ha^{-1}$, backpack sprayer, winter wheat BBCH 15. Air temperature 12 °C, soil temperature (10 cm) 13 °C, wind 0 kph, RH 94 at time of application. Weather data location Nimes, Courbessac. Monthly data 04/1994 – 04/1996, presumably rain is given in 0.1 mm units (report states 1 mm units). Average temperature during experiment 15.5 °C, total rain 2020 mm (80.8 mm per month). Sampling depth 0 - 25 cm. Biomass-C 268 - 329 mg $kg^{-1}$.

**Results**

Recovery DAA0 83%. Quinoxyfen was found in the first layer, detected in the layer 10 – 20 cm except at DAA217. Contents in the 20 – 25 cm layer were < 0.01 – 0.02 mg $kg^{-1}$. First order fit (Berkeley Madonna): 84d (all data points), (report states 174 days from regression line after log transformation). Assuming a Q10 of 2.2, the first order fit for the corrected half-life is 119 days. The 3-hydroxy-metabolite was not detected. Figure A8.9 gives the results for a DFOP fit, while Table A8.6 gives statistical details.

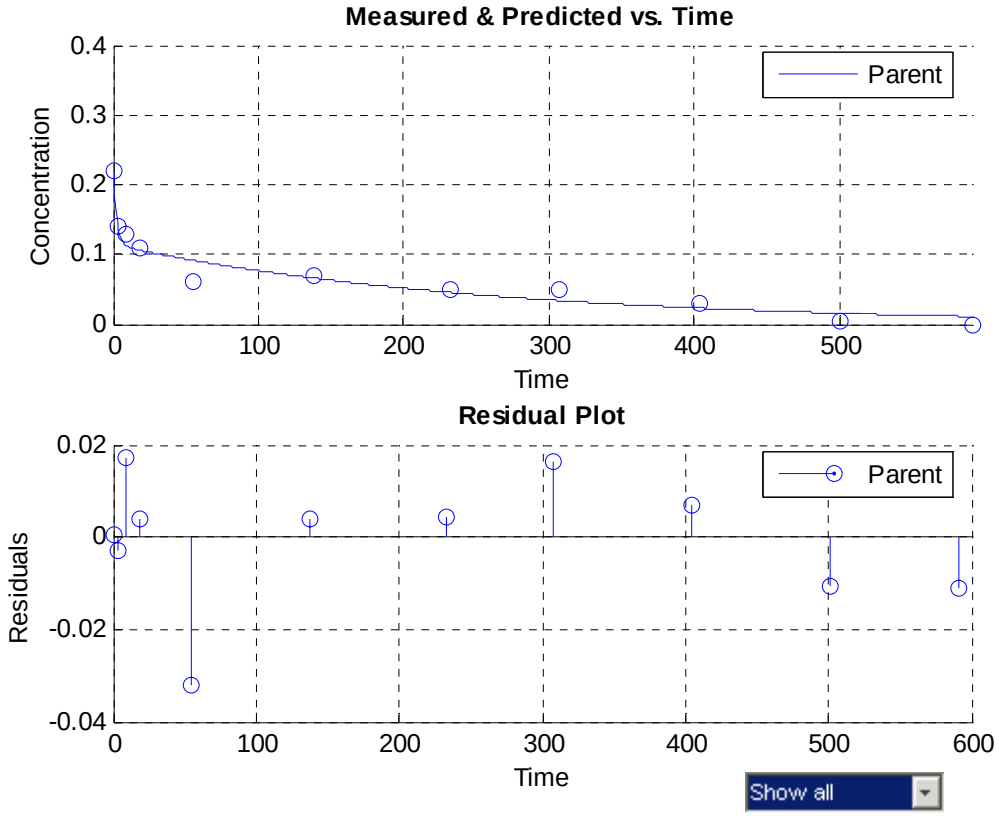



Figure A8.9 DFOP fit for Nimes soil, after time step normalization assuming a Q10 of 2.2

Table A8.6 Nimes fit statistics

| | initial value | estimated value | SD | prob > t |
|---|---|---|---|---|
| SFO | | | | |
| parent_k | 0.01 | 0.0058 | 0.0019 | 0.0077 |
| parent_$M_0$ | 0.2 | 0.15 | 0.017 | |
| DFOP | | | | |
| parent_$k_1$ | 0 | 0.38 | 0.20 | 0.051 |
| parent_$k_2$ | 0 | 0.0040 | 9.1E-4 | 0.0017 |
| parent_g[#] | 0 | 0.48 | 0.069 | 7.0E-5 |
| parent_$M_0$ | 100 | 0.22 | 0.017 | |

[#] The two compartments were switched by the KinGui software, so actually 1-g was given as the result. The statistics refer to 1-g.

**Conclusion**

Conclusion: study result is acceptable. Visually the DFOP fit is quite good and the $Chi^2$-error% is below the value of 15%.

**Reference**

Gambie A. The dissipation of quinoxyfen and its 3-hydroxy metabolite in soil at intervals following a single application of EF-1186, southern France – 1994. Dow Agrosciences, report GHE-P-5441.

## A8.10 Sillery, France

**Description**

Location Sillery, Champagne, France. Sandy silt loam (14/51/35), pH 7.8, OC 2.1%, CEC 126 mmol $kg^{-1}$, spring barley, plot 66 * 3 $m^2$. Application 25 April 1994, 400 g $ha^{-1}$, Cristal boom sprayer, spring barley BBCH15-16. Air temperature 13.3 °C, soil temperature (10 cm) 11.8 °C, wind 0 – 10 km $h^{-1}$, RH 58 at time of application. Weather data location Courcy, decade data 04/1994 – 04/1996, daily for first 8 days, rain 0.9 mm at day of application, 1.9 and 18 at day 1 and 2. Average temperature during experiment 10.8 °C, total rain 1216 mm (50.6 mm per month). Sampling depth 0 - 50 cm. Biomass-C 418 - 629 mg $kg^{-1}$.

**Results**

Recovery at DAA0 was 90%. Quinoxyfen was found in the 0 – 30 cm layer and detected in the 30 - 40 cm layer. First order fit (Berkeley Madonna): 137d (all data points), (report states 203 days from regression line after log transformation). Assuming a Q10 of 2.2, the first order fit for the corrected half-life is 93 days. Figure A8.10 and Table A8.7 give the results for a DFOP fit.

The 3-hydroxy metabolite ND – 0.03 in 0 – 10 cm layer, ND at end, not detected in lower layers except <0.01 in layer 30 – 40 cm at DAA221.

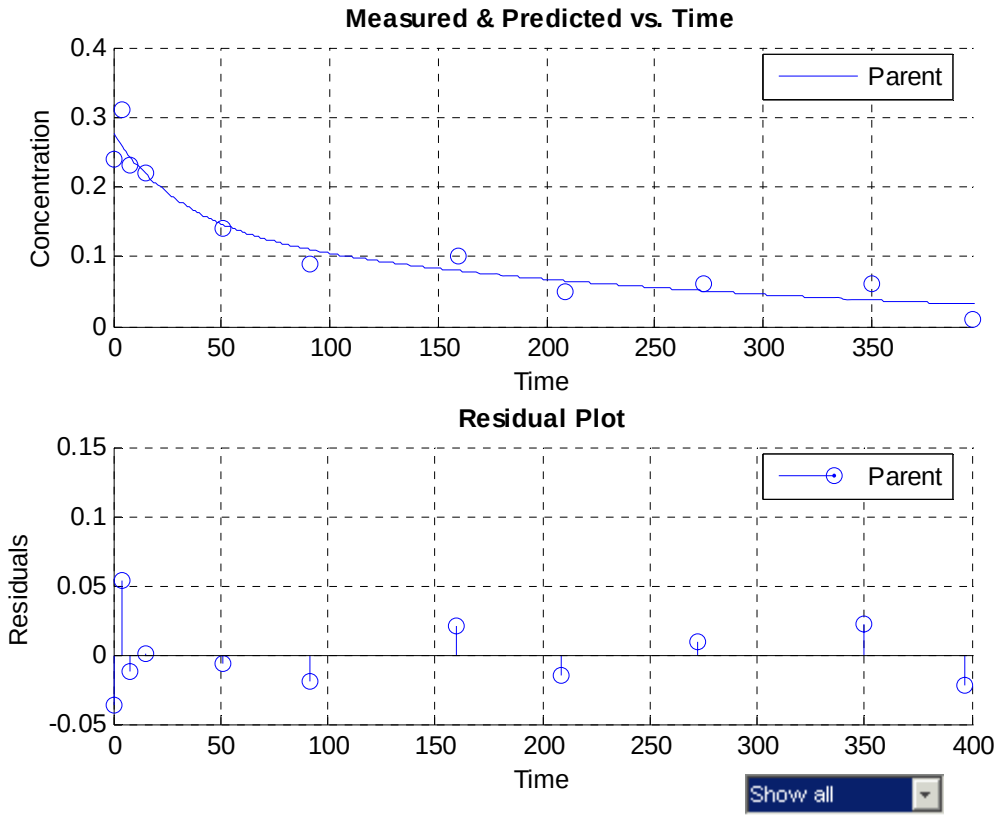



Figure A8.10 DFOP fit for Sillery soil, after time step normalization assuming a Q10 of 2.2

Table A8.7 Sillery fit statistics

| | initial value | estimated value | SD | prob > t |
|---|---|---|---|---|
| SFO | | | | |
| parent_k | 0.01 | 0.0074 | 0.0015 | 3.4E-4 |
| parent_$M_0$ | 0.3 | 0.25 | 0.018 | |
| DFOP | | | | |
| parent_$k_1$ | 0 | 0.0316 | 0.037 | 0.21 |
| parent_$k_2$ | 0 | 0.0039 | 0.0029 | 0.11 |
| parent_g[#] | 0 | 0.47 | 0.34 | 0.08 |
| parent_$M_0$ | 100 | 0.276 | 0.024 | |

[#] The two compartments were switched by the KinGui software, so actually 1-g was given as the result. The statistics refer to 1-g.

**Conclusion**

The study result is acceptable. Visually the DFOP fit is OK and the $Chi^2$-error% is just slightly above the value of 15%.

**Reference**

Gambie A. The dissipation of quinoxyfen and its 3-hydroxy metabolite in soil at intervals following a single application of EF-1186, northern France – 1994. Dow Agrosciences, report GHE-P-5442.

## A8.11 Conclusion from all studies

Table A8.8 gives an overview of the first order and DFOP process parameters for the field dissipation studies. From four field experiments reliable to less reliable $DegT_{50}$ data could be derived (in italics in Table A8.8). Except for one study, first order kinetic fits to the data were not accurate according to the guidelines given by FOCUS (2006). Biphasic behaviour according to DFOP fitted the data much better. The dissipation coefficient of the fast phase is assumed to represent relatively fast processes occurring at or in the surface layer of the soil, including photodegradation and volatilization. The dissipation coefficient of the slow phase is assumed to best represent the degradation in the soil. The geometric mean of the acceptable studies is 232 days and the average of substance in the slow phase is 45%. These values are to be used in the risk assessment.

Table A8.8 Summary of the results of the quinoxyfen field studies

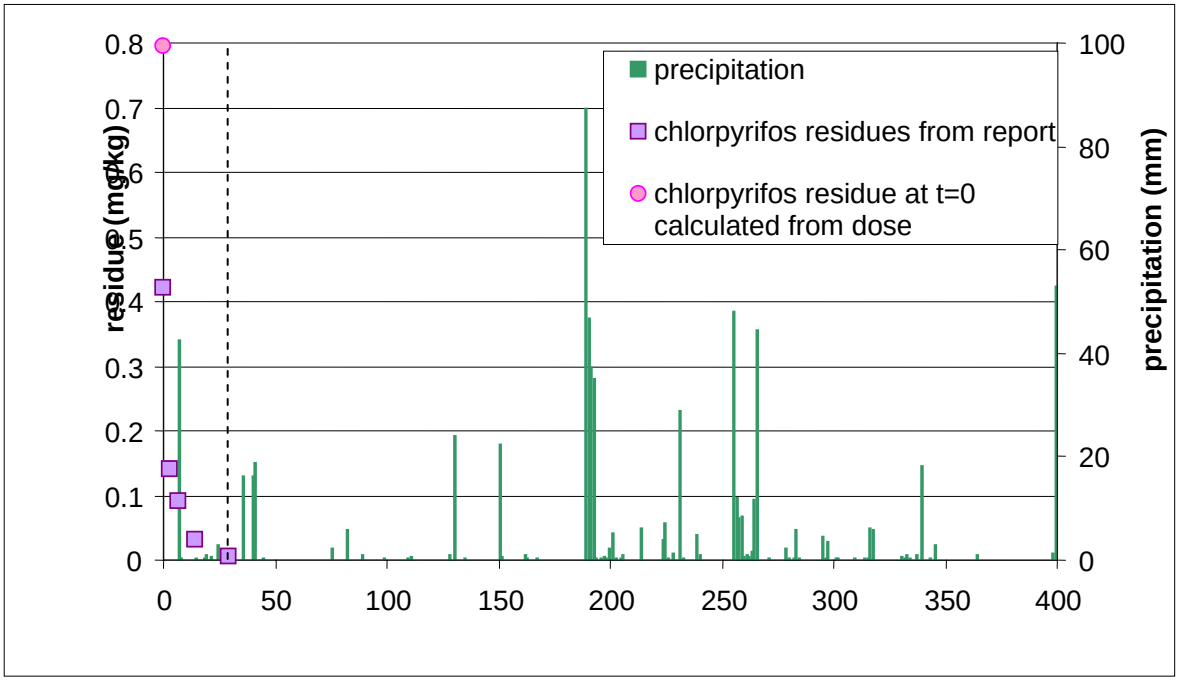
| **study** | **kinetics** | **$DegT_{50,I}$** (d) | **$DegT_{50,II}$** (d) | **g** | **$Chi^2$** | **t-test < 0.05 (for each fitted parameter)** |
|---|---|---|---|---|---|---|
| Ismaning | SFO | 99.2 | | | 23.5 | Y |
| | DFOP | 27.1 | 2.3E9 | 0.71 | 18.8 | N |
| *St-Nicolas*[#] | SFO | 135.3 | | | 10.4 | Y |
| | DFOP | 61.3 | 177.7 | 0.71 | 11.0 | N |
| Warlus | SFO | 10.1 | | | 32.3 | Y |
| | DFOP | 6.1 | 385.1 | 0.8 | 19.4 | N |
| *Laubach*[#] | SFO | 164.3 | | | 17.7 | Y |
| | DFOP | 35.2 | 533.2 | 0.53 | 17.0 | N |
| Crimplesham | SFO | 185 | | | 21.6 | N |
| | DFOP | 13.1 | 266.6 | 0.13 | 25.5 | N |
| *Nimes*[#] | SFO | 120.1 | | | 29.6 | Y |
| | DFOP | 1.8 | 173.3 | 0.48 | 14.9 | Y |
| *Sillery*[#] | SFO | 93 | | | 17.8 | Y |
| | DFOP | 21.9 | 177.7 | 0.47 | 15.5 | N |
| | | | | | | |
| *average*[$] | | | 232 | 0.55 | | |

[#] results of locations in italics were considered acceptable for further use in the evaluation

[$] geometric and arithmetic mean of acceptable results, respectively

# Appendix 9 Details of TCP exposure evaluations

## A9.1 Assessment of field dissipation studies of TCP



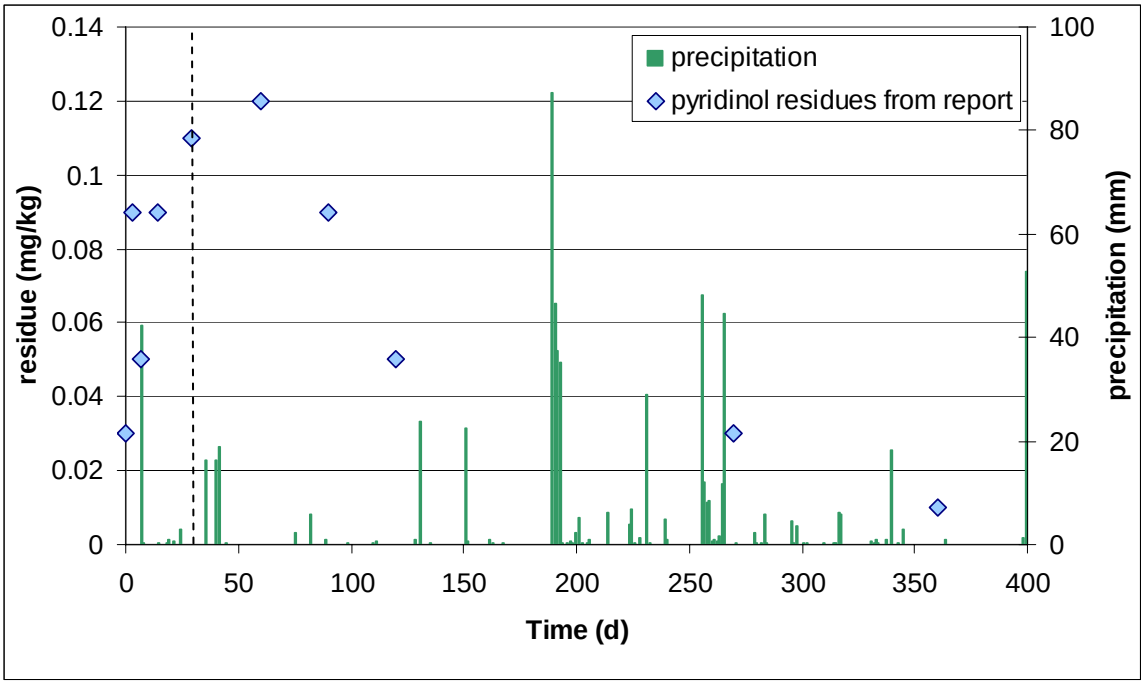




Figure A9.1 Residues of parent chlorpyrifos and metabolite pyridinol/TCP at location Tarragona

Table A9.1 Measured residues of chlorpyrifos and metabolite TCP

| days after application (d) | soil horizon 0 -10 cm | |
|---|---|---|
| | metabolite pyridinol residues (mg $kg^{-1}$) | parent chlorpyrifos residues (mg $kg^{-1}$) |
| | | 0.7936* |
| 0 | 0.03 | 0.42 |
| 3 | 0.09 | 0.14 |
| 7 | 0.05 | 0.09 |
| 14 | 0.09 | 0.03 |
| 29 | 0.11 | 0.005 |
| 60 | 0.12 | <0.01 |
| 90 | 0.09 | ND |
| 120 | 0.05 | ND |
| 270 | 0.03 | ND |
| 360 | 0.01 | ND |

* residue at t = 0 calculated from dose; $\rho_b$ = 1250 kg $m^{-3}$

FOCUS (2006) recommends to consider all measured values, that is measurements of both parent and metabolite, when deriving transformation rate constants. However, the chlorpyrifos measurements of this study were considered not suitable for deriving transformation rate constants, because other dissipation processes might be involved shortly after application. Using the chlorpyrifos measurements, in this case, could possibly lead to an incorrect formation fraction of the metabolite TCP and an incorrect value of the transformation rate. Therefore, only the data for the metabolite were taken into account. Doing this, the transformation rate constant might be slightly underestimated and therefore the $DegT_{50,field}$ slightly overestimated.

At 29 days after application the parent (chlorpyrifos) is almost gone. This point can be considered as the start of the decline pattern of the metabolite TCP. So t = 29 days will be t = 0 days in the kinetic evaluation of the metabolite. The time-step normalization method is used to normalize the measurements to 20 °C. The result; a new pattern of decline in residues is shown in Figure A9.2 (triangles).

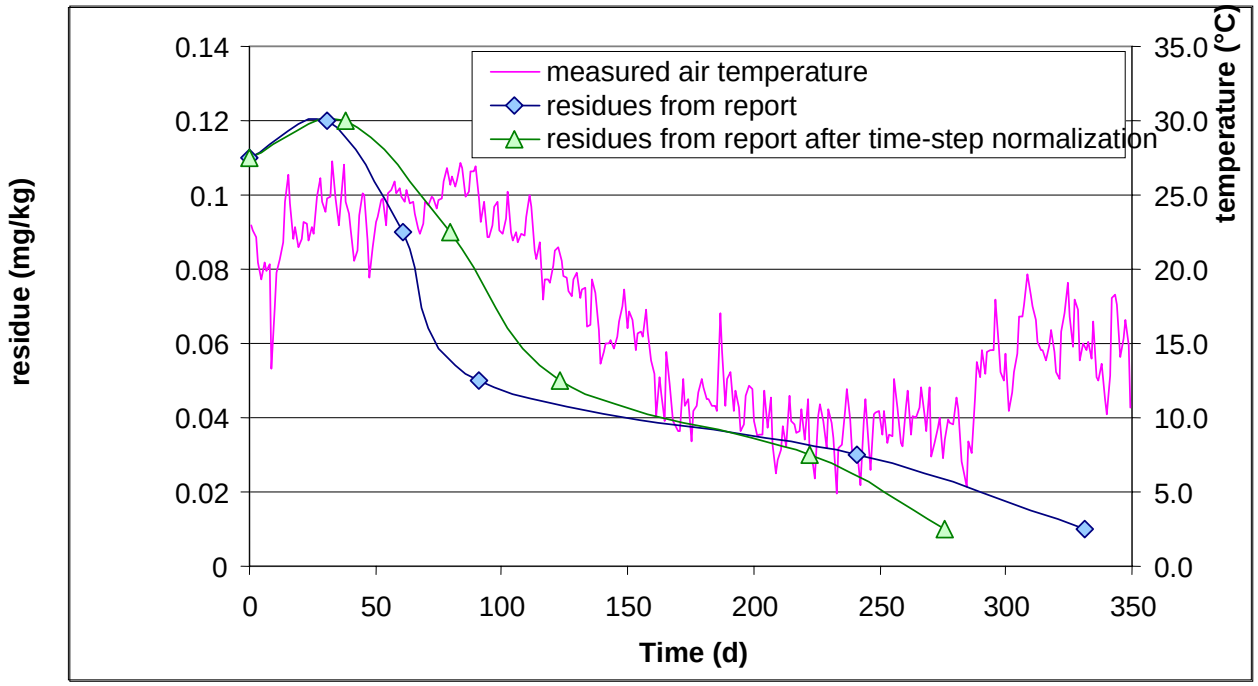



Figure A9.2 Measured residues of metabolite TCP versus time (diamonds) and normalized time (triangles) and measured soil temperature at location Tarragona

The decline pattern of the measured residues of metabolite TCP versus normalized time step is used for the kinetic evaluation. Single First Order (SFO) kinetics was used to model the decline pattern of the residues (see also Table A9.2). The initial amount of the chemical and the rate constant were fitted with the Solver option in Microsoft Excel ®. Results of the spreadsheet provided by the FOCUS workgroup on degradation and kinetics are shown in Figure A9.3.

A $DegT_{50,field}$ value of 111 days was fitted for the metabolite TCP for the field dissipation study at Tarragona.

Table A9.2 Results and statistics of the SFO fit for TCP at Tarragona

| | initial value | estimated value | SD | $Chi^2$ | t-test <0.05 | prob > t |
|---|---|---|---|---|---|---|
| parent_k | 0.01 | 0.0062 | 0.0015 | 15.6 | Y | 0.0071 |
| parent_$M_0$ | 0.12 | 0.13 | 0.014 | | Y | |

**FOCUS_DEGKIN v1**

**Parameter optimisation for SFO kinetics with Excel Solver Add-In**
**Visual assessment and chi2-test**
**For datasets without replicates, optimisation of two parameters (M0 and k)**
1. Enter measured data
2. Enter starting values in cell F19 and F20
3. Optimise parameters (Tools Solver, minimise target cell E23 by changing cells F19 and F20)
**Change number of parameters if M0 is fixed in optimisation!**

User input, all other cells calculated or automated
Optimise using Solver

**Name of dataset:** tcp - Tarragona

| No | Time | Observed | Calculated |
|---|---|---|---|
| 1 | 0.00 | 0.11 | 0.13 |
| 2 | 38.05 | 0.12 | 0.10 |
| 3 | 79.33 | 0.09 | 0.08 |
| 4 | 123.46 | 0.05 | 0.06 |
| 5 | 222.25 | 0.03 | 0.03 |
| 6 | 275.84 | 0.01 | 0.02 |
| 7 | | | |
| 8 | | | |
| 9 | | | |
| 10 | | | |
| 11 | | | |
| 12 | | | |
| 13 | | | |
| 14 | | | |
| 15 | | | |
| 16 | | | |
| 17 | | | |
| 18 | | | |
| 19 | | | |
| 20 | | | |
| 21 | | | |
| 22 | | | |
| 23 | | | |

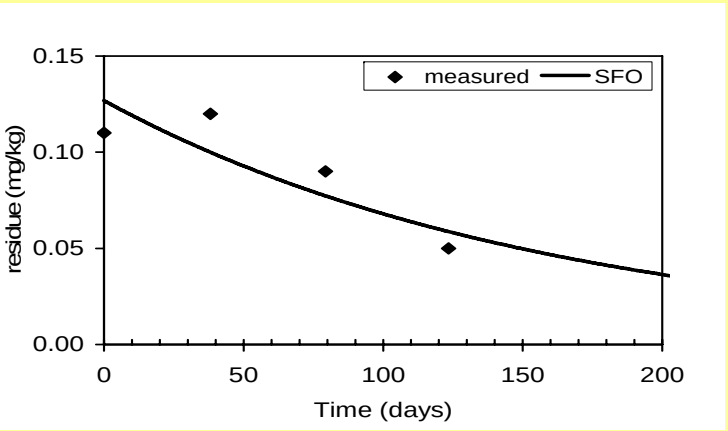
**SFO parameters and endpoints**

| | | | |
|---|---|---|---|
| **M0** | 0.13 | **DT50** | 111.1 |
| **k** | 0.00624 | **DT90** | 369.0 |

**0.001** **Residual Sum of Squares**

**Error level Chi2 test** 15.6

| | |
|---|---|
| 0.001 | **Residual Sum of Squares** |
| 6 | **Number of observations** |
| 2 | **Number of parameters** |
| 0.1 | **Average of observed** |
| 0.01 | **Scaled Error** |
| 9.488 | **Chi2 calculated** |
| 9.488 | **Chi2 Table** |



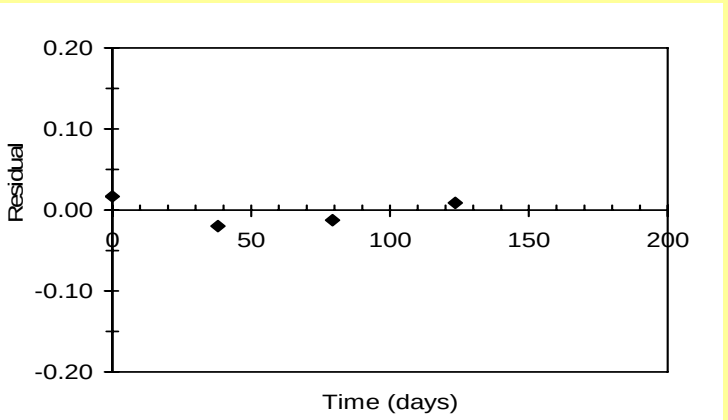




Figure A9.3 Results of the fitting of the initial amount of the chemical and the rate constant of SFO kinetics with the Solver option in Microsoft Excel ®

rivm

National Institute
for Public Health
and the Environment