



# PFOS and other PFASs

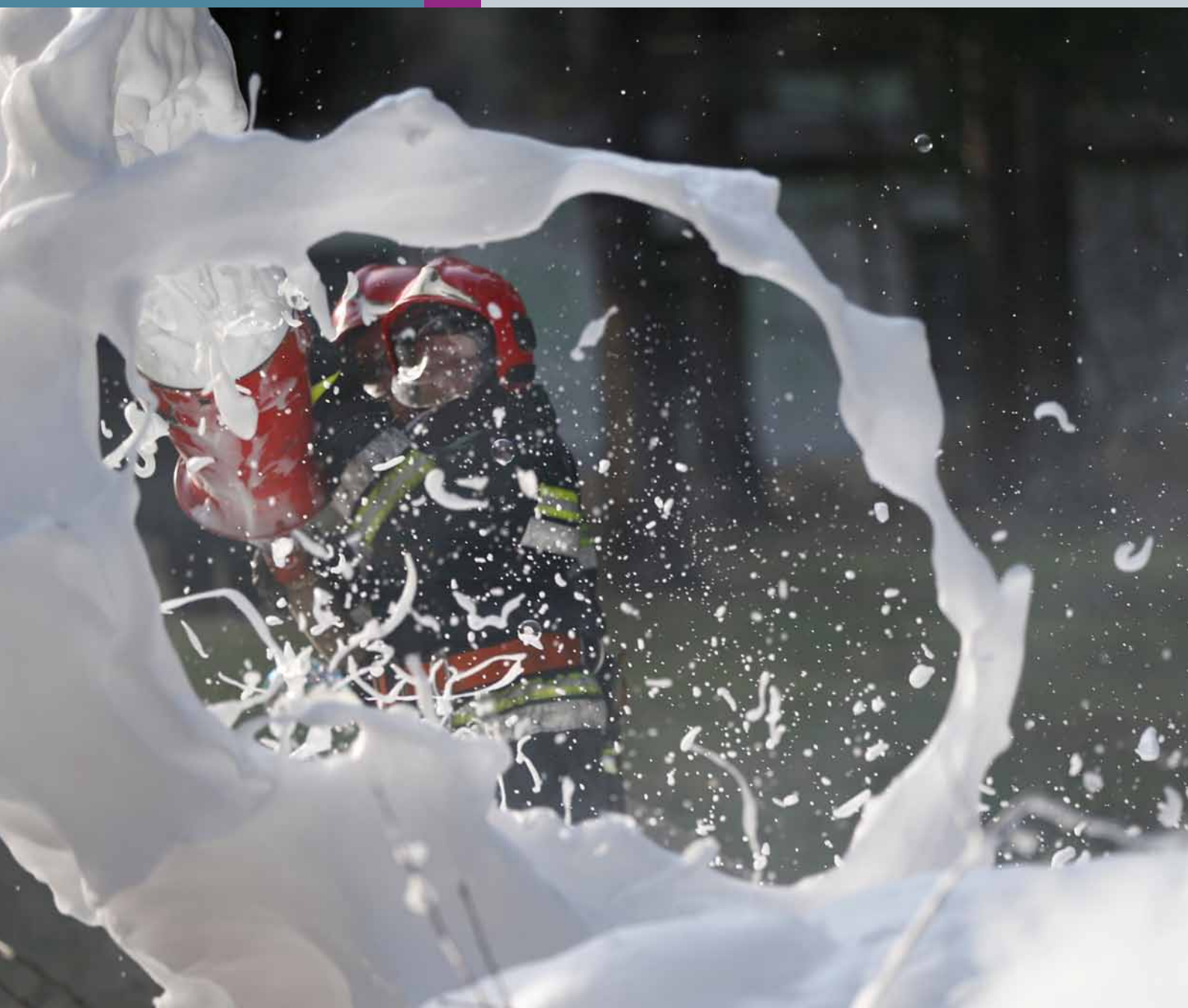
in the Baltic Sea

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Baltic Marine Environment  
Protection Commission

Hazardous substances



BSEP n°173



# Perfluorooctane sulfonate (PFOS) and other perfluorinated alkyl substances (PFASs) in the Baltic Sea – sources, transport routes and trends

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

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

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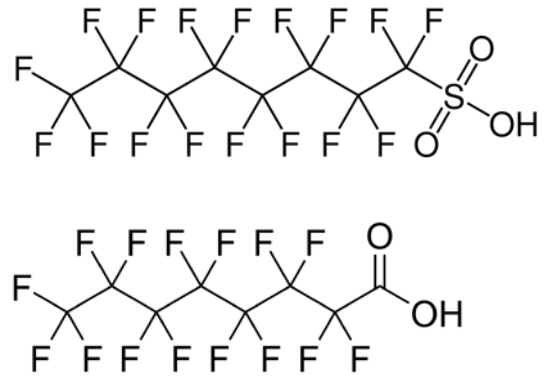
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## Background

As currently defined by the OECD, per- and polyfluorinated alkyl substances (PFAS) are organic chemicals containing at least one perfluorinated carbon moiety (-CF<sub>2</sub>-)<sup>1</sup>. According to recent surveys, over 4000 commercial PFASs are currently on the global market<sup>1,2</sup>. Many PFASs are used as surfactants and surface protectors in industrial and consumer applications. However, the applications and physical-chemical properties of PFASs are diverse, and for many compounds still largely unknown. Due to the high stability of the carbon-fluorine bond, PFASs are expected to be persistent or transform into other persistent PFASs in the environment. Once released into the environment, these chemicals may therefore remain and circulate for a very long time. Knowledge of their use patterns and emissions, as well as hazardous properties and environmental fate, is thus key to understand what risk they may pose to the environment and humans.

Scientific focus has mainly been directed towards understanding properties, environmental occurrence and risk of two sub-groups of PFASs, namely perfluoroalkane sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs), commonly referred to as perfluoroalkyl acids (PFAAs) (see Figure 1)<sup>3</sup>. Long-chain PFSAs (C<sub>n</sub>F<sub>2n+1</sub>SO<sub>3</sub>H, n ≥ 6) and PFCAs (C<sub>n</sub>F<sub>2n+1</sub>COOH, n ≥ 7) have been identified as highly persistent, bioaccumulative, and toxic<sup>3</sup>, as well as widely distributed in the environment<sup>4–6</sup>, biota<sup>7,8</sup>, and humans<sup>9–11</sup>. The high mobility of PFAAs in environmental waters was recently acknowledged as an important contributor to their environmental hazard<sup>12</sup>.

In the following, we review sources and trends of PFASs relevant for the Baltic Sea region. Particular focus is directed at the two most well-studied PFAAs, namely perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).



Molecular structure of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).

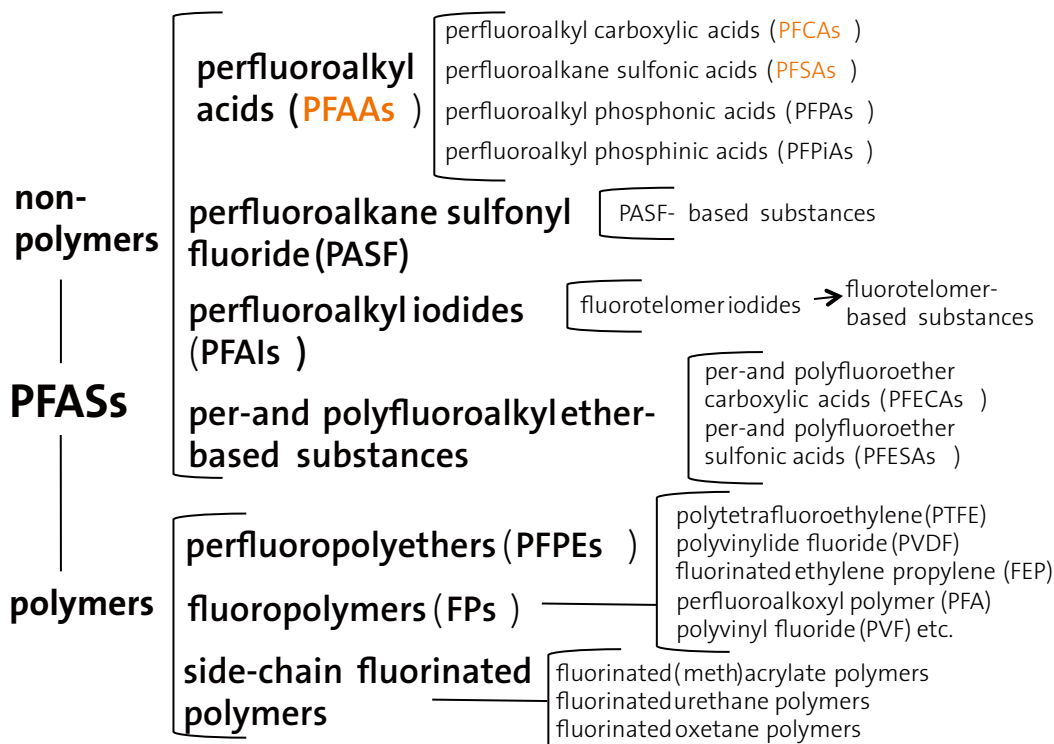


Figure 1. Classification of per- and polyfluoroalkyl substances. Adapted from 3.

## Global production and use of PFASs

PFASs are a large group of substances with diverse properties and uses. Hence their sources to the environment are various. The relative importance of each source is temporally variable, specific to each substance and not well quantified. The following discussion will focus on the major global sources of long-chain PFAAs; sources relevant also for transport to the Baltic Sea as these chemicals are persistent and can be transported over long distances.

Environmental contamination with PFAAs arises both due to emissions of intentionally manufactured PFAAs and due to emissions of other PFASs, which can transform into PFAAs in the environment, so-called precursors. Potential sources of PFAAs, as well as their precursors, include facilities where the substances are manufactured or used in industrial processes (e.g. metal plating, textile industries, manufacturing of fluoropolymers), usage of certain products containing PFASs (e.g. fire-fighting foam, hydraulic oil, ski waxes) and releases at the end of their life cycle (from waste management facilities and waste water treatment plants)<sup>13</sup>.

### PFASs

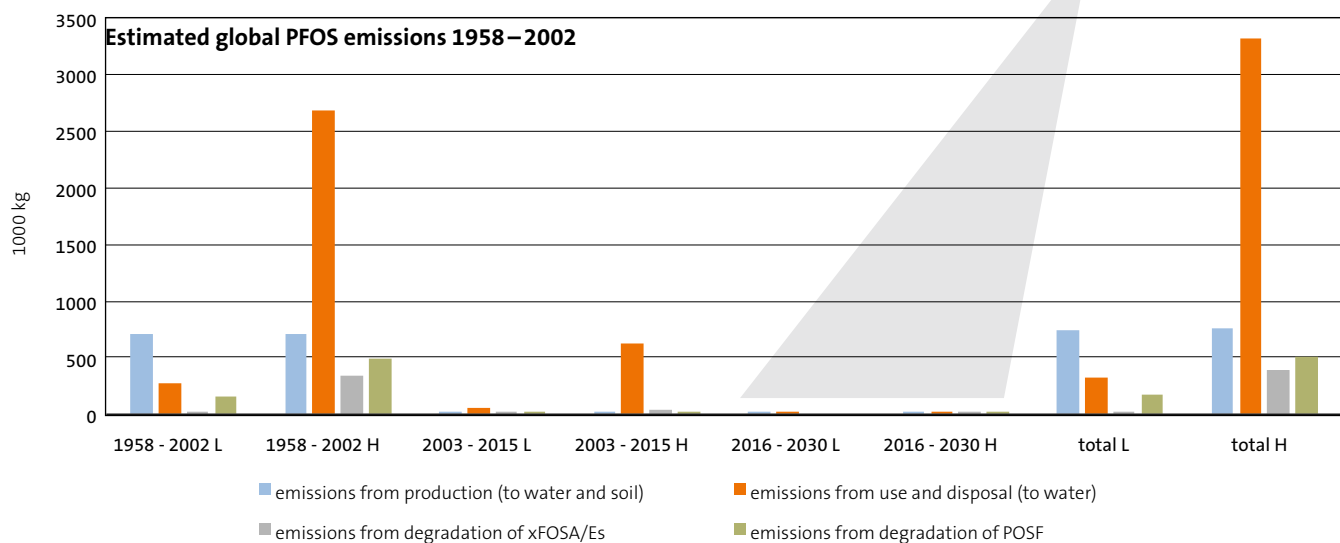
Perfluorooctane sulfonic acid (PFOS) is the PFSA produced in the highest quantity historically<sup>14</sup>. This substance has been used in a wide range of applications, including as a mist-suppressant in metal-plating and as an active ingredient in fire-fighting foam, lubricants and coating formulations<sup>14,15</sup>. PFOS, as well as PFOS-precursors such as perfluorooctanesulfonamides (FOSAs) and perfluorooctanesulfonamido ethanols (FOSEs), are manufactured using the starting material perfluorooctanesulfonyl fluoride (POSF)<sup>14</sup>. The major producer of POSF derivatives (nearly 80% of total production) was the company 3M, with two major production

*PFOS has been used in a wide range of applications, including fire-fighting foams.*



facilities located in the US and Belgium. In addition, six non-3M plants have operated in Europe<sup>16</sup>. 3M started emission reduction measures in 1997 and had phased out manufacture of PFOS, as well as other long-chain PFASs and related precursors, in 2002<sup>16</sup>. After a production history of over half a century, PFOS, its salts and its precursor perfluorooctane sulfonyl fluoride (PFOSF) were listed under Annex B (Restriction) of the Stockholm Convention on Persistent Organic Chemicals in 2009. The listing was recently revised to remove a number of exemptions previously included. The only remaining exemptions are use in certain fire-fighting foams (until the end of 2022) and in metal-plating industries (closed loop systems only)<sup>17</sup>. Manufacture of the insecticide sulfluramid is still included as an acceptable purpose for the production and use of the listed substances<sup>17</sup>. A large proportion of current PFOS precursor emissions globally are attributed to the use of this FOSA-containing insecticide in Brazil<sup>14</sup>.

According to a recent global estimate<sup>14</sup>, emissions of PFOS were historically dominated by direct releases from manufacture, use and disposal (Figure 2). As PFOS production declines, transformation of precursors may instead become the dominant source of PFOS to the environment. Although emissions of PFOS precursors from production sources have declined dramatically since the early 2000s, emissions from use and disposal of products containing the substances still occur<sup>14</sup>. The relative importance of direct releases and precursor transformation for future PFOS emissions will largely depend on the outcome of ongoing efforts to reduce emissions, as outlined by the Stockholm Convention<sup>14</sup>.



**Figure 2.** Estimated global PFOS emissions from different sources between 1958–2002 (when production of PFOS was phased out by the major manufacturer 3M), 2003–2015 and predictions for 2015–2030. L and H = low and high emission scenario, respectively. Note the scale on the y-axis in the bar chart zooming in on 2016–2030. Data extracted from Wang et al 2017.

*PFOA has been used for example in the process of manufacturing teflon.*



Photo: Zlatko Antic/Mostphotos

## PFCAs

Historically, the global emissions of long-chain PFCAs have been dominated by manufacture of perfluorooctanoic acid (PFOA) and fluoropolymers. PFOA and perfluorononanoic acid (PFNA) were used as processing aids in the manufacture of fluoropolymers, while other long-chain PFCAs were often present as impurities in these processing aids<sup>18</sup>. Between 2000 and 2013, major PFOA producers in the US, Japan and Western Europe phased out production of PFOA and substances which can degrade into PFOA, such as fluorotelomer alcohols (FTOHs). Thereafter, production increased rapidly in emerging economies, like China<sup>18</sup>. Import and manufacture of PFOA, as well as substances which can degrade into PFOA, will be restricted under the European Union chemical legislation REACH from 2020<sup>19</sup>. In 2019, it was decided that PFOA, its salts, and substances which can degrade into PFOA will be added to Annex A (Elimination) of the Stockholm Convention, albeit with a number of exemptions<sup>20</sup>.

## Many poorly studied PFASs on the market

The reduction in production and use of long-chain PFASs and PFCAs, has resulted in an industrial transition towards the use of alternative chemicals. Many of these alternative chemicals are also PFASs and may have properties similar to the compounds they replace<sup>21,22</sup>. Hence, there are currently many unregulated PFASs on the market, for which information on their hazardous properties and environmental fate is scarce or even unknown<sup>23</sup>. Recent research has demonstrated that some of these replacement chemicals are persistent, highly mobile and widely distributed in the environment<sup>24-28</sup>.

## Sources and fate of PFASs in the Baltic Sea

PFAAs are generally present in environmental media in the form of deprotonated anions<sup>34–36</sup> as they have acid dissociation constants below one. Because these compounds have high water solubility, environmental waters act both as reservoirs and transport vectors for PFAAs<sup>37,38</sup>. With increasing chain length, their water solubility decreases. Sorption to sediment and soil is thus more important for long-chain PFAAs, whereas short-chain PFAAs are more mobile in the aquatic environment<sup>39,40</sup>. Although, oceanic transport is thought to be the dominant transport pathway for PFAAs on the global scale<sup>37,38</sup>, atmospheric deposition dominates the input to many inland environments, as was demonstrated for e.g. alpine locations<sup>41–44</sup>, background soil<sup>5</sup> and Lake Superior<sup>45</sup>. Mass balances performed in two pristine boreal catchments in Northern Sweden demonstrated that the input of PFAAs via atmospheric deposition exceeded the output via streams<sup>46</sup>. This indicates that a considerable portion of the PFAAs deposited onto background soil is retained and may be released to surface and marine water environments in the future. A review of previously published estimated yearly mass flows of PFOS to the Baltic Sea from WWTPs, rivers and atmospheric deposition is summarized in Table 1.

### Mass balance of PFAAs in the Baltic Sea

In 2013, Filipovic et al. performed a mass balance for the Baltic Sea of PFOS and three PFCAs (perfluorohexanoic acid; PFHxA, PFOA and perfluorodecanoic acid; PFDA)<sup>47</sup>. An important conclusion of their study was that the input of the studied PFAAs to the Baltic Sea exceeds the output, which means that concentrations in the Baltic Sea will increase over time, if emissions are not reduced. The studied PFAAs are largely stored in the water column, which was estimated to contain 78%, 96%, 91% and 46% of the Baltic Sea inventory of PFOS, PFHxA, PFOA and PFDA, respectively. Outflow via the Danish straits was the most efficient output pathway for all studied PFAAs. Sediment burial was an insignificant sink for PFHxA and PFOA (1% and 3%, respectively), while more important as a loss process for the less water-soluble substances (9% for PFOS and 24–32% for PFDA). For PFOS, the input to the Baltic Sea was dominated by riverine discharge (77%), with a lesser contribution from atmospheric deposition (20–21%). For PFHxA, PFOA and PFDA, riverine discharge accounted for 10–73%, 48–59%, 28–67% of the input, respectively. Atmospheric deposition made an important contribution, with 11–37% (PFHxA), 34–43% (PFOA) and 31–72% (PFDA) of total input. A recent study that modelled the input of PFASs to the Baltic Proper<sup>48</sup> confirmed previous findings from Filipovic et al., as it showed that PFOS riverine inflow from the Vistula River and the Oder River is more than three times higher than what is deposited from the atmosphere, while for PFOA, atmospheric deposition exceeds riverine input by a factor of two.



Photo: Tomasz Matuszewski/Mostphotos

*Model estimations have shown that large rivers such as Vistula are important transport routes for PFOS in the Baltic Sea*



## Sources of PFAAs in air in the Baltic Sea region

It is currently not known how much of atmospheric deposition of PFAAs in the Baltic Sea catchment that can be attributed to local versus global (long range atmospheric transport) sources. The European Monitoring and Evaluation Programme (EMEP) has concluded that the data required to estimate this is currently not available<sup>49</sup>. Manufacture and industrial use of long-chain PFCAs has been phased out in the European Union, and thus direct emissions of these substances into air are thought to be small. There are no known current sources emitting PFOS directly into the atmosphere<sup>14</sup>. Direct emissions to air during the use and disposal-phases of PFAA-containing products is also likely negligible, due to the low volatility of PFAAs. Waste incineration has been pointed out as a potential source of PFAAs to air<sup>50,51</sup>, but a lack of published studies on this issue prevents assessment of its relevance. Manufacture and industrial use of PFOA replacements is currently ongoing in Europe (e.g. Germany, the Netherlands, Belgium, the United Kingdom and Italy). The emissions to air from these facilities have not been quantified and the long-range transport potential of any such emissions is unknown. The PFOA replacement GenX has been observed in the environment surrounding a plant located in Dordrecht (Netherlands)<sup>52</sup>. However, it is not clear whether the contamination stems from emissions to air, waterways or a combination of these.

PFAAs that enter the Baltic Sea region via atmospheric long-range transport may stem from transformation of precursors in the atmosphere<sup>14,53</sup> or ocean-to-atmosphere transport on sea spray aerosol<sup>54</sup>. A study using PFOA isomer patterns to elucidate sources of PFCAs in European precipitation<sup>55</sup> concluded that both of these source types, contribute to the observed contamination. However, the relative importance of these sources is not well understood.

*The PFAAs are not volatile but can return from the ocean to the air via sea spray.*

## Sea spray aerosols transport PFAAs from oceans to air

As the global oceans are the major environmental reservoir for PFAAs, an efficient transport vector from seawater to the atmosphere could have major influence on the global circulation of PFAAs. PFOS and other PFAAs present in surface water are not expected to undergo volatilisation<sup>56</sup> but can be transferred into the atmosphere via sea spray aerosol<sup>54</sup>. These droplets of seawater are ejected into the atmosphere when bubbles burst on the ocean surface. The bubbles are formed from air entrained into the ocean by breaking waves. Laboratory studies have demonstrated that PFAAs are highly enriched in sea spray in relation to seawater<sup>54,57,58</sup> and modelling suggests that sea spray-mediated transfer of PFOS to the global atmosphere exceeds emission estimates for other potential sources of PFOS to air by at least one order of magnitude<sup>54</sup>. Although sea spray aerosol undergoes long-range transport, only 2% of the PFAAs aerosolised from the global oceans are estimated to deposit on land<sup>54</sup>. The global oceans are the largest environmental “reservoir” of historically released PFAAs. Since PFAAs are persistent and most PFAAs are not buried in sediments to a substantial degree, sea spray aerosol will act as a continuous source to terrestrial environments long after anthropogenic emissions of PFAAs cease<sup>54</sup>. Predictions of PFOS concentrations in global surface oceans indicate that a slow decline can be expected as a consequence of reduced emissions (see Figure 2 and 3 in Wang et al 2017)<sup>14</sup>. However, in regions affected by substantial downward mixing, surface water concentrations may decline relatively fast<sup>59</sup>.



## Temporal trends of PFASs in air

Temporal trends of concentrations of PFASs in air are assessed as part of the Arctic Monitoring and Assessment Programme<sup>60</sup> and the Global Atmospheric Passive Sampling network<sup>61</sup>. Declining trends of PFOS ( $t_{1/2} = 11$  y) and PFOA ( $t_{1/2} = 1.9$  years) were observed at a station in Northern Norway (2010–2014), while stable levels were observed for PFOS ( $t_{1/2} = 67$  years) and the PFOS precursor perfluorooctane sulfonamide (half-life,  $t_{1/2} = 63$  years) on Svalbard (2006–2014)<sup>60</sup>. However, increasing concentrations of PFOS, PFOA and two fluorotelomer alcohols (PFCA precursors) were observed in the Canadian Arctic<sup>60</sup>. In the Great Lakes region (Canada), declining trends were observed for PFOS, PFOA, PFNA and PFDA in precipitation between 2006 and 2018<sup>62</sup>. No trend was observed for shorter chain PFAAs, which are thus far unregulated in Canada and elsewhere<sup>62</sup>. Declining concentrations or indications of declining concentrations in air have been observed for FOSEs and FOSAs<sup>60,61</sup>.

## Atmospheric deposition

Only three studies relevant to the Baltic Sea region have been published thus far on levels of PFASs in atmospheric deposition. These report on samples collected in Northern Germany (2007–2008)<sup>63</sup>, Northern Sweden (2011–2012)<sup>46</sup> and Southern Sweden (2015–2016)<sup>55</sup>. In the German study, the reported concentration of PFOS and PFOA were 400–9300 pg/L and 100–3300 pg/L, respectively. For PFOA, the two Swedish studies report similar concentrations around 120–1400 pg/L. For PFOS, somewhat lower concentrations were observed in Northern Sweden (<8–160 pg/L) and Stockholm (56–600 pg/L), while concentrations up to 1990 pg/L were observed on the Swedish West coast. This is in line with previous observations from the site on the Swedish West coast, where monitoring of PFOS and PFOA has been performed since 2009 as part of the Swedish national monitoring program. Sea spray aerosol is thought to contribute to the elevated input of PFOS in this coastal site<sup>13,55</sup>. The modelling studies on the Baltic Sea discussed above<sup>47,48</sup> both used the German dataset to calculate the atmospheric deposition of PFASs onto the Baltic Sea. In the more recent Swedish studies<sup>46,55</sup>, lower PFOS concentrations were observed. However, taking these data into account is not expected to alter the conclusion that atmospheric deposition is a minor source of PFOS to the Baltic Sea.

## Riverine discharges

Input to the Baltic Sea via rivers encompasses atmospheric deposition and runoff within the river catchment, as well as point sources within the catchment. River water in the Baltic Sea drainage basin consists almost entirely of shallow groundwater, displaced during rainfall and snowmelt. When washed into the rivers, this water brings PFASs that have been deposited on land<sup>46</sup>. A Finnish research group analysed 23 PFASs in 11 Finnish rivers, selected to represent a range in anthropogenic pressure, from moderate to high with respect to suspected PFAS load<sup>64</sup>. The 11 rivers together represent 62% of the total Finnish riverine discharge into the Baltic Sea. The transport of PFOS from the studied rivers was 10 kg/yr. The discharge of the sum of all studied PFASs into the Baltic Sea was 0.41–18 kg/year for the individual rivers and 76 kg/year in total for all studied rivers. A similar study performed in Sweden<sup>65</sup>, showed that the input of PFOS into the Baltic Sea from 30 monitored Swedish rivers was 105 kg/year. The discharge of the sum of all 13 detected PFASs in the Swedish rivers ranged from 0.23 to 418 kg/year



Photo: Mikael Hjerpe/Mostphotos

*Elevated concentrations of PFOS in atmospheric deposition have been observed on the Swedish West coast.*



Photo: Alexander Malyshev/Mostphotos

*River water in the Baltic Sea drainage basin consists almost entirely of shallow groundwater, displaced during rainfall and snowmelt. When washed into the rivers, this water brings PFASs that have been deposited on land.*

and river, adding up to 1000 kg/year in total. Although a higher total PFAS load was reported from Swedish rivers, the average concentration of total PFASs was similar in the Swedish (10 ng/L) and the Finnish (8 ng/L) rivers.

Absolute concentrations, as well as homologue patterns, were similar across most of the studied Finnish rivers<sup>64</sup>. However, elevated concentrations of perfluoropentanoic acid (PFPeA), PFHxA, PFOA, PFOS and the PFCA precursor 6:2 fluorotelomer sulfonate (6:2 FTSA) were observed in two rivers which flow through a densely populated catchment area in Southern Finland. The concentrations of PFASs in these rivers were especially high in June and July, when input from atmospheric deposition and surface runoff is low and discharges from WWTPs or other point sources are expected to dominate the input. Similarly, the most contaminated Swedish rivers exhibited similar homologue patterns, dominated by PFASs. The spatial trends in homologue patterns observed in both the Finnish study and the Swedish study suggest that rivers in background areas are influenced by similar source types (e.g. atmospheric deposition). It also suggests that one or a few types of sources contribute to elevated levels in waters affected by anthropogenic activities. Rivers in northern Sweden and Finland generally had lower levels of total PFASs compared to rivers in the south. However, this spatial trend was not reflected in total load of PFASs into the Baltic Sea<sup>64,65</sup>, due to the higher water discharge in the North.

The Finnish study reported that the levels of perfluorohexane sulfonic acid (PFHxS), PFOS, perfluorobutanoic acid (PFBA) and PFOA in Swedish rivers were positively correlated with population density. This is in line with previous observations for PFOS and PFOA in other rivers<sup>66-68</sup>, and literature suggesting that WWTPs are major sources of PFASs in European rivers<sup>69,70</sup>. Per capita emissions of 10 mg/year for PFOS and 7 mg/year for PFOA were previously calculated based on data from a survey of 100 European rivers<sup>66</sup>. However, as these samples were collected over a decade ago<sup>71</sup>, the estimated European per capita emissions may

not be representative of current conditions. Furthermore, a modelling study performed on the Danube concluded that estimates of PFOS and PFOA emissions into the river were improved by considering the combined contributions of wealth (based on local gross domestic product) and wastewater treatment technology in addition to human population<sup>68</sup>.

Two modelling studies have performed mass balances of the Oder river, which discharges into the Baltic Sea. According to Filipovic et al.<sup>47</sup>, wastewater treatment plants (WWTPs) make a minor contribution to the total PFAA input to the Baltic Sea and instead atmospheric deposition onto the Baltic Sea catchment is the major source of PFOS and long-chain PFCAs. However, their study did not account for point sources other than WWTPs. Lindim et al.<sup>48</sup> produced a higher estimate of the input of PFOS into the Oder, accounting for contribution from WWTPs, application of sewage sludge on land and atmospheric deposition (onto river surface area only). As Lindim et al. did not present their relative contribution, it is not possible to conclude which of these source types dominate the input into the Baltic Sea.

### Wastewater treatment plants

The emissions via WWTP effluent in Sweden was estimated to 20 kg/year for PFOS and 70 kg/year for the sum of 15 PFASs (Table 1), using data collected between 2006 and 2013<sup>13</sup>. In Finland and Estonia, emissions of PFOS via WWTP effluent was estimated to 12 kg/yr (in 2013)<sup>64</sup> and 1.6 kg (in 2018)<sup>72</sup>, respectively. The total input of PFOS and PFOA into the Baltic Sea via WWTPs was previously estimated to 100 and 200 kg/year respectively, using substance flow analysis<sup>73</sup>. For PFOS, this is consistent with Estonian estimates but lower than Swedish and Finnish estimates. With per capita emissions at Estonian levels (1.2 mg/per/year, see Table 1), the Baltic Sea catchment population of ca 85 million people, would release ca 100 kg PFOS/year into the Baltic Sea, while at Finnish levels (2.2 mg/pers/year) close to 190 kg PFOS/year. According to a recent compilation of data made by HELCOM, higher levels of PFOS were observed in Swedish effluents than in Germany, Denmark and Poland. However, this conclusion is based on few data points, in particular in the case of Poland<sup>74</sup>. Filipovic et al. estimated emissions of PFOS via WWTPs that discharge directly into the Baltic Sea from coastal cities to ca 26 kg<sup>47</sup>, but a recalculation of this number gives only 13 kg PFOS (see Table 1). In their mass balance of the Oder river Filipovic et al. estimated that the amount of PFOS emitted via WWTPs accounts for only 5% of the total mass of PFOS discharged via this river<sup>47</sup>. Based on this finding, in addition to their estimate of WWTP emissions directly into the Baltic Sea, these authors concluded that WWTPs are a minor source of PFOS in the Baltic Sea. However, a recent HELCOM data call<sup>74</sup> indicates that effluent concentrations of PFOS are lower in Poland than in other countries. Consequently, the estimated WWTP emissions to the Oder river may not be suitable for extrapolation to the entire Baltic Sea region.

As part of the Swedish monitoring programme, effluent and sludge is collected from nine municipal wastewater treatment plants yearly. The effluent is analysed for PFASs since 2010, while data on PFASs in sludge have been reported for the time period 2004-2015<sup>76-78</sup>. No time trend analysis has been performed on these data. Nevertheless, declining concentrations are indicated for PFOS, as well as for long-chain PFCAs for some plants. Total organic fluorine analysis, which provides information on how much organic fluorine there is in the sample without identifying the specific compounds that the fluorine is part of (see section on

| ESTIMATED YEARLY MASS FLOWS OF PFOS TO THE BALTIC SEA |                   |                       |               |                      |                                                                                                                                                                   |
|-------------------------------------------------------|-------------------|-----------------------|---------------|----------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                       | Mass flow (kg/yr) | Time period           | Country       | Reference            | Comment                                                                                                                                                           |
| WWTPs                                                 | 26                | 2009 – 2010           | Baltic Sea    | Filipovic et al 2013 | As reported in the publication. Filipovic et al. calculated WWTP emissions from a coastal population of ca 12 160 000 people                                      |
| WWTPs                                                 | 13                | 2009 – 2010           | Baltic Sea    | Filipovic et al 2013 | Corrected by repeating calculation with data from Supplementary Information in Filipovic 2013                                                                     |
| WWTPs                                                 | 44                | 2009 – 2010           | Baltic Sea    | this study           | Mass/PE from Filipovic 2013 multiplied by Helcom PE (population equivalents) data for the entire Baltic Sea catchment, i.e. >80 000 000 (PEs) connected to WWTPs. |
| WWTPs                                                 | 20                | 2006 – 2013           | Sweden        | Hansson et al 2016   | Corresponds to 2.1 mg/pers/year calculated in this study using Swedish population of 9340682 – 9555893                                                            |
| WWTPs                                                 | 12                | 2013                  | Finland       | Junttila et al 2019  | Corresponds to 2.2 mg/pers/year calculated in this study using Finnish population of 5426674                                                                      |
| WWTPs                                                 | 1,6               | 2018                  | Estonia       | EKUK 2019            | Corresponds to 1.2 mg/pers/year calculated in this study using Estonian population of 1319133                                                                     |
| WWTPs                                                 | 100               |                       | Baltic Sea    | COHIBA 2012          |                                                                                                                                                                   |
| Rivers                                                |                   | 2006 – 2007           | Europe        | Pistocchi et al 2009 | Emissions estimated to 10 mg/pers/year                                                                                                                            |
| Rivers                                                | 10                | 2016–2017             | Finland       | Junttila et al 2019  | 11 rivers that contribute 62% of total Finnish river flow                                                                                                         |
| Rivers                                                | 16,1              | 2016-2017             | Finland       | this study           | Junttila et al 2019 upscaled to all Finnish rivers                                                                                                                |
| Rivers                                                | 105               | 2013                  | Sweden        | Nguyen et al 2017    | 30 monitored rivers                                                                                                                                               |
| Rivers                                                | 876 – 952         | 2005 – 2007           | Baltic Sea    | Filipovic et al 2013 | Upscaled from data for rivers contributing 30.7% of total water discharge                                                                                         |
| Atm dep                                               | 238               | 2007 – 2008           | Baltic Sea    | Filipovic et al 2013 | Deposition onto the Baltic Sea surface, atm dep 1070 pg/L and precipitation 236 km <sup>3</sup> /year                                                             |
| Atm dep                                               | 89 – 2074         | 2007 – 2008           | Baltic Sea    | this study           | Filipovic et al 2013 re-calculated with Northern German atm data 400-9300 pg/L and precip 236 km <sup>3</sup> /year.                                              |
| Atm dep                                               | 2 – 36            | 2011 – 2012           | Baltic Sea    | this study           | Filipovic et al 2013 re-calculated with Northern Swedish atm data 8-160 pg/L and precip 236 km <sup>3</sup> /year.                                                |
| Atm dep                                               | 13 – 134          | 2015 – 2016           | Baltic Sea    | this study           | Filipovic et al 2013 re-calculated with Stockholm Swedish atm data 56-600 pg/L and precip 236 km <sup>3</sup> /year.                                              |
| Atm dep                                               | 444               | 2015 - 2016           | Baltic Sea    | this study           | Filipovic et al 2013 re-calculated with West Coast Swedish atm data 1990 pg/L and precip 236 km <sup>3</sup> /year.                                               |
| Atm dep                                               | 1,6 – 22          | 2007–2008, 2011–2012  | Swedish water | Hansson et al 2016   |                                                                                                                                                                   |
| Atm dep                                               | 22 – 290          | 2007–2008, 2011–2012  | Swedish land  | Hansson et al 2016   |                                                                                                                                                                   |
| Fire fighting foams                                   | 10,5              | <2011                 | Sweden        | Hansson et al 2016   |                                                                                                                                                                   |
| Ronneby airport                                       | 2,4               | 2016                  | Sweden        | Koch et al 2019      | Flow from contaminated soil to nearby waterways                                                                                                                   |
| Stockholm Arlanda Airport                             | 0,013             | 2016                  | Sweden        | Koch et al 2019      | Flow from contaminated soil to nearby waterways                                                                                                                   |
| Landfills                                             | 0,2               |                       | Sweden        | Hansson et al 2016   | Emissions to water                                                                                                                                                |
| Landfills                                             | 3,4               |                       | Sweden        | Hansson et al 2016   | Emissions to MWWTPs                                                                                                                                               |
| Non-WWTP sources                                      | 160               |                       | Baltic Sea    | COHIBA 2012          |                                                                                                                                                                   |
| <b>Accumulated emissions and inventories</b>          |                   |                       |               |                      |                                                                                                                                                                   |
| Fire fighting foams                                   | 1000 – 3500       | all years until <2011 | Sweden        | Hansson et al 2016   | Release from Swedish airports until the ban in 2011                                                                                                               |
| Baltic Sea water                                      | 3460              | 2013                  | Baltic Sea    | Filipovic et al 2013 |                                                                                                                                                                   |
| Baltic Sea sediment                                   | 986               | 2013                  | Baltic Sea    | Filipovic et al 2013 |                                                                                                                                                                   |

**Table 1.** Estimated yearly mass flows of PFOS to the Baltic Sea. WWTP = waste water treatment plant, PE = person equivalents

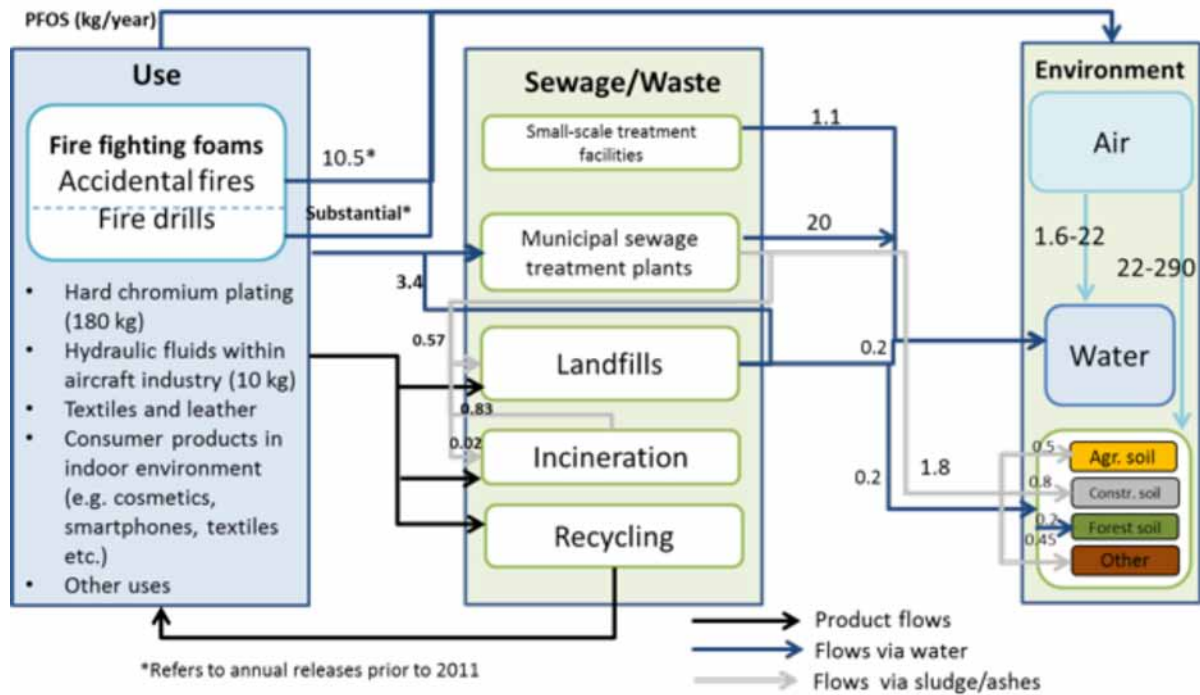


Figure 3. Substance flow analysis for PFOS in Sweden. Figure from 13.

monitoring below) was performed on sludge samples collected in four Swedish WWTPs<sup>77</sup> in order to determine how much of the total organic fluorine the PFASs commonly analysed account for. In these sludge samples, targeted PFAS analysis could account for 5–13% of the total organic fluorine in these samples, indicating that unidentified substances comprise a majority of the total organic fluorine present in WWTP sludge. The proportion of unidentified organic fluorine did not correlate with the number of households served by the WWTP, but seemed to be influenced by industrial input. Higher levels of PFASs have previously been observed in WWTPs receiving industrial wastewater in addition to domestic wastewater<sup>69,76,79</sup>.

Conventional water treatment technologies are largely ineffective at removing PFASs<sup>80</sup>. Furthermore, concentrations of PFAAs may even increase as water passes through a WWTP, i.e. the concentrations are higher in effluent than in influent<sup>81,82</sup>. In three Swedish WWTPs, Eriksson et al. observed a mean mass increase of 83%, 28%, 37% and 58% for PFHxA, PFOA, PFHxS and PFOS, respectively<sup>76</sup>. This phenomenon has been attributed to degradation of precursor compounds into persistent PFAS substances during the wastewater treatment process<sup>81,82</sup>. The hypothesis is supported by observations of declining levels of precursors and intermediates in effluent and sludge in relation to influent<sup>76</sup>. Interestingly, PFOS precursors (such as perfluorooctane sulfonamides and perfluorooctane sulfonamidoacetates) still make a substantial contribution to the overall PFAS levels in Swedish WWTP sludge, although these substances were phased out in the early 2000s<sup>76,77</sup>. Additionally, sludge is an important sink for PFCA precursors, which accounted for on average 67% of the overall loading of identifiable PFASs in Swedish sludge<sup>77</sup>.

When WWTP sludge is applied in the environment as for instance

Waste water treatment plants are transport routes for PFASs. Concentrations of some PFASs may even increase as water passes through a WWTP, a phenomenon attributed to degradation of precursor compounds during the wastewater treatment process.



fertilizer in agriculture, in soil manufacture, or to cover mines and dump sites, it becomes a potential vector for PFAAs and other PFASs (which ultimately degrade into PFAAs) to the environment. Several instances of groundwater and drinking water contamination with PFASs as a consequence of application of sludge or waste-derived soil improver on agricultural land have been identified, such as in the Sauerland region of Germany<sup>83,84</sup>. The relevance of WWTP sludge as a source to the Baltic Sea depends on the degree and geographic distribution of use in the Baltic Sea catchment, as well as on applications and leachate rates from sites of application. In Sweden, environmental releases of PFASs via sludge are estimated to be an order of magnitude lower than emissions via WWTP effluents; for PFOS this means ca 2 kg/year<sup>13</sup>.

### Other point sources

In Sweden, the Environmental Protection Agency has identified over 2000 known or suspected point sources of PFASs to the environment<sup>13</sup>. This geographical survey includes both active points of emission and sites where emissions have occurred historically. Wastewater treatment plants and sites where fire-fighting foam has been used (e.g. airports) make up the majority of the known points of emission (see Figure 3)<sup>13</sup>. Additional sources of potential but unknown importance include landfills and waste management sites, textile and paint industries, metal-plating facilities as well as use of fluorinated ski waxes. Such sources may release PFASs directly into the environment or into wastewater, thereby acting as upstream sources to WWTPs. Screening in surface and ground water impacted by the suspected point sources did in many cases not indicate elevated levels of PFASs<sup>85</sup>. However, considerably elevated levels of PFASs were observed in a lake located adjacent to a hazardous waste management facility<sup>86,87</sup>.

**LANDFILLS.** The total discharge of PFASs (sum of 26 monitored substances) from Swedish landfills was estimated to 0.26–532 kg/year, using data from several screening surveys<sup>13</sup>. The corresponding number for PFOS was 0–134 kg/year (Table 1). Of this, 3.4 kg/year (equal to ca 0.34 mg/pers/year in Sweden) was released to WWTPs and 0.2 kg/year released without treatment to surface water and forests, respectively<sup>13</sup>. A recent study estimated the annual discharge of PFASs from Norwegian landfills to between 3.2 and 110 kg/year (sum of 28 PFASs), corresponding to an average per capita emissions of 3.2 mg/year<sup>88</sup>. These numbers compare well with per capita emission factors from Germany, Spain, China and the United States (0.7–2.2 mg/year)<sup>88</sup>. In the Norwegian study, PFOS contributed with 1–20% to the total PFAS discharge, corresponding to emissions of 0.35 mg PFOS per person and year, which agrees well with the Swedish per capita estimation. While the Norwegian study estimates that 45% of the PFAS emissions are released directly into the environment, the Swedish estimate suggests that only 12% of the total discharges are released into the environment (evenly distributed between surface waters and soil).

**FIRE-FIGHTING FOAMS.** Use of firefighting foam is likely the most important source of PFASs released directly into the environment in Sweden<sup>13,80</sup>. Although PFOS-containing firefighting foams have been totally prohibited in the European Union since 2011 (European Parliament directive 2006/122/EG), the use of foams containing other PFASs has continued due to their effectiveness in putting out fuel fires. Data on emissions due to management of accidental fires is very scarce. Hansson et al. estimated that 150 kg PFOS has been released as a consequence of fire fighting in Sweden 1998–2014 (approximately 9000 fires



Photo: Mostphotos

*Use of firefighting foam is an important source of PFASs released directly into the environment in Sweden.*

recorded)<sup>13</sup>. Based on data from a few commercial and military airport fire training sites, Hansson et al. estimated that approximately 1000-3500 kg PFOS was released from Swedish airports up until the ban on PFOS-containing foam entered into force<sup>13</sup>. In 2016, the yearly flux of PFOS into adjacent rivers was 2.4 kg for Ronneby airport and 0.013 kg for Stockholm Arlanda airport<sup>87</sup>. Measured concentrations of 25 PFASs could explain 39–55% of the extractable organic fluorine (see section on monitoring below) observed in river water samples from Ronneby airport, but only 2–5% of the extractable organic fluorine in corresponding samples from Stockholm Arlanda airport<sup>87</sup>. Approximately half of the historically released PFOS is estimated to remain in the local soil at Stockholm Arlanda airport<sup>89</sup>. The outflow of PFAS from the soil, dominated by leachate into groundwater and subsequent transport to environmental waters, is predicted to decrease by 0.5-1 kg yearly<sup>89</sup>. Although PFOS- and PFAS containing foams were not used in Stockholm Arlanda airport after 2003 and 2011, respectively, no significant decreasing trend of PFASs was observed in adjacent surface waters between 2009 and 2013<sup>90</sup>. This suggests that the contaminated soil in the area may act as a continuous source of PFASs to environmental waters well into the future. Such observations have also been made elsewhere. For example, Filipovic et al. concluded that contaminated soil in a military airfield, abandoned since 1994, still acts as a source of PFASs to the local environment, via leaching into groundwater<sup>91</sup>.

PFAS-containing fire-fighting foams are used on ships in the Baltic Sea by military, coastal guards and likely also commercial shipping companies<sup>92</sup>. However, the emissions from such use have not been quantified.

The releases from non-WWTP sources (mainly the use of firefighting foam on land) into the Baltic Sea watershed was estimated to 160 and 330 kg/year for PFOS and PFOA, respectively (Table 1)<sup>73</sup>. However, these numbers are associated with a high degree of uncertainty as they were estimated using information on usage volumes of PFAS-containing products in the Baltic Sea area. The contribution from contaminated sites to PFAS pollution in the Baltic Sea will depend on e.g. location of the sites, soil type, groundwater hydrology and PFAS contamination level. To our knowledge, no detailed geographic survey has been performed to estimate releases of PFASs into the Baltic Sea from contaminated sites or point sources.



# Monitoring of PFASs in the Baltic Sea

## Most PFASs are not monitored

The PFASs commonly measured in the environment represent a small fraction of the thousands of PFASs in commercial use. A risk of such a narrow scope in monitoring is that important environmental contaminants may go unnoticed. This is illustrated by the discovery that hexafluoropropylene oxide, a substance launched as a replacement for PFOA, currently is the dominant PFAS in the German Bight<sup>93</sup>. Although its presence in the German Bight can be observed in banked samples dating back to 2011, analytical standards and techniques to study this substance have only recently become available.

Despite efforts to inventory all PFASs manufactured<sup>1,2</sup>, it remains challenging to prioritise substances for analytical method development and monitoring. To avert this issue, novel analytical techniques are applied to study a wider range of PFASs in a non-specific way or produce a measure of the total loading of PFASs in sample matrices. An example is analysis of total fluorine or total organic fluorine,<sup>94</sup> using e.g. combustion ion chromatography. When combined with targeted analysis of individual PFASs, measurement of total organic fluorine yields a measure of the contribution from “unknown” PFASs in a sample. Here, the term “unknown” refers to substances which cannot be identified, e.g. due to a lack of tailored compound-specific analytical techniques or reference standards. A survey of PFASs in the Nordic environment was recently published by the Nordic Council of Ministers. This screening effort combined targeted analysis of an extensive list of known PFASs with analysis of the total extractable organic fluorine in a wide range of matrices<sup>95</sup>. The average contribution of known PFASs to the total measured extractable organic fluorine was 8% for surface water, 9% for WWTP sludge, 11% for WWTP effluents, 37% for marine mammals and 42% for marine fish.

## Monitoring within WFD and national monitoring programmes

A suite of PFASs is commonly reported in the scientific literature and included in some of the national monitoring programs in the Baltic Sea area. Generally, 10–30 individual compounds are analysed and a majority of these are PFAAs. Further, PFOS is listed under the Water Framework Directive (WFD) and, as such, included in environmental monitoring programs for surface waters in the EU member states. Within the WFD, the concentration of PFOS in fish muscle should be below the environmental quality standard (EQS) of 9.1 µg/kg wet weight. By applying assumptions on bioconcentration and biomagnification to the biota EQS, a secondary threshold has been derived for water. This value of 0.00013 µg/l should only be used when it is not possible to evaluate an area using the primary biota-based threshold value, and is likely stricter than the corresponding EQS for biota<sup>96</sup>. Between 2011 and 2016, the levels of PFOS in biota were below the EQS in all but one (Merenkurun sisäsaaristo) of the areas monitored by HELCOM<sup>96</sup>. Measurements of PFASs in the Baltic Sea surface water are scarce and were mostly performed in potentially affected coastal areas. These data generally exceed the PFOS EQS set for water<sup>65,96</sup>.

## Spatial differences in Baltic Sea PFAS concentrations

Some general spatial differences in concentrations in the Baltic Sea have been observed. Lower overall PFAA levels were observed in Northern Baltic Sea surface water in comparison to water sampled in Southern Baltic Sea basins<sup>64,65</sup>. In herring liver and white-tailed sea eagle eggs<sup>97,98</sup>, higher PFOS concentrations were observed in the southern Baltic Sea compared to in the Northern Baltic Sea. For long-chain PFCAs fairly uniform levels were observed throughout the Baltic Sea, although the environmental levels are likely influenced by point sources in some areas. It is possible that the spatial concentration differences between PFAS compounds arise because atmospheric deposition is the dominant source for PFCAs, while riverine discharges from densely populated areas in the Southern Baltic Sea catchment is the dominant source for PFOS<sup>97</sup>.

## Temporal trends of PFASs in the Baltic Sea

Sweden is the only Baltic Sea country that has published time trend analyses based on national monitoring data. These are reviewed here, along with trends reported in the scientific literature. A summary of information from other monitoring and screening efforts provided from persons in the HELCOM network is presented in the Appendix. Observed temporal trends of PFASs in the Baltic Sea are summarized in Table 2.

A general increase of PFAAs has been observed in time series recorded since the 1960-80s, both in Baltic Sea biota (e.g. in cod<sup>99</sup>, herring<sup>98</sup>, guillemot egg<sup>98</sup>, white-tailed sea eagle<sup>97</sup> and grey seal<sup>100</sup>) and biota from limnic and terrestrial environments in the region (e.g. peregrine falcon eggs<sup>101</sup>, otter<sup>102</sup>, Arctic char and perch<sup>103</sup>). During recent years (2007-2016), decreasing trends of PFOS were observed in herring liver in two Baltic Sea sampling sites, while no trend was observed in other sampling locations (n = 15)<sup>98</sup>. Insignificant trends were also observed in guillemot eggs (2007-2016)<sup>98</sup>, white-tailed sea eagle eggs (1996-2016)<sup>97</sup>, grey seals (1997-2008)<sup>100</sup>, otters (2002-2011)<sup>102</sup>, peregrine falcon eggs (2000-2007)<sup>101</sup> and cod (2000-2013)<sup>99</sup>. For FOSA, which is a precursor to PFOS, significant decreasing trends have been observed in cod liver (1981-2013)<sup>99</sup>, harbor porpoise (1991-2008)<sup>104</sup>, grey seal (1989-2008)<sup>100</sup> and white-tailed sea eagle (1996-2016)<sup>97</sup>. In herring liver, both decreasing and increasing trends were observed for FOSA between 1980 and 2016<sup>98</sup>. Decreasing trends of PFHxS have been observed in harbor porpoise (199-2008)<sup>104</sup>, grey seals (1997-2008)<sup>100</sup> and, for three sampling locations, in herring liver between 2007 and 2016<sup>98</sup>. Simultaneously, no significant trend was observed in otters (2002-2011)<sup>102</sup> and peregrine falcon eggs (2000-2007)<sup>101</sup>, while an increasing trend was observed in cod liver (2000-2013)<sup>99</sup>.

For PFCAs, several studies report increasing temporal trends over the whole period monitored, but have not specifically analysed trends in recent years<sup>101,104</sup> or have not observed significant trends in recent years<sup>97-100</sup>. In guillemot eggs, decreasing trends were observed for perfluorododecanoic acid (PFDoDA) between 2007 and 2016<sup>98</sup>. In the same time period, decreasing trends were observed in herring liver for some PFCAs at some sites: PFNA, PFDA, perfluoroundecanoic acid (PFUnDA), PFDoDA. Declining concentrations were also observed for PFOA and PFNA in grey seal (1997-2008)<sup>100</sup>. On the contrary, increasing concentrations were observed for long-chain PFCAs in Swedish otters 2002-2011 (PFOA through perfluorotetradecanoic acid) and for in cod liver 2000-2013 (PFDA, PFUnDA, PFDoDA)<sup>99,102</sup>.

The inconsistent trends in PFAA concentrations observed in the Baltic

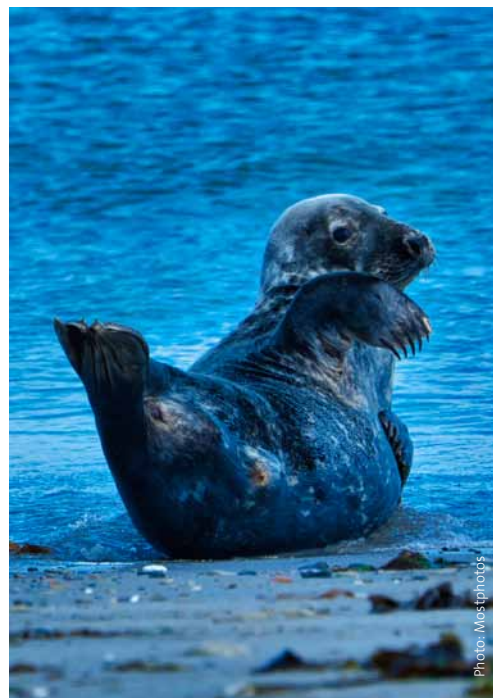


Photo: Mostphotos



Photo: Lukas Kaastner/Mostphotos

*Inconsistent trends in PFAA concentrations in e.g. seals and otters have been observed in the Baltic Sea area during recent years.*

| TIME TRENDS OF PFASs IN BALTIC SEA BIOTA |                             |                                                                                                                                                                                                      |                    |                                                 |                         |                        |
|------------------------------------------|-----------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------|-------------------------------------------------|-------------------------|------------------------|
| PFAS                                     | Matrix                      | Location                                                                                                                                                                                             | Direction of trend | Significance/power                              | Time period             | Reference              |
| PFOS                                     | herring liver               | Ängskärsklubb, Landsort, Utlängan                                                                                                                                                                    | up                 | 5.9%, 7.0%, 4.0% (yearly percentage change)     | 1980–2016               | Bignert et al. Ref 98  |
| PFOS                                     | herring liver               | Fladen, Harufjärden                                                                                                                                                                                  | down               | -8.2%, -3.3% (yearly percentage change)         | 2005–2016               | Bignert et al. Ref 98  |
| PFOS                                     | herring liver               | Harufjärden, Väderöarna; Rånefjärden, Kinnbäcksfjärden, Gaviksfjärden, Långvindsfjärden, Bothnian sea offshore, Lagnö, Byxelkrok, Baltic proper offshore, V hanöbukten, Abbekås, Kullen              | none               |                                                 | 2005, 2007 or 2008–2016 | Bignert et al. Ref 98  |
| PFOS                                     | white-tailed sea eagle eggs | Baltic proper                                                                                                                                                                                        | up                 | 7% (yearly percentage change)                   | 1966–2010               | Faxneld et al. Ref 97  |
| PFOS                                     | white-tailed sea eagle eggs | Baltic proper                                                                                                                                                                                        | none               |                                                 | 2001–2010               | Faxneld et al. Ref 97  |
| PFOS                                     | white-tailed sea eagle eggs | Gulf of Bothnia                                                                                                                                                                                      | up                 | 7% (yearly percentage change)                   | 1969–2010               | Faxneld et al. Ref 97  |
| PFOS                                     | white-tailed sea eagle eggs | Baltic proper                                                                                                                                                                                        | none               |                                                 | 2001–2010               | Faxneld et al. Ref 97  |
| PFOS                                     | grey seal                   | Baltic Sea                                                                                                                                                                                           | up                 | doubling time 6.7 years                         | 1974–2008               | Kratzer et al. Ref 100 |
| PFOS                                     | grey seal liver             | Baltic Sea                                                                                                                                                                                           | up                 | doubling time 4.5 years but more scattered data | 1998–2008               | Kratzer et al. Ref 100 |
| PFOS                                     | otter liver                 | Sweden                                                                                                                                                                                               | up                 | doubling time 13 years                          | 1972–2011               | Roos et al. Ref 102    |
| PFOS                                     | otter liver                 | Sweden                                                                                                                                                                                               | none               |                                                 | 2002–2011               | Roos et al. Ref 102    |
| PFOS                                     | peregrine falcon eggs       | southwest Sweden                                                                                                                                                                                     | none               |                                                 | 2000–2007               | Holmström et al. 101   |
| PFOS                                     | cod liver                   | Baltic proper                                                                                                                                                                                        | none               |                                                 | 2000–2013               | Schultes et al. Ref 99 |
| FOSA                                     | cod liver                   | Baltic proper                                                                                                                                                                                        | down               | half life 15 years                              | 1981–2013               | Schultes et al. Ref 99 |
| FOSA                                     | harbour porposie liver      | German waters of the Baltic Sea                                                                                                                                                                      | down               | not provided                                    | 1991–2008               | Huber et al. ref 104   |
| FOSA                                     | grey seal liver             | Baltic Sea                                                                                                                                                                                           | down               | half-life 18 years                              | 1974–1998               | Kratzer et al. Ref 100 |
| FOSA                                     | grey seal liver             | Baltic Sea                                                                                                                                                                                           | down               | half-life 6 years                               | 1987–2008               | Kratzer et al. Ref 100 |
| FOSA                                     | white-tailed sea eagle eggs | Northern Baltic proper                                                                                                                                                                               | down               | -9.3% (yearly percentage change)                | 2005–2014               | Faxneld et al. Ref 97  |
| FOSA                                     | white-tailed sea eagle eggs | Southern Baltic proper                                                                                                                                                                               | down               | -8.2% (yearly percentage change)                | 2005–2014               | Faxneld et al. Ref 97  |
| FOSA                                     | herring liver               | Ängskärsklubb                                                                                                                                                                                        | down               | -3.3% (yearly percentage change)                | 1980–2016               | Bignert et al. Ref 98  |
| FOSA                                     | herring liver               | Landsort                                                                                                                                                                                             | non-linear         |                                                 | 1980–2017               | Bignert et al. Ref 98  |
| FOSA                                     | herring liver               | Utlängan                                                                                                                                                                                             | up                 | 4.8% (yearly percentage change)                 | 1980–2018               | Bignert et al. Ref 98  |
| FOSA                                     | herring liver               | Harufjärden, Fladen, Väderöarna, Rånefjärden, Kinnbäcksfjärden, Gaviksfjärden, Långvindsfjärden, Bothnian Sea offshore, Lagnö, Byxelkrok, Baltic Proper offshore, Västra Hanöbukten, Abbekås, Kullen | none/non-linear    |                                                 | 2005–2016               | Bignert et al. Ref 98  |
| PFHxS                                    | harbour porposie liver      | German waters of the Baltic Sea                                                                                                                                                                      | down               | not provided                                    | 1991–2008               | Huber et al. Ref 104   |
| PFHxS                                    | grey seals                  | Baltic Sea                                                                                                                                                                                           | down               | half-life 3.8 yrs                               | 1974–2008               | Kratzer et al. Ref 100 |
| PFHxS                                    | grey seals                  | Baltic Sea                                                                                                                                                                                           | down               | half-life 9.9 yrs                               | 1998–2008               | Kratzer et al. Ref 100 |
| PFHxS                                    | herring liver               | Landsort, Utlängan                                                                                                                                                                                   | up                 | 2.0%, 1.9% (yearly percentage change)           | 1980–2016               | Bignert et al. Ref 98  |
| PFHxS                                    | herring liver               | Ängskärsklubb                                                                                                                                                                                        | none               |                                                 | 1980–2016               | Bignert et al. Ref 98  |
| PFHxS                                    | herring liver               | Harufjärden                                                                                                                                                                                          | down               | -4.8% (yearly percentage change)                | 2007–2016               | Bignert et al. Ref 98  |
| PFHxS                                    | herring liver               | Rånöfjärden, Lagnö, Baltic Proper offshore                                                                                                                                                           | down               | not reported                                    | 2007–2017               | Bignert et al. Ref 98  |
| PFHxS                                    | herring liver               | Fladen, Väderöarna, Kinnbäcksfjärden, Gaviksfjärden, Långvindsfjärden, Bothnian Sea offshore, Byxelkrok, Västra Hanöbukten, Abbekås, Kullen                                                          | none               |                                                 | 2005 or 2007–2017       | Bignert et al. Ref 98  |
| PFHxS                                    | otters                      | Sweden                                                                                                                                                                                               | none               |                                                 | 2002–2011               | Roos et al. Ref 102    |
| PFHxS                                    | peregrine falcon eggs       | southwest Sweden                                                                                                                                                                                     | none               |                                                 | 2000–2007               | Holmström et al. 101   |
| PFHxS                                    | cod liver                   | Baltic proper                                                                                                                                                                                        | up                 | doubling time 24 yrs                            | 2000–2013               | Schultes et al. Ref 99 |

**Table 2.** Summary of time trends of PFASs in Baltic Sea biota

Sea during recent years are in line with observations for other parts of the world<sup>105</sup>. Proximity to sources, as well as differences in metabolism of the studied substance in different species, are likely contributing factors to the observed differences. A systematic review of published temporal trends of PFASs<sup>105</sup> concluded that PFOS concentrations in environmental media do not yet appear to be declining on a global scale after the phase outs. The lack of a clear trend may be explained by the short time period elapsed since phase-outs of the individual PFAAs in combination with retention of PFASs in households and in the waste stream (as evidenced by presence of PFOS precursors in sewage sludge almost two decades after their phase out<sup>76,77</sup>). A ten year monitoring period is often too short to statistically detect a trend unless it is of considerable magnitude<sup>97,98</sup>.

The lack of any significant loss mechanisms for PFAAs from the Baltic Sea<sup>47</sup> further prevents a fast response to reduced emissions. Therefore, the insignificant trends observed in the Baltic Sea environment during the most recent years are not necessarily an accurate reflection of the trends in input of PFASs into the Baltic Sea over the period. However, reported increasing trends of some PFCAs<sup>99,102</sup> suggest that the Baltic Sea may still receive increasing inputs of these substances.

In Baltic Sea cod liver, unidentified extractable organic fluorine (i.e. the fraction of extractable organic fluorine unaccounted for by known PFASs) decreased at a rate of 3.3% between 1981 and 2013<sup>99</sup>, in parallel with increasing concentrations of several PFAAs. It is currently not clear whether the decline in unidentified organic fluorine is due to environmental degradation of non-persistent PFASs or declining input of unknown PFASs and other fluorine-containing organic substances (such as pharmaceuticals and pesticides) to the Baltic Sea.

## Conclusions

Due to the long production history, and much reported occurrence in the environment, PFOS and PFOA are the two PFASs for which most data is available. PFOS and PFOA have been added to the Stockholm convention and thus their production and use is being phased out. This has resulted in a transition towards the use of alternative PFAS chemicals, which are not yet well-studied. For PFOS, the riverine input to the Baltic Sea exceeds atmospheric input by a factor of three, according to modelling performed for the Baltic Proper and for the entire Baltic Sea. For PFOA and other PFCAs, atmospheric deposition makes a higher contribution to the total input into the Baltic Sea. Several types of sources may contribute to the loading of PFOS and other PFASs in the Baltic Sea region rivers: i) discharges from WWTPs, ii) atmospheric deposition onto the catchment and subsequent runoff into rivers via groundwater, iii) runoff from contaminated sites via groundwater and drainage ditches. The relative contribution from these sources will likely vary between rivers, depending on population density, catchment size and presence of point sources. Observations in Finland and Sweden demonstrate that many rivers are mainly influenced by atmospheric deposition, while some rivers located in densely populated areas are influenced by additional sources, which give rise to elevated contamination levels. Although primary emissions of many PFAAs globally have decreased during the last decades, secondary sources may be important for future loads and concentrations in the Baltic Sea. These include runoff from background

soil and atmospheric deposition of PFAAs associated with sea spray.

In the Baltic Sea region, there are no known direct sources of PFOS and other PFAAs into the atmosphere. The PFAAs deposited in the region were likely formed in the atmosphere, via conversion of precursors, or transferred from seas to the atmosphere, via sea spray aerosols. The relative importance of these sources is currently not known. While sea spray aerosol is expected to act as a source of PFOS to the atmosphere from oceans well into the future, input of precursor-derived PFOS should decline as a consequence of global bans on their manufacture and use.

In a majority of the studies on Baltic Sea biota no increasing or decreasing temporal trend is observed for PFOS since the late 1990s. This suggests that the transport of PFOS into the Baltic Sea is no longer increasing, but that environmental PFOS concentrations have not yet declined as a response to reduced emissions. For PFOA and other long-chain PFCAs, both increasing and decreasing concentration trends are reported since the late 1990s. The PFASs monitored in environmental samples contribute on average to ca10-40% of the total extractable organic fluorine (surface water, WWTP sludge, WWTP effluent, marine mammals, marine fish), meaning that PFASs which are currently unknown or not included in the monitoring programmes may contribute to the environmental exposure.

## Acknowledgments

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## Appendix

Information from Helcom Contracting Parties regarding PFOS/PFAS emission sources, environmental transport pathways and concentration time trends.

In addition to conducting a literature search in the scientific and grey literature, national representatives active in Helcom working groups were contacted and asked for national information regarding emission estimates covering various sources, information on transport pathways of relevance for the Baltic Sea and time trends observed in environmental concentrations. In general, the information regarding PFOS and other PFASs was scarce, in particular about sources and emissions. National monitoring data is commonly presented as measurements from a single year compared to the EQS with the purpose of determining status, few time trends are presented. More information was available from Sweden, and is included in the main text.

### Estonia

Estonia was the only nation reporting quantitative emission estimates for PFOS. Emissions from industry to surface water was estimated to 0.24 kg/year and to wastewater 0.01 kg/year (EKUK 2018). The total input to WWTPs was 1.6 kg/year, of which 0.04 was estimated to be deposited to land. Zero emissions are expected from production of PFOS, and zero or very little emissions from infrastructure. The contribution from activities from outside Estonia could not be quantified. Estonia has mapped the location of facilities potentially emitting PFOS, several located around Tallinn. The largest number of industries with potential PFOS emissions belong to the metal industry sector and manufacturers of cosmetics and hygiene products and manufacturers of other chemical products. The difference in potential mass emitted is not reported. A source that is separately reported is the activities of the oil shale industry in eastern Estonia, responsible for 0.1 kg perfluorobutanoic acid (PFBA)/year and 0.25 kg perfluoro-n-hexanoic acid (PFHxA) kg/year emitted to surface water.

Estonia report surface water concentrations between 2013 – 2017 that exceed the EQS of 0.00065 µg/L. Less than 20 measurements have been made in Estonian biota. PFOS is measured in surface water, sediment and biota, but no time trends are reported.

### Latvia

Latvia publishes results from environmental monitoring in annual reports. PFOS has been measured in perch (*Perca fluviatilis*), mainly in rivers and some coastal stations, in 2015 (0.43 – 1.97 µg/kg), 2016 (0.16 – 0.85 µg/kg) and 2017 (0.16 – 1.18 µg/kg) at various stations (LGMC 2015, 2016, 2017). The number of stations vary between years with most locations sampled in 2016. The EQS for biota was never exceeded, however for water measurements data was available from 2017 only and the EQS for surface water was then exceeded at two locations. Also PFOA was measured in river water only in 2017.

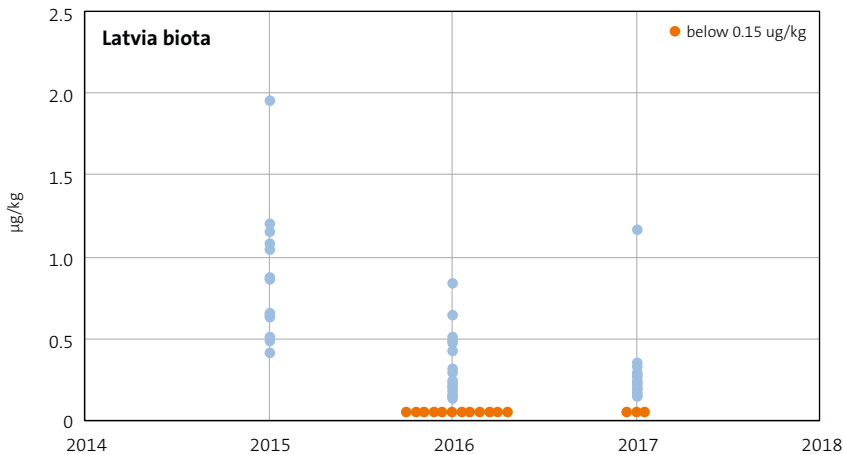
## References Appendix

### Estonia

EKUK Eesti Keskkonnauuringute Keskus, Perfluorooktaan-sulfoonhape ja selle derivaadid (PFOS). Dokument on aruande "Veekeskkonnale ohtlike ainete allikate inventuur." ainepõhine väljavõte. Töö tellija: Keskkonnaministeerium Tellija esindaja veeosakonna peaspetsialist Margus Korsjukov Lepingu nr: 4-1/16/119, Tallinn 2018

### Latvia

LGMC Latvijas vides geoloģijas un meteoroloģijas centrs. Pārskats par virszemes un pazemes ūdeni stavokli 2015, 2016, 2017. Gada. Rīga 2016 - 2018. <https://www.meteo.lv/lapas/vides/udens/udens-kvalitate/udens-kvalitate?id=1100&nid=433>



PFOS concentrations ( $\mu\text{g}/\text{kg}$ ) reported in year 2015, 2016 and 2017 in perch, Latvia. Figure with data extracted from LGMC reports for 2015, 2016 and 2017.

## Germany

Germany has evaluated the WFD priority substances in fish (perch, roach, bream, eelpout) residing in lakes, rivers and coastal waters of Mecklenburg-Vorpommern (LUNG M-V 2018). PFOS concentrations in muscle tissues were measured in four fish species at different locations in the years 2014 – 2017 (see Figure 4-k in LUNG M-V 2018). The maximum concentration observed was  $7.5 \mu\text{g}/\text{kg}$  fresh weight. Levels exceeded the quantification limit of  $2 \mu\text{g}/\text{kg}$  in 10 of the 34 reported data points. The sample locations varied between years. The concentration was  $5.7$  and  $3.8 \mu\text{g}/\text{kg}$  fresh weight in perch in Kleines Haff years 2015 and 2017, respectively. Perch sampled in Tollense Klempenow had levels of  $7.5$  in 2017 but only  $5 \mu\text{g}/\text{kg}$  fresh weight in Tollense-Neddemin in 2015. The data is not sufficient to discern any time trends.

## Denmark

A range of PFASs has been monitored in Denmark between 2007 and 2012 (PFUnA, PFNA, PFOA, PFOSA, PFDA, PFHxS, PFOS), all in effluents, sludge, riverwater and sediments (Hansen 2018). In marine areas in biota (Boutrup et al 2015). PFOS is the most commonly detected PFAS in Danish rivers, and together with PFNA the most frequently detected in WWTP effluents. These PFASs are also those found in highest concentrations. In sludge, PFDA and PFOSA are the most frequently detected PFASs. No time trends have been published as part of the monitoring reporting. A study of PFOS levels in peregrine falcon eggs in Greenland reported that no significant time trend was observed between 1986 – 2014 (see Figure 18 in Vorkamp 2017).

## References Appendix

### Germany

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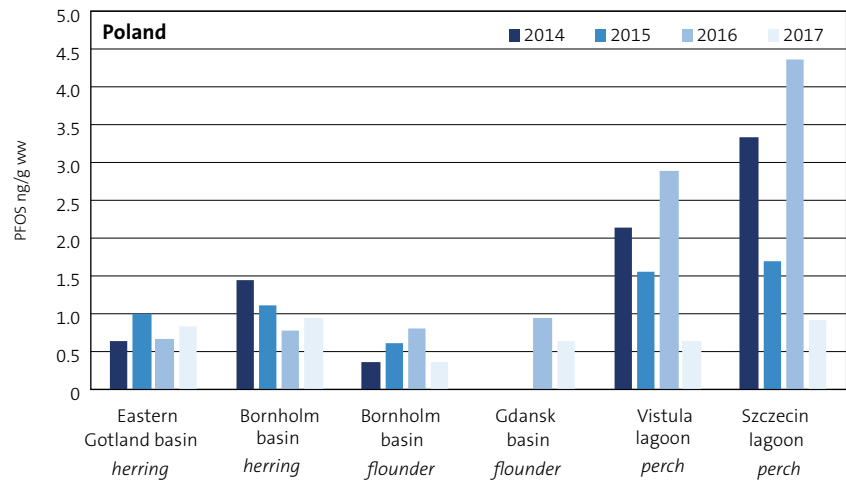


Figure with data extracted from Krzywiński [ed.] 2018.

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### Poland

Poland has monitored PFOS in fish muscle since 2014 in five marine water bodies (Krzywiński [ed.] 2018). During this time period, the measured concentrations has fluctuated between years and appear generally higher in the perch captured in the enclosed Szczecin Lagoon and Vistula Lagoon. In these lagoons the concentrations in 2017 were considerably lower compared to 2016, however no consistent pattern can be discerned in the five locations.

### Finland

Finland provided data on PFASs measured in rivers sampled on several occasions during a one-year period, illustrating the seasonal and spatial variation in concentrations (see Figure 21 and Table 6 in Siimes et al 2019). The PFAS levels were higher in the south, ranging in general between ca 2 – 8 ng/L with some rivers (Porvoonjoki) containing 10 – 14 ng/L or even 50 – 75 ng/L (Vantaanjoki) in the summer months. It was noted that these rivers contained a high proportion of wastewater during the low flow conditions. In the northern rivers, levels ranged between close to zero to at maximum ca 7 ng/L. PFOS was detected in all rivers, at maximum in a concentration of 26 ng/L in Vantaanjoki. The month of peak concentrations observed varied between rivers.

Finland also estimated loads of PFOS to coastal waters from rivers (10 kg/year) and emitted from municipal WWTPs (12 – 37 kg/year in total) (Siimes et al 2019).

Concentrations of PFOS and other PFAS in perch muscle was also measured in years 2014 – 2016 (see Figure 25 in Siimes et al 2019). The concentrations in Vanhankaupunginlahti perch muscle and skin were halved between 2015 and 2016. Also in Vaskiluoto, the levels declined, however more modestly, each year between 2014 and 2016. On the contrary, levels slightly increased in Saaristomeri and Ahlainen between 2015 and 2016, and also in Kellonlahti, Oulu between 2014 and 2016. The EQS of 9.1 µg PFOS/kg was exceeded in Vanhankaupunginlahti in 2015 and in Porvoonjoki in 2016 (Siimes et al 2019). The change of PFAS concentrations in several fish species between 2009 and 2016 was reported in another study, concentrations in Baltic herring, salmon, muikku, pike, perch, made increased whereas a decrease was observed for white fish and pike perch (Airaksinen et al 2018).



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