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Environmental risk limits for kresoxim-methyl

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This investigation has been performed by order and for the account of Directorate-General for Environmental Protection, Directorate for Soil, Water and Rural Area (BWL), within the framework of the project 'Standard setting for other relevant substances within the WFD'.

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Rapport in het kort

Environmental risk limits for kresoxim-methyl

Dit rapport geeft milieurisicogrenzen voor het fungicide kresoxim-methyl in water. Milieurisicogrenzen zijn de technisch-wetenschappelijke advieswaarden voor de uiteindelijke milieukwaliteitsnormen in Nederland. De milieurisicogrenzen zijn afgeleid volgens de methodiek die is voorgeschreven in de Europese Kaderrichtlijn Water. Hierbij is gebruikgemaakt van de beoordeling in het kader van de Europese toelating van gewasbeschermingsmiddelen (Richtlijn 91/414/EEG), aangevuld met gegevens uit de openbare literatuur.

Contents

1 Introduction

1.1 Background and scope of the report

In this report, environmental risk limits (ERLs) for surface water are derived for the fungicide kresoxim-methyl. The derivation is performed within the framework of the project 'Standard setting for other relevant substances within the WFD', which is closely related to the project 'International and national environmental quality standards for substances in the Netherlands' (INS). Kresoxim-methyl is part of a series of 25 pesticides that appeared to have a high environmental impact in the evaluation of the policy document on sustainable crop protection ('Tussenevaluatie van de nota Duurzame Gewasbescherming'; MNP, 2006) and/or were selected by the Water Boards ('Unie van Waterschappen'; project 'Schone Bronnen'; http://www.schonebronnen.nl/).

The following ERLs are considered:

- Maximum Permissible Concentration (MPC) – the concentration protecting aquatic ecosystems and humans from effects due to long-term exposure
- Maximum Acceptable Concentration (MAC_{eco}) – the concentration protecting aquatic ecosystems from effects due to short-term exposure or concentration peaks.
- Serious Risk Concentration (SRC_{eco}) – the concentration at which possibly serious ecotoxicological effects are to be expected.

More specific, the following ERLs can be derived depending on the availability of data and characteristics of the compound:

$MPC_{eco, water}$	MPC for freshwater based on ecotoxicological data (direct exposure)
$MPC_{sp, water}$	MPC for freshwater based on secondary poisoning
$MPC_{hh\ food, water}$	MPC for fresh and marine water based on human consumption of fishery products
$MPC_{dw, water}$	MPC for surface waters intended for the abstraction of drinking water
$MAC_{eco, water}$	MAC for freshwater based on ecotoxicological data (direct exposure)
$SRC_{eco, water}$	SRC for freshwater based on ecotoxicological data (direct exposure)
$MPC_{eco, marine}$	MPC for marine water based on ecotoxicological data (direct exposure)
$MPC_{sp, marine}$	MPC for marine water based on secondary poisoning
$MAC_{eco, marine}$	MAC for marine water based on ecotoxicological data (direct exposure)

1.2 Status of the results

The results presented in this report have been discussed by the members of the scientific advisory group for the INS-project (WK-INS). It should be noted that the Environmental Risk Limits (ERLs) in this report are scientifically derived values, based on (eco)toxicological, fate and physico-chemical data. They serve as advisory values for the Dutch Steering Committee for Substances, which is appointed to set the Environmental Quality Standards (EQSs). ERLs should thus be considered as proposed values that do not have any official status.

2 Methods

The methodology for the derivation of ERLs is described in detail by Van Vlaardingen and Verbruggen (2007), further referred to as the 'INS-Guidance'. This guidance is in accordance with the guidance of the Fraunhofer Institute (FHI; Lepper, 2005).

The process of ERL-derivation contains the following steps: data collection, data evaluation and selection, and derivation of the ERLs on the basis of the selected data.

2.1 Data collection

In accordance with the WFD, data of existing evaluations were used as a starting point. For kresoxim-methyl, the evaluation report prepared within the framework of EU Directive 91/414/EC (Draft Assessment Report, DAR) was consulted (EC, 1997; further referred to as DAR) as well as the review report of 1998 (EC, 1998). An on-line literature search was performed on TOXLINE (literature from 1985 to 2001) and Current Contents (literature from 1997 to 2007). In addition to this, all potentially relevant references in the RIVM e-tox base and EPA's ECOTOX database were checked.

2.2 Data evaluation and selection

For substance identification, physico-chemical properties and environmental behaviour, information from the List of Endpoints of the DAR was used. When needed, additional information was included according to the methods as described in Section 2.1 of the INS-Guidance. Information on human toxicological threshold limits and classification was also primarily taken from the DAR.

Ecotoxicity studies (including bird and mammal studies) were screened for relevant endpoints (i.e. those endpoints that have consequences at the population level of the test species). All ecotoxicity and bioaccumulation tests were then thoroughly evaluated with respect to the validity (scientific reliability) of the study. A detailed description of the evaluation procedure is given in the INS-Guidance (see Section 2.2.2 and 2.3.2). In short, the following reliability indices were assigned:

- Ri 1: Reliable without restriction
  'Studies or data … generated according to generally valid and/or internationally accepted testing guidelines (preferably performed according to GLP) or in which the test parameters documented are based on a specific (national) testing guideline … or in which all parameters described are closely related/comparable to a guideline method.'
- Ri 2: Reliable with restrictions
  'Studies or data … (mostly not performed according to GLP), in which the test parameters documented do not totally comply with the specific testing guideline, but are sufficient to accept the data or in which investigations are described which cannot be subsumed under a testing guideline, but which are nevertheless well documented and scientifically acceptable.'
- Ri 3: Not reliable
  'Studies or data … in which there are interferences between the measuring system and the test substance or in which organisms/test systems were used which are not relevant in relation to the exposure (e.g., unphysiologic pathways of application) or which were carried out or generated according to a method which is not acceptable, the documentation of which is not sufficient for an assessment and which is not convincing for an expert judgment.'

- Ri 4: Not assignable
  'Studies or data … which do not give sufficient experimental details and which are only listed in short abstracts or secondary literature (books, reviews, etc.).'

All available studies were summarised in data-tables, that are included as Appendices to this report. These tables contain information on species characteristics, test conditions and endpoints. Explanatory notes are included with respect to the assignment of the reliability indices.

With respect to the DAR, it was chosen not to re-evaluate the underlying studies. In principle, the endpoints that were accepted in the DAR were also accepted for ERL-derivation with Ri 2, except in cases where the reported information was too poor to decide on the reliability or when there was reasonable doubt on the validity of the tests. This applies especially to DARs prepared in the early 1990s, which do not always meet the current standards of evaluation and reporting.

In some cases, the characteristics of a compound (i.e. fast hydrolysis, strong sorption, low water solubility) put special demands on the way toxicity tests are performed. This implies that in some cases endpoints were not considered reliable, although the test was performed and documented according to accepted guidelines. If specific choices were made for assigning reliability indices, these are outlined in Section 3.3 of this report.

Endpoints with Ri 1 or 2 are accepted as valid, but this does not automatically mean that the endpoint is selected for the derivation of ERLs. The validity scores are assigned on the basis of scientific reliability, but valid endpoints may not be relevant for the purpose of ERL-derivation (e.g. due to inappropriate exposure times or test conditions that are not relevant for the Dutch situation).

After data collection and validation, toxicity data were combined into an aggregated data table with one effect value per species according to Section 2.2.6 of the INS-Guidance. When for a species several effect data were available, the geometric mean of multiple values for the same endpoint was calculated where possible. Subsequently, when several endpoints were available for one species, the lowest of these endpoints (per species) is reported in the aggregated data table.

2.3 Derivation of ERLs

For a detailed description of the procedure for derivation of the ERLs, reference is made to the INS-Guidance. With respect to the selection of the final MPC_{water} and the derivation of the $MAC_{eco,\ marine}$ some additional comments should be made:

2.3.1 Drinking water

The INS-Guidance includes the MPC for surface waters intended for the abstraction of drinking water ($MPC_{dw,\ water}$) as one of the MPCs from which the lowest value should be selected as the general MPC_{water} (see INS-Guidance, Section 3.1.6 and 3.1.7). According to the proposal for the daughter directive Priority Substances, however, the derivation of the AA-EQS (= MPC) should be based on direct exposure, secondary poisoning, and human exposure due to the consumption of fish. Drinking water was not included in the proposal and is thus not guiding for the general MPC value. The exact way of implementation of the $MPC_{dw,\ water}$ in the Netherlands is at present under discussion within the framework of the "AMvB Kwaliteitseisen en Monitoring Water". No policy decision has been taken yet, and the $MPC_{dw,\ water}$ is therefore presented as a separate value in this report. The MPC_{water} is thus derived considering the individual MPCs based on direct exposure ($MPC_{eco,\ water}$), secondary poisoning ($MPC_{sp,\ water}$) or human consumption of fishery products ($MPC_{hh\ food,\ water}$); the need for derivation of the latter two is dependent on the characteristics of the compound.

Related to this is the inclusion of water treatment for the derivation of the $MPC_{dw, water}$. According to the INS-Guidance (see Section 3.1.7), a substance specific removal efficiency related to simple water treatment should be derived in case the $MPC_{dw, water}$ is lower than the other MPCs. For pesticides, there is no agreement as yet on how the removal fraction should be calculated, and water treatment is therefore not taken into account. In case no A1 value is set in Directive 75/440/EEC, the $MPC_{dw, water}$ is set to the general Drinking Water Standard of 0.1 µg/L for organic pesticides as specified in Directive 98/83/EC.

3 Derivation of environmental risk limits for kresoxim-methyl

3.1 Substance identification, physico-chemical properties, fate and human toxicology

3.1.1 Identity

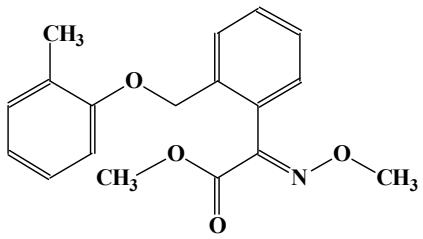

Figure 1. Structural formula of kresoxim-methyl.

Table 1. Identification of kresoxim-methyl.

Parameter	Name or number	Source
Common/trivial/other name	Kresoxim-methyl	EC, 1998
Chemical name	Methyl (E)-2-methoxyimino-2-[2-(o-tolyloxymethyl) phenyl]acetate	EC, 1998
CAS number	143390-89-0	EC, 1998
EC number	-	
SMILES code	Cc1ccccc1OCc2ccccc2C(=NOC)C(=O)OC	U.S. EPA, 2007
Use class	Fungicide	
Mode of action	Inhibition of mitochondrial respiration	Tomlin, 2002
Authorised in NL	Yes	
Annex 1 listing	Yes	

3.1.2 Physico-chemical properties

Table 2. Physico-chemical properties of kresoxim-methyl.

Parameter	Unit	Value	Remark	Reference
Molecular mass	[g/mol]	313.3		EC, 1998
Water solubility	[g/L]	0.002	20 ºC	EC, 1998
pK_a	[-]	-		EC, 1998
log K_{OW}	[-]	3.4	25 ºC	EC, 1998
log K_{OC}	[-]	2.48		EC, 1998
Vapour pressure	[Pa]	2.3×10^{-6}	20 ºC	EC, 1998
Melting point	[°C]	102		EC, 1998
Boiling point	[°C]	n.a.		EC, 1998
Henry's law constant	[Pa.m^3/mol]	3.6×10^{-7}	20 ºC	EC, 1998

n.a. = not applicable.

3.1.3 Behaviour in the environment

Table 3. Selected environmental properties of kresoxim-methyl.

Parameter	Unit	Value	Remark	Reference
Hydrolysis half-life	DT50 [d]	34 d	pH 7	EC, 1998
		875 d	pH 5	
		7 h	pH 9	
Photolysis half-life	DT50 [d]	30 d		EC, 1998
Readily biodegradable		No		EC, 1998
Degradation in water/sediment systems	DT50 (system) [d]	1.3 d		EC, 1998
Relevant metabolites		Kresoxim (acid)	Max. 63-68% in water phase after 7 d	EC, 1998

3.1.4 Bioconcentration and biomagnification

An overview of the bioaccumulation data for kresoxim-methyl is given in Table 4. Detailed bioaccumulation data for kresoxim-methyl are tabulated in Appendix 1.

Table 4. Overview of bioaccumulation data for kresoxim-methyl.

Parameter	Unit	Value	Remark	Reference
BCF (fish)	[L/kg]	220		EC, 1998
BMF	[kg/kg]	1	Default value for BCF < 2000	Van Vlaardingen en Verbruggen (2007)

3.1.5 Human toxicological threshold limits and carcinogenicity

The ADI is 0.4 mg/kg bw. The AOEL(systemic) is 0.9 mg/kg bw/day. Kresoxim-methyl has an R40 (cat. 3) classification for carcinogenicity (ECB, 2008). Kresoxim-methyl is not a mutagen or a substance known or suspected to affect reproduction (EC, 1997).

3.2 Trigger values

This section reports on the trigger values for ERLwater derivation (as demanded in WFD framework).

Table 5. Kresoxim-methyl: collected properties for comparison to MPC triggers.

Parameter	Value	Unit	Method/Source	Derived at section
Log $K_{p,susp\text{-}water}$	1.48	[-]	$K_{OC} \times f_{OC,susp}$ [1]	K_{OC}: 3.1.2
BCF	220	[L/kg]		3.1.4
BMF	1	[kg/kg]		3.1.4
Log K_{OW}	3.4	[-]		3.1.2
R-phrases	R40	[-]		3.1.5
A1 value	1.0	[µg/L]	Total pesticides	
DW Standard	0.1	[µg/L]	General value for organic pesticides	

[1] $f_{OC,susp}$ = 0.1 kg_{OC}/kg_{solid} (EC, 2003).

- Kresoxim-methyl has a log $K_{p,\ susp\text{-}water} < 3$; derivation of $MPC_{sediment}$ is not triggered.
- Kresoxim-methyl has a log $K_{p,\ susp\text{-}water} < 3$; expression of the MPC_{water} as $MPC_{susp,\ water}$ is not required.
- Kresoxim-methyl has a BCF ≥ 100 L/kg; assessment of secondary poisoning is triggered.
- Kresoxim-methyl has an R40 classification. Therefore, the derivation of an MPC_{water} for human health via food (fish) consumption ($MPC_{hh\ food,\ water}$) is required.
- For kresoxim-methyl, no specific A1 value or Drinking Water Standard is available from Council Directives 75/440, EEC and 98/83/EC, respectively. Therefore, the general Drinking Water Standard for organic pesticides applies.

3.3 Toxicity data and derivation of ERLs for water

3.3.1 $MPC_{eco,\ water}$ and $MPC_{eco,\ marine}$

An overview of the selected freshwater toxicity data for kresoxim-methyl is given in Table 6. No data are available on the toxicity of kresoxim-methyl for saltwater organisms. Detailed toxicity data for kresoxim-methyl are tabulated in Appendix 2.
The metabolite kresoxim (free acid) is not toxic for the organisms dealt with (EC_{50} values > 100 mg/L; NOECs > 1 mg/L).

Table 6. Kresoxim-methyl: selected freshwater toxicity data for ERL derivation.

Chronic[a]		Acute[a]	
Taxonomic group	**NOEC/EC10 (µg/L)**	**Taxonomic group**	**L(E)C50 (µg/L)**
Algae	15	Algae	63
Algae	**7**	Algae	490
Crustacea	32 [b]	Crustacea	**293** [d]
Pisces	32 [c]	Pisces	808 [e]
		Pisces	3200
		Pisces	830

[a] For detailed information see Appendix 2. Bold values are used for ERL derivation.
[b] Geometric mean of 0.031 and 0.032 mg/L for *Daphnia magna* (reproduction).
[c] Geometric mean of 0.05 and 0.02 mg/L for *Oncorhynchus mykiss* (mortality).
[d] Geometric mean of 0.09, 0.186 and 1.51 mg/L for *D. magna* (immobilisation).
[e] Geometric mean of 0.86, 1.48 and 0.414 mg/L for *Cyprinus carpio* (mortality).

3.3.1.1 Treatment of fresh- and saltwater toxicity data

ERLs for freshwater and marine waters should be derived separately. For pesticides, data can only be combined if it is possible to determine with high probability that marine organisms are not more sensitive than freshwater organisms (Lepper, 2005). For kresoxim-methyl, no marine toxicity data are available and ERLs for the marine compartment cannot be derived.

3.3.1.2 Mesocosm and field studies

In the DAR (EC, 1997) a summary is given of an outdoor mesocosm study carried out in Germany in 1994. Six applications of kresoxim-methyl (applied as a WG formulation) were performed over a period of 12 weeks. In view of this application pattern, the measured concentration of 1.9 µg/L can be considered to be the lowest concentration to which the system has been exposed for a longer period and becomes the $NOEC_{mesocosm}$.

3.3.1.3 Derivation of $MPC_{eco, water}$ and $MPC_{eco, marine}$

The base-set for freshwater toxicity data is complete. Chronic NOECs for three trophic levels are available for algae, Crustacea and fish. The lowest NOEC is 0.007 mg/L for the alga *Ankistrodesmus bibraianus*. An assessment factor of 10 can be used on the lowest NOEC (0.007 mg/L), and the initial $MPC_{eco, water}$ based on laboratory data is 0.007 / 10 = 0.0007 mg/L (0.7 µg/L).

From the mesocosmstudy, a NOEC of 1.9 µg/L is derived. From a comparison of mesocosm studies with the insecticides chlorpyrifos and lambda-cyhalothrin, it can be concluded that an assessment factor of 3 may be necessary to cover variation at the level of the NOEAEC[1] in case one reliable study is available (De Jong et al., 2008, based on Brock et al., 2006). Lepper (2005) argues that the scope of protection of an environmental quality standard under the WFD is broader than that of the "acceptable concentration" under Directive 91/414. It should be considered that the quality standard must be protective for all types of surface waters and communities that are addressed by the respective standard. Mesocosm studies performed in the context of 91/414 are normally focused on agricultural ditches that can be characterised as eutrophic shallow water bodies. Environmental quality standards under the WFD, however, must assure protection also for water bodies that significantly differ from this paradigm (Lepper, 2005). It is therefore in principle proposed to use an assessment factor of 3 on the NOEC instead of on the NOEAEC. Therefore, the $MPC_{mesocosm}$ becomes 0.63 µg/L.

[1] NOEAEC = No Observed Ecologically Adverse Effect Concentration. Concentration at which effects observed in a study are considered acceptable from a regulatory point of view.

The $MPC_{mesocosm}$ is in good agreement with the MPC based on laboratory data. The lower of the two is chosen as the final $MPC_{eco, water}$, which is therefore set to 0.63 µg/L.

For the marine environment no data are available; therefore an $MPC_{eco, marine}$ is not derived.

3.3.2 $MPC_{sp, water}$ and $MPC_{sp, marine}$

Kresoxim-methyl has a BCF ≥ 100 L/kg, thus assessment of secondary poisoning is triggered. The lowest MPC_{oral} is 16.7 mg/kg diet for the bobwhite quail (see Table 7).

Table 7. Kresoxim-methyl: selected birds and mammal data for ERL derivation

Species[a]	Exposure time	Criterion	Effect concentration (mg/kg diet)	Assessment factor	MPC_{oral} (mg/kg diet)
Bobwhite quail	26 w	NOEC	500	30	**16.7**
Rat	28 d	NOAEC	4000	300	13.3 [b]
Rat	90 d	NOAEC	2000 [b]	90	22.2 [b]
Mouse	90 d	NOAEC	4000	90	44.4
Dog	90 d	NOAEC	5000	90	55.5
Dog	1 y	NOAEC	5000	30	167

[a] For detailed information see Appendix 4. Bold values are used for ERL derivation.
[b] The most sensitive endpoint is the 90 days study; therefore, an overall value for rats of 22.2 mg/kg diet is selected (see INS Guidance).

The $MPC_{sp, water}$ is calculated using the BCF of 220 L/kg and a BMF of 1 (Table 5) and becomes 16.7 / (220 × 1) = 0.076 mg/L (76 µg/L).
Because toxicity data for marine predators are generally not available, the MPCoral, min as derived above is used as a representative for the marine environment also. To account for the longer food chains in the marine environment, an additional biomagnification step is introduced (BMF_2). This factor is the same as given in Table 4. The $MPC_{sp, marine}$ is 16.7 / (220× 1 × 1) = 0.076 mg/L (76 µg/L).

3.3.3 $MPC_{hh\ food, water}$

Derivation of $MPC_{hh\ food, water}$ for kresoxim-methyl is triggered (Table 5). $MPC_{hh,\ food}$ is calculated form the ADI (0.4 mg/kg bw), a body weight of 70 kg and a daily fish consumption of 115 g as $MPC_{hh, food}$ = 0.4 x 0.1 x 70/0.115 = 24.3 mg/kg (Van Vlaardingen en Verbruggen, 2007). Subsequently the $MPC_{water, hh\ food}$ is calculated according to $MPC_{hh\ food, water} = 24.3/(BCF_{fish} \times BMF_1) = 24.3/220 \times 1 = 0.11$ mg/L.

3.3.4 $MPC_{dw, water}$

The Drinking Water Standard is 0.1 µg/L. Thus, the $MPC_{dw, water}$ is 0.1 µg/L.

3.3.5 Selection of the MPC_{water} and MPC_{marine}

The lowest value of the routes included (see Chapter 2.3) is the $MPC_{mesocosm}$ of 0.63 µg/L. Therefore, the MPC_{water} is 0.63 µg/L.

3.3.6 MAC_{eco}

3.3.6.1 $MAC_{eco, water}$

The $MAC_{eco, water}$ may be derived in the first instance from the acute toxicity data. Six short-term values for three trophic levels (fish, *Daphnia*, and algae) are available and kresoxim-methyl has a potential to bioaccumulate (BCF ≥ 100 L/kg). Therefore, an assessment factor of 1000 is applied to the lowest

L(E)C_{50}, i.e. the EC_{50} for *Daphnia magna*: 0.293 mg/L. Therefore, the MAC_{eco} derived from toxicity data is 0.293 / 1000 = 0.000293 mg/L (0.293 µg/L). Since this value is below the MPC_{water} (0.63 µg/L), the $MAC_{eco, water}$ is set equal to the $MPC_{water.}$ Thus, the $MAC_{eco, water}$ is 0.63 µg/L.

3.3.6.2 $MAC_{eco, marine}$

No data are available on the toxicity of kresoxim-methyl for marine organisms. Therefore, no $MAC_{eco, marine}$ can be derived.

3.3.7 $SRC_{eco, water}$

Since three long-term NOECs of all required trophic levels are available, the $SRC_{eco, water}$ is derived from the geometric mean of all available NOECs with an assessment factor 1. The geometric mean is 0.0181 mg/L. Therefore, the $SRC_{eco, water}$ is derived as 0.0181/1 = 0.0181 mg/L (18.1 µg/L).

4 Conclusions

In this report, the risk limits Maximum Permissible Concentration (MPC), Maximum Acceptable Concentration for ecosystems (MAC_{eco}), and Serious Risk Concentration for ecosystems (SRC_{eco}) are derived for kresoxim-methyl in water. No risk limits were derived for the marine compartment because data were not available.

The ERLs that were obtained are summarised in the table below. The MPC value that was set for this compound until now, is also presented in this table for comparison reasons. It should be noted that this is an indicative MPC ('ad-hoc MTR'), derived using a different methodology and based on limited data.

Table 8. Derived MPC, MAC_{eco} and SRC values for kresoxim-methyl.

ERL	Unit	MPC	MAC_{eco}	SRC
Water, old[a]	µg/L	0.015	-	-
Water, new[b]	µg/L	0.63	0.63	18.1
Drinking water[b]	µg/L	0.1[c]	-	-
Marine	µg/L	n.d.[d]	n.d.[d]	-

[a] indicative MPC ('ad-hoc MTR'), source: Helpdesk Water http://www.helpdeskwater.nl/emissiebeheer/normen_voor_het/zoeksysteem_normen/

[b] The $MPC_{dw, water}$ is reported as a separate value from the other MPC_{water} values ($MPC_{eco, water}$, $MPC_{sp, water}$ or $MPC_{hh\ food, water}$). From these other MPC_{water} values (thus excluding the $MPC_{dw, water}$) the lowest one is selected as the 'overall' MPC_{water}.

[c] provisional value pending the decision on implementation of the $MPC_{dw, water}$, (see Section 2.3.1)

[d] n.d. = not derived due to lack of data

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Appendix 1. Information on bioconcentration

Species	Species properties	Test substance	Substance purity(%)	A	Test type	Test water	pH	Hardness/ Salinity [g/L]	Exp. time [d]	Temp. [°C]	Exp. concn.	BCF [$L/kg_{w.w.}$]	BCF type	Method	Ri	Notes	Reference
Oncorhynchus mykiss	5.1± 0.5 cm	[*phenyl-*^{14}*C*]-kresoxim-methyl	97	Y	F	dtw	7.6-7.8		28 d+ 14 d	14	25 µg/L	220	Whole fish	Equilibrium	2	1,2	DAR, Mayo, 1994

1 Loading <4 g fish/L

2 72% to 82% of radioactivity in the fillet was parent compound

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Appendix 2. Detailed aquatic toxicity data

Table A2.1. Acute toxicity of kresoxim-methyl to freshwater organisms.

Species	Species properties	A	Test type	Test compound	Purity [%]	Test water	pH	T [°C]	Hardness $CaCO_3$ [mg/L]	Exp. time	Criterion	Test endpoint	Value [mg/L]	Ri	Notes	Reference
Algae																
Ankistrodesmus bibraianus	$3x10^4$ cells/mL	Y	S	Kresoxim-methyl	94	am	8.0-8.9	22±1		72 h	EC50	growth inhibition	0.063	2		DAR, Dohmen, 1992a
Ankistrodesmus bibraianus	$3x10^4$ cells/mL	Y	S	Kresoxim-methyl	94	am	8.0-8.9	22±1		72 h	EC10	growth inhibition	0.007	2		DAR, Dohmen, 1992a
Pseudokirchneriella subcapitata		Y		BAS 490 04F	50	am	7.9			72 h	EC50	growth rate	0.49	1		Montforts and Linders, 1997
Pseudokirchneriella subcapitata		Y		BAS 490 04F	50	am	7.9			72 h	NOEC	biomass	0.015	1		Montforts and Linders, 1997
Crustacea																
Daphnia magna		Y	S?	BAS 490 04F	50		8.3			48 h	EC50	immobilisation	0.09	1	1	Montforts and Linders, 1997
Daphnia magna	2-24 h old	Y	S	Kresoxim-methyl	93.7	rw	7.5±0.5	20±0.5	270	48 h	EC50	immobilisation	0.186	2	1,7	DAR, Jatzek, 1993a
Daphnia magna similis	4 d old	N	S	Kresoxim-methyl	94		7.7	25±2		24 h	EC50	immobilisation	1.51	2	2	DAR, Nozaka, 1991b
Pisces																
Cyprinus carpio		Y	S	BAS 490 04F	50		8.4			96 h	LC50	mortality	0.86	2	3	Montforts and Linders, 1997
Cyprinus carpio	5-8 cm	Y	S	Kresoxim-methyl	94		8.1-8.6	23		96 h	LC50	mortality	1.48	2	3, 5	DAR, Munk,1993e
Cyprinus carpio	5-8 cm	N	R	Kresoxim-methyl	94		7.5	25±2	107	96 h	LC50	mortality	0.414	2	2	DAR, Nozaka, 1991a
Lepomis macrochirus	1,9 g; 5,49 cm	Y	S	Kresoxim-methyl	94		8.2-8.6	21±1		96 h	LC50	mortality	3.2	2	4	DAR, Munk, 1993d
Lepomis macrochirus	1,9 g; 5,49 cm	Y	S	Kresoxim-methyl	94		8.2-8.6	21±1		96 h	NOEC	mortality	2.15	2		DAR, Munk, 1993d
Oncorhynchus mykiss		Y	S	BAS 490 04F	50		7.5			96 h	LC50	mortality	0.24	1	6	Montforts and Linders, 1997
Oncorhynchus mykiss	4.2 g; 7cm	Y	S	Kresoxim-methyl	94		8.5-8.7	12±1	250	96 h	LC50	mortality	0.83	2	5	DAR, Munk, 1992a

1 According to OECD 202.
2 Nominal value can be accepted because kresoxim-methyl is sufficiently stable in water.
3 According to OECD 203.
4 According to EPA and OECD 203.
5 Geometric mean of highest concentration with 100% mortality and the nearest lower concentration with 0% mortality.
6 Not used for MPC derivation; value < 3 x value of a.s.
7. hardness recalculated from mmol/L

Table A2.2. Chronic toxicity of kresoxim-methyl to freshwater organisms.

Species	Species properties	A	Test type	Test compound	Purity [%]	Test water	pH	T [°C]	Hardness CaCO3 mg /l]	Exp. time	Criterion	Test endpoint	Value [mg/l]	Ri	Notes	Reference
Algae																
Pseudokirchneriella subcapitata		Y		BAS 490 04F	50		7.9			72 h	NOEC	biomass	0.015	1	1	Montforts and Linders, 1997
Ankistrodesmus bibraianus	3x 10^4 cells/mL	Y	S	Kresoxim-methyl	94	am	8.0-8.9	22±1		72 h	EC10	growth inhibition	0.007	2		DAR, Dohmen, 1992a
Crustacea																
Daphnia magna		Y		BAS 490 04F	50		7.9			21 d	NOEC	reproduction	0.031	1	2	Montforts and Linders, 1997
Daphnia magna	2-24 h old	Y	R	Kresoxim-methyl	93.7		7.1-7.9	20±1		21 d	NOEC	reproduction	0.032	2	2	DAR, Jatzek, 1993b
Pisces																
Oncorhynchus mykiss	1.96 g; 6.06 cm	Y	F	BAS 490 04F	50		8.1			28 d	NOEC	mortality	0.05	1	3	Montforts and Linders,1997
Oncorhynchus mykiss	1.5 g; 5.6cm	Y	F	Kresoxim-methyl	94.3		7.5-8.4	14±1	total 2.3 mmol/L	28 d	NOEC	mortality	0.02	2	3	DAR, Munk, 1994c

1 According to OECD 201. EC50 value recalculated using GENSTAT (original EC50 0.222 mg/L for biomass)
2 According to OECD 202.
3 According to OECD 204

Appendix 3. Description of mesocosm studies

Dohmen, G.P. (1995). Source of the summary: DAR (EC, 1997)

Species/Population/ Community	Phytoplankton, chlorophylls, macrophytes, zooplankton, sediment species and macroinvertebrates, emerging insects, fish
Test method	Outdoor microcosm study, outdoor tanks (diam. 2.84 m, 1.5 m high, 100 cm water)
Test substance	BAS 490 02 F (WG formulation, 500 g as/kg)
Analysis	Y
Exposure regime	6 applications with 2-week intervals
T [ºC]	Not reported *
pH	Not reported*
Exposure time	50 wk?
Criterion	NOEC
Test endpoint	*Cryptomonas erosa,* Cladocera, *Daphnia longispina*, *Eudiaptomus gracilis*
Value[µg/L]	1.9
GLP	Y
Validity	**2**

* In the DAR summary

Methods

Design and treatment

The study was conducted in 1994 in Limburgerhof, Germany, in 16 outdoor tanks (1.5 m deep, 2.84 m diameter) buried into the ground. Replicates: 3 tanks + 1 tank for fish *(Cyprinus carpio)* for each treatment and the control.

From the bottom to the edge the tanks contained 15 cm of sand, 5 cm of clay, 10 cm of natural sediment (lake Neuhofener Altrhein) and 100 cm of water. Each tank contained 6335 L of water. Six treatments were made with 2-week intervals (April – June 1994) by overspray. The nominal treatment rates were 4, 20 and 100 g a.s./ha = 1.33, 6.65 and 33.3 µg a.s./L. Biotic and abiotic parameters were monitored up till probably 50 weeks later (April 1995). The summary is not clear on the period observations were made.

Analysis

Samples from the water column and the sediment were analysed for kresoxim-methyl and kresoxim (free acid) during 50 weeks after the first application (no sufficient details given in the summary). O_2, pH, alkalinity, hardness, nutrients, conductivity and organic matter content were measured on a regular base (no details given in the summary).

Biological parameters

The following biological parameters were measured:

Phytoplankton

The abundance of 80 taxa and chlorophyll content were investigated (Cyanophyta, Euglenophyta, Cryptophyta, Dinophyta, Chlorophyta, Chrysophyta, total diversity (Simpson index), Periphyton on glass plates).

Macrophytes

Five aquatic plants were investigated.

Zooplankton

The abundance of 50 taxa was investigated (Cladocera, Copepoda, Rotatoria, Testacea, Heliozoa, Ostracoda, Acari).
Sediment species and macroinvertebrates
Tricladia, Gastropoda, Bivalva, Oligochaeta, Hirudinea, Crustacea (Asellus), Acari (Hydrachnellae), Ephemeroptera, Zygoptera, Heteroptera, Coleoptera, Trichoptera, Diptera were observed.
Emerging insects
25 taxa were identified.
Fish
Mortality and abnormal behaviour in *Cyprinus carpio* were monitored and fish length and weight were recorded. At the end the fish were dissected.

Data analysis
Not reported in the summary in the DAR.

Procedure for evaluation
Not reported in the summary in the DAR.

Results
Residue analysis
Microcosm sediment
Kresoxim-methyl and kresoxim (free acid) in the sediment were analysed at three dates 3 to 13 days after the applications.
Concentrations of a.s. and its metabolite kresoxim (free acid) were absent or sporadically found.
Microcosm water
A summary of the results is shown in Table 3-1.

Table 3-1 Concentrations of kresoxim-methyl and kresoxim (free acid) in microcosm water

Nominal concentration (µg a.s./L)	1.33	6.65	33.3
Theoretical cumulative level of a.s. after last application (µg/L)	7.98	39.9	200
Concentration of a.s. after last application (t = 12 wk) (µg/L)	1.3	1.9	4.3
Concentration of kresoxim (free acid) after last application (t = 12 wk) (µg/L)	4.1 (total 5.4 = 63%)	19.1 (total 21.0 = 53%)	108 (total 112 = 56%)
Concentration of a.s. at t = 24 wk (µg/L)	0.2	0.07	0.9
Concentration of kresoxim (free acid) at t = 24 wk (µg/L)	1.4	2.5	44
Concentration of a.s. at t = 50 wk (µg/L)	0	0	0
Concentration of kresoxim (free acid) at t = 50 wk (µg/L)	0.7	3.2	27.2

Functional parameters
O_2, pH, alkalinity, hardness, nutrients, conductivity and organic matter content
No treatment related effects were observed.

Structural parameters
Phytoplankton and chlorophylls

No treatment related effects were observed, except for Cryptophyta (*Chroomonas nordstedti*, *Cryptomonas erosa*): in the highest concentration higher densities of *C. erosa* compared to control were present. The NOEC was 1.9 µg a.s./L (measured concentration after last application).

Macrophytes

No treatment related effects were observed.

Zooplankton

Cladocera: the highest concentration caused some transient reduction in population levels. There were effects on *Daphnia longispina* at the highest dose (NOEC: 1.9 µg a.s./L (measured concentration after last application)).

Copepoda: the highest dose caused detrimental effects on *Eudiaptomus gracilis* (Calanoida).

For the other taxa no significant treatment related effects were observed.

Sediment species and macroinvertebrates

There was no negative impact on the benthic community.

Emerging insects

There was no negative impact on emerging insects.

Fish

No mortality in the two highest concentrations. Fish behaviour, length and weight were unaffected by the treatments.

Evaluation

Evaluation of the scientific reliability of the field study

Criteria for a suitable (semi)field study:

1. Does the test system represent a realistic freshwater community? Yes
2. Is the experimental set-up adequate and unambiguous? This cannot be judged, because no details of the sampling/monitoring program of phytoplankton, macrophytes, zooplankton and macroinvertebrates were given.
3. Is the exposure regime adequately described? Yes
4. Are the investigated endpoints sensitive and in accordance with the working mechanism of the compound? Yes, crustaceans and algae were included.
5. Is it possible to evaluate the observed effects statistically? This cannot be judged, because no details of the test were given.

Evaluation of the results of the study

A summary of endpoints as derived from this study is presented in the Table below. Kresoxim (acid) is known to have no toxicity to organisms which are sensitive for kresoxim-methyl.

Table 3-2 Summary of endpoints in the outdoor microcosm study with kresoxim-methyl: values based on measured concentrations after 6 applications.

Group	NOEC [µg a.s./L]
Phytoplankton	1.9
Macrophytes	≥ 4.3
Zooplankton	1.9
Sediment species and macroinvertebrates	≥ 4.3
Emerging insects	≥ 4.3
Fish	≥ 4.3

It can be concluded that the NOEC for kresoxim-methyl in this mesocosm study is 1.9 µg/L (measured concentration), based on effects on phytoplankton species and zooplankton species at 4.3 µg/L. Since the test compound has been applied 6 times over a period of 12 weeks, the measured concentration of

1.9 µg/L can be considered to be the lowest concentration to which the system has been exposed for a period of 12 weeks without effects; most concentrations during exposure would have been higher.

Appendix 4. Detailed bird and mammal toxicity data

Species	Species properties (age, sex)	Product Substance	Purity [%]	Application route	Exposure duration	Criterion	Test endpoint	Criterion Oral dosing [mg/kg$_{b.w.}$/d]	Criterion Diet [mg/kg$_{diet}$]	Ri	Notes	Reference
Colinus virginianus	13 d old	Kresoxim-methyl	93.7	Diet	5 d	LC50	Mortality		> 5000	2		DAR, Munk, 1993b
Colinus virginianus	13 d old	Kresoxim-methyl	93.7	Diet	5 d	NOEC	Body weight		≥ 5000	2		DAR, Munk, 1993b
Anas platyrhynchos	8 d old	Kresoxim-methyl	94	Diet	5 d	LC50	Mortality		> 5000	2		DAR, Munk, 1993c
Anas platyrhynchos	8 d old	Kresoxim-methyl	94	Diet	5 d	NOEC	Body weight		≥ 5000	2		DAR, Munk, 1993c
Colinus virginianus	9 m old, ♂♀	Kresoxim-methyl	93.7	Diet	26 w	NOEC	Reproduction		500	2		DAR, Munk, 1994a
Dog	Beagle	Kresoxim-methyl	94	Diet	90 d	NOAEL			5000	2		DAR, Mellert et al., 1994b
Dog	Beagle	Kresoxim-methyl	93.7	Diet	1 y	NOAEL	Body weight	ca. 140	5000♂	2		DAR, Hellwig et al. 1994
Mouse	B6C3F1/CrlBR, ♂♀	Kresoxim-methyl	96.6	Diet	28 d	NOAEL	Body weight	> 2141♂-3755♀	≥ 8000	2	1	DAR, Schilling et al., 1992a
Mouse	B6C3F1/CrlBR, ♂♀	Kresoxim-methyl	98.7	Diet	90 d	NOAEL	Body weight	909♂ - 2583♀	4000♂	2		DAR, Mellert et al., 1994a
Rat	Wistar, ♂♀	Kresoxim-methyl	96.6	Diet	28 d	NOAEL	Body weight	370	4000	2		DAR, Schilling et al., 1992
Rat	♂♀	Kresoxim-methyl	98.7	Diet	90 d	NOAEL	Body weight	577♂-672♀	2000	2		DAR, Mellert et al., 1994
Rat	Wistar, ♂♀	Kresoxim-methyl	94	Diet	2 y	NOAEL	Survival		≥ 16000	2		DAR, Mellert et al., 1994c
Rat	Wistar, ♂♀	Kresoxim-methyl	93.7-96.6	Diet	2 y	NOAEL	Survival		≥ 16000	2		DAR, Mellert et al., 1994d
Rat	Wistar, ♂♀	Kresoxim-methyl	93.7	Diet	2 gen.	NOAEL	Reproduction		≥ 16000	2		DAR, Hellwig et al. 1994a

1 At highest dose only effects on organ weight

Appendix 5. References used in the appendices

DAR: EC. 1997. Kresoxim-methyl, Draft Assessment Report. Rapporteur Member State: Belgium

Montforts and Linders, RIVM, 1997. Adviesrapport 4902-01; Kresoxim methyl: BAS 490 04 F/BAS 490 11F (eerste aanvulling)

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