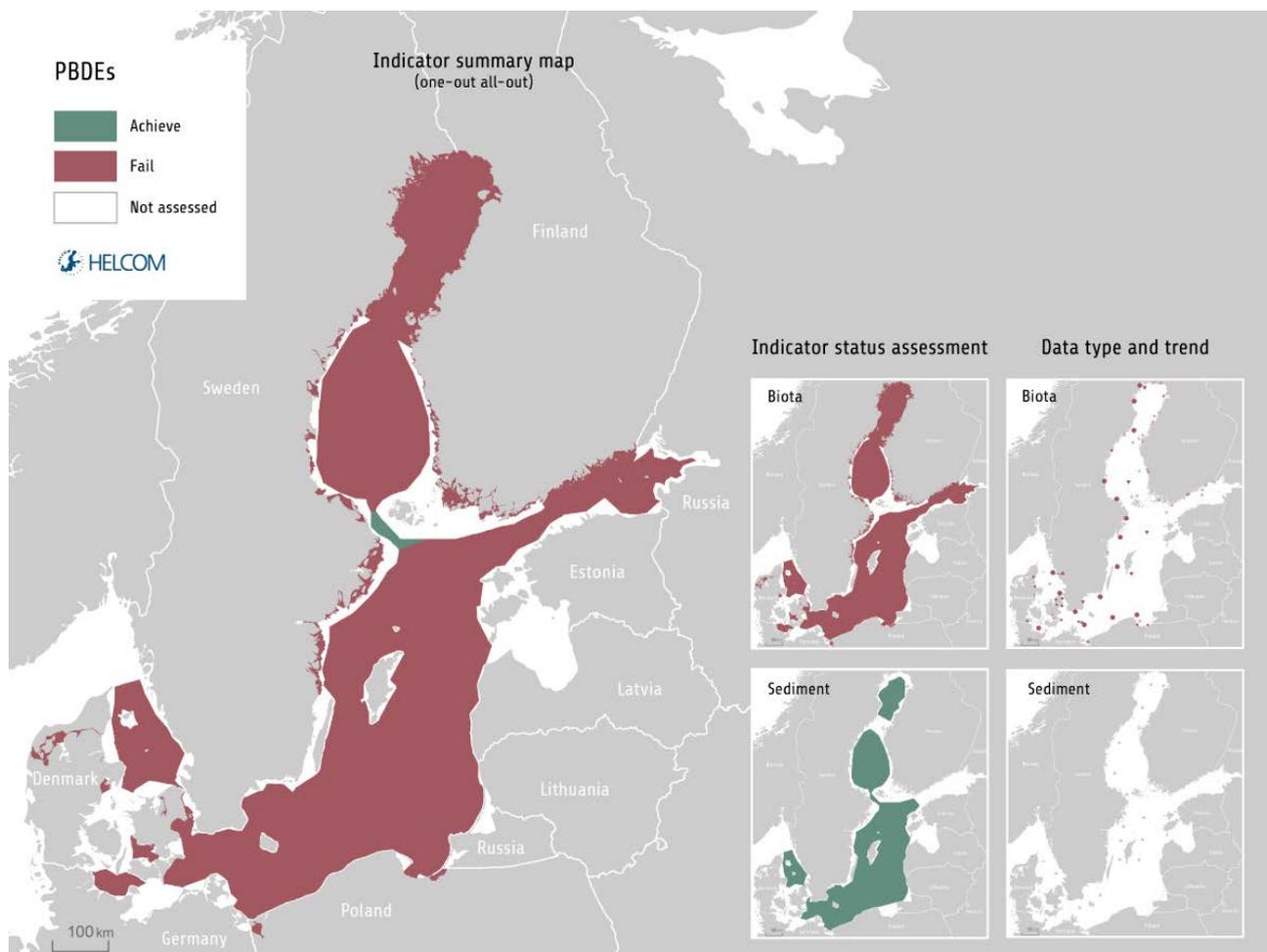


## Polybrominated diphenyl ethers (PBDEs)

### Key Message

The available data and evaluations show that the concentration of polybrominated diphenyl ethers (PBDEs) is high in biota (though less so in sediments) throughout the Baltic Sea. The status of the sum of PBDE congeners (28, 47, 99, 100, 153 and 154) in fish, during the period 2011 to 2016, shows that the threshold is exceeded at every monitoring site in the Baltic Sea, resulting in all fish monitoring areas being classified as ‘not good status’ (Key message figure 1). The core indicator threshold value is the EU Environmental Quality Standard (EQS) of 0.0085 µg kg<sup>-1</sup> wet weight (ww) in fish. The threshold is considered to be very precautionary and is due for review by the EU Chemicals Working Group.



**Key message figure 1.** Status assessment results based on the evaluation of the indicator Polybrominated diphenyl ethers (PBDEs). Status assessments are provided as a summary using the One-Out-All-Out approach (main figure), for biota (upper inset), and for sediment (lower inset). The assessment is carried out using Scale 4 HELCOM assessment units (defined in the [HELCOM Monitoring and Assessment Strategy Annex 4](#)). [Click here to access interactive maps at the HELCOM Map and Data Service: PBDEs.](#)

Concentrations of single PBDE congeners are declining, but the availability of long time series is limited in the Baltic Sea and concentrated to the western parts of the region.

The confidence of the indicator evaluation is **high**.

The indicator is applicable in the waters of all countries bordering the Baltic Sea.

### Relevance of the core indicator

Polybrominated diphenyl ethers (PBDEs) are toxic and persistent substances that bioaccumulate in the marine foodweb. Increasing concentrations of PBDEs were detected in the environment in past decades as their use as commercial flame retardants increased. The use of most PBDE products have been banned in Europe during the last 10 years, and as a result decreasing concentrations are detected for some of the PBDE congeners.

### Policy relevance of the core indicator

	BSAP Segment and Objectives	MSFD Descriptors and Criteria
<b>Primary link</b>	<ul style="list-style-type: none"> <li>Concentrations of hazardous substances close to natural levels</li> </ul>	D8 Contaminants - D8C1 Within coastal and territorial waters and beyond territorial waters the concentrations of contaminants do not exceed the threshold value
<b>Secondary link</b>	<ul style="list-style-type: none"> <li>Fish safe to eat</li> </ul>	D9 Contaminants in fish and other seafood - D9C1 The level of contaminants in edible tissues (muscle, liver, roe, flesh or other soft parts, as appropriate) of seafood (including fish, crustaceans, molluscs, echinoderms, seaweed and other marine plants) caught or harvested in the wild (excluding fin-fish from mariculture) does not exceed the threshold value
<b>Other relevant legislation:</b> The Water Framework Directive and EC regulation No 850/2004 (and its following amendments) and the Stockholm Convention on Persistent Organic Pollutants.		

### Cite this indicator

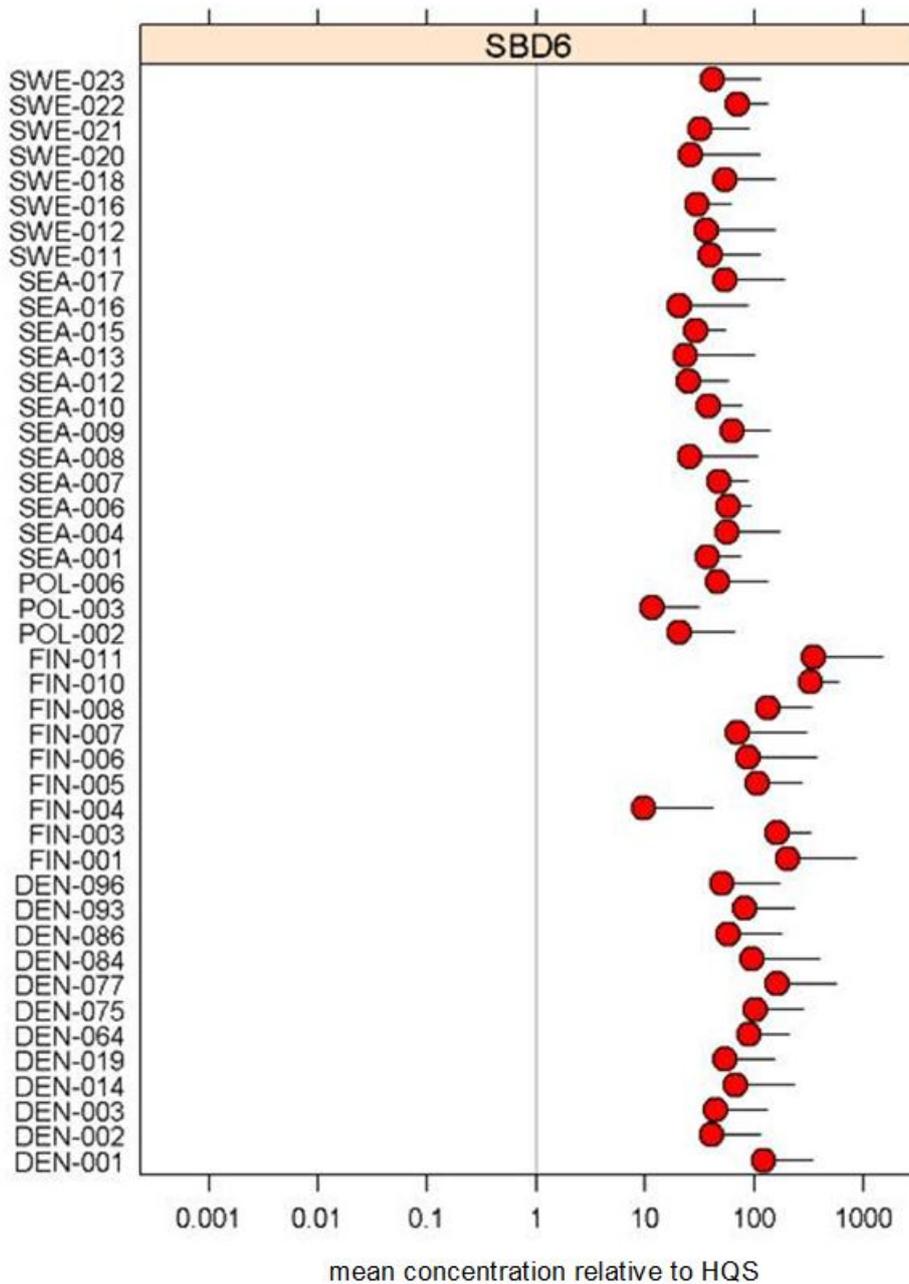
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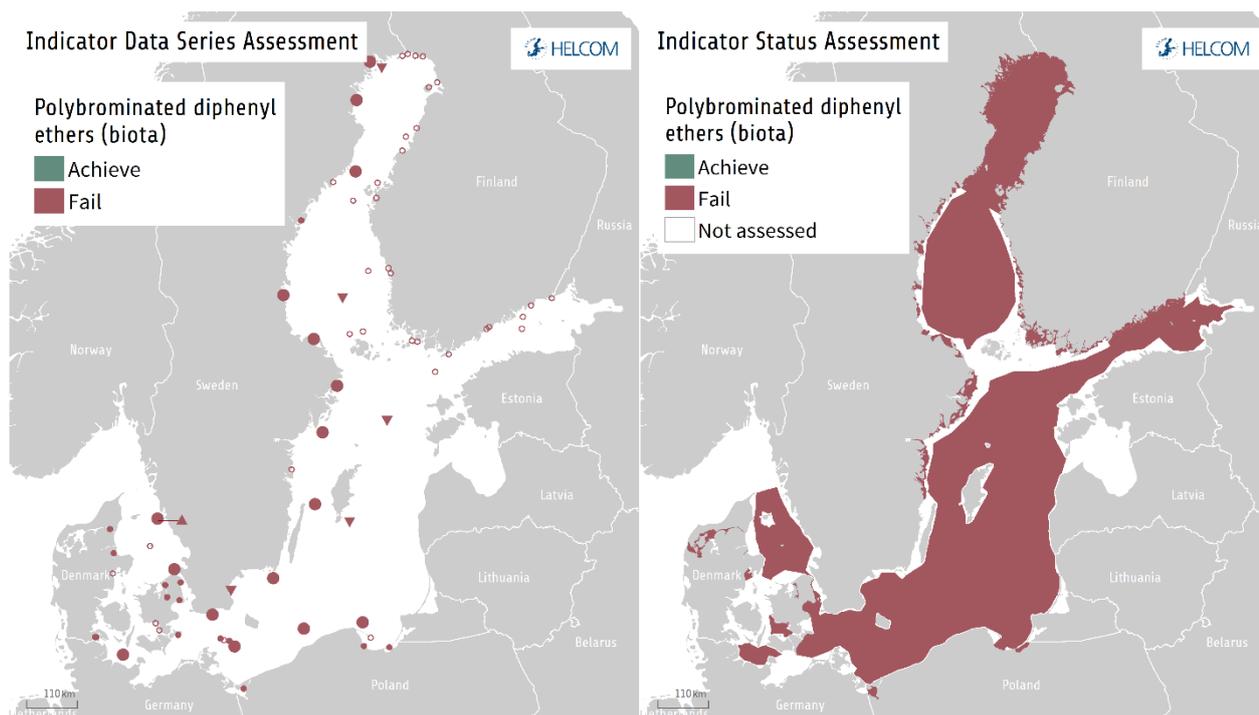
[Polybrominated diphenyl ethers PBDEs HELCOM core indicator 2018 \(pdf\)](#)

## Results and Confidence

Overall the status of polybrominated diphenyl ethers (PBDEs) fail the threshold value (Results figure 1). Data is available across a wide spatial area and shows that the concentrations of PBDEs are above the threshold value in biota throughout the Baltic Sea.



**Results figure 1.** Aggregated mean concentrations in biota per scale 4 HELCOM assessment unit. The bars represent the upper 95% confidence interval. The threshold value is exceeded (failed) in all areas.



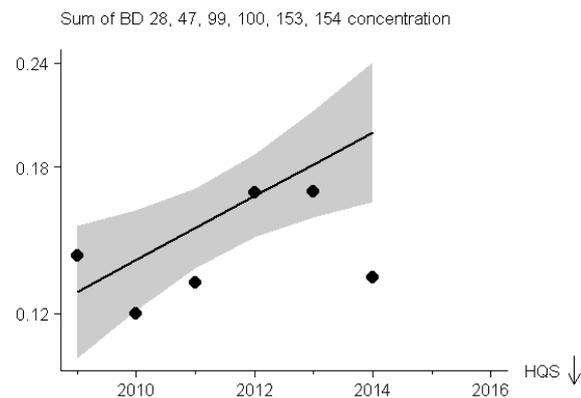
**Results figure 2.** PBDE biota measurements per station in the Baltic Sea (right) and resulting status assessment (left). Red colour indicates that the upper 95 % confidence interval for PBDE concentrations are above the threshold value. Small open circles indicate a status assessment based on only 1-2 years of data, small filled circles indicate that there is not enough data to assess a statistical trend, large filled symbols indicate statistical trends assigned with circles indicating no detectable trend in concentration during the whole monitoring period and the filled arrows indicating significant upward or downward trend in concentration during the monitoring period. [Click here to access interactive maps at the HELCOM Map and Data Service: PBDEs.](#)

The threshold value of 0.0085 µg/kg ww defined by the Environmental Quality Standard (EQS) is exceeded everywhere, but there are regional/local differences in concentration.

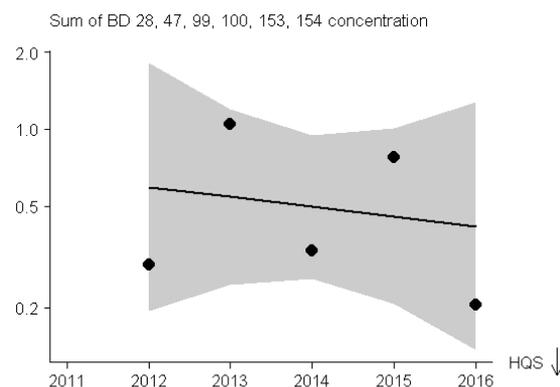
Mean values for the monitoring stations range from 0.03 to 0.82 ng/g ww in fish muscle (0.098 to 3 ng/g ww per scale 4 HELCOM assessment unit). However, the PBDE levels in a single, widespread species, e.g. herring seems to vary less throughout the Baltic Sea than for other substances such as for example PCBs. Generally, PBDEs show higher concentrations in herring muscle in the Baltic compared to the Swedish west coast in the North Sea (Bignert et al. 2017). PBDEs seem to be declining in open sea areas, but the variation both between and within sites is larger in coastal areas (Result figure 2 and 3).

The monitoring has gaps in Estonian, Latvian and Russian waters. In other areas, e.g. Finland, the monitoring period is too short to evaluate the levels with high confidence.

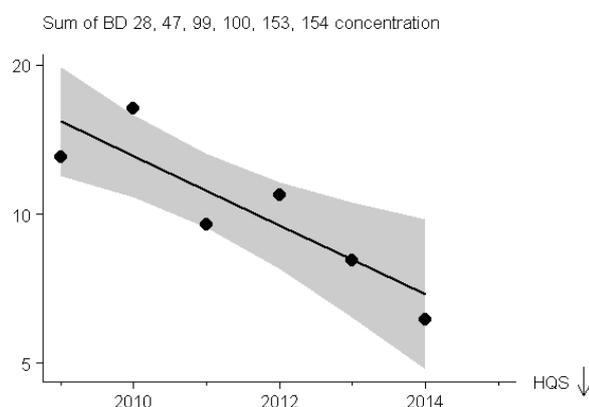
Concentrations of several PBDEs in the marine environment are declining (Bignert et al. 2017). Concentrations of PBDE show decreasing trend in herring muscle from 5 monitoring stations in the Baltic Sea (results figure 2), but in coastal areas the trend is less clear (Results figure 3).



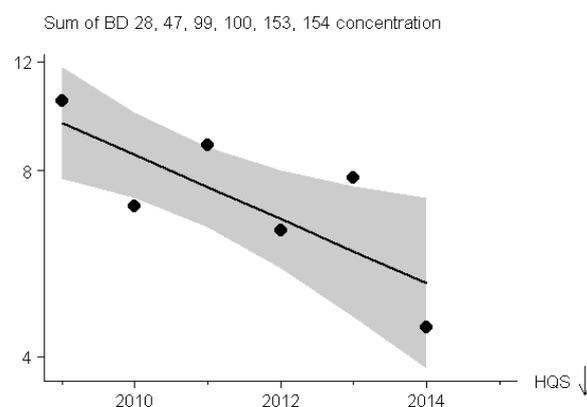
Media: Biota (Herring muscle)  
 Station: E W FLADEN (E W FLADEN)  
 Units:  $\mu\text{g kg}^{-1}$  lipid weight  
 Data extraction: 12 February 2018



Media: Biota (Herring muscle)  
 Station: LWLA (Gdansk Basin (LWLA))  
 Units:  $\mu\text{g kg}^{-1}$  lipid weight  
 Data extraction: 12 February 2018



Media: Biota (Herring muscle)  
 Station: Bothnian Sea off shore (Bothnian Sea off shore)  
 Units:  $\mu\text{g kg}^{-1}$  lipid weight  
 Data extraction: 3 February 2017



Media: Biota (Herring muscle)  
 Station: N Baltic Proper off shore (N Baltic Proper off shore)  
 Units:  $\mu\text{g kg}^{-1}$  lipid weight  
 Data extraction: 3 February 2017

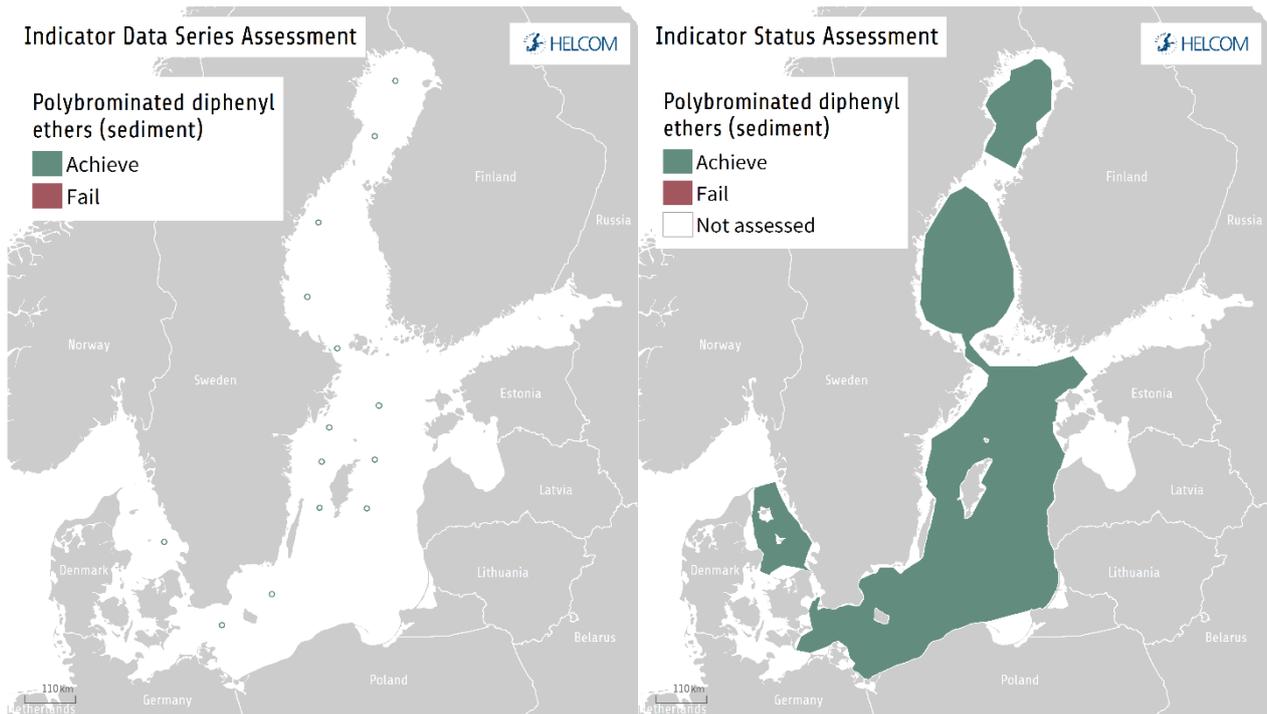
**Results figure 3.** Temporal trends of PBDEs concentration ( $\text{ng/g}$  wet weight – 5% lipid normalized) in herring muscle from stations Fladen Kattegat, Gdansk Basin, Bothnian Sea and north Baltic Proper, (grey colour- confidence level 95% range (see Assessment protocol)).

### Confidence of the indicator status evaluation

The confidence of the status evaluation is considered **high**. Data is available from several regions covering a time period of several years.

### Evaluation of secondary matrices

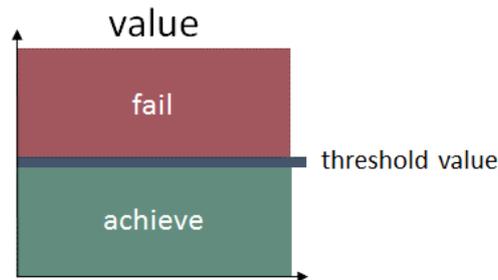
Concentrations of PBDEs has also been measured in sediments. The threshold value for sediment is  $310 \mu\text{g kg}^{-1}$  dry weight (dw). This threshold value is high compared to the threshold value in biota. When these results are assessed against the QS for sediment all assessment units with data show a good status (Results figure 4).



**Results figure 4.** Assessment per station in the Baltic Sea (left) and status assessment results (right) based on the evaluation of the indicator Polybrominated diphenyl ethers (PBDEs) in sediments. Green colour indicates that the upper 95 % confidence interval for PBDE concentrations are below the threshold value. Small open circles indicate a status assessment based on only 1-2 years of data. The assessment is carried out using Scale 4 HELCOM assessment units (defined in the [HELCOM Monitoring and Assessment Strategy Annex 4](#)). [Click here to access interactive maps at the HELCOM Map and Data Service: PBDEs.](#)

## Thresholds and Status evaluation

The threshold value applied for PBDEs is 0.0085 µg/kg fish wet weight (ww). The threshold value is an Environmental Quality Standard (EQS) for biota, where human health is considered the most critical for PBDEs and therefore is defined for edible parts of fish. The value is a sum of PBDE congeners 28, 47, 99, 100, 153 and 154, mainly representing penta- and octa- but not decaBDE.



**Thresholds figure 1.** Schematic representation of the threshold value which indicates good status if the concentration is below the threshold value. The threshold value is EQS biota human health 0.0085 µg/kg fish wet weight (ww).

Good Environmental Status (GES), defined in accordance with the Marine Strategy Framework Directive 2008/56/EC (MSFD), is “concentrations of contaminants at levels not giving rise to pollution effects” (OJEC No. L164 25.6.2008, 2008). PBDEs are included on the priority list under the Water Framework Directive (2000/60/EC) under which the Quality Standards (QSs) have been developed. All QS are based on ecotoxicological studies and derived to protect freshwater and marine ecosystems from potential adverse effects of chemicals, as well as adverse effects on human health via drinking water and food from aquatic environments. QSs are derived for different protection goals. The most stringent of the QSs for the different protection goals is the base for the EQS (2013/39/EU).

In the case of the PBDEs, the EQS is based on the value derived for human health. The EQS is used as a threshold value although it is debated as being very low, and has not been endorsed by the European Food Safety Authority (EFSA). Thus it is not clear if the value is in accordance with the food safety risk assessments.

The EC Guidance Document No. 32 on biota monitoring (the implementation of EQS<sub>biota</sub>) under the Water Framework Directive (EC 2014) was derived for harmonization purposes. This guidance document recommends that for lipid soluble, biomagnifying compounds such as PBDEs the fish assessed for EQS compliance should be at a trophic level of 4.5 for marine environments with a whole body lipid content of 5%. For practical reasons, the guidance opens up for adjustments of results from ongoing monitoring to meet this standard by the use of trophic magnification factors and trophic level. The EU directive on Environmental Quality Standards (2008/105/EC), Article 3, states that also long-term temporal trends should be assessed for substances that accumulate in sediment and/or biota.

In cases where it is not possible to evaluate the environmental status using biota-monitoring, a secondary threshold value based on concentration in sediment can be used as a complement. The threshold value for sediment is 310 µg kg<sup>-1</sup> dry weight (dw). This value has been suggested by the working group on priority substances for the protection of the benthic community.

## Assessment Protocol

The data may require transformation into the relevant unit and base for the threshold value which is  $\mu\text{g kg}^{-1}$  wet weight. Ideally, the data should be expressed in the same matrix which for the purposes of the indicator evaluation ought to be whole body concentrations in fish at a trophic level of 4.5 with a lipid content of 5%.

The majority of the PBDE data reported is analysed in muscle tissue. However, the EC Guidance Document No 32 (European Commission 2014) suggests that the assumption can be made that fat soluble compounds would be evenly distributed in the lipid within the whole organism. With this assumption, a whole body concentration would be possible to calculate from any analysed organ as long as the lipid content in the sample is known/analysed. To harmonize the evaluation across the entire Baltic Sea region, it is recommended to calculate the concentrations into corresponding values to a fish with a general fat content of 5%.

Data is to be normalised to lipid content according to the following equation, where  $\text{Conc}_{\text{norm, lipid}}$  is lipid normalised concentration,  $\text{Conc}_{\text{measurement}}$  is the original value expressed in wet weight (ww) and lipid content<sub>sample</sub> is the actual lipid content of the sample:

$$\text{Conc}_{\text{norm, lipid}} = \text{Conc}_{\text{measurement}} \times 0.05 / \text{lipid content}_{\text{sample}}$$

In case information on lipid content is absent in the data, general fat content values derived in regional studies for the sampled matrix can be applied.

For this evaluation no adjustment for trophic level has been done but is something that needs to be considered in future assessments according to recommendations below.

The EC guidance document (European Commission 2014) recommends making recalculations so the concentrations are standardized to a fish at a trophic level of 4.5 for marine ecosystems to standardise for the biomagnification effect.

## Statistical evaluation

### [Assessment methodology for contaminants in biota, sediment and water](#)

The assessment protocol is structured in three main parts, 1) changes in log concentrations over time are modelled, 2) check for compliance against threshold value and evidence for temporal change of contaminant concentration per station and 3) a spatial aggregation of status per assessment unit.

It should be noted that the assessment protocol makes the assumption that monitoring data stems from the same monitoring stations during consecutive years. The stations used by the protocol are defined in the ICES Station Dictionary. Stations with similar station name are grouped together, but it is also possible to define a group of stations with different names to be defined as the same station in the Station Dictionary. Usually a station is defined in the Station Dictionary with coordinates and a valid box around these coordinates, but coordinates outside of the box will only give a warning when reporting the data, and are not used in the actual data extraction.

## Overview

Time series of contaminant concentrations are assessed in three stages:

1. For sediment, the concentrations are normalized prior to the assessment to account for changes in the bulk physical composition of the sediment such as particle size distribution or organic carbon content. The concentrations are log transformed and changes in the log concentrations over time are modelled using linear mixed models. The type of temporal change that is considered depends on the number of years of data:
  1. 1-2 years: no model is fitted because there are insufficient data
  2. 3-4 years: concentrations are assumed to be stable over time and the mean log concentration is estimated
  3. 5-6 years: a linear trend in log concentration is fitted
  4. 7+ years: more complex (smooth) patterns of change over time are modelled
2. The fitted models are used to assess status against available threshold value and evidence of temporal change in contaminant levels in the last twenty years
3. The fitted models are also used for spatial aggregation to assess status against available threshold value and evidence of temporal change in contaminant levels on a scale 4 level HELCOM assessment unit.

All initial data is handled in a highly precautionary manner to further ensure that the risk of false positives is minimalised. For all initial data the 95% confidence limit on the mean concentration, based on the uncertainty seen in longer time series throughout the HELCOM area, is used. Applying a precautionary approach, the 90% quantile (psi value,  $\Psi$ ) of the uncertainty estimates in the longer time series from the entire HELCOM region are used. The same approach is used for time series with three or more years of data, but which are dominated by less-than values (i.e. no parametric model can be fitted). The mean concentration in the last monitoring year (meanLY) is obtained by: restricting the time series to the period 2011-2016 (the last six monitoring years), calculating the median log concentration in each year (treating 'less-than' values as if they were above the limit of detection), calculating the mean of the median log concentrations, and then back-transforming (by exponentiating) to the concentration scale. The upper one-sided 95% confidence limit (cLY) is then given by:  $\exp(\text{meanLY} + q_{\text{norm}}(0.95) * \Psi / \sqrt{n})$ , where n is the number of years with data in the period 2011-2016 (HELCOM 2018).

These stages are described in more detail in the link below. There is also information on how the methodology is adapted when there are 'less-than' measurements, i.e. some concentrations are reported as below the detection limit, and missing uncertainties, i.e. the analytical variability associated with some of the concentration measurements was not reported.

<http://www.helcom.fi/action-areas/monitoring-and-assessment/monitoring-and-assessment-strategy>

## Relevance of the Indicator

### Hazardous substances assessment

The status of hazardous substances is assessed using several core indicators. Each indicator focuses on one important aspect of the complex issue. In addition to providing an indicator-based evaluation of the concentration of polybrominated diphenyl ethers (PBDEs), this indicator will also contribute to the overall hazardous substances assessment along with the other hazardous substances core indicators.

### Policy relevance

The polybrominated diphenyl ethers (PBDEs) have mainly been used as flame retardants in plastic materials and polyurethane foams. PBDEs are diphenyl ethers with different degrees of bromination varying from 2 to 10. PentaBDEs refer to the congeners 82–127, 47 and 99 being the most abundant, octaBDEs refer to the congeners 194–205 and decaBDEs mainly refers to the congener 209.

PBDEs are on the HELCOM BSAP priority list and in the Stockholm Convention Annex A (Elimination). The use of substance groups pentaBDE and octaBDE is banned in the EU since 2004 (Commission regulation EC 552/2009). PentaBDE and octaBDE are not allowed to be placed on the market as substances, in mixtures or in articles in higher concentration than 0.1 % by weight. The substance group decaBDE that is restricted but not completely banned, is currently found in biota and is able to degrade into lower brominated congeners. The European Food Safety Authority (EFSA) has encouraged countries to also monitor decaBDE.

The substance groups pentaBDE and octaBDE have been prioritised through two consecutive prioritisation procedures under the WFD: pentaBDE were prioritised following COMMPS (Combined Monitoring-based and Modelling-based Priority Setting scheme) procedure in 2001, while octaBDE was prioritised in the context of the second European Commission proposal for a new list of priority substances, for the reason that they are PBT (Persistent, Bioaccumulative and Toxic) and vPvB (very Persistent and very Bioaccumulative) substances.

The use of PBDEs in electrical and electronic products (E&Es) was restricted even earlier than 2004 by the Directive 2002/95/EC (RoHS). From June 30, 2008, this directive covers also decaBDE. This implies that the only permitted use of PBDEs in Europe is now the application of decaBDE in products other than E&Es. As a result of this new regulation, the majority of the previous use of decaBDE in the EU is now prohibited (corresponding to ca 80 percent of the total EU use in 2001). It is, however, still possible for industries to apply for exemptions for certain applications under the procedure laid out in article 5 of the RoHS Directive.

PentaBDE is now included in Annex A (Elimination) in the Stockholm Convention and should no longer be on the EU market as well as hexaBDE and heptaBDE contained in octaBDE. In 2017, DecaBDE was added in Annex A with specific exemptions.

### Role of PBDEs in the ecosystem

#### *General properties*

PBDEs with smaller molecules are more toxic and bioaccumulative than larger ones. The biotic and abiotic debromination of highly brominated PBDEs, such as decaBDE, to these smaller forms is a possibility and

justifies that monitoring is based on a broad set of congeners. All PBDEs are hydrophobic or very hydrophobic substances, that are very likely to adsorb on particulate matter and not likely to volatilize from the water phase. The higher the bromination degree, the lower the water solubility. Therefore decaBDE is found only in low concentrations in fish, in contrast to lower-brominated PBDEs which are more commonly found in marine organisms. PBDEs have the potential to photodegrade in the environment.

The occurrence of PBDEs is widespread in the Baltic marine environment. It is probable that current legislative measures (penta- and octaBDE banned in the EU since 2004) have already decreased penta- and octaBDE levels in the Baltic Sea.

According to EU-RAR (2000), concentrations increased with the age of the fish and were higher in seals than in fish in the Baltic Sea, indicating bioaccumulation and biomagnification.

DecaBDE (BDE 209) is the dominant congener from sources (e.g. WWTPs) and in the Baltic Sea sediments; it can also be found in Baltic Sea fish, although tetraBDE is the most dominant congener in biota. Levels of decaBDE may be increasing because its use is only partly restricted. However, because of the environmental problems of decaBDE and anticipating regulatory measures, the European industry has taken voluntary action to reduce releases of decaBDE. This would be expected to lead – over time – to decreasing concentrations.

*Main impacts on the environment and human health*

PBDEs are categorized as endocrine disrupters (Category 2) for animals and humans. This means that the substances have the potential to disrupt endocrine functions, such as hormone regulation in the organisms. PBDEs have been shown to have endocrine-disrupting effects, in particular, on estrogen and thyroid hormone levels and functioning. It has been shown to disturb development of the nervous system.

Human pressures linked to the indicator

	General	MSFD Annex III, Table 2a
<b>Strong link</b>		Substances, litter and energy - Input of other substances (e.g. synthetic substances, non-synthetic substances, radionuclides) – diffuse sources, point sources, atmospheric deposition, acute events
<b>Weak link</b>		

PBDEs mainly spread to the Baltic Sea via the atmosphere, rivers and waste water treatment plants (WWTPs). PBDEs are mainly discharged from landfills and waste sorting sites or emitted via atmosphere to the environment. The substances accumulate on waste sites as a result of production and use of flame-protected materials. More information on the occurrence of penta-, octa- and deca-BDE discharges is needed from the whole Baltic Sea area also including from WWTPs.

## Monitoring Requirements

### Monitoring methodology

HELCOM monitoring of relevance to the indicator is documented in the on-line **HELCOM Monitoring Manual** in the [sub-programme: Contaminants in biota](#). Monitoring guidelines on the determination of persistent organic compounds in biota are currently documented in the [HELCOM COMBINE manual](#). The guidelines are to be updated and included in the HELCOM monitoring manual in the future.

The concentration of PBDEs in environmental monitoring is to be determined in an appropriate biota matrix that includes muscle of herring, perch, cod and eelpout. The basis for determination of the concentration is the lipid or wet weight with lipid content (%) in fish.

### Current monitoring

The monitoring activities relevant to the indicator that are currently carried out by HELCOM Contracting Parties are described in the **HELCOM Monitoring Manual**

**Sub-programme:** [Contaminants in biota monitoring concepts table](#)

Denmark, Finland, Germany, Lithuania, Poland and Sweden presently monitor PBDEs in fish. Lithuania and Sweden monitor PBDEs in sediments. Germany prepares for monitoring in sediment. Estonia and Latvia have screening or research data. No information is available from Russia.

When time series have started to accumulate data from the new monitoring stations in Finland, Lithuania and Poland, the monitoring of temporal trends of PBDEs will be considered adequate in the Baltic Sea. The current time series stations use highly mobile sample species (herring, cod and flounder) which makes the network of time series stations geographically representative. The adequacy of the current network could be further tested through power analysis.

### Description of optimal monitoring

## Data and updating

### Access and use

The data and resulting data products (tables, figures and maps) available on the indicator web page can be used freely given that the source is cited. The indicator should be cited as following:

HELCOM (2018) Polybrominated diphenyl ethers (PBDEs). HELCOM core indicator report. Online. [Date Viewed], [Web link].

ISSN 2343-2543

### Metadata

[Result: Polybrominated diphenyl ethers \(PBDEs\)](#)

[Data: Polybrominated diphenyl ethers \(PBDEs\) biota data](#)

[Data: Polybrominated diphenyl ethers \(PBDEs\) sediment data](#)

Data are extracted from the HELCOM COMBINE database, hosted by ICES. The data is based on regular monitoring activities carried out by Contracting Parties of HELCOM.

Most data sets cover only short time series which prevent temporal analyses. With the available data, status maps can be produced adequately for most parts of the western Baltic Sea, covering data up to 2016.

## Contributors and references

### Contributors

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Elisabeth Nyberg, Sara Danielsson, Anders Bignert, Swedish Museum for Natural History

HELCOM Expert Network on Hazardous Substances

### Archive

This version of the HELCOM core indicator report was published in July 2018:

[Polybrominated diphenyl ethers PBDEs HELCOM core indicator 2018 \(pdf\)](#)

Previous versions of the core indicator report:

[HOLAS II component - Core indicator report – July 2017 \(pdf\)](#)

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