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Status and Trends of Organotin in Sediments in the Southern North Sea

Common Indicator Assessment

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Trends of Organotin in Sediments in the Southern North Sea

Contributors

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Citation

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Contents

Key Message

Following the total ban on tributyltin in marine applications, mean concentrations in sediment have measurably reduced (with a trend of approx. -10% per year) in the Southern North Sea but no monitoring station is yet significantly below the EQS value proposed by Sweden of 0,8 µg kg^{-1} at 2,5% OC (https://www.ospar.org/documents?v=43227) assessment criteria. The need for follow-up of the situation is still apparent.

Background (brief)

Tributyltin (TBT) and other organotin compounds are found globally, throughout the marine environment. Organotins have many applications and TBT was extensively used in antifouling paints on watercraft **(Figure a**), buoys, and mariculture equipment, which led to the widespread distribution of TBT in water, sediment, and biota. TBT is prone to oxidation, so in a well-mixed water column without any input, concentrations decrease rapidly, the same is true for oxygenated sediments, whilst under anoxic conditions, the substance is stable.

High concentrations of TBT in sediment are generally associated with commercial ports, harbours, shipyards, shipping lanes and previously also marinas. Organotins are toxic to many marine organisms even at very low concentrations. For example, widespread declines in some snail populations have occurred due to hormone disruption by TBT, and TBT was the cause for the slow but steady decrease of brown shrimp in impacted areas, although this was only recently concluded. However, the situation is improving following legislation banning the use of TBT in all marine applications and restrictions for product use within the EU.

TBT use was banned in the late 1980s for smaller vessels and has been prohibited on all vessels and offshore installations since 2008, or ships must bear at least a barrier coating. However, inputs of TBT to the aquatic environment are likely to continue, from countries not in compliance with the ban, from disused vessels or installations, from land-based applications and by redistribution of contaminated soils and sediments.

Figure a: TBT has been used as an antifoulant in paint on ship hulls (image from Parmentier et al., 2019)

Background (extended)

Tributyltin (TBT) and other organotin compounds are contaminants found globally, throughout the marine environment. Organotins have many applications, such as coatings, anti-odour/anti-fungal additives, pesticides, biocides in marine antifoulant paints, catalysts, wood treatments and preservatives. Extensive use in antifouling paints on watercraft and protection of other sea-based installations led to the widespread distribution of TBT in estuarine and marine water, sediment, and biota.

Organotins are toxic to many marine organisms even at very low concentrations. High concentrations of TBT in sediment are generally associated with commercial ports, harbours, shipyards, shipping lanes and marinas (**Figure b**) and can cause shell deformities in oysters and impair reproduction, which was the first reported deleterious effect (Alzieu *et al.*, 1982). Subsequently, it was noted that female marine snails develop male sexual characteristics due to hormone disruption by TBT. This has led to widespread declines in some snail populations (Imposex Indicator Assessment). France was the first responding country by issuing a ban in 1982 on the application of organotin-based paints on ships < 25 m waterline and fish farms. Similar bans followed suit between 1987 and 1991 throughout the North Sea countries. In 1989, the EU imposed such measures on all Member States (EU Council Directive 89/677/EEC, European Commission, 1989) and the IMO acted accordingly on a global scale in 1990 (IMO resolution MEPC. 29 (25), 1990). In 2001, the IMO adopted the 'International Convention on the Control of Harmful Antifouling Systems, 2001,' formalising a global ban on the application of organotin antifouling agents on marine vessels after the deadline of 17 September 2008 [AFS Convention, modified in 2010 (IMO resolution MEPC. 195 (61), 2010)] to include guidelines on survey and certification of antifouling systems on ships). The EU transposed the 2001 AFS Convention into Regulation (EC) 782/2003 (EU Regulation No. 782/2003, European Union, 2003) which banned the application of TBT on EU-flagged vessels starting on 1 January 2003. That regulation further obliged all ships visiting EU ports from 1 January 2008 onwards to be free of TBT or at least to bear a barrier coating (Parmentier *et al.*, 2019).

Figure b: High concentrations of TBT in sediment are normally associated with commercial ports, harbours, shipyards, shipping lanes and marinas.

The consecutive ban on different vessels led to a decline of environmental TBT concentrations, especially after 2008 (Verhaegen *et al.*, 2012). TBT is quite sensitive to oxidation processes leading to dealkylation, rendering the substance much less toxic. These processes occur fast in a fully oxygenated water column or oxygenated sediments, whilst TBT can persist in anoxic sediments. Especially in highly impacted areas, like estuaries and along the major shipping routes, the concentrations dropped significantly over the entire North Sea since 2008, and the entire ecosystem got a positive stimulus because of the reduced stress due to TBT (Parmentier *et al.*, 2019). As most organisms are vulnerable in their early development stages, the resilience of several marine populations increased. There are several reasons to do a follow-up of concentrations in sediments: the concentrations determined are quality assured, and readily comparable for temporal and spatial trend assessment, the indicator “imposex” can be biased by mutant strains of snails that support higher concentrations of TBT, whilst the objective is to protect the wild type organisms, and a low VDSI index can give a false sense of safety, as larvae, especially fish larvae, can be even more sensitive to TBT.

OSPAR’s North-East Atlantic Environment Strategy (NEAES 2030) aims to achieve and maintain concentrations in the marine environment close to zero for human made hazardous substances. Despite the TBT ban for marine applications, inputs of TBT to the aquatic environment are likely to continue, arising from countries not in compliance with the ban, from disused vessels or installations, through the redistribution of already contaminated sediments. Wastewater treatment plants and landfills are another potential source of TBT to the marine environment, as organotin compounds are sometimes applied to consumer products. The use of organotins in consumer products is regulated in the EU through Decision 2009/425/EC and afterward by Regulation No. 276/2010 that amended Annex XVII of the REACH Regulation (EC) No. 1907/2006. Articles and mixtures not meeting the imposed threshold limits of TBT may not be sold or used in the EU since 2012. The follow-up of all these potential sources necessitates a continued monitoring of the presence of TBT in the environment.

Assessment Method

Assessment methods for trends and status were made using the methods described in the contaminant online assessment tool https://dome.ices.dk/OHAT/trDocuments/2021/help_ac_sediment_contaminants.html Assessment Criteria are described at https://dome.ices.dk/OHAT/trDocuments/2022/help_ac_sediment_contaminants.html

Trend assessment

The results from the individual time series at each monitoring site were synthesised at an assessment area scale in a series of meta-analyses.

A time series of organotin concentrations in sediment is assessed for trend if:

- there is at least one year with data in the period 2015 to 2020
- there are at least five years of data over the whole time series
- a parametric model can be fitted to the data

For the synthesis at the assessment area scale, data were used only from monitoring sites considered representative of general conditions or baseline stations. Data from monitoring sites impacted by point sources were excluded. The analysis was also restricted to assessment areas with at least three monitoring sites with trend information and where those monitoring sites had good geographic spread. The criteria for trend assessment were only fulfilled in one assessment area: the Southern North Sea.

For a regional trend assessment, the trend in each time series is summarised by the estimated change in log concentration over the last twenty years (or shorter if the time series does not extend that far back). A regional (Southern North Sea) trend for each organotin is then estimated by fitting the following linear mixed model by restricted maximum likelihood:

- response: trend (yearly change in log concentration)
- fixed model: organotin
- random model: station + residual variation

The fixed model means that a separate regional trend is estimated for each organotin. The random effects allow for variation in trend between stations common to all organotins (station). The residual variation is made up of two terms: the variation associated with the estimate of the trend from the individual time series, which is assumed known (and given by the square of the standard error); and a term which accounts for any additional residual variation not explained by the other fixed and random effects.

Status assessment

A time series of organotin concentrations in sediment is assessed for status if:

- there is at least one year with data in the period 2015 to 2020;
- there are at least three years of data over the whole time series;
- a parametric model can be fitted to the data and used to estimate the mean concentration in the final monitoring year (or, occasionally, if a non-parametric test of status is applied).

There are no restrictions on data used in the status meta-analysis based on the classification of the monitoring station; time series data from baseline, representative and impacted stations are all included. However, the few time series with a non-parametric assessment of status must be excluded, because there is no summary measure of status to use in the mixed model. The criteria for status assessment were only fulfilled in one assessment area: the Southern North Sea.

For a regional status assessment, the status of each time series is summarised by the difference between the estimated mean log concentration in the final monitoring year and the log assessment concentration. Essentially the same linear mixed model as for trends is then fitted:

- response: status (mean log concentration - log assessment concentration)
- fixed model: intercept
- random model: residual variation

Where the residual variation is made up of the status estimation variation, the variation in the status estimates from the individual time series analysis, and a term which accounts for any additional variation not explained by the other fixed and random effects. The fixed model only includes an intercept since there is an assessment concentration for only one organotin and region.

Data from monitoring sites available to assess the status of organotin concentrations in the Irish and Scottish West Coast, Irish Sea, Southern North Sea and Channel (**Table a**). Time series data available to assess temporal trends for the Southern North Sea and Irish and Scottish West Coast (**Table b**).

Table a: Number of monitoring sites used to assess organotin concentration status in sediment, by OSPAR contaminants assessment area and organotin compound. TBT: tributyltin, DBT: dibutyltin, MBT: monobutyltin, TPhT: triphenyltin

OSPAR contaminants assessment areas	Stations	TBT	DBT	MBT	TPhT
Irish Sea	5	5	0	0	0
Irish and Scottish West Coast	2	2	0	0	0
Southern North Sea	36	31	29	32	2
Channel	4	4	2	2	0

Table b: Number of monitoring sites used to assess temporal trends in organotin concentrations in sediment, by OSPAR contaminants assessment area and organotin compound. TBT: tributyltin, DBT: dibutyltin, MBT: monobutyltin, TPhT: triphenyltin

OSPAR contaminants assessment areas	Stations	TBT	DBT	MBT	TPhT
Southern North Sea	32	31	29	32	2
Channel	4	4	2	2	0
Irish Sea	5	5	0	0	0
Irish and Scottish West Coast	2	2	0	0	0

The location of the monitoring sites in the Southern North Sea, Channel, Irish Sea, and the Irish and Scottish West Coast are shown in **Figure c**.

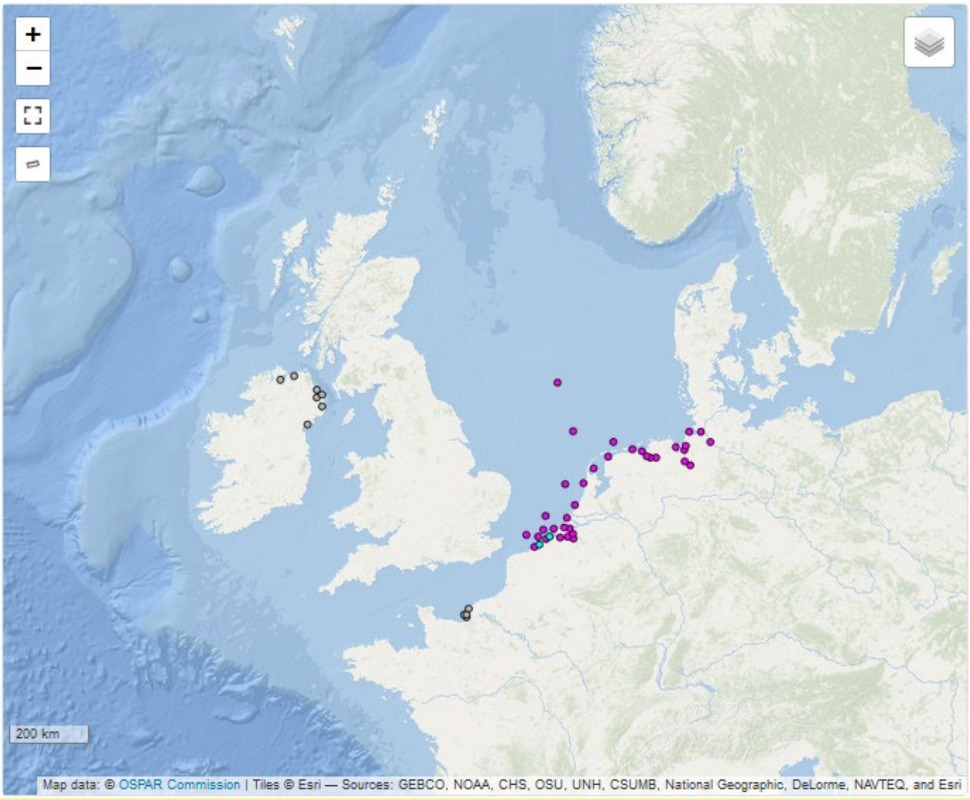

Figure c: Monitoring sites available to assess organotin concentrations in sediment in the Southern North Sea, Channel, Irish Sea and the Irish and Scottish West Coast. The purple circles are stations where there is a trend assessment for at least one organotin, the light blue circles are stations where there are only status assessments, and the grey circles are stations which were not included in the assessment as they did not meet the criteria for inclusion. Available via ODIMS.

Differences in methodology used for the IA 2017 compared with the QSR 2023

For the QSR 2023, a meta-analysis is used to synthesise the individual time series results and provide an assessment of status and trend at the assessment area level. Meta-analyses take into account both the estimate of status or temporal trend in each time series and the uncertainty in that estimate. They provide a more objective regional assessment than was possible in the QSR 2010, where a simple tabulation of the trend and status at each monitoring site was presented.

The EQS value used for the evaluation of the environmental quality of sediment is the one proposed by Sweden and adopted by OSPAR, namely 0,8 µg kg^{-1} at 2,5% OC (https://www.ospar.org/documents?v=43227; the value was originally set at 1,6 µg kg-1 at 5% OC). Denmark has a reservation against the use of this threshold value, as they agreed nationally on another, more stringent one.

Results (brief)

The regional trend as well as status of TBT in sediments could only be assessed for the Southern North Sea. The current trend estimate for the Southern North Sea is a yearly 10% decrease of TBT concentration. The assessment of status for TBT in sediments for the Southern North Sea shows that the EQS is not met and that estimated mean concentration relative to the EQS is approximately 3,6. If current rates of decrease continue it will take more than one decade to reach EQS levels.

Results (extended)

Results can be found at the dedicated OHAT page for organotins in sediment:

https://dome.ices.dk/OHAT/trDocuments/2022/regional_assessment_sediment_organotins.html

Organotin profiles

The profile of concentrations across organotins can sometimes be useful for examining sources, and for comparing concentrations across regions where assessment criteria are not available for each organotin time series. The estimated organotin concentration profiles for the Southern North Sea are shown in **Figure e**.

As the toxicity of organotin compounds rapidly decreases when the number of organic ligands decreases, the TBTSn+ and TPhTSn+ are the compounds that are the main reason for concern. The loss of organic substituents is an oxidation process, this explains why organotins are remarkably stable in sediments, especially in oxygen-deficient sediments, but are readily degraded in the water column except for anoxic water layers. This property explains why after 15 years of TBT ban on ships sailing in European waters, there are still regions where detected TBT is significantly above the EQS value, and it is most probable that these areas are along the major shipping lanes and big ports. The TBT embedded in the sediment is only released slowly, though faster release occurs during dredging operations, the major impact being reduced to the dredged and the disposal area.

The different processes governing the release of organotins from the sediment is complex and depends on numerous parameters, so the easiest follow-up is by trend analysis of the monitoring results combined with a risk-based choice of the stations near ports and along major shipping lanes.

Exceedance of the EQS value for TBT in sediments was noted for the major part of the Southern North Sea, the Channel and the Irish Sea. It should be noted that the major TBT monitoring effort is concentrated in that area, in view of the intense shipping traffic this can be considered a logical choice. When looking at individual stations, EQS exceedance can be as high as 30-fold, which necessitates a follow-up over at least a decade.

Assuming that the current yearly change of –10,2% will continue and that the current mean regional status for TBT (TBSN+) for the Southern North Sea is 3,6 times the EQS value, it will require 12 years until the mean value is approximately at the EQS level. It is not well-documented whether the lower butylated products degrade even faster, but in any case, the major toxicological concern arises from TBT. The concentration of TPhT is significantly lower.

Table c: Estimates of the regional (Southern North Sea) trend by organotin.

organotin	trend	se	lower	upper	% yearly change	%yc lower	%yc upper
TBT	-10,77	0,66	-12,05	-9,48	-10,21	-11,35	-9,05
DBT	-7,33	0,70	-8,71	-5,96	-7,07	-8,34	-5,78
MBT	-0,99	0,65	-2,26	0,28	-0,99	-2,24	0,28

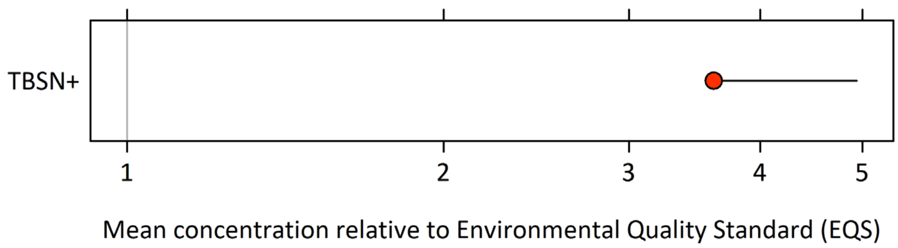

Figure d: Mean regional status for TBT (TBSN+) for the Southern North Sea with estimated mean concentration relative to the EQS and pointwise upper one-sided 95% confidence interval

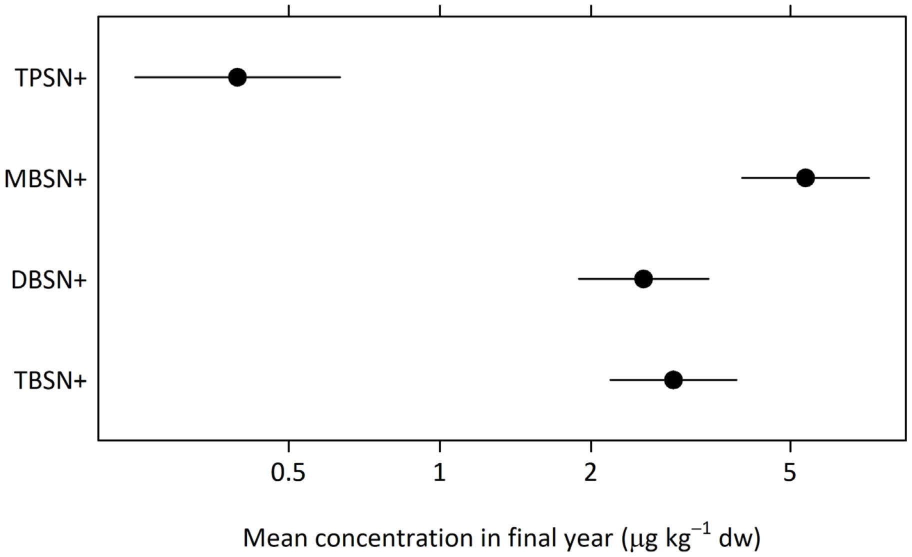

Figure e: The estimated organotin concentration profiles for the Southern North Sea with pointwise 95% confidence limits. The units are ug/kg dw normalised to 2,5% organic carbon. The EQS for TBT (TBSN+) is 0,8 µg/kg dw sediment normalized to 2,5% OC, other organotins do not have generally agreed EQS values.

Conclusion (brief)

It is clear that the regulation of TBT has been effective in reducing the input to the Southern North Sea in general. However, the general levels of TBT concentration levels are still at levels where effects on the marine environment cannot be excluded. Based on the current trend with a decrease of about 10% per year, it is expected that TBT levels in the sediment will exceed EQS for at least another decade. The data availability for the Southern North Sea is relatively good and the assessment of trends and status has a high degree of confidence.

Conclusion (extended)

Relatively soon after the start of widespread use of TBT as an antifoulant, effects were demonstrated and attributed to its presence. The impact on molluscs occurred at very low concentrations, and the associated biological effects (Imposex or VDSI index) led to its use as a Biological Effects Indicator. Indeed, at that period it was hard to accurately determine the presence of TBT with analytical chemical methods. The threshold for VDSI was much lower than for oysters. Oyster malformations in Arcachon Bay prompted a serious response from the French Environmental Agency. Other countries and the EU followed suit by banning TBT on small ships. Many scientists considered imposex a suitable indicator, and little work was done to further unravel the mechanism of action, and the effect of TBT on other marine organisms. In fact, as extensively demonstrated in Parmentier et al., (2019) and references therein, effects of TBT on larval stages, in particular on fish larvae, occur at even lower concentration levels than for dogwhelk.

The TBT ban on small ships was issued for economic reasons (oyster culture), but it took considerably longer for a total ban, as the general feeling was that only molluscs were at stake. Their limited economic importance did not trigger a fast ban on all marine applications. It took until 2008 to have a ban in full force, together with the publication of effects on a number of other marine organisms, occurring at extremely low concentrations, and revealing the Endocrine Disruptive power of the booster biocide TBT. For example, TBT was shown to be causing effects in the stock of brown shrimp *Crangon crangon*.

More recent evaluations by Sweden and Denmark set levels even lower, as recent publications reveal more and more effects of TBT. As lesson learnt, it should be noted that, whenever a substance is supposed to enter the marine environment in important quantities, and there is a demonstrated effect on any organism at levels in the range of ng/L, a full suite of toxicity tests needs to be undertaken to properly evaluate the risk, and to be able to adequately demonstrate safe levels using adequate evaluation methodology, based on a Species Sensitivity Distribution containing sufficient genera and taxa. If that had been done for TBT, the substance would have been banned a lot earlier. Actually, it is strange that the substance was not immediately banned for all applications, as the risk of having the substance leached to the marine environment cannot be ruled out.

Knowledge Gaps (brief)

Although direct inputs of TBT to the marine environment have been banned in the OSPAR maritime area and mostly in the rest of the world, general levels are such that ecological effects cannot be excluded, non-pesticidal use of TBT is still ongoing in some countries, release from contaminated sites is ongoing and thus further monitoring of TBT concentrations in the marine environment is warranted.

The OSPAR EQS value is based on the Swedish EQS but has recently been replaced in HELCOM with the Danish EQS due to availability of new data. OSPAR experts should consider if the OSPAR EQS should also be updated, reflecting availability of new data.

Knowledge Gaps (extended)

Full evaluation of the toxicity of TBT should have been triggered by the work of Alzieu et al., (1982). The conclusions of this article should have sent marine scientists a high alert signal, indicating that a vast research effort needed to be undertaken. For only a fraction of the money earned by the sale of TBT and the economic benefits on shipping, a complete study could have been financed to cover the costs.
The ban of TBT has not solved the problem of fouling on ships and marine infrastructure. Alternatives prove to be as problematic, and so there is a real need for an antifoulant with limited environmental impact. Candidate substances must be thoroughly evaluated with regard to toxicity.

A further evaluation of TBT toxicity, even after the ban, will generate knowledge and expertise to carry out an enhanced evaluation in the future, in order to prevent another worldwide problem for the marine environment. When the fisheries in Europe are considered, an improvement of the situation in the last decade is observed. As measures have been taken on different aspects of the ecosystem, it is hard to evaluate to what extent the ban of TBT has contributed to the revival of certain fish stocks, yet the sentiment amongst a lot of analytical marine chemists is that it cannot be underestimated.

A holistic approach, taking into account all aspects, as suggested in Parmentier et al., (2019), should be the standard for evaluation of all new antifoulants and substances used in comparable applications.

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Assessment Metadata

Field	Data Type	
Assessment type	List	Indicator Assessment
Summary Results (template Addendum 1)	URL	https://odims.ospar.org/en/submissions/ospar_tbt_sediment_msfd_2022_06/
SDG Indicator	List	14.1 By 2025, prevent and significantly reduce marine pollution of all kinds, in particular from land-based activities, including marine debris and nutrient pollution
Thematic Activity	List	Hazardous Substances
Relevant OSPAR Documentation	Text	Agreement 2002-16 CEMP Guidelines for Monitoring Contaminants in Sediments. Revised in 2018 Agreement 2016-04 CEMP Guidelines for coordinated monitoring for hazardous substances. Revised in 2021
Linkage	URL	https://www.frontiersin.org/articles/10.3389/fmars.2019.00633/full https://www.ospar.org/documents?v=43227 https://www.ices.dk/news-and-events/news-archive/news/Pages/Tributylin.aspx
Date of publication	Date	2022-06-30
Conditions applying to access and use	URL	https://odims.ospar.org/en/data_policy/
Data Snapshot	URL	https://doi.org/10.17895/ices.data.21229139
Data Snapshot	URL	https://doi.org/10.17895/ices.data.18601820
Data Results	Zip File	https://odims.ospar.org/en/submissions/ospar_tbt_sediment_results_2022_06/
Data Source	URL	https://dome.ices.dk/ohat/?assessmentperiod=2022

OSPAR's Quality Status Report 2023

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Our vision is a clean, healthy and biologically diverse North-East Atlantic Ocean, which is productive, used sustainably and resilient to climate change and ocean acidification.

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