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Per- and polyfluoroalkyl substances (PFAS) within the Swedish Monitoring Programme for Contaminants in Marine Biota

Report 6:2023

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Department of Environmental Research and Monitoring

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Summary
This report present an overview of spatio-temporal trends, bioaccumulation and compliance with new environmental quality standards for Per- and polyfluoroalkyl substances within the Swedish National Monitoring Programme for Contaminants in Marine Biota.

Content

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1 Summary

The aim of the report is three-fold. Firstly, to evaluate to what extent phase-out of certain per- and polyfluoroalkyl substances (PFAS) first initiated in the early 2000s are reflected in the biota concentration within the Baltic Sea. Secondly, to investigate the spatial differences of PFAS across the Baltic Sea, which has not previously been evaluated, and couple these results to PFAS observations in other matrices to better understand the flow of PFAS through the Baltic Sea ecosystem. Lastly, to investigate the implication of a proposed PFAS EQS dossier on the evaluation of Good Environmental Status in the Baltic Sea.

We use data on PFAS from the Swedish Monitoring Program for Contaminants in Marine Biota covering 40 years for the longest time series (four Time Trend Stations) and 26 stations at present day. The program covers stations from the Bothnian Bay in the north to Skagerrak at the Swedish west coast (referred to as the Greater Baltic Sea) and PFAS is analyzed in four fish species and three bird species. The target compounds are perfluoroalkyl sulfonic acid (PFSA; C4-C8), perfluoroalkyl carboxylic acid (PFCA; C6-C15) and FOSA. In the data evaluation, observations from other monitoring programmes and research campaigns are included (river, marine surface water, sediment, and top predators) to set the observations from the Swedish Monitoring Program for Contaminants in Marine Biota into context.

After an initial exponential increase in PFAS concentrations, we found that PFAS displayed a rapid response to phase-out and regulations in the early 2000s. As a result, PFAS concentrations stabilized (rather than displaying an immediate decrease). This is linked to the few removal pathways of the long lived PFAS homologues in the Baltic Sea water column. However, within the last decade PFAS has started to show significant declines at many stations, the exception being a few PFAS homologues (PFOA (C8) and PFNA (C9)).

Two distinct water masses are present in the Greater Baltic Sea, North Sea water and Baltic Sea water, the latter with origin in the Baltic Sea drainage basin. Differences in the PFAS loads of these water masses likely drives geographical differences seen in the PFAS concentrations and homologue distribution between fish in Kattegat and the Baltic Sea. Different water mass lifetimes in the Baltic Sea basins further affect the concentration and response time with regards to changes in external sources for individual homologues.

A proposed PFAS EQS dossier presents an EQS (with the PFAS sum expressed as PFOA-equivalents) a factor 100 lower than the current PFOS EQS. We find that PFOS, PFNA and PFUnDA contribute more than 80% to the sumPFAS-equivalent. PFNA is the only homologue that is currently increasing in some parts of the Baltic Sea and special attention should be on this homologue in the future. Despite the slow recovery with regards to PFAS concentrations over the past decade the biota PFAS concentrations are still 5-230 times higher than the threshold proposed in the PFAS EQS dossier. Screening studies has further identified a range of PFAS in the Greater Baltic Sea not currently part of the Swedish Monitoring Program for Contaminants in Marine Biota. As an example the cyclic PFECHS has been found at various trophic levels in the food web at concentrations indicating biomagnification potential. These findings indicate that PFAS is still affecting the Greater Baltic Sea environment negatively and the development in concentrations of individual homologues should be followed closely over the coming decade both for those PFAS included in the current program but also the emergence of novel PFAS through screening program.

2 Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of organic chemicals, which are persistent (or transform to persistent products) in the environment. There has been continued international efforts to reduce PFAS releases over the past two decades beginning in 2002 with the voluntary phase-out of perfluorooctane sulfonyl fluoride-based chemistries by the 3M Co. The United Nations Stockholm Convention on Persistent Organic Pollutants now include regulation on Perfluorooctanesulfonic acid (PFOS; 2009), perfluorooctanoic acid (PFOA; 2019) and perfluorohexanesulfonic acid (PFHxS; 2022) and PFCAs (C9-C14) are from 2023 included in annex XVII of REACH. However, within the Baltic Sea PFAS concentrations in biota have so far been very slow to respond to voluntary phase-outs and regulations [*Faxneld et al.*, 2016; *Johansson and Undeman*, 2020; *Schultes et al.*, 2019].

A switch of laboratories, the proposal of a PFAS threshold limit and the addition of a decade of new data since the last large evaluation, has resulted in the work presented in this report on PFAS within the Swedish Monitoring Program for Contaminants in Marine Biota (from here on referred to as the Marine Monitoring Program). Firstly, from the introduction of PFAS into the Marine Monitoring Program and until 2019 PFAS has been analyzed at the Department of Environmental Science at Stockholm University. From 2020 analysis are conducted at the Swedish Agricultural University. An intercalibration between the two laboratories indicated limited discrepancies in concentrations of PFAS homologue concentrations [*Faxneld et al.*, 2022] but there are differences in the calculation of LOQ between the two labs that short term can affect trend analysis of homologues close to the detection limit. A thorough evaluation focused on the data analyzed at Stockholm University therefore seems appropriate. Secondly, the current European threshold (EQS), which is used to evaluate observations within the Marine Monitoring Program, has for PFAS homologues been restricted to PFOS [*EU*, 2013]. Biota observations from the Marine Monitoring Program is consistently below the PFOS EQS. However, a proposal with a focus on a range of PFAS homologues that includes new toxicity studies, has been prepared for consideration by the Joint Research Centre (JRC) [*EU*, 2021]. An evaluation of the biota concentrations from the Marine Monitoring Program against this new threshold is therefore relevant in preparation for the EU implementation of the EQS. And lastly, within the Marine Monitoring Program PFAS is determined for several species of fish and bird eggs providing information on both spatio-temporal trends and trophic level distribution. The latest in depth analysis of PFAS data was published in 2014 as part of a bigger ecosystem study including also data on contaminants in Baltic Sea top predators [*Faxneld et al.*, 2014b]. At that time PFAS concentrations did not show signs of slowing down their exponential increase (newest data from 2010). Furthermore, the spatial variability was not investigated. With a doubling of the number of years of data available for most stations and another decade for regulations to have had an effect on the Baltic Sea PFAS concentrations in biota, a re-evaluation of the temporal trends and a first evaluation of the spatial variability is therefore needed.

Here we evaluate to what degree regulations on PFAS, first initiated in the early 2000s, are reflected in biota concentration within the Baltic Sea. Further, the report investigates the spatial differences of PFAS across the Baltic Sea not previously evaluated and couples these results to PFAS data from other matrices in

order to understand the flow of PFAS through the Baltic Sea ecosystem. In addition, the report looks ahead at the importance that the new restriction proposal on PFAS, if implemented in its current form, will have for the evaluation of Good Environmental Status (GES) in the Baltic Sea.

3 Methods

3.1 Geographical area

The Marine Monitoring Program covers the Northern Baltic Sea to the Swedish west coast (Kattegat and Skagerrak - hereafter referred to as Kattegat). The Baltic Sea is a coastal sea with limited inflow of marine water from the North Sea through the Danish straits of which Kattegat is a part. This impact the salinity, which increases in offshore surface water from <3 PSU in the northern Baltic Sea, to 6-8 PSU in the southern Baltic Proper and 20-30 in Kattegat, and >30 in Kattegat water below the halocline [*Nilsson*, 2023]. Few fish sampled in the program can therefore be considered to represent a truly marine environment (close to the standard salinity of 35 PSU of marine waters) but instead represent brackish water. For this work, the geographical area is split into five basins as indicated on Figure 1. The greater Baltic Sea will refer to all five basins, while Baltic Sea refers only to the four eastern basins. The five basins represent salinity, temperature and DOC gradients but also represent different human induced pressures, with the largest population and industry located around the three southern basins.

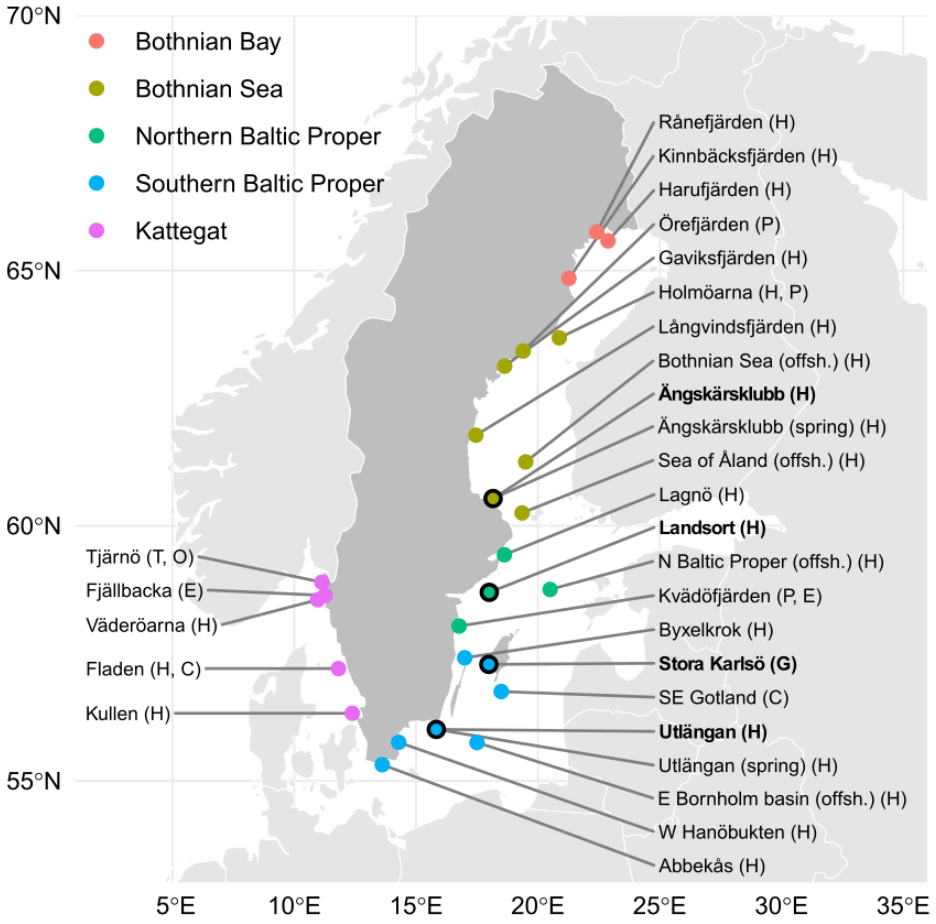

Figure 1. PFAS sampling sites within the Swedish National Monitoring Programme for Contaminants in marine biota (H=herring, P=perch, E=eelpout, G=common guillemot, C=cod, T=common tern, O=Eurasian oystercatcher). The sites are divided into five larger areas, from here on referred to as basins. The Kattegat basin includes station both in Kattegat and in the eastern Skagerrak. Data aggregated at a basin level is used for some of the statistical analysis. Black circles indicate Time Trend Stations with data on herring and guillemot.

3.2 Sampling and sample preparation

Fish and bird eggs are collected as part of the Marine Monitoring Program [*Soerensen and Faxneld*, 2020]. Eggs have been collected during May and fish every fall (August to November) from the early 1970s and 1980s (for a few Time Trend Stations), respectively. Collected eggs are kept refrigerated during transport and at the Swedish Museum of Natural History until they are prepared for analysis. Caught fish are placed individually in polyethylene bags, frozen, and transported to the Swedish Museum of Natural History. Fish and egg samples are prepared for analysis while fish (or leftover parts of fish) and homogenized egg (yolk and albumen) samples not going for contaminant analysis right away are stored at -25°C in the Swedish Environmental Specimen Bank located at the Swedish Museum of Natural History [*Odsjö*, 2006]. In general, samples were handled following the Swedish National Monitoring Program's manual for collection, preparation, and storage of biota [*Soerensen and Faxneld*, 2020].

The Marine Monitoring Program has grown over the years from a few selected stations to a total of 27 stations today (PFAS is analyzed in at least one species at 26 of these stations; Figure 1). The Time Trend Stations are Ängskärsklubb, Landsort, Utlängan, and Stora Karlsö. Within the Marine Monitoring Program, liver from four fish species (herring, cod, eelpout and perch), eggs from three birds species (common guillemot, common tern, and Eurasian oystercatcher) and one mussel species are collected across the Swedish coastal and offshore area (Figure 1). PFAS is not measured in the mussels due to low concentrations; see for examples result from the Norwegian monitoring program showing only FOSA above the detection limit [*Green et al.*, 2022]. PFAS analyses were introduced in to the monitoring program in 2004 and 2005 at Stora Karlsö (guillemot) and Ängskärsklubb, Landsort, and Utlängan (herring). In connection to this, retrospective analyses were conducted every second year (approximately) on samples for the three herring stations from 1980 to 2003 followed by yearly analysis and with 5 years interval for guillemot from 1973 to 2003 followed by yearly analysis. From 2007 more fish and later bird stations were included in the PFAS program but no more retrospective studies were conducted. In this report the four stations with the longer time series will be referred to as Time Trend Stations (Figure 1).

PFAS are analyzed for at least one species at each station (from Holmöarna, Fladen and Kvädofjärden two fish species are analyzed every year). Table 1 gives information on the tissue, number of stations and the start of the PFAS time series for different species.

Table 1. The start year for the monitoring of PFAS and PFAS isomers. For herring the time series for PFAS measurements vary with the Time Trend Stations going back to 1980 (3 stations), most stations starting 2002-2009 (15 stations) and the Sea of Åland and Eastern Bornholm basin being added in 2015.

Species	Tissue	# of stations	Start year$_{PFAS}$	Start year$_{isomers}$
Herring	Liver	20	1980, 2004-2009, 2015	2011
Perch	Liver	2	2016	2016
Eelpout	Liver	2	2016	2016
Cod	Liver	2	2016	2016
Guillemot	Egg	1	1973	2011
Common tern	Egg	1	2011	2011
Eurasian Oystercatcher	Egg	1	2011	2011

3.3 Analytical methods

Samples were analyzed at the Department of Environmental Science at Stockholm University. The target compounds were PFBS, PFHxS, PFOS, PFDS, FOSA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, and PFPeDA (abbreviations of PFAS are according to *Buck et al.* [2011]). In some cases, linear and branched isomers of PFOS, FOSA PFHxS and PFDS were reported separately (Table 1). Homologues were quantified with authentic standards and, in most cases, exactly matched isotopically labeled internal standards. The specific procedure for extraction is described in *Faxneld et al.* [2014a]. The analyses were conducted using UPLC-MS/MS. Data on PFDS, PFBS, PFHxA, PFHpA, is excluded from all analysis due to more than 90 % samples <LOQ values except in the calculation of sumPFAS-equivalents in chapter 12 Compliance with environmental quality standards (EQSs).

3.4 Data from other studies

To put the PFAS results from the fish and bird's eggs in the Marine Monitoring Program into context, a number of other previously published data is included in this report (Table 2). What is included is not an exhaustive list of previously published observations. Instead, the observations have been chosen in order to help highlight different aspects of the data from the Marine Monitoring Program with a preference for data with a spatial distribution across all five basins (Figure 1) and top predators. Focus has furthermore been on picking observations that matches as close as possible in time to the observations in the Marine Monitoring Program. River and marine water samples are from 2013, sediments are from 2014, 2020 and 2021, zooplankton sample from 2013-2014, seals from 2006-2016, common eider from 2015-2016, and white-tailed sea eagle from 2019-2021 (references found in Table 2). As these data contains different matrices, are analyzed at different labs and with different methodology as well as different study focus, the reported PFAS and their detection limits differs between studies. We try to account for this as best possible in the comparison and a full overview of targeted homologues and detection limits reported in the various studies can be found in Table S 2.

Table 2. Greater Baltic Sea PFAS data from our (grey) and other sources. Columns indicate the presence of data for the five basins. The PFAS homologues targeted in each study and the detection limit (as defined for each study) is found in Table S 2.

Matrix	Tissue	Bothnian Bay	Bothnian Sea	Northern Baltic Proper	Southern Baltic Proper	Kattegat
Swedish rivers	Water	Nguyen et al. 2017	Nguyen et al. 2017	Nguyen et al. 2017	Nguyen et al. 2017	Nguyen et al. 2017
Surface water (2 m)	Water	Nguyen et al. 2017	Nguyen et al. 2017	Nguyen et al. 2017	Nguyen et al. 2017	Nguyen et al. 2017
Sediment	Sediment	Josefsson et al 2022	Josefsson et al 2022	Josefsson et al 2022	Josefsson et al 2022	Josefsson et al 2022
Zooplankton	Whole organism			Gebbink et al 2016		
Herring	Liver	Soerensen & Faxneld 2020	Soerensen & Faxneld 2020	Soerensen & Faxneld 2020	Soerensen & Faxneld 2020	Soerensen & Faxneld 2020
Perch	Liver		Soerensen & Faxneld 2020	Soerensen & Faxneld 2020		
Eelpout	Liver			Soerensen & Faxneld 2020	Soerensen & Faxneld 2020	Soerensen & Faxneld 2020
Cod	Liver			Soerensen & Faxneld 2020		Soerensen & Faxneld 2020
Guillemot	Egg Liver Muscle			Soerensen & Faxneld 2020 Holmström & Berger 2008 Holmström & Berger 2008		
Common tern	Egg					Soerensen & Faxneld 2020
European oystercatc.	Egg					Soerensen & Faxneld 2020
White-tailed sea eagle	Egg Liver Muscle		Haque et al. 2023	Haque et al. 2023 Vainio et al. 2022 Vainio et al. 2022	Haque et al. 2023	
Common eider	Egg Liver					De Wit et al. 2020 De Wit et al. 2020
Grey seal	Liver				De Wit et al. 2020	
Harbor seal	Liver				De Wit et al. 2020	
Harbor porpoise	Liver				De Wit et al. 2020	

3.5 Statistical treatment

A graphical and statistical presentation of PFAS time trends from the Marine Monitoring Program can be found in the appendix of *Soerensen and Faxneld* [2020] and (including 2020 data analyzed by a different laboratory) in *Soerensen and Faxneld* [2022].

LOQ

For determination of sum and relative distribution of PFAS, values below LOQ were replaced with 0. For evaluating time series change points and trends for individual PFAS, concentrations below LOQ were substituted with LOQ/√2. No outliers were removed from the data.

Spatial analysis

For analysis of the "current day" spatial distribution and composition of PFAS by individual homologues, measurements from 2018 and 2019 are used. For measurements aggregated for historic analysis, the temporal range of the measurements used for the analysis is described in figure or table text.

Change point / structural change analysis

We carried out statistical change point (CP) analyses for the PFAS time series by fitting two-piece linear regressions to yearly average log-concentrations, with the CP represented by the unknown join point estimated by least squares [*Chappell*, 1989; *Hudson*, 1966]. In comparison to e.g. *Nyberg et al.* [2018] and *Miaz et al.* [2020], who fit separate log-linear regression before and after the CP, this has the advantage of forcing the trend-lines to meet at the same point in the CP year. No outliers were excluded from the data prior to doing the analysis. In order to test the null hypothesis (that there is no structural change in the time series) we used the supF test [*Andrews*, 1993; *Andrews and Ploberger*, 1994] with a p value approximated by parametric bootstrap. The full fitting process is implemented as a package for the R computing environment [*R Core Team*, 2022], lmcp, freely available at https://github.com/mskoldSU/lmcp.

PFTeDA and PFPeDA had almost exclusive LOQ values for herring prior to 2010 and the LOQ values were in many cases high than observations from 2010 and onwards. Further, there was an average of three observations below LOQ during the last 10 years (2010-2019) for each time series. For these time series PFTeDA and PFPeDA CP analysis were therefore not included. For guillemot, concentrations of the two PFCAs were higher and CP analysis were conducted.

Time trend analysis

For time trends, we used log-linear regression on the whole time series, on the period from the CP to the last year of the time series (CP year-2019), and on the last 10 years (2010-2019). The slope of the log-linear regression represents the yearly average increase or decrease of the time series. Statistics for the log-linear

regression was extracted using the “lmcp” function in R. Statistic results at the stations scale is extracted from *Soerensen and Faxneld* [2020].

Bioaccumulation factors

Bioaccumulation factors (BAF) are calculated as basin averages of herring liver concentrations (ng kg^{-1} wet weight) divided by surface water concentration (ng L^{-1}; [*Nguyen et al.*, 2017]). The calculation relies on detectable PFAS concentrations (>LOQ) in both water and fish liver. As longer-chained PFAS are often below LOQ in the water, although found in detectable concentrations in herring liver, this limits the estimation of BAF for the longer-chained PFAS. To explore the minimum BAF (referred to as potential BAF) for basins where the water concentrations is <LOQ, additional BAF are calculated including water observations <LOQ as LOQ/√2 [*Pickard et al.*, 2022].

Biomagnification factors

Biomagnification factors (BMF) for PFAS are calculated as basin averages of predator liver concentration (ng kg^{-1} wet weight) divided by herring liver concentrations (ng kg^{-1} wet weight). For birds, egg contaminant concentration is converted to a liver equivalent using the conversion factors from Table 4.

4 Trophic position of Greater Baltic Sea biota

Table 3 gives the approximate trophic position of the fish and birds that are part of the Marine Monitoring Program. The trophic level calculation is based on mussel isotope data from as close as possible to the stations where fish or bird eggs were caught/collected. Table S 3 gives an overview of preferred food items for each species.

Eelpout and herring has similar low trophic levels (3.0-3.7) while perch and cod having a trophic level 0.4-0.7 higher than herring in any given basin. This reflects the feeding habits of the pelagic zooplanktivorous herring and the stationary, bottom dwelling, eelpout that feeds on insect larvae, molluscs, crustaceans, worms and small fish. This is compared to the coastal perch, that is an omnivore that feed opportunistic on fish, and cod, that lives below the halocline and feed on preyfish like herring but also benthic invertebrates [*Funk et al.*, 2021].

Table 3. Stable isotope values (mean ± standard deviation) for mussels, fish and bird eggs. Trophic level (TL) is calculated as (δ^{15}Npredator - δ^{15}Nmussel)/3.4 + 2 assuming a TL of 2 for mussels [Post, 2002]. The trophic level difference (TL_{diff}) indicate the distance from other species to herring. δ^{13}C has not been lipid adjusted.

Basin	Species	Station	δ^{13}C	δ^{15}N	TL	TL_{diff}
Kattegat	Blue mussel	Fjällbacka	-18.75±0.53	9.04±0.54		
	Eelpout	Fjällbacka	-16.93±0.58	12.69±0.41	3.1	-0.3
	Herring	Väderöarna	-20.00±0.60	13.65±0.58	3.4	
	Eurasian oystercatcher	Tjärnö	-17.19±1.67	11.59±0.76	2.8	-0.6
	Common Tern	Tjärnö	-17.20±1.28	14.13±0.56	3.5	0.1
	Blue mussel[1]	Glommen	~-19.3	~8.8		
	Cod	Fladen		~16	~4.1	0.7
S. Baltic Proper	Blue mussel[1]	Högby fyr	~-19.25	~5.0		
		Östergarnsholm		~4.5		
	Herring	Byxelkrok		~11	~3.7	
	Cod	SE Gotland		~12.5	~4.2	0.5
	Guillemot	Stora Karlsö	-19.18±0.64	12.51±0.25	~4.2	0.5
	WTSE[2]	Coastline		~12 (7.0-15.0)	~4.0	0.3
N. Baltic Proper	Blue mussel	Kvädofjärden	~-22.6	~7.0		
		Dragviksfärden[1]		~5.8		
	Herring			~11	~3.3	
	Eelpout	Kvädofjärden		~10.5	~3.2	-0.1
	Perch	Kvädofjärden		~12.5	~3.7	0.4
	WTSE[2]	Coastline		~12 (7.5-14.0)	~3.7	0.4
Bothnian Sea	Baltic clam[1]	Gaviksfjärden	~-22	~6.0		
		Örefjärden	~-23	~7.5		
	Herring	Gaviksfjärden		~10	~3.0	
	Perch	Holmöarna		~12.0	~3.5	0.5
	WTSE[2]	Coastline		~12 (9.0-17.0)	~3.5	0.5

1. Data taken from *Karlsson et al.* [2019]. 2. Data approximated from graph in *Hellström* [2016].

The Eurasian oystercatcher is below herring (-0.6 TL) and common tern is at the same trophic level, while guillemot and white-tailed sea eagle are 0.3-0.5 higher in trophic level. The δ^{15}N is determined in different matrices for herring (muscle) and birds (egg) but *Vainio* [2022] found the same distance when looking at muscle concentrations in a study on white-tailed sea eagles at the Finnish coast in the Northern

Baltic Proper. They found the muscle $\delta^{15}N$ to be 12.09±1.83 and the trophic position to be 3.6-4.6 similar to ours (3.5-4.0). For Eurasian oystercatcher and common tern, the trophic levels can be explained by their diet. The Eurasian oystercatcher feeds mainly on worms and shellfish while the common tern feed mainly on small fish [*Lemmetyinen*, 1973; *Reindl and Falkowska*, 2019]. The lack of fish in the diet of the Eurasian oystercatcher explains its low trophic level below the common tern, and the small fish diet of the common tern explain the level only slightly higher than herring. Guillemot mostly feed on the zooplanktivorous sprat [*Österblom et al.*, 2001], while the white-tailed sea eagle has a diet at Baltic coastal locations mostly consisting of larger fish and sea birds. The trophic level for the guillemot and white-tailed sea eagle could therefore seem slightly low as also noted by *Vainio* [2022] for the white-tailed sea eagle.

5 Bird matrix conversion factors

Bird eggs are an easy matrix to collect and is therefore used in the Marine Monitoring Program and in other monitoring programs [*Dittmann et al.*, 2011; *Mattig*, 2017]. However, the egg PFAS concentration are not directly comparable to measurements in liver or muscle from other species in the food web. It is therefore important to get a general sense of the conversion factors between contaminant concentrations in eggs and other common used tissues within monitoring like liver and muscle. Table 4 show the PFAS concentrations and approximate conversion factors (*k*) between egg, liver and muscle for three different bird species in the Greater Baltic Sea. The data is from three previously published studies [*De Wit et al.*, 2020; *Holmström and Berger*, 2008; *Vainio*, 2022]. For a detailed description of the theory behind tissue conversion factors see *Soerensen et al.* [2023]. It should be noted that the white-tailed sea eagle eggs are collected at a different location than the birds for the liver and muscle samples (Figure 2) and the result should be viewed with caution. However, taken together with the results from the other two bird species it gives a broad idea of the concentration differences in eggs and adult bird tissues for various PFAS.

PFAS egg concentrations are mostly elevated compared to liver and muscle and liver concentrations are elevated compared to muscle. This makes sense as PFAS tends to bind to protein rich tissue such as liver, egg yolk and serum. For the three bird species, PFOS has the highest $k_{egg/liver}$ (1.4-4.6) and $k_{egg/muscle}$ (14.8-23.2) while FOSA is consistently at or below one (0.65-1.0) suggesting FOSA is not transferred to the chick. For the PFCAs the $k_{egg/liver}$ are relative close to one (0.4-4.3) while the $k_{egg/muscle}$ are all above two (2.5-19.1). *Holmström and Berger* [2008] suggest a more efficient transfer of PFOS than other PFAS from mother to eggs. However, for both $k_{egg/liver}$ and $k_{egg/muscle}$ the longer chain lengths (C_{11}-C_{13}) seems to have the higher values, indicating that also these are preferentially transferred to the eggs. Such a preferential transfer from mother to egg is problematic because it suggests that birds during the early developmental phase and as chicks are exposed to higher concentrations of PFAS than we expect by just looking at adult concentrations [*Holmström and Berger*, 2008].

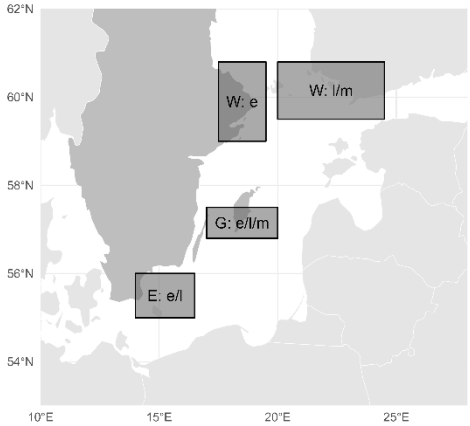

Figure 2. Map indicating where samples presented in Table 4 are collected. W: white-tailed sea eagle, G: guillemot, E: eider, e: egg, l: liver, m: muscle.

The results indicate that for some PFAS like PFOS and long chained PFCAs, egg concentrations will overestimate concentrations in adult birds considerably. This should be taken into consideration when calculating Biomagnification factors (BMF) or relate concentrations to threshold values set for other tissues.

Table 4. Concentration of selected PFAS in three different matrices of white-tailed sea eagle and guillemot. Location of collection indicated on Figure 2. Guillemot data (medians) is from *Holmström and Berger* [2008] collected on Stora Karlsö, Gotland. The liver and muscle concentrations are from *Vainio* [2022] from white-tailed eagles collected in Finland at the border between the Northern Baltic Proper and the Bothnian Sea and egg concentrations are from coastal stations (<10 km inland: Östhammar and Värmdö stations) in Stockholm county (2019 data [*Haque et al.*, 2023]). Common eider data is from *De Wit et al.* [2020].

	Egg (ng g^{-1} ww)	**Liver** (ng g^{-1} ww)	**Muscle** (ng g^{-1} ww)	$k_{egg/liver}$	$k_{egg/muscle}$
Guillemot					
PFOS	325 (243-432)	121 (91-150)	14 (9.8-17)	2.69	23.21
PFNA	1.1 (0.76-1.8)	2.8 (1.3-5.7)	0.24 (0.17-0.42)	0.40	4.58
PFDA	2.0 (1.7-2.6)	3.5 (2.4-8.5)	0.44 (0.31-0.61)	0.57	4.55
PFUnDA	12 (7.6-13)	12 (6.6-28)	0.63 (0.33-1.2)	1.00	19.05
PFDoDA	3.6 (2.7-4.1)	3.4 (2.1-8.5)	0.53 (<MDL-0.77)	1.06	6.79
PFTrDA	11 (8.8-14)	7.1 (3.9-15)	1.3 (1.0-1.9)	1.55	8.46
White-tailed sea eagle					
FOSA	0.21±0.11	0.32±0.32	0.21±0.19	0.65	1
PFOS	293±329	63.08±38.59	19.77±18.24	4.64	14.8
PFHxS	1.37±1.93	0.9±0.82	0.29±0.35	1.52	4.72
PFOA	0.53±0.33	0.28±0.16	0.21±0.18	1.89	2.52
PFNA	11.14±7.11	10.08±7.04	2.88±1.86	1.11	3.87
PFDA	6.63±4.50	2.6±1.37	0.79±0.46	2.55	8.39
PFUnDA	9.04±6.27	3.69±2.13	1.15±0.95	2.45	7.86
PFDoDA	3.78±3.06	0.87±0.65	0.29±0.29	4.34	13.03
PFTrDA	4.15±3.48	1.71±1.26	0.64±0.49	2.43	6.48
Common eider					
FOSA	0.25	0.31		0.81	
PFHpS	0.36	0.12		3	
PFOS	17	12		1.42	
PFNA	1.4	1.4		1	
PFDA	0.74	0.86		0.86	
PFUnDA	1.3	0.98		1.33	
PFDoDA	0.81	0.46		1.76	
PFTrDA	1.0	1.3		0.77	
PFTeDA	0.22	0.24		0.92	

6 Spatial variability

6.1 Spatial distribution in fish

Figure 3 shows the distribution of PFAS (total and relative) and PFCAs for the four fish species in the Marine Monitoring Program. PFOS is the dominant homologue for all four fish species as also observed by others for the Baltic Sea [*De Wit et al.*, 2020; *Kumar et al.*, 2022] and other marine systems [*Houde et al.*, 2011; *Lin et al.*, 2021]. PFOS (including FOSA) contribute >60% of PFAS in all basins.

Herring is the only species with stations in all five basins. The results indicate the same spatial pattern for concentrations of both PFAS and PFCA with slightly increasing concentrations from the Bothnian Bay to the Southern Baltic Sea and the lowest concentrations in Kattegat. Although observations are only available from two basins, something similar is seen for cod (pelagic) but not to the same degree for eelpout (coastal). While the Σ(PFOS+FOSA) concentration is similar for all basins, fish from Kattegat have a larger fraction of FOSA to Σ(PFOS+FOSA) than the other basins. This is true for herring, cod and eelpout although the fraction decreases from herring (63%) to cod (35%) to eelpout (8%; see chapter 9 PFOS and FOSA distribution for a discussion of the drivers).

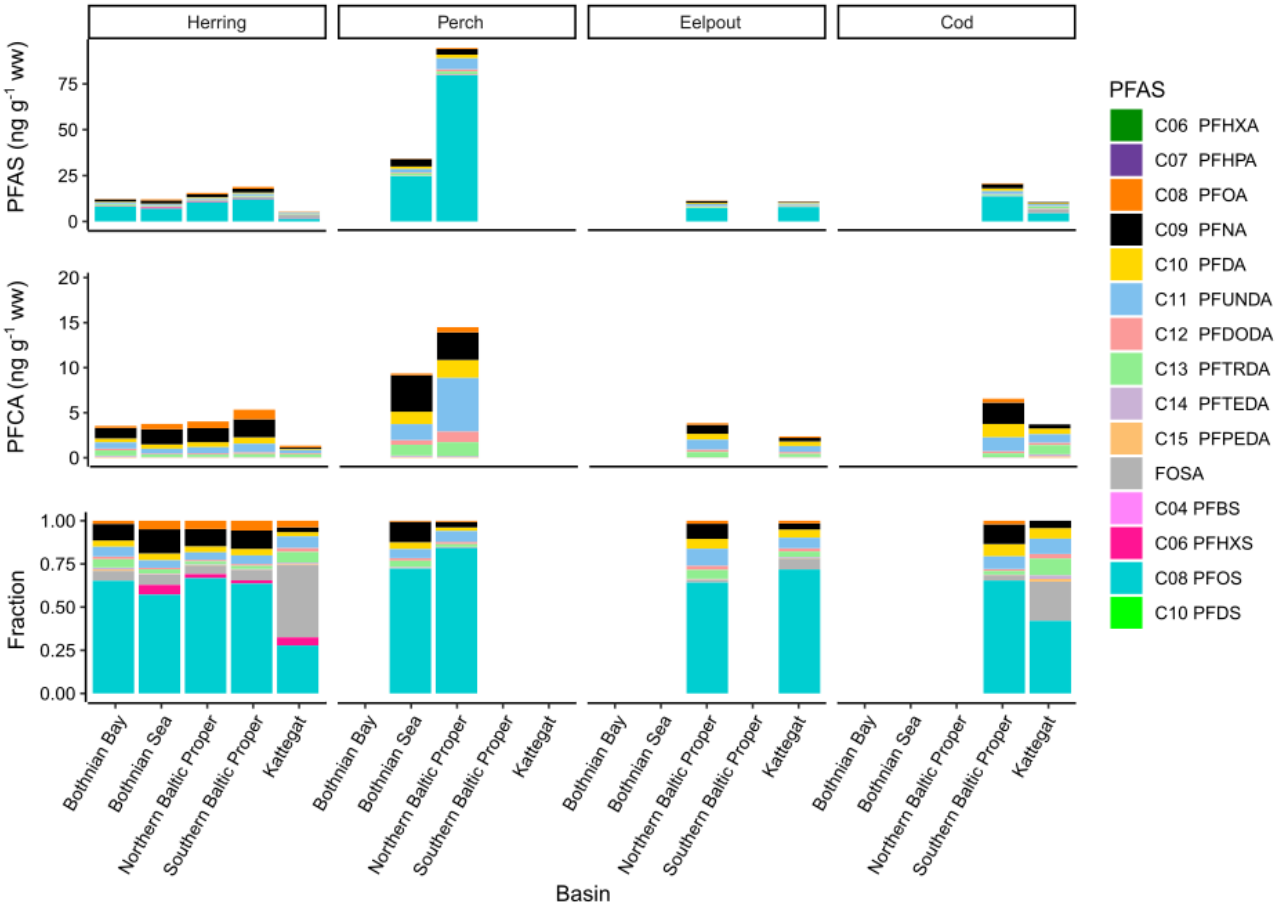

Figure 3. Concentrations (ng g^{-1} ww liver) of A) PFAS and B) PFCA, and C) the fractional PFAS distribution in fish within the Marine Monitoring Program. Figure 1 shows the areas and station distribution within five basins. The concentration at individual stations for 2017-2019 can be found in *Soerensen and Faxneld* [2020].

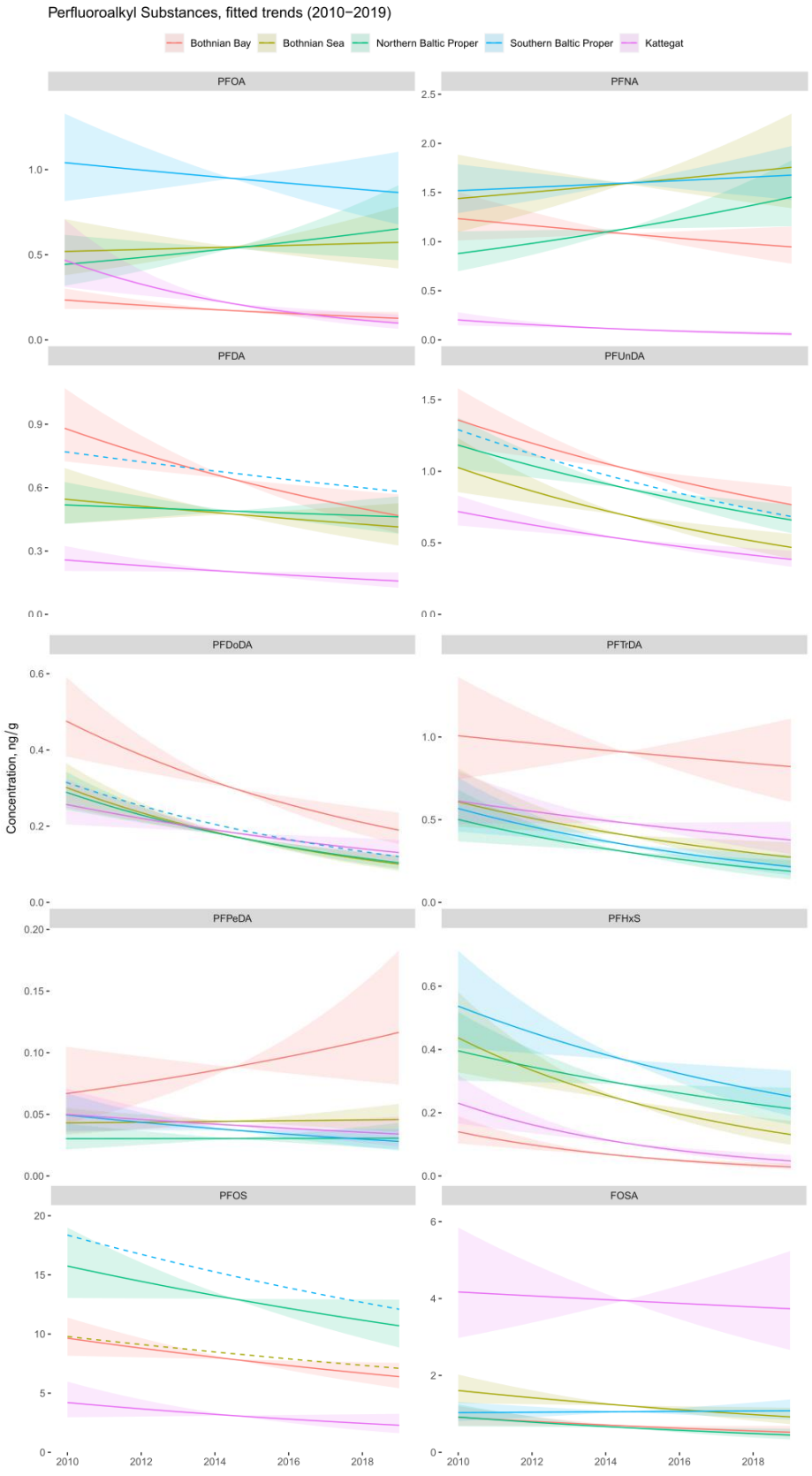

Figure 4. The spatial and temporal (2010-2019) distribution of PFAS homologues in herring liver (ng g^{-1} ww) from the basins of the Greater Baltic Sea including 95% confidence bands. The dashed line indicates that both positive and negative slopes are included in the basin average. Stations within each basin have been combined to give basin averages. The confidence band reflect the uncertainty in the trend given a fixed level at the midpoint. Hence, the bands cannot be used to assess uncertainty in contaminant level, since uncertainty in the intercept is not taken into account (see *Soerensen and Faxneld* [2020]).

Concentrations for perch in the Northern Baltic Proper is elevated (<75 ng g^{-1} ww) compared to perch in the Bothnian Sea and cod (that has a similar trophic level). Concentrations from possible contaminated sites at the Greater Baltic Sea coast found that PFAS concentration ranged between 20-70 ng g^{-1} ww (except for two outliers at Lilla Värtan in the Stockholm harbor with >200 ng g^{-1} ww) [*Danielsson et al.*, 2014]. This suggest that perch in Kvädofjärden (Northern Baltic Proper) could be influenced by local sources. This contamination could be localized to the pelagic prey of perch as elevated concentrations are not seen for eelpout (benthic prey) at the same station. Concentration differences of metals and other organic contaminants between perch and eelpout in Kvädöfjärden has previously been linked to the differences in food choices of the two species [*Hanson et al.*, 2020].

Figure 4 shows the herring concentrations per basin and trends for the 2010-2019 period for individual PFAS homologues (for a discussion of the trends see chapter 11 Change points and trends for individual homologues). For the PFCAs, the basin averages are in general close together. For PFNA (C9) and PFDA (C10) the Kattegat basin is an outlier with much lower concentrations than the other basins. PFUnDA (C11) has no clear outliers although there is spread across the basins, while the Bothnian Bay has an outlier with elevated concentration for PFDoDA (C12), PFTrDA (C13) and PFPeDA (C14). Both the perfluoroalkyl carboxylic acid (PFCA) PFOA (C8) and perfluoroalkyl sulfonic acid (PFSA) PFHxS (C5) has lowest concentrations in the Bothnian Bay and Kattegat and highest in the Southern Baltic Proper (for a discussion of this see chapter 11 Change points and trends for individual homologues). For PFOS (C8) the Baltic Proper basins have highest concentrations with low concentrations in Kattegat. This is opposite to FOSA that has four times higher concentrations in Kattegat than in the other basins (Figure 3, see chapter 9 PFOS and FOSA distribution for a discussion of the drivers).

6.2 Spatial distribution from sources to top predators

Figure 5 and Figure 6 show the concentration and relative distribution of PFAS in various matrices across the Greater Baltic Sea ecosystem from sources to top predators. The river water has considerable higher concentrations, including a larger fraction of short chain homologues like PFBA (C4) and PFBS (C4), than the offshore surface water suggesting that concentrations closer to the coast (for both water and biota) could be higher than what is indicated by the offshore seawater concentrations. For surface water and sediment, the concentration is increasing and decreasing, respectively, from the Bothnian Bay to Kattegat. This could suggest high adsorption and sedimentation in the river impacted northern basins (mainly PFOA, PFNA and PFOS) where allochthonous dissolved organic carbon (DOC) rich in aromatic functional groups have a higher impact [*Deutsch et al.*, 2012] and a limited dilution of PFAS entering the Kattegat basin from rivers, industry and run-off due to the small water mass and a strong stratification separating surface water from the water below the halocline. It should be noted that many of the Baltic Proper sediment samples are from anoxic areas and the PFAS concentrations are therefore not likely to reflect the exposure of bottom feeders in other areas of the Baltic Proper.

The herring PFAS distribution does not follow that of either the surface water or the sediment (Figure 5). Most noticeable is the decrease in the herring concentration from the Southern Baltic Proper to Kattegat, where the surface water concentrations increases. Furthermore, although the PFOS fraction in the Kattegat surface water is similar to the other basins the fraction in the herring is less than half that seen for the other basins (Figure 6). Instead a large fraction of FOSA is present in the Kattegat herring, a substance contributing <5% in the surface water samples. This will be discussed further in chapter 9.2 Intra-species FOSA:PFOS distribution.

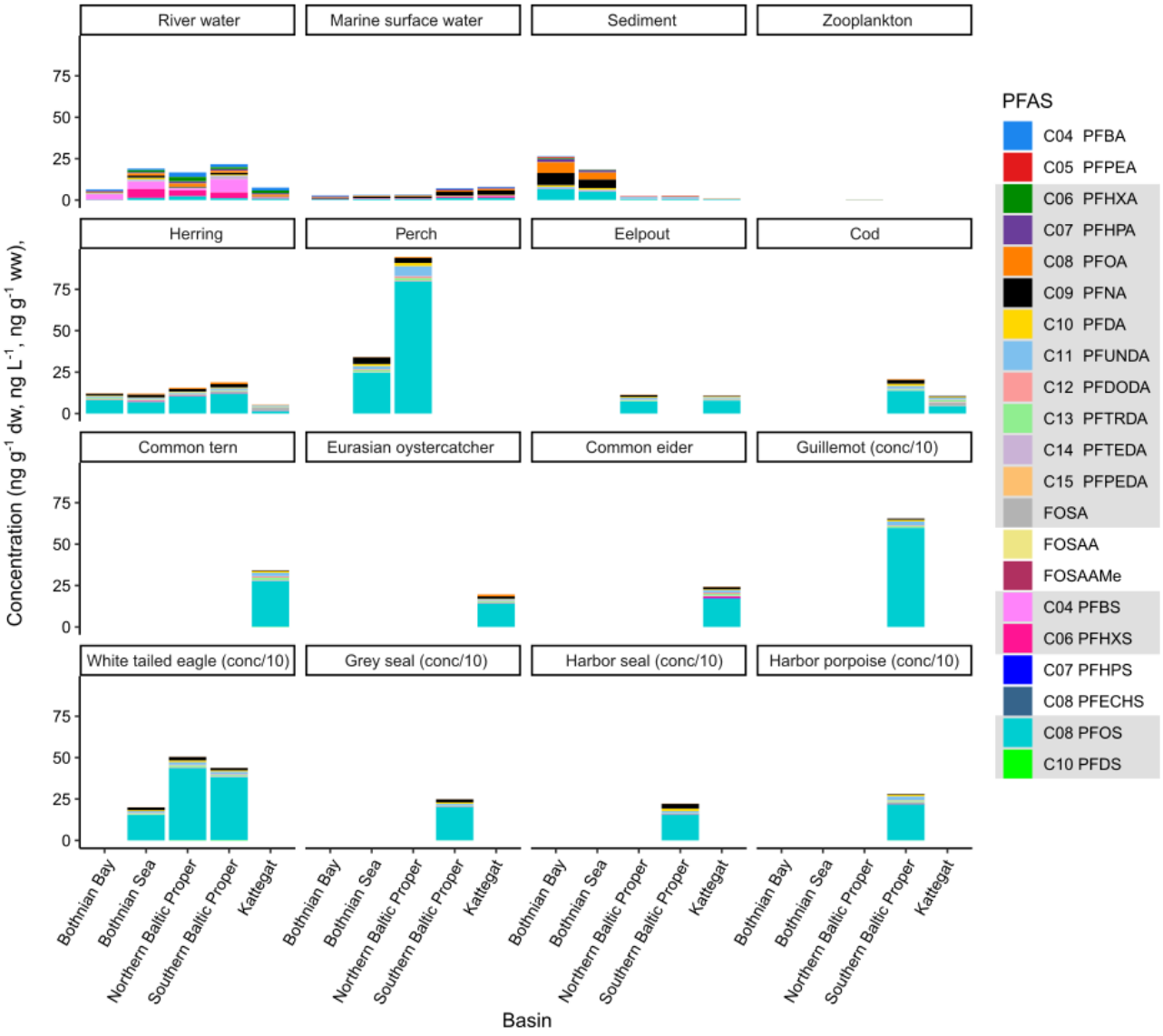

Figure 5. PFAS concentrations in different media from the Greater Baltic Sea grouped by basins. Water samples are in ng L^{-1}, sediment ng g^{-1} dw, and biota ng g^{-1} ww. Analyzed tissue is liver for fish and seals, and egg for birds. Indicated with grey on the legend are the PFAS that are targeted within the Marine Monitoring Program, other PFAS are found in the other studies. For zooplankton, DiPAP concentrations (sum of DiPAP 0.56±0.10) has not been included in the graph. Note that the concentrations for the top predators shown on the figure are divided by 10.

Bird egg PFAS concentrations seem to be controlled by their trophic level with the Eurasian oystercatcher and the common eider (feeding on crustaceans and molluscs) having the lowest concentrations, common tern (TL 3.5) having slightly higher concentration and guillemot and white-tailed sea eagle more than 10 times higher concentrations. The PFOS to PFAS fraction also increases from 60-80% to 80-90% with the increase in trophic level. Table 4 showed the importance of the efficiency of transfer of different PFAS homologues from mother to egg for the different bird species. The biomagnification and importance of the mother to egg transfer is discussed further in chapter 8 Biomagnification.

The marine mammals also have a high PFOS fraction (>75%) although slightly smaller than for guillemot and white-tailed sea eagles. In a direct comparison, the marine mammal concentrations are smaller than for the two avian birds. However, using an approximate conversion factor $k_{egg/liver}$ for PFOS of 3.5 (2.7-4.6; Table 4) to calculate bird liver concentrations suggest that the liver concentrations of the two birds are below or aligned with the marine mammal liver concentrations.

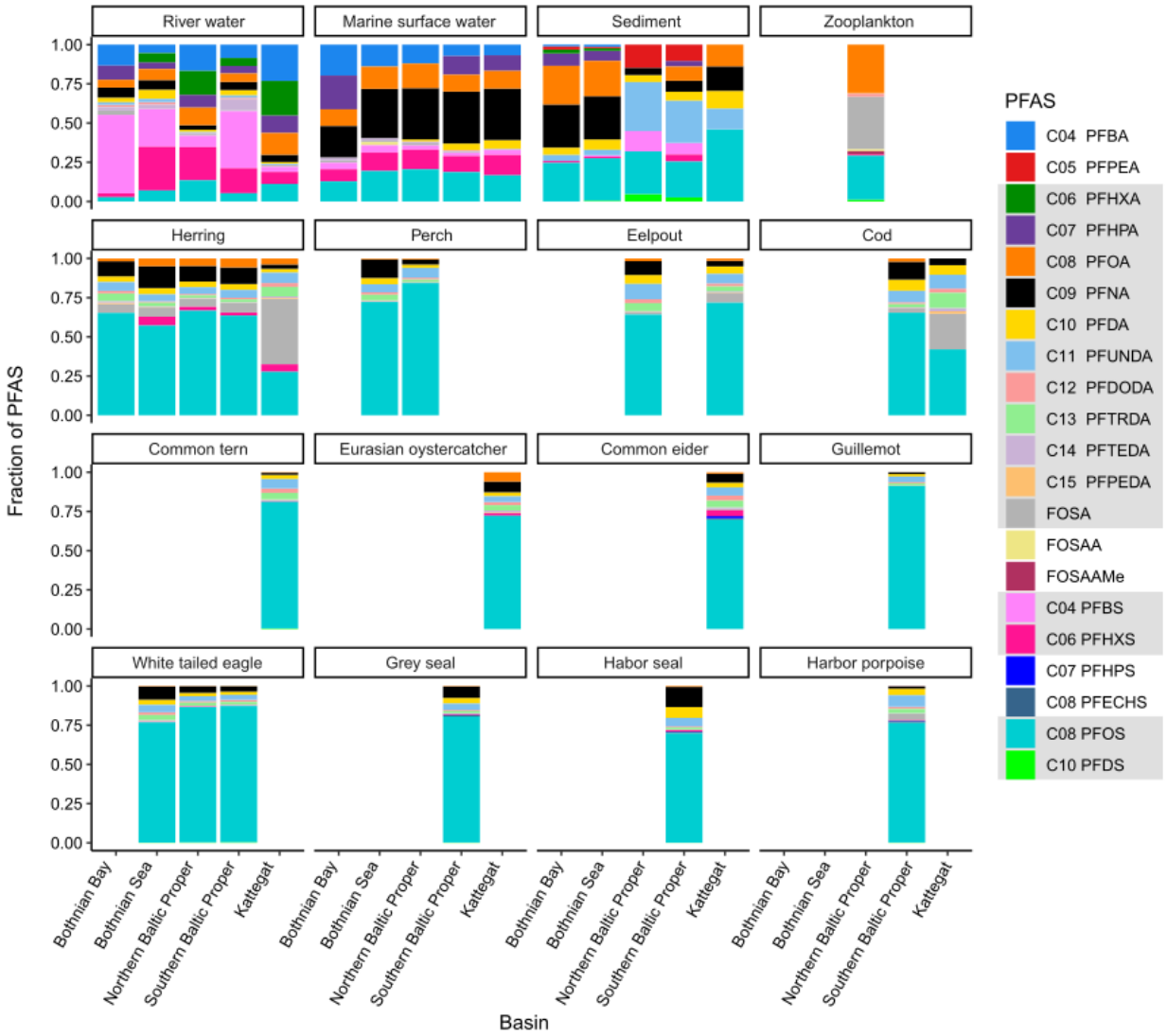

Figure 6. Fractional distribution of PFAS in different media from the greater Baltic Sea grouped by basins. Indicated with grey on the legend is the PFAS that are targeted within the marine monitoring program, other PFAS can be found for some of the other studies. For zooplankton, DiPAP concentrations has not been included in the graph as part of the PFAS distribution (represents ~50% of the observed PFAS in the zooplankton [Gebbink et al., 2016]).

7 Bioaccumulation

Many PFAS have been found to bioconcentrate and accumulate in the lower food web [*Gebbink et al.*, 2016; *Zhang et al.*, 2019]. Calculating empirical bioconcentration factors can give an idea of the initial increase of PFAS from water and into the food web and thereby indicate the potential for PFAS to affect food web concentrations. Ideally, plankton measurements would be used for this calculation to avoid any impact of food web biomagnification from prey to predator. For the Greater Baltic Sea, there is no spatially resolved measurements of PFAS in plankton. As an approximation, Figure 7 present BAFs from water to herring liver for the PFAS homologues. These BAF thus include both the bioconcentration and any biomagnification from plankton to herring. For the analysis, it should be kept in mind that the surface water PFAS data is from just one campaign, which could impact the results. The BAF for PFCAs indicate an overall increase with chain length from C8 to C10 followed by a decrease from C10 to C14 similar to previous findings. The decrease with increasing chain length for >C11 has been linked to reduced bioavailability of larger molecules due to steric hindrance to uptake past a certain chain length [*Pickard et al.*, 2022]. An increase in BAF from C7 to C11 has also been found previously for plankton and fish (muscle or whole body) [*Pickard et al.*, 2022; *Shi et al.*, 2018; *Zhang et al.*, 2019](no BAF was calculated for PFunDA in our study as all water observations were >LOQ). However, the increase from C8 to C10 for herring liver in the Greater Baltic Sea is lower (factor 10, log BAF from ~3 to ~4; Table 5) compared to other studies that showed an increase in BAF of a factor 100 (log BAF from ~2 to ~4 for fish muscle and ~3.5 to ~5.5 for whole fish) [*Gebbink et al.*, 2016]. The liver to muscle conversion factor ($k_{liver/muscle}$) is 10-20 for the different PFCAs. However, the $k_{liver/muscle}$ from *Soerensen et al.* [2023] for PFOA (k=12.9) and PFDA (k=18) actually suggest a slightly smaller BAF difference if converting the herring liver concentrations to muscle equivalent before calculating the BAF. That the observations are from liver rather than muscle therefore do not explain the smaller difference in BAF between C8 and C10 in the data from the Marine Monitoring Program. It is unclear what causes this inconsistency with previous observations. An increase in BAF for C10-C14 when including the potential BAFs (see method description in chapter 3.5 Statistical treatment) suggest that problems with the detection of the longer chain PFAS in the surface water could result in an underestimation of the empirically calculated BAF for these homologues.

Table 5. Average bioacumulation factors (BAF) from water to herring liver for the four Baltic Sea basins: Bothnian Bay, Bothnian Sea, Northern Baltic Proper, and Southern Baltic Proper (excluding Kattegat).

PFAS	logBAF	logBAF including potential BAF
PFCA		
PFOA (C8)	3.08±0.14	3.08±0.14
PFNA (C9)	3.16±0.17	3.16±0.17
PFDA (C10)	3.73±0.51	4.08±0.47
PFDoDA (C12)	3.65	3.84±0.11
PFTeDA (C14)	3.24±0.15	3.39±0.20
PFSA		
PFHxS (C6)	2.98±0.29	2.98±0.29
PFOS (C8)	4.14±0.17	4.14±0.17
FOSA (C8)	4.33±0.11	4.37±0.10

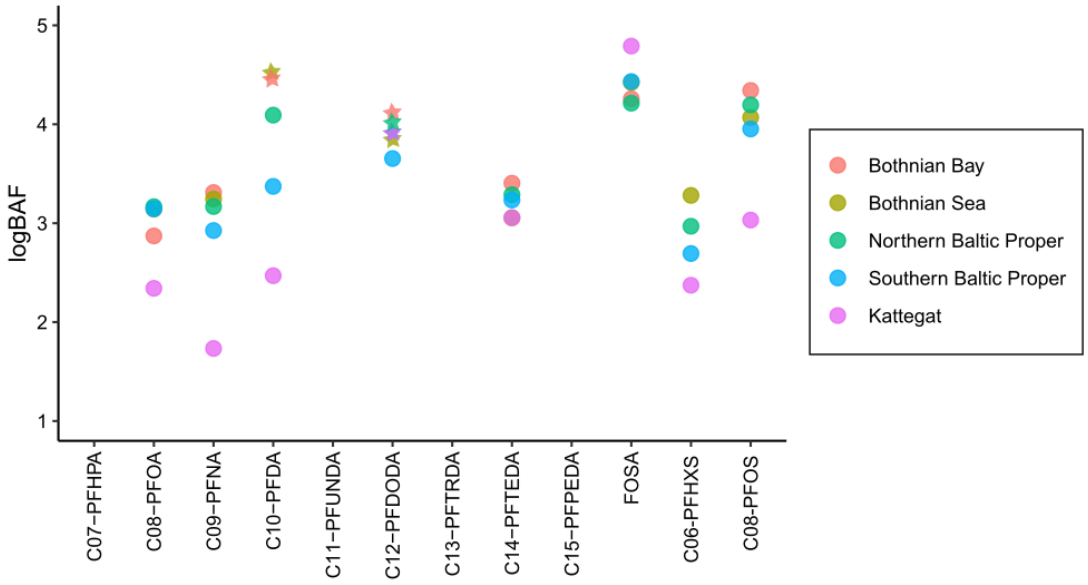

Figure 7. Empirically derived bioaccumulation factors (BAF, L kg^{-1}) from water to herring liver for PFAS homologues in the five basins. Circle: BAF calculated including only observation >LOQ; Star: BAF for PFAS homologues with only <LOQ observations for marine water (see method description in chapter 3.5 Statistical treatment; BAF calculated using LOQ/√2 for the water samples). PFAS with no information on observations or LOQ in water: PFUnDA, PFTrDA and PFPeDA [*Nguyen et al.*, 2017].

A chain length dependence is also seen for the two PFSAs PFHxS and PFOS (C6 and C8). Similar to the BAF from *Pickard et al.* [2022] based on fish muscle in north-eastern US lakes, the BAF for the PFOS precursor FOSA is the same or higher than the BAF for PFOS. This underlines the importance of the precursor as a potential source of PFOS due to biotransformation in the food-web.

For almost all PFAS homologues, the BAF from Kattegat deviates the most from the Greater Baltic Sea average indicating that something is different for this basin (Figure 7). Kattegat is influenced both by the outflow of surface water from the Baltic Sea and inflow of saltier water below the halocline from the North Sea [*Omstedt et al.*, 2014] as well as from local rivers. A different PFAS profile in the North Sea water compared to that of the Baltic Sea could be reflected in the PFAS uptake into the food web if it happens below the halocline. The deviations in BAF therefore suggest that the surface water concentrations of PFAS measured by *Nguyen et al.* [2017] is not representative of the food web exposure to PFAS in Kattegat. For PFCA and PFSA, the Kattegat BAFs are considerably lower than for the other basins, which could reflect a combination of both the higher surface water concentrations and lower herring concentrations presented in Figure 5. North Sea water, potentially less contaminated than the Baltic Sea water, could cause a dilution of the BAF signal in the Kattegat food web compared to the surface water concentration. On the other hand BAF for FOSA is higher for Kattegat than the other basins, reflecting a much larger fraction of FOSA to both PFAS and PFOS than for the other basins. This is likely also linked to the impact of the North Sea water and will be discussed in detail in chapter 9 PFOS and FOSA distribution. Given the possible influence of North Sea water on the Kattegat biota PFAS profile, the BAF for the other four basins should be seen as better representing BAF for PFAS in the Baltic Sea (Table 5).

8 Biomagnification

Calculating empirical PFAS BMFs for the Greater Baltic Sea food web is made difficult by the use of different matrices (liver and egg) for different biota (Table 1). Furthermore, the different metabolisms and migration (exposure) pattern of biota can impact the BMF calculation. For the calculation of the BMF, the $k_{egg/liver}$ for guillemot and white-tailed sea eagle (Table 4) is used to convert egg concentrations to liver concentrations for the birds, so that the tissue used for the calculation of the BMF is the same for all biota (liver). It should be noted that the conversion factors are based on a small number of samples and have a high degree of uncertainty. Therefore, only a BMF_{liver} for PFOS, constituting 80% of PFAS in top predators, is calculated. For PFCA, the BMF is calculated without normalizing the egg concentration to liver and the change in relative distribution across the food web is further investigated. In this case, the use of different matrices is less problematic but should still be kept in mind ($k_{egg/liver}$ range: 0.4-1.6 and 1.9-4.3 for PFCA in guillemot and white-tailed sea eagle, respectively). To simplify the comparison of the BMF and the relative PFCA contribution, the focus is on herring, cod, white-tailed sea eagle, and guillemot. While only cod and guillemot has a fraction of herring in their diet (Table S 3), the trophic position of all three predators is above that of herring (Table 3) and their food preferences suggest a higher trophic level than herring.

8.1 PFOS

Table 6 show a high BMF for PFOS in the Greater Baltic Sea as consistently found by others [*De Wit et al.*, 2020; *Gebbink et al.*, 2016]. While the trophic level distance to herring is very similar for the three predator species, the PFOS biomagnification potential varies by a factor of 10 (Table 6). *Vainio* [2022] found that Baltic Sea white-tailed sea eagles often had lower empirically estimated trophic levels than suggested by their known prey indicating higher trophic position of prey than predator. Thus, the BMF cannot always be normalized to a trophic level distance. Instead food preferences might provide more information than the trophic level. Cod feed mostly on herring and benthic invertebrates and guillemot mostly prey on another zooplanktivorous species, sprat [*Funk et al.*, 2021; *Österblom et al.*, 2001]. However, in a study from the Southern Baltic Proper, *Gebbink et al.* [2016] found that the PFOS concentration in sprat and herring differed with only a few percent. The exposure for these two species should therefore be fairly similar, while the white-tailed sea eagle may have a higher exposure through the consumption of larger fish and birds. It is therefore not clear from food preferences what causes the difference in BMF.

In addition to prey exposure level, the food consumption and excretion levels could also impact the BMF. *Vainio* [2022] for example mentions the higher energy consumption of birds compared to fish. However, considering intake and common bird excretion rates (although no specific excretion rates were determined for guillemot) did not lead to an explanation of high PFOS concentrations found in Southern Baltic Proper guillemot [*Holmström and Berger*, 2008]. It is therefore unclear why there is such a large variability in the magnification potential between predators, with similar trophic distance to the main prey. But the results suggest that birds has a higher magnification potential than fish with similar food sources such as seen for cod and guillemot.

Table 6. PFOS predator-prey relationship indicating the biomagnification potential. PFOS egg concentrations from the marine program has been converted to liver concentrations using conversion factors from Table 4.

	Trophic level distance to herring	PFOS BMF	PFOS BMF liver-normalized	ΣPFCA BMF
Cod	0.5-0.7	1.1-3.1	1.1-3.1	1.2-2.8
White-tailed sea eagle	0.3-0.5	22.3-41.8	4.8-9.0	10.1-16.2
Guillemot	0.5	49.9	18.6	10.5

8.2 PFCA

Table 6 presents the herring to predator PFCA BMFs (without conversion of egg concentration to liver). These results suggest a similar magnification of PFCA for cod and even the two birds as that seen for PFOS. A better understanding of the $k_{egg/liver}$ conversion factor for the birds has to be established to narrow down the biomagnification potential.

Figure S 2 shows the relative distribution of PFCA for all biota and Figure 8 focus on the four focus species. A shift is seen in the relative distribution of PFCA homologue across fish and bird species in the order herring → cod → white-tailed sea eagle → guillemot with a relative decrease in the small chain length PFCA (≤C8) and an increase in the longer chain length PFCA (≥11). This is in line with previous findings of increasing bioavailability of long chain PFCAs [*Miranda et al.*, 2022].

For all species in the marine program there is also a high odd/low even chain length distribution for PFCA pairs (PFOA:PFNA, PFDA:PFUnDA, PFDoDA:PFTrDA, PFTeDA:PFPeDA). This has repeatedly been reported for biota [*Bossi et al.*, 2015; *Schultes et al.*, 2019; *Spaan et al.*, 2020]. The distribution is suggested to be caused by two main processes, atmospheric x:2 FTOH degradation and subsequent bioaccumulation [*Ellis et al.*, 2004] with a higher bioaccumulation potential for longer PFCAs [*Miranda et al.*, 2022; *Zhang et al.*, 2019]. The lower chain length are found at higher concentrations in the Greater Baltic Sea water than the long [*Nguyen et al.*, 2017]. The difference in bioaccumulation potential means that the longer chain length should get closer to, or surpass, the concentration of the shorter chain length higher in the food web [*Zhang et al.*, 2019] as seen in Figure 8. Despite the generality of the odd/even PFCA pattern, there is still basin differences in the relative PFCA distribution as best seen for herring (Figure S 2) indicating that the availability of the different PFCAs are changing across the Greater Baltic Sea.

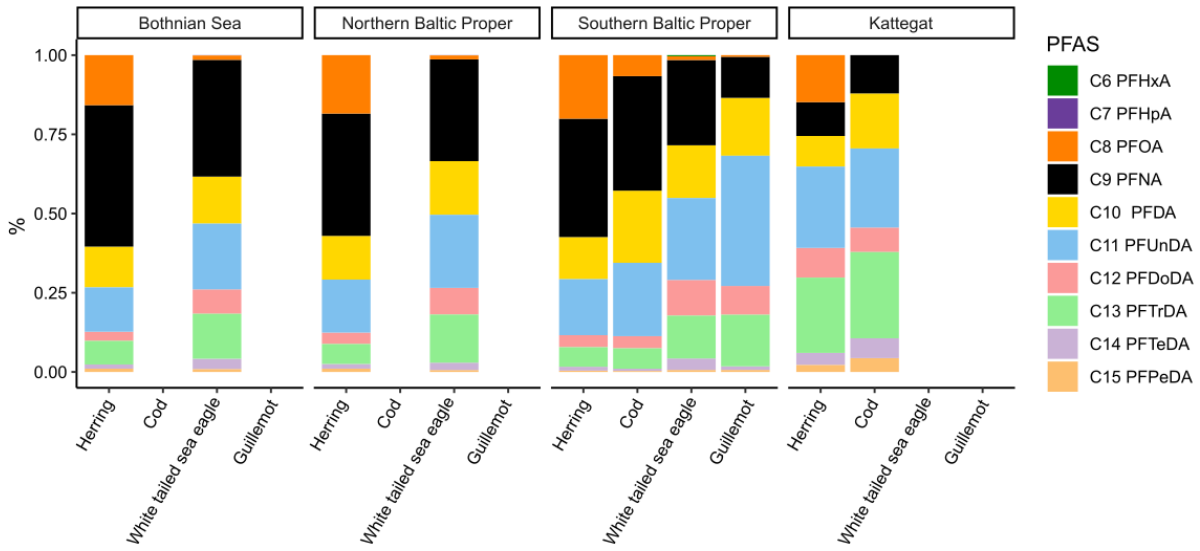

Figure 8. Fractional distribution of PFCAs in fish liver and bird eggs from the monitoring program. The fractional values can be found in Table S 5.

9 PFOS and FOSA distribution

Figure 6 present an overview on the fractional distribution of PFAS. It indicates that the FOSA fraction is higher and PFOS fraction lower in Kattegat compared to the four Baltic Sea basins for some of the species but that the sum of PFOS and FOSA is similar for all basins. In a study focused on PFOS precursors from the southern Baltic Proper, *Gebbink et al.* [2016] found that FOSA contributed 42-85% to the sum of all PFOS precursors. FOSA should therefore be a good indicator of the precursor pattern in the Baltic Sea. FOSA can degrade to PFOS in the water column or in the food web [*Gaillard et al.*, 2017; *Tomy et al.*, 2004], while PFOS is a stable end product. Here we focus on the FOSA to Σ(PFOS+FOSA) fraction and refer to it below as $FOSA_{frac}$ (%). Figure 9 presents a more detailed view on the $FOSA_{frac}$ for the species within the Marine Monitoring Program (Table S 6 provides mean and standard deviations). There is both a geographical difference in $FOSA_{frac}$ as well as an inter-species difference.

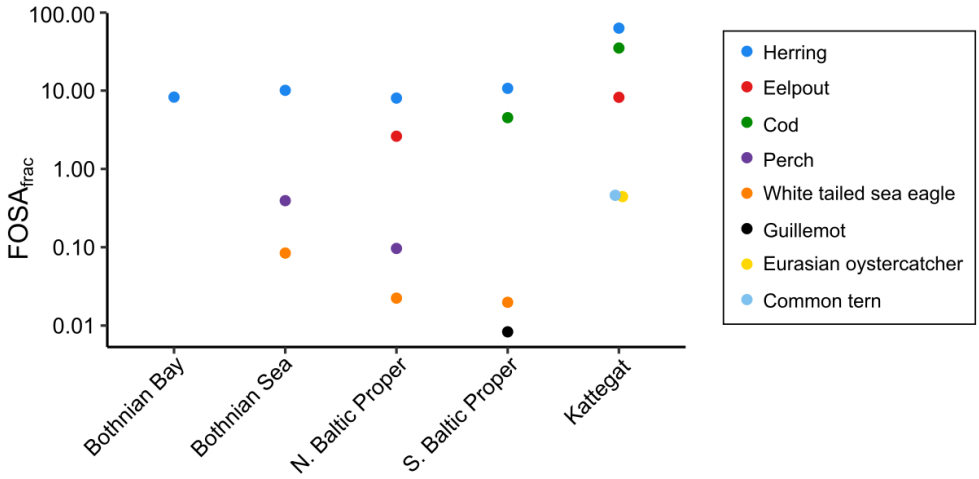

Figure 9. $FOSA_{frac}$ (%) grouped by basins and species based on samples from 2018-2019 [*Soerensen and Faxneld*, 2020]. The graph include <LOQ values but excluding these does not make significant differences to spatial patterns. Mean and standard deviations are found in Table S 6.

9.1 Inter-species FOSA:PFOS distribution

The inter species difference is likely a reflection of preferred prey items for the different species, the trophic level and the ability of the species to transform FOSA and other precursors into the stable end product PFOS. While both PFOS and FOSA has a high potential for bioconcentration (Figure 7), FOSA can also be transformed to PFOS within the food web [*Tomy et al.*, 2004]. Different fish and bird species likely have different abilities to carry out such a transformation as previously reported for marine mammals [*Galatius et al.*, 2013; *Spaan et al.*, 2020]. The $FOSA_{frac}$ is therefore likely to decrease with increasing trophic position, which can explain the decrease of a factor $10\text{-}10^2$ from herring to perch and $10^2\text{-}10^3$ from herring to guillemot and white-tailed sea eagle. For the birds the more efficient transfer of PFOS compared to FOSA from bird to egg will also have an effect on the decrease seen in $FOSA_{frac}$ in our bird egg samples (Table 4). Both cod (5-35) and eelpout (3-8) has a lower $FOSA_{frac}$ than herring (8-63), respectively) but much higher than perch ($FOSA_{frac}$ <0.5). Cod and eelpout have a more diverse diet than herring, consuming

benthic animals and smaller fish (cod also consume herring). The $FOSA_{frac}$ for zooplankton and benthic animals is not well established for the Baltic Sea. *Gebbink et al.* [2016] and *Vainio* [2022] found $FOSA_{frac}$s of ~50% and <7%, respectively while *Vainio* [2022] found $FOSA_{frac}$ for invertebrates including benthic invertebrates of 5-60%. Perch is the only one of the fish species that we know are capable of in vivo transformation of PFOS precursors including FOSA to PFOS [*Gaillard et al.*, 2017]. This ability might be an additional reason to prey preferences that the $FOSA_{frac}$ for perch (<1%) is much lower than for cod (>5%) at the same trophic level. More studies on in vivo transformation and $FOSA_{frac}$ in fish are needed.

The Eurasian oystercatcher and common tern have a $FOSA_{frac}$ a factor 10^2 lower than that of herring similar to that of the other two birds. This makes sense for the common tern that has a diet of fish (see Table S 3) but less so for the Eurasian oystercatcher that forage more on worms and shellfish but also more inland than the other birds. However, the fraction could be affected by the difference in prey for the Eurasian oystercatcher.

The FOSA and PFOS isomer ratios do not show a clear trophic level difference (Figure 11; Table S 4). Some previous studies have found that branched PFOS isomers are selectively degraded and metabolized while linear isomers are selectively enriched via preferential bioconcentration, uptake, and accumulation [*Houde et al.*, 2011; *Shi et al.*, 2018]. The high fraction of *n*-PFOS in fish supports an enrichment to the trophic level of fish (compared to 70% *n*-PFOS in releases [*Houde et al.*, 2011]) but no preferential accumulation is observed from herring to higher trophic levels in the Greater Baltic Sea.

9.2 Intra-species FOSA:PFOS distribution

The geographical difference in $FOSA_{frac}$ seen in Figure 6 and Figure 9 distinguish two regions, the Kattegat and the Baltic Sea (the four easterly basins). For the three fish species (herring, cod and eelpout) for which there are observations in both regions, the $FOSA_{frac}$ increases from 10% to 63%, from 5% to 35% and from 3% to 8%, respectively from the Baltic Sea to Kattegat. The elevated $FOSA_{frac}$ in Kattegat is supported by a $FOSA_{frac}$ for cod of 18±4% from a study on possibly contaminated sites in coastal Kattegat [*Danielsson et al.*, 2014] and a $FOSA_{frac}$ of 50-65% and 20-50% in two studies in coastal Skagerrak (the water connecting Kattegat with the North Sea) [*Green et al.*, 2022; *Valdersnes et al.*, 2017]. Figure 10 show the historic development of the herring $FOSA_{frac}$. The historic data shows that the high $FOSA_{frac}$ has been consistent across the past three decades (at least since 1991) despite changes in PFAS source distribution and concentrations. Figure 10B,C further show a proportional decrease in both PFOS and FOSA in Kattegat since the 1990s. For the Baltic Sea, the historic $FOSA_{frac}$ show some divergence not seen in the present day data. Both the Bothnian Sea and the Northern Baltic Proper had higher historic $FOSA_{frac}$, for the Bothnian Sea the fraction in the 1980s was similar to what is seen in Kattegat today. The higher historic $FOSA_{frac}$ in these basins seems to be driven by a fast increase and later decrease of FOSA compared to PFOS (Figure 10B,C). This could be driven by industry with high FOSA and FOSA precursor (like DiSAmPAP) releases during the 1980s-1990s from for example paper mills located along the Bothnian Bay and Sea coastline [*Kärrman et al.*, 2022].

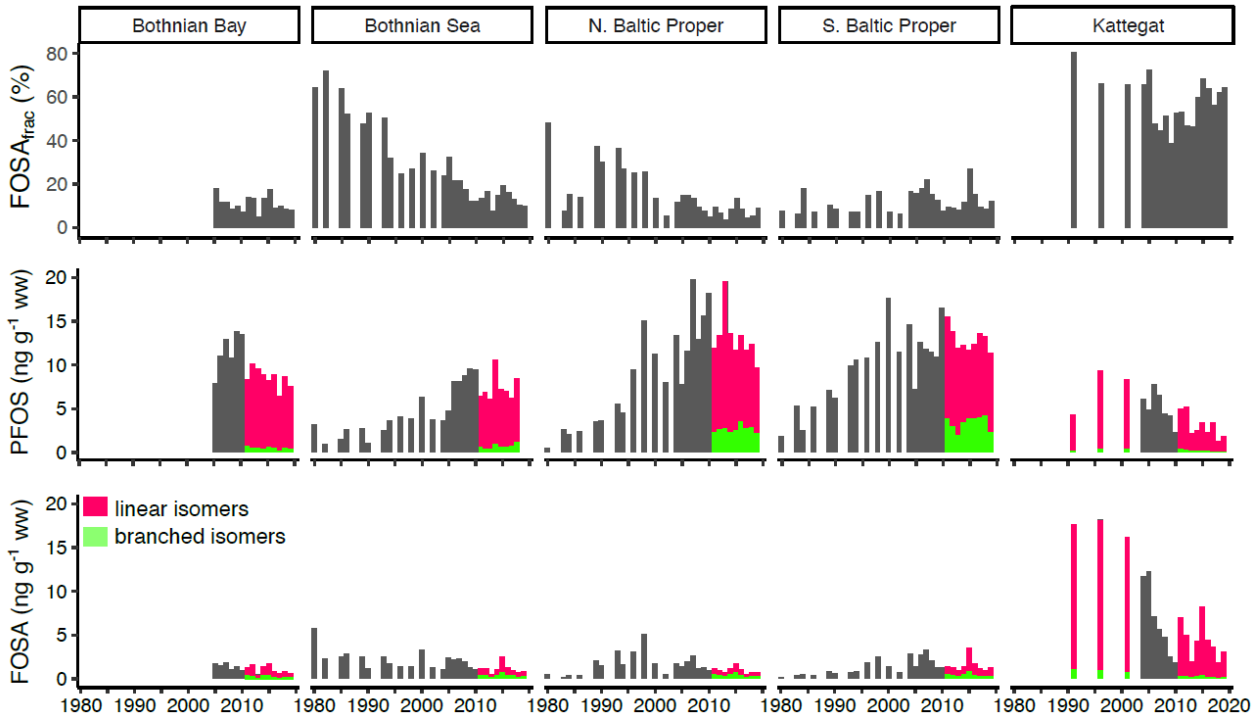

Figure 10. Herring $FOSA_{frac}$, PFOS and FOSA grouped by sub-basin and years with observations. Data for Kattegat from 1991, 1996 and 2001 are from *Ullah et al.* [2014]. Data from Bothnian Sea, Northern Baltic Proper and Southern Baltic Proper from before 2002 is from only one station in each basin (Time Trend Station, see Figure 1) while later data is the average of the multiple stations in each basin that are part of the Marine Monitoring Program.

Since 2011, branched and linear PFOS and FOSA has been analyzed in herring within the Marine Monitoring Program (Table 1; other species from 2011 or 2016). The isomer FOSA concentrations and the *n*-$FOSA_{frac}$ (*n*-FOSA/(*n*-FOSA+*b*-FOSA)) indicate that it is only *n*-FOSA that is elevated in Kattegat compared to the four Baltic Sea basins (Figure 10C; Figure 11). For example, the herring *n*-FOSA is 63-74% in the Baltic Sea and 96% in Kattegat. While there is also a difference in the distribution of the PFOS isomers, the difference between Kattegat and the Baltic Sea is smaller and there is more variability within the Baltic Sea with the Bothnian Bay being similar to Kattegat with 95% *n*-PFOS and the Northern and Southern Baltic Proper being lower with 77-89%. Also for *n*-FOSA Figure 11 indicate the lowest fractions are found in the Baltic Proper.

Elevated FOSA, *n*-FOSA, $FOSA_{frac}$ and (partly) *n*-PFOS and lower PFOS is thus found in Kattegat compared to the Baltic Sea. These differences are not driven by elevated FOSA or lower PFOS in the surface water in Kattegat compared to the Baltic Sea (see chapter 7 [*Nguyen et al.*, 2017], no information on the isomers exist for the water). The FOSA concentration in water in this study was not related to salinity, DOC or latitude while PFOS was positively associated with salinity and population density. Further, this is not a tissue specific issue as muscle studies show the same geographical differences in the distribution [*Faxneld et al.*, 2014a; *Ullah et al.*, 2014]. Previous fish studies have shown an increase in PFOS and other PFAS at higher salinity (summarized in *Bangma et al.* [2022]), which would suggest an increase in PFOS

concentration rather than decrease from the Baltic Sea to Kattegat. An inhibition of *n*-FOSA *in vivo* degradation driven by the increase in salinity could potentially explain the high $FOSA_{frac}$ in Kattegat and the similarity in the Σ(PFOS + FOSA) concentrations across basins. For another precursor, DiSAmPAP, biotransformation through a range of intermediate products including FOSA was observed in freshwater fish and freshwater sediments but not marine sediments [*Benskin et al.*, 2013; *Gaillard et al.*, 2017; *Zhang et al.*, 2018]. Furthermore, a long half-life of EtFOSA was found for marine sediments [*Benskin et al.*, 2013]. Whether *in vivo* FOSA degradation could be specifically inhibited at a certain salinity level should be investigated.

Water from the North Sea and Skagerrak flow into Kattegat below the outflowing low salinity surface water and is then transported along the bottom into the Baltic Proper [*Højerslev et al.*, 1996; *Omstedt et al.*, 2014]. Thus, distinctive water masses are found above and below the halocline in Kattegat [*Yi et al.*, 2012]. The food web uptake of PFAS in water masses originating in the North Sea and carrying different salinity and PFAS concentrations as well as homologue signature than that of the Baltic Sea could explain the discrepancy between observations in Kattegat biota and surface water. This is in line with the conclusion from the BAF results discussed in chapter 7 Bioaccumulation and would further explain the similar $FOSA_{frac}$ signatures between Kattegat cod and those observed in coastal Skagerrak [*Green et al.*, 2022; *Valdersnes et al.*, 2017].

The theories presented here could to some extend be confirmed by PFAS water column profiles in the North Sea, Kattegat and the Baltic Proper. Furthermore, the reason for the difference in the $FOSA_{frac}$ between the North Sea and Baltic Sea water masses, possibly influenced by differences in sources, residence times and salinity, should be investigated further.

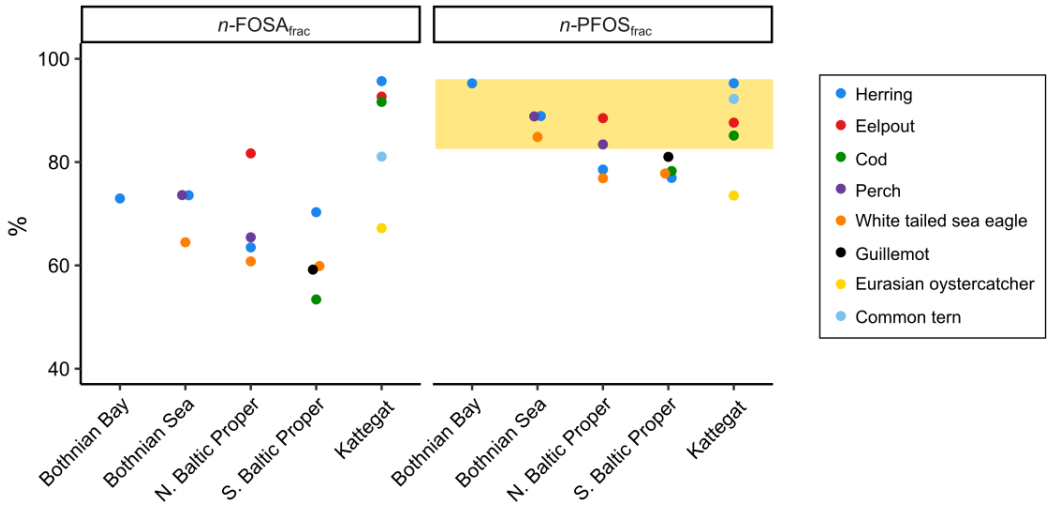

Figure 11. Fraction of FOSA and PFOS found as branched forms grouped by fish species and basin. The yellow square indicates the *n*-PFOS (83-95%) found in fish with a focus on Northern European freshwater or brackish (Baltic Sea) samples [*Ullah et al.*, 2014].

10 Decadal changes in PFAS and homologue distribution

It is important to monitor the effect on environmental concentrations following the voluntary phase-out of perfluorooctane sulfonyl fluoride-based chemistries by industry and the increasing implementation of regulation to control the use and release of PFAS. Despite the phase-out, studies on Baltic biota have not shown a deviation from exponential increases in concentrations of PFAS homologues [*Faxneld et al.*, 2016; *Johansson and Undeman*, 2020; *Schultes et al.*, 2019]. With the inclusion of 2010-2019 data, the time series from the Marine Monitoring Program has been extended compared to previous analysis. Figure 12 shows the decadal change in the PFAS concentration and the change in homologue distribution for herring and guillemot at the Time Trend Stations. PFAS concentrations increase from the 1970/1980s to the 2000s followed by a beginning decrease in the past decade. During the entire period, PFOS (including the precursor FOSA) has been dominant (>60%).

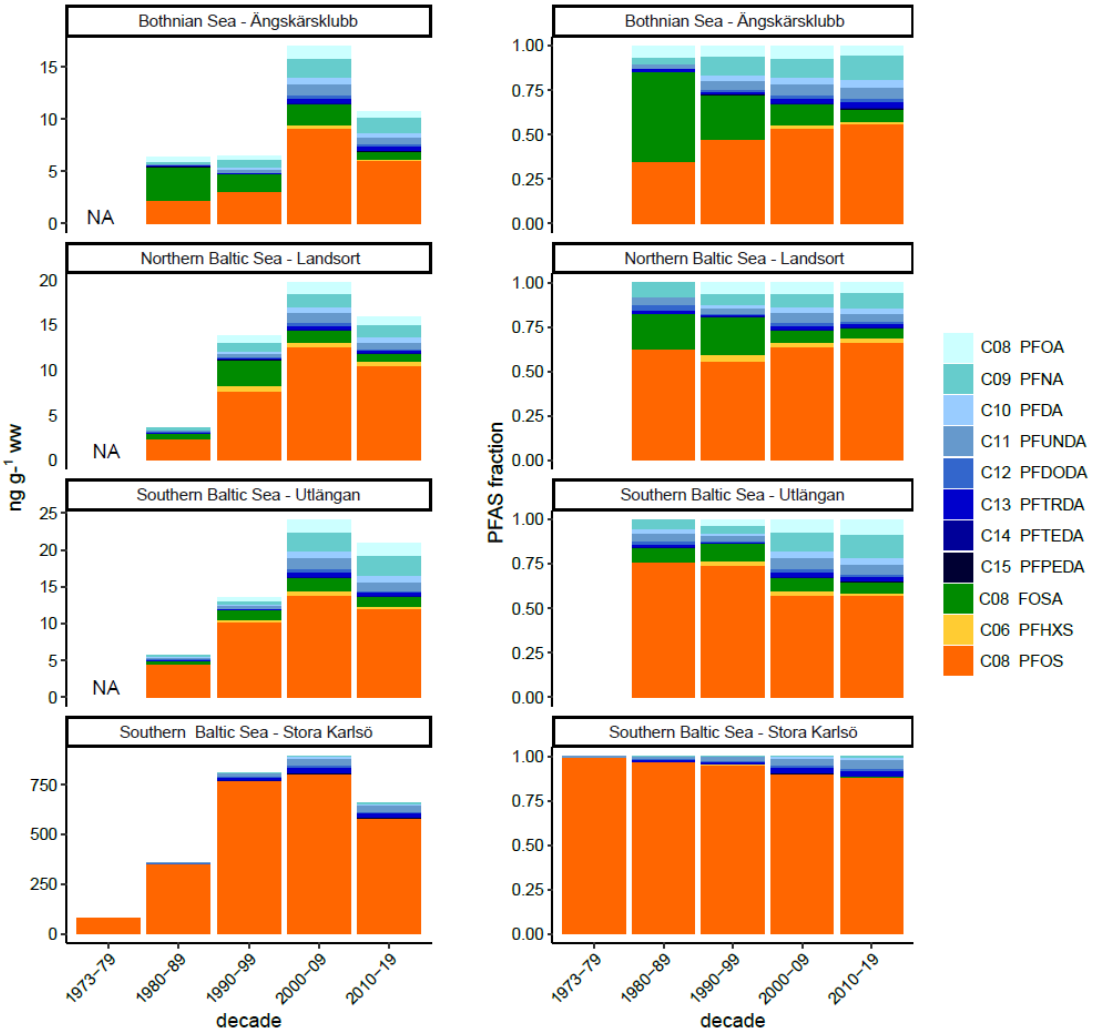

Figure 12. Decadal sum and fractional distribution of PFAS at the Time Trend Stations in the Baltic Sea. Herring: Ängskärsklubb, Landsort and Utlängan; guillemot: Stora Karlsö. No samples were collected for Ängskärsklubb, Landsort and Utlängan prior to 1980. Table S 7 present the values of the fractional distribution (%).

While PFOS is dominant, the PFCA fraction has been increasing until the 2000s and been stable the last two decades for herring. The PFCA fraction increased from 13-18% in the 1980s to 27-37% in the 2000s and 2010s (Table S 5). For the two northern Time Trend Stations, the FOSA fraction has decreased from 20-50% to 5-6%, possibly reflecting the phase-out of direct sources such as paper industries [*Kärrman et al.*, 2022], while it has been stable at Utlängan (Southern Baltic Proper) at 6-10%, maybe reflecting low FOSA entries to the Baltic Proper already in the 1980s. The decadal decrease in FOSA concentrations suggest a reduction in the release of FOSA and its precursors to the Baltic Sea while the decrease in the FOSA fraction likely reflect the longer lifetime of PFOS in the water column than its precursors and that PFOS therefore represents the sum of both legacy precursor and direct PFOS inputs.

In the last decade, the Bothnian Bay show higher PFCA(C12-C14) concentrations compared to the other four basins (Figure 4). *Nguyen et al.* [2017] found that for the discharge of PFCA to the Baltic Sea longer chain lengths were associated with higher latitude indicating higher prevalence in northern areas (only C3-C11 was observed above LOQ due to the low water concentrations of longer chain lengths). Another reason could be a small dilution effect on river concentrations in this basin with low volume and high river discharge. The strong particle binding of the longer chained PFCAs and the high amount of settling organic material from the terrestrial landscape could also result in a removal of these PFCA homologues before they research other basins.

For PFOA, PFNA, PFDA and the PFSA PFHxS, Kattegat has lower concentrations compared to the Baltic Sea (the exception being low PFOA also in the Bothnian Bay) and no increasing trends (Figure 4, Table 7). Homologues with shorter chain-lengths are more water soluble and may therefore be transported through soil and reach water bodies more easily than homologues with longer chains [*Nguyen et al.*, 2017]. The Baltic Sea water column is impacted by terrestrial sources due to the large watershed. In Kattegat the main influence below the halocline is from the North Sea and Skagerrak and the surface water from the Baltic Sea will be transported through Kattegat and into the Skagerrak (see chapter 7 Bioaccumulation and 9 PFOS and FOSA distribution). The North Sea water flowing into Kattegat below the halocline is likely less historically impacted by the shorter chained homologues, which could explain the lower concentrations.

For guillemot, which is found 0.5-1.0 trophic level higher in the food web than herring, PFOS still dominates the PFAS only decreasing from 99% in the 1970s to 88% in the 2000s (Figure 12).

The decadal changes seen for PFAS in the Marine Monitoring Program follow the temporal emission and regulation patterns. However, the lack of any significant loss mechanism for PFSA and PFCA from the Baltic Sea results in a long lifetime [*Faxneld et al.*, 2016; *Johansson and Undeman*, 2020] and a delayed reaction to changes in inputs. Thus, the phase-out of PFOS manufacturing (except from China) and regulations from the early 2000s is only becoming evident in the Baltic Sea biota during the last decade (2010-2019).

11 Change points and trends for individual homologues

While the decadal changes at the Time Trend Stations in chapter 10 give an overview of the general changes in PFAS, a CP analysis can indicate when a change take place in a time series. The CP year indicates a change in the behavior of the temporal observations, but it should be kept in mind that such a change does not have to be an increase that turns into a decrease. Examples of different types of trends before and after a CP year are found in Figure 13 that highlight the trends associated with the herring Time Trend Stations. Table 7 presents the CP year and statistics for the Time Trend Stations (trends for the Time Trend Stations as well as a summary of trends from all stations in the five basins). The results suggest different temporal behavior amongst the PFAS homologues in the Baltic Sea basins.

It should be noted that almost all the homologues show significant increasing log-linear trends ($p<0.001$) when investigating the entire length of the time series. The discussion below focuses on examining change points and recent trends in the time series. The log-linear trends for the entire time series will therefore not be addressed but the results can be found in Table 7 and *Soerensen and Faxneld* [2020].

11.1 PFSA and FOSA

Significant changes in the time series for PFOS and FOSA are only found for the Baltic Proper herring. However, the best estimate for a CP year for the other time series still gives an indication on when a change is likely to have happened. Both PFOS and FOSA time series have CP years in the 1990s for the Baltic Proper but later (2008-2012) for the Bothnian Sea. The herring muscle time series available for Kattegat (Fladen) from *Ullah et al.* [2014] suggest similar CP years for Kattegat and the Baltic Proper (Table 7). While FOSA show decreases of >2.1% y^{-1} after the CP year in herring in all the long time series, the decrease for PFOS on the other hand is <0.4% y^{-1} for the Baltic Proper stations (Figure 13). This indicates that the phase-out of the perfluorooctane sulfonyl fluoride-based chemistries in the early 2000s had an immediate effect on FOSA in all basins, a result that is supported by its shorter lifetime.

For PFOS, which is more persistent in the environment, the sources and physical removal pathways (due to slow degradation) have had a much large impact in shaping the temporal pattern in the basins. *Ullah et al.* [2014] found that PFOS began to decrease almost immediately in Kattegat after a peak in 2002 and PFOS has had a significant decrease in the herring liver time series at Fladen (Kattegat) since it was included in the Marine Monitoring Program in 2005 ($p<0.001$). Ängskärsklubb (Bothnian Sea) also show a rapid change from increasing to decreasing trends in concentrations after the CP year in 1997. Landsort (Northern Baltic Proper) and Utlängan (Southern Baltic Proper) on the other hand has stayed at a plateaued since the CP year (1995-1998, trend -0.4% y^{-1} to 0.1% y^{-1}) (Table 7). Kattegat exchanges water with the North Sea through Skagerrak [*Omstedt et al.*, 2014]. Once local sources started decreasing due to the phase-out, the exchange of water with the North Sea is likely to have caused a fast reversal of the trend. Similarly, freshwater discharges into the Bothnian Bay and Sea result in an almost unidirectional exchange of water with the Baltic Proper. The lifetime of PFOS in these proportionally smaller basins is therefore likely to be shorter and a decrease in

sources after the phase-out will have had a fast effect on biota concentrations. However, for the Baltic Proper, there are no significant physical loss mechanism for PFOS due to the closed nature of the system. There is a long circulation time with only a slow outflow through the Danish straits. Sediment concentrations of PFAS in the Baltic Proper is also similar to that in Kattegat and the North Sea (North Sea 0.1-0.6 ng g^{-1} dw with decreasing concentrations from 2013-2016 [*Josefsson*, 2022; *Logemann et al.*, 2022]) and thus do not reflect the higher surface water or herring concentrations in the Baltic Proper, suggesting that the sedimentation is relatively slow. This allows for the build-up of PFOS from precursor degradation and result in a long lifetime of PFOS already present in the basin. However, it takes a long time for PFOS to decrease in the Baltic Proper, 33-40% of herring stations in the two basins now show significant decreases over the past 10 years and guillemot has been decreasing significantly since 1996. This suggest that even in the Baltic Proper the effects of the phase-out is now emerging and suggest that the Baltic Proper will get a better environmental status regarding PFOS in the coming decade.

PFHxS is close to or below LOQ especially in the older data and a significant change in the time series is only found for Stora Karlsö (CP year 2001). However, 42% of the herring time series indicate a significant decrease over the last 10 years suggesting that also PFHxS has peaked in the Baltic Sea.

11.2 PFCA

The PFCA(C10-C13) peaked in 2007-2012. For PFUnDA (C11) and PFDoDA (C12) a decrease for most basins is under way as indicated by the fact that >50% of herring time series across the Greater Baltic Sea show significant decreases for the last 10 years. For PFDA (C10) and PFTrDA (C13) less stations (~30%; 0-60% for each basin) has begun to show significant decreases (Figure 13). A delay is seen for PFCA (>C14) with the CP years for PFTeDA (C14) and PFPeDA (C15) suggesting a peak followed by a decrease between 2013-2015 (guillemot data only). The increase in environmental persistency with chain length can explain the slower reaction to the phase-out of the longer chain homologues. Still, the number of stations experiencing significant decreasing trends over the past 10 years suggest that despite a lag, the PFCA(>C14) will also slowly be removed from the Baltic Sea biota over the coming decades.

PFOA (C8) and PFNA (C9) show the most spread in the CP years and trends. The CP years range from 1998 to 2017 and as seen on Figure 13 for PFNA at Utlängan, the increase even continue after the estimated CP year in some cases. For the Time Trend Stations, no significant trends were found for the last 10 years but looking across all stations within the Marine Monitoring Program increases for 17-33% of stations in Northern Baltic Proper for both PFOA and PFNA and 33% in the Bothnian Sea for PFNA are found, with most other stations showing no significant trends. These shorter chained PFCAs are thus still increasing their presence or remaining at stable concentrations in the Baltic Sea biota with especially the increase of PFNA being a concern due to its high toxicity (see chapter 12 Compliance with environmental quality standards (EQSs) and Table 9).

Table 7. Change point (CP) year, log linear regression (including significance level) for the four long time series (1980-2019) and overview at basin level. The slope of the log-linear regression also approximate a yearly percent change. $Trend_{cp-2019}$: log linear regression from the CP year to 2019; $Trend_{all}$: log linear regression for all years in the dataseries; $Trend_{10}$: log linear regression for 2010-2019. The last columns indicate the percent of stations within each basin where herring has a significant trend (decreasing unless otherwise indicated) for the last 10 years. The number of stations per basin is Bothnian Bay: 3, Bothnian Sea: 6, Northern Baltic Proper: 3, Southern Baltic Proper: 5, Kattegat: 3.

PFAS	Basin	Station	Cp_{year}	$Trend_{CP-2019}$ (% y^{-1})	$Trend_{all}$ (% y^{-1})	$Trend_{10}$ (% y^{-1})	# sign $Trend_{10}$ per basin
PFCA	Bothnian Bay						
	Bothnian Sea	Ängskärsklubb	2009	-7.4*	5.7***	-3.6	
	N. Baltic Proper	Landsort	2007	-5.2*	5.7***	-5.5	
	S. Baltic Proper	Utlängan	2007	0.1	7.4***	2.4	
	S. Baltic Proper	St. Karlsö	**2009***	-8.0***	7.1***	-8.3***	
	Kattegat						
PFOA	Bothnian Bay						0
	Bothnian Sea	Ängskärsklubb	2009	-2.9	3*	14.1	17%
	N. Baltic Proper	Landsort	2016	-36.2*	4.5***	-7.3	33% up
	S. Baltic Proper	Utlängan	2017	-28.1	7.1***	2.5	0
	S. Baltic Proper [A]	St. Karlsö					
	Kattegat						0
PFNA	Bothnian Bay						0
	Bothnian Sea	Ängskärsklubb	2008	-2.8	6.7***	0.7	17% up
	N. Baltic Proper	Landsort	**1998***	-0.1	6.2***	0.5	33% up
	S. Baltic Proper	Utlängan	2007	1.5	8.5***	4.7	0
	S. Baltic Proper	St. Karlsö	2013	-4.8	7.8***	-2	
	Kattegat						33%
PFDA	Bothnian Bay						33%
	Bothnian Sea	Ängskärsklubb	2010	-14.6*	6.1***	-13.1	33%
	N. Baltic Proper	Landsort	2007	-4.6*	7***	-4.8	0
	S. Baltic Proper	Utlängan	2007	0.6	8.3***	0.7	60%
	S. Baltic Proper	St. Karlsö	2009	-0.5	7.8***	0.1	
	Kattegat						0
PFUNDA	Bothnian Bay						33%
	Bothnian Sea	Ängskärsklubb	**2010***	-17.2***	6.3***	-17.3*	50%
	N. Baltic Proper	Landsort	**2008***	-8.8***	6.1***	-10.6*	33%
	S. Baltic Proper	Utlängan	**2008***	-3.8	5.9***	1.8	60%
	S. Baltic Proper	St. Karlsö	**2007*****	-7*	9***	-6.1	
	Kattegat						66%
PFDODA	Bothnian Bay						66%
	Bothnian Sea	Ängskärsklubb	2012	-23.8***	4.5***	-22.2*	83%
	N. Baltic Proper	Landsort	2011	-15.2***	3.4*	-14.2*	100%
	S. Baltic Proper	Utlängan	2008	-6*	4.7***	-1	40%
	S. Baltic Proper	St. Karlsö	**2009***	-9.1*	8.1***	-10.7***	
	Kattegat						33%
PFTRDA	Bothnian Bay						0
	Bothnian Sea	Ängskärsklubb	**2012***	-20*	6.5***	-12	17%
	N. Baltic Proper	Landsort	2012	-18.6***	5.7***	-12	33%
	S. Baltic Proper	Utlängan	2007	-3.2	7.5***	1.3	40%
	S. Baltic Proper	St. Karlsö	**2008***	-12***	8.6***	-14.9*	
	Kattegat						0
PFTEDA	S. Baltic Proper [B]	St. Karlsö	2013	-20.3*	2.5*	-11.4	
PFPEDA	S. Baltic Proper [B]	St. Karlsö	2015	-27.9	0.2	-2.2	
PFHXS	Bothnian Bay						66%
	Bothnian Sea [A]	Ängskärsklubb					33%
	N. Baltic Proper	Landsort	2016	-35***	0.8	-10.1	0
	S. Baltic Proper	Utlängan	2017	-34.5*	1.4*	-3.6	40%
	S. Baltic Proper	St. Karlsö	**2001***	-5.8***	3.2*	2.4	
	Kattegat [C]						100%
PFOS	Bothnian Bay						33%
	Bothnian Sea	Ängskärsklubb	2012	-16.1*	4.5***	-11.9	17%
	N. Baltic Proper	Landsort	**1998*****	-0.4	5.6***	-4.2	33%
	S. Baltic Proper	Utlängan	**1995***	0.1	3.5***	1.4	40%
	S. Baltic Proper	St. Karlsö	1996	-2.6*	3.7***	4.3	
	Kattegat [D]	Fladen	1997	-5.8***	-1.7	-	33%
FOSA	Bothnian Bay						66%
	Bothnian Sea	Ängskärsklubb	2008	-11.1*	-3.9***	-6.1	40%
	N. Baltic Proper	Landsort	**1995***	-7***	0	-6.3	33%
	S. Baltic Proper	Utlängan	**1998***	-2.1	3.8***	-2	0
	S. Baltic Proper [A]	St. Karlsö					
	Kattegat [D]	Fladen	2000	-16.5***	-10.0***	-	0

[A] The LOQ value is higher than later observations above LOQ due to increased instrument accuracy. [B]Only St. Karlsö (guillemot) station included as herring concentrations are mostly below LOQ. [C]Kullen removed due to many <LOQ values. [D]CP analysis conducted on muscle PFOS measurements from *Ullah et al.* [2014].

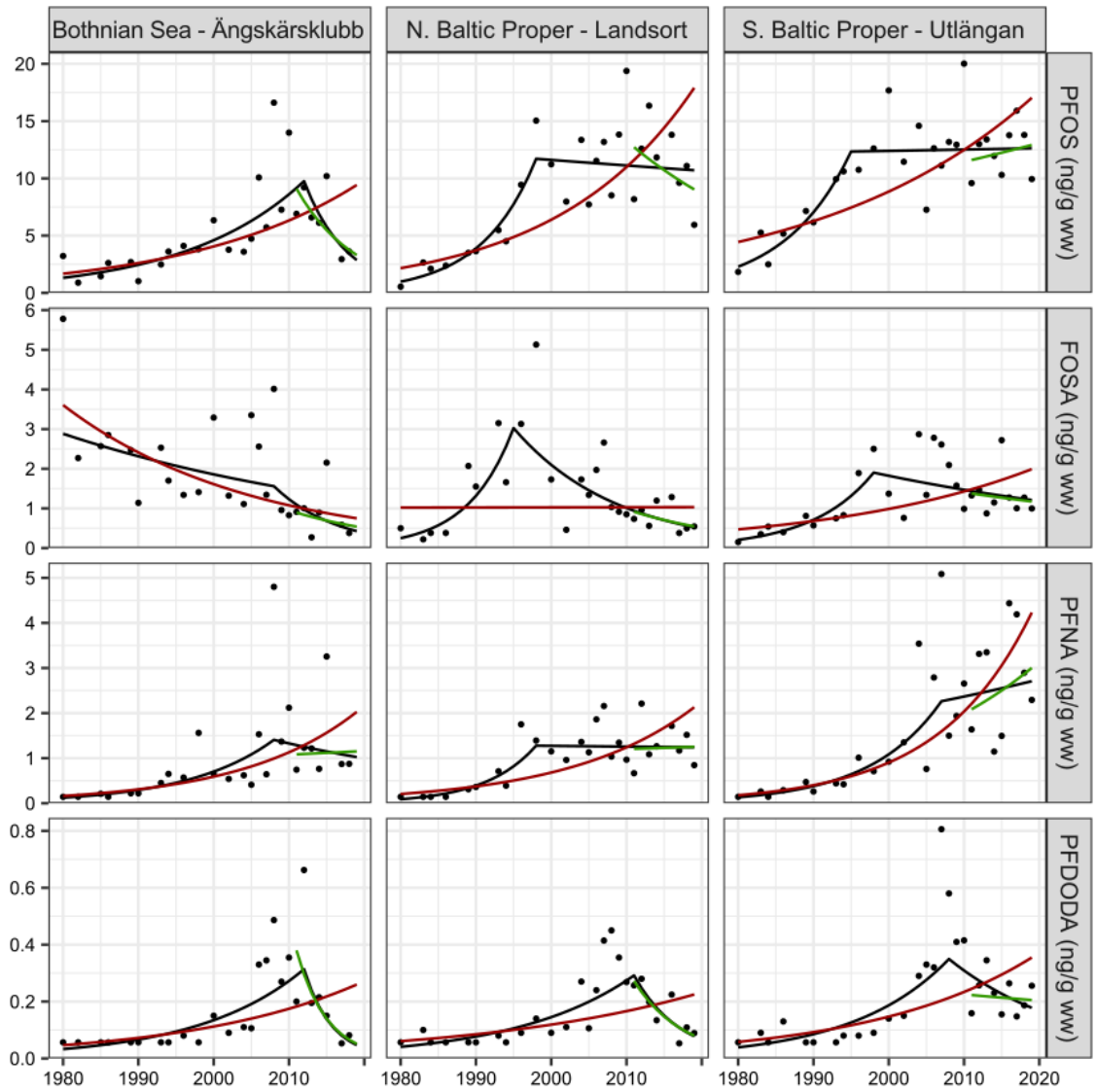

Figure 13. Linear regression (log concentration) and CP analysis for selected PFAS from the three herring Time Trend Stations. Significance levels are found in Table 7. Black line: CP regression, green line: last 10 years regression, red line: total time series regression.

11.3 Comparison to time series studies in the Swedish population

There is a limited number of temporal trend studies on PFAS in water, biota and humans within Sweden and the Baltic Sea [*Haque et al.*, 2023; *Miaz et al.*, 2020; *Nyberg et al.*, 2018; *Sun et al.*, 2019]. Several biota studies have not been able to detect any significant decreasing trends prior to 2013 [*Faxneld et al.*, 2016; *Schultes et al.*, 2019]. In a global review of PFAS trends in the ocean, *Muir and Miaz* [2021] reported declining median concentrations of ΣPFCA(C7-C12) and PFSA in the Baltic Sea since 2003 (last data point 2017) but this was based on only 7 years with observations and the trend looked to be driven by high concentrations during the first observation in 2003. The major problems with assessing temporal trends in water is the lack of systematic sampling at fixed sites and inter-annual variability in river inflow [*Muir and Miaz*, 2021]. Biota smooths out some of the inter-annual variability. Human time series have some of the same qualities but represents different, to a certain extend more global, exposure pathways.

Two human time series from Sweden [*Miaz et al.*, 2020; *Nyberg et al.*, 2018] were more likely to have 1) an earlier CP year and 2) a significant decrease after a CP year compared to the Baltic Sea biota (Table 8). For PFOS, the two human studies have a CP year followed by a decreasing trends in 1988 and 2001. While biota from the Marine Monitoring Program had similar CP year (CP: 1995-1998) concentrations plateaued after the CP year and only in the last 10 years are concentrations beginning to decrease for some stations (Table 7). In humans, there is a decrease in the PFOS precursors (both FOSA and the FOSA precursors) that follows the timeline for the phase out of PFOS [*Miaz et al.*, 2020] resulting in a FOSA CP year for human milk already in 1984 and a decrease to below LOQ for most precursors in serum by 2011. This is similar to the decrease seen across the herring data although the FOSA decrease comes slightly later.

Table 8. Comparison between CP year for herring and guillemot and human samples from Sweden.

PFAS	**CP year** **Herring and guillemot** (Table *7*)	**CP year** **Swedish (Stockholm) human milk**	**CP year** **Swedish (Uppsala) serum**
PFNA	1998, n.s.	2010	2007
PFDA	n.s.	n.s.	2004
PFUnDA	2007-2010	1984	2008
PFDoDA	2009, n.s.	n.s	Not determined
PFTrDA	2008, 2012, n.s.	n.s.	2009
PFTeDA	n.s.		
PFPeDA	n.s.		
PFHxS	2001, n.s.	2004	2010/2011
PFOS	1995, 1998, n.s.	1988	2001
FOSA	1995, 1998, n.s.	1984[A]	2004-2011[B]

[A]data (1972-2015) from *Nyberg et al.* [2018] – FOSA represented by CP for lin-FOSA and br-FOSA
[B]data (1996-2017) from *Miaz et al.* [2020] – FOSA represented by CP in FOSA precursors lin-FOSAA, br-FOSAA, EtFOSA, MeFOSAA, EtFOSAA

For PFCA(C8-C10) the human time series start decreasing right after the CP year in 2008 and 2010 while biota time series continue to increase or have unchanging concentrations. For PFCA(C11-C13) both human and biota samples mostly show significant decreases after the CP year and the CP year are similar for biota and humans (2007-2012) with the exception of a 1984 CP year for human milk. There is no human data on the longer PFCA (>C14). The results indicate that the shorter chain PFCAs are still increasing in Baltic Sea biota but not in humans while the longer chain PFCAs are decreasing in both matrices.

When comparing time series for human and short lived biota (such as fish) it should be considered that the differences in lifetime exposure and metabolism could be important for trends likely resulting in a slower response in humans. Here we see the opposite, with a faster response in humans. The more immediate PFOS decrease in human time series compared to the Baltic Sea biota is likely driven by several factors. The lag time between phase out of PFOS and a response in the form of a decrease in biota is long for the Baltic Sea, especially the Baltic Proper, compared to some other systems [*Johansson and Undeman*, 2020] due to the small water exchange with the North Sea. Human PFAS intake comes from various sources including food, house dust, air and drinking water [*De Silva et al.*, 2021]. Following a phase out, some of the direct sources such as drinking water and house dust could have a more immediate impact on the exposure than seen for ecosystem scale processes in the marine system [*Miaz et al.*, 2020]. Further, the human exposure through fish in Sweden will not necessarily be linked directly to the temporal trend in the Baltic Sea. A part of the fish consumed by the Swedish population are caught in other parts of the world, with a primary import from Norway [*EUMOFA*, 2021]. A different lifetime of PFOS in these ecosystems could result in different exposure patterns for these fish compared to those from the Baltic Sea.

In the case of Sweden and the Baltic Sea, human trends in the Swedish population seems to be a predictor of future changes in the Baltic Sea environment. The lag time between the two matrices is unknown and likely differentiate between different PFAS homologues. Such a lag in the response is similar to the manner that the Baltic Proper trends mimic the two Northern basin trends with a lag time although this lag time is likely shorter than the one to humans (response to phase out: Humans → biota Bothnian Bay and Sea → biota Baltic Proper). For the longer chain PFCAs (C11-C13) and PFOS the biota is already following the human trends and the hypothesis is further supported by the number of stations for these homologues showing significant decrease the last 10 years across the Baltic Sea (Table 7). If this holds up, PFCA(C8-C10) can be expected to peak, plateau and start decreasing in the Baltic Sea in the coming years.

12 Compliance with environmental quality standards (EQSs)

An EQS for PFOS in biota has existed since 2011 but a new PFAS EQS has recently been prepared for consideration by the Joint Research Centre (JRC) [*EU*, 2021]. The new draft EQS dossier for the risk assessment of PFAS includes 24 per- and polyfluoroalkyl substances. It is based on three approaches 1) a relative toxicity approach 2) a key study of the EFSA conclusion on combined exposure of four PFAS and 3) criteria for selection of the 24 PFAS. The proposed EQS is calculated using Relative Potency Factors (RPF). This approach is a way to assess the risk from mixture exposure and is based on rat liver toxicity data or read-across and is described in detail in *Bil et al.* [2021]. Each of the 24 PFAS has a RPF, which has been derived using PFOA as an index compound. Among the selected PFAS are six perfluoroalkyl sulfonic acids, 13 perfluorocarboxylic acids, three perfluoroalkyl ether carboxylic acids, and two fluorotelomer alcohols. The list of all PFAS with their respective RPF is found in Table 9. Only 13 of the proposed 24 PFAS are today analyzed in the Marine Monitoring Program.

The $EQS_{biota,\ hh}$ in the proposed draft EQS dossier for the sum of the 24 PFAS (expressed as PFOA-equivalents) is 77.30 ng kg^{-1} ww (0.077 ng g^{-1} ww) [*EU*, 2021]. The new EQS for the sum of PFAS is an improvement to the already established EQS for PFOS [*EU*, 2013]. In addition to including a wider range of the most common PFAS homologues, it is also based on a more extensive knowledge on PFAS toxicity. This has resulted in a factor of two reduction in the target level compared to the PFOS EQS (Table 10).

Table 9. PFAS selected for the draft EQS dossier [EU, 2021]. Homologues in bold are analyzed in the Marine Monitoring Program. Tissue conversion factors (k) are from *Soerensen et al.* [2023].

Acronym	Relative potency factors (RPF)	$k_{liver/muscle}$
PFBA	0.05	
PFPeA	0.01≤RPF≤0.05*	
PFHxA	0.01	12.9#
PFHpA	0.01≤RPF≤1*	12.9#
PFOA	1	12.9
PFNA	10	14.9
PFDA	4≤RPF≤10*	18
PFUnDA	4	13.9
PFDoDA	3	14.3
PFTrDA	0.3≤RPF≤3*	10.6
PFTeDA	0.3	10.6#
PFHxDA	0.02	
PFODA	0.02	
PFBS	0.001	19.2#
PFPeS	0.001≤RPF≤0.6*	
PFHxS	0.6	19.2#
PFHpS	0.6≤RPF≤2*	
PFOS	2	19.2
PFDS	2*	28.9
6:2 FTOH	0.02	
8:2 FTOH	0.04	
HFPO-DA (Gen X)	0.06	
ADONA	0.03	
C6O4	0.06*	

* Based on read-across

Indicate that there is no homologue specific *k* and the *k* from the homologue closest in chain length to the given homologue is used instead

Table 10. PFOS and PFAS environmental quality standards [*EU*, 2013; 2021]. Standard set according to human health via consumption of fishery products.

	Goal	Target level (µg kg^{-1} ww muscle)
PFOS	EQS human health	9.1
PFAS	EQS human health	0.077

Within the Marine Monitoring Program, biota concentrations have consistently been below the PFOS EQS indicating good environmental status [*Soerensen and Faxneld*, 2020]. However, the new PFOS EQS is much more restrictive. The 13 homologues currently analyzed within the Marine Monitoring Program were used to investigate how Baltic Sea fish (herring) concentrations compare with the proposed sum-PFAS EQS. Since concentrations are measured in liver in the Marine Monitoring Program, liver concentrations were first converted to muscle concentrations using conversion factors for single homologues from *Soerensen et al.* [2023] and then multiplied with their respective RPFs (only values above LOQ were included in the RPF calculations). The sum of the 13 recalculated homologue concentrations produce a sumPFAS-equivalent for muscle.

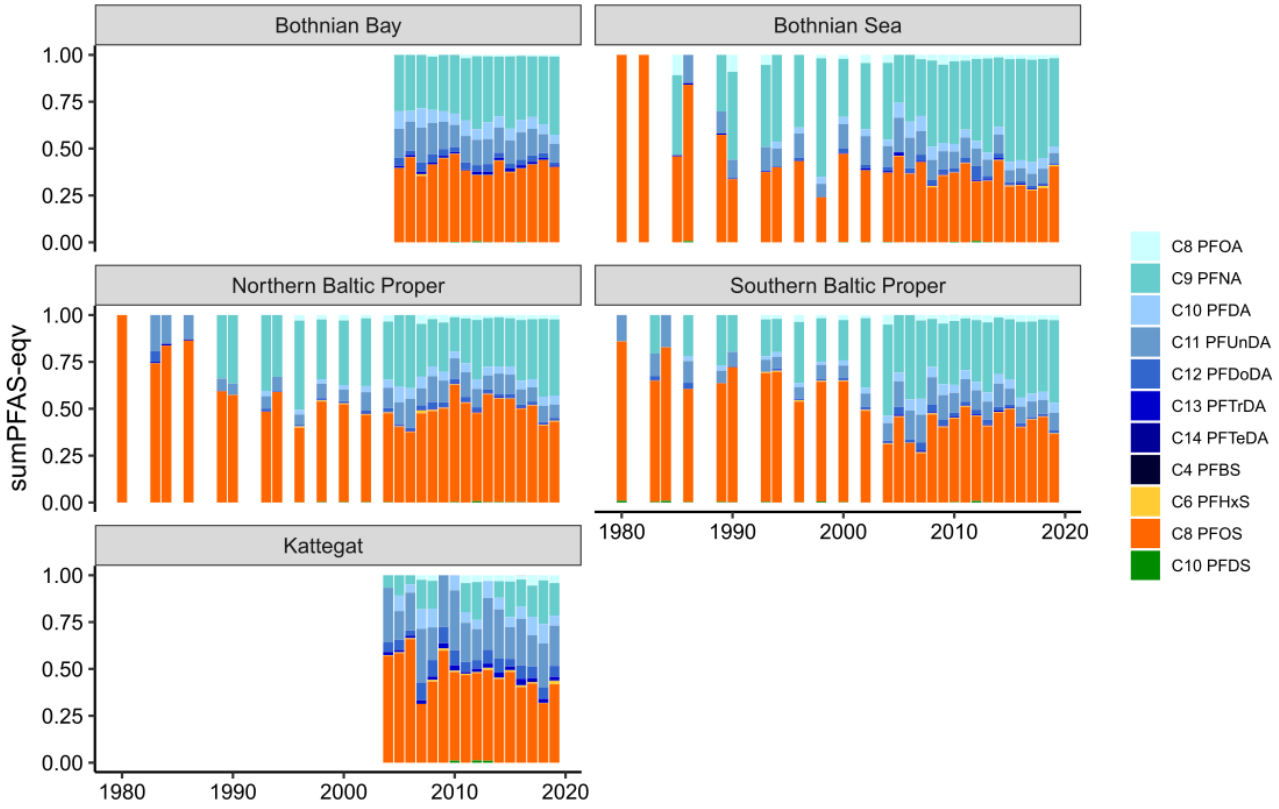

Figure 14. Fractional distribution of the PFAS-equivalence for the individual homologues. Data from Bothnian Sea, Northern Baltic Proper and Southern Baltic Proper from before 2002 is from only one station in each basin (Time Trend Station, see Figure 1) while later data is the average of the multiple stations in each basin that are part of the Marine Monitoring Program.

Table 11 present the sumPFAS-equivalents for herring and perch and the new proposed $EQS_{biota, hh}$. Even though the monitoring stations represent background conditions with no direct pollution in the Baltic Sea, all stations are well above the proposed PFAS EQS. Herring in Kattegat which has the lowest PFAS concentrations has a sumPFAS-equivalent 5 times above the threshold and perch in the Northern Baltic proper has a sumPFAS-equivalent 230 times above the threshold.

Figure 14 show the contribution of each PFAS homologue to the sumPFAS-equivalence over time. PFNA, PFUnDA and PFOS mostly contribute >80% to the sumPFAS-equivalent, with PFUnDA and PFOS being most important historically in Kattegat and PFNA and PFOS most important in the Baltic Sea. While these three homologues also contribute 70-80% of the PFAS concentration (PFNA: 9-13%, PFUnDA: 4-6%, PFOS: 55-65; Figure 12), the higher toxicity of PFNA and PFUnDA means that they mostly represent >40% of the sumPFAS-equivalent. PFUnDA and to some degree PFOS concentrations are decreasing in the Baltic Sea and can therefore be expected to contribute less to the sumPFAS-equivalent in the coming years (Table 7). On the other hand, PFNA is still increasing at some stations in the Bothnian Sea and the Northern Baltic Proper, while it is stable at others. PFNA are therefore likely to increase in importance for the sumPFAS-equivalent in the coming years.

Table 11. SumPFAS-equivalents (±standard deviation) and comparison to $EQS_{biota, hh}$ for herring and perch. The data has been recalculated from liver values to muscle values using conversion factors in table 4 before being multiplied with their respective RPF (Table 9).

Basin	**sumPFAS-eqv** (ng g^{-1} ww muscle)	**$EQS_{biota, hh}$** (ng g^{-1} ww muscle)	**sumPFAS-eqv/ $EQS_{biota, hh}$**
Herring			
Bothnian Bay	1.84±0.39	0.077	24
Bothnian Sea	2.26±1.99	0.077	29
N. Baltic Proper	2.49±1.27	0.077	32
S. Baltic Proper	3.17±1.24	0.077	41
Kattegatt	0.39±0.32	0.077	5
Perch			
Bothnian Sea	7.31±1.56	0.077	95
N. Baltic Proper	17.7±6.86	0.077	230

13 Other PFAS of possible concern for the Baltic Sea

In the Marine Monitoring Program, 15 PFAS are analyzed regularly (if including linear and branched variations, 19 PFAS are analyzed). However, this is only a fraction of all PFAS that exist in the environment and could pose potential problems. While many of these are not important for the Baltic Sea and detection is further hampered by analytical limitations, there could still be PFAS of relevance not covered by the current monitoring framework. This chapter presents a synthesis of PFAS homologues from the draft PFAS EQS dossier and PFAS homologues detected in the Baltic Sea but not included in the Marine Monitoring Program.

Only ~50 % of the PFAS that are included in the proposed draft EQS are analyzed in the Marine Monitoring Program (Table 12). The compounds in the draft EQS were chosen based on having the most (eco)toxicity data and physico-chemical parameters including analytical methods, the availability of a RPF (see chapter 12 Compliance with environmental quality standards (EQSs)), being the most recent PFAS on the market and being coherence with other directives (the Drinking Water Directive and Ground Water Directive [*EU*, 2021]). According to the draft PFAS EQS dossier, monitoring data from the member states is lacking for six of the 24 PFAS (ADONA, 6:2 FTOH, 8:2 FTOH, C6O4, PFHxDA, and PFODA). These are a subset of the ones not currently in the Marine Monitoring Program. HFPO-DA (Gen X) is another homologue on the list not monitored in Sweden. This compound is under assessment as PBT compound and listed as SVHC (Substance of very high concern). ADONA and HFPO-DA (Gen X) are also included in the Annex I of the FCM Recycled Plastic & Articles Regulation. These homologues thus requires special attention.

Table 12. PFAS homologues included in the proposed PFAS EQS but not part of the Marine Monitoring Program.

Draft dossier	PFAS congeners	Drinking water directive	Ground water directive	mobility	Bioaccumulability
PFBA	Carboxylic acid	yes	yes	mobile	Not likely bioaccumul
PFPeA	Carboxylic acid	yes	yes	mobile	Not likely bioaccumul
PFHxDA	Carboxylic acid	no	yes	Not mobile	Potentially bioaccumul
PFODA	Carboxylic acid	no	yes	Not mobile	No data
PFPeS	Sulfonic acid	yes	no	mobile	Potentially bioaccumul
PFHpS	Sulfonic acid	yes	yes	mobile	Potentially bioaccumul
6:2 FTOH	Telomer alcohol	no	no	PFHxA precursor	No data
8:2 FTOH	Telomer alcohol	no	no	Not mobile (PFOA precurs.)	Potentially bioaccumul
HFPO-DA (Gen X)	Ether carboxylic acid	no	no	mobile	Evaluation of bioaccumul
ADONA	Ether carboxylic acid	no	no	mobile	Not bioaccumul
C6O4	Ether carboxylic acid	no	no	mobile	Not bioaccumul

Table 13 lists PFAS homologues detected in the Baltic Sea that are not currently included in the Marine Monitoring Program. Several of these homologues are also found in the draft PFAS EQS dossier (Table 12), both PFSA and PFCA precursors (PFBA, PFPeA, PFPeS, PFHpS) and novel PFAS (HPFO-DA). Some of the PFAS are so far only found in surface water (PFBA, PFPeA, HFPO-DA) or sediment (PFBA, 6:6

PFPiAs, 6:8 PFPiAs) and are likely not relevant for biota at the moment. Further, while some studies, detect certain homologues in biota, they do not necessarily show up in all studies, suggesting that their presence is still limited (at least in concentrations above the level of detection). As an example, *Kärrman et al.* [2019] screened various matrices in the marine environment but did not find HFPO-DA (Gen X), ADONA, and diPAPs.

It is worth noting that many of the studies listed in Table 13 is focused on pristine sites often using samples from the stations included in the Marine Monitoring Program [*De Wit et al.*, 2020; *Kärrman et al.*, 2019; *Schultes et al.*, 2019]. The detections are therefore not limited to polluted sites but represent a presence in the most pristine sites of the Baltic Sea. Table 12 and Table 13 should in unison be used as a basis for evaluating whether these substances might be relevant to follow more closely in the future through screening or monitoring.

Table 13. PFAS homologues that have been found in various biota or in surface water or sediment in the Greater Baltic Sea. Bold text indicate that the PFAS homologues are part of the draft PFAS EQS dossier.

Class	Detected	Biota	Reference
PFSA and PFCA precursors	**PFBA**	**Surface water** **Sediment**	**[*Joerss et al.*, 2019; *Nguyen et al.*, 2017]**
	PFPeA	**Surface water**	**[*Joerss et al.*, 2019]**
	PFPeS	**Bird egg: guillemot**	**[*Kärrman et al.*, 2019]**
	PFHpS	**Fish liver: herring** **Marine mammal liver: grey seal, harbor seal, harbor porpoise** **Bird egg: eider, white-tailed sea eagle, guillemot**	**[*De Wit et al.*, 2020; *Kärrman et al.*, 2019; *Kratzer et al.*, 2011]**
	DiPAPs	Sediment Zooplankton	[*Gebbink et al.*, 2016; *Kärrman et al.*, 2022]
	diSAmPAP	Sediment	[*Kärrman et al.*, 2022]
FTSA	4:2 FTSA	Sediment* Fish liver: herring	[*Kärrman et al.*, 2022; *Kärrman et al.*, 2019]
	6:2 FTSA	Fish liver: herring, cod	[*Kärrman et al.*, 2019; *Schultes et al.*, 2019]
FTCA	7:3 FTCA	Sediment* Fish liver: herring Marine mammal liver: harbor porpoise	[*Kärrman et al.*, 2019]
FTUCA	FTUCA	Sediment*	[*Kärrman et al.*, 2022]
PFPiA	6:6 PFPiAs	Sediment	[*Joerss et al.*, 2019]
	6:8 PFPiAs	Sediment	[*Joerss et al.*, 2019]
Novel PFAS	PFECHS	Surface water Fish liver: herring, cod, flounder Marine mammal liver: grey seal, harbor seal, harbor porpoise Bird egg: eider, white-tailed sea eagle, guillemot	[*De Wit et al.*, 2020; *Joerss et al.*, 2019; *Kärrman et al.*, 2019; *Vainio*, 2022]
	HFPO-DA (Gen X)	**Surface water**	**[*Joerss et al.*, 2019]**
	11-Cl-PF	Bird egg: guillemot	[*De Wit et al.*, 2020]

* indicates that the presence has only been given at the level of class, not the specific homologue.

PFECHS is an example of a novel PFAS homologue detected in the Baltic Sea but not included in the PFAS EQS draft dossier. It is a cyclic PFSA (C8) and it is the PFAS homologue from Table 13 detected in most studies and matrices in the Baltic Sea. It has been found both in water and at different levels of the food

web. *Joerss et al.* [2019] detected PFECHS in 86% of water samples from the south eastern Baltic Sea coastline. It has furthermore shown up in biota screening studies and research projects in the past years [*De Wit et al.*, 2020; *Kärrman et al.*, 2019; *Vainio*, 2022]. Figure 15 show the concentrations in the species where PFECHS was detected. Similar to what has been observed for PFOS it looks to have a high BMF potential from lower trophic levels to top predators of birds and marine mammals. However, from herring to cod, there is a decrease in PFECHS. It should be noted that while PFECHS is detected in some cases it is not always observed above the level of detection when looked for. It did not show up above level of detection in invertebrate and zooplankton samples and only a few fish samples in the study by *Vainio* [2022] and was further below level of detection for herring in the study by *De Wit et al.* [2020]. Most noticeable was the lack of concentrations above the quantification limit for guillemot eggs in the *Kärrman et al.* [2019] screening study. Given the BMF potential regular screening with a focus on top predators might be the best option for following the temporal development of PFECHS in the Baltic Sea environment.

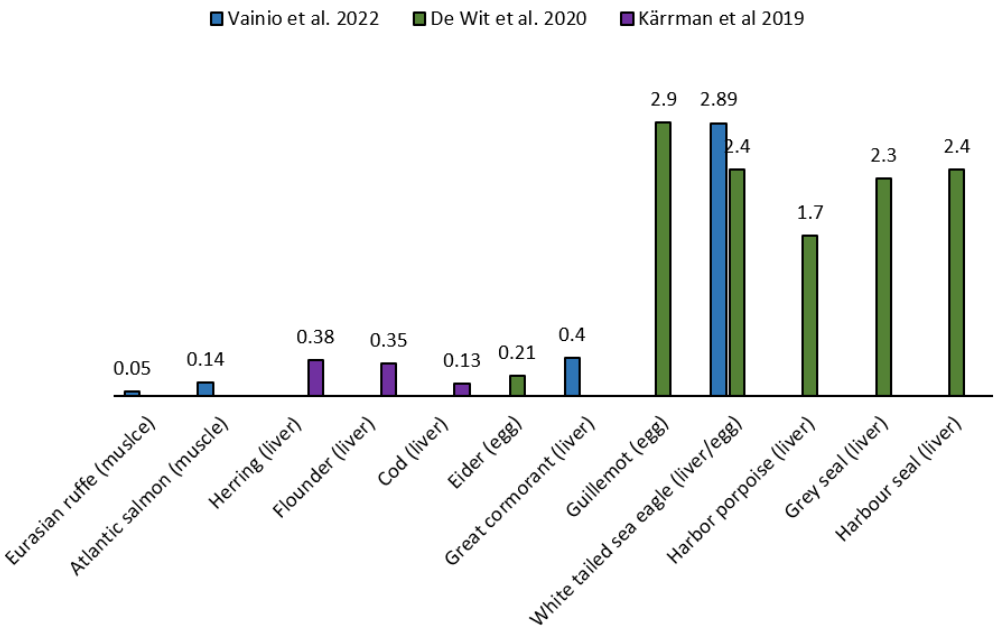

Figure 15. PFECHS (ng g^{-1} ww) detected in Baltic Sea biota. Note the different tissue used for analysis.

14 Conclusion

We find two distinct PFAS profiles in biota with regards to concentration, and homologue and isomer distribution separating the Kattegat basin from the rest of the Baltic Sea. These are linked to different source patterns and water mass lifetimes. North Sea subsurface water entering the Kattegat through Skagerrak likely has a strong influence on the Kattegat biota PFAS profile, while the Baltic Sea biota is more influenced by river discharge from the Baltic Sea drainage basin and atmospheric deposition. In addition to sources, also differences in the lifetime of water masses likely play a role in driving spatial and temporal differences in biota. Water mass lifetimes is shorter in Kattegat and the river impacted Bothnian Bay and Sea compared to the Baltic Proper. This has the effect that regulation and phase-out of PFAS sources are very slow to manifest themselves especially in the Baltic Proper biota. This is evident when looking at the change point analysis of the four Time Series Stations (~40 year) for Baltic Sea herring and guillemot. While the PFOS change point analysis suggest a change in the exponential increase around the time of the phase-out of perfluorooctane sulfonyl fluoride-based chemistries, the PFOS concentrations stayed at a plateau for a long time and it is only in the last decade that significant decreasing trends in the biota PFOS concentration are observed. Over the past four decades, the proportional contribution to the observed PFAS have decreased for FOSA and PFOS and increased for PFCA, showing the impact of regulation and a shift towards alternative substances. For the last 10 year period PFAS observations are available for 26 stations in the Marine Monitoring Program. These observations indicate that for the PFSAs and PFCAs with chain lengths longer than C9 at least some stations are showing decreasing trends for all homologues. PFOA and PFNA are the only homologues that are still showing significant increasing trends at some stations.

We used PFAS water concentrations from across a Greater Baltic Sea offshore transect to calculate BAF from water to herring. PFOS, FOSA and PFDA were shown to have the highest BAF for herring. For PFCA, PFDA has the highest BAF with decreasing BAF for both shorter and longer chain lengths.

An evaluation of a PFAS EQS draft dossier based on new knowledge on PFAS toxicity indicate that the Greater Baltic Sea is not in good environmental status (GES) for any basins. Observed sumPFAS-equivalence are 5 times higher than the EQS for herring in the basins with the lowest pressure and 41 times higher in the basin with the highest pressure. PFOS and PFNA are responsible for the highest pressure on the Baltic Sea system. As PFOS is currently decreasing or stable while PFNA is still increasing at some stations in the Baltic Sea, specific attention should be given to the change in PFNA concentrations in the future. A synthesis of screening and research studies further highlight the presence of PFAS homologues in the Greater Baltic Sea that are currently not part of the Marine Monitoring Program. Some of these are part of the PFAS in the EQS draft dossier and some, like PFECHS, are already seen to bioaccumulate in Baltic biota. The development in their concentrations should be followed, possibly with a focus on top predators.

In January 2023 a broad restriction proposal on PFAS was submitted by authorities in Sweden, the Netherlands, Germany, Denmark and Norway for consideration by European Chemicals Agency (ECHA). If implemented, this initiative could play a vital part in reducing PFAS concentrations and moving towards future GES in the Baltic Sea.

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17 Appendix

Table S 1. Full name and abbreviation of all homologues referred to in the report.

Abbreviation	Full name
PFCA	**Perfluoroalkyl carboxylate**
PFBA	Perfluorobutanoic acid
PFPEA	Perfluoropentanoic acid
PFHxA	Perfluorohexanoic acid
PFHpA	Perfluoroheptanoic acid
PFOA	Perfluorooctanoic acid
PFNA	Perfluorononanoic acid
PFDA	Perfluorodecanoic acid
PFUnDA	Perfluoroundecanoic acid
PFDoDA	Perfluorododecanoic acid
PFTrDA	Perfluorotridecanoic acid
PFTeDA	Perfluorotetradecanoic acid
PFPeDA	Perfluoropentadecanoic acid
PFOCDA	Perfluorooctadecanoic acid
PFSA	**Perfluoroalkyl sulfonate**
PFBS/LFBS	Perfluorobutane sulfonate
PFHxS	Perfluorohexane sulfonate
n-PFHxS	Linear PFHxS
PFHxS Br	Branched PFHxS
PFHPS	Perfluoroheptane sulfonate
PFOS	Perfluorooctane sulfonate
n-PFOS	Linear PFOS
PFOS Br	Branched PFOS
PFOS-99	
PFOS-80	
PFDS	Perfluorodecane sulfonate
n-PFDS	Linear PFDS
PFDS Br	Branched PFDS
PFECHS	Perfluoro-4-ethylcyclohexanesulfonates
FOSAA	**Perfluorosulfonamides**
FOSA	Perfluorooctane sulfonamide
n-FOSA	Linear FOSA
FOSA Br	Branched FOSA
Me-FOSA	N-Methyl-N-(2-hydroxyethyl)perfluorooctanesulfonamide
Et-FOSA	N-ethyl(perfluorooctane)sulfonamide
FOSAA	2-(perfluorooctanesulfonamido) acetic acid
Me-FOSAA	Metyl perfluorooctane sulfonamidoacetic acid
Me-FOSE	N-Methyl-N-(2-hydroxyethyl)perfluorooctanesulfonamide
Et-FOSE	N-Ethyl-N-(2-hydroxyethyl)perfluorooctylsulphonamide
FTSA	**Fluorotelomer sulfonic acid**
4:2 FTSA	4:2 Fluorotelomer sulfonic acid
6:2 FTSA	6:2 Fluorotelomer sulfonic acid
FTCA	**Fluorotelomer acids**
7:3 FTCA	7:3 Fluorotelomer carboxylic acid
8:2 CL-PFESA	8:2 chlorinated polyfluorinated ether sulfonate
diPAP	**Polyfluoroalkyl phosphate diesters**
6:2/6:2 diPAP	6:2/6:2 Fluorotelomer phosphate diester
6:2/8:2 diPAP	6:2/8:2 Fluorotelomer phosphate diester
8:2/8:2 diPAP	8:2/8:2 Fluorotelomer phosphate diester
6:2/10:2 diPAP	6:2/10:2 Fluorotelomer phosphate diester
8:2/10:2 diPAP	8:2/10:2 Fluorotelomer phosphate diester
6:2/12:2 diPAP	6:2/12:2 Fluorotelomer phosphate diester
10:2/10:2 diPAP	10:2/10:2 Fluorotelomer phosphate diester
8:2/12:2 diPAP	8:2/12:2 Fluorotelomer phosphate diester
6:2/14:2 diPAP	6:2/14:2 Fluorotelomer phosphate diester

Table S 2. Limit of detection for the datasets used in this report. For details see the references studies. LOQ: level of quantification, LOD: level of detection, MDL: method detection limit, MQL: method quantification limit, RL: reporting limit which can be either LOQ or LOD or a mix of the two across years.

	Nguyen et al. 2017	Josefsson et al 2022	de Witt et al 2021	Haque et al 2023	Soerensen and Faxneld 2020	Gebbink et al 2016 Zooplankton
	MDL (ng/L)	RL (µg/kg dw)	LOD (ng g ww)	LOQ (ng g ww)	LOQ (ng g ww)	MQL (ng/g ww)
PFBA	0.12	0.1				
PFPEA	0.76	0.1				
PFHXA	0.49	0.08	0.53	0.124-0.143	0.041	0.04
PFHPA	0.27	0.05	0.07	0.035-0.041	0.041	0.1
PFOA	0.087	0.05	0.03	0.035-0.042	0.041	0.01
PFNA	0.03	0.05	0.07	0.035-0.043	0.041	0.05
PFDA	0.03	0.05	0.11	0.124-0.143	0.041	0.001
PFUNDA	0.03	x	0.09	0.124-0.143	0.041	0.008
PFDODA	0.03		0.07	0.124-0.143	0.041	0.001
PFTRIDA	0.03		0.19	0.035-0.043	0.041	0.004
PFTEDA	0.03		0.08	0.124-0.143	0.041	0.1
PFPEDA				0.124-0.143	0.041	0.05
PFOCDA	0.03					
PFBS/LFBS	0.03	0.3	0.1	0.028-0.036	0.036	0.002
PFHXS		0.3	0.62	0.031-0.038	0.039	0.0005
PFHXS L				0.031-0.038	0.039	
PFHXS Br				0.031-0.038	0.039	
PFHPS			0.62			
PFOS	0.03	x	0.19		0.088	
PFOS L					0.088	0.02
PFOS Br					0.039	0.02
PFOS-99				0.118-0.137		
PFOS-80				0.118-0.137		
PFDS		0.3	0.08	0.031-0.039	0.04	0.0003
PFDS L				0.031-0.039	0.04	
PFDS Br				0.031-0.039	0.04	
FOSA	0.03	0.3	0.02	0.033-0.041	0.067	
FOSA L				0.033-0.041	0.067	0.04
FOSA Br				0.033-0.041	0.042	0.007
Me-FOSA	0.03					
Me-FOSE	0.15					
Et-FOSE	0.17					
FOSAA	0.03					0.0008
Me-FOSAA	0.03					0.0001
Et-FOSAA	0.03					0.0004
6:2 FTSA	0.03	0.05/0.08				
PFECHS			0.04			
8:2 CL-PFESA			0.01			
6:2/6:2 diPAP						0.0001
6:2/8:2 diPAP						0.0001
8:2/8:2 diPAP						0.0001
6:2/10:2 diPAP						0.0001
8:2/10:2 diPAP						0.0001
6:2/12:2 diPAP						0.0001
10:2/10:2 diPAP						0.0003
8:2/12:2 diPAP						0.0002
6:2/14:2 diPAP						0.0003

Table S 3. Information on food preferences for species in the marine monitoring program and white tailed sea eagle. References from De Wit et al. [2020],[Funk et al., 2021], [Reindl and Falkowska, 2019], [Österblom et al., 2001].

Species	Food items
Herring	Plankton
Cod	Herring, benthic invertebrates
Perch	Fish
Eelpout	Benthic invertebrates, fish egg, fry, small fish
Eurasian oystercatcher	Worms, shellfish
Common tern	Small fish
Guillemot	Common sprat, Atlantic herring
White tailed sea eagle	Large fish, game, seabirds

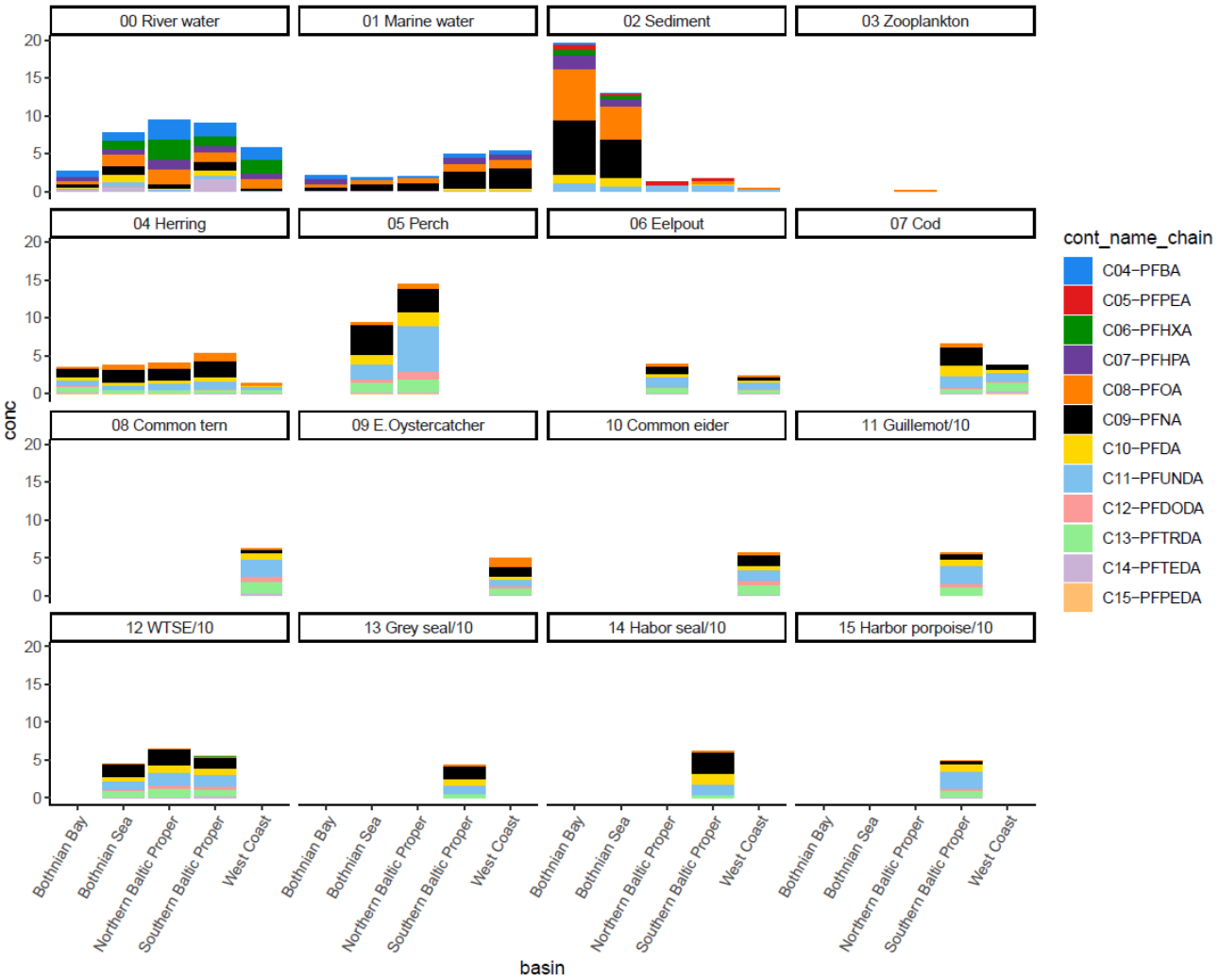

Figure S 1. Concentration of PFCA in source water and biota from the Baltic Sea.

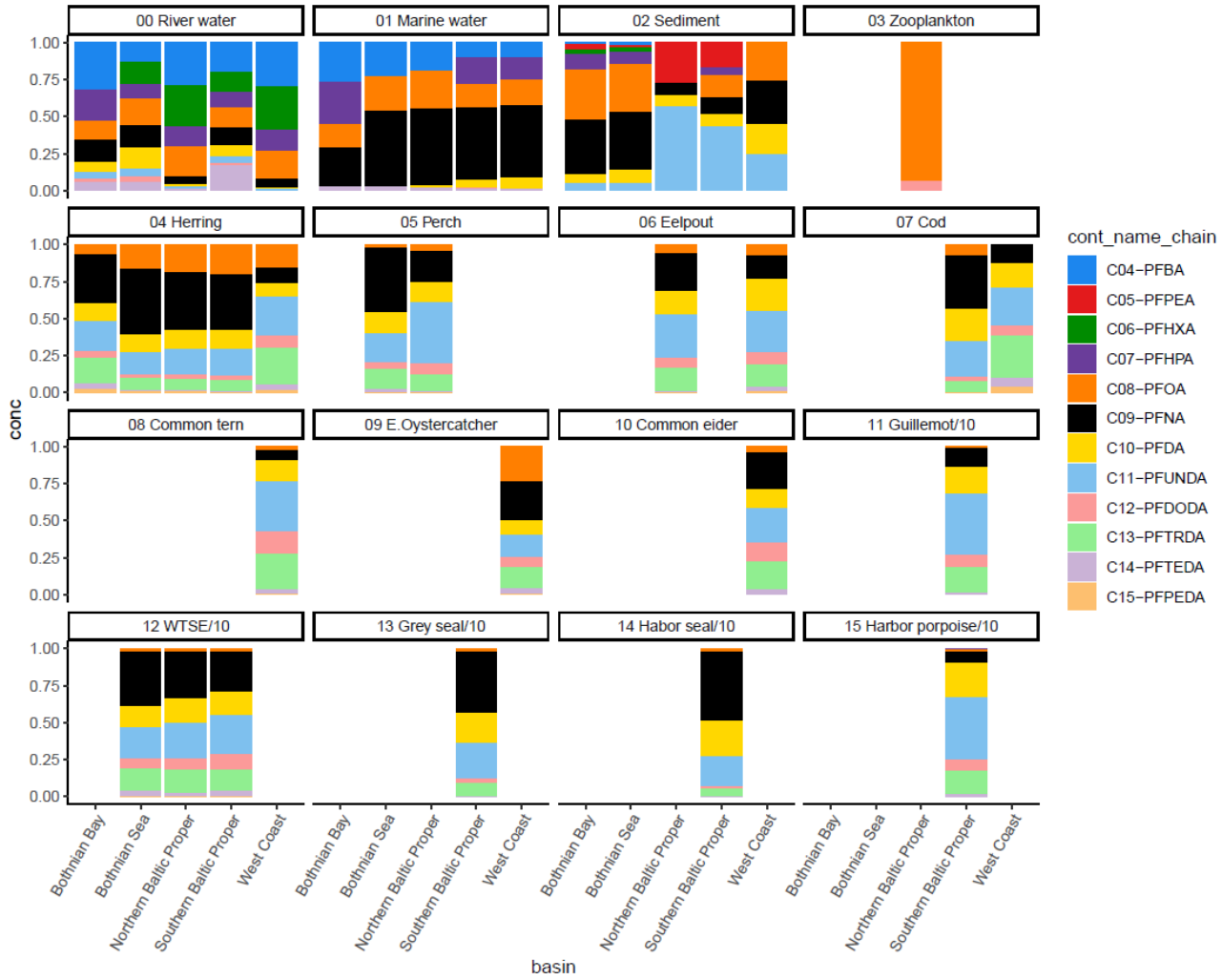

Figure S 2. Relative distribution of PFCA in source water and biota from the Baltic Sea.

Table S 4. The BMF from herring to cod, guillemot and WTSE. In recent years, br-FOSA has been <LOQ for guillemot at St Karlsö and there is therefore no FOSA BMF for guillemot. Primary BMF is calculated by setting values <LOQ to zero, the BMF in parenthesis is calculated by setting values <LOQ to NA and only shown if they differ from the primary BMF.

BFM	l-PFOS	Br-PFOS	l-FOSA	Br-FOSA
Bothnian Sea, herring:WTSE	17.4	20.6	0.14 (0.21)	0.07 (0.26)
Northern Baltic Proper, herring:WTSE	32.9	35.5	0.10 (0.15)	0.09 (0.51)
Southern Baltic Proper, herring:cod	1.2	1.0	0.4	1.1
Southern Baltic Proper, herring:guillemot	53.8	37.9	0 (na)	0 (na)
Southern Baltic Proper, herring:WTSE	25.5	25.2	0.04 (0.09)	0 (na)
Kattegat, herring:cod	2.7	13.9 (5.7)	1.0	2.4

Table S 5. Distribution (%) of PFCA in Baltic Sea biota. Odd-even pairs are indicated in with shading.

Basin	PFCA	Herring	Cod	White tailed sea eagle	Guillemot
Bothnian Sea	C07-PFHPA			0.1%	
	C08-PFOA	15.8%		1.4%	
	C09-PFNA	44.6%		36.8%	
	C10-PFDA	12.9%		14.8%	
	C11-PFUNDA	14.0%		20.8%	
	C12-PFDODA	2.9%		7.7%	
	C13-PFTRDA	7.5%		14.2%	
	C14-PFTEDA	1.3%		3.2%	
	C15-PFPEDA	1.0%		0.9%	
Northern Baltic Proper	C07-PFHPA			0.1%	
	C08-PFOA	18.4%		1.3%	
	C09-PFNA	38.6%		32.1%	
	C10-PFDA	13.8%		16.9%	
	C11-PFUNDA	16.7%		23.1%	
	C12-PFDODA	3.6%		8.4%	
	C13-PFTRDA	6.3%		15.2%	
	C14-PFTEDA	1.5%		2.3%	
	C15-PFPEDA	1.0%		0.6%	
Southern Baltic Proper	C06-PFHXA			0.4%	
	C08-PFOA	20.1%	6.6%	1.2%	0.5%
	C09-PFNA	37.4%	36.1%	26.9%	13.0%
	C10-PFDA	13.3%	22.8%	16.7%	18.3%
	C11-PFUNDA	17.7%	23.1%	25.8%	41.1%
	C12-PFDODA	3.8%	3.8%	11.3%	9.1%
	C13-PFTRDA	6.2%	6.4%	13.5%	16.3%
	C14-PFTEDA	1.2%	0.7%	3.6%	1.1%
	C15-PFPEDA	0.4%	0.3%	0.6%	0.7%
Kattegat	C08-PFOA	14.8%			
	C09-PFNA	10.7%	12.1%		
	C10-PFDA	9.7%	17.4%		
	C11-PFUNDA	25.7%	25.0%		
	C12-PFDODA	9.4%	7.7%		
	C13-PFTRDA	23.8%	27.2%		
	C14-PFTEDA	3.8%	6.3%		
	C15-PFPEDA	2.3%	4.4%		

Table S 6. The fractional distribution among FOSA and PFOS as well as their isomers. Data from 2018-2019 for all species except white tailed sea eagle for which 2021 data is used.

Species	Fraction (%)	Bothnian Bay	Bothnian Sea	N. Baltic Proper	S. Baltic Proper	Kattegat
Herring	$FOSA_{frac}$	8±3	10±4	8±6	11±8	63±14
	n-$FOSA_{frac}$	73±5	74±11	63±19	70±19	96±2
	n-$PFOS_{frac}$	95±2	89±7	79±10	77±11	95±3
Eelpout	$FOSA_{frac}$			3±1		8±2
	n-$FOSA_{frac}$			82±5		93±2
	n-$PFOS_{frac}$			89±2		88±4
Cod	$FOSA_{frac}$				5±1	35±3
	n-$FOSA_{frac}$				53±5	92±1
	n-$PFOS_{frac}$				78±2	85±3
Perch	$FOSA_{frac}$		0.4±0.1	0.1±0.04		
	n-$FOSA_{frac}$		74±13	65±10		
	n-$PFOS_{frac}$		89±1	83±2		
White tailed sea eagle	$FOSA_{frac}$		0.08±0.09	0.02±0.01	0.02±0.01	
	n-$FOSA_{frac}$		64±15	61±12	60±15	
	n-$PFOS_{frac}$		85±3	77±3	78±4	
Guillemot	$FOSA_{frac}$				0.01±0.003	
	n-$FOSA_{frac}$				59±3	
	n-$PFOS_{frac}$				81±1	
Eurasian Oyestercatcher	$FOSA_{frac}$					0.4±0.1
	n-$FOSA_{frac}$					67±8
	n-$PFOS_{frac}$					74±3
Common tern	$FOSA_{frac}$					0.5±0.1
	n-$FOSA_{frac}$					81±2
	n-$PFOS_{frac}$					92±2

Table S 7. Decadal distribution (%) of PFAS at Baltic Sea Time Series Stations.

Station	Species	Homologues	Decades				
			1973-79	1980-89	1990-99	2000-09	2010-19
Ängskärsklubb	Herring	C08-PFOA		7.3%	6.4%	7.4%	5.9%
		C09-PFNA		3.4%	10.7%	10.6%	13.4%
		C10-PFDA			3.0%	4.1%	4.7%
		C11-PFUNDA		2.9%	4.9%	6.1%	6.0%
		C12-PFDODA			1.2%	1.8%	1.9%
		C13-PFTRDA		1.6%	1.5%	2.8%	3.3%
		C14-PFTEDA				0.3%	0.7%
		C15-PFPEDA		0.2%	0.3%	0.2%	0.4%
		FOSA		50.3%	25.2%	11.8%	6.6%
		C06-PFHXS				1.9%	1.8%
		C08-PFOS		34.3%	46.7%	52.8%	55.2%
Landsort	Herring	C08-PFOA			6.6%	6.8%	6.0%
		C09-PFNA		8.6%	6.6%	7.2%	8.6%
		C10-PFDA			1.8%	3.4%	3.4%
		C11-PFUNDA		4.6%	2.7%	5.8%	4.5%
		C12-PFDODA		2.8%	0.7%	1.6%	1.0%
		C13-PFTRDA		2.2%	0.9%	2.3%	2.0%
		C14-PFTEDA			0.4%	0.2%	0.4%
		C15-PFPEDA			0.2%	0.1%	0.3%
		FOSA		19.7%	21.1%	7.1%	5.4%
		C06-PFHXS			3.8%	2.3%	2.4%
		C08-PFOS		62.1%	55.0%	63.3%	65.8%
Utlängan	Herring	C08-PFOA			4.3%	7.9%	9.2%
		C09-PFNA		5.9%	4.2%	10.1%	12.6%
		C10-PFDA		2.2%	1.2%	3.8%	4.2%
		C11-PFUNDA		4.4%	2.8%	6.6%	5.6%
		C12-PFDODA		1.9%	0.6%	1.8%	1.2%
		C13-PFTRDA		1.3%	1.0%	2.7%	2.1%
		C14-PFTEDA		0.7%		0.2%	0.5%
		C15-PFPEDA				0.1%	0.4%
		FOSA		7.8%	9.6%	7.6%	6.0%
		C06-PFHXS			2.6%	2.1%	1.6%
		C08-PFOS		75.7%	73.7%	57.0%	56.6%
Stora Karlsö	Guillemot	C08-PFOA				0.1%	0.1%
		C09-PFNA		0.3%	0.3%	0.5%	1.1%
		C10-PFDA		0.3%	0.5%	1.0%	1.6%
		C11-PFUNDA	0.9%	1.3%	2.1%	4.1%	4.5%
		C12-PFDODA		0.6%	0.5%	1.2%	1.3%
		C13-PFTRDA		0.9%	1.6%	3.1%	3.1%
		C14-PFTEDA			0.2%	0.2%	0.3%
		C15-PFPEDA				0.2%	0.2%
		FOSA				0.0%	0.2%
		C06-PFHXS		0.1%	0.2%	0.2%	0.2%
		C08-PFOS	99.1%	96.4%	94.6%	89.3%	87.6%

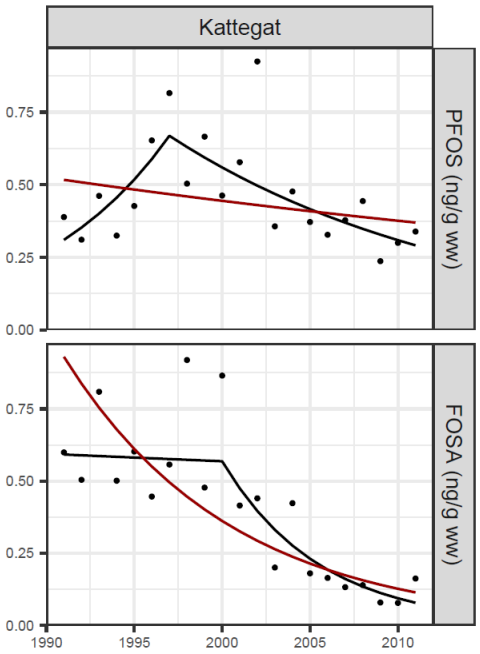

Figure S 3. CP analysis and log linear regression for herring muscle at Fladen (Kattegat) from Ullah et al. [2014]. Black: regression before and after CP, red: regression for the entire data series. Significance level are listed in Table 7.