Hexabromocyclododecane (HBCDD)

Key Message

This core indicator evaluates the status of the marine environment based on concentrations of hexabromocyclododecane (HBCDD) in Baltic Sea fish. Good status is achieved when the concentrations of HBCDD are below the threshold value. The current evaluation is based on data up to 2015 to evaluate the assessment period 2011-2015.

Key message figure 1: Status assessment results based on evaluation of the indicator 'hexabromocyclododecane (HBCDD)'. The assessment is carried out using Scale 4 HELCOM assessment units (defined in the HELCOM Monitoring and Assessment Strategy Annex 4), based on data from stations where 3 or more years of data are available.

Good status is achieved for all assessed areas since the concentrations of HBCDD in fish are below the threshold value in all monitored areas. However, there are areas where data are absent and thus extended monitoring is required to enable a status evaluation in the entire Baltic Sea.

Time series of HBCDD levels in biota show increasing concentrations since 1980s in Baltic Proper and Bothnian Sea. However, since 2000s no increases are observed and decreasing HBCDD concentrations are seen in fish from the west coast and southern coast of Sweden since late 1990s.
Confidence of the indicator evaluation results is considered to be high. It should also be noted, however, that the majority of the stations are selected as reference stations while potential local problems with HBCDD may occur in areas not included in the current monitoring programmes.

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

Relevance of the core indicator

HBCDD is a persistent, bioaccumulative and toxic compound with possible impacts on the reproductive and developmental system. The main use of HBCDD is in insulation material in the building industry or as coating of textiles to improve the fire resistance of the materials. The presence of HBCDD in biological samples gives information of the contaminant load of the Baltic Sea and reflects the bioavailable part of the contaminant. The species selected for monitoring acts as an exposure route via food to (top) predators and humans.

Policy relevance of the core indicator

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HOLAS II component - core indicator report – web-based version July 2017 (pdf)
Results and Confidence

Good status was achieved in terms of concentrations of hexabromocyclododecane (HBCDD) in fish in all evaluated assessment units during the period 2011-2015 as the average concentrations were below the threshold value of 167µg/kg ww (or 167ng/g ww) (Results figure 1).

The results are based on HBCDD concentrations in different fish species, but also different matrixes, i.e. muscle and liver (Results figure 1). This brings extra variability in the results due to species differences and matrix specific properties. It should be noted that monitoring data from Finland is not included in this assessment due to problems with data reporting and processing. A revision of flounder data for the period 2012-2015 is also envisaged. The data will be included in the updated indicator by mid-2018.

Results figure 1. Spatial variation of the HBCDD sampling stations, herring, cod, perch and eelpout represented. Green colour indicates that the measured HBCDD concentrations are below the threshold value. Small open circles indicate an ‘initial status assessment’ with only 1-2 years of data, small filled circles indicate that there is not enough data to assess a trend, large filled circles that concentrations has been stable during the whole monitoring period and the filled arrow that there is an upward or downward trend during the monitoring period.
Mean concentration values of HBCDD for fish from all monitored stations were well below the threshold value. The upper 95% confidence interval for the modelled most recent year ranged from 0.15 (herring from south Baltic Proper, Abbekås) to 3.1 (eelpout from the coast of Denmark, Langerak) ng/g ww in fish adjusted to a mean lipid content of 5%. The threshold value is more than 50 times higher than the maximum reported value.

**Evaluation of temporal trends**

The data from biota trend monitoring stations show increasing HBCDD concentrations from the 1970s and 1980s to the 2000s (Bignert et al. 2017). Cod from southeastern Gotland show a high increase with concentration values four times higher in the 2000s compared to the 1980s. Since the end of the 1990s, decreasing levels are seen at the Swedish west coast station Fladen for both herring and cod, and the same trend is also detected for herring from Utlängan in the southern Baltic Proper and in herring from two stations in the Bothnian Sea (Results figure 2 and Bignert et al. 2017).
Results figure 2. Temporal trend of HBCDD concentration (ng/g wet weight) in herring muscle from the Bothnian Sea, the south Baltic Proper and in Kattegat (HQS – threshold level, grey colour - confidence level 95% range (see Assessment protocol) [source: http://dome.ices.dk/HELCOMHZ2016/main.html].

Confidence of indicator status evaluation

The overall confidence of the assessment is high.

The geographical resolution of the current dataset for the coverage of the whole Baltic Sea is low. No detailed geographical studies to investigate the variability in HBCDD concentrations across the region have yet been carried out. However, the distance from the measured concentrations in fish to the current threshold value is large, with a minimum distance observed for cod from the Baltic Proper where the threshold value is 50 times higher than the reported mean value. Therefore the confidence that the observed levels do not exceed the current threshold value is high.

It should also be noted that the majority of the monitoring stations are selected as reference stations and potential local problems with HBCDD may occur in areas not included in the current monitoring programmes.
Good Environmental Status

Good status is achieved if the concentration of hexabromocyclododecane (HBCCD) is below the threshold value of 167 µg kg\(^{-1}\) fish wet weight (Good Environmental Status figure 1).

The threshold value is an environmental quality standard (EQS), derived at EU level as a substance included on the priority list under Directive 2008/105/EC regarding priority substances in the field of water policy (EQSD) (European Commission 2008a). GES in accordance with the MSFD is defined as 'concentrations of contaminants at levels not giving a rise to pollution effects'.

The EQS are derived from ecotoxicological and toxicological studies to protect freshwater and marine ecosystems from potential adverse effects of chemicals, as well as protection of human health in connection with consumption of drinking water and food from aquatic environments. Quality Standards (QS) are derived for different protection goals, i.e. pelagic and benthic communities, top-predators in these ecosystems, and human health. The most stringent of these QS are the basis for the EQS. The EQS boundary for HBCDD is based on the QS set for biota, to protect from secondary poisoning, defined for prey tissue, i.e. fish whole body. For harmonization purposes, the EC Guidance Document No. 32 on biota monitoring (the implementation of EQS\textsubscript{biota}) under the Water Framework Directive was developed (European Commission 2014). This guidance document recommends that for lipid soluble, biomagnifying compounds such as HBCDD 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%. The aim of the recommendation is to obtain comparable monitoring data.

An alternative, secondary threshold value at 170 µg kg\(^{-1}\) dw is set for concentrations in sediment. It is derived within the EQS process and is a QS in sediment, set to protect the marine benthic community. The secondary threshold value should only be used when it is not possible to evaluate an area using the primary biota-based threshold value.

The technical HBCDD products consist of three stereoisomers, α-, β- and γ-HBCDD, but the QSs and EQS are derived for the sum of the three stereoisomers. More detailed information concerning the derivation of the threshold value can be found in HBCDD EQS dossier (HBCDD EQS dossier 2011).

Article 3 of the EQSD states that also long-term temporal trends should be assessed for substances that accumulate in sediment and/or biota, such as HBCDD. A trend indicates if the state of the environment is approaching the threshold value or if the state is deteriorating.
Assessment Protocol

Data processing

The data may require transformation into the relevant unit and base for the threshold value which is µg 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%. However, for this evaluation no adjustments for lipid content or trophic level have been done but is something that needs to be considered in future assessments according to recommendations below.

The majority of the HBCDD data reported are 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 analyzed organ as long as the lipid content in the sample is known/analyzed. 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 Concent, lipid is lipid normalised concentration, Concent, measurement is the original value expressed in wet weight (ww) and lipid content, sample is the actual lipid content of the sample:

\[
\text{Concent}_{\text{norm, lipid}} = \frac{\text{Concent, measurement} \times 0.05}{\text{lipid content, sample}}.
\]

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.

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 standardize 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 normalised 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.

These stages are described in more detail 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.

Assessment units

HBCDD is a globally used chemical, widely spread in biological samples and even present in samples from remote places such as the Arctic region. The HBCDD indicator is therefore relevant for the whole Baltic Sea area and can theoretically be applied in all regions.

The core indicator evaluates the status with regard to concentration of HBCDD using HELCOM assessment unit scale 4 (division of the Baltic Sea into 17 sub-basins and further division into coastal and offshore areas and division of the coastal areas by WFD water types or water bodies). This division is applied in order to take into account the different routes by which HBCDD enters the Baltic Sea - via air and via run-off from land, including also potential point sources.

The assessment units are defined in the HELCOM Monitoring and Assessment Strategy Annex 4.
Relevance of the Indicator

Hazardous substances assessment

The status of the Baltic Sea marine environment in terms of contamination by 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 status of the Baltic Sea in terms of concentrations of hexabromocyclododecane (HBCDD) in the marine environment, this indicator along with the other hazardous substances core indicators is used to develop an overall assessment of contamination status.

Policy relevance

The core indicator on HBCDD concentrations addresses the Baltic Sea Action Plan's (BSAP) hazardous substances segment's ecological objectives 'Concentrations of hazardous substances close to natural levels' and 'All fish safe to eat'.

The core indicator is relevant to the following specific BSAP commitment:

- Agree by 2009, if relevant assessments show the need, to initiate adequate measures such as the introduction of use restrictions and substitutions in the most important sectors identified by the Contracting Parties and taking as a starting point the HELCOM list of substances or substance groups of specific concern to the Baltic Sea (in which HBCDD is included).

The core indicator also addresses the following qualitative descriptors of the MSFD for determining good environmental status (European Commission 2008b):

- Descriptor 8: 'Concentrations of contaminants are at levels not giving rise to pollution effects' and
- Descriptor 9: 'Contaminants in fish and other seafood for human consumption do not exceed levels established by Community legislation or other relevant standards'.

and the following criteria of the Commission Decision (European Commission 2010):

- Criterion 8.1 (concentration of contaminants)
- Criterion 9.1 (levels, number and frequency of contaminants).

HBCDD is a substance (group) on the revised Water Framework Directive (WFD) Priority Substance list. It has also been identified as a Substance of Very High Concern (SVHC), meeting the criteria of a PBT (persistent, bioaccumulative and toxic) substance pursuant to Article 57(d) in the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulation.

HBCDD is included in Annex XIV of the REACH regulation based on its hazardous properties, the volumes used and the likelihood of exposure to humans or the environment (European Commission 2011). This means that HBCDD cannot be used or placed on the market without first being approved by the European Chemicals Agency, ECHA. According to the harmonized classification and labelling (ATP03) approved by the European Union, this substance is suspected of damaging fertility or the unborn child and may cause harm to breast-fed children.
In December 2009, HBCDD was considered by the Executive Body (EB) of the UNECE (United Nations Economic Commission for Europe) Convention on Long-Range Transboundary Air Pollution (LRTAP) to meet the criteria for POPs, set out in EB decision 1998/2. Since 26th of November 2014, HBCDD is listed in Annex A of the Stockholm Convention, meaning that parties must take measures to eliminate the production and use of the chemical.

Role of HBCDD in the ecosystem

The commercially available brominated flame retardant hexabromocyclododecane (HBCDD or HBCD) is lipophilic, has a high affinity to particulate matter and low water solubility. The technical product consists of three stereoisomers, 70–95 % γ-HBCDD and 3–30% of α- and β-HBCDD, proportions depending on the manufacturer and the production method used. However, HBCDD is known to undergo thermal rearrangement, i.e. a shift in the relative amount of each stereoisomer can be seen if HBCDD, or a material containing HBCDD, is heated above 140°C. This has for instance been shown by Peled et al. (1995) and Heeb et al. (2010). The result of the transformation is that a relative increase of α-HBCDD and a relative decrease of γ-HBCDD could be observed. The transformation rate is dependent on time and temperature. HBCDD in this core indicator refers to the sum of the three diastereoisomers unless otherwise stated.

HBCDD is persistent in air and is subject to long-range transport. It is found to be widespread also in remote regions, and found in e.g. air and biological samples in the Arctic region (de Wit et al. 2006, EFSA 2011). The low volatility of HBCDD has been predicted to result in significant sorption to atmospheric particulates, with the potential for subsequent removal by wet and dry deposition. The transport potential of HBCDD was considered to be dependent on the long-range transport behaviour of the atmospheric particles to which it sorbs.

HBCDD has a strong potential to bioaccumulate and biomagnify. Available studies demonstrate that HBCDD is well absorbed from the rodent gastro-intestinal tract. Of the three diastereoisomers constituting HBCDD, the α-form is much more bioaccumulative than the other forms. HBCDD is very toxic to aquatic organisms. In mammals, studies have shown reproductive, developmental and behavioural effects with some of the effects being trans-generational and detectable even in unexposed offspring (Eriksson et al. 2006; Viberg et al. 2006, 2007). Beside these effects, data from laboratory studies with Japanese quail and American kestrels indicate that HBCDD at environmentally relevant doses could cause eggshell thinning, reduced egg production, reduced egg quality and reduced fitness of hatchlings (Fernie et al. 2009). Recent advances in the knowledge of HBCDD-induced toxicity includes a better understanding of the potential of HBCDD to interfere with the hypothalamic-pituitary-thyroid (HPT) axis, its potential ability to disrupt normal development, to affect the central nervous system, and to induce reproductive and developmental effects.

HBCDD has been found in human blood, plasma and adipose tissue. The main sources of exposure to humans presently known is through contaminated food and dust. For breast feeding children, mothers’ milk is the main exposure route, but HBCDD exposure also occurs at early developmental stages as it is transferred across the placenta to the foetus. Swedish human breast milk data from 1980 to 2004 show that HBCDD levels have increased since HBCDD was commercially introduced as a brominated flame retardant in the 1980s (Fängström et al. 2008). Though information on the human toxicity of HBCDD is to a great extent lacking, and tissue concentrations found in humans are seemingly low. Embryos and infants
are vulnerable groups that could be at risk, particularly to the observed neuroendocrine and developmental toxicity of HBCDD.

Because of the properties of HBCDD as a persistent, bioaccumulating, and toxic compound and in combination of the globally extensive use, HBCDD is considered a relevant substance to monitor in the entire Baltic Sea area. Monitoring species are available, and the substance is expected to be found in the whole area.

Human pressures linked to the indicator

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<td>Strong link</td>
<td>Use of synthetic compounds to increase fire resistance of materials</td>
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<tr>
<td>Weak link</td>
<td>Substances, energy and litter - Input of other substances (e.g. synthetic substances, non-synthetic substances, radionuclides) – diffuse sources, point sources, atmospheric deposition, acute events</td>
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The HBCDD is mainly used in expanded polystyrene (EPS) and extruded polystyrene (XPS) in the construction industry (as thermal insulation), as well as coating of textiles to improve their fire resistance (Marvin et al. 2011; ECB 2008; EFSA 2011). Furthermore, HBCDD is present in a number of different consumer products, mainly packaging material but also polystyrene food containers and foam boards (Rani et al. 2014). The use of HBCDD globally is extensive and the use in EU (not counting imported articles and products containing HBCDD) was estimated to be around 12,000 tonnes in 2006 (Relevance figure 1).

Since HBCDD is used as an additive flame retardant (i.e. not chemically bound to the material) the release of HBCDD occurs by leaching from the material to which it was added (http://chm.pops.int; EFSA 2011). There are a number of studies which identify HBCDD in different media, e.g. in air (EFSA 2011), moss – atmospheric deposition (Schlabach et al. 2002) and soil (Covaci et al. 2009). Furthermore, HBCDD has been shown to be taken up by plants (Li et al. 2011). Covaci et al. (2006) concludes that α-HBCDD is the most commonly occurring diastereoisomer in wildlife.

Estimated emissions within EU from HBCDD production and handling, associated with micronizing (fine grade grinding) of HBCDD is estimated to be 3 kg per year. The estimated release of particles during usage of EPS and XPS has been estimated to 100 g per tonne EPS and 5 g per tonne XPS. This amounts to an estimated release of approximately 560 kg HBCDD per year (of which 530 kg and 30 kg are from the use of EPS and XPS, respectively, assuming a use of 3% HBCDD in both EPS and XPS). This can be compared to a total estimated release of around 3000 kg per year in the EU, including all known sources (ECHA, 2009).
The use of HBCDD in the EU during the years 2006–2007 expressed in tonnes per year. EPS = Expanded polystyrene, XPS = Extruded polystyrene and HIPS = High impact polystyrene, minor sources are not shown as bars. Adapted from ECHA 2009.

The estimated degradation and persistence of HBCDD differs somewhat depending on type of test and experimental setup, but some studies have identified debrominated transformation products, and a shorter half-life has been seen in anaerobic compared to aerobic conditions (EFSA 2011). In vitro experiments have shown that mammalian hepatic microsomes can debrominate HBCDD and that γ-HBCDD is metabolized faster than α-HBCDD (MacInnis et al. 2010).
Monitoring Requirements

Monitoring methodology

Environmental monitoring of hexabromocyclododecane (HBCDD) in biota is currently not coordinated in the HELCOM community, implying that national guidelines are applied in the sampling as documented in the monitoring concepts table in the HELCOM Monitoring Manual under the sub-programme: Contaminants in biota.

So far, there are no technical guidelines related to HBCDD monitoring in biota in the HELCOM Monitoring Manual and there is a need to develop such common monitoring guidelines.

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 in the relevant Monitoring Concept Table.

Sub-programme: Contaminants in biota

Presently, only Denmark, Poland and Sweden have permanent monitoring of HBCDD in biota. Germany monitors HBCDD in biota on a project basis, national water monitoring is under development and sediment monitoring is in a planning phase. Finland and Lithuania have results from a few years and are planning to include the substance in their national monitoring programmes. Estonia will include HBCDD analysis (sediment and biota) in coastal areas from 2017. Latvia has only screening data and there is no information from Russia.

Description of optimal monitoring

The performance of existing monitoring should be evaluated in relation to the monitoring objectives, but first there is a need to quantify these objectives. These quantitative objectives need to be specified for each kind of monitoring, e.g. temporal trend-, incident-, geographical (spatial)- and compliance monitoring. For example, for temporal trend monitoring: what statistical power is required, during what time period should a certain trend be possible to detect and with what specified power (with certain one-or two-tailed statistical tests at a specified significant level)? With these definitions at hand it is possible to estimate e.g. required sample sizes and sampling frequencies. It can be shown that for a monitoring period of 12 years or shorter, generally the power to detect trends will decrease substantially if the sampling is carried out every second or every third year compared to annual sampling. For geographical studies the required spatial resolution should be determined. For compliance monitoring, it is imperative to know the distance to target levels (and variance) before sample sizes are estimated.

Time series of HBCDD concentrations in fish are missing or too short to enable evaluation for several sub-basins in the Baltic Sea region. Also biological variables, possible confounding factors (e.g. age, fat content) are often missing (not reported) disabling means to make samples comparable between areas and over time. The geographical resolution is generally too poor to make reliable generalized maps from interpolation of the existing stations using Kriging. No serious attempts to study patterns of variation in fish (coastal- offshore) through variograms have been made that could give guidance to the uncertainty and to the distance between sites required to achieve required confidence in generalized maps.
Some areas of the Baltic Sea have no HBCDD monitoring at present. The eastern parts of the Baltic Sea and the eastern coastline lack reported HBCDD concentrations. Thus increased monitoring is needed to enable both a status and trend evaluation for the entire Baltic Sea.
Data and updating

Access and use

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

HELCOM (2017) Hexabromocyclododecane (HBCDD). HELCOM core indicator report. Online. [Date Viewed], [Web link].
ISSN: 2343-2543

Metadata

Result: Hexabromocyclododecane (HBCDD)

Data: Hexabromocyclododecane (HBCDD)

The data used in the assessment is based on HELCOM COMBINE data reported by Contracting Parties as part of regular environmental monitoring activities. The data was extracted in accordance with the HELCOM core indicator extraction table, which specifies the matrix and metadata required.
Contributors and references

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Archive
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References


EFSA (European Food Safety Authority) (2011) Scientific Opinion on Hexabromocyclododecanes (HBCDDs) in Food. European Food Safety Authority, Parma, Italy.


**Additional relevant publications**


