ASSESSMENT OF HAZARDOUS SUBSTANCES IN DANISH SEDIMENT AND BIOTA ACCORDING TO NORWEGIAN, SWEDISH AND DUTCH QUALITY STANDARDS

Technical Report from DCE – Danish Centre for Environment and Energy No. 146 2019

AARHUS
UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

[Blank page]

ASSESSMENT OF HAZARDOUS SUBSTANCES IN DANISH SEDIMENT AND BIOTA ACCORDING TO NORWEGIAN, SWEDISH AND DUTCH QUALITY

Technical Report from DCE – Danish Centre for Environment and Energy No. 146 2019

John Jensen[1]
Hans Sanderson[2]
Martin M. Larsen[1]
Liselotte Sander Johansson[1]
Helena Kallestrup[1]

[1] Aarhus University, Department of Bioscience
[2] Aarhus University,Department of Environmental Science

AARHUS UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

Data sheet

Series title and no.: Technical Report from DCE – Danish Centre for Environment and Energy No. 146

Title: Assessment of hazardous substances in Danish sediment and biota according to Norwegian, Swedish and Dutch quality standards

Authors: John Jensen[1], Hans Sanderson[2], Martin M. Larsen[1], Liselotte Sander Johansson[1] & Helena Kallestrup[1]
Institutions: Aarhus University, [1]Department of Bioscience & [2]Department of Environmental Science

Publisher: Aarhus University, DCE – Danish Centre for Environment and Energy ©
URL: http://dce.au.dk/en

Year of publication: June 2019
Editing completed: June 2019

Referee: Patrik Fauser
Quality assurance, DCE: Susanne Boutrup

Financial support: The Danish Environmental Protection Agency

Please cite as: Jensen, J., Sanderson, H., Larsen, M.M., Johansson, L.S. & Kallestrup, H. 2019. Assessment of hazardous substances in Danish sediment and biota according to Norwegian, Swedish and Dutch quality standards. Aarhus University, DCE – Danish Centre for Environment and Energy, 38 pp. Technical Report No. 146
http://dce2.au.dk/pub/TR146.pdf

Abstract: This report compares monitoring data in sediment and biota for 14 hazardous substances found in Denmark with quality standards (EQS) used in Sweden, Norway and the Netherlands. Firstly, the Swedish, Norwegian and Dutch EQSs were assessed according to transparency in derivation and usability in assessment of the status in Danish surface water bodies. When comparing with the identified usable EQS the concentrations found in Danish biota samples are with the exemption of TBT, generally below the used EQS values, whereas sediment samples frequently are found in concentrations that exceed the EQS for metals, especially zinc, nickel and arsenic. However, the comparisons for metals are without considering natural background concentrations, as these have not been stablished for Danish sediments. Firm conclusions regarding the status of the observed concentrations of metals in Danish sediment samples therefore await the identification of such background concentrations.

Keywords: Environmental Quality Standards; Hazardous substances; Monitoring data

Layout: Graphic Group, AU Silkeborg
Front page photo: Colourbox

ISBN: 978-87-7156-415-0
ISSN (electronic): 2245-019X

Number of pages: 38

Internet version: The report is available in electronic format (pdf) at
http://dce2.au.dk/pub/TR146.pdf

Contents

[Blank page]

1. Introduction

The overall purpose of this project is to compare monitoring data in sediment and biota for 14 hazardous pollutants found in Denmark with environmental quality standards (EQS) used in Sweden, Norway and the Netherlands. To aid this assessment, the occurrence, i.e. concentration levels, in Danish environmental samples as reported in the NOVANA program are compared with environmental quality standards (EQS) selected from a smaller set of European countries assumed to have derived EQS, which could be used for a comparison in a Danish context, i.e. Sweden, Norway and The Netherlands.

Part one of this report provides information on EQS collected from three countries, Norway, Sweden and The Netherlands, for 14 environmentally hazardous pollutants. The quality of the relevant EQS including transparency in how the EQS was derived in relation to databases, assessment factors and agreement with the EU Technical Guidance Document for Deriving Environmental Quality Standards (EQS), a.k.a. TDG#27 (EU 2011) are assessed. Furthermore, it is assessed whether the individual criteria and requirements can be used meaningfully in the assessment of the environmental status in Danish surface water bodies, or whether altered conditions mean that one or more criteria or requirements cannot meaningfully be applicable to such a state assessment.

The collected EQS are assessed according to validity and usefulness in a Danish context including the need of correction and normalization to conditions found in Danish waters and sediment. The most useful of the valid EQS values are then used in part two of the project.

The report is organized in a part devoted to the evaluation and selection of EQS (Chapter 2-4) and a part where these EQS are compared with monitoring data for biota and sediment in Danish freshwater streams and lakes and marine waters (Chapter 5).

2. Procedure for identifying relevant and useful EQS

On request to key personnel, reports and documentation were received directly from the EPAs in Netherlands, Norway and Sweden for the compounds of interest in Table 1.

The received documentations were used to evaluate the usefulness of the available EQS in a Danish context. To guide and aid the evaluation, the received / collected information were queried and quality checked against a set of criteria and essential questions. These are listed in Appendix A.

Table 1. Compounds included in the investigation.

Compound	CAS#
Butylbenzylphthalate (BBP)	85-68-7
di(2-ethylhexyl)adipat (DEHA)	103-23-1
di-2-ethylhexyl phthalate (DEHP)	117-81-7
diisononylphthalate (DINP)	28553-12-0
Non-dioxin-like PCBs (e.g. congener #28, 52,101,138,153, 180)	Na
As	7440-38-2
Cu	7440-50-8
Cr	7440-47-3
Ni	7440-02-0
Zn	7440-66-6
Benz[a]pyrene	50-32-8
Fluoranthene	206-44-0
Tributyltin (TBT)	36643-28-4
Hexachlorocyclohexane (HCH)	608-73-1

The results are listed in Table 3 (biota) and 4 (sediment). Inorganic metals are generally not biomagnifiable and hence biota EQS are frequently not derived.

Chapter 3 contains a short description of the various methodologies and overall concepts used in the three selected countries, including references to key background documents. In Chapter 4, conclusions regarding the availability and most suited EQS values are discussed for each major chemical groups, e.g. phthalates, metals, including TBT, PAHs and PCB. Based on the availability of EQS values from the three countries, we have indicated the most robust and relevant EQS for Danish conditions for further use in part two of this report.

For each substance, all available EQS are summarized and listed in Table 3 (biota) and Table 4 (sediment) along with the EQS selected for the comparison study in Chapter 5 of this project.

3. National methodologies and concepts for deriving EQS

3.1 Norway

In 2015, the Norwegian EPA updated their EQS values for priority pollutants to allow a classification of their aquatic environments into five groups or environmental classification classes, ranging from background (best) to very bad (worst). As metals generally are considered non-biomagnifiable, EQS are not derived for biota in Norway, which is in line with recommendations from e.g. the UK Environmental Protection Agency. Instead, Tolerable Daily Intake (TDI) are provided for the metals in the background documents. All the Norwegian results comply with the TGD#27 (EU 2011) except that they all are normalized to a fraction of organic carbon (F_{oc}) of 1% due to the Norwegian geology rather than the usual of 5% recommended in the TGD#27. The EQS were updated and re-analyzed in 2014 by NIVA in the report M241 (NIVA 2014) and reported in 2016 by the Ministry in the report M608 (Miljødirektoratet, 2016). Throughout this report, these two central documents are referred to as M241 and M608.

For metals in sediments, all Norwegian EQS are set using a risk approach including the background concentrations in sediments. The used background concentrations all originate from an OSPAR agreement on marine background concentrations reported in 2006 (OSPAR 2006). Here “Background concentrations” (BCs) are defined as assessment tools intended to represent the concentrations of certain hazardous substances that would be expected in the North-East Atlantic if certain industrial developments had not happened. They represent the concentrations of those substances at “remote” sites, or in “pristine” conditions based on contemporary or historical data respectively, in the absence of significant mineralization and / or oceanographic influences. In a Danish context, it should be noted that the background concentrations “approved” by OSPAR only covers marine sediments in the North East Atlantic and not for example the Baltic Sea. Since the background concentration from Norway only partly covers Danish marine waters, e.g. Nordsøen, the EQS for metals from Norway are hence corrected for the addition of the background concentration, and these “core” EQS are evaluated as suitable conservative estimates for use in part two of the project.

3.2 Sweden

The Swedish EQS have been published in a report from 2008 (Naturvådsverket 2008). The derivation of the EQS follows generally the recommendation in the TGD#27 (EU 2011).

3.3 The Netherlands

All official EQS in The Netherlands are available from the homepage[1] of RIVM (Rijksinstituut voor Volksgezondheid en Milieu), the Dutch Research Institute for Human Health and the Environment. From the homepage, it may be possible to access the background documentation underpinning the EQS. For the

[1] https://rvszoeksysteem.rivm.nl/

set of EQS evaluated in this report, especially four background documents have been referred to, i.e. Metals: Crommentuijn et al (1997a), PAH: Kalf et al (1995), TBT: Crommentuijn et al (1997b) and Phthalates: Hansler et al (2007).

For metals, two set of EQS values are available: MTR (Maximaal Toelaatbaar Risiconiveau) and VR (Verwaarloosbaar Risiconiveau). The MTR and VR levels correspond to the Maximum Permissible Concentrations (MPCs) and Negligible Concentrations (NCs) derived by Crommentuijn et al (1997ab) and generally equals the so-called *intervention values* and *target values* terms often used in the context of contaminated land to name EQS in The Netherlands. The MPCs and NCs for metals are all based on the added-risk approach. In the added-risk approach, a Maximum Permissible Addition (MPA) and Negligible Addition (NA) have been adopted according to the national policy on radiation. For naturally occurring compounds, the MPC/NC is constructed from the background concentration (Cb) and the MPA/NA, and expressed as MPC=Cb+MPA and NC=Cb+(MPA/100).

The EQS for metals are based on data originating back to early 90's and would need a revision in order to make them updated. Furthermore, as mentioned above, they are based upon background concentrations found in The Netherlands. As the soil types and natural origin are very different from The Netherlands and Denmark, these values are not considered useful in a Danish context.

The EQS for PAH are derived parallel to the EQS for metals, i.e. in early 1990’s, using the same approach. The EQS sediment for benz(a)pyrene and fluoranthene are both based upon the principle of equilibrium partitioning (EqP). Due to the age, the Dutch EQS for PAH (and metals) are not updated regarding data and furthermore most likely not in full accordance with TGD#27.

The EQS for phthalates, e.g. BBP and DEHP, are so-called indicative environmental quality standards used to indicate the maximum permissible concentration of a substance in water, air or soil. Indicative environmental quality standards are derived using a simple step-by-step plan. This approach is quicker than the common procedure for deriving environmental quality standards, mainly because the method for literature searches and validation of data is less exhaustive. Uncertainty factors are applied as a precaution to prevent underestimation of a potential risk to humans or the environment. Despite the indicative nature, the indicative EQS included in this report to a large extend (if not completely) follows the methods outlined by EU in their own risk assessment reports and TGD#27. The Dutch EQS for phthalates have hence been assessed useful and valid for the screening purpose of this report with a general remark of a need for reassessing the underpinning ecotoxicological data if a national EQS would have to be established.

4. EQS for specific substances

4.1 Phthalates

4.1.1 Butylbenzylphthalate (BBP).

The Netherlands has an indicative EQS (See Chapter 3.3) for sediment, but not for biota (Hansler et al 2007). The Dutch sediment EQS of 4.66 mg/kg dw is an indicative MTR (See Chapter 3) and is based upon the $PNEC_{sediment}$ from the EU Risk Assessment Report (EU 2007), which is derived by the use of EqP method assuming a fraction of suspended organic carbon of 10% and a Koc of 10,500 L/kg. The EQS for fresh- and marine waters used in the EqP were determined to 7.5 µg/L and 0.75 µg/L, respectively (EU 2007). The available data included data for algae, fish and daphnia with the latter as the most sensitive (NOEC = 75 µg/L). The EQS were derived by the use of an AF of 10 and 100 for fresh and marine waters, respectively. A partition coefficient for suspended matter/water of 263 was used by EU in the equation to calculate the $PNEC_{sediment}$. The Netherlands recalculated the EU PNEC values expressed as wet weight to dry weight by the use of a conversion factor of 2.71, i.e.

EQS-sediment for freshwater: 1.72 mg/kg ww x 2.71 = 4.66 mg/kg dw (10% OC)

EQS-sediment for marine water: 0.172 mg/kg ww x 2.71 = 0.466 mg/kg dw (10% OC)

Norway has no EQS for BBP in neither sediment nor biota.

Conclusion for BBP:
No EQS for biota is available, and only The Netherlands has a useful EQS for BBP in freshwater and marine sediment, i.e. 4.66 and 0.466 mg/kg dw, respectively. These are based upon aquatic data from the EU RAR and the use of EqP. They are hence considered relevant and valid although associated to substantial uncertainty due to the use of EqP.

$EQS_{sediment}$ of 2.33 mg/kg dw for freshwaters and 0.233 mg/kg for marine waters, both based upon the EU and Dutch EQS normalised to 5% from 10% OC, i.e. divided by two, is evaluated as suitable for the comparison study found in Chapter 5.

4.1.2 Di-2-ethylhexyl phthalate (DEHP)

Biota
Norway has an EQS_{biota} of 2,900 mg/kg ww. The $EQS_{biota,hh}$ is based upon a TDI of 48 µg/kg bw/day, a body weight of 70 kg and an intake of fish of 0.115 kg/day. 10% of TDI has been used for the consumption of fish and seafood. If focusing on the risk of secondary poisoning, Norway has calculated an $EQS_{biota,sec\ pois}$ of 3.2 mg/kg ww, using BCF of 2500 for blue mussels eaten by birds. This is very similar to the $PNEC_{oral,\ mammals}$ of 3.3 mg/kg ww presented in the EU RAR for DEHP (EU 2005).

Sediment
The Netherlands has an EQS for sediment as an indicative MTR (See Chapter 3), which is based upon the $EQS_{sediment}$ from the EU Risk Assessment Report for DEHP (EU 2008) converted to Dutch standard sediment (Hansler et al

2007). The $PNEC_{sediment}$ in the EU-RAR is >100 mg/kg dw (EU 2008). The available studies with sediment-dwelling organisms exposed to DEHP show largely varying results although in general the toxicity was relative low. A NOEC of > 1,000 mg/kg derived from a frog study was chosen for the derivation of a $PNEC_{sediment}$. Effect studies existed with organisms from at least three trophic levels, wherefore an assessment factor of 10 is used, resulting in a PNEC of >100 mg/kg dw. The Dutch conversion relates to differences in default OC content of 10% OC in the EU assessment and a Dutch standard of 5.9 % OC. The Dutch EQS is hence 100 mg/kg dw X (5.9/10) = 59 mg/kg dw.

Norway has an EQS for both fresh and marine sediment of 10 mg/kg dw. The EQS are based upon the same frog study from the EU RAR (EU 2008), resulting in an $EQS_{sediment}$ of 10 mg/kg dw, normalized to 1% OC.

Conclusion for DEHP
Both The Netherlands and Norway has EQS for DEHP in sediment.

The $EQS_{sediment}$ is based upon data from the EU RAR and hence considered relevant and valid. The Dutch EQS of 59 mg/kg dw and the Norwegian of 10 mg/kg dw are both normalised to organic carbon, i.e. 5.9 and 1% OC, respectively. For the comparison study in Chapter 5, an $EQS_{sediment}$ of 50 kg/kg dw based upon the EU, Norwegian and Dutch EQS normalised to 5% OC is evaluated as suitable for use in Chapter 5.

For biota, the Norwegian $EQS_{biota,sec\ pois}$ of 3.2 mg/kg ww is evaluated as suitable for use in the comparison study found in Chapter 5.

4.1.3 Di(2-ethylhexyl)adipate (DEHA) and diisononylphthalate (DINP)

None of the three countries has national EQS for these two phthalates. The European Union Risk Assessment Report for DINP from 2003 was unable to derive a suitable PNEC for sediment or biota.

The OECD lists in its *Screening Information Dataset (SIDS)* for DEHA an aquatic PNEC of 0.0035 mg/L based upon a NOEC from a chronic daphnia study and an AF of 10. The same report holds NOAEL values potentially enabling the establishment of EQS for biota.

For DINP, the SIDS Initial Assessment Profile (SIAM) report concluded: "*Due to its very low solubility, no acute toxicity in fish, invertebrates or algae could be observed. No long-term toxicity could be observed in algae or invertebrates at the limit of solubility. No valid long-term fish studies are available, but a read-across from tests performed with other long-chain phthalates (> C6) indicates that no effects are to be expected for DINP at the limit of water solubility or above. No effects were observed in acute toxicity studies with sediment organisms. No effects were observed in studies with terrestrial organisms.*" The same report holds NOAEL values potentially enabling the establishment of EQS for biota.

4.2 Metals

For metals, The Netherlands has two sets of EQS values corresponding to what was used to named *intervention value* (MTR) and *target value* (VR) (See Chapter 3.3), where the latter is most relevant for an EQS having e.g. sediment multifunctionality as endpoint. The EQS are based on data and methodologies originating back to early 90's. Furthermore, the most relevant EQS (multi-functionality) are typically based upon background concentrations. Due to the age of the EQS and the widely use of national background concentrations as EQS, the Dutch EQS values for metals, and TBT, are hence not assessed to be useful in a Danish context and consequently not discussed further in this chapter.

In Norway, updated and more recent EQS values are available. These are explained and discussed in more details below. Metals are not considered to biomagnify (see Chap. 2), hence only EQS for sediment has been derived in Norway, as they therefore do not represent a risk to the consumer or top predators.

In Sweden, the calculations of EQS are performed according to the requirements in the Water Framework Directive, but only EQS for zinc in sediment and chrome in sediment and biota are available.

4.2.1 Arsenic (As)

In Norway, an EQS for sediment is set at 18 mg/kg dw and includes the addition of Norwegian background concentrations in sediments of 15 mg/kg dw. The EQS is based upon EqP using an EQS for freshwater of 0.5 µg/L derived from data from the most sensitive group of organisms being *Daphnia pulex* with an EC10 of 5.0 µg/L and an AF of 10. The Kd for sediment-water is set as 6607 l/kg dw. The EQS sediment is hence calculated according to TGD#27 as:

$PNEC_{sediment}$ = (0.5 µg/L * 6,607 l/kg dw / 1000) + 15 mg/kg dw = 18 mg/kg dw.

Sweden has not derived/recommended any $EQS_{sediment}$ for arsenic.

The Norwegian EQS_{added} of 3 mg/kg dw for both marine and freshwater sediments, excluding the background concentration of 15 mg/kg, is evaluated as suitable for the comparison study found in Chapter 5.

4.2.2 Copper (Cu)

In Norway, an EQS for sediment is set at 84 mg/kg dw in marine waters and 210 mg/kg dw in freshwaters, and includes in both cases the addition of Norwegian background concentrations in sediments of 20 mg/kg dw. The EQS is based upon EqP using an EQS for freshwater of 7.8 µg/L and 2.6 µg/L for marine waters, both from the Voluntary EU Risk Assessment Report for copper (EU 2008). The Kd for sediment-water is set as 24,409 l/kg dw. The EQS sediment is hence calculated according to TGD#27 as:

FW: $PNEC_{sediment}$ = (7.8 µg/L * 24409 l/kg dw / 1000) + 20 mg/kg dw = 210 mg/kg dw

SW: $PNEC_{sediment}$ = (2.6 µg/L * 24409 l/kg dw / 1000) + 20 mg/kg dw = 84 mg/kg dw

The Voluntary EU Risk Assessment Report for copper (EU 2008) includes a $PNEC_{sediment}$ based upon numerous sediment studies (available single species sediment exposure tests resulted in 106 individual chronic NOEC values), which could void the need of using EqP. Here a HC5(50) based upon benthic species sensitivity distribution was used to derive a PNEC of 87.1 mg Cu/kg dry weight (5% OC) for both marine- and freshwater. The Species Sensitivity Distribution (SSD) was based on a log-normal distribution and an AF of 1, which may be questioned, as it indicates that no uncertainty remains in the

PNEC derivation. Norway omitted this value as national EQS due to the fact it – when normalized to 1% OC – would approach the background concentration.

Sweden has not derived / recommended any $EQS_{sediment}$ for copper.

The Norwegian EQS_{added} of 190 mg / kg dw for freshwater and 64 mg / kg for marine water sediment, excluding the background concentration of 20 mg / kg dw, are evaluated as suitable for the comparison study found in Chapter 5.

4.2.3 Chrome (Cr)

Chrome may exist as both Cr III and Cr VI. In sediment the dominate state is considered to be Cr III, wherefore the EQS are established as Cr total. In Norway, the EQS for sediment is set at 660 mg / kg dw in marine waters and 112 mg / kg dw in fresh waters, and includes in both cases the addition of Norwegian background concentrations in sediments of 60 mg / kg dw. The EQS is based upon EqP using an EQS for both marine - and freshwater of 4.7 µg Cr III / L originating from the EU Risk Assessment Report for Chrome (EU 2005). The PNEC in the EU RAR is based upon a NOEC from a reproduction test with *Ceriodaphnia dubia* and the use of an AF of 10. In Norway, the Kd for sediment-water is set as 11,000 and 120,000 l / kg dw for fresh- and marine water, respectively. The EQS sediment is hence calculated according to TGD#27 as:

FW: $PNEC_{sediment}$ = (4.7 µg / L * 11,000 l / kg dw / 1000) + 60 mg / kg dw = 112 mg / kg dw

SW: $PNEC_{sediment}$ = (4.7 µg / L * 120,000 l / kg dw / 1000) + 60 mg / kg dw = 624 mg / kg dw

In the Norwegian background report (M-241), the $PNEC_{sediment}$ for marine water is falsely presented as 664 mg / kg dw, which must be a typo. Nevertheless, the official EQS for Cr in Norway is set at 112 and 660 mg / kg dw for fresh- and marine waters in M-608 (Miljødirektoratet 2016). For comparison, the EU RAR arrives at a $PNEC_{sediment}$ of 31 mg / kg ww or 80 mg / kg dw, also based upon EqP. This EU PNEC is set as total concentration of Cr, i.e. including background concentration.

The Swedish $EQS_{sediment}$ for chrome is also based upon EqP calculation using EQS_{water} of 3.4 and 4.7 µg / L for CrVI and CrIII, respectively. The EQS_{water} for Cr VI is based upon a HC5 coming from a SSD and an AF of 3, whereas the EQS_{water} for CrIII is based upon the AF method using an AF of 10 and the lowest NOEC of 47 µg / L for *Daphnia magna*. The EqP calculation uses a sediment density of 1150 kg / m3 and partitioning coefficients as listed below between suspended matter and water depending on the pH, i.e. in neutral or alkali environments versus acidic environments.

Cr III: 75,000 and 7,500 L / kg in neutral / alkali and acidic environments, respectively

Cr VI: 500 and 50 L / kg in neutral / alkali and acidic environments, respectively

Altogether, it results in $EQS_{sediments}$ shown below. The EQS are shown as mg / kg dw and in brackets as mg / kg wet weight. In Sweden no differentiation between fresh- and marine sediments are indicated.

Chrome mg/kg dw (mg/kg ww)	neutral/alkali environments	acidic environments
Cr III	1426 (307)	143 (31)
Cr VI	0.69 (0.15)	6.9 (1.5)

Sweden has published an EQS_{biota} protecting human health against chrome intake from marine food. The EQS_{biota} of 4.3 mg/kg biota ww is based upon a TDI of 0.07 mg Cr (VI)/kg/day, a body weight of 70 kg and daily consumption of fish products of 0.115 kg/day/person.

The Norwegian EQS_{added} of 52 mg/kg dw (total Cr) for freshwater sediments and 600 mg/kg dw for marine sediments, excluding the background concentration of 60 mg/kg dw, are evaluated as suitable for the comparison study found in Chapter 5 for the sediment. For biota, the EQS_{biota} of 4.3 mg/kg ww from Sweden is evaluated as suitable for the comparison study found in Chapter 5.

4.2.4 Nickel (Ni)

In Norway, the EQS for sediment is set at 42 mg/kg dw and includes the Norwegian background concentrations in sediments of 30 mg/kg dw. The EQS is based upon EqP using an EQS for freshwater of 1.7 µg/L originating from EU Risk Assessment Report for Nickel and derived from the output of a SSD with HC5 of 5.1 and an AF of 3. The Kd for sediment-water is set as 7079 l/kg dw. The $EQS_{sediment}$ is hence calculated according to TGD#27 as:

$PNEC_{sediment}$ = (1.7 µg/L * 7,079 l/kg dw / 1000) + 30 mg/kg dw = 42 mg/kg dw.

No $PNEC_{sediment}$ can be extracted from the EU RAR, as it concluded: "*The current sediment data set should not be used to derive a PNEC sediment and that additional research is warranted to allow scientifically justified approaches to be incorporated into the nickel sediment toxicity test program in order to derive a reliable PNEC for the sediment compartment*". Therefore, a multi-laboratory, multiphase research project was conducted to provide a scientific basis for a bioavailability based approach for assessing risks of nickel in sediments[2]. Promoted and organized by the nickel industry, i.e. NIPRA - Nickel Health and Environmental Science, a subset of 6 nickel-spiked sediments was deployed in the field to examine benthic colonization and community effects. Furthermore a testing program yielded a broad, high quality data set that was used to develop a SSD for benthic organisms in various sediment types, a reasonable worst case predicted no-effect concentration for nickel in sediment. HC5 values normalized according to bioavailability (ASV/TOC modelling) for 12 eco-regions revealed HC5 value between 109 and 305 mg/kg dw, i.e. significantly higher than the Norwegian EQS. Sweden has not derived/recommended any $EQS_{sediment}$ for nickel.

The Norwegian EQS expressed as added nickel (EQS_{added}) of 12 mg/kg dw for freshwater and marine sediments, excluding the background concentration of 30 mg/kg, is evaluated as suitable for the comparison study found in Chapter 5.

[2] https://www.nickelinstitute.org/media/3721/eu-ni-ra-fact-sheet-8-2017-january.pdf

4.2.5 Zinc (Zn)

In Norway, an EQS for sediment is set at 139 mg/kg dw in marine- and freshwaters, and includes the addition of Norwegian background concentrations in sediments of 90 mg/kg dw. The EQS originates from the PNEC of 49 mg/kg dw from the EU Risk Assessment Report for zinc (EU 2010). The PNEC is based upon ecotoxicological test with four benthic species and an AF of 10 with the lowest NOEC of 488 mg/kg dw being for *Hyalella Azteca*. Sweden uses the same EQS_{added} of 49 mg/kg dw.

The Norwegian and Swedish EQS expressed as added zinc (EQS_{added}) of 49 mg/kg dw for freshwater and marine sediments, excluding the background concentration, is evaluated as suitable for the comparison study found in Chapter 5.

4.2.6 Tin (Tri-butyl-tin – TBT)

Norway has EQS for both biota and sediment. The EQS_{biota} for protection of human health is based upon a TDI of 0.25 µg/kg body weight/day, an intake of fish/shellfish of 0.115 kg/day, and a body weight of 70 kg, which is in full accordance with the EU EQS dossier. The Norwegian $EQS_{biota,\ hh}$ is hence = (0.25*70) / 0.115 = 152 µg/kg ww, which is round off as 150 µg/kg ww. In Norway seafood are considered the only source of TBT, wherefore 100% of the ADI can be used. In the EU EQS dossier, only 10% of the ADI can be used for aquatic sources, wherefore the $EQS_{biota,hh}$ is set as 15.2 µg/kg ww.

For sediments, Norwegian EQS are fully in line with the EU derived $EQS_{sediment}$ of 0.02 µg/kg dw, except that is an order of magnitude lower, i.e. 0.002 µg/kg dw, due to the normalisation to 1% OC instead of the 10% OC used in the EU EQS dossier. The Norwegian EQS is based upon EqP using the EU derived EQS_{water} of 0.0002 µg/L and a Koc of 1084 L/kg. The EQS_{water} of 0.0002 µg/L is based upon data from approximately 25 species and a $HC5_{(50)}$ derived from a species sensitivity distribution of 0.00083 µg/L and an AF of 4.

In Sweden, Stockholm University has recently (ACES, 2018) published a report deriving an $EQS_{sediment}$ value for TBT. The report was commissioned by the Swedish Agency for Marine and Water Management (SwAM) to prepare a Water Framework Directive (WFD) sediment Environmental Quality Standard (EQS) dossier. It is, however, unclear what the legal status of the EQS is at current state.

In the literature search conducted in 2013, 10 sediment studies were available investigating toxicity to 9 freshwater species, 3 marine species and marine meiobenthic communities. All studies were assessed as reliable. The critical study with the highest observed sensitivity was the study by Duft et al. (2003), who investigated effects from TBT exposure on the freshwater Gastropoda *Potamopyrgus antipodarum* using artificial spiked sediment (OC 2.3 %) with a duration of 2, 4 and 8 weeks. The most sensitive endpoint was the number of new embryos (without shells) after 4 weeks of exposure. The EC10 was higher after 8 weeks compared to 4 weeks (2.98 µg/kg dw), which most likely is due to reduced bioavailability of TBT over time. As the dose-response curve was clearer after 8 weeks compared to 4 weeks and chemical analysis of sediment concentration only was made at week 8, the EC10 after 8 weeks was assessed to be more reliable. This EC10 was recalculated to 16 µg/kg dw expressed as 5% TOC. An AF of 10 was assessed as sufficient, since effect-data for three chronic freshwater studies were available investigating at least three sediment-dwelling species representing different living-conditions. Based on the above, a Swedish EQS of 1.6 µg/kg dw (5% OC) was derived assumed to protect both freshwater and marine sediment dwelling species.

Conclusion of TBT

The Norwegian EQS_{biota} of 15.2 µg/kg ww is evaluated as suitable for the comparison study found in Chapter 5, although it is based upon an accepted consumption of 100 % of the ADI from seafood, which may be in contrast to the policy in EU and many countries.

$EQS_{sediment}$ values are available from Norway, EU and Sweden. Where the two former is based on the EqP method, Sweden has derived an EQS based upon studies with sediment dwelling species exposed in spiked sediments. The TGD#27 states: "*Where sediment ecotoxicity data are available, ecotoxicity data from experiments with benthic organisms is preferred over water column ecotoxicity data used in conjunction with equilibrium partitioning, because of the assumptions and uncertainties inherent in the equilibrium partitioning approach*"

The Swedish $EQS_{sediment}$ of 1.6 µg/kg dw (5 % OC) for freshwater and marine sediments, is evaluated as suitable for the comparison study found in Chapter 5.

4.3 PAHs

For PAHs only $EQS_{sediment}$ are evaluated here as EQS_{biota} are covered by existing EU regulations.

4.3.1 Benz(a)pyren (B(a)P)

For sediment the Dutch EQS is 0.003 mg/kg dw with references to an older report by Kalf et al (1995), despite new $EQS_{sediment}$ values are available in the EU dossier (EU 2011a) (see below). Kalf et al (1995) list a MCP value (see Section 3.3) of 2.7 mg/kg dw for B(a)P, being derived by the use of EqP. Consequently, NC values are derived as 0.027 mg/kg dw, as these are defined as MPC/100. The NC for B(a)P in Kalf et al (1995) is an order of magnitude higher than the $EQS_{sediment}$. It has not been possible to determine this difference although the MPC for soil (0.26 mg/kg dw) is in fact an order of magnitude lower than for sediment, and soil and sediment in the Netherlands frequently is considered analogous.

In Norway, the marine $EQS_{sediment}$ for B(a)P is 0.18 mg/kg dw (1% OC), and is based upon the use of EqP with a K_D value of 8318 L/kg (Koc of 831,764) and an $EQS_{freshwater}$ of 0.22 µg/L. The use of an $EQS_{freshwater}$ of 0.22 µg/L in Norway is somehow in conflict with as well the EU EQS of 0.022 µg/L (see below) and the national $EQS_{freshwater}$ of 0.00017 µg/L apparently coming from a new EU EQS dossier not made available in the references of the M241 report. The calculations is hence not fully transparent.

Sweden has no $EQS_{sediment}$ for B(a)P.

EU EQS dossier

In the EU EQS dossier, the $EQS_{sediment}$ is presented as 91.5 µg/kg dw or 35.2 µg/kg ww covering both fresh- and marine sediments. No ecotoxicological data are available for sediment-dwelling organisms. Therefore, EqP method was applied to derive the $EQS_{sediment}$. The used $EQS_{freshwater}$ of 0.022 µg/L for the EqP was based upon an EC10 of 0.22 µg/L for shell development of the marine mollusc *Crassostrea gigas* and an AF of 10.

4.3.2 Fluoranthene (FLU)

The Dutch EQS for sediment is referred to an older Dutch report from 1995 (Kalf et al 1995), despite new $EQS_{sediment}$ values are available in the EU dossier. Kalf et al (1995) list a MCP value (see Section 3.3) of 2.6 mg/kg for FLU, being derived by the use of EqP. The NC value are derived as 0.026 mg/kg dw, as it is defined as MPC/100. The Dutch $EQS_{sediment}$ for FLU of 0.03 mg/kg is hence based on the NC value.

In Norway, the $EQS_{sediment}$ is 0.4 mg/kg dw (1% OC) being an OC-normalization of the $EQS_{sediment}$ from the EU EQS Dossier for Fluoranthene (see below).

Sweden has no $EQS_{sediment}$ for FLU.

EU EQS Dossier

The EU EQS dossiers (EU 2011b) include an $EQS_{sediment}$ value based upon a rather substantial sediment dataset covering annelids, insects and crustaceans. The lowest relevant value was a 14d-EC10 of 41 mg/kg dw for reproduction of the marine crustacean *Schizopera knabeni*. This value was based upon an organic carbon content of 10%. Based upon an OC-normalized EC10 of 20 mg/kg (5% OC) and an AF of 10, the $EQS_{sediment}$ for FLU was suggested as 2.0 mg/kg dw (5% OC) covering both marine and freshwater sediments.

4.3.3 Conclusions on PAH

Regarding sediment, the EQS in The Netherlands are based upon older data and hence not assessed very useful. Sweden has no $EQS_{sediment}$ for PAHs. The $EQS_{sediment}$ from Norway for B(a)P of 0.18 µg/kg dw is somehow non-transparent and should hence be used with caution. For comparison, the PNEC from the EU EQS dossier is 91.5 µg/kg dw (5% OC). The Norwegian $EQS_{sediment}$ for FLU is in line with the EQS from the EU Dossier, normalized to Norwegian sediments.

The Norwegian $EQS_{sediment}$, i.e. 0.9 µg/kg dw for benz(a)pyrene and 2.0 mg/kg dw for fluoranthene (both normalized to 5% OC), are evaluated as suitable for the comparison study found in Chapter 5. Both cover sediments from as well freshwater as marine waters.

4.4 PCBs

Only none dioxin-like are included here as dioxin-like substances are covered by existing EU regulations.

4.4.1 Sediment

In The Netherlands, a number of EQS for sediments are available. The scientific background of these are, however, not fully transparent as they apparently is set as background concentrations in Dutch sediments and/or soils.

In Norway, a sum of 4.1 µg/kg for PCBs, i.e. PCB# 28, 52, 101, 118, 138, 153 and 180, is recommended as $EQS_{sediment}$. As reference for the Norwegian EQS, a published study by de Deckere et al (2011) is used. The EQS published in that study is apparently already incorporated into Flemish legislation. The study by de Deckere et al (2011) has not been evaluated within this project. Furthermore, the Norwegian EQS is based upon PCB including the dioxin-like PCB#118.

In Sweden, an $EQS_{sediment}$ of 30 µg/kg in freshwaters and 20 µg/kg in marine waters, covering the total sum of all PCBs, has been suggested in a report by Naturvådsverket (2008). However, these are apparently not currently incorporated into the Swedish legislation (HVMFS 2013). These EQS are based upon an adaptation of Canadian interim Quality Standards derived by the Canadian Council of Ministers (CCME). The Canadian EQS has not been evaluated in this report.

4.4.2 Biota

In Norway, an EQS_{biota} 0.6 µg/kg biota covering the seven PCBs with number 28, 52, 101, 118, 138, 153 and 180, i.e. including the dioxin-like PCB#118. The EQS is derived by the use of a TDI of 0.01 µg/kg body weight, a body weight of 70 kg and an intake of marine products covering 10% of TDI. The TDI of 0.01 µg/kg body weight used by Norway is paying reference to a report by RIVM from 2001 (RIVM 2001), which has not been evaluated in this report.

In Sweden, an EQS_{biota} for freshwater of 125 µg/kg fish muscle (ww) covers the six non-dioxin like PCBs # 28, 52, 101, 138, 153 and 180 (HVMFS 2013). For eels the EQS is 300 µg/kg ww. The Swedish EQS_{biota} for marine waters, covering the same six PCBs, are set at 75 µg/kg ww for fish muscle and/or crustaceans. This is in agreement with the work of HELCOM, who has, as part of its work with core indicators, identified a level of non-dioxin PCB ensuring a Good Environmental Status of 75 µg/kg fish muscle (ww) for the six non-dioxin like PCBs # 28, 52, 101, 138, 153 and 180 (HELCOM 2018). The scientific background for the EQS_{biota} in Sweden and HELCOM has not been evaluated in this report, as the background information has not been available.

4.4.3 Conclusions on non-dioxin like PCB

The $EQS_{sediment}$ available are all derived with relative low transparency with references to documents and studies not evaluated within this project. Both the Norwegian EQS of 4.1 µg/kg dw and the Swedish EQS values of 30 (fresh water) and 20 µg/kg dw (marine waters) includes at least one dioxin-like PCB (e.g. #118) wherefore they are evaluated as unsuitable for the comparison study found in Chapter 5. For biota, the Swedish EQS of 125 and 75 µg/kg ww for 6 non-dioxin-like PCBs in fresh and marine waters, respectively, is evaluated as suitable for the comparison study found in Chapter 5.

4.5 Hexachlorocyclohexan (HCH)

No EQS for HCH is available from The Netherlands.

In Norway, an EQS_{biota} of 61 µg/kg ww is available. This is based upon an ADI of 0.001 µg/kg/day (coming from a NOAEL of 0.47 mg/kg body weight/day set in a chronic toxicity study with rats (EU 2005), a body weight of 70 kg and a maximum intake via seafood of 10%).

The EQS_{biota} from Norway is in full agreement with the one for lindane (γHCH) from the EU Dossier (EU 2005) protecting human health. However, it should be noted that the EU EQS for secondary poisoning, i.e. $EQS_{biota.sec\ pois}$, is 33 µg/kg ww, i.e. lower than the $EQS_{biota,hh}$. As highlighted, the EQS used in Norway is for lindane. For HCHs other than lindane, i.e. Σα-, β-, δ-, ε- HCH, no $EQS_{biota,hh}$ is available in the EU dossier, but an $EQS_{biota.sec\ pois}$, is set at 67 µg/kg ww.

In sediment, Norway has established an EQS of 0.74 µg/kg dw for freshwater and ten times lower for marine sediments, i.e. 0.074 µg/kg dw. Both are normalized to 1% OC and both are based upon EqP calculations using the EQS_{water} from the EU EQS Dossier for HCH (EU 2005) using the lowest chronic NOEC of 0.2 µg/L obtained for the increased drift of an aquatic insect of the mayfly genus *Baetis*. Long-term toxicity data are available for at least three trophic levels. Therefore, the lowest NOEC is divided by an assessment factor of 10 or 100 in order to derive the EQS_{fw} and EQS_{sw} of 0.02 and 0.002 µg/L, respectively. The Norwegian $EQS_{sediment}$ was based on these EQS and the use of a Kd value of 37 L/kg.

4.5.1 Conclusions on hexachlorcyclohexan

For biota, the Norwegian EQS_{biota} of 61 µg/kg ww is evaluated as suitable for the comparison study found in Chapter 5. For sediment, the Norwegian EQS of 0.74 µg/kg dw is evaluated as suitable for the comparison study found in Chapter 5.

4.6 Summary of EQS

Although three different countries, i.e. Norway, The Netherlands and Sweden, have been included in this review over national EQS for sediment and biota, a relative limited set of EQS were evaluated as suitable for use in this report. Mostly EQS from Norway and Sweden was considered relevant, useful and up to date as many of the Dutch EQS were of older origin. The conclusions from the evaluations can be found in Table 3 (biota) and Table 4 (sediment).

Table 3. Collected EQS values (µg/kg ww) for biota (EQS_{biota}) from Sweden, Norway and The Netherlands and comments on the evaluation of suitability for the comparison study found in Chapter 5 of this report.

Compound (CAS#)	**Sweden**	**Norway**	**The Netherlands**	**EQS used in Comparison Study**	**Comments (See also specific comments in Chapter 4)**
BBP (85-68-7)	-	-	-	-	-
DEHA (103-23-1)	-	-	-	-	-
DEHP (117-81-7)	3000	3.2 (sec. pois) 2900 (human health)	-	3.2 (sec. pois.)	EQS covers secondary poisoning
DINP (28553-12-0)	-	-	-	-	-
PCB (-)	75 (PCB_6)*	0.6 (PCB_7)**		75	The Swedish EQS is in agreement with the criteria for Good Environmental Status in the HELCOM
As (7440-38-2)	-	-	-	-	Not biomagnifying hence no EQS in any country
Cu (7440-50-8)	-	-	-	-	Not biomagnifying hence no EQS in any country
Cr (7440-47-3)	4.3	-	-	4300	The EQS_{biota} is based upon human health protection from fish consumption
Ni (7440-02-0)	-	-	-	-	Not biomagnifying hence no EQS in any country
Zn (7440-66-6)	-	-	-	-	Not biomagnifying hence no EQS in any country
Tributyltin (TBT) (36643-28-4)	-	150	-	150	Human health. 100% of ADI is used for marine food
Hexachlorocyclohexan (γHCH) (608-73-1)	-	61	-	61	EQS is for γHCH and based upon human health protection from fish consumption

§ *) Mixture sum of PCB# 28, 52, 101, 138, 153 and 180; **) Mixture sum of PCB # 28, 52, 101, 118, 138, 153, 180

Table 4. Collected EQS values (mg/kg dw) for sediment ($EQS_{sediment}$) from Sweden (S), Norway (N) and The Netherlands (NL) and conclusion on the evaluation of suitability for the comparison study found in Chapter 5 of this report. Unless otherwise specified the $EQS_{sediment}$ covers both marine- (SW) and freshwater (FW) sediments. For Part two, selected EQS is aimed normalized to 5% OC. In cases where no national indication of OC normalization is available, the EQS is adopted directly.

Compound (CAS#)	Sweden	Norway	The Netherlands	EQS used in Comparison Study	Comments (See also specific comments in Chapter 4)
BBP (85-68-7)	-	-	4.66 (FW) 0.466 (SW) [10% OC]	2.33 (FW) 0.233 (SW)	2.33/0.233 mg/kg dw is NL EQS[§] normalized to 5% OC
DEHA (103-23-1)	-	-	-	-	-
DEHP (117-81-7)	-	10 [1% OC]	59 [5.9 % OC]	50	50 mg/kg dw is NL/N EQS normalized to 5% OC
DINP (28553-12-0)	-	-	-	-	-
PCB (-)**	0.03 (FW) 0.02 (SW) (PCB_{total})	0.0041 (PCB_7)	0.02 (PCB_7)	None	No information about OC % in any of the national EQS. All EQS includes dioxin-like PCBs, which is out of the scope of this report
As (7440-38-2)	-	3	-	3	Added risk approach, i.e. EQS exclude background concentrations
Cu (7440-50-8)	-	64 (SW) 190 (FW)	-	64 (SW) 190 (FW)	Added risk approach, i.e. EQS exclude background concentrations
Cr (7440-47-3)*	Cr_{VI}: 0.69-6.9 Cr_{III}: 143-1426	600 (SW) 52 (FW)	-	600 (SW) 52 (FW)	Added risk approach, i.e. EQS exclude background concentrations
Ni (7440-02-0)	-	12	-	12	Added risk approach, i.e. EQS exclude background concentrations
Zn (7440-66-6)	-	49	-	49	Added risk approach, i.e. EQS exclude background concentrations
Benz[a]pyrene (50-32-8)	-	0.18 [1% OC]	-	0.9	0.9 mg/kg dw is the EQS from N normalized to 5% OC
Fluoranthene (206-44-0)	2.0	0.4 [1% OC]		2.0	2.0 mg/kg dw is the EQS from S/N normalized to 5 % OC
Tributyltin (TBT) (36643-28-4)	0.0016 [5% OC]	0.000002 [1% OC]	-	0.0016	The EQS from S is based on sediment data in contrast to the EQS from N being based on EqP.
Hexachlorocyclohexan (γHCH) (608-73-1)	-	0.00074 (FW) 0.000074 (SW) [1% OC]	-	0.0037 (FW) 0.00037 (SW)	0.0037/0.00037 mg/kg dw is EQS from N normalized to 5 % OC

§ So-called indicative environmental quality standards (See Chapter 3.3 for more details)

*) Swedish EQS for Chrome differs according to alkali/neutral or acidic sediments. **) Mixture of PCBs, i.e. Mixture sum of total PCBs or Mixture sum of PCB_7 - # 28, 52, 101, 118, 138, 153, 180

5. Methodology and data for the comparison study

Comparison of EQS identified in Chapter 4 with sediment and biota concentrations found in marine and freshwater sediment and biota are based upon data from NOVANA, the National Monitoring and Assessment Programme for Aquatic and terrestrial Environments (Naturstyrelsen, 2011; Miljøstyrelsen, 2017). In NOVANA, each subprogram on surface water includes surveillance monitoring and operational monitoring. Surveillance monitoring shall provide information on ecological and chemical status on surface waters while operational monitoring shall be carried out in water bodies, which are identified as being at risk of failing to meet their environmental objectives.

The monitoring data are stored in a database for surface waters, ODA (https://oda.dk/main.aspx) where data for this project are extracted from.

This project includes quality assured data from the period 2010 and onward. Data included are data on sediment from surveillance and operational monitoring in lakes and streams. Monitoring of biota in lakes and streams is not included since none of the hazardous substances included in this project are measured in biota from lakes and streams. In marine waters surveillance monitoring is covered by monitoring in biota and operational monitoring in sediment. These data are included as well.

Denmark is in the context of the water framework directive split into three major and one minor water districts[3].

The comparison study used an adopted excel-based model, which has been developed to assess normalized environmental data from the national ODA database against Danish EQS (Miljøkvalitetskrav, MKK) and OSPAR/HELCOM EAC/EQS values (Larsen and Strand, 2018).

5.1 Adjustment of the model

In the model outlined above, the Danish environmental quality criteria are replaced by the EQS listed in Table 3 and 4 in Chapter 4 and the measured concentrations are normalized and assessed in relation to these criteria, mentioned to ensure comparative assessments.

If relevant, the observed concentrations are normalized. This accounts particularly for sediments and organic fractions, as the normalization based on TOC can be of a factor 50 or more for sandy sediments. In the open North Sea, sediments typically have less than 0.5% TOC, and in a few cases with very organic sediments, the normalization may be from 10% to 5% TOC. For the metals, normalization are based on Al or Li, and can also be a factor of 0.5 to 10 with the highest difference for the sandy sediments as for TOC. Normalization is necessary as sand accumulate less organic substances and metals compared to clay sediment. Furthermore, sediment dwellers need to process larger quantities of sandy sediment than organic/clay sediments to get the same amount of food. Normalization is in line with the recommendations made by

[3] https://www.retsinformation.dk/Forms/R0710.aspx?id=161600

both OSPAR and the EU. Further details on the model can be found in Larsen and Strand (2018).

5.2 Comparison study in Danish lakes

Data from lakes included in NOVANA during the period 2010-2017. None of the compounds in this project are measured in biota, as only mercury is included in the Danish surveillance of toxic substances in freshwater biota (fish).

The lake program is divided into control (surveillance) and operational monitoring. Therefore, Table 5 and 6 presents comparison with data from control and operational monitoring. In Table 5, results for sediments include summary data as well (total dataset).

Table 5. Lake sediment. Number of observations (OBS) where measurements are lower than the suggested EQS (Table 4), higher than EQS, but lower than 2*MKK (MKK<OBS≤2*MKK) or higher than 2*MKK. The inventory is divided into water districts and program types (OPE=operational monitoring, CON=control monitoring and TOTAL data set). Furthermore, the mean, maximum and minimum concentrations in the data set is shown for each substance.

Substance	Water district	Program	OBS≤EQS	EQS<OBS≤2*EQS	OBS>2*EQS	Avg. Conc. (mg/kg dw)	Range (min-max) mg/kg dw
DEHP	1 Jylland/Fyn	CON	94	0	0	0.196	0.01-1.8
		OPE	102	0	0	0.406	0.01-3.4
		TOTAL	196	0	0	0.305	0.01-3.4
	2 Sjælland	CON	17	0	0	0.306	0.01-1.5
		OPE	20	0	0	1.66	0.01-12
		TOTAL	37	0	0	1.04	0.01-12
	3 Bornholm	CON	0	0	0	0	0-0
		OPE	1	0	0	0.180	0.18-0.18
		TOTAL	1	0	0	0.180	0.18-0.18
	4 Vidå/Kruså	CON	5	0	0	0.312	0.01-0.59
		OPE	2	0	0	0.055	0.01-0.1
		TOTAL	7	0	0	0.239	0.01-0.59
Arsenic	1 Jylland/Fyn	CON	15	15	41	14.87	1.3-120
		OPE	0	4	6	60.40	3.5-510
		TOTAL	15	19	47	20.49	1.3-510
	2 Sjælland	CON	2	3	9	8.43	2.1-26
		OPE	1	0	3	6.14	0.65-9.2
		TOTAL	3	3	12	7.92	0.65-26
	3 Bornholm	CON	0	0	0	0.00	0-0
		OPE	0	1	0	3.80	3.8-3.8
		TOTAL	0	1	0	3.80	3.8-3.8
	4 Vidå/Kruså	CON	0	2	2	9.45	4-22
		OPE	0	0	0	0.00	0-0
		TOTAL	0	2	2	9.45	4-22
Chrome	1 Jylland/Fyn	CON	93	0	1	17.68	2.2-260
		OPE	101	0	1	29.34	1.3-1200
		TOTAL	194	0	2	23.75	1.3-1200
	2 Sjælland	CON	16	0	1	21.96	7.5-130
		OPE	20	0	0	19.89	2.3-49
		TOTAL	36	0	1	20.84	2.3-130
	3 Bornholm	CON	0	0	0	0.00	0-0
		OPE	1	0	0	30.00	30-30
		TOTAL	1	0	0	30.00	30-30

	4 Vidå/Kruså	CON	5	0	0	19.70	7.5-34
		OPE	2	0	0	20.95	6.9-35
		TOTAL	7	0	0	20.06	6.9-35
Copper	1 Jylland/Fyn	CON	93	1	0	23.28	0.94-270
		OPE	101	0	1	88.63	0.97-6200
		TOTAL	194	1	1	57.29	0.94-6200
	2 Sjælland	CON	16	0	1	83.12	10-800
		OPE	19	1	0	67.82	2.1-240
		TOTAL	35	1	1	74.85	2.1-800
	3 Bornholm	CON	0	0	0	0.00	0-0
		OPE	1	0	0	31.00	31-31
		TOTAL	1	0	0	31.00	31-31
	4 Vidå/Kruså	CON	5	0	0	23.20	13-34
		OPE	2	0	0	11.00	9-13
		TOTAL	7	0	0	19.71	9-34
Nickel	1 Jylland/Fyn	CON	33	38	23	21.95	0.78-180
		OPE	30	40	32	22.77	0.82-170
		TOTAL	63	78	55	22.38	0.78-180
	2 Sjælland	CON	6	10	1	15.39	7.6-27
		OPE	9	7	4	16.55	2.3-56
		TOTAL	15	17	5	16.02	2.3-56
	3 Bornholm	CON	0	0	0	0.00	0-0
		OPE	0	0	1	24.00	24-24
		TOTAL	0	0	1	24.00	24-24
	4 Vidå/Kruså	CON	2	1	2	28.64	6.4-86
		OPE	0	1	1	33.00	17-49
		TOTAL	2	2	3	29.89	6.4-86
Zinc	1 Jylland/Fyn	CON	22	26	46	162.87	3.2-3000
		OPE	11	28	63	285.90	4.6-9600
		TOTAL	33	54	109	226.90	3.2-9600
	2 Sjælland	CON	0	3	14	180.18	66-440
		OPE	3	5	12	299.20	15-830
		TOTAL	3	8	26	244.51	15-830
	3 Bornholm	CON	0	0	0	0.00	0-0
		OPE	0	0	1	180.00	180-180
		TOTAL	0	0	1	180.00	180-180
	4 Vidå/Kruså	CON	0	1	4	142.60	73-210
		OPE	1	0	1	163.00	26-300
		TOTAL	1	1	5	148.43	26-300
	1 Jylland/Fyn	CON	93	0	1	0.149	0.001-8.2
		OPE	100	2	0	0.121	0.001-1.3
		TOTAL	193	2	1	0.134	0.001-8.2
	2 Sjælland	CON	16	0	1	0.295	0.017-2
		OPE	19	1	0	0.229	0.0018-1
		TOTAL	35	1	1	0.259	0.0018-2
	3 Bornholm	CON	0	0	0	0.00	0-0
		OPE	1	0	0	0.059	0.059-0.059
		TOTAL	1	0	0	0.059	0.059-0.059
	4 Vidå/Kruså	CON	5	0	0	0.0381	0.0065-0.075
		OPE	2	0	0	0.00680	0.004-0.0096
		TOTAL	7	0	0	0.0292	0.004-0.075

Fluoranthene	1 Jylland/Fyn	CON	93	0	1	0.358	0.003-21
		OPE	101	1	0	0.246	0.003-2.2
		TOTAL	194	1	1	0.300	0.003-21
	2 Sjælland	CON	16	1	0	0.503	0.039-3
		OPE	20	0	0	0.439	0.012-2
		TOTAL	36	1	0	0.468	0.012-3
	3 Bornholm	CON	0	0	0	0.00	0-0
		OPE	1	0	0	0.100	0.1-0.1
		TOTAL	1	0	0	0.100	0.1-0.1
	4 Vidå/Kruså	CON	5	0	0	0.152	0.017-0.35
		OPE	2	0	0	0.016	0.01-0.021
		TOTAL	7	0	0	0.113	0.01-0.35
Tributyltin (TBT)	1 Jylland/Fyn	CON	50	18	14	0.00257	0.001-0.025
		OPE	17	23	16	0.00601	0.001-0.13
		TOTAL	67	41	30	0.00397	0.001-0.13
	2 Sjælland	CON	7	1	6	0.00650	0.001-0.046
		OPE	4	1	0	0.00124	0.001-0.0022
		TOTAL	11	2	6	0.00512	0.001-0.046
	3 Bornholm	CON	0	0	0	0	0-0
		OPE	0	0	0	0	0-0
		TOTAL	0	0	0	0	0-0
	4 Vidå/Kruså	CON	3	1	0	0.00125	0.001-0.002
		OPE	0	1	0	0.00200	0.002-0.002
		TOTAL	3	2	0	0.00140	0.001-0.002

In total, 242 lakes are included in the project. 197 lakes are situated in water-district 1 (Jylland / Fyn), 37 in water district 2 (Sjælland), one in water district 3 (Bornholm) and seven in water district 4 (Vidå / Kruså).

Among the 14 chosen substances, BBP, PCB and HCH are not included in the monitoring program for lake sediments in the period 2010-2017. For DEHA and DINP no suitable EQS were found for freshwater sediments. The remaining nine substances are listed in Table 5. Arsenic was only measured in 104 and TBT in 232 of the 242 lakes. The remaining seven substances were measured in all lakes.

For all substances, except DEHP, the sediment EQS in table 4 were exceeded in one or more of the 242 lakes. EQS for arsenic, nickel, zinc and TBT are exceeded in the majority, i.e. 65-85%, of lakes. In most cases concentrations of arsenic exceeds 2*EQS. In 8 lakes the ratio between the observed concentration and the EQS was larger than 10 with the highest ration being 170 in Geding Sø. The nickel concentrations exceeds 2*EQS in 64 lakes and in four lakes the ratio is higher than 10. Zinc exceeds the observed / EQS ratio with a factor 2 in two-third of the lakes, i.e. 164 of the 242, of which 8 lakes exceeds a ratio of 10. The largest ratio, 195, was, as for arsenic observed in Geding Sø. For TBT, the ratio between the measured concentration and the EQS exceeds 2 in 36 lakes. In five lakes the ratio exceeds 10, with the highest values in Bagsværd Sø and Svanholm Sø having ratios of 29 and 81, respectively.

The EQS for chrome, benz[a]pyrene, fluroanthene and copper were exceeded in 3-5% of the lakes. There are no obvious differences in these relations between the four water districts.

For arsenic and copper there seems to be a difference in the average concentrations between water district 1 and 2. However, in both cases the concentration ranges are quite large with a few lakes showing high concentrations for both substances. In Byn, Geding Sø and Grov Sø, all in water district 1, sediment concentrations ≥ 100 mg As/kg have been found. In Geding Sø and Lyngsø in water district 1 copper concentrations of 6200 mg/kg and 270 mg/kg, respectively, have been found followed by Frederiksborg Slotssø and Lyngby Sø where concentrations of 240 and 800 mg/kg have been found.

In almost half of the lakes in this project, i.e. 102 of 242, three or more substances have been found in concentrations exceeding the EQS values in Table 4. There is not found obvious difference between the water districts, as about half of the lakes in both water district 1, 2 and 4 and the only lake in water district 3 meet the EQS values.

Table 6 gives an overview of these lakes, together with the substances causing the exceedance. It is obvious that arsenic, nickel, zinc and TBT are the most critical substances in this respect. In a few lakes, Geding Sø, Lyng Sø, Silkeborg Langsø, Peblinge Sø and Søllerød Sø, other substances or more than 3 substances are non-compliant. As mentioned above, arsenic and TBT are not measured in all lakes, indicating that the number of non-compliant substances in some lakes could be higher.

It should, once more, be mentioned that the conclusions on metals above, is based upon a comparison of measured total metal concentrations and EQS values expressed as added concentrations. An inclusion of natural background concentrations in Denmark would most likely alter the outcome of the comparison, at least with regards to the ratios of exceedance, but likely also the number of exceedance.

Table 6. Lake sediment. Lakes, in which the number of toxic substances exceeding EQS is at least 3. The water districts and programme types are explained above in e.g. Table 5. The substances are separated according to their level of concentrations, i.e. lower or higher than 2*EQS. [1)]Arsene is not measured [2)]TBT is not measured, [3)]Neither arsen nor TBT are measured.

Lake	Water district	Program	Substances EQS<OBS≤2*EQS	Substances OBS>2*EQS
ALMINDSØ[1)]	1	OPE	TBT	Nickel, Zinc
ARRESKOV SØ	1	CON	Arsenic, Nickel, Zinc, TBT	
AVNSØ,SILKEBORG[1)]	1	OPE	Nickel, Zinc	TBT
BORBJERG MØLLESØ[1)]	1	OPE	TBT	Nickel, Zinc
BRAHETROLLEBORG SLOTSSØ[1)]	1	OPE	Nickel, TBT	Chrome, Zinc
BRASSØ	1	CON	Nickel	Arsenic, Zinc, TBT
BRYRUP LANGSØ	1	CON		Arsenic, Nickel, Zinc, TBT
BRÆNDEGÅRD SØ[1)]	1	OPE		Nickel, Zinc, TBT
BYN	1	CON		Arsenic, Nickel, Zinc
DALLERUP SØ[1)]	1	OPE	Nickel, Zinc, TBT	
DONS NØRRESØ	1	CON	Nickel, Zinc	Arsenic
DYBVAD SØ	1	OPE	Nickel, TBT	Arsenic, Zinc
EJSTRUP SØ[1)]	1	OPE		Nickel, Zinc, TBT
ENGETVED SØ[2)]	1	OPE		Arsenic, Nickel, Zinc
ENSØ	1	CON	Nickel, Zinc, TBT	Arsenic
FJELLERUP SØ	1	CON	Arsenic, TBT	Zinc
FLYNDER SØ	1	CON	Nickel, Zinc	Arsenic
FÅRESØEN	1	CON	Nickel	Arsenic, Zinc
FÅRUP SØ	1	CON	Nickel, Zinc, TBT	Arsenic
GEDING SØ[2)]	1	OPE	Nickel	Arsenic, kobber, Zinc

GROV SØ	1	CON	Nickel, TBT	Arsenic, Zinc
GRÅSTEN SLOTSØ	1	CON	Arsenic, Nickel	Zinc
HALE SØ	1	OPE	Arsenic	Zinc, TBT
HALKÆR SØ[1)]	1	OPE	Nickel, Zinc	TBT
Hals sø[1)]	1	OPE	Nickel	Zinc, TBT
HAMPENSØ	1	CON	Nickel	Arsenic, Zinc, TBT
HINGE SØ	1	CON		Arsenic, Nickel, Zinc
HJERK NOR[1)]	1	OPE		Nickel, Zinc, TBT
HOLSTEBRO SØ/VANDKRAFT SØEN[1)]	1	OPE	TBT	Nickel, Zinc
HUMMELSØ[1)]	1	OPE	TBT	Nickel, Zinc
HVIDKILDE SØ	1	CON	Arsenic, Nickel, Zinc	
JELS OVERSØ	1	CON		Arsenic, Nickel, Zinc
KARL SØ[2)]	1	CON		Arsenic, Nickel, Zinc
KILEN	1	CON		Arsenic, Nickel, Zinc, TBT
KNUDSØ	1	CON	Nickel	Arsenic, Zinc, TBT
Kul sø[2)]	1	OPE	Arsenic, Nickel, Zinc	
KULSØ V. BRYRUP	1	CON		Arsenic, Nickel, Zinc
KULSØ VED TROLHEDE	1	CON		Arsenic, Nickel, Zinc, TBT
KÅS SØ	1	CON	Zinc	Arsenic, Nickel
LADING SØ	1	CON	Arsenic, Nickel	Zinc
LANGESØ[1)]	1	CON	Nickel	TBT
LEGIND SØ	1	CON	Nickel	Arsenic, Zinc
LUND FJORD	1	CON	Arsenic, Nickel, Zinc	
LYNGSØ	1	CON	Copper, TBT	Benz[a]pyrene, Fluoranthene, Arsenic, Chrome, Nickel, Zinc,
MADUM SØ	1	CON	Nickel	Arsenic, Zinc
MELLEMVESE	1	CON	Arsenic, Nickel, Zinc, TBT	
MOSSØ[1)]	1	OPE	Nickel, Zinc, TBT	
MUNKESØEN[1)]	1	OPE	TBT	Nickel, Zinc
NEDERSØ[2)]	1	OPE	Arsenic, Nickel	Zinc
NORDBORG SØ	1	CON	Arsenic, Nickel	Zinc
NR. SØBY SØ, ÅRSLEV[1)]	1	OPE	Nickel, Zinc	TBT
NØRHÅ SØ	1	CON	Nickel, Zinc	Arsenic, TBT
NØRRESØ, FYN	1	CON	Nickel	Arsenic, Zinc
OLDENOR[1)]	1	OPE	Nickel, Zinc	TBT
RAVNSØ	1	CON	Nickel	Zinc, TBT
RYGBJERG SØ[1)]	1	CON	Nickel, TBT	Zinc
RØDESØ[1)]	1	OPE	Nickel	Zinc, TBT
SILKEBORGLANGSØ ØST [3)]	1	OPE	Benz[a]pyrene, Fluoranthene, Nickel, Zinc	
SKØR SØ	1	CON	Nickel, Zinc, TBT	Arsenic
SLIVSØ [1)]	1	OPE	Nickel, Zinc	TBT
SNÆBUM SØ[1)]	1	OPE	Nickel	Zinc, TBT
SPØTTRUP SØ[1)]	1	OPE	Nickel, Zinc, TBT	
STEVNING DAM	1	CON	Arsenic, Nickel	Zinc
STIGSHOLMSØ	1	CON	Nickel	Arsenic, Zinc
STORE ØRESØ[1)]	1	CON	Nickel, TBT	Zinc
STORMOSE[1)]	1	OPE	TBT	Nickel, Zinc
STRANDSØ 1[1)]	1	OPE	Nickel, Zinc	TBT
SULDRUP SØ	1	CON	Arsenic	Zinc, TBT
SVANHOLM SØ[1)]	1	OPE		Nickel, Zinc, TBT
SØBY SØ, MIDTJYLLAND	1	CON		Arsenic, Nickel, Zinc
SØGÅRD SØ, JYLLAND	1	OPE		Arsenic, Nickel, Zinc
SØNDERSUND OG BYN[1)]	1	OPE	TBT	Nickel, Zinc
SØVIGSUND SØ[1)]	1	CON	TBT	Nickel, Zinc

TANG SØ[2)]	1	CON		Arsenic, Nickel, Zinc
TANGE SØ[2)]	1	OPE	Nickel	Arsenic, Zinc
TEBSTRUP SØ	1	CON	Nickel, Zinc	Arsenic
THORSØ	1	CON		Arsenic, Nickel, Zinc, TBT
TILLERUP SØ[1)]	1	CON	Nickel, Zinc	TBT
TRANEKÆR SØ[1)]	1	OPE	Nickel, Zinc, TBT	
VEDBØL SØ[2)]	1	OPE	Nickel	Arsenic, Zinc
VELLING IGELSØ	1	CON	TBT	Arsenic, Nickel, Zinc
VESSØ	1	CON	Nickel, Zinc, TBT	Arsenic
ØRNSØ[2)]	1	CON		Arsenic, Nickel, Zinc
BAGSVÆRD SØ	2	CON	Nickel	Arsenic, TBT
BASTRUP SØ[1)]	2	CON	Nickel	Zinc, TBT
FAVRHOLM SØ	2	CON	Nickel	Arsenic, TBT
FREDERIKSBORG SLOTSØ[2)]	2	OPE	Kobber, Nickel	Arsenic, Zinc
FURESØEN STORESØ	2	CON	Nickel, TBT	Arsenic, Zinc
HVIDSØ[2)]	2	OPE	Nickel	Arsenic, Zinc
KORNERUP SØ[1)]	2	OPE	Nickel, TBT	Zinc
LYNGBY SØ	2	CON	Nickel	Arsenic, Chrome, Copper, Zinc, TBT
PEBLINGESØ	2	CON	Fluoranthene	Benz[a]pyrene, Arsenic, Nickel, Zinc, TBT
ROSENGÅRD SØ[2)]	2	CON	Nickel	Arsenic, Zinc
SKT. JØRGENS SØ SYD-BASSIN	2	CON	Nickel	Arsenic, Zinc, TBT
SØLLERØD SØ[3)]	2	OPE	Benz[a]pyrene, Nickel	Zinc
VESTERBORG SØ	2	CON	Arsenic, Nickel	Zinc
ØSTRUP-GUNDSØMAGLE SØ	2	CON	Nickel	Arsenic, Zinc
HUNDSEMYR[2)]	3	OPE	Arsenic	Nickel, Zinc
HOSTRUP SØ	4	CON	Nickel, TBT	Arsenic, Zinc
RALSØEN	4	CON		Arsenic, Nickel, Zinc
STORE SØGÅRD SØ	4	CON	Arsenic	Nickel, Zinc

5.3 Comparison study in Danish streams

Data from Danish streams covered by the NOVANA program 2010-2018 was analyzed for comparison using EQS values identified as suitable in Chapter 4 (Table 3 and 4). None of the selected compounds are measured in stream biota, as only mercury is included for freshwater fish in the NOVANA program.

Like for lakes, streams are covered by a surveillance and an operational monitoring program. Data is hence presented in Table 7 and 8 according to the two sub-programs (surveillance and operational) as well as for the total data set.

Arsenic and benz[a]pyrene have been found in two and one stream, respectively, in concentrations above 2*EQS, while concentrations above EQS with respect to nickel, zink, and TBT have been found in multiple streams. In five streams, three compounds have been found in concentrations above EQS, and in one stream (Damhusåen) four compounds exceeded EQS (Table 8).

Table 7. Stream sediments. Number of observations (OBS) where measurements are lower than the suggested EQS (Table 4), higher than EQS, but lower than 2*EQS (EQS<OBS≤2*EQS) or higher than 2*EQS. The inventory is separated into water distric and program types (OPE=operational monitoring, CON=control monitoring and TOTAL data set). Furthermore, the mean concer tration in the data set is shown for each substance.

Substance	Water District	Program	OBS≤EQS	EQS<OBS≤ 2*EQS	OBS>2*EQS	Avg. Conc. mg/kg dw	Range (min-max) mg/kg dw
DEHP	1 Jylland/Fyn	CON	10	0	0	2.08	0.01-19
		OPE	34	0	0	1.021	0.1-11
		TOTAL	44	0	0	1.262	0.01-19
	2 Sjælland	CON	8	0	0	0.6975	0.01-3.8
		OPE	9	0	0	2.892	0.06-19
		TOTAL	17	0	0	1.859	0.01-19
	3 Bornholm	CON	0	0	0	-	-
		OPE	0	0	0	-	-
		TOTAL	0	0	0	-	-
Arsenic	1 Jylland/Fyn	CON	0	0	1	21.00	21-21
		OPE	0	0	0	-	-
		TOTAL	0	0	1	21.00	21-21
	2 Sjælland	CON	0	0	1	13.00	13-13
		OPE	0	0	0	-	-
		TOTAL	0	0	1	13.00	13-13
	3 Bornholm	CON	0	0	0	-	-
		OPE	0	0	0	-	-
		TOTAL	0	0	0	-	-
Chrome	1 Jylland/Fyn	CON	8	0	0	15.32	4.1-24
		OPE	7	0	0	17.66	9.3-43
		TOTAL	15	0	0	16.41	4.1-43
	2 Sjælland	CON	8	0	0	12.17	2.4-39
		OPE	2	0	0	24.00	24-24
		TOTAL	10	0	0	14.54	2.4-39
	3 Bornholm	CON	0	0	0	-	-
		OPE	0	0	0	-	-
		TOTAL	0	0	0	-	-
Copper	1 Jylland/Fyn	CON	8	0	0	22.025	2.9-60
		OPE	17	0	0	22.32	1.6-59
		TOTAL	25	0	0	22.22	1.6-60
	2 Sjælland	CON	8	0	0	29.14	1.5-170
		OPE	3	0	0	37.00	28-55
		TOTAL	11	0	0	31.28	1.5-170
	3 Bornholm	CON	0	0	0	-	-
		OPE	0	0	0	-	-
		TOTAL	0	0	0	-	-
Nickel	1 Jylland/Fyn	CON	3	1	4	20.47	7.8-39
		OPE	7	5	5	18.85	2.6-62
		TOTAL	10	6	9	19.37	2.6-62
	2 Sjælland	CON	6	2	0	8.712	1.8-23
		OPE	1	2	0	12.90	8.7-18
		TOTAL	7	4	0	9.855	1.8-23
	3 Bornholm	CON	0	0	0	-	-
		OPE	0	0	0	-	-
		TOTAL	0	0	0	-	-

Zinc	1 Jylland/Fyn	CON	1	3	4	128.37	38-250
		OPE	2	6	9	163.7	18-380
		TOTAL	3	9	13	152.4	18-380
	2 Sjælland	CON	4	2	2	132.4	1-690
		OPE	0	0	3	216.7	170-260
		TOTAL	4	2	5	155.4	1-690
	3 Bornholm	CON	0	0	0	-	-
		OPE	0	0	0	-	-
		TOTAL	0	0	0	-	-
Benz[a]pyrene	1 Jylland/Fyn	CON	6	0	0	0.094	0.005-0.26
		OPE	53	0	0	0.075	0.003-0.27
		TOTAL	59	0	0	0.07694	0.003-0.27
	2 Sjælland	CON	2	0	0	0.1325	0.045-0.22
		OPE	16	0	1	0.3687	0.0073-4.7
		TOTAL	18	0	1	0.3439	0.0073-4.7
	3 Bornholm	CON	0	0	0	-	-
		OPE	0	0	0	0.205	0.11-0.3
		TOTAL	0	0	0	0.205	0.11-0.3
Fluoranthene	1 Jylland/Fyn	CON	13	0	0	0.1193	0.006-0.56
		OPE	53	0	0	0.1379	0.006-054
		TOTAL	66	0	0	0.1342	0.006-0.56
	2 Sjælland	CON	9	0	0	0.1313	0.0035-0.46
		OPE	17	0	0	0.2218	0.018-1.5
		TOTAL	26	0	0	0.1905	0.0035-1.5
	3 Bornholm	CON	0	0	0	-	-
		OPE	0	0	0	0.325	0.2-0.45
		TOTAL	0	0	0	0.325	0.2-0.45
Tributyltin (TBT)	1 Jylland/Fyn	CON	5	5	1	0.00549	0.001-0.045
		OPE	0	0	0	-	-
		TOTAL	5	5	1	0.00549	0.001-0.045
	2 Sjælland	CON	6	2	1	0.003	0.001-0.017
		OPE	0	0	0	-	-
		TOTAL	6	2	1	0.003	0.001-0.017
	3 Bornholm	CON	0	0	0	-	-
		OPE	0	0	0	-	-
		TOTAL	0	0	0	-	-

Table 8. Streams, in which the number of substances exceeding EQS is at least 3. The water districts and programme types are explained above in e.g. Table 7. The substances are separated according to their level of exceedance of EQS, i.e. lower or higher than 2*MKK.

Vandløb (Obs.number)	Water district	Program	EQS<OBS≤2*EQS	OBS>2*EQS
Skjern Å (25000097)	1	CON	TBT	Nickel, Zinc
Skjern Å (25000097)	1	CON	0	Arsen, Nickel, Zinc
Ejstrup Bæk (25000707)	1	CON	Nickel, TBT, Zinc	0
Solkær Å (37000011)	1	CON	TBT	Nickel, Zinc
St. Vejle Å (53000011)	2	CON	Nickel, TBT	Zinc
Damhusåen (53000028)	2	CON	Nickel, TBT	Arsen, Zinc

5.4 Comparison study in Danish marine waters.

Data from the marine part of the NOVANA program 2010-2018 was analyzed using the EQS values, which were identified for such a comparison study in Chapter 4. Marine data on biota is available for all parameters with EQS values. The same is the case for sediments, except for BBP and γ-HCH.

For the non-dioxin like PCBs, i.e. PCB_6, monitoring was stopped in 2010, due to very few results above the detection limits for sediments. Therefore, no data was available in sediments after 2009. From 2010, only monitoring data for PCB #118 is available for sediments and biota. PCB#118 is a dioxin-like PCB and is hence out of the scope of this report focusing on non-dioxin-like PCBs. The group of PCBs is hence not assessed in this report with regards to sediments.

In the period 2010-2017, the marine program has not been separated in programs for surveillance and operational monitoring. Generally, data on biota has been characterized as surveillance monitoring and sediment data as operational monitoring. For that reason, the results in Table 9 and 10 are shown for the total data set, i.e. not separated in observations from surveillance and operational monitoring.

In sediment, TBT, zinc, arsenic, nickel and copper have been found in concentrations above EQS, i.e. percentages of samples with ratios OBS/EQS above 1. Only TBT had ratios above 10, i.e. as high as 2250. For metals, maximum ratios were in the range of 2-8.5. The used EQS for metals are, as discussed in Chapter 4, added concentrations, i.e. without background concentrations. As metals are naturally occurring substances, the added risk approach makes good sense. In order to get a more realistic comparison, information about background levels would need to be included. These may be defined from undisturbed sediment cores after age determination and analysis of pre-industrial segments of the sediment core.

Phthalates and nonylphenols have been measured in sediments since 2010 for DEHP and diisononylphthalate (DINP), but di(2-ethylhexyl)adipat (DEHA) was first introduced in the monitoring from 2015 and butylbenzylphtahalate (BBP) from 2017. Around Bornholm (water district 3) only sediment data from 2017 and 1028 are available. For DINP and DEHA, no EQS was found, so they are not assessed any further. From 2017, the monitoring of sediment samples was changed to include only phthalates and nonylphenols. It can furthermore be noted that although the concentrations in the North Sea samples generally are very low, the sediments are very sandy, wherefore normalization increases the concentrations significantly.

For biota, most of the data, except for one DEHP and one chrome sample, are found to be lower than the EQS (Table 10). Both samples above are found in the Jutland area. For chrome it was in a Sand gaper (*Mya arenaria*), a species living buried in the sediment and often exhibiting higher metal concentrations of particularly chrome and nickel than blue mussels. For DEHP it was in the one mussel measured for DEHP around Funen. In total, this sums up to less than 1% of samples exceeding the biota EQS. Data on PCB_6 are still measured in fish muscle, and for one time-trend station in liver. Measurements in mussels was stopped due to many "less than" values in 2011. The EQS is shown for all three matrices in table 10. Only measurements in fish liver occasionally (6 out of 209 samples) exceeds the EQS, as all samples with fish muscle and mussels had measured concentrations below the EQS (Table 10).

Table 9. Results for marine sediment samples from 2010-2018, with available sampling years indicated in brackets. Number of observations (OBS) where measurements are lower than the EQS (Table 4), higher than EQS, but lower than 2*EQS (EQS<OBS≤2*EQS) or higher than 2*EQS.

Substance (period)	Water district	OBS≤EQS	EQS<OBS≤2*EQS	OBS>2*EQS	Avg. Conc. mg/kg dw	Range (min-max) mg/kg dw
Arsenic	Jylland/Fyn	29	31	92	8.1	<DL-25.1
(2010-2016)	Sjælland	28	12	24	3.0	<DL-16.5
	Bornholm	n.m.**	n.m.	n.m.	n.m.	n.m.
	Vidå/Kruså	0	4	9	9.9	3.9-22
Chrome	Jylland/Fyn	153	0	0	32.2	<DL-92
(2010-2016)	Sjælland	60	0	0	15.9	<DL-64
	Bornholm	n.m.	n.m.	n.m.	n.m.	n.m.
	Vidå/Kruså	13	0	0	41.1	9,8-70
Nikkel	Jylland/Fyn	74	26	54	16.46	<DL-62
(2010-2016)	Sjælland	49	5	9	7.6	<DL-36
	Bornholm	n.m.	n.m.	n.m.	n.m.	n.m.
	Vidå/Kruså	6	2	6	17.3	2.7-35
Copper	Jylland/Fyn	155	3	1	17.1	<DL-138
(2010-2016)	Sjælland	60	3	0	10.4	<DL-97
	Bornholm	n.m.	n.m.	n.m.	n.m.	n.m.
	Vidå/Kruså	13	0	0	12.8	1.2-38
Zinc	Jylland/Fyn	60	28	67	87.6	<DL-312
(2010-2016)	Sjælland	34	9	20	48.5	<DL-315
	Bornholm	n.m.	n.m.	n.m.	n.m.	n.m.
	Vidå/Kruså	3	5	5	89.8	12-203
DEHP	Jylland/Fyn	186	0	0	0.14	<DL-1.6
(2010-2018)	Sjælland	75	0	0	0.08	<DL-1.1
	Bornholm	6	0	0	0.14*	0.02-0.24
	Vidå/Kruså	19	0	0	0.06	<DL-0.14
BBP	Jylland/Fyn	33	0	0	0.0024	0.001-0.013
(2017-2018)	Sjælland	13	0	0	0.0033	0.001-0.017
	Bornholm	4	n.m.	n.m.	0.0031	0.003-0.004
	Vidå/Kruså	8	0	0	0.0010	0.001-0.001
Benz(a)Pyrene	Jylland/Fyn	124	0	0	0.07	<DL-0.56
(2010-2015)	Sjælland	57	0	0	0.10	<DL-0.85
	Bornholm	n.m.	n.m.	n.m.	n.m.	n.m.
	Vidå/Kruså	9	0	0	0.06	0.0005-0.16
Fluoranthene	Jylland/Fyn	151	0	0	0.10	<DL-0.75
(2010-2016)	Sjælland	63	0	0	0.09	<DL-0.68
	Bornholm	n.m.	n.m.	n.m.	n.m.	n.m.
	Vidå/Kruså	13	0	0	0.07	0.004-0.24
Tribultyltin (TBT)	Jylland/Fyn	25	55	81	0.041	<DL-3.6
(2010-2016)	Sjælland	8	18	29	0.009	<DL-0.05
	Bornholm	n.m.	n.m.	n.m.	n.m.	n.m.
	Vidå/Kruså	4	4	4	0.004	<DL-0.01

* DL = Detection limits; ** n.m.=no measurements

Table 10. Results for marine biota samples 2010-2018. Number of observations (OBS) where measurements are lower than the EQS (Table 4), higher than EQS, but lower than 2*EQS (EQS<OBS≤2*EQS) or higher than 2*EQS.

Substance	Water districts	OBS≤EQS	EQS<OBS≤2*EQS	OBS>2*EQS	Avg. Conc.	Range (min-max) μg/kg ww
					μg/kg ww	
Chrome	Jylland/Fyn	320	1	0	226	16-5856
	Sjælland	201	0	0	157	16-1285
	Bornholm	9	0	0	360	109-835
	Vidå/Kruså	1	0	0	141	-
DEHP	Jylland/Fyn	0	1	0	5.1	-
	Sjælland	n.m.*	n.m.	n.m.	n.m.	n.m.
	Bornholm	n.m.	n.m.	n.m.	n.m.	n.m.
	Vidå/Kruså	n.m.	n.m.	n.m.	n.m.	n.m.
γ HCH	Jylland/Fyn	102	0	0	0.16	0.01-0.56
	Sjælland	170	0	0	0.18	0.01-1.1
	Bornholm	n.m.	n.m.	n.m.	n.m.	n.m.
	Vidå/Kruså	n.m.	n.m.	n.m.	n.m.	n.m.
Tributyltin (TBT)	Jylland/Fyn	216	13	6	6.4	0.4-102
	Sjælland	119	0	0	2.6	0.7-8.1
	Bornholm	12	0	0	1.8	0.5-2.4
	Vidå/Kruså	1	0	0	2.4	-
PCB_6 ** Fish liver (1998-2016)	Jylland/Fyn	139	2	2	9.8	<0.4-198
	Sjælland	70	1	1	14.2	<0.3-198
	Bornholm	n.m.	n.m.	n.m.	n.m.	n.m.
	Vidå/Kruså	n.m.	n.m.	n.m.	n.m.	n.m.
PCB_6 Fish muscle (1998-2018)	Jylland/Fyn	33	0	0	1.8	0.2-8.4
	Sjælland	20	0	0	1.6	0.4-6.9
	Bornholm	n.m.	n.m.	n.m.	n.m.	n.m.
	Vidå/Kruså	n.m.	n.m.	n.m.	n.m.	n.m.
PCB_6 mussels (1998-2011)	Jylland/Fyn	2226	0	0	0.34	0.03-1.68
	Sjælland	230	0	0	0.36	0.06-2.98
	Bornholm	1	0	0	0.12	-
	Vidå/Kruså	5	0	0	0.43	0.32-0.57

* n.m.=no measurements ** PCB_6 =sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180

6. Summary and conclusions

Based upon international environmental quality standards (EQS) and Danish monitoring data, the main objective of this report has been to compare monitoring data with EQS originating from Norway, Sweden and The Netherlands for 14 hazardous substances found in sediment and biota in Denmark. To obtain the most useful EQS values for such a comparison study, EQS found in Norway, Sweden and The Netherlands were identified and evaluated according to what extent they were derived by following the recommendation and guidance laid down by the EU in support of the Water Frame Directive.

For phthalates, no EQS could be identified for DEHA and DEHP, whereas useful EQS from The Netherlands and Norway were identified for DEHP and BBP. Regarding metals, it was concluded that the sediment EQS from The Netherlands were relative old and consequently not in agreement with the current recommendations for derivation of EQS. Sweden only had a few available EQS whereas Norway has EQS for all the investigated metals. These are all derived as EQS including the natural background concentration relevant for Norwegian situations. Denmark has not established such natural background concentrations in freshwater and marine sediments for all metals. The Norwegian EQS values for metals used for the comparison study in this report are hence excluding background concentrations, i.e. EQS subtracted the background concentration, which is also named EQS_{added}, as it refers to the fraction of the total concentration added by anthropogenic activities. The comparison of EQS_{added} with monitoring data presented as total sediment concentrations can hence be considered a worst-case consideration. For other organic pollutants, the Norwegian EQS has generally been adopted for use in this report, as they in large are in line with the EU recommendations for derivation of EQS. An exception is tributyltin (TBT) in sediment, where the Swedish EQS has been chosen as it is based upon ecotoxicological data for sediment dwellers in contrast to the Norwegian EQS where extrapolation from aquatic pelagic species have been made. Chapter 4 outline all the details in the discussions regarding EQS including an evaluation of whether the Norwegian, Swedish and Dutch EQS are suitable for being used in a Danish context.

The comparison of the suitable EQS with Danish monitoring data for sediment in freshwater streams and lakes as well as marine waters and biota in marine waters revealed that except for TBT, concentrations found in biota were generally below the EQS. For TBT approximately 5% of the biota samples had concentrations higher than the EQS. The situation was somehow similar for sediments in Danish streams where the vast majority of substances were measured in concentrations lower than EQS in (almost) all samples. However, in six Danish streams the sediment concentrations of at least three substances (arsenic, nickel and zinc or TBT) were found to exceed the EQS. The metal most frequently exceeding the EQS is zinc, as for example 22 of 25 sediment samples collected in streams from Jylland / Fyn exceeded the EQS. In the other water districts, no exceedance have been observed. In district Sjælland, the same comparison sums up to 64%. The same comparisons for nickel result in exceedance fractions of 60 and 36% for Jylland / Fyn and Sjælland, respectively.

For lake sediments, it is the same trend. More than 80% of the samples exceeded the suitable EQS for zinc in Jylland, and more than 90% in Sjælland.

For nickel, the same comparisons identified 68 and 59% of lakes in Jylland / Fyn and Sjælland with monitored concentrations exceeding EQS. Arsenic has been investigated in fewer lakes, but in water district 1 and 2, more than 80% of the sediment samples had arsenic concentration exceeding the EQS. In approximately 50 and 40% of the lake sediments in Sjælland / Fyn and Sjælland, respectively, the TBT concentration exceeded the EQS. All other substances were with a few exemptions found in lower concentrations than the suitable EQS.

For marine sediments, the average concentrations were generally lower. Nevertheless, a high number of samples has been found to exceed the EQS for arsenic and TBT. The concentration of arsenic was higher than EQS in 57 and 76% of all samples in Jylland / Fyn without taking natural background into account.

The comparisons for metals are made without any consideration about natural background concentrations. According to the water framework directive background concentrations can be taken into consideration in cases where monitoring data in sediment exceeds the EQS. There is not yet established natural background concentrations for metals in Danish sediments, but it is very likely that if including these in the assessment, the outcome will change. However, the ratio between the average concentration in streams and the EQS for zinc and nickel in for example Jylland / Fyn is approximately 3, and for lake sediments it is even higher. For arsenic the ratio in lake sediment for example is approaching 7 and in the operational monitoring program it is as high as 20. It is hence by no means certain that an inclusion of natural background concentrations would result in no exceedance for sediments in streams and lakes, whereas it is more likely to influence the outcome for marine sediments markedly, as the ratio between measured total concentrations and EQS are lower.

In short, the concentrations found in Danish biota samples are with the exemption of TBT, generally found to be below EQS values derived according to international standards, whereas sediment samples frequently have been shown to exceed the EQS for metals, especially zinc, nickel and arsenic. Inclusion of natural background concentration of metals is, however, essential to conclude on the status of the observed environmental concentrations in Danish sediments.

7. References

ACES. 2018. Tributyltin – TBT. Sediment EQS Derivation. ACES report 29. Sara Sahlin, Marlene Ågerstrand. Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Sweden.

Crommentuijn T, Kalf DF, Polder MD, Posthumus R, van de Plassche EJ. 1997. Maximum Permissible Concentrations and Neglible Concentrations for pesticides. RIVM Report 601501 002.

Crommentuijn, T., Polder, M.D. and van der Plassche, E.J. 1997. Maximum permissible concentrations and negligible concentrations for metals, taking background concentrations into account. RIVM report 601501 001.

de Deckere, E., De Cooman, W., Leloup, V., Meire, P., Schmitt, C., & Peter, C. (2011). Development of sediment quality guidelines for freshwater ecosystems. *Journal of soils and sediments*, *11*(3), 504-517.

Duft, M. , Schulte-Oehlmann, U. , Tillmann, M. , Markert, B. and Oehlmann, J. (2003), Toxicity of triphenyltin and tributyltin to the freshwater mud snail *Potamopyrgus antipodarum* in a new sediment biotest. Environmental Toxicology and Chemistry 22: 145-152. doi:10.1002/etc.5620220119

EU 2003. European Union Risk Assessment Report, 1,2-Benzenedicarboxylic acid, Di-C8-C10 branched alkyl esters, C9-rich and di-"isononyl" phthalate (DINP). European Commission, 2003.

EU 2005. Common Implementation Strategy for the Water Framework Directive, Environmental Quality Standard (EQS) Substance Data Sheet, Priority Substance no. 18, Hexachlorocyclohexanes (incl. Lindane), 2005.

EU 2005. EQS dossier, TBT. Environmental quality standards (EQS) substance data sheet. Priority substance NO. 30. Tributyl compounds (TBT-ion) CAS no 688-73-3, 36643-28-4. EU dossier.

EU 2005. European Union Risk Assessment Report. Chromium trioxide, sodium chromate, sodium dichromate, ammonium dichromate, potassium dichromate. Volume 53. EUR 21508 EN, JRC, 2005.

EU 2007. European Risk Assessment Report. Benzyl butyl phthalate (BBP). EUR 22773. EN ISSN 1018-5593. Luxembourg: Office for Official Publications of the European Communities, 2007. © European Communities, 2007.

EU 2008. European Risk Assessment Report. Di-2-ethylhexyl phthalate (DEHP). EUR 23384 EN. ISSN 1018-5593. Luxembourg: Office for Official Publications of the European Communities, 2008. © European Communities, 2008

EU 2008. European Risk Assessment Report. Nickel.

EU 2008. Voluntary risk assessement of copper, copper II sulphate pentahydrate, copper(I)oxide, copper(II)oxide, dicopper chloride trihydroxide.- VOLUNTARY RISK ASSESSMENT.

EU 2010. European Union Risk Assessment Report. Zinc metal. EUR 24587 EN 2010.

EU 2011. EU EQS dossier, 5,6-ring PAH. Common Implementation Strategy for the Water Framework Directive, Environmental Quality Standard (EQS) Substance Data Sheet, Priority Substance no. 28, 5-6 ring polyaromatic hydrocarbons, 2011.

EU 2011. EU EQS dossier, Fluoranten. Common Implementation Strategy for the Water Framework Directive, Environmental Quality Standard (EQS) Substance Data Sheet, Priority Substance no. 15, Fluoranthene, 2011.

EU 2011. Technical Guidance for Deriving Environmental Quality Stanmdards. Common Implememtation Strategy for the Water Framework Directive (200/60/EC). Guidance Document No. 27. European commission.

Hansler RJ, Fleuren RHLJ, Heugens EHW, Janssen PJCM, Posthumus R, Smit CE. 2007. Indicatieve milieukwaliteitsnormen 2005-2006. Overzicht van in 2005 en 2006 door het RIVM afgeleide indicatieve milieukwaliteitsnormen voor stiffen. RIVM Report 601570001/2007.

HELCOM (2018). PCBs, dioxins and furans. HELCOM core indicator report. Online. ISSN 2343-2543

HVMFS. 2013. Havs- och vattenmyndighetens föreskrifter om klassificering och miljökvalitetsnormer avseende ytvatten. HVMFS 2013:19.

Kalf DF, Crommentuijn T, Posthumus R, van de Plassche EJ. 1995. Integrated Environmental Quality Objective for Polycyclic Aromatic Hydrocarbons (PAHs). RIVM Report 679101 018.

Larsen, M.M. & Strand, J. 2018. Værktøj til håndtering og behandling af data for miljøfarlige forurenende stoffer. Aarhus Universitet, DCE – Nationalt Center for Miljø og Energi, 42 s. - Teknisk rapport nr. 127

Miljødirektoratet 2014. Kvalitetssikring av miljøkvalitetsstandarder Quality assurance of environmental quality standards. Report M-241.

Miljødirektoratet 2016. Grenseverdier for klassifisering av vann, sediment og biota - Quality standards for water, sediment and biota. Report M-608.

Miljøstyrelsen, DCE-Nationalt Center for Miljø og Energi ved Aarhus Universitet samt GEUS – De Nationale Geologiske Undersøgelser for Danmark og Grønland (2017) NOVANA Det nationale program for overvågning ag vandmiljøet og naturen 2017-2021. Programbeskrivelse

Miljø- og Fødevareministeriet (2017) Bekendtgørelsen nr. 1625 om fastlæggelse af miljømål for vandløb, søer, overgangsvande, kystvande og grundvand af 19. december 2017

Naturvådsverket. 2008. Förslag till gränsvärden för särskilda förorenande ämnen. Stöd till vattenmyndigheterna vid statusklassificering och fastställande av MKN. Report No. 5799. ISBN 978-91-620-5799-2.pdf.

Naturstyrelsen, Danmark Miljøundersøgelser, Aarhus Universitet, De Nationale Geologiske Undersøgelser for Danmark og Grønland (2011) NOVANA Det nationale program for overvågning af vandmiljøet og naturen 2011-2015. Programbeskrivelse 2. del

OSPAR 2006. Agreement on Background Concentrations for Contaminants in Seawater, Biota and Sediment. OSPAR Agreement 2005-6 Revised by ASMO 2006 (ASMO 2006 Summary Record ASMO 06/12/01).

RIVM (2001). Baars A.J., Theelen R.M.C., Janssen P.J.C.M., Hesse J.M., van Apeldoom M.E., Meijerink M.C.M., Verdam L. and Zeilmaker M.J. (2001). Re-evaluation of human-toxicological maximum permissible risk levels. RIVM report 711701 025. RIVM, Bilthoven. March 2001.

APPENDIX A

Table A. Assessment criteria

Year of publication
Was the principles of TDG#27 used?
Was improvements/updates to TDG#27 (March 2018) used?
PNEC from EU risk assessments used?
What and why was the AF used?
What was the key tox study used – CRED or Klimish?
Which species was used in the study?
Was higher tier SSD or cosm testing tox values used?
Was an added risk model used for metals?
What type of sediment was used in the test?
What is the protection aim (multifunctional, hum or eco)?
Any country specific aspects driving the EQS?
What is the legal status (binding or guidance) of the EQS in the country (up for review?)
Is the EQS recalculated from freshwater (EqP modelling)?
Is there a differentiation between sediment and freshwater EQS (e.g. for DEHP)?
How reliable is the PNEC (1-3)? (1= fully reliable according to TGD#27, 2= reliable as few deviations to TGD#27, 3= not reliable as a new derivation according to TGD#27 is like to result in markedly different result)
How relevant for DK is the PNEC (1-3)? (1= fully relevant, 2= somehow relevant, 3= not relevant as national aspects, e.g. background concentrations, are driving the derivation)

[Blank page]

ASSESSMENT OF HAZARDOUS SUBSTANCES IN DANISH SEDIMENT AND BIOTA ACCORDING TO NORWEGIAN, SWEDISH AND DUTCH QUALITY STANDARDS

This report compares monitoring data in sediment and biota for 14 hazardous substances found in Denmark with quality standards (EQS) used in Sweden, Norway and the Netherlands. Firstly, the Swedish, Norwegian and Dutch EQSs were assessed according to transparency in derivation and usability in assessment of the status in Danish surface water bodies. When comparing with the identified usable EQS the concentrations found in Danish biota samples are with the exemption of TBT, generally below the used EQS values, whereas sediment samples frequently are found in concentrations that exceed the EQS for metals, especially zinc, nickel and arsenic. However, the comparisons for metals are without considering natural background concentrations, as these have not been stablished for Danish sediments. Firm conclusions regarding the status of the observed concentrations of metals in Danish sediment samples therefore await the identification of such background concentrations.

ISBN: 978-87-7156-415-0
ISSN: 2245-019X