ACES REPORT 28

Copper in sediment

EQS data overview

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EQS DATA OVERVIEW

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Preface

The Department of Environmental Science and Analytical Chemistry (ACES) at Stockholm University was commissioned, by the Swedish Agency for Marine and Water Management and the Swedish Environmental Protection Agency, to perform a literature overview and EQS derivation for the specific pollutant copper in sediment. The work was performed under the Water Framework Directive (2000/60/EC) using the European Communities's guidance document "Technical Guidance for Deriving Environmental Quality Standards".

The report was prepared by Sara Sahlin and Marlene Ågerstrand.

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The Department of Environmental Science and Analytical Chemistry (ACES)
Stockholm University

Förtydligande från Havs- och Vattenmyndigheten

Havs- och vattenmyndigheten planerar att ta med sedimentvärden för koppar bland de bedömningsgrunder som ingår i Havs- och vattenmyndighetens föreskrifter (HVMFS 2013:19) om klassificering och miljökvalitetsnormer avseende ytvatten[1]. Stockholm Universitet har därför på uppdrag av Havs- och vattenmyndigheten och Naturvårdsverket tagit fram beslutsunderlag för att kunna etablera bedömningsgrunder för koppar i sediment. Utifrån litteratursökning och granskning av underlag har förslag på värden beräknats utifrån de riktlinjer som ges i CIS 27 (European Communities, 2011). I denna rapport har flera alternativa värden tagits fram utifrån olika beräkningssätt. Slutgiltigt val av värden att utgå ifrån vid statusklassificering har föreslagits av Havs- och vattenmyndigheten och efter dialog med deltagare i en arbetsgrupp (representanter från Kemikalieinspektionen, Naturvårdsverket och Läkemedelsverket).

I enlighet med detta föreslås för limnisk miljö respektive marin miljö **36 och 52 mg/kg torrvikt**. Båda värdena avser sediment med 5% TOC. Värdena är framtagna utifrån en deterministisk beräkning och en ”added risk” approach, vilket innebär att det har tagits fram för att man i samband med utvärderingen ska beakta naturlig bakgrundshalt om den annars hindrar efterlevnaden av värdet.

Bedömningsgrunder för koppar i sediment har ännu inte beslutats.

[1] https://www.havochvatten.se/hav/vagledning--lagar/foreskrifter/register-vattenforvaltning/klassificering-och-miljokvalitetsnormer-avseende-ytvatten-hvmfs-201319.html

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1. METHOD CONSIDERATION

The work was performed under the Water Framework Directive (2000/60/EC) using the European Communities's (2011) guidance document "Technical Guidance for Deriving Environmental Quality Standards".

Environmental Quality Standards (EQS) for pelagic communities has previously been derived for copper (HVMFS 2013:19). This derivation aims to derive complementary EQS for the sediment compartment for protection of benthic communities.

Data sources

Ecotoxicity studies were collected from the REACH registration dossier for copper and the European Union Risk Assessment Report: *Voluntary Risk assessment of copper, copper II sulphate pentahydrate, copper(I)oxide, copper (II) oxide, dicopper chloride trihydroxide* (ECI, 2008). A complementary search for peer-reviewed studies in the scientific literature was conducted. The following databases were used: Scopus; Web of science; Google Scholar; ETOX; Ekotoxzentrum; UBA; INERIS; RIVM; The following keywords were used: Copper* sediment* toxicity* chronic* NOEC* EC10* LC10* EC50* dietary exposure* freshwater* marine waters* saltwater* Mollusca* macrophytes* echinoderms* mesocosm* microcosm* field study* field SSD (short for species sensitivity distributions).

Due to time restrictions, reliability and relevance evaluations were not performed. In addition, only data from studies investigating chronic duration and endpoints have been considered.

Bioavailability of copper

The bioavailability of copper in sediment is controlled by multiple factors such as physico-chemical (e.g. pH, redox potential, particle size), geochemical (e.g. organic matter, metal oxide, sulfide) and biological (e.g. feeding behavior, uptake rates). Several methods are available to describe the bioavailability fraction of metals in anoxic sediments, such as EqP (Equilibrium partitioning) and the SEM-AVS (Simultaneously Extracted Metals – Acid Volatile Sulfides) approach. The SEM-AVS approach is based on the concept that the relation of metals and reactive sulfides controls the bioavailability (and toxicity) in sediment by controlling metal concentration in pore water. Basically, one mole of SEM will react with one mole of AVS and in case where AVS exceeds SEM concentrations (SEM/AVS ratio <1), all metals will be bound to sulfides leading to decreased concentration of free metal ions in the pore water and consequently reduced toxicity. Some organism accumulate metals even under conditions where AVS do not exceed SEM (i.e. the metal should not be bioavailable according to the SEM/AVS method) (Camusso et al. 2012; Méndez-Fernandez et al. 2014). This can be explained by the fact that this approach consider exposure from pore water only and does not consider metals that are ingested through sediment particles and become bioavailable in the gut (Camusso et al. 2012; Méndez-Fernández et al. 2014) and may exhibit different mode of action and accumulate in different tissues when ingested (Hook et al. 2014). However, bioaccumulation does not directly relate to toxic effects since copper is an essential metal that can be regulated through accumulation strategies such as active elimination of excess copper or by storage as detoxified forms. Nevertheless, when the uptake exceeds the rate of combined excretion and detoxification, copper can induce toxic responses to aquatic organisms (Rainbow et al. 2002). Other aspects that have been criticized with the SEM-AVS approach is the impact of spatial, temporal and vertical (with depths) variation of AVS within a recipient. In addition, the total AVS depends on other metals that bind to sulfides, and consequently the concentrations of metals that bind stronger to sulfides (e.g. mercury and silver) needs to be known for the sites that are being considered. The SEM-AVS approach has therefore not been considered in this EQS derivation. Nevertheless, AVS concentrations are tabulated in table S1-S2.

Another common method to take bioavailability of especially organic contaminants in sediment into account is to normalize measured concentrations to organic carbon (OC). This is based on the observation that sediments with higher OC (i.e. greater sorption potential) reduce the bioavailable fraction (in pore water) and therefore also the toxicity. Expressing the EQS as concentrations in sediment with a standard OC concentration of 5% is appropriate when a relationship with OC can be discerned (European Communities 2011). Studies where different OC content has been measured show that the toxicity of copper tends to decease with increased percentage of OC, which makes this approach applicable. Recalculating the measured whole sediment concentration, based on site specific OC content, will consider the site specific Cu concentrations in pore water. However, aspects related to dietary exposure will then not be taken into account. The route of dietary exposure was not considered important in ECI (2008). Nevertheless, to compare the outcome, two alternative values were calculated in this dossier: one where effect values were normalized to 5% OC and the second where toxicity data was used without taking the OC content into account.

Added risk approach (ARA)

The EQS values was derived using the added risk approach (ARA), meaning that natural background concentrations should be taken into account when evaluating monitoring data. However, to compare outcomes a total risk approach (TRA) was also undertaken and is presented under supportive information (section 7).

Added effect values were calculated by subtracting the copper concentration used in the control medium from the effect value (European Communities, 2011) in cases where natural sediment was used. In studies using artificial OECD guideline sediment (e.g. OECD 218) the background concentrations were assumed to be negligible since the guideline requires that sediment used should be checked for absence of contaminations e.g. heavy metals.

2. PROPOSED ENVIRONMENTAL QUALITY STANDARDS

	$EQS_{sediment}$ (mg/kg dw)			
	ARA at 5% OC	**ARA[1]**	**TRA at 5% OC**	**TRA[1]**
Freshwater	36 (see section 5.1)	28 (see section 5.1)	44[2] (see section 9.1)	- (see section 9.1)
Marine	52 (see section 5.2)	16 (see section 5.2)	60 (see section 9.2)	18 (see section 9.2)

1 = Overall standard, regardless of organic carbon content. 2 = PNEC from ECI (2008) with assessment factor (AF) 2.

3. MEASURED ENVIRONMENTAL CONCENTRATIONS

Measured sediment concentrations for freshwater (tables 1-3) and marine and coastal environments (tables 4-6) was provided from the Swedish Agency for Marine and Water Management, and the Geological Survey of Sweden (SGU). Statistics are reported as min, average (mean), standard deviation (SD), median, percentiles (25, 75, 90, 95, 99) and max concentration (mg/kg dw). Data provided from SGU (table 3 and 6), included measurements of TOC which enabled normalization of copper concentrations for TOC. Due to limited number of freshwater stations, only statistic of normalized data from marine and coastal areas are reported (table 6), however, of the freshwater measurements (in table 3) the normalized concentrations ranged between 5.3-13.1 mg/kg dw. It is not certain if data provided from SGU belongs to unaffected locations or not, however, when comparing data from table 3 and background concentrations given in table 1 it seems reasonable that the data belongs to somewhat affected locations.

Table 1. Screening data of background concentrations in freshwater sediment, data not normalized for TOC (not reported).

min	mean	SD	median	P25	P75	P90	P95	P99	max	n
2.7	28.7	18.3	24	16.0	38.0	50.0	68.5	78.8	86	91

Table 2. Screening data from freshwater sediment at point sources and urban locations, data not normalized for TOC (not reported).

min	mean	SD	median	P25	P75	P90	P95	P99	max	n
3.2	50.6	62.3	34	17	53.3	90.9	169.0	350.0	420	152

Table 3. Measured concentrations of freshwater sediment, concentrations not normalized for TOC. Data from six stations could be normalized for TOC with concentrations ranging between 5.3-13.1 mg/kg dw.

min	mean	SD	median	P25	P75	P90	P95	P99	max	n
12	64.3	46.3	39.5	26.4	113.8	135	140	140	140	26

Table 4. Screening data from coastal areas at urban locations. Data not normalized for TOC (not reported).

min	mean	SD	median	P25	P75	P90	P95	P99	max	n
26.0	46.0	14.9	43	38.0	49.0	55.5	71	97	97	34

Table 5. Screening data from marine environments at urban locations. Data not normalized for TOC (not reported).

min	mean	SD	median	P25	P75	P90	P95	P99	max	n
9.1	97.4	162.2	45	39.8	48.0	172.0	361.0	512.2	550	10

Table 6. Measured concentrations (mg/kg dw) from the North Sea and the Baltic Sea, normalized to site-specific TOC (based on geometric mean of Cu and TOC for 16 stations). Data not normalized for TOC is given in brackets (n= 135).

min	mean	SD	median	P25	P75	P90	P95	P99	max	n
10	44 (66.7)	9 (82)	42 (47)	37 (32)	50 (82)	57 (118)	61 (132)	62 (166)	63 (914)	16 (135)

4. EFFECTS IN FIELD, MESOCOSMS AND MICROCOSMS

4.1 Studies combining different type of data

Approaches using field data, in which matched sediment chemistry and biological effects data are analyzed using various statistical methods to relate chemical concentrations to the frequency of biological effects can be used in the EQS derivation (European Communities, 2011). One should however remember that in studies based on field sediments, also other contaminants can contribute to the observed toxicity.

Threshold concentrations developed in other legal contexts but at least partly based on field assessments can be useful as supportive information. Several types of sediment quality guidelines for copper have been developed during the years, including 'threshold effect levels' (TEL), 'effect range low' (ERL) or 'no-effect level' (NEL), and referring to concentrations where biological effects are unlikely to occur, based also on field observations. Values referring to concentrations associated with a significant biological impact is called 'Probable effect levels' (PEL). These particular guideline values were derived using matched biological and chemical data from several modeling, laboratory and field studies collected from the biological effect database for sediment (BEDS) compiled based on studies conducted in North America. Adverse effects were determined as altered benthic communities (reduced species richness or total abundance), toxicity, histopathological disorders (fish), E(L)C50 from ecotoxicity studies or toxicity predicted by EqP from water (in total two EqP studies with acute and chronic values of 216 and 136 mg/kg dw).

The lower 10th percentile of the effect data in the dataset to determine ERL for copper was 34 mg/kg dw for the marine and estuarine environment and 70 mg/kg dw for combined freshwater and marine data (Long and Morgan, 1990; Long et al. 1995). 89 reports passed the screening criteria (e.g. method considerations, chemical analysis and control survival) and were therefore included. The mean total organic carbon (TOC) of the entire dataset was 1.2 % (Long and Morgan, 1990; Long et al. 1995).

MacDonald et al. (1996) used the same dataset as was used to develop the ERL but modified the approach and used information from both the 'effects' and 'no effects' datasets. Distributions were used to calculate TEL based on the 15th percentile of the 'effects' data set and the 50th percentile of the 'no effects' dataset. The TEL for copper was calculated to 18.7 mg/kg dw (PEL calculated to 108) based on at least 20 data in both the "effects" and "no effects" category for marine and estuarine data. OC levels were rarely reported and the TEL could therefore not be recalculated and expressed on the basis for OC normalization. The same approach was used by Smith et al. (1996) calculating TEL to 35.7 mg/kg dw for freshwater sediments. The TEL for freshwater was based on 56 studies which met all of the screening criteria (but OC % unknown).

Kwok et al. (2008) used field-based SSD of benthic communities in marine sediment from the Hong Kong area, with calculated hazardous concentrations (HC) considering the responses of the sensitive species based on abundance. The HC5 and HC10 were calculated to 23.5 and 33.9 mg Cu/kg dw, respectively including 13 species of which the polychaetes *Aglaophamus lyrochaeta and Mediomastus sp.* showed highest sensitivity (Kwok et al. 2008). Gillbert et al. (2014) used community sensitivity distribution (CSD) to derive field-based sediment quality guidelines using field sediment data from the Norwegian Continental Shelf. Data were collected between 1996-2001 from 2,015 stations, including some stations near oil platforms. The relationship of species density and copper concentrations was fitted by a logistic-type regression model and then used to determine HC5 and HC10 values. They concluded that the lower confidence limits of HC5 could be regarded as safe levels, which were calculated to 3.1 and 4.88 mg/kg dw (based on median or mode values, respectively). Compared to Kwok et al. (2008), all species in the communities (and not only the most sensitive) were considered in the calculated hazardous concentrations. Neither of these studies determined the OC %. For the studies above, it is not clear whether copper is the dominant contaminant and investigation of the potential contribution from other contaminants is not reported. It could therefore not be excluded that at least part of the effects observed could rather be related to other contaminants or mixture effects as well as other factors.

4.2 Field observations

In a Swedish assessment of the contaminated lakes Skutbosjön and Dovern (in Östergötland) effects on benthic fauna were examined. The sediment was contaminated with metals, PCB and PAH. Copper was the dominating contaminant of the surface sediment with concentrations varying between 220 to 1100 mg/kg dw compared to approximately 60 mg/kg dw of the reference site nearby. There were no significant differences in biodiversity between the different sites; however, the number of detrivores was significantly lower at contaminated locations. Copper and PAH concentrations explained about 25-35% of the reduction of detrivores and the remaining variation was explained by other factors such as oxygen conditions, availability of food, predation, or random variations during sampling. Effects at individual level were assessed using Chironomidae and the biomarker mouth deformation, which showed a correlation with the copper concentration. The deformation occurred at concentrations approximately above 350 mg/kg dw (at OC > 5%) and ARA was estimated to 290 mg/kg dw (at OC > 5%). This indicates that the bioavailability of copper was low, which could be explained by copper being tightly bound in the sediments, as previously leaching tests has shown (WSP, 2017).

Olsgard (1999) investigated the marine macrobenthic community structure of copper spiked sediment relocated into field at 63 meter depth (Oslofjord, Norway). Sediments were collected in field, spiked with copper and placed into field (defaunated) to investigate the recolonization patters. Mean copper concentrations were 70 (control), 150, 300, 900 and 2000 mg/kg dw with mean OC of 3.2%. After 7 month there was no significant effect for number of taxa among the treatments, however, at 900 and 2000 mg/kg dw the number of individuals was significantly lower. The abundance of Individual species (total 16 taxa) in relation to copper concentrations was also investigated showing a negative correlation for the polychaetes *Pectinaria koreni, Prionospio cirrifera, Capitella capitata, Pseudopolydora paucibranchiata, Harmothoe spp*. and *Chaetozone setosa,* the bivalve *Thyasira sarsi* and the brittle star *Ophiura affinis*. For most of the species the reduced abundance was seen at 900 mg/kg dw, however, for *Pectinaria koreni* and *Prionospio cirrifera* lower abundance was significant at 300 mg/kg dw (giving a NOEC of 150 mg/kg dw). This NOEC normalized to 5% OC was 234 mg/kg dw. The analysis showed that 17.4% of the total fauna variance could be explained by copper concentrations, while OC, total sedimentary carbon, total nitrogen and grain size explained only an insignificant part of the fauna variance.

Neira et al. (2011) conducted a field study investigating the marine macrobenthic community in the north end of San Diego Bay, California. 26 sampling stations were included with copper concentrations categorized as high, medium, low and reference site corresponding to mean measured concentrations of 236.1, 183.2, 111.5, and 18.9 mg/kg dw, respectively. The results showed that biomass significantly decreased with increasing copper in sediment, with “medium” and “high” concentrations being significantly lower compared to control and “low” copper levels (giving a NOEC of 111 mg/kg dw). In addition, at sites with elevated copper concentrations the communities exhibited reduced individual body size and diversity while density was not changed. Of the 48 taxa identified, annelid polychaetes and crustacean were most dominant (>77% of total). Polychaete families had a higher family richness at “low” copper levels and reference sites compared to sites categorized as “high”. At “high” copper concentration (236.1 mg/kg dw) the peracarid crustaceans (class Malacostraca) were most affected, with number of amphipod species reduced to 4 compared to 10 at reference sites and sites with “low” copper. Average species richness and diversity was greater at sites with lowest copper (111.5 mg/kg dw) compared to elevated copper concentrations, but evenness was not significantly different. Types of feeding strategies was also different among the sites, with omnivores being dominant at sites with high copper concentrations, while subsurface-deposit feeders were the most dominant at reference sites. The change of community parameters was compared to the following environmental variables: copper of pore water, copper of sediment, total organic matter (TOC), sediment chlorophyll *a*, copper of surface water, mud content, sediment redox potential, and sediment phaeopigments. 18.3% of the variance of biological species composition was explained by copper (sediment and porewater) and 34.4% was explained by the covariance of TOM and chlorophyll *a*. The remaining percentages was assumed to be explained by other physical and biological factor such as presence of other contaminants, hydrodynamics, sediment stability, predations, bioturbation, recruitment or natural variability. The OC was not measured in this study, however, organic matter (OM) varied between 1.3-6.3% at different sites. To enable comparison of single-species toxicity studies a factor of 1.7 can be used to recalculate OM to OC. The OC could then be roughly estimated to 3.7 % (European Communities, 2008). This gives a NOEC of 151 mg/kg dw at 5% OC (125 as ARA at 5% OC).

Using the same study area, Neira et al. (2015) conducted further investigations of benthic communities in terms of recolonization of macrofauna of copper contaminated sediments. Two different locations were used either associated with low (30 mg/kg dw) or high (196 mg/kg dw) copper contamination. Collected sediments from both sites were defaunated and either kept with natural copper concentrations or spiked (i.e. increased levels) and then translocated back into field either at the original site or at the opposite site (in total 7 different “designs” of treatments). After three month of exposure to sediments with varying copper levels (30-1256 mg/kg dw), changes in recolonizing fauna composition with reduced biodiversity and lower structural complexity were observed. Two primary colonizing communities were identified; (1) similar adjacent background fauna associated with low copper levels, that showed increased diversity and was dominated by surface- and subsurface-deposit feeders, burrowers, and tube builders and (2) similar adjacent background fauna associated with high copper levels with few dominant species and an increasing importance of carnivores and mobile epifauna. At sites with high copper, shifts of the community composition of macrofauna was observed with reduced crustaceans (primary amphipods) and polychaete family richness. At sites with spiked sediment reduced species richness and diversity were evident and elevated dominance compared to sites with lower copper levels. It was difficult to establish a cause-effect relationship between copper however, this study concludes that recolonization of copper enriched sediment indicates that macrofauna evolved tolerance to copper. This was shown in the different recolonizations patterns and composition of translocated copper-spiked sediment that strongly suggested that fauna coming from the areas associated with high enriched copper were more tolerant and most likely recovered faster compared to the fauna from the areas associated with low natural copper concentrations.

4.3 Mesocosms studies

Gardham et al. (2014a) constructed pond mesocosms with copper spiked sediments (equilibrated for two month) using four copper concentrations ranging from 71 to 711 mg/kg dw with control sediment having a concentration of 4.6 mg/kg dw. In total, 35 taxa were found in the mesocosms dominated by

Ostracoda, Nemotoda and Diptera. After 497 days, high copper concentrations (>400 mg/kg dw) caused clear effects on the richness, abundance and structure of the benthic communities, while concentrations below 100 mg/kg dw had no effect. In this study 7% (1840 total count) of the total abundance contained the taxa Chironominae (critical taxa in the freshwater derivation). In general, the abundance of Chironominae exposed to 711 mg/kg dw was significantly lower compared at lower copper concentrations and control. The abundance at 410 mg/kg dw was also lower compared to control and the intermediate levels of treatment, however, at the last two sampling points (407 and 497 d) the abundance was higher compared to all other treatments.

In a similar mesocosm set-up, Gardham et al. (2015) investigated the influence of copper on phytoplankton, macrophytes, periphyton and organic matter decomposers. Copper significantly reduced the growth (in terms of reduced shoot density) of the macrophyte *Vallisneria spiralis* at concentration of 97 mg/kg dw (NOEC 62 mg/kg dw), showing a dose-depending relationship (control concentrations of 5.8 mg/kg dw). A decreasing effect was observed for subsurface organic matter decomposition and phytoplankton chlorophyll (a) concentrations. However, the periphyton cover of the walls of the mesocosms was significantly higher at concentrations of 310 and 650 mg/kg dw, which was assumed to be attributed by reduced grazing pressure from snails. The OC content in these studies was 2% (Gardham et al. 2014b).

4.4 Microcosms studies

Jeppe et al. (2017) conducted a field-based microcosm to investigate effects of copper exposure in terms of changes in abundance of colonizing macroinvertebrates. Sediment was spiked with concentrations of 62.5, 125, 250, 500 and 750 mg/kg dw (reference sediment with background concentration of 11 mg/kg dw). After 7 weeks a total of 45 taxa was colonized in the microcosms, mainly abundant with the family Chironomidae (94.5%). The total abundance was reduced with increased copper, with EC_{50} of 133 mg/kg dw. The five most common species of the family Chironomidae showed individual EC_{50} varying between 89-681 mg/kg dw. The taxon *Chironomus* (critical genus in the freshwater derivation) had a EC_{50} of 97 mg/kg dw, however, the large standard error of ± 222 mg/kg dw and the lack of percentage OC, makes it difficult to compare this effect value to single-species observations used in the EQS derivation. The result from the colonizing microcosms was compared with microcosms of laboratory organisms (two snails, *Potamopyrgus antipodarum* and *Physella acuta* and the chironomid, *Chironomus tepperi).* EC_{50} (reproduction) for the laboratory bred organisms was 121 mg/kg and 298 mg/kg for *P. antipodarum* and *P. acuta*, respecively, and 238 mg/kg for *C. tepperi* (growth).

Ho et al. (2018) exposed field-collected marine benthic communities to copper spiked sediments, with mean measured concentrations of 235 mg/kg dw (single dose investigated). The communities included for instance; Malacostraca, Ostracoda, Polychaeta, Bivalvia, Maxillopoda, Gastropoda, Nemertea, Nematodes, and Harpacticoids. Changes of the community were assessed as differences in total abundance, taxa richness, diversity and evenness and the abundances of selected taxa. There was no significant difference of the relative percentage of some of the taxa. However, the total abundance was significantly reduced in copper sediment compared to both field and laboratory control (background concentrations of 7.7 and 25.5 mg/kg, respectively). For example, mean macrofauna per treatment decreased from 3500 (field control) to approximately 1110, and meiofauna decreased from 1500 to 200. The percentage of OC was 2% (personal communication with Kay Ho, US Environmental Protection Agency, Atlantic Ecology Division) which gives an effect concentration of 588 mg/kg dw at

5% OC. In this study, however, there was no significant change in the relative percentage of the Maxillopoda, Malacostraca, Gastropoda, or Nemertea observed among the laboratory control or the copper concentrations of 235 mg/kg dw. The most sensitive species of marine single-species studies were the crustacean *Nitocra spinipes* and *Meltia plumulosa* belonging to the taxonomic class of Maxillopoda and Malacostraca, respectively.

Table 7. Summary of field studies, microcosms, mesocosms from the literature search and information reported in ECI (2008).

Type of study	Type of value	Effect value (mg/kg dw)	Comment	Reference
Information from the literature search				
Field, laboratory, and Eqp studies (m)	ERL	34	The lower 10th percentile of the effect data. Mean OC 1.2 %	Long et al. 1995
	ERL at 5% OC	≈142		
Field, laboratory, and Eqp studies (f/m)	ERL	70	The lower 10th percentile of the effect data (based on 51 input data). OC not reported.	Long and Morgan, 1990
Field, laboratory, and Eqp studies (f/m)	TEL	18.7	Based on "effect" and "no effect" data (>40 input data). OC not reported.	MacDonald et al. 1996
Field, laboratory, and Eqp studies (f)	TEL	35.7	Based on "effect" and "no effect" data (>40 input data). OC not reported.	Smith et al. 1996
Field SSD (m)	HC5	23.5	Field-SSD (13 species) based on abundance. OC not reported.	Kwok et al. 2008
	HC10	33.9		
Field CSD (m)	HC5 (lower confidence level)	3.1-4.9	Field-SSD based on species community density. OC not reported.	Gillbert et al. 2014
	HC5	8.3-10.8		
Field spiked sediment (m)	NOEC	150	Copper-spiked sediment. Reduced abundance of the polychaetes: *Pectinaria koreni* and *Prionospio cirrifera.* Duration 8 month.	Olsgard 1999
	at 5% OC	234		
Field observation (m)	NOEC	111	Reduced biomass. OC estimated to 3.7% (recalculated from OM).	Neira et al. 2011
	at 5% OC	152		
	ARA	92		
	ARA at 5% OC	126		
Field observation (f)	Threshold (OC >5%)	350	Increased mouth deformations of Chironomidae above this concentration.	WSP 2017
	ARA (OC > 5%)	290		

Type of study	Type of value	Effect value (mg/kg dw)	Comment	Reference
Mesocosm (f)	NOEC	62	Reduced shoot density (*Vallisneria spiralis*) at 97 mg/kg dw. OC 2%. Duration 62 weeks	Gardham et al. 2015
	at 5% OC	155		
	ARA	56		
	ARA at 5% OC	141		
Mesocosm (f)	NOEC	100	Effects on the richness, abundance and structure of the benthic communities was seen at >400 mg/kg dw. OC 2%. Duration 71 week	Gardham et al. 2014a
	at 5% OC	250		
Microcosm (m)	NOEC	< 235	Significantly reduced abundance of several taxa. OC not reported. Duration 21 day.	Ho et al. 2018
Microcosm (f)	EC_{50}	133	Total abundance of colonized biota reduced by 50%. OC% not reported. Duration 7 week	Jeppe et al. 2017
Information available in ECI (2008)[1]				
PNEC derivation (f)	HC5 (at 5% OC)	87	SSD based on laboratory studies (6 species included). Does not consider added risk values.	ECI 2008
PNEC derivation (m)	PNEC	676	Eqp method	ECI 2008
Field accumulation study (f)	-	100	No accumulation observed in *C. riparius.* At concentrations above 700 mg/kg dw, accumulation was observed	Bervoets et al, 2004 (in ECI 2008)
	at 5% OC	263		
Mesocosms (f)	NOEC	≥ 142 (added as 160 µg/L to water phase)	No effect on abundance of benthic macro-invertebrates (Cyclopoida, Ostracoda, Chironomidae and Tubicidae) and Nematodae. Duration 111 day	Schaefers 2003 (in ECI 2008)
	at 5% OC	213		
Mesocosm (f)	NOEC	80 (added as 25 µg/L to water phase)	Decreased leaf litter decomposition, decreased sporulation of fungi and decreased abundance/richness of litter associated invertebrates was seen at 75µg Cu/L (corresponds to 196 mg/kg dw). OC not reported in the original study, assumed to be around 1-2 % (ECI, 2008). Duration 18 months	Roussel 2005 (in ECI 2008)
	at 5% OC	200-400		
	ARA	63		
	ARA at 5% OC	157		

Type of study	Type of value	Effect value (mg/kg dw)	Comment	Reference
Microcosm (f)	NOEC	37 mg/kg dw (added as 8.8 µg/L to water phase)	Benthic diversity. No effect on snails (Viviparus), oligochaetes – Lumbricidae, Naididae *(Uncinais, Paranais, Pristina*) and Tubicidae (*Tubifex)*. Clear effects were seen at 56.7 mg/kg dw (absence of certain species). Duration 32 weeks	Hedtke 1984 (in ECI 2008)
	at 5% OC	214		

1 = For full summary see ECI (2008) (CHAPTER 3.2 – Environmental effects: 3.2.4. Effects to Freshwater sediment organisms). f = freshwater, m = marine water, ERL = effect range low, TEL = threshold effect levels, HC5/HC10 = Hazardous concentration causing 5 and 10% effect in species sensitivity distributions (SSD), NOEC = No observed effect concentration, ARA = Added risk approach, OC = Organic carbon content, PNEC = Predicted no effect concentration.

5. EFFECTS AND QUALITY STANDARDS (ARA)

5.1 Freshwater sediment toxicity

Effect values investigating chronic toxicity to 10 species were available (table S1). Of these, six species could be used to determine added effect values (i.e. reported background concentrations in natural sediments, or used artificial OECD guideline sediments). The three lowest effect values representing three different living and feeding conditions are presented in Table 8.

Table 8. Lowest effect value for three different species (critical effect values, i.e. used in the EQS derivation, in bold), representing three different living and feeding conditions, and the critical mesocosm observation.

FRESHWATER EFFECTS		**Effect value (ARA)**	**Normalized to 5% OC (ARA)**	**Reference**
Annelida (mg/kg dw)	*Lumbriculus variegatus*/ 28d NOEC/EC_{10}: 74.9 (Biomass) OECD sediment, OC 2.6%	74.9	143.4	Roman et al. 2007; REACH registration dossier ref. 008 (REACH, 2018a)
Insecta (mg/kg dw)	*Chironomus riparius* / 28d NOEC/EC_{10}: 83.3 (Emergence) OECD sediment, OC 2.6-30 %	83.3	**70.9**	Roman et al. 2007; REACH registration dossier ref. 008 (REACH, 2018a)
Mollusca (mg/kg dw)	*Potamopyrgus antipodarum*/ 28d NOEC: 73.2 (Growth) Natural sediment, OC 2.2%	**55.8**	126.8	Pang et al. 2013
Critical mesocosm NOEC (LOEC)		56.2 (91.2)	140.5 (228)	Gardham et al. 2015

According to the European Communities (2011), the criterion for use of assessment factor (AF) 10 is fulfilled (three species representing three different living and feeding conditions). However, there are numerous field, mesocosms, and microcosm studies that suggest that AF 10 would lead to a value that is probably over conservative (see section 3 and Table 7). Smith et al. (1996) derived a TEL of 35.7 mg/kg dw based on 56 studies investigating either spiked-sediment toxicity, EqP, or field investigations (not possible to estimate ARA and OC% normalization). In addition, four freshwater mesocosms were available with three NOECs of approximately 200 mg/kg dw at 5% OC (80-100 mg/kg dw without normalization). These studies included endpoints such as abundance, diversity of benthic communities, leaf litter decomposition, and sporulation of fungi. The lowest NOEC from mesocosms was 155 mg/kg dw at 5% OC (62 mg/kg dw without normalization) for the endpoint reduced shoot density of the aquatic plant *Vallisneria spiralis* (143.5 mg/kg dw ARA at 5% OC) (Gardham et al. 2015).

According to European Communities (2011) the AF can be reduced when e.g. mesocosm NOECs are higher than the derived EQS. Therefore, on the basis of the availability of several field and mesocosm data and the results from these, the AF was reduced to 2. The choice of AF was further supported by data on species-specific and subfamily level of the most sensitive species (i.e. *C. riparius* when normalizing for OC) that confirms that the derived EQS will be sufficiently protective (see table 2):

- Chironominae abundance was not affected below concentrations of 94.4 mg/kg dw ARA (226 at 5% OC) (Gardham et al. 2014b).
- Mouth deformation of Chironomidae was not seen at concentrations below 350 mg/kg dw (WSP 2017).
- No effect was seen on Chironomidae abundance in a mesocsosm at 142 mg/kg dw (213 at 5% OC) (Schaefers 2003, in ECI 2008).
- *C. riparius* collected at 19 different river locations representing sediments with different physico-chemical properties showed no evidence of accumulation at 100 mg/kg dw (263 at 5% OC). Bioaccumulation was observed at 700 mg/kg dw (Bervoets et al. 2004, in ECI 2008).

Deterministic derivation (ARA)

Two different scenarios were proposed, using either the added effect value normalized to 5% OC or the added effect value regardless of OC content.

1. Critical effect value (ARA at 5% OC) was *C. riparius* with geometric mean NOEC[2] of 70.9 mg/kg dw. Using AF 2 gives an **ARA EQS of 35.5 mg/kg at 5% OC.**
2. Critical effect value (ARA) was *P. antipodarum* with NOEC of 55.8 mg/kg dw. Using AF 2 gives an **ARA EQS of 27.9 mg/kg.**

Probabilistic derivation (ARA)

The total dataset included five major taxonomic groups and six species with ARA values. The dataset does not fulfill the requirements for performing a SSD according to the European Communities (2011), and a probabilistic derivation was therefore not considered applicable.

[2] This geometric mean includes data from study conditions using 30% OC (REACH registration dossier ref. 008 in REACH, 2018a), which may not represent realistic environmental conditions. If excluding this data, the critical NOEC was 86, which results in a EQS ARA of 43 mg/kg dw.

5.2 Marine sediment toxicity

Effect values investigating chronic toxicity to five species were available (table S2). For all of these, added effect values could be determined (the studies reported background concentrations in natural sediments). The three lowest effect values representing three different living and feeding conditions are presented in Table 9.

Table 9. Lowest effect value for three different species (critical effect values, i.e. used in the EQS derivation, in bold), representing three different living and feeding conditions, and the critical field observation.

MARINE EFFECTS		**Effect value (ARA)**	**Normalized to 5% OC (ARA)**	**Reference**
Annelida (mg/kg dw)	*Neanthes arenaceodentata* / 28d NOEC : 230 (growth) Natural sediment, OC 0.8 %, salinity ≈ 28 ppm	200.2	1320.6	Ward et al. 2015
Crustacean (mg/kg dw)	*Nitocra spinipes*/ 11d EC_{10} **:** 90 (reproduction) Natural sediment, OC 1.5%, salinity 30 ppm	**77.5**	**258.3**	Campana et al. 2012
Mollusca (mg/kg dw)	*Hydrobia ulvae*/ 10d NOEC: 247 (reporduction) Natural sediment, OC 3%, salinity 33 ppm	224	373.3	Campana et al. 2013
Critical field NOEC (LOEC)		80 (230)	125 (359)	Olsgard et al. 1999

As for freshwater, the criterion for AF 10 is fulfilled but there are field observations suggesting that the AF would lead to a too conservative EQS. The field observation by Long et al. (1995) and Kwok et al. (2008) are consistent, suggesting that 34 mg/kg dw is expected to cause 10% effect of benthic communities (in terms of e.g. reduced abundance) (Table 7, section 3). Long et al. (1995) assumed that the TOC was approximately 1.2%, which gives a threshold concentrations of 141.7 mg/kg dw at 5% OC (not possible to estimate ARA value). In addition, other field studies investigating benthic community structure, abundance, biomass and richness were available, suggesting NOEC of 126 and 125 mg/kg dw at 5% OC ARA (92 and 80 mg/kg dw ARA without normalization to OC) (Neira et al. 2011; Olsgard et al. 1999).

Of the marine field and microcosm observations, Neira et al. (2014) and Ho et al. (2018) provides supporting information that the taxonomic classes Maxillopoda and Malacostraca (of which the most sensitive crustaceans, *Nitocra spinipes* and *Meltia plumulosa,* belongs to) were not affected at concentrations of 125 and 568 mg/kg dw ARA at 5% OC. However, species-specific information from field was not available. The ARA effect values from single-species toxicity and mesocosm studies (without normalization) was consistent, however, when normalizing to 5% OC the mesocosm NOEC was 2-fold lower (in contrast to freshwater field observations which was nearly 2-fold higher). Due to available supporting field observations, it is justified to reduce the AF. However, the AF was set to 5 and not 2 since the evidence was not as convincing as for freshwater (AF 2 would result in a EQS equivalent to the critical mesocosm NOEC). Additionally, there were more available field and mesocosms information regarding toxicity to the most sensitive freshwater species (*C. riparius*) used as critical data in the derivation (when normalizing to OC%). European Communities (2011) does not stipulate how to reduce the AF when field observations suggest lower toxicity.

Deterministic derivation (ARA)

Two different scenarios were proposed, using either the added effect value normalized to 5% OC or the added effect value regardless of OC content.

1. Critical effect value (ARA at 5% OC) was *N. spinipes* with NOEC of 258.3 mg/kg dw. Using AF 5 gives an **ARA EQS of 52 mg/kg at 5% OC**.
2. Critical effect value (ARA) was *N. spinipes* with NOEC of 77.5 mg/kg dw. Using AF 5 gives an **ARA EQS of 16 mg/kg dw.**

Probabilistic derivation (ARA)

The total dataset included three major taxonomic groups and five species. The dataset does not fulfill the requirements to perform a SSD according to the European Communities (2011), and a probabilistic derivation was therefore not considered applicable.

6. IDENTIFICATION OF ISSUES RELATING TO UNCERTAINTY IN RELATION TO THE EQSs DERIVED

Benthic organisms using sediment particles (or e.g. algae) as their main food source has been shown to be more sensitive to copper (Camusso et al. 2012; Jeppe et al. 2017) and this route of exposure is therefore considered relevant. Studies used as critical data in the derivations used uncontaminated food in the bioassays, but in natural ecosystems food sources would also contain copper and contribute to the total exposure. Observations in field likely take aspects of both dietary and exposure from pore water into account, and effect values derived from field studies suggest that the derived EQS should be protective of both routes.

Assuming that artificial OECD guideline sediments contains negligible amount of copper might underestimate the added effect values (in the case of freshwater sediment). On the other hand, using artificial sediments under controlled laboratory conditions does probably reflect a worst-case scenario, since these conditions tend to promote the bioavailability of copper. The single species observations from laboratory studies suggest higher sensitivity compared to observations in the field. However, it is reasonable that certain environmental conditions could promote the bioavailability of copper and give rise to similar toxicity levels as those shown under laboratory conditions. The derived ARA values are believed to be sufficient protective. This was also supported by field observations, which suggest that effects are unlikely to occur at the EQS concentration.

The complexity of copper toxicity, which is influenced by several environmental factors, complicates the derivation. Normalizing to OC entails that the bioavailability is taken into account, however, several other factors would necessarily be considered in a case-by-case basis to take bioavailability fully into account. These factors include particle size, pH, redox potential, depths and other geochemistry variables.

Uncertainties remains regarding the sensitivity of aquatic plants. Gardham et al. (2015) suggest that *V. spiralis* was among the most sensitive in their mesocosms. Likewise, there was evidence from single-species studies (e.g Caillat et al. 2014; Zhu et al. 2016, see table S1) suggesting toxicity, however, these could not be used in the derivation due to limited reporting.

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8. SUPPORTIVE INFORMATION - TOXICITY DATA

Table S1 and S2 summarize all available freshwater and marine water sediment toxicity data. All studies were conducted using either $CuCl_2$ or $CuSO_4$. Studies collected from the REACH registration dossier have previously been evaluated as "Reliable with restriction" (R2). OECD 218 sediment was assumed to contain negligible backgrounds concentrations (tabulated as 0 mg/kg dw).

Table S1. Freshwater sediment toxicity. Lines in bold text = possible to calculate added risk value, Grey cell= used in the base set for the EQS derivation.

Species	OC %	AVS (µmol/g dw)	Duration and Endpoint			Value total (mg/kg dw)	Background conc.	Normalized to 5% OC	Reference	Sediment
Insecta										
Chironomus riparius	1.81	-	-	NOEC	Growth	90	-	248.6	Pery et al. 2005	Artificial
Chironomus riparius	**2.6**	**<0.06**	**28 d**	**NOEC**	**Growth**	**89.2**	**0**	**171.5**	**Roman et al. 2007**	**OECD 218**
Chironomus riparius	**2.6**	**<0.06**	**28 d**	**EC10**	**Growth**	**92.5**	**0**	**177.9**	**Roman et al. 2007**	**OECD 218**
Chironomus riparius	**29.81**	**0.3**	**28 d**	**NOEC**	**Growth rate**	**505.9**	**0**	**84.9**	**REACH registration dossier ref. 008 (REACH, 2018a)**	**OECD 218**
Chironomus riparius	2.83	0.15	28 d	NOEC	Growth rate	75.4	-	133.2	REACH registration dossier ref. 008	Natural
Chironomus riparius	1.96	0.11	28 d	NOEC	Growth rate	55.5	-	141.6	REACH registration dossier ref. 008	Natural
Chironomus riparius	2.12	0.28	28 d	NOEC	Growth rate	54.2	-	127.8	REACH registration dossier ref. 008	Natural
Chironomus riparius	**2.6**	**<0.06**	**28 d**	**NOEC**	**Emergence**	**59.5**	**0**	**114.4**	**Roman et al. 2007**	**OECD 218**
Chironomus riparius	**2.6**	**<0.06**	**28 d**	**EC10**	**Emergence**	**33.3**	**0**	**64.0**	**Roman et al. 2007**	OECD 218
Chironomus riparius	**2.62**	**0.05**	**28 d**	**NOEC**	**Emergence**	**59.5**	**0**	**113.5**	**REACH registration dossier ref. 008 (REACH, 2018a)**	OECD 218
Chironomus riparius	**29.81**	**0.3**	**28 d**	**NOEC**	**Emergence**	**292**	**0**	**49.0**	**REACH registration dossier ref. 008 (REACH, 2018a)**	OECD 218
Chironomus riparius	**2.62**	**0.05**	**28 d**	**NOEC**	**Survival**	**59.5**	**0**	**113.5**	**REACH registration dossier ref. 008 (REACH, 2018a)**	**OECD 218**
Chironomus riparius	**29.81**	**0.3**	**28 d**	**NOEC**	**Survival**	**292**	**0**	**49.0**	**REACH registration dossier ref. 008 (REACH, 2018a)**	**OECD 218**
Chironomus riparius	2.83	0.15	28 d	NOEC	Survival	177.1	-	312.9	REACH registration dossier ref. 008 (REACH, 2018a)	Natural
Chironomus riparius	2.12	0.28	28 d	NOEC	Survival	54.2	-	127.8	REACH registration dossier ref. 008 (REACH, 2018a)	Natural
Chironomus riparius	**2.6**	**<0.06**	**28 d**	**NOEC**	**Survival**	**<180**	**0**	**-**	**Roman et al. 2007**	**OECD 218**

Species	OC %	AVS (µmol/g dw)	Duration and Endpoint			Value total (mg/kg dw)	Background conc.	Normalized to 5% OC	Reference	Sediment
Chironomus riparius	**2.6**	**<0.06**	**28 d**	**EC10**	**Survival**	**150**	**0**	**288.5**	**Roman et al. 2007**	**OECD 218**
Chironomus riparius	1.96	0.11	28 d	NOEC	Survival	85.4	-	217.9	REACH registration dossier ref. 008 (REACH, 2018a)	Natural
Hexagenia spp.	0.5[1]	-	21 d	NOEC	Survival	39.2	-	392.0	Milani et al. 2003[2]	Natural
Hexagenia spp.	0.5[1]	-	21 d	NOEC	Survival	33.9	-	339.0	Milani et al. 2003[2]	Natural
Hexagenia spp.	0.5[1]	-	21 d	NOEC	Survival	44.9	-	449.0	Milani et al. 2003[2]	Natural
Hexagenia spp.	0.5[1]	-	21 d	NOEC	Growth	44.9	-	449.0	Milani et al. 2003[2]	Natural
Hexagenia spp.	0.5[1]	-	21 d	NOEC	Growth	23.4	-	234.0	Milani et al. 2003[2]	Natural
Hexagenia spp.	0.5[1]	-	21 d	NOEC	Growth	29.2	-	292.0	Milani et al. 2003[2]	Natural
Annelida										
Lumbriculus variegatus	**2.6**	**<0.06**	**28 d**	**NOEC**	**Survival**	**114**	**0**	**219.2**	**Roman et al. 2007**	**OECD 218**
Lumbriculus variegatus	**2.6**	**<0.06**	**28 d**	**EC10**	**Survival**	**126**	**0**	**242.3**	**Roman et al. 2007**	**OECD 218**
Lumbriculus variegatus	**2.6**	**<0.06**	**28 d**	**NOEC**	**Biomass**	**80.5**	**0**	**154.8**	**Roman et al. 2007**	**OECD 218**
Lumbriculus variegatus	**2.6**	**<0.06**	**28 d**	**EC10**	**Biomass**	**69.6**	**0**	**133.8**	**Roman et al. 2007**	**OECD 218**
Lumbriculus variegatus	**2.62**	**0.05**	**28 d**	**NOEC**	**Biomass**	**80.5**	**0**	**153.6**	**REACH registration dossier ref. 008 (REACH, 2018a)**	**OECD 218**
Lumbriculus variegatus	1.96	0.1	28 d	NOEC	Biomass	91.8	-	234.2	REACH registration dossier ref. 008 (REACH, 2018a)	Natural
Lumbriculus variegatus	**2.6**	**<0.06**	**28 d**	**NOEC**	**Reproduction**	**80.5**	**0**	**154.8**	**Roman et al. 2007**	**OECD 218**
Lumbriculus variegatus	**2.6**	**<0.06**	**28 d**	**EC10**	**Reproduction**	**96.9**	**0**	**186.3**	**Roman et al. 2007**	**OECD 218**
Tubifex tubifex	**2.6**	**<0.06**	**28 d**	**NOEC**	**Survival**	**138**	**0**	**265.4**	**Roman et al. 2007**	**OECD 218**
Tubifex tubifex	**2.6**	**<0.06**	**28 d**	**EC10**	**Survival**	**160**	**0**	**307.7**	**Roman et al. 2007**	**OECD 218**
Tubifex tubifex	0.5[1]	-	28 d	NOEC	Survival	237.8	-	2378.0	Milani et al. 2003[2]	Natural
Tubifex tubifex	0.5[1]	-	28 d	NOEC	Survival	246.9	-	2469.0	Milani et al. 2003[2]	Natural
Tubifex tubifex	0.5[1]	-	28 d	NOEC	Survival	270.5	-	2705.0	Milani et al. 2003[2]	Natural
Tubifex tubifex	**1.56**	**-**	**28 d**	**NOEC**	**Survival**	**358.8**	**58**	**964.1**	**Vecchi et al. 1999[3]**	**Natural**
Tubifex tubifex	**1.03**	**-**	**28 d**	**NOEC**	**Survival**	**101.4**	**21**	**382.9**	**Vecchi et al. 1999[3]**	**Natural**

Species	OC %	AVS (µmol/g dw)	Duration and Endpoint			Value total (mg/kg dw)	Background conc.	Normalized to 5% OC	Reference	Sediment
Tubifex tubifex	**1.05**	**-**	**28 d**	**NOEC**	**Survival**	**69.1**	**21**	**229.0**	**Vecchi et al. 1999[3]**	**Natural**
Tubifex tubifex	**2.62**	**0.05**	**28 d**	**NOEC**	**Survival**	**138.5**	**0**	**264.3**	**REACH registration dossier ref. 005 (REACH, 2018b)**	**OECD 218**
Tubifex tubifex	2.83	0.27	28 d	NOEC	Survival	54	-	95.4	REACH registration dossier ref. 005 (REACH, 2018b)	Natural
Tubifex tubifex	2.12	0.28	28 d	NOEC	Survival	95.3	-	224.8	REACH registration dossier ref. 005 (REACH, 2018b)	Natural
Tubifex tubifex	**9.81**	**0.59**	**28 d**	**NOEC**	**Survival**	**580.9**	**0**	**296.1**	**REACH registration dossier ref. 005 (REACH, 2018b)**	**OECD 218**
Tubifex tubifex	**2.6**	**<0.06**	**28 d**	**NOEC**	**Growth**	**78.3**	**0**	**150.6**	**Roman et al. 2007**	**OECD 218**
Tubifex tubifex	**2.6**	**<0.06**	**28 d**	**EC10**	**Growth**	**43.3**	**0**	**83.3**	**Roman et al. 2007**	**OECD 218**
Tubifex tubifex	0.5[1]	-	28 d	NOEC	Growth	23.4	-	234.0	Milani et al. 2003[2]	Natural
Tubifex tubifex	**2.62**	**0.05**	**28 d**	**NOEC**	**Growth**	**78.3**	**0**	**149.4**	**REACH registration dossier ref. 005 (REACH, 2018b)**	**OECD 218**
Tubifex tubifex	**9.81**	**0.59**	**28 d**	**NOEC**	**Growth**	**580.9**	**0**	**296.1**	**REACH registration dossier ref. 005 (REACH, 2018b)**	**OECD 218**
Tubifex tubifex	2.12	0.28	28 d	NOEC	Growth rate	32.2	-	75.9	REACH registration dossier ref. 005 (REACH, 2018b)	Natural
Tubifex tubifex	1.96	0.2	28 d	NOEC	Growth rate	53	-	135.2	REACH registration dossier ref. 005 (REACH, 2018b)	Natural
Tubifex tubifex	**2.6**	**<0.06**	**28 d**	**NOEC**	**Reproduction**	**78.3**	**0**	**150.6**	**Roman et al. 2007**	**OECD 218**
Tubifex tubifex	**2.6**	**<0.06**	**28 d**	**EC10**	**Reproduction**	**79.2**	**0**	**152.3**	**Roman et al. 2007**	**OECD 218**
Tubifex tubifex	0.5[1]	-	28 d	NOEC	Reproduction	127.8	-	1278.0	Milani et al. 2003[2]	Natural
Tubifex tubifex	0.5[1]	-	28 d	NOEC	Reproduction	129	-	1290.0	Milani et al. 2003[2]	Natural
Tubifex tubifex	0.5[1]	-	28 d	NOEC	Reproduction	270.5	-	2705.0	Milani et al. 2003[2]	Natural
Tubifex tubifex	**1.41**	**-**	**28 d**	**NOEC**	**Reproduction/ survival**	**67.25**	**36**	**110.8**	**Vecchi et al. 1999[3]**	**Natural**
Tubifex tubifex	**1.56**	**-**	**28 d**	**NOEC**	**Reproduction**	**231.7**	**58**	**556.7**	**Vecchi et al. 1999[3]**	**Natural**
Tubifex tubifex	**1.03**	**-**	**28 d**	**NOEC**	**Reproduction**	**62.64**	**21**	**202.1**	**Vecchi et al. 1999[3]**	**Natural**
Tubifex tubifex	**1.03**	**-**	**28 d**	**IC10**	**No of cocoons**	**84**	**20**	**310.7**	**Pasteris et al. 2003[4]**	**Natural**
Tubifex tubifex	**1.03**	**-**	**28 d**	**IC10**	**No of young**	**81.7**	**20**	**299.5**	**Pasteris et al. 2003[4]**	**Natural**
Tubifex tubifex	**1.03**	**-**	**28 d**	**IC10**	**No of embryos**	**111**	**20**	**441.7**	**Pasteris et al. 2003[4]**	**Natural**

Species	OC %	AVS (µmol/g dw)	Duration and Endpoint			Value total (mg/kg dw)	Background conc.	Normalized to 5% OC	Reference	Sediment
Tubifex tubifex	**1.03**	**-**	**28 d**	**IC10**	**Total offspring**	**91.7**	**20**	**348.1**	**Pasteris et al. 2003[4]**	**Natural**
Tubifex tubifex	**2.62**	**0.05**	**28 d**	**NOEC**	**Reproduction**	**78.3**	**0**	**149.4**	**REACH registration dossier ref. 005 (REACH, 2018b)**	**OECD 218**
Tubifex tubifex	**9.81**	**0.59**	**28 d**	**NOEC**	**Reproduction**	**580.9**	**0**	**296.1**	**REACH registration dossier ref. 005 (REACH, 2018b)**	**OECD 218**
Tubifex tubifex	2.83	0.27	28 d	NOEC	Reproduction	18.3	-	32.3	REACH registration dossier ref. 005 (REACH, 2018b)	Natural
Tubifex tubifex	2.12	0.28	28 d	NOEC	Reproduction	56.1	-	132.3	REACH registration dossier ref. 005 (REACH, 2018b)	Natural
Tubifex tubifex	1.96	0.1	28 d	NOEC	Reproduction	98.3	-	250.8	REACH registration dossier ref. 005 (REACH, 2018b)	Natural
Crustacea										
Hyalella azteca	**2.6**	**<0.06**	**28 d**	**NOEC**	**Growth**	**53.2**	**0**	**102.3**	**Roman et al. 2007**	**OECD 218**
Hyalella azteca	**2.6**	**<0.06**	**28 d**	**EC10**	**Growth**	**75.3**	**0**	**144.8**	**Roman et al. 2007**	**OECD 218**
Hyalella azteca	0.5[1]	-	28 d	NOEC	growth	59.3	-	593.0	Milani et al. 2003[2]	Natural
Hyalella azteca	0.5[1]	-	28 d	NOEC	growth	66.9	-	669.0	Milani et al. 2003[2]	Natural
Hyalella azteca	0.5[1]	-	28 d	NOEC	growth	155.1	-	1551.0	Milani et al. 2003[2]	Natural
Hyalella azteca	0.5[1]	-	28 d	NOEC	Growth	52.3	-	523.0	Milani et al. 2003[2]	Natural
Hyalella azteca	**2.62**	**0.05**	**28 d**	**NOEC**	**Growth rate**	**53.2**	**0**	**101.5**	**REACH registration dossier ref. 005 (REACH, 2018b)**	**OECD 218**
Hyalella azteca	**9.66**	**0.27**	**28 d**	**NOEC**	**Growth rate**	**538.6**	**0**	**278.8**	**REACH registration dossier ref. 005 (REACH, 2018b)**	**OECD 218**
Hyalella azteca	2.12	0.28	28 d	NOEC	Growth rate	21.8	-	51.4	REACH registration dossier ref. 005 (REACH, 2018b)	Natural
Hyalella azteca	1.96	0.10	28 d	NOEC	Growth rate	49.9	-	127.3	REACH registration dossier ref. 008 (REACH, 2018b)	Natural
Hyalella azteca	0.5[1]	-	28 d	NOEC	Survival	59.3	-	593.0	Milani et al. 2003[2]	Natural
Hyalella azteca	0.5[1]	-	28 d	NOEC	Survival	66.9	-	669.0	Milani et al. 2003[2]	Natural
Hyalella azteca	0.5[1]	-	28 d	NOEC	Survival	155.1	-	1551.0	Milani et al. 2003[2]	Natural
Hyalella azteca	2.83	0.18	28 d	NOEC	Survival	171	-	302.1	REACH registration dossier ref. 005 (REACH, 2018b)	Natural
Hyalella azteca	2.12	0.28	28 d	NOEC	Survival	141	-	332.5	REACH registration dossier ref. 005 (REACH, 2018b)	Natural

Species	OC %	AVS (µmol/g dw)	Duration and Endpoint			Value total (mg/kg dw)	Background conc.	Normalized to 5% OC	Reference	Sediment
Hyalella azteca	1.96	0.10	28 d	NOEC	Survivial	140	-	357.1	REACH registration dossier ref. 008 (REACH, 2018a)	Natural
Gammarus pulex	**2.62**	**0.05**	**35 d**	**NOEC**	**Survival**	**94.7**	**0**	**180.7**	**REACH registration dossier ref. 008 (REACH, 2018a)**	**OECD 218**
Gammarus pulex	2.83	0.21	35 d	NOEC	Survival	94.7	-	167.3	REACH registration dossier ref. 008 (REACH, 2018a)	Natural
Gammarus pulex	**2.6**	**<0.06**	**28 d**	**NOEC**	**Survival**	**94.7**	**0**	**182.1**	**Roman et al. 2007**	**OECD 218**
Gammarus pulex	**2.6**	**<0.06**	**28 d**	**EC10**	**Survival**	**73.2**	**0**	**140.8**	**Roman et al. 2007**	**OECD 218**
Gammarus pulex	**2.62**	**0.05**	**35 d**	**NOEC**	**Growth rate**	**94.7**	**0**	**180.7**	**REACH registration dossier ref. 008** (REACH, 2018a)	**OECD 218**
Gammarus pulex	**2.6**	**<0.06**	**28 d**	**NOEC**	**Growth**	**94.7**	**0**	**182.1**	**Roman et al. 2007**	**OECD 218**
Gammarus pulex	**2.6**	**<0.06**	**35 d**	**EC10**	**Growth**	**102**	**0**	**196.2**	**Roman et al. 2007**	**OECD 218**
Mollusca										
Potamopyrgus antipodarum	**2.2**	**-**	**28 d**	**NOEC**	**Growth**	**73.2**	**17.4**	**126.8**	**Pang et al. 2013**	**Natural**
Aquatic plants										
Typha latifolia	0.26	-	7 d	NOEC	Root lengt	14	-	269.2	Mulller et al. 2001	Natural
Typha latifolia	0.26	-	7 d	NOEC	Shoot lengt	89.4	-	1719.2	Mulller et al. 2001	Natural
Typha latifolia	2		7 d	NOEC	Root growth	663	-	1657.5	Huggett et al. 2001	Natural
Myriophyllum aquaticum	-	-	14 d	IC23	Growth rate	5	-	-	Caillat et al. 2014	Artificial
Vallisneria natans	-	-	14 d	NOEC	Root growth	< 125	25.75	-	Zhu et al. 2016	-

1 = Organic carbon content not reported in the original study, 0.5% seems to be an estimation made in ECI (2008). 2 = Milani et al. (2003) also available in REACH registration dossier ref. 006. 3 = Vecchi et al. (1999) also available in REACH registration dossier ref. 007. 4 = Pasteris et al. (2003) also available in REACH registration dossier ref. 003.

Table S2. Marine sediment toxicity. Studies were conducted in salinity 25-33 ‰ (not tabulated). Lines in bold text= possible to calculate added risk value, Grey cell= used in the base set for the EQS derivation.

Species	OC %	AVS (µmol/g dw)	Duration and Endpoint			Value total (mg/kg dw)	Background conc.	Added value at 5% OC	Reference	Sediment
					Annelida					
Neanthes arenaceodentata	**0.76**	**0.28**	**28 d**	**LC10**	**Survival**	**514**	**29.8**	**3193.9**	**Ward et al. 2015**	**Natural**
Neanthes arenaceodentata	**0.76**	**0.28**	**28 d**	**NOEC**	**Survival**	**506**	**29.8**	**3141.2**	**Ward et al. 2015**	**Natural**
Neanthes arenaceodentata	**0.76**	**0.76**	**28 d**	**NOEC**	**Growth**	**230**	**29.8**	**1320.6**	**Ward et al. 2015**	**Natural**
					Crustacea					
Leptocheirus plumulosus	**0.76**	**0.05-0.15**	**28 d**	**NOEC**	**Growth**	**199**	**40.4**	**1046.2**	**Ward et al. 2016**	**Natural**
Leptocheirus plumulosus	0.76	0.05-0.15	28 d	NOEC	Survival	>605	40.4	-	Ward et al. 2016	Natural
Leptocheirus plumulosus	**0.76**	**0.05-0.15**	**28 d**	**NOEC**	**Reproduction**	**418**	**40.4**	**2490.8**	**Ward et al. 2016**	**Natural**
Melita plumulosa	-	-	42 d	NOEC	Fertility/ growth	250	-	-	Gale et al. 2006	Natural
Melita plumulosa	0.4	<4.5	10 d	EC10	Reproduction	11	-	-	Campana et al. 2012	Natural
Melita plumulosa	0.7	<4.5	10 d	EC10	Reproduction	39	-	-	Campana et al. 2012	Natural
Melita plumulosa	**1.5**	**<4.5**	**10 d**	**EC10**	**Reproduction**	**91**	**12.5**	**261.7**	**Campana et al. 2012**	**Natural**
Nitocra spinipes	0.4	<4.5	11 d	EC10	Reproduction	20	-	-	Campana et al. 2012	Natural
Nitocra spinipes	0.7	<4.5	11 d	EC10	Reproduction	40	-	-	Campana et al. 2012	Natural
Nitocra spinipes	**1.5**	**<4.5**	**11 d**	**EC10**	**Reproduction**	**90**	**12.5**	**258.3**	**Campana et al. 2012**	**Natural**
Nitocra spinipes	-	-	7 d	NOEC	Development	600	-	-	Perez-Landa et al. 2011	Natural
					Mollusca					
Hydrobia ulvae	**3**	**-**	**10 d**	**NOEC/LC10**	**Reproduction/ Mortality**	**247**	**23**	**373.3**	**Campana et al. 2013**	**Natural**

9. SUPPORTIVE INFORMATION - TOTAL RISK APPROACH (TRA)

When using the total risk approach (TRA), i.e. not considering background concentrations, the datasets looks different in terms of number of species, most sensitive species and effect values. This is because all effect values can be used in this derivation. The same taxonomic orders (Insecta and Crustacean) as when using the ARA approach were among the most sensitive.

9.1 Freshwater sediment toxicity

In total, 8 species were considered in the TRA derivation. The assumption that artificial sediments contains negligible amount of copper complicates the comparison of ARA and TRA. This is because the same species (*C. riparius*) was the critical species in both approaches, leading to an equivalent EQS at 5% OC (scenario 1) (table S3).

In scenario 2, when OC was not normalized to standard content, the lowest effect value was *Hexagenia spp.* with NOEC of 31.3 mg/kg dw (at 0.5 % OC). Using AF 2 the **TRA EQS was set to 15.7 mg/kg dw**. This EQS falls nearly 2-fold below the ARA EQS.

On this basis, the HC5 of 87 mg/kg dw (at 5% OC) derived in ECI (2008) was proposed as EQS sediment for TRA. This HC5 was derived based on toxicity data for six species not considering background concentrations. It seems reasonable to apply AF 2 to take into account the limited number of species used in the SSD. This gives an **EQS TRA of 44 mg/kg dw at 5% OC.** However, in case of environmental conditions with OC less than 2 % background copper concentrations (estimated to 20 mg/kg dw) would exceed the EQS, which limits the practical usability**.**

Table S3. Lowest effect value for three different species (critical effect value, i.e. used in the EQS derivation, in bold), representing three different living and feeding conditions, and the critical mesocosm observation.

FRESHWATER EFFECTS		**Effect value (TRA)**	**Normalized to 5% OC (TRA)**	**Reference**
Annelida (mg/kg dw)	*Tubifex tubifex*/ 28d/ NOEC / Growth OECD sediment, OC 0.5-9.8%	65.5	143.8	Roman et al. 2007; REACH registration dossier ref. 008
Insecta (mg/kg dw)	*Chironomus riparius* / 28d NOEC-EC_{10} / Emergence OECD sediment, OC 2.6-30 %	44.5	**85.4**	Roman et al. 2007; REACH registration dossier ref. 008
	Hexagenia spp. /28d / NOEC/ Growth Natural sediments, OC 0.5%	**31.3**	313	Milani et al. 2003
Mollusca (mg/kg dw)	*Potamopyrgus antipodarum*/ 28d/ NOEC / Growth Natural sediment, OC 2.2%	73.2	166.4	Pang et al. 2013
Critical mesocosm NOEC		62	155	Gardham et al. 2015

9.2 Marine sediment toxicity

The most sensitive species when considering TRA values was *Metia plumulosa* (table S4). Using the critical effect value normalized to 5% OC (300 mg/kg dw) and AF 5 gives a **TRA EQS of 60 mg/kg dw.** However, in case of environmental conditions with OC less than 1.7 % background copper concentrations (estimated to 20 mg/kg dw) would exceed this EQS, which limits the practical usability. Using the critical effect value (not normalized to OC) of 90 mg/kg dw and AF 5, gives a **TRA EQS of 18 mg/kg dw.** This TRA EQS is in line with natural background concentrations, which limits the practical usability.

Table S4. Lowest effect value for three different species (critical effect values, i.e. used in the EQS derivation, in bold), representing three different living and feeding conditions, and the critical field observation.

MARINE EFFECTS		**Effect value (TRA)**	**Normalized to 5% OC (TRA)**	**Reference**
Annelida (mg/kg dw)	*Neanthes arenaceodentata* / 28 d / NOEC / Growth Natural sediment, OC 0.8 %, salinity ≈ 28 ppm	230	1517.2	Ward et al. 2015
Crustacean (mg/kg dw)	*Meltia plumulosa* / 10 d/ EC_{10} / Reproduction Natural sediment, OC 1.5%[1], salinity 30 ppm	**90**	**300**	Campana et al. 2012
Mollusca (mg/kg dw)	*Hydrobia ulvae*/ 10d/ NOEC / reporduction Natural sediment, OC 3%, salinity 33 ppm	247	411.7	Campana et al. 2013
Critical field observation		34	142	Long et al.1 995

1 = Only data for 1.5 % OC was considered (same OC as in the ARA derivation), because when using the geometric mean for all OC (0.4-1.5%) the TRA effect value were lower compared to the ARA value.

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