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Environmental risk limits for dithianon

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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 dithianon

Dit rapport geeft milieurisicogrenzen voor het fungicide dithianon 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 dithianon. 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). Dithianon 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 pesticides, the evaluation report prepared within the framework of EU Directive 91/414/EC (Draft Assessment Report, DAR) was consulted (EC, 2006; 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}, 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 ($MPC_{hh food, water}$); 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 dithianon

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

3.1.1 Identity

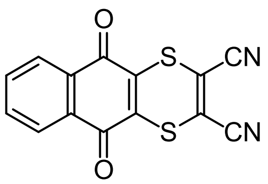

Figure 1. Structural formula of dithianon.

Table 1. Identification of dithianon.

Parameter	Name or number	Source
Common/trivial/other name	dithianon	EC, 2006
Chemical name	5,10-dihydro-5,10-dioxonaphtho[2,3-*b*]-1,4-dithiine-2,3-dicarbonitrile (IUPAC) 5,10-dihydro-5,10-dioxonaphtho[2,3-*b*]-1,4-dithi-in-2,3-dicarbonitrile (CA)	EC, 2006
Molecular formula	$C_{14}H_4N_2O_2S_2$	EC, 2006
CAS number	3347-22-6	EC, 2006
EC number	222-098-6	EC, 2006
SMILES code	N#CC=1S\C3=C(/SC=1C#N)C(=O)c2ccccc2C3=O	
Use class	Fungicide	EC, 2006
Mode of action	Dithianon is a conventional broad-spectrum protectant fungicide. It is a multi-site inhibitor that acts by modification of sulfydryl (SH) groups found in the cysteine residues of many proteins.	EC, 2006
Authorised in NL	Yes	
Annex 1 listing	No	

3.1.2 Physico-chemical properties

Table 2. Physico-chemical properties of dithianon

Parameter	Unit	Value	Remark	Reference
Molecular weight	[g/mol]	296.3		EC
Water solubility	[mg/L]	0.27	pH 5	EC
		0.14	pH 7	
		0.19	pH 9	
		0.31	pH 4	EC, 2006
		0.38	pH 7	
		0.36	pH 9	
pK_a	[-]	n.a.		
log K_{OW}	[-]	3.2	HPLC-method	EC, 2006
		>3.5	Flask-method	
		0.61	BioLoom	Biobyte, 2006
log K_{OC}	[-]	**4.17**	HPLC-method	EC, 2006
Vapour pressure	[Pa]	2.71×10^{-9}		EC, 2006
Melting point	[°C]	215-216		EC, 2006
Boiling point	[°C]	n.a.		EC, 2006
Henry's law constant	[Pa.m^3/mol]	2.97×10^{-6}	calculated using sol. 0.25 mg/L and VP 2.97×10^{-6}	EC, 2006

n.a. = not applicable.

3.1.3 Behaviour in the environment

Selected environmental properties of dithianon are presented in Table 3.

Table 3. Selected environmental properties of dithianon

Parameter	**Unit**	**Value**	**Remark**	**Reference**
Hydrolysis half-life	DT_{50} [d]	10.7	pH 5, 20 °C	EC, 2006
		0.6	pH 7, 20 °C	
		9.8 min	pH 9, 20 °C	
Photolysis half-life	DT_{50} [h]	0.5	pH 4, 20 °C	EC, 2006
Readily biodegradable		No		EC, 2006
Water/sediment systems	DT_{50} [h]	1.4 – 2.4	not detected in sediment; $DT_{50,water} = DT_{50, system}$	EC, 2006
Relevant metabolites	water/sediment systems (dark): CO_2, no major metabolites and many minor metabolites photolysis: phthalic acid, phthaldialdehyde and 1,2-benzenedimethanol			EC, 2006

3.1.4 Bioconcentration and biomagnification

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

Table 4. Overview of bioaccumulation data for dithianon.

Parameter	Unit	Value	Remark	Reference
BCF (fish)	[L/kg]	28		EC, 2006
BMF	[kg/kg]	1	Default value for BCF < 2000	

3.1.5 Human toxicological threshold limits and carcinogenicity

The following risk phrases related to human toxicology are proposed for dithianon in the DAR: R23, R48/22, R22, R41, R43. Dithianon is assigned R22 according to ESIS (http://ecb.jrc.it/esis/; date of search 17 March 2008). The ADI was set at 0.01 mg/kg_{bw}/d, based on the NOAEL of 1.0 mg/kg_{bw}/d from a long-term toxicity/carcinogenicity study in rats, 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. Dithianon: collected properties for comparison to MPC triggers.

Parameter	Value	Unit	Method/Source	Derived at section
Log $K_{p,susp-water}$	3.17	[-]	$K_{OC} \times f_{OC,susp}$ [1]	K_{OC}: 3.1.2
BCF	28	[L/kg]		3.1.4
BMF	1	[kg/kg]		3.1.4
Log K_{OW}	3.2	[-]		3.1.2
R-phrases	R23, R48/22, R22, R41, R43, R50	[-]		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).

- Dithianon has a log $K_{p,\ susp-water} \geq 3$; derivation of $MPC_{sediment}$ is triggered.
- Dithianon has a log $K_{p,\ susp-water} \geq 3$; expression of the MPC_{water} as $MPC_{susp,\ water}$ is required.
- Dithianon has a BCF < 100; assessment of secondary poisoning is not triggered.
- Dithianon has no (proposed) classification on carcinogenicity. Dithianon is assigned R22, but the BCF is < 100 L/kg. Therefore, an MPC_{water} for human health via food (fish) consumption ($MPC_{water,\ hh\ food}$) need not to be derived.
- For Dithianon, 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

Dithianon has a DT_{50} for hydrolysis of 0.6 days at pH 7, 20 °C. The $DT_{50,system}$ in water/sediment studies was 1.4 – 2.4 hours. Due to these characteristics, it appears impossible to maintain test concentrations in aquatic toxicity tests. In all cases where test concentrations were determined, actual concentrations were below the limit of quantification (LOQ) before renewal or at the end of the test period.

In a number of studies, radioactively labelled dithianon was used. If test concentrations were only determined by radioactivity measurements (Liquid Scintillation Counting, LSC), this was not considered adequate because this method does not distinguish between parent and metabolites.

Therefore, only tests that comply with the following criteria were accepted with Ri 2:

- the test should have been performed under renewal or flow-through conditions
- analysis of the test water should have been performed by specific identification methods (HPLC or GC)
- the endpoint should be based on mean measured concentrations, or if the endpoint is based on initial concentrations, initial recovery should have been 80-120% of nominal

Because algae tests can hardly be performed under renewal conditions, Ri 2 was assigned in case of HPLC/GC-measurements and initial recovery of 80-120% of nominal.

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

An overview of the selected freshwater toxicity data for dithianon is given in Table 6. Detailed toxicity data for dithianon are tabulated in Appendix 2. There are no data on toxicity for marine organisms.

Table 6. Dithianon: 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	250[b]	algae	298[d]
crustacea	60	fish	**36**
fish	8.3		
fish	**0.97**[c]		

[a] For detailed information see Appendix 2. Bold values are used for ERL derivation.
[b] preferred endpoint growth rate for *Pseudokirchneriella subcapitata*
[c] lowest endpoint mortality for *Oncorhynchus mykiss*, geometric mean of 2.2 and 0.43 µg/L
[d] preferred endpoint growth rate for *P. subcapitata*

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

3.3.1.2 Mesocosm and field studies

A pond enclosure study with fish and zooplankton was included in the DAR. This study was not considered reliable due to the absence of water analysis. The study is evaluated in Appendix 3.

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

Acute data are available for algae and fish, but not for *Daphnia*. Chronic data are available for algae, *Daphnia* and fish. Fish are the most sensitive group of the organisms tested. It is therefore accepted that the absence of acute data for *Daphnia* is compensated for by the presence of a chronic study, and the $MPC_{eco, water}$ can be derived by applying an assessment factor of 10 to the lowest NOEC. The $MPC_{eco, water}$ is 0.97 / 10 = 0.097 µg/L.

There are no marine toxicity data, the $MPC_{eco, marine}$ cannot be derived.

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

Dithianon has a BCF < 100 L/kg, thus assessment of secondary poisoning is not triggered.

3.3.3 $MPC_{hh food, water}$

Derivation of $MPC_{hh food, water}$ for dithianon is not triggered.

3.3.4 $MPC_{dw, water}$

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

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

The MPC_{water} is set equal to the $MPC_{eco, water}$ of 0.097 µg/L.

Because the log $K_{p\ susp\text{-}water} \geq 3$, the final MPC_{water} has to be recalculated into 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 4.17 (K_{oc} 14791 L/kg) an $f_{OC,susp,Dutch\ standard}$ of 0.1176, the $K_{p,susp\text{-}water,Dutch\ standard}$ is calculated to be 1740 L/kg.

The $MPC_{susp, water}$ is 0.097 x 10^{-3} / (30 × 10^{-6} + (1 / 1740)) = 0.16 mg/kg_{dw} = 160 $\mu g/kg_{dw}$.

3.3.6 MAC_{eco}

3.3.6.1 $MAC_{eco, water}$

In the absence of data for *Daphnia*, the acute base set is not complete. Fish are the most sensitive species group of the organisms tested, and the NOEC for *Daphnia* is higher than the lowest LC_{50}. It is considered justified to derive the $MAC_{eco, water}$ as if the base set were complete. Dithianon has no potential to bioaccumulate (BCF 28 L/kg), and the mode of action is not specific. Although fish are represented in the acute dataset, chronic data indicate that there might be a large difference in sensitivity within this species group. The fish species that is most sensitive on the basis of chronic data (*Oncorhynchus mykiss*) is not represented in the acute dataset. Therefore, an assessment factor of 100 is applied to the lowest LC_{50} of 36 µg/L. The $MAC_{eco, water}$ is 0.36 µg/L.

3.3.6.2 $MAC_{eco,\ marine}$

There are no marine toxicity data, the $MAC_{eco,\ marine}$ cannot be derived.

3.3.7 $SRC_{eco,\ water}$

NOECs are available for four species belonging to algae, *Daphnia* and fish (Table 6). The $SRC_{eco,\ water}$ is calculated as the geometric mean of all available NOECs, and is 19 µg/L.

3.4 Toxicity data and derivation of ERLs for sediment

The log $K_{p,\ susp\text{-}water}$ of dithianon is above the trigger value of 3, therefore, ERLs should be derived 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 0.097 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 $K_{susp\text{-}water}$:

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

Using $K_{p,susp}$ = 1479 L/kg (log $K_{p,\ susp}$ = 3.17), $F\text{air}_{susp}$ = 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 371, and the $MPC_{sediment,\ TGD,\ EqP,\ ww}$ as 0.0313 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 $MPC_{\text{Dutch standard sediment, EqP, dw}}$ = 85 µg/kg$_{dw}$.

3.4.3 Derivation of $SRC_{eco, sediment}$

The $SRC_{eco, sediment}$ is derived by applying the above described equilibrium partitioning method on the (unrounded) $SRC_{eco, water}$. The resulting $SRC_{eco, sediment}$ for Dutch standard sediment is 1.6×10^3 µg/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 dithianon 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 7. Derived MPC, MAC_{eco}, and SRC values for dithianon.

ERL	Unit	MPC	MAC_{eco}	SRC
Water, old	µg/L	0.4[a]	-	-
Water, new[b]	µg/L	0.097	0.36	19
Water, suspended matter	$\mu g/kg_{dw}$	160	-	-
Drinking water[d]	µg/L	0.1	-	-
Marine	µg/L	n.d.[c]	n.d.[c]	-
Sediment	$\mu g/kg_{dw}$	85	-	1.6×10^3

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

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

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Appendix 1. Information on bioconcentration

Species	Species properties	Test substance	Substance purity(%)	Analysed	Test type	Test water	pH	Hardness/ Salinity [g/L]	Temperature [°C]	Exposure time [h]	Exp. concn.	BCF [L/kg_{ww}]	BCF type	Method	Notes	Ri	Reference
Oncorhynchus mykiss	2g	dithianon	90/>98	Y	F					72 (dep. 144)	0.4	26	whole, ww	OECD 305E	1,2,3,4	2	EC, 2006 (Van Dijk 1992)

NOTES

1 analysis by LSC/TLC
2 total radioactive residues (TRR) at start 0.55 and 1.98 µg/L (dithianon equivalents); active substance hardly detectable
3 RA reached plateau after 12-24h
4 BCF based on total TRR

Appendix 2. Detailed aquatic toxicity data

Table A2.1. Acute toxicity of dithianon 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	1.00E+04	Y	S	dithianon	95.1		7.2-8.3	22-24		72 h	EC50	biomass	0.090	2	1,13,14,16	EC, 2006 (Drottar, 2001b)
Pseudokirchneriella subcapitata	1.00E+04	Y	S	dithianon	95.1		7.2-8.3	22-24		72 h	EC50	growth rate	0.298	2	1,13,14,16	EC, 2006 (Drottar, 2001b)
Pseudokirchneriella subcapitata	1.00E+04	Y	S	dithianon	99.2		7.6-9.8	23-24		72 h	EC50	biomass	> 0.140	3	1,9,14,16	EC, 2006 (Toy and Gray, 1993)
Pseudokirchneriella subcapitata	1.00E+04	Y	S	dithianon	99.2		7.6-9.8	23-24		72 h	EC50	growth rate	> 0.140	3	1,9,14,16	EC, 2006 (Toy and Gray, 1993)
Pseudokirchneriella subcapitata	1.00E+04	Y	S	Delan70WG	70		7.4-8.5	24		72 h	EC50	growth rate	0.064	3	1,11,14,16	EC, 2006 (Mitchell, 1996a)
Fungi																
Saccharomyces cerevisiae		N	S	dithianon	a.g.	am	3.2	28		16-18 h	EC20	fermentation	0.020	3	8	Weber, 2000
Crustacea																
Daphnia magna	<24h	Y	S	dithianon	95		8.3	20		48 h	EC50	immobilisation	0.260	3	2,13,14,16	EC, 2006 (Drottar,2001c)
Daphnia magna	<24h	Y	S	dithianon	92		7.9-8.1	20		48 h	EC50	immobilisation	0.610	3	2,20,14,18,19	EC, 2006 (Ellgehausen, 1987)
Daphnia magna	<24h	Y	S	Delan70 WG	70		7.0-7.9	19-21		48 h	EC50	immobilisation	0.110	3	2,9,14,16	EC, 2006 (Mitchell, 1996c)
Pisces																
Lepomis macrochirus	2.5cm; 0.32g	Y	R	dithianon	92		7.5-8.1	21		96 h	LC50	mortality	0.0360	2	3,4,9,14,16	EC, 2006 (Douglas, 1988)
Brachydanio rerio	2.6cm;0.15g	Y	S	dithianon	96.6/99.9		8.2-8.4	23-24		96 h	LC50	mortality	0.0478	3	6,13,15,16	EC, 2006 (Olivieri, 1999)
Carassius auratus	1.00 g	N	S	dithianon	100		7.4	18	44	96	LC50	mortality	0.150	3	8	Mayer and Ellersieck, 1986
Carassius auratus		N	S	dithianon				23		96 h	LC50	mortality	4-5	3	8,18	EC, 2006 (Dense, 1969)
Carassius auratus	2.3cm;0.13g	Y	S	dithianon	96.6/99.9		8.2	23		96 h	LC50	mortality	0.0475	3	6,13,15,16	EC, 2006 (Olivieri, 1999)
Cyprinus carpio	3.1cm;0.38cm	Y	S	dithianon	96.6/99.9		8.1-8.3	22-24		96 h	LC50	mortality	0.0596	3	6,13,15,16	EC, 2006 (Olivieri, 1999)
Gasterosteus aculeatus	2.5cm;0.11g	Y	S	dithianon	96.6/99.9		8.2-8.3	23-24		96 h	LC50	mortality	0.0273	3	6,13,15,16	EC, 2006 (Olivieri, 1999)
Ictalurus punctatus	1.60 g	N	S	dithianon	100		7.4	18	44	96	LC50	mortality	0.130	3	8	Mayer and Ellersieck, 1986
Ictalurus punctatus	2g	N	S	dithianon				23		96 h	LC50	mortality	0.04	3	8,18	EC, 2006 (Dense, 1969)
Ictalurus punctatus	2.2cm;0.07g	Y	S	dithianon	96.6/99.9		8.2-8.5	23-24		96 h	LC50	mortality	0.0143	3	6,13,15,16	EC, 2006 (Olivieri, 1999)
Onchorhynchus mykiss	4g	N	S	dithianon				15		96 h	LC50	mortality	0.07	3	8,18	EC, 2006 (Dense, 1969)
Onchorhynchus mykiss	6.5cm;2.4g	Y	S	dithianon	92		7.8-8.3	15-16		96 h	LC50	mortality	0.044	3	3,10,14,16	EC, 2006 (Ritter, 1987)
Onchorhynchus mykiss	4.2cm;0.8g	Y	S	dithianon	92		7.8-8.4	14-15		96 h	LC50	mortality	0.03-0.054	3	3,12,14,17	EC, 2006 (Wuerthrich, 1991)
Onchorhynchus mykiss		Y	S	Delan70WG	70		7.2-7.8	14-15		96 h	LC50	mortality	0.023	3	3,11,14	EC, 2006 (Mitchell, 1996)
Orizias latipes	2.9cm;0.31g	Y	S	dithianon	96.6/99.9		8.1-8.3	24-25		96 h	LC50	mortality	0.0416	3	6,13,15,16	EC, 2006 (Olivieri, 1999)
Pimephales promelas	0.90 g	N	S	dithianon	100		7.4	18	44	96	LC50	mortality	0.165	3	8	Mayer and Ellersieck, 1986
Pimephales promelas	1.8cm;0.04g	Y	S	dithianon	96.6/99.9		8.0-8.3	23-24		96 h	LC50	mortality	0.0536	3	6,13,15,16	EC, 2006 (Olivieri, 1999)
Poecilia reticulata	2.5cm;0.23g	Y	S	dithianon	96.6/99.9		8.2-8.4	24-25		96 h	LC50	mortality	0.0508	3	6,13,15,16	EC, 2006 (Olivieri, 1999)

NOTES

1 test procedure according to OECD 201
2 test procedure according to OECD 202
3 test procedure according to OECD 203
4 test procedure according to EPA 72-1
5 test procedure according to EPA 72-2
6 test procedure according to EPA 40 CFR 158 (E)
7 based on active substance
8 result based on nominal concentration; actual not measured
9 result based on nominal; measured initial 80-120% of nominal
10 result based on nominal; measured initial <80% of nominal
11 result based on nominal; measured in stock and fortified samples 80-120% of nominal
12 result based on measured initial; initial <80% of nominal
13 result based on measured initial; initial 80-120% of nominal
14 analysis by HPLC/GC
15 analysis by LSC; metabolites may have accounted for (part of) total radioactivity
16 concentrations at test termination were below LOQ
17 test water pre-incubated for 48 h
18 precipitation observed
19 endpoint ca. 3 times above water solubility (0.22 mg/L)
20 result based on nominal; measured initial >120% of nominal

Table A2.2. Chronic toxicity of dithianon 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	1.00E+04	Y	S	dithianon	95.1		7.2-8.3	22-24		72 h	NOEC	biomass	0.250	2	1,9,10,14	EC, 2006 (Drottar, 2001b)
Pseudokirchneriella subcapitata	1.00E+04	Y	S	dithianon	95.1		7.2-8.3	22-24		72 h	NOEC	growth rate	0.250	2	1,9,10,14	EC, 2006 (Drottar, 2001b)
Pseudokirchneriella subcapitata	1.00E+04	Y	S	dithianon	99.2		7.6-9.8	23-24		72 h	NOEC	biomass	≥ 0.140	3	1,6,10,14	EC, 2006 (Toy and Gray, 1993)
Pseudokirchneriella subcapitata	1.00E+04	Y	S	dithianon	99.2		7.6-9.8	23-24		72 h	NOEC	growth rate	≥ 0.140	3	1,6,10,14	EC, 2006 (Toy and Gray, 1993)
Pseudokirchneriella subcapitata	1.00E+04	Y	S	Delan70 WG	70		7.4-8.5	24		72 h	NOEC	growth rate	0.01	3	1,8,10,14	EC, 2006 (Mitchell, 1996a)
Insecta																
Chironomus riparius	1st instar	Y	S	dithianon	95.1-96.6	am	6.4-6.7	20-22		28 d	emergence	NOEC	0.125	3	6,10,11,16	EC, 2006 (Mattock, 2000)
Chironomus riparius	1st instar	Y	S	dithianon	95.1-96.6	am	6.4-6.7	20-22		28 d	development	NOEC	0.250	3	6,10,11,16	EC, 2006 (Mattock, 2000)
Crustacea																
Daphnia magna	<24h	Y	R	dithianon	95.1	rw	8.2	19-21		21 d	mortality F0	NOEC	0.06	2	2,6,10,14	EC, 2006 (Dohmen, 2002)
Daphnia magna	<24h	Y	R	dithianon	95	rw	8.2	20		21 d	reproduction	NOEC	>0,24	2	2,6,10,14	EC, 2006 (Dohmen, 2002)
Daphnia magna	<24h	Y	R	dithianon	91.6	rw/nw	7.9-8.8	19-20		21 d	immobilisation F0	NOEC	0.100	3	5,7,10	EC, 2006 (Wuethrich, 1991d)
Daphnia magna	<24h	Y	R	dithianon	91.6	rw/nw	7.9-8.8	19-20		21 d	reproduction	NOEC	0.100	3	5,7,10	EC, 2006 (Wuethrich, 1991d)
Pisces																
Gasterosteus aculeatus	3.3cm;0.42g	Y	R	dithianon	95.5-97.4	7.2-8.4	17-18			28 d	mortality	NOEC	0.0083	2	3,10,11,13	EC, 2006 (Drottar, 2001a)
Onchorhynchus mykiss	juveniles;2.5cm;0.14g	Y	R	dithianon	94.7-95.1		7.6-8.2	12		79 d	mortality	NOEC	0.0039	2	9,10,11,12	EC, 2006 (Drottar, 1999)
Onchorhynchus mykiss	embryo, <3h	Y	R	dithianon	95.1		7.8-8.4	14-16		90 d	growth	NOEC	0.0047	2	4,9,10,14	EC, 2006 (Drottar, 2000)
Onchorhynchus mykiss	embryo, <3h	Y	R	dithianon	95.1		7.8-8.4	14-16		90 d	mortality	NOEC	0.0047	2	4,9,10,14	EC, 2006 (Drottar, 2000)
Onchorhynchus mykiss	4.7cm;1.1g	Y	R	Delan70 WG	70		7.7-8.3	14-16		28 d	growth	NOEC	0.0022	2	9,10,14	EC, 2006 (Drottar et al., 1999)
Onchorhynchus mykiss	4.7cm;1.1g	Y	R	Delan70 WG	70		7.7-8.3	14-16		28 d	mortality	NOEC	0.0022	2	9,10,14	EC, 2006 (Drottar et al., 1999)
Onchorhynchus mykiss	4.8cm	Y	F	Delan70 WG	70		8.1-8.4	14-15		28 d	growth	NOEC	<0.00043	2	3,10,15	EC, 2006 (Drottar et al., 2000)
Onchorhynchus mykiss	4.8cm	Y	F	Delan70 WG	70		8.1-8.4	14-15		28 d	mortality	NOEC	0.00043	2	3,10,15	EC, 2006 (Drottar et al., 2000)
Onchorhynchus mykiss	5.7cm;1.8g	Y	F	dithianon	91.6		7.8-8.1	14-16		21 d	mortality	NOEC	0.011	3	3,7,10	EC, 2006 (Wuerthrich, 1991b0
Onchorhynchus mykiss	5.7cm;1.8g	Y	F	dithianon	91.6		7.8-8.1	14-16		21 d	growth	NOEC	0.011	3	3,7,10	EC, 2006 (Wuerthrich, 1991b0
Onchorhynchus mykiss	4.8cm;1.2g	Y	F	dithianon	91.6		6.3-6.8	14-16		21 d	mortality	NOEC	0.0025	3	3,7,10	EC, 2006 (Wuerthrich, 1991c)
Onchorhynchus mykiss	4.8cm;1.2g	Y	F	dithianon	91.6		6.3-6.8	14-16		21 d	growth	NOEC	0.0025	3	3,7,10	EC, 2006 (Wuerthrich, 1991c)

NOTES

1 test procedure according to OECD 201
2 test procedure according to OECD 211
3 test procedure according to OECD 215/204
4 test procedure according to EPA 72-4
5 test procedure according to OECD 202
6 result based on nominal; measured initial 80-120% of nominal
7 result based on nominal; measured initial <80% of nominal
8 result based on nominal; measured in stock and fortified samples 80-120% of nominal
9 result based on measured initial; initial 80-120% of nominal
10 analysis by HPLC/GC
11 sediment added
12 concentrations at renewal were 30-50% of nominal; concentrations at test end were < 0.2 µg/L
13 result based on measured initial; daily average 59-96% of nominal
14 concentrations in old solutions/at test end were below LOQ
15 results based on measured concentrations; 29-54% of nominal
16 concentrations after 28 days 13-20% of nominal in water

Appendix 3. Description of mesocosm studies

A pond enclosure study with fish and zooplankton is included in the DAR, an unchanged copy of the summary is given below. Based on mortality of fish, the NOEC is reported as 4.3 µg as/L, the LC_{50} as 13-43 µg as/L. These concentrations refer to nominal concentrations after single application of 43 g as/ha, calculated assuming mixing over 1 m depth.

Evaluation of the scientific reliability of the mesocosm study
Criteria for a suitable (semi)field study:

1. Does the test system represent a realistic freshwater community? No, fish, zooplankton and macrophytes were present, but macro-invertebrates were not included.
2. Is the description of the experimental set-up adequate and unambiguous? Yes.
3. Is the exposure regime adequately described? No. The test compound was sprayed twice, and nominal concentrations are calculated based on one application and assuming complete mixing over 1 m depth. Chemical analyses were, however, not performed.
4. Are the investigated endpoints sensitive and in accordance with the working mechanism of the compound? Yes. Dithianon is a fungicide, fish are shown to be the most sensitive species group in acute and chronic laboratory tests.
5. Is it possible to evaluate the results statistically? No, descriptive statistics are reported to have been applied, but results are not presented as such.

These criteria result in an overall assessment of the study reliability. The study is considered to be not reliable due to the lack of chemical analyses (Ri 3).

Toy R. 1993. Dithianon: The effects of Delan 500 g/L SC (DF07459) on *Oncorhynchus mykiss* and zooplankton in enclosures within ponds.

Sittingbourne Research Centre; Kent ME9 8AG; United Kingdom, unpublished, BASF DocID DT-560-050

Guidelines:	<none>
GLP:	No, studies were conducted prior to the implementation of GLP but are scientifically valid
Validity:	Acceptable

Material and methods:

Test item:	Delan 500 g/L SC (BAS 216 05 F), batch no. Ht 10/91/1, content of a.s.: Dithianon (BAS 216 F) 500 g/L (nominal).
Test species:	Rainbow trout (*Oncorhynchus mykiss* WALBAUM 1792), mean body length 6.1 (5.4 - 6.6) cm, mean body weight 2.2 (1.6 - 2.7) g; animal supplier: Zeals Trout Farm, Wolverton, Wiltshire, UK. Zooplankton, naturally occurring populations of Cladocera (*Daphnia*, *Cyclops*, *Diaptomus* etc.) from Grigg Farm, Headcorn, Kent, UK.
Test system:	Outdoor mesocosm site consisting of 15 steel enclosures set into a pond (12 m x 5 m x 1.4 m, 0.98 m diameter), 6 enclosures with a water depth of 1.1 m (fish test), 9 with a water depth of 0.97 m (zooplankton test). The mesocosm site was located within Grigg Farm, Headcorn, Kent. The enclosures were largely embedded in the ground. The bottom was covered by a mature pond sediment. The deep-water area of the

ponds (in which the enclosures were placed) contained *Potamogeton* spp. and filamentous algae. The leaves of *Potamogeton* were mostly submersed so the surface of the water in the enclosures was largely clear of plants.

Test design: Fish-test: 2 applications, 2 controls, 1 replicate per treatment. Spraying interval 7 days. 10 fish per enclosure; new fish were added to enclosures in which all fish had died. Daily assessment of mortality and sublethal effects. Test termination after 14 days.

Zooplankton-test: 1 application, 3 controls, 3 replicates per treatment. Assessment of zooplankton population density on day -1, 0, 1, 3 and 7 after treatment. Test termination after 7 days.

Endpoints: Biological endpoints: mortality and sublethal effects on fish, population density of zooplankton.

Test concentrations: Fish test: 1st application: control, 4.3, 13.0, 43.0 and 130 µg a.s./L (based on over spray of 1 m deep water body this would correlate to application rates of 43, 130, 430 and 1300 g a.s./ha).

2nd application: control, 43, 130 and 430 g a.s./ha.

Zooplankton test: control, 130 and 1300 g a.s./ha (corresponding to 13 and 130 µg a.s./L)

The test item was sprayed from a height of 10 - 15 cm onto the water in the enclosures by using a hand-held DeVilbiss sprayer.

Test conditions: Fish test: temperature: 12 °C - 21 °C, pH 7.3 - 8.0, dissolved oxygen: 37% - 81%.

Zooplankton study: temperature: 12 °C - 20 °C, pH 7.6 - 8.0, dissolved oxygen: 43% - 98%.

Analytics: none

Statistics: Descriptive statistics.

Findings:

Fish:

Ten rainbow trout were added to each enclosure prior first application to the system. A second application was made seven days after the first application and observations of fish survival were made for an additional seven days for a total test period of 14 days. In the enclosure where there was 100% mortality, new fish were added at various intervals to evaluate the persistence of toxicity. No mortality of fish was observed in the control and the lowest test item rate (4.3 µg a.s./L). There was 100% mortality of rainbow trout at the two highest levels of 43 and 130 µg a.s./L. In the 130 µg a.s./L treatment, all fish added 4 days after the first application died, while one fish died when rainbow trout were added 5 days after the first application. In the 43 µg a.s./L treatment, the water remained acutely toxic for 2 days after the first application. In the 13 µg a.s./L treatment, three fish died after the first treatment. When a second application of 13 µg a.s./L was made, additional four fish died. The remaining fish (three) survived for the complete 14 day observation period. In the 4.3 µg a.s./L treatment, there were no mortalities after both the first and second treatments. Thus, the NOEC after 2 applications under field conditions was 4.3 µg a.s./L, the LOEC was 13 µg a.s./L.

Zooplankton:

Taxa initially appeared sufficiently abundant to warrant counting their abundance: Cladocera, *Diaptomus* spp, *Cyclops* and copepodites, juveniles of *Diaptomus* and *Cyclops*. None of the taxa show significant changes in population density when compared to the control. Only *Diaptomus* spp. proved too scarce to determine whether or not there was a change in population.

Conclusion:

The results of the study show likely effects following direct over spray of a 1 m deep waterbody during a commercial application of the test item. Such over spray would be unlikely to affect zooplankton populations but would be toxic to fish. If the water body was static, it would be likely to remain toxic for several days after over-spray. The NOEC for rainbow trout was determined to be 4.3 µg a.s./L, the LC50 was 13 – 43 µg a.s./L. The zooplankton NOEC was determined to be 130 µg a.s./L, the EC50 was > 130 µg a.s./L.

Appendix 6. References used in the appendices

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