

Hexabromocyclododecane (HBCD)

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Key messages

HBCD has not exceeded the threshold levels and thus indicates Good Environmental Status in herring muscle, cod liver and eggs of Common Guillemot and Herring Gull.

Time series of HBCD show a recent decrease in the eggs of Common Guillemot and Herring Gull but herring concentrations do not show temporal trends.

The current assessment applies to a limited sea area only and thus extended monitoring of the substance is needed.

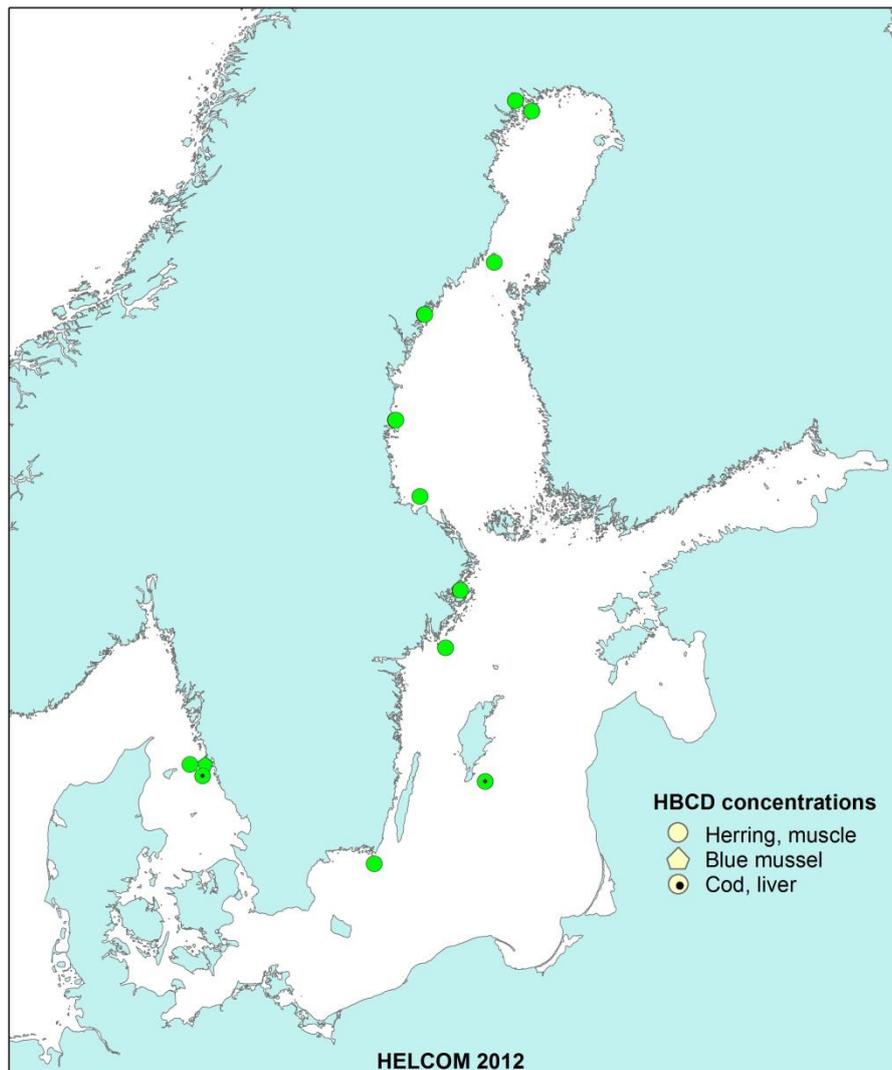


Figure 1. Status of hexabromocyclododecane (HBCD) in 2005-2010. The average is compared against the GES boundary (GES denoted by green color and 'moderate status' by yellow color) and a level three times the GES boundary i.e. the 'bad status' (red color). See Metadata for the threshold concentrations.

Current status in the Baltic Sea

HBCD is found to be widespread in the global environment, with elevated levels in top predators in the Arctic. In biota, HBCD has been found to bioconcentrate, bioaccumulate and to biomagnify at higher trophic levels.

The average concentration of HBCD in the Baltic Sea in the period of 2005–2010 does not exceed the threshold level in any of the monitoring stations (Figure 1). Thus, the substance indicates Good Environmental Status (GES) in blue mussel, herring muscle and cod liver. However, the spatial distribution of the assessment is very limited.

The Swedish results (Bignert et al. 2011) show that HBCD levels in Baltic Sea herring muscle are generally low and always lower than the GES boundary, which is the EU Environmental Quality Standard ($167 \mu\text{g kg}^{-1} \text{ ww}$). The highest concentrations ($25 \mu\text{g kg}^{-1} \text{ lw}$ or around $1 \mu\text{g kg}^{-1} \text{ ww}$) were found from the southern sea areas (Bornholm Basin and Western Gotland Basin) and the lowest levels in Kattegat ($2 \mu\text{g kg}^{-1} \text{ lw}$) (Figure 2).

Also the levels in the sediments of the Swedish coastal area are very low compared to the GES boundary for sediments ($170 \mu\text{g kg}^{-1} \text{ dw}$).

The spatial analysis of HBCD levels in herring muscle during 1999–2004 does not show any firm geographical differences, except that the level in the Southern Baltic Proper seems to be higher than another six sites from Skagerrak to Bothnian Bay. In general, HBCD seems to be more evenly distributed in the Swedish marine environment compared to, e.g. PCBs (Bignert et al. 2006).

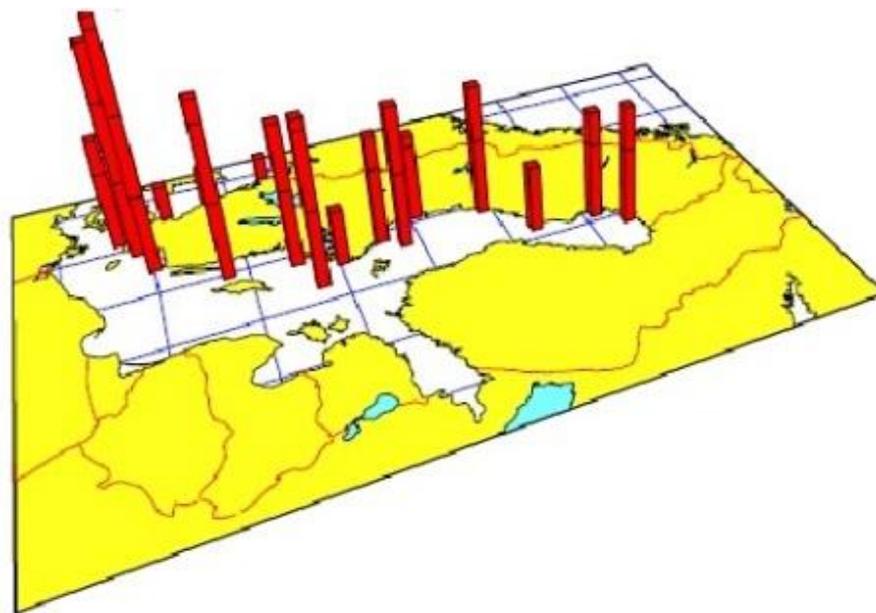


Figure 2a. Spatial variation in mean concentration (2008–2010 in ng/g lipid weight) of HBCDD in herring muscle. The highest concentration (22 ng/g) was found in the southern Baltic Proper (Utlängan), the lowest (2.6 ng/g) in Skagerrak (Väderöarna). Data originates from the Swedish national monitoring programme and are analysed at the Department of Applied Environmental Science, Stockholm University.

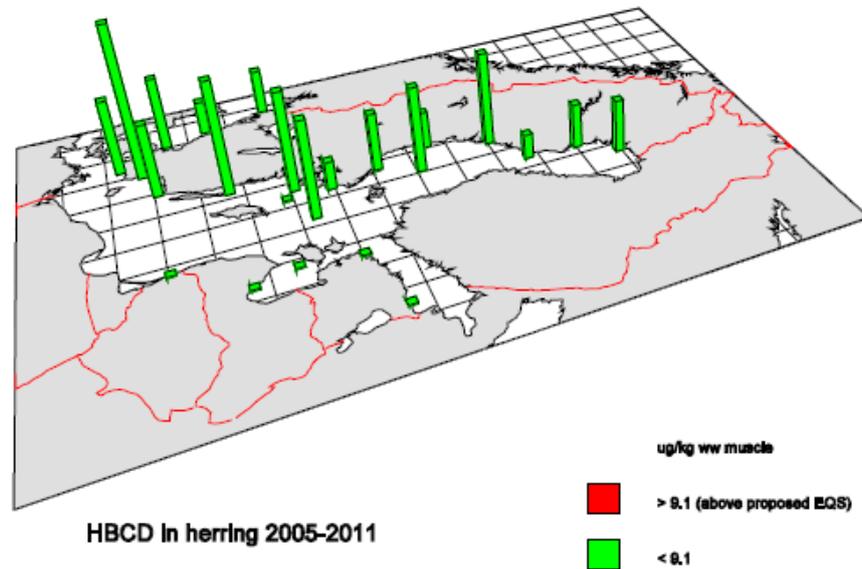


Figure 2b. Spatial variation in mean concentration (2005–2011 in $\mu\text{g}/\text{kg}$ wet weight) of HBCDD in herring muscle. The highest concentration (0,81 $\mu\text{g}/\text{kg}$) was found on Hanöbukten, Sweden.

General information

General properties (e.g. herbicide, lipophilic, bioaccumulating, persistence, volatile)

The commercially available brominated flame retardant hexabromocyclododecane (HBCD or HBCDD) is lipophilic, has a high affinity to particulate matter and low water solubility. Depending on the manufacturer and the production method used, technical HBCD consists of 70–95 % γ -HBCD and 3–30% of α - and β -HBCD.

HBCD has a strong potential to bioaccumulate and biomagnify. Available studies demonstrate that HBCD is well absorbed from the rodent gastro-intestinal tract. Of the three diastereoisomers constituting HBCD, the α -form is much more bioaccumulative than the other forms. HBCD is persistent in air and is subject to long-range transport. HBCD is found to be widespread also in remote regions such as in the Arctic, where concentrations in the atmosphere are elevated.

The low volatility of HBCD 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 HBCD was considered to be dependent on the long-range transport behaviour of the atmospheric particles to which it sorbs.

Main impacts on the environment and human health

HBCD is very toxic to aquatic organisms. In mammals, studies have shown reproductive, developmental and behavioral effects with some of the effects being trans-generational and detectable even in unexposed offspring (Eriksson et al. 2006, Viberg et al. 2006, 2007). Besides these effects, data from laboratory studies with Japanese quail and American kestrels indicate that HBCD 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 HBCD-induced toxicity includes a better understanding of the potential of HBCD 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.

HBCD has been found in human blood, plasma and adipose tissue. The main sources of exposure presently known are contaminated food and dust. For breast feeding children, mothers' milk is the main exposure route but HBCD exposure also occurs at early developmental stages as it is transferred across the placenta to the foetus. Human breast milk data from the 1970s to 2000 show that HBCD levels have increased since HBCD was commercially introduced as a brominated flame retardant in the 1980s. Though information on the human toxicity of HBCD 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 HBCD.

The HELCOM thematic assessment of hazardous substances in the Baltic Sea showed that HBCD exceeds threshold values in several parts of the Baltic Sea and increasing trends have been found in the eggs of common guillemot (HELCOM 2010).

Policy relevance

Status of a compound on international priority lists and other policy relevance

HBCD has attracted attention as a contaminant of concern in several regions, by international environmental forums and academia. In the EU, HBCD has 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 regulation. In December 2009, HBCD was considered by the Executive Body (EB) of the UNECE Convention on Long-Range Transboundary Air Pollution (LRTAP) to meet the criteria for POPs, set out in EB decision 1998/2.

HBCD is a substance (group) of specific concern to the Baltic Sea. It is on the HELCOM BSAP priority list and on the revised WFD Priority Substance list (a proposal from EC).

Status of restrictions, bans or use

In the EU, HBCD has 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 regulation. In May 2009, HBCD was included in the European Chemicals Agency (ECHA) recommendation list of priority substances to be subject to Authorisation under REACH, based on its hazardous properties, the volumes used and the likelihood of exposure to humans or the environment. A proposal on classification and labeling of HBCD as a possible reprotoxic substance is currently under discussion within the EU (Proposal for Harmonised Classification and Labelling, Based on the CLP Regulation (EC) No 1272/2008, Annex VI, Part 2 Substance Name: Hexabromocyclododecane Version 2, Sep. 2009).

At the meeting of the parties of the Stockholm Convention in 2013, decisions will be made on phase-out or other restriction of HBCD.

HBCD concentrations are recently declining

Temporal trends

Swedish monitoring data on HBCD in herring muscle shows that no temporal trend is seen in the Baltic Sea (Figure 3, Bignert et al. 2012).

Figure 4 shows an increase of HBCD in the guillemot eggs of about 3 % per year until recent years. Similar result was found from the eggs of herring gull in German coast (Figure 5).

A temporal analysis (EU-RAR 2006) showed that HBCD levels in seals in the Baltic Sea have increased. The median levels in the 1980s ranged between 16 and 35 $\mu\text{g kg}^{-1}$ lw with a median concentration of 28 $\mu\text{g kg}^{-1}$ lw (n=7). In the

1990s, the levels ranged between 34 and 177 $\mu\text{g kg}^{-1}$ lw with a median of 73 $\mu\text{g kg}^{-1}$ lw ($n=12$). From 2000, data from only one seal are available and has a HBCD concentration of 64 $\mu\text{g kg}^{-1}$ lw. However, another study found that the HBCD level in the blubber of 30 grey seals during 2000–2002 ranged from 31–554 $\mu\text{g kg}^{-1}$ lw with a mean of 101 $\mu\text{g kg}^{-1}$ lw. The results indicate that the HBCD levels in seals have not decreased.

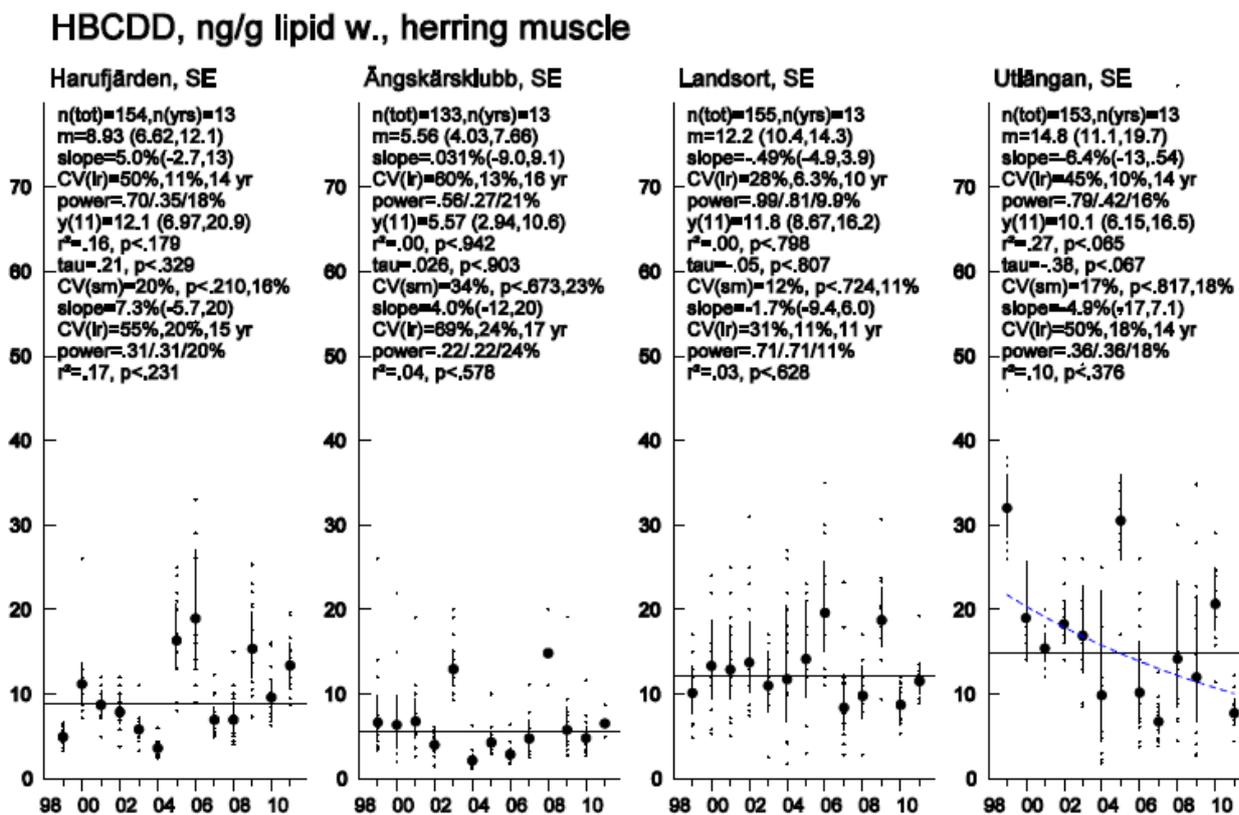


Figure 3. Temporal trends of HBCDD concentration (ng/g lipid weight) in herring muscle from four different sampling sites in the Baltic Sea (1999–2011). Harufjärden (Bothnian Bay), Ångskärsklubb (S. Bothnian Sea), Landsort (N. Baltic Proper), Utlängan (Bornholm Basin). The horizontal line is the mean concentration of the analysed period

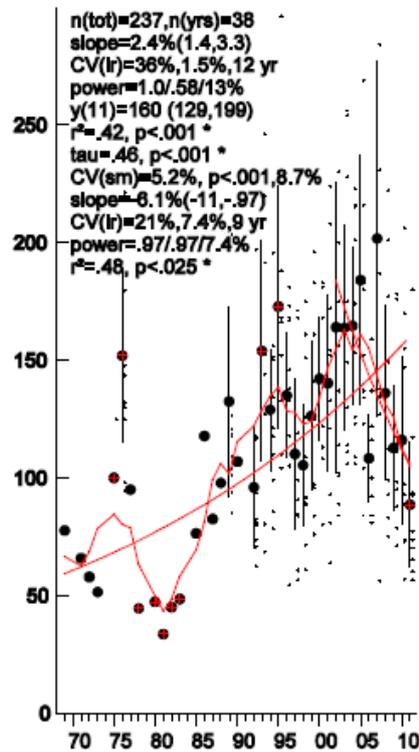


Figure 4. Temporal trend of HBCDD concentration (ng/g lipid weight) in guillemot egg (1969-2011) from St. Karlsö (S. Baltic Proper). The red linear line presented in the figure is based on a log-linear regression analysis and shows an increasing trend of 3% per year and the non-linear red line is a simple 3-point running mean smoother fitted to the annual geometric mean values. The dashed light blue line represent a trend for the last 10 years if $0.05 < p < 0.15$. A red cross represents a suspected outlier.

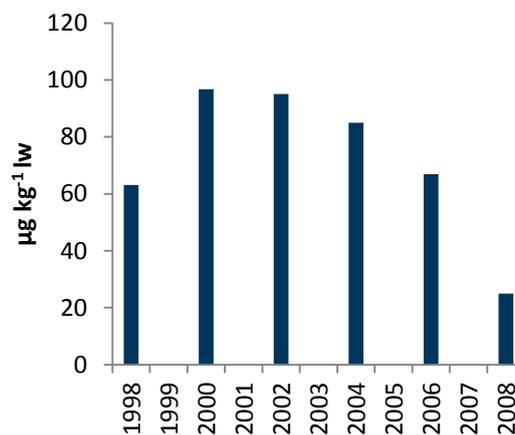


Figure 5. Temporal trend of HBCD concentrations in the eggs of herring gull in the German coast of Arkona Basin from a retrospective study of specimen bank. Note that no replication of concentrations was made. Source: Umwelt Probenbank des Bundes (<http://www.umweltprobenbank.de/de>).

Metadata

Data source

ICES and EIONET data bases: HBCD in fish and other biota and sediment.

National Swedish Monitoring Programme of Contaminants in Biota.

Umwelt Probenbank des Bundes (<http://www.umweltprobenbank.de/de>).

Description of data

Status map was based on average concentrations of the time period 2005-2010. All concentrations are presented as lipid-weight basis, if possible.

Swedish data

Trend (in %) assessed from the annual geometric mean of concentrations of **HBCDD** (ng/g lipid weight) in various matrices and sites during the time period 1969/99-2010 and the estimated mean concentration for the last year (2010). The trend is reported, if $p < 0.1$. The age interval, the total number of analyses and the number of years are also presented. The numbers presented in brackets are the 95% confidence intervals.

Matrix	age	n analyses	n yrs	year	trend (95% ci)	mean concentration of last year (95% ci)
Herring muscle						
Harufjärden	3–4	143	12	1999-2010		8.6 (6.3-12)
Ängskärsklubb	3–5	129	11	1999-2010		4.0 (2.1-7.3)
Landsort	3–5	143	12	1999-2010		12 (8.5-17)
Utlängan	3–4	143	12	1999-2010		11 (6.9- 20)
Guillemot egg						
St. Karlsö		227	37	1969-2010	2.6 (1.6,3.5)*	166 (134, 205)

* significant trend, $p < 0.05$

Methodology and frequency of data collection

See Bignert *et al.* 2012.

Analyses

Sampling, sample preparation, storage in specimen bank and evaluation of results are carried out by the *Department of Contaminant Research* at the Swedish Museum of Natural History, Stockholm. Chemical Analysis is carried out at *Institute of Applied Environmental Research* at Stockholm University.

Preferred matrix

Biota and sediment are preferred. The measured data on HBCD concentration in Baltic Sea water is very scarce and the detection limit has been too high to draw any conclusions (HELCOM 2010).

GES boundaries

The GES boundary is the Environmental Quality Standard (EQS), proposed by the European Commission to the revised EQS Directive (31.1.2012). The EQS is $167 \mu\text{g kg}^{-1}$ fish ww. An alternative approach is to use the Quality Standard for sediment ($170 \mu\text{g kg}^{-1}$ dw) (WFD WG E Dossier 19.1.2012).

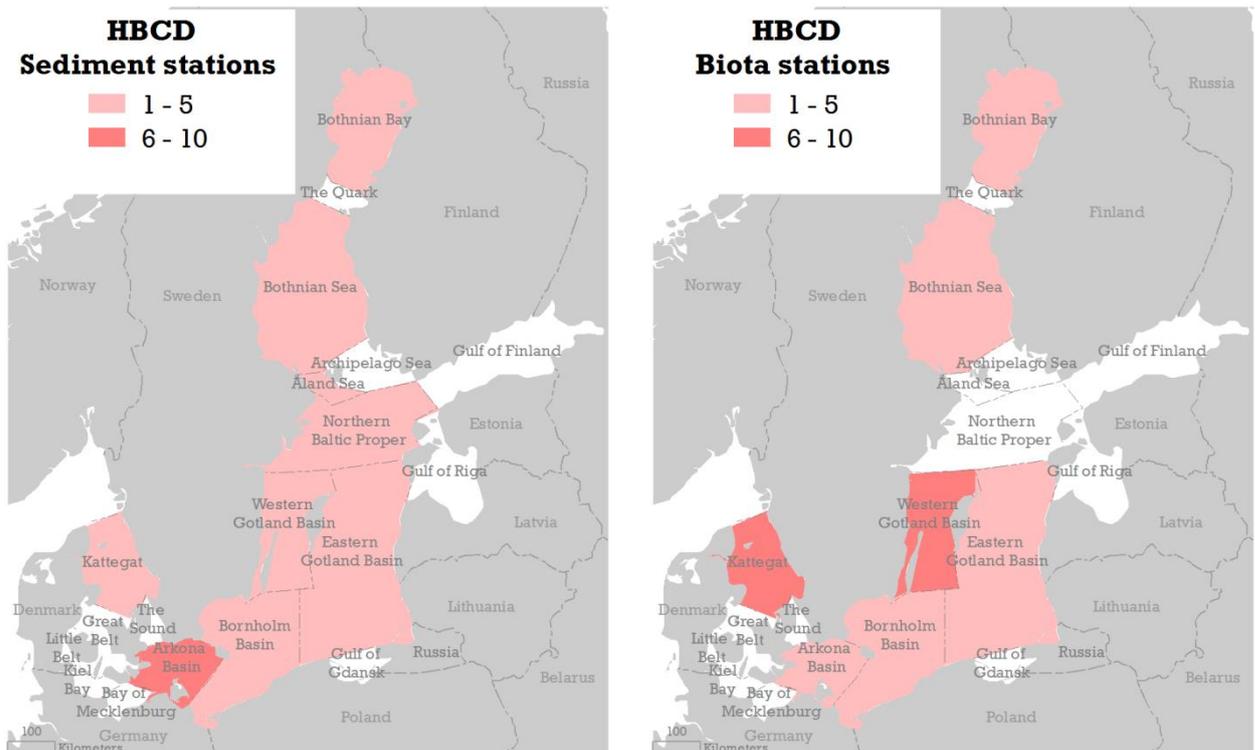
The EU directive on environmental quality standards (2008/105/EC), Article 3, states that also long-term temporal trends should be assessed for substances that accumulate in sediment and/or biota.

Table 1. Quantitative targets for HBCD (WFD WG E dossier 19 Jan 2011).		
Protection objective	Unit	Value
Pelagic community (marine waters)	$[\mu\text{g.l}^{-1}]$	0.031
Benthic community (marine)	$[\mu\text{g.kg}^{-1} \text{ dw}]$	170
Predators (secondary poisoning)	$[\mu\text{g.kg}^{-1} \text{ biota ww}]$	167 (Critical QS)
Human health via consumption of fishery products	$[\mu\text{g.kg}^{-1} \text{ biota ww}]$	6100

Monitoring the compound

Only Denmark, Poland and Sweden have permanent biota monitoring presently. Germany monitors HBCD in biota on the project basis, but national water monitoring is under development and sediment monitoring in a planning phase. Finland and Lithuania are planning to include the substance to the national monitoring programme. Estonia and Latvia have only screening data and there is no information from Russia.

Annex 1 gives an overview of the current monitoring.



Gaps in the monitoring of the compound

There is a geographical gap in the monitoring of the substance in the eastern Baltic Sea, especially in Gulf of Finland and Gulf of Riga. At the moment there is no monitoring in Estonia, Finland, Latvia, Lithuania and Russia.

The monitoring of HBCD is not considered adequate in the Baltic Sea, because most of the data series are too short for temporal assessments and there are spatial gaps. The time series stations use highly mobile sample species (herring, cod and flounder) which makes the network of time series stations as geographically more representative. A power analysis was, however, recommended to be made.

Geographical relevance of the indicator

HBCD is considered a relevant substance to monitor in the entire Baltic Sea area.

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Annex 1.

Hexabromocyclododecane (HBCD) in national monitoring programmes in sediment and biota. Number of stations and frequency of monitoring (interval in years) is shown for each sub-basin. Some recent screenings have also been included. Species key: her=herring, per=perch, flo=flounder, eelp=eelpout, sal=salmon, mus=mussel.

Subbasin	Sweden			Germany			Estonia			Poland			Lithuania			Latvia			Finland			Denmark		
	Sedim.	Biota		Sedim.	Biota		Sedim.	Biota		Sedim.	Biota		Sedim.	Biota		Sedim.	Biota		Sedim.	Biota		Sedim.	Biota	
	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.
Archipelago Sea																								
Arkona Basin	1		1 her	1	7 project	1 bird project																1 flo	1	
Bay of Mecklenburg																								
Bornholm Basin	1		2 her	1							1her+1flo+1mus	1												
Bothnian Bay	2		3 her	1																				
Bothnian Sea	2		4 her	1																				
Eastern Gotland	2		1 her+ cod	1							1 her	1		2 her, flo project										
Great Belt																						5 eelp+flo	1	
Gulf of Finland																								
Gulf of Gdansk											1 flo+ 1 mus	1												
Gulf of Riga																2 her, per project								
Kattegat	1		4 her, cod+mus	1																		4 eelp	1	
Kiel Bay																								
Little Belt																							2 eelp	1
North Baltic Proper	2		3 her	1			5her, per project																	
The Quark			1 her	1																				
The Sound																						1 flo	1	

