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Environmental risk limits for dodine

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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 dodine

Dit rapport geeft milieurisicogrenzen voor het fungicide dodine in water en sediment. 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.

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1 Introduction

1.1 Background and scope of the report

In this report, environmental risk limits (ERLs) for surface water and sediment are derived for the fungicide dodine. 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). Dodine 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 dodine, the evaluation report prepared within the framework of EU Directive 91/414/EC (Draft Assessment Report, DAR) was consulted (EC, 2005; 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 depends 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 dodine

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

3.1.1 Identity

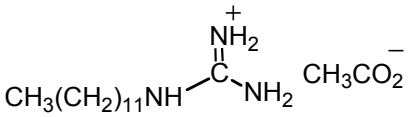

Figure 1. Structural formula of dodine.

Table 1. Identification of dodine.

Parameter	Name or number	Source
Common/trivial/other name	dodine, doguadine, dodine acetate	Tomlin, 2003; EC, 2006
Chemical name	1-dodecylguanidinium acetate (IUPAC) dodecylguanidine monoacetate	Tomlin, 2003; EC, 2006
CAS number	2439-10-3	EC, 2006
EC number	219-459-5	EC, 2006
SMILES code	CCCCCCCCCCCCNC(N)=N(H)(H)OC(=O)C free base: CCCCCCCCCCCCNC(N)=[N+](H)(H)	
Use class	Fungicide	EC, 2006
Mode of action	multisite inhibitor acting mainly on the fungus membranes	EC, 2006
Authorised in NL	Yes	
Annex 1 listing	No	

3.1.2 Physico-chemical properties

Physico-chemical properties of dodine are summarised in Table 2.

Table 2. Physico-chemical properties of dodine.

Parameter	Unit	Value	Remark	Reference
Molecular weight	[g/mol]	287.4		EC, 2006
		227.4	free base	
Water solubility	[mg/L]	870	pH 4.9, 20 ºC	EC, 2006
		930	pH 6.9, 20 °C	
		790	pH 9.1, 20 °C	
pK_a	[-]	-		
log K_{OW}		0.96	shake flask	EC, 2006
		4.31	Calculated for the free-base	Biobyte, 2006
log K_{OC}	[-]	6.6	Arithmeic mean	EC, 2006
Vapour pressure	[Pa]	$<5.49 \times 10^{-6}$	Calculated	EC, 2006
Melting point	[°C]	133.2		EC, 2006
Boiling point	[°C]	n.a.	Decomposition prior to boiling	EC, 2006
Henry's law constant	[Pa.m^3/mol]	$< 1.7 \times 10^{-3}$	20 °C	EC, 2006

n.a. = not applicable.

In view of the characteristics of dodine, being a surfactant with a dodecyl-group, it is hardly possible to experimentally derive the log K_{ow}. The log K_{ow} of 0.96 as given in the DAR is considered unrealistically low in view of the structural formula of dodine. The estimated log K_{ow} of 4.31 for the free base is considered to be more relevant, and is used as a worst case for risk assessment.

3.1.3 Behaviour in the environment

Table 3. Selected environmental properties of dodine.

Parameter	Unit	Value	Remark	Reference
Hydrolysis half-life	DT50 [d]	576	pH 5, 25 °C (extrapolated)	EC, 2006
Photolysis half-life	DT50 [d]	12.6	28 d under natural light at 40 °N	EC, 2006
Readily biodegradable		No		EC, 2006
Biodegradation in water/ sediment systems	DT50 [d]	0.71	whole system, 20 °C	EC, 2006
Relevant metabolites	guanidine		photometabolite	EC, 2006

3.1.4 Bioconcentration and biomagnification

An overview of the bioaccumulation data for dodine is given in Table 4.

Table 4. Overview of bioaccumulation data for dodine.

Parameter	Unit	Value	Remark	Reference
BCF (fish)	[L/kg]	919	calculated with log K_{ow} 4.31	Veith et al., 1979
BMF	[kg/kg]	1	Default value for log $K_{ow} < 4.5$	

3.1.5 Human toxicological threshold limits and carcinogenicity

The following R-phrases related to human toxicology are proposed in the DAR: R22, R23, R38, R41. According to ESIS, dodine is assigned R22, R36/38 (http://ecb.jrc.it/esis/; date of search 17 March 2008). Dodine is not classified as being carcinogenic.

An ADI of 0.1 mg/kg_{bw}/d is proposed in the DAR, based on a 1-year dog study with NOAEL values of 10 mg/kg_{bw}/d with a safety factor of 100.

3.2 Trigger values

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

Table 5. Dodine: collected properties for comparison to MPC triggers.

Parameter	Value	Unit	Method/Source	Derived at section
Log $K_{p,susp\text{-}water}$	5.6	[-]	$K_{OC} \times f_{OC,susp}$ [1]	K_{OC}: 3.1.2
BCF	919	[L/kg]		3.1.4
BMF	1	[kg/kg]		3.1.4
Log K_{OW}	4.2	[-]		3.1.2
R-phrases	R22,R23,R36/38, R41, R50/R53	[-]		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).

- dodine has a log $K_{p,\ susp\text{-}water} \geq 3$; derivation of $MPC_{sediment}$ is triggered.
- dodine has a log $K_{p,\ susp\text{-}water} \geq 3$; expression of the MPC_{water} as $MPC_{susp,\ water}$ is required.
- dodine has a BCF $\geq$ 100 L/kg; assessment of secondary poisoning is triggered.
- dodine has an R22 classification and the log K_{ow} is $\geq$ 3; the MPC_{water} for human health via food (fish) consumption ($MPC_{hh\ food,\ water}$) need to be derived.
- For dodine, 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 toxicity data for dodine is given in Table 6 for freshwater, marine toxicity data are given in Table 7. Detailed toxicity data for dodine are tabulated in Appendix 1.
With respect to the selection of data for derivation of the MPC, the following should be noted:
Dodine shows a fast decline of concentrations in water over time. Therefore, studies in which the concentrations were not measured were assigned Ri 3. Studies in which concentrations were measured, were only assigned Ri 2 when the endpoint could be based on time weighted average concentrations. Otherwise, Ri 3 was assigned.

Table 6. Dodine: 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	4.8[b]	Algae	**6.9**[d]
Crustacea	**4.4**	Crustacea	30[e]
Pisces	99[c]	Pisces	700
		Pisces	840
		Pisces	598

a. For detailed information see Appendix 1.
b. Preferred endpoint growth rate for *Pseudokirchneriella subcapitata*
c. Most sensitive endpoint for *Pimephales promelas*, parameter growth
d. Preferred endpoint growth rate for *Pseudokirchneriella subcapitata*.
e. Geometric mean of 18 and 49 µg/L, parameter mortality/immobility for *Daphnia magna*

Table 7. Dodine: selected marine toxicity data for ERL derivation.

Chronic[a]		Acute[a]	
Taxonomic group	**NOEC/EC10 (µg/L)**	**Taxonomic group**	**L(E)C50 (µg/L)**
		Crustacea	390
		Pisces	3700

[a] For detailed information see Appendix 1.

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 dodine, there are not sufficient marine toxicity data (acute base set not complete; no chronic data) and ERLs for the marine compartment cannot be derived.

3.3.1.2 Mesocosm and field studies

An outdoor mesocosm study was performed with the product Dodine 400 SC. An evaluation of the study is included in Appendix 4. From this study, a NOEC of 6 µg as/L was derived, based on the absence of effects at this treatment level. Because dodine concentrations in water show a fast decline with time (DT_{50} 0.83 days), the study does not allow for the assessment of effects due to chronic exposure. It will, however, be considered for the derivation of the MAC.

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

The base-set for freshwater toxicity data is complete. Chronic NOECs are available for algae, crustaceans, and fish. An assessment factor of 10 is applied to the lowest NOEC of 4.4 µg/L for crustacea. The $MPC_{eco, water}$ is 0.44 µg/L.

For the marine environment, only acute data are available. The base-set is not complete because data for algae are missing. The $MPC_{eco, marine}$ cannot be derived.

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

In view of the log $K_{ow} \geq 3$, derivation of the $MPC_{sp, water}$ and $MPC_{sp, marine}$ is triggered. The available toxicity data for mammals and birds are presented in Appendix 2. In Table 8, the MPC_{oral} is derived applying the appropriate assessment factors to the data. No default assessment factors are available for a 56-days mammal and a 6-weeks bird test, a factor of 300 is used as a worst case.

Table 8. Dodine: derivation of the $MPC_{oral, min}$.

Species	Exposure time	NOAEC [mg/kg_{diet}]	LC_{50} [mg/kg_{diet}]	AF_{oral}	MPC_{oral}
dog	1 y	400		30	13.33
mouse	56 d	625		300	2.08
mouse	56 d	625		300	2.08
mouse	91 d	600		90	6.67
mouse	91 d	600		90	6.67
mouse	78 w	200		30	**6.67**
rat	28 d	200		300	0.67
rat	28 d	200		300	0.67
rat	90 d	200		90	2.22
rat	90 d	200		90	2.22
rat	2 y	400		30	13.33
rat	2 gen	200		30	**6.67**
rat	2 gen	200		30	**6.67**
Mallard duck	5 d		325	3000	0.11
Mallard duck	6 w	750		300	2.50
Mallard duck	20+11+2 w	200		30	**6.67**

The lowest $MPC_{oral, duck}$ for Mallard ducks is 0.11 mg/kg_{diet}, based on a short-term toxicity study. There are, however, also long-term data available, which according to the INS-Guidance prevail over the short-term study. The $MPC_{oral, duck}$ for Mallard ducks based on the long-term test is 6.67 mg/kg_{diet}.
A similar reasoning leads to a $MPC_{oral, mouse}$ of 6.67 mg/kg_{diet} for mice, and $MPC_{oral, rat}$ of 6.67 mg/kg_{diet} for rat. The overall lowest $MPC_{oral, min}$ is thus 6.67 mg/kg_{diet}.

The $MPC_{sp, water}$ is derived as $MPC_{oral, min}$ / (BCF × BMF) = 6.67 / (919 × 1) = 7.3×10^{-3} mg/L = 7.3 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 derived as $MPC_{oral, min}$ / (BCF × BMF_1 × BMF_2) = 6.67 / (919 × 1 × 1) = 7.3×10^{-3} mg/L = 7.3 µg/L.

3.3.3 $MPC_{hh\ food, water}$

Derivation of $MPC_{hh\ food, water}$ for dodine is triggered (Table 5). The $MPC_{hh\ food}$ is calculated from the ADI (0.1 mg/kg_{bw}/d), a body weight of 70 kg and a daily fish consumption of 115 g, as $MPC_{hh\ food}$ = 0.1 x 0.1 x 70/0.115 = 6.1 mg/kg.
Subsequently the $MPC_{hh\ food, water}$ is calculated as 6.1 / (BCF_{fish} x BMF_1) = 6.1 / (919 x 1) = 6.6 µg/L.

3.3.4 $MPC_{dw, water}$

The Drinking Water Standard is 0.1 µg/L, 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 Section 2.3.1) is the ecotoxicological $MPC_{eco, water}$. The MPC_{water} = 0.44 µg/L..

No MPC_{marine} can be selected due to the absence of data.

3.3.5.1 $MPC_{susp, water}$

Because the log $K_{p, susp\text{-}water} \geq 3$ (Table 5), the final MPC_{water} has to be recalculated in an $MPC_{susp, water}$, which refers to the concentration in suspended matter. The $MPC_{susp, water}$ is calculated according to:

$MPC_{susp, water} = MPC_{water, total} / (C_{susp, Dutch\ standard} \times 10^{-6} + (1/ K_{p,susp\text{-}water,Dutch\ standard}))$, with $MPC_{water, total}$ being the above derived MPC_{water} in mg/L and $C_{susp, Dutch\ standard}$ is 30 mg/L.

For this calculation, $K_{p,susp\text{-}water,Dutch\ standard}$ is calculated as K_{OC} x $f_{OC,susp,Dutch\ standard}$. This is not the same as the European standard $f_{OC,susp}$ which is used in the table with trigger values. With a log K_{OC} of 6.6 (K_{oc} 3981072 L/kg) an $f_{OC,susp,Dutch\ standard}$ of 0.1176, the $K_{p,susp\text{-}water,Dutch\ standard}$ is calculated to be 468361 L/kg.

The $MPC_{susp, water}$ is 0.44 x 10^{-3} / (30 × 10^{-6} + (1 / 468361)) = 14 mg/kg_{dw}.

3.3.6 MAC_{eco}

3.3.6.1 $MAC_{eco, water}$

The MAC_{eco} is based on the acute toxicity data. The compound has a potential to bioaccumulate; the mode of action is most likely non-specific, but there is a high interspecies variation. Therefore, an assessment factor of 1000 should be applied. The lowest EC_{50} is 6.9 µg/L, leading to a $MAC_{eco, water}$ of 6.9/1000 = 6.9 ng/L. This value is below the $MPC_{eco, water}$ of 0.44 µg /L, and since it is not realistic to assume that acute effects on species occur below a level that is deemed to be protective for chronic exposure, the $MAC_{eco, water}$ is initially set to 0.44 µg/L.

A NOEC of 6 µg as/L was derived from an outdoor mesocosm study, based on initial concentrations (see Appendix 3). 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 NOEAEC1 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). In addition, dodine is a fungicide, which may affect several taxonomic groups. It is therefore in principle

[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.

proposed to use an assessment factor of 3 on the NOEC instead of on the NOEAEC. The $MAC_{mesocosm}$ is 2.0 µg/L.

Since the most sensitive group from the acute dataset is also represented in the mesocosm, the $MAC_{eco, water}$ is set to 2.0 µg/L.

3.3.6.2 $MAC_{eco, marine}$

Since the marine base set is not complete, it is not possible to derive the $MAC_{eco, marine}$

3.3.7 $SRC_{eco, water}$

Three chronic NOECs are available for algae, *Daphnia* and fish. In this case, the $SRC_{eco, water}$ is set to the geometric mean of the aggregated chronic toxicity values (see Table 6), which is 13 µg/L.

3.4 Toxicity data and derivation of ERLs for sediment

3.4.1 Sediment toxicity data

There are no sediment toxicity data available.

3.4.2 Derivation of $MPC_{sediment}$

Because there are no sediment toxicity data, the $MPC_{sediment}$ needs to be derived by applying the equilibrium partitioning method on the $MPC_{eco,water}$ of 0.44 µg/L

First, the $MPC_{sediment}$ is calculated using TGD default values, and subsequently this $MPC_{sediment}$ is recalculated to Dutch standard sediment.

$$MPC_{\text{sediment, TGD, EqP, ww}} = \frac{K_{susp-water}}{RHO_{\text{susp}}} \times MPC_{\text{eco, water}} \times 1000$$

with $K_{susp\text{-}water}$:

$$K_{\text{susp-water}} = F\text{air}_{\text{susp}} \times K_{\text{air-water}} + F\text{water}_{\text{susp}} + F\text{solid}_{\text{susp}} \times \frac{K\text{p}_{\text{susp}}}{1000} \times RHO\text{solid}$$

Using $K_{p,susp}$ = 398107 L/kg (log $K_{p, susp}$ = 5.6), $F\text{air}_{susp}$ = 0, $F\text{water}_{susp}$ = 0.9, $F\text{solid}_{susp}$ = 0.1, RHO_{susp} = 1150 kg/m^3, $F\text{solid}_{susp}$ = 0.1, RHO_{solid} = 2500 kg/m^3, the $K_{susp\text{-}water}$ is calculated as 99528, and the $MPC_{sediment, TGD, EqP, ww}$ as 38 mg/kg$_{ww}$.
This value is converted to dry weight and subsequently to Dutch standard sediment using the following equations:

$$MPC_{\text{sediment, TGD, EqP, dw}} = \frac{RHO_{\text{susp}}}{F\text{solid}_{\text{susp}} \times RHO\text{solid}} \times MPC_{\text{sediment, TGD, EqP, ww}}$$

$$MPC_{\text{Dutch standard sediment, EqP, dw}} = \frac{Foc_{\text{Dutch standard sediment}}}{Foc_{\text{susp, TGD}}} \times MPC_{\text{sediment, TGD EqP, dw}}$$

With $Foc_{\text{Dutch standard sediment}}$ = 0.0588 and $Foc_{\text{susp,TGD}}$ = 0.1, the $MPC_{\text{Dutch standard sediment, EqP, dw}}$ = 103 mg/kg_{dw}.

3.4.3 Derivation of $SRC_{eco, sediment}$

Since no valid sediment toxicity data are available, the $SRC_{eco, sediment}$ is calculated using the (unrounded) $SRC_{eco, water}$ and the partitioning method, analogous to the calculation of the $MPC_{sediment}$. The $SRC_{eco,sediment}$ is 2995 mg/kg_{dw}.

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 dodine in water and sediment. 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 9. Derived MPC, MAC_{eco}, and SRC values for dodine.

ERL	Unit	MPC	MAC_{eco}	SRC
Water, old[a]	µg/L	5.1×10^{-3}		
Water, new[b]	µg/L	0.44	2.0	13
Water, suspended matter	mg/kg_{dw}	14	-	-
Drinking water[b]	µg/L	0.1[c]	-	-
Sediment	$µg/kg_{dw}$	1.0×10^{5}	-	3.0×10^{6}
Marine	µg/L	n.d.[d]	n.d.[d]	-
Marine, suspended matter	mg/kg_{dw}	n.d.[d]	n.d.[d]	-
Marine sediment	mg/kg_{dw}	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 dodine 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	S	dodine	94	dw		25		120 h	growth rate	EC50	0.01100	3	1,2	EC, 2006 (Hoberg, 1993)
Pseudokirchneriella subcapitata		Y	S	dodine	94	dw		25		120 h	cell density	EC50	0.00095	3	1,2	EC, 2006 (Hoberg, 1993)
Pseudokirchneriella subcapitata		Y	S	dodine	99			24		120 h	growth rate	EC50	0.00910	3	1,3,5	EC, 2006 (Hoberg, 1995)
Pseudokirchneriella subcapitata		Y	S	dodine	99			24		120 h	cell density	EC50	0.00250	3	1,3,5	EC, 2006 (Hoberg, 1995)
Pseudokirchneriella subcapitata		Y	S	400 SC	40			23		72 h	growth rate	EC50	0.00690	2	4	EC, 2006 (Migchielsen, 2004)
Pseudokirchneriella subcapitata		Y	S	400 SC	40			23		72 h	biomass	EC50	0.00560	2	4	EC, 2006 (Migchielsen, 2004)
Crustacea																
Daphnia magna	<24 h		F	dodine	94					48 h	immobility	EC50	0.018	2	5	EC, 2006 (Putt, 1992)
Daphnia magna	<24 h		R	dodine	95					48 h	immobility	EC50	0.053	3	5	EC, 2006 (Caley, 1989)
Daphnia magna	<24 h	Y	S	dodine	98					48 h	immobility	EC50	0.146	3	6	EC, 2006 (Migchielsen, 2002)
Daphnia magna	<24 h	Y	R	400 SC	40					48 h	immobility	EC50	0.049	2		EC, 2006 (Migchielsen, 2004)
Daphnia magna	<24 h	N	S	dodine		am				26 h	mortality	EC50	0.058	3	7	Frear and Boyd, 1967
Gammarus fasciatus	mature	N?	S	dodine	97.6		7.1	15	44	96 h	mortality	LC50	1.100	3	7	Mayer and Ellersieck, 1986
Mollusca																
Cipangopaludina malleata		N	S	dodine		dtw		22		48 h	mortality	LC50	2.70	4	8,9	Nishiuchi and Yoshida, 1972
Indoplanorbis exustus		N	S	dodine		dtw		22		48 h	mortality	LC50	2.30	4	8,9	Nishiuchi and Yoshida, 1972
Physa acuta		N	S	dodine		dtw		22		48 h	mortality	LC50	2.40	4	8,9	Nishiuchi and Yoshida, 1972
Semisulcospira libertina		N	S	dodine		dtw		22		48 h	mortality	LC50	2.00	4	8,9	Nishiuchi and Yoshida, 1972
Pisces																
Gambusia affinis	Juvenile	N	S	dodine	95					24 h	mortality	LC50	0.930	3	7	Hourdakis et al., 1995
Gambusia affinis	Mature	N	S	dodine	95					24 h	mortality	LC50	2.990	3	7	Hourdakis et al., 1995
Lepomis macrochirus	mature	Y	R	dodine	95.3			22		96 h	mortality	LC50	0.700	2	4	EC, 2006 (Caley et al., 1990b)
Onchorhynchus mykiss	mature	Y	R	dodine	95.3			14		96 h	mortality	LC50	0.840	2	4	EC, 2006 (Caley et al., 1990a)
Rasbora heteromorpha	mature	N	S	Melprex 65	65		8.1	20	20	96 h	mortality	LC50	0.92	3	7	Tooby et al., 1975
Cyprinus carpio	2.3cm 0.33g	Y	R	dodine	99	dw	8	21	367	96 h	mortality	LC50	0.598	2	5	Mighielsen, 2005
Cyprinus carpio		Y		400 SC	40	am	7.7		180	96 h	mortality	LC50	1.400	3	10	Mighielsen, 2007

Notes

1 control growth not exponential and irregular
2 endpoint based on initial measured; strong decline
3 5-days value from 15-days test
4 endpoint recalculated based on measured concentrations
5 original endpoint based on measured concentrations
6 sediment added; concentration during test not given
7 static, concentrations not measured
8 article in Japanese; original result as TLm
9 purity unknown
10 sediment added; concentrations decline to < 50% after 24 h

Table A1.2. Chronic toxicity of dodine 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	S	dodine	94	dw				120 h	NOEC	growth rate	0.00600	3	1,2	EC, 2006 (Hoberg, 1993)
Pseudokirchneriella subcapitata		Y	S	dodine	94	dw				120 h	NOEC	cell density	0.000082	3	1,2	EC, 2006 (Hoberg, 1993)
Pseudokirchneriella subcapitata		Y	S	dodine	99					120 h	NOEC	growth rate	0.00042	3	1,3,4	EC, 2006 (Hoberg, 1995)
Pseudokirchneriella subcapitata		Y	S	dodine	99					120 h	NOEC	cell density	0.000059	3	1,3,4	EC, 2006 (Hoberg, 1995)
Pseudokirchneriella subcapitata		Y	S	400 SC	40					72 h	NOEC	growth rate	0.0048	2	4	EC, 2006 (Migchielsen, 2004)
Crustacea																
Daphnia magna	<24 h	Y	F	dodine	99	tw		20		21 d	reproduction	NOEC	0.0044	2	4	EC, 2006 (Putt 1995)
Daphnia magna	<24 h	Y	F	dodine	99	tw		20		21 d	immobility	EC50	0.0300	2	4	EC, 2006 (Putt 1995)
Pisces																
Pimephales promelas	eggs	Y	F	dodine	97	tw		25		5 d	hatching		>0,4	2	4	EC, 2006 (Sousa, 1995)
Pimephales promelas	eggs	Y	F	dodine	97	tw		25		35 d	mortality	NOEC	0.200	2	4	EC, 2006 (Sousa, 1995)
Pimephales promelas	eggs	Y	F	dodine	97	tw		25		35 d	growth	NOEC	0.099	2	4	EC, 2006 (Sousa, 1995)

Notes

1 control growth not exponential and irregular
2 endpoint based on initial measured; strong decline
3 5-days value from 15-days test
4 original endpoint based on measured concentrations

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Table A1.3. Acute toxicity of dodine to marine 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
Crustacea																
Mysidopsis bahia	<24 h	Y	F	dodine	94	nw		25	32	96 h	mortality	LC50	0.390	2	1	EC, 2006 (Bettencourt, 1992)
Mollusca																
Crassostrea virginica	juvenile	Y	F	dodine		nw			31	96 h	shell growth	EC50	0.098	3	1,2	EC, 2006 (Dionne, 1992)
Crassostrea virginica	juvenile	Y	F	dodine		nw			31	96 h	mortality	LC50	> 0.120	3	1,2	EC, 2006 (Dionne, 1992)
Pisces																
Cyprinodon variegates	mature	Y	F	dodine	94	nw		22		96 h	mortality	LC50	3.700	2	1	EC, 2006 (Bettencourt, 1992)

Notes

1 original endpoint based on measured concentrations

2 difference between control and solvent control; solvent control does not meet validity criteria

Appendix 2. Detailed bird and mammal toxicity data

Table A2.1. Toxicity of dodine to birds and mammals.

Species	Species properties (age, sex)	Purity [%]	Application route	Exp. time	Criterion	Test endpoint	NOAEL [mg/kg$_{bw}$/d]	NOAEC Diet [mg/kg$_{diet}$]	LC50 Diet [mg/kg$_{diet}$]	Ri	Notes	Reference
birds												
Bobwhite quail	20 g, 11 days old	95.3	diet	5 d	LC50	mortality	> 976		> 5200	2		EC, 2006 (Hakin 1990a)
Mallard duck	8 days, 100g	95.3	diet	5 d	LC50	mortality	280		325	2		EC, 2006 (Hakin 1990b)
Bobwhite quail	49 weeks, 220-300 g	94	diet	6 w	NOEC	mortality	≥ 135	≥ 1500		2	4	EC, 2006 (Pedersen & Mumper 1993a
Mallard duck	110 weeks, 1000-1400 g	94	diet	6 w	NOEC	mortality	50	750		2	4	EC, 2006 (Pedersen 1993b
Bobwhite quail	20 weeks, 150-250 g	94	diet	24+13+2 w	NOEC	reproduction	≥ 95	≥ 1000		2	4	EC, 2006 (Pedersen 1994a
Mallard duck	24 weeks, 1200 g	94	diet	20+11+2 w	NOEC	reproduction	20	200		2	4	EC, 2006 (Pedersen 1994b
mammals												
dog	6-9 kg, 7 months	94	capsules	6 w	NOAEL		1.25			3	1, 2	EC, 2006 (Smith 1994)
dog	6 months, 6-9 kg	99	capsules	1 y	NOAEL	body weight	10	400		2	3	EC, 2006 (Trutter 1996)
mice	4 weeks, 18-21g, Male	95	diet	56 d	NOAEL	body weight	109.4	625		2	4	EC, 2006 (Mulhern et al., 1988)
mice	4 weeks, 18-21g, female	95	diet	56 d	NOAEL	body weight	150.4	625		2	4	EC, 2006 (Mulhern et al., 1988)
mice	28 d, 23.2-30.1g, male	94	diet	91 d	NOAEL	body weight	94	600		2	4	EC, 2006 (Kangas 1994)
mice	28 d, 17.3-23.9g, female	94	diet	91 d	NOAEL	body weight	116	600		2	4	EC, 2006 (Kangas 1994)
mice		98.6	diet	78 w	NOAEL	body weight	29-36	200		2	4	EC, 2006 (Williams, 1998)
rat	28 d, 182-228g, male	94	diet	28 d	NOAEL	body weight	< 47	< 500		3	2,4	EC, 2006 (Batham 1994b)
rat	28 d,131-173g, female	94	diet	28 d	NOAEL	body weight	< 50	< 500		3	2,4	EC, 2006 (Batham 1994b)
rat	5 weeks, male	99	diet	28 d	NOAEL	food uptake	17.7	200		2	2,4	EC, 2006 (Dange 1997)
rat	5 weeks, female	99	diet	28 d	NOAEL	food uptake	19.2	200		2	2,4	EC, 2006 (Dange 1997)
rat	3,5 w, 35-50g, male	95	diet	90 d	NOAEL	body weight	14.1	200		2	4	EC, 2006 (Lina et al., 1984)
rat	3,5 w, 35-50g, female	95	diet	90 d	NOAEL	body weight	14.9	200		2	4	EC, 2006 (Lina et al., 1984)
rat		98.6	diet	2 y	NOAEL	body weight	20-26.5	400		2	4	EC, 2006 (Dange, 1998)
rat		98.6	diet	2 gen	NOAEL	body weight	13.14	200		2	4,5	EC, 2006 (Henwood, 1996)
rat		98.6	diet	2 gen	NOAEL	reproduction	52.6	≥ 800		2	4	EC, 2006 (Henwood, 1996)
rat		98.6	diet	2 gen	NOAEL	pup development	13.14	200		2	4	EC, 2006 (Henwood, 1996)

Notes

1 dosing adjusted during study in 2 groups
2 range-finding
3 NOAEC calculated with default conversion factor
4 NOEAC based on dietary concentrations used in test
5 maternal toxicity

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Appendix 3. Description of mesocosm study

Reference	Foekema EM, Lewis WE, Hoornsman G, Van het Groenewoud H, Van der Vlies EM. 2007. Determination of the biological effects and fate of Dodine 400CS in outdoor ponds. Den Helder, The Netherlands: IMARES. Report no. C111/07, 87 pp. (with Annexes). Data provided by Agriphar SA, Belgium.
Species; Population; Community	phytoplankton; zooplankton; periphyton; gastropods; crustaceans; insects; macrophytes
Test Method	outdoor mesososm
System properties	ca. 2200 L, natural sediment ca. 10 cm
Formulation	Dodine 400 SC (384-315 g as/L)
Exposure regime	3, 6, 16, 41 and 109 µg as/L; two applications with 5-d interval; calculated initial, based on measured Dodine in dosing solutions
Analysed	Y; starting at 1 h post-application until 28 d
Temperature [°C]	14-22; > 17 as from one week after 2nd application
pH range	8.5-9.5; treatment effect at 41 and 109 µg as/L
Hardness [mg $CaCO_3$/L]	
Exposure time	63 d
Criterion	NOEC
Test endpoint	phytoplankton, zooplankton
Value [µg as/L]	6
GLP	Y
Guideline	OECD; SETAC; CLASSIC
Notes	
Ri	1

An outdoor mesocosm study was performed with the fungicide Dodine 400 SC in compliance with GLP. The present evaluation of the study is based on the original study report.
Test system. Glass-fibre tanks (∅ 190-200 cm; 110 cm deep). Mesocosms set-up in April 2007 with sediment (ca. 10 cm; 3.3% OM) and water (86-90 cm) from Lake Markermeer. Additional organisms were introduced (snails, 30 *Bithynia tentaculata* and 20 *Lymnea stagnalis*; crustaceans, 50 *Asellus aquaticus* and 60 *Gammarus* sp.; macrophytes, ca. 4 g wwt *Elodea canadensis* and 11 g wwt *Myriophylum spicatum*) and water was re-circulated for 37 days prior to application. Mesocosms were treated twice (24 and 29 May; interval 5 d) with Dodine 400 SC, nominal application rates 3, 7, 18, 45 and 110 µg as/L applied evenly on the surface. Internal circulation (100 L/h) throughout the study. Replicate ponds for treatments, three control ponds.
Analytical sampling. Treatment solutions analysed. Water samples taken 1, 3, 24 h after each application, 5 d after 1st application (before 2nd), and on days 10 and 28 after 1st application (5 and 23 after 2nd). Sediment samples on days 5 (before 2nd application), 10 and 63. Analysis by LC/MS-MS, LOQ 0.1 µg/L water, 0.01 mg/kg wwt sediment.
Biological sampling. Zooplankton, phytoplankton, periphyton, emerged insects (floating traps), (macro-)invertebrates were sampled before and until 63 days after treatment. Macrophyte biomass was determined at the end of the study.
Data treatment and statistics. Half-life of test compound with first-order kinetics. Differences between controls and treatments analysed by ANOVA with Bonferroni post-test. Numeric data transformed log(n+0.1). Multivariate statistics (PRC) on zooplankton, fytoplankton, macro-invertebrates and water quality parameters with CANOCO. Data transformation (either log(n+0.1), log or square root). Significance of PRC analysed by Monte-Carlo permutation.

RESULTS

Chemical analysis. Calculated average nominal concentration based on actual amount in dosing solutions was 3, 6, 16, 41 and 109 µg as/L. Actual concentrations in replicate samples 1 h post-application were 55-288% and 43-143% of nominal after 1st and 2nd application, respectively. Overall average concentrations 1, 3 and 24 h after both applications are given in the table below. Concentrations just before the 2nd application were <1 µg as/L, except for the highest treatment level. Calculated average DT_{50} was 0.83 days. There is no evidence of accumulation of the compound in the water column. Calculated nominal concentrations were used to express endpoints.

Nominal	1 hour post application[1]		3 h post application[1]		24 h post application[1]	
[µg as/L]	[µg as/L]	[% of nominal]	[µg as/L]	[% of nominal]	[µg as/L]	[% of nominal]
2 x 3	3	100	4*	149	1	32
2 x 6	8	136	6	99	3	48
2 x 16	19	120	16	100	9	55
2 x 41	42	102	35	86	17	42
2 x 109	117	107	87	79	51	47

1: average of measurements after 1st and 2nd application

* high value due to sample contamination after 1st application, recovery after 2nd application is 113% of nominal

Physico-chemical parameters. Significant effects on DO, pH and turbidity at 2 x 41 and 2 x 109 µg as/L, partly explained as secondary effects due to changes in primary production.

Biological system. No significant effect were observed on biomass and community structure of periphyton, nor on macrophytes. The PRC-analysis showed a significant effect on zooplankton, phytoplankton, macro-invertebrates and water quality parameters at 2 x 41 and 2 x 109 µg as/L. Significant effects per treatment level are summarised in the table below.

Table: summary of effects in mesocosm study

Treatment [µg as/L]	Group	Species/taxon	Significant effect on day									Notes
			4	11	18	25	32	39	46	53	60	
2 x 3	phytoplankton	*Scenedesmus* sp.		↑								effect not present at 2 x 6 and 2 x 16 µg as/L
	zooplankton	*Filinia longiseta*			↑	↑						low numbers/absent in control as from day 18
2 x 6	phytoplankton	unidentified micro-algae		↓								low numbers/absent in control as from day 18
	zooplankton	*Filinia longiseta*			↑							low numbers/absent in control as from day 18
		Keratella quadrata					↓					increase at 2 x 16 µg as/L; no effect at 2 x 41 and 2 x 109 µg as/L
2 x 16	phytoplankton	unidentified micro-algae		↓								low numbers/absent in control as from day 18
		Crucigenia sp.		↑	↑							low numbers/absent in control
		Mycrocystis aeruginosa	↑	↑								low numbers/absent in control
	zooplankton	*Filinia longiseta*			↑	↑						low numbers/absent in control as from day 18
		Keratella quadrata					↑					no effect at 2 x 41 and 2 x 109 µg as/L
		Polyartha sp.				↓						

Table: summary of effects in mesocosm study (cont.)

Treatment	Group	Species/taxon	Significant effect on day									Notes
[µg as/L]			4	11	18	25	32	39	46	53	60	
2 x 41	water quality	DO	increase on day 32; n.s. at next sampling (day 35)									indicative of enhanced primary production
		pH	increase on day 32,35; n.s. at next sampling (day 39)									indicative of enhanced primary production
		turbidity	increase on day 4-6,14,18; n.s. at next sampling (day 21)									indicative of enhanced primary production
	phytoplankton	chlorophyll a	increase on day 5,6,14; n.s. at next sampling (day 18)									
		unidentified micro-algae		↑								low numbers/absent in control after day 18
		Ankristodesmus angustus		↑								low numbers/absent in control
		Scenedesmus sp.		↑	↑							
		Crucigenia sp.		↑								low numbers/absent in control
		Ankyra ancora				↓						
		Mycrocystis aeruginosa		↑								low numbers/absent in control
		flagellates < 3 µm	↓	↓								
	zooplankton	*Daphnia longispina*	↓									
		Filinia longiseta			↑	↑	↑					low numbers/absent in control as from day 18
		Polyartha sp.	↓									
2 x 109	water quality	DO	increase on day 7,14,49; decrease on day 28,32,35; n.s. at next sampling (day 39)									indicative of enhanced primary production
		pH	increase on day 11; decrease on day 28-46; n.s. at next sampling (day 49)									indicative of enhanced primary production
		turbidity	increase on day 4-6,14-21; n.s. at next sampling (day 25)									indicative of enhanced primary production
	phytoplankton	chlorophyll a	increase on day 11,18; n.s. at next sampling (day 25)									
		unidentified micro-algae			↑	↑						low numbers/absent in control after day 18
		Ankristodesmus angustus	↑	↑	↑							low numbers/absent in control
		Scenedesmus sp.			↑							
		Crucigenia sp.		↑								low numbers/absent in control
		Ankyra ancora				↓	↓	↓	↓			
		Mycrocystis aeruginosa		↑								low numbers/absent in control
		flagellates < 3 µm	↓									
		flagellates 3-10 µm				↑	↑					
	zooplankton	*Bosmina* sp.	↓	↓								
		Daphnia longispina	↓	↓	↓	↓	↓	↓	↓			
		Ceriodaphnia sp.	↓	↓	↓							
		Simocephalus vetulus	↓									
		Filinia longiseta	↓			↑	↑					low numbers/absent in control as from day 18
	macro-invertebrates	*Asellus aquaticus*	no effect until day 33; significant increase on day 61									cumulative numbers on traps day 0-33 and day 61
		Gammarus sp.	trend towards decrease until day 33; significant decrease on day 61									cumulative numbers on traps day 0-33 and day 61
		Procladius choreus	significant increase towards study end									

The authors conclude that effects at treatment levels 2 x 3, 2 x 6 and 2 x 16 µg as/L can be classified as Class 2: slight effects, short-term and/or quantitatively restricted response of one or a few sensitive endpoints and only observed at individual samplings; effects at treatment level 2 x 41 µg as/L as Class 3: clear response of sensitive endpoints at some subsequent sampling dates, total recovery within 8 weeks; effect at treatment level 2 x 109 µg as/L as Class 5: clear response of sensitive endpoints, total recovery longer than 8 weeks after last application.

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 description of the experimental set-up adequate and unambiguous? Yes.
3. Is the exposure regime adequately described? Yes. Overall mean measured concentrations after application are in good agreement with calculated nominal concentrations. There is no evidence of accumulation of the compound in the water column between applications and calculated nominal concentrations can be used to express the endpoints.
4. Are the investigated endpoints sensitive and in accordance with the working mechanism of the compound? Yes. Algae and crustaceans are most sensitive in laboratory studies, representatives of these groups are present in the mesocosms and show effects.
5. Is it possible to evaluate the observed effects statistically? Yes. Full statistical analyses are presented, including multi-variate statistics

This criteria result in an overall assessment of the study reliability. The study is considered to be reliable (Ri 1).

Evaluation of the endpoint to be used for standard setting

The effect on *Scenedesmus* sp. observed at 2 x 3 µg as/L is considered not to be related to the test substance, because it was not observed at the two next higher treatment levels. The increase of the rotifer *Filinia longiseta* is observed in all treatments. However, population density of this species was already declining at the time of application, and the observed increase is in fact a delayed decline, most probably due to reduced predation. In the control, total numbers of *F. longiseta* on day 18 were 4, 4 and 0 and it was absent as from day 25. At 2 x 3 µg as/L, numbers were 7 and 46 on day 18, and 4 and 2 on day 25. Although significant, the effect on day 25 is not considered crucial for classification of effects. At 2 x 6 µg as/L, a similar reasoning applies. The decrease on *Keratella quadrata* at 2 x 6 µg as/L is considered not to be related to the test substance, because at the same sampling date an increase was observed at 2 x 16 µg as/L and no effects were seen at 2 x 41 and 2 x 109 µg as/L. The unidentified algae species shows an effect at 2 x 6 µg as/L and higher, the increase observed at 2 x 41 and 2 x 109 µg as/L is merely a delayed decline. Considering the extent and duration of effects at the respective treatments, treatment level **2 x 6 µg as/L** is considered as the NOEC. Since there is no evidence of accumulation of residues, the NOEC can be set to **6 µg as/L**. Because dodine concentrations show a relatively fast decline with time (DT_{50} 0.83 days), the study does not allow for the assessment of effects due to chronic exposure, it can, however, be considered for the derivation of the MAC.

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Appendix 4. Detailed sediment toxicity data

Table A4.1. Toxicity of dodine to sediment organisms.

Species	Species properties (age, sex)	Sediment type	A	Test compound	Purity [%]	pH	o.m. [%]	Clay [%]	T [°C]	Exp. time	Criterion	Test endpoint	Result test water [mg/L]	Result std. sediment [mg/kg_{dw}]	Validity	Notes	Reference
Chironomus riparius	larvae,2-3d	OECD	S	dodine	96.2		2.72		20	28 d	NOEC NOEC	emergence development	≥ 3.2 ≥ 3.2		3 3	1,2,3 1,2,3	EC, 2006 (Desmares-Koopmans, 2002)

Notes

1 water spiked
2 endpoint based on nominal initial in water phase, actual initial 72-82% after 20 min.
3 OECD artificial soil, 5% peat (1.6% OC) water:sediment 4:1

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Appendix 6. References used in the appendices

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