### NAPHTHALENE

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), whose comments have been addressed as follows: Where possible, the concentrations (i.e. whether nominal or measured) used in the cited studies have been indicated. Further explanation has been added regarding the non-use of a SSD approach to determine the AA-QS, and regarding the application of an additional assessment factor for the marine sediment EQS.

This dossier is a revision of the 2005 EQS fact sheet for naphthalene, which was not totally consistent with the revised Technical Guidance for deriving EQS (E.C., 2011) and did not include the latest ecotoxicological and toxicological data contained in the final version of the European Union Risk Assessment Report (E.C., 2003) made available in the context of the assessment of existing chemicals (Regulation 793/93/EEC). The present fact sheet reviews the EQS for naphthalene based on this new document and on a report in preparation provided by RIVM (Verbruggen, in prep.) which was made available to the assessor.

### 1 <u>CHEMICAL IDENTITY</u>

Common name	Naphthalene
Chemical name (IUPAC)	Naphthalene
Synonym(s)	-
Chemical class (when available/relevant)	Polyaromatic hydrocarbons (PAH)
CAS number	91-20-3
EC number	202-049-5
Molecular formula	C <sub>10</sub> H <sub>8</sub>
Molecular structure	
Molecular weight (g.mol <sup>-1</sup> )	128.2

### 2 EXISTING EVALUATIONS AND REGULATORY INFORMATION

Legislation	
Annex III EQS Dir. (2008/105/EC)	No (existing priority substance included in Annex I EQS Dir.)
Evisting Substances Dec. (702/02/EC)	Priority List #1. Substance #020. Rapporteur: UK
Existing Substances Reg. (793/93/EC)	EU-RAR finalised 2003
Pesticides(91/414/EEC)	No
Biocides (98/8/EC)	Product Type #19 (Repellents and attractants) – To be phased out by 21/08/2009
	Decision Reference: Commission Decision 2008/681/EC
PBT substances	Not investigated by EU-PBT Working Group
Substances of Very High Concern (1907/2006/EC)	Not investigated

POPs (Stockholm convention)	Not investigated
Other relevant chemical regulation (veterinary products, medicament,)	No
Endocrine disrupter (E.C., 2004 and E.C., 2007 <sup>1</sup> )	Not investigated

<sup>1</sup> Commission staff working document on implementation of the Community Strategy for Endocrine Disrupters.

### 3 PROPOSED QUALITY STANDARDS (QS)

### 3.1 ENVIRONMENTAL QUALITY STANDARD (EQS)

 $QS_{water_{eco}}$  for protection of pelagic organisms is 2  $\mu g.\Gamma^1$  for both freshwater and marine waters, and is deemed the "critical QS" for derivation of an Environmental Quality Standard.

Data are available on 3 trophic levels for both acute and chronic ecotoxicity. Many acute data are available, including 7 and 6 taxonomic groups of freshwater and marine organisms, respectively. Many chronic data are also available, including 5 and 6 taxonomic groups of freshwater and marine organisms, respectively. Significant differences between freshwater and marine species cannot be demonstrated from the information available. An assessment factor of 10 was applied to derive the AA-QS<sub>water eco</sub> (using the assessment factor method) and no additional assessment factor was applied to derive the marine EQS in view of the substantial marine dataset and the presence of specific taxonomic groups (echinoderms). An assessment factor of 5 was applied to the chronic-HC<sub>5</sub> for derivation of the MAC-QS for both freshwater and marine water.

	Value	Comments
Proposed AA-EQS for [freshwater] [µg.I <sup>-1</sup> ]	2	Critical QS is QS <sub>water eco</sub>
Proposed AA-EQS in [marine water] [µg.l <sup>-1</sup> ]	2	See section 7
Proposed MAC-EQS for [freshwater] [µg.I <sup>-1</sup> ]	130	See section 7.1
Proposed MAC-EQS for [marine water] [µg.l <sup>-1</sup> ]	130	See Section 7.1

### 3.2 SPECIFIC QUALITY STANDARD (QS)

Protection objective <sup>2</sup>	Unit	Value	Comments
Pelagic community (freshwater)	[µg.l <sup>-1</sup> ]	2	See section 7.1
Pelagic community (marine water)	[µg.l <sup>-1</sup> ]	2	
Benthic community (freshwater)	[µg.kg⁻¹ <sub>dw</sub> ]	138	See section 7.1
Benthic community (marine)	[µg.kg⁻¹ <sub>dw</sub> ]	138	See Section 7.1
	[µg.kg <sup>-1</sup> <sub>biota ww</sub> ]	12 266	
Predators (secondary poisoning)	[µg.l <sup>-1</sup> ]	23.8 (fresh water)	See section 7.2
		23.8 (marine water)	
	[µg.kg <sup>-1</sup> <sub>biota ww</sub> ]	2 435	
Human health via consumption of fishery products	[µg.l <sup>-1</sup> ]	4.7 (fresh water)	See section 7.3
		4.7 (marine water)	
Human health via consumption of water	[µg.l <sup>-1</sup> ]	140	

<sup>&</sup>lt;sup>2</sup> Please note that as recommended in the Technical Guidance for deriving EQS (E.C., 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

All data hereunder are extracted from Naphthalene EU-RAR (E.C., 2003).

### 4.1 USES AND QUANTITIES

There are two sources for the manufacture of naphthalene in the EU. These are coal tar (which accounts for the majority of the production) and petroleum. For the purposes of the assessment the total annual production of naphthalene in the EU has been taken to be 200,000 tonnes based on site-specific information. This figure includes a production tonnage of 20,000 tonnes per annum of "naphthalene oil" which is understood to be at least 90% pure. Lower grade naphthalene oil, containing about 60% naphthalene, has a separate CAS number and has not been considered in the assessment. Companies producing naphthalene are located in the UK, Belgium, France, Italy, Netherlands, Denmark, Germany, Austria and Spain. Production figures from individual producers ranged from 4,000 to 70,000 tonnes per annum.

Figures for the amount of naphthalene used within the EU vary. For the purposes of the assessment a value of approximately 140 000 tonnes per annum has been taken in the EU-RAR, with the remaining tonnage being exported. This value was derived from the most recent information available for the specific uses summarised in the table below.

Process	Approximate annual continental tonnages used in assessment
Phthalic anhydride production	40 000
Manufacture of dyestuffs	46 000
Naphthalene sulphonic acid manufacture	24 000
Alkylated naphthalene solvent production	15 000
2-naphthol production	12 000
Pyrotechnics manufacture	15
Mothballs manufacture	1 000
Grinding wheels manufacture	350

Approximate tonnages of naphthalene assumed in the assessment

### 4.2 ESTIMATED ENVIRONMENTAL EMISSIONS

The EU-RAR (E.C., 2003) considers the release of naphthalene to the environment from its production, its use as a chemical intermediate, the formulation and use of pyrotechnics, the formulation and use of mothballs and the production of grinding wheels. Releases of naphthalene to the environment also arise from indirect sources, particularly from vehicle emissions. Releases from these sources have been estimated and included in calculating PECs at the regional and continental levels. The vast majority (~99.5%) of emissions occur initially to air. Emissions from traffic are estimated to account for 87% of the total emissions to air.

### 5 ENVIRONMENTAL BEHAVIOUR

### 5.1 ENVIRONMENTAL DISTRIBUTION

			Master reference	
	$L(m \propto 1^{-1})$	31.9	Mackay <i>et al.</i> , 1992	
Water solubility (mg.l <sup>-1</sup> )		51.9	<i>in</i> E.C., 2003; E.C., 2008b	
Volatilisation		Naphthalene is readily volatilised from surfa volatilisation from water up to 1m deep is a		
Vanaur prog		11.2 at 25°C	Mackay <i>et al.</i> , 1992	
Vapour pres	sure (Pa)	11.2 at 25 C	<i>in</i> E.C., 2003; E.C., 2008b	
Henry's Law	constant		Mackay <i>et al.</i> , 1992	
(Pa.m <sup>3</sup> .mol <sup>-1</sup> )	)	50 at 25°C	in E.C., 2003; E.C., 2008b	
Adsorption		Naphthalene is expected to adsorb to sedin The value 1 349 is used as K <sub>oc</sub> for deriva		
Organic carb	oon – water	log $K_{OC}$ = 3.13 (calculated from $K_{OW}$ )	Karialdaff at at 4070	
partition coefficient	cient (K <sub>oc</sub> )	K <sub>OC</sub> = 1 349	Karickhoff <i>et al.</i> , 1979	
Sediment - water partition coefficient( $K_{sed-water}$ )35 (calculated from $K_{OC}$ )E.C.,		E.C., 2011		
Bioaccumulatio	on	The BCF value of 515 is used for derivat $BMF_1 = BMF_2 = 1$ (Bleeker, 2009; E.C., 20		
Octanol-water partition		3.34	Mackay <i>et al.</i> , 1992	
coefficient (	Log Kow)	0.04	<i>in</i> E.C., 2003; E.C., 2008b	
Annelids		<i>Arenicola marina</i> (marine worms): 160 (oesophageal glands), 300 (stomach wall)	Lyes, 1979 <sup>3</sup>	
	Molluscs	Mytilus edulis (marine bivalve): 27 – 38	Hansen <i>et al.</i> , 1978 <sup>3</sup>	
		Daphnia magna: 50	Eastmond <i>et al.</i> , 1984 <sup>3</sup>	
	Crustaceans	Daphnia pulex: 131	Southworth <i>et al.</i> , 1978 <sup>3</sup>	
		Diporeia spp.: 311, 459, 736	Landrum <i>et al.</i> , 2003	
BCF		Pimephales promelas: 427	Call & Brook (1977) <sup>3, 4</sup>	
	Fish	Cyprinodon variegatus: 895, 999	Jonsson <i>et al.</i> , 2004	
FISH	FISH	Cyprinus carpio: 66, 76	RIITI, 1979	
		Lepomis macrochirus: 300	McCarthy and Jimenez, 1985	
If normalised to 5% lipid weight, values from Jonsson et al. (2004) result in a worst BCF for fish of 515. This latter value is chosen for back calculation of QS <sub>biota</sub> into wate well as default BMF values of 1 according to Draft Technical Guidance Document on derivation (E.C., 2011).			culation of QS <sub>biota</sub> into water as	

<sup>&</sup>lt;sup>3</sup> As cited *in* Veith *et al.*, 1979, cited itself *in* E.C., 2003.

<sup>&</sup>lt;sup>4</sup> Note that this reference can not be traced back. Therefore, it can not be used with confidence.

### 5.2 ABIOTIC AND BIOTIC DEGRADATIONS

		Master reference
	ion, oxidation and hydrolysis are not considered to be significant pathways f rbon degradation in the soil environment (Sims and Overcash, 1983 <i>as cited</i>	
Hydrolysis	PAH are chemically stable, with no functional groups that results in hydrolysis. Under environmental conditions, therefore, hydrolysis does not contribute to the degradation of anthracene (Howard <i>et al.</i> , 1991).	E.C., 2008b
Photolysis	The main abiotic transformation is photochemical decomposition, which in natural water takes place only in the upper few centimetres of the aqueous phase. PAHs are photodegraded by two processes, direct photolysis by light with a wavelength < 290 nm and indirect photolysis by least one oxidizing agent (Volkering and Breure, 2003). Singlet oxygen usually plays the main role in this process. The degradation is related to the content of oxygen dissolved (Moore and Ranamoorthy, 1984). When PAHs are absorbed on particles, the accessibility for photochemical reactions may change, depending on the nature of the particles. It was shown by Zepp and Schlotzhauer that for PAHs in true solution in "pure" water or seawater, direct photolysis is considerably more significant than photooxidation by means of singlet oxygen. There are great differences in photochemical reactivity between the various PAHs.	E.C., 2008b
	The half-life for photolysis in water lies in the range $25 - 550$ hours depending on the experimental conditions used.	E.C., 2003
Biodegradation	The results of the only standardised screening test for inherent biodegradability for naphthalene suggest that naphthalene is not inherently biodegradable (2% degradation after 4 weeks). However, numerous other 'non-standard' biodegradation tests suggest that it is easily degraded under aerobic and denitrifying conditions, particularly where acclimated microorganisms are used, with naphthalene falling below measurable levels within 8-12 days in a number of tests. Naphthalene has therefore been considered to be inherently biodegradable in the Final EU-RAR (E.C., 2003).	E.C., 2003

## 6 AQUATIC ENVIRONMENTAL CONCENTRATIONS

### 6.1 ESTIMATED CONCENTRATIONS

Compartment		Predicted environmental concentration (PEC)	Master reference
Freshwater (µg.l <sup>-1</sup> )	PEC <sub>continental</sub>	0.0025	E.C., 2003
	PEC <sub>regional</sub>	0.03	
	PEC <sub>local – production</sub> (worst case)	0.31	
	PEC <sub>local –</sub> use as intermediate (site-sp.)	0.031	
	PEC <sub>local</sub> – use as intermediate	0.042	

	PEClocal – pyrotechnics manufacture	2.35		
	PEClocal – mothballsmanufacture	0.03		
	PEClocal - grinding wheels manufacture	294		
Marine waters (µg.l <sup>-1</sup> )	-	No data available	E.C., 2003	
	PEC <sub>continental</sub>	0.075		
	PEC <sub>regional</sub>	1		
	PEC <sub>local – production (worst case)</sub>	8.7		
Freebuster and ment (up kg <sup>-1</sup> du)	PEC <sub>local –</sub> use as intermediate (site-sp.)	0.87		
Freshwater sediment (µg.kg <sup>-1</sup> dw)	PEC <sub>local – use as intermediate</sub>	1.2	E.C., 2003	
	PEClocal – pyrotechnics manufacture	66		
	PEClocal – mothballsmanufacture	0.83		
	PEClocal - grinding wheels manufacture	8 232		
Marine sediment (µg.kg <sup>-1</sup> dw)	-	No data available	E.C., 2003	
Biota (freshwater)		No data availat	ble	
Biota (marine)		No data availat	ble	
Biota (marine predators)		No data available		

## 6.2 MEASURED CONCENTRATIONS

Compartment		Measured environmental concentration (MEC)		Master reference
		PEC 1:	0.12	James <i>et al.</i> ,
Freshwater (µg.l <sup>-1</sup> )		PEC 2:	1.17	2009 <sup>(1)</sup>
		0.005 –	2.24	E.C., 2003
Marine waters (coastal a	nd/or transitional) (µg.l <sup>-1</sup> )	0.3	3	E.C., 2003
WWTP effluent (µg.l <sup>-1</sup> )		N	o data available	
	Sed . 0 mm	PEC 1:	117	
	Sed < 2 mm	PEC 2:	97	
	Sed 20 µm	PEC 1:	766	James <i>et al.</i> ,
Sediment (µg.kg <sup>-1</sup> dw)		PEC 2:	655	2009 <sup>(1)</sup>
	Sed 63 µm	PEC 1:	54	
		PEC 2:	41	
	Freshwaters	Up to 750		
	Estuarine and coastal	Up to 91		E.C., 2003
	Urban areas	Up to 7 720		
Biota (µg.kg <sup>-1</sup> ww)	Invertebrates	PEC 1:	6	
		PEC 2:	6	James <i>et al.</i> ,
		PEC 1:	79	2009 <sup>(1)</sup>
	Fish	PEC 2:	19	

Compartment		Measured environmental concentration (MEC)	Master reference
	Marine predators	No data available	

<sup>(1)</sup> data originated from EU monitoring data collection

### 7 EFFECTS AND QUALITY STANDARDS

Final Coal Tar Pitch High Temperature EU-RAR (E.C., 2008b) states that "PAHs can be toxic via different modes of action, such as non-polar narcosis and phototoxicity. The last is caused by the ability of PAHs to absorb ultraviolet A (UVA) radiation (320-400 nm), ultraviolet B (UVB) radiation (290-320 nm), and in some instances, visible light (400-700 nm). This toxicity may occur through two mechanisms: photosensitization, and photomodification. Photosensitization generally leads to the production of singlet oxygen, a reactive oxygen species that is highly damaging to biological material. Photomodification of PAHs, usually via oxidation, results in the formation of new compounds and can occur under environmentally relevant levels of actinic radiation (Lampi et al., 2006). The photo[induced]toxic effects can be observed after a short period of exposure, which explains why for PAHs like anthracene, fluoranthene and pyrene, where photo[induced]toxicity is most evident, the acute toxicity values are even lower than the chronic toxicity values. According to some authors (Weinstein and Oris, 1999) there is a growing body of evidence which suggests that photo[induced] toxic PAHs may be degrading aquatic habitats, particularly those in highly contaminated areas with shallow or clear water. For example, the photoinduced chronic effects of anthracene have been reported at those UV intensities occurring at depths of 10 to 12 m in Lake Michigan (Holst and Giesy, 1989). In addition to direct uptake of PAHs from the water column, another potential route of exposure for aquatic organisms is their accumulation from sediments (see e.g. Clements et al., 1994; Kukkonen and Landrum, 1994), followed by subsequent solar ultraviolet radiation exposures closer to the surface. Ankley et al. (2004) also concluded in their peer review that PAHs are present at concentrations in aquatic systems such that animals can achieve tissue concentrations sufficient to cause photoactivated toxicity. Although UV penetration can vary dramatically among PAH-contaminated sites, in their view it is likely that at least some portion of the aquatic community will be exposed to UV radiation at levels sufficient to initiate photoactivated toxicity. They do recognize that at present time, the ability to conduct PAH photoactivated risk assessment of acceptable uncertainty is limited by comprehensive information on species exposure to PAH and UV radiation during all life stages. PAH exposure and uptake, as well as UV exposure, are likely to vary considerably among species and life stages as they migrate into and out of contaminated locations and areas of high and low UV penetration. For all but sessile species, these patterns of movements are the greatest determinant of the risk for photoactivated toxicity."

Despite these uncertainties, it is thought that the photo[induced]toxic effects cannot be ignored in the effects assessment and EQS derivation processes. Therefore these effects are also considered in this dossierand it should be noted that the UV exposure levels of the selected studies did not exceed the UV levels under natural sun light conditions.

### 7.1 ACUTE AND CHRONIC AQUATIC ECOTOXICITY

Ecotoxicity data reported in the tables hereunder were extracted exclusively from the finalised version of EU-RAR (E.C., 2008b) and a RIVM report in preparation (Verbruggen, in prep.) which was made available to the assessor.

Final naphthalene EU-RAR (E.C., 2003) indicates that care must be taken when interpreting data from tests based on nominal concentrations because naphthalene can rapidly volatilise from solution in case of e.g. poorly sealed test beakers. Therefore, whenever it was possible, for each species, endpoints were reported for tests for which results were based on measured concentrations (reported as (m) in the tables hereunder) rather than nominal concentrations (reported as (n) in the tables hereunder). Also, when available, information was given on the type of exposure, i.e.: static (s), static closed (sc), renewal (r), renewal closed (rc), or continuous flow (cf).

Given that many PAH chemicals are phototoxic, information on the absence/presence of light as well as the type of light was reported in the tables as much as possible.

In the tables below, all data reported were considered valid for effects assessment purposes when they could be given a reliability index (Klimisch code) of 1 or 2, or were considered useful as supporting information for effects assessment purposes, i.e. could be given a reliability index (Klimisch code) of 2/3. Information on reliability was retrieved from the RIVM report in preparation (Verbruggen, in prep.). Information on reliability was not available in the finalised version of EU-RAR (E.C., 2008b) but no data

#### Naphthalene EQS dossier 2011

extracted only from the RAR that were not also evaluated by RIVM are key data for QS derivation. Finally, it is to be noted that naphthalene is highly volatile and that many toxicity studies were therefore rejected by RIVM "due to high uncertainty in exposure concentrations, either because analysis showed that the concentrations in static systems dropped very quick or because exposure concentrations were not analytically verified" (Verbruggen, in prep.). Still, there are many valid toxicity data available for this substance.

### 7.1.1 Organisms living in the water column

### ACUTE EFFECTS

ACUTE EFFEC	TS		Klimisch code	Master reference	
	Freshwater	Nitrosomonas / unknown duration	Assessed by E.C., 2003	Blum and Speece,	
		$IC_{50 - inhibition ammonia consumption} = 29 (n, sc)$	4 acc <sup>ing</sup> to RIVM	1991	
		Tetrahymena pyriformis / 60h		Schultz <i>et al.</i> ,	
		IC <sub>50 - growth</sub> = 188.85	Assessed by E.C., 2003	1983	
Micro- organisms		Anabaena flos-aqua / 2h			
Bacteria		$EC_{50 - nitrogen fixation - continuous light} = 24 (m, s)$	2 acc <sup>ing</sup> to RIVM	Bastian and Toetz, 1985	
(µg.l <sup>-1</sup> )	Marine	Vibrio fischeri / 15mn			
		EC <sub>50 – bioluminescence – dark</sub> = 0.72 (n, s)	2 acc <sup>ing</sup> to RIVM	El-Alawi <i>et al.</i> , 2001	
		$EC_{50-bioluminescence-visible light} = 0.7 (n, s)$		2001	
		Vibrio fischeri / 30mn / Lumistox test	ing	Loibner <i>et al.</i> ,	
		EC <sub>50 - bioluminescence - dark</sub> = 1.89 (m, s)	2 acc <sup>ing</sup> to RIVM	2004	
	Freshwater	Pseudokirchneriella subcapitata / 4h	Assessed by E.C., 2003	Millemann <i>et al.</i> ,	
		EC <sub>50 – growth (photosynthesis)</sub> =2.96 (m, s)	2 acc <sup>ing</sup> to RIVM	1984	
		Nitzschia palae / 4h	Assessed by E.C., 2003		
		$EC_{50 - growth (photosynthesis)} = 2.82 (m, s)$	2 acc <sup>ing</sup> to RIVM	Millemann <i>et al.</i> , 1984	
		Scenedesmus vacuolatus / 24h			
Algae &		EC50 – growth (cell number) = 3.8 (m, sc)	2 acc <sup>ing</sup> to RIVM	Walter <i>et al.</i> , 2002	
aquatic plants	Marine	Skeletonema costatum / unknow duration	Østgaard <i>et al.</i> ,		
(mg.l⁻¹)		$EC_{30 \text{ to } 50 - \text{growth}} = 0.4$	Assessed by E.C., 2003	1984	
		Champia parvula / 14d / female			
		$EC_{50 - growth - light:dark=16:8h} = 2.2$ (n, rc)			
		Champia parvula / 14d /	2 acc <sup>ing</sup> to RIVM	Thursby et al.,	
		tetrasporophyte		1985	
				1985	
Invertebrates	Freshwater	tetrasporophyte $EC_{50-growth-light:dark=16:8h} = 1.378$ (n, rc,	Assessed by E.C., 2003	1985 Millemann <i>et al.</i> ,	
	Freshwater Molluscs	tetrasporophyte EC <sub>50 - growth - light:dark=16:8h</sub> = 1.378 (n, rc, geo. mean)	Assessed by E.C., 2003 2 acc <sup>ing</sup> to RIVM		
		tetrasporophyte EC <sub>50 - growth - light:dark=16:8h</sub> = 1.378 (n, rc, geo. mean) <i>Physa gyrina</i> / 48h		Millemann <i>et al.</i> , 1984	
	Molluscs	tetrasporophyte $EC_{50 - growth - light:dark=16:8h} = 1.378$ (n, rc, geo. mean) <i>Physa gyrina /</i> 48h $LC_{50} = 5.02$ (m, rc)	2 acc <sup>ing</sup> to RIVM	Millemann <i>et al.</i> , 1984	
	Molluscs	tetrasporophyte $EC_{50-growth-light:dark=16:8h} = 1.378$ (n, rc, geo. mean) <i>Physa gyrina /</i> 48h $LC_{50} = 5.02$ (m, rc) <i>Daphnia magna /</i> 48h	2 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003	Millemann <i>et al.</i> , 1984 Crider <i>et al.</i> , 1982	
	Molluscs	tetrasporophyte $EC_{50 - growth - light:dark=16:8h} = 1.378$ (n, rc, geo. mean) <i>Physa gyrina</i> / 48h $LC_{50} = 5.02$ (m, rc) <i>Daphnia magna</i> / 48h $LC_{50 - light:dark=16:8h} = 3.4$ or $4.1^5$ (m, s)	2 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003 2/3 acc <sup>ing</sup> to RIVM	Millemann <i>et al.</i> , 1984	
	Molluscs	tetrasporophyte $EC_{50 - growth - light:dark=16:8h} = 1.378$ (n, rc, geo. mean) Physa gyrina / 48h $LC_{50} = 5.02$ (m, rc) Daphnia magna / 48h $LC_{50 - light:dark=16:8h} = 3.4$ or $4.1^5$ (m, s) Daphnia magna / 48h	2 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003 2/3 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003 2 acc <sup>ing</sup> to RIVM	Millemann <i>et al.</i> , 1984 Crider <i>et al.</i> , 1982 Millemann <i>et al.</i> , 1984	
	Molluscs	tetrasporophyte $EC_{50 - growth - light:dark=16:8h} = 1.378$ (n, rc, geo. mean) <i>Physa gyrina</i> / 48h $LC_{50} = 5.02$ (m, rc) <i>Daphnia magna</i> / 48h $LC_{50 - light:dark=16:8h} = 3.4$ or $4.1^5$ (m, s) <i>Daphnia magna</i> / 48h $EC_{50 - immobility} = 2.16$ (m, sc)	2 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003 2/3 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003	Millemann <i>et al.</i> , 1984 Crider <i>et al.</i> , 1982 Millemann <i>et al.</i> , 1984	
Invertebrates (mg.I <sup>-1</sup> )	Molluscs	tetrasporophyte $EC_{50 - growth - light:dark=16:8h} = 1.378 (n, rc, geo. mean)$ <i>Physa gyrina /</i> 48h $LC_{50} = 5.02 (m, rc)$ <i>Daphnia magna /</i> 48h $LC_{50 - light:dark=16:8h} = 3.4 \text{ or } 4.1^5 (m, s)$ <i>Daphnia magna /</i> 48h $EC_{50 - immobility} = 2.16 (m, sc)$ <i>Daphnia magna /</i> 48h	2 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003 2/3 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003 2 acc <sup>ing</sup> to RIVM	Millemann <i>et al.</i> , 1984 Crider <i>et al.</i> , 1982 Millemann <i>et al.</i> , 1984 Bisson <i>et al.</i> , 2000	
	Molluscs	tetrasporophyte $EC_{50 - growth - light:dark=16:8h} = 1.378$ (n, rc, geo. mean)         Physa gyrina / 48h $LC_{50} = 5.02$ (m, rc)         Daphnia magna / 48h $LC_{50 - light:dark=16:8h} = 3.4$ or $4.1^5$ (m, s)         Daphnia magna / 48h $EC_{50 - light:dark=16:8h} = 3.4$ or $4.1^5$ (m, s)         Daphnia magna / 48h $EC_{50 - light:dark=16:8h} = 2.16$ (m, sc)         Daphnia magna / 48h $EC_{50 - immobility - dark} = 1.664$ (m, s)         Daphnia pulex / 96h	2 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003 2/3 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003 2 acc <sup>ing</sup> to RIVM 2 acc <sup>ing</sup> to RIVM	Millemann <i>et al.</i> , 1984 Crider <i>et al.</i> , 1982 Millemann <i>et al.</i> , 1984	
	Molluscs	tetrasporophyte $EC_{50-growth-light:dark=16:8h} = 1.378 (n, rc, geo. mean)$ $Physa gyrina / 48h$ $LC_{50} = 5.02 (m, rc)$ $Daphnia magna / 48h$ $LC_{50-light:dark=16:8h} = 3.4 \text{ or } 4.1^5 (m, s)$ $Daphnia magna / 48h$ $EC_{50-immobility} = 2.16 (m, sc)$ $Daphnia magna / 48h$ $EC_{50-immobility-dark} = 1.664 (m, s)$	2 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003 2/3 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003 2 acc <sup>ing</sup> to RIVM 2 acc <sup>ing</sup> to RIVM Assessed by E.C., 2003	Millemann <i>et al.</i> , 1984 Crider <i>et al.</i> , 1982 Millemann <i>et al.</i> , 1984 Bisson <i>et al.</i> , 2000 Trucco <i>et al.</i> ,	

<sup>&</sup>lt;sup>5</sup> Value depending on data treatment (3.4 applying linear regression versus 4.1 applying probit analysis)

#### ACUTE EFFECTS

тѕ		Klimisch code	Master reference	
	Gammarus minus / 48h	Assessed by E.C., 2003	Millemann et al.,	
	LC <sub>50</sub> = 3.93 (m, sc)	2 acc <sup>ing</sup> to RIVM	1984	
Marine	Neanthes arenaceodentata / 96h	2 acc <sup>ing</sup> to RIVM	Rossi and Neff, 1978	
Annelids	LC50 = 1.069 (m, s)			
Molluscs	<i>Mytilus edulis /</i> 48h EC <sub>50 - feeding filtration</sub> = 0.922 (m, r)	2 acc <sup>ing</sup> to RIVM	Donkin <i>et al.</i> , 1991; Donkin <i>et</i> <i>al.</i> , 1989	
Crustaceans	Artemia salina / larvae nauplii / 24h	Assessed by E.C., 2003		
	$EC_{50 - immobility - constant illumination} = 3.19$ (m, s)	2 acc <sup>ing</sup> to RIVM	Foster and Tullis, 1984	
	Callinectes sapidus / adult / 48h	Assessed by E.C., 2003		
	$LC_{50 - constant artificial illumination} = 2.3 (m, cf, geo. mean)$	2 acc <sup>ing</sup> to RIVM	Sabourin, 1982	
	<i>Cancer magister</i> / 1 <sup>st</sup> instar larvae / 96h	Assessed by E.C., 2003	Caldwell et al.,	
	$LC_{50-\text{light:dark}=13:11h} > 2 (m, r)$	2 acc <sup>ing</sup> to RIVM	1977	
	Calanus finmarchicus / 96h	2 acc <sup>ing</sup> to RIVM	Falk-Petersen <i>et</i>	
	LC50 = 2.4 (m, sc)		<i>al.</i> , 1982	
	Elasmopus pectenicrus / 96h		Lee and Nicol,	
	LC <sub>50</sub> = 2.68 (n, rc)	2/3 acc <sup>ing</sup> to RIVM	1978a	
	<i>Eualis suckleyi /</i> 96h	Assessed by E.C., 2003	Rice and Thomas	
	LC <sub>50</sub> = 1.39 (m, cf)	2 acc <sup>ing</sup> to RIVM	1989	
	Eurytemora affinis / adult / 24h	Assessed by E.C., 2003	Ott at al. 1079	
	LC <sub>50</sub> = 3.8 (m, sc)	2 acc <sup>ing</sup> to RIVM	Ott <i>et al.</i> , 1978	
	<i>Hemigrapsus nudus /</i> 8d			
	LC <sub>50</sub> = 1.863 (n, cf, geo. mean)	2 acc <sup>ing</sup> to RIVM	Gharrett and Rice	
	$EC_{50 - locomotory dysfunction} = 1.648$ (n, cf, geo. mean)		1987	
	Neomysis Americana / 96h	Assessed by E.C., 2003	Smith and	
	LC <sub>50</sub> = 1.043 (m, cf, geo. mean)	2 acc <sup>ing</sup> to RIVM	Hargreaves, 198	
	Neomysis Americana / 96h	Assessed by E.C., 2003	Hargreaves et al	
	LC <sub>50</sub> = 1.066 (m, r, geo. mean)	2 acc <sup>ing</sup> to RIVM	1982	
	<i>Oithona davisae / </i> 48h			
	LC <sub>50</sub> = 7.19 (m, s)	2 acc <sup>ing</sup> to RIVM	Barata <i>et al.</i> , 200	
	$EC_{50 - immobility} = 4.48 \text{ (m, s)}$			
	Palaemonetes pugio / adult / 24h	4 acc <sup>ing</sup> to RIVM	Anderson et al.,	
	LC <sub>50</sub> = 2.6 (s)		1974	
	Palaemonetes pugio / adult / 24 – 96h	4 acc <sup>ing</sup> to RIVM	Tatem, 1975	
	LC <sub>50</sub> = 2.35 (n, s)			
	Palaemonetes pugio / 48h	2 acc <sup>ing</sup> to RIVM	Under et al 200	
	$LC_{50-fluorescent constant light} = 2.111 (m, r)$		Unger <i>et al.</i> , 2008	

#### Klimisch code Master reference **ACUTE EFFECTS** Paracartia grani / 48h $LC_{50 - light:dark=12:12h} = 2.517$ (m, s, geo. 2 acc<sup>ing</sup> to RIVM Calbet et al., 2007 mean) $EC_{50 - immobility - light:dark=12:12h} = 2.467$ (m, s) Parhyale hawaiensis / 24h Lee and Nicol, 2 acc<sup>ing</sup> to RIVM 1978b $LC_{50} = 6 (n, sc)$ Penaeus aztecus / 24 - 96h Anderson et al.. 4 acc<sup>ing</sup> to RIVM 1974 $LC_{50} = 2.5$ (s) Scylla serrata / intermoult juvenile / Kulkarni and 96h Assessed by E.C., 2003 Masurekar, 1983 $LC_{50} = 17 (n)$ Chironomus tentans / 4th instar larvae Sediment Assessed by E.C., 2003 Millemann et al... / 48h Insects 1984 2 acc<sup>ing</sup> to RIVM $EC_{50 - immobility - dark} = 2.81 (m, sc)$ Chironomus riparius / 96h / 1<sup>st</sup> instar, <24h Bleeker et al., 2 acc<sup>ing</sup> to RIVM $LC_{50-mercury light} = 0.6 (m, s)$ 2003 $LC_{50 - UV \text{ light}} = 0.65 \text{ (m, s)}$ Somatochlora cingulata / 96h Correa and Coler, 4 acc<sup>ing</sup> to RIVM 1983 $LC_{50} = 1 - 2.5$ (n) Fish Freshwater Oncorhynchus kisutch / 96h / fry, 1g Assessed by E.C., 2003 Moles et al., 1981 2 acc<sup>ing</sup> to RIVM $(mg.l^{-1})$ $LC_{50} = 2.1 (m, cf)$ Oncorhynchus kisutch / 96h / fry, 0.3g, 7d 2 acc<sup>ing</sup> to RIVM Moles, 1980 LC<sub>50</sub>= 3.22 (m, cf) Oncorhynchus mykiss / 96h Assessed by E.C., 2003 DeGraeve et al., 1982 2 acc<sup>ing</sup> to RIVM $LC_{50-light:dark=16:8h} = 1.6 (m, cf)$ Oreochromis mossambicus / 96h 4 acc<sup>ing</sup> to RIVM Dangé, 1986 $LC_{50} = 7.9 (n, r)$ Pimephales promelas / 96h / 31 - 35d Holcombe et al., 2 acc<sup>ing</sup> to RIVM 1984 LC<sub>50</sub> =6.08 (m, cf) Pimephales promelas / 96h / 1-2 mo, Millemann et al., 0.27g 2 acc<sup>ing</sup> to RIVM 1984 $LC_{50-light:dark=16:8h} = 1.99 (m, sc)$ Pimephales promelas / 96h / 0.9g, Assessed by E.C., 2003 DeGraeve et al., 46mm 1982 2 acc<sup>ing</sup> to RIVM $LC_{50-light:dark=16:8h} = 7.8 (m, cf)$ Cyprinodon variegatus / 24 - 96h Marine Anderson et al.. 4 acc<sup>ing</sup> to RIVM 1974 $LC_{50} = 2.4$ (s) Fundulus heteroclitus / 96h / 8.2±2cm DiMichele and 2 acc<sup>ing</sup> to RIVM Taylor, 1978 LC<sub>50 - light:dark=14:10h</sub> =5.3 (m, r) Onchorhynchus gorbuscha / 96h / Assessed by E.C., 2003 Moles and Rice, 325mg, 32mm 1983 2 acc<sup>ing</sup> to RIVM $LC_{50} = 1.2 (m, cf)$

Naphthalene EQS dossier 2011

ACUTE EFFEC	тѕ		Klimisch code	Master reference
		Onchorhynchus gorbuscha / 48h / fry	Assessed by E.C., 2003	Rice and Thomas,
		LC <sub>50</sub> = 0.961 (m, cf)	2 acc <sup>ing</sup> to RIVM	1989
	Sediment	No inforr	mation available	
	Freshwater	<i>Xenopus laevis /</i> 96h / larvae, 3w	Assessed by E.C., 2003	Edmisten and
		$LC_{50-light:dark=12:12h} = 2.1 (m, cf)$	2/3 acc <sup>ing</sup> to RIVM	Bantle, 1982
Amphibians		<i>Xenopus laevis /</i> 96h		
(mg.l <sup>-1</sup> )		Frog Embryo Teratogenesis Assay- Xenopus (FETAX). No effects at saturated concentrations.	Assessed by E.C., 2003	Schultz and Dawson, 1995

#### Master reference CHRONIC EFFECTS Valid according to Pseudokirchneriella subcapitata / 72h Freshwater 2 acc<sup>ing</sup> to RIVM Bisson et al., 2000 Algae $EC_{10-arowth} > 4\ 270\ (m, s)$ Scenedesmus vacuolatus / 24h 2 acc<sup>ing</sup> to RIVM Walter et al., 2002 $NOEC_{growth (cell number) - fluorescent light} = 1.2$ (m, sc) Algae & *Lemna gibba /* 8d Macrophytes aquatic plants 2 acc<sup>ing</sup> to RIVM Ren et al., 1994 $EC_{10-growth rate-partial UV light} = 32 (m, r)$ (mg.l<sup>-1</sup>) Marine Champia parvula / 14d / female Macrophytes $EC_{10-growth-light:dark=16:8h} = 0.85$ (n, rc) Thursby et al., 2 acc<sup>ing</sup> to RIVM Champia parvula / 14d / 1985 tetrasporophyte $EC_{10-growth-light:dark=16:8h} = 0.47$ (n, rc) Invertebrates Daphnia magna / 28d Freshwater 4 accing to E.C., 2003 Parkhurst, 1982 $(mg.l^{-1})$ Crustaceans NOEC = 3Ceriodaphnia dubia / 7d / ind<24h 2 acc<sup>ing</sup> to RIVM Bisson et al., 2000 EC<sub>10</sub> - reproduction light:dark=16:8h = 0.514 (m, r) Hyalella azteca / 10d / org.=2-3w, 0.5-1mm 2 acc<sup>ing</sup> to RIVM Lee et al., 2002 $NOEC_{mortality} = 1.161 (m, r)$ Mytilus edulis / 48h / fertilized eggs Marine Molluscs $EC_{10-larval development-dark} = 4.037 (m,$ 2 acc<sup>ing</sup> to RIVM sc, average) Bellas et al., 2008 EC<sub>10 - larval development - light:dark=14:10h</sub> = 8.241 (m, sc, average) Crustaceans Cancer magister / 40d / Alaska larvae NOEClarval development - ligh:dark=13:11h = 0.021 (m, cf) Caldwell et al., 2 acc<sup>ing</sup> to RIVM Cancer magister / 60d / Oregon 1977 larvae $NOEC_{larval\ development\ -\ ligh:dark=13:11h} \geq$ 0.17 (m, cf) Eurytemora affinis / 10d Berdugo et al., 2 acc<sup>ing</sup> to RIVM 1977 $NOEC_{feeding \; rate, \; egg \; production} \geq 0.05 \; (m, \; r)$ Eurytemora affinis / lifetime, 15d 2 acc<sup>ing</sup> to RIVM Ott et al., 1978 NOEC<sub>repro</sub> < 0.014 (m, sc, one concentration tested) Paracartia grani / 48h / eggs **Echinoderms** 1.3 < NOEC<sub>egg hatching -</sub> 2 acc<sup>ing</sup> to RIVM Calbet et al., 2007 light:dark=12:12h < 6.4 (m. r. one concentration tested) Paracentrotus lividus / 48h / fertilized eggs $EC_{10-larval development-dark} = 0.649 (m,$ 2 acc<sup>ing</sup> to RIVM Bellas et al., 2008 sc, average) $EC_{10-larval development-light:dark=14:10h} =$ 0.741 (m, sc, average)

CHRONIC EFI	FECTS		Valid according to	Master reference
		Psammechinus miliaris / 48h / fertilized eggs, 2-8 cells, <4 h NOEClarval development – light:dark=16:8h ≥	2 acc <sup>ing</sup> to RIVM	AquaSense, 2005
		0.355 (m, sc) Strongylocentrus droebachiensis / eggs / ELS / 96h LC <sub>10</sub> = 0.94 (m, s)	2 acc <sup>ing</sup> to RIVM	Falk-Petersen <i>et al.</i> , 1982
		Strongylocentrus droebachiensis / eggs / ELS / 96h	2 acc <sup>ing</sup> to RIVM	Saethre <i>et al.</i> , 1984
		$LC_{10} = 0.58 \text{ (m, s)}$		
	Sediment	<i>Tanytarsus dissimilis /</i> life-cycle / spiked water, no sediment	2-3 acc <sup>ing</sup> to RIVM 3 acc <sup>ing</sup> to the assessor	Darville and
	(freshwater)	NOEC <sub>egg</sub> hatching, adult emergence – light:dark=16:8h < 0.5 (m, cf)	(see text hereunder)	Wilhm, 1984
	Freshwater	Danio rerio / 96h / larvae NOEC <sub>malformations</sub> ≥ 0.388 (m, r, one concentration tested)	io rerio / 96h / larvae $C_{malformations} \ge 0.388$ (m, r, one $2 \operatorname{acc}^{\operatorname{ing}}$ to RIVM K	
		<i>Micropterus salmoides /</i> 7 d incl. 4 post-hatch / eggs 2-4 d post spawning	2 acc <sup>ing</sup> to RIVM	Black <i>et al.</i> , 1983
		LC <sub>10</sub> = 0.037 (m, cf)		
		<i>Oncorhynchus kisutch</i> / 40d / fry, 1g NOEC <sub>growth</sub> = 0.37 (m, cf)	2 acc <sup>ing</sup> to RIVM	Moles <i>et al.</i> , 1981
		Oncorhynchus mykiss / 27 d incl. 4 post-hatch / eggs 20 min post fertilization	2 acc <sup>ing</sup> to RIVM	Black <i>et al.</i> , 1983
Fish		LC <sub>10</sub> = 0.02 (m, cf)		
(mg.l <sup>-1</sup> )		<i>Pimephales promelas /</i> 30d / embryo- larvae	2 acc <sup>ing</sup> to RIVM	DeGraeve <i>et al.</i> , 1982
		$NOEC_{growth - light:dark=16:8h} = 0.45 (m, cf)$		
	Marine	Gadus morhua / 4d / eggs / ELS LC <sub>10</sub> = 1 (m, s, geo. mean)	2 acc <sup>ing</sup> to RIVM	Falk-Petersen <i>et al.</i> , 1982
		Gadus morhua / 4d / eggs / ELS	ing	Saethre <i>et al.</i> ,
		$LC_{10} > 0.7$ (m, s, weighted average)	2 acc <sup>ing</sup> to RIVM	1984
		<i>Oncorhynchus gorbuscha</i> / 40d / 325 mg, 32 mm	2acc <sup>ing</sup> to RIVM	Moles and Rice, 1983
		$NOEC_{growth} = 0.12 (m, cf)$		
	Sediment		mation available	1
	<b>Marine</b> Ascidians	Ciona intestinalis / 20h / fertilized eggs		
Tunicates		$EC_{10-larval development-dark} = 0.61$ (m, sc, average)	2 acc <sup>ing</sup> to RIVM	Bellas <i>et al.</i> , 2008
		EC <sub>10</sub> - larval development - light:dark=14:10h =3.025 (m, sc, average)		

	Available ecotoxicological information for organisms living in water column					
	Fresh water species	Marine species				
	7 taxonomic groups	6 taxonomic groups				
Acute	- algae, crustaceans, and fish	- algae, crustaceans and fish				
	<ul> <li>micro-organisms, molluscs, insects, amphibians</li> </ul>	- micro-organisms, annelids, molluscs				
	5 taxonomic groups	6 taxonomic groups				
Chronic	- algae, crustaceans, and fish	- algae, crustaceans and fish				
	- macrophytes and insects	- cnidarians, molluscs, and echinoderms				

The Technical Guidance Document on EQS derivation (E.C., 2011) states that "*in principle, ecotoxicity data* for freshwater and saltwater organisms should be pooled for organic compounds, if certain criteria are met" and that "the presumption that for organic compounds saltwater and freshwater data may be pooled must be tested, except where a lack of data makes a statistical analysis unworkable."

For naphthalene in fact, there are enough data to perform a "*meaningful statistical comparison*" and the statistical analysis made showed no evidence of "*a difference in sensitivity between freshwater vs saltwater organisms*" (F-test 0.19; t-test 0.99; Verbruggen, in prep.). Moreover, the mode of action (cf. reference to narcosis above) is an additional information allowing no to differentiate between the two media.

Therefore, in this case, the data sets may be combined for QS derivation according to the Technical Guidance Document on EQS derivation (E.C., 2011).

#### **Determination of the MAC**

#### Assessment Factor Method

The majority of the results from short-term tests lie in the range 1-10 mg.l<sup>-1</sup>, except for some data on prokaryotes (bacteria and cyanophyta). All of the organisms tested appear to show similar sensitivity in the short-term tests, which is characteristic of narcotic effects. The predicted values were 7.8 mg.l<sup>-1</sup> (LC<sub>50</sub> for fish), 6.1 mg.l<sup>-1</sup> (LC<sub>50</sub> for daphnia) and 3.8 mg.l<sup>-1</sup> (EC<sub>50</sub> for algae), all of which fit closely the range of measured values whilst being towards the high end. Therefore, assessment factors of 10 and 100 applied to the lowest acute data seem conservative enough for derivation of MAC-QS<sub>freshwater, eco</sub> and MAC-QS<sub>marine water, eco</sub>, respectively. The effect concentration of 0.4 mg.l<sup>-1</sup> for *Skeletonema costatum* is the lowest value of the dataset. However, exposure duration is unknown and the percentage of affected organisms is unclear (30 to 50%). Therefore, the value obtained on *Chironomus riparius* with a 96h exposure *via* water – which is of the same order of magnitude as for the diatom *Skeletonema* – is preferred for derivation of the MAC<sub>water, eco</sub> of 60 µg.l<sup>-1</sup>.

#### SSD Method

If the acute data sets for freshwater and marine species are combined, the combined data set appears sufficient to apply a statistical derivation approach to derive the MAC-QS<sub>water, eco</sub> values. Indeed, data appropriate for the derivation of a Species Sensitivity Distribution (SSD) include 7 taxonomic groups (algae, annelids, bacteria, crustaceans, molluscs, fish and amphibians) but it is not deemed necessary to include macrophytes as sensitive species to naphthalene given the high  $EC_{10}$  obtained for *Lemna gibba* after a chronic exposure of 8d, i.e. 32 mg.l<sup>-1</sup>.

In its report in preparation (Verbruggen, in prep.), RIVM proposes such an assessment based on the combined freshwater and marine datasets. The Species Sensitivity Distribution (SSD) curves after the goodness of fit has been tested are reported hereunder for acute ecotoxicity.

## LC50 or EC50 [ug 1<sup>-1</sup>] Taxon Species

#### Selected acute toxicity data of naphthalene to freshwater species (Verbruggen, in prep.)

Taxon	Species	
Algae	Nitzschia palea	2820
Algae	Pseudokirchneriella subcapitata	2960
Algae	Scenedesmus vacuolatus	3800
Amphibia	Xenopus laevis	2100
Crustacea	Daphnia magna	1896 a
Crustacea	Diporeia spp.	1587
Crustacea	Gammarus minus	3930
Cyanophyta	Anabaena flos-aqua	24000
Insecta	Chironomus riparius	600 b
Mollusca	Physa gyrina	5020
Pisces	Oncorhynchus mykiss	2212 c
Pisces	Pimephales promelas	4572 d

<sup>a</sup> Geometric mean of 2160 and 1664 μg/L for the most sensitive parameter (immobility) at a standard exposure time of 48 h <sup>b</sup> Most sensitive lifestage exposed under light conditions including some UV-A <sup>c</sup> Geometric mean of 2100, 3220, and 1600 μg.l<sup>1</sup>

<sup>d</sup> Geometric mean of 1680, 1990, and 7900 µg.I<sup>-1</sup>

#### Selected acute toxicity data of naphthalene to marine species (Verbruggen, in prep.)

Taxon	Species	LC50 or EC50 [µg.l <sup>-1</sup> ]
Algae	Champia parvula	1378 <sup>a</sup>
Annelida	Neanthes arenaceodentata	1069
Bacteria	Vibrio fischeri	710 <sup>b</sup>
Crustacea	Artemia salina	3190
Crustacea	Calanus finmarchicus	2400
Crustacea	Elasmopus pectenicrus	2680
Crustacea	Eualis suckleyi	1390
Crustacea	Eurytemora affinis	3800
Crustacea	Hemigrapsus nudus	1100 <sup>c</sup>
Crustacea	Neomysis Americana	825 <sup>d</sup>
Crustacea	Oithona davisae	4480 <sup>e</sup>
Crustacea	Palaemonetes pugio	2111
Crustacea	Paracartia grani	2467 <sup>e</sup>
Crustacea	Parhyale hawaiensis	6000
Mollusca	Callinectus sapidus	2301 <sup>f</sup>
Mollusca	Mytilus edulis	922
Pisces	Fundulus heteroclitus	5300
Pisces	Oncorhynchus gorbuscha	1200 <sup>g</sup>

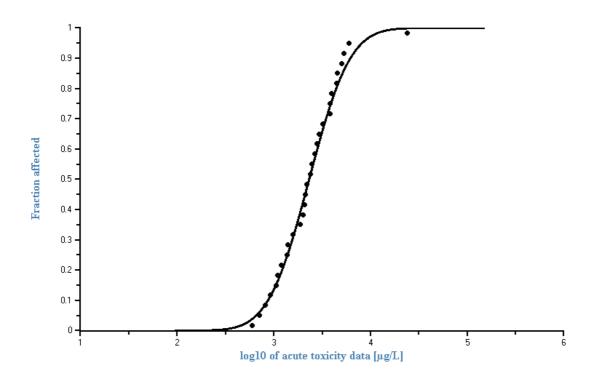
<sup>a</sup> Geometric mean of 1000 and 1900 μg.l<sup>-1</sup> for the most sensitive lifestage (tetrasporophyte) <sup>b</sup> Geometric mean of 700 and 720 μg.l<sup>-1</sup> at standard exposure time (15 min)

<sup>c</sup> Lowest value obtained with continuous exposure instead of intermittent exposure <sup>d</sup> Geometric mean of 800 and 850  $\mu$ g.l<sup>-1</sup> at highest test temperature of 25 °C

<sup>e</sup> Most sensitive parameter (immobility)

<sup>f</sup> Lowest value at highest salinity of 30‰

<sup>9</sup> Most relevant exposure time (96 h) and probably also most relevant life-stage for acute toxicity testing



# Species sensitivity distribution for the acute toxicity of naphthalene to freshwater and marine species (Verbruggen, in prep.).

The HC<sub>5</sub> of this SSD is 650  $\mu$ g.l<sup>-1</sup>, the HC<sub>50</sub> is 2324  $\mu$ g.l<sup>-1</sup>. The MAC<sub>water, eco</sub> is by default derived applying an assessment factor of 10 to the HC<sub>5</sub>. However, in their report in preparation, the RIVM states that "*the number of toxicity data and the taxonomic diversity is high and the differences in species sensitivity are low, which is characteristic of narcotic effects.*"

The RIVM proposes the above direct comparison for nine species from five taxonomic groups of the noeffect level and the 50% effect levels. The values are different by a factor of 5 or less.

Taxon	Species	EC50/EC10 or LC50/LC10 (mg.l <sup>-1</sup> )
Amphibia	Xenopus laevis	1.6
Algae	Scenedesmus vacuolatus	2.2
Algae	Champia parvula	1.4 – 2.1
Bacteria	Vibrio fischeri	4.8
Crustacea	Calanus finmarchicus	1.1
Crustacea	Oithona davisae	1.8
Crustacea	Paracartia grani	1.6
Crustacea	Parhyale hawaiensis	1.6
Cyanophyta	Anabaena flos-aqua	2.5

Acute no effect le	evels (10%	cut-off	by	means	of	EC10)	versus	50%	effect	levels	(EC50)	for
naphthalene												

Given that the MAC<sub>water, eco</sub> has to be protective of any acute toxicity effects but that the values used in the SSD are 50% effective concentrations and given the little difference between 50% effect levels and no effect levels, RIVM considered an assessment factor of 5 as sufficient to apply to the HC5 to derive the MAC<sub>freshwater, eco</sub>. Given the large number of marine data in the dataset and the presence of non standard species such as seaweed, annelids and molluscs, an extra assessment factor for the MAC<sub>marine water, eco</sub> was not deemed necessary. Thus, both MAC<sub>freshwater, eco</sub> and MAC<sub>marine water, eco</sub> could be set to 130  $\mu$ g.l<sup>-1</sup>.

There are no acute data below these proposed values of 130  $\mu$ g.l<sup>-1</sup>. Therefore, this value seems sufficiently conservative and is proposed as MAC<sub>freshwater, eco</sub> and MAC<sub>marine water, eco</sub> rather than the values obtained by the assessment factor method.

### Determination of the AA-QS<sub>water, eco</sub>

#### <u>Assessment Factor Method</u>

Longer-term studies are also available to derive AA-QS<sub>water, eco</sub>. Species sensitivities are again rather comparable between taxa but less than for acute data as fish and daphnia appear to be more sensitive than algae. The RIVM report (Verbruggen, in prep.) justifies the use of the two results on fish reported by Black et al. (1983) data – while it was disregarded by naphthalene RAR – as follows: The data reported for Black et al. (1983) show a clear dose-response relationship.

"The  $LC_{10}$  for survival after 4 days post-hatching is 20 µg/L. Clearly, this is the lowest usable effect concentration for naphthalene in freshwater species. In the RAR of naphthalene the study of Black et al., was disregarded because the method could not be repeated with toluene and it generally gives much lower results than standard studies. After reconsideration, it was concluded in the RAR of coal tar pitch that the value could be used.

There are some differences between the studies with toluene and naphthalene. First, for toluene the difference with the other toxicity data is several orders of magnitude, while for naphthalene, there are several studies which show the onset of chronic effects or effects on sensitive life stages around the value of 20 µg/L. For the most sensitive strain of Dungeness crabs a NOEC of 21 µg/L was found in a 40-d study (Caldwell et al., 1977). In this study only two exposure concentrations are used. Although well-performed, the statistical power of this test is limited. For the marine herbivorous copepod Eurytemora affinis one concentration of 14 µg/L tested in a 15-d study resulted in significant effects (Ott et al., 1977).

Second, the EC10 for toluene is also an order of magnitude lower than that for naphthalene, while naphthalene is a compound with a log  $K_{ow}$  that is 0.6 unit higher than that of toluene. For this reason, the EC10 for naphthalene would be expected to be lower than the EC10 for toluene, which is apparently not the case.

Further, both EC10s do not originate from the same publication, or at least toluene has been omitted from the publication. If a read-across is performed with the data for phenanthrene instead of toluene with data from the same study (Black et al., 1983), the data are very well in line with another study with the same species and with data for other species tested with phenanthrene. Therefore, the EC10 is considered to be useful in this case."

The available data cover 5 freshwater taxonomic groups as well as 6 marine taxonomic groups, including echinoderms. Hence an assessment factor of 10 applied to the lowest chronic value of 0.02 mg.l<sup>-1</sup> obtained from a 27d-study on salmonid *Oncorhynchus mykiss* is deemed relevant to derive both AA-QS<sub>freshwater, eco</sub> and AA-QS<sub>marine water, eco</sub>.

#### SSD Method

Valid chronic toxicity data are available for more than 10 species originating from seven taxonomic groups. Usable value for an additional eighth taxa representing the insects is missing. Indeed, in a full life-cycle study with the midge *Tanytarsus dissimilis*, it was concluded that concentrations below 500  $\mu$ g.l<sup>-1</sup> resulted in minimal effects (Darville and Wilhm, 1984) but details on the dose-response relationship for this species are missing and some results are ambiguous (deletion of results of one control and one treatment subunits for the reason that no hatching was observed). With this value missing on insects, a species sensitivity distribution can in principle not be applied. For comparative purposes the SSD was tentatively realised by RIVM in their report (resulting in a HC<sub>5</sub> of 25  $\mu$ g.l<sup>-1</sup>) but the data did not fit well to a log-normal distribution and effects for one species that were observed in one study were not always observed in the other or differences existed even between different strains for the same species. Moreover, there were some effects observed even below the lowest EC<sub>10</sub>. The wide range of NOEC or EC<sub>10</sub> values for different species, also

raised some question whether there were "more specific modes of toxic action involved besides the baseline toxicity caused by narcosis". RIVM considered that "part of the differences might also be explained from the difficulties in maintaining constant exposure concentration in toxicity".

Because of all these uncertainties, a species sensitivity distribution can in principle not be applied and assessment factor method is applied exclusively to derive AA-QS<sub>water, eco</sub>.

Tentative QS <sub>water</sub> Assessment factor method	Relevant study for derivation of QS	AF	Tentative QS
MAC <sub>freshwater</sub> , eco	SSD-HC₅ = 0.65 mg.l <sup>-1</sup>	5	130 µg.l⁻¹
MAC <sub>marine water, eco</sub>	$33D - HC_5 = 0.05$ Hig.i	5	130 µg.l⁻¹
AA-QS <sub>freshwater</sub> , eco	Oncorhynchus mykiss / 27 d incl. 4	10	2 µg.l <sup>-1</sup>
AA-QS <sub>marine water, eco</sub>	post-hatch / eggs 20 min post fertilization $LC_{10} = 0.02 \text{ mg.I}^{-1}$	10	2 µg.l <sup>-1</sup>

### 7.1.2 Sediment-dwelling organisms

The toxicity of naphthalene was studied exposing the sediment-dwelling crustacean *Rhepoxynius abronius* during 10d *via* spiking of muddy sand (2.58% organic matter) (Boese *et al.*, 1998). The endpoints were mortality and reburial and irradiation of the crustaceans with UV light had little effect on these parameters. The EC<sub>50</sub> for reburial of *Rhepoxynius abronius* after 10 days of exposure is 227  $\mu$ mol.g<sup>-1</sup> for an OC content of 2.58%. This value corresponds to a concentration of 29 101 mg.kg<sup>-1</sup> for the same OC content and to a value of 56 397 mg.kg<sup>-1</sup> when normalized to an OC content of 5% as recommended by the Draft Technical Guidance Document on EQS derivation (E.C., 2011).

RIVM notes in its report that although this value is an  $EC_{50}$ , the exposure time (10-d) as well as the endpoint (reburial) are rather chronic than acute. Nevertheless, the difference with the  $LC_{50}$  is negligible ( $LC_{50}$  normalised to 5% OC content is 57 889 mg.kg<sup>-1</sup><sub>dw</sub>). The long-term test on the freshwater sediment species *Tanytarsus* cited here before (see section 7.1.1., SSD method) can not be used for the above cited reasons, and in particular because the test was carried out in the absence of sediment.

Because of the dataset available (one acute test but no true long-term sediment test available and no saltwater sediment test representing different living and feeding conditions), assessment factors of 1000 and 10 000 should be applied to derive  $QS_{freshwater, sed}$  and  $QS_{marine water, sed}$  of 56 397 µg.kg<sup>-1</sup><sub>dw</sub>, respectively 56 397 µg.kg<sup>-1</sup><sub>dw</sub> as recommended by the TGD on EQS derivation (E.C., 2011).

Tentative QS <sub>water, sed</sub> Assessment factor method	Relevant study for derivation of QS	AF	Tentative QS
AA-QS <sub>freshwater</sub> , sed.	Rhepoxynius abronius / 10d	1 000	56 397 µg.kg⁻¹ <sub>dw</sub>
AA-QS <sub>marine water, sed.</sub>	$LC_{50}$ of 57 889 mg.kg $^{-1}_{dw}$ EC <sub>50</sub> of 56 397 mg.kg $^{-1}_{dw}$	10 000	5 639 µg.kg <sup>-1</sup> <sub>ww</sub>
AA-QS <sub>freshwater</sub> , sed.	Oncorhynchus mykiss / 27 d incl. 4 post-hatch / eggs 20 min post	EqP	53 µg.kg <sup>-1</sup> <sub>ww</sub> 138 µg.kg <sup>-1</sup> <sub>dw</sub>
AA-QS <sub>marine water, sed.</sub>	fertilization $LC_{10} = 0.02 \text{ mg.I}^{-1}$	EqP	53 µg.kg <sup>-1</sup> <sub>ww</sub> 138 µg.kg <sup>-1</sup> <sub>dw</sub>

The values derived via the equilibrium partitioning approach are more conservative and therefore proposed as the  $QS_{water, sed}$  values.

#### Naphthalene EQS dossier 2011

As a matter of comparison, provisional ecotoxicological assessment criteria for naphthalene in seawater and sediment were agreed in November 1993 (Oslo and Paris Commissions, 1994). For seawater, the ecotoxicological assessment criteria was provisionally set as 1-10  $\mu$ g.l<sup>-1</sup>, based on a NOEC of 40  $\mu$ g.l<sup>-1</sup> and an assessment factor of 10. Concentrations in sediment were calculated by applying the equilibrium partitioning approach and the provisional assessment criteria for sediment is 10-100  $\mu$ g.kg<sup>-1</sup><sub>dw</sub>.

### 7.2 SECONDARY POISONING

Based on the Technical Guidance Document on EQS derivation (E.C., 2011), this substance does trigger the bioaccumulation criteria (e.g. log  $K_{OW} = 3.34$ ) although the toxicological data available do not seem to demonstrate a high toxicological potential (NOEC > 1 000 mg.kg<sup>-1</sup><sub>feed ww</sub>).

Secondary poisoning of to	Master reference	
	Mouse / Oral / 90d / absolute brain, liver and spleen weights for females NOAEL = 133 mg.kg <sup>-1</sup> <sub>bw</sub> .d <sup>-1</sup> NOEC = 1 104 mg.kg <sup>-1</sup> <sub>feed ww</sub> (CF=8.3)	Shopp et al (1984) <i>in</i> E.C., 2003
Mammalian oral toxicity	Dog / Oral / 7d / Haemolytic anaemia LOAEL = 220 mg.kg <sup>-1</sup> <sub>bw</sub> .d <sup>-1</sup> LOEC = 8 800 mg.kg <sup>-1</sup> <sub>feed ww</sub> (CF=40) <i>Poorly conducted study with no control</i> (as cited in E.C., 2003)	Zuelzer and apt (1949) <i>in</i> E.C., 2003
	Reprotoxicity: Overall naphthalene only produces fetotoxicity at maternally toxic doses in animals, and does not produce developmental toxicity at maternally subtoxic doses.	E.C., 2003
Avian oral toxicity		

For the back calculation of  $QS_{biota, hh}$  into water, the BCF value of 515 is used as well as  $BMF_1 = BMF_2 = 1$  (cf. section 5.1).

Tentative QS <sub>biota secpois</sub>	Relevant study for derivation of QS	AF	Tentative QS
Biota	NOEC = 1 104 mg.kg <sup>-1</sup> <sub>feed ww</sub>	90	12 266 µg.kg <sup>-1</sup> <sub>biota ww</sub>
			corresponding to
			23.8 µg.l <sup>-1</sup> (freshwater)
			23.8 µg.l <sup>⁻1</sup> (marine water)

### 7.3 HUMAN HEALTH

Based on the Technical Guidance Document on EQS derivation (E.C., 2011), this substance does trigger the criteria defined on the basis of the hazardous properties of the chemical of interest. Specific triggers include classification criteria according to the Regulation on classification, labelling and packaging of substances and mixtures (E.C., 2008a), which are H302 (Harmful if swallowed) and H351 (Suspected of causing cancer). Based on this information, a QS<sub>biota, hh</sub> should be derived.

Human health via consumption of fishery products		Master reference	
Mammalian oral toxicity	Mouse / Oral / 90d / absolute brain, liver and spleen weights for females	Shopp et al (1984) <i>in</i> E.C., 2003	
	NOAEL = $133 \text{ mg.kg}^{-1}_{bw}.d^{-1}$		
	NOEC = 1 104 mg.kg <sup>-1</sup> <sub>feed ww</sub> (CF=8.3)		
	If naphthalene is considered to be not carcinogenic, due to its negative genotoxicity as suggested in an RIVM report (Baars <i>et al.</i> , 2001), then it is deemed acceptable to use the proposed TDI of 0.04 mg.kg <sup>-1</sup> <sub>bw</sub> .d <sup>-1</sup> as the Threshold Level.	Baars <i>et al.</i> , 2001	
	Not classified as mutagenic nor reprotoxic.		
	Classified as Carcinogenic category 2: suspected carcinogenic substance	E.C., 2008a	
	No oral threshold values are available in the EU-RAR.	E.C., 2008b	
CMR	Potential of naphthalene for carcinogenicity is questioned and discussed by ATSDR, RIVM, and U.S. EPA. Conclusions are controversial:	US-EPA, 1998	
	- EPA classifies this compound as C, a possible human carcinogen, using criteria of the 1986 cancer guidelines (US-EPA, 1986). Using the 1996 Proposed Guidelines for Carcinogen Risk Assessment (US-EPA, 1996), the human carcinogenic potential of naphthalene via the oral or inhalation routes "cannot be determined" at this time based on human and animal data; however, there is suggestive evidence [observations of benign respiratory tumors and one carcinoma in female mice only exposed to naphthalene by inhalation (NTP, 1992]. Additional support includes increase in respiratory tumors associated with exposure to 1-methylnaphthalene. An oral slope factor for naphthalene was not derived because of a lack of chronic oral naphthalene studies.		
	- RIVM questioned the potential for carcinogenicity of naphthalene but concluded that it is not carcinogenic due to its negative genotoxicity, therefore basing their risk estimate on the threshold approach (Baars <i>et al.</i> , 2001).		
	- ATSDR has published a Toxicological Profile for Naphthalene (ATSDR, 2005). Although ATSDR discusses the carcinogenicity data in its evaluation, it does not currently assess cancer potency or perform cancer risk assessments.		

According to the evaluations reported above, a clear conclusion cannot be drawn on the carcinogenic potential of naphthalene. There is no evidence of naphthalene being a genotoxic substance; therefore, it is considered acceptable to base the  $QS_{biota, hh}$  on a Tolerable Daily Intake of 40  $\mu$ g.kg<sup>-1</sup><sub>bw</sub>.d<sup>-1</sup> as the Threshold Level.

For the back calculation of  $QS_{biota, hh}$  into water, the BCF value of 515 is used as well as  $BMF_1 = BMF_2 = 1$  (cf. section 5.1).

Tentative QS <sub>biota hh</sub>	Relevant data for derivation of QS	AF	Threshold Level (mg.kg <sup>-1</sup> <sub>bw</sub> .d <sup>-1</sup> )	Tentative QS <sub>biota, hh</sub>
Human health	TPH fraction specific RfD of t TPHCWG method (TPHCWG 1997) <sup>(1)</sup>		0.04	2 435 μg.kg <sup>-1</sup> <sub>biota ww</sub> corresponding to 4.7 μg.l <sup>-1</sup> (fresh and marine waters)

<sup>(1)</sup> TPH = Total Petroleum Hydrocarbons; TPHCWG = Total Petroleum Hydrocarbons Criteria Working Group, Toxicology Technical Action Group

Human health via consumption of drinking water		Master reference
Existing drinking water standard(s)	No existing regulatory standard	Directive 98/83/EC
Provisional calculated drinking water standard	140 μg.l <sup>-1</sup>	Baars <i>et al.</i> , 2001 and E.C., 2011

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