HELCOM INDICATORS

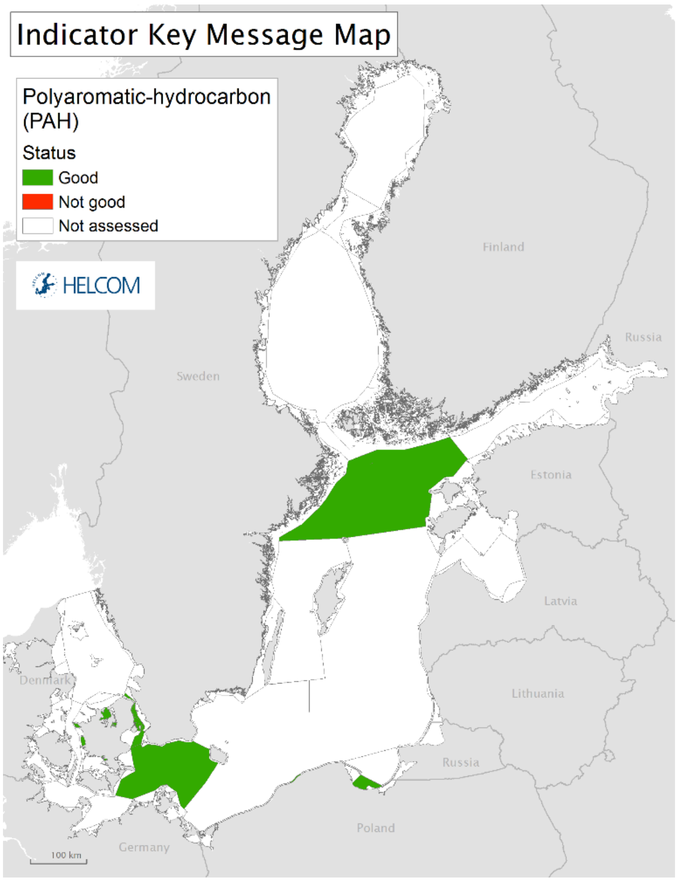
HELCOM core indicator report
July 2017

Polyaromatic hydrocarbons (PAH) and their metabolites

Key Message

The concentrations of benzo(a)pyrene, representing the concentration of polyaromatic hydrocarbons (PAH), achieve the threshold value in the open sea assessment units of the Norther Baltic Proper, the Arkona Basin and the Sound (Key message figure 1). The concentrations are below the threshold value in all evaluated coastal assessment units, namely in the Gdansk Basin, The Sound and The Great Belt. There are many areas for which data were not available for the evaluated assessment period of 2011-2015 and for which there is currently no evaluation (Key message figure 1).

As there is no commonly agreed threshold value for measuring metabolites available, this report only considers concentrations of PAH.



Key message figure 1: Status assessment results based evaluation of the indicator 'PAH and metabolites'. The assessment is carried out using Scale 4 HELCOM assessment units (defined in the [HELCOM Monitoring and Assessment Strategy Annex 4]).

The confidence of the indicator evaluation is high, however the spatial coverage of available data is currently not sufficient to evaluate the whole Baltic Sea area.

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

Relevance of the core indicator

Polycyclic aromatic hydrocarbons (PAHs) are of concern due to their persistence and potential to accumulate in aquatic organisms, particularly invertebrates such as bivalves and crustaceans. In most vertebrates, PAHs are fairly rapidly metabolized however PAHs and the toxic intermediates that are formed during metabolic degradation can cause harmful effects in fish. PAHs associate with particles in the water accumulate in sediments, and are persistent especially in anaerobic sediments.

Some PAHs are formed naturally, but the majority of PAHs in the marine environment stem from human activity. Sources of PAH include the release of crude oil products into the sea (oil-spills), as well as all types of incomplete combustion of fossil fuels and waste incineration.

Policy relevance of the core indicator

	BSAP Segment and Objectives	**MSFD Descriptors and Criteria**
Primary link	Concentrations of hazardous substances close to natural levels	D8 Concentration of contaminants - 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 seafood - D9C1 The level of contaminants in edible tissues (muscle, liver, roe 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 the exceed threshold values.
Other relevant legislation: EU Water Framework Directive		

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Results and Confidence

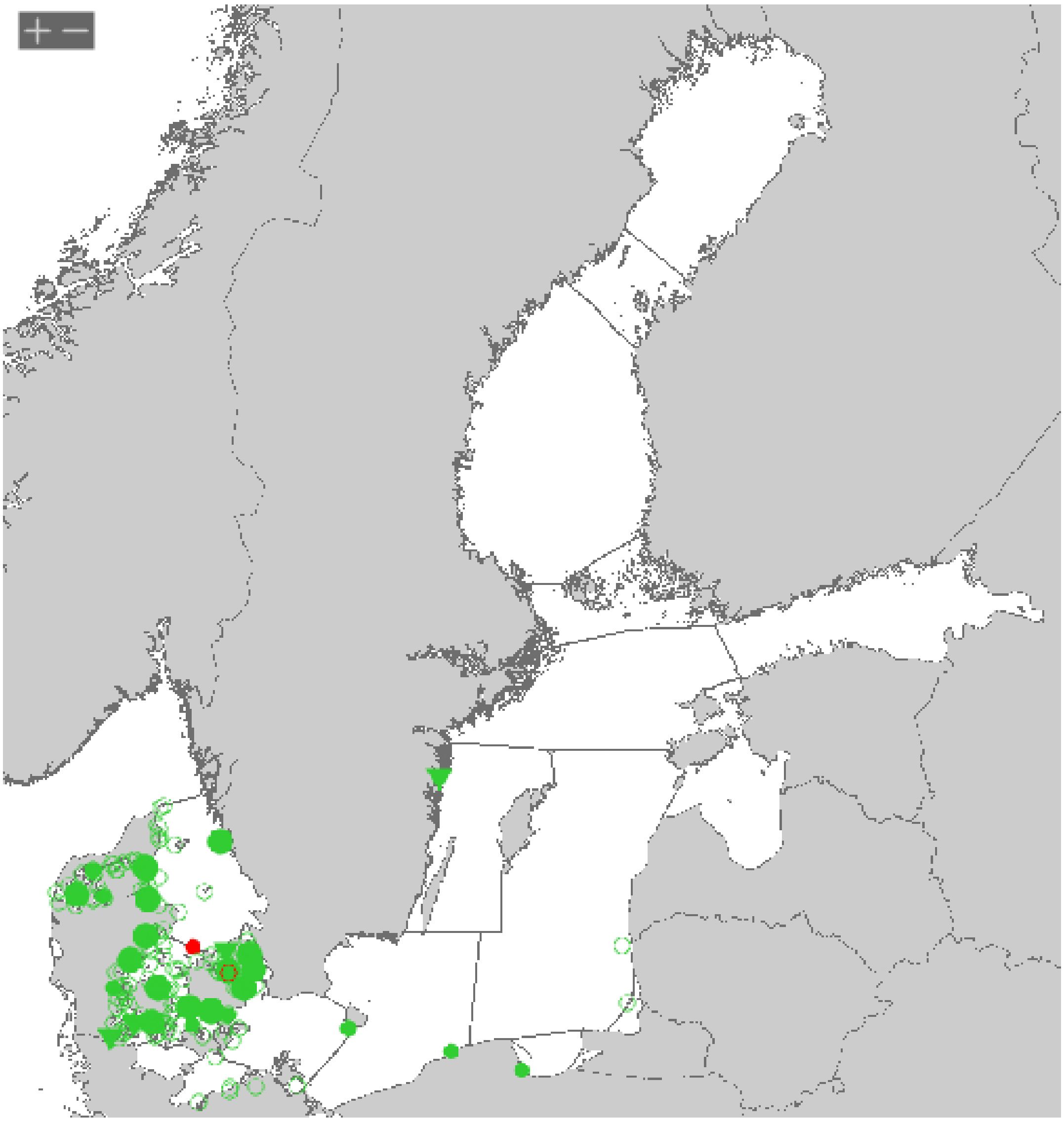
The core indicator is evaluated to achieve the threshold value in all assessment units where a full evaluation of the dataset was possible with aggregated results calculated for each assessment unit (Results table 1). A full evaluation was only possible for 3 out of 17 open sea assessment units, namely the Sound (SEA-003), Arkona Sea (SEA-006) and Northern Baltic Proper (SEA-012), and 10 coastal assessment units (Results table 1). To carry out a full assessment, a minimum of three years of data per monitoring station is required (see section Assessment Protocol). Concentration measurements are available for the primary substance benzo(a)pyrene for all the evaluated assessment units, and the threshold value was achieved in all units. It could furthermore be noted that the secondary substance fluoranthene was also evaluated in all of the evaluated assessment units, and that while the evaluation outcomes do not affect the overall status the threshold value was also achieved in all units for the secondary substance (Results table 1).

Results tale 1. The core indicator results per assessment unit based on the data that passed the full statistical treatment (see section Assessment protocol). In assessment units where a status assessment is available for the primary substances benzo(a)pyrene this will be given also as the overall status assessment, and the overall status assessment will only be influenced by the secondary substances assessment if no assessment is available for the primary substance. Confidence (conf.) is expressed as H-high, M-moderate or L-low. Status is expressed as A-achieve of F-failed threshold value.

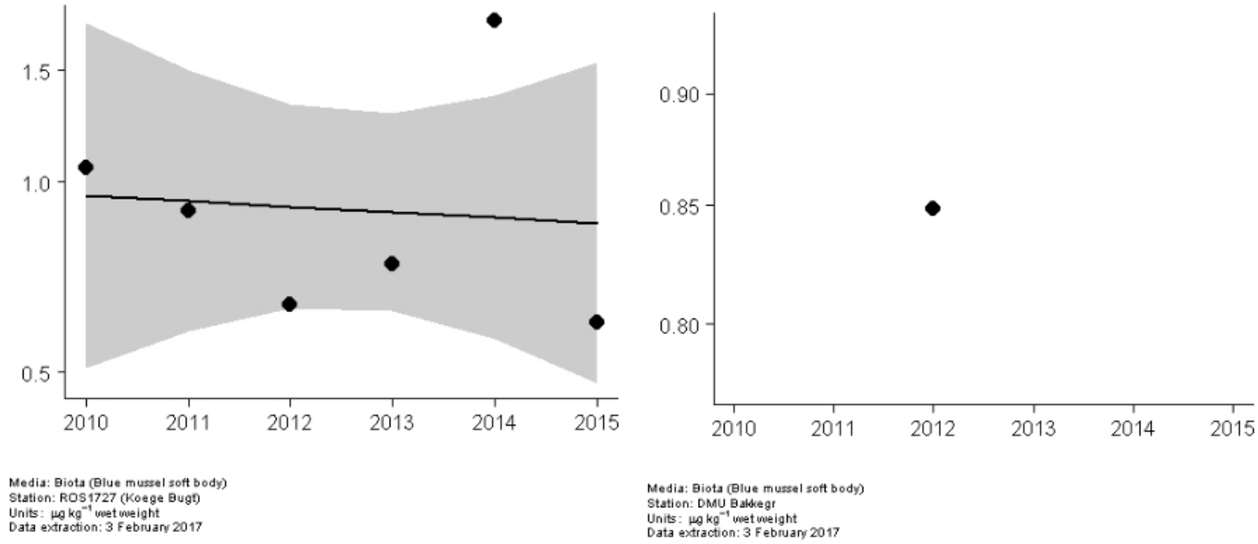
Assess ment unit	Primary substance: benzo(a)pyrene						*Secondary substance: Flu-fluranthane, Ant-anthracene*							Overall Status achieve / fail thresh old
	Matrix	Thresh old value [µg/kg ww]	Concentra tion [µg/kg ww]	Upper ratio to thresh old value	Conf.	Status	*Flu/ Ant*	*Matrix*	*Threshol d value [µg/kg ww]*	*Concentr ation [µg/kg ww]*	*Upper ratio to threshol d value*	*Conf.*	*Status achieve / fail thresho ld*	
Open sea														
SEA-003	crustacean and molluscs	5	0,2	0,03	H	A	Flu	crustacean and molluscs	30	2,0	0,07	H	A	A
SEA-006	crustacean and molluscs	5	1,6	0,31	H	A	Flu	crustacean and molluscs	30	4,9	0,16	H	A	A
SEA-012	crustacean and molluscs	5	0,5	0,09	H	A	Flu	crustacean and molluscs	30	1,8	0,06	H	A	A
coastal														
DEN-002	crustacean and molluscs	5	1,8	0,36	H	A	Flu	crustacean and molluscs	30	5,3	0,18	H	A	A
DEN-003	crustacean and molluscs	5	1,1	0,23	H	A	Flu	crustacean and molluscs	30	7,2	0,24	H	A	A
DEN-008	crustacean and molluscs	5	1,2	0,23	H	A	Flu	crustacean and molluscs	30	4,2	0,14	H	A	A
DEN-009	crustacean and molluscs	5	0,8	0,16	H	A	Flu	crustacean and molluscs	30	4,9	0,16	H	A	A
DEN-010	crustacean and molluscs	5	2,0	0,41	H	A	Flu	crustacean and molluscs	30	9,6	0,32	H	A	A
DEN-012	crustacean and molluscs	5	0,9	0,18	H	A	Flu	crustacean and molluscs	30	6,5	0,22	H	A	A
DEN-014	crustacean and molluscs	5	1,1	0,21	H	A	Flu	crustacean and molluscs	30	4,9	0,16	H	A	A
DEN-015	crustacean and molluscs	5	1,3	0,26	H	A	Flu	crustacean and molluscs	30	4,3	0,15	H	A	A
POL-006	crustacean and molluscs	5	3,9	0,78	H	A	Flu	crustacean and molluscs	30	6,7	0,22	H	A	A
POL-015	crustacean and molluscs	5	0,9	0,18	H	A	Flu	crustacean and molluscs	30	1,1	0,04	H	A	A

Results based on both the full data and initial status assessment data

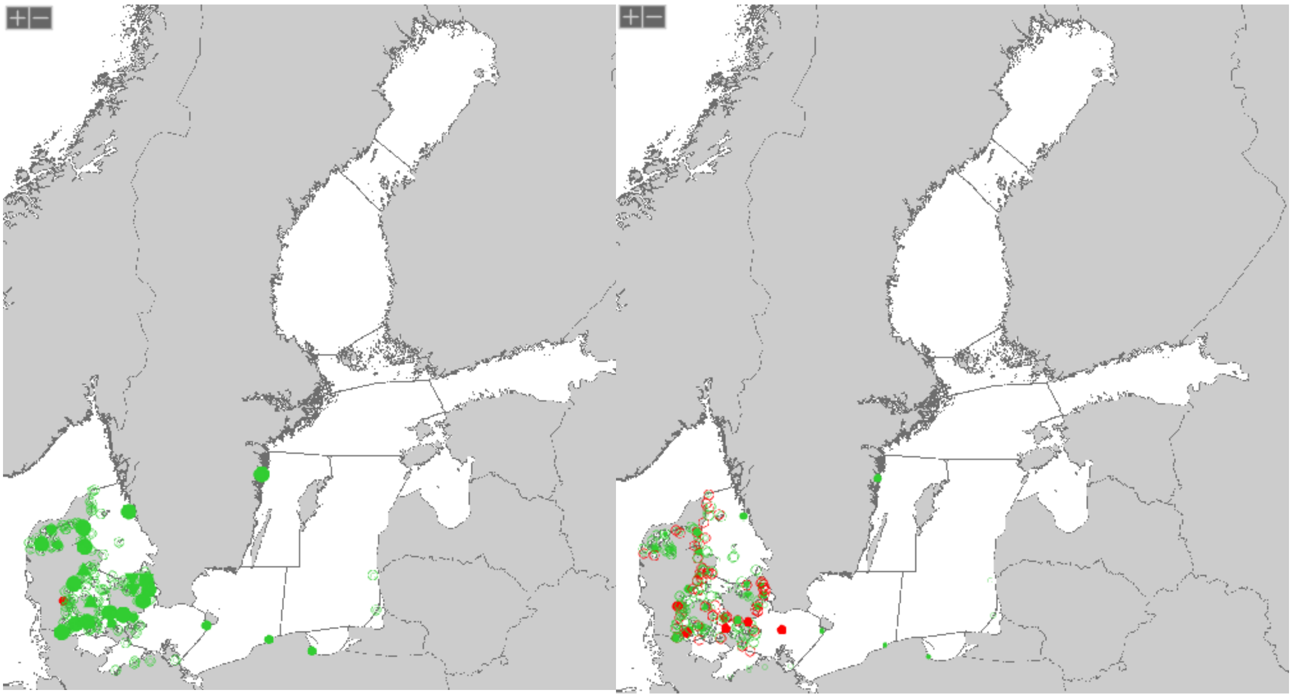
It should be noted that in addition to the data that supports a full assessment using the core indicator assessment protocol, there is also initial status assessment data available meaning that measurements are only available for 1-2 years per station. In order to achieve a better spatial coverage, the initial status assessment data could also be considered. The results per station show details of the data, and includes both the stations for which a full evaluation was possible and based on which the aggregated results were produced, as well as the initial status assessment stations that are not included in the key message result of the indicator. The maps and figures of the results per station are also available online: http://dome.ices.dk/HELCOMHZ2016/main.html



Results figure 1. Benzo(a)pyrene concentration measurements per station. Green indicates that the threshold value is achieved and red that the threshold value is failed. Large filled circles indicate a stable status, triangles pointing down indicate a significant downward trend and triangles pointing up indicate a significant upward trend. Small empty circles indicate initial status assessment data.



Results figure 2. Examples of benzo(a)pyrene concentration measurements in blue mussel (soft body) at two stations in the Arkona Basin selected for illustrative purposes, showing a station with full assessment possible (left) and initial status assessment data (right).



Results figure 3. Secondary substances (left) fluoranthene concentration measurements in biota and (right) anthracene measurements in sediment per station. Green indicates that the threshold value is achieved and red that the threshold value is failed. Large filled circles indicate a stable status, triangles pointing down indicate a significant downward trend and triangles pointing up indicate a significant upward trend. Small empty circles indicate initial status assessment data.

Confidence of the indicator status evaluation

The indictor evaluation for the assessment units where a full assessment was possible is evaluated to be **high**.

Even if PAH metabolites are not included in the present version of this report it should be mentioned that they are valuable HELCOM core indicators and would be included in environmental assessment as soon as agreed threshold levels are available. Many countries in Europe including Germany and Poland can provide long term monitoring data on PAH metabolites. The analytical methods are quality assured, well documented and PAH metabolites can be turned into a proper environmental assessment as soon as there is an agreed threshold.

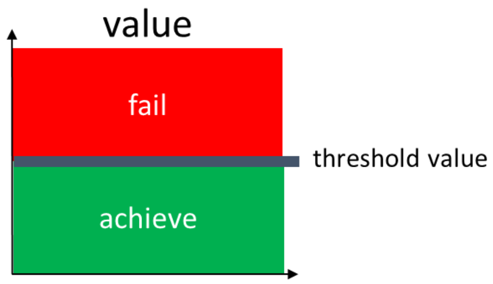
The data is considered to be reliable and the evaluation accurate, indicating a high confidence in the evaluation. The threshold value is based on an EU Environmental Quality Standard (EQS) which is considered to have a high confidence.

It should be well noted that a full evaluation was only possible for three open sea assessment units and ten coastal assessment units, indicating that there is a lack of data that meets the core indicator assessment protocol requirements in the Baltic Sea.

There are data from Germany that are not included due to lack of supplemental parameters and from Poland due to informal status of the data; also Estonia experienced data reporting issues. All these issues will be fixed in the final report (June 2018).

Good Environmental Status

Good status is evaluated for the core indicator 'Polyaromatic hydrocarbons (PAH) and metabolite' by comparing the measured concentrations of benzo(a)pyrene in the fish muscle and shellfish soft body matrix against the EU Environmental Quality Standard (EQS) of 5 µg/kg wet weight (Good environmental status figure 1). The threshold value is an EQS derived for the protection goal of human health via consumption of fishery products.



Good environmental status figure 1. Schematic representation of the threshold value for which the measured concentration of the primary substance benzo(a)pyrene, or the secondary substances fluoranthene and anthracene, should be lower than the threshold value concentration in order for the threshold value to be achieved.

The threshold value for benzo(a)pyrene concentration 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 and as a pragmatic approach secondary threshold values for secondary substances have also been agreed to be used to evaluate assessment units where no measurements are available for the primary substance and threshold value. The threshold values were agreed at HELCOM HOD 50-2016 (outcome para 4.47).

Good environmental status table 1. Threshold value for the primary substance benzo(a)pyrene and the two secondary substances fluoranthene and anthracene.

Substance	**Threshold value**	**Reference**
Benzo(a)pyrene	5 µg/kg wet weight crustaceans and molluscs	EQS $_{\text{biota human health}}$
Secondary substance fluoranthene	*30 µg/kg wet weight crustaceans and molluscs*	*EQS $_{\text{biota human health}}$*
Secondary substance anthracene	*24 µg/kg dw sediment (Normalized to 5% TOC)*	*QS*

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.

Assessment Protocol

Assessment units are evaluated using the primary substance benzo(a)pyrene concentration measured in edible parts of fish and crustaceans. If no evaluation is possible using the primary substance, then the secondary substances can be used to develop an evaluation for an assessment unit.

Sediment measurements were normalized to 5% total organic content (TOC) before being evaluated against the threshold value.

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.

Assessment units

The core indicator evaluation is carried out on the HELCOM assessment unit scale 4, including 17 open sea assessment units delimitated by the so called 1 nautical mile boundary from the baseline, and with the coastal areas split into WFD waterbodies or –types. The assessment units are defined in the HELCOM Monitoring and Assessment Strategy Annex 4.

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 PAH and metabolites, this indicator will also contribute to the overall hazardous substances assessment along with the other hazardous substances core indicators.

Policy relevance

Benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, indeno(1,2,3-cd), anthracene, pyrene, fluoranthene and naphthalene are identified as priority substances by European Commission (Directive 2008/105/EC).

The maximum levels of benzo(a)pyrene, and also a sum of benzo(a)pyrene, benz(a)anthracene, benzo(b)fluoranthene and chrysene, are regulated in food stuff according to the Commission Regulation (EC) No 835/2011.

Role of PAH and their metabolites in the ecosystem

Polycyclic aromatic hydrocarbons (PAHs) are of concern due to their persistence and potential to accumulate in aquatic organisms, particularly invertebrates, such as bivalves and crustaceans. In most vertebrates, PAHs are fairly rapidly metabolized, but they and their toxic intermediates emerging during metabolic degradation can cause deleterious effects in fish.

The PAH compounds identified as priority pollutants include low-molecular-weight PAH compounds, containing two-ring compounds (naphthalene) and three-ring compounds (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene) that are acutely toxic to a broad spectrum of marine organisms. The compounds also include high-molecular-weight PAHs with four-ring compounds (fluoranthene, pyrene, benzo(a)anthracene, chrysene); five-ring compounds (benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene) and six-ring compounds (indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene) that are less toxic but have greater carcinogenic potential (Kennish 1997).

Indeno(1,2,3-c,d)pyrene and chrysene have been shown to cause carcinogenic effects in experimental animals (IARC class 2b), and benzo(a)pyrene to cause cancer in humans (IARC class 1). Weakly- or non-carcinogenic PAHs can modify the carcinogenic activity of other PAHs in complex mixtures (Marston et al. 2001). Therefore, synergistic effects of PAHs can be larger than the total levels of PAHs would indicate. Also PAHs are transformed in the marine environment, e.g. when exposed to sunlight, the mechanism known as phototoxicity is involved, producing reactive and toxic photomodification products (HELCOM 2010). Thus, evaluating the overall environmental status based on PAHs has to take this complexity into consideration.

PAHs tend to associate with particulate material due to their low water solubility and hydrophobic nature. Deposition of these particles can lead to an accumulation of PAHs in the sediment. PAHs are persistent, especially in anaerobic sediments, with the higher molecular weight PAHs being more persistent than the lower molecular weight compounds (Kennish 1997; Webster et al. 2003).

Bioaccumulation of PAHs in marine organisms from sediments is dependent, thermodynamically, on the ratio between adsorption capacity of the sediment and absorption capacity of the organism. Different profiles of contaminants have been observed in organisms of different trophic levels that have been attributed to a partial biotransformation of the contaminants in the organisms of higher trophic levels (Baumard et al. 1998b). Increased levels of neoplastic aberrations or tumors have been found in fish exposed to PAH contaminated sediments. High concentrations of PAHs are also harmful to reproduction of fish and can damage cellular membrane structures (Knutzen 1995). Oxidised PAH in an organism are known to bind to DNA and/or cause mutations which may lead to cancer.

To evaluate effects of PAH exposure on fish, concentrations of the main metabolites such as 1-hydroxypyrene, 1-hydroxyphenanthrene and 3-hydroxybenzo(a)pyrene can be determined in bile by HPLC with fluorescence detection (HPLC-F), by synchronous fluorescence scanning, gas chromatography with mass selective detection (GC/MS) and also by UPLC/MS/MS (Ariese et al. 2005). PAH metabolites in fish bile reflects the level of exposure during the last few days before sampling, varying to some degree depending on the feeding activity of the fish.

Human pressures linked to the indicator

	General	MSFD Annex III, Table 2a
Strong link	PAH introduced to the marine environment through spills of petrochemical substances	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	Atmospheric deposition may be a significant pathway	

Some polyaromatic hydrocarbons (PAHs) are formed naturally, but the majority of PAHs in the marine environment stem from anthropogenic activity. Anthropogenic PAH sources in the marine environment include the release of crude oil products (petrogenic source) and all types of incomplete combustion of fossil fuels – coal, oil and gas or wood and waste incineration (pyrolytic sources) (Neff 2004).

Each source generates a characteristic PAH pattern enabling distinction of the sources in a sample by analyzing the concentration relationships of individual PAH compounds (Baumard et al. 1998, Sicre et al. 1987, Yunker et al. 2002). The PAH contamination in the Gulf of Finland and some areas in the western Baltic Sea (Sound, Belt Sea and Kattegat) have been identified as having a significant contribution of petrogenic PAHs, compared to the rest of the Baltic Sea where pyrolytic sources predominate. PAH from pyrolytic sources may be introduced through atmospheric deposition, however no reliable information is available on the airborne deposition of PAHs onto Baltic Sea surface waters (Pikkarainen 2004). In the areas where petrogenic PAHs are identified as a significant source, PAHs contamination is likely to originate from atmospheric deposition combined with shipping activities.

PAH compounds are pervasive in the Baltic Sea. Anthracene has been detected in fish from Swedish monitoring stations selected to reflect reference conditions. Anthracene has also has been measured in sediment from the Stockholm area (with concentrations falling inversely with distance from central Stockholm) and homogeneous coastal samples, indicating small local impact. It has also been measured in detectable concentrations in water areas sampled with the use of passive sampling devices. Fluoranthene is frequently present in fish from Swedish background stations, and also found in sediment and sludge. It has been found in all water samples from Sweden taken by means of passive sampling devices, and it is detectable in groundwater samples (Swedish EPA 2009).

In distance of point sources there are no temporal trends of PAH contamination mirrored as PAH metabolites detectable in dab and flounder from the North Sea and the western Baltic Sea caught during 1997 and 2004 (Kammann 2007). Lower values than in North Sea (dab, cod, flounder, haddock) and Baltic Sea (flounder, cod, herring, Vuorinen et al. 2006; eelpout) have been detected in Barents Sea (cod) and near Iceland (dab). Higher concentrations are present in fish caught in harbour regions or in coastal areas (eelpout, Kammann and Gercken 2010).

Monitoring Requirements

Monitoring methodology

HELCOM common monitoring of relevance to the indicator is documented in the on-line **HELCOM Monitoring Manual in the sub-programme: Contaminants in biota** and sub-programme: Contaminants in sediment.

Monitoring guidelines on the determination of persistent organic compounds in biota are currently documented in the HELCOM COMBINE manual, and are under review.

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 **and the** monitoring concepts table for sediment**.**

PAHs are monitored in biota in Denmark, Poland and Sweden and in sediments in Denmark, Poland and Sweden.

PAH metabolites in fish bile are regularly monitored by Denmark, Germany and Poland. Pre-monitoring stage of PAH metabolites investigations exist in Finland and Poland.

Description of optimal monitoring

PAHs or their metabolites are not monitored adequately in the eastern parts of the Baltic Sea. Especially, the lack of monitoring in Gulf of Finland is noteworthy.

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 (2017) PAH and metabolites. HELCOM core indicator report. Online. [Date Viewed], [Web link].

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Metadata

Result: Polyaromatic hydrocarbons (PAH) and their metabolites

Data: Polyaromatic hydrocarbons (PAH) and their metabolites sediment data

Data: Polyaromatic hydrocarbons (PAH) and their metabolites biota data

The core indicator evaluation is based on an extraction of data from the HELCOM COMBINE database, hosted by ICES. The database contains data from regular environmental monitoring carried out by the Contracting Parties of HELCOM.

The dataset has been used to evaluate the assessment period 2011-2015 for the purposes of the 'Status of the Baltic Sea' report.

Contributors and references

Contributors

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Archive

This version of the HELCOM core indicator report was published in July 2017:

HOLAS II component - Core indicator report – web-based version July 2017 (pdf)

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