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White-Tailed Eagle (*Haliaeetus albicilla*) Body Feathers Document Spatiotemporal Trends of Perfluoroalkyl Substances in the Northern Environment

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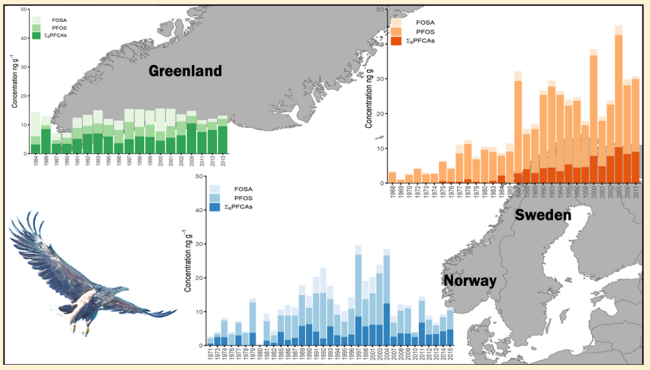
Supporting Information

ABSTRACT: We reconstructed the first long-term (1968−2015) spatiotemporal trends of perfluoroalkyl substances (PFAS) using archived body feathers of white-tailed eagles (*Haliaeetus albicilla*) from the West Greenland (n = 31), Norwegian (n = 66), and Central Swedish Baltic coasts (n = 50). We observed significant temporal trends of perfluorooctane sulfonamide (FOSA), perfluorooctane sulfonate (PFOS), and perfluoroalkyl carboxylates (∑PFCAs) in all three subpopulations. Concentrations of FOSA and PFOS had started decreasing significantly since the mid-1990s to 2000 in the Greenland and Norwegian subpopulations, consistent with the 3M phase-out, though in sharp contrast to overall increasing trends observed in the Swedish subpopulation. Moreover, ∑PFCA concentrations significantly increased in all three subpopulations throughout the study periods. These temporal trends suggest on-going input of PFOS in the Baltic and of ∑PFCAs in all three regions. Considerable spatial variation in PFAS concentrations and profiles was observed: PFOS concentrations were significantly higher in Sweden, whereas FOSA and ∑PFCA concentrations were similar among the subpopulations. PFOS dominated the PFAS profiles in the Swedish and Norwegian subpopulations, in contrast to the domination of FOSA and ∑PFCAs in the Greenland one. Our spatiotemporal observations underline the usefulness of archived



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bird of prey feathers in monitoring spatiotemporal PFAS trends and urge for continued monitoring efforts in each of the studied subpopulations.

1. INTRODUCTION

Perfluoroalkyl substances (PFAS) have been used in a variety of applications such as protective coating and textiles, fire-fighting foams, and electronic industries since the 1950s.[1,2] The ubiquity and persistence of PFAS in the general population and wildlife have caused major concerns about their potential health and environmental impact.[3−6] PFAS manufacturers, for example, 3M, voluntarily phased-out the production of perfluorooctane sulfonyl fluoride (PFOSF)-based compounds in 2000−2002, following negotiations with USEPA.[7] Moreover, in 2009, perfluorooctane sulfonate (PFOS), its salts, and related substances were included in the list of persistent organic pollutants (POPs) under Annex B (restriction) by the Stockholm Convention.[8] PFOA, its salts, and related compounds have been recently listed under Annex A (elimination).[9] However, global regulations on the production and use of other long-chain perfluoroalkyl carboxylates (PFCAs) and their precursors are currently in progress.[10]

Despite being partially phased-out more than a decade ago, their extreme persistence and ubiquitous distribution warrant further monitoring of spatiotemporal PFAS trends.[11] Museum collections or specimen banks have high potential to retrospectively construct temporal trends of PFAS, as shown by studies using archived bird eggs.[12−16] Compared to eggs, feathers are not only nondestructive and minimally invasive but also more economical in terms of storage and transportation. Moreover, feathers are available in relatively large quantities from museum collections, allowing for the systematic sampling for long-term trend studies as has been shown repeatedly in mercury monitoring.[17−19] Museum feathers have been frequently used to reconstruct temporal trends in foraging ecology, for example, food chain or habitat source and trophic level (as proxied by feather stable carbon and nitrogen isotopes, respectively).[20−22] The usefulness of feathers for biomonitoring of legacy organochlorines (OCs) has also been demonstrated.[23−27] Recently, several studies have also explored the potential of feathers to monitor PFAS and found significant correlations between feather and plasma concentrations of certain homologues, which suggests the feasibility of using feathers.[28−33] However, the usefulness of feathers to study temporal trends of PFAS has yet to be shown. In addition to temporal trends, studying spatial variation of PFAS is important for the understanding of their dispersal and distribution. This is not always reliable when comparing different studies using different sentinel species, matrices, analytical laboratories, and statistical methods. Combining spatial and temporal trends in different populations of the same species can thus lead to valuable information on, for instance, the effectiveness of industrial phase-outs and pollution hotspots and subsequently contribute to risk assessment as well as policy-making.

In the present study, we obtained white-tailed eagle (*Haliaeetus albicilla*) feather samples from various museums and specimen banks. The feathers were collected from three northern subpopulations over a 47 year period (1968−2015). Being a widely distributed top predator, white-tailed eagles have long been used to monitor environmental contaminants.[16,34−38] To our knowledge, this is the first study documenting long-term and large-scale spatiotemporal trends of PFAS using archived feathers. The objectives of the present study are (1) to evaluate the feasibility of archived feathers in reconstructing temporal trends of PFAS and (2) to investigate spatial variation in these trends with regard to potentially varying the intensity of environmental sources, pathways, and phase-outs. Finally, since dietary plasticity may influence individual contaminant exposure,[39−42] we included stable isotope proxies in the retrospective spatiotemporal modeling.

2. MATERIALS AND METHODS

2.1. Sample Collection and Preparation. The present study used body (chest and back contour) feathers of white-tailed eagles from subpopulations in West Greenland (n = 31; 1984−2013), along the Norwegian coast (n = 66; 1971−2015), and the Central Swedish Baltic Sea coast (n = 50; 1968−2011; Figure S1). Feathers were obtained from various natural history museums (NHMs) and specimen bank collections as previously reported.[43] The Swedish samples consisted of molted feathers from breeding pairs identified by territory and subsequently stored in polyethylene bags. None of the feathers have been treated with preservatives prior to or during storage at the museum. The Norwegian samples comprised feathers of individual birds preserved as museum skins, mounted specimens, and frozen carcasses. Based on the communication with museum correspondents, the skins and mounted specimens have not been treated with any PFAS-containing products, whereas the frozen carcasses were stored directly in the freezer without any pretreatment. The Greenland feathers were entirely from frozen carcasses and thus have not been treated with any chemicals. To conclude, we are confident that external PFAS contamination during storage in museums is unlikely to have occurred. All the molted feathers, skins, and mounted specimens have been stored at ambient temperature and humidity conditions across museums, whereas the frozen specimens have been wrapped in polyethylene bags and stored under dark conditions at −20 °C. On average, 10 body feathers per year per breeding pair/individual were sampled from the original collections, and all body feathers were consequently stored in polyethylene bags under dark, ambient temperature, and humidity conditions until preparation for chemical analysis. After removal of the calamus, feathers were thoroughly cleaned in distilled water, homogenized using stainless steel scissors, and stored in aluminum foil at ambient conditions until chemical analysis. Due to the opportunistic banking activity of the Greenland and Norwegian collections, there are differences among subpopulations with regard to the storage condition as detailed above (i.e., ambient temperature versus frozen and closed bags versus skin/mounted specimens), as well as the biology of the sampled eagles (e.g., age and sex). All Swedish samples were banked systematically from breeding adult pairs loyal to their territory, whereas Greenland and Norwegian samples comprised both immatures and adults of both sexes.

2.2. PFAS Analysis. The analysis was performed at the Department for Environmental Science at Aarhus University, Denmark. 15 PFAS were targeted, including one perfluor-

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oalkane sulfonamide (FASA): perfluorooctane sulfonamide (FOSA), five perfluoroalkane sulfonates (PFSAs) (PFBS, PFHxS, PFHpS, PFOS, and PFDS), and nine perfluoroalkyl carboxylates (PFCAs) (PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, and PFTeDA) (full names are given in Table S1). The compounds were quantified using an Agilent 1200 Series HPLC (Agilent Technologies, Palo Alto, CA, USA) interfaced to a triple quadrupole QTrap 5500 (Sciex, Framingham, CT, USA) operated in negative electrospray ionization (ESI) mode, applying the isotope dilution method.

The extraction method presented by Jaspers et al.[29] was slightly modified. Before extraction, the homogenized feather material was milled into fine powder using a ball mill (Mixer Mill MM 400, Retsch, DE). On average, 183 ± 24 mg of feather material was weighed into polypropylene tubes and spiked with ^{13}C-labeled compounds (PFHxS, PFOS, FOSA, PFHxA, PFOA, PFNA, PFDA, PFUnDA, and PFDoDA), submerged in 2 mL of 200 mM NaOH for an hour to resolve the bounded PFAS from the keratin matrix. Subsequently 10 mL of MeOH was added; the mixture was sonicated and left to digest overnight at ambient temperature. A 200 μL volume of HCl (2 M) was added to the samples the following day, before transferring the extract to a new polypropylene tube. The extract was then evaporated to 2 mL under a gentle nitrogen flow at 32 °C. Fifty μL of glacial acetic acid was added, and the extract was cleaned up on a MeOH and glacial acetic acid conditioned ENVI-Carb column (100 mg; Supelco). The target analytes were collected in new polypropylene tubes, and the columns were further eluted with 3 mL of MeOH. The final extract was evaporated to dryness under a gentle nitrogen flow, reconstituted in 500 μL of MeOH:2 mM ammonium acetate (50:50, v:v), vortexed, and subsequently filtered over a nylon filter (17 mm syringe filter 0.2 μm; Thermo Scientific) into a polypropylene injection vial.

Quality assurance/quality control (QA/QC) procedures included addition of ^{13}C-labeled PFAS as surrogate standards, procedural blanks, random sample duplicates, and analysis of Certified Reference Material (CRM; IRMM 427 − pike/perch tissue, European Commission Joint Research Centre, BE) in duplicate with each batch of samples. QA/QC details are further listed in Table S1. Recoveries for the CRMs ranged between 92 and 97% of the certified values (PFOS, PFDA, PFUnDA, and PFDoDA) and 89 and 119% of the indicated values (FOSA, PFNA, and PFTrDA; Table S1). All reported concentrations are corrected for average procedural blank values (i.e., 0.01 ng g^{-1} for PFOS, PFNA, PFOA, PFUnDA and 0.02 ng g^{-1} for PFDA). Relative percent differences (Table S1) inferred from duplicate samples were 51% for PFTrDA and below 15% for all other PFAS. Concentrations of PFTrDA reported in the present study should rather be considered indicative. All body feather concentrations are expressed in ng g^{-1}. The method detection limit (MDL) was set for each PFAS as three times the SD of the procedural blank value or a 10:1 signal-to-noise ratio when not detected in the blank samples.

2.3. Stable Isotope Analysis. The analysis for stable carbon (^{13}C and ^{12}C) and nitrogen (^{15}N and ^{14}N) isotopes was performed at the Stable Isotope Lab of the University of Koblenz-Landau (Greenland and Norwegian samples) and the Laboratory of Oceanology of the University of Liège, Belgium (Swedish samples). For the analysis of the Greenland and Norwegian samples, the internal reference material (i.e., casein) was measured in duplicate every 10 samples revealing an imprecision (±SD) of ≤0.06‰ for both δ^{13}C and δ^{15}N, while for the Swedish samples, glycine was used as the internal reference material and was measured every 15 samples, showing an imprecision (±SD) of ≤0.20‰ for both δ^{13}C and δ^{15}N. Further details of the quantitative instrumentation are reported in detail by Sun et al.[43]

2.4. Statistical Analyses. All statistical analyses were performed using R 3.5.2.[44] Two samples from the Norwegian subpopulation had high concentrations of PFNA (3.5 ng g^{-1}; 1987) and PFOA (11.2 ng g^{-1}; 2009) compared to the population mean ± 5SD of 0.5 ± 2.6 and 0.8 ± 8.5, respectively, and were therefore regarded as outliers and removed from further statistical analysis. δ^{13}C values were corrected for the oceanic Suess effect as outlined in further detail by Sun et al.[43] Age and sex were not included in the statistical analysis as such information was only sporadically available.

Only compounds with a detection frequency above 50% in each subpopulation were analyzed. We did not detect PFBS, PFHxS, PFHpS, PFDS, PFHxA, or PFHpA in any sample, whereas PFTeDA was detected in less than 40% of the samples (Table S2). Thus, the following eight PFAS were analyzed for spatiotemporal trends and profiles: FOSA, PFOS, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFTrDA. Non-detects were excluded for individual compound analysis and set to zero for summary statistics and proportions. Detection frequencies were high for PFOS and FOSA (≥97%) in all three subpopulations. Likewise, $\sum_6$PFCAs (sum of PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFTrDA) were detected in 100, 91, and 78% of the Greenland, Norwegian, and Swedish samples, respectively. We therefore expect limited bias by exclusion and substitution of non-detects as described above. For individual PFCAs, the bias might be slightly stronger due to relatively higher censoring proportions in some compounds (up to 50%).

We used Generalized Additive Models (GAM)[45] for the investigation of temporal trends of PFAS in each subpopulation. Year and dietary proxies (δ^{13}C and δ^{15}N) were included as predictors, whereas PFAS concentrations were response variables. Due to the high variance inflation factor (>3;[46] Table S3) between δ^{13}C and δ^{15}N in the Norwegian subpopulation, we did not include them simultaneously in the same model in this specific subpopulation. We used penalized thin plate splines (ts) for smoothing to automatically penalize the smooth terms to zero if the smooth parameter went to infinity.[47] Therefore, instead of removing insignificant variables, all predictors including the dietary proxies were kept in the model. Considering the positive and positively skewed concentration data (Table S4), we chose Gamma family with a log link. We validated model adequacy visually using residual plots. Finally, the spatiotemporal trends were evaluated based on model output (i.e., P values and adjusted R^2). We also inspected the trend lines and 95% confidence intervals fitted using model predictions. Annual percent changes were calculated using annual predicted concentrations (median).

We additionally compared concentrations and profiles among subpopulations. To account for temporal variation, we calculated average concentrations of each individual PFAS and $\sum_6$PFCAs per 10 year interval, as well as proportions of FOSA, PFOS, and $\sum_6$PFCAs against $\sum$PFAS. For concentration data, we fitted ANOVA models with the interaction between subpopulation and compound and compared differ-

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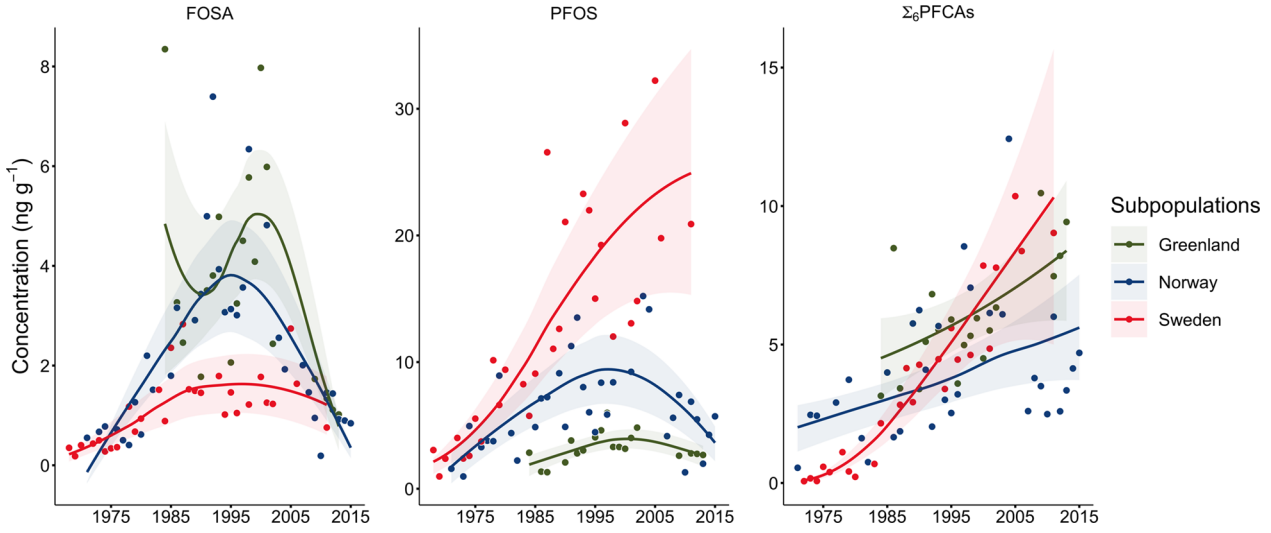

Figure 1. Temporal trends of FOSA, PFOS, and $\sum_6$PFCAs (PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFTrDA) in body feathers of white-tailed eagles from West Greenland, the Norwegian, and the Central Swedish Baltic coasts. Trend lines and 95% prediction intervals (shaded) are fitted using GAM models (see Table S6). Dots represent annual median values.

ences per decade using Tukey pairwise comparison. For proportion data, beta regressions (package "betareg"[48]) were fitted and compared.

3. RESULTS AND DISCUSSION

3.1. Spatial Trends of PFAS. While concentrations of FOSA and Σ_6PFCAs were similar among the regions, there was clear spatial variation in PFOS concentrations (Figure 1 and Figure S2). This difference was most pronounced in the recent decade (2006−2015) when the median concentration of PFOS in the Swedish subpopulation (20.1 ng g^{-1}) was 5 times higher than that in the Norwegian one (4.2 ng g^{-1}; $P < 0.01$) and 7 times higher than that in the Greenland one (2.8 ng g^{-1}; $P < 0.01$; Table S5). Comparable spatial variations in PFOS concentrations have been reported in previous studies. PFOS concentrations (ng g^{-1}; ww) in guillemot (*Uria aalge*) eggs were significantly higher (5 times) in Sweden (mean = 400; range = 200−760; 2003) compared to Norway (mean = 85; range = 54−110; 2005), while concentrations were lowest in Iceland (mean = 16; range = 5−22; 2002) and the Faroe Islands (mean = 15; range = 6−34; 2003).[49] Moreover, PFOS in white-tailed eagle eggs in Sweden showed a northward decreasing trend, with lowest concentrations found in those from inland freshwater: estimated concentrations in 1990 were 223 and 38 ng g^{-1} ww in eggs from Baltic Proper and northern Inland, respectively.[16] This pattern was attributed to the greater emissions in the South Swedish coastal area versus atmospheric input in the northern inland area.[16] Indeed, PFAS consumption in the Swedish market in 1999 alone (38 tons) was higher than the estimated total PFOS use in Norway (23−26 tons),[50] which is consistent with the higher PFOS exposure in the Swedish compared to the Norwegian subpopulation in the present study. In contrast, PFOS use in Greenland was likely limited to point sources such as airports, indoor uses, or storage facilities.[51] In addition, the exposure to PFOS in white-tailed eagles could be influenced by long-range atmospheric transport (LRAT) of volatile precursors, such as *N*-ethyl perfluorobutanesulfonamide,[52−55] which can subsequently biotransform and degrade to FOSA and eventually to PFOS.[53,55,56] The fact that we observed consistently higher FOSA:PFOS ratios in Greenland (median: 1.0) in contrast to Norway (median: 0.3) and Sweden (median: 0.1) also suggests the presence of PFOS precursors in Greenland.

There were no significant differences in the concentrations of Σ_6PFCAs per 10 year period among the three subpopulations from 1966 to 2005. However, in 2006−2015, Σ_6PFCA concentrations were significantly higher in both the Greenland (median: 8.2 ng g^{-1}) and Swedish subpopulations (median: 9.0 ng g^{-1}), compared to the Norwegian one (3.8 ng g^{-1}; both $P < 0.01$; Figure S2). The high Σ_6PFCA concentrations in Greenland might be caused by the contribution of precursor compounds such as fluorotelomer alcohols (FTOHs) to the Arctic region through LRAT[57,58] and/or potential local sources (e.g., waterproofed textiles).

For each individual PFCA, the concentrations were not significantly different among the three subpopulations across the entire study period, except for significantly higher PFTrDA concentrations in Greenland (median 4.0 ng g^{-1} in 2006−2015) and in Norwegian feathers (median 3.7 ng g^{-1} in 1996−2005) compared to other subpopulations (all $P < 0.05$; Figure S3). The general lack of geographical variation in PFCAs compared to PFOS is in line with spatial trends of PFUnDA observed in white-tailed eagle eggs in the Swedish Baltic region.[16] Faxneld et al.[16] reported more homogeneously distributed concentrations of PFUnDA than PFOS and suggested that the disparity was likely a result of different transport pathways between PFOS (water-bound) and long-chain PFCAs (atmospheric/particle bound or secondary sources). A previous study on common guillemot eggs also found concentrations of PFUnDA to be similar in Sweden and Faroe Islands, with significantly lower concentrations in Norway.[49]

3.2. Temporal Trends of PFAS. The increases of FOSA in the Norwegian (10.2% year^{-1}; 1971−1995) and Swedish (9.9% year^{-1}; 1968−1987) subpopulations observed in the present study are higher than the 4.5% annual increase reported in white-tailed eagle eggs from the Baltic proper in 1966−2010.[16] FOSA decreased significantly in the later period in Norway (7.6% year^{-1}; $P < 0.01$; 1995−2015), but not in Sweden (1.8% year^{-1}; $P = 0.90$; 1987−2011), indicating the likely diminishing FOSA influx at the Norwegian coast but a

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Table 1. Temporal Trend Model Predictions of FOSA, PFOS, and ∑PFCAs in Three White-Tailed Eagle Subpopulations[a]

compound	country	period (peak year)	median$_{start}$ (95% PI)	median$_{peak}$ (95% PI)	median$_{end}$ (95% PI)	annual (↑)	annual (↓)
FOSA	Greenland	1984−2013 (1999)	5.1 (1.9−8.3)	5.2 (3.9−6.4)	1.0 (0.6−1.4)	0.1%	−11.1%*
	Norway	1971−2015 (1995)	0.4 (0.2−0.7)	4.6 (3.1−6.0)	0.9 (0.6−1.3)	10.2%*	−7.6%*
	Sweden	1968−2011 (1987)	0.3 (0.2−0.4)	1.8 (1.1−2.5)	1.1 (0.5−1.7)	9.9%*	−1.8%
PFOS	Greenland	1984−2013 (2000)	2.0 (1.1−2.8)	3.9 (3.2−4.7)	2.7 (1.8−3.5)	4.4%*	−2.9%*
	Norway	1971−2015 (1998)	2.3 (0.9−3.7)	12.0 (8.6−15.4)	4.9 (2.8−7.1)	6.3%*	−5.1%*
	Sweden	1968−2011 (2005)	2.3 (1.4−3.1)	25.0 (16.8−33.3)	24.3 (14.1−34.5)	6.7%*	−0.5%
$\sum_6$PFCAs	Greenland	1984−2013 (-)	4.5 (3.1−5.9)	-	8.4 (5.9−10.9)	2.2%*	-
	Norway	1971−2015 (-)	1.8 (1.0−2.5)	-	6.3 (3.8−8.9)	2.9%*	-
	Sweden	1972−2011 (-)	0.2 (0.1−0.2)	-	10.2 (4.4−16.0)	11.4%*	-

[a]Modeled median predicted concentrations of the starting and ending years, as well as the peak years (if applicable), are presented, with 95% prediction intervals (PI). Annual increase (↑) and decline rates (↓) were computed using the predicted median concentrations of the starting and ending years compared to the peak year, respectively. Asterisks indicate significant temporal trends. - means not applicable.

prolonged one in the Baltic. The lack of a decrease in Sweden agrees with the FOSA trend in eggs of white-tailed eagles from the Gulf of Bothnia but contrasts the significant decrease in those from the Baltic proper in 2001−2010.[16] On the other hand, FOSA concentrations in Greenland were relatively constant from 1984 throughout the 1990s (P = 0.40; 0.1% year^{-1}; Table 1 and Figure 1). The following decreasing rate (11.1% year^{-1}; P < 0.01) until 2013 is in line with the average annual decrease (9%) in Arctic marine and freshwater biota,[59] and the peaking time is also consistent with the peaking of atmospheric FOSA in the North Atlantic (between 1997 and 2001).[60] Trends of FOSA in the Arctic region reported in the literature do not appear to be universally consistent: polar bears (*Ursus maritimus*) seem to undergo decreasing exposure since the 1970s in the Canadian Arctic[61] but an increasing one until the mid-2000s in East Greenland.[62,63] In beluga whales (*Delphinapterus leucas*) from the Canadian Arctic, FOSA concentrations increased during the 1990s and then decreased during the 2000s.[64] Given that FOSA is a precursor of PFOS,[53,55,56] temporal trends of FOSA may reflect a potential mixture of anthropogenic input and biotransformation over time.

We observed a continuous increase of PFOS in the Swedish subpopulation until 2005 (6.7% year^{-1}; P < 0.01), several years after the phase-out, before concentrations leveled off until 2011 (P = 0.90; Figure 1 and Table 1). The observed increase rate is consistent with the annual increase observed in Baltic guillemot (7−11%)[12] and white-tailed eagle eggs (7%)[16] during the period of 1960s−2000s. These results are comparable with the geographical pattern of PFOS reviewed by Land et al.,[11] still showing increasing trends in the Baltic contrasting the decreasing trends that have started to appear in other areas. The semienclosed Baltic Sea has unique geographic and hydrological features such as the small water volume, large drainage area, and low water exchange rate.[11,65] These features may enhance the contamination and result in a long residing time of contaminants, which may also explain the delayed onset of decreasing PFOS trends in the Swedish Baltic eagles. Similar carry over effects of PFOS have also been reported in top predators from the South San Francisco Bay, USA.[66] The increasing trend of PFOS in the Greenland subpopulation observed for the period between 1984 and 2000 (4.4% year^{-1}; P < 0.01) is in agreement with the increase reported in ringed seals (*Phoca hispida*) from West Greenland (4.7% year^{-1}; 1982−2003) and lower than those from East Greenland,[67] as well as in polar bears from East Greenland (4.7% year^{-1}) in 1984−2006.[62] Following this period, we observed decreasing PFOS concentrations until 2013 (2.9% year^{-1}; P = 0.03) in line with a general decline across Arctic biota.[59] Trends of PFOS in the Norwegian subpopulation increased by 6.3% year^{-1} (P < 0.01) from 1971 to 1998 followed by a pronounced annual 5.1% decrease up to 2015 (P = 0.01). The decreasing trends in the Greenland and Norwegian subpopulations highlighted an almost immediate response to the phase-out of PFOSF-based compounds in 2000.[7] This peak is a few years earlier than detected for Greenland ringed seals and polar bears, which were reported to be around 2005−2006.[59,63] Nevertheless, comparably prompt decreasing trends have been reported in herring gull (*Larus argentatus*) eggs from the Great Lakes, USA, since the 1990s[14] and in auklet (*Cerorhinca monocerata*) and cormorant (*Phalacrocorax auritus*) eggs from the Pacific coast of Canada since the early 2000s.[15] PFOS has been decreasing since 2001 in sea otters (*Enhydra lutris kenyoni*) from Alaska[68] and in two ringed seal populations from Canadian Arctic since 1998−2000.[69] Given that we observed significant effects of δ^{15}N or δ^{13}C in the trend models (Table S6), the slightly earlier onset of a decrease in Norway may also be attributed to a dietary shift (reflected by decreasing δ^{13}C and δ^{15}N) mediated contaminant exposure in this subpopulation during recent decades.

We found significantly increasing $\sum_6$PFCAs in all three subpopulations throughout the study periods (all P < 0.05; Table S6 and 1). The annual increase was lower in Greenland (2.2%) and Norway (2.9%) compared to Sweden (11.4%). The increase rate in Sweden is in agreement with the annual 10−15% in eggs of the same white-tailed eagle population in 1966−2010,[16] as well as the 6−13% reported in Scandinavian otters (*Lutra lutra*) in 1972−2011.[70] Comparable to the general increase of $\sum_6$PFCAs, we observed increasing concentrations in all individual PFCAs with the exception of PFOA in all three subpopulations and PFTrDA in Norway (see Figure S4 and Tables S6 and S7 for trends of individual PFCAs). PFOA decreased significantly in Greenland after 1998 (8.8% year^{-1}; P < 0.01) and in Norway from 1971 to 2015 (4.6% year^{-1}; P < 0.01) but remained approximately constant from 1975 to 2011 in Sweden. Unlike the here observed decreasing/constant trends, modeled PFOA in seawater showed continuous increasing trends until 2010 in northern temperate zone and until 2030 in the Arctic region.[52,71] Such differences can be attributed to the different environmental matrices modeled, as PFOA is less prevalent in biotic samples. Therefore, the PFOA trends observed in the present study are likely not representative of the PFOA contamination trends in

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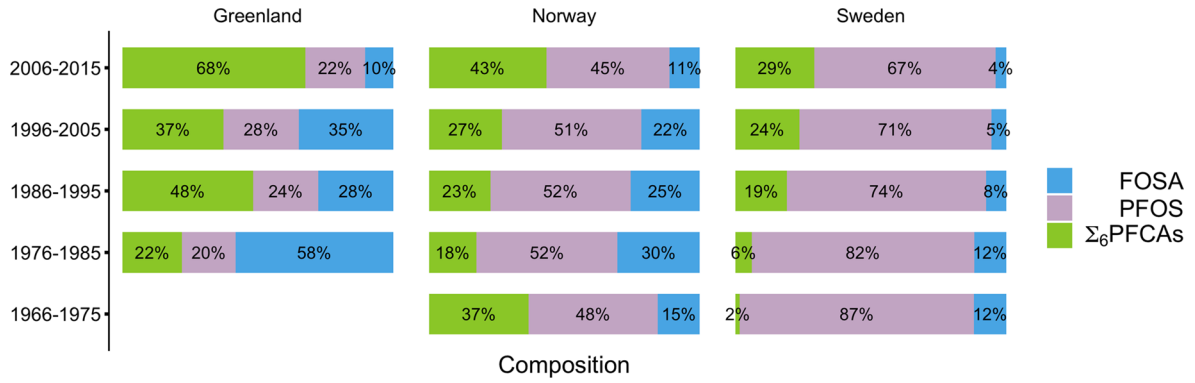

Figure 2. Composition of PFAS in feathers of white-tailed eagle from the West Greenland, the Norwegian, and the Central Swedish Baltic coasts.

the general environment. Inconsistencies in PFAS concentrations between biotic and abiotic samples have been reported previously. For example, PFOA was present at higher concentrations in surface water compared to fish in the Faroe Islands, and short-chain PFAS such as perfluorobutanoate (PFBA) dominated the PFAS profile in surface water.[72] In contrast, in fish from the Faroe Islands and Greenland, longer-chain PFCAs showed higher concentrations, whereas short-chain PFCAs such as PFHpA and PFHxA were not detected.[72,73] Compared to PFOA, longer-chain PFCAs tend to bioaccumulate and biomagnify in food webs.[56,74] In accordance, trends of C9−C13 across subpopulations have been generally increasing in the present study. These trends appear to be in line with the regulations on PFCAs. PFOA has been subjected to regulatory effort in the EU since 2017.[10,75] However, the initiative for replacing and eliminating longer-chain PFCAs is still in progress.[2,10] The increasing production in Asia[2] and the numerous secondary sources of PFCAs via precursor degradation likely additionally explain our observation that levels of long-chain PFCAs have not yet equilibrated in the environment.

3.3. Spatiotemporal Variation of the PFAS Profile. Consistent with the general pattern in most biological samples,[76,77] the observed PFAS profile was dominated by PFOS (60−80%) in the Swedish subpopulation (Figure 2), which is comparable with the profile reported in eggs from the same population.[16] Proportions of PFOS per 10 year period were consistently significantly higher in the Swedish subpopulation than in the Norwegian and Greenland ones during the entire study period (all $P < 0.05$) except between Sweden and Greenland in 1976−1985 ($P = 0.08$; Figure S5). Proportions of PFOS (around 50%) were significantly higher in the Norwegian than in the Greenland subpopulation in 1986−2015 (all $P < 0.05$). In contrast, the PFAS profile was dominated by FOSA and Σ_6PFCAs in the Greenland subpopulation, whereas PFOS accounted for 20−30% only (Figure 2). Accordingly, the proportions of Σ_6PFCAs were significantly higher in the Greenland subpopulation compared to the ones in Norway and Sweden during the last decade ($P < 0.05$; Figure S5). In addition, we observed significantly higher concentrations of odd-chain PFCAs (C9, C11, and C13) compared to even-chain PFCAs (C10 and C12) in Greenland in most decades (Figure S3). We also observed consistently positive ratios of odd- to even-chain PFCAs, as well as increasing trends of PFNA:PFOA ratios in all three subpopulations (Figure S6). The dominating Σ_6PFCAs and odd-chain homologues in the Greenland subpopulation appear to indicate an important role of LRAT of precursor FTOHs in PFCA exposure in the Greenland biota.[58,78] In addition, in line with the increasing concentrations, the proportions of Σ_6PFCAs have been increasing across all subpopulations. The major contributing individual PFCA homologue however seems to be dependent on the subpopulation and study period, as we observed significantly higher proportions of odd-chain PFCA (C13 or C11) in Greenland and Norway in some decades, whereas in Sweden, the proportions between odd- and even-chain PFCA homologues were not significantly different across the study periods (Figure S7). This could be due to different contamination pathways, for example, high local contamination in Sweden, contrasting the LRAT influence in Norway and Greenland.

3.4. Feathers as a Biomonitoring Tool for PFAS and Limitations of Our Study. Several studies have reported significant associations between PFAS concentrations in feathers and in internal tissues. Jaspers et al.[29] found significant correlations between barn owl (*Tyto alba*) feather and liver concentrations of PFOS, and a similar correlation has been reported for several other bird species.[28] Significant associations between PFDA, PFDoDA, and PFTrDA in plasma and body feathers have been shown in nestling white-tailed eagles as well,[31] whereas a lack of such association between feathers and internal tissues has also been reported.[30] Strong and significant correlations were found between feather and plasma in nestling northern goshawks (*Accipiter gentilis*) for PFOS, PFUnDA, PFDoDA, and PFTeDA but not for PFHxS, PFNA, or PFTrDA.[33] These results suggest that the usefulness of feathers for biomonitoring PFAS might be compound-specific. The inconsistencies in the correlations between PFAS concentrations in feathers and internal tissues warrant further investigations[27] in order to better evaluate the suitability of feathers for representing internal PFAS exposure and eventually to predict the toxicological potential from feather PFAS.

PFOS and FOSA concentrations observed in the present study are within the ranges reported previously in birds of prey feathers, such as body feathers of white-tailed eagles from West Greenland (median = 8 and 2 ng g^{-1}; 1997−2009; $n = 11$),[32] body feathers of nestling white-tailed eagles from northern Norway (median = 6 and 1 ng g^{-1}; 2014; $n = 14$),[31] and PFOS in tail feathers of Belgian barn owls (median = 16 ng g^{-1}; 2008−2009; $n = 13$).[29] It is however challenging to compare the exposure levels due to possible effects of feather types, as demonstrated for OCs,[26] and age.[42] Body feathers are replaced approximately each year in white-tailed eagles, whereas the big

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flight feathers are molted across multiple years.[79,80] This makes body feathers more suitable for temporal trend monitoring than flight feathers where unknown multiple variations in year of growth could be a confounding factor.

In conclusion, the PFAS trends and profiles we reconstructed here are in general agreement with previous studies using soft tissues or eggs and show clear spatial differences corresponding to contamination sources. The temporal trends also appear to indicate the effectiveness of phase-outs or continued emissions of major PFAS. While our study strongly suggests the feasibility of using archived feathers in spatiotemporal trend monitoring of PFAS as an alternative to soft tissues or eggs, there are some limitations that should be acknowledged and ideally addressed in future work. First, as mentioned earlier, age and sex could not be included in the retrospective modeling analysis due to the sample banking protocols (necessarily) accepting such specimens. Second, different storage conditions among the subpopulations may have had a minor impact on some of the results: for example, the precursor compound FOSA[53,55,56] may potentially degrade/transform at differing rates depending on the storage condition. Finally, although we applied a consistent washing procedure across the three subpopulations, there is uncertainty regarding the effective removal of potential external contamination due to wet/dry deposition. In that respect, feather concentrations may not only reflect internal body burdens.[27] Despite these shortcomings, our careful experimental design and analytical quality are advantageous and do result in reliable spatiotemporal trends and further underline the promising avenue of using archived feathers in retrospective PFAS trend monitoring. Finally, the distinctive spatiotemporal trends we reconstructed also warrant the need for continued monitoring, in particular PFOS in the Baltic and PFCAs in general, and should align well with the banking philosophy and modus operandi of NHMs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b03514.

Precursor and product ions and QA/QC for the compounds analyzed; detection frequencies of perfluoroalkyl substances; variance inflation factors; data descriptive statistics of feather concentrations; mean and median feather concentrations of PFAS at 10 year intervals; GAM model output; temporal trend predictions of PFCAs; sample size per year per subpopulation; comparisons of mean PFAS and PFCA concentrations in white-tailed eagles; temporal trends of PFCAs; comparisons of PFAS and PFCA compositions per 10 year period; temporal trends of odd:even chained PFCA ratios (PDF)

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