



# Dioxins and PCBs

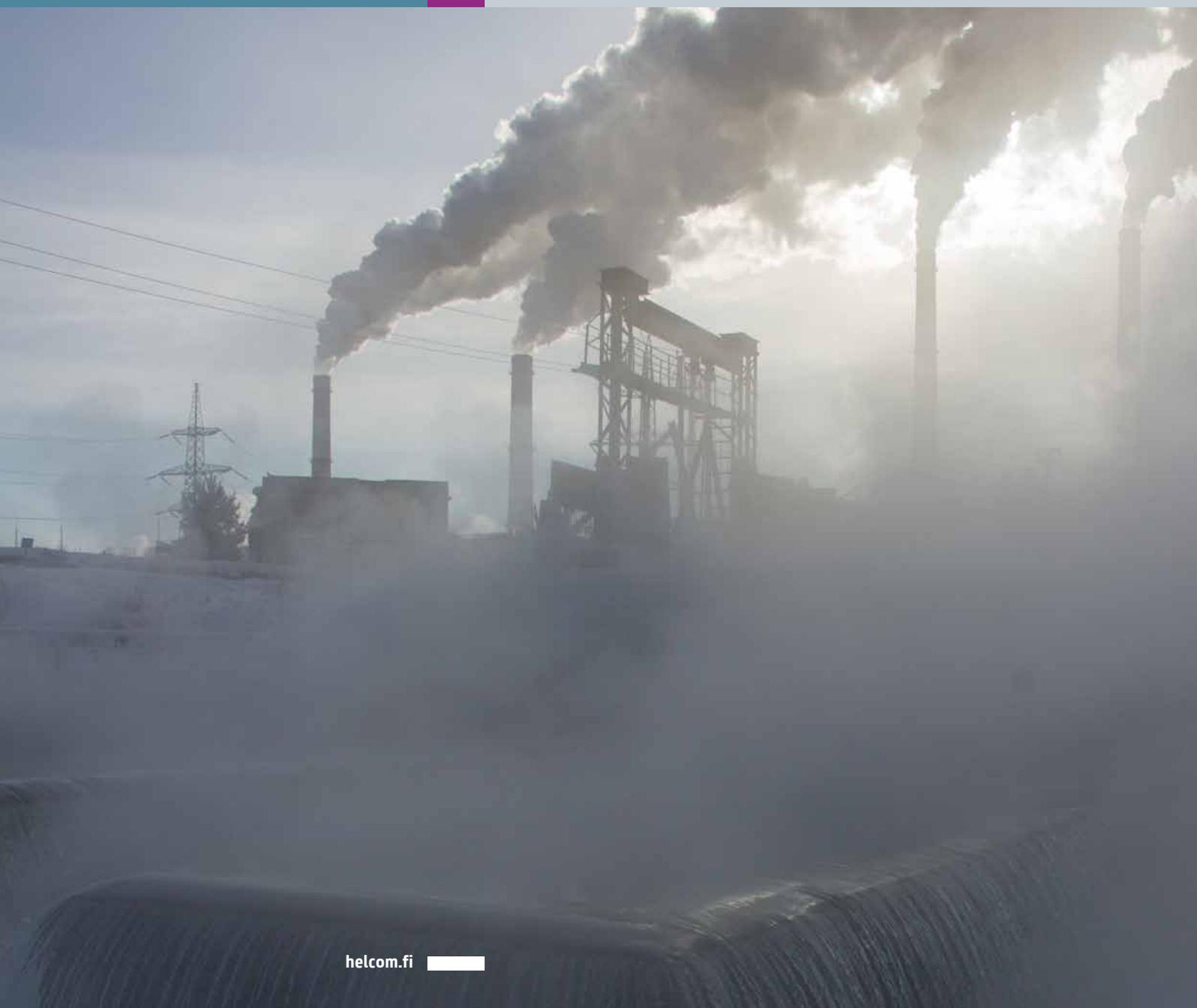
## in the Baltic Sea

  
Baltic Marine Environment  
Protection Commission

Hazardous substances



BSEP n°171



# Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) in the Baltic Sea

## – Sources, transport routes and trends

*The report was written to support the update of the HELCOM Baltic Sea Action Plan (BSAP). The BSAP is a programme to restore good ecological status of the Baltic marine environment by 2021 and was adopted in 2007 by all the HELCOM Contracting Parties. The study addresses the thematic area “Hazardous substances”.*

*It provides background information that is relevant in the process of evaluating the efficiency of currently implemented measures, and for suggesting additional measures, needed to achieve good environmental status in the Baltic Sea*

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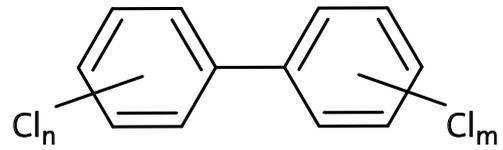
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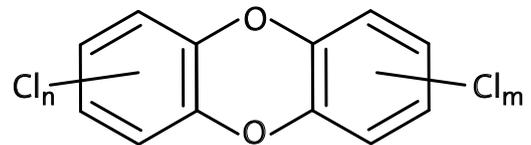
## Background

Polychlorinated biphenyl is a chemical structure consisting of 2 directly linked benzene rings that are substituted with between one and ten chlorine atoms. There are 209 possible unique structures (called congeners), depending on where chlorine is substituted on the rings. Technical mixtures of polychlorinated biphenyls (PCBs) were produced as industrial chemicals that were used in a wide range of applications. Some of the most important were as insulating fluids in electrical transformers and capacitors in fluorescent light fixtures, as plasticizers and flame retardants in building materials, and in carbonless copy paper. Large scale industrial production began in the 1930s and peaked in the 1970s when efforts began to phase them out. Common ways of entry into the environment include improper handling/spills of transformer oil and volatilization from open or semi-open uses such as in building materials. Once in the environment PCBs are very persistent, lipophilic (i.e., they tend to accumulate in lipid like material, which can lead to pronounced bioaccumulation), hydrophobic (i.e., they tend to migrate out of water into organic matter) and somewhat volatile (sufficient to make atmospheric transport possible). These properties vary widely among the congeners, whereby increasing degree of chlorination generally means increasing lipophilicity and increasing hydrophobicity. Several of the PCBs congeners produce dioxin-like toxicity. Abbreviated dl-PCBs, they have been included in the toxicity equivalent system for assessing dioxin toxicity risk.

Polychlorinated dibenzo-p-dioxin (PCDD) is a chemical structure consisting of 2 benzene rings linked to each other via two oxygen bridges located at adjacent carbon atoms on each ring, substituted with between one and eight chlorine atoms. The polychlorinated dibenzofuran (PCDF) structure is similar, except that one of the oxygen bridges is replaced by a direct carbon-carbon bond. There are 75 PCDD congeners and 135 PCDF congeners. PCDD/Fs have not been produced intentionally for



Molecular structure of PCBs.



Molecular structure of polychlorinated dibenzo-p-dioxins (PCDD).

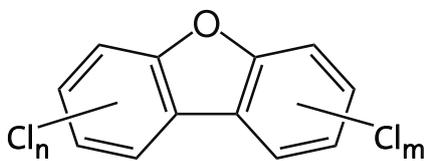
*PCDDs and PCDFs are unintentionally formed during synthesis of other chemicals, in certain industrial processes (e.g. chlorine bleaching) and in combustion processes.*



One of the major uses of PCBs was as insulating fluids in electrical transformers.



Photo: Chico Doaf/Mostphotos



Molecular structure of polychlorinated dibenzofurans.

commercial use. They are formed during the synthesis of other chemicals and are consequently present as contaminants in a range of industrial products. Of particular relevance for the Baltic Sea are chlorinated phenol wood preservatives. PCDD/Fs are also formed in certain industrial processes, whereby chlorine bleaching of pulp has been important for the Baltic Sea. Finally, they are formed in combustion processes, most efficiently where there is a strong source of chlorine, whereby waste incineration, ferrous and non-ferrous metal production, power generation and heating, and uncontrolled combustion processes are particularly relevant in the Baltic region (Lassen et al., 2003). Like PCBs, PCDD/Fs are very persistent in the environment, lipophilic and hydrophobic. They are less volatile, making them less likely to migrate out of surface media via the atmosphere. The different PCDD/F congeners have different toxicity, and toxicity equivalency factors are used to calculate the equivalent toxicity (TEQ) of PCDD/F congener mixtures with respect to 2,3,7,8-tetrachlorodibenzo-p-dioxin.

Concern about these chemicals in the Baltic Sea arises from the high levels measured in biota. This has resulted in restrictions on the use of fish, and in the most recent HELCOM core indicator report, good status was not achieved for the indicator dioxin-like PCBs, dioxins and furans, with exceedances being found primarily in the Bothnian Bay (HELCOM, 2018). dl-PCBs contribute approximately one third of the total dl-PCB+PCDD/F toxicity in Baltic Sea herring from Finnish waters (Airaksinen et al., 2014). One PCB congener, PCB 126, contributes 85% - 91% of the total PCB dioxin-like toxicity in zooplankton in the Baltic Sea (Peltonen et al., 2014) and 65% of the total PCB dioxin-like toxicity in a range of fish species from Finnish waters (Isosaari et al., 2006), which makes this congener especially relevant from a risk management perspective. In Baltic herring, one congener, 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-PeCDF), typically contributes more than half of the PCDD/F toxicity, followed in importance by 1,2,3,7,8-pentachlorodibenzo-p-dioxin (1,2,3,7,8-PeCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). The contribution of the other 207 PCDD/F congeners is generally minor or negligible (Airaksinen et al., 2014). Thus, the dioxin problem in the Baltic Sea is essentially attributable to 4 substances: PCB 126, 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, and 1,2,3,7,8-PeCDD. The non-dl-PCBs are exceeding the threshold for sum of congeners 28, 52, 101, 138, 153, 180 at several monitoring stations, including those where dl-PCB+PCDD/F levels are too high.

## Sources and pathways to the Baltic Sea

### PCBs

PCBs enter the Baltic Sea mainly through the atmosphere. There are different streams of evidence to support this conclusion. One is that the PCB pattern was uniform in sediments collected through the Baltic Sea – North Sea transition region, suggesting that there must be a common source (Christiansen et al., 2009). PCB concentrations in sediment are also uniform across the Baltic Sea when normalized to organic carbon, suggesting that one source influences the whole sea (Axelman et al., 2001; Jonsson, 2000). Modeled estimates of riverine input of PCBs were two orders of magnitude less than atmospheric deposition (Wiberg et al., 2009). In the North Sea, highly industrialized rivers do contribute a PCB load which is comparable to atmospheric deposition (O'Driscoll et al., 2013). However, such strong riverine impacts are characterized by strong gradients in PCB concentrations in the rivers' estuaries. Strong gradients in PCB concentration in sediments are virtually absent in the Vistula and Oder estuaries, two of the most industrialized rivers in the Baltic watershed (Dannenberger et al., 1997; Szlinder-Richert et al., 2012). In sediments from the Neva delta, dl-PCB-TEQ concentration were on average 17 times higher in the river itself than in the reference area in the Gulf of Finland, which indicates that the Neva could be a more significant PCB source (Metelkova et al., 2019). However, the impact appears to have been comparatively minor, as PCB levels in sediments from the Gulf of Finland have been found to be low (Isosaari et al., 2002).

PCB contamination in the atmosphere is believed to arise primarily from remobilization of PCB residues already in the environment, also called reemission or secondary emissions. While it was originally thought that residues in soil and sediments were the primary source of PCB reemission (Wania and Mackay, 1996), sources in urban environments have been shown to play a notable role (Harner et al., 2004). PCBs are also formed as unintentional byproducts during combustion. While this source is generally insignificant for PCBs as a group, it has been postulated to be an important source of atmospheric PCB 126, contributing even more than the PCB technical mixtures to atmospheric levels at some locations in Asia (Kishida et al., 2010; Li et al., 2016). However, combustion has been found to be an unimportant source of PCB 126 to atmospheric levels of PCBs in southern Germany (Weber et al., 2018), indicating that the PCB source distribution in Europe and Asia are different.

EMEP uses emissions data provided by signatory countries to the UNECE LRTAP Convention and mathematical models of atmospheric transport and environmental fate to assess atmospheric contamination with PCBs. They focus on one PCB congener, PCB 153, that does not contribute to TEQ. Their latest analysis indicates that 26% of PCB 153 in the atmosphere in the EMEP region originates from primary emissions in EMEP countries, 6% from primary emissions in other countries, and 68% from reemission. PCB 153 concentrations are highest in the south-western part of the Baltic Sea and lowest in Bothnian Bay. Although it is recognized that the nationally reported emissions estimates are uncertain, the agreement between modeled concentrations of PCB 153 in ambient air and measurements from the EMEP monitoring network is reasonably good. Of the primary emissions in EMEP countries, 79% are

*Most PCB contamination in the atmosphere arise from remobilization of PCBs that have already been emitted (i.e. secondary emissions). Primary emissions that are still ongoing in the Baltic Sea region are dominated by industrial emissions.*



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*Some rivers in the Baltic Sea catchment are highly contaminated by industrial emissions of PCDD/Fs. Atmospheric deposition is, however, believed to be the major source in offshore and pristine areas.*

attributed to industry and 10% to other stationary sources (Gusev et al., 2019). There is no comparable analysis for PCB 126 or PCB TEQ, but this work supports the statement above that PCB contamination is largely due to reemission.

### PCDD/Fs

There are several different major source categories of PCDD/Fs to the Baltic Sea including chlorinated phenol wood preservatives, chlorine bleaching in the pulp & paper industry, and combustion processes such as waste incineration and metal production. These source categories have different temporal characteristics. Chlorinated phenol wood preservatives and chlorine bleaching were used extensively from the 1950s into the 1980s, but their use has since been largely eliminated. Combustion processes have been a significant primary source of PCDD/Fs for much longer periods (Meharg and Killham, 2003) and continue to be so today, but some emissions sources such as municipal waste incineration have a temporal characteristic similar to that of chlorinated phenols.

The different source categories take different pathways to the Baltic Sea. PCDD/Fs originating from chlorinated phenols are transported from sites where they were used (e.g., sawmills) into coastal waters where they accumulate in nearshore sediments. Discharges from chlorinated phenol production sites have also contaminated coastal sediments (Salo et al., 2008). PCDD/Fs from chlorine bleaching were also discharged directly into coastal waters where they accumulated in sediments. PCDD/Fs from combustion sources, on the other hand, are transported in the atmosphere and deposited across the Baltic Sea (Rappe et al., 1989). They also accumulate in vegetation in soils in the watershed, which can then become secondary sources to the Baltic Sea.

The different source categories possess different PCDD/F congener patterns or signatures. Due to the persistence and hydrophobicity of PCDD/Fs, these signatures are largely conserved in sediments. Thus, sediments can be used to identify the sources of PCDD/Fs to the Baltic Sea. The

strongest point source of PCDD/F contamination in the Baltic Sea is the Kymijoki River, which was contaminated by emissions from a plant that produced Ky-5, a chlorinated phenol-based wood preservative. Analysis of sediments indicates that the contamination plume extends 75 km from the river mouth and that it contains about about 12.4 kg WHO TEQ (Isosaari et al., 2002). However, it has been suggested that atmospheric deposition is a stronger contributor than the Ky-5 source to the TEQ contamination of fish in the region because the congeners contributing most to the TEQ in the Ky-5 signature are not strongly accumulated in fish (Korhonen et al., 2016). For 2,3,4,7,8-PeCDF, the congener that makes the biggest contribution to the PCDD/F TEQ in fish, the Ky-5 source was estimated to have contributed just 13% of the total amount deposited in Gulf of Finland sediments during 1986-1997 (Verta et al., 2007).

Statistical methods have been used to estimate the relative contributions of different PCDD/F source signatures to environmental samples. Assessment of 146 surface sediment samples collected along the Swedish coast and in offshore areas led to the conclusion that atmospheric sources were the dominant contributor of the  $\Sigma$ PCDD/F in offshore and pristine areas while chlorophenol based wood preservatives were important contributors in coastal areas close to relevant sources (Sundqvist et al., 2010). Chlorine bleaching was an important source category at just one coastal site, while another source signature that appeared to be linked to the pulp & paper industry made a major contribution at two further coastal locations (Sundqvist et al., 2009a). This technique was later applied to sediment cores, allowing assessment of source contributions over the period 1919-2010, and a similar conclusion was reached: atmospheric sources have always contributed >80% of the  $\Sigma$ PCDD/F in the Baltic Proper and >50% in the Bothnian Sea and Bothnian Bay (Assefa et al., 2014a). Recently the technique was also applied to herring, and atmospheric sources were again found to be the dominant contributor, this time to TEQ in herring (Assefa et al., 2019). It was also reported that the contribution of tetrachlorophenol sources had increased at the cost of atmospheric sources in herring sampled post-2000 compared to pre-2000, and it was suggested that the importance of atmospheric sources would continue to decrease over time. This finding stands in contrast to the same authors' observations in sediment cores, where such a temporal trend was not observed (Assefa et al., 2014a). The dataset for the sediment study was much larger, whereas a strength of the herring study is that it calculates the contribution of the different sources to TEQ (i.e., the basis of the HELCOM core indicator) instead of  $\Sigma$ PCDD/F.

Mass balance modeling has been used to estimate current sources of PCDD/F to the Baltic Sea. Estimates of discharges from contaminated sites were found to be insignificant compared with atmospheric deposition (Armitage et al., 2009). This corroborates the conclusion that atmospheric sources are and have been the major contributor to PCDD/F contamination of the Baltic Sea.

The PCDD/F contamination in air over the Baltic Sea depends on the season and where the air comes from. PCDD/F concentrations are more than an order of magnitude higher during winter than summer. Air masses that originate from the south and east have much higher PCDD/F concentrations than air masses that originate from the north and west. Furthermore, the PCDD/F congener pattern differs, with PCDFs making a stronger contribution to the PCDD/F TEQ in air from the south and east (Sellström et al., 2009; Assefa et al., 2018). Soot concentration was found to be a good predictor of the concentration of all



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*PCDD/F congener patterns in sediment cores have been studied to estimate the relative contributions of different sources in the environment.*

2,3,7,8-substituted PCDD/Fs during the winter half year at Aspvreten, Sweden (Sellström et al., 2009). This indicates that most of the atmospheric deposition to the Baltic Sea occurs during winter and that the atmospheric sources of PCDD/Fs are considerably stronger during winter.

Identifying the specific atmospheric sources of PCDD/Fs has proven difficult. Efforts to predict atmospheric concentrations from emissions inventories provided by European countries to the UNECE failed; the modeled concentrations were less than the observed concentrations by a factor of 5.3 (median) (Shatalov et al., 2012a,b). Since the uncertainty in the modeled transport and removal of PCDD/Fs in the atmosphere is low, this indicates that emissions are vastly underestimated. Despite efforts to improve the reporting of emissions data, the most recent EMEP status report on transboundary pollution of POPs concludes “Estimates of PCDD/F emissions officially reported by the EMEP countries are most likely subject to considerable uncertainties due to underestimation of releases from some source categories (e.g. 'Residential combustion', 'Open burning of wastes') and incomplete coverage of all potential sources.” To cope with this in their transboundary modeling work, EMEP uses the upper uncertainty bound of the national emissions inventories when these are provided, and applies a factor 3 multiplier to the emissions inventories of countries that do not report uncertainty bounds (Gusev et al., 2018). The enormous emissions gap has still not been closed, and thus available emissions inventories cannot identify the nature and location of the dominant sources of PCDD/F emissions that are impacting the Baltic Sea. Although the UNECE CLRTAP emissions have

*Small scale uncontrolled combustion is suspected to be a major source of PCDD/Fs in the Baltic Sea.*



been broken according to emissions category and country (EEA, 2019, Barnicki 2017), these breakdowns are not relevant for assessing the sources of PCDD/Fs to the Baltic Sea due to this emissions gap.

There are indications of the source category responsible for the emissions gap. Large commercial and industrial combustion facilities were major sources of atmospheric PCDD/Fs in the 1970s and 1980s, but abatement measures have greatly reduced emissions in many cases. According to the UNECE CLRTAP reporting at the European scale emissions from the categories “public electricity and heat production” and “iron and steel production” have decreased by 83% and 69%, respectively, between 1990 and 2017, whereas estimated emissions from “residential:stationary”, “clinical waste” and “other waste” are at approximately the same level today as almost 30 years ago (EEA, 2019). According to the 2015 UNECE inventories, the contribution of the source categories “public power”, “industry”, “road traffic”, “waste” and “agriculture” to the total PCDD/F TEQ emissions of the HELCOM countries (except Russia) was 7%, 24%, 3%, 13% and 4%, respectively, while the contribution of “other stationary sources” was 46% (Barnicki et al., 2017). As a result of the implementation of abatement technology, it was predicted in 2004 that emissions were likely to be dominated by small sources in the future (Quass et al., 2004). In 2003 uncontrolled combustion was identified as the largest source of PCDD/F emissions in Poland using the UNEP Chemicals toolkit for quantification of dioxin and furan releases, although the uncertainty was high (Lassen et al., 2003). Twelve years later, there was not much more quantitative information on the magnitude of this source category. In a review of PCDD/F sources, Dopico and Gomez (2015) write “Open waste burning, backyard barrel burning, or biomass waste burning ... is probably the most important nonindustrial source and one of the most difficult to determine precisely, given the variability in composition of waste and mostly uncontrolled combustion techniques”. In summary, small scale uncontrolled combustion is suspected to be the primary explanation for the emissions gap. This would make it a major source of PCDD/Fs to the Baltic Sea.

Some of the PCDD/Fs from atmospheric sources enter the Baltic Sea via rivers. PCDD/Fs that have been deposited to the terrestrial environment accumulate in vegetation and soil, and from there they can be carried by surface runoff to the Baltic Sea. PCDD/F transport in rivers is closely linked to the transport of particulate matter (Josefsson et al., 2016). PCDD/Fs are mobilized from the watershed during floods, which can result in higher concentrations in river water and PCDD/F loads that are an order of magnitude higher than during low flow conditions (Urbaniak et al., 2015). In the Gulf of Gdansk, the sedimentation basin for several major rivers from the more densely populated and industrialized regions of the Baltic Sea drainage basin, the PCDD/Fs in the sediments are primarily of atmospheric origin (Niemirycz and Jankowska, 2011). In a modeling study, riverine inputs were estimated to equal 20% and 40% of atmospheric deposition of PCDD/F TEQ to the Baltic Sea and Bothnian Sea, respectively (Armitage et al., 2009). If emission reduction measures lead to a decrease in atmospheric deposition in the future, riverine input of PCDD/F residues from the terrestrial environment can be expected to contribute a larger percentage of PCDD/F inputs to the Baltic Sea. No studies were found about how the magnitude of these inputs can be expected to develop in the future.



Photo: SeaWiFSProject/NASA

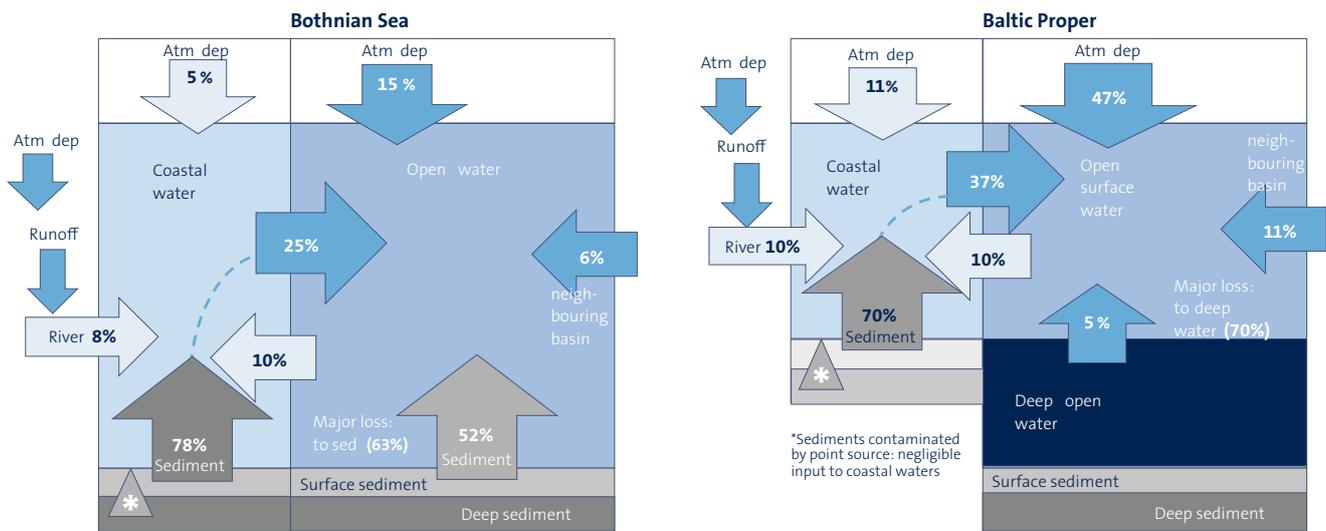
## Cycling in the Baltic Sea

PCB and PCDD/F contamination in pelagic fish is primarily determined by the chemicals' concentrations in the water column. The concentrations in the water column are determined by the balance between the rate of chemical input to the water column and the rate of chemical removal. As noted above, atmospheric deposition is an important source of PCBs and PCDD/Fs to the pelagic environment of the Baltic Sea, while for PCDD/Fs riverine inputs or discharges from point sources on the coast can also contribute. In addition, sediments can be a source to the water column, as well as a sink. Due to the hydrophobic properties of PCBs and PCDD/Fs, they sorb strongly to organic material in sediment. This conveys upon sediments the role of a buffer for contaminant levels in the water column. They soak up PCBs and PCDD/Fs from the water column when concentrations in sediment are low compared to water, and release chemicals to the water column when concentration in sediment are comparatively high. Other important sinks for PCDD/Fs in the water column of the Baltic Sea include loss to the atmosphere via volatilization, degradation, and transport into other parts of the Baltic Sea or out of the Baltic Sea entirely. The PCB and PCDD/F levels in the water column are the result of the interaction of these many sources and sinks, each of which can vary in time and space, which yields a complex contaminant cycling puzzle.

A basin scale chemical fate and transport model was parameterized for the Baltic Sea in order to unravel this puzzle (Armitage et al., 2009; Wiberg et al., 2009). The simulations yielded the following features of PCDD/F TEQ behavior for the year 2007:

**A) INPUTS TO COASTAL WATERS CAME PRIMARILY** from sediments, while inputs from rivers and the atmosphere were insignificant in comparison. Hence the concentrations in the water column were determined by the concentrations in sediments (i.e., the sediment buffer function). The major loss from coastal waters was deposition to sediments, but 20%-30% of the total input was exported to offshore waters.

**B) ABOUT HALF OF THE INPUTS TO OFFSHORE WATERS** in the Bothnian Sea came from sediments, while the other half came from coastal water, atmospheric deposition, and neighbouring basins. Thus sediment played



**Figure 1.** Overview and approximate relative importance of input routes for PCDD/Fs to coastal and open waters in the Bothnian Sea (left) and Baltic Proper (right) in year 2007. Adopted from mass balance calculated using the Popcycling-Baltic model by Armitage et al. 2009. The blue triangle signifies that PCDD/F-levels can be elevated in sediments in close proximity of industrial point sources.

a less dominant but still important role in determining the concentrations in water. The major loss from the Bothnian Sea offshore water was deposition to sediment. The dominant removal process from the sediment-water system as a whole was sediment burial, while degradation, volatilization (transfer to the atmosphere as a gas) and transfer to other basins were negligible in comparison. Sediment burial is the process whereby sediment material (and the associated contaminants) is transferred to deeper layers due to the accrual of fresh sediment material on the sediment surface.

**C) INPUTS TO OFFSHORE SURFACE WATER IN THE BALTIC PROPER** were equally divided between coastal water/other basins and atmospheric deposition. Hence the PCDD/F concentrations in the water were determined by both atmospheric deposition and the levels in the coastal sediments (i.e., sediments above the halocline). Loss from the Baltic Proper surface water was almost exclusively due to transport into deep water (below the halocline). In the deep water the large input from the surface water was transferred to the sediments. The modeled loss of PCDD/Fs due to sediment burial exceeded net input from the water column, so that surface sediment concentrations were predicted to be decreasing in 2007.

This work illuminates the important role that sediment plays in determining PCDD/F levels in the water column. The model findings are corroborated by empirical measurements showing: a) PCDD/Fs in offshore sediments in 2007 were in equilibrium with the overlying water, i.e. that there was no net tendency for them to either soak up or release PCDD/Fs in their buffer function (Cornelissen et al., 2008); b) on the other hand, contaminated coastal sediments from the Bothnian Sea sampled in 2010 displayed a strong tendency to release PCDD/Fs to the water column (Sobek et al., 2014). The sediment buffering function is particularly relevant for the response time to changes in PCDD/F inputs. A decrease in PCDD/F input is expected to result in a slower decrease in contamination levels in the Bothnian Sea than in the Baltic Proper (surface water) due to the stronger sediment buffering in the Bothnian Sea

(Armitage et al., 2009). This may be a partial explanation for the fact that the Bothnian Sea and the Bothnian Bay are the regions where herring most frequently exceed the PCDD/F quality standard for secondary poisoning (Bignert et al., 2017).

Although sediment contamination hotspots apparently have little impact on PCDD/F levels in water on a basin scale or in widely ranging pelagic fauna, they can have impacts on local benthic fauna and stationary pelagic fauna feeding on a food web impacted by the benthic environment (Sobek et al.; 2014; Vuorinen et al., 2017).

The analogous assessment for PCBs was done for the sum of PCB congeners 28, 52, 101, 118, 138, 153 and 180. In contrast to the PCDD/Fs, atmospheric deposition equaled input from sediment in coastal waters and dominated input in offshore waters. This is due to the greater volatility of the PCBs compared to the PCDD/Fs. Losses from coastal water were equally divided between sedimentation and volatilization in coastal water, and volatilization was the dominant loss process in offshore water. PCB concentrations in most surface waters were governed by the concentrations in the atmosphere, while concentrations in the deep water of the Baltic Proper were influenced by both the atmospheric deposition arriving via the surface water and the PCB residues in sediment. As a result of the more rapid air/sea exchange compared to PCDD/Fs, there was a closer link between concentrations in air and concentration in water and sediment. The buffering effect of the sediments was much less than for the PCDD/Fs, which was reflected in shorter contaminant residence times: ~2 years for PCBs in the Bothnian Sea and Baltic Proper compared with 11 years for the PCDD/Fs (Wiberg et al., 2009).

On a smaller spatial and temporal scale, the cycling behavior of PCBs and PCDD/Fs is more complex. High resolution models can provide useful insight. For instance, they have shown the effect of storm events on the cycling of PCB 153 in the North Sea (O'Driscoll et al., 2013). No model simulations of this kind were found for the Baltic Sea.



## Time trends in emissions

### PCBs

The primary emissions of PCB 153 by HELCOM countries are estimated to have decreased by 78% between 1990 and 2016. The change varies broadly from country to country, with Latvia showing a decrease of 95% while Sweden and Finland show slight increases. These estimates are based on official reporting of the countries to UNECE and on expert judgement (Gusev, 2018a). No estimates were found for PCB 126. As noted above, primary emissions of PCBs currently make a comparably small contribution to PCB levels in the atmosphere.

### PCDD/Fs

According to the official reporting to UNECE, atmospheric emissions of PCDD/F TEQs by HELCOM countries have decreased by 31% between 1990 and 2015 (Barnicki et al., 2017). However, as noted above the official reporting vastly underestimates the emissions. Hence this is not a reliable estimate of the time trend of total atmospheric emissions. Since the major source of current atmospheric emissions has not been characterized, it is not possible to directly estimate their time trend.

## Time trends in environmental levels

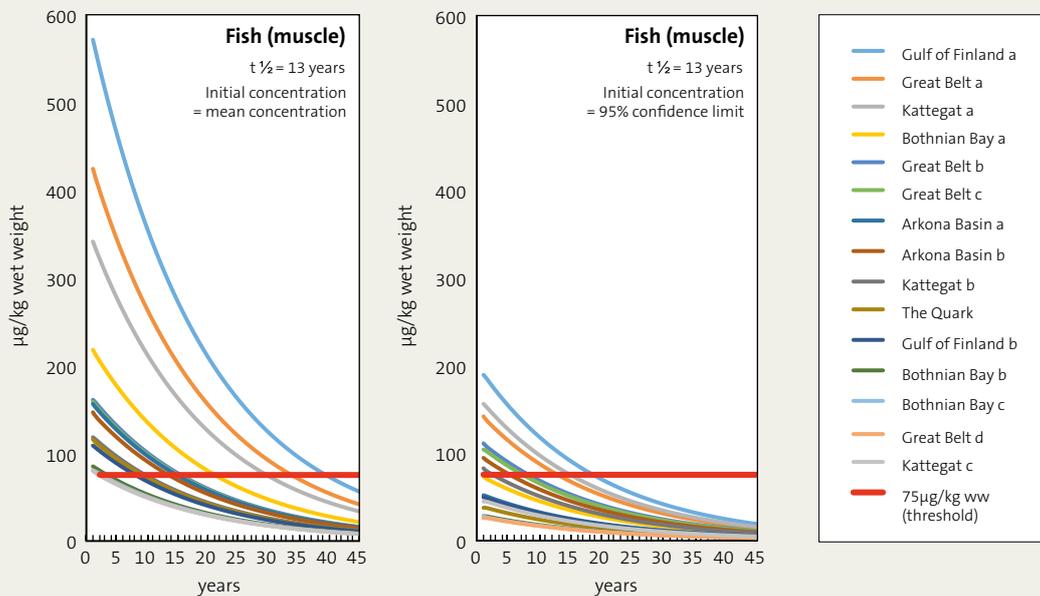
### PCBs

The herring and guillemot egg archives maintained by the Swedish Museum of Natural History have provided the longest datasets for analysis of time trends in Baltic Sea biota. Concentrations are highest in herring from the Bothnian Sea and the Baltic Proper. The time trends at the three long-term monitoring stations in these water bodies, Ångskärsklubb, Landsort and Utlängan, show a continual decrease of PCB 153 concentrations between 1988 and 2016, with a fitted annual average decrease of 5.3%, 5.8%, and 1.8%, respectively. For PCB 118 the annual average decrease was 6.1%, 7.2%, and 4.9%, respectively (Bignert et al., 2017). Significant decreases have also been observed for the period 2008-2017 for a range of PCB congeners in herring from Utlängan, Byxelkrok and Rånefjärden and perch from Örefjärden, indicating that the decreases continue today (Danielsson et al., 2019). Guillemot eggs from Stora Karlsö showed similar decreases: 7.2% and 7.6% for PCB 153 and PCB 118, respectively, between 1988 and 2016, and 4.7% and 5.6%, respectively, between 2007 and 2016 (Bignert et al., 2017).

Other time trend studies support the above results. The  $\Sigma$ PCB (20 congeners) decreased in juvenile ringed seals collected from the Swedish waters of the Baltic Sea decreased by a factor of ~5 between 1975 and 2015 (Bjurlid et al., 2018). PCB TEQ in herring samples collected all along the Finnish coast decreased significantly between 2002 and 2009 in old herring (> 5 years) but not in young (< 5 years) (Airaksinen et al., 2014).

### BALTIC SEA AREA – SAMPLING LOCATIONS



PCBs IN FISH (*Perca fluviatilis*, *Zoarcetes viviparus*, *Gadus morhua*)

**Figure 2.** Estimated time for concentrations of PCBs (sum of congeners 28, 52, 101, 138, 153, 180) to decrease below the threshold of 75 µg/kg ww fish muscle where this threshold was exceeded in the most recent HELCOM status assessment (performed in 2018) assuming that  $[PCB](t)=[PCB]_{initial}e^{-kt}$ . The last year of monitoring in the dataset was 2012 to 2016 depending on station. The initial value is the observed concentration at the last year of monitoring or mean log concentration during 3–4 years (left panel) or the upper one-sided 95% confidence limit on the fitted value in last monitoring year (right panel) (<http://metadata.helcom.fi/geonetwork/srv/eng/catalog.search#/metadata/33505b4a-ee14-4544-9e1d-d155548004e4>).

The table (below) shows time to reach good status depending on assumptions regarding degradation half-life (initial value upper one-sided 95% confidence limit).

Names refer to basins and monitoring stations: Gulf of Finland a = Seurasaarenselk, Great Belt a = ARH170009, Kattegat a = Anholt, Bothnian Bay a = Kemlin edusta Ajos Poh, Great Belt b = SJY FFML5014, Great Belt c = SJY FFML5012, Arkona Basin a = OMTF0112, Arkona Basin b = DMU KB, Kattegat b = FRB 65, The Quark = Vaskiluoto, Gulf of Finland b = Vanhankaupunginlahti, Bothnian Bay b = Tornion edusta, Bothnian Bay c = SIMONNIEMEN EDUSTA 1, Great Belt d = ST00102400, Kattegat c = DMU 2R.

TIME (in years) FOR CONCENTRATIONS TO DECREASE BELOW 75 µg/kg ww				
Assumed half life (years)	9	14	18	39
% yearly decline	7.4%	5.0%	3.8%	1.8%
Gulf of Finland a	27	42	53	115
Great Belt a	23	35	45	98
Kattegat a	20	31	40	86
Bothnian Bay a	14	22	28	60
Great Belt b	10	16	20	44
Great Belt c	10	16	20	42
Arkona Basin a	10	15	19	42
Arkona Basin b	9	14	18	38
Kattegat b	6	10	12	26
The Quark	6	9	12	25
Gulf of Finland b	5	8	10	21
Bothnian Bay b	2	3	4	8
Bothnian Bay c	2	2	3	5
Great Belt d	1	2	2	4
Kattegat c	1	2	2	3

Although the wide and non-systematic spatial range of sample collection is a limitation of the Finnish study, it is the only one to report PCB TEQs. Overall the data indicated that PCB concentrations in biota from the most contaminated regions of the Baltic Sea have been decreasing at about 5% per year for the last 3 decades, which corresponds to a half-life of 14 years.

Differences in time trends are often observed between different species, or even within different sub-groups of the same species. This is because the relationship between a chemical's concentrations in the physical environment and in biota is not fixed. Variables affecting bioaccumulation include the age, size, lipid content, growth rate, reproductive history and feeding habits of the individual, the trophic level of the species, the food web structure that it is feeding on, and the contaminant exposure of that food web (Miller et al., 2014; Vuorinen et al., 2012; Vuorinen et al., 2017). The relationship between the contaminant time trends in the environment and in biota can be disturbed when one of these variables changes. This restricts the utility of time trends in biota levels as markers of environmental quality; they provide insight into the time trend of the environmental quality for the organism, but not necessarily into the time trend of contamination levels in the physical environment.

PCB time trends in the physical environment have been studied using sediment cores. They show that PCB concentrations in sediments have decreased across the Baltic Sea during the last 20 years. For cores taken in offshore areas, the half-lives in sediment of PCBs 118, 138, 153 and 180 averaged 17, 14, 17 and 17 years, respectively, in good agreement with the half-lives in biota (Sobek et al., 2015).

The atmospheric deposition of PCBs to the Baltic Sea has been estimated to have decreased by 61% between 1990 and 2016 (Gusev, 2018b). This estimate was obtained with the EMEP model based on the emissions estimates mentioned above. The model's predictions of PCB concentrations in air agree well with concentrations measured at 11 EMEP monitoring sites (Gusev et al., 2019), which lends confidence to the deposition predictions. A loss of 61% over 25 years corresponds to a half-life of 18 years, which is in good quantitative agreement with the observed time trends in sediment and biota. The similarity in time trends is consistent with our understanding of the cycling of PCBs (summarized above), which says that concentrations in the water column and sediment are closely linked to concentrations in the atmosphere.

Future trends of PCB concentrations in the Baltic Sea are thus expected to be closely linked to future trends in PCB concentrations in the atmosphere. Given that the majority of the current atmospheric deposition to the Baltic Sea originates from secondary emissions, and that the sources of these secondary emissions are not well characterized, it is difficult to predict future trends in atmospheric concentrations.

The latest HELCOM Status Assessment (2018) indicated that levels of non-dioxin like PCBs were still exceeding the threshold for good status (75 µg/kg ww) in fish at 15 of 107 monitoring sites; at several of these the dl-PCB+PCDD/F levels were also too high. The 15 stations are located in coastal areas around the Gulf of Finland, the Bothnian Bay and Denmark, and in open waters of the Kattegat. Note that HELCOM uses the 95% confidence limit of the mean concentration, based on the uncertainty seen in longer time series throughout the HELCOM area, for comparison to the threshold at stations with less than 4 years of monitoring (which is the case at all stations with deteriorated status). If one assumes that PCB-levels continue to decrease at the current rate (half-life ca 13 years, corresponding to a first order rate constant  $k$  of 0.053 1/yr or a yearly decrease of ca 5.2%) observed in guillemots and herring in recent years (Bignert et al., 2017), then the levels at the most contaminated sites will drop below the threshold for good status in ca 40 years (Figure 2). For most monitoring sites, good status will be reached within 10-20 years or less. The table in Figure 2 shows how time to good status is influenced by assumptions regarding yearly % reductions in fish. Mean concentrations in fish at several of these stations are already below the threshold. With a half-life of 13 years, mean concentrations at all stations will be below the threshold within 20 years time.

### PCDD/Fs

Regarding PCDD/F time trends in biota, the concentrations of PCDD/F TEQs in guillemot eggs from Stora Karlsö decreased significantly between 1969 and 2016. The decrease was still significant during the last 10 years of this period, but small (~20%) (Bignert et al., 2017). In herring muscle, there was no significant decrease in PCDD/F TEQs between 1990 and 2016 at the two long-term monitoring locations in the Bothnian Bay (Harufjärden) and the Baltic Proper (Utlängan), but there was a significant decrease over the whole period in the Bothnian Sea

*PCDD/Fs and PCBs are monitored in guillemot eggs from Stora Karlsö.*



(Ängkärsklubb). The concentrations in Ängkärsklubb were 3-4 times higher than at the other two sites in 1990, whereas in 2016 they were similar at all three sites (Bignert et al., 2017). The differences between the sites may be due to higher exposure arising from point sources on the west coast of the Bothnian Sea and their legacy impact on sediments there. The year to year variability in PCDD/F TEQ concentrations was much greater in herring from Ängkärsklubb compared to the other sites, which could be an indication of more heterogeneous PCDD/F contamination in their habitat range.

Others studies report decreasing PCDD/F time trends in biota, whereby these datasets are not as strong as those above. The  $\Sigma$ PCDD/F decreased in juvenile ringed seals collected from the Swedish waters of the Baltic Sea decreased by a factor of ~2 between 1990 and 2015 (Bjurlid et al., 2018). PCDD/F+PCB TEQ in eelpout sampled in the western Baltic Sea (Zingst) decreased significantly (by ~25%) between 2003 and 2017 (Fliedner et al., 2018). A meta-analysis of PCDD/F TEQ in herring samples all along the Finnish coast showed a decrease of ~80% between 1978 and 2009, whereby young (< 5 year) herring showed no decrease after 1993, while in old (>5 year) herring concentrations decreased over the whole period (Airaksinen et al., 2014). Similar concentrations of 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF were found in zooplankton sampled in 2001/2002 and 2010 in offshore waters adjacent to the Finnish coast (Peltonen et al., 2014). Overall the data indicate that PCDD/F concentrations in Baltic Sea biota have decreased markedly since the 1970s, but that in most cases most of the decrease occurred prior to 1990.

As PCDD/F concentrations in water have seldom been measured, time trends of PCDD/F levels in the physical environment are most readily examined using depth profiles in stratified sediment cores. PCDD/F degradation in sediments is negligible (Mäntynen et al., 2017), so PCDD/F delivered to and buried in the sediment is conserved. In 4 offshore cores (2 from the Gulf of Finland, 1 from the Bothnian Sea and 1 from the Baltic Proper), peak PCDD/F TEQ concentrations were found below the surface, and in 3 cases the peak concentrations were dated to the 1970s (Verta et al., 2007). In 6 other offshore cores (1 from the Bay of Bothnia, 2 from the Bothnian Sea, and 3 from the Baltic Proper), the peak PCDD/F TEQ concentrations were found to be considerably later (1985 for 1 core, 1993-1995 for 4 cores, and 2002 for 1 core) (Assefa et al., 2014b).

Other archives of atmospheric contamination with PCDD/Fs have earlier peak years. Sediments from two remote/pristine freshwater lakes in Germany had peak PCDD/F deposition in 1959 and 1979. Vegetation samples from 3 archives in Germany and England had peak concentrations prior to 1960, 1985, and 1991, respectively. Finally, long term monitoring of ambient air in 3 urban centres in England all indicated that the peak PCDD/F concentrations occurred prior to 1991 (Assefa et al., 2014b). Clearly there is a significant delay between reductions in atmospheric emissions and reduction in contaminant levels in accumulation sediments in the Baltic Sea.

The delayed response of the accumulation sediments to changes in atmospheric emissions can be partly explained by the fact that part of the input to the Baltic Sea comes indirectly via runoff from the drainage basin. This vector is supplied by PCDD/F residues in soil, which are very persistent and not expected to respond rapidly to changes in emissions. In addition, particulate organic matter (and its associated PCDD/F load) circulates in the Baltic Sea for longer periods of time in a process of



Photo: David Thyberg/Mostphotos

deposition and resuspension before it finally settles in deposition basins and is sequestered (Assefa et al., 2014b). This further delays the response of accumulation sediments to changes in inputs.

Due to the underlying complexity of the processes affecting the response time of the Baltic Sea to changes in atmospheric concentrations and the lack of information on PCDD/F time trends in the atmosphere, it is difficult to forecast future trends of PCDD/F contamination in the Baltic Sea. A simple box model predicted that between 2007 and 2017 the PCDD/F TEQ concentrations would decrease by ~10% in offshore surface water of the Baltic Proper and ~30% in Bothnian Sea offshore water if there were no changes in atmospheric deposition during this period (Armitage et al., 2009).

These predictions are generally consistent with the herring and guillemot biomonitoring data for this period (Bignert et al., 2017). Looking further into the future, the same model scenario of constant air concentrations predicted that PCDD/F TEQ concentrations in Baltic Proper offshore surface water would stabilize at 2017 levels, while concentrations in the Bothnian Sea would continue to decrease slowly, stabilizing around 2045 at a level about 30% lower than 2017 levels (Armitage et al., 2009). The latest HELCOM Status Assessment (2018) indicates that the threshold for the sum of PCDDs, PCDFs, dl-PCBs of 0.0065 µg TEQ/kg ww fish, crustaceans or mollusks was exceeded at 6 out of 43 monitoring stations in year 2013 – 2016, and just below the limit in two other stations. The upper 95% confidence limit of the concentrations were a factor 1.23 to 2.37 higher than the threshold, which is the EQS for human consumption. The exceedances occur mainly in eelpout in the Danish stations in Great Belt, Kattegat and Arkona basin. At one station in the Bothnian Bay observed levels in herring were 2.1 times higher than the threshold. If the predicted 30% reduction in water concentrations in 2045 in the Bothnian Sea applies also to the Bothnian Bay, this will not be enough to reach good status, and further reductions of air concentrations are warranted. Nevertheless, there are considerable uncertainty in these model simulations, in particular with respect to the time trends in atmospheric concentrations of PCDD/Fs, transfer of PCDD/Fs from the terrestrial environment to the Baltic Sea, and the residence time of PCDD/Fs in surface sediments (Wiberg et al., 2013).

Another approach to assessing the time to achieve good environmental status is to assume that current trends will continue as observed in Baltic Sea biota. Figure 3 shows how concentrations will decline at the monitoring stations where levels of dioxins and dl-PCBs exceed the threshold for good status, under assumptions of two different half-lives: 12 years as observed in herring in the Bothnian Sea and 31 years as observed in guillemot at Stora Karlsö in the Baltic Proper. Note that these stations are not located in the basins with deteriorated status. With these decline rates, the status in the Bothnian Bay will be good within 10 – 30 years,

## BALTIC SEA AREA – SAMPLING LOCATIONS



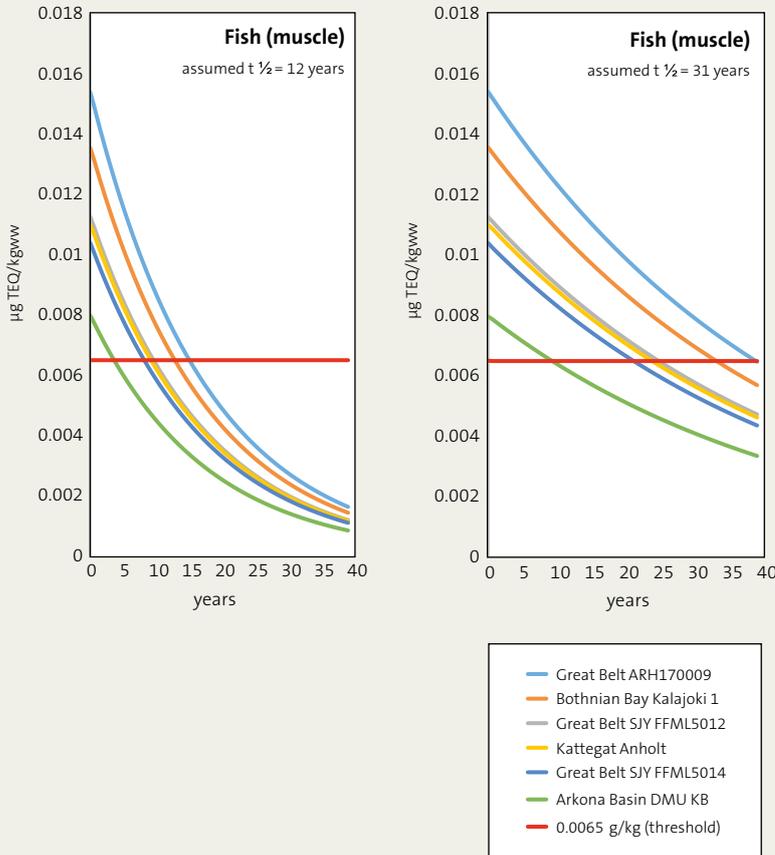
*PCDD/Fs and PCBs are monitored in herring and eelpout.*



Photo: Hans Christiansson/Mostphotos



Photo: Tony Holm/Azote

PCDD/FS AND DIOXIN-LIKE PCBs IN FISH (*Zoarces viviparus*, *Clupea harengus*)

**Figure 3.** Estimated time for TEQ concentrations to reach the threshold ( $0.0065 \mu\text{g TEQ/kg ww}$ ) assuming that  $[\text{TEQ}](t) = [\text{TEQ}]_{\text{initial}} e^{-kt}$ . Names and numbers refer to basin and name of monitoring station. The threshold was exceeded at 6 monitoring stations in the most recent HELCOM status assessment (performed in 2018). The last year of monitoring in the data-set was 2013 to 2016 depending on station. The initial value is the upper one-sided 95% confidence limit of the fitted value in the last monitoring year.

(<http://metadata.helcom.fi/geonetwork/srv/eng/catalog.search#metadata/33505b4a-ee14-4544-9e1d-d155548004e4>)

The left graph shows how concentrations will decrease with time  $t$  if the half-life is 12 years, which corresponds to a first order rate constant  $k$  of  $0.057 \text{ 1/yr}$  or a yearly decrease of ca 5.6%. This is the rate of decrease observed in herring lipids at Ångskärsklubb (Bothnian Sea) 2007 to 2016. In the right graph, a half-life of 31 years is assumed, i.e.  $k = 0.022$  corresponding to yearly decrease = 2.2%, which is the observed decrease in guillemots at Stora Karlsö (Baltic Proper) 1979 to 2016 (Bignert et al. 2017).

The concentrations are estimated as  $[\text{TEQ}](t) = [\text{TEQ}]_{\text{initial}} e^{-kt}$ . Note that HELCOM uses the 95% confidence limit of the mean concentration, based on the uncertainty seen in longer time series throughout the HELCOM area, for comparison to the threshold at stations with less than 4 years of monitoring (which is the case at all stations with deteriorated status).

in the southern parts of the Baltic Sea this will happen in less than 10-20 years except for the most contaminated station in the Great Belt. With the faster decline rate all mean concentrations would be below the threshold for in good status within 5 years.

Note that the threshold for dioxins and dl-PCBs is set based on limits in the European foodstuff legislation. This threshold is pragmatically set according to the ALARA-principle (As Low As Reasonably Achievable), which in the case of dioxins means that the limit is set at the 95% percentile of observed concentrations, i.e. the 5% most contaminated fish should not be consumed (Karlsson and Malmaeus, 2014). This also means that the threshold should be lowered when levels decline in the environment. The limit is thus not connected to for example the Tolerable Weekly Intake (TWI), or observations of ecotoxicity of dioxins. For a woman weighing 60 kg, a weekly consumption of 150 g of fish at the  $0.0065 \mu\text{g TEQ/kg ww}$  limit would result in 16 pg/kg body weight/week, which exceeds the previous TWI of 14 pg/kg. Moreover, the European Food Safety Authority, EFSA, lowered the tolerable weekly intake of dioxins by a factor 7 to just 2 pg TEQ/kg body weight in 2018. If this will have consequences for the dioxin threshold, which is currently not set to protect human health, is not clear.

## Conclusions

- The atmosphere is the primary source of both PCBs and PCDD/Fs to the Baltic Sea. To reduce levels in Baltic Sea biota, measures should address emissions to air.
- PCBs in the atmosphere over the Baltic Sea originate primarily from diffuse secondary emissions within the EMEP region, and there are indications that urban areas are important sources of PCBs. The most important primary sources are industrial emissions.
- The source of the majority of the PCDD/Fs in the atmosphere over the Baltic Sea is not known. This hampers evaluations of the effectiveness of measures to reduce dioxin levels in the Baltic Sea.
- The levels of PCDD/Fs in the water column are buffered by the PCDD/F residues in sediments, which leads to a slow response to reductions in external inputs. PCBs, on the other hand, are more weakly buffered and respond more rapidly to reductions in external inputs. Contaminated sediments near coastal point sources impact dioxin concentrations locally, but not in the coastal waters in general.
- PCB concentrations in biota have decreased at ~5% per year during the last 15 years, and concentrations in sediment and atmospheric deposition to the Baltic Sea have decreased at similar rates.
- PCDD/F concentrations in biota have decreased little since 1990 in many parts of the Baltic Sea (e.g. ~50% in guillemot eggs).
- Good environmental status for the HELCOM core indicator non-dioxin like PCBs will be achieved at all stations in the Baltic Sea in ~2055, and at most stations around 2025-2035, assuming that concentrations continue to decrease at a rate of ca 5% per year, based on the definition of good status being that the upper 95 % confidence interval of the concentration is below the threshold value.
- Good environmental status for the HELCOM core indicator dioxins, furans, and dl-PCBs will be achieved at all stations in the Baltic Sea in ~2025-2045 assuming that concentrations continue to decrease at a rate of 2-6% per year, based on the definition of good status being that the upper 95 % confidence interval of the concentration is below the threshold value.

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