Perfluorooctane sulphonate (PFOS)

Authors

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Text is partly based on the HELCOM Thematic Assessment of Hazardous Substances, Chapter by Urs Berger.

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Contents

Key messages

PFOS concentrations exceed the threshold concentrations in several monitoring sites in the Baltic Sea, indicating moderate or even bad environmental status.

Time series data in a fish-feeding bird (Common guillemot) shows that the concentrations have increased since the late 1960s, but first signs of decline are already noted.

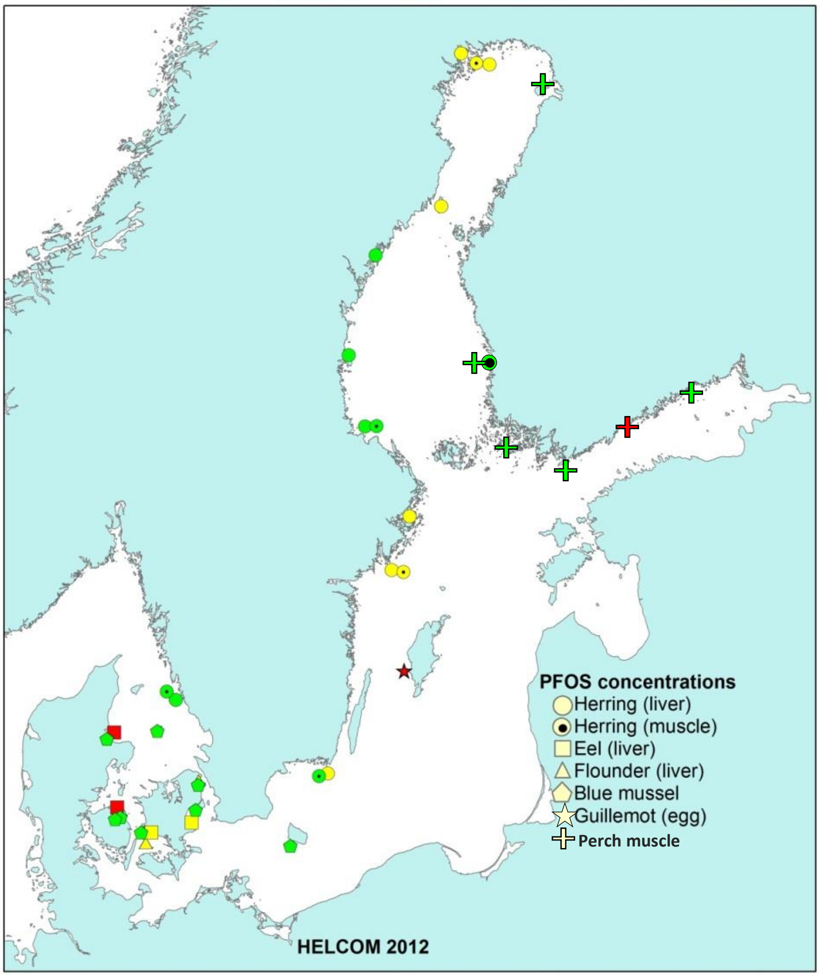


Figure 1. *Status of hexabromocyclododecane (HBCD) in 2005-2010. The average is compared against the GES boundary (GES denoted by green color and 'moderate status' by yellow color) and a level three times the GES boundary i.e. the 'bad status' (red color). See Metadata for the threshold concentrations.*

Concentrations and temporal trends of PFOS in the Baltic Sea

This core indicator report shows that the concentrations of PFOS exceed the GES boundary of 9.1 µg kg^{-1} ww in some parts of the Baltic Sea. The status assessment is based on herring muscle and liver, flounder liver, eel liver, perch muscle and blue mussels. In addition, concentrations in bird eggs and predatory fish and seals are given in the text. PFOS concentrations seem to exceed the GES boundary in polluted areas and they accumulate in predators of the food web.

Exponentially increasing concentrations of some perfluoroalkyls (PFA) in wildlife have been reported during the 1990s (Holmström et al. 2005). According to the HELCOM thematic assessment of hazardous substances in the Baltic Sea (HELCOM 2010), PFOS concentrations are generally below the threshold level of 9.1 µg kg^{-1} ww, but frequently exceed them in many parts of the Baltic Sea. The PFOS and PFOA (perfluorooctanoid acid) levels in fish and water seem to be similar in different parts of the Baltic Sea. There is not enough data to assess temporal changes in PFOS concentrations in fish. However, the data to assess the current status covers several fish species and blue mussel and can therefore be considered quite exhaustive, whereas the lack of time series inhibits making of a comprehensive assessment.

Concentrations in fish exceed the threshold level

PFOS levels in fish liver (e.g. herring, perch, pike, eelpout, flounder, eel and cod) exceeded the threshold level for the protection of predators via secondary poisoning (9.1 µg kg^{-1} wet weight in prey tissue which is used as the GES boundary, see Metadata) in several areas of the Baltic Sea (HELCOM 2010). Thus, PFOS may cause adverse effects for top predators.

One of the highest concentrations was found from the liver of pike (*Esox lucius*) from the Gulf of Finland (close to Helsinki and Espoo) containing 200 to 550 µg PFOS kg^{-1} ww, as well as up to 140 µg kg^{-1} ww of PFOSA, a non-persistent precursor compound of PFOS (Nordic Council of Ministers 2004). Screening data from Finland shows other very high liver concentrations: salmon liver concentrations ranged between 25 and 72 µg kg^{-1} ww along the Finnish coast line and in a polluted bay in Helsinki a perch liver concentration of 141 µg kg^{-1} ww was observed. Additional hot spots seem to be the mouth of the river Oder in the Bornholm Basin (coast of Poland; Lilja et al. 2009), the Hanö Bight (Bornholm Basin, coast of Sweden; SEPA 2006) and the Kattegat (Nordic Council of Ministers 2004). In all these regions, fish liver values of around 60 µg PFOS kg-1 ww have been observed (perch, cod and eelpout, respectively). According to Bignert et al. (2011) the highest concentrations of PFOS in herring muscle in Swedish samples were found from the Northern Baltic Proper (18 µg kg^{-1} ww) and the lowest in the Kattegat (around 4 µg kg^{-1} ww).

In regions less affected by anthropogenic pollution, typical PFOS levels in fish were in the range 1–5 µg kg^{-1} ww (see also Theobald et al. 2007, Berger et al. 2009b). Liver concentrations of predatory fish seem to be much higher. In blue mussels from the Kattegat, Great Belt and the Sound, PFOS was below the detection limit of 0.2 µg kg^{-1} ww (NERI 2007).

The distribution of PFOS in herring liver was found to be quite homogeneous throughout the Baltic Sea (around 10 µg kg^{-1} ww), which probably is a result of the extraordinary persistence of the compound and its use for more than three decades. A somewhat higher level of 26 µg kg^{-1} ww was found along the Swedish coast of the Northern Baltic Proper, reflecting the proximity of the city of Stockholm.

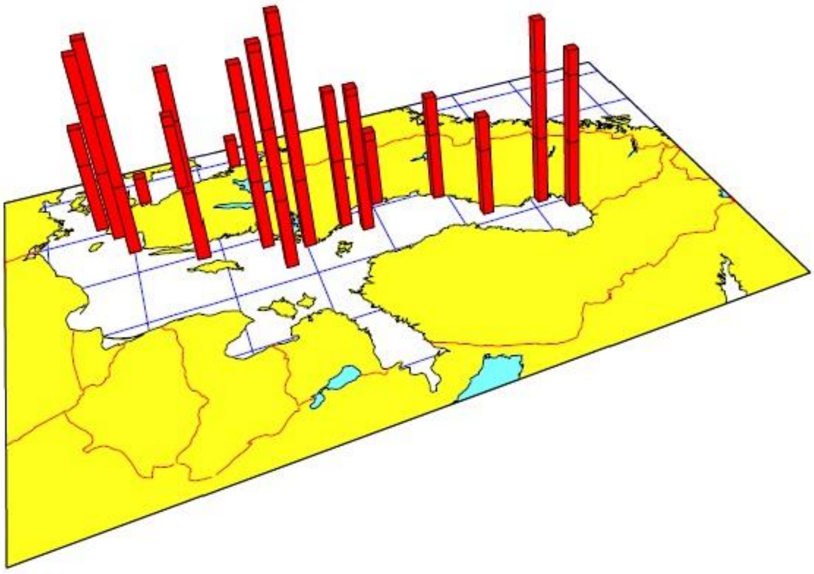


Figure 2a. *Spatial variation in geometric mean concentration (2008–2010, µg kg^{-1}ww) of PFOS in herring liver. The highest concentration (16 µg kg^{-1}ww) was found in the northern part of the Baltic Proper (Lagnö), the lowest (2.0 µg kg^{-1}ww) at Väderöarna in Skagerrakk. Data originates from the Swedish national monitoring programme, and analyses were performed at the Department of Applied Environmental Science, Stockholm University.*

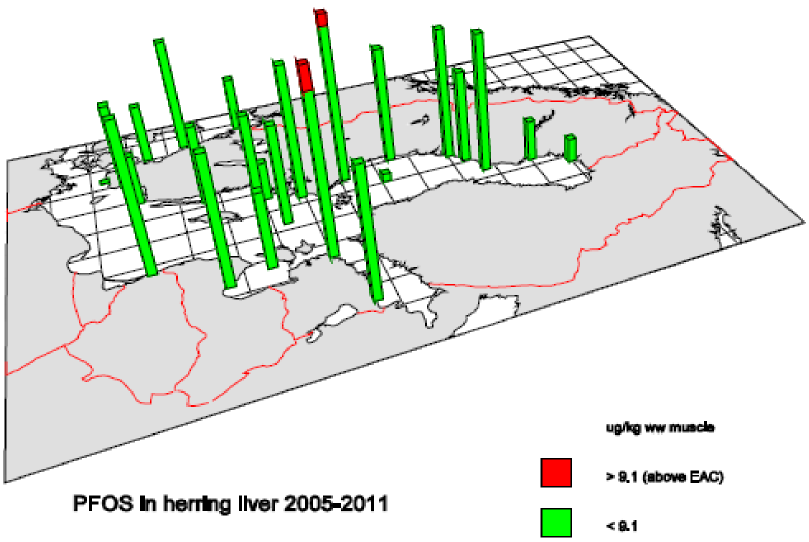


Figure 2b. *Spatial variation in geometric mean concentration (2005–2011, µg kg^{-1}ww) of PFOS in herring liver. The highest concentration (10.4 µg kg^{-1}ww) was found in the Gulf of Finland.*

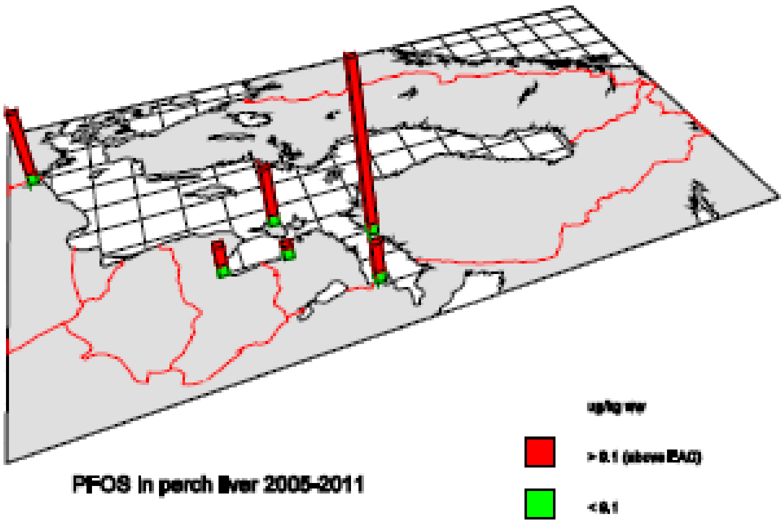


Figure 2c. *Spatial variation in geometric mean concentration (2005–2011, µg kg^{-1}ww) of PFOS in perch liver. The highest concentration (141 µg kg^{-1}ww) was found in Vanhankaupunginlahti, Helsinki.*

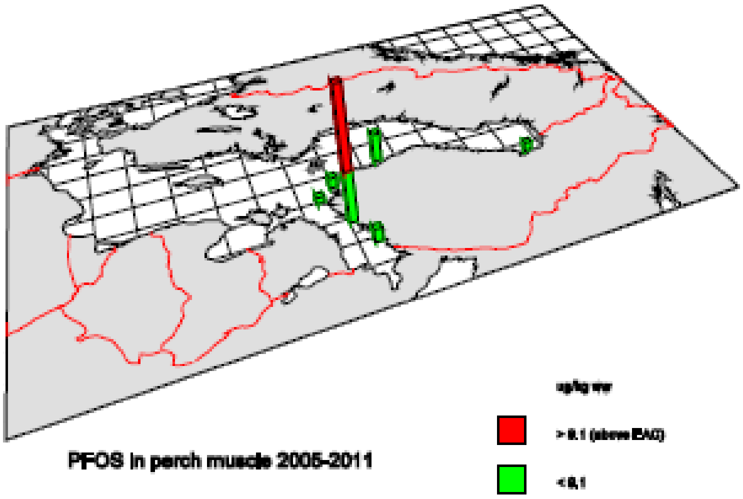


Figure 2d. *Spatial variation in geometric mean concentration (2005–2011, µg kg^{-1}ww) of PFOS in perch muscle. The highest concentration (23,8 µg kg^{-1}ww) was found in Vanhankaupunginlahti, Helsinki*.

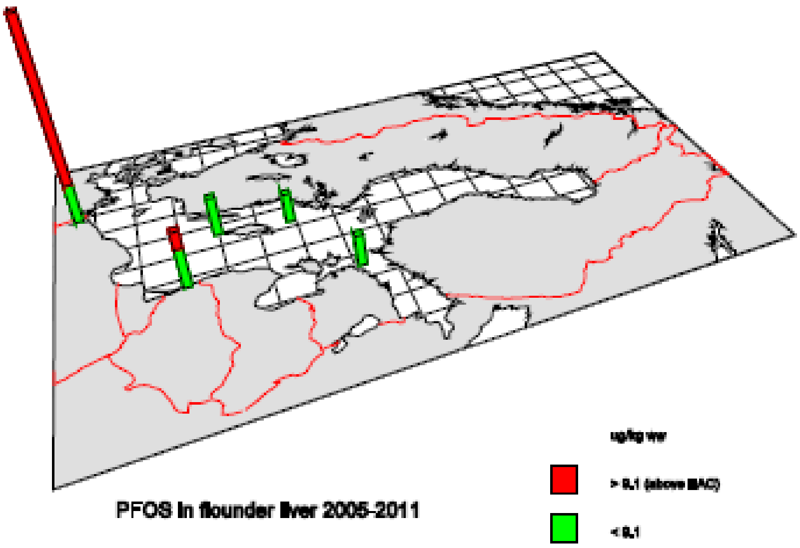


Figure 2e. *Spatial variation in geometric mean concentration (2005–2011, µg kg^{-1}ww) of PFOS in flounder liver. The highest bar (Szczecin Lagoon, Poland) represents a value of 47.7 µg/kg ww.*

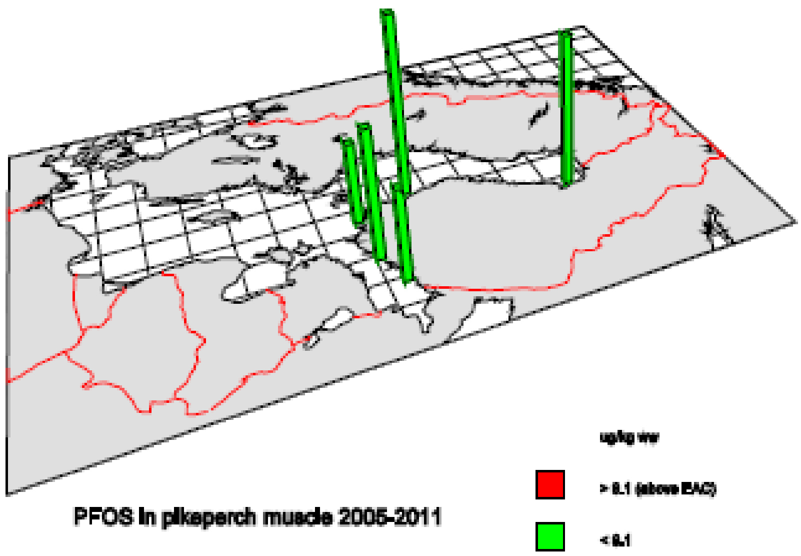


Figure 2f. *Spatial variation in geometric mean concentration (2005–2011, µg kg^{-1}ww) of PFOS in pike-perch muscle. The highest bar (Pori, Finland) represents a value of 4.95 µg/kg ww.*

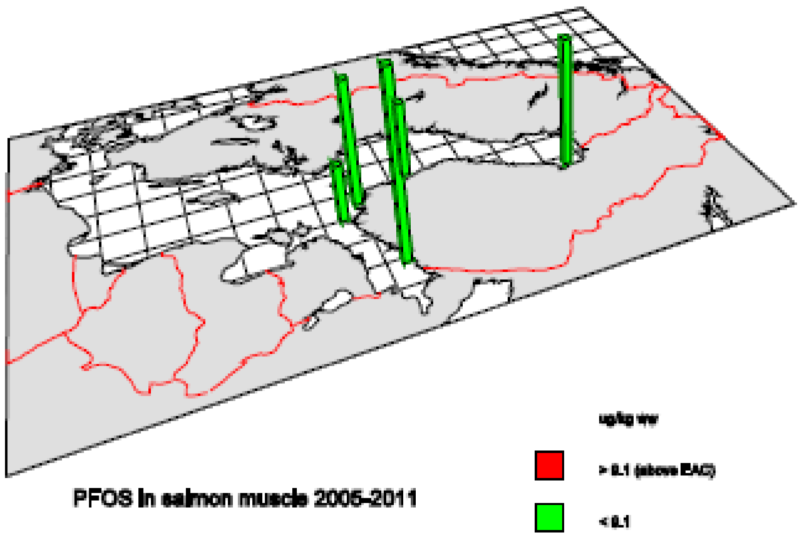


Figure 2g. *Spatial variation in geometric mean concentration (2005–2011, µg kg^{-1}ww) of PFOS in salmon muscle. The highest bar (Kotka, Finland) represents a value of 5.0 µg/kg ww.*

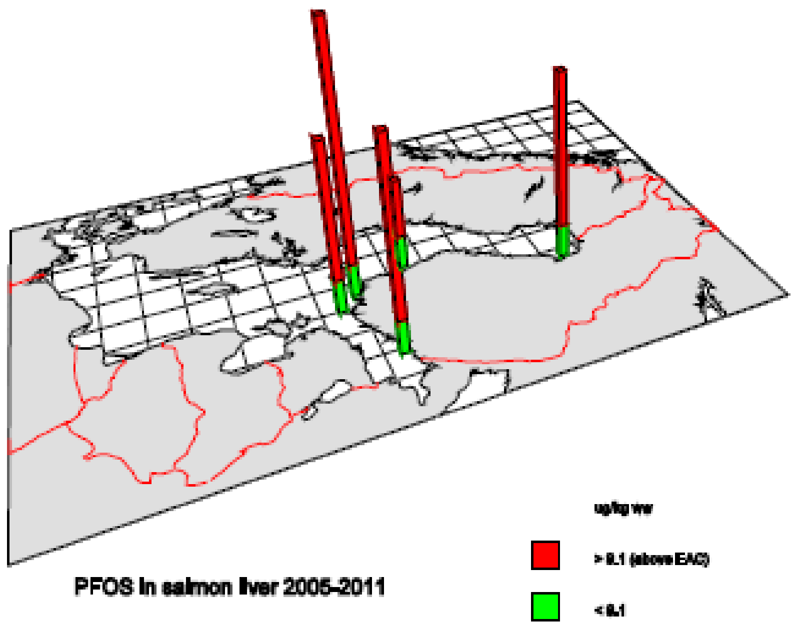


Figure 2h. *Spatial variation in geometric mean concentration (2005–2011, µg kg^{-1}ww) of PFOS in salmon liver. The highest bar (Turku, Finland) represents a value of 72.0 µg/kg ww.*

High concentrations in mammals and birds

Marine mammals are considerably higher contaminated with PFOS than marine and freshwater fish, and were found to be the most contaminated of all Nordic biota studied (HELCOM 2010). Several hundreds to one thousand µg kg^{-1} ww of PFOS have been found in the livers of grey seals (Southern Baltic Proper and Bothnian Sea; Nordic Council of Ministers 2004), harbour seals (Great Belt and the Sound; Nordic Council of Ministers, 2004) as well as ringed seals (Bothnian Bay; Kannan et al. 2002). In the eggs of common guillemots (Western Gotland Basin), PFOS concentrations were greater than 1000 µg kg^{-1} ww (Holmström et al. 2005). OSPAR risk assessment (OSPAR 2005) on marine environment concluded that the major area of concern for PFOS is the secondary poisoning of top predators, such as seals and predatory birds.

Concentrations in surface waters

Only a few measurements of PFAs in the Baltic Sea surface water exist (Nordic Council of Ministers 2004, Theobald et al. 2007, Lilja et al. 2009). They were mostly performed in potentially affected coastal areas. Perfluoro octanoid acid (PFOA) and PFOS dominated the water samples. Concentrations of PFOA were determined in the range 0.57-0.68 ng l^{-1} (Little Belt, Kiel Bight, Mecklenburg Bight, Arkona Basin) up to 4–7 ng l^{-1} (Little Belt, the Sound, coast of Poland, Gulf of Finland). PFOS was found at levels 0.34-0.90 ng l^{-1} for all locations mentioned, with the exception of single measurements of 2.9 ng l^{-1} (coast of Poland) and 22 ng l^{-1} close to Helsinki (Gulf of Finland). Further away from the coast in the Arkona Basin, PFOA and PFOS levels were 0.35-0.40 ng l^{-1}.

Concentrations in surface sediments

Limited data exist for PFA concentrations in Baltic Sea sediments (Nordic Council of Ministers 2004, SEPA 2006, NERI 2007, Theobald et al. 2007). PFOS and/or PFOA were occasionally detected, but consistently at levels below 1 µg kg^{-1} dw or ww. The highest levels reported so far have been from the Gulf of Finland close to Helsinki (PFOS 0.9 µg kg^{-1} ww), close to Stockholm (PFOS 0.6 µg kg^{-1} ww) and along the coast of Poland (PFOS and PFOA both around 0.6 µg kg^{-1} dw). In the German Baltic coast, concentrations of PFOS in sediments were on the order of 0.02-0.67 µg kg^{-1} dw, those of PFOA 0.09-0.68 µg kg^{-1} dw (Theobald et al. 2007).

General information

General properties

Perfluorooctane sulphonate (PFOS), perfluoro octanoic acid (PFOA) and other perfluorinated compounds are considered as global environmental contaminants. PFOS and PFOA are chemically and biologically inert and very stable (Poulsen et al. 2005). PFOS meets the P (Persistent) and vP (very Persistent) criteria due to slow degradation. PFOS is also bioaccumulative (B) and toxic (T) (RPA & BRE 2004, OSPAR 2005). PFOA is considered as very persistent (vP) and toxic (T), but not bioaccumulative (Van der Putte et al. 2010). It has a capacity to undergo long-range transport.

PFOS related substances and PFOA are members of the larger family of perfluoroalkylated substances (PFAS). Perfluorooctanyl sulfonate compounds are all derivatives of PFOS and can degrade to PFOS, also called as PFOS-related compounds. The abbreviation PFOA is used as a group name for perfluorooctanoic acid and its salts. Some 100–200 PFOS-related compounds have been identified (KEMI 2006). PFOS binds to blood proteins and bioaccumulates in the liver and gall bladder unlike most POP compounds, which accumulate into fat (Renner 2001). Some indicative compounds related to use are presented e.g. in HELCOM report on selected hazardous substances (HELCOM 2009).

Main impacts on the environment and human health

PFOS has been shown to disturb immune system, development and reproduction (endocrine disruption) of organisms and influence the lipid metabolism, to reduce weight gain and food consumption. It is also suspected to induce liver necrosis. Falandysz et al. (2006) have suggested that the consumption of contaminated fish from the Baltic Sea contributes significantly to human blood levels of perfluoroalkyl compounds.

Pathways of PFOS to the Baltic ecosystem

Some PFAS have been manufactured for more than five decades. They are applied in industrial processes (e.g., production of fluoropolymers) and in commercial products such as water- and stain-proofing agents and fire-fighting foams, electric and electronic parts, photo imaging, hydraulic fluids and textiles.

PFOS is both intentionally produced and an unintended degradation product of related anthropogenic chemicals. PFOS is still produced in several countries.

Policy relevance

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

PFOS is included in the Stockholm Convention list of POPs, Annex B, which requires the parties to the convention to restrict the production and use of the substance.

The HELCOM Baltic Sea Action Plan has the objective of “Hazardous substances close to natural levels” and PFOS and PFOA are chosen as priority substances under the BSAP.

PFOS is included on the revision list of the EU Priority Substances. The EU Marine Strategy Framework Directive requires that “contaminants are at levels that do not give rise to pollution effects” (GES Descriptor 8).

Status of restrictions, bans or use

The production and use of perfluorooctane sulfonate (PFOS), one of the major PFA representatives, have been regulated in some countries (e.g., Canada and the EU), but large-scale PFOS production continues in other parts of the world. PFOS has been produced and used since the 1950s, but due to findings of detectable concentrations in human blood in the general population and negative health effects on living organisms, PFOS has been phased out in 2002 by its main producer 3M.

PFOS concentrations are high in predators and still increasing

Assessment of temporal trends of PFOS

According to Swedish data on common guillemot eggs, a significant increasing trend is observed for PFOS in guillemot eggs with 7–10 % per year (Figure 3), which is equal to an increase to 25–30 times higher levels in the early 2000s as compared to the late 1960s (Bignert et al. 2009). It is noteworthy, however, that the time series shows considerable variation in the latest years, perhaps indicating also a levelling-off of the PFOS concentrations.

The concentrations in herring liver in Bothnian Bay, Bothnian Sea, Northern Baltic Proper and Bornholm Basin do not show any temporal changes (Figure 4).

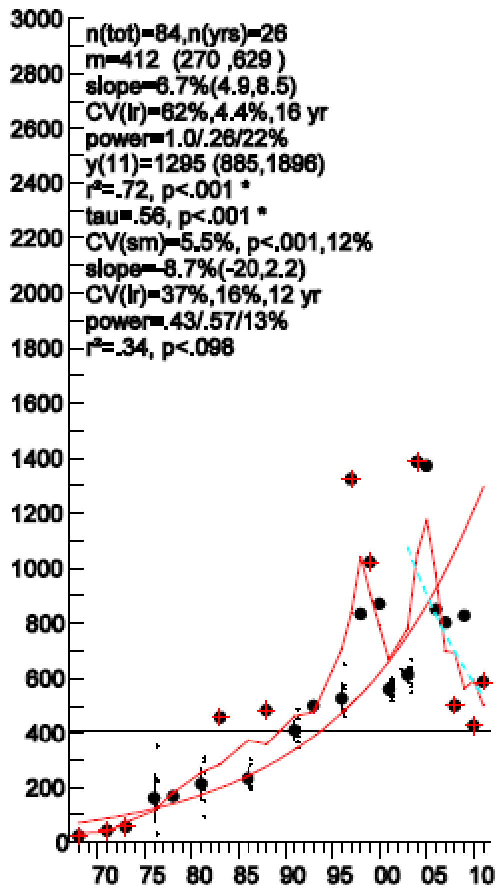


Figure 3. *Temporal trend of PFOS concentration (ng/g fresh w.) in guillemot eggs (1968–2011). The linear red line presented in the figure is based on a log-linear regression analysis and shows an increasing trend of 7-10 % per year and the non linear red line is a simple 3-point running mean smoother fitted to the annual geometric mean values. The horizontal line is the mean concentration over the whole period. A red cross represents a suspected outlier.*

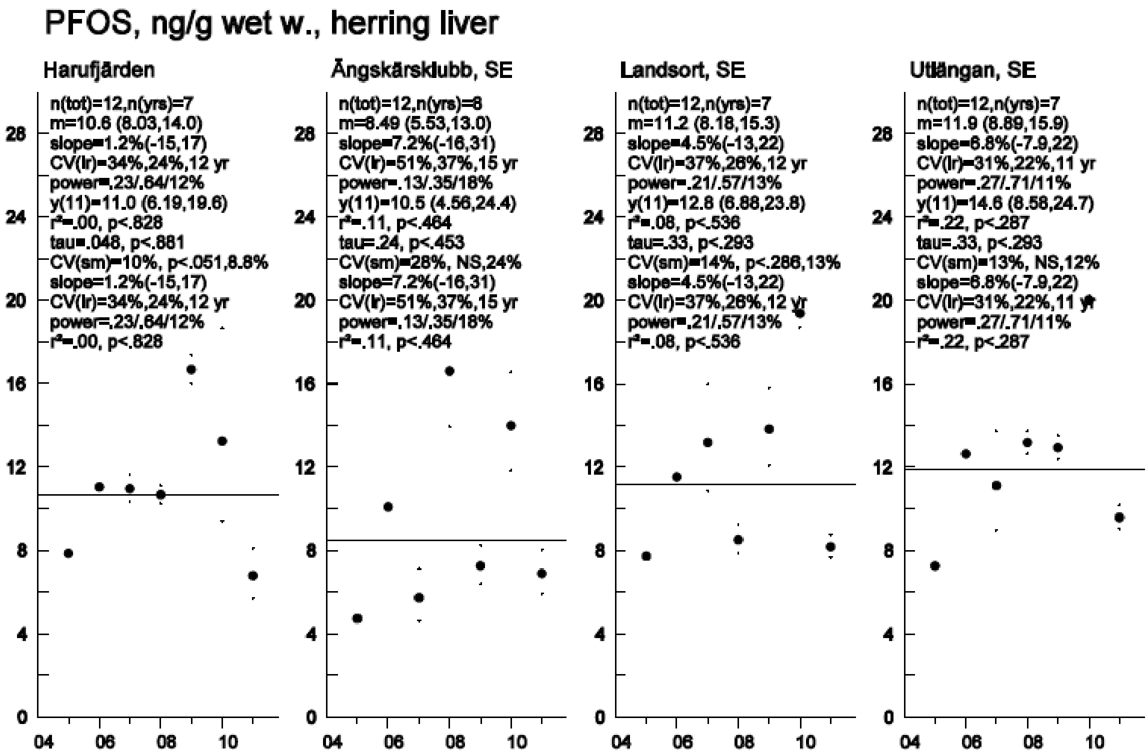


Figure 4. *Temporal trend of PFOS concentration (pg kg^{-1} ww) in herring liver (2004-2011). The horizontal line is the mean concentration over the whole period.*

Metadata

Data source

ICES and EIONET databases of the monitoring data of the HELCOM Contracting Parties.

HELCOM SCREEN project, data from 2008 (Lilja et al. 2009).

Project 202 22 213 of the Federal Environmental Agency, Germany. Data from 2003-2005 (Theobald et al. 2007).

Strand, et al. (2007). DMU (NERI) Rapport 608. Data from 2003.

Nordic Council of Ministers (NMR) (2004): TemaNord 2004:552. Data from 2003.

Screening data in Finland (EU-kalat II project)

Description of data

The average of the time period 2005–2010 has been used as the basis for the status classification. Time series graphs use annual averages. The data is in wet weight basis.

Trend (in %) assessed from the annual geometric mean of concentrations of PFOS (ng/g fresh weight) in guillemot egg at St. Karlsö during the time period 1968–2010 and the estimated mean concentration for the last year (2010). The trend is reported, if p<0.1. The total number of analyses and the number of years are also presented. The numbers presented in brackets are the 95 % confidence intervals.

Matrix	n analyses	n yrs	year	trend (95% ci)	mean concentration of last year (95 % ci)
Guillemot egg.					
St. Karlsö	83	25	68-10	7.1(5.3,8.9)*	1325 (907–1935)

* significant trend, $p < 0.05$

Preferred matrix

Fish and sediment are appropriate matrixes to be used in the monitoring of PFOS in the Baltic Sea. Instead, water is more appropriate matrix to be used in the monitoring of PFOA. Sediment data is currently not appropriate for the core indicator, because of the lack of a proper GES boundary.

GES boundaries

The GES boundary is the Environmental Quality Standard (EQS), proposed by the European Commission to the revised EQS Directive (31.1.2012). The EQS is 9.1 µg kg-1 fish ww. An alternative approach is to use the Quality Standard for water (0.23 µg l-1) (WFD WG E Dossier 19.1.2012). There is no QS for benthic organisms (sediment).

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.

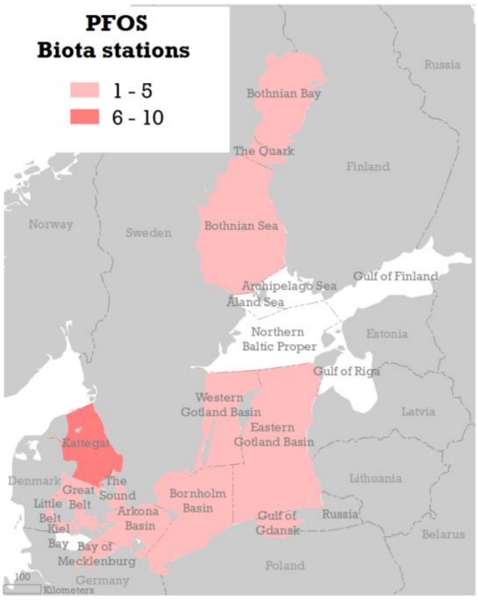
Monitoring of PFOS

Only Sweden and Denmark have PFOS in the national monitoring programme. Germany monitors PFOS in biota on the project basis. Finland (fish) and Lithuania (sediment) are planning to include PFOS in the monitoring programmes. The substance is not included in the monitoring programmes in Latvia and Poland. No information from Estonia or Russia. A few measurements in water and fish (flounder and herring) are taken from Estonia, Latvia, Lithuania and Poland in the HELCOM SCREEN project (2009). Finland has screening data from several fish species along the coast line.

Annex 1 presents an overview of the current monitoring.

The core indicator for PFOS requires better geographical coverage in national monitoring programmes and time series data to assess temporal trends. In the Swedish guillemot monitoring, the number of years required to detect an annual change of 10 % with a power of 80 % was 15 years for the guillemot eggs time-series.

In addition, common HELCOM sampling and analysis procedures should be agreed on.



Relevance of the indicator in the Baltic Sea

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

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Annex 1.

Perfluorooctanesulphonate (PFOS) in national monitoring programmes in sediment and biota. Some screening data has been added. Number of stations and frequency of monitoring (interval in years) is shown for each sub-basin. Species key: her=herring, per=perch, flo=flounder, eelp=eelpout, sal=salmon, mus=mussel

	Sweden				**Germany**				**Estonia**				**Poland**			
	Sedim.		Biota		Sedim.		Biota		Sedim.		Biota		Sedim.		Biota	
Subbasin	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.
Archipelago Sea																
Arkona Basin			1 her	1			1 bird	project								
Bay of Mecklenburg							1 eelp	project								
Bornholm Basin			2 her	1											1per+ 1 flo	project
Bothnian Bay			3 her	1												
Bothnian Sea			4 her	1												
Eastern Gotland																
Great Belt																
Gulf of Finland																
Gulf of Gdansk															1her+ 1 flo	project
Gulf of Riga																
Kattegat			2 her	1												
Kiel Bay																
Little Belt																
North Baltic Proper			3 her	1												

	Lithuania				**Latvia**				**Finland**				**Denmark**			
	Sedim.		Biota		Sedim.		Biota		Sedim.		Biota		Sedim.		Biota	
Subbasin	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.	St	Inter.
Archipelago Sea																
Arkona Basin															1 flo	1
Bay of Mecklenburg																
Bornholm Basin																
Bothnian Bay																
Bothnian Sea																
Eastern Gotland			2	project												
Great Belt															5eelp, 1flo	1 1
Gulf of Finland																
Gulf of Gdansk																
Gulf of Riga							1her+ 1 per	project								
Kattegat															4 eelp	1
Kiel Bay																
Little Belt															2 eelp	1
North Baltic Proper																

The Quark		1 her 1														
The Sound																1 flo 1
Western Gotland		2 her,bird 1														
Åland Sea																