# Mass Balance of Perfluoroalkyl Acids in the Baltic Sea

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S *Supporting Information*

ABSTRACT: A mass balance was assembled for perfluorohexa-noic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluoro-decanoic acid (PFDA), and perfluorooctanesulfonic acid (PFOS) in the Baltic Sea. Inputs (from riverine discharge, atmospheric deposition, coastal wastewater discharges, and the North Sea) and outputs (to sediment burial, transformation of the chemical, and the North Sea), as well as the inventory in the Baltic Sea, were estimated from recently published monitoring data. Formation of the chemicals in the water column from precursors was not considered. River inflow and atmospheric deposition were the dominant inputs, while wastewater treatment plant (WWTP) effluents made a minor contribution (<5%). A mass balance of the Oder River watershed was assembled to explore the sources of the perfluoroalkyl acids (PFAAs) in the river inflow. It indicated that WWTP effluents made only a moderate contribution to riverine discharge (21% for PFOA, 6% for PFOS), while atmospheric deposition to the watershed was 1−2 orders of magnitude greater than WWTP discharges. The input to the Baltic Sea exceeded the output for all four PFAAs, suggesting that inputs were higher during 2005−2010 than during the previous 20 years despite efforts to reduce emissions of PFAAs. One possible explanation is the retention and delayed release of PFAAs from atmospheric deposition in the soils and groundwater of the watershed.
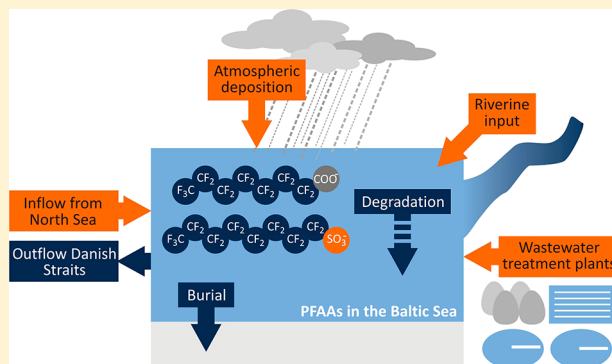
1. INTRODUCTION

Perfluoroalkyl acids (PFAAs) have been produced since the 1950s. Their unique amphiphilic properties have been exploited in a wide range of industrial and consumer applications. PFAAs are exceptionally stable chemicals that have a very long degradation half-life in the environment.[1,2] They can also be formed in the environment from the transformation of other industrially produced precursor compounds.[3,4] Long-chain PFAAs bioaccumulate and magnify in food webs.[5,6] Of these, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) have been associated with a wide range of adverse effects on both mammalian[7] and aquatic organisms.[8]

The Baltic Sea is one of the world's largest brackish water systems with a highly populated and industrialized catchment. The long water residence time of ∼20 years makes the Baltic Sea particularly susceptible to pollution, and high levels of a range of persistent organic pollutants such as polychlorinated biphenyls, dibenzo-*p*-dioxins, and dibenzofurans have been found in Baltic Sea sediments and food webs.[9] In recent years, high levels of PFAAs have also been found in Baltic Sea biota.[10] PFOS concentrations in the eggs of Baltic Sea guillemots are among the highest ever reported in birds,[11] and they are close to the levels that have been shown to cause adverse effects in other bird species.[12] Furthermore, temporal trend monitoring in Baltic Sea herring (1980−2010) and sea eagle eggs (1966−2010) showed increasing concentrations of PFOS and long-chain perfluoroalkylcarboxylic acids (PFCAs, C8−C15) (personal communication, Anders Bignert). There is clearly a need

to control PFAA levels in the Baltic Sea environment. In order to develop effective management strategies, the major sources (both emissions to the environment and transport pathways) of PFAAs to the Baltic Sea must be identified.

Different conclusions have been drawn about the major transport pathways of PFAA contamination to surface waters. In a study of several small rivers in Germany, it was concluded that the major part of PFAAs entered the rivers via municipal wastewater treatment plants (WWTPs).[13] In the first attempt at a PFAA mass balance of a large lake, Boulanger et al.[14] concluded that WWTP discharges represented a minor input pathway of PFOA to Lake Ontario compared to inflow from the other Great Lakes. Scott et al.[15] did a similar study for Lake Superior, a large lake with a much lower population density in the watershed and no known PFAA manufacturing sites. In contrast to Boulanger et al.,[14] this study included even precipitation, and it was concluded that wet deposition and riverine discharges represented the dominant PFAA inputs to the lake.

To identify the major input pathways of PFAAs to the Baltic Sea, a PFAA mass balance was assembled. Available monitoring data were used to estimate PFAA inputs (from river inflow, atmospheric deposition, wastewater discharges directly to the

Baltic Sea, and inflow from the North Sea via the Danish Straits) and outputs (to sediment burial, transformation of the chemical, and outflow via the Danish Straits to the North Sea) as well as the PFAA inventory in the Baltic Sea. In addition, a PFAA mass balance was conducted for the Oder River watershed that compared the atmospheric deposition to the watershed with the inputs via WWTPs throughout the watershed and the output from the watershed via Oder River's discharge to the Baltic Sea.

2. MATERIALS AND METHODS

Mass balances were conducted for four PFAAs: perfluorohexanoic acid (PFHxA), PFOA, perfluorodecanoic acid (PFDA) and PFOS (see abbreviation list in the Supporting Information for further frequently used abbreviations and Table S1 in Supporting Information for structures of the target chemicals). These compounds were chosen on the basis of availability of literature monitoring data. The data used were reported after 2006. Some of the data sets contained data points that were below the method detection limit (MDL; see Table S2 in the Supporting Information). This introduced uncertainty into the calculation of the chemical fluxes and inventories. To set bounds on the uncertainty, two estimates were calculated: high-bound estimate (HBE), for which all of the data points reported as nondetected were set to the MDL; and low-bound estimate (LBE), for which all of the data points reported as nondetected were set to 0. Calculated PFAA fluxes and inventories are given as ranges (LBE−HBE) throughout the paper and the Supporting Information. Despite this and other uncertainties, the fluxes and inventories are reported with three significant digits due to the need for aggregation for the overall mass balance.

2.1. Study Areas. Two mass balances were conducted, one for the Baltic Sea and one for the Oder River catchment area. Figure 1 shows the Baltic Sea and its catchment. The rivers for which PFAA data were available are marked in the figure, and the Oder River is highlighted. The Baltic Sea catchment has a population of 85 million, whereby approximately 15 million live within 10 km of the Baltic Sea coast.[16] The economies of the countries within the watershed vary widely. Sweden, Germany, Denmark, and Finland have high per capita gross domestic products (GDP) (>U.S. $37 000) compared to Russia, Poland, Latvia, Estonia, and Lithuania (<U.S. $20 400).[17] There are no PFAA manufacturing sites in the Baltic Sea catchment to our knowledge.

The properties of the Baltic Sea of most relevance for the mass balance models are summarized in Table 1. Although a one-box model was used for the mass balance of the Baltic Sea, it was divided into five basins for interpolation of the riverine input (see Figure 1 and Table S3 in Supporting Information). Each of the basins contained rivers for which PFAA concentration data were available: Vindelälven and Kalixälven in the Bothnian Bay (BB), Kokemäen and Dalälven in the Bothnian Sea (BS), Narva, Purtse, and Vantaa in the Gulf of Finland (GoF), Daugava in the Gulf of Riga (GoR), and Vistula, Oder, Eman, Nemunas, Norrström, and Motala in the Baltic proper (BP).

The processes considered in the mass balances for the Baltic Sea and the Oder River catchment are illustrated in Figure 2. The system boundary for the Baltic Sea mass balance enclosed water and surface sediment. The input pathways (hereafter also called sources) treated were river inflow, atmospheric deposition (which also includes PFAAs that were formed
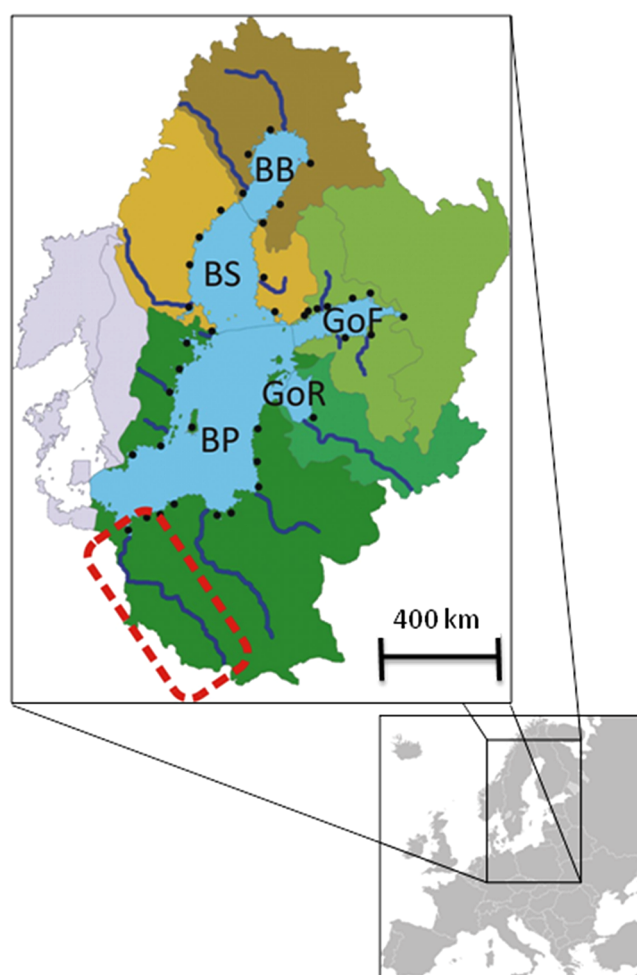

Figure 1. Illustration of the study region. The five basins of the Baltic Sea are shown separated by gray lines (BB, Bothnian Bay; BS, Bothnian Sea; GoF, Gulf of Finland; GoR, Gulf of Riga; BP, Baltic proper). The colored landmasses represent the watersheds of the basins. The black dots are coastal cities with population >35 000, and the blue lines represent the rivers for which measurements of PFAA concentrations were available. The Oder River is highlighted within the red box.

Table 1. Properties of the Baltic Sea and the Oder River Catchment

	Baltic Sea	Oder River catchment
catchment area (km²)	1 633 290[a]	118 938[f]
population/coastal population (million)	85/15.0[b]	16.2[f]
area of the sea (km²)	372 858[c]	
water volume (km³)	20 958[c]	
average depth (m)	52.3[c]	
inflow from rivers/river flux (km³/yr)	436[d]	15.0[f]
inflow from North Sea (km³/yr)	475[d]	
precipitation onto (km³/yr)	223[d]	17.8[f]
outflow Danish Straits (km³/yr)	950[d]	
sediment burial rate (10³ kg dry matter/yr)	95 520 000[e]	

[a]Reference 46. [b]Reference 16. [c]Reference 47. [d]Reference 48. [e]Reference 9. [f]Average 1996−2006; personal communication from Erik Smedberg.

from precursors in the atmosphere), coastal wastewater discharges, and inflow from the North Sea via the Danish
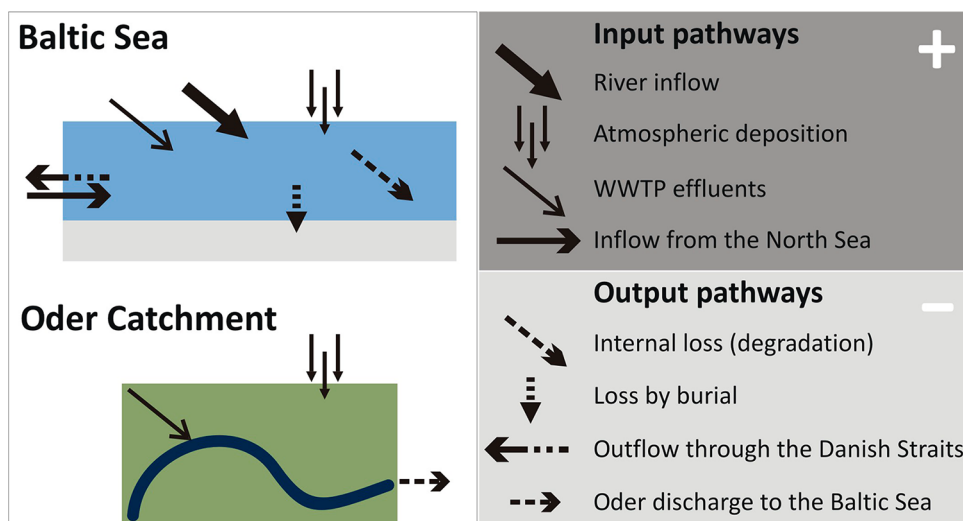
Figure 2. Schematic illustration of the processes included in PFAA mass balances of the Baltic Sea and the Oder River catchment.

Straits, while the loss processes considered were sediment burial, transformation of the PFAAs, and outflow via the Danish Straits to the North Sea. The system boundary for the Oder catchment mass balance enclosed the nonatmospheric portions of the catchment (i.e., land, surface water, groundwater, and associated solids). The input processes treated were atmospheric deposition and wastewater discharges, while the outflow from the Oder to the Baltic Sea was the only loss process considered.

2.2. Input Pathways. *2.2.1. Riverine Inflow.* The riverine input of PFAAs, N_{river} (kilograms per year), was calculated according to

$$N_{river} = C_{river}Q_{river} \qquad (1)$$

where C_{river} is the PFAA concentration in river water (kilograms per cubic meter) and Q_{river} is the river discharge rate (cubic meters per year). C_{river} was compiled from two studies that analyzed water samples collected close to the mouths of major European rivers during autumn 2005 (three rivers)[18] and 2007 (11 rivers).[19] The detection frequencies of PFHxA, PFOA, PFDA, and PFOS in the rivers were 14%, 71%, 14%, and 71%, respectively. The data were scaled up from the river to the basin level by use of the river discharge weighted average concentration (see section 2.1 in the Supporting Information for details). Q_{river} was taken from the same sources.[18,19]

2.2.2. Atmospheric Deposition. The input of PFAAs via atmospheric deposition, $N_{deposition}$ (kilograms per year), was calculated according to

$$N_{deposition} = C_{precip}Q_{precip} \qquad (2)$$

where C_{precip} is the PFAA concentration in precipitation (kilograms per cubic meter of water) and Q_{precip} is the amount of precipitation deposited directly on the Baltic Sea (cubic meters of water per year). C_{precip} was estimated from the mean PFAA concentrations (see section 2.2 in the Supporting Information) measured in 20 bulk deposition samples that were collected continuously between October 1, 2007, and May 8, 2008, at a site close to the southwestern corner of the Baltic Sea.[20] The values were typically in the sub to low nanograms per liter range. Concentrations in a similar range have been reported in wet deposition from Northern Finland, the Swedish

west coast,[21] the United States, and Asia.[22] Q_{precip} was taken from Table 1.

2.2.3. Wastewater Treatment Plant Effluents. The PFAA input from WWTP discharges directly into the Baltic Sea, N_{WWTP} (kilograms per year), was estimated according to

$$N_{WWTP} = C_{WWTP}q_{WWTP}P_{equiv} \qquad (3)$$

where C_{WWTP} is the PFAA concentration in the WWTP effluent (kilograms per cubic meter), q_{WWTP} is the amount of wastewater discharged annually per population equivalent [cubic meters per year per population equivalent (pe)], and P_{equiv} is the number of population equivalents connected to WWTPs discharging directly into the Baltic Sea. C_{WWTP} was estimated from recent measurements of PFAA concentrations in effluents from WWTPs discharging directly to the Baltic Sea. Two to four WWTPs were studied for six of the nine countries bordering on the Baltic Sea. Most of the WWTPs served large populations. Two to six samples were collected from each WWTP between October 9, 2009, and August 10, 2010.[23−28] The values of q_{WWTP} were taken from the literature,[23−30] while P_{equiv} was estimated by selecting coastal cities with populations greater than 35 000 inhabitants (which serve >80% of the population in the coastal region). Details of the calculations are provided in section 2.3 in the Supporting Information.

2.2.4. Inflow from the North Sea through the Danish Straits. Input of PFAAs from the North Sea through the Danish Straits, N_{NS} (kilograms per year), was estimated as

$$N_{NS} = C_{NS}Q_{NS} \qquad (4)$$

where C_{NS} is the PFAA concentration in North Sea water (kilograms per cubic meter) and Q_{NS} is the annual inflow of water from the North Sea through the Danish Straits (cubic meters per year). C_{NS} was estimated from PFAA concentrations measured in surface water samples collected at three stations along the southern coast of Norway in 2007[31] (Table S11 in Supporting Information). For annual water inflow Q_{NS}, an average value of 475×10^9 m^3/year was used (Table 1).

2.3. Output Pathways. *2.3.1. Transformation in Water.* The lower limit for the phototransformation half-life of PFOA in coastal oceans was recently estimated to be 25 600 years.[1] We are not aware of any evidence showing PFAA transformation in water via other mechanisms. Hence the trans-

Table 2. Summary of PFAA Mass Balance for the Baltic Sea[a]

	PFHxA	PFOA	PFDA	PFOS
	Input (kg/yr)			
riverine discharges	16.4−426	401−641	53.8−311	876−924
atmospheric deposition	60.2−62.9	365−367	141−144	238[b]
WWTP discharges	6.84[b]	11.1[b]	0.743−0.964	25.8[b]
North Sea inflow	80.8−85.5	66.5−69.4	0−6.18	0−14.3
sum	164−582	843−1090	195−462	1140−1200
	Output (kg/yr)			
sediment burial	2.36[b]	14.0[b]	5.68−22.5	18.7[b]
Danish Straits outflow	155[b]	370[b]	16.4−47.4	177[b]
transformation	0.0834[b]	0.197[b]	0.00704−0.279	0.0936[b]
sum	157[b]	384[b]	22.2−70.3	196[b]
	Inventory (kg)			
Baltic Sea water	3080[b]	7270[b]	260−1030	3460[b]
sediment	125[b]	727[b]	305−1210	986[b]
sum	3200[b]	8000[b]	565−2240	4450[b]

[a]Ranges are delineated by low-bound estimates (LBE) and high-bound estimates (HBE). [b]Here LBE = HBE.

formation half-life $t_{0.5}$ of PFOA in Baltic Sea water was assumed to be 25 600 years and the loss due to transformation, N_{tran} (kilograms per year), was calculated according to

$$N_{tran} = \frac{\ln(0.5)}{t_{0.5}} C_{Baltic} V_{Baltic} \tag{5}$$

where V_{Baltic} is the volume of water in the Baltic Sea (cubic kilometers) and C_{Baltic} is the PFAA concentration in the Baltic Sea (kilograms of PFAA per cubic kilometer). V_{Baltic} is given in Table 1 and C_{Baltic} is given in Table S16 (Supporting Information). In the absence of information on the transformation of other PFAAs besides PFOA, $t_{0.5}$ was assumed to be 25 600 years for all four chemicals.

2.3.2. Outflow through the Danish Straits. Outflow of PFAAs through the Danish Straits, N_{DS} (kilograms per year), was determined according to

$$N_{DS} = C_{BP}Q_{DS} \tag{6}$$

where C_{BP} is the PFAA concentration in water in the Baltic proper (kilograms per cubic meter) and Q_{DS} is the annual outflow of water from the Baltic Sea through the Danish Straits (cubic meters per year). The estimation of C_{BP} is described in section 2.4.1, and Q_{DS} is given in Table 1. C_{BP} and N_{DS} are listed in Table S14 (Supporting Information).

2.3.3. Sediment Burial of PFAAs. The rate of loss of PFAA due to sediment burial, N_{burial} (kilograms per year), was calculated according to

$$N_{burial} = C_{sed}Q_{burial} \tag{7}$$

where Q_{burial} is the rate at which sediment is buried in the Baltic Sea (kilograms of sediment dry weight per year; see Table 1) and C_{sed} is the PFAA concentration in the sediment being buried (kilograms of PFAA per kilogram of sediment dry weight). The estimation of C_{sed} is made from PFAA concentrations measured in Baltic Sea water and K_d values taken from the literature as described in section 2.4.2. K_d, C_{sed}, and N_{burial} are listed in Table S15 (Supporting Information).

2.4. Baltic Sea Inventory of PFAAs. *2.4.1. Water.* The PFAA inventory in Baltic Sea water, M_{water} (kilograms), was calculated according to

$$M_{water} = \sum_{basin=1}^{5} (C_{water,basin}V_{basin}) \tag{8}$$

where $C_{water,basin}$ is the PFAA concentration in water in the basin (kilograms per cubic meter) and V_{basin} is the volume of water in the basin (cubic meters). The basins and their water volumes are listed in Table S3 (Supporting Information). $C_{water,basin}$ was estimated from PFAA concentrations measured in 62 water samples collected at depths of 2−3 and 5 m on two cruises in the Baltic Sea during the summer of 2008.[32] The number of samples collected, detection frequency of the PFAAs, average PFAA concentrations, and PFAA inventories are given for each basin in Tables S16 and S17 (Supporting Information). The concentrations did not differ to a great extent between the basins. The lack of strong spatial gradients supports the use of the simple box model to assess the chemical mass balance.

2.4.2. Sediment. The PFAA inventory in Baltic Sea sediment, M_{sed} (kilograms), was calculated according to

$$M_{sed} = \sum_{basin=1}^{5} [C_{sed,basin}A_{basin}d_{sed}(1-\phi_{sed})\rho_{sed}] \tag{9}$$

where $C_{sed,basin}$ is the PFAA concentration in the surface sediment of the basin (kilograms of PFAA per kilogram of sediment dry weight), A_{basin} is the surface area of the basin (square meters), d_{sed} is the average depth of the surface sediment (meters), ϕ_{sed} is the porosity of the sediment (cubic meters of nonsolids per cubic meter of bulk sediment), and ρ_{sed} is the density of the dry sediment (kilograms per cubic meter of solids). A_{basin} is given in Table S3 (Supporting Information). d_{sed} was assumed to be 0.05 m throughout the Baltic Sea. ϕ_{sed} was set to 0.89,[33] while ρ_{sed} was assumed to equal 2500 kg/m³.

The PFAA concentration in sediment, $C_{sed,basin}$ (kilograms of PFAA per kilogram of sediment dry weight), was calculated from the PFAA concentration in water, $C_{water,basin}$, with the assumption of equilibrium partitioning:

$$C_{sed,basin} = C_{water,basin}K_d \tag{10}$$

where K_d is the equilibrium partition coefficient (cubic meters per kilogram of sediment dry weight). $C_{water,basin}$ (kilograms of PFAA per cubic meter) was determined as in section 2.4.1, and K_d values measured for Baltic Sea sediments (168, 423, 4795, and 1185 m³/kg$_{sediment\ dry\ weight}$ for PFHxA, PFOA, PFDA, and

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PFOS, respectively)[34] were used. The PFAA inventories in sediment are given in Table S18 (Supporting Information).

2.5. Mass Balance of the Oder Catchment. The mass balance of the Oder catchment considered PFAA inputs from WWTPs and atmospheric deposition, while riverine discharge was the only output included (transformation and sedimentation were assumed to be negligible). Input from WWTPs was calculated by multiplying the annual PFAA input per population equivalent for Poland (see section 2.2.3) by the total population within the catchment. Atmospheric deposition was calculated from eq 2, where Q_{precip} was the amount of precipitation to the Oder catchment (cubic meters per year), which was taken from the data supporting the Nest decision support system (Erik Smedberg, personal communication).[35] The riverine discharge was equal to the riverine input of the Oder to the Baltic Sea (see Table S4 in Supporting Information). As with the Baltic Sea model, this was an input/output mass balance that made no assumptions about how the chemicals behaved within the model domain.

3. RESULTS

The results of the mass balance for the Baltic Sea are summarized in Table 2. Detailed results per basin for the LBE and HBE input scenarios are given in Tables S12 and S13, respectively (Supporting Information).

3.1. PFAA Input to the Baltic Sea. Rivers were a major source of the four PFAAs to the Baltic Sea (Table 2). They accounted for 10−73% of the total input of PFHxA, 48−59% of PFOA, 28−67% of PFDA, and 77% of PFOS (Tables S12 and S13, Supporting Information). Atmospheric deposition was also an important source. It accounted for 11−37% of the total input of PFHxA, 34−43% of PFOA, 31−72% of PFDA, and 20−21% of PFOS. The North Sea made a significant contribution to the LBE scenario for PFHxA (49%), but otherwise its contribution to the mass balance was insignificant.

WWTP discharges directly to the Baltic Sea made a negligible contribution to the overall mass balance. They accounted for 4% of the LBE of the PFHxA mass balance; otherwise their contribution was ≤2%. The mean concentrations of PFHxA, PFOA, and PFOS in effluent waters were significantly higher for the group of countries with higher per capita GDP (>U.S. $37 000) (i.e., 4.97, 8.98, and 8.45 ng/L, respectively) in comparison to the group with lower per capita GDP (<U.S. $20 500) (i.e., 1.07, 5.33, and 1.67 ng/L, respectively) ($p < 0.05$, t-test). In Tables S12 and S13 (Supporting Information), the inputs from rivers, atmospheric deposition, and WWTPs are compared on a basin basis. The LBE estimates suggest that WWTPs could 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 on a basin scale is minor.

The differences between LBE and HBE in Table 2 show that a large fraction of nonquantifiable data points imparts considerable uncertainty to some of the input estimates. This is particularly true for the riverine inputs of PFHxA and PFDA and the North Sea inputs of PFDA and PFOS. Improved monitoring data for rivers would be helpful in reducing the uncertainties. 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.

3.2. PFAA Output from the Baltic Sea. Outflow through the Danish Straits is the most important output pathway for PFAAs in the Baltic Sea (Table 2). Transformation accounted for <0.04% of the total outputs. Sediment burial is most important for the most strongly sorbing of the PFAAs. It accounts for 24−32% of the total output of PFDA and 9% for PFOS, while it is an insignificant sink for PFHxA and PFOA (1% and 3%, respectively).

3.3. Inventory of PFAAs in the Baltic Sea. The inventory of most of the PFAAs is largely stored in the water column, not in the sediment. Water was estimated to contain 96%, 91%, 46%, and 78% of the Baltic Sea inventory of PFHxA, PFOA, PFDA, and PFOS, respectively.

3.4. Oder River Catchment Input and Output of PFAAs. The results of the PFAA mass balance of the Oder catchment are presented in Table 3. Atmospheric deposition

Table 3. Summary of PFAA Mass Balance for the Oder Catchment[a]

	PFHxA	PFOA	PFDA	PFOS
		Input (kg/yr)		
WWTP discharges	1.84[b]	6.21[b]	0.292−0.397	3.28[b]
atmospheric deposition	17.1−17.8	103−104	39.8−40.4	67.6[b]
sum	18.9−19.6	110−111	40.1−40.8	70.9[b]
		Output (kg/yr)		
river discharge	0−15.0	30.1[b]	0−15.0	60.2[b]

[a]Ranges are delineated by low-bound estimates (LBE) and high-bound estimates (HBE). [b]Here LBE = HBE.

accounts for almost all of the PFAA input into the catchment. WWTPs are an insignificant source of all four PFAAs except for PFHxA, for which they contribute 9%. The total inputs and the total outputs are similar for PFHxA and PFOS. For PFOA and PFDA, the inputs are 3.7 and >2.7 times greater, respectively, than the outputs.

4. DISCUSSION

A major observation in this study is that WWTPs make a minor contribution to the total PFAA input to the Baltic Sea. The results for the Oder catchment mass balance show that this is also true when the indirect inputs of WWTP discharges to rivers flowing into the Baltic Sea are considered. COHIBA, a recent project on the control of hazardous substances in the Baltic Sea region, estimated the total discharges of PFOA and PFOS via WWTPs to the Baltic Sea catchment to be 200 and 100 kg/year, respectively.[36] These are similar to our estimates when they are scaled up to the whole Baltic Sea catchment. The small contribution of PFAAs from WWTP effluents is also consistent with the observations of Boulanger et al.,[14] who estimated WWTP discharges of PFOA to Lake Ontario to be considerably smaller than riverine input via the Niagara River. It is also in agreement with the findings of Scott et al.,[15] who found that WWTPs contributed just 6% and 8% of the PFOA and PFOS input, respectively, to Lake Superior.

A second major observation is that atmospheric deposition is a dominant source of PFAAs to the Baltic Sea. This conclusion is reinforced by the indirect contribution of atmospheric deposition through riverine input as indicated by the Oder catchment mass balance. Other emissions from the technosphere may contribute to PFAAs at the catchment level. For

instance, the COHIBA project estimated that other sources besides WWTP effluent (largely the use of firefighting foams on land) result in emissions of 160 kg/year PFOS and 330 kg/year PFOA to the Baltic Sea watershed.[36] This is <25% of our estimates of the total input to the Baltic Sea and <25% of the atmospheric deposition to the Baltic Sea catchment (scaled up from the Oder catchment). The dominant impact of atmospheric deposition is consistent with the work of Scott et al.,[15] who concluded that this is the dominant source of PFAAs to Lake Superior. Lake Superior has a large and sparsely populated watershed. The fact that atmospheric deposition also dominates in the highly populated Baltic Sea watershed provides stronger evidence that atmospheric deposition is currently a more important source of PFAA contamination of the environment than known anthropogenic emissions to land and water.

The importance of atmospheric deposition observed in this study is consistent with the results of a mass balance conducted on a smaller spatial scale.[37] A study of two rain events in a 10 km^2 watershed in Switzerland showed that rain, WWTP effluent, and surface runoff in stormwater all contributed significantly to the fluxes of a range of PFAAs. An explanation for the greater importance of WWTP effluent in the Swiss study is the higher population density of 2100 persons/km^2 compared with 49 and 136 persons/km^2 for the Baltic Sea and Oder catchments, respectively.

The dominance of atmospheric deposition as a PFAA source to a highly developed region such as the Baltic Sea has consequences for the environmental risk management of PFAAs. Focusing management efforts on reducing municipal WWTP emissions of PFAAs will not lead to marked reductions of PFAA inputs to the Baltic Sea. This can only be achieved by measures that lead to a reduction of atmospheric deposition of PFAAs. It is currently not clear what the sources of the PFAAs in the atmosphere are. One explanation is direct emissions of the chemicals. For instance, emissions from fluoropolymer production facilities have been proposed as a major source of PFOA to the atmosphere.[38] A second hypothesis is that they are formed from precursor compounds.[4] A third possibility is that PFAAs are being transferred via sea spray to the atmosphere,[39,40] and that the levels in atmospheric deposition are thus coming (at least partly) from environmental recirculation and not from primary emissions. Armitage et al.[41] used multimedia models and available data to assess the contributions of different sources to PFOA levels in the atmosphere, but they were unable to clearly identify the dominant source(s) due to large uncertainties in key parameters. The understanding of the sources of PFOS in the atmosphere is also incomplete, whereby a major contributor is believed to be the transformation of precursor compounds emitted from production facilities and fluorochemical products.[42] Research is urgently needed to identify the sources of PFAAs in the atmosphere.

A third major observation of the present study was that the input of the PFAAs to the Baltic Sea exceeds the output. This was the case for all four chemicals, regardless of whether the LBE or HBE results were used. This mass balance excess indicates that the concentrations of all chemicals are increasing in the Baltic Sea. When the difference between PFAA input and output is compared with the PFAA inventory, the doubling time for the concentration in the Baltic Sea can be estimated. This amounts to 8–94 years for PFHxA, 12–16 years for PFOA, 3–5 years for PFDA, and 4 years for PFOS. General

trends of increasing concentrations of PFOA, PFDA, and PFOS have been observed in biomonitoring data for Baltic Sea herring up to 2010 (Anders Bignert, personal communication). Although the year-to-year variability is considerable, these biomonitoring data suggest doubling times on the order of 10–15 years for PFOA, 4–8 years for PFDA, and 5–10 years for PFOS during the first decade of the millennium. This is broadly consistent with the mass balance results.

A positive mass balance for the Baltic Sea suggests that inputs during the period when the samples were collected (2005–2011) must have been higher than the average input during the previous 20 years (the water residence time in the Baltic Sea). No time trend data are available for atmospheric deposition.

It is notable that the contribution of direct atmospheric deposition to the total input to the Baltic Sea was smaller for PFOS than for the other substances; the dominant source was the rivers (Table 2). There are significant nonatmospheric sources of PFOS to river water, such as the use of firefighting foam. Firefighting foam is known to have been a major source of PFOS to the Norrström River,[21] which has elevated PFOS concentrations compared to the bulk of the rivers (see Table S4 in Supporting Information). The input from such sources could have increased over time. After firefighting training exercises, PFOS is known to be transferred into groundwater, from which it will eventually be discharged to surface water. The transfer of PFOS from training sites to groundwater has been shown to continue for years after PFOS release has ceased.[43] This can result in the peak in PFOS release to surface water being delayed compared to the peak in firefighting foam usage.

Another factor that could have caused an increase in riverine inputs of PFOS and other PFAAs during the 2000s is release of residues stored in the watershed. The median PFOS concentration in the world's background soils was recently estimated to be 0.47 ng/g dry weight, whereby one-sixth of the soil samples included in the international survey were from Norway.[44] Assuming that the Baltic Sea watershed is covered with a 10 cm deep layer of soil with this PFOS concentration, this soil would contain ~60 000 kg of PFOS. This is more than an order of magnitude greater than the PFOS inventory in the Baltic Sea (see Table 2). This illustrates that soil potentially is a large reservoir of PFOS that will buffer PFOS inputs from atmospheric deposition, delaying and modulating their transfer via surface runoff and groundwater to surface water. Currently little is known about the fate of PFAAs in watersheds. Research is needed to overcome this knowledge gap if we are to be able to develop effective strategies for reducing PFOS levels in surface waters and to predict how PFOS concentrations in surface waters will change as a result of management strategies.

In 2012 the European Commission proposed that concentrations of PFOS should not exceed 0.13 ng/L in marine waters.[45] PFOS concentrations in the Baltic Sea have already exceeded this limit. There is clearly a need to reduce the inputs of PFOS and other PFAAs to the Baltic Sea. This will require identifying and controlling the sources of PFAAs in the atmosphere and obtaining a better understanding of how they travel through the terrestrial environment to surface water.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Additional text and 18 tables with details of the mass balance calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Vaalgamaa, S.; Vähätalo, A. V.; Perkola, N.; Huhtala, S. Photochemical reactivity of perfluorooctanoic acid (PFOA) in conditions representing surface water. *Sci. Total Environ.* **2011**, *409*, 3043–3048.

(2) Annex Xv dossier proposal for identification of a substance as a cmr cat 1a or 1b, PBT, vPvB or a substance of an equivalent level of concern; BAuA Federal Office for Chemicals, Dortmund, Germany, 2011; http://echa.europa.eu/proposals-to-identify-substances-of-very-high-concern-previous-consultations/-/substance/1513/search/+/del/20/col/PUBLICATIONDATEAXVR/type/asc/pre/8/view.

(3) Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. Atmospheric chemistry of perfluoroalkanesulfonamides: Kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-ethyl perfluorobutanesulfonamide. *Environ. Sci. Technol.* **2006**, *40*, 864–872.

(4) Young, C. J.; Mabury, S. A. Atmospheric perfluorinated acid precursors: Chemistry, occurrence, and impacts. In *Reviews of Environmental Contamination and Toxicology*; De Voogt, P., Ed.; Springer: New York, 2010; Vol. *208*, pp 1–109.

(5) Kannan, K.; Tao, L.; Sinclair, E.; Pastva, S. D.; Jude, D. J.; Giesy, J. P. Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. *Arch. Environ. Contam. Toxicol.* **2005**, *48*, 559–566.

(6) Conder, J. M.; Hoke, R. A.; Wolf, W. de; Russell, M. H.; Buck, R. C. Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. *Environ. Sci. Technol.* **2008**, *42*, 995–1003.

(7) Chen, T.; Zhang, L.; Yue, J.; Lv, Z.; Xia, W.; Wan, Y.; Li, Y.; Xu, S. Prenatal PFOS exposure induces oxidative stress and apoptosis in the lung of rat off-spring. *Reprod. Toxicol.* **2012**, *33*, 538–545.

(8) Mhadhbi, L.; Rial, D.; Pérez, S.; Beiras, R. Ecological risk assessment of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in marine environment using *Isochrysis galbana, Paracentrotus lividus, Siriella armata* and *Psetta maxima. J. Environ. Monit.* **2012**, *14*, 1375–1382.

(9) Sources, transport, reservoirs and fate of dioxins, PCBs and HCB in the Baltic Sea environment; Swedish Environmental Protection Agency Report 5912; Stockholm, Sweden, 2009; http://naturvardsverket.se/Documents/publikationer/978-91-620-5912-5.pdf, pp 11–131.

(10) Kratzer, J.; Ahrens, L.; Roos, A.; Bäcklin, B.-M.; Ebinghaus, R. Reprint of: Temporal trends of polyfluoroalkyl compounds (PFCs) in liver tissue of grey seals (*Halichoerus grypus*) from the Baltic Sea, 1974–2008. *Chemosphere* **2011**, *85*, 253–261.

(11) Holmström, K. E.; Järnberg, U.; Bignert, A. Temporal trends of PFOS and PFOA in guillemot eggs from the Baltic Sea, 1968–2003. *Environ. Sci. Technol.* **2005**, *39*, 80–84.

(12) Nøst, T. H.; Helgason, L. B.; Harju, M.; Heimstad, E. S.; Gabrielsen, G. W.; Jenssen, B. M. Halogenated organic contaminants and their correlations with circulating thyroid hormones in developing Arctic seabirds. *Sci. Total Environ.* **2012**, *414*, 248–256.

(13) Becker, A.; Gerstmann, S.; Frank, H. Perfluorooctane surfactants in waste waters, the major source of river pollution. *Chemosphere* **2008**, *72*, 115–121.

(14) Boulanger, B.; Peck, A. M.; Schnoor, J. L.; Hornbuckle, K. C. Mass budget of perfluorooctane surfactants in Lake Ontario. *Environ. Sci. Technol.* **2005**, *39*, 74–79.

(15) Scott, B. F.; De Silva, A. O.; Spencer, C.; Lopez, E.; Backus, S. M.; Muir, D. C. G. Perfluoroalkyl acids in Lake Superior water: Trends and sources. *J. Great Lakes Res.* **2010**, *36*, 277–284.

(16) Helcom Website finding Baltic Sea facts: http://www.helcom.fi/environment2/nature/en_GB/facts/ (accessed January 4, 2013).

(17) CIA - The World Factbook, tracking the gross domestic product: https://www.cia.gov/library/publications/the-world-factbook/rankorder/2004rank.html (accessed July 6, 2012).

(18) McLachlan, M. S.; Holmström, K. E.; Reth, M.; Berger, U. Riverine discharge of perfluorinated carboxylates from the European continent. *Environ. Sci. Technol.* **2007**, *41*, 7260–7265.

(19) EU Wide Monitoring Survey of Polar Persistent Pollutants in European River Waters; European Comission, Joint Research Centre, Institute for Environment and Sustanability, Luxembourg, 2008; http://publications.jrc.ec.europa.eu/repository/bitstream/111111111/7489/1/48459%20-%20new%20correct%20version_-_eumore_eur_report_loos_28_11_08%20errata%20corrige.pdf.

(20) Dreyer, A.; Matthias, V.; Weinberg, I.; Ebinghaus, R. Wet deposition of poly- and perfluorinated compounds in Northern Germany. *Environ. Pollut.* **2010**, *158*, 1221–1227.

(21) Results from the Swedish National Screening Programme 2005, Subreport 3: Perfluorinated Alkylated Substances (PFAS); IVL Swedish Environmental Research Institute, Norwegian Institute for Air Research NILU, Sweden, Stockholm, 2005; http://www.ivl.se/download/18.7df4c4e812d2da6a416800071897/B1698.pdf.

(22) Kwok, K. Y.; Taniyasu, S.; Yeung, L. W. Y.; Murphy, M. B.; Lam, P. K. S.; Horii, Y.; Kannan, K.; Petrick, G.; Sinha, R. K.; Yamashita, N. Flux of perfluorinated chemicals through wet deposition in Japan, the United States, and several other countries. *Environ. Sci. Technol.* **2010**, *44*, 7043–7049.

(23) WP3 Innovative approaches to chemical controls of hazardous substances, national report of Latvia: Latvian Institute of Aquatic Ecology, Riga, Latvia, 2011; http://www.cohiba-project.net/identification/results/en_GB/results/_files/86204541090333826/default/COHIBA-WP3_National%20Report%20Latvia.pdf.

(24) WP3 Innovative approaches to chemical controls of hazardous substances, national report of Lithuania: Institute of Botany, Nature Research Centre, Vilnius, Lithuania, 2010; http://www.cohiba-project.net/publications/en_GB/publications/_files/87105800188200474/default/COHIBA-WP3_National%20Report%20Lithuania.pdf.

(25) WP3 Innovative approaches to chemical controls of hazardous substances, national report of Estonia: Estonian Environmental Research Centre; Tallinn, Finland, 2011; http://www.cohiba-project.net/identification/results/en_GB/results/_files/86074458170261965/default/augusti_parandused_wp3nr_uk050911_templiidil_kaantega.pdf.

(26) WP3 National report of Sweden: IVL Swedish Environmental Research Institute, Stockholm, Sweden, 2011; http://www.cohiba-project.net/identification/results/en_GB/results/_files/86289229930497499/default/COHIBA-WP3_National_report_SE_Final_20sep11.pdf.

(27) Cohiba WP3 national report, Polish results: The Institute for Ecology of Industrial Areas (IETU), Katowice, Poland, 2011; http://www.cohiba-project.net/identification/results/en_GB/results/_files/86074482568397267/default/20111021%20COHIBA-WP3_National%20report%20Germany_fin.pdf.

(28) WP3 Innovative approaches to chemical controls of hazardous substances, results from chemical analysis, national report of Finland: Finnish Environment Institute SYKE, Helsinki, Finland, 2011; http://www.cohiba-project.net/identification/results/en_GB/results/_files/86074462319739344/default/National%20report%20-%20Finland%20-%2019072011%20final.pdf.

(29) National report of the German results of Cohiba WP 3 work: Agency for Environment, Nature Conservation and Geology Mecklenburg-Vorpommern; Güstrow, Germany, 2011; http://www.cohiba-project.net/identification/results/en_GB/results/_files/86074482568397267/default/20111021%20COHIBA-WP3_National%20report%20Germany_fin.pdf.

(30) WP3 Innovative approaches to chemical controls of hazardous substances, results from chemical analysis, acute and chronic toxicity tests in sase studies, Danish national report: http://www.cohiba-project.net/publications/en_GB/publications/_files/8710580018820047/default/COHIBA-WP3_National%20Report%20Lithuania.pdf.

(31) Ahrens, L.; Gerwinski, W.; Theobald, N.; Ebinghaus, R. Sources of polyfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea: Evidence from their spatial distribution in surface water. *Mar. Pollut. Bull.* **2010**, *60*, 255–260.

(32) Kirchgeorg, T.; Weinberg, I.; Dreyer, A.; Ebinghaus, R. Perfluorinated compounds in marine surface waters: data from the Baltic Sea and methodological challenges for future studies. *Environ. Chem.* **2010**, *7*, 429–434.

(33) The POPCYCLING-Baltic model: a non-steady state multi-compartment mass balance model of the fate of persistent organic pollutants in the Baltic Sea environment. Norwegian Institute for Air Research, Kjeller, Norway, 2000; http://www.utsc.utoronto.ca/~wania/downloads3.html.

(34) Theobald, N.; Baldwin, W.; Artsalee, C.; Haarich, M. Entwicklung und Validierung einer Methode zur Bestimmung von polyfluorierten organischen Substanzen in Meerwasser, Sedimenten und Biota; Untersuchungen zum Vorkommen dieser Schadstoffe in der Nord- und Ostsee, Im Auftrag des Umweltbundesamtes Deutschland, Texte 41/07, ISSN 1862–4804; http://172.16.1.5/ajax/actions.hsp?_h=4cb0a4a2128737d44620a079d761b351&action=viewattachment&mid=1&fid=306_67114557&attid=3 (accessed November 21, 2011).

(35) Baltic Nest Institute Web site; http://www.balticnest.org/ (accessed March 12, 2013).

(36) COHIBA Guidance document no. 4 for PFOS and PFOA: Federal Environment Agency of Germany (UBA) and Finnish Environment Institute (SYKE), Helsinki, Finland, 2011; http://www.cohiba-project.net/publications/en_GB/publications/_files/87107446768797277/default/PFOA-PFOS.pdf.

(37) Müller, C. E.; Spiess, N.; Gerecke, A. C.; Scheringer, M.; Hungerbühler, K. Quantifying diffuse and point inputs of perfluoroalkyl acids in a nonindustrial river catchment. *Environ. Sci. Technol.* **2011**, *45*, 9901–9909.

(38) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40*, 32–44.

(39) McMurdo, C. J.; Ellis, D. A.; Webster, E.; Butler, J.; Christensen, R. D.; Reid, L. K. Aerosol enrichment of the surfactant PFO and mediation of the water–air transport of gaseous PFOA. *Environ. Sci. Technol.* **2008**, *42*, 3969–3974.

(40) Reth, M.; Berger, U.; Broman, D.; Cousins, I. T.; Nilsson, E. D.; McLachlan, M. Water-to-air transfer of perfluorinated carboxylates and sulfonates in a sea spray simulator. *Environ. Chem.* **2011**, *8*, 381–388.

(41) Armitage, J. M.; MacLeod, M.; Cousins, I. T. Modeling the global fate and transport of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources using a multispecies mass balance model. *Environ. Sci. Technol.* **2009**, *43*, 1134–1140.

(42) Armitage, J. M.; Schenker, U.; Scheringer, M.; Martin, J. W.; MacLeod, M.; Cousins, I. T. Modeling the global fate and transport of perfluorooctane sulfonate (PFOS) and precursor compounds in relation to temporal trends in wildlife exposure. *Environ. Sci. Technol.* **2009**, *43*, 9274–9280.

(43) Moody, C. A.; Field, J. A. Determination of perfluorocarboxylates in groundwater impacted by fire-fighting activity. *Environ. Sci. Technol.* **1999**, *33*, 2800–2806.

(44) Strynar, M. J.; Lindstrom, A. B.; Nakayama, S. F.; Egeghy, P. P.; Helfant, L. J. Pilot scale application of a method for the analysis of perfluorinated compounds in surface soils. *Chemosphere* **2012**, *86*, 252–257.

(45) Circa Webpage tracking PFOS dossier; http://circa.europa.eu/Public/irc/env/wfd/library?l=/framework_directive/thematic_documents/priority_substances/supporting_substances/eqs_dossiers/pfos_dossier_2011pdf/_EN_1.0_&a=d (accessed Aug 30, 2012).

(46) HELCOM 2004, The Fourth Baltic Sea Pollution Load Compilation (PLC-4); Baltic Sea Environmental Proceedings no. 93; http://www.helcom.fi/stc/files/Publications/Proceedings/bsep93.pdf.

(47) Al-Hamdani, Z., Reker, J., Eds. Towards marine landscapes in the Baltic Sea. BALANCE interim report no. 10, 2007. Available at http://balance-eu.org/.

(48) Aniansson, B. H. Nordic Council; International Conference on the Pollution of the Seas Northern Europe's seas, Northern Europe's environment: report to the Nordic Council's International Conference on the Pollution of the Seas, 16–18 October 1989; Nordic Council, Stockholm, Sweden, 1989.

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dx.doi.org/10.1021/es400174y | *Environ. Sci. Technol.* 2013, 47, 4088–4095