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J.W.A. Scheepmaker | J.W. Vonk

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J.W. Vonk

Contact:
J.W.A. Scheepmaker
Expertise Centre for Substances
Jacqueline.scheepmaker@rivm.nl

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 metsulfuron-methyl

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

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# 1 Introduction

## 1.1 Background and scope of the report

In this report, environmental risk limits (ERLs) for surface water (freshwater and marine) are derived for the herbicide metsulfuron-methyl. The derivation is performed within the framework of the project 'Standard setting for other relevant substances within the WFD', which is closely related to the project 'International and national environmental quality standards for substances in the Netherlands' (INS). Metsulfuron-methyl is part of a series of 25 pesticides that appeared to have a high environmental impact on 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, 2000; 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 Appendices to this report. These tables contain information on species characteristics, test conditions and endpoints. Explanatory notes are included with respect to the assignment of the reliability indices.

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

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

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

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

## 2.3 Derivation of ERLs

For a detailed description of the procedure for derivation of the ERLs, reference is made to the INS-Guidance. With respect to the selection of the final $MPC_{water}$, 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 ($MPC_{hh\ food,\ water}$); the need for derivation of the latter two is dependent on the characteristics of the compound.

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

# 3 Derivation of environmental risk limits for metsulfuron-methyl

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

### 3.1.1 Identity

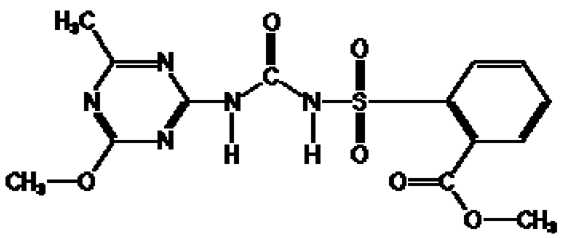

Figure 1. Structural formula of metsulfuron-methyl.

Table 1. Identification of metsulfuron-methyl.

| Parameter | Name or number | Source |
|---|---|---|
| Common/trivial/other name | Metsulfuron-methyl | EC, 2000 |
| Chemical name | Methyl 2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)benzoate | EC, 2000 |
| CAS number | 74223-64-6 | EC, 2000 |
| EC number | - | |
| SMILES code | COC(=O)c1ccccc1S(=O)(=O)NC(=O)Nc2nc(OC)nc(C)n2 | U.S. EPA, 2007 |
| Use class | Herbicide | |
| Mode of action | Acetolactate synthase inhibitor | Tomlin, 2002 |
| Authorised in NL | Yes | |
| Annex I listing | Yes | |

### 3.1.2 Physico-chemical properties

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

| Parameter | Unit | Value | Remark | Reference |
|---|---|---|---|---|
| Molecular weight | [g/mol] | 381.4 | | EC, 2000 |
| Water solubility | [g/L] | 2.79 | pH 7, 25 ºC; at pH 5: 0.548 | EC, 2000 |
| p$K_a$ | [-] | 3.75 | | EC, 2000 |
| log $K_{OW}$ | [-] | -1.7 | pH 7, 25 ºC | EC, 2000 |
| log $K_{OC}$ | [-] | 1.60 | | EC, 2000 |
| Vapour pressure | [Pa] | 1.1 x $10^{-10}$ | 20 ºC | EC, 2000 |
| Melting point | [°C] | 162 | | EC, 2000 |
| Boiling point | [°C] | n.a. | | EC, 2000 |
| Henry's law constant | [Pa.$m^3$/mol] | 4.5 x $10^{-11}$ | pH 7 | EC, 2000. |

n.a. = not applicable.

### 3.1.3 Behaviour in the environment

Table 3. Selected environmental properties of metsulfuron-methyl.

| Parameter | Unit | Value | Remark | Reference |
|---|---|---|---|---|
| Hydrolysis half-life | DT50 [d] | > 30 | pH 7; at pH 5: 22 d at 25 ºC | EC, 2000 |
| Photolysis half-life | DT50 [d] | No photolysis | | EC, 2000 |
| Readily biodegradable | | No | | EC, 2000 |
| Degradation in water/sediment systems | DT50 (system) [d] | 105 - 175 | | EC, 2000 |
| Relevant metabolites | | Bis-O-demethyl metsulfuron-methyl | 25% in water after 91 d (maximum) | EC, 2000 |

### 3.1.4 Bioconcentration and biomagnification

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

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

| Parameter | Unit | Value | Remark | Reference |
|---|---|---|---|---|
| BCF (fish) | [L/kg] | < 1 | Experimentally determined | EC, 2000 |
| | | 0.007 | Calculated from log $BCF_{fish}$ = 0.85 x log $K_{ow}$ – 0.70 | Veith et al. (1979) |
| BMF | [kg/kg] | 1 | Default value for BCF < 2000 | |

### 3.1.5 Human toxicological threshold limits and carcinogenicity

No toxicological R phrases are assigned. The substance is not carcinogenic or mutagenic and has no effects on reproduction. The human health protection assessment is not triggered (Draft Assessment Report, European Commission, 1997).

## 3.2 Trigger values

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

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

| Parameter | Value | Unit | Method/Source | Derived at section |
|---|---|---|---|---|
| Log $K_{p,susp-water}$ | 0.60 | [-] | $K_{OC} \times f_{OC,susp}$[1] | $K_{OC}$: 3.1.2 |
| BCF | 0.007 | [L/kg] | | 3.1.4 |
| BMF | 1 (default) | [kg/kg] | | 3.1.4 |
| Log $K_{OW}$ | -1.7 | [-] | | 3.1.2 |
| R-phrases | - | [-] | | 3.1.5 |
| A1 value | 1.0 | [µg/L] | Total pesticides | |
| DW standard | 0.1 | [µg/L] | Generic value for organic pesticides | |

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

- Metsulfuron-methyl has a log $K_{p,\ susp-water}$ < 3; derivation of $MPC_{sediment}$ is not triggered.
- Metsulfuron-methyl has a BCF < 100 L/kg; assessment of secondary poisoning is not triggered.
- Metsulfuron-methyl has no toxicological R classification. Therefore, the derivation of an $MPC_{water}$ for human health via food (fish) consumption ($MPC_{hh\ food,\ water}$) is not required.
- For metsulfuron-methyl no specific A1 value or Drinking Water Standard are 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 $MPC_{water,\ eco}$ and $MPC_{marine,\ eco}$

An overview of the selected aquatic toxicity data for metsulfuron-methyl is given in Table 6 for freshwater and in Table 7 for the marine environment. Detailed aquatic toxicity data for metsulfuron-methyl are tabulated in Appendix 2.
For the aquatic macrophyte *Lemna minor* the chronic (7/14 d) $EC_{50}$ can be used as a virtual acute $EC_{50}$-value because of the theoretically logarithmic growth rate of the fonts. The value is useful for the derivation of the $MAC_{eco}$ (see 3.3.6.1).

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

| **Chronic**[a] | | **Acute**[a] | |
|---|---|---|---|
| **Taxonomic group** | **NOEC/EC10 (µg/L)** | **Taxonomic group** | **L(E)C50 (µg/L)** |
| Algae | 87.3 [b] | Cyanobacteria | 49.6 |
| Macrophyta | 54 | Cyanobacteria | 2.3 |
| Macrophyta | 0.287 [c] | Algae | 800 |
| Macrophyta | **0.10** | Algae | 1030 |
| Crustacea | >150000 [d] | Algae | 9150 |
| Pisces | 68000 | Algae | 55700 |
| | | Algae | 28200 |
| | | Algae | 122000 |
| | | Algae | 48400 |
| | | Algae | 267 |
| | | Algae | 153 |
| | | Algae | 2780 |
| | | Algae | 1190 [e] |
| | | Algae | 5720 |
| | | Algae | 191 |
| | | Algae | 24410 |
| | | Algae | 24700 |
| | | Macrophyta | 0.718 [f] |
| | | Macrophyta | 10 |
| | | Macrophyta | **0.3** |
| | | Macrophyta | 1 |
| | | Crustacea | > 150000 [g] |
| | | Pisces | > 150000 [g] |

[a] For detailed information see Appendix 2. Bold values are used for ERL derivation.
[b] Geometric mean of 0.29, 0.50, 0.04 and 0.01 mg/L for *Pseudokirchneriella subcapitata* (growth rate).
[c] Geometric mean of 0.00037, 0.00011, 0.00030, 0.0015, 0.00019 and 0.00016 mg/L for *Lemna minor* (growth rate).
[d] This value completes the base set but is not used for further calculations.
[e] Geometric mean of 2.9, 0.85 and 0.68 mg/L for *Pseudokirchneriella subcapitata* (growth rate).
[f] Geometric mean of chronic EC50 values: 0.00079, 0.0004, 0.00031, 0.00088, 0.0048, 0.00043, 0.0011 and 0.00036 mg/L for *Lemna minor* (growth rate).
[g] These figures show the absence of toxicity to Crustacea (*Daphnia*) and fish, but are not used for further calculations.

Table 7. Metsulfuron-methyl: selected marine toxicity data for ERL derivation.

| Chronic | | Acute [a] | |
|---|---|---|---|
| Taxonomic group | NOEC/EC10 (mg/L) | Taxonomic group | L(E)C50 (mg/L) |
| | | Cyanobacteria | 7.63 |
| | | Cyanobacteria | 0.0343 |
| | | Algae | 21.0 |
| | | Algae | 20.6 |
| | | Algae | 16.8 |
| | | Algae | 5.34 |
| | | Algae | 9.15 |
| | | Algae | 1.53 |
| | | Algae | 25.2 |
| | | Algae | 0.381 |
| | | Algae | 38.5 |
| | | Algae | 139 |
| | | Algae | 0.305 |
| | | Algae | 8.01 |
| | | Algae | 175 |
| | | Algae | 1.53 |
| | | Algae | 215 |

[a] For detailed information see Appendix 2.

#### 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 metsulfuron-methyl, such a comparison cannot be made and datasets are kept separated.

#### 3.3.1.2 Mesocosm and field studies

Studies have been carried out with enclosures in natural and artificial water bodies. Details are given in Appendix 3. In one study actual concentrations during the exposure period not were determined. This makes the study not sufficiently reliable for MPC derivation. It should be remarked, however that distinct effects on Macrophyta were present already in the lowest tested concentration (1 µg/L). In a second study no Macrophyta were included. At the lowest concentration tested (10 µg/L) distinct effects were observed on Cyanophyta. The NOEC was < 10 µg/L. The study could therefore not be used for the derivation of ERLs.

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

The base set for freshwater organisms is complete. Chronic NOEC values are available for three trophic levels (fish, *Daphnia*, algae and Macrophyta). Therefore, the assessment factor is 10. The lowest available NOEC is that obtained with *Elodea nuttallii*: 0.10 µg/L. The $MPC_{eco,\ water}$ is derived as 0.10/10 = 0.01 µg/L.

Because the basis set for marine organisms is not complete the $MPC_{eco,\ marine}$ cannot be derived.

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

Metsulfuron-methyl 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 metsulfuron-methyl is not required (Table 5).

### 3.3.4 $MPC_{dw,\ water}$

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

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

The lowest value of the routes included is the $MPC_{eco,\ water}$. Therefore, the $MPC_{water}$ is 0.010 µg/L.

The $MPC_{marine}$ cannot be derived.

### 3.3.6 $MAC_{eco}$

#### 3.3.6.1 $MAC_{eco,\ water}$

The $MAC_{eco,\ water}$ is derived from the acute toxicity data. Since short-term values for three trophic levels (fish, *Daphnia*, Macrophyta and algae) are available and because:

- there is no potential to bioaccumulate,
- the mode of action is known and specific and
- the potentially most sensitive species group (Macrophyta) is included in the data set,

an assessment factor of 10 is applied to the lowest $EC_{50}$ of 0.3 µg/L (*Elodea nutallii*). Therefore, the $MAC_{eco}$ is derived as 0.3 /10 = 0.03 µg/L.

#### 3.3.6.2 $MAC_{eco,\ marine}$

Because not sufficient data on marine organisms are available (the marine base set is not complete) the $MAC_{eco,\ marine}$ cannot be derived.

### 3.3.7 $SRC_{eco,\ water}$

Since more than three long-term NOECs of all required trophic levels are available, the $SRC_{eco,\ water}$ is derived from the geometric mean of all available NOECs with an assessment factor 1. The geometric mean is 24.7 µg/L. Therefore, the $SRC_{eco,\ water}$ is derived as 24.7/1 = 24.7 µg/L.

## 3.4 Toxicity data and derivation of ERLs for sediment

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

# 4 Conclusions

In this report, the risk limits Maximum Permissible Concentration (MPC), Maximum Acceptable Concentration for ecosystems ($MAC_{eco}$), and Serious Risk Concentration for ecosystems ($SRC_{eco}$) are derived for metsulfuron-methyl in water. No risk limits were derived for the marine compartment because not enough data were available. Derivation of ERLs for sediment is not triggered.

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

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

| ERL | Unit | MPC | $MAC_{eco}$ | SRC |
|---|---|---|---|---|
| Water, old[a] | µg/L | 0.00036 | - | - |
| Water, new[b] | µg/L | 0.010 | 0.03 | 24.7 |
| Drinking water[b] | µg/L | 0.1[d] | - | - |
| Marine | µg/L | n.d.[c] | n.d.[c] | - |

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 [mg/L] | Exp. time [d] | Temp. [°C] | Exp. concn. | BCF [L/kg$_{w.w.}$] | BCF type | Method | Validity | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Lepomis macrochirus* | 2-3 g, 4-5 cm | [14C-phenyl]metsulfuron-methyl | > 98 | Y | F | nw | 7.2-7.7 | 102 | 28+14 d | 23±1 | 10 µg/L | < 1 | Muscle | Equili-brium | 2 | DAR, Han and Anderson, 1982 |
| *Lepomis macrochirus* | 2-3 g, 4-5 cm | [14C-phenyl]metsulfuron-methyl | > 98 | Y | F | nw | 7.2-7.7 | 102 | 28+14 d | 23±1 | 1118 µg/L | < 1 | Muscle | Equili-brium | 2 | DAR, Han and Anderson, 1982 |

# Appendix 2. Detailed aquatic toxicity data

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

| Species | Species properties | A | Test type | Test compound | Purity [%] | Test water | pH | T [°C] | Hardness $CaCO_3$ [mg/L] | Exp. time | Criterion | Test endpoint | Value [mg/L] | Ri | Notes | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Cyanobacteria** | | | | | | | | | | | | | | | | |
| *Anabaena flos-aquae* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | < 0.00038 | 2 | 5 | Nyström et al., 1999 |
| *Anabaena flos-aquae* | | Y | S | a.i. | | am | | | | 120 h | EC50 | | 0.0954 | 4 | | DAR, Evaluation Table, 1999 |
| *Phormidium luridum* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 0.0496 | 2 | 5 | Nyström et al., 1999 |
| *Synechococcus leopoliensis* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 0.0023 | 2 | 5 | Nyström et al., 1999 |
| **Algae** | | | | | | | | | | | | | | | | |
| *Asterionella formosa* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 0.8 | 2 | 5 | Nyström et al., 1999 |
| *Bumilleriopsis filiformis* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | > 0.38 | 2 | 5 | Nyström et al., 1999 |
| *Chlamydomonas dysosmos* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 1.03 | 2 | 5 | Nyström et al., 1999 |
| *Chlamydomonas reinhardtii* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 9.15 | 2 | 5 | Nyström et al., 1999 |
| *Chlorella emersonii* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 55.7 | 2 | 5 | Nyström et al., 1999 |
| *Chlorella pyrenoidosa* | 4 x $10^5$ cells/mL | N | S | a.i. | 90 | am | | 25 | | 96 h | EC50 | Biomass | 14.22 | 3 | 9 | Ma, 2002 |
| *Chlorella pyrenoidosa* | 3 x $10^5$ cells/mL | N | S | a.i. | >95 | am | | 20 | | 96 h | EC50 | Biomass | 0.62 | 3 | 9 | Wei et al., 1998 |
| *Cryptomonas pyrenoidifera* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 28.2 | 2 | 5 | Nyström et al., 1999 |
| *Cyclotella cryptica* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 122 | 2 | 5 | Nyström et al., 1999 |
| *Diatoma elongata* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 48.4 | 2 | 5 | Nyström et al., 1999 |
| *Monoraphidium contortum* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 0.267 | 2 | 5 | Nyström et al., 1999 |
| *Monoraphidium pusillum* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 0.153 | 2 | 5 | Nyström et al., 1999 |
| *Pediastrum sp.* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 2.78 | 2 | 5 | Nyström et al., 1999 |
| *Pseudokirchneriella subcapitata* | 1.2 x $10^5$ cells/mL | N | S | a.i. | 99.2 | am | | 24 | | 72 h | EC50 | biomass | 3.5 | 2 | 8, 11 | DAR, Douglas and Handley, 1988a |
| *Pseudokirchneriella subcapitata* | 1.2 x $10^5$ cells/mL | N | S | a.i. | 99.2 | am | | 24 | | 72 h | EC50 | Growth rate | 2.9 | 2 | 8 | DAR, Douglas and Handley, 1988a |
| *Pseudokirchneriella subcapitata* | 3.3 x $10^3$ cells/mL | N | S | a.i. | 99 | am | | 24±1 | | 72 h | NOEC | Growth rate | 0.01 | 2 | | DAR, Frobis (no date) |
| *Pseudokirchneriella subcapitata* | 3.3 x $10^3$ cells/mL | N | S | a.i. | 99 | am | | 24±1 | | 72 h | EC50 | Growth rate | > 0.045 | 2 | | DAR, Frobis (no date) |
| *Pseudokirchneriella subcapitata* | $10^4$ cells/mL | N | S | a.i. | 98.5 | am | | | | 48 h | EC50 | Growth rate | 0.85 | 2 | | Cedergreen et al., 2007 |
| *Pseudokirchneriella subcapitata* | $10^4$ cells/mL | N | S | a.i. | 98.5 | am | 8 | 22 | | 48 h | EC50 | Growth rate | 0.68 | 2 | | Cedergreen and Streibig, 2005 |
| *Pseudokirchneriella subcapitata* | $10^4$ cells/mL | N | S | a.i. | 98.5 | am | 8 | 22 | | 48 h | EC10 | Growth rate | 0.29 | 2 | | Cedergreen and Streibig, 2005 |
| *Pseudokirchneriella subcapitata* | 2 x $10^4$ cells/mL | N | S | a.i. | | am | | 25 | | 96 h | EC50 | Biomass | 0.19 | 2 | 4, 11 | Fairchild et al., 1997 |
| *Pseudokirchneriella subcapitata* | 2 x $10^4$ cells/mL | N | S | a.i. | | am | | 25 | | 96 h | NOEC | Biomass | < 0.019 | 2 | 4 | Fairchild et al., 1997 |
| *Pseudokirchneriella subcapitata* | 10 ng chlorophyll-a/mL | N | S | a.i. | | am | | | | 6 d | NOEC | biomass | 0.04 | 3 | 6 | Nyström and Blanck, 1998 |
| *Pseudokirchneriella subcapitata* | 10 ng chlorophyll-a/mL | N | S | a.i. | | am | | | | 6 d | EC50 | biomass | 1.56 | 3 | 6 | Nyström and Blanck, 1998 |
| *Pseudokirchneriella subcapitata* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 4.96 | 2 | 5, 11 | Nyström et al., 1999 |
| *Raphidocelis subcapitata* | 5 x $10^4$ cells/mL | | | TC product | 90 | am | | 25 | | 96 h | EC50 | Cell biomass | 24.7 | 2 | | Ma et al., 2006 |
| *Raphidonema longiseta* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | < 0.38 | 2 | 5 | Nyström et al., 1999 |
| *Scenedesmus obliquus* | 4 x $10^5$ cells/mL | N | S | a.i. | 90 | am | | 25 | | 96 h | EC50 | Biomass | 72.9 | 3 | 9 | Ma, 2002 |
| *Scenedesmus obtusiusculus* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 5.72 | 2 | 5 | Nyström et al., 1999 |
| *Scenedesmus vacuolatus* | $10^6$ cells/mL | N | S | a.i. | >99 | am | 6.7 | 28 | | 24 h | EC50 | Biomass | 1.2 | 3 | 1 | Fahl et al., 1995 |
| *Scenedesmus vacuolatus* | $10^6$ cells/mL | N | S | a.i. | >99 | am | 6.7 | 28 | | 24 h | EC50 | Growth rate | 0.85 | 3 | 1 | Fahl et al., 1995 |
| *Staurastrum gracile* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 0.191 | 2 | 5 | Nyström et al., 1999 |
| *Stichococcus chloranthus* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7 | 20 | | | EC50 | biomass | 24.41 | 2 | 5 | Nyström et al., 1999 |
| **Crustacea** | | | | | | | | | | | | | | | | |
| *Daphnia magna* | < 48 h old | N | S | a.i. | 92.9 | | 7.4-7.9 | 20.2 | 160 | 48 h | LC50 | Mortality | > 150 | 1 | 7 | DAR, Phillips, 1982a |
| *Daphnia magna* | < 48 h old | Y | S | Ally 20 DF | 20 | nw | 7.2-7.6 | 20.2-20.5 | 77 | 48 h | EC50 | Immobility | > 200 | 2 | | DAR, Hutton, 1989 |
| **Macrophyta** | | | | | | | | | | | | | | | | |
| *Batrachium trichophyllum* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Growth rate (biomass) | > 0.1 | 2 | | Cedergreen et al., 2004 |
| *Batrachium trichophyllum* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Reduction of Specific Leaf Area | 0.00007 | 3 | 3 | Cedergreen et al., 2004 |
| *Batrachium trichophyllum* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Growth rate (biomass) | > 0.1 | 2 | | Cedergreen et al., 2004 |

| Species | Species properties | A | Test type | Test compound | Purity [%] | Test water | pH | T [°C] | Hardness $CaCO_3$ [mg/L] | Exp. time | Criterion | Test endpoint | Value [mg/L] | Ri | Notes | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Batrachium trichophyllum* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Reduction of Specific Leaf Area | 0.00007 | 3 | 3 | Cedergreen et al., 2004 |
| *Berula erecta* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Growth rate (biomass) | > 0.1 | 2 | | Cedergreen et al., 2004 |
| *Berula erecta* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Reduction of Specific Leaf Area | 0.0039 | 3 | 3 | Cedergreen et al., 2004 |
| *Callitriche platycarpa* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Growth rate (biomass) | > 0.1 | 2 | | Cedergreen et al., 2004 |
| *Ceratophyllum demersum* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Growth rate (biomass) | > 0.1 | 2 | | Cedergreen et al., 2004 |
| *Ceratophyllum demersum* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Reduction of Specific Leaf Area | 0.0002 | 3 | 3 | Cedergreen et al., 2004 |
| *Ceratophyllum submersum* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Growth rate (biomass) | > 0.1 | 2 | | Cedergreen et al., 2004 |
| *Ceratophyllum submersum* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Reduction of Specific Leaf Area | 0.0022 | 3 | 3 | Cedergreen et al., 2004 |
| *Elodea canadensis* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Growth rate (biomass) | > 0.1 | 2 | | Cedergreen et al., 2004 |
| *Elodea canadensis* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Reduction of Specific Leaf Area | 0.00057 | 3 | 3 | Cedergreen et al., 2004 |
| *Elodea nutallii* | | Y | S | a.i. | 99 | am | 9-10.2 | 22 | | 21 d | EC50 | Total length of shoots | 0.0003 | 2 | 12 | Dorsman, 2007 |
| *Lemna minor* | | N | S | a.i. | 98.5 | am | 5 | 24 | | 7 d | EC10 | Growth rate | 0.00037 | 2 | | Cedergreen and Streibig, 2005 |
| *Lemna minor* | | N | S | a.i. | 98.5 | am | 5 | 24 | | 7 d | EC50 | Growth rate | 0.00079 | 2 | | Cedergreen and Streibig, 2005 |
| *Lemna minor* | | N | S | a.i. | 98.5 | am | 5 | 24 | | 7 d | EC50 | Growth rate | 0.0004 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | a.i. | tg | am | | 24 | | 7 d | EC50 | Growth rate | 0.00031 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | a.i. | tg | am | | 24 | | 7 d | EC10 | Growth rate | 0.00011 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | a.i. | tg | am | | 24 | | 7 d | EC50 | Growth rate | 0.00088 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | a.i. | tg | am | | 24 | | 7 d | EC10 | Growth rate | 0.0003 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | a.i. | tg | am | | 24 | | 7 d | EC50 | Growth rate | 0.0048 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | a.i. | tg | am | | 24 | | 7 d | EC10 | Growth rate | 0.0015 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | a.i. | tg | am | | 24 | | 7 d | EC50 | Growth rate | 0.00043 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | a.i. | tg | am | | 24 | | 7 d | EC10 | Growth rate | 0.00019 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | Y | F | a.i. | | am | | 24 | | 14 d | EC50 | Growth rate (biomass) | 0.0008 | 3 | 2 | Cedergreen et al., 2004 |
| *Lemna minor* | | Y | F | a.i. | | am | | 24 | | 14 d | EC50 | Growth rate (biomass) | 0.0011 | 2 | | Cedergreen et al., 2004 |
| *Lemna minor* | | Y | F | a.i. | | am | | 24 | | 14 d | EC50 | Reduction of Specific Leaf Area | 0.00018 | 3 | 3 | Cedergreen et al., 2004 |
| *Lemna minor* | | Y | F | a.i. | | am | | 24 | | 14 d | EC50 | Reduction of Specific Leaf Area | 0.0001 | 3 | 3 | Cedergreen et al., 2004 |
| *Lemna minor* | | N | | a.i. | | am | | 25 | | 4 d | EC50 | Biomass (# fronds) | 0.0004 | 3 | 10 | Fairchild et al., 1997 |
| *Lemna minor* | | N | | a.i. | | am | | 25 | | 4 d | NOEC | Biomass (# fronds) | < 0.0002 | 3 | 10 | Fairchild et al., 1997 |
| *Lemna minor* | 2-3 fronds per plant | N | R | a.i. | 99.2 | am | 5 | 21±1 | | 14 d | EC50 | Growth | 0.00036 | 2 | | DAR, Douglas and Handley, 1988b |
| *Lemna minor* | 2-3 fronds per plant | N | R | a.i. | 99.2 | am | 5 | 21±1 | | 14 d | NOEC | Growth | 0.00016 | 2 | | DAR, Douglas and Handley, 1988b |
| *Lemna trisulca* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Growth rate (biomass) | 0.01 | 2 | | Cedergreen et al., 2004 |
| *Lemna trisulca* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Reduction of Specific Leaf Area | 0.00062 | 3 | 3 | Cedergreen et al., 2004 |
| *Myriophyllum spicatum* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Growth rate (biomass) | > 1 | 2 | | Cedergreen et al., 2004 |
| *Myriophyllum spicatum* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Reduction of Specific Leaf Area | 0.00029 | 3 | 3 | Cedergreen et al., 2004 |
| *Potamogeton cripus* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Growth rate (biomass) | > 0.1 | 2 | | Cedergreen et al., 2004 |
| *Potamogeton cripus* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Reduction of Specific Leaf Area | 0.00023 | 3 | 3 | Cedergreen et al., 2004 |
| *Sparganium emersum* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Growth rate (biomass) | > 0.1 | 2 | | Cedergreen et al., 2004 |
| *Spirodela polyrrhiza* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Growth rate (biomass) | > 1 | 2 | | Cedergreen et al., 2004 |
| *Spirodela polyrrhiza* | Collected from wild | Y | F | a.i. | | am | 8.5 | 15-18 | | 14 d | EC50 | Reduction of Specific Leaf Area | 0.00019 | 3 | 3 | Cedergreen et al., 2004 |
| **Pisces** | | | | | | | | | | | | | | | | |
| *Lepomis macrochirus* | 3.6 cm, av. 0.87 g | N | S | a.i. | 92.9 | nw | 7.2-7.6 | 22.2 | 114 | 96 h | LC50 | Mortality | > 150 | 2 | 7 | DAR, Phillips, 1982b |
| *Lepomis macrochirus* | 3.6 cm, av. 0.87 g | N | S | a.i. | 92.9 | nw | 7.2-7.6 | 22.2 | 114 | 96 h | NOEC | Sublethal effects | ≥ 150 | 2 | 7 | DAR, Phillips, 1982b |

| Species | Species properties | A | Test type | Test compound | Purity [%] | Test water | pH | T [°C] | Hardness $CaCO_3$ [mg/L] | Exp. time | Criterion | Test endpoint | Value [mg/L] | Ri | Notes | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Lepomis macrochirus* | Av. 3.0 cm, av. 0.66 g | Y | S | Ally 20 DF | 20 | nw | 6.9-7.5 | 21.5-22.5 | 77 | 96 h | LC50 | Mortality | > 200 | 2 | | DAR, Hutton, 1988a |
| *Oncorhynchus mykiss* | Av. 2.8 cm, av. 0.17 g | N | S | a.i. | 92.9 | nw | 6.9-7.5 | 12.2 | 110 | 96 h | LC50 | Mortality | > 150 | 2 | 7 | DAR, Muska, 1982 |
| *Oncorhynchus mykiss* | Av. 5.2 cm, av. 2.1 g | Y | S | Ally 20 DF | 20 | nw | 7.1-7.4 | 11.5-11.9 | 79 | 96 h | LC50 | Mortality | > 200 | 2 | | DAR, Phillips, 1988 |

1 Test deviates too much from OECD 201. No continuous light.
2 No proper evaluation. 50% effect at ca. 0.1 mg/L.
3 The test parameter is not suitable for EC50 derivation
4 Biomass measured by fluorescence.
5 The incubation period was not reported. AUGC = Area Under the Growth Curve.
6 The experiment is poorly described and essential data are missing.
7 The test concentrations were not measured but due to the stability of the test compound the data are considered to be valid.
8 The growth rate was lower than usual in these studies, but yet fulfilled the validation criterion.
9 Unusual regression model.
10 Exposure period too short.
11 Value for $EC_{50}$(biomass) not taken for MPC derivation, because growth data are available.
12 Plants planted in clay.
13 Plants planted in agar.

Table A2.2. Acute toxicity of metsulfuron-methyl to marine organisms.

| Species | Species properties | A | Test type | Test compound | Purity [%] | Test water | pH | T [°C] | Salinity [‰] | Exp. time | Criterion | Test endpoint | Value [mg/L] | Ri | Notes | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Cyanobacteria** | | | | | | | | | | | | | | | | |
| *Anacystis montana* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 7.63 | 2 | 1 | Nyström et al., 1999 |
| *Nodularia harveyana* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 0.0343 | 2 | 1 | Nyström et al., 1999 |
| **Algae** | | | | | | | | | | | | | | | | |
| *Amphidinium carterae* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | < 0.00038 | 2 | 1 | Nyström et al., 1999 |
| *Chlorella ovalis* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 21.0 | 2 | 1 | Nyström et al., 1999 |
| *Cryptomonas baltica* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 20.6 | 2 | 1 | Nyström et al., 1999 |
| *Ditylum brightwellii* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 16.8 | 2 | 1 | Nyström et al., 1999 |
| *Dunaliella tertiolecta* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 5.34 | 2 | 1 | Nyström et al., 1999 |
| *Emiliana huxleyi* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 9.15 | 2 | 1 | Nyström et al., 1999 |
| *Isochrysis galbana* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 1.53 | 2 | 1 | Nyström et al., 1999 |
| *Pavlova lutherii* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 25.2 | 2 | 1 | Nyström et al., 1999 |
| *Phaeodactilum tricornutum* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | > 381 | 2 | 1 | Nyström et al., 1999 |
| *Platymonas subcordiformis* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 0.381 | 2 | 1 | Nyström et al., 1999 |
| *Porphyridium aerugineum* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 38.5 | 2 | 1 | Nyström et al., 1999 |
| *Porphyridium cruentum* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 139 | 2 | 1 | Nyström et al., 1999 |
| *Prorocentrum minimum* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 0.305 | 2 | 1 | Nyström et al., 1999 |
| *Rhodella sp.* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | > 381 | 2 | 1 | Nyström et al., 1999 |
| *Rhodomonas lens* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 8.01 | 2 | 1 | Nyström et al., 1999 |
| *Skeletonema costatum* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 175 | 2 | 1 | Nyström et al., 1999 |
| *Skeletonema costatum* | | Y | S | a.i. | | am | | | | 120 h | EC50 | | 0.0936 | 4 | | DAR, Evaluation Table |
| *Tetraselmis sp.* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 1.53 | 2 | 1 | Nyström et al., 1999 |
| *Thalassiosira pseudonana* | 10 ng chlorophyll-a/mL | N | S | Ally | 20 | am | 7.0 | 20 | 26 | | EC50 | Biomass | 215 | 2 | 1 | Nyström et al., 1999 |

1 The incubation period was not reported.

Table A2.3. Chronic toxicity of metsulfuron-methyl to freshwater organisms.

| Species | Species properties | A | Test type | Test compound | Purity [%] | Test water | pH | T [°C] | Hardness CaCO3 [mg /L] | Exp. time | Criterion | Test endpoint | Value [mg/L] | Ri | Notes | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Algae** | | | | | | | | | | | | | | | | |
| *Pseudokirchneriella subcapitata* | $10^4$ cells/mL | N | S | A.i. | 98.5 | am | 8 | 22 | | 48 h | EC10 | Growth rate | 0.29 | 2 | | Cedergreen and Streibig, 2005 |
| *Pseudokirchneriella subcapitata* | 2 x $10^4$ cells/mL | N | S | A.i. | | am | | 25 | | 96 h | NOEC | Biomass | < 0.019 | 2 | 2 | Fairchild et al., 1997 |
| *Pseudokichneriella subcapitata* | 1.2 x $10^5$ cells/mL | N | S | A.i. | 99.2 | am | | 24 | | 120 h | NOEC | Growth rate | 0.50 | 2 | 3 | DAR, Douglas and Handley, 1988a |
| *Pseudokirchneriella subcapitata* | 10 ng chlorophyll-a/mL | N | S | A.i. | | am | | | | 6 d | NOEC | Growth rate | 0.04 | 2 | 2 | Nyström and Blanck, 1998 |
| *Pseudokichneriella subcapitata* | 3.3 x $10^3$ cells/mL | N | S | A.i. | 99 | am | | 24±1 | | 120 h | NOEC | Growth rate | 0.01 | 2 | | DAR, Frobis (no date) |
| **Macrophyta** | | | | | | | | | | | | | | | | |
| *Elodea canadensis* | Collected from wild, 19.5 cm long shoots | Y | S | A.i. | ag | nw | | 22 | | 8 d | NOEC | Shoot length | 0.054 | 2 | 1 | Wendt-Rasch et al., 2003 |
| *Elodea nuttallii* | | Y | S | A.i. | 99 | am | 9-10.2 | 22 | | 21 d | NOEC | Total length of shoots | 0.00010 | 2 | 5 | Dorsman, 2007 |
| *Lemna minor* | | N | S | A.i. | 98.5 | am | 5 | 24 | | 7 d | EC10 | Growth rate | 0.00037 | 2 | | Cedergreen and Streibig, 2005 |
| *Lemna minor* | | N | S | A.i. | tg | am | | 24 | | 7 d | EC10 | Growth rate | 0.00011 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | A.i. | tg | am | | 24 | | 7 d | EC10 | Growth rate | 0.00030 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | A.i. | tg | am | | 24 | | 7 d | EC10 | Growth rate | 0.0015 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | A.i. | tg | am | | 24 | | 7 d | EC10 | Growth rate | 0.00019 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | | A.i. | | am | | 25 | | 4 d | NOEC | Biomass (frond count) | < 0.0002 | 3 | 4 | Fairchild et al., 1997 |
| *Lemna minor* | 2-3 fronds per plant | N | R | A.i. | 99.2 | am | 5 | 21±1 | | 14 d | NOEC | Growth | 0.00016 | 2 | | DAR, Douglas and Handley, 1988b |
| *Lemna minor* | | N | S | A.i. | 98.5 | am | 5 | 24 | | 7 d | EC50 | Growth rate | 0.00079 | 2 | | Cedergreen and Streibig, 2005 |
| *Lemna minor* | | N | S | A.i. | 98.5 | am | 5 | 24 | | 7 d | EC50 | Growth rate | 0.0004 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | A.i. | tg | am | | 24 | | 7 d | EC50 | Growth rate | 0.00031 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | A.i. | tg | am | | 24 | | 7 d | EC50 | Growth rate | 0.00088 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | A.i. | tg | am | | 24 | | 7 d | EC50 | Growth rate | 0.0048 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | N | S | A.i. | tg | am | | 24 | | 7 d | EC50 | Growth rate | 0.00043 | 2 | | Cedergreen et al., 2005 |
| *Lemna minor* | | Y | F | A.i. | | am | | 24 | | 14 d | EC50 | Growth rate (biomass) | 0.0011 | 2 | | Cedergreen et al., 2004 |
| *Lemna minor* | 2-3 fronds per plant | N | R | A.i. | 99.2 | am | 5 | 21±1 | | 14 d | EC50 | Growth | 0.00036 | 2 | | DAR, Douglas and Handley, 1988b |
| **Crustacea** | | | | | | | | | | | | | | | | |
| *Daphnia magna* | < 24 h old | Y | R | A.i. | 98.8 | nw | 7.1-7.7 | 19.9 | 78 | 21 d | NOEC | Reproduction | ≥ 150 | 1 | | DAR, Hutton, 1989 |
| **Pisces** | | | | | | | | | | | | | | | | |
| *Oncorhynchus mykiss* | Av. 4.7 cm, av. 2.52 g | Y | F | A.i. | 98.8 | nw | 7.4-8.7 | 10.9-12.8 | 72 | 21 d | NOEC | Length | 68 | 2 | | DAR, Hutton, 1988b |
| *Oncorhynchus mykiss* | Av. 4.7 cm, av. 2.52 g | Y | F | A.i. | 98.8 | nw | 7.4-8.7 | 10.9-12.8 | 72 | 21 d | LC50 | Mortality | > 150 | 1 | | DAR, Hutton, 1988b |

1 Four apical shoots planted in plastic jars with sediment and placed in 9 L aquaria.
2 Biomass measured by fluorescence.
3 The growth rate was lower than usual in these studies, but yet fulfilled the validation criterion
5 Plants planted in clay
4 Exposure period too short.

# Appendix 3. Enclosure studies

**Wendt-Rasch et al., 2003**

| Species/ Population/ Community | Test method | Test substance | Anal. | Exposure regime | T [ºC] |
|---|---|---|---|---|---|
| Macrophytes<br>Phytoplankton<br>Zooplankton<br>Periphytic algae | 80 L enclosures in artificial pond with natural lake sediment, open to air, precipitation and sunlight | Metsulfuron-methyl, anal. grade | N | Single application, acetone solution mixed through water | Not reported |

| pH | Exp. time | Criterion | Test endpoint | Value [μg/L] | GLP | Validity |
|---|---|---|---|---|---|---|
| 8.5 | 14 d | NOEC | Macrophyte root formation | < 1 | N | 3 |

**Description**
Twenty-four plastic enclosures (height 0.65 m, diam. 0.4 m) were placed in an artificial lake in Sweden. The time of the year was not reported.
Each system enclosed a portion of sediment (natural lake sediment mixed with fine gravel) and 80 L of water. The systems were open to air, precipitation and sunlight. The sediment was macrophyte-free before the experiment started. In each enclosure, 200 g (fresh weight) shoots of *Elodea Canadensis* from a nearby stream were introduced. Metsulfuron-methyl was dissolved in acetone (< 0.009%) and added to the enclosures. Nominal concentrations were: 0, 1, 5 and 20 μg metsulfuron-methyl/L. In some enclosures cypermethrin was also added, but the results of these enclosures are not reported here. The number of replicates per concentration was 3.
Four apical shoots of *Myriophyllum spicatum* and five apical shoots of *E. canadensis* were planted in plastic jars containing natural sediment from a nearby lake. In each enclosure, four jars with *M. spicatum* and five jars with *E. canadensis* were placed 40 cm below the water surface at the beginning of the experiment. At the end of the experiment (day 14), the plants were harvested, the occurrence of roots noted and the dry weight of the shoots determined.
Further parameters investigated were: phytoplankton community (species composition, chlorophyll-a), zooplankton community (rotatoria and nauplii), periphytic algae (species and chlorophyll-a) and physicochemical parameters: pH, conductivity, total N and P.
No macrofauna was included, but macrofauna is known to be insensitive for metsulfuron-methyl.
Results were analysed by multivariate analysis.

**Results**
No influence of metsulfuron-methyl on phytoplankton species and total chlorophyll-a was found. After 14 days the chlorophyll-a content of periphytic algae was enhanced in comparison with the control in all three test item concentrations. A distinct effect was found in the 5 and 20 μg/L enclosures. The species *Tetraspora* sp. and *Apiocysitis* sp. decreased in number by exposure to metsulfuron-methyl. There was no effect on zooplankton.
Effects on macrophytes were most distinct. No significant difference in the dry weight of either *M. spicatum* or *E. canadensis* was found between the control and the metsulfuron-methyl exposed plants. However, no roots were found on the *M. spicatum* plants in any of the exposed enclosures, while all the plants in the control enclosures had developed roots. Similarly, none of the *E. canadensis* plants exposed to 5 or 20 μg/L had developed any roots. In the enclosures exposed to 1 μg/L 43% of the plants had developed a few short roots (< 3 cm), while the rest of the plants in these enclosures lacked roots at the time of harvesting. All *E. canadensis* plants not exposed to the herbicide had developed long roots.

pH had increased after 10 days in all concentrations.

**Conclusion**

Because in the 1 µg/L enclosures serious effects on macrophytes were found the NOEC is < 1 µg metsulfuron-methyl/L.
Since no actual concentrations were measured during the experiment the reliability is low (validity code 3).

**Thompson et al., 1993a, 1993b**

| | |
|---|---|
| Species/ Population/ Community | Phytoplankton, Zooplankton |
| Test method | 90 $m^3$ enclosures including sediment, in mesotrophic boreal lentic lake |
| Test substance | Escort, 60% DF formulation of metsulfuron-methyl |
| Analysis | Y |
| Exposure regime | Single application, sprayed on the surface |
| T [ºC] | 22 |
| pH | 6.7-7.3 |
| Expose time | 77 d |
| Criterion | NOEC |
| Test endpoint | Cyanophyta |
| Value [µg/L] | < 10 |
| GLP | N |
| Validity | 2-3 |

**Description**

Fifteen plastic enclosures (4.2 x 4.9 m, average depth to sediment 4.3 m) were placed in a mesotrophic, boreal lentic lake in Canada. The start of the experiment was August 1, 1989.
Each system enclosed a portion of bottom sediment and ca. 90,000 L of water. The systems were open to air, precipitation and sunlight. The pH was 6.7-7.3, DO 7.2-8 mg/L and conductivity 0.03 mS/cm.
A parallel experiment with hexazinone was also performed, but is not reported here.
Metsulfuron-methyl was applied by spraying Escort, 60% DF formulation of metsulfuron-methyl on the enclosure surface. Nominal concentrations were: 0, 0.01, 0.1, 0.5 and 1.0 mg metsulfuron-methyl/L. The number of replicates per concentration was 3.
Concentrations of metsulfuron-methyl were quantified throughout the study by GLC.
The following parameters were investigated: phytoplankton (species and total counts) and zooplankton (Rotifera, Cladocera, Nauplii and other Copepoda). No macrofauna was included, but macrofauna is known to be insensitive for metsulfuron-methyl.
The following chemical parameters were measured: DO, pH, temperature, conductivity.
Analysis of the results included linear and non-linear correlation of effects with concentration.

**Results**

Analysis showed that the concentration of metsulfuron-methyl at the 1.0 mg/L level decreased with a $DT_{50}$ > 84 d, whereas at the 0.01 mg/L level the $DT_{50}$ was 29 d.
No inhibitory effects of metsulfuron-methyl were observed on zooplankton.

Phytoplankton biomass was inhibited by metsulfuron-methyl. Non-linear correlation analysis showed that the log inhibition of Cyanophyta could be correlated with the concentration of metsulfuron-methyl ($r^2 = 0.99$). An $EC_{50}$ of 0.002 mg/L was calculated. Other groups of phytoplankton did not correlate well with the concentration of metsulfuron-methyl.
Dissolved Oxygen was reduced maximally 23% after 50 days at 0.5 mg/L. Lower concentrations showed lower reductions. However, at 1.0 mg/L a 5% stimulation after 50 days was observed. These results were statistically not significant.

**Conclusion**
Metsulfuron-methyl decreased strongly the number of Cyanophyta in lake enclosures in Canada. The NOEC was < 0.01 mg/L. The $EC_{50}$ value calculated for the dose-response relationship for Cyanophyta was 0.002 mg/L, therefore the NOEC is most likely < 0.002 mg/L.
The study was not carried out under GLP and no raw data were given. Macrophyta, known to be most sensitive for metsulfuron methyl, were not included in the study. Therefore, a validity code 2-3 is assigned to the study.

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National Institute
for Public Health
and the Environment

P.O. Box 1
3720 BA Bilthoven
The Netherlands
www.rivm.com