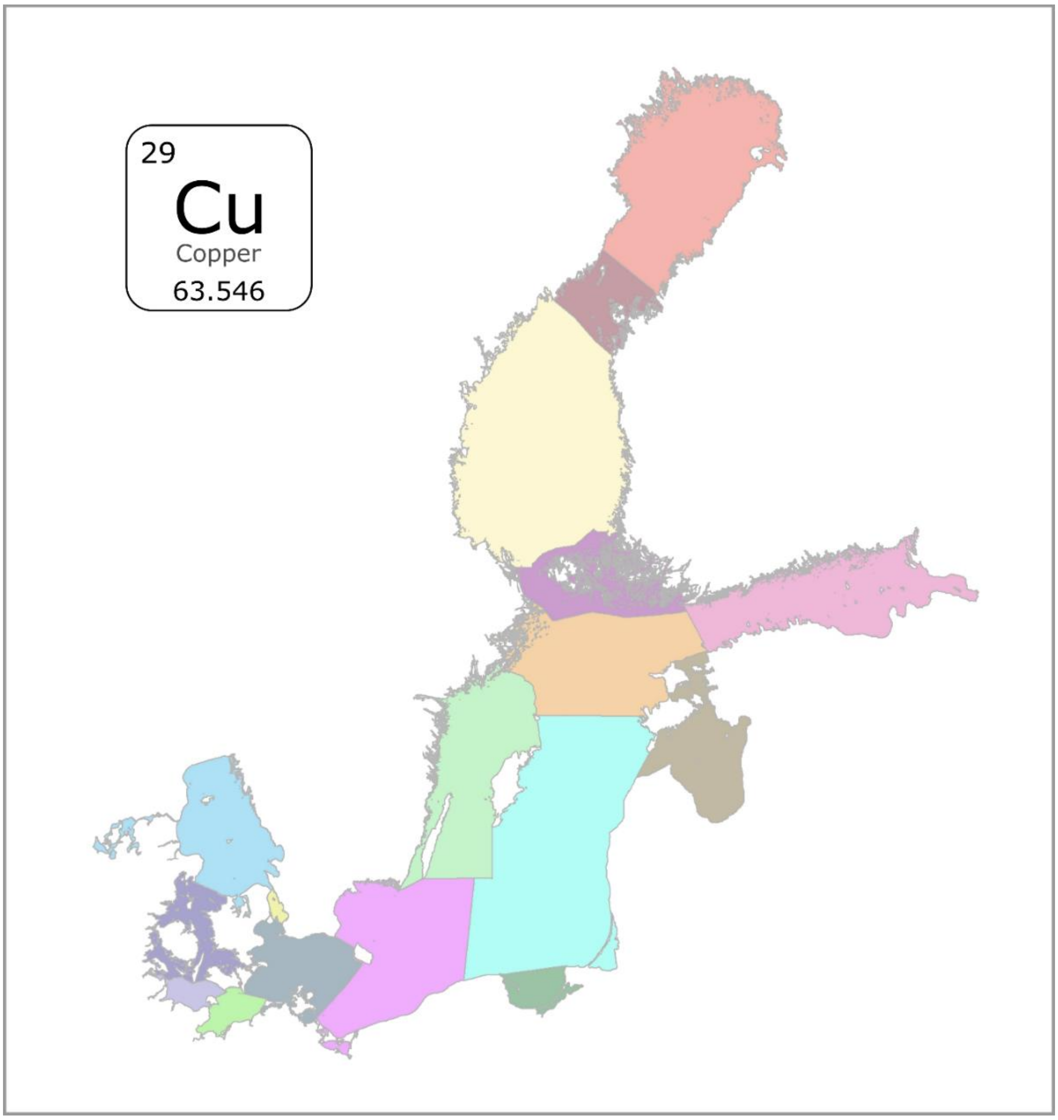
Copper as a HELCOM core indicator

Part 1: Sources, environmental concentrations and state assessments in the Baltic Sea

Part 2: EQS derivation for copper in sediment



Maria Lagerström, Anna Lunde Hermansson and Erik Ytreberg

Department of Mechanics and Maritime Sciences, Chalmers University of Technology, SE 412 96 Gothenburg, Sweden

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INTRODUCTION

Copper is an essential element for organisms but may also be toxic to most species when concentrations exceed levels that are physiologically required. The bioavailability of copper in freshwater, estuarine and marine waters is governed by the free ion concentration, as predicted by the free ion activity model (FIAM) (Campbell, 1994; Brown and Markich, 2000). Although current water quality criteria (WQC) and environmental quality standards (EQS) are based on total dissolved concentrations, there are ongoing attempts to incorporate metal speciation into WQC via the biotic ligand model (BLM). The BLM is derived from the FIAM and takes into consideration the properties of the water in terms of dissolved organic carbon (DOC), hardness and pH to account for the competition between cations for the biotic ligand (e.g. fish gill or algal cell membrane). The BLM is currently in use to assess the state of freshwater bodies in the EU, e.g. in Sweden (Swedish Agency for Marine and Water Management, 2019), but so far, no validated models are in use for the marine environment. Instead, the EU copper Voluntary Risk Assessment Report (VRAR-Cu) recommend that a marine EQS value based on total dissolved copper concentrations (normalized to ambient DOC concentration) shall be used (European Copper Institute, 2008). The VRAR-Cu report did however not consider marine sediments.

In north Atlantic surface waters, dissolved copper concentrations are rather constant and on average 0.075 µg/L (Pohl et al., 1993). In the Baltic Sea, concentrations are significantly higher, about 0.6 µg/L (Pohl and Hennings, 2005), mainly due to the low water exchange capacity of the Baltic Sea and a larger input of copper from both natural and anthropogenic sources. Elevated aquatic copper concentrations have also been reported from Baltic water bodies with high anthropogenic loads, e.g. in marinas (Kylin and Haglund, 2010; Lagerström et al., 2020) and commercial harbours (Fathollahzadeh et al., 2014). Copper concentrations in surface seawater, sediment and biota are actively monitored in the Baltic Sea, but the monitoring programs, EQS threshold values, and the status assessment under the Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD) differ between the HELCOM contracting parties. Hence, there is a need to harmonize the work within HELCOM regarding how the environmental monitoring is conducted and what EQS (threshold values) to use in the status assessment of the different matrices (surface seawater, sediment and biota).

Aims and report structure

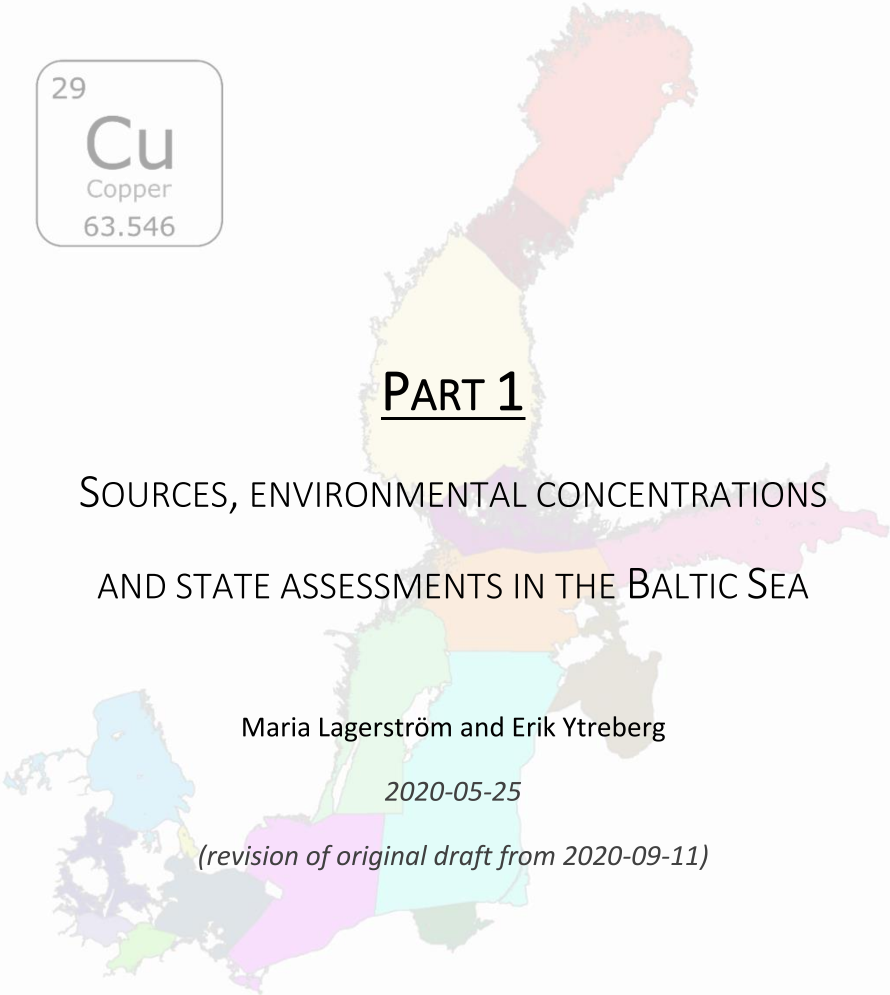
The overall aim of this report was to propose a harmonized threshold value for copper in sediments for the Baltic Sea region and assess how the implementation of the threshold value will affect the status classification of copper in different Baltic subbasins. An additional aim was to compile the EQS values (threshold values) currently in use by different HELCOM contracting parties and to summarize anthropogenic and natural sources of copper to the Baltic Sea. The report comprises of two parts. The first part focuses on sources of copper, environmental concentrations and state assessments in the Baltic Sea. During the drafting of the first part of the report, we received an additional assignment by the Swedish Agency for Marine and Water Management to organize a series of workshops with the aim to propose a harmonized approach for the derivation of an EQS for copper in marine sediments. Thus, three workshops were organised in March to April 2021 with experts representing academia, industry, consulting agencies and governmental authorities to discuss how bioavailability, natural background and ecotoxicological data should be treated when deriving an EQS for copper in marine sediments. The results and outcome from these workshops are described in part 2 of this report, where we also propose a harmonized threshold value for copper in sediments for the Baltic Sea region.

The specific aims of the first part of this report was to:

1. Summarize anthropogenic and natural sources of copper to the Baltic Sea.
2. Compile existing monitoring data of copper in surface seawater, sediment and biota and to investigate for potential time trends.
3. Summarize EQS values (threshold values) used by different HELCOM contracting parties in their status assessment of copper in surface water, sediment and biota.
4. Analyse how the copper concentrations in the different matrices relate to the EQS values currently in use by the HELCOM contracting parties.
5. Compile the countries' status classifications of coastal surface waters and sediments under the WFD, with regard to copper.

The specific aims of the second part of this report was to:

1. Summarize the main outcome from the workshops regarding how to derive an EQS-value for copper in marine sediments.
2. Propose a harmonized EQS value for copper in sediments for the Baltic Sea region.
3. Assess how the concentrations of copper in sediment in different HELCOM subbasins compare to the proposed EQS value.



PART 1

SOURCES, ENVIRONMENTAL CONCENTRATIONS AND STATE ASSESSMENTS IN THE BALTIC SEA

Maria Lagerström and Erik Ytreberg

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(revision of original draft from 2020-09-11)

1.1 SOURCES OF COPPER TO THE BALTIC SEA

The sources of copper to the aquatic environment can be either anthropogenic (e.g. mining activities, use as pesticide/biocide and wastewater treatment plants) or natural (e.g. weathering of rocks and windblown dust). The waterborne inputs of copper to the Baltic Sea have been compiled in the HELCOM PLC-5 report (HELCOM, 2011). However, due to shortcomings in national monitoring program and lack of proper laboratory equipment, some knowledge gaps exist. For example, no data have been reported from Denmark. Despite the lack of data, the total annual input (in 2006) of copper from riverine sources has been estimated to be 886 tonnes (**Table 1**). Emissions where highest from Sweden (239 tonnes), followed by Russia (184 tonnes) and Poland (142 tonnes). The copper load was highest in the Baltic sub-regions Gulf of Finland (290 tonnes) and Baltic Proper (201 tonnes).

Table 1. *Waterborne copper inputs (in tonnes) to the Baltic Sea in 2006 by country and sub-region. Data from HELCOM (2011).*

Country	inputs (tonnes)	Sub-region	inputs (tonnes)
Denmark	n/a	Archipelago Sea	12.61
Estonia	110.41	Baltic Proper	200.62
Finland	127.94	Bothnian Bay	136.74
Germany	8.03	Bothnian Sea	106.03
Latvia	74.70	Gulf of Finland	290.31
Lithuania	0.14	Gulf of Riga	92.35
Poland	141.76	Kattegat	39.79
Russia	184.39	Sound	2.83
Sweden	238.90	Western Baltic	5.00
Total	886.3	Total	886.3

No further information about the magnitude of the different natural and anthropogenic sources is presented in the HELCOM document. However, for Sweden, high resolution data is available for different diffusive sources (

Table 2) and point sources (**Table 3**) per Baltic Sea river basin district (Ejhed et al., 2011; Hansson et al., 2012). Note however that the inputs of these sources are expressed as loads per river basin district, and not net inputs to the Baltic Sea. Thus, it is unknown in what extent these loads of copper is reaching the Baltic Sea. Nonetheless, the results show forest, stormwater and agriculture to be the main diffusive source of copper to the Baltic Sea river basin districts. For point sources, industry facilities under the European Pollutant Release and Transfer Register (E-PRTR) emitted the highest load of copper. Inputs of copper in higher resolution (i.e. per emission sources) from other HELCOM Contracting Parties were not accessible.

Atmospheric deposition data on the Baltic Sea was not available and are hence not included in the current copper load compilation.

Table 2. *Gross inputs (kg/year) of copper per diffusive source and river basin district. Processed data from Hansson et al., 2012.*

Gross load, Kg Cu/year	Storm-water	Agri-culture	Forest	Other land				Depos-ition on water	Local on-site wastewater treatment	M-WWTP not E-PRTR	Industries not E-PRTR	Total diffusive sources
				Moun-tain	Mire	Unfor-ested	Oth-er					
Bothnian Bay	3,800	1,400	13,000	6,700	2,100	570	590	3,200	150	580	120	32,000
Bothnian Sea	6,300	2,900	13,000	2,800	1,400	930	520	3,300	390	940	180	33,000
Northern Baltic	7,200	4,100	2,800		89	140	1,100	1,400	510	870	140	18,000
Southern Baltic	7,800	8,100	3,800		120	170	1,500	1,200	570	2,000	160	26,000
Skagerrak and Kattegat	13,000	14,000	17,000	230	1,400	670	3,100	5,200	930	1,200	440	57,000
Total	**38,000**	**30,000**	**49,000**	**9,700**	**5,100**	**2,500**	**6,800**	**14,000**	**2,500**	**5,500**	**1000**	**160,000**

Table 3. *Gross input (kg/year) of copper to Swedish river basin districts, per point source and river basin district. Processed data from Ejhed et al., 2011.*

Gross load, Kg Cu/year	Municipal wastewater treatment plants, E-PRTR	Industry, E-PRTS	Total point sources
Bothnian Bay	434	2,322	2,756
Bothnian Sea	926	13,887	14,813
Northern Baltic	2,804	1,082	3,886
Southern Baltic	2,830	805	3,635
Skagerrak and Kattegat	4,229	3,326	7,555
Total	11,224	21,422	32,646

Another large source of copper to the Baltic Sea, that is not included in the HELCOM or Swedish load compilation is the shipping and leisure boat sector. Copper is currently the main biocide (often included as cuprous oxide or copper thiocyanate) in antifouling paints used on ships and leisure boats (Amara et al., 2018). Other sources of copper from shipping include emissions of greywater (i.e. drainage from dishwater, shower, laundry bath and washbasin drains), sewage, bilge water and scrubber discharge water. In **Figure 1**, the total volume of bilge water, greywater, sewage and scrubber water discharged to the Baltic Sea in 2018 is presented (Jalkanen and Johansson, 2019).

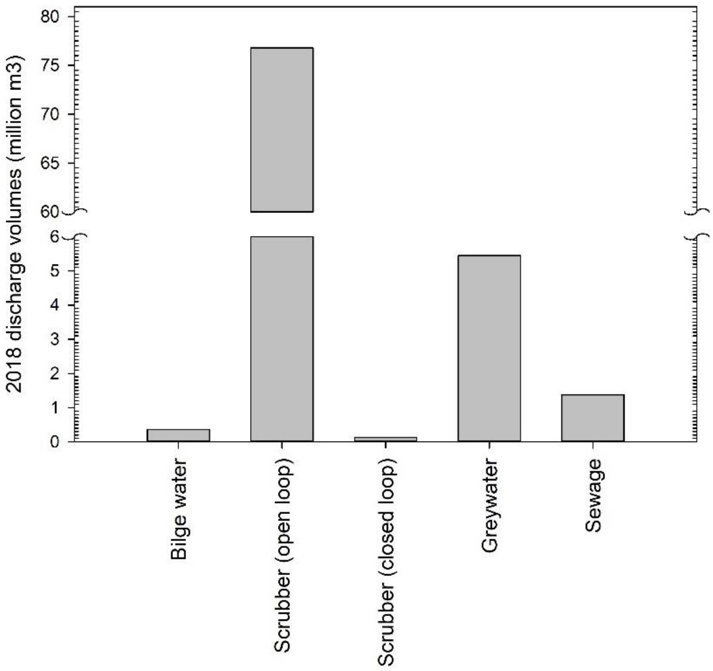


Figure 1. *2018 discharge volumes of bilge water, scrubber water, greywater and sewage from Baltic shipping in million m^3.*

The discharged volumes were multiplied with the average concentration of copper to calculate yearly loads of copper from Baltic shipping. The average concentration of copper in the respective waste stream was obtained from an extensive literature review (Jalkanen et al., 2020). As shown in **Figure 2**, the largest source of copper from Baltic shipping is the use of copper-based antifouling paints which is estimated to be 366 tonnes annually. Antifouling paints on leisure boats is also a significant source of copper and amount to 57 tons annually (based on leisure boat activity data for 2014) (Johansson et al., 2020). In total, the load of copper from the shipping and leisure boat sector was calculated to 428 tonnes annually.

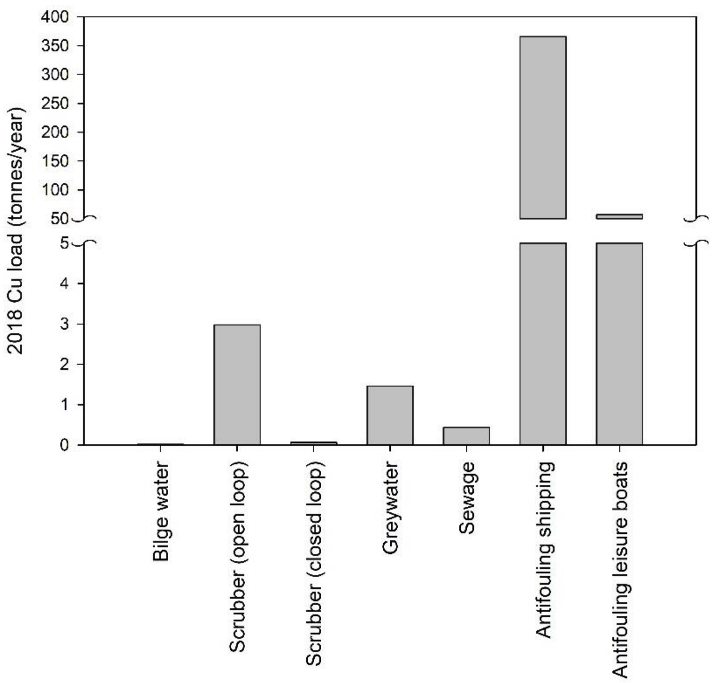


Figure 2. *Total load of copper from Baltic shipping and Baltic leisure boating during 2018 in tonnes.*

1.2 COPPER CONCENTRATIONS IN VARIOUS MATRICES IN THE BALTIC SEA

1.2.1 SURFACE SEAWATER

1.2.1.1 Data collection

Seawater data was collected from the ICES DOME (Marine Environment) data portal (ICES, 2020). The following procedure was used to treat and filter the data:

- The units of the reported concentrations were harmonized to µg/L
- Several samples from Germany with concentrations >10,000 and reported units of µg/kg were suspected of being sediment or biota samples. These were therefore excluded.
- Some 30-40 sampling points reported with extremely low concentrations (<0.01 µg/L) from Poland in 2015 (station SWIZP) due to suspected of reporting error.
- Data reported as < LOD or < LOQ were set to LOD/2 or LOQ/2, respectively. If LOD or LOQ was not specified, the data point was removed.
- Only samples with a specified pre-treatment method involving filtration through a 0.45 µm filter were included.
- Samples were labelled as either "BF" (before filtration), "AF" (after filtration) or "WT" (Water). As the aim was to map dissolved concentrations, all measurement corresponding to unfiltered samples (labelled "BF") were excluded.
- Only samples with specified sampling depth within 0-2 m of the surface were included.

Out of the 2,215 data points in the ICES data portal, 1,012 remained after data filtering according to the outlined criteria.

Only data from Estonia, Lithuania, Germany and Poland have been reported into the ICES data portal. Attempts to retrieve additional data were therefore carried out. A large dataset (1,091 data points from https://itameri.fi/) with concentrations of copper in seawater in Finland was found but could not be included as water samples were reported as unfiltered. Additionally, a large dataset was downloaded from the IOW database ODIN 2 (1,427 data points) but could not be included as sampling depths were all ≥ 11 m. A literature search was conducted, particularly aimed at finding more data from sampling stations in the main and Northern parts of the Baltic Sea but was unfortunately not fruitful.

Although concentrations of dissolved copper are measured in several Swedish coastal water bodies for their status assessment, only the average measured concentration for a given water body is available through the WISS (Water Information System Sweden) database (WISS, 2020). Hence, data from WISS could not be used in the compilation of individual data points in surface seawater or sediment. The data from WISS is instead used in section 1.6 to evaluate the status classifications of Swedish coastal surface waters and sediments in the Baltic Sea.

1.2.1.2 Measured concentrations

The sampling locations of the 1,048 surface seawater concentrations (≤ 2 m depth) included in the analysis are shown on the map in **Figure 3**. Most samples are from coastal locations with a limited number of measurements from the open sea. The number of data points per subbasin are displayed in **Table 4**. Data was only obtained for 6 out of 17 subbasins. No data was obtained for the Northern Baltic Sea subbasins (e.g. Bothnian Bay, Bothnian Sea, Åland Sea or Northern Baltic Proper). The two subbasins of Bornholm Basin (405 data points) and the Eastern Gotland Basin (229 data points), were by far the ones with the most data and represent together roughly 60 % of the dataset.

As seen in **Figure 3**, data was available for all years between 2006 and 2018, with the majority of data points in the 0.1 – 10 µg/L range. The average concentration per subbasin ranges from 0.5 to 3.6 µg/L with a Baltic Sea average at 2.4 µg/L. A few data points have been reported in the very high range of 10 – 100 µg/L range. Whether these concentrations were in fact correctly reported can be questioned. As discussed in the next section, it appears that some entries into the ICES data portal have been entered incorrectly.

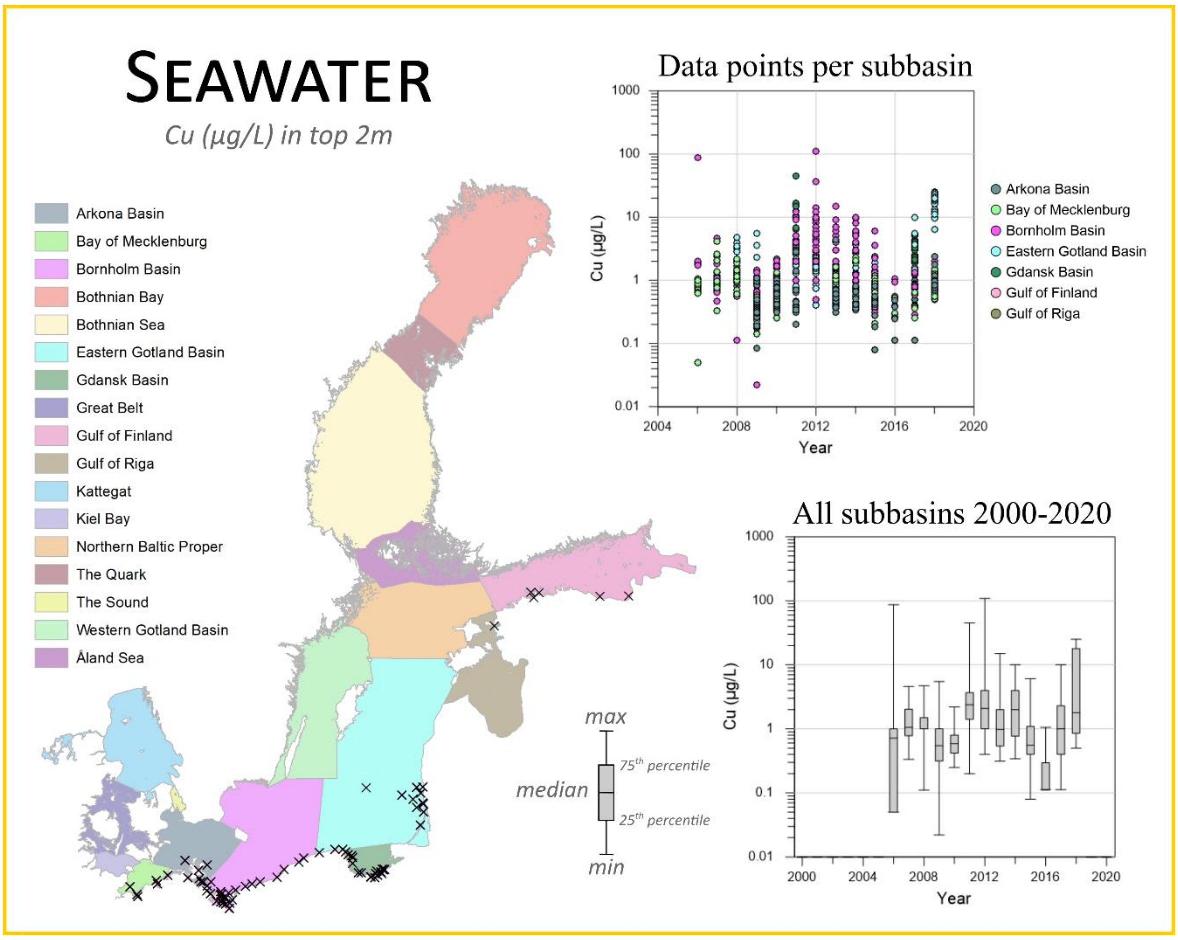


Figure 3. *Dissolved copper concentrations (in µg/L) in surface seawater (≤ 2 m depth) in the Baltic Sea. The map shows the sampling locations of seawater samples in the HELCOM subbasins. All measured concentrations in the different subbasins are shown in the top right graph. The boxplot on the lower right-hand side shows the yearly average concentrations in the whole of the Baltic Sea between 2000 – 2020.*

Table 4. *Number of observations and their concentration range per subbasin.*

HELCOM subbasin	Number of data points	Time period	Concentration (µg/L))		
			Minimum	Maximum	Average
Kattegat	0				
Great Belt	0				
The Sound	0				
Kiel Bay	0				
Bay of Mecklenburg	168	2006–2018	0.05	4.1	0.7
Arkona Basin	106	2009–2018	0.08	4.3	0.6
Bornholm Basin	369	2006–2018	0.02	109.0	3.0
Gdansk Basin	133	2011–2017	0.5	45.0	3.6
Eastern Gotland Basin	229	2008–2018	0.25	25.0	3.2
Western Gotland Basin	0				
Gulf of Riga	1	2018	0.5	0.5	0.5
Northern Baltic Proper	0				
Gulf of Finland	6	2017	0.5	3.5	1.7
Åland Sea	0				
Bothnian Sea	0				
The Quark	0				
Bothnian Bay	0				
All subbasins	1012	2006–2018	0.02	109.0	2.5

1.2.1.3 Time trends

The dataset consisted of 77 individual sampling stations, of which 18 were sampled during at least three different years, allowing for an assessment of potential time trends. The 18 stations are grouped and plotted by subbasin in **Figure 4**. The sampling depth was not always consistent between years at a given station but was always between 0.5 and 1.5 m depth. The displayed data points are the average of 1 - 10 measurements per year.

A measurement of 87 µg/L reported for 2006 for station OMMVKHM (blue dots) in the Bornholm Basin was excluded as all other measurements from that year were < 2 µg/L. It is possible that the entry was in fact supposed to be 0.87 µg/L, i.e. that the decimal point was misplaced. All measurement points for the stations in the Eastern Gotland Basin during 2018 are similarly questionable as they hold concentrations in great excess compared to previous years. These were nonetheless plotted but should be interpreted with caution (**Figure 4**).

With the exception of the high concentrations reported for 2018 at the stations in the Eastern Gotland Basin, the highest concentrations are found for the stations sampled in Bornholm Basin. The high concentrations measured at stations EZP, CZP, HZP and OMMVKHM here are to be expected as these stations are located in the enclosed waters of the Szczecin Lagoon in the Oder estuary.

No clear time trends can be seen from the data in **Figure 4**. Generally, concentrations seem to be rather constant with small interannual variations and, with the exception of stations in the Szczecin Lagoon, concentrations are mostly ≤ 2 µg/L.

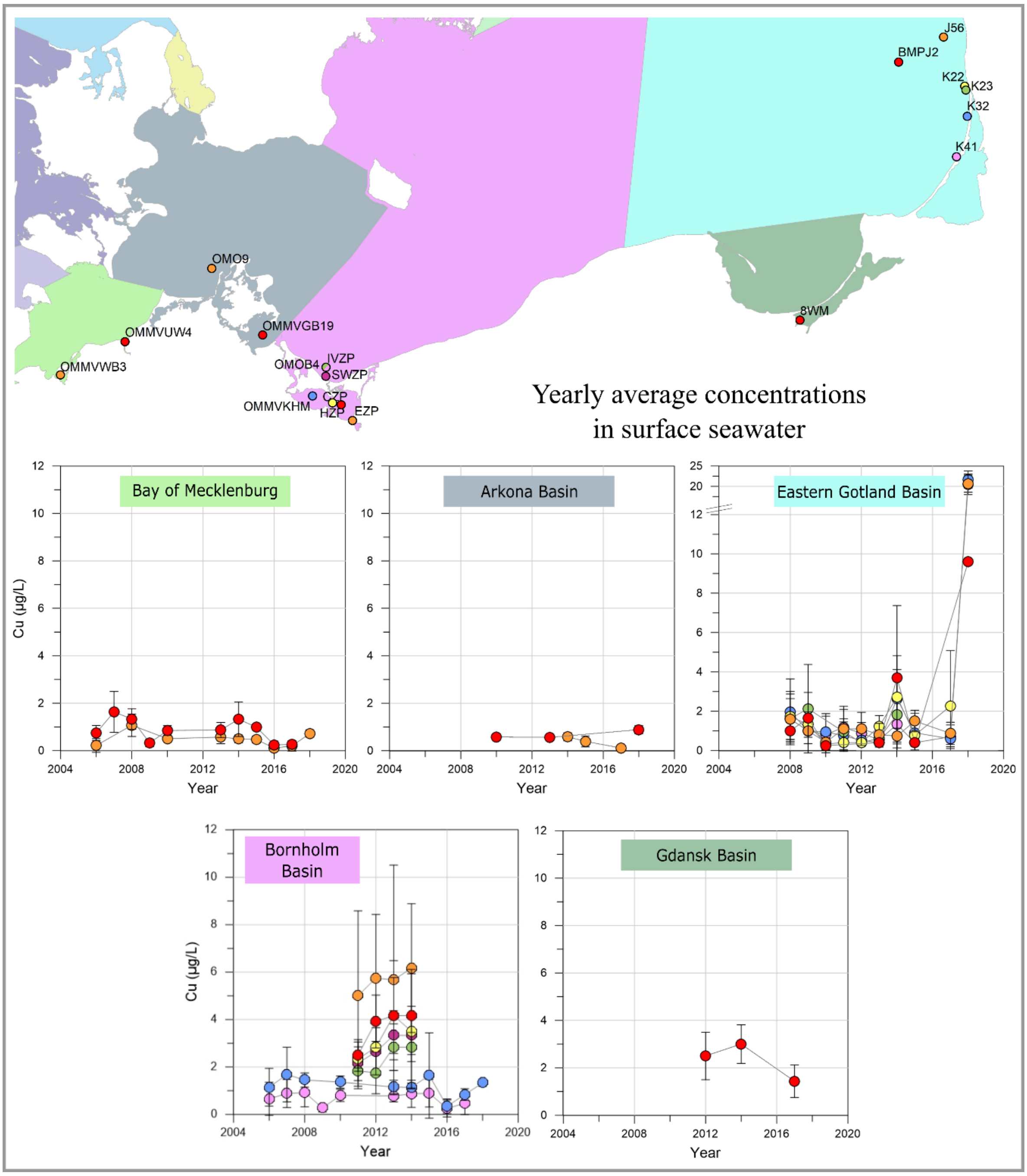


Figure 4. *Average yearly concentrations in surface seawater at stations with at least three sampling years Dots on the maps show station locations. Error bars in the graphs show the standard deviation. Note the break in the y-axis in the plot with the Eastern Gotland Basin stations.*

1.2.2 SURFACE SEDIMENT

1.2.2.1 Data collection

Sediment data was firstly collected from the ICES DOME (Marine Environment) data portal (ICES 2020). The following procedure was used to treat and filter the data (1,415 data points):

- The units of the reported concentrations were harmonized to mg/kg.
- Data reported as < LOD or < LOQ were set to LOD/2 or LOQ/2, respectively (57 data points).
- Only concentrations reported in dry weight (dw) were included. Sediment data reported in wet weight (ww) were removed.
- Only samples with specified sampling depth or sampling ranges within 0-2 cm of the sediment surface were included (i.e. the lower limit of the sampling range was ≤ 2 cm).

As concentrations mainly from the Southern Baltic were reported into the ICES data portal, a search for additional data was conducted. 807 data points with copper concentrations were downloaded from the European Marine Observation and Data Network data portal (EMODnet, 2020). A literature search was also carried out to find data published in peer reviewed scientific journals. Out of 22 publications where concentrations of copper in sediments in the Baltic Sea were reported, less than half contained data within the desired depth range. Of these, there were only two where the concentrations and coordinates of the sampling stations were reported in tables in the text and for which the data could be added directly to the dataset (Leivuori et al., 2000; Vallius et al., 2007). The first authors of several of the other publications were contacted with a request to share the published data with the omitted station information. Two replied with the requested information and data, all from the Gulf of Finland (Vallius, 2015a, 2015b; Ryabchuk et al., 2017). A dataset from The Sound was retrieved from publicly available sediment survey reports carried out by Öresunds Vattenvårdsförbund (ÖVF, 2020). The final compiled dataset was checked for duplicate samples in case of overlaps between the differently sourced sets of data.

A total of 1,599 data points remained after data filtering according to the previously outlined criteria. Data from the following sources were included in the final dataset:

- ICES DOME data portal (907 data points)
- EMODnet (370 data points)
- ÖVF (21 data points)
- Scientific publications (301 data points):
    - Leivuori et al. 2000 (9 data points)
    - Vallius et al. 2007 (14 data points)
    - Vallius et al. 2015a (45 data points)
    - Vallius et al. 2015b (47 data points)
    - Ryabchuk et al. 2017 (186 data points)

Note that no criteria for size fraction was applied as this information was not always specified.

1.2.2.2 Measured concentrations

A total of 643 surface sediment samples were included in the analysis. Their sampling locations are shown on the map in **Figure 5**. Samples from both coastal and open sea locations were included. The number of data points per subbasin, which varies widely, are also displayed in **Table 5**. Of all the subbasins, the Gulf of Finland (285 data points) and Kattegat (184 data points) were by far the ones with the most data. Oppositely, no data from the Great Belt, Gdansk Basin or the Quark could be included. Out of the 17 subbasins, only 10 subbasins had 10 or more data points. With regards to the distribution in time, the majority of data points (88%) were sampled between 2001 and 2017.

The plotted data (graphs in **Figure 5**) shows the distribution of concentrations to be very large: from < 1 mg/kg (i.e. samples < LOD or < LOQ) to nearly 500 mg/kg dw. The average concentration in the subbasins range from 12 to 92 mg/kg dw, with an average concentration for all subbasins of 42 mg/kg dw (**Table 5**).

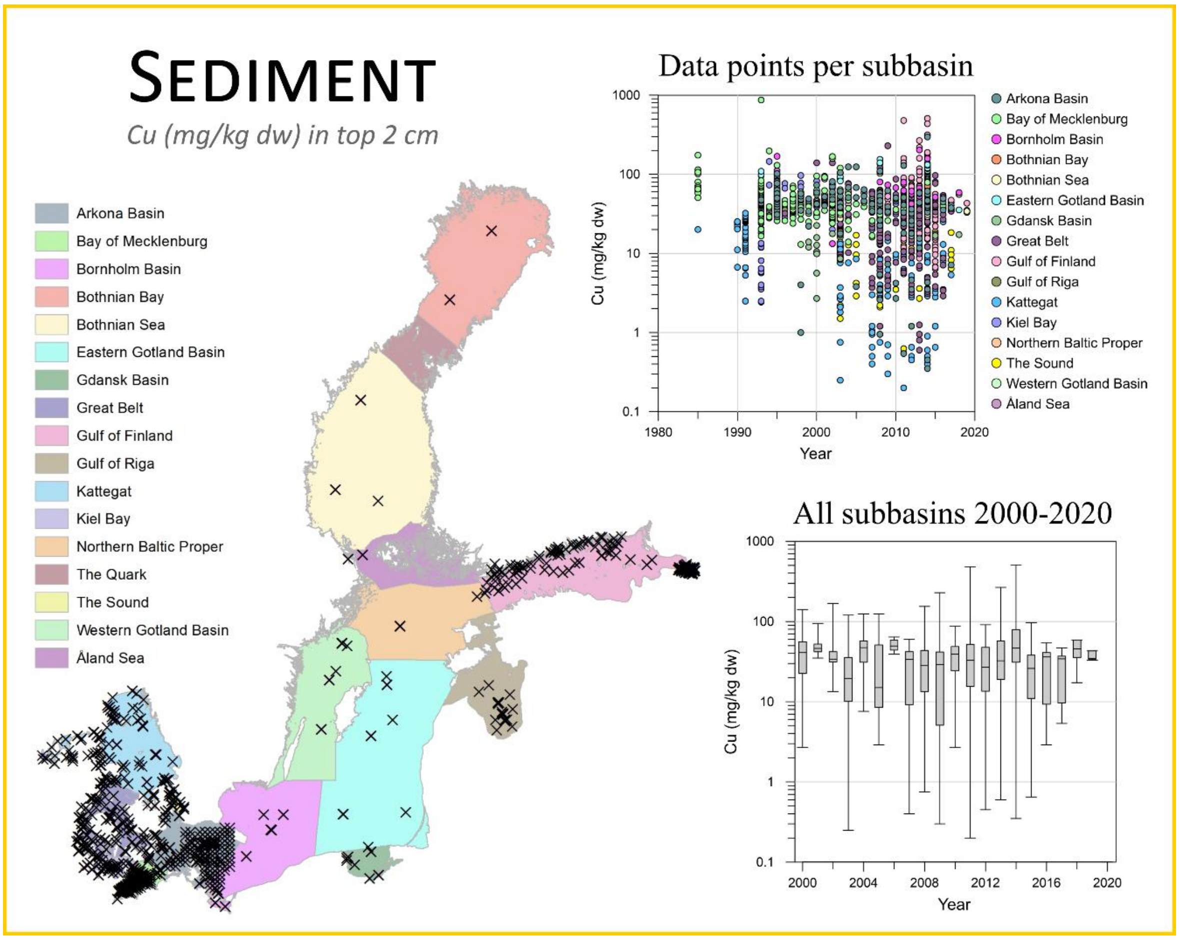


__Figure 5.__ Copper concentrations (in mg/kg dry weight) in surficial sediments (≤ 2 cm depth) in the Baltic Sea. The map shows the sampling locations of seawater samples in the HELCOM subbasins. All measured concentrations in the different subbasins are shown in the top right graph. The boxplot on the lower right-hand side shows the yearly average concentrations in the whole of the Baltic Sea between 2000 – 2020.

Table 5. *Number of observations and their concentration range per subbasin.*

HELCOM subbasin	Number of data points	Time period	Concentration (mg/kg dw)		
			Minimum	Maximum	Average
Kattegat	197	1985–2017	0.2	138.4	14.5
Great Belt	191	1994–2016	0.6	228.7	28.9
The Sound	42	2003–2017	0.6	49.1	12.0
Kiel Bay	111	1993–2017	2.4	312.0	42.3
Bay of Mecklenburg	285	1985–2017	13.0	867.0	49.5
Arkona Basin	237	1993–2017	0.4	297.0	45.8
Bornholm Basin	64	1993–2018	13.3	203.0	59.3
Gdansk Basin	25	1998–2018	13.3	203.0	59.3
Eastern Gotland Basin	32	1993–2018	32.4	154.0	85.7
Western Gotland Basin	31	1993–2014	16.3	136.0	88.3
Gulf of Riga	25	1994–2002	28.0	39.0	32.8
Northern Baltic Proper	13	2003–2014	33.0	182.0	75.3
Gulf of Finland	294	2001–2019	6.4	508.2	51.7
Åland Sea	14	2001–2014	29.1	94.6	47.5
Bothnian Sea	20	2003–2019	27.4	47.0	35.6
The Quark	0				
Bothnian Bay	18	2003–2014	18.8	70.6	48.9
All subbasins	1599	1985–2019	0.2	867	32.2

1.2.2.3 Time trends

The collected dataset consisted of 857 individual sampling stations. Out of these, 97 were sampled during at least three different years, allowing for the assessment of potential time trends. As mainly recent time trends were of interest, only stations sampled during at least three years from 2000 and onward were considered. For stations where the analysed grain size fraction differed between years, only the most frequently analysed size fraction for all years was included. If several samples were reported for the same year, the average concentration was used. The stations (82 stations) were grouped by monitoring programme, study or reporting country to allow for comparisons between years of cohesive datasets, i.e. sampling depth and analysed grain size fraction were the same for all stations and years. This resulted in the division of the data into 7 sets, as outlined next.

Open sea transect in the Baltic Sea

Sediment surface samples (0 – 1 cm, <63 µm fraction) were sampled at 13 off-shore stations by the Swedish Geological Survey (SGU) along the transect in **Figure 6** in three different years: 2003, 2008 and 2014. Single samples were collected in 2003 and 2008, while 7 replicate samples were reported for 2014 (average concentrations are plotted in the graph for this year, error bars show the standard deviation).

The transect data shows the differences in concentration to generally be larger between locations than between years. The highest concentrations were typically detected in the Eastern and Western Gotland basins and in the Northern Baltic Proper (~100 – 150 mg/kg dw), while lower concentrations (≤ 50 mg/kg dw) were found in the other locations e.g. Kattegat and the Northern part of the Baltic Sea.

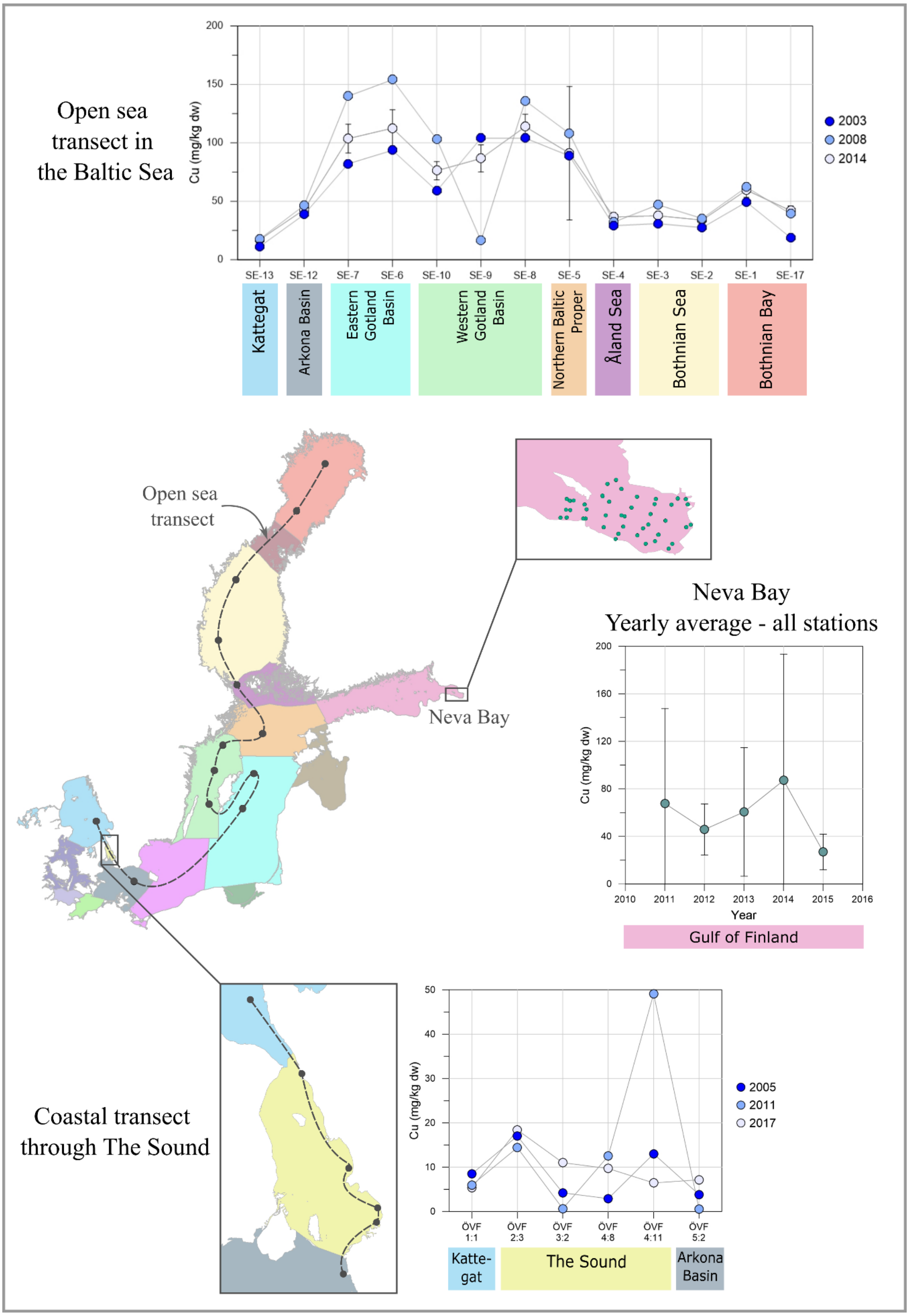


Figure 6. *Concentrations in sediment at stations with at least three sampling years from an open sea transect in the Baltic Sea (top), in Neva Bay (center) and from a coastal transect across the Sound (bottom). Dots on maps show station locations. Error bars in the graphs show the standard deviation.*

The summary report by SGU associated to the transect dataset concludes that the geographical pattern in sediment copper concentration does not reflect that of land-based sources. Instead, the high concentrations of copper in the Eastern and Western Gotland basins and the Northern Baltic Proper are more likely due to the reducing conditions of both surface sediments and bottom waters of the Baltic Proper which would promote the formation of insoluble copper sulphides in these subbasins (Josefsson and Apler, 2019). Although lower concentrations are found in the other sampled subbasins, all data points except for that from 2003 at the Kattegat station exceed what is currently defined as natural background levels (15 mg/kg dw) for Swedish coastal waters (see **Table 8**).

Variations between years are typically small, although the data series from 2003 generally held the lowest concentrations, while the dataset for 2008 was typically highest. A new analytical procedure for the extraction of metals from sediments was applied for the 2014 dataset. Whilst total digestion with hydrofluoric acid was used for the samples collected in 2003 and 2008, extraction by nitric acid was used for the samples collected in 2014. The observed differences between 2003 and 2008 should therefore not be related to the analytical method (Josefsson and Apler, 2019).

Neva Bay

The dataset originates from a published scientific study (Ryabchuk et al. 2017) in which surface sediment samples (0 – 1 cm, all grain size fractions) were collected 2011 – 2015 at 39 stations in Neva Bay, i.e. the innermost part of the Gulf of Finland. The geographical distribution of the stations as well as the yearly average of all stations are shown in **Figure 6**.

The yearly average copper concentrations range from 27 to 87 mg/kg dw. There was no significant difference in concentration between the five sampled years. Thus, even though the last sampled year (2015) holds the lowest, no time trend can be discerned within the time frame of the dataset.

Coastal transect through the Sound

Surface sediments (0 – 2 cm, <63 µm fraction) were collected in three different years (2005, 2011 and 2017) at 6 coastal stations in a transect stretching across The Sound, from Kattegat in the north to the Arkona Basin in the south.

Concentrations were low (< 20 mg/kg dw) for all stations and sampling years, except for station ÖVF 4:11 where a concentration of nearly 50 mg/kg dw was measured in 2011. According to the sediment survey report, the loss on ignition, i.e. concentration of organic matter, was unusually high in this sample compared to previous and subsequent years (ÖVF 2020). This could perhaps explain the higher measured concentrations of copper that year. Concentrations measured in 2005 and 2017 are lower, and more similar around roughly 10 mg/kg dw. Interannual variations at the individual stations are otherwise small and typically < 5 mg/kg dw. No clear time trends can thus be discerned. The smallest interannual variations are found for the Kattegat station (ÖVF 1:1) and the most northern station in the Sound (ÖVF 2:3), with average concentrations of 6.6 and 16.6 mg/kg dw, respectively. The latter station, ÖVF 2:3, is located just outside the city of Helsingborg, which could account for the higher concentrations. Nonetheless, the concentrations of all the sampled locations are below or close to what is currently defined as natural background levels (15 mg/kg dw) for Swedish coastal waters (see **Table 8**).

Comparison with concentrations at other coastal stations in the Baltic Sea, e.g. those in Neva Bay, is made difficult by the fact that the size fraction of the analysed sediment samples differs. Comparison can however be made to the open sea transect, where the analysed size fraction is indeed the same. The concentrations from the coastal Sound transect are closest to those measured concentrations at the Kattegat station of the open sea transect (SE-13, at roughly 15 mg/kg dw), which is also geographically closest. All other sampled stations in the open sea transect are higher, as even the lowest concentrations are between 30 – 50 mg/kg dw.

Stations divided by reporting country

The remaining 24 stations were divided into 4 sets based on reporting country, sampling depth and analysed grain size fraction:

- data reported by Germany (9 stations), 0-2 cm, <20µm
- data reported by Denmark (8 stations), 0-1 cm, <2mm
- data reported by Poland (6 stations), 0-2 cm, <63µm
- data reported by Sweden (1 station), 0-2 cm, total sediment

For most sampled stations, concentrations tend to remain fairly constant over time with reported concentrations are ≤ 50 mg/kg dw (**Figure 7**). Higher and more variable concentrations are however observed for a few stations. At station OMBMPK8 in the Arkona Basin, concentrations vary between years from 40 to nearly 300 mg/kg dw. The station's location next to a major shipping lane could perhaps explain this variability. However, other stations such as OMBMPK8 (Arkona Basin) and OMBMPN1 (Kiel Bay) are also located in the middle of major shipping lanes without similarly elevated concentrations suggesting other factors are involved. Another elevated measurement (312 mg/kg dw) was also recorded for a single data point in 2014 in Kiel Bay (OMBMPN3) but may possibly be a misreported value given that the concentrations for all other years are an order of magnitude lower.

The data reported by Poland (3 subbasins) can be compared to those of the open sea transect and the coastal transect across the Sound as the analysed size fraction was the same. In Bornholm Basin, concentrations are in the 40-60 mg/kg dw range which is comparable to those measured in the neighbouring Arkona Basin at station SE-12 of the open sea transect. The lowest concentrations, around 17 mg/kg dw, were found in the Gdansk Basin at coastal station BMPL10 which is comparable to those measured along the coastal transect across the Sound. For the Eastern Gotland Basin, concentrations are half (40 mg/kg dw) of those measured at stations SE-6 and SE-7 of the open sea transect, suggesting that reducing conditions were not prevailing at the location of station BMPK1.

In conclusion, geographical differences, even within the same subbasin tend to exceed interannual differences at most sampled stations. No time trends could thus be discerned from the studied dataset.

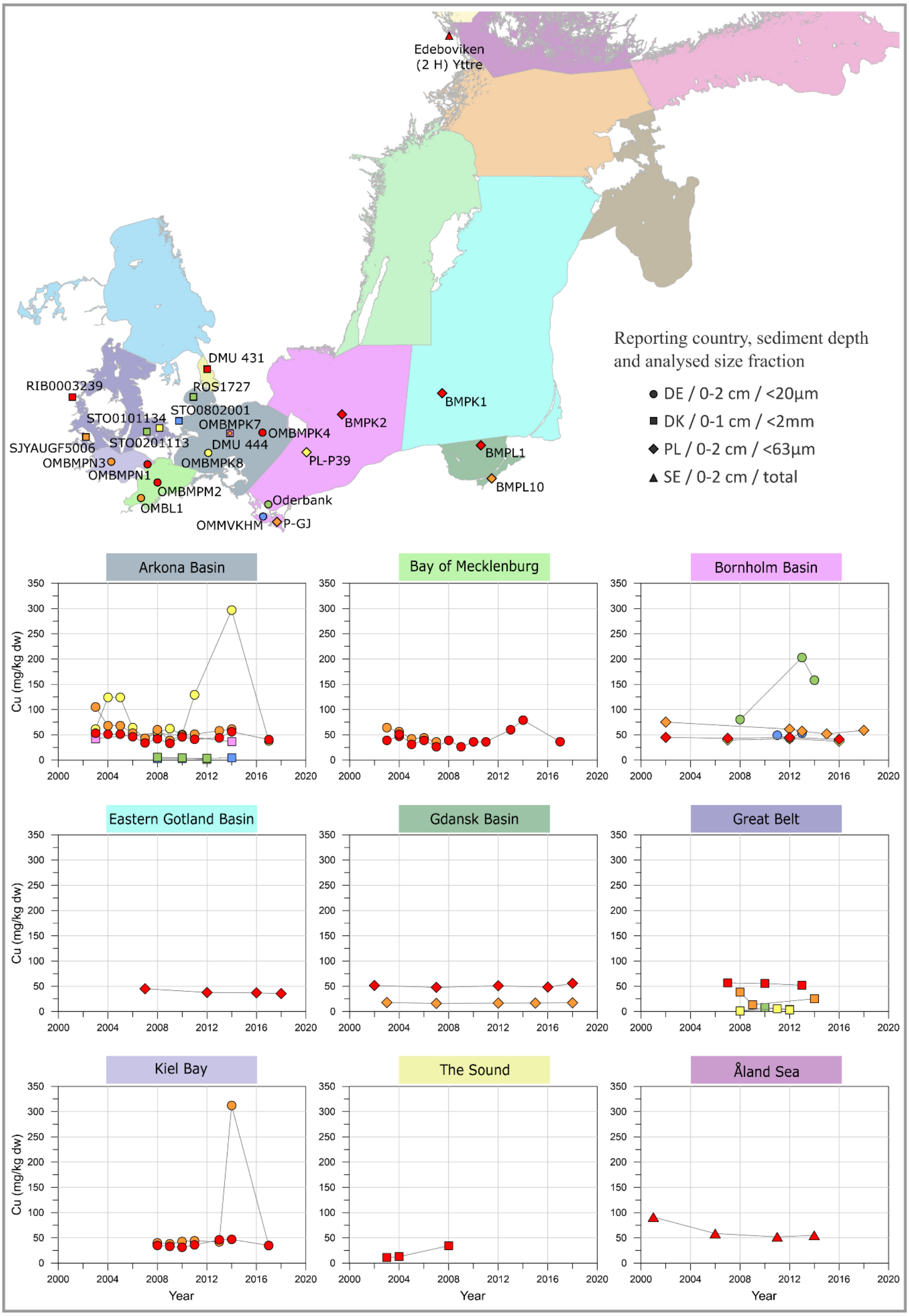


Figure 7. *Concentrations in sediment at stations with at least three sampling years by reporting country. Station names and locations are shown on the map. Note that the different symbols represent different size fractions (see legend). Note that the positions of stations OMBMPK7 (orange circle) and DMU 444 (pink square) in the Arkona Basin overlap.*

1.2.3 BIOTA

1.2.3.1 Data collection

Biota data was collected from the ICES DOME (Marine Environment) data portal (ICES 2020). The following procedure was used to treat and filter the data:

- The units of the reported concentrations were harmonized to mg/kg.
- Data reported as < LOD or < LOQ were set to LOD/2 or LOQ/2, respectively. If LOD or LOQ were not specified or if only a value of "0" for the concentration was entered, the data point was removed.
- Data reported to be greater than a certain value were reported at that value.
- Data points labelled as "Suspect" were removed.
- Bird species (2 species) were removed.

As the filtered dataset collected from the ICES data portal was quite large (12,909 data points) and had a fairly even distribution amongst subbasins, no attempts to collect additional data were made.

The dataset was split in two, depending on whether concentrations were reported in wet weight (5,782 points) or dry weight (7,127 points). For the data reported in in dry weight, the corresponding dry weight percentage, if also reported, was used to relate the concentrations to wet weight (6,145 points). This yielded a final dataset with 11,927 values in mg/kg ww. Concentrations for a total of 15 different species were reported (**Table 6**). Species were divided into three categories: fish, bivalves and crustaceans. 92% of fish samples were liver samples and 8% were muscle sample. For the bivalves, soft body were indicated as the analysed matrix for all but two data points.

Table 6. *Number of data points per species in the biota dataset and the measured organs for each species. LI – Liver, MU – Muscle, SB - Whole soft-body or WO - Whole organism.*

	Species	**Number of data points**	**Measured organs (number of data points)**
Fish	*Abramis brama*	1	MU (1)
	Clupea harengus	5447	LI (4868), MU (579)
	Gadus morhua	1815	LI (1760), MU (55)
	Limanda limanda	397	LI (397)
	Neogobius melanostomus	2	LI (1), MU (1)
	Perca fluviatilis	621	LI (500), MU (121)
	Platichthys flesus	1657	LI (1625), MU (32)
	Pleuronectes platessa	10	LI (10)
	Sprattus sprattus	28	MU (28)
	Zoarces viviparus	187	LI (156), MU (31)
Bivalves	*Dreissena polymorpha*	36	SB (36)
	Macoma balthica / Limecola balthica	49	MU (1), SB (48)
	Mya arenaria	9	SB (9)
	Mytilus edulis	1611	MU (1), SB (1610)
Crustaceans	*Saduria entomon (crayfish)*	57	WO (57)
	Total	11927	

As seen in **Table 6**, most of the data consist of various fish species, followed by bivalves. Herring (*Clupea harengus*) is the most sampled fish species, followed in decreasing order by cod (*Gadus morhua*), flounder (*Platichthys flesus*) and perch (*Perca fluviatilis*). As for the bivalves, blue mussel (*Mytilus edulis*) is by far the most sampled species.

1.2.3.2 Measured concentrations

Only the species with more than 10 data points were included in the analysis (**Table 6**). The sampling locations and copper concentrations in **Figure 8** thus correspond to 7 fish species, 3 bivalve species and 1 crustacean species. For the fish species, liver tissue has been much more frequently sampled than muscle tissue, whereas soft-body tissue is by far the most commonly samples for bivalves. The data for the fish species were divided by tissue sampled (liver or muscle). For the bivalves, only the concentrations reported for the soft-body are shown.

As seen in the map of **Figure 8**, biota samples have been collected and analysed from all 17 subbasins. The geographical distribution for this matrix is thus better than that of seawater and sediment. For all three categories, concentrations reported from as early as 1979 can be found. Time series for copper concentration in fish liver from the 1980's and onward are available for herring (*Clupea harengus*), cod (*Gadus morhua*) and perch (*Perca fluviatilis*), whereas most bivalve data (mainly *Mytilus edulis*) are only available from the late 1990's. Data for crustaceans is scarce and only available for a few years.

The compiled data shows that the concentrations of copper are highest in crustaceans (typically > 10 mg/kg ww, average of 26.0 mg/kg ww) followed by liver tissue in fish (typically 1 – 50 mg/kg ww, average of 6.8 mg/kg ww), soft-body tissue of bivalves (0.5 - 5 mg/kg ww, average of 1.8 mg/kg ww) and muscle tissue in fish (0.1 – 1 mg/kg ww, average of 0.9 mg/kg ww). Some measurements of copper in herring (*C. Harengus*) muscle tissue reported in 1999 and 2000 are unusually high and more on par with those in liver tissue. Possibly, the wrong organ was specified in the DOME database for these data points.

Previous studies of metal concentrations in various tissues of herring and perch have found that metals such as Ag, Cd, Cu, Zn and Pb are typically found in higher concentrations in liver as compared to muscle (Faxneld et al., 2015; Danielsson et al., 2018). This is consistent with the, on average, 7.6 times higher concentrations of copper in liver compared to muscle for the 7 fish species in **Figure 8**. Differences in liver concentration between fish species can however also be observed here, with higher concentrations in e.g. perch (*P. Flesus*) than in herring (*C. Harengus*) and cod (*G. Morhua*).

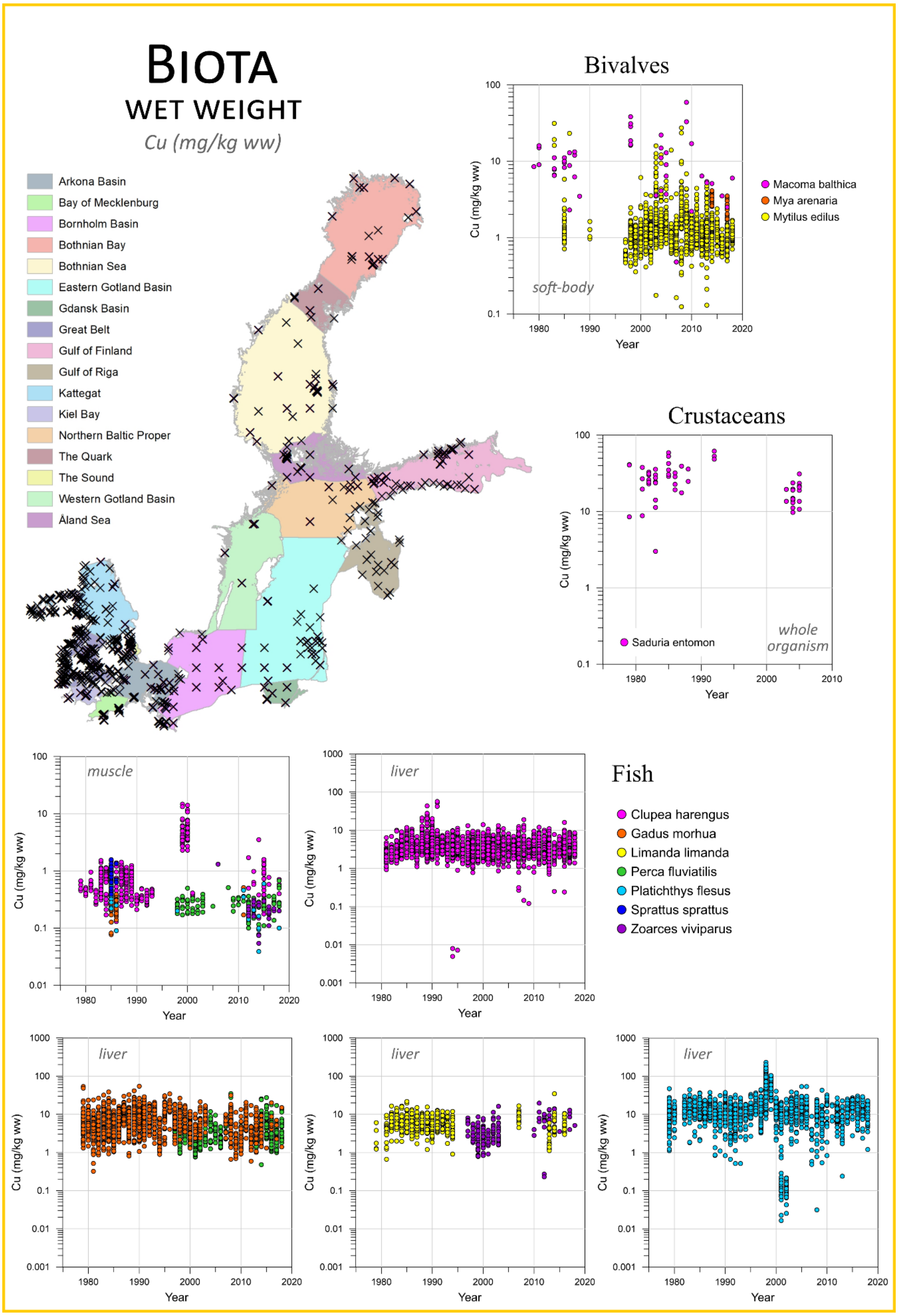


Figure 8. *Copper concentrations (in mg/kg wet weight) in biota in the Baltic Sea. The map shows the sampling locations of biota samples in the HELCOM subbasins. All measured concentrations for the different species (divided into three categories: fish, bivalves and crustaceans) are shown in the graphs. Sampled tissue is indicated in grey in the graphs.*

1.2.3.3 Time trends

The fish and bivalve species with the most data points respectively were selected to evaluate potential time trends. Only concentrations in the most commonly analysed organ was included in the analysis. Thus, time series of concentrations in liver tissue in herring (*C. harengus*) and in the soft-body tissue of blue mussel (*M. edulis*), are presented next. While herring migrates/roams over larger areas, the blue mussel is a stationary bivalve.

Herring – concentrations in liver tissue

The concentration of copper in the liver tissue of herring as measured in the Baltic Sea over time are shown in **Figure 9**. The interannual variation of copper concentration was higher during the period 1980 – 1991 with concentrations increasing from 2 to 6 mg/kg ww, as compared to the period 1991 – 2018 where the concentrations are rather constant around 3 – 4 mg/kg ww for all years.

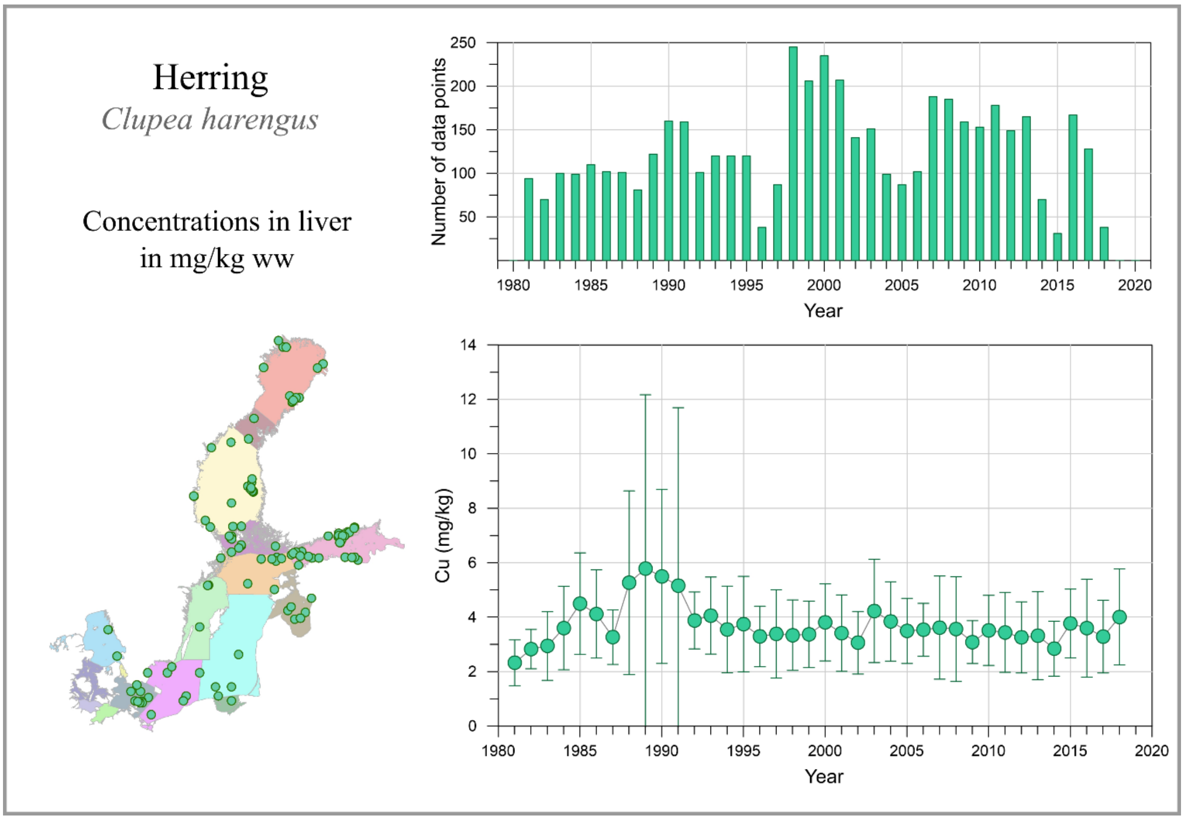


Figure 9. *Concentrations in herring liver 1980 – 2020 in mg/kg per wet weight. The map shows the sampling locations. The top graph shows the number of observations per year. The bottom graph shows average yearly concentration. Error bars show the standard deviation.*

Blue mussel – concentrations in the soft-body tissue

The wet weight copper concentrations in blue mussel are shown in **Figure 10**. As for herring, the concentrations appear to be rather constant and typically range between 0.5 - 2 mg/kg ww. Two years in the 1980's have however concentrations that are one order of magnitude higher than those reported for all other years. These data (1983 and 1986) are however only based on a few data points (≤ 3) as compared to the dataset from the 1998 – 2018 which for most years is based on ≥ 40 data points. Possibly, these high concentrations may have been entered incorrectly into the ICES database. The data points from 1983 were all sampled in Bothnian Bay (see the most northern data point in map in **Figure 10**) where blue mussels are not typically found, suggesting the values correspond to another organism or that the coordinates are incorrect.

Although some years between 1998 – 2018 show somewhat more elevated concentrations than most (e.g. most years 2003 – 2008), these increased yearly averages appear to be driven by a few high data points, as indicated by correspondingly large error bars. For the years just prior to this time period (1998 – 2002) as well as all those following (2009 – 2018), concentrations are more similar and vary little between years with an average of 1.2 ± 0.2 mg/kg ww.

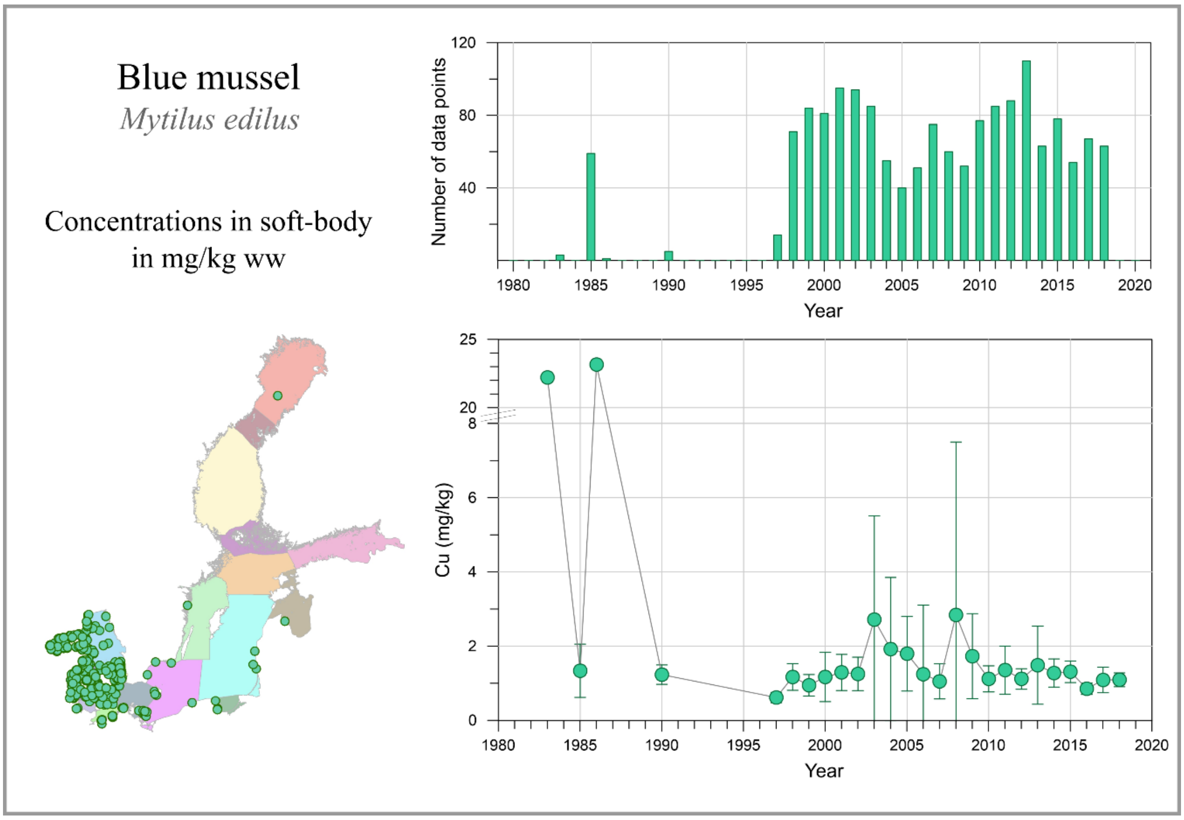


Figure 10. *Concentrations in blue mussel soft-body 1980 – 2020 in mg/kg per wet weight. The map shows the sampling locations. The top graph shows the number of observations per year. The bottom graph shows average yearly concentration. Error bars show the standard deviation.*

1.3 EQS VALUES IN USE BY THE HELCOM CONTRACTING PARTIES FOR STATUS CLASSIFICATION

As shown in section 1.2, surface seawater, sediment and biota are routinely monitored for copper in the Baltic Sea. However, the interpretation of the results and how the copper data are used for status classification within the WFD and MSFD differs substantially between countries. In a survey across HELCOM contracting parties, national monitoring and threshold values used for copper in seawater, sediment and biota have been compiled (**Table 7** and **Table 8**). The document confirms a large variation in the countries' monitoring program. In Sweden, copper concentrations in both surface seawater and sediment are used for status classification under the WFD while only sediment data is used under the MSFD. Germany on the other hand, uses sediment data for status classification under the WFD while surface water is used for trend analysis only. In Poland and Estonia, copper concentrations in surface seawater are used for status classification under both the WFD and the MSFD. In Denmark, surface seawater is used for status classification under the WFD while sediment is not included. No information about if and how the other HELCOM contracting parties (Lithuania, Latvia, Finland and Russia) are using copper in their status assessment were available.

1.3.1 THRESHOLD VALUE FOR SURFACE WATERS

The HELCOM contracting parties are using different threshold values (Environmental Quality Standard - EQS) for copper to determine the environmental state in surface water (**Table 7**). Sweden uses 0.87 µg Cu/L (dissolved bioavailable fraction) where site-specific DOC concentrations are taken into consideration. If DOC-data is absent, a default value of 1.45 µg Cu/L (dissolved fraction) is used. Sweden's EQS-value is based on the EU voluntary risk assessment of copper (I) oxide (VRAR-Cu) which was conducted in 2008 under the Council Regulation 793/93/EEG (Existing Substances regulation) (European Copper Institute, 2008). In the VRAR-Cu, Predicted-No-Effect-Concentrations (PNEC) were developed for terrestrial, freshwater and marine ecosystems. For the marine environment, 57 chronic toxicity data (No Observed Effect Concentrations, NOECs) on 24 species (4 algae, 18 invertebrates, and 2 fishes) were selected as highly reliable. Species sensitivity distribution (SSD) curves were developed with these data and a PNEC-value was derived using the 50% confidence value of the 5th percentile value (HC5) of the SSD-curve. The reported HC5 value was 5.2 µg/L (when normalized to DOC = 2 mg/L), but due to the absence of high quality marine mesocosm data and other field data an assessment factor (AF) of 2 was applied for the marine environment (European Copper Institute, 2008). Therefore, a $PNEC_{marine}$ of 2.6 µg Cu/L is proposed which was also accepted by the European Commissions' Scientific Committee on Health and Environmental Risks (SCHER). In Sweden, an additional AF of 3 is used with the arguments that Baltic Sea species and ecosystems are considered to be more sensitive to hazardous compounds as compared to marine ecosystems in which the $PNEC_{marine}$ was developed to protect. Thus, $PNEC_{Baltic} = 2.6/3 = 0.87$ µg/L. This $PNEC_{Baltic}$ is categorized as the bioavailable copper concentration and before comparing in-field measured dissolved copper concentrations, site-specific DOC concentrations need to be considered. Therefore, measured dissolved (< 0.45 µm) copper concentration shall be divided by $(DOC_{conc}/2)^{0.6136}$) before comparison with the $PNEC_{Baltic}$. The reason behind this is that $PNEC_{marine}$ was developed based on chronic toxicity studies using a DOC concentration of 2 mg/L and the DOC concentrations are typically higher in the Baltic Sea (4-5 mg/L). If site-specific DOC concentration is absent, a default $PNEC_{Baltic}$ value of 1.45 µg Cu/L (dissolved fraction, <0.45 µm) is used. The latter assumes a DOC concentration of 4.6 mg/L which results in **$PNEC_{Baltic}$** (DOC= 4.6 mg/l) = 0.87 * $(4.6/2)^{0.6136}$= **1.45 µg/l**.

Table 7. *Threshold values for copper in surface seawater used by HELCOM contracting parties for status classification within MSFD and WFD.*

Matrix	Country	Threshold value	Relates to	Background and rationale	Used for
Water	Poland	50 µg/L	Filtered (0.45 µm)	Species, endpoint, AF	MSFD, WFD
Water	Estonia	15 µg/L	Filtered (0.45 µm)	Based on expert report (that takes into account EQS dossiers or other similar international risk assessments, ecotoxicological surveys, monitoring data, available data on limit valus in other countries)	MSFD, WFD
Water	Sweden	0.87 µg/L	Filtered (0.45 µm) and bio-available conc. (measured conc./ (site-specific $DOC/2)^{0,613}$)	Derived from EU Risk Assessment Report (VRAR-Cu 2008) and the $PNCE_{marine}$ proposed in the report, but with a DOC normalization approach and an extra AF of 3 as Baltic Sea ecosystems are more sensitive to hazardous compounds than marine water	WFD (since 2019)
Water	Sweden	1.45 µg/L	Filtered (0.45 µm) default value if DOC concentration is unknown	Derived from EU Risk Assessment Report (VRAR-Cu 2008) and the $PNCE_{marine}$ proposed in the report, but with a DOC normalization approach and an extra AF of 3 as Baltic Sea ecosystems are more sensitive to hazardous compounds than marine water	WFD (since 2019)
Water	Germany	No threshold, trend assessment only	Filtered (0.45 µm)		
Water	Denmark	1 µg/L	Filtered (0.45 µm). Threshold added to the natural background concentration. However only the upper concentration limit given below	Weight of evidence approach considering 2 SSDs, NOECs and EC10 values	WFD
Water	Denmark	4.9 µg/L	Filtered (0.45 µm). Upper concentration limit regardless of the natural background concentration		WFD

As shown in **Table 7**, Poland and Estonia are using considerably higher threshold values, 50 µg/L and 15 µg/L, respectively, compared to Sweden. The scientific rationale behind these threshold values is unknown to the authors of this report but the survey across HELCOM contracting parties suggest they are based on (unspecified) expert reports. Denmark has also established threshold values based on SSDs and chronic data (NOECs and EC10). References are however not included so no assessment on the scientific evidence behind the threshold values could be performed in this study. The threshold values used by Denmark are 1.0 µg/L (dissolved) where background concentration shall be added to the threshold value and 4.9 µg/L (dissolved) without background.

1.3.2 THRESHOLD VALUE FOR SEDIMENT

Sweden and Germany are the only countries that have established threshold values for copper in sediment (**Table 8**). Sweden uses 52 mg/kg dw (normalized to 5% Total Organic Carbon - TOC) as threshold value where background concentrations (15 mg/kg dw) shall be added to the measured concentration prior to comparison to the threshold value. In Germany, 160 mg/kg dw is used, and no information is given whether natural background concentrations shall be accounted for or if the data shall be normalized to TOC concentrations. Notable, this threshold value is from the 1990s and has not been applied under the WFD assessment.

Table 8*. Threshold values for copper in sediment used by HELCOM contracting parties for status classification within MSFD and WFD.*

Matrix	Country	Threshold value	Relates to	Background and rationale	Used for
Sediment	Sweden	52 mg/kg dw	<63µm fraction. 5% TOC. If exceeded account for natural background (15 mg/kg)	Based on report by Sahlin and Ågerstrand (2018), prepared on behalf of the Swedish Agency for Marine and Water Management and the Swedish Environmental Protection Agency. EQS based on Nitocra spinipes, NOEC/EC10, AF 5.	MSFD, WFD (since 2019)
Sediment	Germany	160 mg/kg dw	<63µm fraction		WFD

The Swedish threshold value is based on the study by Sahlin and Ågestrand, 2018. The work was performed under the Water Framework Directive (2000/60/EC) using the European Communities's guidance document No 27 "Technical Guidance for Deriving Environmental Quality Standards" (European Commission, 2018). The total dataset included studies on three major taxonomic groups and five species, where NOEC, EC10 or LC10 were produced for different endpoints (survival, growth, reproduction and development). The dataset did not fulfil the requirements to perform an SSD according to the Guidance Document No 27 and therefore the most sensitive species, the crustacean *Nitocra spinipes*, of the marine single-species studies was selected to derive an EQS value. The lowest effect value was obtained in the work by Campana et al., 2012 where an EC10 on the endpoint reproduction was observed at a copper concentration of 77.5 mg/kg dw (TOC concentration 1.5% and salinity 30 ppm). As the bioavailability (and toxicity) of copper in sediment are known to decrease with increasing concentration of TOC, the effect value (EC10) was normalized to 5% TOC, i.e. 77.5 mg/kg * 1.5% (TOC) / 5% (TOC) = 258.3 mg/kg dw. An AF of 5 was further used to account for limited number of field and mesocosm observations. Hence, the proposed added EQS-value for marine sediments is **52 mg/kg dw at 5% TOC.** This is also used by the Swedish Agency for Marine and Water Management (SwAM) in status classification under MSFD and WFD since 2019 (Swedish Agency for Marine and Water Management, 2019).

No details about the threshold value used by Germany is given in the survey across HELCOM contracting parties. Hence, no evaluation regarding the scientific justification and rationale behind the threshold value could be performed in this report.

1.3.3 Threshold value for biota

No threshold values for biota are currently used by any HELCOM contracting party.

1.4 MEASURED CONCENTRATIONS RELATIVE TO EQS VALUES IN USE

The concentrations in seawater (**Figure 3**) and sediments (**Figure 5**) were used to assess the proportion of data points that would exceed the different national EQS-values in use (EQS values are shown in **Table 7** and **Table 8**). For seawater, 40% of the data points exceeded the Swedish threshold value for copper in seawater (**Figure 11**). The corresponding exceeding proportion of data points was 9.9% when the Danish threshold value was used and 2.8% and 0.2% when Estonian and Polish threshold values were used, respectively.

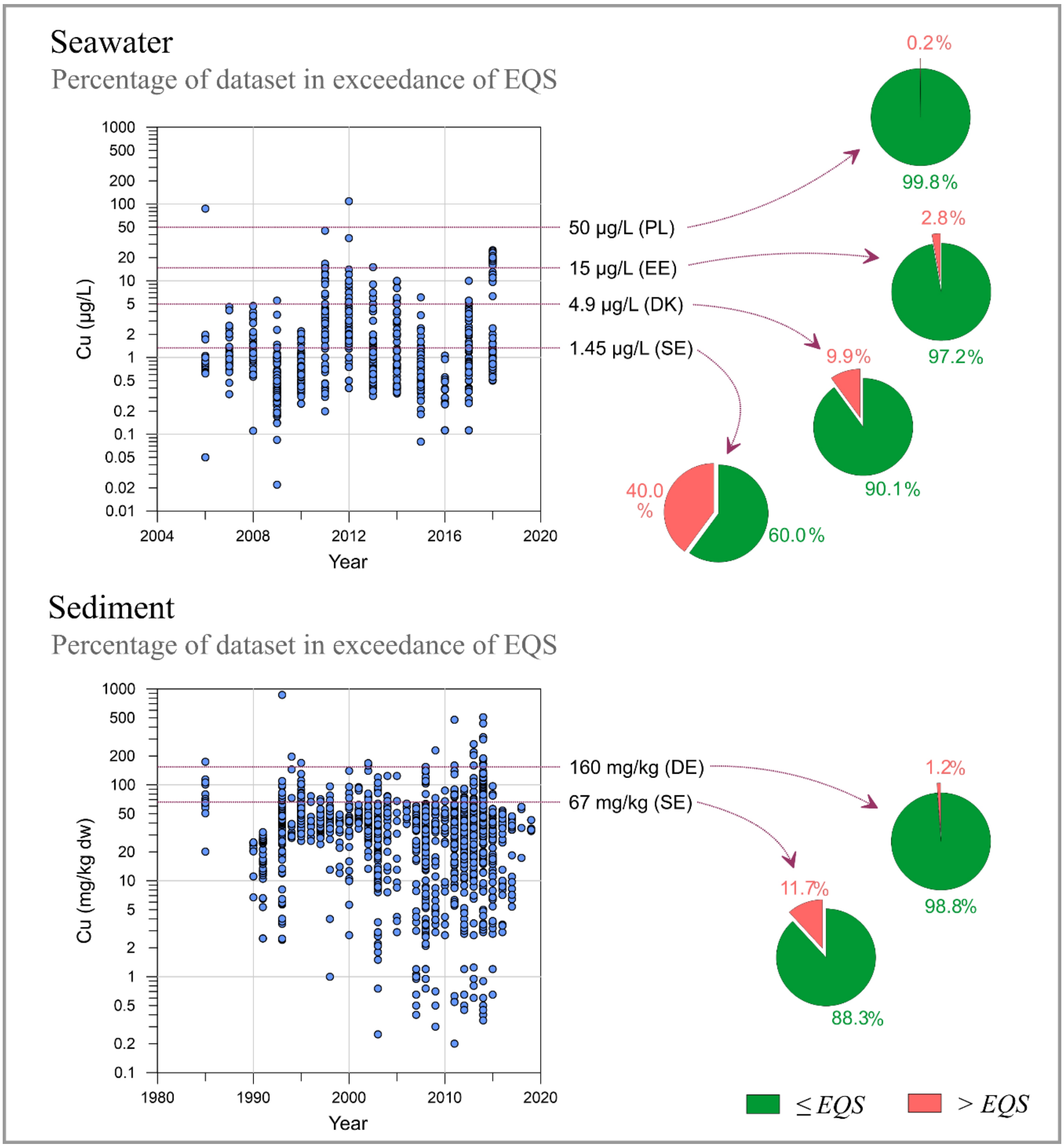


Figure 11. *Proportion of data points in exceedance of different national EQS-values for copper in seawater (0-2 m) and surface (0-2 cm) sediment. PL=Poland, EE=Estonia, DK=Denmark, DE=Germany and SE=Sweden.*

For copper in sediment, only Sweden and Germany have established threshold values. The Swedish threshold value was derived using the added risk approach and hence background concentrations should be considered when assessing monitoring data. Therefore, 67 mg/kg dw (52 mg/kg + 15 mg/kg background) was used as a threshold value in the current assessment. Since the threshold value is normalized to 5% TOC, site-specific TOC concentration is required. In the current assessment it was assumed that all data points had a TOC-concentration of 5%. The results showed 11.7% of the data points to exceed the Swedish threshold value (**Figure 11**). When the German threshold value was used, the proportion of data points exceeding the threshold value decreases to 1.2%.

1.5 Status classification of Swedish coastal waters under the WFD, with regard to copper

In Sweden, copper is listed as a river basin specific pollutant in the Swedish Agency for Marine and Water Management's regulation *on classification and environmental quality standards regarding surface water (HVMFS 2019:25)*. River basin specific pollutants that pose a significant pressure on a specific water body shall be monitored and classified under ecological status in the WFD. Sweden's coastal waters have been divided into 554 coastal water bodies of which 154 have been assessed based on the copper concentrations in surface seawater (28 water bodies) or sediment (125 water bodies) (WISS, 2020). The assessments were in most cases based on average concentrations originating from a set of subsamples in surface seawater or sediment. The threshold values for copper in Sweden, as shown in **Table 7** and **Table 8**, have been used in the status classification of surface seawater and sediment, respectively. In total, 42 water bodies (27% of the assessed coastal water bodies) did not fulfil the requirements for good ecological status, i.e. they displayed copper concentrations in surface seawater or in sediment exceeding the threshold value (EQS) (**Figure 12**). For the surface seawater, 12 out of the 28 assessed water bodies did not fulfil good status with respect to copper. For sediment, 30 out of in total 126 assessed water bodies failed to reach good status. Due time constraints, we were not able to compile data from other HECLOM contracting parties.

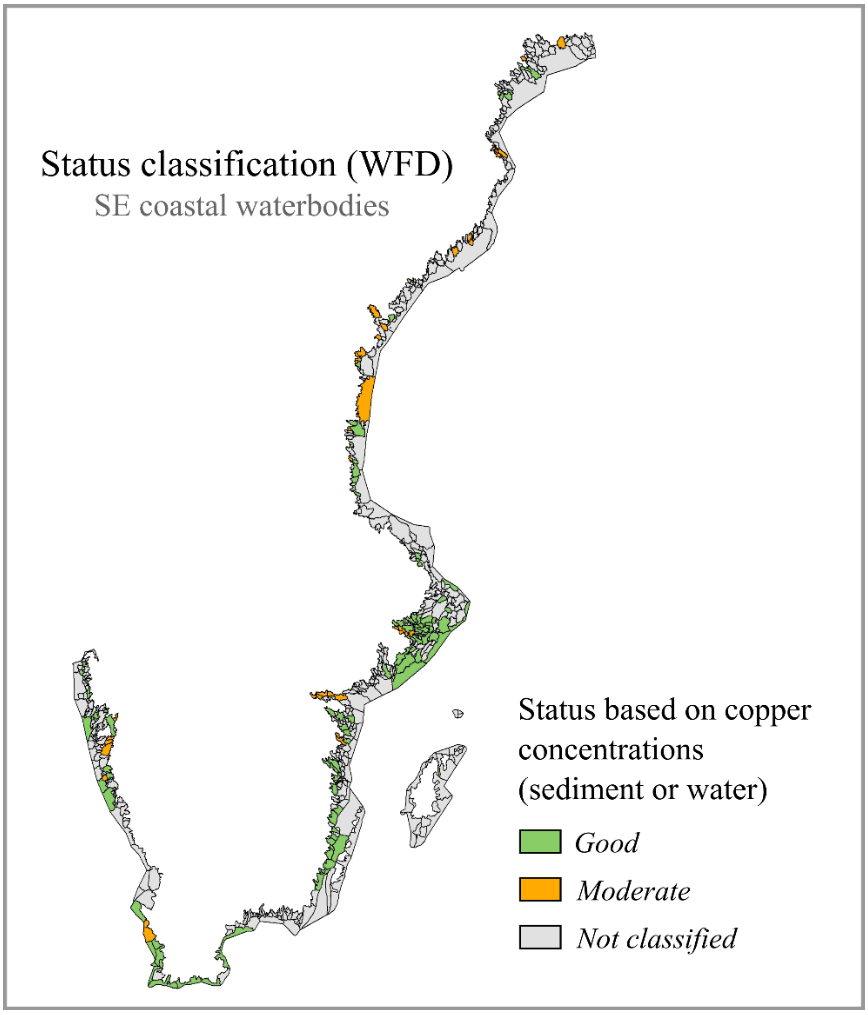
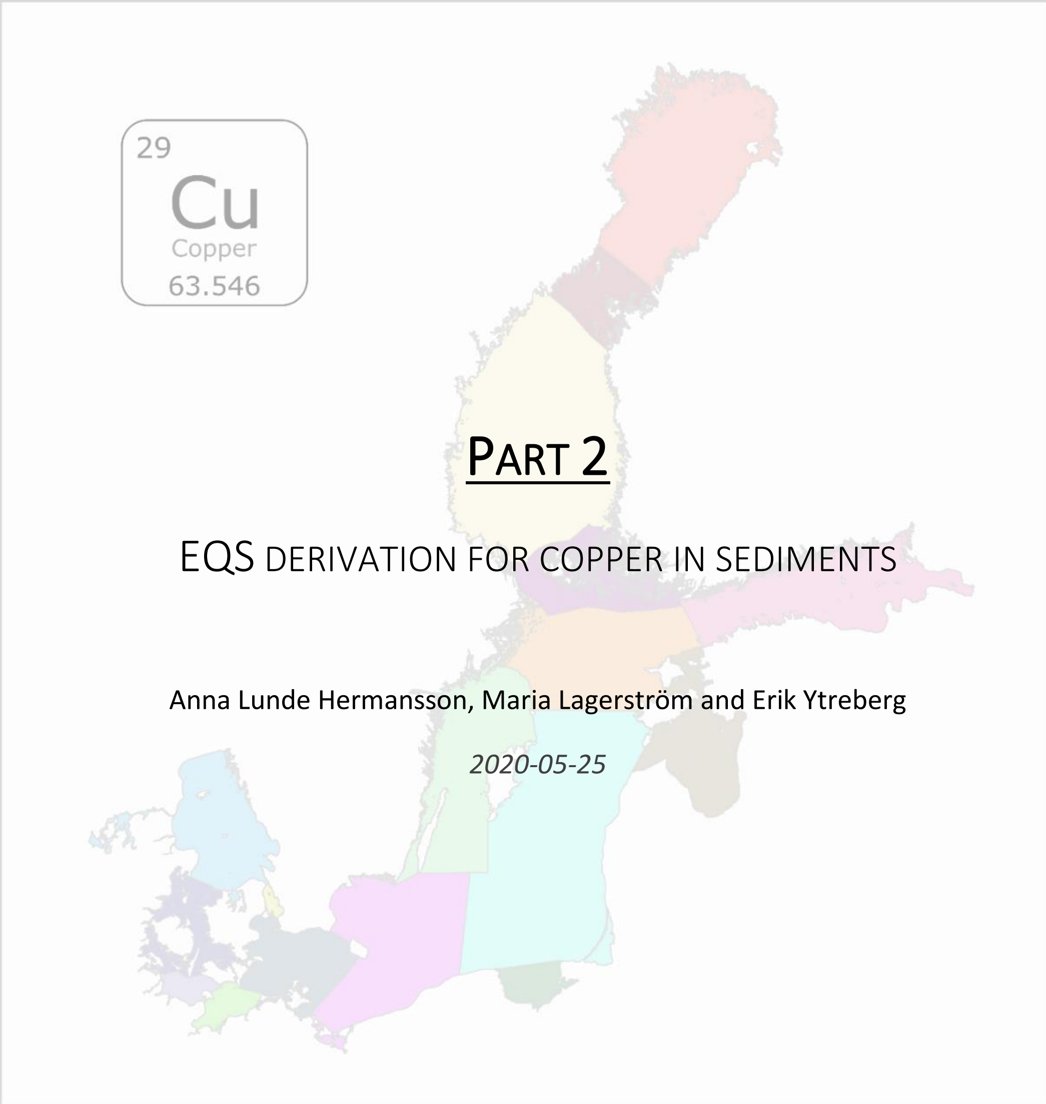


Figure 12. *Swedish status classification in coastal water bodies based on copper concentrations in sediment or water. Status classification data from WISS, 2020.*



Part 2

EQS derivation for copper in sediments

Anna Lunde Hermansson, Maria Lagerström and Erik Ytreberg

2020-05-25

2.1. METHOD SELECTION/CONSIDERATION

The process of deriving a new EQS for copper in sediment was separated into two parts. The first part was focused on collecting input from several sectors and expert judgement through three workshops. The second part consisted of an extensive literature study where ecotoxicological data was collected for further analysis. The Technical Guidance Document No. 27 (European Commission, 2018), hereafter TGD 27, served as a starting point for deriving the EQS of copper in sediment and has been used as the main supporting guidance document during decision making. When guidance on derivation of metals in the sediment matrix were lacking, expert judgement and interpretation from guidance of deriving EQS in the water matrix have also been important.

2.1.1 EXPERT ELICITATION THROUGH WORKSHOPS

As shown in **Table 7** and **Table 8**, the EQS-values of copper in use by different HELCOM contracting parties differ by a factor of up to 50. The main reasons for the substantial differences in national EQS for sediment and water originates from different assumptions regarding bioavailability, natural background, as well as quality assessment and data treatment of available ecotoxicological data. To discuss and hopefully resolve some of these issues, Chalmers University of Technology, together with the Swedish Agency for Marine and Water Management and the Danish Ministry of Environment organised three workshops in the spring of 2021. The workshop series was entitled "*Towards a harmonised approach for the derivation of an EQS for copper in marine sediments*". Participants were experts representing academia, industry, consulting agency and governmental authorities. Three main topics were discussed: 1) bioavailability, 2) natural background and 3) how ecotoxicological data should be treated when deriving an EQS for copper in marine sediments. The main objective of this expert elicitation endeavour was to provide concrete suggestions on each of the three topics, combining both scientific knowledge and practical feasibility. The main conclusions from the three workshops have been summarised below. Details on each of the workshops, as well as all group discussion notes can be found in **Appendix A**.

Workshop 1 – Bioavailability

To account for bioavailability, normalisation to organic carbon can be justified if it reduces the variability in the dataset. This is stated in TGD 27 and was also supported by participants at Workshop 1 on bioavailability and Workshop 3 on ecotoxicological data and EQS derivation. Even though it was recognised that other factors such as particle size and AVS may be important to consider, there was generally an agreement that the lack of data make these difficult to consider during EQS derivation at this time.

Workshop 2 – Natural background

During the derivation of an EQS, the total risk approach (TRA), referring to the total measured concentration, is preferable over the added risk approach (ARA), where the background concentration is first subtracted from the measured concentration before determining an EQS. As organisms inhabiting the sediment have no ability of distinguishing between natural or anthropogenic sources, the ARA is ecologically inappropriate. This conclusion was supported by workshop participants.

Workshop 3 – treatment of ecotoxicological data

During workshop 3, there was an agreement that marine and freshwater data could be pooled to perform a probabilistic approach (i.e. a species sensitivity distribution (SSD)) to derive an EQS for copper in sediment, if the marine data is insufficient and if statistics can show that there is not difference in sensitivity between the two types of species. This approach was also preferred over the deterministic one, used in previous dossiers on copper thresholds in sediment (e.g. Sahlin and Ågestrand, 2018; DK-EPA, 2019).

2.1.2 Selected approach for EQS derivation

TGD 27 suggests that background concentrations should be assessed during the implementation of the EQS rather than during the derivation process. This was also supported by participants at workshop 2. A decision to use TRA (rather than ARA) was therefore applied for the EQS derivation. At workshop 3, participants expressed a clear preference for a probabilistic approach over a deterministic one. A probabilistic approach (i.e. an SSD) was therefore selected to derive the HC5 (i.e. the concentration where 5% of the species included are affected). Since the Baltic Sea has a unique environment consisting of freshwater, brackish and marine species, participants at workshop 3 suggested that pooling of freshwater and marine ecotoxicological data could be appropriate. Additionally, this would provide a more extensive dataset allowing the application of the preferred probabilistic approach.

2.2 SSD ANALYSIS AND ESTIMATION OF HC5

2.2.1 COLLECTION OF ECOTOXICOLOGICAL DATA

Ecotoxicological studies and data was compiled from previous EQS dossiers (e.g. European Copper Institute, 2008; Sahlin and Ågestrand, 2018) and complemented with newer studies on the toxicity of copper in marine and freshwater sediments. The ecotoxicological data and studies used to derive an EQS for copper are described in detail in **Appendix B**. All studies included in the final SSD have been analysed with respect to reliability and relevance, either by the extensive Cu-VRAR (European Copper Institute, 2008) where all studies assigned Q1 (highest quality) are included or, for the more recent data, according to the CRED-model (Moermond et al., 2016) where only studies assigned C1 or C2 (relevant without/with restrictions) and R2 (reliable and relevant with some restrictions) where selected and used. No studies were assessed as R1 (reliable without restrictions).

In accordance with TGD 27, a statistical two tailed t-test (assuming unequal variances (F-test confirmation)) between the marine and freshwater datasets confirmed that pooling of the data was supported. There was no significant difference between freshwater and marine NOEC/EC10 values ($p=0.36$ non-normalised data and $p=0.64$ for TOC-normalised data). The final dataset of ecotoxicological test results represented a total of 12 species from 9 taxonomic groups (on order level) (**Figure 13**). TGD 27 does not provide guidance on the number of taxonomic groups required to perform an SSD for metals in the sediment but due to pooling, a total of 9 taxonomic groups (on order level) was achieved, fulfilling the minimum required number of taxa for the water column.The dataset included 4 marine species (4 taxonomic groups) and 8 freshwater species (5 additional taxonomic groups + amphipoda already represented by marine species) where the species represent different feeding and living conditions from both the marine and limnic environment (**Figure 13** and more detailed description in **Appendix B**).

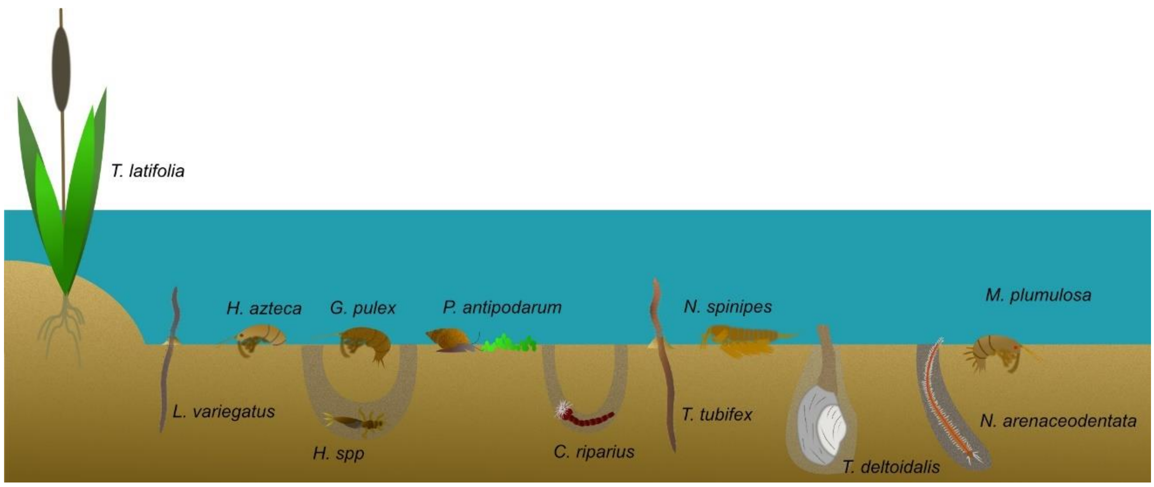


Figure 13. *All species, and an illustration of their feeding/living conditions, that were included in the final SSD analysis (Figure 15) where the four species to the right (N. spinipes, T.deltoidalis, N. arenaceodentata and M. plumulosa) are tested in marine sediments while the rest are tested in freshwater sediments. More detailed information on the species can be found in Appendix B.*

2.2.2 BIOAVAILABILITY

As described in section 2.1 , one outcome from workshop 1 was that the data should be normalized to organic carbon if it reduces the variability in the dataset. Based on calculations of the Max:Min ratios of the different species-specific endpoints it can be argued that the variability within the dataset is reduced by normalisation to organic carbon (**Figure 14**). A comparison of the relative standard deviations (RSDs) for 6 species and endpoints also showed a decrease when data was normalised to organic carbon (Table 1 in **Appendix B**). Based on this, it was decided to normalise the data to 5% organic carbon (following TGD 27 recommendations) prior to the SSD analysis.

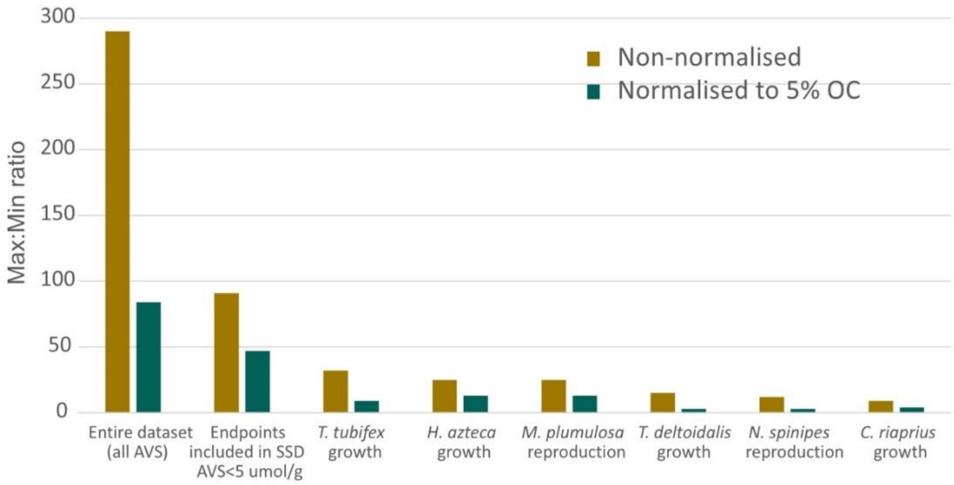


Figure 14. *The Max:Min ratios of the 1) entire dataset, 2) the "low AVS" data and 3) the most sensitive endpoints of species with more than 3 NOEC/EC10 values. The bars represent data that has not been normalised (brown) vs. normalised to 5% organic carbon (green).*

As TGD 27 highlights the importance of using worst-case scenario ecotoxicological tests, and that the acid volatile sulphides (AVS) can reduce the bioavailability and thus increase the apparent tolerance of copper in sediment, studies with high AVS levels were removed from the final SSD analysis. Most studies where AVS > 1 µmol/g were thus excluded from the dataset to follow TGD 27 recommendations. However, several of the ecotoxicology studies on marine species were conducted under conditions where AVS is defined as being <4.5 µmol/g (see **Appendix B**), but as these tests included some of the more sensitive species and end-points they were nonetheless included in the final analysis. Where no information on AVS was provided, expert judgement considering oxygen supply, redox potential and sediment origin determined whether or not the test results were included in the final SSD (see table 3 in **Appendix B**).

2.2.3 SSD ANALYSIS

SSD analysis was conducted using the US-EPA SSD toolbox (US-EPA, 2020), allowing for several different fitting methods and distribution functions that could be compared to obtain the best fit for the available data (**Appendix B**). Maximum likelihood was used as the fitting method for all analysis as this is a commonly applied and preferred approach when performing SSD for regulatory purposes

(Carr and Belanger, 2019; Fox et al., 2021). The selection of data, based on AVS and organic carbon properties as described previously, resulted in a total of 49 test results (NOEC and EC10 values) from 12 species that was used in the final SSD analysis (Figure 6 and Table 3 in **Appendix B**). The geometric mean of all toxicity values ranged from 50 to 1513 mg/kg dw, with max-to-min ratio of 30. The logistic distribution offered the best fit (**Appendix B** for comparison), especially in the left tail of the curve, with an overall R^2 value of 0.97 (Q-Q plot, **Figure 15**). Despite this, the generated HC5 value (61 mg/kg dw) is not protective of the most sensitive species/endpoints of *M. plumulosa* (40 mg/kg dw), *H. Azteca* (51 mg/kg dw), *T. tubifex* (32 mg/kg dw) and *T. deltoidalis* (37 mg/kg dw).

Applying the logistic distribution, the derived HC5=61 mg/kg dw (Lower limit 33 mg/kg; upper limit 124 mg/kg) (**Figure 15**).

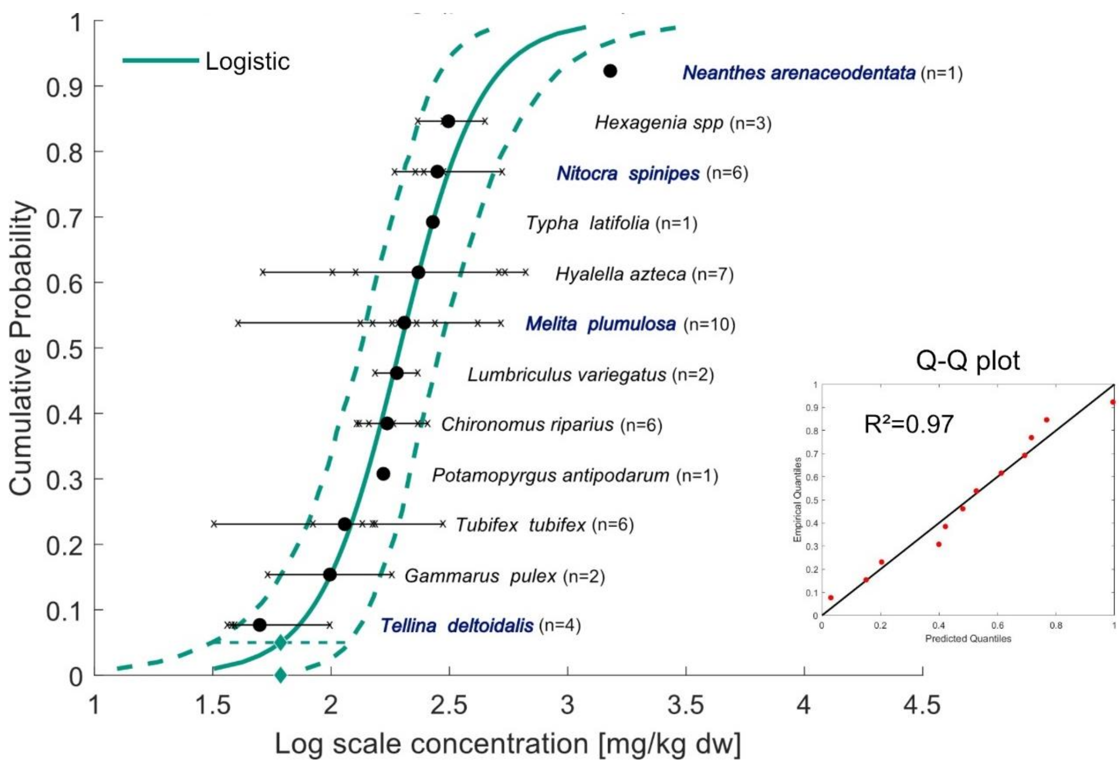


Figure 15. *The log logistic SSD curve based on NOEC/EC10 values normalised to 5% organic carbon. The dots represent the geometric mean (or single value) of each species (written to the right of the curve, dark blue and bold show marine species) with the horizontal line representing the range and the X showing the discrete NOEC/EC10 value for each species (number of values=n). The full line represents the fitted curve and the dashed lines are the upper and lower confidence interval of the fitting of the curve. The diamond shows the HC5 value (and is also put on the x-axis for better read) and the horizontal dashed line shows the 95% confidence interval of the HC5 value. The inset "Q-Q plot" represents the goodness-of-fit of the curve where the R2 value=0.97.*

2.3 PROPOSED EQS FOR COPPER IN BALTIC SEA SEDIMENTS

The HC5 derived from the best fitting distribution (61 mg/kg dw normalized to 5% TOC) was used for the EQS setting. Considering the lower limit of the HC5 value and the absence of ecotoxicological data and high quality marine mesocosm/field data from the Baltic Sea, an AF = 3 was applied and **an EQS of 20 mg/kg dw normalised to 5% TOC** is proposed to be used.

2.3.1 SELECTION OF ASSESSMENT FACTOR

The derived HC5 value was used to calculate a protective EQS value for copper in sediments for the Baltic Sea region by dividing the HC5 value with an additional safety factor, also known as assessment factor (AF). To set an appropriate AF, several aspects were considered in the weight-of-evidence approach suggested by TGD 27.

First, the lower limit of the HC5 value (=33 mg/kg dw) is 1.8 times lower than the HC5-50 (=61 mg/kg dw), suggesting that an AF of at least 2 should be used. The lower limit of the confidence interval is however not protective for the lowest NOEC/EC10 value (=32 mg/kg dw of *T. tubifex*), which could justify an AF>2. In addition, if an SSD curve is performed using only the lowest reported EC10/NOEC from each species/endpoint (see **Appendix B**), the derived HC5 (=19 mg/kg dw) is 3.2 times lower than HC5-50 value (=61 mg/kg dw). This again could justify an AF > 2.

Secondly, even though the number of species and taxonomic groups are fulfilled to perform an SSD, only 5 of the species used in the SSD can be found the Baltic Sea region and no testing was conducted on Baltic populations. Baltic ecosystems are considered more vulnerable to pollution than most other marine or freshwater ecosystems due to its unique combination of low salinity, low biodiversity and limited food-web with only a few key-species (Kautsky and Svensson, 2003; Magnusson and Norén, 2012). Therefore, following the precautionary principle, a more conservative assessment factor (>2) is required to adequately protect the Baltic Sea ecosystem.

Further, the results from marine and freshwater mesocosm and field studies show effect values in the approximate range of 100-400 mg/kg dw normalised to 5% TOC (**Appendix B**). Even though none of the studies have been performed using species and/or communities from the Baltic Sea the results indicated that an AF above 3 will most likely be overprotective for the Baltic Sea.

Other parameters that were considered in the weight-of-evidence approach included short-term (acute) test results, the taxonomic groups and their respective feeding and living conditions and the quality assessment of the studies (**Appendix B)**. The weighing of the arguments regarding these parameters, however, balanced each other out, resulting in no change of the selection of AF.

Based on reasoning and arguments following TGD 27 and the outcomes from the workshops (**Appendix A**), with the strongest weight assigned to the confidence interval and the sensitivity of the Baltic Sea area**, an AF of 3** is recommended and used for the derivation of an EQS for copper in marine sediments for the Baltic Sea region.

As the proposed EQS should protect Baltic Sea species, more effort should be made to perform ecotoxicological studies and mesocosm/field studies using Baltic species before lowering the AF to 2.

2.3.2 CONSIDERATION OF NATURAL BACKGROUND CONCENTRATIONS

TGD 27 specifies that the size of the AF should not normally result in a quality standard below typical natural background concentrations (NBC). This is particularly stressed for metals. Studies on the background concentrations of copper in the Baltic Sea are however currently lacking. Nonetheless, to attempt to evaluate whether an AF of 3 would lead to an EQS < NBC, the sediment data set presented in part 1 of this report (see section 1.2.2), was searched for samples collected at depths below 10 cm. A total of 17 stations, of which some had been sampled recurringly, were found. As shown by the map in **Figure 16**, the stations were located in 8 different subbasins of the southern Baltic Sea. Hence, no deep samples for the northern and eastern Baltic Sea (e.g. Gulf of Finland) were part of this analysis. Although the sediments have not been dated, the plotted profiles show that the concentrations typically vary little at depths below 15-20 cm (**Figure 16**). The concentration in such deep samples could thus give an idea of the range of background concentrations of Cu in the Baltic Sea. Below 20 cm, concentrations of Cu (not normalized to TOC) are typically between 10-50 mg/kg, dw, except for the Eastern Gotland Basin where concentrations as high as nearly 100 mg/kg dw have been measured.

To assess the applicability of the proposed EQS, concentrations need to be normalised to 5% TOC. TOC concentrations were only reported for sediment samples from 3 of the 8 subbasins (**Figure 17**). At depths of 30 cm, the normalised concentrations in the three subbasins range from 4.3 to 23.3 mg/kg dw, with an average ± 1 standard deviation of 13.6 ± 4.6 mg/kg dw (5% TOC normalisation). These results suggest that the proposed EQS value of 20 mg/kg dw, at 5% TOC would be close to, but not necessarily below NBC. More studies in different HELCOM subbasins and preferably with dating of the sediments are however needed to allow for a more accurate determination of the NBC. If such studies would reveal that an EQS based on an AF of 3 is indeed below the NBC, TGD 27 states the first step is to investigate how to reduce the uncertainty of the EQS. If the uncertainty cannot be reduced, for example through additional ecotoxicological studies, the natural background can be taken into account when assessing compliance. In locations where the EQS value exceeds the natural background, the natural background could for instance be used as the threshold value instead, as proposed by participants at Workshop 2 (**Appendix A**). However, the implementation of the EQS value and the corresponding status classification is beyond the scope of this report.

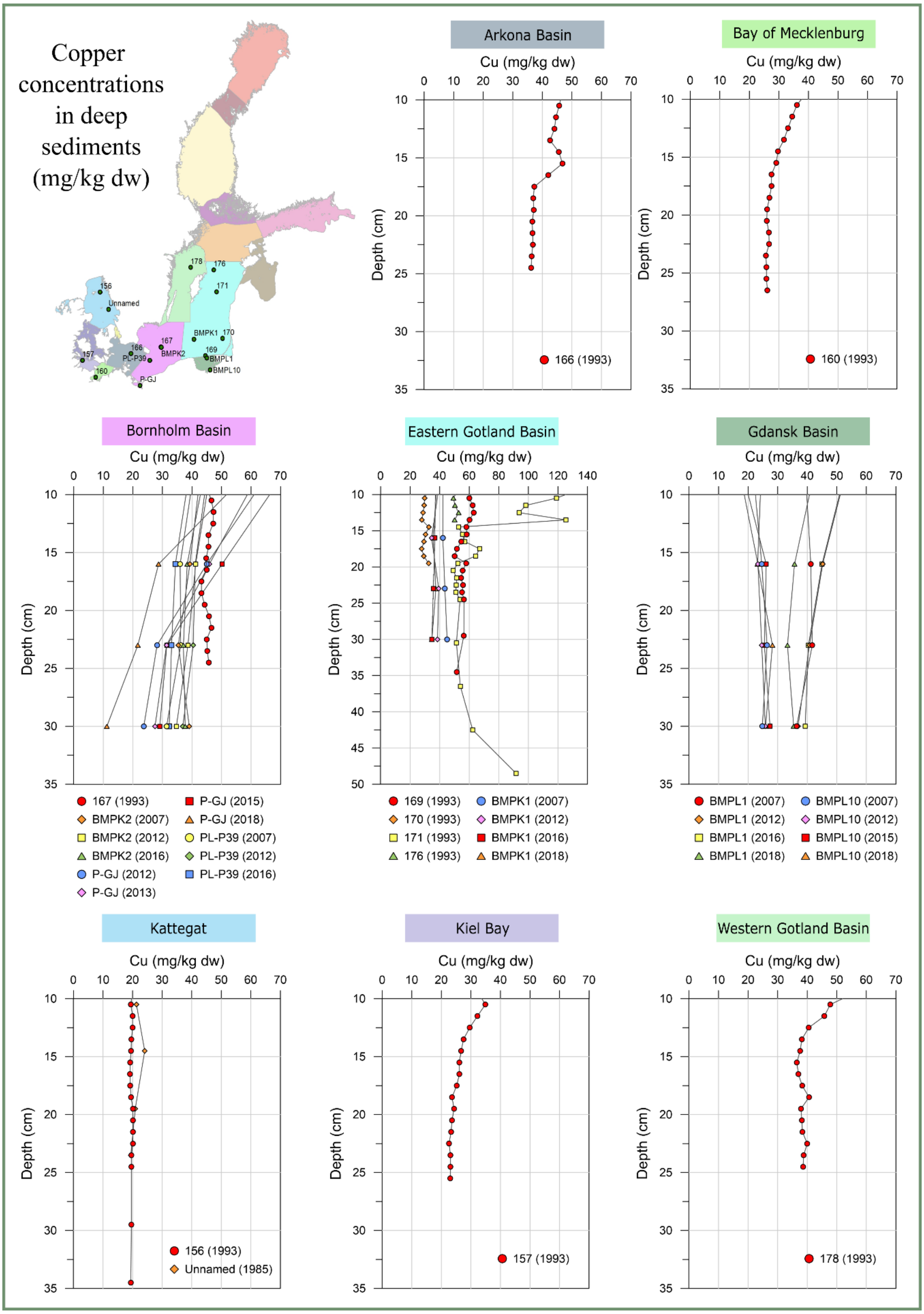


Figure 16. *Sediment depth profiles with sampling depths > 10 cm. The scales of the x- and y-axis's are the same for all graphs except the Easter Gotland Basin. Note that some of the stations were sampled several years.*

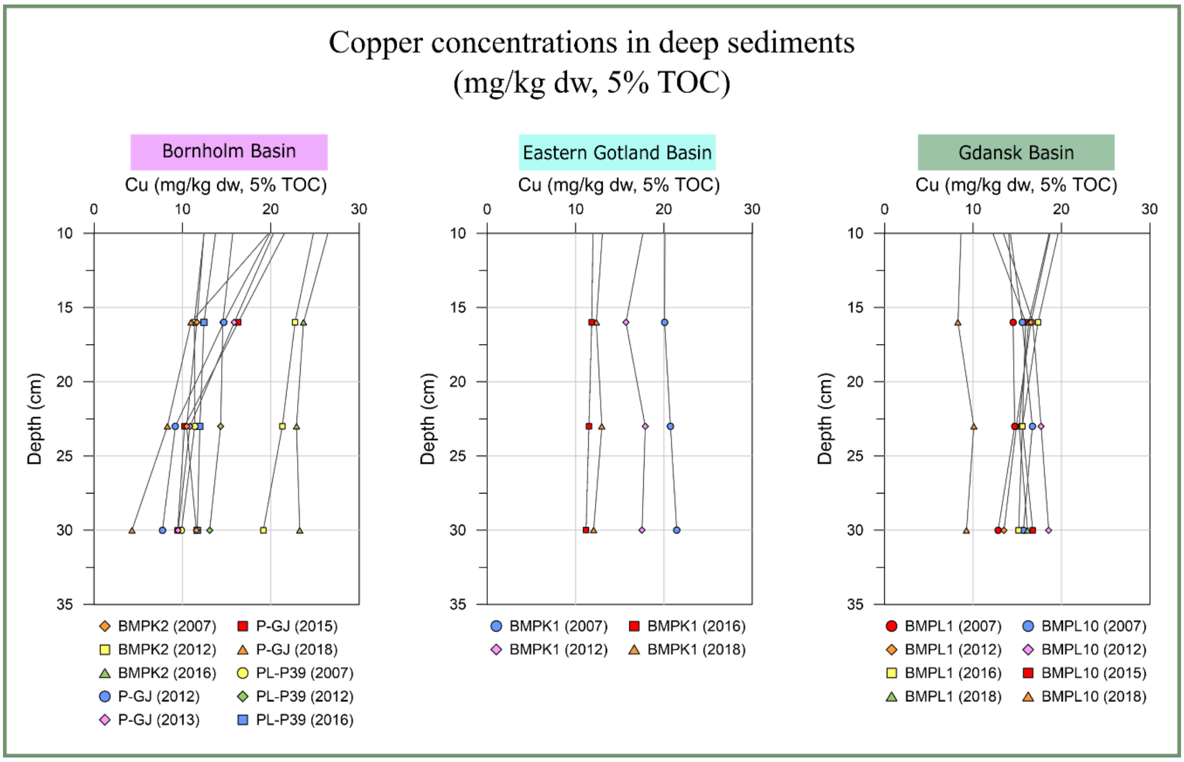


Figure 17. *Sediment depth profiles with sampling depths > 10 cm, normalised to 5% organic carbon. See the map in Figure 17 for the sampling locations.*

2.4 Application of the proposed EQS

2.4.1 Organic carbon concentrations in Baltic Sea sediments

As the proposed EQS requires normalisation to organic carbon, the concentrations of TOC in the Baltic subbasins as reported on dry weight basis into the ICES Dome portal were mapped (**Figure 18**). The data shows that the TOC concentration in Baltic Sea sediments varies widely, both within and between basins and ranges from nearly 0 to 25%, dw. As the box plot shows, 50% of the data points are found between 1.6 and 6.0%, with a median OC concentration of 4.2%. The corresponding EQS values for these TOC concentrations would be: 6.4 (at 1.6% TOC), 16.8 (at 4.2% TOC) and 24.0 (at 6.0% TOC) mg Cu/kg dw.

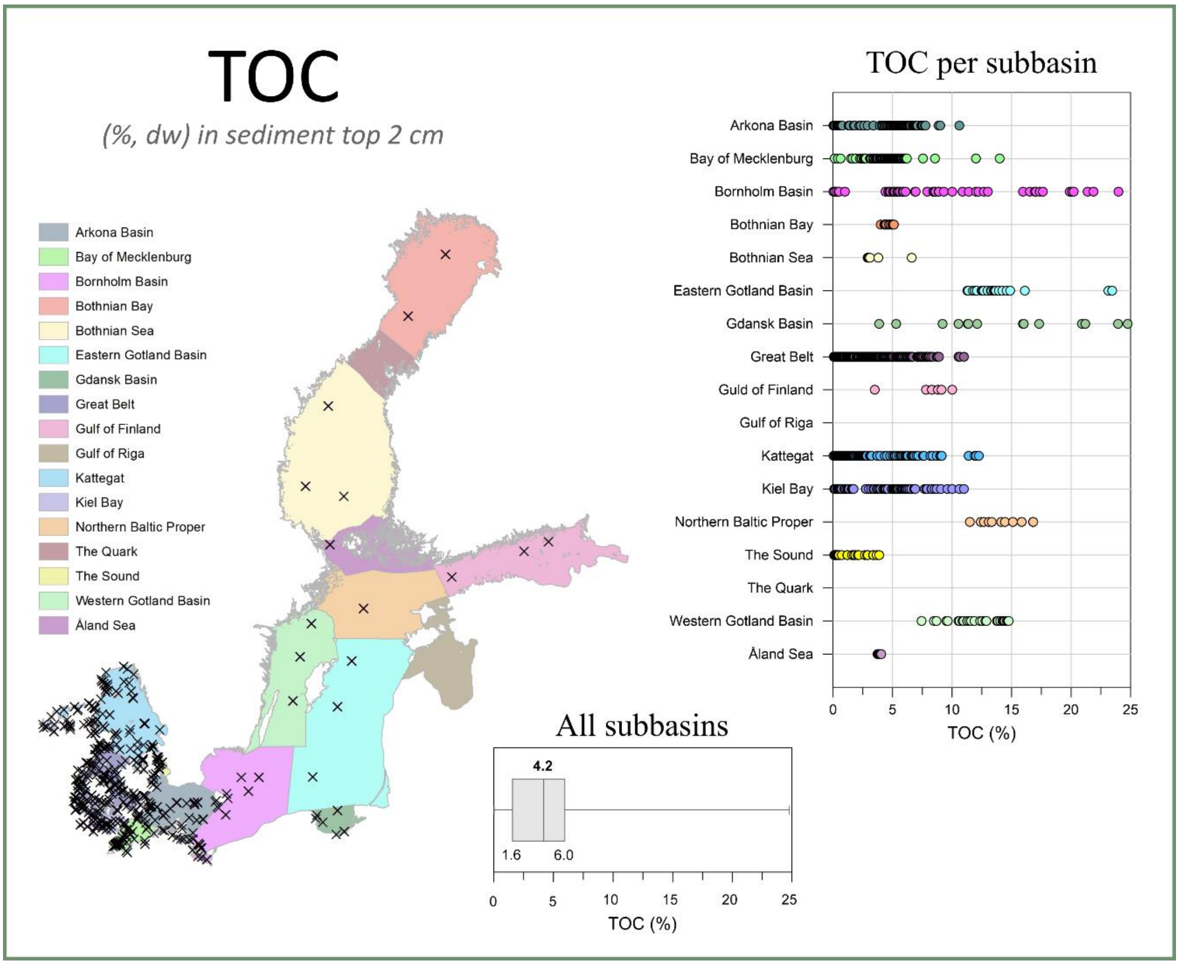


__Figure 18.__ Organic carbon concentrations in percent dry weight in surface sediments (top 2 cm) as reported into the ICES Dome portal. Sampling locations are shown on the map. The dataset includes samples from 1990 – 2019. The top graph shows the individual data points per subbasin. The bottom graph is a box plot of all measured concentrations (n = 1052).

2.4.2 COMPARISON OF EQS VALUE WITH MEASURED CONCENTRATIONS

The collected sediment concentrations for Cu in surface sediments (top 2 cm, see section 1.2.2) were normalised to 5% TOC. Such metadata was available for 809 out of the total 1,599 data points. Samples were collected from 1985 to 2019, the bulk of which were between the years 2000 and 2019 (86%) and, more specifically, between the years 2003 and 2014 (73%). Hence, data for more recent years and the suggested assessment period (2016-2021) are lacking.

The normalised concentrations are shown, per subbasin, in **Figure 19**. The results show that there is a wide variation between and within basins, with concentrations mainly between 10 and 100 mg/kg dw at 5% TOC. Some samples of very high concentrations (> 10,000 mg/kg dw, 5% TOC) are suspected to be the result of misreported TOC data.

The maps in figure 19 show that 90% of data points would be in exceedance of the proposed EQS (AF = 3) of 20 mg/kg, dw at 5% TOC. Even if a lower AF of 2 had been proposed, a vast majority (76%) of data points would still be in exceedance.

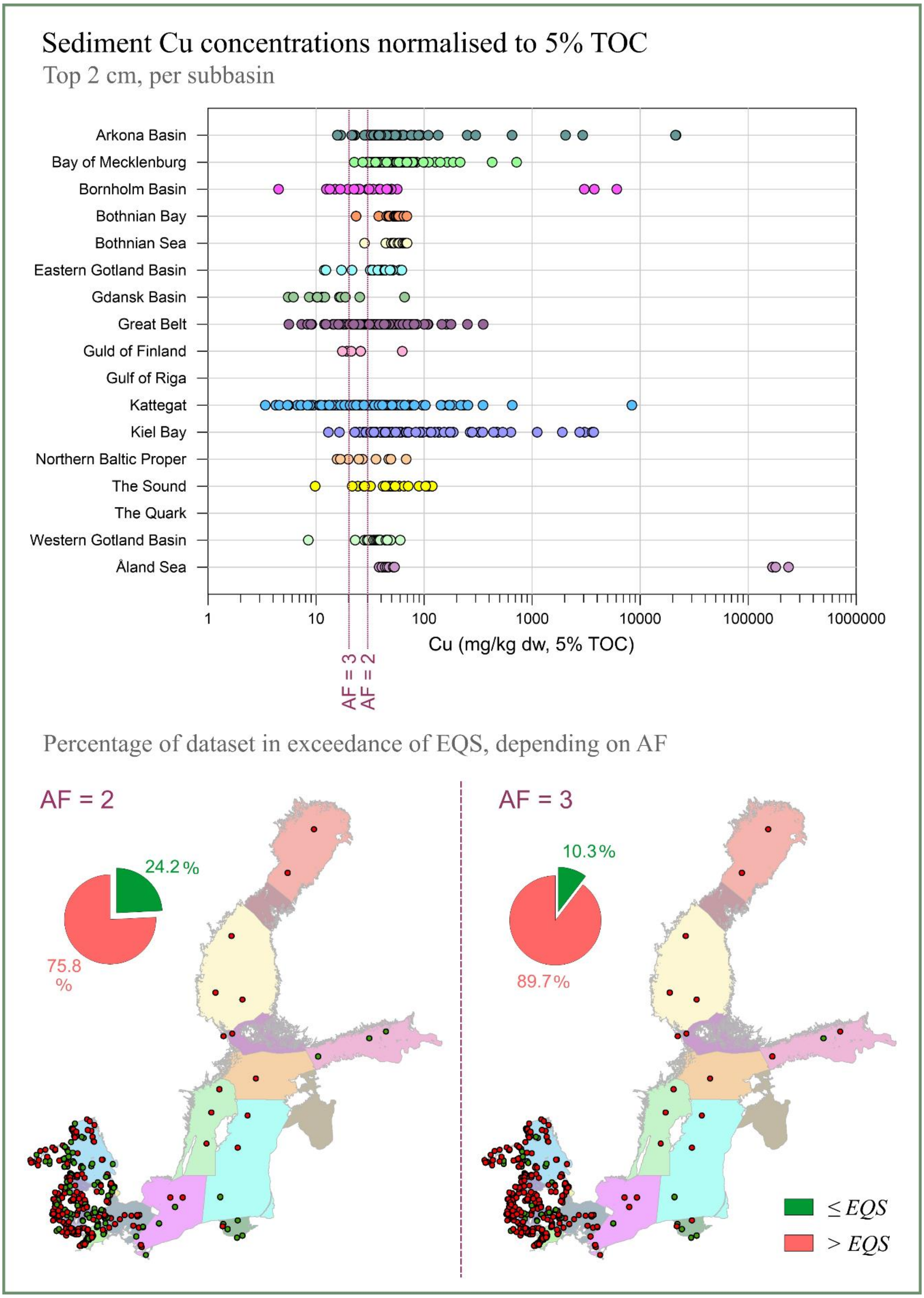


Figure 19. *Normalised copper concentrations (in mg/kg dry weight, at 5% TOC) in surficial sediments (≤ 2 cm depth) in the Baltic Sea per subbasin (top graph). The maps at the bottom show the data points below (green) and above (red) the proposed EQS, as well as the overall proportion of data points in exceedance of the proposed EQS-values given an AF of 2 (left) or 3 (right).*

References

Amara, I., Miled, W., Slama, R.B., Ladhari, N., 2018. Antifouling processes and toxicity effects of antifouling paints on marine environment. A review. Environ. Toxicol. Pharmacol. 57, 115–130. https://doi.org/10.1016/j.etap.2017.12.001

Brown, P.L., Markich, S.J., 2000. Evaluation of the free ion activity model of metal-organism interaction: extension of the conceptual model. Aquat. Toxicol. 51, 177–194. https://doi.org/10.1016/S0166-445X(00)00115-6

Campana, O., Simpson, S.L., Spadaro, D.A., Blasco, J., 2012. Sub-Lethal Effects of Copper to Benthic Invertebrates Explained by Sediment Properties and Dietary Exposure. Environ. Sci. Technol. 46, 6835–6842. https://doi.org/10.1021/es2045844

Campbell, P.G.C., 1994. Interactions between trace metals and aquatic organisms: a critique of the Free-ion Activity Model. Met. Speciat. Bioavailab. 45–102.

Carr, G.J., Belanger, S.E., 2019. SSDs Revisited: Part I—A Framework for Sample Size Guidance on Species Sensitivity Distribution Analysis. Environ. Toxicol. Chem. 38, 1514–1525. https://doi.org/10.1002/etc.4445

Danielsson, S., Bignert, A., Faxneld, S., Nyberg, E., Andersson, M., Jones, D., Kylberg, E., Strömquist, J., Johansson, A.-M., Hjelmquist, P., Mechedal, J., Sundbom, M., Bizkarguenaga, E., Benskin., J., de Wit, Egebäck, A.-L., Eriksson, U., Kruså, M., 2018. Distribution and conversions of metal-and POP concentrations among various tissues in herring. Swedish Museum of Natural History.

DK-EPA, 2019. Fastsættelse af kvalitetskriterier for vandmiljøet - Kobber (Draft asssessment). Ministry of Environment of Denmark - Envrionmental Protection agency.

Ejhed, H., Palm Cousins, A., Karlsson, M., Köhler, S., Huser, B., Westerberg, I., 2011. Feasibility study of net load of metals, SMED report No 50 2011 (No. 50).

EMODnet, 2020. European Marine Observation and Data Network, Data portal, Chemistry. [WWW Document]. Cent. Portal. URL https://www.emodnet.eu/en/chemistry (accessed 8.11.20).

European Commission, 2018. Technical guidance for deriving environmental quality standards. Guidance document no. 27. Updated version 2018.

European Copper Institute, 2008. Voluntary Risk Assessment Report (VRAR) for copper, copper(II) sulfate pentahydrate, copper(I) oxide, copper(II) oxide, dicopper chloride trihydroxide.

Fathollahzadeh, H., Kaczala, F., Bhatnagar, A., Hogland, W., 2014. Speciation of metals in contaminated sediments from Oskarshamn Harbor, Oskarshamn, Sweden. Environ. Sci. Pollut. Res. 21, 2455–2464. https://doi.org/10.1007/s11356-013-2173-0

Faxneld, S., Danielsson, S., Nyberg, E., Bignert, A., 2015. Conversion factors for metals between liver, muscle and wholebody in perch.

Fox, D.R., Dam, R.A. van, Fisher, R., Batley, G.E., Tillmanns, A.R., Thorley, J., Schwarz, C.J., Spry, D.J., McTavish, K., 2021. Recent Developments in Species Sensitivity Distribution Modeling. Environ. Toxicol. Chem. 40, 293–308. https://doi.org/10.1002/etc.4925

Hansson, K., Andersson, H., Ejhed, H., Liljeberg, M., Olshammar, M., Skårman, T., Sörme, L., Dunsö, O., Segersson, D., 2012. Diffuse emissions to air and water, SMED Report No 164 2012 (No. 164 2012).

HELCOM, 2011. Fifth Baltic Sea Pollution Load Compilation (PLC-5). Baltic Sea Environment Proceedings No. 128.

ICES, 2020. DOME (Marine Environment) data portal. [WWW Document]. URL https://www.ices.dk/data/data-portals/Pages/DOME.aspx (accessed 8.11.20).

Jalkanen, J.P., Johansson, L., 2019. Discharges to the sea from Baltic Sea shipping in 2006 - 2018. Finnish Meteorological Institute, Baltic Marine Environment Protection Commission, Maritime Working Group, Lisbon, Portugal.

Jalkanen, J.-P., Johansson, L., Wilewska-Bien, M., Granhag, L., Ytreberg, E., Eriksson, K.M., Yngsell, D., Hassellöv, I.-M., Magnusson, K., Raudsepp, U., Maljutenko, I., Styhre, L., Winnes, H., Moldanova, J., 2020. Modeling of discharges from Baltic Sea shipping. Ocean Sci. Discuss. 1–54. https://doi.org/10.5194/os-2020-99

Johansson, L., Ytreberg, E., Jalkanen, J.-P., Fridell, E., Eriksson, K.M., Lagerström, M., Maljutenko, I., Raudsepp, U., Fischer, V., Roth, E., 2020. Model for leisure boat activities and emissions – implementation for the Baltic Sea. Ocean Sci. 16, 1143–1163. https://doi.org/10.5194/os-16-1143-2020

Josefsson, S., Apler, A., 2019. Miljöföroreningar i utsjösediment – geografiska mönster och tidstrender, SGU-rapport 2019:06, Diarie-nr: 35-778/2017 och 35-1141/2018.

Kautsky, L., Svensson, S., 2003. 6. Life in the Baltic Sea. Baltic University Press, pp. 148–181.

Kylin, H., Haglund, K., 2010. Screening of Antifouling Biocides Around a Pleasure Boat Marina in the Baltic Sea After Legal Restrictions. Bull. Environ. Contam. Toxicol. 85, 402–406. https://doi.org/10.1007/s00128-010-0094-x

Lagerström, M., Ferreira, J., Ytreberg, E., Eriksson-Wiklund, A.-K., 2020. Flawed risk assessment of antifouling paints leads to exceedance of guideline values in Baltic Sea marinas (under review).

Leivuori, M., Jokšas, K., Seisuma, Z., Kulikova, I., Petersell, V., Larsen, B., Pedersen, B., Floderus, S., 2000. Distribution of heavy metals in sediments of the Gulf of Riga, Baltic Sea. Boreal Environ. Res. 5.

Magnusson, K., Norén, K., 2012. The sensitivity of the Baltic Sea ecosystems to hazardous compounds, PM 9/12. Swedish Chemicals Agency.

Moermond, C.T.A., Kase, R., Korkaric, M., Ågerstrand, M., 2016. CRED: Criteria for reporting and evaluating ecotoxicity data. Environ. Toxicol. Chem. 35, 1297–1309. https://doi.org/10.1002/etc.3259

ÖVF, 2020. Öresunds vattenvårdsförbund, undersökningar. [WWW Document]. URL http://www.oresunds-vvf.se/undersokningar/ (accessed 8.14.20).

Pohl, C., Hennings, U., 2005. The coupling of long-term trace metal trends to internal trace metal fluxes at the oxic–anoxic interface in the Gotland Basin (57°19,20′N; 20°03,00′E) Baltic Sea. J. Mar. Syst. 56, 207–225. https://doi.org/10.1016/j.jmarsys.2004.10.001

Pohl, C., Kattner, G., Schulz-Baldes, M., 1993. Cadmium, copper, lead and zinc on transects through Arctic and Eastern Atlantic surface and deep waters. J. Mar. Syst. 4, 17–29. https://doi.org/10.1016/0924-7963(93)90017-G

Ryabchuk, D., Vallius, H., Zhamoida, V., T. Kotilainen, A., Rybalko, A., Malysheva, N., Deryugina, N., Sukhacheva, L., 2017. Pollution history of Neva Bay bottom sediments (eastern Gulf of Finland, Baltic Sea). Baltica 30, 31–46. https://doi.org/10.5200/baltica.2017.30.04

Sahlin, S., Ågestrand, M., 2018. Copper in sediment EQS data overview. ACES report number 28. Department of Environmental Science and Analytical Chemistry (ACES) Stockholm University.

Swedish Agency for Marine and Water Management, 2019. HVMFS 2019:25, Havs- och vattenmyndighetens föreskrifter om klassificering och miljökvalitetsnormer avseende ytvatten.

US-EPA, 2020. Center for Computational Toxicology and Exposure, EPA's (2020): Species Sensitivity Distribution (SSD) Toolbox. The United States Environmental Protection Agency's Center for Computational Toxicology and Exposure. Software. [WWW Document]. URL https://doi.org/10.23645/epacomptox.11971392.v1

Vallius, H., 2015a. Applying sediment quality guidelines on soft sediments of the Gulf of Finland, Baltic Sea. Mar. Pollut. Bull. 98, 314–319. https://doi.org/10.1016/j.marpolbul.2015.06.036

Vallius, H., 2015b. Quality of the surface sediments of the northern coast of the Gulf of Finland, Baltic Sea. Mar. Pollut. Bull. 99, 250–255. https://doi.org/10.1016/j.marpolbul.2015.07.070

Vallius, H., Ryabchuk, D., Kotilainen, A., 2007. Distribution of heavy metals and arsenic in soft surface sediments of the coastal area off Kotka, North-Eastern Gulf of Finland, Baltic Sea. Spec. Pap. - Geol. Surv. Finl. 45, 33–48.

WISS, 2020. Water Information System Sweden, a database developed by the Competent Authorities of the Swedish Water Districts, the County Administrative Boards and the Swedish Agency for Marine and Water Management. [WWW Document]. URL https://viss.lansstyrelsen.se/ (accessed 6.23.20).