

## Abstract

Perfluoroalkyl acids (PFAAs) are man-made chemicals. Their unique properties make them beneficial for a wide range of industrial and consumer applications, such as constituents in fire fighting foams, hydraulic oils and food packaging materials.

PFAAs have shown to be highly persistent in the environment, and the toxicological potential of long chain PFAA homologues is of a concern. International regulation and voluntary actions by the industry have been implemented and led to reduced primary emissions of PFAAs to the environment. However, the concentrations of some PFAAs in e.g. birds from the Baltic Sea are still very high and of ecotoxicological concern. Measures to reduce the PFAA contamination require an understanding of the sources and how the PFAAs are being transported in the environment.

In this licentiate thesis a mass balance was assembled for perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorodecanoic acid (PFDA) and perfluorooctane sulfonic acid (PFOS) in the Baltic Sea. A one-box model was used including the input pathways river inflow, atmospheric deposition, wastewater discharges and inflow from the North Sea via the Danish Straits, while the loss processes considered were sediment burial, transformation of the chemicals and outflow to the North Sea via the Danish Straits. Additionally, the inventories of the four target PFAAs in the Baltic Sea were estimated. Both chemical fluxes and inventories were estimated using recently published monitoring data (2005-2010).

In order to obtain a detailed perspective on the current knowledge regarding PFAAs in the Baltic Sea, challenges and uncertainties in data selection were discussed for the most dominant input pathways. This included WWTP emissions and calculation of emission factors (EFs), atmospheric deposition and riverine inflow.

River inflow and atmospheric deposition were the dominant inputs, while wastewater treatment plant (WWTP) effluents made a minor contribution. The input to the Baltic Sea exceeded the output for all 4 PFAAs, suggesting that inputs were higher during 2005-2010 than during the previous 20 years despite efforts to reduce emissions of PFAAs. Comparing the difference between PFAA input and output with the PFAA inventory, the doubling time for the concentration in the Baltic Sea was estimated to be 8-94 yr for PFHxA, 12-16 yr for PFOA, 3-5 yr for PFDA and 4 yr for PFOS. The surplus of the input can be an effect of retention and delayed release of PFAAs from atmospheric deposition in the soils and groundwater of the watershed.

The licentiate thesis contributes to a holistic understanding of the major input and output pathways and inventories of PFAAs in the Baltic Sea. Furthermore, it points out current knowledge gaps in our understanding of sources and fate of PFAAs in the aquatic environment.

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## **List of papers:**

The licentiate thesis is based on the following paper, referred to as **Paper I**.

### **Paper I**

“Mass balance of perfluoroalkyl acids in the Baltic Sea”. Filipovic M, Berger U, McLachlan M.S. (submitted to *Environmental Science and Technology*)

### **Aim**

#### **Main aim:**

The aim of this licentiate thesis was to assemble a mass balance of perfluorinated alkyl acids (PFAAs) including perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorodecanoic acid (PFDA) and perfluorooctane sulfonic acid (PFOS) in the Baltic Sea.

#### **Sub goals:**

- Identify the major input/output pathways of PFAAs in the Baltic Sea.
- Predict future concentration trends of PFAAs in the Baltic Sea.
- Increase the current level of knowledge regarding environmental transport and fate of PFAAs and identify current knowledge gaps.
- Evaluate the state of contamination of the Baltic Sea with PFAAs relatively to European guidelines on environmental quality standards for PFOS.

## Abbreviations

BB	Bothnian Bay
BP	Baltic Proper
BS	Bothnian Sea
GoF	Gulf of Finland
GoR	Gulf of Riga
HBE	High bound estimate
LBE	Low bound estimate
MDL	Method detection limit
MLQ	Method quantification limit
PFDA	Perfluorodecanoic acid
PFHxA	Perfluorohexanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFAAs	Perfluoroalkyl acids
PFASs	Per- and polyfluoroalkyl substances
PFCAs	Perfluoroalkyl carboxylic acids
PFSAs	Perfluoroalkane sulfonic acids
K <sub>d</sub>	Sediment/water distribution coefficient

Terminology fact box: Per- and polyfluoroalkyl substances.<sup>1</sup>

Per- and polyfluoroalkyl substances (PFASs) is a generic name for all highly fluorinated aliphatic substances that contain one or more fully fluorinated carbon atoms, in such a manner that they contain the perfluoroalkyl moiety  $C_nF_{2n+1}$ .

Perfluoroalkyl acids (PFAAs) are a subgroup of PFASs, consisting of a fully fluorinated (perfluorinated) carbon chain and an acidic (hydrophilic) group. All PFAAs are thus fluorosurfactants.

Perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) are subgroups of PFAAs. Representatives of PFCAs studied in this thesis are perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA) and perfluorodecanoic acid (PFDA), while perfluorooctane sulfonic acid (PFOS) is the only PFSA included.

## 1. Introduction

### 1.1 A brief history of fluorine chemistry

The element fluorine was discovered by Mosander in 1886.<sup>2</sup> More than 50 years later, in 1938, the fluorine chemistry took a big step forward. This occurred in a laboratory of the DuPont Company when Dr. Roy J Plankett in the search of a new refrigerant developed the fluoropolymer polytetrafluoroethylene (PTFE).<sup>3</sup> PTFE was registered in 1945 and became later one of the best known trademarks of the DuPont Company known as Teflon®. The high-volume production of PTFE was eventually made possible by using perfluorooctanoic acid (PFOA), a representative of the perfluorocarboxylic acids (PFCAs), as a polymerization aid. During the same period of time, chemists at the 3M Company accidentally synthesized a new perfluorinated compound, perfluorooctane sulfonic acid (PFOS).<sup>4</sup> PFOS became a key ingredient of another famous trademark registered as Scotchgard® by 3M. These two trademarks introduced the perfluoroalkyl acids (PFAAs) to mainstream consumers, and they are still used today. In the early 1940s, during World War II, the Manhattan project required new inert materials for separation of uranium isotopes via gas diffusion from their corrosive hexafluorides.<sup>5</sup> Fluorinated materials were uniquely suited for the task. The Manhattan project gave great momentum to the development of new fluorine based chemicals. Ever since, the fluorine industry has grown exponentially and a large variety of poly- or perfluorinated organochemicals have become ingredients in the products of everyday life. The success story of per- and polyfluoroalkyl substances (PFASs) started thus with the accidental synthesis of new chemicals and chemists serendipitously discovering the extraordinary physical-chemical properties of these new materials.

### 1.2 PFAS production, properties and use

The first industries producing PFASs were established in the USA. However, in 1971 3M opened the first PFOS production facility in Europe located in Antwerp, Belgium. The cumulative historic production of PFCAs between the 1950s and 2004 has been estimated to range between 4400 and 8000 tonnes.<sup>6</sup> The historical production of PFSA based products from 1970 to 2002 was estimated to be 122 500 tonnes.<sup>7</sup> The unique physical-chemical properties of PFASs (e.g. surface activity, thermal and chemical stability)<sup>8</sup> make them favorable in a wide range of consumer products. PFASs are used in everyday products such as water resistant outdoor clothing,<sup>9</sup> non-stick cookware, paper coatings and fire-fighting foams. They are also used in a wide range of industrial applications such as the production of semi conductors, the metal plating industry and the production of fluoropolymers.<sup>10</sup>

### 1.3 Environmental occurrence, trends and transport of PFAAs

Starting from the early 2000s, numerous environmental monitoring studies have shown that PFAAs are ubiquitously present in the global environment. PFAAs have e.g. been detected in the Baltic Sea region in sea water,<sup>11</sup> river water,<sup>12,13</sup> sediment<sup>14</sup> and atmospheric deposition.<sup>15</sup> Trend studies from the Baltic Sea region of PFOS in guillemot eggs and grey seal liver collected over the years 1968 to 2003 and 1969 to 2008, respectively, showed a significant increasing trend of PFOS at least until the late 1990s.<sup>16,17</sup>

Research has demonstrated that emissions of PFAAs to the aquatic environment occur via five routes: (1) discharge from wastewater treatment plants (WWTPs),<sup>18</sup> (2) discharge by urban runoff,<sup>19</sup> (3) leakage from disposal and spill sites to groundwater,<sup>20,21</sup> (4) atmospheric deposition,<sup>15</sup> and (5) direct discharge by industrial production sites.<sup>22</sup> Two previously

conducted mass balances of PFAAs in the Great Lakes by Boulanger et al.<sup>23</sup> and Scott et al.<sup>24</sup> showed that the importance of input pathways was in the order of riverine inflow > atmospheric deposition > WWTPs. However, in a study of a number of rivers in Germany, Becker and co-workers came to a different conclusion, i.e. that WWTP effluents were the most important input sources for PFAAs.<sup>18</sup>

#### **1.4 PFAA toxicity**

PFOS has been shown to be toxic in laboratory tests to rodents<sup>25</sup> and aquatic organisms.<sup>26</sup> Moreover, epidemiological studies on newborns have shown a negative correlation between PFOA concentrations in serum and birth weight and size.<sup>27</sup> Meltzer et al. showed that concentrations of PFOS and PFOA in blood positively correlated with thyroid disease in the US general population.<sup>28</sup> In addition, concentrations of PFAAs in serum were negatively correlated with concentrations of semen in the Danish male population.<sup>29</sup>

#### **1.5 European regulation on PFOS and PFOA**

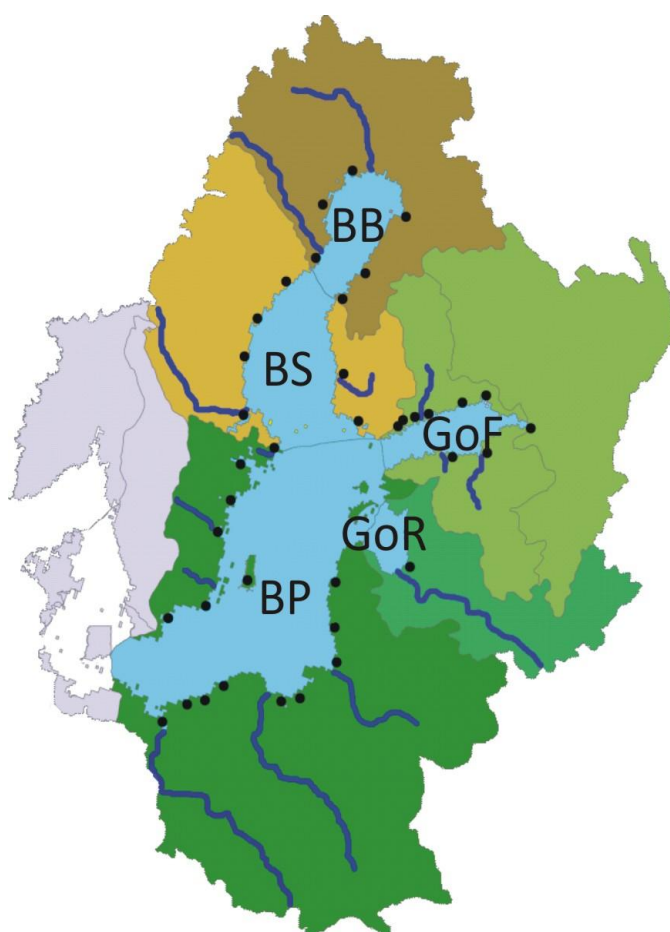
In 2002 the 3M Company voluntarily phased out the production of PFOS-based chemicals, based on the concern that had arisen due to the ubiquitous presence of PFOS in the blood of their employees.<sup>30</sup> In 2005 Sweden proposed to add PFOS to the Stockholm Convention on Persistent Organic Pollutants, as it fulfilled the criteria to be persistent, bioaccumulative and toxic (PBT).<sup>31</sup> In 2009 PFOS was finally listed in Annex B of the Stockholm Convention.<sup>32</sup> In 2006 the EU Directive 2006/122/EC amending directive 76/769/EEC restricted the marketing and use of perfluorooctane sulfonates.<sup>33</sup> The directive became effective in 2008 and applied to substances and preparations with concentrations equal to or higher than 0.005 % by mass. In 2010 the EU lowered the limit to 0.001 % by mass. Semi-finished products, articles or parts thereof may not be placed on the market if the concentration of perfluorooctane sulfonates is equal to or higher than 0.1 % by mass. For textiles or other coated materials, the limit is 1 µg/m<sup>2</sup> of the coated material. Furthermore, the European Commission defined Environmental Quality Standards (EQS) in 2012 including PFOS.<sup>34</sup> The EQS document states that PFOS concentrations should not exceed 0.13 ng/L in marine waters.

PFOA is not regulated in the EU or at an international level. It does not fulfill the criterion of a bioaccumulative compound according to the Stockholm Convention. Nevertheless, in 2006 the US Environmental Protection Agency agreed with eight major global PFAS producers (Arkema, Asahi, BASF Corporation (successor to Ciba), Clariant, Daikin, 3M/Dyneon, DuPont and Solvay Solexis) to launch the “PFOA Stewardship Program”. The program agreed on a reduction of global facility emissions and product content of PFOA by 95% by 2010 (measured against a year 2000 baseline) and to work towards completely eliminating emissions and product content by 2015.<sup>35,36</sup> However, fluorotelomer based precursor compounds, which can be transformed to PFCAs (including PFOA) metabolically or in the environment, are currently not regulated and no voluntary commitment to reduce emissions exists.

## 1.6 The Baltic Sea and its catchment

The Baltic Sea is one of the world's largest brackish water bodies with an area of 415 266 km<sup>2</sup> and a volume of 21 721 km<sup>3</sup>. It can be divided into five sub-basins, i.e. Bothnian Bay (BB), Bothnian Sea (BS), Baltic Proper (BP), Gulf of Finland (GoF) and Gulf of Riga (GoR) (Figure 1). Details on the five basins (volume, depth, river inflow, wet deposition) are given in Table S3 in the supporting information of Paper I. The salinity varies between the basins from 20 psu (parts per thousand) in the Kattegat (BP) to 1–2 psu in the Bothnian Bay and the Gulf of Finland. The large variation in salinity makes every basin unique in an ecological perspective.

The Baltic Sea is only connected with the North Sea via a narrow and shallow opening close to the Kattegat. This narrow connection limits the water exchange and makes the Baltic Sea an almost enclosed Sea with a water residence time between 20 and 30 years. This long residence time makes the ecosystems of the Baltic Sea basins highly sensitive to human impacts and climate changes. The Baltic Sea has in fact proven to be a long-term reservoir for many persistent organic pollutants.<sup>37</sup>



The total area of the Baltic Sea catchment is 1 720 270 km<sup>2</sup>. In Figure 1 the catchments of the different basins are shown with different colors. Nine countries border the Baltic Sea, i.e. Sweden, Finland, Russia, Estonia, Latvia, Lithuania, Poland, Germany and Denmark. In total there are more than 85 million people living in the catchment and approximately 15 million live within 10 km of the coastline. The population density varies widely from over 500 inhabitants per km<sup>2</sup> in urbanized regions of Poland, Germany and Denmark to less than 10 inhabitants per km<sup>2</sup> in northern parts of Finland and Sweden.<sup>38</sup> There is also a great variation in gross domestic product (GDP) between the countries, as outlined in **Paper I**. Within the Baltic Sea catchment there are no known PFAS manufacturing industries. However, there are industries that use PFAS formulations for various industrial applications.<sup>39</sup>

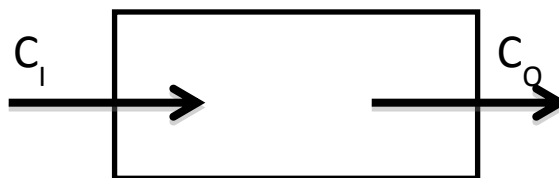
**Figure 1:** Baltic Sea catchment and basins.

## 2. Method

### 2.1 Input data and one box model

A mass balance was conducted for four PFAAs, i.e. PFHxA, PFOA, PFDA and PFOS, for the Baltic Sea (Figure 1). Literature data of PFAA concentrations in various media reported after 2006 were employed. To set bounds on the uncertainty, two estimates were calculated: a) High bound estimate (HBE) for which all of the data points reported as non-detected were set to the method detection limit (MDL); b) Low bound estimate (LBE) for which all of the data points below MDL were set to 0.

A simple one box model was applied in this study due to the homogeneity of the PFAA concentrations in the basins of the Baltic Sea (see Table S16 in the supporting information of Paper I). The methodology of the model including equations for the calculation of chemical fluxes and inventories is described in Paper I (sections 2.2 to 2.5). A typical one box model is shown in Figure 2 including the chemical input ( $C_I$ ) and the chemical output ( $C_O$ ).

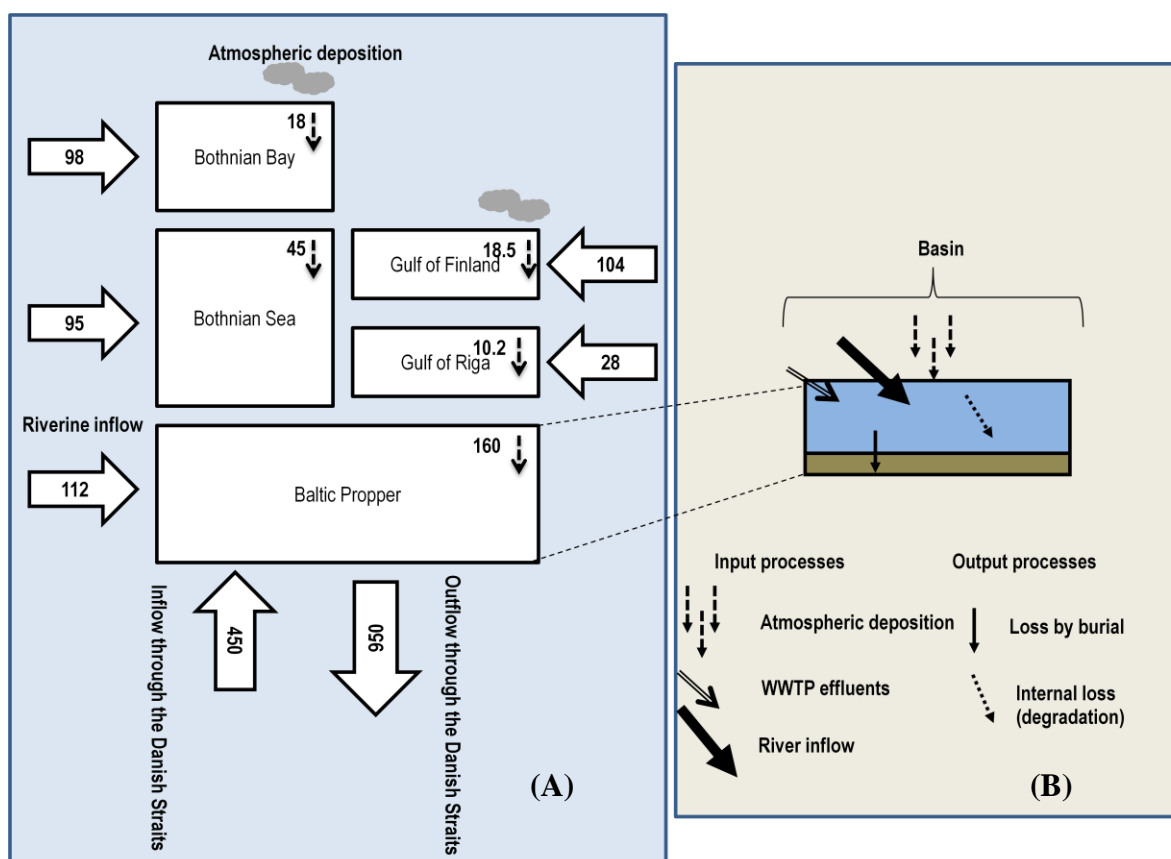


**Figure 2:** One box model including chemical input ( $C_I$ ) and output ( $C_O$ ).

### 2.2 Basin specific calculation of the river and wet deposition fluxes

The hydrological model used in this study is shown in Figure 3 A. All of the input and output processes within a basin are shown in Figure 3 B. In order to be able to calculate basin specific chemical fluxes, the riverine water discharges had to be calculated on a basin basis. This was done using basin specific river runoff data from a model by the Nordic Council<sup>40</sup> (for BB and BS) or data assembled by Helcom (for BP, GoR and GoF, see section 2.1 in the supporting information in **Paper I**). Furthermore, basin specific data for wet deposition were needed. These were also taken from the model by the Nordic Council<sup>40</sup> for BB and BS. This model did not distinguish between BP, GoR and GoF. Basin specific wet deposition was thus estimated by assuming that the wet deposition rate per surface area is equal for these three basins.





**Figure 3:** (A) The hydrological model of the Baltic Sea used in the present study. All water fluxes are presented as km<sup>3</sup>/yr. (B) Input and output processes within a basin.

### 3. Results and discussion

#### 3.1 Challenges and uncertainties in input calculations

In a mass balance study data selection is one of the most influential parameters for the outcome of the study. The input data shall thus be closely evaluated before being put into the model. In this chapter the data used for three of the most important PFAA input pathways to the Baltic Sea (i.e. WWTP emissions, atmospheric deposition and riverine input) are evaluated.

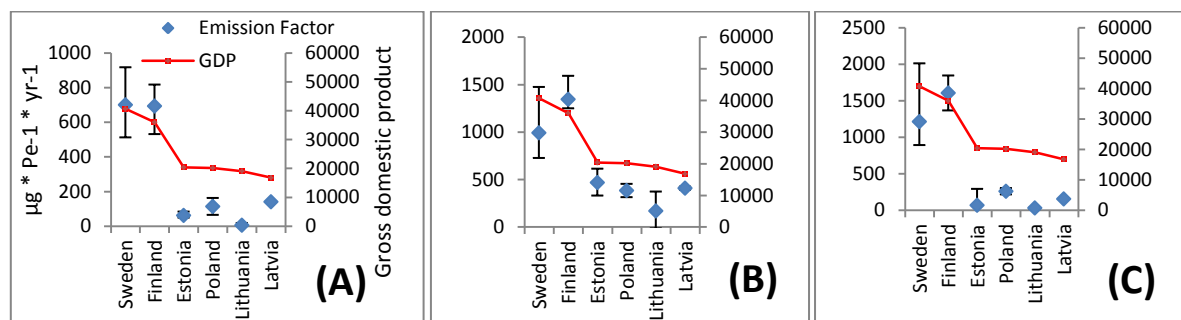
##### 3.1.1 Emission factors

The most common way to estimate chemical discharges by humans is by using emission factors (EF) (see **Paper I**, section 2.2.3). An emissions factor is a representative value that attempts to relate the quantity of a pollutant released to the environment with an activity associated with the release of that pollutant. WWTP effluents discharging the treated waste water from the coastal population into the Baltic Sea are a direct pathway of PFAAs to the Baltic Sea.

One of the challenges in this study was to calculate basin specific PFAA input fluxes. This was done by estimating country specific WWTP EFs ( $\mu\text{g} \cdot \text{Pe}^{-1} \cdot \text{yr}^{-1}$ ) for the countries in the Baltic Sea catchment and applying these to all coastal cities with a population greater than

35 000 in the respective countries. The PFAA data used for the calculation of EFs were taken from a recent study, in which PFAAs in WWTP effluents from Sweden, Finland, Lithuania, Poland, Latvia and Estonia were quantified.<sup>41–47</sup> For more details see Table S8-S10 in the supporting information of **Paper I**.

In Figure 4 the calculated average EFs for PFHxA, PFOA and PFOS are compared to the gross domestic product (GDP) for six countries. The EFs for countries with a GDP >37 000 US\$ (Sweden and Finland) ranged from 649-701, 993-1346 and 1215-1607  $\mu\text{g} \cdot \text{Pe}^{-1} \cdot \text{yr}^{-1}$  for the three chemicals, respectively, whereas for countries with a GDP <20 500 US\$ (Lithuania, Poland, Latvia and Estonia) the respective ranges were 5.63-141, 170-469 and 33.6-262  $\mu\text{g} \cdot \text{Pe}^{-1} \cdot \text{yr}^{-1}$ .



**Figure 4:** Comparisons between (A) PFHxA, (B) PFOA and (C) PFOS EFs ( $\mu\text{g} \cdot \text{Pe}^{-1} \cdot \text{yr}^{-1}$ , min-max and average values) and the gross domestic product (GDP) in US\$ for six countries bordering the Baltic Sea.

Interestingly, the concentrations of PFHxA, PFOA and PFOS in effluent waters were significantly higher for the countries with a high GDP in comparison to the group of countries with a lower GDP (see also **Paper I**, section 2.1). This might be due to differences in use and application of PFAA containing products such as (pricey) water resistant outdoor clothing.<sup>9</sup>

### 3.1.2 Atmospheric deposition

Lipophilic persistent organic pollutants which are prone to long range atmospheric transport have frequently been analyzed in atmospheric deposition. However, PFAAs such as PFOA and PFOS, which have low acid dissociation constants ( $\text{pK}_a$ ) and are ionic under environmental pH's, are not expected to volatilize to a significant extent and are thus not under surveillance by national monitoring programs. Only a handful of reports reporting concentrations of PFOA and PFOS in atmospheric deposition in the Baltic Sea region have been published (Table 1). There is only one peer reviewed scientific article available that includes the concentrations of several PFAA homologues in atmospheric deposition in the Baltic Sea catchment.<sup>15</sup> PFAA concentrations from this paper were used in our calculations (Table 1, Northern Germany). From Table 1 it can be seen that the German data used in the present study for PFOA and PFOS are comparable to data from the Swedish west coast (Råö and Landvetter) and also to the data from the remote location Pallas in northern Finland. It was thus concluded that the northern German data were suited to represent the atmospheric deposition on the whole Baltic Sea.

**Table 1:** Reported PFAA concentrations (ng/L) in atmospheric deposition within the greater Baltic Sea region.

Location		n	ng/L				Ref
			PFHxA	PFOA	PFDA	PFOS	
Northern Germany	average	20	0.270	1.64	0.630	1.07	15
Sweden	range	4	0.81-1.18	10.7-16.8	N.A	0.83-2.97	48
Sweden	average	-	1.06	14.48	N.A	2.18	49
Pallas, Finland	range	3	N.A	2.0-3.1	N.A	0.22-0.47	49
Råö, Sweden	range	4	N.A	2.3-13	N.A	2.2-7.7	49
Råö, Sweden	range	6	N.A	1.7-8.3	N.A	1.7-7.5	49
Stockholm, Sweden	range	3 <sup>a</sup> , 2 <sup>b</sup>	N.A	7.2-13	N.A	2.6-3.9	49
Landvetter, Sweden	range	23 <sup>a</sup> , 2 <sup>b</sup>	N.A	1.3-2.3	N.A	0.81-0.96	49

N.A= not analyzed, <sup>a</sup> refers to number of samples analyzed for PFOA, <sup>b</sup> refers to number of samples analyzed for PFOS

### 3.1.3 Rivers

PFAA concentrations from 14 rivers were available from two reports and used in this study.<sup>12,13</sup> The water flux from the 14 rivers contributed approximately 30% of the total riverine runoff to the Baltic Sea. The PFAA concentrations measured in the 14 rivers were also used (on a basin specific basis) for the rivers for which no data were available. Some of the largest rivers lacked PFAA data, e.g. Neva discharging into the Gulf of Finland and the Kemijoki discharging into the Bothnian Bay. This led to elevated uncertainty of estimated PFAA inputs to the basins of GoF and BB (see also Table S5 in **Paper I**). Furthermore, the number of analyzed river water samples was low, as only concentration data from single water samples were available for all 14 rivers.<sup>12,13</sup> In addition, the results of 11 rivers were reported with only one significant digit and with a relatively high method detection limit of 1 ng/L. Taken together, this led to considerable uncertainties in the final input calculations of riverine discharges, as reflected by large LBE-HBE ranges (Table S5 in **Paper I**).

### 3.2 Mass balance of PFAAs in the Baltic Sea

The results of the mass balance are summarized in Table 2. Rivers were a major source of the investigated PFAAs to the Baltic Sea as was atmospheric deposition followed by the inflow from the North Sea and WWTP discharges. These results are generally consistent with previous studies from the Great Lakes by Boulanger et al. and Scott et al.<sup>23,24</sup> The annual input in kg/yr and the percent contributions of the input pathways is presented in **Paper I** (SI Tables S12 and S13). The inflow from the North Sea made a significant contribution to the LBE scenario for PFHxA (49%), but otherwise its contribution to the mass balance was insignificant.

A major observation was that WWTP discharges directly to the Baltic Sea made a negligible contribution to the overall inputs in the mass balance. They accounted for 4% of the LBE of PFHxA; otherwise their contribution was  $\leq 1\%$ . The LBE estimates on a basin specific basis suggest that WWTPs make a significant contribution to the total input of PFHxA, PFOA and PFOS to the Gulf of Finland (20%, 15% and 13%, respectively). Otherwise the contribution of WWTPs is also minor on a basin scale. In **Paper I** (SI Tables S12 and S13), the inputs from rivers, atmospheric deposition and WWTPs are compared on a basin basis.

The differences between LBE and HBE show that a large fraction of non-quantifiable data points imparts considerable uncertainty to some of the input estimates (Table 2). This is particularly true for the river inputs of PFHxA and PFDA (as discussed above) and the North Sea inputs of PFDA and PFOS. However, this uncertainty does not affect the major

observation that rivers and atmospheric deposition are much more important sources of PFAAs to the Baltic Sea than WWTPs.

**Table 2.** Summary of the PFAA mass balance for the Baltic Sea. The ranges are delineated by the low bound estimates (LBE) and high bound estimates (HBE).

<b>Input [kg/yr]</b>	<b>PFHxA</b>	<b>PFOA</b>	<b>PFDA</b>	<b>PFOS</b>
Riverine discharges	16-426	401-641	54.4-311	876-924
Atmospheric deposition	60.2-62.9	365-367	141-144	239*
WWTP discharges	6.84*	11.1*	0.743-0.964	12.7*
North Sea inflow	80.8-85.5	66.5-69.4	0-6.18	0-14.3
<b>Sum</b>	<b>164-582</b>	<b>843-1 090</b>	<b>195-462</b>	<b>1 130-1 190</b>
<b>Output [kg/yr]</b>				
Sediment burial	2.36*	14.0*	5.68-22.5	18.7*
Danish Straits outflow	155*	370*	16.5-47.5	177*
Transformation	0.0834*	0.197*	0.00704-0.279	0.0936*
<b>Sum</b>	<b>157*</b>	<b>384*</b>	<b>22.2-70.3</b>	<b>196*</b>
<b>Inventory [kg]</b>				
Baltic Sea water	3 080*	7 270*	260-1 030	3 460*
Sediment	125*	727*	305-1 210	986*
<b>Sum</b>	<b>3 200*</b>	<b>8 000*</b>	<b>565-2 240</b>	<b>4 450*</b>

\* LBE=HBE

The environmental behaviour and transport of PFAAs within watersheds is still a largely unexplored study field. Studies conducted at former fire-fighting training sites, where PFAAs were discharged during the usage of aqueous film forming foam (AFFF), show continuous leakage of PFAAs to groundwater.<sup>50</sup> Furthermore, a recent study on PFAA concentrations in soil collected worldwide showed that some PFAAs were ubiquitously present.<sup>51</sup> An estimation of the total amount of PFOS in soil in the Baltic Sea catchment, based on the concentrations measured in this worldwide study,<sup>13</sup> showed that the soil could be a larger reservoir of PFOS than the Baltic Sea itself (for details see **Paper I**, section 4).

Another major observation was the importance of atmospheric deposition as a pathway of PFAAs to the Baltic Sea. This observation revealed an important knowledge gap, i.e. how PFAAs are being released/transferred to the atmosphere. Are industrial emissions to air most important? Are waste incineration plants a major contributor? Is degradation of volatile, airborne PFAA precursor compounds an important pathway? Or are atmospheric levels of PFAAs primarily the result of environmental circulation from surface water, e.g. via sea spray?<sup>52</sup> These are some of the research questions that are still unanswered. However, if the last hypothesis on the importance of environmental circulation was true, then at least a part of the input surplus observed in the mass balance (see the section below) would be compensated by sea spray as an output pathway, which was not considered in the present study.

The last major observation was the positive mass balance for the Baltic Sea, i.e. a surplus of chemical input fluxes compared to output fluxes (Table 2). From this surplus and from the chemical inventory in the Baltic Sea water (Table 2) doubling times for the different PFAAs could be calculated. The doubling times for PFOA and PFOS were 12-16 yr and 4yr, respectively. These were broadly consistent with the doubling times observed in bio-monitoring data for Baltic Sea herring (pers. comm. Anders Bignert). The EQS defined by the European Commission in 2012 propose that concentrations of PFOS should not exceed 0.13 ng/L in marine waters.<sup>34</sup> The PFOS concentrations in the Baltic Sea have already exceeded this value, and the positive mass balance for PFOS suggests that the contamination will increase in the near future. There is a need to reduce the input of PFAAs to the Baltic Sea. This will require identifying and reducing the sources of PFAAs to the atmosphere and gaining a better understanding of the chemicals' transfer within the catchment to surface water.

#### **4. Conclusions and outlook**

This is the first mass balance conducted for PFAAs in the Baltic Sea. The licentiate thesis contributes to a holistic understanding of the major input and output pathways and inventories of PFAAs in the Baltic Sea. The results identified several knowledge gaps. First, the transport of PFAAs from atmospheric deposition through the terrestrial environment to surface water is not well understood. An understanding of this transport process is important in order to understand if surface soil is an important reservoir of PFAAs, which could lead to contaminant releases even after emissions have ceased. A study is ongoing investigating the transport of PFAAs in a boreal watershed.

Second, the relative contributions of different PFAA sources to the EFs from WWTPs are not well understood. A new study was initiated investigating the role of PFAA concentrations present in drinking water and of diffuse sources during use of drinking water for the PFAA concentrations detected in the influents/effluents from the WWTPs.

Third, the ubiquitous presence of PFAAs in atmospheric deposition is of concern and poorly understood. Research is urgently needed in this field, as atmospheric deposition is a major source/pathway of PFAAs to the Baltic Sea.

#### **5. Acknowledgements**

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