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Environmental risk limits for aldicarb sulfoxide

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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 aldicarb sulfoxide

Dit rapport geeft milieurisicogrenzen voor aldicarb sulfoxide, een metaboliet van het insecticide aldicarb, 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 van aldicarb in het kader van de Europese toelating van gewasbeschermingsmiddelen (Richtlijn 91/414/EEG), aangevuld met gegevens uit de openbare literatuur.

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1 Introduction

1.1 Background and scope of the report

In this report, environmental risk limits (ERLs) for surface water are derived for aldicarb sulfoxide, a metabolite of the insecticide aldicarb. 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). Aldicarb sulfoxide is part of a series of 25 pesticides or related compounds 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 aldicarb sulfoxide, the evaluation report prepared for aldicarb within the framework of EU Directive 91/414/EC (Draft Assessment Report, DAR) was consulted (EC, 1996; further referred to as DAR). 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 Annexes 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}, an additional comment 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 ($MPC_{hh\ food, water}$); 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 aldicarb sulfoxide

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

3.1.1 Identity

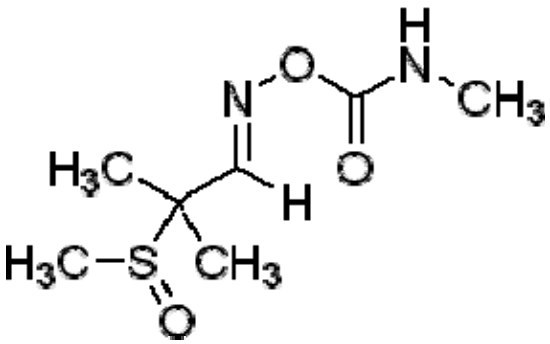

Figure 1. Structural formula of aldicarb sulfoxide

Table 1. Identification of aldicarb sulfoxide.

Parameter	Name or number	Source
Common name	aldicarb sulfoxide	
Chemical name	(1E)-2-methyl-2-(methylsulfinyl)propanal O-(methylcarbamoyl)oxime	www.chemspider.com
	2-methyl-2-(methylsulfinyl)-propanal-O-(methylcarbamoyl) oxime	www.chemspider.com
CAS number	001646-87-3	
EC number		
SMILES code	O=S(C(\C=N\OC(=O)NC)(C)C)C	www.chemspider.com
Use class	parent aldicarb is used as insecticide/acaricide/nematicide	
Mode of action	inhibition of cholinesterase	EC, 1996
Authorised in NL	no products with aldicarb authorised	
Annex 1 listing	parent aldicarb is not listed	

3.1.2 Physico-chemical properties

Physico-chemical properties of aldicarb sulfoxide are summarised in Table 2.

Table 2. Physico-chemical properties of aldicarb sulfoxide

Parameter	Unit	Value	Remark	Reference
Molecular weight	[g/mol]	206.27		
Water solubility	[mg/L]	28 x 10^3	at 25 ºC	SRC PhysProp Database
		1.0 x 10^6	EpiWin	US EPA, 2007
pK_a	[-]			
log K_{OW}	[-]	-0.78	EpiWin	US EPA, 2007
		-0.39	ClogP	BioByte, 2006
log K_{OC}	[-]	1.39	K_{oc} 24.6 L/kg, mean of 4 soils	EC, 1996
Vapour pressure	[Pa]	1.0 x 10^{-4}	at 25 ºC	SRC PhysProp Database
		9.3 x 10^{-3}	25 °C	Luttik and Linders, 1989
		1.8 x 10^{-4}	EpiWin	US EPA, 2007
Melting point	[°C]			
Boiling point	[°C]			Luttik and Linders, 1989
Henry's law constant	[Pa.m^3/mol]	2.8 x 10-8	EpiWin	US EPA, 2007

3.1.3 Behaviour in the environment

Table 3. Selected environmental properties of aldicarb sulfoxide.

Parameter	Unit	Value	Remark	Reference
Hydrolysis half-life	DT50 [d]	1.115	pH 4, 14 ºC	EC, 1996
		345	pH 4, 23 ºC	
		> 4	pH 5, 14 ºC	
		3.378	pH 5, 23 ºC	
		> 4	pH 6, 14 ºC	
		2.477	pH 6, 23 ºC	
		797	pH 7, 14 ºC	
		186	pH 7, 23 ºC	
		131	pH 8, 14 ºC	
		25	pH 8, 23 ºC	
		11.1	pH 9, 14 ºC	
		2.2	pH 9, 23 ºC	
		65	pH 8.5, 5 ºC	
		10	pH 8.5, 15 ºC	
Photolysis half-life	DT50 [d]			
Readily biodegradable				
Water/sediment systems	DT50 [d]	3.5 -4.0	dissipation in water	EC, 1996

3.1.4 Bioconcentration and biomagnification

There are no experimental data available for aldicarb sulfoxide.

Table 4. Overview of bioaccumulation data for aldicarb sulfoxide.

Parameter	Unit	Value	Remark	Reference
BCF (fish)	[L/kg]		not applicable, log K_{ow} -0.78[a]	
BMF	[kg/kg]	1	Default value for log K_{ow} < 4.5	

[a] log K_{ow} outside range applicable to QSARs

3.1.5 Human toxicological threshold limits and carcinogenicity

Human toxicological threshold limits and classification are not available for aldicarb sulfoxide. The parent compound aldicarb is assigned R24, R26/28. Aldicarb is not carcinogenic.

3.2 Trigger values

This section reports on the trigger values for ERL_{water} derivation (as demanded in WFD framework).

Table 5. Aldicarb sulfoxide: collected properties for comparison to MPC triggers.

Parameter	Value	Unit	Method/Source	Derived at section
Log $K_{p,susp\text{-}water}$	0.39	[-]	$K_{OC} \times f_{OC,susp}$[1]	K_{OC}: 3.1.2
BCF		[L/kg]		3.1.4
BMF	1	[kg/kg]		3.1.4
Log K_{OW}	-0.78	[-]		3.1.2
R-phrases	-	[-]		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).

- Aldicarb sulfoxide has a log $K_{p,\ susp\text{-}water}$ < 3; derivation of $MPC_{sediment}$ is not triggered.
- Aldicarb sulfoxide has a log $K_{p,\ susp\text{-}water}$ < 3; expression of the MPC_{water} as $MPC_{susp,\ water}$ is not required.
- Aldicarb sulfoxide has a log K_{ow} < 3; assessment of secondary poisoning is not triggered.
- Aldicarb sulfoxide has no classification. The parent compound aldicarb is assigned R24, R26/28, but the log K_{ow} of aldicarb sulfoxide is < 3. Therefore, derivation of an MPC_{water} for human health via food (fish) consumption ($MPC_{hh\ food,\ water}$) is not triggered
- For aldicarb sulfoxide, 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 aldicarb sulfoxide is given in Table 6. Marine toxicity data are not available. Detailed toxicity data for aldicarb sulfoxide are tabulated in Appendix 1.

Table 6. Aldicarb sulfoxide: 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	4800	algae	16000
crustacea	89	crustacea	**69**[b]
pisces	1020	crustacea	800
		pisces	4000

[a] For detailed information see Appendix 1. Bold values are used for ERL derivation.

[b] geometric mean of 84 and 57 µg/L, parameter mortality/immobility for *Daphnia laevis*, juveniles

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 aldicarb sulfoxide, no marine toxicity data are available and ERLs for the marine compartment cannot be derived.

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

The acute base-set for freshwater toxicity data is complete. Chronic NOECs are available for algae, crustaceans and fish. However, the acute EC_{50} of 69 µg/L for *Daphnia laevis* is lower than the chronic NOEC for *D. magna*. In this case, an assessment factor of 100 is applied to the EC_{50} µg/L for *D. laevis* (see INS-Guidance, p. 72, 2nd part of note c). The $MPC_{eco, water}$ is 69 / 100 = 0.69 µg/L.

For the marine environment, no data are available to derive an $MPC_{eco, marine}$.

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

Aldicarb sulfoxide has a log K_{ow} < 3, assessment of secondary poisoning is not triggered.

3.3.3 $MPC_{hh\ food,water}$

Derivation of $MPC_{hh\ food, water}$ for aldicarb sulfoxide is not triggered (Table 5).

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 only route included is direct toxicity ($MPC_{eco, water}$). The MPC_{water} is 0.69 µg/L.

3.3.6 MAC_{eco}

3.3.6.1 $MAC_{eco, water}$

At least one short-term $L(E)C_{50}$ from each of three trophic levels or the base set is available. Aldicarb sulfoxide has no potential to bioaccumulate, and it has a specific mode of action. Insects are not present in the dataset, but *Daphnia* sp. are known to be susceptible to carbamates. It is therefore considered that the potentially most sensitive species group is included in the dataset and an assessment factor of 10 can be applied to the lowest acute LC_{50} of 69 µg/L for *Daphnia laevis*. The $MAC_{eco, water}$ is set at 69/10 = 6.9 µg/L.

3.3.6.2 $MAC_{eco, marine}$

No data are available for derivation of the $MAC_{eco, marine}$.

3.3.7 $SRC_{eco, water}$

Chronic data are available for algae, crustaceans (among which *Daphnia*) and fish, the geometric mean of all chronic data is 758 µg/L. When three or more NOEC values are available, a comparison with acute data is not considered necessary. The $SRC_{eco, water}$ can be derived using an assessment factor of 1, resulting in an $SRC_{eco, water}$ of 758 µg/L.

3.4 Toxicity data and derivation of ERLs for sediment

The log $K_{p, susp-water}$ of aldicarb sulfoxide is below the trigger value of 3, therefore, ERLs are not derived for sediment.

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 aldicarb sulfoxide in freshwater. Derivation of ERLs for the marine compartment was not possible due to lack of data. Derivation of risk limits for sediment was not triggered.

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 7. Derived MPC, MAC_{eco}, and SRC values for aldicarb sulfoxide.

ERL	Unit	MPC	MAC_{eco}	SRC
Water, old[a]	µg/L	0.043	-	-
Water, new[b]	µg/L	0.69[c]	6.9	758
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. Detailed aquatic toxicity data

Table A1.1. Acute toxicity of aldicarb sulfoxide 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																
Scenesdesmus subspicatus				aldicarb sulfoxide						96 h	growth rate	EC50	16	2		EC, 1996
Scenesdesmus subspicatus				aldicarb sulfoxide						96 h	biomass	EC50	7.6	2		EC, 1996
Crustacea																
Daphnia laevis	mature females	Y	S	aldicarb sulfoxide		tw	6.9	21	58	48 h	mortality	LC50	0.103	1		Foran *et al.*, 1985
Daphnia laevis	mature females	Y	S	aldicarb sulfoxide		tw	6.9	21	58	48 h	immobility	EC50	0.043	1		Foran *et al.*, 1985
Daphnia laevis	juveniles (1-3 days)	Y	S	aldicarb sulfoxide		tw	6.9	21	58	48 h	immobility	EC50	0.057	1		Foran *et al.*, 1985
Daphnia laevis	juveniles (1-3 days)	Y	S	aldicarb-sulfoxide		tw	6.9	21	58	48 h	mortality	LC50	0.084	1		Foran *et al.*, 1985
Daphnia magna				aldicarb sulfoxide								LC50	0.8	2		EC, 1996
Insectae																
Culex pipiens L.	early 4th instar			aldicarb sulfoxide	98%					24 h		LC50	> 5	3	1	Bayoumi *et al.,* 1988
Pisces																
Danio rerio	eggs	Y	S	aldicarb sulfoxide	98%	ISO-water		27.5 ± 1		48 h	mortality	LC50	> 61.88	2	2	Küster and Altenburger, 2007
Lepomis macrochirus	7 cm, 5 g	N	S	aldicarb sulfoxide	95%	pond water	n.r.	22		72 h	mortality	LC50	4	2	3	Luttik and Linders, 1989

NOTES

1 test conditions poorly reported
2 max. conc. 300 µmol/L
3 milieufiche
4 According to OECD 202

Table A1.2. Chronic toxicity of aldicarb sulfoxide 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																
Scenedesmus subspicatus				aldicarb sulfoxide							growth rate	NOEC	4.8	2		EC, 1996
Crustacea																
Daphnia magna		Y	R	aldicarb sulfoxide	96.5		7.5-8.1	20-23		21	reproduction	NOEC	0.0894	1		De Knecht, 1999
Pisces																
Oncorhynchus mykiss	1-5 g			aldicarb sulfoxide	96.5		7.2-7.6	13.6-14.6		28	mortality	NOEC	1.02	1		De Knecht, 1999

Appendix 2. References used in the appendices

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