VIDEREUDVIKLING AF TÆRSKELVÆRDIER FOR EN RÆKKE METALLER OG PAH'ER (MILJØFARLIGE STOFFER)

Notater til HELCOM og OSPAR

Teknisk rapport fra DCE – Nationalt Center for Miljø og Energi nr. 233 2022

AARHUS UNIVERSITET
DCE – NATIONALT CENTER FOR MILJØ OG ENERGI

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Sammenfatning:	For at undgå dansk fodnote politik på tærskelværdier i regionale assessments, er notater om udviklingen af de danske EQS værdier for cadmium, bly, tributyltin, fluoranthen og anthracen udformet på engelsk, og fremsendt til HELCOM og OSPARs arbejdsgrupper for miljøfarlige stoffer (EN-HZ og MIME) for at påvirke tærskelværdierne, der anvendes i HELCOM og OSPARs kommende holistiske assessment og Quality Status Report. Ved udgangen af 2021 ser det ud til, at det lykkes at harmonisere DK og HELCOMs tærskelværdier for cadmium, delvist bly, tributyltin og anthracen, mens der for OSPAR bliver sat et arbejde i gang med at udvikle metoder til at inkludere nationale tærskelværdier i Nordsø assessments fremover.

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Indhold

Forord

Miljøstyrelsen har anmodet DCE om 'Udvikling af indikatorer og tærskelværdier under havstrategidirektivet'. Projektet omfatter syv delprojekter, herunder delprojektet 'Videreudvikling af tærskelværdier for en række metaller og PAH'er (miljøfarlige stoffer), som er beskrevet i dette notat. Miljøstyrelsen har beskrevet delprojektet således: *Videreudvikling og tilpasning af regionale tærskelværdier for miljøfarlige stoffer med det formål, at de eksisterende danske forbehold for en række tærskelværdier kan fjernes.*

Notatet beskriver forløbet og afklaringen af anvendelsen af regionale tærskelværdier i Østersøkonventionen (HELCOM) og Nordsøkonventionen (OSPAR). DCE har i dialog med Departementet og Miljøstyrelsen, udarbejdet en række mødedokumenter, som afklarer og oversætter Miljøstyrelsens miljøkvalitetskriterier for cadmium, bly, TBT, fluoranthen og anthracen. Miljøkvalitetskriterierne danner grundlag for de lovfastsatte miljøkvalitetskrav.

Projektet startede primo 2021. HELCOM-arbejdsgruppen Expert Network for Hazardous Substance (EN-HZ) udarbejdede i løbet af 2021 forslag til tærskelværdier, med henblik på at de skulle anvendes i HELCOM til 'holistic assessment' (HELCOM HOLAS III). EN-HZ rapporterede udkommet til Conservation and State arbejdsgruppen, der i efteråret 2021 sendte tærskelværdierne videre til Heads of delegation mødet i foråret 2022, hvor det vil blive endeligt besluttet, hvilke værdier der skal indgå i den Holistiske Assessment III.

Projektet indgik ligeledes i forarbejde i OSPAR til Quality Status Report (OSPAR Q0SR 2023), der udkommer i 2023, her via en intersessionel arbejdsgruppe under Working Group on Monitoring and on Trends and Effects of Substances in the Marine Environment (MIME). MIME har sendt sine anbefalinger videre til Hazardous Substances & Eutrophication Committee (HASEC) som står for den politiske accept af tærskelværdierne.

Projektet beskriver baggrunden for de danske forbehold for en række metaller og PAH'er. Der fremlægges beskrivelser af baggrunden for de danske miljøkvalitetskrav (angivet i BEK nr 1625 af 19/12/2017) for metaller (inkl. TBT) og PAH'er for arbejdsgrupperne EN-HZ og MIME. Formålet var, at få dem anerkendt som regionale tærskelværdier i henholdsvis HELCOM og OSPAR, således som beskrevet ovenfor, så der var overensstemmelse mellem danske miljøkvalitetskrav og regionale tærskelværdier.

Dokumenter til møderne i HELCOM og OSPAR (bilag 1-3) er udarbejdet af DCE ved Martin M. Larsen (MML) i samarbejde med Miljøministeriets Departement v/Anne Munch Christensen (AMC). Dokumenterne blev fremlagt på møderne i EN-HZ og MIME på vegne af Danmark af MML. AMC deltager i møderne som head of delegation og MML som faglig ekspert. Det faglige indhold har været DCE's ansvar. Da Miljøstyrelsen har udarbejdet de underliggende dokumenter med beskrivelse af miljøkvalitetskriterier (Kvalitetskriterier for miljøfarlige forurenende stoffer i vandmiljøet (mst.dk)), har der været afholdt web møder med deltagelse af MML, AMC og Miljøstyrelsen ved Janni Magelund Degn Larsen (JMDL), ligesom miljøkvalitetskriteriet for TBT blev genberegnet af JMDL efter kommentering fra Sverige af det oprindelige udkast.

Der er under projektet udarbejdet og justeret to notater, som er anvendt som underlag i HELCOM EN-HZ og OSPAR MIME arbejdsgrupperne (bilag 2 og bilag 3), en oversigt over danske forbehold (bilag 1) samt en oversigt over afholdte møder (bilag 4).

Sammenfatning

Den danske fremlæggelse af uddrag af dokumenterne med de danske miljøkvalitetskriterier for cadmium, bly, tributyltin, fluoranthen og anthracen i OSPAR og HELCOM resulterede i en diskussion om tærskelværdierne til de kommende OSPAR QSR 2023 og HELCOM HOLAS III rapporteringer.

Efter det seneste HELCOM 'state and conservation' møde d. 4.-8. oktober 2021 blev det besluttet at anbefale HELCOMs heads of delegation (HOD), at de danske miljøkvalitetskrav bruges som regionale tærskelværdier for cadmium i biota, bly i muslinger, fluoranthen og tributyltin i sediment. Anbefalingen behandles på møde i december 2021 (efter redaktionens afslutning).

Diskussionen i regi af OSPAR resulterede i forslag til en arbejdsgruppe, der skal definere en fremgangsmåde til at gennemgå og acceptere fremtidige nationale dokumenter vedrørende miljøkvalitetskrav som regionale tærskelværdier for Nordsøen. Derimod var der ikke tilslutning til at revidere de nuværende tærskelkriterier til QSR 2023.

Summary

The Danish presentation of translated parts of Danish language documents on the development of EQS and QS for cadmium, lead, tributyltin, fluoranthene og anthracene in OSPAR and HELCOM resulted in a debate about which target values should be used in the upcoming OSPAR QSR 2023 og HELCOM HOLAS III reports.

After the latest HELCOM 'state and conservation' meeting on 4th.-8th. october 2021 it was decided to recommend to HELCOMs heads of delegation, that Danish EQS / QS values for cadmium in biota, lead in mussels, fluoranthene and tributyltin in sediment. The recommendation will be discussed in the HELCOM HOD meeting of December 2021.

Discussion under OSPAR resulted in the suggestion to establish a working group with the purpose to define the way National EQS / QS documents could be evaluated and accepted as future target values for the North Sea, but for the QSR 2023, no changes to current criteria will be made based on the Danish suggestions.

Notater til OSPAR og HELCOM

Som optakt til årets første HELCOM EN-HZ møde d. 17.-19. februar 2021 fremsendte Anna M. Christensen et mødedokument udarbejdet af DCE til HELCOM sekretariatet d. 5. februar 2021 (bilag 1, med fremhævelser tilføjet af HELCOMs sekretariat) til EN-HZ 14-2021, som redegjorde for de danske forbehold for eksisterende tærskelværdier. Dokumentet var blevet til i samarbejde mellem Departementet og DCE/AU, og som bilag var alle baggrundsdokumenterne for de danske miljøkvalitetskrav (EQS-værdier) vedlagt (på dansk). For at gøre disse operationelle var det nødvendigt at oversætte dem til engelsk, så de kunne diskuteres i EN-HZ med henblik på at opnå accept og dermed kunne forelægges som forslag til regionale tærskelværdier for den kommende HELCOM HOLAS III og OSPAR QSR 2023.

DCE udarbejdede herefter i samarbejde med MST og Departementet et mødedokument, der blev fremsendt til HELCOM sekretariatet forud for det næste EN-HZ 15 møde d. 15.-16. juni 2021 (bilag 2). Mødedokumentet gennemgik hovedpunkterne i dokumenter om de danske miljøkvalitetskrav (Kvalitetskriterier for miljøfarlige forurenende stoffer i vandmiljøet (mst.dk), og belyste forskellene mellem de danske og evt. andre landes EQS-værdier (især mht. TBT). Dokumenterne blev forfattet og præsenteret af DCE, med assistance og gennemlæsning af både Departementet og MST, som havde produceret de underliggende dokumenter.

På baggrund af kommentarer fra Sverige reviderede Miljøstyrelsen baggrundsdokumentet for TBT med en genberegning af EQS-værdien efter EN-HZ 15, ligesom bly i biota og anthracen blev tilføjet, og et nyt dokument blev fremsendt til EN-HZ 16. Efter endnu en mindre justering i samarbejde med Miljøstyrelsen og Departementet på basis af EN-HZ 16, blev dokumentet introduceret af Departementet på HELCOMs State and Conservation 15-2021 (online møde den 4.-8- oktober 2021). Indstillingen efter dette møde blev, at de danske miljøkvalitetskrav for cadmium (sekundær QS grænse, som anvendes hvis der ikke findes data for den primære grænse af EQS for vand) blev accepteret (160 µg Cd/kg VV) i fisk og muslinger. Derudover, blev miljøkvalitetskravet for bly i muslinger (sekundære QS grænse) på 110 µg Pb/kg VV accepteret, men for fiskelever blev OSPARs BAC fastholdt. Det danske forslag (der retter en fejl i EU's baggrundsdokument for fluoranthen) blev også accepteret, så en sekundær QS for fluoranthen i sediment blev fastsat til 3500 µg/kg (5% C_{ORG}) i sediment fra tidligere 2000. Endelig blev værdien for TBT sediment accepteret efter mødet. Sverige havde et lille forbehold, men på et efterfølgende møde i EN-HZ blev de lidt lavere danske værdier (1,3 mod 1,6 µg TBT/kg i sediment) accepteret på baggrund af tidligere diskussioner om anvendelsen af artsfølsomhedsindeks kurver.

Efterfølgende blev samme mødedokument efter en mindre revision forelagt for OSPAR på MIME møde i ICES den 22.-26. november 2021, ved fremsendelse til OSPAR sekretariatet den 12. november-2021 (bilag 3). Det afstedkom ikke anbefaling om revision af tærskelværdierne for QSR 2023 til næste niveau (OSPAR HASEC) fra MIME. I stedet er der forslag fra MIME om at nedsætte en intersessionel arbejdsgruppe med det formål at lave et mere formelt netværk og møderække for at diskutere en fremgangsmåde til at inkludere nationalt udviklede EQS/QS værdier som regionale tærskelværdier. Det vil give de enkelte lande mulighed for at konsultere deres økotoksikologiske netværk for at vurdere, om der er tilstrækkelig dokumentation til at foreslå MIME at inkludere nye tærskelværdier i fremtidige QSR arbejder, som f.eks. de danske EQS beregninger.

Bilag 1: Notat til HELCOM EN-HZ 14-2021

Document title	HELCOM HZ indicator threshold values
Code	4-1
Category	DEC
Agenda Item	Threshold values – progress towards overview and review (if needed)
Submission date	8.2.2021
Submitted by	Secretariat
Reference	

Background

The purpose of this document is to gather as much relevant information as possible to support harmonisation across the region, where possible, and to address known issues related to threshold values in the existing hazardous substances indicators.

Contracting Parties are invited to fill in relevant information where other substances are assessed nationally (providing relevant details) or where national threshold values conflict with those already provided in the table (providing relevant national information). Once information is received from all Contracting Parties a summary and comparison will be compiled to support next steps on the topic.

The table provided below builds on discussion at EN-HZ 13-2020 (Outcomes agenda item 6, in particular paragraph 6.11). On this basis the table below gathers information from the EH-HZ 'extraction table' (i.e. indicator parameter summary) and is complimented by relevant information from Denmark.

Items in grey text are where know study reservations or open issues are known.

Action requested

The Meeting is invited to:

- Review the information provided and discuss the issues raised.
- Plan next steps ahead (with the HOLAS III deadlines in mind).
- Agree on any changes to the threshold values applied, where possible, so that new recommendations can be presented to State and Conservation 14-2021.

Collation of substances assessed and their threshold values (HELCOM and national) in the Baltic Sea region.

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Items in grey text are where know study reservations or open issues are known.

Substance	Matrix (details)	Threshold value applied (type)	Contracting Party	Other important notes (if needed)	DK national threshold
Cadmium	Water (filtered or unfiltered)	0.2 µg/l (EQS)	HELCOM indicator	Surface water layer (≤ 5.5 m)	EU EQS (equal to HELCOM threshold)
Cadmium	Biota	960 µg/kg dw (OSPAR BAC)	HELCOM indicator	Molluscs (M edulis + M. baltica)	In DK 160 µg/kg ww is used for both fish and molluscs Will be reviewed
Cadmium	Biota	26 µg/kg ww fish liver (OSPAR BAC)	HELCOM not implemented currently	Herring & cod (open sea) Flounder, dab, eelpout & perch (coastal)	DK reservation 160 µg/kg ww – nationally developed National threshold will be reviewed
Cadmium	Sediment	2.3 mg/kg dw (QS from EQS dossier)	HELCOM indicator	Sediment (surface, ICES 'upper sediment layer - 0-X cm')	DK reservation 3.8 mg/kg dw - nationally developed based on EU EQS dossier and additional data
Lead	Water (filtered or unfiltered)	1.3 µg/l (EQS)	HELCOM indicator	Surface water layer (≤ 5.5 m)	EU EQS (equal to HELCOM threshold)
Lead	Biota	26 µg/kg ww fish liver (OSPAR BAC)	HELCOM indicator	Herring & cod (open sea) Flounder, dab, eelpout & perch(coastal)	DK reservation 110 µg/kg ww - nationally developed
Lead	Biota	1300 µg/kg dw (OSPAR BAC)	HELCOM indicator	Molluscs (M edulis + M. baltica)	DK reservation In DK 110 µg/kg ww is used for both fish and molluscs
Lead	Sediment	120 mg/kg (QS from EQS dossier)	HELCOM indicator	Sediment (surface, ICES 'upper sediment layer - 0-X cm')	DK reservation 163 mg/kg dw - nationally developed based on EU EQS dossier https://mst.dk/media/202438/7439-92-1-bly-sediment.pdf

Mercury	Biota	20 µg/kg ww (EQS biota secondary poisoning)	HELCOM indicator	Herring & cod (open sea) Flounder, dab, eelpout & perch (coastal) Molluscs (M. edulis + M. baltica)	EU EQS (equal to HELCOM threshold)
HBCDD (HBCD or HBCDA,HBCDB, and HBCDG)	Biota	167 µg/kg ww 5% lipid content (EQS biota human health)	HELCOM indicator	Herring & cod (open sea) Flounder, dab, eelpout & perch (coastal)	EU EQS (equal to HELCOM threshold)
HBCDD (HBCD, HBCDA,HBCDB, HBCDG)	Sediment	170 µg/kg dw (QS from EQS dossier)	HELCOM indicator	Sediment (surface, ICES 'upper sediment layer - 0-X cm')	No national value has been develop
PBDEs (BD28, BD47, BD99, BD100, BD153, BD154)	Biota	0.0085 µg/kg ww 5% lipid content (EQS biota human health)	HELCOM indicator	Herring & cod (open sea) Flounder, dab, eelpout & perch (coastal)	EU EQS (equal to HELCOM threshold)
PBDEs (BD28, BD47, BD99, BD100, BD153, BD154)	Sediment	310 µg/kg dw sediment (QS protection objective benthic community marine)	HELCOM indicator	Sediment (surface, ICES 'upper sediment layer - 0-X cm')	No national value has been developed (This has not been part of the indicator earlier)
PFOS	Biota	9.1 µg/kg ww (EQS biota human health)	HELCOM indicator	Herring & cod (open sea) Flounder, dab, eelpout & perch (coastal)	EU EQS (equal to HELCOM threshold)
PFOS	Water	0.00013 µg/l (EQS)	HELCOM indicator	Surface water layer (≤ 5.5 m)	EU EQS (equal to HELCOM threshold)
dl-PCBs, dioxins and furans (CB77, CB81, CB105, CB118, CB126, CB156, CB157, CB167, CB169, CDD1N, CDD4X, CDD6P, CDD6X, CDD9X, CDDO, CDF2N, CDF2T, CDF4X, CDF6P, CDF6X, CDF9P, CDF9X, CDFO, CDFP2, CDFX1, TCDD)	Biota	0.0065 TEQ/kg ww 5% lipid content (EQS biota human health)	HELCOM indicator	Herring & cod (open sea) Flounder, dab, eelpout & perch (coastal)	EU EQS/food limit (equal to HELCOM threshold)
CB-118	Biota	24 µg/kg lw fish liver of muscle (EAC)			DK reservation, No national threshold exist

Non dl-PCBs (PCBs) (sum of congeners CB28, CB52, CB101, CB138, CB153, CB180)	Biota	75 µg/kg ww 5% lipid content (EC 1881/2006)	HELCOM indicator	Herring & cod (open sea) Flounder, dab, eelpout & perch (coastal)	EU food limit (equal to HELCOM threshold)
PAHs (benzo(a)pyrene)	Biota	5 µg/kg ww (EQS biota human health)	HELCOM indicator	Molluscs & Crustaceans (M. edulis, M. baltica & S. entomon)	EU EQS (equal to HELCOM threshold)
PAHs (fluoranthene)	Biota	30 µg/kg ww (EQS biota human health)	HELCOM indicator	Molluscs & Crustaceans (M. edulis, M. baltica & S. entomon)	EU EQS (equal to HELCOM threshold)
PAHs (fluoranthene)	Sediment	2000 µg/kg dw (QS)	HELCOM indicator		DK reservation In process nationally- there seems to be a mistake in the EU EQS dossier for the QS value for sediment
PAHs (anthracene)	Sediment	24 ug/kg dw (QS)	HELCOM indicator	Sediment (surface, ICES 'upper sediment layer - 0-X cm')	DK reservation – DK value is 4.8 µg/kg dw – Based on EU EQS dossier. DK value is being checked
PAH Metabolite 1-hydroxypyrene	Biota	483 ng/g fish bile	HELCOM indicator	Herring & cod (open sea) Flounder, dab, eelpout & perch (coastal)	DK reservation, no regular monitoring is being performed in Danish waters. Is this endpoint needed as a part of the indicator?
TBT (TBTIN, TBSN+)	Sediment	1.6 µg /kg dw 5% TOC (QS)	HELCOM indicator	Sediment (surface, ICES 'upper sediment layer - 0-X cm')	DK reservation - In process nationally
TBT (TBTIN, TBSN+)	Water (ideally unfiltered)	0.2 ng/l water (EQS)	HELCOM indicator	Surface water layer (≤ 5.5 m)	EU EQS (equal to HELCOM threshold)
TBT	Biota	12 µg/kg dw (OSPAR EAC)	HELCOM indicator	Molluscs	DK reservation - In process nationally
Imposex (VDS, VDSI, INTS, INTSI, IMPF%, IMPS, IMPSI, PCI, %FemalePOP Assisting parameters: PARAM = MBTIN, MBSN+, DBTIN, DBSN+,	Biological effects	Gercken & Sordyl 2009; Magnusson et al 2016 EAC: *Peringia ulvae*: 0.1 VDSI *Nucella lapillus*: 2.0 VDSI *Neptunea antiqua*: 2.0 VDSI	HELCOM indicator	Gastropods	HELCOM/OSPAR thresholds for imposex/intersex are used nationally

TBTIN, TBSN+, TPTIN, TPSN+)		*Hinia reticulata*: 0.3 VDSI *Buccinum undatum*: 0.3 VDSI *Littorina littorea*: <0.3 ISI			
Please add further substances or information of relevance…					

Bilag 2: Notat til EN-HZ 15-2021

Document title	Proposal on QS threshold values from Denmark
Code	4-1
Category	DEC
Agenda Item	4 - Threshold values
Submission date	25.5.2021
Submitted by	Secretariat
Reference	

The purpose of this document is to gather as much relevant information as possible to support harmonisation across the region, where possible, and to address known issues related to threshold values in the existing hazardous substances indicators.

Background

As part of an extensive national review process related to the threshold values for hazardous substances Denmark has recalculated several QS values with relevance to HELCOM (and OSPAR) indicators. The recalculation is generally supported by greater data availability and the inclusion of more species or relevance, and the newly proposed values are therefore considered to be more accurate / appropriate. The recalculation follow the appropriate guidelines set out under relevant legislation and are thus suitable for application under EU policies, for those Contracting Parties that are also EU Member States.
The document below provides a summary of each aspect addressed and supporting information (in Danish) is also provided in Documents 4-1 Att1-4.
The EN-HZ meeting is requested to review and discuss the proposed changes and to decide if these should be transferred to State and Conservation for endorsement (and subsequent approval at HOD). This process needs to be implemented by the 7 September 2021 deadline for the approval procedure.

Action requested

The Meeting is invited to:
- Take note of the work carried out by Denmark,
- Consider and discuss the new proposals,
- Decide on any changes to the HELCOM indicator threshold values (i.e. decide on proposing these changes to the Working Group and HOD level).

Danish quality standards for selected indicator substances.

Introduction

A number of EU QS values have been re-evaluated by the Danish EPA, and are hereby suggested to be taken onboard in OSPAR and HELCOM assessments as assessment criteria for the QSR 2023 and HELCOM HOLAS III. For each substance and specific matrices, the rationale behind the recalculated values is presented below. All calculations follow the EU guideline, with summary of the factors used. The background documents are in Danish, but the main table and summaries are included below. References are not given in full for each substance, but a selection of the most relevant are given, and the remainder references can be found in these selected references.

For most datasets, new data or re-interpretation of existing data lead to lower assessment factors, or an increase in the number of species, facilitating calculation of species sensitive distribution in some cases, again reducing the assessment factors compared to selecting the lowest NOEC/EC_{10} values. A summary is given in the table below, details follow.

Overview of existing and suggested revised QS values for the different substances

Substance	Type	OSPAR	HELCOM	Revised QS	unit
Fluoranthene	$QS_{sediment}$		2000 (QS)	3500 (5%TOC)	µg/kg dw
		600 (ERL)		1750 (2.5%TOC)	µg/kg dw
Lead	$QS_{sediment}$	47 (ERL)	131 (QS)	163	µg/kg dw
Cadmium	$QS_{sediment}$	1.2 (EAC)	2.3 (QS)	3.8$	mg/kg dw
Shellfish	$QS_{sec.pois.}$	1.0 (Food)	0.137 (QS)	0.32$	mg/kg ww
Fish		0.05 (Food)			mg/kg ww
TBT	$QS_{sediment}$		1.6 (S-QS)	1.1 (5%TOC)	µg/kg dw
		0.8 (S-QS)		0.55 (2.5%TOC)	µg/kg dw
Shellfish	$QS_{sec.pois.}$	12 (EAC)	12 (EAC)	1.8	µg/kg ww
Fish	$QS_{sec.pois.}$			2.3	µg/kg ww

$: Note that the current danish QS values, under review in 2021.

Fluoranthene

The EU EQS datasheet (2005 and revised in 2011) present different values for QS benthic community:
$QS_{sediment,\ Equilibrium\ partitioning\ 2005}$: 173 µg/kg DW
$QS_{sediment,\ Assessment\ factor\ 2005}$: 129 µg/kg DW

$QS_{sediment, Equilibrium partitioning 2011}$: 2.000 µg/kg DW, same for fresh- and marine waters

OSPAR assessment criteria currently in use:
BAC 39 (14.4 not normalised) µg/kg DW 2.5% TOC, ERL 600 µg/kg DW

HELCOM assessment criteria currently in use:
2000 µg/kg (EU $QS_{sediment}$)

The Danish EPA review of fluoranthene only found few new data during a literature search, the main difference is the conversion of the critical study converting the organic carbon content of 41 mg/kg from 10% TOC to 5% TOC, where the EU just convert by dividing with 2, and the Danish EPA converts from standard sediment with 10% OM (taken as standard sediment with conversion of TM to TOC with a factor of 0,588), resulting in 35 mg/kg instead of 20 mg/kg before applying the assessment factor of 10, leading to:
3500 µg/kg sediment (5% OC, HELCOM) and 1750 µg/kg (2.5% OC, OSPAR).

English summary of sediment quality standards for the Danish assessment of fluoranthene

Fluoranthene has a log K_{ow} of 5.2 (EU-dossier, 2011) and is likely to sorb to sediment. Ecotoxicity data have been taken from the EU-dossier (2011) and from Verbruggen (2012) and are presented in table 4.1. Further a search for data was conducted[1].

There are EC_{10} or NOEC values for nine species and three major taxonomic groups. The lowest toxicity value is a LOEC of 8.8 mg/kg sediment (with 10% OM) for *Chironomus riparius* (Verrhiest et al. (2001), cfr. Verbruggen (2012)). The EU-dossier (2011) and Verbruggen (2012) mention this value but choose not to use it, with a remark that the *C. riparius* data "vary widely". The study is rated with a Klimisch score of 2 in the EU-dossier (2011) and Verbruggen (2012), and by the Danish EPA, so it is regarded as reliable and relevant. A LC_{50} has also been calculated, indicating, that there must be a dose-response correlation, though since no raw data has been presented in the study, this cannot be validated and the percentage effect is also not noted. Therefore, according to TGD no. 27 (table 20, page 154, version 2018), LOEC can only be used as additional information.

Verbruggen, 2012 chose the second lowest toxicity value, EC_{10} of 41 mg/kg dw (with 10% OM). EU-dossier, 2011 chose the same value, but notes it as 41 mg/kg dw (with 10% OC), leading to a lower sediment quality standard than found in Verbruggen, 2012. The value used by Verbruggen, 2012, was chosen to set the national sediment quality standard.

Statistically, the difference in sensitivity between freshwater and saltwater species is insignificant (Mann-Whitney U test, P > 0.2, two-tailed). If anything, the freshwater species are the more sensitive. Therefore, marine and freshwater data are pooled, and the same assessment factor is employed for the fresh- and saltwater environments.

With three major taxonomic groups represented, an assessment factor of 10 can be used to derive a $PNEC_{Sediment}$ from the EC_{10}:

$PNEC_{Sediment}$ = 41 mg/kg sed. / 10 = 4.1 mg/kg sed. (with 10% OM),

This value is, following conversion to an EU standard sediment with 5% OC using the conversion factor %OM = 1.7 * %OC (EU, 2018), used as $QS_{Sediment}$ for fluoranthene:

3 500 µg/kg sediment (5% OC) = 69 700 µg/kg OC = $QS_{Sediment}$

[1] In ECHA's REACH database, US EPA's ECOTOX database, via OECD's eChemPortal meta-database as well as by conducting a literature search focused on sediment-dwellling organisms using Google Scholar.

Table 4.1 chronic effects of fluoranthene on sedimentdwelling organisms

	Expo-suretime	Effect type	EC_{10} or NOEC mg/kg Dry-weigh; 10% OM	EC_{10} or NOEC mg/kg Dry-weigh; 5% OC	EC_{10} or NOEC mg/kg OC	Reference queted in Verbruggen (2012)
Annelida						
Stylaria lacustris s	10 days	Mortality	112	95	1904	Suedel & Rodgers, 1996
Crustacea						
Corophium spinicorne s	10 days	Mortality	108	92	1836	Swartz et al. 1990
Coullana sp. f	10 days	Mortality, LC_{10}	157	133,5	2670	Lotufo 1998
Diporeira sp. f	30 days	Mortality	≥2979	≥2533	≥50643	Driscoll & Landrum 1997
*Hyalella azteca** f	16 days	Mortality	600*	510	10200	Driscoll & Landrum 1997
	10 days	Mortality	<54	<46	918	Suedal & Rodgers 1996
	14 days	Mortality	9*	7,7	153	Verrhiest et al. 2001
Rhepoxynius abronius s	10 days	Mortality	58	49	986	Swartz et al. 1990
	10 days	Mortality	113	96	1921	Swartz et al. 1988
	10 days	Mortality	83	71	1411	Swartz et al. 1997
	10 days	Mortality	117	99	1989	Swartz et al. 1997
	10 days	Mortality	235	200	3995	De Witt et al. 1992
	10 days	Mortality	173	147	2941	De Witt et al. 1992
	10 days	Mortality	188	160	3196	De Witt et al. 1992
	10 days	Mortality	141	120	2397	De Witt et al. 1992
	10 days	Mortality	218	185	3706	De Witt et al. 1992
R. abronius geometric mean			135	115	2295	
Schizopera knabeni s	14 days	Reproduction	41	35	697	Lotufo 1997
	10 days	Reproduction	58	49	986	Lotufo 1997
Insecta						
*Chironomus riparius*** f	10 days	Mortality	<8,8	7,5	150	Verrhiest et al. 2001
*Chironomus tentans**** f	10 days	Immobility	58	49	986	Suedel & Rodgers 1996
	10 days	Immobility, EC_{50}	40***	34	680	Suedel et al. 1993

*Verbruggen (2012) uses the geometriske mean (73 mg/kg) af values from Driscoll & Landrum (1997) (600 mg/kg) and the value from Verrhiest et al. (2001) (9 mg/kg). But the two studies have been performed using different circumstances, e.g. animals have been exposed to ultraviolet light in Verhiest et al., but not in Driscoll & Landrum, and different sediment types was used. An average is hence no applicable. The EU-dossiet (2011) do not include a geometric mean of the values.
**10-11 day mortality is a more sensitive effect type than hathching. Two studies include10-11 days toxicity values (Stewart & Thompson, 1995 and Verrhiest et al., 2001).
***Lowest EC_{50} in Suedel et al. (1993) is lower than the NOEC from Suedel & Rodgers (1996). In the latter, clay content is about 3 times larger than the first study, while pH is 6 Suedel & Rodgers and 6,5-8,5 in Suedel et al. (1993).
f: freshwater species; s: marine species

Lead in sediment

EQS for lead was developed in 2005 and revisited in 2011 EU EQS datasheet.

$QS_{benthic\ community,\ 2005}$: 53.4 mg/kg + $C_{background}$ (i.e. $MPA_{sediment}$ = 53,4)

$QS_{benthic\ community,\ marine\ 2011}$: 123 mg/kg dw
$QS_{benthic\ community,\ freshwater\ 2011}$: 131 mg/kg dw total Pb; 41 mg/kg DW bioavailable fraction using AVS/SEM correction

OSPAR assessment criteria currently in use:
BAC 38 (22.4 not normalised) µg/kg DW 5% Al, ERL 47 mg/kg DW

HELCOM assessment criteria currently in use:
120 mg/kg (rounded EU $QS_{sediment}$)

Lead QS for sediments was developed using a SSD analysis on combined marine and freshwater species, as no difference between the two water types was evident.
The Danish EPA arrived at a **$QS_{sediment}$ = 163 mg/kg DW** for total lead.

Based on NOEC or EC_{10} from 8 species representing three systematic groups and at least four food strategies, a species sensitivity distribution was performed and an assessment factor of three used (reduced from 10 based on two seawater species and six freshwater species combined), with a HC_5 of 490 mg/kg DW (90% range from 212 to 756). It should also be noted that applying the simultaneous extracted metal/acid volatile sulphide (SEM-AVS) model resulted in negative NOEC values so the use of SEM-AVS was abandoned, and the result is thus valid for total lead only.

English Summary and conclusions for the Danish assessment of lead

Quality standards (QS) for sediment for lead were developed based on data in industry's voluntary risk assessment report (VRAR).

There are chronic values for 8 sediment species, of which 2 are marine. The species represent 3 major taxonomic groups, and at least 4 different foraging strategies.

The two marine species, a crustacean and an oligochaete, are neither more nor less sensitive than their freshwater taxonomic counterparts, and so the freshwater and saltwater data are combined.

An SSD analysis was employed, and an assessment factor of 3 applied for derivation of the freshwater as well as the saltwater sediment QS.

HC_5 = 490 mg Pb/kg sediment, d.w.
Sediment $QS_{freshwater}$ = sediment $QS_{saltwater}$ = (490 mg/kg)/3 = 163 mg Pb/kg sediment, dry weight

Toxicity data from VRAR

Organism	Most sensitive endpoint	EC10 or NOEC (mg total Pb/kgDW)	Remark
Worms (annalida, Oligocheta)			
Tubifex tubifex	reproduction 28 days	573	EC10
Lumbriculus variegatus	survival 28 days	2100	EC10
Neanthes arenaceodentata	28 days NOEC	801	Marine species
Insets (Insecta)			
phoron virgo	Survival 21 days	1126	NOEC (EC10 = 1616 but no reliable CL) a
Hexagenia limbata	Survival, growth 21 days	>2903	NOEC Unbounded: >2903 with 13.3 % effect observed

			at this tested concentration = similar to what was observed in the control)
Chironomus tentans	Survival 20 days	3390	NOEC (no monotonic trend in survival concentration)
Crustations (Crustacea)			
Hyalella azteca	survival 28 days	1416	EC10
Lumbriculus variegatus	growth 35 days	1745	EC10
Leptocheirus plumulosus (Amphipoda)	28 days NOEC	931	Marine species
Amphiascus tenuiremis (Copepoda)	4 days LC50	2465	Marine species

Cadmium in sediment and biota

EQS for cadmium was developed in 2005 but not revisited in the 2011 EU EQS dossiers

$QS_{Sediment, assessment factor, 2005}$: added risk approach 2.3 mg/kg dw + background
$QS_{biota secpois}$: 160 µg/kg ww

OSPAR assessment criteria currently in use:
Sediment: BAC 0.31 (0.129 not normalized) µg/kg DW 5% Al, ERL 1.2 mg/kg DW
Biota: BAC mussels 960, fish liver 26 µg/kg dw.
MPC mussel, fish muscle 1000, fish liver 50 µg/kg ww

HELCOM assessment criteria currently in use:
Sediment: 2.3 mg/kg DW (EU $QS_{sediment}$)
Biota: HQS mussel 137.3 µg/kg ww (OSPAR BAC, recalculated to wet weight)

Cadmium QS for sediments was developed using a SSD analysis on combined marine and freshwater species, as no difference between the two water types was evident. The Danish EPA arrived at a $QS_{sediment}$ = 3.8 mg/kg DW and biota criteria $QS_{secpois}$ 0.32 mg/kg ww, QS_{HH} 0.044 mg/kg ww.

The original EU risk assessment for sediment used an uncertainty factor of 50 due to only one chronic dataset for freshwater (Chironomus sp), reduced from 100 as most short-term test showed very little difference in species sensitivity. In the Danish evaluation, three species representing three systematic groups and reducing the uncertainty factor to 10, including two marine species. Lowest observed NOEC or EC_{10} was 38 mg/kg, applicable to both fresh water and seawater. It should be noted that the cadmium concentration in many cases was lower than the acid volatile sulphur, but still had a clear dose-response signal. The use of SEM-AVS models for cadmium was therefore abandoned. The suggested cadmium $QS_{sediment}$ is close to expected background levels, and should be used as added risk approach.
The original EU risk assessment for biota included a species sensitivity distribution with a HC_5 of 1.6 mg/kg food, but mainly based on mammal and birds, so the EQS datasheet resorted to using the assessment factor method, with 10 as the factor. Concidering the lack of lower trophic levels, the danish EPA used the SSD value, with an uncertainty factor of 5, resulting in 1.6/5 =0.32 mg/kg $QS_{secpois}$. For human health, the EFSA ADI of 0,36 µg/kg body weight/day, and 20% of food intake from fish, assuming a 70 kg person eats 0.115 g fishproduct/day yields 0,36 µg/kg body weight per day* 70 kg *0,2 / 0,115 g per day = 0.044 mg/kg $QS_{HH.}$

English Summary and conclusions for Danish assessment of cadmium

All data and calculations were taken from the EU risk assessment report (RAR) and the addendum thereto, plus from Hansen et al. 1996, and DeWin et al. 1996. The environmental quality standard (EQS) values for freshwater and saltwater and the corresponding maximal acceptable concentrations (MAC) are all in Directive 2008/105/EC, and in the draft new directive amending Directive 2008/105/EC.

Calculation of available Cd in sediments is based on the SEM-AVS model (Technical Guidance (EU vejledning) 2011), and requires measurements of sulphides, copper and lead, and preferably also mercury. However, as clear dose-response relationships were observed in Hansen et al. 1996, where AVS was in excess of the metal concentrations, the reliability of the SEM / AVS model is questioned.

With the extra data of Hansen et al. 1996 and DeWin et al. 1996 there are chronic values for more than 3 species representing more than 3 major taxonomic groups, including more than 2 marine species. Therefore, an assessment factor (AF) of 10 is applied to the lowest EC_{10} or NOEC for both the marine and fresh-water environments.

The EC_{10} values from Hansen et al. 1996 were estimated by the Danish Environmental Protection Agency from the data in the article.

Concerning the biota QS, the RAR calculated an HC5 = 1.6 mg / kg feed, fresh weight, but chose to use the AF method because of lack of guidance on how to employ an SSD for mammals and birds. However, there is data for 4 species of mammals and 3 species of birds covering 6 different orders. Given that the evaluation is for birds and mammals only compared to the multitude of major taxonomic groups to be protected by the EQS_{water}, it is here accepted to employ the SSD method, applying an AF of 5.

Thus, the $EQS_{biota,\ secondary\ poisoning}$ = 1.6 mg / kg:5 = 0.32 mg CD / kg feed, fresh weight.

The ADI employed = 0.36 µg / kg bw*day (EFSA 2009). Seafood should only contribute with 20 % of this daily intake. A 70 kg person is expected to eat 0.115 kg fish / day. This results in an $EQS_{biota,\ human\ health}$ = 0.044 mg / kg food, wet weight.

Quality standards for the water column

Hardness	EQS µg/l (VKK)		MAC µg/l (KVKK)
	Freshwater	Saltwater	Fresh- and saltwater
≤40	≤0.08	0.2	≤0.45
10-<50	0.08	0.2	0.45
50 - <100	0.09	0.2	0.6
100 - <200	0.15	0.2	0.9
≥200	0.25	0.2	1.5

Quality standards for sediment and biota are as follows:

$EQS_{sediment,\ freshwater}$:

Added 3.8 mg / kg dw

Available 3.8 mg / kg dw

$EQS_{sediment,\ saltwater}$:

Added 3.8 mg / kg dw

Available 3.8 mg / kg dw

$EQS_{biota,\ secondary\ poisoning}$: 0.32 mg / kg feed, wet weight

$EQS_{biota,\ human\ health}$: 0,044 mg / kg seafood, wet weight

TBT in sediment and biota

The EU EQS datasheet (2005) present different values for QS benthic community:
$QS_{sediment,\ Equilibrium\ partitioning\ 2005}$: 0.02 µg / kg DW (tentative)
$QS_{biota,\ secpois}$: 230 µg / kg ww prey

$QS_{biota,HH}$: 15.2 µg / kg ww seafood

OSPAR assessment criteria currently in use:
Sediment: 0.8 µg / kg DW (2.5% TOC)
Shellfish: BAC 5 µg / kg DW , EAC 12 µg / kg DW

HELCOM assessment criteria currently in use:
Sediment: 1.6 µg / kg DW (5% TOC)
Biota: 12 µg / kg dw (EAC)

The Danish EPA suggest $QS_{sediment}$ of 1.1 µg / kg DW, and secondary poisoning QS values of 2.3 µg / kg for fish and 1.8 µg / kg for mussels, with a human health QS for fish products as 30 µg / kg DW

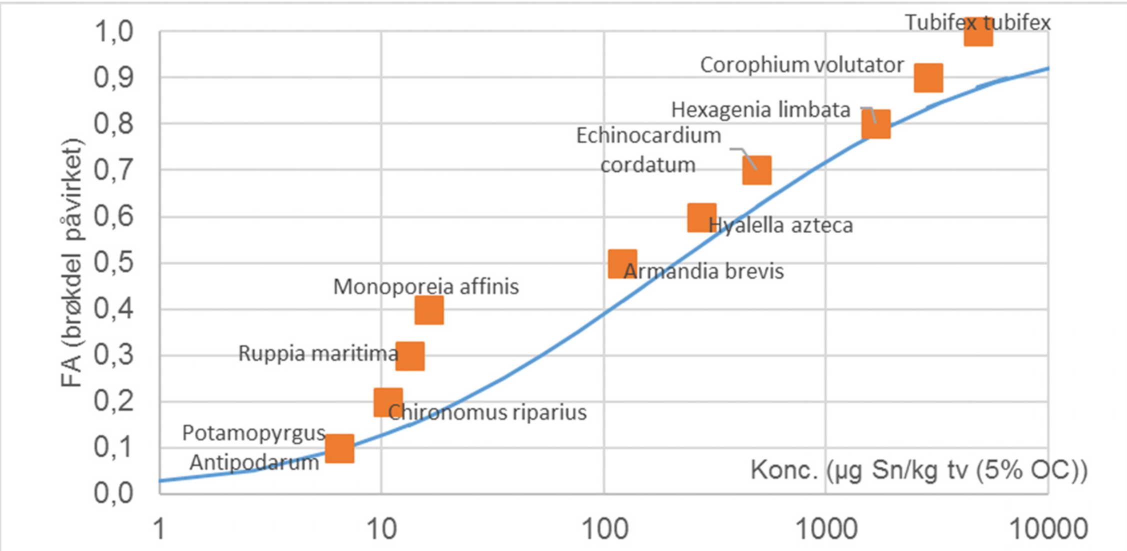
For sediment, the Swedish EPA re-calculated a $QS_{sediment}$ instead of the tentative EU $QS_{sediment\ EP}$ in 2018. The outcome of this review is in the process of being adopted in HELOM and OSPAR. The Danish EPA propose a slightly lower value in a preliminary study, pending a peer review among EU, HELCOM and OSPAR countries. The main difference in the Danish and Swedish project is the use of a species sensitivity distribution test, resulting higher effect level but a lower assessment factor, together resulting in a lower assessment value.

Differens between Swedish and Danish QS for TBT in sediment

S	DK	Comment
1.6 µg/kg 5%TOC	1.1 µg/kg DW (5% OC)	Proposed QS based on SSD
32 µg/kg OC	22 µg/kg OC	based on OC
0.4 µg/kg 5%TOC		QS based on EqPt (not used)

The discrepancy between Danish and Swedish outcome is mainly based on the Species Sensitivity Distribution test used in the Danish document, based on 10 species in six species groups (figure 1). For the critical study method both end up with EC_{10} of 16 µg / kg dw (5% TOC) and an assessment factor of 10. The SSD results in a HC_5 of 2.3 µg Sn / kg DW (5% TOC) with 90% confidensinterval 0.09 to 14.1. Converted to TBT cation this is 5.6 µg TBT / kg DW. The assessment factor for the SSD value is 5, leading to the $QS_{sediment}$ of 1.1 µg / kg DW (5%TOC).

Some discrepancy is also found in the used K_{OC}, but both studies conclude that the Equilibrium partitioning method is unsuitable (as do the EU guideline) for TBT.



Species sensitivity distribution for sediment dwelling organisms showing concentration of TBT expressed as ratio of affected specimens to the µg Sn/kg DW normalized to 5% TOC. HC_5 is estimated at 2.3 µg Sn/kg DW.

The Biota QS are based on energy normalized calculation of the critical studies for marine mammals, recalculated to fish and mussels using bioconcentration factors for TBT. TBT is usually not lipid normalized in assessments, as it is more bound to sulfur-groups (proteins) than lipids, the lipid normalization might not be helpful despite K_{OC}>3 due to relative high water solubility.

English Summary and conclusions for the Danish assessment of TBT

Tributyltin compounds with the tributyltin cation (TBT) have been used primarily in anti-fouling paints for ships since the 1950s but have also been used in wood preservatives and as catalysts and stabilizers in PVC. It is estimated that about 2,000-3,000 tonnes were used per year in TBT-based paints (Mathiessen, 2019) in the mid-1980s, before the ban on using TBT in anti-fouling paints. It is thus estimated that shipping traffic contributed with about 0.2-1.4 tonnes of Sn-TBT in Danish waters.

Derivation of environmental quality standards (EQS) for the aquatic environment is following the EU Guidance Document No. 27. Technical Guidance Document for Deriving Environmental Quality Standards (EU, 2018).

QS for water has already been derived in EU for the tributyltin cation (EC, 2018) at:

$EQS_{freshwater, saltwater}$: 0.0002 µg TBT/l $MAC_{freshwater, saltwater}$: 0.0015 µg TBT/l

Relevant ecotoxicity data for benthic organism, mammals and birds have primarily been retrieved from reviews and summary reports. An additional data search in the SETAC's database (SETAC Sediment Advisory Group (SEDAG), Spiked Sediment Toxicity Database) and US EPA's database (ECOTOXicology knowledgebase) was prepared as well.

QS for sediment

It is relevant to derive a QS for sediment-dwelling organisms for TBT as the log K_{OW} >3 (3.1-4.1) (EU, 2018).

The ICES database (ICES, 2020) contains data on measurements of VDSI (Vas Deferens Sequence Index) for Nassarius reticulatus, concentration of TBT and organic carbon content for some sediments. In the database, 218 related measurements of TBT, organic carbon content and VDSI were found for Nassarius reticulatus. 48 measurements have been found for which the VDSI is measured to be below 0.3, which is considered as the non-effect level. The concentrations in these 48 measurements were between 0.5-5.6 µg Sn/kg (5% OC) with a 10% percentile value of 1.0 µg Sn/kg (5% OC) - corresponding to 2.4 µg TBT/kg (5% OC) (using a conversion factor of 2.44 (MST, 2004)).

Ecotoxicity data for benthic organisms are shown in appendix A, where the data used for the SSD analysis to establish the QS_{sed} are shown with bold.

The available laboratory data on marine sediment-dwelling organisms suggest that marine species are less sensitive compared to freshwater species. However, the marine dataset lacks data for the most sensitive taxonomic group: Gastropoda (snails).

In the derivation of the QS_{sed}, data for freshwater and marine sediment-dwelling organisms were pooled since statistical tests showed no significant differences (see appendix C). After pooling data suitable chronic data have been found for 10 different species with different living and feeding conditions (Potamopyrgus antipodarum, Chironomus riparius, Monoporeia affinis, Hyalella azteca, Hexagenia limbata, Tubifex tubifex, Echinocardium cordatum, Amandia brevis, Corophium volutator, Ruppia maritima). These species represent six systemic groups (Gastropoda, Insecta, Macrophyte, Annelida, Echinodermata, Amphipoda), which are considered sufficient to determine the QS_{sed} from, based on a Species Sensitivity Distribution (SSD).

To perform the SSD, all effect concentrations are converted to an EU standard sediment with a 5% content of organic carbon. LOEC values are converted to NOEC by dividing by 2 (EU, 2018).

Via the establishment of the SSD, the HC_5 is found at 5.6 µg TBT/kg dry weight (5% OC).

QS (both freshwater and marine sediment) is found by dividing HC_5 with an AF of 5:

$QS_{sed,\ freshwater,\ saltwater}$ = 1.1 µg TBT / kg dry weight (5% OC) = 22 µg TBT / kg OC

An $OS_{sed,\ freshwater,\ saltwater}$ obtained using uncertainty factors is also derived.
QS for sediment can be determined, when three or more NOEC / EC_{10} values are found.

The critical EC_{10} of 2.98 µg / kg dry weight (2.3% OC) for the freshwater snail, Potamopyrgus antipodarum, is converted to an EC_{10} in standard sediment (5% OC) of 16 µg / kg dry weight. An uncertainty factor of 10 is applied and results in:

$QS_{sed,\ freshwater,\ saltwater}$ = 1.6 µg TBT / kg dry weight (5% OC) = 32 µg TBT / kg OC

It is noted that the $QS_{sed,\ freshwater,\ saltwater}$ derived using the SSD-method (1.1 µg TBT / kg dry weight (5% OC)) is at the same level but slightly lower than the $QS_{sed,\ freshwater,\ saltwater}$ derived using uncertainty factors (1.6 µg TBT / kg dry weight (5% OC)).
It is also noted that the $QS_{sed\ freshwater,\ saltwater}$ derived using the SSD-method is below but very comparable to the 10% percentile of the measured concentrations where VDSI is measured to be below the threshold of 0.3 (2.4 µg TBT / kg (5% OC)).

Overall, it is concluded that the QS_{sed} to be used for both freshwater and marine sediments is: $QS_{sed,\ freshwater,\ saltwater}$ = 1.1 µg TBT / kg dry weight (5% OC)
$QS_{sed,\ freshwater,\ saltwater}$ = 22 µg TBT / kg OC

It can be further mentioned that the EU dossier (EC, 2005) has derived a QS_{sed} based on the EqP- method to 0,02 µg TBT / kg dry weight (10% OC) with a K_{oc} value of 1084, corresponding to 0,01 µg TBT / kg dry weight (5% OC). The EU dossier is from 2005, and uses an older version of the guidance document. Using the newest guidance document (EU, 2018) the QS_{sed} would be 0.02 µg TBT / kg dry weight (5% OC) with K_{oc} 1965 (calculations in appendix D). Since data is available now, this method is not used to set the QS_{sed} in this dossier.

QS for biota, secondary poisoning

The BCF for TBT is significantly >100 and log K_{OW} >3 (3.1-4.1). It is therefore relevant to derive $QS_{sec.\ pois.}$. Further, TBT biomagnifies in the food web, so it is also relevant to derive a biota QS for marine mammals.

Mammals, freshwater

The toxicity data for birds and mammals are listed in appendix B, where the data used to establish the $QS_{sec.\ pois.}$ is shown with bold.

The lowest NOAEL (No Observed Adverse Effect Level), which QS_{biota} is calculated from, is 0.025 mg / kg bw / day for mammals in a study with rats with test duration greater than 24 months. As the NOAEL is based on a chronic test with mammals (in this case rats), the total AF according to EU (2018) is a factor of 1 and 10, respectively (table 9 and table 10 in EU, 2018).

$PNEC_{feed}$ = NOAEL / 1 / 10 = 0.0025 mg TBT / kg bw / day

$PNEC_{feed}$ is then energy normalized based on method A (p. 85-86) in EU (2018). The original study was not available, so an assumed bodyweight at 250 g for an adult rat was used in the calculation of the daily energy expenditure (DEE).

Log DEE [kJ / d] =0.8136 + 0.7149 * log bw [g] =0.8136 + 0.7149 * log 250 g = 2.53

DEE = $10^{2.53}$ = 338.8 kJ / day

Then using DEE, the bodyweight in kg and $PNEC_{oral}$ (0.0025 mg TBT / kg bw / day), $PNEC_{feed}$ is energy normalized:

$PNEC_{feed,\ energy\text{-}normalized}$ [mg / kJ] = 0.0025 mg TBT / kg bw / day * (0.25 kg bw / 338.8 kJ / day) = 0.0000018 mg / kJ

PNEC expressed as content in fish, $PNEC_{fish}$, is determined from an energy content of fish of 21,000 kJ / kg dry weight, a dry matter content of 26% and a lipid content of 5% stated in EU (2018):

$PNEC_{fish}$ = 0.0000018 mg / kJ × 21,000 kJ / kg dry weight × 0.26 = 0.01 mg / kg fish, wet weight $PNEC_{fish, lipid}$ = 0.01 mg / kg fish / 0.05 = 0.2 mg / kg lipid

A $PNEC_{feed}$ expressed as mussel content, $PNEC_{mussels}$, is determined from an energy content of bivalves of 19,000 kJ / kg dry weight, a dry matter content of 8% and a lipid content of 1% stated in EU (2018):

$PNEC_{mussels}$ = 0.0000018 mg / kJ × 19,000 kJ / kg dry weight × 0.08 = 0.003 mg / kg mussels, wet weight

$PNEC_{mussels, lipid}$ = 0.003 mg / kg mussels / 0.01 = 0.3 mg / kg lipid

Birds, freshwater

Only one data set for birds (Japanese quail) with a NOEC of 24 mg / kg food was found. The study lasted for 6 weeks (appendix B). Based on the duration (42 days), and the lifespan of a Japanese quail (approximately 6 years), the study should be characterized as sub-acute. However, as the studied effect was reproduction, it is considered too conservative to set the study to a subacute study, which is why the study as a whole is handled as a subchronic study. When NOEC originates from a sub-chronic toxicological experiment, the total uncertainty factor (according to tables 9 and 10 in the EU, 2018) is a factor of 3 × 10.

NOEC = 20 mg / kg feed
$PNEC_{feed}$ = NOEC / 30 = 0.8 mg / kg feed

According to method B in EU (2018), the $PNEC_{feed}$ should be energy normalized to calibrate the energy content of the food used in the toxicological study (here feed) with the energy content of the food for the organisms that are to be protected. Regarding eiders feeding primarily on mussels, mussels was here considered the critical food item.

$PNEC_{feed}$ is energy normalized on the basis of an energy content in grass and grain seeds, of 18,400 kJ / kg dry weight and a dry matter content of 85.3% stated in table 8 in EU (2018), as the energy content of the food in the relevant bird experiment is not stated:

$PNEC_{feed, energy-norm.}$ = 0.8 mg / kg food / (18,400 kJ / kg dry weight × 0.853) = 0.000051 mg / kJ

PNEC expressed as content in mussels, $PNEC_{mussels}$, is determined on the basis of an energy content in mussels of 19.000 kJ / kg dry weight, a dry matter content of 8% and a lipid content of 1% (table 7 in EU, 2018):

$PNEC_{mussels}$ = 0.000051 mg / kJ × 19,000 kJ / kg dry weight × 0.08 = 0.078 mg / kg wet weight $PNEC_{mussels, lipid}$ = 0.078 mg / kg mussels / 0.01 = 7.8 mg / kg lipid

The PNEC values for birds are noted to be higher than the values derived from the study with rat , so values for $QS_{sec.pois.freshwater}$ are based on the study with rat .

Overall, $QS_{sec.pois.freshwater}$ is determined as: $QS_{sec.pois.freshwater}$ = 0.01 mg/kg fish, wet weight

$QS_{sec.pois.freshwater}$ = 0.2 mg/kg lipid
$QS_{sec.pois.freshwater}$ = 0.003 mg/kg mussels, wet weight

$QS_{sec.pois.freshwater}$ = 0.3 mg/kg lipid

Marine mammals, saltwater

A derivation of QS for marine water is relevant as TBT biomagnifies in the marine food chain with BMF values for TBT of 5.6 for harbour porpoise with cod, squid and flounder as the main food source (based on wet weight) (see figure 3.1).

Derivation of QS for saltwater is calculated for marine mammals as a food basis on the basis of the lowest energy normalized PNEC, which is 0.0000018 mg / kJ for mammals. The Technical Guidance Document (EU,

2018) also states the energy content of marine mammals at 23,200 kJ / kg dry weight and a dry matter content of 32%, as well as a lipid content of 10% (table 7, vertebrates). This gives to:

$PNEC_{marine\ mammals}$ = 0.0000018 mg / kJ × 23,200 kJ / kg dry weight × 0.32 = 0.013 mg / kg marine mammal, wet weight

$PNEC_{marine\ mammals,\ lipid}$ = 0.013 mg / kg marine mammal wet weight / 0.10 = 0.13 mg / kg lipid

This value is calculated back to a PNEC for fish and mussels using the page 89 in the EU (2018). For fish the BMF of 5,6 is used as well as the fraction of lipid in fish (5%) respectively (table 7 in EU, 2018) and gives the following $QS_{sec.pois.marine\ water}$:

$QS_{sec.pois.,\ saltwater}$ = 0.013 mg / kg marine mammals, wet weight / 5.6 = 0.0023 mg/kg fish, wet weight
$QS_{sec.pois.,\ saltwater}$ = 0.0023 mg / kg fish wet weight / 0.05 = 0.046 mg/kg lipid

For mussels the BMF from mussels to marine mammals (figure 3.1) is used as well as a fraction of lipid in mussels (1%) (table 7 in EU, 2018). The BMF used is calculated as, $BMF_{marine\ mammals\forall fish}$ [5.6] × $BMF_{fish\forall crustaceans/snails}$ [1.9] × $BMF_{crustaceans/snails\forall mussels}$ [0.7] = 7.4.

$QS_{sec.pois.,\ saltwater}$ = 0.013 mg / kg marine mammals, wet weight / 7.4 = 0.0018 mg/kg mussels, wet weight

$QS_{sec.pois.,\ saltwater}$ = 0.0018 mg / kg fish wet weight / 0.01 = 0.18 mg/kg lipid

QS for human consumption

As TBT is classified H301, H372 and H360, then according to the Technical Guidance Document (EU, 2018), a QS for human consumption, $QS_{biota,\ hh\ food}$, of aquatic organisms must be calculated.

A maximum tolerable daily intake for humans (TDI - Tolerable Daily Intake) for TBT of 0.00025 mg / kg bw / day has been established (EFSA, 2004).

According to EU (2018), $QS_{biota,\ hh\ food}$ is calculated on the assumption that a maximum of 20% of TDI must be derived from fish and seafood and that a standard food intake from this source corresponds to 0.00163 kg fish / kg bw / day.

Hereby $QS_{biota,\ hh\ food}$ can be calculated as:
QS_{HH} = 0.2 × TDI / 0.00163 = 0.2 × 0.00025 / 0.00163 = 0.03 mg / kg fish, wet weight

With a standard lipid content in fish of 5%, a lipid-normalized $PNEC_{fish}$ can be calculated as: $QS_{biota,\ hh\ food,\ lipid}$ = 0.03 mg / kg fish / 0.05 kg lipid / kg fish = 0.6 mg / kg lipid

$QS_{biota,\ hh\ food}$ = 0.03 mg/kg fish, wet weight $QS_{biota,\ hh\ food}$ = 0.6 mg/kg lipid

QS_{water} based on $QS_{biota,\ hh\ food}$ and $QS_{sec.\ pois.}$
According to the EU (2018) the found quality criteria for biota ($QS_{sec.\ pois.}$ and $QS_{biota,\ hh\ food}$) should be converted to a water quality criteria to ensure that the found effects of direct effects are sufficiently conservative to protect against secondary effects through bioaccumulation in food chains.

The lowest QS value for biota is derived for secondary poisoning in saltwater ($QS_{sec.\ pois,\ saltwater}$) which is used to derive QS_{water}:

$QS_{water} = QS_{sec.\ pois,\ saltwater}$ / BAF

The bioaccumulation, BAF, for saltwater is calculated here as BCF × BMF1 × BMF2, where BCF is the bioconcentration factor in mussels and BMF1 (0.7, figure 3.1) is the trophic biomagnification factor covering the food chain from mussels to crustaceans, snails etc., BMF2 (1.9, figure 3.1) is the biomagnification factor from crustaceans / snails to predatory fish.

BCF in mussels is highly variable - with laboratory-determined BCF values between 10,400 - 37,500 L / kg. The geometric mean of the values, 19,748 L / kg was applied.

Based on the above BCF and BMF factors, QS_{water} is found to be:

$QS_{water} = QS_{sec. pois, saltwater}$ / BAF = 0.0023 mg/kg fish, wet weight / (19,748 l/kg × 0.7 × 1.9) = 0.000000088 mg/l = 0.000088 µg/l

$QS_{water} = QS_{sec. pois, saltwater}$ / BAF = 0.0018 mg/kg mussels, wet weight / (19,748 l/kg × 0.7 × 1.9) = 0.000000069 mg/l = 0.000069 µg/l

It should be noted that $EQS_{freshwater, saltwater}$ (0.0002 µg TBT/l) is higher than QS_{water}, which suggest that the water criteria does not protect biota.

In conclusion, the following EQS for the aquatic environment have been derived for TBT:

QS for sediment

QS_{sed} = 1.1 µg/kg dry weight (5% OC); 22 µg/kg OC

QS for secondary poisoning

$QS_{freshwater, fish}$ = 0.01 mg/kg fish, wet weight; 0.2 mg/kg lipid $QS_{freshwater, mussels}$ = 0.003 mg/kg mussels, wet weight; 0.3 mg/kg lipid $QS_{saltwater, fish}$ = 0.0023 mg/kg fish, wet weight; 0.046 mg/kg lipid $QS_{saltwater, mussels}$ = 0.0018 mg/kg mussels, wet weight; 0.18 mg/kg lipid

QS for human consumption

$QS_{biota, hh food}$ = 0.03 mg/kg fish, wet weight; 0.6 mg/kg lipid

Summary of suggestions

Based on the recent Danish efforts for setting EQS values, the revised assessment criteria (see table in introduction) are suggested.

For TBT in general and cadmium in shellfish the assessment criteria are lower than currently in use in OSPAR and HELCOM, whereas for the reminder, lower assessment factors and use of species sensitivity distributions when possible, leads to a more lenient assessment criteria for lead, fluoranthene and and cadmium in fish and sediment.

The background documents are unfortunately in Danish mainly, with the English summaries and selected figures/tables included in this document. Any further information will be made available as quickly as possible if needed.

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Bilag 3: Notat til OSPAR MIME 2021

Agenda Item 5.2 MIME 21/5/2(L)

OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic

Working Group on Monitoring and on Trends and Effects of Substances in the Marine Environment (MIME)

Hybrid meeting in Denmark (Copenhagen) and videoconference: 22-26 November 2021

Development and status for Danish EQS values

Presented by Denmark

Issue:

To follow-up of relevant national or regional projects on monitoring and assessments, including development of EQS thresholds from Sweden, Denmark, and Norway.

Action requested

1. MIME is invited to;
   a. **note** the current Danish EQS values and the derivation they are based upon as at Annex 1;
   b. **note** the status for use in HELCOM EN-HZ (cf. introduction);
   c. **review** the difference between OSPAR MIME and HELCOM EN-HZ;
   d. **agree** on any acceptable adjustments of OSPAR MIME assessment criteria to bring OSPAR and HELCOM assessment into closer agreement.

Background

2. The national Danish EQS documentation (in Danish) have been added an extended English abstract, and presented at HELCOM EN-HZ and OSPAR MIME pre-assessment meetings, resulting in both recalculation of the Danish TBT assessment criteria and updates to the extended abstracts presented during the preliminary work, after receiving comments from several HELCOM partners and some bi-lateral discussion with primarily Sweden.

3. Status for HELCOM. The following adjustments to HELCOM use of EQS was accepted by HELCOM State and Conservation 15-2021 held online 4-8 October 2021 (the final version of the outcome from S&C 15-2021 are available here – maybe only to HELCOM contracting parties):
   a. TBT in sediments adjusted to 1.3 µg/kg dw sediment (5% TOC) based on the Danish revised TBT EQS, after a consensus EN-HZ meeting following the S&C 15-2021 meeting.
   b. Cadmium secondary threshold: QS derived from EQS (whole fish, secondary poisoning) of 160 µg/kg ww mussels and fish used instead of OSPAR BAC previously
   c. Lead secondary threshold: add the new **proposal of 110 ug/kg ww** for mussels but to maintain the existing OSPAR proxy BAC 26 µg/kg ww fish liver
   d. PAHs (fluoranthene): Secondary threshold - **proposal for 3500 µg/kg (5% CORG)** in sediment to replace current 2000 µg/kg (5% CORG)

4. OSPAR MIME is invited to discuss the revised HELCOM thresholds and decide if any could be applicable in the OSPAR OHAT, except normalization to 2.5% CORG for sediments.

5. The use of cadmium and lead in fish is noted to still need recalculation factors from liver or muscle to whole organisms, and Denmark would like information from other contracting parties about any relevant data available to accommodate such recalculation factors.

Annex 1

Danish quality standards for selected indicator substances - update.

Introduction

A number of EU QS values have been re-evaluated by the Danish EPA, and are hereby suggested to be taken onboard in OSPAR and HELCOM assessments as assessment criteria for the QSR 2023 and HELCOM HOLAS III. For each substance and specific matrices, the rationale behind the recalculated values is presented below. All calculations follow the EU guideline, with summary of the factors used. The background documents are in Danish, but the main table and summaries are included below. References are not given in full for each substance, but a selection of the most relevant are given, and the remainder references can be found in these selected references.

For most datasets, new data or re-interpretation of existing data lead to lower assessment factors, or an increase in the number of species, facilitating calculation of species sensitive distribution in some cases, again reducing the assessment factors compared to selecting the lowest NOEC/EC_{10} values. A summary is given in the table below, details follow.

Overview of existing and suggested revised QS values for the different substances (changes and additions have been highlighted in yellow)

Substance	Type	OSPAR	HELCOM	QS suggested by DK	unit
Fluoranthene	$QS_{sediment}$	600 (ERL)	2000 (QS)	3500 (5%TOC) 1750 (2.5%TOC)	µg/kg dw µg/kg dw
Anthracen	$QS_{sediment}$	24 (S-QS)		4.8 (5%TOC) 2.4 (2.5 TOC)	µg/kg dw µg/kg dw
Lead	$QS_{sediment}$ QS_{mussel} QS_{fish}	47 (ERL) 1500 (MPC) 300 (muscle)	131 (QS) 26 (BAC)	163 110 (110)	µg/kg dw µg/kg ww µg/kg ww
Cadmium Shellfish Fish	$QS_{sediment}$ $QS_{sec.pois.}$	1.2 (EAC) 1000 (Food) 50 (Food)	2.3 (QS) 0.137 (QS)	3.8$ 160$ (160$)	mg/kg dw µg/kg ww µg/kg ww
TBT	$QS_{sediment}$	0.8 (S-QS)	1.6 (S-QS)	1.3 (5%TOC) 0.65 (2.5%TOC)	µg/kg dw µg/kg dw
Shellfish Fish	$QS_{sec.pois.}$ $QS_{sec.pois.}$	12 (EAC)	12 (EAC)	3 3	µg/kg ww µg/kg ww

$: Note that the current danish QS values, under review in 2021.

The following adjustments to HELCOM use of EQS was accepted by HELCOM State and Conservation 15-2021 held online 4-8 october 2021 (the final version of the outcome from S&C 15-2021 are available here):

- TBT in sediments adjusted to 1.3 µg/kg dw sediment (5% TOC) based on the Danish revised TBT EQS, after a concensus EN-HZ meeting following the S&C 15-2021 meeting.
- Cadmium secondary threshold: QS derived from EQS (whole fish, secondary poisoning) of 160 µg/kg ww mussels and fish used instead of OSPAR BAC previously
- Lead secondary threshold: add the new **proposal of 110 ug/kg ww** for mussels but to maintain the existing OSPAR proxy BAC 26 µg/kg ww fish liver as no conversion factors are available
- PAHs (fluoranthene): Secondary threshold - **proposal for 3500 µg/kg (5% CORG)** in sediment to replace current 2000 µg/kg (5% CORG)

The EU EQS datasheet (2005 and revised in 2011) present different values for QS benthic community:
$QS_{sediment,\ Equilibrium\ partitioning\ 2005}$: 173 µg/kg DW
$QS_{sediment,\ Assessment\ factor\ 2005}$: 129 µg/kg DW

$QS_{sediment,\ Equilibrium\ partitioning\ 2011}$: 2.000 µg/kg DW, same for fresh- and marine waters

OSPAR assessment criteria currently in use:
BAC 39 (14.4 not normalised) µg/kg DW 2.5% TOC, ERL 600 µg/kg DW

HELCOM assessment criteria currently in use:
2000 µg/kg (EU $QS_{sediment}$)

The Danish EPA review of fluoranthene only found few new data during a literature search, the main difference is the conversion of the critical study converting the organic carbon content of 41 mg/kg from 10% TOC to 5% TOC, where the EU just convert by dividing with 2, and the Danish EPA converts from standard sediment with 10% OM (taken as standard sediment with conversion of TM to TOC with a factor of 0,588), resulting in 35 mg/kg instead of 20 mg/kg before applying the assessment factor of 10, leading to:

3500 µg/kg sediment (5% OC, HELCOM) and 1750 µg/kg (2.5% OC, OSPAR).

English summary of sediment quality standards for the Danish assessment of fluoranthene

Fluoranthene has a log K_{ow} of 5.2 (EU-dossier, 2011) and is likely to sorb to sediment. Ecotoxicity data have been taken from the EU-dossier (2011) and from Verbruggen (2012) and are presented in table 4.1. Further a search for data was conducted[2].

There are EC_{10} or NOEC values for nine species and three major taxonomic groups. The lowest toxicity value is a LOEC of 8.8 mg/kg sediment (with 10% OM) for *Chironomus riparius* (Verrhiest et al. (2001), cfr. Verbruggen (2012)). The EU-dossier (2011) and Verbruggen (2012) mention this value but choose not to use it, with a remark that the *C. riparius* data “vary widely”. The study is rated with a Klimisch score of 2 in the EU-dossier (2011) and Verbruggen (2012), and by the Danish EPA, so it is regarded as reliable and relevant. A LC_{50} has also been calculated, indicating, that there must be a dose-response correlation, though since no raw data has been presented in the study, this cannot be validated and the percentage effect is also not noted. Therefore, according to TGD no. 27 (table 20, page 154, version 2018), LOEC can only be used as additional information.

Verbruggen, 2012 chose the second lowest toxicity value, EC_{10} of 41 mg/kg dw (with 10% OM). EU-dossier, 2011 chose the same value, but notes it as 41 mg/kg dw (with 10% OC), leading to a lower sediment quality standard than found in Verbruggen, 2012. The value used by Verbruggen, 2012, was chosen to set the national sediment quality standard.

Statistically, the difference in sensitivity between freshwater and saltwater species is insignificant (Mann-Whitney U test, $P > 0.2$, two-tailed). If anything, the freshwater species are the more sensitive. Therefore, marine and freshwater data are pooled, and the same assessment factor is employed for the fresh- and saltwater environments.

With three major taxonomic groups represented, an assessment factor of 10 can be used to derive a $PNEC_{Sediment}$ from the EC_{10}:

$PNEC_{Sediment}$ = 41 mg/kg sed. / 10 = 4.1 mg/kg sed. (with 10% OM),

[2] In ECHA's REACH database, US EPA's ECOTOX database, via OECD's eChemPortal meta-database as well as by conducting a literature search focused on sediment-dwellling organisms using Google Scholar.

This value is, following conversion to an EU standard sediment with 5% OC using the conversion factor %OM = 1.7 * %OC (EU, 2018), used as $QS_{Sediment}$ for fluoranthene:

3 500 µg/kg sediment (5% OC) = 69 700 µg/kg OC = $QS_{Sediment}$

Table 4.1 chronic effects of fluoranthene on sedimentdwelling organisms

	Expo-sure-time	Effect type	EC_{10} or NOEC mg/kg Dry-weigh; 10% OM	EC_{10} or NOEC mg/kg Dry-weigh; 5% OC	EC_{10} or NOEC mg/kg OC	Reference queted in Verbruggen (2012)
Annelida						
Stylaria lacustris s	10 days	Mortality	112	95	1904	Suedel & Rodgers, 1996
Crustacea						
Corophium spinicorne s	10 days	Mortality	108	92	1836	Swartz et al. 1990
Coullana sp. f	10 days	Mortality, LC_{10}	157	133,5	2670	Lotufo 1998
Diporeira sp. f	30 days	Mortality	≥2979	≥2533	≥50643	Driscoll & Land-rum 1997
*Hyalella azteca** f	16 days	Mortality	600*	510	10200	Driscoll & Land-rum 1997
	10 days	Mortality	<54	<46	918	Suedal & Rodgers 1996
	14 days	Mortality	9*	7,7	153	Verrhiest et al. 2001
Rhepoxynius abronius s	10 days	Mortality	58	49	986	Swartz et al. 1990
	10 days	Mortality	113	96	1921	Swartz et al. 1988
	10 days	Mortality	83	71	1411	Swartz et al. 1997
	10 days	Mortality	117	99	1989	Swartz et al. 1997
	10 days	Mortality	235	200	3995	De Witt et al. 1992
	10 days	Mortality	173	147	2941	De Witt et al. 1992
	10 days	Mortality	188	160	3196	De Witt et al. 1992
	10 days	Mortality	141	120	2397	De Witt et al. 1992
	10 days	Mortality	218	185	3706	De Witt et al. 1992
R. abronius geometric mean			135	115	2295	
Schizopera knabeni s	14 days	Reproduc-tion	41	35	697	Lotufo 1997
	10 days	Reproduc-tion	58	49	986	Lotufo 1997
Insecta						
*Chironomus riparius*** f	10 days	Mortality	<8,8	7,5	150	Verrhiest et al. 2001
*Chironomus tentans**** f	10 days	Immobility	58	49	986	Suedel & Rodgers 1996
	10 days	Immobility, EC_{50}	40***	34	680	Suedel et al. 1993

*Verbruggen (2012) uses the geometriske mean (73 mg/kg) af values from Driscoll & Landrum (1997) (600 mg/kg) and the value from Verrhiest et al. (2001) (9 mg/kg). But the two studies have been performed using different circumstances, e.g. animals have been exposed to ultraviolet light in Verhiest et al., but not in Driscoll & Landrum, and different sediment types was used. An average is hence no applicable. The EU-dossiet (2011) do not include a geometric mean of the values.

**10-11 day mortality is a more sensitive effect type than hathching. Two studies include10-11 days toxicity values (Stewart & Thompson, 1995 and Verrhiest et al., 2001).
***Lowest EC_{50} in Suedel et al. (1993) is lower than the NOEC from Suedel & Rodgers (1996). In the latter, clay content is about 3 times larger than the first study, while pH is 6 Suedel & Rodgers and 6,5-8,5 in Suedel et al. (1993).

f: freshwater species; s: marine species

EQS for lead in sediment was developed in 2005 and revisited in 2011 EU EQS datasheet.

$QS_{benthic\ community,\ 2005}$: 53.4 mg/kg + $C_{background}$ (i.e. $MPA_{sediment}$ = 53,4)

$QS_{benthic\ community,\ marine\ 2011}$: 123 mg/kg dw
$QS_{benthic\ community,\ freshwater\ 2011}$: 131 mg/kg dw total Pb; 41 mg/kg DW bioavailable fraction using AVS/SEM correction

OSPAR assessment criteria currently in use:
BAC 38 (22.4 not normalised) µg/kg DW 5% Al, ERL 47 mg/kg DW

HELCOM assessment criteria currently in use:
120 mg/kg (rounded EU $QS_{sediment}$)

The Danish Lead QS for sediments was developed using a SSD analysis on combined marine and freshwater species (NOEC or EC_{10} from 8 species representing three systematic groups and at least four optimal foraging strategies), as no difference between the two water types was evident.
The Danish EPA arrived at a **$QS_{sediment}$ = 163 mg/kg DW** for total lead, using an assessment factor of 3 instead of 4 as suggested by the EU 2011 derivation. This was based on the combined freshwater and marine species SSD. There are two marine species with different optimal foraging strategies and NOEC available, and the Polychaeta is specific to marine water, so the same assessment factor of 3 is used for both fresh- and marine species, with no extra assessment factor for the marine QS. The assessment factor of 4 was set by the EQS dossier based on number of species and higher toxanomic groups included, that the proposed MAX (14.25 µg/l) was below both the ETX lower confidence limit and Mytilus edulis lowest acute dataset (25.8 and 25 µg/l). The same arguments hold for an assessment factor of 3 (MAX eqs 19 µg/l). This difference in assessment factors accounts for most of the difference between 123 and 163 mg/kg DW between the 2011 benthic community QS and the Danish QS.

Note also that the rounded HC_5 of 490 mg/kg DW (90% range from 212 to 756) compared to the EU 2011 HC_5 of 492.5 mg/kg DW reduces the $QS_{sediment}$ from 164 to 163 only, given the 90% range of it seems that the EU 2011 document has overstated the significant number of digits on the HC_5.

It should also be noted that applying the simultaneous extracted metal/acid volatile sulphide (SEM-AVS) model resulted in negative NOEC values so the use of SEM-AVS was abandoned, and the result is thus valid for total lead only.

$QS_{sec\ pois}$ for lead in biota was set in 2011 to 3.6 mg/kg ww for predators and 16.9 µg/kg ww for avian predators.

$QS_{human\ health}$ from EC food regulation (2001) was 200 µg/kg ww for fish muscle (changed to 300 µg/kg in EC 1881 (2006)), 1000 µg/kg ww for molluscs (changed to 1500 µg/kg in EC 1881 (2006)).

In the Danish legislation (BEK nr 1625 af 19/12/2017, table 4), a national QS_{biota} for softparts has been set for both freshwater and marine waters at 110 µg/kg wet weight.

Quality standards (QS) for sediment for lead were developed based on data in industry's voluntary risk assessment report (VRAR).

There are chronic values for 8 sediment species, of which 2 are marine. The species represent 3 major taxonomic groups, and at least 4 different foraging strategies.

The two marine species, a crustacean and an oligochaete, are neither more nor less sensitive than their freshwater taxonomic counterparts are, and so the freshwater and saltwater data are combined.

An SSD analysis was employed, and an assessment factor of 3 applied for derivation of the freshwater as well as the saltwater sediment QS.

HC_5 = 490 mg Pb/kg sediment, d.w.
Sediment $QS_{freshwater}$ = sediment $QS_{saltwater}$ = (490 mg/kg)/3 = 163 mg Pb/kg sediment, dry weight

Toxicity data from VRAR

Organism	Most sensitive endpoint	EC10 or NOEC (mg total Pb/kgDW)	Remark
Worms (annalida, Oligocheta)			
Tubifex tubifex	reproduction 28 days	573	EC_{10}
Lumbriculus variegatus	survival 28 days	2100	EC_{10}
Neanthes arenaceodentata	28 days NOEC	801	Marine species
Insets (Insecta)			
Ephoron virgo	Survival 21 days	1126	NOEC (EC10 = 1616 but no reliable CL) [a]
Hexagenia limbata	Survival, growth 21 days	>2903	NOEC Unbounded: >2903 with 13.3 % effect observed at this tested concentration = similar to what was observed in the control)
Chironomus tentans	Survival 20 days	3390	NOEC (no monotonic trend in survival concentration)
Crustations (Crustacea)			
Hyalella azteca	survival 28 days	1416	EC_{10}
Lumbriculus variegatus	growth 35 days	1745	EC_{10}
Leptocheirus plumulosus (Amphipoda)	28 days NOEC	931	Marine species
Amphiascus tenuiremis (Copepoda)	4 days LC_{50}	2465	Marine species

Cadmium in sediment and biota

EQS for cadmium was developed in 2005 but not revisited in the 2011 EU EQS dossiers

$QS_{Sediment, assessment factor, 2005}$: added risk approach 2.3 mg/kg dw + background
$QS_{biota secpois}$: 160 µg/kg ww

OSPAR assessment criteria currently in use:
Sediment: BAC 0.31 (0.129 not normalized) µg/kg DW 5% Al, ERL 1.2 mg/kg DW
Biota: BAC mussels 960, fish liver 26 µg/kg dw.
MPC mussel, fish muscle 1000, fish liver 50 µg/kg ww

HELCOM assessment criteria currently in use:
Sediment: 2.3 mg/kg DW (EU $QS_{sediment}$)
Biota: HQS mussel 137.3 µg/kg ww (OSPAR BAC, recalculated to wet weight)

Cadmium QS for sediments was developed using a SSD analysis on combined marine and freshwater species, as no difference between the two water types was evident. The Danish EPA arrived at a $QS_{sediment}$ = 3.8 mg/kg DW and biota criteria $QS_{secpois}$ 0.32 mg/kg ww, QS_{HH} 0.044 mg/kg ww.

The original EU risk assessment for sediment used an uncertainty factor of 50 due to only one chronic dataset for freshwater (Chironomus sp), reduced from 100 as most short-term test showed very little difference in species sensitivity. In the Danish evaluation, two extra studies was added increasing the number of species to three, representing three systematic groups and reducing the uncertainty factor to 10, including two marine species. The Hansen study will be examined more closely in the ongoing revision of the Cd EQS in sediment, taking into account the Swedish concerns of possible limitations from using colonization studies, and natural sediments and water, which could contain other contaminants and potentially affect the results.
Lowest observed NOEC or EC_{10} was 38 mg/kg, applicable to both fresh water and seawater. It should be noted that the cadmium concentration in many cases was lower than the acid volatile sulphur, but still had a clear dose-response signal. The use of SEM-AVS models for cadmium was therefore abandoned. The suggested cadmium $QS_{sediment}$ is close to expected background levels, the added risk approach should therefore be used with expected background sediment concentrations in the range of 0.33 to 0.62 mg/kg (i.e. 10-16% of the calculated QS_{sed} value).

The original EU risk assessment for biota included a species sensitivity distribution with a HC_5 of 1.6 mg/kg food, but mainly based on mammal and birds, so the EQS datasheet resorted to using the assessment factor method, with 10 as the factor. Concidering the lack of lower trophic levels, the danish EPA used the SSD value, with an uncertainty factor of 5, resulting in 1.6/5 =0.32 mg/kg $QS_{secpois}$. For human health, the EFSA ADI of 0,36 µg/kg body weight/day, and 20% of food intake from fish, assuming a 70 kg person eats 0.115 g fishproduct/day yields 0,36 µg/kg body weight per day* 70 kg *0,2 / 0,115 g per day = 0.044 mg/kg $QS_{HH.}$

English Summary and conclusions for Danish assessment of cadmium

All data and calculations were taken from the EU risk assessment report (RAR) and the addendum thereto, plus from Hansen et al. 1996, and DeWin et al. 1996. The environmental quality standard (EQS) values for freshwater and saltwater and the corresponding maximal acceptable concentrations (MAC) are all in Directive 2008/105/EC, and in the draft new directive amending Directive 2008/105/EC.

Calculation of available Cd in sediments is based on the SEM-AVS model (Technical Guidance (EU vejledning) 2011), and requires measurements of sulphides, copper and lead, and preferably also mercury. However, as clear dose-response relationships were observed in Hansen et al. 1996, where AVS was in excess of the metal concentrations, the reliability of the SEM/AVS model is questioned.

With the extra data of Hansen et al. 1996 and DeWin et al. 1996 there are chronic values for more than 3 species representing more than 3 major taxonomic groups, including more than 2 marine species. Therefore, an assessment factor (AF) of 10 is applied to the lowest EC_{10} or NOEC for both the marine and fresh-water environments.

The EC_{10} values from Hansen et al. 1996 were estimated by the Danish Environmental Protection Agency from the data in the article.

Concerning the biota QS, the RAR calculated an HC5 = 1.6 mg/kg feed, fresh weight, but chose to use the AF method because of lack of guidance on how to employ an SSD for mammals and birds. However, there is data for 4 species of mammals and 3 species of birds covering 6 different orders. Given that the evaluation is for birds and mammals only compared to the multitude of major taxonomic groups to be protected by the EQS_{water}, it is here accepted to employ the SSD method, applying an AF of 5.

Thus, the $EQS_{biota, secondary poisoning}$ = 1.6 mg/kg : 5 = 0.32 mg CD/kg feed, fresh weight.

The ADI employed = 0.36 µg/kg bw*day (EFSA 2009). Seafood should only contribute with 20 % of this daily intake. A 70 kg person is expected to eat 0.115 kg fish/day. This results in an $EQS_{biota, human health}$ = 0.044 mg/kg food, wet weight.

Quality standards for the water column

Hardness	EQS µg/l (VKK)		MAC µg/l (KVKK)
	Freshwater	Saltwater	Fresh- and saltwater
≤40	≤0.08	0.2	≤0.45
10-<50	0.08	0.2	0.45
50 - <100	0.09	0.2	0.6
100 - <200	0.15	0.2	0.9
≥200	0.25	0.2	1.5

Quality standards for sediment and biota are as follows:

$EQS_{sediment, freshwater}$:

Added 3.8 mg/kg dw

Available 3.8 mg/kg dw

$EQS_{sediment, saltwater}$:

Added 3.8 mg/kg dw

Available 3.8 mg/kg dw

$EQS_{biota, secondary poisoning}$: 0.32 mg/kg feed, wet weight

$EQS_{biota, human health:}$ 0,044 mg/kg seafood, wet weight

Note that the $EQS_{biota, secondary poisoning}$ in the Danish legislation have not been changed, so currently the $EQS_{sec pois}$ from EU of 160 µg/kg wet weight is used. The implementation of 320 µg/kg wet weight awaits the Cd review in 2021.

TBT in sediment and biota

The EU EQS datasheet (2005) present different values for QS benthic community:
$QS_{sediment, Equilibrium partitioning 2005}$: 0.02 µg/kg DW (tentative)
$QS_{biota, secpois}$: 230 µg/kg ww prey
$QS_{biota,HH}$: 15.2 µg/kg ww seafood

OSPAR assessment criteria currently in use:
Sediment: 0.8 µg/kg DW (2.5% TOC)
Shellfish: BAC 5 µg/kg DW , EAC 12 µg/kg DW

HELCOM assessment criteria currently in use:
Sediment: 1.6 µg/kg DW (5% TOC)
Biota: 12 µg/kg dw (EAC)

After revision of the calculation of the SSD august 2021, the Danish EPA arrived at a $QS_{sediment}$ of 1.3 µg/kg DW, and secondary poisoning QS values of 3 µg/kg for fish and 3 µg/kg for mussels, with a human health QS for fish products as 30 µg/kg DW

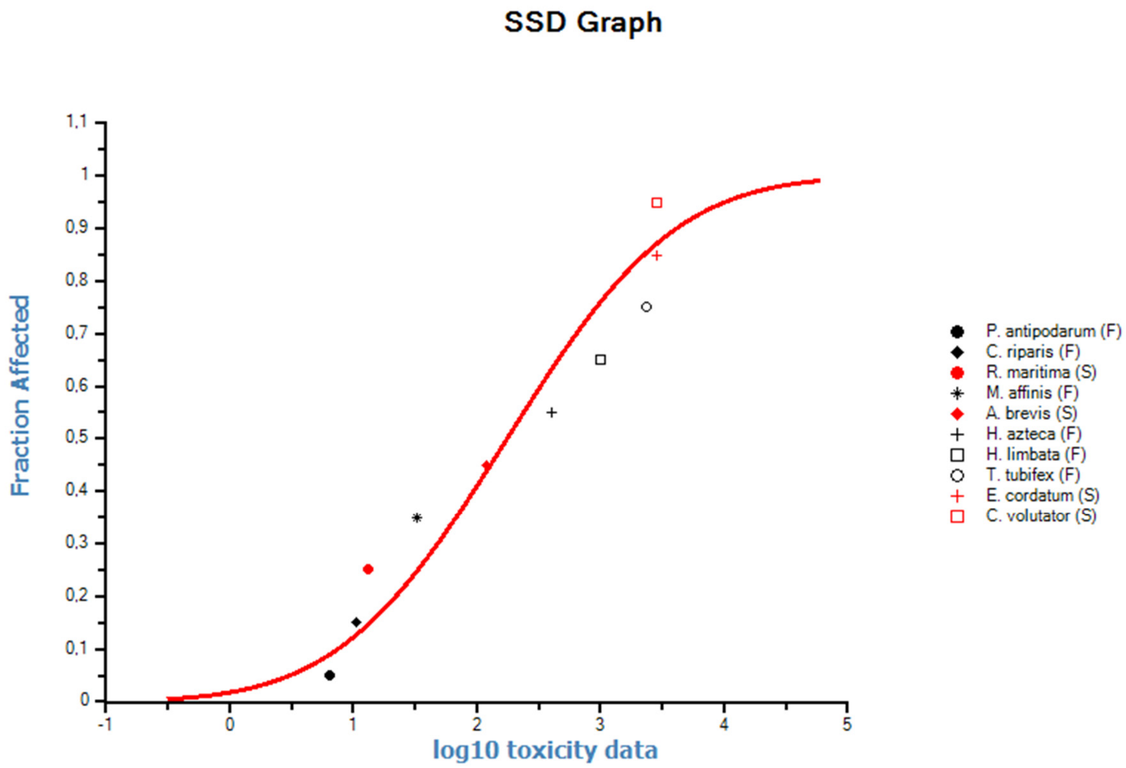
For sediment, the Swedish EPA re-calculated a $QS_{sediment}$ instead of the tentative EU $QS_{sediment\ EP}$ in 2018. The outcome of this review is in the process of being adopted in HELOM and OSPAR. The Danish EPA originally propose a slightly lower value in a preliminary study, pending a peer review among EU, HELCOM and OSPAR countries. The main difference in the Danish and Swedish project is the use of a species sensitivity distribution test, resulting higher effect level but a lower assessment factor, together resulting in a lower assessment value.

Differens between Swedish and Danish QS for TBT in sediment

S	**DK**	Comment
1.6 µg/kg 5%TOC	**1.3 µg/kg DW (5% OC)**	Proposed QS based on SSD
32 µg/kg OC	**26 µg/kg OC**	based on OC
0.4 µg/kg 5%TOC		QS based on EqPt (not used)

The discrepancy between Danish and Swedish outcome is mainly based on the Species Sensitivity Distribution test used in the Danish document, based on 10 species in six species groups (figure 1). For the critical study method both end up with EC_{10} of 16 µg/kg dw (5% TOC) and an assessment factor of 10. The SSD results in a HC_5 of 2.3 µg Sn/kg DW (5% TOC) with 90% confidensinterval 0.09 to 14.1. Converted to TBT cation this is 5.6 µg TBT/kg DW. The assessment factor for the SSD value is 5, leading to the $QS_{sediment}$ of 1.1 µg TBT/kg DW (5%TOC). Note that there *H. limbate* datapoint at in the SSD was updated in august, and the endpoint for *T. tubifex* was changed from 4026 to 2349 µg Sn/kg dw (5% OC) so the HC_5 have been recalculated to 2.7 with the endpoint chosen. The Danish EPA original paper was revised in august, and the new English abstract and results are included in this revised document.

Some discrepancy is also found in the used K_{OC}, but both studies conclude that the Equilibrium partitioning method is unsuitable (as do the EU guideline) for TBT.



*Revised species sensitivity distribution for sediment dwelling organisms showing concentration of TBT expressed as ratio of affected specimens to the µg Sn/kg DW normalized to 5% TOC. HC_5 is estimated at 2.7 µg Sn/kg DW using ETX v 2.2, with a 90% confidence interval of 0.01 to 14.3 µg Snkg ww. Recalculating to TBT cation gives a HC_5 =2.7 * 2.44 = 6.6 µg TBT/kg dry weight.*

The Biota QS are based on energy normalized calculation of the critical studies for marine mammals, recalculated to fish and mussels using bioconcentration factors for TBT. TBT is usually not lipid normalized in assessments, as it is more bound to sulfur-groups (proteins) than lipids, the lipid normalization might not be helpful despite K_{OC}>3 due to relative high water solubility.

English Summary and conclusions for the Danish assessment of TBT (revised august 2021)

Tributyltin compounds with the tributyltin cation (TBT) have been used primarily in anti-fouling paints for ships since the 1950s but have also been used in wood preservatives and as catalysts and stabilizers in PVC. It is estimated that about 2,000-3,000 tonnes were used per year in TBT-based paints (Mathiessen, 2019) in the mid-1980s, before the ban on using TBT in anti-fouling paints. It is thus estimated that shipping traffic contributed with about 0.2-1.4 tonnes of Sn-TBT in Danish waters.

Derivation of environmental quality standards (EQS) for the aquatic environment is following the EU Guidance Document No. 27. Technical Guidance Document for Deriving Environmental Quality Standards (EU, 2018).

QS for water has already been derived in EU for the tributyltin cation (EC, 2018) at:

$EQS_{freshwater, saltwater}$: 0.0002 µg TBT/l
$MAC_{freshwater, saltwater}$: 0.0015 µg TBT/l

Relevant ecotoxicity data for benthic organism, mammals and birds have primarily been retrieved from reviews and summary reports. An additional data search in the SETAC's database (SETAC Sediment Advisory Group (SEDAG), Spiked Sediment Toxicity Database) and US EPA's database (ECOTOXicology knowledgebase) was prepared as well.

QS for sediment

It is relevant to derive a QS for sediment-dwelling organisms for TBT as the log K_{OW} >3 (3.1-4.1) (EU, 2018).

The ICES database (ICES, 2020) contains data on measurements of VDSI (Vas Deferens Sequence Index) for *Nassarius reticulatus*, concentration of TBT and organic carbon content for some sediments. In the database, 218 related measurements of TBT, organic carbon content and VDSI were found for *Nassarius reticulatus*. 48 measurements have been found for which the VDSI is measured to be below 0.3, which is considered as the non-effect level. The concentrations in these 48 measurements were between 0.5-5.6 µg Sn / kg (5% OC) with a 10% percentile value of 1.0 µg Sn / kg (5% OC) - corresponding to 2.4 µg TBT / kg (5% OC) (using a conversion factor of 2.44 (MST, 2004)).

Ecotoxicity data for benthic organisms are shown in appendix A, where the data used for the SSD analysis to establish the QS_{sed} are shown with bold.

In the derivation of the QS_{sed}, data for freshwater and marine sediment-dwelling organisms were pooled since statistical tests showed no significant differences (see appendix C). After pooling data suitable chronic data have been found for 10 different species with different living and feeding conditions (*Potamopyrgus antipodarum, Chironomus riparius, Monoporeia affinis, Hyalella azteca, Hexagenia limbata, Tubifex tubifex, Echinocardium cordatum, Amandia brevis, Corophium volutator, Ruppia maritima*). These species represent six systemic groups (*Gastropoda, Insecta, Macrophyte, Annelida, Echinodermata, Amphipoda*), which are considered sufficient to determine the QS_{sed} from, based on a Species Sensitivity Distribution (SSD).

To perform the SSD, all effect concentrations are converted to an EU standard sediment with a 5% content of organic carbon. LOEC values are converted to NOEC by dividing by 2 (EU, 2018).

The available laboratory data on marine sediment-dwelling organisms suggest that marine species are less sensitive compared to freshwater species. However, the marine dataset lacks data for one of the most sensitive taxonomic groups: Gastropoda (snails). In the EU EQS dossier (EC, 2005) it was concluded that the two groups show similar sensitivity to TBT-compounds. Furthermore, TBT-cations in the marine is assumed to have a reduced bioavailability compared to freshwater due to higher salinity and increased pH – meaning less free TBT-cations will be available in the marine environment (Parmentier et al., 2019). Based on this and that is has been concluded that freshwater and marine data can be pooled it is assumed that the derived QS_{sed} protects both freshwater and marine sediment-dwelling organisms.

Via the establishment of the SSD in the program ETX v. 2.2 developed by RIVM, the HC_5 is found at 2.7 µg TBT/kg dry weight (5% OC).

Since only 10 different species and 6 taxonomic groups are represented, the HC_5 is divided with an assessment factor of 5 resulting in the following QS for both freshwater and marine sediment:

$QS_{sed,\ freshwater,\ saltwater}$ = 1.3 µg TBT/kg dry weight (5% OC)
= 26 µg TBT/kg OC

An $OS_{sed,\ freshwater,\ saltwater}$ obtained with the deterministic approach using assessment factors is also derived. QS for sediment can be determined, when three or more NOEC / EC_{10} values are found.

The critical EC_{10} of 2.98 µg / kg dry weight (2.3% OC) for the freshwater snail, *Potamopyrgus antipodarum*, is converted to an EC_{10} in standard sediment (5% OC) of 16 µg / kg dry weight. An assessment factor of 10 is applied and results in:

$QS_{sed,\ freshwater,\ saltwater}$ = 1.6 µg TBT / kg dry weight (5% OC)
= 32 µg TBT / kg OC

It is noted that the $QS_{sed, freshwater, saltwater}$ derived using the SSD-method (1.3 µg TBT/kg dry weight (5% OC)) is a bit lower than the $QS_{sed, freshwater, saltwater}$ derived using assessment factors (1.6 µg TBT/kg dry weight (5% OC)).
It is also noted that the $QS_{sed\ freshwater, saltwater}$ derived is below but very comparable to the 10% percentile of the measured concentrations where VDSI is measured to be below the threshold of 0.3 (2.4 µg TBT/kg (5% OC)).

Overall, it is concluded that the QS_{sed} to be used for both freshwater and marine sediments is:

$QS_{sed, freshwater, saltwater}$ = 1.3 µg TBT/kg dry weight (5% OC)
= 26 µg TBT/kg OC

It can be further mentioned that the EU dossier (EC, 2005) has derived a QS_{sed} based on the EqP-method to 0,02 µg TBT/kg dry weight (10% OC) with a K_{oc} value of 1084, corresponding to 0,01 µg TBT/kg dry weight (5% OC). The EU dossier is from 2005, and uses an older version of the guidance document (Lepper, 2004). Using the newest guidance document (EU, 2018) the QSs_{ed} would be 0.02 µg TBT/kg dry weight (5% OC) with K_{oc} 1965 (calculations in appendix E). Since ecotoxicity data is available now, this method is not used to set the QS_{sed} in this dossier.

QS for biota, secondary poisoning

The BCF for TBT is significantly >100 and log K_{OW} >3 (3.1-4.1). It is therefore relevant to derive $QS_{sec.\ pois.}$. Further, TBT biomagnifies in the food web, so it is also relevant to derive a biota QS for marine mammals.

Mammals, freshwater

The toxicity data for birds and mammals are listed in appendix B, where the data used to establish the $QS_{sec.\ pois.}$ is shown with bold.

The lowest NOAEL (No Observed Adverse Effect Level), which QS_{biota} is calculated from, is 0.025 mg/kg bw/day for mammals in a study with rats with test duration greater than 24 months. As the NOAEL is based on a chronic test with mammals (in this case rats), the total assessment factor (AF) according to EU (2018) is a factor of 1 and 10, respectively (table 9 and table 10 in EU, 2018).

$PNEC_{feed}$ = NOAEL/1/10 = 0.0025 mg TBT/kg bw/day

$PNEC_{feed}$ is then energy normalized based on method A (p. 85-86) in EU (2018). The original study was not available, so an assumed bodyweight at 250 g for an adult rat was used in the calculation of the daily energy expenditure (DEE).

Log DEE [kJ/d] =0.8136 + 0.7149 * log bw [g]
=0.8136 + 0.7149 * log 250 g = 2.53

DEE = $10^{2.53}$ = 338.8 kJ/day

Then using DEE, the bodyweight in kg and $PNEC_{oral}$ (0.0025 mg TBT/kg bw/day), $PNEC_{feed}$ is energy normalized:

$PNEC_{feed, energy-normalized}$ [mg/kJ] = 0.0025 mg TBT/kg bw/day * (0.25 kg bw / 338.8 kJ/day) = 0.0000018 mg/kJ

PNEC expressed as content in fish, $PNEC_{fish}$, is determined from an energy content of fish of 21,000 kJ/kg dry weight and a dry matter content of 26% stated in EU (2018):

$PNEC_{fish}$ = 0.0000018 mg/kJ × 21,000 kJ/kg dry weight × 0.26 = 0.01 mg/kg fish, wet weight

A $PNEC_{feed}$ expressed as mussel content, $PNEC_{mussels}$, is determined from an energy content of bivalves of 19,000 kJ/kg dry weight and a dry matter content of 8% stated in EU (2018):

$PNEC_{mussels}$ = 0.0000018 mg / kJ × 19,000 kJ / kg dry weight × 0.08 = 0.003 mg / kg mussels, wet weight

Birds, freshwater

Only one data set for birds (Japanese quail) with a NOEC of 24 mg / kg food was found. The study lasted for 6 weeks (appendix B). Based on the duration (42 days), and the lifespan of a Japanese quail (approximately 6 years), the study should be characterized as sub-acute. However, as the studied effect was reproduction, it is considered too conservative to set the study to a subacute study, which is why the study as a whole is handled as a subchronic study. When NOEC originates from a sub-chronic toxicological experiment, the total AF (according to tables 9 and 10 in the EU, 2018) is a factor of 3 × 10.

NOEC = 20 mg / kg feed
$PNEC_{feed}$ = NOEC / 30 = 0.8 mg / kg feed

According to method B in EU (2018), the $PNEC_{feed}$ should be energy normalized to calibrate the energy content of the food used in the toxicological study (here feed) with the energy content of the food for the organisms that are to be protected. Regarding eiders feeding primarily on mussels, mussels were here considered the critical food item.

$PNEC_{feed}$ is energy normalized on the basis of an energy content in grass and grain seeds, of 18,400 kJ / kg dry weight and a dry matter content of 85.3% stated in table 8 in EU (2018), as the energy content of the food in the relevant bird experiment is not stated:

$PNEC_{feed,\ energy\text{-}norm.}$ = 0.8 mg / kg food / (18,400 kJ / kg dry weight × 0.853) = 0.000051 mg / kJ

PNEC expressed as content in mussels, $PNEC_{mussels}$, is determined based of an energy content in mussels of 19.000 kJ / kg dry weight and a dry matter content of 8% (table 7 in EU, 2018):

$PNEC_{mussels}$ = 0.000051 mg / kJ × 19,000 kJ / kg dry weight × 0.08 = 0.078 mg / kg wet weight

The PNEC values for birds are noted to be higher than the values derived from the study with rats, so values for $QS_{sec.pois.freshwater}$ are based on the study with rats.

Overall, $QS_{sec.pois.freshwater}$ is determined as:

$QS_{sec.pois.freshwater}$ = **0.01 mg/kg fish, wet weight**

$QS_{sec.pois.freshwater}$ = **0.003 mg/kg mussels, wet weight**

Marine mammals, saltwater

A derivation of QS for marine water is relevant as TBT biomagnifies in the marine food chain with BMF values for TBT of 4.4 for harbour porpoise with cod, squid and flounder as the main food source (based on wet weight) (see table 3.2).

Derivation of QS for saltwater is calculated for marine mammals as a food basis on based of the lowest energy normalized PNEC, which is 0.0000018 mg / kJ for mammals. The Technical Guidance Document (EU, 2018) also states the energy content of marine mammals at 23,200 kJ / kg dry weight and a dry matter content of 32% (table 7, vertebrates). This gives to:

$PNEC_{marine\ mammals}$ = 0.0000018 mg / kJ × 23,200 kJ / kg dry weight × 0.32 = 0.013 mg / kg marine mammal, wet weight

This value is calculated back to a PNEC for fish and mussels using the page 89 in the EU (2018). For fish the BMF of 4.4 is used and results in the following $QS_{sec.pois.marine\ water}$:

$QS_{sec.pois.,\ saltwater}$ = 0.013 mg / kg marine mammals, wet weight / 4.4 = **0.003 mg/kg fish, wet weight**

For mussels the BMF from marine mammals to mussels is used (table 3.2). The BMF is calculated as, $BMF_{marine\ mammals \rightarrow fish}$ [4.4] × $BMF_{fish \rightarrow crustaceans/snails}$ [1.2] × $BMF_{crustaceans/snails \rightarrow mussels}$ [0.9] = 4.8.

$QS_{sec.pois.,\ saltwater}$ = 0.013 mg/kg marine mammals, wet weight / 4.8 = **0.003 mg/kg mussels, wet** weight

QS for human consumption

As TBT is classified H301, H372 and H360, then according to the Technical Guidance Document (EU, 2018), a QS for human consumption, $QS_{hh\ food}$, of aquatic organisms must be calculated.

A maximum tolerable daily intake for humans (TDI - Tolerable Daily Intake) for TBT of 0.00025 mg/kg bw/day has been established (EFSA, 2004).

According to EU (2018), $QS_{hh\ food}$ is calculated on the assumption that a maximum of 20% of TDI must be derived from fish and seafood and that a standard food intake from this source corresponds to 0.00163 kg fish/kg bw/day.

Hereby $QS_{hh\ food}$ can be calculated as:

$QS_{hh,\ food}$ = 0.2 × TDI / 0.00163 = 0.2 × 0.00025 / 0.00163 = **0.03 mg/kg fish, wet weight**

QS_{water} based on $QS_{biota,\ hh\ food}$ and $QS_{sec.\ pois.}$

According to EU (2018) the found quality criteria for biota ($QS_{sec.\ pois.}$ and $QS_{hh\ food}$) should be converted to a water quality criteria (QS_{water}) to ensure that the found effects of direct effects are sufficiently conservative to protect against secondary effects through bioaccumulation in food chains. QS_{water} is derived as followed:

QS_{water} = $QS_{sec.\ pois,}$ or $QS_{hh,\ food}$ / BAF

The BAF for freshwater is calculated here as BCF × BMF1, where BCF is the bioconcentration factor in fish (rainbow trout, 406 l/kg, table 3.1) and BMF1 is the trophic biomagnification factor covering the food chain from algae to predatory fish. Table 3.2 notes BMF-values from mussels to crustaceans/snails (0.9) and from crustaceans/snails to predatory fish (1.2). This gives the following BAF for freshwater (fw):

BAF_{fw} = BCF × BMF1 = 406 l/kg × 0.9 × 1.2 = 438.5 l/kg

For saltwater an extra BMF has to be added in order to protect marine mammals (porpoise). BAF for saltwater is derived as BCF × BMF1 × BMF2, where BMF2 is the biomagnification factor from predatory fish to marine mammals (porpoise) (4.4, table 3.2). This results in the following BAF for saltwater (sw):

BAF_{sw} = BCF × BMF1 × BMF2 = 406 l/kg × 0.9 × 1.2 × 4.4 = 1929 l/kg

Based on the above BAF factors, QS_{water} is found to be:

$QS_{freshwater}$ = $QS_{sec.\ pois,\ freshwater}$ / BAF_{fw} = 0.01 mg/kg fish, wet weight / 438.5 l/kg = 0.000023 mg/l = 0.02 µg/l

$QS_{saltwater}$ = $QS_{sec.\ pois,\ saltwater}$ / BAF_{sw} = 0.003 mg/kg fish, wet weight / 1929 l/kg = 0.0000016 mg/l = 0.002 µg/l

$QS_{hh\ food,\ water}$ = $QS_{hh\ food}$ / BAF_{fw} = 0.03 mg/kg fish, wet weight / 438.5 l/kg = 0.000068 mg/l = 0.07 µg/l

It should be noted that the EU $EQS_{freshwater,\ saltwater}$ (0.0002 µg TBT/l) is lower than $QS_{freshwater}$, $QS_{saltwater}$ and $QS_{hh\ food,\ water}$ which suggest that the water criteria does protect biota.

In conclusion, the following EQS for the aquatic environment have been derived for TBT:

QS for sediment

QS_{sed} = 1.3 µg/kg dry weight (5% OC); 26 µg/kg OC

QS for secondary poisoning

$QS_{freshwater, fish}$ = 0.01 mg/kg fish, wet weight
$QS_{freshwater, mussels}$ = 0.003 mg/kg mussels, wet weight
$QS_{saltwater, fish}$ = 0.003 mg/kg fish, wet weight
$QS_{saltwater, mussels}$ = 0.003 mg/kg mussels, wet weight

QS for human consumption

$QS_{biota, hh food}$ = 0.03 mg/kg fish, wet weight

Antracene in sediment

The EU EQS datasheet (2011) present the same values for QS benthic community in marine water and freshwater, as no data on marine sediment dwelling species was available:
$QS_{sediment, Benthic community}$: 24 µg/kg DW

OSPAR assessment criteria currently in use:
BAC 5 (1.8 not normalised) µg/kg DW 2.5% TOC, ERL 85 µg/kg DW

HELCOM assessment criteria currently in use:
24 µg/kg (EU $QS_{sediment}$)

The Danish evaluation adds a safety factor of five for marine benthic community on top of the freshwater, due to the lack of sediment dwelling species, but reduced from 10 to five due to the large amount of data on freshwater species. The EU anthacen dossier also uses an assessment factor of 50, but does not include the extra factor of 5 to go from freshwater to marine water, .

English Summary for anthracene

24 µg/kg (EU QSsediment)

Data and calculations were taken from the EU datasheet (15/2-2011) on which the quality standards in the Water Framework Directive are based. That datasheet is attached to the present document as an annex ("bilag").

$EQS_{freshwater}$ = 0.1 µg/l
$EQS_{saltwater}$ = 0.1 µg/l
MAC = 0.1 µg/l
$EQS_{sediment, freshwater}$ = 24 µg/kg dw
$EQS_{sediment, saltwater}$ = 4.8 µg/kg dw
Biota EQS = 2.4 mg/kg feed, wet weight

Summary of suggestions

Based on the recent Danish efforts for setting EQS values, the revised assessment criteria (see table in introduction) are suggested.

For TBT in general, anthracene in sediment and cadmium in shellfish the assessment criteria are lower than currently in use in OSPAR and HELCOM, whereas for the reminder, lower assessment factors and use of species sensitivity distributions when possible, leads to a more lenient assessment criteria for lead, fluoranthene and cadmium in fish and sediment.

The background documents are unfortunately in Danish mainly, with the English summaries and selected figures/tables included in this document. Any further information will be made available as quickly as possible if needed.

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Fluoranthene EQS dossier 2011. Fluoranthene
Anthracene EQS dossier 2011. Anthracene.
02_Anthracene_EQSdatasheet_310705.pdf Environmental Quality Standards (EQS) Substance Data Sheet. Priority Substance No. 2 Anthracene CAS-No. 120-12-7
06_Cadmium_EQSdatasheet_310705.pdf: Environmental Quality Standards (EQS) Substance Data Sheet. Priority Substance No. 6 Cadmium and its Compounds CAS-No. 7440-43-9
15_Fluoranthene_EQSdatasheet_150105.pdf: : Environmental Quality Standards (EQS) Substance Data Sheet. Priority Substance No. 15 Fluoranthene CAS-No. 206-44-0
20_Lead_EQSdatasheet_310705.pdf: Environmental Quality Standards (EQS) Substance Data Sheet. Priority Substance No. 20 Lead and its Compounds CAS-No. 7439-92-1
30_Tributyltin_EQSdatasheet_150105.pdf: : Environmental Quality Standards (EQS) Substance Data Sheet. Priority Substance No. 30 Tributyltin compounds (TBT-ion) CAS-No. 688-73-3 (36643-28-4)

Bilag 4: Tidslinje for møder i HELCOM og OSPAR

På grund af COVID 19 er ingen af møderne holdt som fysiske møder, bortset fra MIME 2021, der blev afholdt som hybrid møde med 10 lande repræsenteret i ICES' mødelokale og de øvrige over nettet.

Hvor det er muligt at finde møde dokumenterne er navn og nr. angivet nedenfor, for undergruppe møderne i OSPAR / MIME er der ikke udarbejdet formelle møde registreringer, da det er arbejdsgrupper der forbereder dokumenter og holdninger til MIME mødet og diskuterer anvendelsen af tærskelværdier i OHAT, Ospars Holistic Assessment Tool

HELCOM møde ID	**Dato**	**Dokument nr.**	**Deltager**
EN-HZ 14-2021	17-19 februar	4-1 HELCOM HZ indicator threshold values	MML, AMC
EN-HZ 15-2021	15-16 juni	4-1 Danish suggestions for QS values in OSPAR and HELCOM	MML
EN-HZ 16-2021	2. september	3-4 Danish suggestions for QS values in OSPAR and HELCOM revised 1-9-2021	MML
State&Conservation 15-2021	4-8 oktober	Presentation 14	AMC
EN-HZ follow up	20. oktober		MML

OSPAR møde ID	**Dato**	**Dokument nr.**	**Deltager**
MIME QSR subgroup	25 maj	(uformelt møde)	MML
MIME QSR subgroup	1. juli	(uformelt møde)	MML
MIME QSR subgroup	25. august	(uformelt møde)	MML
MIME QSR subgroup	22. november	(uformelt møde)	MML
MIME QSR subgroup	24. november	(uformelt møde)	MML
MIME 2021	22-26 november	MIME 21/05/02 (L) Development and status for Danish EQS values	MML, AMC

VIDEREUDVIKLING AF TÆRSKELVÆRDIER FOR EN RÆKKE METALLER OG PAH'ER (MILJØFARLIGE STOFFER)

Notater til HELCOM og OSPAR

For at undgå dansk fodnote politik på tærskelværdier i regionale assessments, er notater om udviklingen af de danske EQS værdier for cadmium, bly, tributyltin, fluoranthen og anthracen udformet på engelsk, og fremsendt til HELCOM og OSPARs arbejdsgrupper for miljøfarlige stoffer (EN-HZ og MIME) for at påvirke tærskelværdierne, der anvendes i HELCOM og OSPARs kommende holistiske assessment og Quality Status Report. Ved udgangen af 2021 ser det ud til, at det lykkes at harmonisere DK og HELCOMs tærskelværdier for cadmium, delvist bly, tributyltin og anthracen, mens der for OSPAR bliver sat et arbejde i gang med at udvikle metoder til at inkludere nationale tærskelværdier i Nordsø assessments fremover.

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