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Mass Balance of Perfluorinated Alkyl Acids in a Pristine Boreal Catchment

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Ⓢ Supporting Information

ABSTRACT: Mass balances of ten individual perfluorinated alkyl acids (PFAAs) in two nested pristine catchments in Northern Sweden with different sizes and hydrological functions were assembled for 2011−2012. Concentrations of PFAAs in rain and snowmelt, as well as in streamwater at the outlet of the two watersheds were measured and used to calculate PFAA atmospheric inputs to and riverine outputs from the catchments. The results generally showed a great excess of PFAA inputs for both catchments over the whole study year. However, during the spring flood period, the inputs and outputs were within a factor of 2 for several PFAAs and the streamwater showed PFAA patterns resembling the patterns in rain (as opposed to snowmelt), suggesting that snowmelt water infiltrating the ground had displaced water from the previous summer. Comparison of PFAA mass balances between the two catchments further suggested that atmospheric inputs of short-chain (replacement) perfluoroalkyl carboxylic acids had increased in the years before sampling, while inputs of the legacy perfluorooctane sulfonic acid had decreased. Overall, the mass balances indicate that a considerable portion of the PFAAs deposited from the atmosphere are stored in soil and may be released to surface and marine water environments in the future.
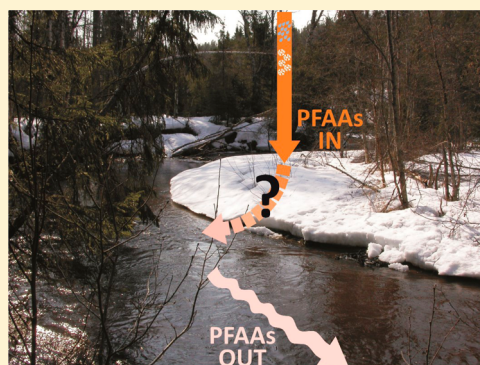
1. INTRODUCTION

Perfluorinated alkyl acids (PFAAs) are a class of anthropogenic surfactants with a fully fluorinated carbon chain attached to an acid group. Two subgroups of PFAAs of environmental concern are perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs).[1] The most-studied PFCA and PFSA are the C8-homologues perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), respectively. Some PFAAs have been produced for more than 60 years. The cumulative global production volume of PFOS-based chemicals between 1970 and 2002 has been estimated to be 96 000 t,[2] and for PFCAs to be 2610−21400 t between 1951 and 2015.[3] The unique properties of highly fluorinated compounds (e.g., thermal stability, extraordinary potential to lower the surface tension, water/oil repellence) make them suitable for a broad range of industrial and consumer product applications, such as in the production process of fluoropolymers, as impregnating agents for clothing and food packaging material, in thermostatic oils, and as surface tension lowering agents in aqueous film forming fire-fighting foams. PFAAs are environmentally persistent and long-chain PFAAs (>C5 PFSAs and >C7 PFCAs) are bioaccumulative and toxic.[4,5] PFAAs have been detected in environmental matrixes such as different water bodies including snow,[6−8] and in wildlife.[9]

The ubiquitous presence of PFAAs in the environment has raised concerns among researchers and authorities regarding the environmental fate and transport of these chemicals. The transport of PFAAs in the atmosphere has been hypothesized to occur via two routes. First, nonionic precursor compounds such as fluorotelomer alcohols (FTOHs) are transported in the gas phase where they can undergo transformation before being deposited as PFAAs.[10] Second, the ionic PFAAs can undergo atmospheric transport sorbed to airborne particles,[11] which can be transported long distances due to the intermittent nature of their primary removal process, rain.[12] PFAAs have been detected in atmospheric deposition including rain and snow in low concentrations (<1 ng L^{−1}) in both industrialized and remote regions in North America, Asia, Europe, and Antarctica.[13−17] A recent modeling study suggested that atmospheric deposition is the dominant input pathway of PFAAs to the Baltic Sea.[18]

A number of studies have reported the occurrence of PFAAs in seemingly pristine groundwater and rivers worldwide.[19,20] However, so far there have been no studies that systematically

investigated the fate of PFAAs in pristine watersheds. The aim of this study was to gain insight into transport processes and retention of different PFAA homologues within a watershed, as well as to understand the influence of temporal trends in atmospheric inputs on riverine outputs of PFAAs. For this purpose, mass balances were assembled for PFAAs in a remote, pristine environment, unaffected by local human activities. The Krycklan Catchment Study site, a low population, uniquely instrumented research catchment in Northern Sweden, was chosen as the study area. PFAA concentrations were measured in atmospheric bulk deposition and snowmelt as well as in two streams with different catchment areas and hydrological function over the course of one year. PFAA mass balances over the two catchments were assembled separately for the spring flood period, for the rest of the year, and for the whole year.

2. MATERIALS AND METHODS

2.1. Site Description. The present study was conducted at the Krycklan Catchment Study (KCS), located approximately 60 km inland from the Baltic Sea in Northern Sweden (64° 14′ N, 19° 46′ E; Figure 1).[21] KCS is located in the Boreal biome,
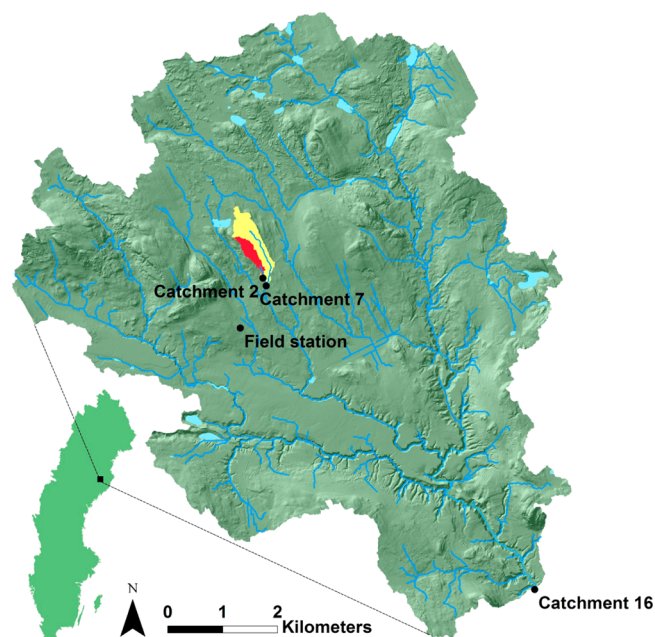

Figure 1. Illustration of the study site. Small figure: Map of Sweden with the black square showing the location of the Krycklan Catchment Study (KCS). Large figure: Whole KCS watershed (catchment 16) with the subcatchments 2 (red area) and 7 (yellow and red area) and the position of the Svartberget field station where atmospheric deposition samples were collected (black dot). The sampling sites for stream 2 and stream 16 and the runoff measuring site C7 are also indicated by black dots.

with a cold temperate humid climate. Snow, which makes up approximately 50% of the annual precipitation, covers the ground for on average 168 days each year. The 30-year mean annual temperature (1981−2010) was 1.8 °C, annual precipitation 614 mm, and stream runoff 311 mm (i.e., 0.311 m^3 per m^2 catchment area).[22]

Two of the 17 long-term monitored KCS streams were included in this study; Västrabäcken (stream 2) and the Krycklan outlet (stream 16) (Figure 1). The selection of the

two study catchments was based on already existing research infrastructure and ancillary data that helped obtaining a mechanistic insight into transport processes of PFAAs. The stream 2 catchment (C2) is one of the most studied within KCS and is described in detail elsewhere.[23,24] In short, the 0.12 km^2 catchment is underlain by unsorted till soils. The area is entirely forested, primarily with Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*), with an understory dominated by ericaceous shrubs, mostly bilberry (*Vaccinium myrtillus*). The much larger stream 16 catchment (C16; 67.8 km^2) provides the outlet of KCS. It has been closely studied in recent years.[25] Soils consist of unsorted sand/silt till in the upper half of the catchment and sorted sand/silt in the lower lying regions. The vegetation is similar to C2, but C16 also includes 9% mires and 1% lakes.

C2 is pristine with no human population and very limited forestry activity during the last 100 years. In C16, less than 2% is arable land used for low intensity farming. Forestry is practiced using conventional methods in approximately 60% of the area. The population comprises fewer than 100 people, and there are no known wastewater outlets or anthropogenic pollution sources that would affect surface water quality.[21]

2.2. Samples. *2.2.1. Atmospheric Deposition.* Field duplicates of 11 sequential atmospheric bulk deposition samples were collected covering the period from May 5th to November 21st, 2011 (hereafter called rain samples), and 9 sequential snowmelt samples were collected from a snow lysimeter during April and May 2012, representing the complete snowfall and dry deposition from the winter 2011/ 2012 (hereafter called snowmelt samples) at an open field at the Svartberget field station in KCS (Figure 1). The atmospheric bulk deposition sampler consisted of a 15 cm diameter polypropylene funnel connected via an 80 cm polypropylene tube (i.d., 1 cm, with a constriction at the lower end of the tube to minimize evaporation of collected rainwater) to a 1 L high-density polyethylene bottle. All parts of the atmospheric deposition sampler were rinsed with methanol before sampling. The sampling bottle (wrapped in aluminum foil) was placed on the ground and the funnel was mounted 1 m above the ground. The snow lysimeter has been described in detail elsewhere.[26] In short, the snow accumulation part consisted of a 1.44 m^2 square area with a drain in one corner. The lysimeter was cleaned with ethanol during late autumn prior to any snow accumulation. The change from rain sampling to snow sampling was made as soon as snow began to permanently accumulate in the catchment to build up the seasonal snow cover. Any precipitation as rain or snow prior to this time was accounted for as rain, and any afterward as snow. The sampling occasions for all atmospheric deposition samples are shown in Figure S1 in the Supporting Information.

2.2.2. Streamwater. The two streams, 2 and 16, were selected for the study because of their differences in size (Figure 1) and hydrological function as well as based on available research infrastructure and ancillary data. Stream water was usually sampled on the same days at both sites. The sampling procedure has previously been described in detail.[21] Generally, two samples per month were taken from June 2011 to November 2011 (December 2011 for stream 2), while ten (stream 2) and 11 (stream 16) samples were taken during spring flood in April and May 2012 (Figure S1). Additionally, two samples per month were taken from June and July 2012 for comparison with the respective months in 2011. In this way, a total of 26 and 25 samples were collected for stream 2 and 16,

respectively. From December 2011 (January 2012 for stream 2) to March 2012, stream samples were not available and PFAA concentrations measured in November 2011 (December 2011 for stream 2) were used in the PFAA stream discharge calculations for the winter months. Winter base flow (from the start of snow accumulation in November to the onset of snowmelt in early April) is a stable water quality period[27] constituting less than 20% of the annual runoff.[28] All water samples were stored in a cold room at 4 °C before extraction. All meteorological and hydrological records used in this study are freely available data from the KCS infrastructure (www.slu. se/Krycklan). The meteorological data were collected at the Svartberget field station, whereas the stream runoff data for stream 2 and 16 were extrapolated from measurements (measured every 10 min and averaged to daily values) of the runoff at field site C7 30 m downstream of the sampling point for stream 2 (Figure 1). The extrapolation was based on scaling the C7 runoff to the catchment sizes of C2 (factor 0.240) and C16 (factor 144) following earlier published work.[29−31] The long-term monitored catchment C7 provides an average runoff per area for the whole Krycklan and is thus representative also for other catchments within the KCS.[32]

2.3. Chemical Analysis. *2.3.1. Chemicals and Reagents.* Stable isotope labeled and native PFAA standards were purchased from Wellington Laboratories (Guelph, ON, Canada) in 2 μg mL^{-1} solution mixtures dissolved in methanol. The 10 target analytes were perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluoro-dodecanoic acid (PFDoDA), perfluorohexane sulfonic acid (PFHxS), perfluorooctane sulfonic acid (PFOS), and perfluoro-decane sulfonic acid (PFDS).

The following stable isotope labeled PFAAs containing <0.5% of their native analogs were used as surrogate internal standards (IS): $^{13}C_2$−PFHxA, $^{13}C_4$−PFHpA, $^{13}C_4$−PFOA, $^{13}C_5$−PFNA, $^{13}C_2$−PFDA, $^{13}C_2$−PFUnDA, $^{13}C_2$−PFDoDA, $^{18}O_2$−PFHxS, and $^{13}C_4$−PFOS. $^{13}C_8$−PFOA and $^{13}C_8$−PFOS were used as volumetric internal standards for calculation of total method recovery of the IS. Solvents and reagents used in this work were of HPLC grade or highest commercial purity. Methanol and 1-methylpiperidine were purchased from Merck (Hohenbrunn, Germany) and acetonitrile was purchased from Sigma-Aldrich (Steinheim, Germany).

2.3.2. Sample Extraction. All water samples were allowed to reach room temperature prior to analysis. The two streamwater samples collected in the same month were pooled (1:1) before analysis for each of the streams. Stream water samples from the spring flood and all atmospheric deposition samples were analyzed individually. A volume of 60 μL IS solution (10 pg μL^{-1} of each IS in methanol) was added directly to the sampling bottle containing rainwater or snowmelt water (400−1000 mL). For streamwater samples, 30 μL IS solution (20 pg μL^{-1} of each IS in methanol) was added to 500 mL of sample. The water samples were then shaken for 24 h using a KS501 digital orbital shaker (IKA, Staufen, Germany) and thereafter placed in an ultrasonic bath (Ultrasonic cleaner, USC-TH, VWR International) for 30 min prior to extraction.

All samples were extracted and extracts were cleaned up using a method described for drinking water and wastewater.[33] Briefly, the bulk samples (including particles) were extracted on prewashed (16 mL of 2 vol % 1-methylpiperidine in methanol/ acetonitrile (80/20)) mixed mode C8+quaternary amine solid

phase extraction cartridges (CUQAX256, 500 mg, 6 mL, UTC, Bristol, PA). The water samples were loaded at 5 mL min^{-1} using a vacuum manifold. The target compounds were eluted by gravity with 8 mL of 2 vol % 1-methylpiperidine in methanol/acetonitrile (80/20), which took up to 30 min. The extracts were evaporated to dryness under a gentle stream of nitrogen at 40 °C and the residuals were reconstituted in 70 μL methanol and 100 μL 4 mM aqueous ammonium acetate. A volume of 30 μL of a 20 pg μL^{-1} solution of the volumetric standards in methanol was added before instrumental analysis.

2.3.3. Instrumental Analysis and Quantification. The extracts were analyzed on an Acquity ultraperformance liquid chromatography system coupled to a Xevo TQ-S tandem mass spectrometer (UPLC/MS/MS; Waters Corp., Milford, MA) according to a previously published method.[33] Briefly, 5 μL of the extracts were injected and the analytes were separated on a BEH C18 (50 mm × 2.1 mm i.d., 1.7 μm particle size; Waters Corp.) analytical column kept at 50 °C using a flow rate of 0.4 mL min^{-1} and a binary gradient of mobile phase (A) 90% water and 10% acetonitrile and (B) acetonitrile, both containing 2 mM ammonium acetate.

The mass spectrometer was operated in negative electrospray ionization mode using the following settings: capillary voltage 1.0 kV, source temperature 150 °C, desolvation temperature 450 °C, desolvation and cone gas flow (nitrogen) 800 and 200 L h^{-1}, respectively. The cone voltage and collision energy were optimized compound-specifically and are given in the Table S1, together with the measured MS/MS transitions for all analytes. For PFOS two product ions were measured (m/z 80 and m/z 99).

PFAAs were quantified using the internal standard method and a five point external calibration curve, spanning concentrations from the individual method detection limits (MDLs) to 5 pg μL^{-1}. All analytes had authentic stable isotope labeled IS except for PFDS, for which $^{13}C_4$−PFOS was employed. However, PFDS was not detected in the samples. For PFOS the linear isomer (L-PFOS) and the sum of branched isomers (br-PFOS) were quantified separately using the calibration curve of the linear standard. This procedure is known to overestimate the concentration of br-PFOS when using the transition to m/z 80 and underestimate when using m/z 99.[34] Branched PFOS concentrations given in this study are therefore averages of the concentrations calculated using the two transitions. PFOS (without prefix) refers to the sum of L-PFOS and br-PFOS.

2.3.4. Analytical Quality Control. Analytical quality control included a minimum of six procedural blank replicates with each batch of samples. Quantified PFAA concentrations in the blanks were used to estimate the individual method detection limits (MDLs, Table S2) for the respective batch of samples. The MDLs were calculated as the arithmetic mean plus three times the standard deviation in the procedural blanks. This is a conservative approach of defining the MDL.[35] Therefore, all signals above MDL in sample chromatograms were quantified and used in statistical analysis. Blank correction was not performed. The analytical procedure was further quality controlled through calculation of absolute IS recoveries and by precision testing using the atmospheric deposition field duplicate samples. Details are given in the section "Analytical quality control" in the SI including Tables S3−S5.

2.4. Mass Balance Model. PFAA mass balances were assembled for the watersheds of C2 and C16 considering inputs from rain and snow (including particles and dry deposition),

while stream runoff was the only output pathway considered. Earlier studies have shown that volatilization, hydrolysis, and sediment burial of PFAAs are not significant output or loss mechanisms under environmental conditions.[18,36] Export to other watersheds via deep groundwater was neglected since it does not notably contribute to the total water flow in the catchment.[37] This is related to the glacial history of the region that resulted in a base till with extremely low hydrological conductivity underlying the catchment. Hence, most of the hydrological pathways in the catchment are shallow, occurring in the upper meters of the soil.[24]

In the calculation of atmospheric inputs of PFAAs via rain, averages of the PFAA concentrations in the field duplicates were used. The amount of precipitation during the individual sampling periods for rain samples is shown in Figure S2. In the calculation of stream outputs, the total flow for the whole month was multiplied by the PFAA concentrations in the monthly pooled samples (June 2011 to March 2012), while during spring flood (April–May 2012) the PFAA concentrations in the individual samples were multiplied by the flows that had occurred during the time period defined by the midpoints of the intervals between the samples. The calculated water flows for stream 2 and stream 16 for the time periods represented by the individual samples are presented in Figures S3 and S4, respectively. A detailed description of the calculations of inputs and outputs is provided in the SI in the section "Calculation of PFAA inputs and outputs".

Three mass balances for different time periods were assembled for each catchment: (i) Spring flood, including all snowmelt water (lysimeter samples) as input and stream discharges from April and May 2012 (the two months covering the complete hydrological spring flow, see Figures S3 and S4) as output; (ii) rest of the year, including bulk deposition samples from May to November 2011 as input and stream discharges from June 2011 to March 2012 as output; and (iii) whole year (June 2011 to May 2012), combining the inputs and the outputs from (i) and (ii). Two estimates were calculated: a high-bound estimate (HBE), for which all of the PFAA concentrations <MDL were set to the respective MDL and a low-bound estimate (LBE), for which all of the PFAA concentrations <MDL were set to 0.

3. RESULTS AND DISCUSSION

3.1. Concentrations and Patterns of PFAAs in Rain and Snowmelt.
PFAA concentrations in the individual rain and snowmelt samples are presented in the Tables S6–S9. PFCAs with 6 to 12 carbons (PFHxA to PFDoDA) and PFSAs with 6 and 8 carbons (PFHxS and PFOS) were detected in both types of deposition samples. For each season, the PFAA concentrations in the atmospheric deposition for the whole season (referred to as bulk concentrations) were calculated by dividing the total mass of chemical deposited during the season by the total volume of precipitation (as water); see Figure 2A for summer (rain) and Figure 2B for winter (snowmelt). PFHxA, PFHpA, PFOA, and PFNA were the dominant PFAAs with bulk concentrations of several hundred pg L^{-1}. PFOS showed the highest levels among the PFSAs in both rain and snowmelt, with a bulk concentration of 76 and 29 pg L^{-1}, respectively, and an average percentage of br-PFOS relative to total PFOS of 39 and 52%, respectively (Figure 2, parts A and B). Current atmospheric inputs of PFSAs to this remote region of Northern Europe are thus very low compared to PFCAs. This is likely due to the phase-out of the manufacturing of
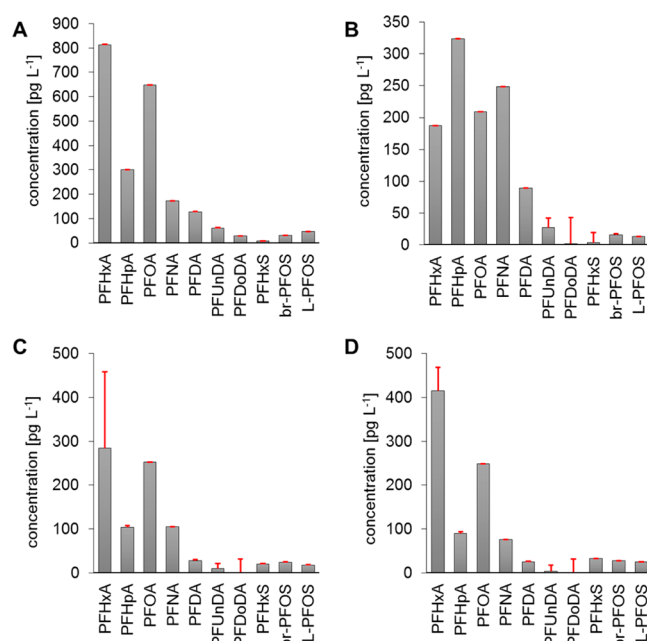

Figure 2. Bulk concentrations of PFAAs in (A) rain and (B) snowmelt and in stream 2 during (C) spring flood and (D) rest of the year. Bulk concentrations were calculated as the total mass of chemical deposited during the season divided by the total volume of precipitation (A and B) or the total mass of chemical discharged in the stream divided by the total water discharge (C and D). The low-bound estimate concentrations are shown with solid bars and the high-bound estimate values with error bars.

PFOS and its precursors by the 3 M Company in 2002, while the production and use of PFCAs and their fluorotelomer-based precursors is still continuing. The PFAA concentrations in snowmelt in the present study were comparable to PFAA levels determined in snow samples from Krycklan collected in 2009[38] and in Tibetan mountain snow collected in 2010.[39] The PFHxA, PFOA, and PFOS concentrations in the present study ranged from 105 to 477, 116–808, and <4–49 pg L^{-1}, respectively, in Krycklan samples from 2009 from 17.5 to 154, < MDL-122, and 2.6–253 pg L^{-1}, and in the Tibetan snow from 63.5 to 140, 68–191, and 25–64.2 pg L^{-1}.

The elution profiles of the PFAAs from the snow lysimeter during snowmelt are shown in the Figure S5. They are in agreement with the elution profiles determined in an earlier study in a snowmelt simulator,[40] showing an early elution (first flush) of the short-chain PFCAs (PFHxA and PFHpA) and a late elution of the long-chain homologues, as well as a significant fraction of all PFAAs in the last sample containing most of the particles.

The PFAA pattern in rain was dominated by PFHxA and PFOA (Figure 2A), while PFHpA and PFNA dominated in snowmelt (Figure 2B). Looking at the individual precipitation samples, there were statistically significant differences in PFAA concentrations between rain and snowmelt. The mean concentrations of PFHxA and PFOA in rain (826 and 650 pg L^{-1}, respectively) were significantly higher than in the snowmelt samples (227 and 270 pg L^{-1}, respectively) ($p <$ 0.05, t test), while the mean concentration of PFNA in rain was lower than in the snowmelt samples (179 versus 300 pg L^{-1}, p < 0.05, t test). The higher concentrations of PFHxA and PFOA, both in absolute terms and relative to PFHpA and PFNA, in rain compared to snowmelt could possibly be explained by
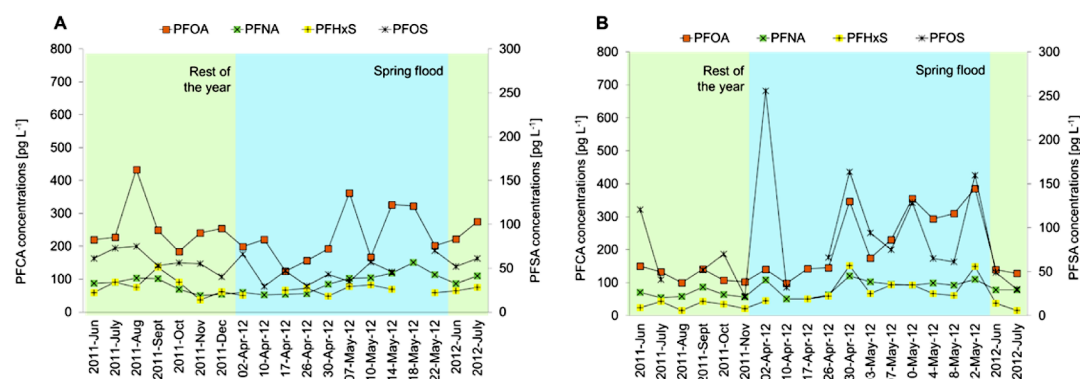
Figure 3. Concentrations of selected PFAAs in (A) stream 2 samples and (B) stream 16 samples. The PFAAs with a detection frequency ≥90% are shown. The results are shown sequentially according to the time point of sampling. Results for samples from June and July 2012 are shown to demonstrate the comparability between years (compared to June and July 2011). However, these results were not used in the mass balance calculations.

transformation of airborne 6:2 and 8:2 fluorotelomer-based precursors to PFHxA and PFOA, respectively. Young and Mabury have reviewed the current knowledge on atmospheric chemistry of PFASs.[10] Different transformation pathways of airborne precursors to PFCAs have been suggested, leading to different chain length patterns of PFCAs. For example, transformation via a perfluorinated radical at low NO_x concentrations would predominantly result in even chain PFCAs, as observed in the rain samples of the present study, but not in the snow samples. PFCA pattern differences between different deposition samples could thus potentially be used to elucidate the relative importance of the suggested transformation pathways under certain environmental conditions (NO_x concentration, temperature, and solar irradiation). Alternatively, the PFHxA and PFOA enriched pattern in rain could be the result of direct emissions of these chemicals to the atmosphere, as demonstrated by the measurements from Hazelrigg performed by Barber et al. 2007.[41]

3.2. Concentrations and Patterns of PFAAs in Streamwater. Concentrations of PFAAs in the samples from streams 2 and 16 are presented in Figure 3, and Tables S10–S11. The detection frequencies of the individual PFAAs in the samples from the two streams are summarized in the Table S4. Bulk concentrations during spring flood and during the rest of the year were calculated for stream 2 in a manner analogous to the precipitation samples; the total mass of chemical discharged by the stream during the season was divided by the total water discharge (Figure 2, parts C and D). Our results were comparable to PFAA concentrations in river samples from Vindelälven (a river located near Krycklan in Northern Sweden) collected in 2005[19] and 2013.[42] The PFHpA, PFOA, PFNA, and PFOS concentrations in the streams analyzed in the present study ranged from <23−166 pg L^{-1}, 98−434 pg L^{-1}, 50−151 pg L^{-1}, and <44−256 pg L^{-1}, respectively, while for Vindelälven they were reported as 200 pg L^{-1}, < 650 pg L^{-1}, 220 pg L^{-1}, and "not analyzed" in 2005, and as <30 pg L^{-1}, < 170−260 pg L^{-1}, 260−360 pg L^{-1}, and 74− 250 pg L^{-1} in 2013.

Peralta-Tapia et al. have reported for the C2 catchment that snowmelt water in spring displaces shallow groundwater,[24] resulting in a spring flood in stream 2 that is dominated by water from the previous summer and autumn.[43] In line with this finding, the PFCA pattern observed in the water from stream 2 during spring flood (Figure 2C) shows a dominance of PFHxA and PFOA, which is more comparable to rain

samples than snowmelt (Figure 2, parts A and B). Thus, our results confirm that a significant amount of water from the previous summer/autumn was discharged in stream 2 during the spring flood of 2012.

A significant difference between the two stream systems was observed when comparing PFAA concentrations between spring flood and the rest of the year. For stream 2, there was no noteworthy seasonal difference for any of the investigated PFAAs (Figure 2, parts C and D), though the sample to sample variability was relatively high (Figure 3A). The concentrations in stream 16 during spring flood were comparable to the concentrations in stream 2 (Figure 3, parts A and B), which is likely a reflection of both streams receiving a large contribution of shallow groundwater containing recent PFAA deposition during the spring.[43] However, stream 16 showed considerably lower levels of PFOA and PFHxS during the rest of the year compared to the spring flood (Figure 3B, Table S11). This can be explained by the much older age of the water in stream 16 during base flow. Using stable oxygen isotopes as a tracer, a contribution of 82% of old groundwater to stream 16 has been demonstrated, while only 18% of deeper groundwater reaches stream 2.[27] Additionally, the deep groundwater in C16 is considerably older compared to C2, due to the much larger size of C16 and the correspondingly longer water residence time of at least a decade in the subsurface environment. Our results indicate that this old groundwater reaching stream 16 during base flow likely had considerably lower concentrations of several PFAAs. The only PFAA with a comparable average concentration during the rest of the year in stream 16 and stream 2 was PFOS, which suggests that the deep groundwater feeding stream 16 and the shallow groundwater feeding stream 2 had similar concentrations of this chemical (despite retention in the soil column). The global production and emission maximum of PFOS and its precursors was in the late 1990s, before the 3M Company started to phase out the production in 2000. The relatively high PFOS levels in stream 16 could thus originate from atmospheric inputs from the late 20th century. For a discussion of temporal changes of atmospheric PFAA inputs, see section 3.3.2 below.

3.3. Mass Balance of PFAAs in Krycklan Catchments. *3.3.1. Boundary Conditions for the Mass Balance.* The water mass balance during the study period was close to a steady state, with precipitation close to the long-term average, streamwater outflow during the spring flood about equal to meltwater from the winter's precipitation, and streamwater
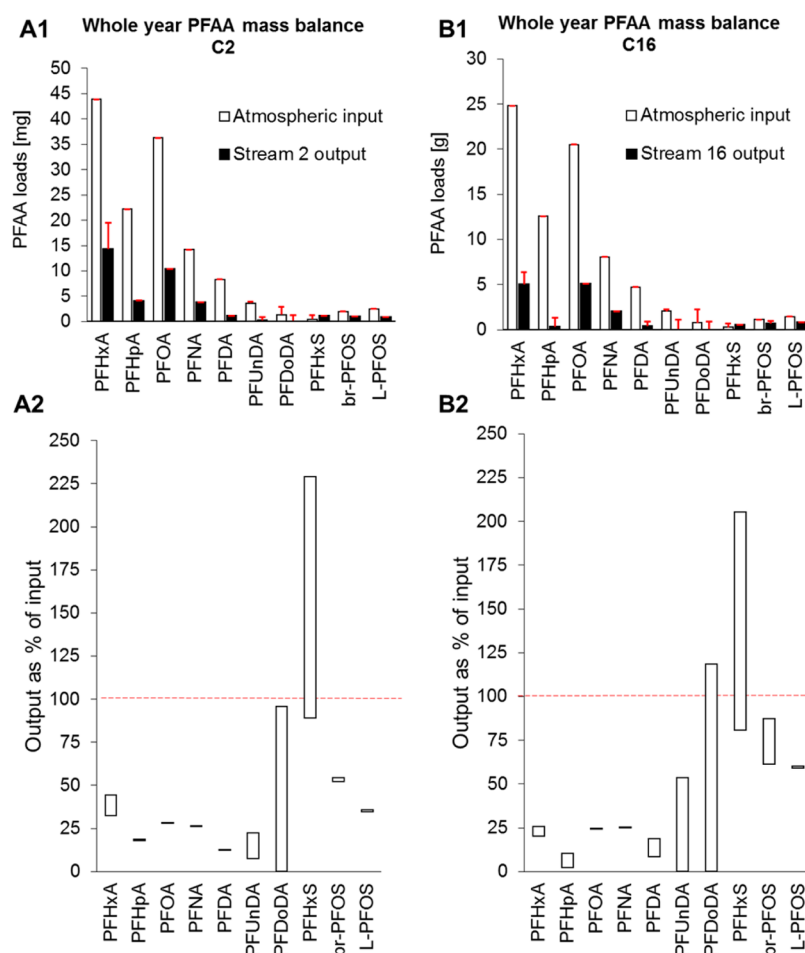
Figure 4. Total PFAA atmospheric inputs (white bars) and stream discharges (black bars) over the whole year are compared for (A1) C2 and (B1) C16. The LBE values are shown with solid bars and the HBE values with error bars. The output expressed as percentage of the input is shown for (A2) C2 and (B2) C16. The ranges depict LBE$_{output}$/HBE$_{input}$ to HBE$_{output}$/LBE$_{input}$. A closed mass balance would correspond to 100% (dashed line).

outflow during the rest of the year equal to about half of the precipitation, while the other half returned to the atmosphere by evapotranspiration.[31] Details are given in the SI section "Water mass balance for C2 and C16" including Table S12. However, steady state conditions were not expected for PFAAs for the following reasons. (i) Emissions of PFAAs and their precursors to the atmosphere have been changing over the last decades as a result of changes in production and use. Changing atmospheric inputs of PFCAs to remote regions have been demonstrated by sediment core analysis from alpine lakes.[44] (ii) The age of the streamwater varies over the course of a year. During spring flood (as well as during high rainfall episodes in summer) the bulk of the water in both streams is from shallow groundwater displaced by snowmelt (or rainwater), whereas during the rest of the year a large portion of the streamwater consists of old groundwater, especially for stream 16 (see also section 3.2).[24,27] (iii) The long-chain PFAAs are relatively poorly water-soluble and can sorb strongly to surfaces. They are thus retained during passage through the soil column. The short-chain analogs, however, are more mobile, and the time lag between their atmospheric deposition on the watershed and their export via the streams may rather reflect the residence time of the water. These factors need to be considered in interpreting the PFAA mass balances.

3.3.2. General Observations for Whole-Year Mass Balances. The whole-year mass balances for the individual PFAAs in C2 and C16 are shown in Figure 4. The calculated input and output loads are listed in the Tables S13–S16. The PFAA mass balances in C2 and C16 were generally similar. Marked differences in the output/input ratios (Figure 4, parts A2 and B2) were only apparent for PFHxA and PFHpA (higher value for C2) as well as for br-PFOS and L-PFOS (lower value for C2). This can be explained by a combination of the expected recent temporal trends of emissions and therewith atmospheric inputs and the average age of the water in the streams (older water in C16). Wang and co-workers[3] estimated continuously increasing global emissions for 6:2 FTOH, a volatile precursor of PFHxA and PFHpA, as well as a sharp drop of emissions for airborne PFOS precursors after the year 2000 due to the production phase-out by the 3M Company. Emissions of volatile precursors of long-chain PFCAs were estimated to have peaked around 2008 and are since decreasing,[3] due to the shift in production from long-chain compounds to short-chain homologues. The difference between PFAA concentrations in bulk deposition samples taken in Northern Germany in 2007–2008[17] and the present study is consistent with the expected temporal trends in atmospheric inputs. Mean PFOS concentrations were 13 times higher in the German study, whereas mean PFHxA and PFHpA
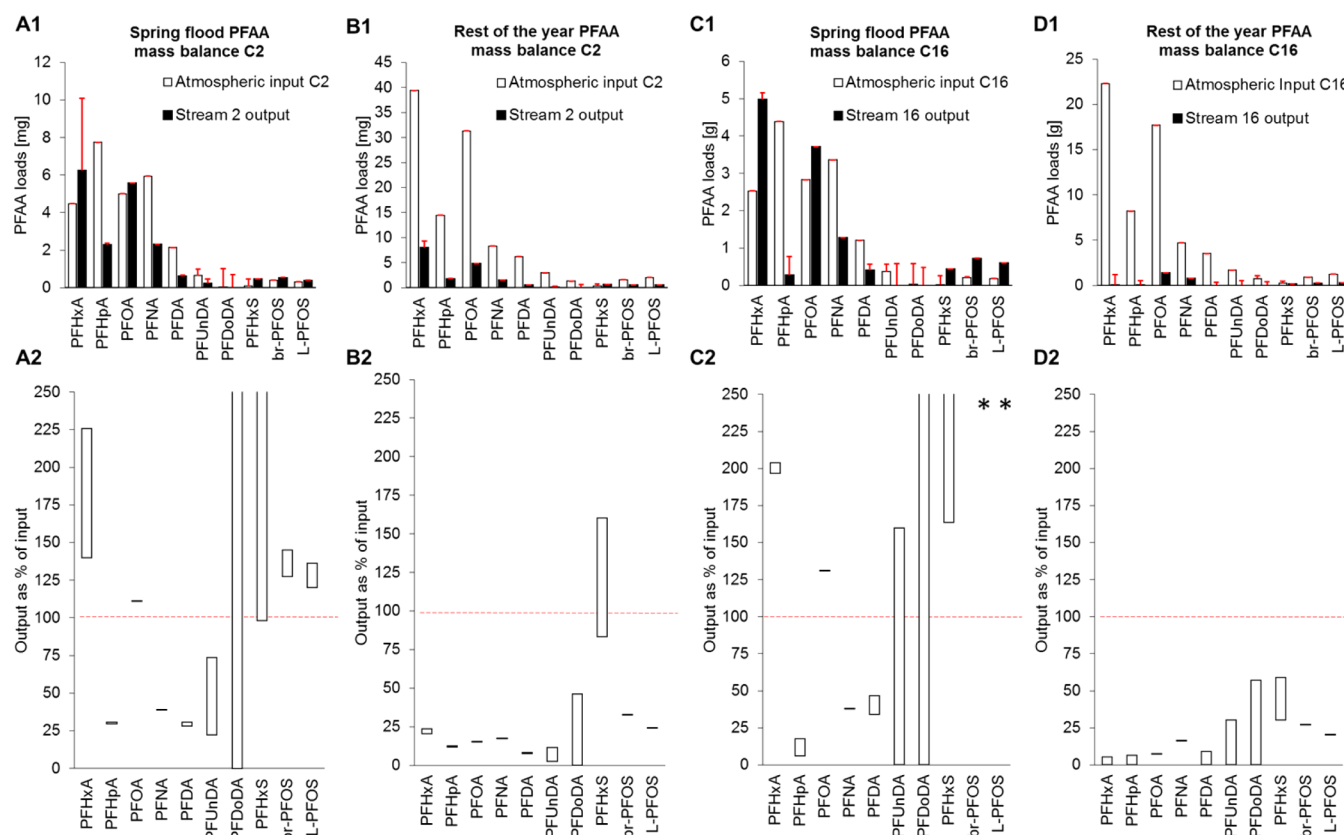
Figure 5. Total PFAA atmospheric inputs (white bars) and stream discharges (black bars) are compared for (A1) spring flood in C2, (B1) rest of the year in C2, (C1) spring flood in C16, and (D1) rest of the year in C16. The LBE values are shown with solid bars and the HBE values with error bars. The output expressed as percentage of the input is shown for the respective scenarios and catchments in (A2) to (D2). The ranges depict LBE_{output}/HBE_{input} to HBE_{output}/LBE_{input}. A closed mass balance would correspond to 100% (dashed line). The asterisks in Figure (C2) indicate that the bars for br-PFOS and L-PFOS are outside the shown range (>250%).

concentrations in bulk deposition were 2.9 and 1.3 times higher, respectively, in the present study, despite the remote sampling site.

The atmospheric input was larger than the riverine output for all PFAAs (except PFHxS) in both catchments. As PFAAs are not expected to degrade in the environment, nor to volatilize, the positive mass balances suggest that the PFAA inventories in the soil of the watersheds or in deep groundwater were increasing. This is in agreement with previous work hypothesizing that a considerable fraction of PFOS entering the Baltic Sea catchment by atmospheric deposition was "stored" in the soil.[18] The surplus of input over output was higher for PFCAs than for PFSAs, which was especially pronounced in C16 (Figure 4, parts A2 and B2). This could again be explained by the global emission trends of PFHxS and PFOS, which likely decreased sharply after the 3M production phase-out in 2000−2002. The PFSAs observed in the streams partly originated from years (C2) to decades (C16) old atmospheric inputs that were higher than the atmospheric inputs measured in the present study for 2011−2012 (see also above). The higher output/input ratio for PFHxS compared to PFOS may partly reflect the weaker sorption of PFHxS to soil, which would lead to a shorter travel time and lesser attenuation of the PFHxS concentration during groundwater transport. Analogously, br-PFOS had a higher output/input ratio in the two catchments than L-PFOS, reflecting the lower soil/water partition coefficient of the branched isomers compared to L-PFOS.[45]

PFUnDA and PFDoDA are expected to sorb strongly to soil.[45] In this case, the chemicals would move very slowly through the groundwater system, and the output/input ratio would be expected to be low. Although there is considerable uncertainty in the output/input ratios for these chemicals, the results are consistent with this expectation (Figure 4).

3.3.3. Comparison of Spring Flood Scenario and Rest of the Year. In Figure 5, the PFAA mass balances for C2 for the spring flood period (Figure 5, parts A1 and A2) and for the rest of the year (Figure 5, parts B1 and B2) are shown. The PFAA mass balances during the rest of the year were similar to the whole-year mass balances (Figure 4) with a net input for all PFAAs except PFHxS. The excess of inputs was even more pronounced than in the whole-year mass balance. Because deep groundwater only contributes on average 18% to stream 2 during base flow,[27] the average water is relatively young and historical changes in atmospheric inputs to C2 over the scale of years to decades were expected to have a small influence on the measured mass balances. Considering this, the low output/input ratios for the PFCAs suggest that the PFAAs deposited on C2 during summer and autumn were predominantly retained in the soil in the shallow groundwater zone or were transferred into deeper groundwater zones.

During spring flood output/input ratios were much higher than during the rest of the year (Figures 5A2 and 5B2). This was due to the fact that in spring the water in stream 2 consists mainly of shallow groundwater being displaced by the snowmelt.[23,24] As discussed in section 3.2, this shallow

groundwater consisted predominantly of rainwater from the previous summer and autumn, which contained considerably higher bulk concentrations of several PFAAs than the snowmelt (Figure 2). In fact, higher outputs than inputs were observed during spring flood for PFHxA, PFOA, PFHxS, br-PFOS, and L-PFOS (Figure 5A2). These were the PFAAs with >80% of their annual atmospheric inputs via rain and <20% via snow (Table S13).

Season-specific PFAA mass balances for C16 are shown in Figure 5, parts C1, C2, D1, and D2. During spring flood, the PFCA mass balances for C2 and C16 were similar, which may reflect the fact that much of the streamwater in both catchments originated from shallow groundwater displaced by snowmelt. However, the output/input ratio was a factor of 2.4 and 2.6 higher for br-PFOS and L-PFOS, respectively, in C16 than in C2. This indicates that the spring flood is particularly efficient at mobilizing older residues of PFOS stored in the C16 catchment. Seen over the whole year, the PFOS output/input ratios are more similar in the two watersheds (Figure 4).

Markedly lower output/input ratios of PFHxA and PFHpA were measured in C16 compared to C2 during the rest of the year. Possible explanations for these observations were already discussed in sections 3.2 and 3.3.2, including temporal trends in atmospheric inputs and the significance of old groundwater infiltration into stream 16.

The present study demonstrates that a large portion of PFAAs deposited in remote regions is retained in soils and groundwater aquifers, probably for years to decades, before being released to surface water and transported to the oceans. While the atmospheric inputs of the legacy PFOS likely have decreased over the past decade, the peak of releases to surface water and the marine environment may still come in the future. Furthermore, the present study suggests that environmental inputs of short-chain (replacement) PFCAs such as PFHxA and PFHpA to remote regions are currently increasing. The mass balance calculations are a first step in understanding the transport of PFAAs through and retention in watersheds. This is essential for our understanding of historic and potential future releases of PFAAs to freshwater (e.g., for drinking water production) and to the marine environment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03403.

> Detailed information on the sampling, analytical procedure, quality assurance, precipitation and stream-water flows, input and output calculations, measured PFAA concentrations in all samples, and calculated inputs, outputs and mass balances (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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