

HELCOM core indicator report July 2017

PCB, dioxin and furan

Key Message

This core indicator evaluates the status of the marine environment based on concentrations of dioxin and dioxin like compounds in Baltic Sea fish, crustacean and molluscs as well as on concentrations of non-dioxin like PCB in Baltic Sea fish. Good status is achieved when the concentrations of PCBs, dioxins and furans are below the threshold values. 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 evaluation of the indicator 'PCB, dioxin and furan'. The assessment is carried out using Scale 4 HELCOM assessment units (defined in the <u>HELCOM Monitoring and</u> <u>Assessment Strategy Annex 4</u>).

Good status was achieved in the majority of coastal and open sea areas. PCBs were responsible when the overall good status was not achieved. The concentrations of dioxins and furans in fish were 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 PCB levels in biota show decreasing concentrations at some stations, e.g. in the Bornholm Basin, the Easter Gotland Basin and the Bothnian Bay. However, most of the stations show steady concentrations.

The confidence of the indicator assessment is moderate. It should however be noted that there has been major data reporting problems, and that the dioxin-parameter has not been fully assessed in this version of the indicator report.

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

Relevance of the core indicator

PCBs are synthetic chemicals which do not occur naturally in the environment. Due to their properties, PCBs have been used in a wide variety of applications and manufacturing processes, especially as plasticizers, insulators and flame-retardants. They are widely distributed in the environment through, for example, inappropriate handling of waste material or leakage from transformers, condensers and hydraulic systems. Long-term effects of PCBs include increased risk of cancer, infections, reduced cognitive function accompanied by adverse behavioural effects, as well as giving birth to infants of lower than normal birth weight (Carpenter 1998, Carpenter 2006). There are also indications that PCBs are associated with reproductive disorders in marine top predators.

Dioxins (PCDD/Fs) were never produced intentionally, but they are minor impurities in several chlorinated chemicals (e.g., PCBs, chlorophenols, hexachlorophene, etc.) and are formed in several industrial processes and from most combustion processes, such as municipal waste incineration and small-scale burning under poorly controlled conditions. The most relevant toxic effects of PCDD/Fs are developmental toxicity, carcinogenity and immunotoxicity.

	BSAP Segment and Objectives	MSFD Descriptors and Criteria
Primary link	Concentrations of hazardous substances	D8 Concentrations of contaminants
	close to natural levels	- D8C1 Within coastal and territorial and beyond
		territorial waters, the concentrations of contaminants
		do not exceed the threshold values
Secondary link	Fish safe to eat	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 does not
		exceed the threshold.
		Deignity Substances Discritica (2012/20/EU)

Policy relevance of the core indicator

Other relevant legislation: EU Water Framework Directive; EU Priority Substances Directive (2013/39/EU)



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Results and Confidence

Non-dioxin like PCBs

Good status was achieved in terms of concentrations of non-dioxin like PCB (Sum of 6 CB: 28, 52, 101, 138, 153 and 180, see Good Environmental status table 1) in fish in most evaluated assessment units during the period 2011-2015, as the average concentrations were below the threshold value of 75 μ g/kg ww in fish muscle (or 75 ng/g ww) (Results figure 1). At some stations, in the Eastern Gotland Basin, the Arkona Basin and in the Kiel Bay, good status was not achieved. While in the Eastern Gotland basin a decreasing trend was observed, the concentrations of PCB in the Arkona Basin and the Kiel Bay showed no trend.

The results are based on PCB 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.



Results figure 1. Spatial variation of the non-dioxin like PCBs (Sum of 6 PCB) sampling stations, flounder, dab, herring, cod, perch and eelpout are represented. Green colour indicates that the measured non-dioxin like PCBs 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 have been stable during the whole monitoring period and the filled arrow that there is an upward or downward trend during the monitoring period.



Dioxins, furans and dl-PCBs:

Good status was achieved in terms of concentrations of dioxins and furans in fish in all evaluated assessment units during the period 2011-2015, as the average concentrations were below the threshold value of 0.0065 TEQ/kg ww (fish muscle, crustaceans or molluscs) (Results figure 2 and 3).

The results are based on dioxin and furan concentrations in different fish species (perch and eelpout) (Results figure 2 and 3), which lead to an extra variability in the results due to species differences.



Results figure 2. Spatial variation of dioxin and furan sampling stations, perch and eelpout are represented. Green colour indicates that the measured dioxin and furan 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 have been stable during the whole monitoring period and the filled arrow that there is an upward or downward trend during the monitoring period.





Results figure 3. Aggregated mean concentrations per HELCOM assessment unit. Concentrations of dioxins (SDX) and furans are way below the threshold value in the assessed Danish assessment areas. (HQS = Human-health Quality Standard).

Evaluation of temporal trends

Non dioxin-like PCBs:The data from biota trend monitoring stations show decreasing or no trend for PCBs. Results figure 4 shows examples of decreasing trends at stations in the Baltic Sea. Monitoring data for dioxins and furans are only available since 2011 at three stations, which all showed no trend (Results figure 5 shows an example). Furthermore, the dioxin data from Finland is not sufficient for trend assessment (at least 3 years) and is therefore only shown as initial status assessment data in Results figure 1.







Results figure 4. Temporal trend of the Sum of 6 PCB concentration (ng/g wet weight) in flounder, dab, herring, cod, perch and eelpout from the Bothnian Bay, the Eastern Gotland Basin and in the Bornholm Basin (HQS – threshold level (Human-health Quality Standard), grey colour- confidence level 95% range (see Assessment protocol)) [source: http://dome.ices.dk/HELCOMHZ2016/main.html].



Dioxins, furans and dl-PCBs:

Results figure 5. Temporal trend of the Sum of dioxin and furan concentration (ng/g wet weight) in eelpout muscle from the Kattegat (HQS – threshold level (Human-health Quality Standard), grey colour- confidence level 95% range (see Assessment protocol)) [source: http://dome.ices.dk/HELCOMHZ2016/main.html].

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Confidence of the indicator status evaluation

The overall confidence of the assessment is moderate.

The geographical resolution of the current dataset for the coverage of the whole Baltic Sea is high, mainly due to measurements of non-dioxin like PCBs, even so dioxin and furan data were only assessed in Denmark and Finland so far. No detailed geographical studies to investigate the variability in dioxin and furan concentrations across the region have yet been carried out.

It should also be noted that the majority of the monitoring stations are selected as reference stations and potential local problems with PCBs, dioxins and furans may occur in areas not included in the current monitoring programmes.

The confidence of the threshold for the Sum of 6 PCB is low as this value is derived from the food safety directive and no environmental quality standard is available. Thus, the overall confidence is moderate.

It should be noted that several countries encountered problems with data reporting and processing. The data will be included in the updated indicator by mid-2018.



Good Environmental Status

The core indicator evaluates whether an area reflects good status by comparing the concentration to a threshold value which should not be exceeded (Good environmental status figure 1).



Good environmental status figure 1. Schematic representation of the threshold value which indicates good status when the measured concentration is below the threshold value.

Good Environmental status table 1. Threshold value for the core indicator 'PCB, dioxin and furan'. The secondary threshold value for dioxin is not yet fully agreed in HELCOM and therefore not used in the assessment and marked *.

	Primary threshold value	reference	Secondary threshold value*	reference
Dioxin and dioxin-	Sum of PCDD, PCDF,	EQS biota human health	CB-118 24 µg/kg lw	FAC
like compounds	PCB-DL	2013/39/EU	fish liver or muscle	27.0
	0.0065 TEQ/kg ww			
	fish, crustaceans or			
	molluscs			
Non-dioxin like PCBs	sum of congeners	EC 1881/2006 and		
	(28, 52, 101, 138,	1259/2011		
	153, 180) 75 μg/kg			
	ww fish muscle			

The threshold value for each compound is defined based on Ecological Quality Standards (EQS) derived for the purposes of the EU Water Framework Directive, and where EQS values are not available on Environmental Assessment Criteria (EAC) values developed in the OSPAR framework.

The threshold value is matrix sensitive, and only applicable if the concentrations are measured in the appropriate matrix. For historical reasons, the Contracting Parties around the Baltic Sea have differing monitoring strategies. As a pragmatic approach, a threshold value is defined in this indicator (based on 2013/39/EU GES boundary), however if suitable monitoring data is not available in a region the secondary threshold value can be used for the evaluation.

The threshold value for PCB is defined for the Sum of 6 congeners (non-dioxin like) (Good Environmental status Table 1**Error! Reference source not found.**). Other congeners included in current monitoring programmes can be included when suitable boundary values become available. For dioxins, the threshold value is defined as the QS-value for secondary poisoning.



This core indicator is used to evaluate the status of the environment and the logical target for this specific indicator expressing pollution effects, is the secondary poisoning of predators. In the Water Framework Directive, the most stringent EQS is derived for water ecosystems and the human health protection goal and is designated as the EQS-boundary. If the indicator is used to evaluate risks to human health, then the following boundary values can be applied:

dioxin EQS $_{\text{biota human health}}$ 0.0065 (TEQ) $\mu g/kg$ ww

EU foodstuff regulation 1881/2006 (amendment 5 changed with regulation 1259/2011): seafood Σ (WHO-PCDD/F-TEQ) 0.0035 $\mu g/kg$ ww

 Σ (WHO-PCDD/F-PCB-TEQ) 0.0065 µg/kg ww

Non-dioxin like PCBs (28,52,101,138,153,180) 75 $\mu g/kg$ ww

The EU directive on environmental quality standards (2008/105/EC and 2013/39/EU), Article 3, states that also long-term temporal trends should be assessed for substances that accumulate in sediment and/or biota.



Assessment Protocol

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:

- 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 is 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 in the core indicator <u>general assessment protocol</u>. 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

PCBs, dioxin and furan are considered relevant substances to evaluate in the entire Baltic Sea area. Concentrations may be higher in the coastal areas compared to the offshore areas, and therefore the indicator is evaluated on HELCOM assessment unit scale 3.



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 PCB, dioxin and furan 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 "ICES 7" non-dioxin like PCBs (non-dl-PCB) and dioxin like PCBs (dl-PCB), i.e. congeners CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180, are listed as mandatory contaminants that should be analysed and reported within both HELCOM and OSPAR, and are classed as priority POPs under the Stockholm Convention. In the proposed revised guidelines for OSPARCOM (1996) the congeners CB-105 and CB-156 are added to this list. Non-dioxin like PCBs are not included in the Water Framework Directive (WFD) priority substance lists, but they are included in the Marine Strategy Framework Directive (MSFD).

The Helsinki Convention (1974, 1992) has recommended special bans and restrictions on transport, trade, handling, use and disposal of PCBs. The Ministerial Declaration from 1998, within HELCOM and the 1995 Declaration of the Fourth international conference of the protection of the North Sea called for measures against toxic, persistent, bioaccumulating substances like PCBs to cease their inputs to the environment completely by the year 2020.

Dioxins and furans (PCDD/Fs) are included in several international agreements, of which the Stockholm Convention and the Convention on Long Range Transboundary Air are among the most important for the control and reduction of sources to the environment. World health organization (WHO) and Food and Agriculture Organization of the United Nations (FAO) have jointly established a maximum tolerable human intake level of dioxins via food, and within the EU there are limit values for dioxins in food and feed stuff (EC 2006). Several other EU legislations regulate dioxins, e.g. the plan for integrated pollution prevention and control (IPPC 2010/75/EC) and directives on waste incineration (EC, 2000, 2008). The EU has also adopted a Community Strategy for dioxins, furans and PCBs (EC 2001). PCDD/Fs are currently not included in the Water Framework Directive but are on the list of substances to be revised for adoption in the near future. HELCOM has listed PCDD/Fs and dI-PCBs as prioritized hazardous substances of specific concern for the Baltic Sea (HELCOM 2010), like OSPAR on the List of Chemicals for Priority Action (OSPAR 2010b).

Under the Stockholm Convention, releases of unintentionally produced by-products listed in Annex C4, including dioxins and dl-PCBs, are subject to continuous minimization with the ultimate goal of elimination where feasible. The main tool for this is a National Action Plan which should cover the source inventories and release estimates as well as plans for release reductions. At the EU level, a Strategy for dioxins and PCBs was adopted in 2001. The Strategy includes actions in the area of feed and food contamination and actions related to the environment, including release reduction. Over the past decade, important legislation has been adopted to reduce the emissions of PCDD/Fs, in particular in the areas of waste incineration and integrated pollution prevention and control. Releases of POPs, including dioxins, from industrial installations have been regulated by the IPPC Directive and the Waste Incineration Directive, the former



requiring Member States to establish permit conditions based on the Best Available Techniques (BAT) for a wide variety of industry sectors, and the latter setting maximum permissible limit values for PCDD/F emissions to air and water from waste incineration. Currently these releases of these substances are regulated by the Directive on industrial emissions (IED, 2010/75/EU). The proper and timely implementation and enforcement of the IED remains a key priority in order to ensure the necessary reduction of emissions from major industrial sources. However, at present or in the near future, non-industrial sources are likely to exceed those from industrial ones (Quass et al. 2004).

Role of PCBs, dioxins and furans in the ecosystem

Polychlorinated biphenyls (PCBs) and PCDD/Fs (dioxins and furans) are persistent organic pollutants (POPs) that can cause severe, long-term impacts on wildlife, ecosystems and human health. The substance groups are characterized by low water solubility and low vapour pressure. Due to their persistent and hydrophobic properties, the substances accumulate in sediments and organisms in the aquatic environment. In the environment, dioxins can undergo photolysis, however, they are generally very resistant to chemical and biological degradation.

Polychlorinated biphenyls (PCBs) consist of two linked benzene rings with chlorine atoms substituted for one or more hydrogen atoms. Theoretically, 209 congeners are possible, but only around 130 are found in commercial mixtures. Some PCBs are called dioxin-like (dl-PCBs) because they have a co-planar structure very similar to that of dioxins and have dioxin-like effects (i.e. four non-ortho substituted PCBs: CB-77, CB-81, CB-126, CB-169, IUPAC and eight mono-ortho substituted: CB-105, CB-118, CB-156, CB-157, CB-167, CB-114, CB-123, CB-189, IUPAC) (Burreau et al. 2006).

The name 'dioxin' refers to polychlorinated dibenzo-*p*-dioxin (PCDD) and dibenzofuran (PCDF) compounds, i.e. two benzene rings with one (furans) or two (dioxins) oxygen bridges and substituted with 1–8 chlorine atoms. Of the 210 possible congeners, the 17 compounds (10 furans, 7 dioxins) substituted in positions 2, 3, 7 and 8 are considered to be of highest toxicological importance.

The PCBs included in this core indicator report are the 7 PCB congeners that have been monitored since the beginning of the HELCOM and OSPARCOM monitoring programmes, carefully selected mainly by ICES working groups due to their relatively uncomplicated identification and quantification in gas chromatograms and as they usually contribute a very high proportion of the total PCB content in environmental samples. These are the 'ICES 7': CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180.

Long-term effects of PCBs from human and laboratory mammal studies include increased risk of cancer, infections, reduced cognitive function accompanied by adverse behavioural effects, as well as giving birth to infants of lower than normal birth weight (Carpenter 1998, Carpenter 2006). There are also indications that PCBs are associated with reproductive disorders in marine top predators. PCBs are also assumed, together with p,p'-DDE, to cause eggshell thinning and reduced number of offspring in white-tailed eagles and uterine leioymas in grey seal in the Baltic Sea (Helander et al 2002, Bäcklin et al. 2010).

The most relevant toxic effects of PCDD/Fs are developmental toxicity, carcinogenity and immunotoxicity. The sensitivity of various species to the toxic effects of PCDD/Fs varies significantly. 2,3,7,8-TCDD is the most toxic and well-studied congener and is used as a reference for all other related chemicals. Each of the 17 relevant congeners is assigned a toxic equivalency factor (TEF), where 2,3,7,8-TCDD equals 1 (Van den Berg et al., 1998; Van den Berg et al., 2006). Dioxin concentrations are commonly reported as toxic or TCDD

equivalents (TEQ), which is the sum of the individual congener concentrations multiplied with its specific TEF.

Human pressures linked to the indicator

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

PCBs are synthetic chemicals and do not occur naturally in the environment. Due to their properties, PCBs have been used in a wide variety of applications and manufacturing processes, especially as plasticizers, insulators and flame-retardants. They are widely distributed in the environment through, for example, inappropriate handling of waste material or leakage from transformers, condensers and hydraulic systems. According to some estimates, the total global production of PCBs from 1930 until the bans that were implemented in most countries by the 1980s had already been in the order of 1.5 million tons.

Dioxins (PCDD/Fs) were never produced intentionally, but they are minor impurities in several chlorinated chemicals (e.g., PCBs, chlorophenols, hexachlorophene, etc.), and are formed in several industrial processes and from most combustion processes, such as municipal waste incineration and small-scale burning under poorly controlled conditions. Formerly, pulp bleaching using chlorine gas was an important source of PCDD/Fs.

Numerous recent papers have shown differences in PCDD/F and dl-PCB concentrations in Baltic herring, sprat and salmon between the Baltic Sea basins (e.g., Bignert et al. 2010; Karl et al. 2010). Higher concentrations have been detected in the northern basins where dioxin and dl-PCB levels in herring exceed established maximum limit concentrations for human consumption. Regional variation within a sub-basin has been found in the Swedish coastal region of the Bothnian Sea (Bignert et al. 2007), where the concentrations are higher than in other Swedish areas (Bignert et al. 2011). Since the atmospheric deposition pattern (lowest in the north) is different compared to the patterns detected in the concentrations in fish (generally highest in the north), other factors or sources than atmospheric deposition are thus likely to be involved. The reasons remain unclear, but higher historical PCDD/F discharges from point sources in the northern basins have been suggested. In general, the contribution from the dl-PCBs to the TEQ is substantial and seems to increase the further south in the Baltic region the samples are collected.



Monitoring Requirements

Monitoring methodology

Monitoring of PCB, dioxin and furan in the Contracting Parties of HELCOM is described on a general level in the **HELCOM Monitoring Manual in the** <u>sub-programme Concentration of Contaminants</u>.

Specific monitoring guidelines have previously been documented in the HELCOM COMBINE manual, and are currently under review with the aim of being updated and included in the HELCOM Monitoring Manual.

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: monitoring concepts table for biota

The monitoring of temporal trends of PCBs is considered adequate in the Baltic Sea. There are no big gaps in the monitoring programme of PCBs. The monitoring of PCBs focuses on the seven classical "ICES 7" congeners: CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180. The time series stations use highly mobile sample species (herring, cod and flounder) which makes the network of time series stations as geographically representative for HELCOM sub-basins and coastal areas.

Monitoring of temporal trends of dioxin and furan is carried out by a few countries only.

Description of optimal monitoring

Monitoring stations for dioxins and furans seem to be lacking from the Bornholm Basin, the Gulf of Gdansk and the German Bight and increasing the spatial coverage of the monitoring program would allow for higher confidence evaluations from a scientific point of view. For temporal trend monitoring an annual sampling is required to detect trends more adequate than if sampling is only performed every second or third year. The present lack of monitoring stations and data for PCDD/Fs might also be a result of the high analytical costs which are contradicting the scientific demands.

Therefore, time series of dioxin and furan concentrations in fish are missing or too short to enable evaluation for several sub-basins in the Baltic Sea region. Also sample metadata (e.g. age, fat content) are often missing (not reported) reducing sample comparability between areas and over time. The geographical resolution is generally too poor to make reliable generalized maps from interpolation of the existing stations using statistical interpolation methods (e.g. Kriging).



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:

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Metadata

Result: PCB, dioxin and furan

Data: PCB, dioxin and furan data

Data are extracted from the HELCOM COMBINE database, hosted by ICES. The COMBINE data stem from regular environmental monitoring programmes of the coastal countries.



Contributors and references

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Archive

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