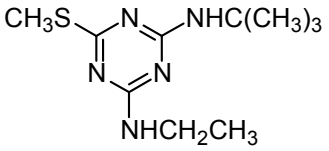
TERBUTRYN

This EQS dossier was prepared by the Sub-Group on Review of the Priority Substances List (under Working Group E of the Common Implementation Strategy for the Water Framework Directive).

The dossier was reviewed by the Scientific Committee on Health and Environmental Risks (SCHER), which commented that it did not agree with the use of an additional assessment factor of 10 for the marine AA-QS and MAC-EQS. Reference has been made to the TGD-EQS to explain this use. Explanation has also been added regarding the non-use of a different endpoint to derive the marine MAC-QS.

1 CHEMICAL IDENTITY

Common name	Terbutryn
Chemical name (IUPAC)	2-(Ethylamino)-4-(tert-butylamino)-6-(methylthio)-1,3,5-triazine
Synonym(s)	N-(1,1-Dimethylethyl)-N'-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine
Chemical class (when available/relevant)	Triazine
CAS number	886-50-0
EU number	212-950-5
Molecular formula	$C_{10}H_{19}N_5S$
Molecular structure	
Molecular weight ($g.mol^{-1}$)	241.36

2 EXISTING EVALUATIONS AND REGULATORY INFORMATION

Annex III EQS Dir. (2008/105/EC)	Not Included
Existing Substances Reg. (793/93/EC)	Not listed
Pesticides(91/414/EEC)	Not included in Annex I
Biocides (98/8/EC)	In review for Annex I listing (RMS Slovakia; supported uses PT 7: Film preservatives, main use in paints; PT 9: Polymer preservatives, main use in sealing bands around windows; PT10: Masonry preservatives, main use in cement-based material)
PBT substances	Does not fulfil PBT criteria
Substances of Very High Concern (1907/2006/EC)	No
POPs (Stockholm convention)	No

Other relevant chemical regulation (veterinary products, medicament, ...)	Information / No
Endocrine disrupter	Available information / Not investigated

3 PROPOSED QUALITY STANDARDS (QS)

3.1 ENVIRONMENTAL QUALITY STANDARD (EQS)

$QS_{water,eco}$ is the "critical QS" for derivation of an Environmental Quality Standard

	Value	Comments
Proposed AA-EQS for [freshwater] [µg.L^{-1}] **Proposed AA-EQS for [marine water] [µg.L^{-1}]**	**0.065** **0.0065**	**Critical QS is $QS_{water,eco}$** **See section 7**
Proposed MAC-EQS for [freshwater] [µg.L^{-1}] **Proposed MAC-EQS for [marine water] [µg.L^{-1}]**	**0.34** **0.034**	**See section 7.1**

3.2 SPECIFIC QUALITY STANDARD (QS)

Protection objective*	Unit	Value	Comments
Pelagic community (freshwater)	[µg.l^{-1}]	0.065	See section 7.1
Pelagic community (marine water)	[µg.l^{-1}]	0.0065	
Benthic community (freshwater)	[µg.kg^{-1} $_{dw}$]		e.g. EqP, see section 7.1
	[µg.l^{-1}]		
Benthic community (marine)	[µg.kg^{-1} $_{dw}$]		
	[µg.l^{-1}]	-	
Predators (secondary poisoning)	[µg.kg^{-1} $_{biota\ ww}$]	67	See section 7.4
	[µg.l^{-1}]	0.37 (freshwater and marine water)	
Human health via consumption of fishery products	[µg.kg^{-1} $_{biota\ ww}$]	61	See section 7.5
	[µg.l^{-1}]	0.34 (freshwater and marine water)	
Human health via consumption of water	[µg.l^{-1}]		

* Please note that as recommended in the Technical Guidance for deriving EQS (2011), "EQSs […] are not reported for 'transitional and marine waters', but either for freshwater or marine waters". If justified by substance properties or data available, QS for the different protection objectives are given independently for transitional waters or coastal and territorial waters.

4 MAJOR USES AND ENVIRONMENTAL EMISSIONS

4.1 USES AND QUANTITIES

Terbutryn is a selective herbicide and a triazine compound. It is absorbed by the roots and foliage and acts as an inhibitor of photosynthesis ([http://pmep.cce.cornell.edu/profiles/extoxnet/pyrethrins-ziram/terbutryn-ext.html).

Terbutryn is no longer registered in the EU under Annex I of 91/414/EEC, but it still has biocidal uses.

4.2 ESTIMATED ENVIRONMENTAL EMISSIONS

No information available.

5 ENVIRONMENTAL BEHAVIOUR

5.1 ENVIRONMENTAL DISTRIBUTION

		Master reference
Water solubility ($mg.L^{-1}$)	25 - 58 $mg.L^{-1}$ at 20°C	HVBG, 2002
	25 $mg.L^{-1}$ at 20°C	Industrieverband Agrar, 1990; BCPC, 1983; US EPA, 2008
	22 $mg.L^{-1}$ at 20°C	Vogue et al., 1994; BCPC, 2002
Volatilisation		
Vapour pressure (Pa)	1.3 x 10^{-4} Pa at 20°C	Industrieverband Agrar, 1990; Mensink and Linders, 1991
	2.7 x 10^{-4} Pa at 20 °C	Mensink and Linders, 1991
	6.3 x 10^{-4} Pa at 40 °C	Mensink and Linders, 1991
Henry's Law constant ($Pa.m^3.mol^{-1}$)	1.5 x 10^{-3} (calculated)	BPCP, 2002
Adsorption	**The mean measured Koc of 663 $L.kg^{-1}$ (log Koc 2.8) is used for derivation of quality standards.**	
Organic carbon – water partition coefficient (K_{OC}) ($L.kg^{-1}$)	2000	PPDB, 2009
	663 (average K_{om} 390 $L.kg^{-1}$, range 195-880 $L.kg^{-1}$, n=8)	Mensink and Linders, 1991
	609 (calculated)	US EPA, 2008
Suspended matter – water partition coefficient($K_{susp-water}$)	log Kp,susp = 1.8	
Bioaccumulation	**The BCF value of 181 $L.kg^{-1}$ on fish is used for derivation of quality standards.**	
Octanol-water partition coefficient (Log Kow)	**3.48** (experimental)	BioLoom, 2006
	3.50 (estimated, ClogP)	Bioloom, 2006
	3.65	PPDB, 2009
	3.74 (experimental)	US EPA, 2008
	3.77 (calculated)	US EPA, 2008
BCF	10-12 (see note below)	Mensink and Linders, 1991
	41 (calculated)	US EPA, 2008
	82 (calculated; upper trophic	US EPA, 2008

	level)	
	181 (calculated)	acc. to Veith et al., 1979 with log Kow 3.48

BCF-values of 12 and 10 L.kg^{-1} are reported in for muscle of *Cyprinus* sp. after exposure for 7 and 56 days to terbutryn in water (0.05 mg.L^{-1}) and algae (0.04 mg.L^{-1}). BCF in intestines was 80 L.kg^{-1} after 10 days and 10 L/kg after 56 days. Further details are not known and the reliability of the underlying study could not be assessed (Mensink and Linders, 1991).

5.2 ABIOTIC AND BIOTIC DEGRADATIONS

		Master reference
Hydrolysis	Stable	BPCP, 1983
Photolysis	DT_{50}=	
Biodegradation	$DT_{50\ (fresh\ water)}$= ~28 d	Jungmann et al., 2001 Brust et al., 2001

6 AQUATIC ENVIRONMENTAL CONCENTRATIONS

6.1 ESTIMATED CONCENTRATIONS

Compartment	**Predicted environmental concentration (PEC)**	**Master reference**
Freshwater		
Marine waters (coastal and/or transitional)	-	
Sediment		
Biota (freshwater)	-	
Biota (marine)	-	
Biota (marine predators)	-	

6.2 MEASURED CONCENTRATIONS

Compartment	**Measured environmental concentration (MEC)**	**Master reference**
Freshwater	PEC 1 = 0.125 µg.L^{-1} PEC 2 = 0.05 µg.L^{-1} Maximum of the average by station (n=2429) 1.04 µg.L^{-1} Maximum of analyses (n= 47201) 11.8 µg.L^{-1}	DGEnv (2010)
Marine waters (coastal and/or transitional)	-	
WWTP effluent	-	

Sediment	PEC 1 = - PEC 2 = 25 µg.kg_{dw}^{-1} Maximum of the average by station (n=1086) 25 µg.kg_{dw}^{-1}	DGEnv (2010)
	Maximum of analyses (n=1786) 25 µg.kg_{dw}^{-1}	DGEnv (2010)
Biota		
Biota (marine predators)		

7 EFFECTS AND QUALITY STANDARDS

7.1 ACUTE AND CHRONIC AQUATIC ECOTOXICITY

Detailed toxicity data are presented in Annex I.

Several sources were used to retrieve ecotoxicity data. Syngenta provided original study reports on algae, daphnids, fish and aquatic macrophytes. The report of Mensink and Linders (1991) that was prepared for authorisation of terbutryn as plant protection product in the Netherlands was consulted, as well as the German report on water quality standards by Nendza (2003). The EPA ecotox database was searched for additional data, and references with potentially sensitive endpoints were retrieved where possible. In addition, the open literature was screened via SCOPUS, available via www.scopus.com. All studies were evaluated for their reliability in view of their use for quality standard derivation.

Chemical analysis of test concentrations is lacking in a lot of the (older) studies. Terbutryn is hydrolytically stable, degradation in water is relatively slow and the compound is not volatile. In addition, water solubility is relatively high and sorption relatively low. Stability of test concentrations was demonstrated in some tests and from this it may be concluded that endpoints based on nominal concentrations may be used. However, in one algae test there was a decline of test concentrations (Shabana and Abou-Waly, 1995). Rapid uptake of terbutryn by algae was demonstrated by Gonzalez-Barreiro et al. (2006) and Rioboo et al. (2007), and this may have caused a decline in concentrations during the test. From the data of Shabana and Abou-Waly (1995) there appears to be a trend towards a decreased decline in concentrations at higher test levels. It may be possible that uptake by algae, and thus depletion from the test medium, is reduced at higher exposure levels due to toxicity. This implies that decreasing test concentrations over time do not necessarily relate to inadequate exposure.

In view of the above, it was decided to accept endpoints based on nominal concentrations with Ri 2, if the other aspects of the study do not give rise to concern with respect to quality.

ACUTE EFFECTS			**Master reference**
Bacteria ($\mu g.L^{-1}$)	**Marine**	*Vibrio fischeri* / 15 min. EC_{50}: 13[b] bioluminescence	Gaggi et al., 1995
Cyanobacteria ($\mu g.L^{-1}$)	**Freshwater**	*Anabaena flos-aqua* / 7 d EC_{50}: 3.4 dry weight	Mensink and Linders, 1991
		Nostoc muscorum / 7 d EC_{50}: 107[a] growth rate	Shabana and Abou-Waly, 1995
Algae & aquatic plants ($\mu g.L^{-1}$)	**Freshwater**	*Chlorella vulgaris* / 48 h EC_{50}: 13[b] growth rate	Rioboo et al., 2002
		Pseudokirchneriella subcapitata / 96 h EC_{50} : 3.4 growth rate[a]; geometric mean 3.3, 3.6	Grade, 1997; Okamura et al., 2000
		Lemna gibba / 6 d EC_{50}: 17.6 growth rate[a]; most relevant duration	Ward, 1982
	Sediment	*Myriophyllum aquaticum* / 14 d EC_{50}: 2.0 $mg.kg_{dw}^{-1}$ sediment	Gonsior, 2009
	Marine	*Dunaliella tertiolecta* / 96 h EC_{50} : 3.1 cell number	Gaggi et al., 1995
		Skeletonema costatum / 9 d EC_{50}: 0.91 dry weight	Mensink and Linders, 1995
Crustacea ($\mu g.L^{-1}$)	**Freshwater**	*Daphnia magna* / 48 h EC_{50} : 5259 immobilisation/mortality; geometric mean 7100, 2660, 7700	Marchini et al., 1988; Vilkas, 1977; LeBlanc, 1982a
	Marine	*Artemia salina* / 24 h EC_{50}: 22 immobilisation	Gaggi et al., 1995
	Sediment	no data available	
Oligochaeta ($\mu g.L^{-1}$)	**Freshwater**	*Lumbriculus variegatus* / 96 h LC_{50}: 23700	Brust et al., 2001
Fish ($\mu g.L^{-1}$)	**Freshwater**	*Danio rerio* / 96 h LC_{50}: 5710	Plhalova et al., 2009
		Lepomis macrochirus / 96 h LC_{50}: 2720	Mayer and Ellersieck, 1987
		Oncorhynchus mykiss / 96 h LC_{50} : 950 geometric mean 820, 1100	Mayer and Ellersieck, 1987; LeBlanc, 1982b
	Marine	no data available	

a: growth rate is preferred if more endpoints are available for one species

b: most sensitive endpoint or test duration

CHRONIC EFFECTS			**Master reference**
Cyanobacteria ($\mu g.L^{-1}$)	**Freshwater**	*Nostoc muscorum* / 7 d EC_{10}: 35[a] growth rate	Shabana and Abou-Waly, 1995
Algae & aquatic plants ($\mu g.L^{-1}$)	**Freshwater**	*Chlorella vulgaris* / 48 h EC_{10}: 11[b] growth rate	Rioboo et al., 2002
		Pseudokirchneriella subcapitata / 96 h NOEC: 0.65 growth rate[a]	Grade, 1997
		Lemna gibba / 6 d EC_{10}: 6.3 growth rate[a]; most relevant duration	Ward, 1982
	Sediment	*Myriophyllum aquaticum* / 14 d NOEC: 0.977 $mg.kg_{dw}^{-1}$ sediment (corresponding pore water concentration 22 $\mu g.L^{-1}$)	Gonsior, 2009
	Marine	no data available	
Crustacea ($\mu g.L^{-1}$)	**Freshwater**	*Daphnia magna* / 21d NOEC : 1300 mortality/reproduction	LeBlanc, 1982a
	Marine	no data available	
	Sediment	no data available	
Fish ($\mu g.L^{-1}$)	**Freshwater**	*Danio rerio* / 21 d NOEC: 200 length	Plhalova et al., 2009
		Oncorhynchus mykiss / 21d NOEC : 150 mortality (see notes below)	Ritter, 1990
		Pimephales promelas / 34 d NOEC: 840 ELS	Surprenant, 1987
	Marine	no data available	

a: growth rate is preferred if more endpoints are available for one species

b: most sensitive endpoint or test duration

In previous versions of this dossier, there was discussion on the validity of the NOEC for *Oncorhynchus mykiss* from the study by Ritter (1990). A NOEC of 9 $\mu g.L^{-1}$was reported, as well as a NOEC of 0.15 $mg.L^{-1}$. It was reported that INERIS (2009) considered this study not reliable. The study was reviewed again for the purpose of this dossier. The study was assigned Ri 2 because of fluctuations in the measured concentrations, but still considered reliable for QS-derivation. The previously used NOEC of 9 $\mu g.L^{-1}$, however, is not taken forward, because this is based on clinical signs which are not necessarily related to population effects. Instead, the NOEC for mortality of 150 $\mu g.L^{-1}$ is adopted.

7.2 OTHER STUDIES

Three (semi-)field studies are available in which the effects of terbutryn on algae and organisms depending on algae as a food source were studied. See Annex II for summaries and evaluation.

Brust et al. (2001) used indoor artificial streams to study the effects of terbutryn on *aufwuchs* (mainly periphytic algae *Ulothrix* sp. and *Cladophora* sp. and bacillariophyceae *Achnanthes* sp., *Nitzschia* sp.) and bacillariophyceae (*Achnanthes* sp., *Nitzschia* sp.) and detritivores (*Lumbriculus variegatus*) in a 72-days experiment. Effects on *aufwuchs* biomass were present at the lowest test concentration of 0.6 $\mu g.L^{-1}$nominal. Initial measured concentrations at this test level were 0.43 $\mu g.L^{-1}$. Effects on population growth of *L. variegatus* were present at the next higher concentration, this was considered to be a secondary effect due to food limitation. Concentrations gradually decreased with a DT_{50} of 28.2 days. Biomass increase in the control was exponential over 50 days, which is considered as the relevant period to express effects. Starting from 0.43 $\mu g.L^{-1}$, the time-weighted average concentration over 50 days is 0.25 $\mu g.L^{-1}$. The NOEC for aufwuchs is thus < 0.25 $\mu g.L^{-1}$, the NOEC for population growth of *L. variegatus* is 0.25 $\mu g.L^{-1}$.

Goldsborough and Robinson (1983) and Gurney and Robinson (1989) used field enclosures in a marsh on the southern end of Lake Manitoba, Canada, to study the effects of terbutryn on freshwater marsh periphyton. Both studies were consistent in showing effects on algae communities at a nominal initial test concentration of 10 $\mu g.L^{-1}$. Actual concentrations over the full study are not known. Both studies have deficiencies in experimental set-up and/or reporting, the study of Goldsborough and Robinson (1983) can be used as supporting information.

In another non-standard study, Rioboo et al. (2007) studied population development of the rotifer *Brachionus* sp. after feeding with terbutryn-exposed algae. *Chlorella vulgaris* were exposed to 12.5, 100 and 500 nM terbutryn (3.0, 24 and 124 $\mu g.L^{-1}$) for 24 hours, after which they were used as exclusive food source for *Brachionus* in a 5-days renewal test. After five days, rotifers were fed non-exposed algae for two days to study recovery. Algae removed 90% of the terbutryn from the exposure medium, while cell integrity was not affected. Population growth rate of *Brachionus* was significantly decreased and generation time significantly increased when fed algae exposed to 3.0 and 24 $\mu g.L^{-1}$. Population growth was absent when fed on algae exposed to 124 $\mu g.L^{-1}$, animals did not survive beyond four days. After returning to herbicide-free algae, recovery was observed in the 3.0 and 24 $\mu g.L^{-1}$ treatments, but not in rotifers that had been fed algae exposed to 124 $\mu g.L^{-1}$.

7.3 DERIVATION OF THE QS-WATER

There are too few data to perform a meaningful statistical comparison and there are no further indications (spread of the data, read-across, expert judgement) of a difference in sensitivity between freshwater and saltwater organisms. Therefore, the data sets may be combined for QS derivation.

7.3.1 MAC-$QS_{freshwater, eco}$

For derivation of the $MAC_{freshwater, eco}$, acute toxicity values are available for bacteria, cyanobacteria, algae, macrophyta, crustacea, oligochaeta and fish. The lowest endpoint is the EC_{50} of 0.91 $\mu g.L^{-1}$. for *Skeletonema costatum*. The test duration of 9 days, however, is considered too long for derivation of the MAC-$QS_{freshwater, eco}$. In addition, the endpoint dry weight is probably not representative of growth rate after prolonged testing. This also holds for the 7-days test with *Anabaena flos-aquae*. The 96-h EC_{50} of 3.1 $\mu g.L^{-1}$ for cell number of the marine algal species *Dunaliella tertiolecta* is almost identical to the 72-h EC_{50} of 3.4 $\mu g.L^{-1}$ for growth rate of the green algae *Pseudokirchnerialla subcapitata; the latter is based on a study with a higher reliabiability index*..Terbutryn is a herbicide and the potentially most sensitive species groups (algae, macrophyta) are represented in the dataset. The aquatic macrophyte *Lemna gibba* is less sensitive than algae. In addition, information from a sediment-spiked water/sediment study with the macrophyte *Myriophyllum aquaticum* was available. At the level of the NOEC (0.977 $mg.kg_{dw}^{-1}$ sediment), corresponding pore water concentrations were 22 $\mu g.L^{-1}$. This indicates that algae are indeed the most sensitive species group. Therefore, an assessment factor of 10 can be applied to the more reliable lowest endpoint (3.4 $\mu g.L^{-1}$) and the MAC-$QS_{freshwater, eco}$ is 0.34 $\mu g.L^{-1}$. This value is a factor of 10 lower than the concentration that induced effects on *Brachionus* sp. fed on short-term exposed algae (Rioboo, 2007 ; see above).

7.3.2 MAC-$QS_{saltwater, eco}$

Terbutryn is a herbicide and the potentially most sensitive species groups (algae, macrophyta) are represented in the dataset. There are, however, no acute data for additional typically marine species. The

MAC-$QS_{saltwater, eco}$ is therefore derived by applying an assessment factor of 100 to the lowest EC50 of 3.4 µg.L^{-1}. The MAC-$QS_{saltwater, eco}$ is 0.034 µg.L^{-1}. As explained in the TGD-EQS this factor takes account of the uncertainties associated with extrapolation to the marine ecosystem, i.e. with the greater species diversity in the marine environment and the possibly greater sensitivity of marine species and taxa not in the experimental dataset.

7.3.3 AA-$QS_{freshwater, eco}$

For derivation of the AA-$QS_{freshwater, eco}$, chronic NOEC/EC10 values are available for cyanobacteria, algae, macrophyta, crustacea and fish. The lowest NOEC is 0.65 µg.L^{-1} for growth rate of *Pseudokirchnerialla subcapitata*. This is the species that was also most sensitive in acute studies. In view of the laboratory dataset, an assessment factor of 10 would be justified, resulting in an AA-$QS_{freshwater, eco}$ of 0.065 µg.L^{-1}. In indoor artificial streams effects were seen at an initial concentration of 0.43 µg/L, corresponding with a time-weighted average concentration over 50 days of 0.25 µg.L^{-1}. The AA-$QS_{freshwater, eco}$ of 0.065 µg.L^{-1} is a factor of 4 lower than this value. It seems reasonable to consider the value of 0.065 µg.L^{-1} protective for ecosystem effects.

7.3.4 AA-$QS_{saltwater, eco}$

There are no additional chronic data for typically marine species. As explained for the MAC-$QS_{saltwater, eco}$, the AA-$QS_{saltwater, eco}$ is therefore derived by applying an assessment factor of 100 to the lowest NOEC of 0.65 µg.L^{-1}. The AA-$QS_{saltwater, eco}$ is 0.0065 µg.L^{-1}.

Tentative QS_{water}	Relevant study for derivation of QS	Assessment factor	Tentative QS
$MAC_{freshwater, eco}$	*Pseudokirchneriella subcapitata*/ 72 h EC_{50} 3.4 µg.L^{-1}	10	0.34 µg.L^{-1}
$MAC_{marine\ water, eco}$		100	0.034 µg.L^{-1}
AA-$QS_{freshwater, eco}$	*Pseudokirchneriella subcapitata* / 72 h NOEC 0.65 µg.L^{-1}	10	0.065 µg.L^{-1}
AA-$QS_{marine\ water, eco}$		100	0.0065 µg.L^{-1}
AA-$QS_{freshwater, sed.}$	-	EqP	- µg.kg^{-1}_{ww} - µg.kg^{-1}_{dw}
AA-$QS_{marine\ water, sed.}$	-	EqP	- µg.kg^{-1}_{ww} - µg.kg^{-1}_{dw}

7.4 SECONDARY POISONING

The calculated BCF is > 100 L/kg and the risks for secondary poisoning should be assessed. There are no chronic studies with birds available, Mensink and Linders (1991) report a LC_{50} for *Colinus virginianus* of > 7025 mg/kg food, which was classified as not reliable due to lack of study details. The critical human-toxicological endpoint (NOAEL is 0.1 mg.kg_{bw}^{-1}.d^{-1}) is based on haematological effects in female rats in a 2-years study. This endpoint is used for the assessment of secondary poisoning, considering that it is a worst-case because the NOAEL is based on haematology instead of body weight or reproduction.

Secondary poisoning of top predators		Master reference
Mammalian oral toxicity	rat / Oral / 2 Years / Haematological effects in females NOAEL: 0.1 mg.kg_{bw}^{-1}.d^{-1} NOEC: 2 mg/kg fd (conversion factor 20)	http://www.epa.gov/IRIS/subst/0285.htm
Avian oral toxicity	no chronic data available	

Tentative QS_{biota}	Relevant study for derivation of QS	Assessment factor	Tentative QS

Biota	NOEC: 2 $mg.kg^{-1}_{biota\ ww}$	30	67 $\mu g.kg^{-1}_{biota\ ww}$ corresponding to 0.37 $\mu g.L^{-1}$ (freshwater/saltwater)

7.5 HUMAN HEALTH

Human health via consumption of fishery products		**Master reference**
Mammalian oral toxicity	rat / Oral / 2 Years / Hematologic effects in females NOAEL : 0.1 $mg.kg^{-1}_{bw}.d^{-1}$ (RfD : 0.001 $mg.kg^{-1}_{bw}.d^{-1}$)	US EPA/IRIS (2010)
CMR	no	

Tentative $QS_{biota, hh}$	**Relevant study for derivation of $QS_{biota, hh}$**	**Assessment Factor**	**Tentative $QS_{biota, hh}$**
Human health	RfD: 1 $\mu g.kg^{-1}_{bw}.d^{-1}$		61 $\mu g.kg^{-1}_{biota\ ww}$ corresponding to 0.34 µg/L (BCF 181 L/kg)

Human health via consumption of drinking water		**Master reference**
Existing drinking water standard(s)	0.1 $\mu g.L^{-1}$ (preferred regulatory standard)	Directive 98/83/EC
Any guideline		

8 BIBLIOGRAPHY, SOURCES AND SUPPORTIVE INFORMATION

This list also contains references that are included in Annex I from which endpoints are not taken forward for QS-derivation.

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Annex I. Detailed aquatic toxicity data

Legend to column headings	
A	test water analysed Y(es)/N(o)
Test type	S(tatic), R(enewal), F(low through)
Test compound	a.s. = active substance
Purity	refers to purity of active substance or content of active in formulation
Test water	am = artificial medium; rw = reconstituted water; d(t)w = deionised/dechlorinated/distilled (tap)water; nw = natural water; tw = tap water
T	temperature
Ri	Reliability index according to Klimisch et al. (1997); asterisk indicates citation
Reference	see Section 8 of main report

Acute toxicity 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-aqua	6 d old culture, 2E4 cells/mL	Y	S	terbutryn	96.6	am		24		7 d	EC50	dry weight	3.4	2	1	Mensink and Linders, 1991
Nostoc muscorum			S	terbutryn	98			25		7 d	EC50	chlorophyll a	5.16	2	2	Abou-Waly and Shabana, 1993
Nostoc muscorum		Y	S	terbutryn	99.9			25		3 d	EC50	growth rate	544	2	3	Shabana and Abou-Waly, 1995
Nostoc muscorum		Y	S	terbutryn	99.9			25		7 d	EC50	growth rate	107	2	3	Shabana and Abou-Waly, 1995
algae																
Chlamydomonas geitleri	4000 cells/mL	N	S	terbutryn	99.9	am		23			EC50	growth rate	4.8	3	4	Francois and Robinson, 1990
Chlamydomonas geitleri	4000 cells/mL	N	S	terbutryn	99.9	am		23			EC50	final yield	7.2	3	4	Francois and Robinson, 1990
Chlorella vulgaris	3 d old culture; 9E6 cells/mL	N	S	terbutryn	ag	am		18		48 h	EC50	growth rate	**13**	2	5	Rioboo et al., 2002
Chlorella vulgaris	3 d old culture; 9E6 cells/mL	N	S	terbutryn	ag	am		18		96 h	EC50	growth rate	**23**	2	5	Rioboo et al., 2002
Chlorella vulgaris	3 d old culture; 9E6 cells/mL	N	S	terbutryn	ag	am		18		24 h	EC50	growth rate	**< 6**	2	6	Gonzalez-Barreiro et al., 2006
Pseudokirchneriella subcapitata		Y	S	terbutryn		rw	7.7		100	96 h	EC50	biomass	**2.7**	2	7	Gaggi et al., 1995
Pseudokirchneriella subcapitata	1E4 cells/mL	N	S	terbutryn	98	am		25		72 h	EC50	growth rate	**3.3**	2	8	Okamura et al., 2000
Pseudokirchneriella subcapitata	1E4 cells/mL	N	S	terbutryn	98	am		25		72 h	EC50	biomass	2.0	2	8	Okamura et al., 2000
Pseudokirchneriella subcapitata	10800 cells/mL	Y	S	terbutryn	97.4	rw	7.9-8.0	23	30.3	72 h	EC50	growth rate	**3.6**	1	9	Grade, 1997
Pseudokirchneriella subcapitata	10800 cells/mL	Y	S	terbutryn	97.4	rw	7.9-8.0	23	30.3	72 h	EC50	biomass	1.7	1	9	Grade, 1997
Pseudokirchneriella subcapitata	5 d old culture, 2E4 cells/mL	Y	S	terbutryn	96.6	am		24		7 d	EC50	dry weight	**13.1**	2	1	Mensink and Linders, 1991

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
Synechococcus elongatus	3 d old culture; 9E6 cells/mL	N	S	terbutryn	ag	am		18		24 h	EC50	growth rate	3.3	3	10	Gonzalez-Barreiro et al., 2006
crustacea																
Daphnia magna	< 24 h old	N	S	terbutryn	≥ 96	dtw	8.4	21	250	48 h	EC50	immobilisation	**7100**	2	11	Marchini et al., 1988
Daphnia magna	< 20 h old	N	S	terbutryn		nw	7.6	17	36	48 h	LC50	mortality	**2660**	2	12	Vilkas, 1977
Daphnia magna	< 20 h old	N	S	terbutryn	ag	nw	7.6	17	36	48 h	LC50	mortality	2700	2*	13	Mensink and Linders, 1991
Daphnia magna				terbutryn						48 h	LC50	mortality	2660	2*	14	PPDB, 2009
Daphnia magna	< 24 h old	N	S	terbutryn	94	rw	7.9-8.3	22	160	48 h	LC50	mortality	**7700**	2	15	LeBlanc, 1982a
Daphnia magna	< 24 h old	N	S	terbutryn	94	nw	7.9-8.3	22	160	48 h	LC50	mortality	7700	2*	16	Mensink and Linders, 1991
oligochaeta																
Lumbriculus variegatus		N	S	terbutryn	98.8	rw				96 h	LC50	mortality	**23700**	2	17	Brust et al., 2000
Lumbriculus variegatus		N	S	terbutryn	98.8	rw				96 h	EC50	deformation	**16500**	2	17	Brust et al., 2000
macrohpyta																
Lemna gibba		Y	S	terbutryn	96.6	am		24		14 d	EC50	frond production	16	3	18	Ward, 1982
Lemna gibba		Y	S	terbutryn	96.6	am		24		6 d	EC50	growth rate	**17.6**	2	18,19	Ward, 1982
Lemna gibba		Y	S	terbutryn	96.6	am		24		12 d	EC50	growth rate	15.9	2	18,19	Ward, 1982
Lemna gibba		Y	S	terbutryn	96.6	am		24		14 d	EC50	growth rate	15.8	3	18,19	Ward, 1982
pisces																
Carassius auratus				terbutryn						96 h	LC50	mortality	1400	4	14	BCPC, 2002
Carassius auratus				terbutryn						96 h	LC50	mortality	1400	4*	14	Nendza, 2003
Danio rerio	juv. 30 mm, 0.3 g	N	R	terbutryn			8.1-8.5	23		96 h	LC50	mortality	**5710**	2	20	Plhalova et al., 2009
Lepomis macrochirus				terbutryn						96 h	LC50	mortality	1300	4	14	BCPC, 2002
Lepomis macrochirus				terbutryn						96 h	LC50	mortality	1300	4	14	Nendza, 2003
Lepomis macrochirus	1.3 g	N	S	terbutryn	80		7.1	18	44	96 h	LC50	mortality	**2720**	2	21	Mayer & Ellersieck, 1986
Lepomis macrochirus				terbutryn						96 h	LC50	mortality	4000	4	14	BCPC, 1983
Lepomis macrochirus		N	S	product	80	nw				96 h	LC50	mortality	4500	3	22	Mensink and Linders, 1991
Oncorhynchus mykiss	0.8 g	N	S	terbutryn	80		7.1	13	44	96 h	LC50	mortality	**820**	2	21	Mayer & Ellersieck, 1986
Oncorhynchus mykiss	0.65 g, 43 mm	Y	S	terbutryn	96.6	rw	7.8	12	46	96 h	LC50	mortality	**1100**	2	23	LeBlanc, 1982b
Oncorhynchus mykiss				terbutryn						96 h	LC50	mortality	1100	4*	14	Nendza, 2003
Oncorhynchus mykiss				terbutryn						96 h	LC50	mortality	1100	4*	14	PPDB, 2009
Oncorhynchus mykiss				terbutryn						96 h	LC50	mortality	1100	4*	14	BCPC, 2002
Oncorhynchus mykiss				terbutryn						96 h	LC50	mortality	1800	4	14	BCPC, 1983
Oncorhynchus mykiss		N	S	product	80	nw				96 h	LC50	mortality	3500	3	24	Mensink and Linders, 1991

NOTES
1 solvent acetone, solvent control included; reported source could not be checked, details from summary; dry weight probably not considered representative for growth rate after prolonged testing
2 endpoint recalculated from reported data;tablehead refers to "applied measured concentrations", but the methods section does not refer to analytical measurements
3 endpoint recalculated from reported data; based on nominal concentrations; measured concentrations on t=7 were 23-49% of nominal; growth rate based on chlorophyll a content
4 endpoint based on nominal concentrations; solvent methanol (max. 0.05%), solvent control included; test duration not clear; reported as 3 days in EPA ecotox database; text states that growth curves were made from 6-12 datapoints, with 2 cell counts daily duration could be 3-6 days; read from figure: <10% effect at 0.01 µM
5 endpoint recalculated from reported data; endpoint based on nominal concentrations; solvent methanol (max. 0.05%), solvent control included
6 endpoint based on nominal concentrations; solvent methanol (max. 0.05%), solvent control included; 60% effect at lowest test concentration; no growth at 6 µg/L and higher; only three concentrations tested
7 solvent acetone (0.5 mg/L), solvent control included;stability of test compound confirmed in preliminary 96 h algal test; endpoint based on nominal concentrations
8 endpoint based on nominal concentrations; solvent DMSO
9 measured concentration at start and end >80% of nominal, except for 3 samples; endpoint based on mean measured
10 endpoint recalculated from reported data; endpoint based on nominal concentrations; solvent methanol (max. 0.05%), solvent control included; only 3 concentrations tested
11 according to OECD 202; stock analysed
12 endpoint based on nominal concentrations; solvent acetone, solvent control included
13 endpoint based on nominal concentrations; solvent acetone, solvent control included; remark by authors that LC50 is approximate value most likely refers to 24 h value (> 5.6 mg/L)
14 (primary) source unknown
15 endpoint based on nominal concentrations; solvent DMF (max. 0.5 mL/L), solvent control included
16 endpoint based on nominal concentrations; solvent DMF
17 endpoint based on nominal concentrations; tested in multiwell plates

18 endpoint recalculated from reported data; solvent acetone (10 µL/L), solvent control included; initial measured concentrations 87-92% of nominal; endpoint based on initial measured; frond production at 9.1 µg/L is inhibited by 8-34% as compared to solvent control during days 0-12, stimulation by 10% after 14 days; this indicates recovery between 12- and 14 days; final frond number is therefore not appropriate and growth rate should be used
19 duration of Lemna test according to OECD 221 is 7 days; average specific growth rate in solvent control over 0-6 days is 0.26 (doubling time 2.7 days), which is close to validity criterion of OECD 221 (0.275/d; 2.5 days); control growth rate over 0-9 and 0-12 days is lower (3.2-3.0/d); recalculcated EC50 for growth rate over 0-6 days is considered to be most appropriate endpoint from this study
20 endpoint based on nominal concentrations; solvent DMSO (0.1%), solvent control included; according to OECD 203; test concentrations reported as 82-88% of measured initial; author confirmed that mean measured were >80% of nominal (pers. comm. L. Plhalova, 23-06-2010)
21 endpoint based on nominal concentrations
22 endpoint based on nominal concentrations; classified as not reliable by Mensink and Linders, 1991; reported source could not be checked, details from summary
23 solvent DMF (max. 0.5 mL/L), solvent control included; concentrations measured at t=0 are 62-72% of nominal, procedural recovey average 80% (71-92%); endpoint based on initial measured
24 endpoint based on nominal concentrations; reported source could not be checked, details from summary

Acute toxicity 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 as/L]	Ri	Notes	Ref
bacteria																
Vibrio fischeri		Y	S	terbutryn				15		15 min	EC50	bioluminescence	13	2	1	Gaggi et al, 1995
Vibrio fischeri		N	S	terbutryn	ag			15		5 min	EC50	bioluminescence	> 6800	2	2	Hernando et al., 2007
Vibrio fischeri		N	S	terbutryn	ag			15		15 min	EC50	bioluminescence	> 6800	2	2	Hernando et al., 2007
Vibrio fischeri		N	S	terbutryn	ag			15		30 min	EC50	bioluminescence	> 6800	2	2	Hernando et al., 2007
algae																
Dunaliella tertiolecta		Y	S	terbutryn		nw				96 h	EC50	cell number	3.1	2	3	Gaggi et al, 1995
Skeletonema costatum	5 d old culture, 2E4 cells/mL	Y	S	terbutryn	96.6	am		20		9 d	EC50	dry weight	0.91	2	4	Mensink and Linders, 1991
crustacea																
Americamysis bahia		Y	S	terbutryn						96 h	EC50	mortality	740	4	5	Nendza, 2003
Artemia salina	2-3rd instar larvae	Y	S	terbutryn				25		24 h	EC50	immobilisation	22	2	6	Gaggi et al, 1995

NOTES
1 Microtox test; solvent acetone (0.5 mg/L), solvent control included; endpoint based on nominal concentrations; stability of test compound confirmed in preliminary 96 h algal test
2 Microtox test; endpoint based on nominal concentrations; solvent DMSO (2%), solvent control included
3 solvent acetone (0.5 mg/L), solvent control included; endpoint based on nominal concentrations; stability of test compound confirmed in preliminary 96 h algal test

4 solvent methanol (max. 0.05%), solvent control included; solvent acetone, solvent control included; endpoint based on measured concentrations; reported source could not be checked, details from summary; dry weight probably not considered representative for growth rate after prolonged testing
5 primary source unknown; Ri 1 according to German ETOX-database
6 Artoxkit test; solvent acetone (0.5 mg/L), solvent control included; endpoint based on nominal concentrations; stability of test compound confirmed in preliminary 96 h algal test;

Chronic toxicity 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																
Nostoc muscorum	log-phase		S	terbutryn	98	am		25		7 d	EC10	chlorophyll a after 7 d	0.17	2	1	Abou-Waly and Shabana, 1993
Nostoc muscorum		Y	S	terbutryn	99.9	am		25		3 d	EC10	growth rate	321	2	2	Shabana and Abou-Waly, 1995
Nostoc muscorum		Y	S	terbutryn	99.9	am		25		7 d	EC10	growth rate	35	2	2	Shabana and Abou-Waly, 1995
algae																
Chlamydomonas geitleri	4000 cells/mL	N	S	terbutryn	99.9	am		23			NOEC	growth rate	2.4	3	3	Francois and Robinson, 1990

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
Chlamydomonas geitleri	4000 cells/mL	N	S	terbutryn	99.9	am		23			NOEC	final yield	2.4	3	3	Francois and Robinson, 1990
Chlorella vulgaris	3 d old culture; 9E6 cells/mL	N	S	terbutryn	ag	am		18		48 h	EC10	growth rate	11	2	4	Rioboo et al., 2002
Chlorella vulgaris	3 d old culture; 9E6 cells/mL	N	S	terbutryn	ag	am		18		96 h	EC10	growth rate	16	2	4	Rioboo et al., 2002
Pseudokirchneriella subcapitata	10800 cells/mL	Y	S	terbutryn	97.4	rw	7.9-8.0	23	30.3	72 h	NOEC	growth rate	0.65	1	5	Grade, 1997
Pseudokirchneriella subcapitata	10800 cells/mL	Y	S	terbutryn	97.4	rw	7.9-8.0	23	30.3	72 h	NOEC	biomass	0.4	1	5	Grade, 1997
Synechococcus elongatus	3 d old culture; 9E6 cells/mL	N	S	terbutryn	ag	am		18		24 h	NOEC	growth rate	< 6.0	2	6	Gonzalez-Barreiro et al., 2006
macrohpyta																
Lemna gibba		Y	S	terbutryn	96.6	am		24		14 d	EC10	frond production	15	3	7	Ward, 1982
Lemna gibba		Y	S	terbutryn	96.6	am		24		6 d	EC10	growth rate	6.3	2	7,8	Ward, 1982
Lemna gibba		Y	S	terbutryn	96.6	am		24		12 d	EC10	growth rate	7.0	2	7,8	Ward, 1982
Lemna gibba		Y	S	terbutryn	96.6	am		24		14 d	EC10	growth rate	12.5	3	7,8	Ward, 1982
crustacea																
Daphnia magna		Y	F	terbutryn	94	rw	7.9-8.3	22	160	21 d	NOEC	mortality	**1300**	1	9	LeBlanc, 1982a
Daphnia magna		Y	R	terbutryn	94	nw	7.9-8.3	22	160	21 d	NOEC	mortality	1300	1*	10	Mensink and Linders, 1991
Daphnia magna		Y	R	terbutryn						21 d	NOEC	mortality	1300	1*	11	Nendza, 2003
mollusca																
Lymnea stagnalis	eggs, < 24 h	N	S	terbutryn	ag					9 d	LC100	mortality	2400	3	12	Kosanke et al., 1988
pisces																
Danio rerio	juv. 20 d, 9 mg	Y	R	terbutryn			8.0-8.5	23		28 d	NOEC	length	200	2	13	Plhalova et al., 2009
Oncorhynchus mykiss	0.6 g, 39 mm; 0.1 g/L	Y	F	terbutryn	100	tw	7.1-8.2	14.5-16		21 d	NOEC	clinical signs	9	2	14,15	Ritter, 1990
Oncorhynchus mykiss	0.6 g, 39 mm; 0.1 g/L	Y	F	terbutryn	100	tw	7.1-8.2	14.5-16		21 d	NOEC	mortality	150	2	14	Ritter, 1990
Oncorhynchus mykiss	0.6 g, 39 mm; 0.1 g/L	Y	F	terbutryn	100	tw	7.1-8.2	14.5-16		21 d	NOEC	length, weight	≥ 600	2	14	Ritter, 1990
Oncorhynchus mykiss			F							21 d	NOEC	sublethal effects	9	4*	11	Nendza, 2003
Pimephales promelas	fertilised eggs	Y	F	terbutryn	97.3	nw	7	25	26-36	34 d	NOEC	growth	840	1	16	Surprenant, 1987

NOTES

1 endpoint recalculated from reported data; tablehead refers to "applied measured concentrations", but the methods section does not refer to analytical measurements
2 endpoint recalculated from reported data; based on nominal concentrations; measured concentrations on t=7 were 23-49% of nominal; growth rate based on chlorophyll a content
3 endpoint based on nominal concentrations; solvent methanol (max. 0.05%), solvent control included; test duration not clear; reported as 3 days in EPA ecotox database; text states that growth curves were made from 6-12 datapoints, with 2 cell counts daily duration could be 3-6 days; read from figure: <10% effect at 0.01 µM
4 endpoint recalculated from reported data; endpoint based on nominal concentrations; solvent methanol (max. 0.05%), solvent control included
5 measured concentration at start and end >80% of nominal, except for 3 samples; endpoint based on mean measured
6 endpoint based on nominal concentrations; solvent methanol (max. 0.05%), solvent control included; 60% effect at lowest test concentration; only three concentrations tested, not possible to calculate reliable EC10
7 endpoint recalculated from reported data; solvent acetone (10 µL/L), solvent control included; initial measured concentrations 87-92% of nominal; endpoint based on initial measured; frond production at 9.1 µg/L is inhibited by 8-34% as compared to solvent control during days 0-12, stimulation by 10% after 14 days; this indicates recovery between 12- and 14 days; final frond number is therefore not appropriate and growth rate should be used
8 duration of Lemna test according to OECD 221 is 7 days; average specific growth rate in solvent control over 0-6 days is 0.26 (doubling time 2.7 days), which is close to validity criterion of OECD 221 (0.275/d; 2.5 days); control growth rate over 0-9 and 0-12 days is lower (3.2-3.0/d); recalculcated EC50 for growth rate over 0-6 days is considered to be most appropriate endpoint from this study
9 solvent DMF (16 µL/L), solvent control included; mean measured concentrations 48-74% of nominal, endpoint based on mean measured
10 reported source could not be checked, details from summary; authors report endpoint as MATC, this should read NOEC
11 primary source unknown; Ri 1 according to German ETOX-database
12 endpoint based on nominal concentrations; details on test system and conditions not reported
13 endpoint based on nominal concentrations; solvent DMSO (0.1%), solvent control included; according to OECD 215; test concentrations reported as 82-88% of measured initial; author confirmed that mean measured were >80% of nominal (pers. comm. L. Plhalova, 23-06-2010)
endpoint based on nominal concentrations; solvent Tween (0.001%), solvent control included; analysis of samples from 0.009, 0.015 and 2.4 mg/L on day 0, 12 and 21; 68-106% of nominal at t=0, 90-92% at t=12 and
14 98/134% at t=21, overall average 95% of nominal
15 clinical signs at 0.15 mg/L: hypoactivity 30-50%, remaining at bottom/top of tank 10-30%; clinical signs are not considered appropriate endpoint for EQS-derivation
16 solvent acetone 99 uL/L, solvent control included; measured concentrations 80-85% of nominal; endpoint based on measured concentrations

Annex II. Summary of non-standard studies

Reference	Brust K, Licht O, Hultsch V, Jungmann D, Nagel R. 2001. Effects of terbutryn on aufwuchs and Lumbriculus variegatus in artificial indoor streams. Environ Toxicol Chem 20, 2000-2007.
Species; Population; Community	algae, *Lumbriculus variegatus*
Test Method	indoor artificial stream
System properties	3.7 m long, flow rate 0.2 m/s
Compound	terbutryn 98.8% pure
Exposure regime	0, 0.6, 6, 60 and 600 µg/L
Analysed	Yes
Temperature [°C]	14-14.5
pH range	8.4-8.5
Hardness [mg $CaCO_3$/L]	Not reported
Exposure time	single
Criterion	NOEC
Test endpoint	biomass of aufwuchs (periphytic algae, bacteria, fungi)
Value [µg/L]	< 0.25 µg/L (50-d TWA at 0.6 µg/L nominal; 0.43 µg/L measured initial)
GLP	No
Guideline	No
Notes	This study is most likely the same experiment as referred to in Nendza, 2003 as Jungmann, D., Brust, K., Hultsch, V., Licht, O., Mählmann, J., Schmidt, J., Nagel, R. (2001). Stellenwert von Ökosystemtests bei der ökologischen Risikobewertung gefährlicher Stoffe in Oberflächengewässern. Teil II: Wirkung des Herbizides Terbutryn. Umweltbundesamt, Berlin, UBA-FB 000261/2.e
Ri	2

Description

Experimental system

Artificial indoor streams were set-up in a greenhouse 20 days before application.

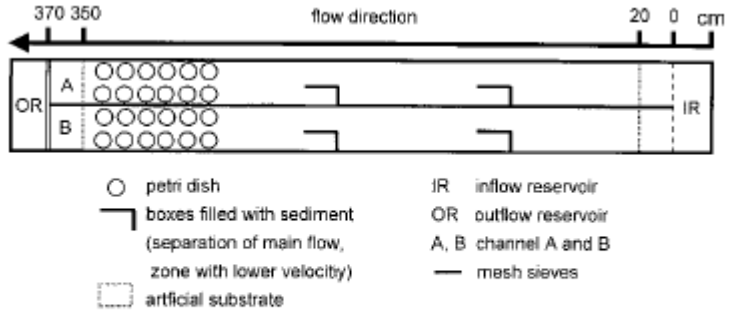


Fig. 1. Top view of the design for the artificial indoor streams. Only the set-up relevant for *Lumbriculus variegatus* and aufwuchs is shown.

Streams were made of stainless steel, streambed was divided lengthwise into two channels. Artificial sediment (washed gravel, free of clay and organics), 500 L tap water (10 cm) with nutrients. Water circulated by pump at 0.2 m/s, temperature 15 °C, daily sunlight regime. Aufwuchs was established by exposing five stones in a natural stream (Lockwitzbach, southeast of Dresden, Germany) to develop inoculum. Stones were transferred to the laboratory, invertebrates were removed, aufwuchs was washed with a water-jet, and filtered through 100 µm mesh. A suspension of the precipitate was distributed to the streams on day -19. Petri dishes with a monolayer of glass beads were used as artificial substrates. Initial biomass 0.3-0.5 g/cm^2. Successfully established periphyton consisted of green algae (*Ulothrix* sp., *Cladophora* sp.) and bacillariophyceae (*Achnanthes* sp., *Nitzschia* sp.).

Lumbriculus variegatus (100 of comparable physiological state per channel obtained from laboratory culture) were added on day -5 by fitting boxes with animals to the channels so that worms could colonise the streams.

Tebutryn was applied to the systems on day 0, nominal concentrations 0.6, 6, 60 and 600 µg/L by addition of a stock solution in water to the flow system.

Sampling

Water samples were taken from the inflow reservoir after 1 h, 3, 6, 9 days and then weekly thereafter. Chemical analysis by GC-MS after solid-phase extraction. LOQ 0.18 µg/L (detection limit 0.06 µg/L).

Biological sampling: artificial substrates were sampled every 10 days and biomass was determined. *Lumbriculus* individuals were collected at the end of the 72-days exposure period, population structure, number of segments, dry weight, migration behaviour and population growth were determined.

Results

Chemical analysis. Measured concentrations of terbutryn after 1 h were 0.43, 5.2, 53 and 519 µg/L (72-88% of nominal). Concentrations gradually declined to 0.043, 0.9, 10 and 129 µg/L after 72 days (see copied figure below). DT_{50} was estimated as 28.2 days. The metabolite desethyl terbutryn was detected after 72 days at 5% of initial added terbutryn.

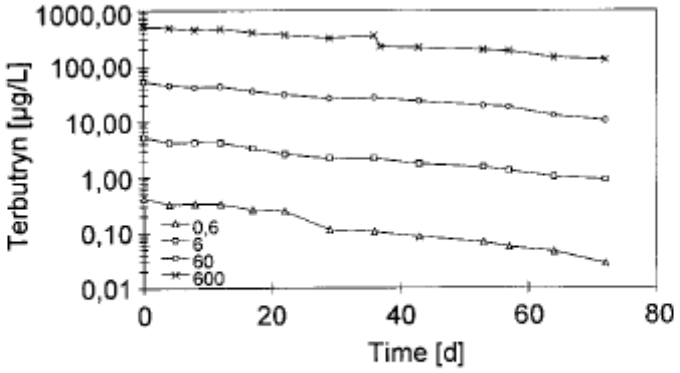


Fig. 2. Terbutryn concentration in the water of the artificial streams during 72 d of exposure.

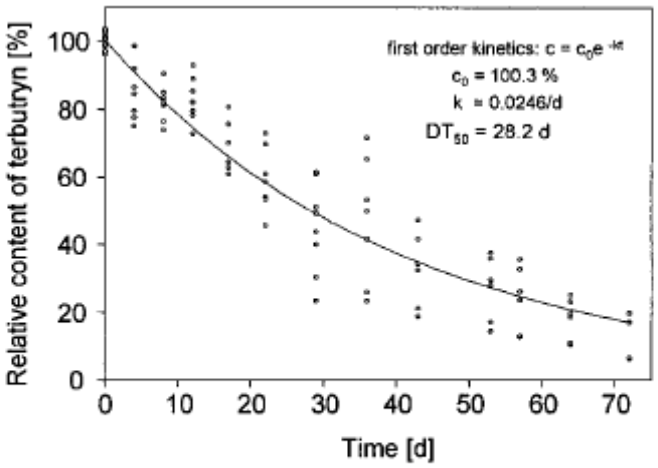


Fig. 3. Relative content of terbutryn (based on applied concentrations) in water of the treatments over time. Circles represent two water samples per treatment.

Physico-chemical characteristics. Nitrite-N, nitrate-N and ammonia-N were increased at 60 and 600 µg/L, as were ortho-phosphate-P and silicon-Si. No differences in oxygen, temperature, and pH, higher conductivity at 6 µg/L and higher.

Biological observations.

Aufwuchs. Control biomass of aufwuchs increased to 4.3 mg/cm^2 on day 50, and declined thereafter. At 0.6 µg/L, the maximum level of 2.4 mg/cm^2 was reached on day 40. No increase of biomass was found at 6 (max. 0.6 mg/cm^2 on day 30), 60 and 600 µg/L (decrease to 0.1 mg/cm^2 by day 19).

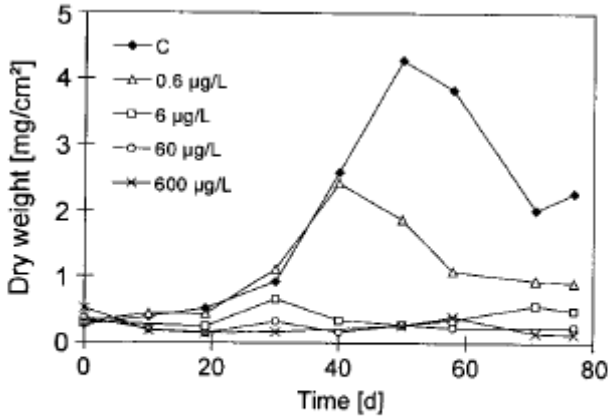


Fig. 4. Development of aufwuchs during the experiment in the artificial streams. The first sample was taken on day 0 (before terbutryn was applied).

Worms. See table from paper copied below. Total number of worms after 72 days was 1221 in the control, 1333 at 0.6 µg/L (+0.7%) and was 609 at 6 µg/L (-50%), 275 at 60 µg/L (-78%) and 241 at 600 µg/L (-81%). Reproduction occurred in all streams and different developmental stages could be observed. A concentration-related decrease was observed for the parameters number of large worms, incomplete small worms, complete small worms, dry weight/worm. No clear effect on the number of segments per worm. The numbers of worms that were retrieved on the meshes of the artificial streams, which is an indication of population stress, increased with increasing concentrations from 0.8% in the control to 10% in at 600 µg/L. Worms were observed on the meshes as from day 59.

Table 2. Effects of terbutryn on *Lumbriculus variegatus* in the artificial indoor streams (pooled results from sides A and B of each stream)

	Treatment (µg/L)				
	Control	0.6	6	60	600
Total worms[a]	1,221	1,333	609	275	241
Large worms[a]	897	975	392	232	198
Incomplete small worms[a]	209	212	120	19	26
Complete small worms[a]	115	146	97	24	17
Number of segments/worm[a,b]	118.8	117.4	85.7	97.9	105.8
Dry weight/worm (mg)[a,c]	0.72	0.70	0.42	0.26	0.35
Relative inhibition (%)[d]	0	−7.2	49.9	78.4	80.9
Σ Individuals on mesh[a]	1	8	18	24	26

[a] Total worms, large worms, incomplete small worms, complete small worms, number of segments, dry weight per worm, and Σ individuals on mesh represent pooled total from entire stream.
[b] Number of segments is the average of $n = 60$ worms per stream, except for treatment 60 ($n = 30$).
[c] Dry weight per worm is the average of $n = 60$ worms per stream, except for treatment 60 ($n = 30$).
[d] Relative inhibition of population growth of *L. variegatus* using Equation 1.

There was a clear correlation between the biomass development of aufwuchs and the number of worms, indicating that the effect on worms was due to limitations in food. This is supported by the observed decline in dry weight per worm.

Conclusions of the author

Authors report a LOEC for aufwuchs of 0.6 µg/L nominal, corresponding to 0.43 µg/L based on initial measured. The NOEC for worms is reported as 0.6 µg/L nominal, the EC50 as 6 µg/L. Effects in the artificial streams are observed at much lower concentrations than the acute LC50 of 23.7 mg/L and EC50 for deformation of 16.5 mg/L obtained from a laboratory test (see Annex 1).

Remarks

The following criteria are used to evaluate the reliability and relevance of this (semi)field study:

1. Does the test system represent a realistic freshwater community? No, the system represents a simple food-web, consisting of algae and detritivores.
2. Is the description of the experimental set-up adequate and unambiguous? Yes, details about the test system, biological and chemical sampling are reported.
3. Is the exposure regime adequately described? Yes, results of chemical sampling were presented in the text and in a figure. The reported DT50 is considered reliable and can be used to calculate time-weighted average concentrations.
4. Are the investigated endpoints sensitive and in accordance with the working mechanism of the compound? Yes. From the laboratory data it appears that algae are the potentially most sensitive species group.

The authors do not discuss the development of aufwuchs biomass in the control over time. The decline that is seen from day 50 onwards is most likely due to the increased worm populations. Algae growth rate is apparently not high enough to make up for the increased food demand. The fact that at 0.6 µg/L this point is reached 10 days earlier is consistent with this. Population development of worms at 0.6 µg/L is not affected as compared to the control, while aufwuchs biomass is likely to be directly affected as well. In this way, the disruption of the equilibrium between worm population growth and food availability is enhanced by exposure of terbutryn. The difference in aufwuchs development over time between 0.6 µg/L and the control is therefore considered as a treatment related effect.

From the study it can be concluded that the NOEC for algae is lower than 0.43 µg/L (initial measured). Since terbutryn was present for a considerable period of time, the study is considered suitable for derivation of the AA-EQS. The 50 days period in which the control showed exponential growth should be considered for the evaluation of effects. Using the DT50 of 28.2 days, the time-weighted average concentration over 50 days is 0.25 µg/L.

The result NOEC < 0.25 µg/L for aufwuchs and NOEC 0.25 µg/L for population growth of *Lumbriculus variegatus* is used for EQS-derivation.

Reference	Goldsborough LG, Robinson GGC. 1983. The effect of two triazine herbicides on the productivity of freshwater marsh periphyton. Aquat Toxicol 4, 95-112.
Species; Population; Community	periphyton
Test Method	outdoor enclosures
System properties	60 cm water depth
Compound	terbutryn > 98% pure
Exposure regime	0, 0.01, 0.1 and 1.0 mg/L
Analysed	Yes
Temperature [°C]	14-24.7
pH range	Not reported
Hardness [mg $CaCO_3$/L]	Not reported
Exposure time	single
Criterion	NOEC
Test endpoint	chlorophyll a, carbon assimilation
Value [µg/L]	< 10 µg/L
GLP	No
Guideline	No
Notes	
Ri	2 (supportive only)

Description

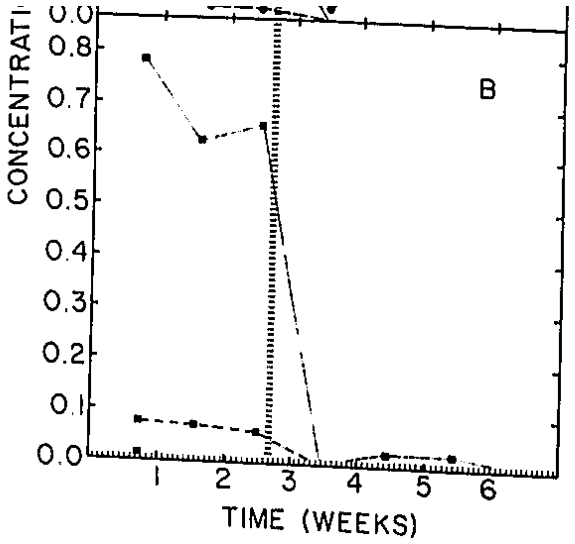
Experimental system

Littoral enclosures were set up in the Blind Channel of the Delta Marsh, southern end of Lake Manitoba. Enclosures (made of PVC-sheets, 300 L) were placed into water of ca. 60 cm depth, embedded into sediments to 45 cm. Submersed macrophytes were removed to minimise variation between enclosures. Acrylic rods were placed into the enclosures for periphytal algal colonisation. Teburtryn (0.01, 0.1 and 1 mg/L) was applied by suspension of gauze sacs with the appropriate solutions into the water, mixing was enhances by squeezing the sacs at regular time intervals during 2 days. One enclosure per treatment. Colonised substrates were sampled as from 9 days after treatment and at weekly intervals for 5 weeks thereafter. Periphyton was sampled for determination of chlorophyll a and for use in carbon assimilation experiments.

Water was sampled daily and analysed for dissolved silicon and ammonia. Terbutryn concentrations were analysed by UV-spectrophotometry. DO, light extinction and temperature were monitored weekly.

Results

Chemical analysis. Measured concentrations of terbutryn were in agreement with nominal at the start of the experiment. The lowest level of 0.01 mg/L was below the limit of detection. After 18 days, enclosures were immersed due to a strong north wind, and concentrations fell below the LOD (see figure).



Biological observations. Before the flood, al levels of terbutryn resulted in >90% reduction in chlorophyll a. Photosynthetic activity was significantly reduced at all levels, a reduction of appr. 50% was seen after 1 week. Specific productivity (carbon fixed per unit of chlorophyll a) was significantly reduced. (see figures)

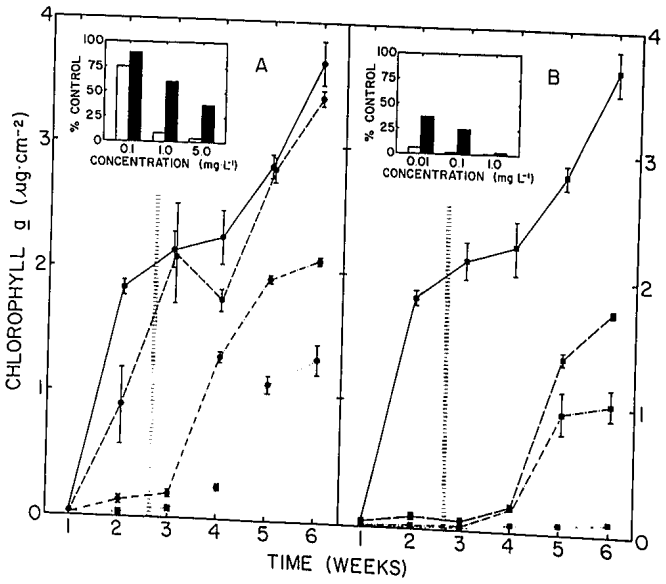


Fig. 2. A. Chlorophyll *a* levels of periphyton over the 6-wk period of the experiment in the control enclosure (●——●) and in enclosures treated with 0.1 (●----●), 1.0 (●—·—·—●) and 5.0 (●·····●) mg/l simazine. Inset: mean pre-flood (□) and post-flood (■) chlorophyll *a* in each enclosure relative to the untreated control. B. Chlorophyll *a* levels of periphyton in the control enclosure (■——■) and in enclosures treated with 0.01 (■----■), 0.1 (■—·—·—■) and 1.0 (■·····■) mg/l terbutryn. Inset: mean pre-flood (□) and post-flood (■) chlorophyll *a* in each enclosure relative to the untreated control. Error bars are the SE of replicates. The approximate period of enclosure flooding is indicated by the vertical bar.

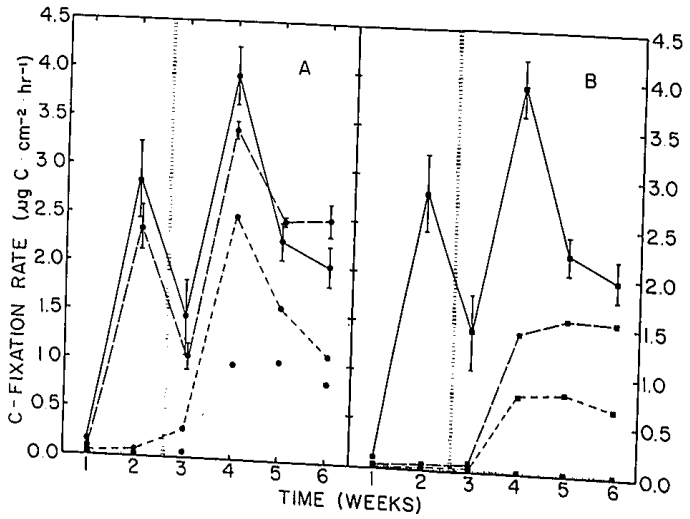


Fig. 3. A. Photosynthetic rates of periphyton over the 6-wk period of the experiment in the control enclosure (●———●) and in enclosures treated with 0.1 (●----------●), 1.0 (●—·—·—●) and 5.0 (●·····●) mg/l simazine. B. Photosynthetic rates of periphyton in the control enclosure (■———■) and in enclosures treated with 0.01 (■----------■), 0.1 (■—·—·—■) and 1.0 (■·····■) mg/l terbutryn. Error bars are the SE of replicates. The approximate period of enclosure flooding is indicated by the vertical bar.

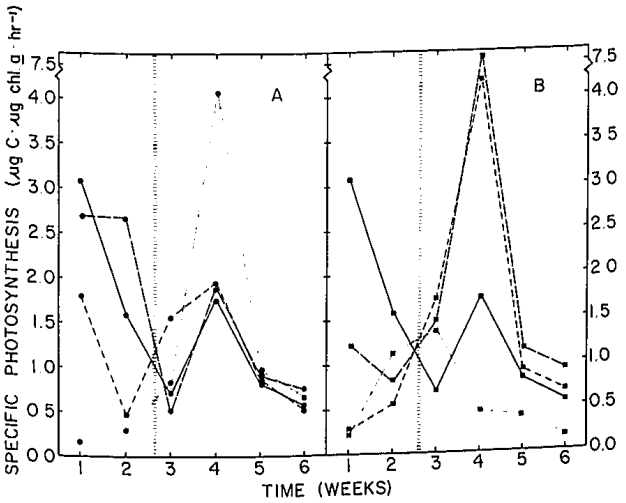


Fig. 4. A. Specific photosynthetic rate of periphyton over the 6-wk period of the experiment in the control enclosure (●———●) and in enclosures treated with 0.1 (●----------●), 1.0 (●—·—·—●) and 5.0 (●·····●) mg/l simazine. B. Specific photosynthetic rate of periphyton in the control enclosure (■———■) and in enclosures treated with 0.01 (■----------■), 0.1 (■—·—·—■) and 1.0 (■·····■) mg/l terbutryn. Vertical bars indicate the approximate period of enclosure flooding.

Recovery of all parameters was observed after the flooding had caused a drop in terbutryn levels. At the highest exposure level, water concentrations of terbutryn increased again after 5 weeks, causing a decrease in productivity. Ammonia and silicon concentrations increased as a result of decreased productivity.

Conclusions of the author

Authors report that the minimum effective concentration of terbutryn is < 0.01 mg/L, but conclude that the long-term impact after a single dosage may be minimal.

Remarks

The following criteria are used to evaluate the reliability and relevance of this (semi)field study:

1. Does the test system represent a realistic freshwater community? No, the system only covers algae.
2. Is the description of the experimental set-up adequate and unambiguous? Yes/No. The test system and chemical analysis is briefly described, biological sampling is reported adequately. Only one replicate enclosure per treatment.
3. Is the exposure regime adequately described? No, results are only presented in figures, The LOD is not adequate for the lowest treatment level. The data for the two higher treatment levels indicate that initial measured concentrations were in agreement with nominal and that concentrations remain more or less constant for 2.5 weeks.
4. Are the investigated endpoints sensitive and in accordance with the working mechanism of the compound? Yes. From the laboratory data it appears that algae are the potentially most sensitive species group.

The results indicate that strong effects on algae are to be expected after exposure to 10 µg/L and higher. Terbutryn remains present in the water phase over a longer time period, which makes this study not suitable for derivation of a MAC-QS. Furthermore, in view of the remarks above, this study can only be used as supporting information.

Reference	Gurney SE, Robinson GGC. 1989. The influemce of two triazine herbicides on the productivity, biomass and community composition of freshwater marsh periphyton. Aquat Bot 36, 1-22.
Species; Population; Community	periphyton
Test Method	outdoor enclosures
System properties	water volume 320 L, surface area/volume ratio ca. 5.2
Compound	terbutryn technical grade
Exposure regime	0, 0.01 mg/L
Analysed	Yes (end of study)
Temperature [°C]	Not reported
pH range	Not reported
Hardness [mg $CaCO_3$/L]	Not reported
Exposure time	single
Criterion	NOEC
Test endpoint	chlorophyll a, carbon assimilation
Value [µg/L]	< 10 µg/L
GLP	No
Guideline	No
Notes	
Ri	3

Description

Experimental system

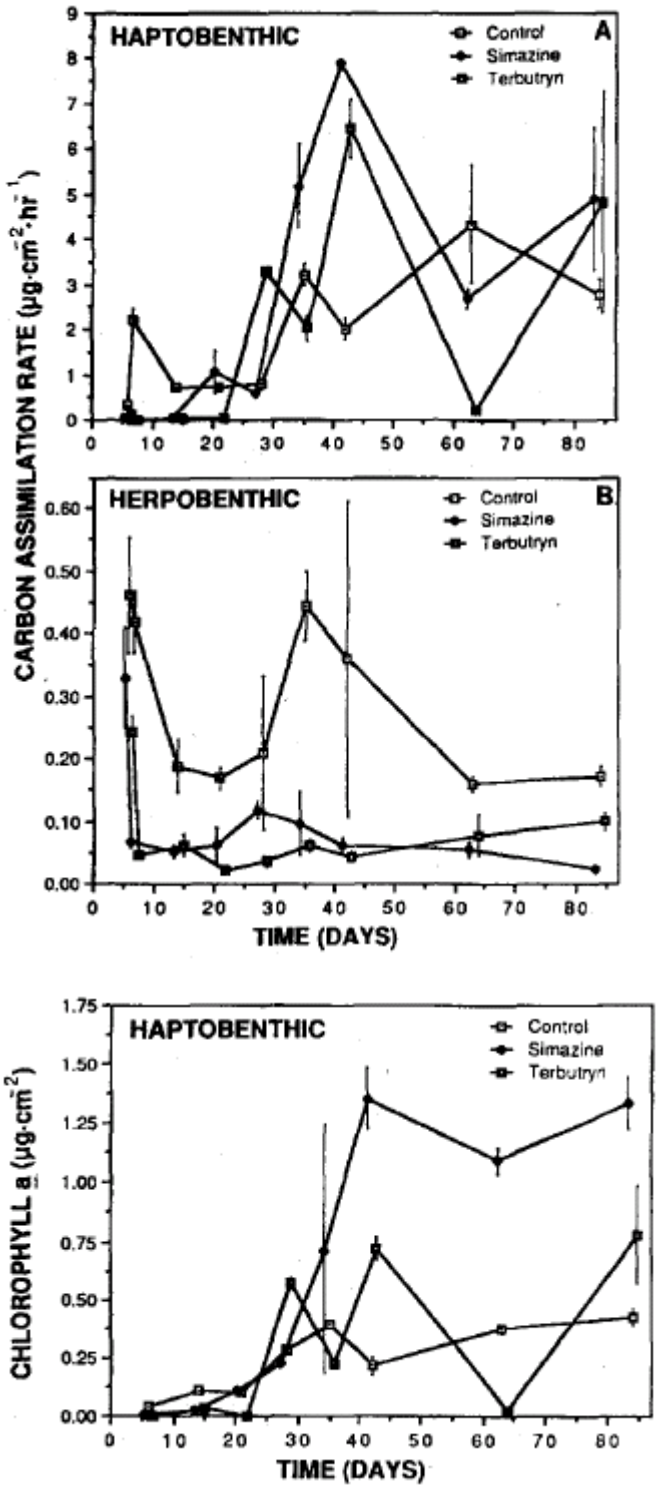
Littoral enclosures were set up in the Blind Channel of the Delta Marsh, southern end of Lake Manitoba. Enclosures (made of PVC-sheets, 120 cm high, Ø 76 cm, n=2) were placed into water. Systems were telescoping enclosures, modified from Goldsborough and Robinson (1983, see above), that allowed for 50 cm fluctuation in water level. Submersed macrophytes were absent at the time of placement, but vegetation had to be removed occasionally from the control to minimise variation between enclosures. Acrylic rods (n=84) were placed into one of the two replicate enclosures at 23 cm depth in the sediment for colonisation of haptobenthic algae. Enclosures without rods were used to sample herpobenthic (sediment living) periphyton. Teburtryn was applied six days later. Pre-weighed terbutryn was placed in a gauze sac and suspended in each enclosure. Haptobenthic algae were sampled between 28 May 1984 and 21 August 1984 on nine sampling days, eight of them after herbicide application. Colonised substrates (n=4) were removed and sub-sampled. Algae samples were removed for chlorophyll a determination. On six of the nine sampling days, algae cell counts were made and identified. Herpobenthic communities were sampled from within a 11-cm diameter PVC coring cylinder. One sediment sample was taken on each of the nine sampling days. Three cellulose tissue traps (4 cm^2) were used to determine carbon assimilation and one as dark assimilation control.

Water was sampled three times a week and analysed for DO, silicon, ammonia and total reactive phosphorous (TRP). Terbutryn concentrations were analysed by UV-spectrophotometry, LOD was too high, final concentrations were determined using GLC 86 days after herbicide application (91 days after set-up).

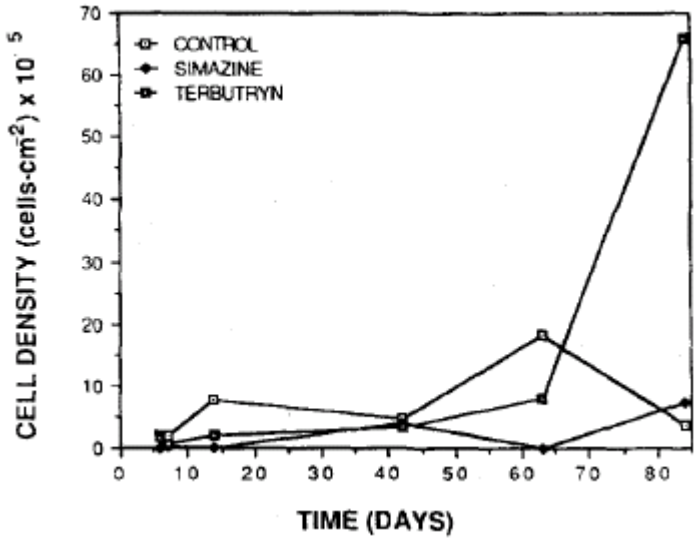
Results

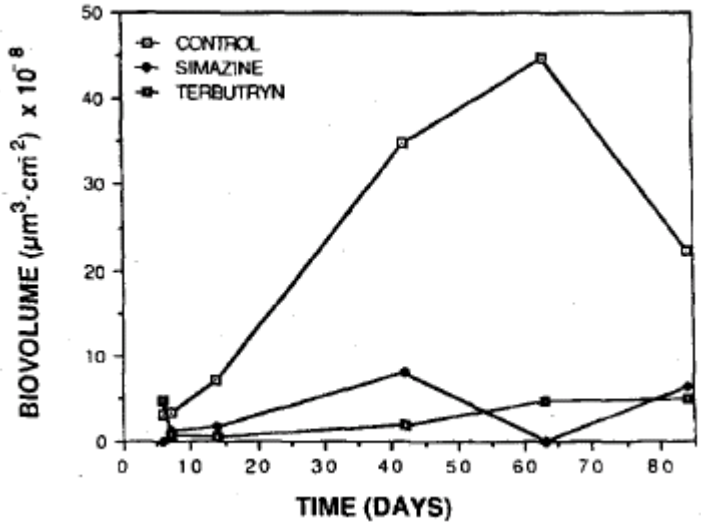
Chemical analysis. Measured concentrations of terbutryn after 86 days were in agreement 0.005 and 0.00315 mg/L (5 and 3 µg/L, 50 and 32% of nominal), indicating relatively high persistence in the water column.

Biological observations. Photosynthetic activity (measured as carbon assimilation) of haptobenthic algae was decreased for ca. 2 weeks, between 30 and 53 days a stimulation as compared to the control was present followed by a sharp decline on day 60 and a stimulus on day 84. Overall mean assimilation rate was 99% of the control. Carbon assimilation in the herpobenthic enclosures was always decreased as compared to the control (see figure). Mean assimilation rate was 27% of the control. Similar patterns were found for chlorophyll a content.



Terbutryn did not result in consistent decrease of cell density of haptobenthic algae, but biovolume was severely decreased (see figure). Differences in biovolume appeared to be related in to differences in species composition. Where the control was dominated by relatively large Chlorophyta taxa, terbutryn treatments were dominated by Bacillariophyta taxa. Mean biovolume per cell was 3050 μm^3 in the control and 216 μm^3 in the terbutryn treatment.





DO in the treated enclosures was generally lower than in the control, dissolved ammonia was substantially higher. TRP followed a similar trend as ammonia. Increased TRP and ammonia are probably related with the inhibition of algae, that normally intercept nutrients. Recovery of haptobenthic algae after 30 days caused a decrease in nutrients. Nutrient status seems to be a secondary effect. PRC-analysis was used to evaluate the relationship between nutrient concentrations and carbon assimilation, there was no statistically significant relationship in the terbutryn treatment. Silicon concentrations were roughly similar to the control. Comparison of DO, TRP, ammonia and silicon concentrations in the enclosures with those from the adjacent marsh were indicative of an enclosure effect. Authors propose that differences are due to the fact that sediment within the enclosures is less vulnerable to disturbance.

Conclusions of the author

Authors conclude that the effects of terbutryn are complex and that physiological and structural endpoints should be considered. Depending on the spatial location, algae communities may respond differently. Although functional response of haptobenthic algae recovers within about two weeks, secondary effects on nutrient conditions have a longer impact.

Remarks

The following criteria are used to evaluate the reliability and relevance of this (semi)field study:

1. Does the test system represent a realistic freshwater community? No, the system only covers algae.
2. Is the description of the experimental set-up adequate and unambiguous? Yes/No. The test system and chemical analysis is briefly described, biological sampling is reported more in details but not fully clear. Only one replicate enclosure.
3. Is the exposure regime adequately described? No, chemical analysis results are only presented briefly. The LOD is not adequate and measured concentrations are available for the end of the study only.
4. Are the investigated endpoints sensitive and in accordance with the working mechanism of the compound? Yes. From the laboratory data it appears that algae are the potentially most sensitive species group.

The results indicate that strong effects on algae are to be expected after exposure to 10 µg/L. Final concentrations after 86 days were 3 and 5 µg/L, the actual exposure concentration at the start of the test and in between is not known. Terbutryn remains present in the water phase over a longer time period, which makes this study not suitable for derivation of a MAC-QS. Furthermore, in view of the remarks above, a reliable endpoint for AA-QS derivation cannot be derived from this study.