Prevalence of Long-Chained Perfluorinated Carboxylates in Seabirds from the Canadian Arctic between 1975 and 2004

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Perfluorinated Sulfonate and Carboxylate Compounds in Eggs of Seabirds Breeding in the Canadian Arctic: Temporal Trends (1975–2011) and Interspecies Comparison

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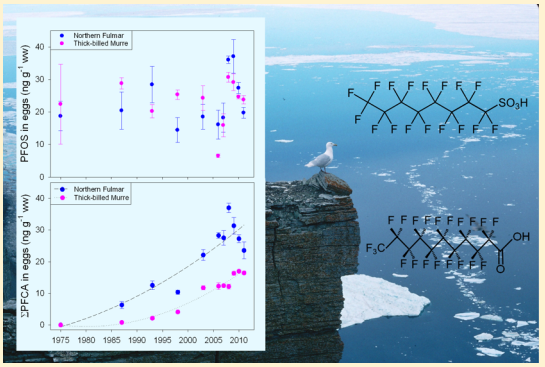
Supporting Information

ABSTRACT: Perfluorinated sulfonates (PFSAs) and perfluorinated carboxylates (PFCAs), as well as selected precursor compounds, were measured in eggs of thick-billed murres (*Uria lomvia*) and northern fulmars (*Fulmarus glacialis*) from Prince Leopold Island in the Canadian Arctic between 1975 and 2011 as well as in eggs of three additional species (black guillemot *Cepphus grylle*, black-legged kittiwake *Rissa tridactyla*, glaucous gull *Larus hyperboreus*) sampled in 2008. ΣPFCA concentrations increased significantly from 1975 to 2011 in the murre and fulmar eggs at an average annual rate of 0.56 and 0.91 ng g^{-1} ww, respectively, whereas perfluorooctane sulfonate (PFOS) concentrations did not change significantly. The interspecies comparison of eggs sampled in 2008 found that black guillemots had the highest PFOS and lowest ΣPFCA levels, and northern fulmars had the highest ΣPFCA levels. PFUnA (C_{11}) and PFTrA (C_{13}) were the predominant PFCAs measured in eggs of all five species except for the black guillemot where PFDA (C_{10}) contributed almost equally with PFTrA (C_{13}) to the PFCA profile. Based on published toxicity thresholds, levels of neither perfluorooctanoate (PFOA) nor PFOS in seabird eggs from the Canadian Arctic are of toxicological concern. These are the first interspecies comparisons for PFASs in seabirds from the Canadian Arctic.



INTRODUCTION

The chemical and thermal stability of a large number of per- and poly-fluoroalkyl substances (PFASs) led to the manufacture of a range of fluorinated polymers used as lubricants, adhesives, stain and soil repellants, paper coatings, nonstick surfaces on cookware, and fire-fighting foams.[1] Although PFASs were commercialized over 50 years ago, they received little attention as contaminants in wildlife until Giesy and Kannan[2] reported their presence in marine mammals, fish-eating birds, and marine and freshwater fish from around the world. Perfluorooctane sulfonate (PFOS) was the dominant PFAS found in all samples analyzed. Since then, perfluorinated sulfonates (PFSAs) and carboxylates (PFCAs), in particular, have been shown to be widespread in the environment and in wildlife, including ecosystems in the Arctic.[3−6]

Air is the most important transport route to the Arctic for volatile and semivolatile contaminants[7] but cannot account for the presence of nonvolatile but highly stable compounds such as the PFSAs and PFCAs in the Arctic. It has been proposed that neutral, volatile precursor compounds (e.g., PFCA and PFSA precursor compounds such as fluorotelomer alcohols (FTOHs) and sulfonamide alcohols) could undergo long-range atmospheric transport and be degraded in remote regions.[8−11] Conversely, given that transport via ocean currents may be more important than the atmospheric route for more water-soluble, less volatile contaminants,[7] ionic PFASs, such as PFSAs and PFCAs, could be transported directly to the arctic marine environment via ocean currents.[12,13] Unlike the atmospheric transport pathway which can deliver contaminants from midlatitudes to the Arctic within a few days or weeks, ocean transport is relatively slow, and it may take decades before contaminants reach the Arctic from other parts of the world.[14]

To date, PFAS monitoring in biological samples has focused largely on PFCAs and PFSAs with very few measurements reported for their precursors.[6] Food web studies in marine ecosystems suggest that PFCAs and PFSAs can biomagnify,[15−21] and these compounds have been found in arctic seabirds along with a variety of other arctic biota.[6,22] Seabirds feed at relatively high trophic positions in arctic marine food webs,[23,24] and, therefore, eggs of seabirds have been used to monitor contamination of the marine environment in the Canadian Arctic since 1975.[25] Unlike lipophilic halogenated organic contaminants, which are transferred along with fat to the eggs at the time of egg formation,[26,27] perfluoroalkyl acids such as PFCAs and PFSAs appear to bind to proteins rather than partition into lipid.[6] Nonetheless, PFCAs and PFSAs and other PFASs are transferred to bird eggs,[3,4,28] and eggs have been used in a number of studies to monitor PFASs.[29−33]

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Table 1. Mean Concentrations (ng g^{-1} ww ± standard error) of Perfluorinated Carboxylates and Sulfonates in Eggs of Northern Fulmars and Thick-Billed Murres from Prince Leopold Island, Nunavut, Canada, 1975−2011

species	year	*n* (# pools)[a]	ΣPFCA	PFBS (C_4)	PFHxS (C_6)	PFOS (C_8)	PFDS (C_{10})
northern fulmar	1975	15 (5)	0.03 ± 0.02	<0.1	<0.1	18.7 ± 4.53	<0.2
	1987	6 (2)	6.33	<0.1	<0.1	20.4	<0.2
	1993	15 (5)	12.6 ± 1.35	<0.1	<0.1	28.4 ± 5.59	<0.2
	1998	15 (5)	10.4 ± 0.70	<0.1	<0.1	14.5 ± 3.82	<0.2
	2003	15 (5)	22.1 ± 1.69	<0.1	<0.1	18.5 ± 3.86	<0.2
	2006	15 (5)	28.3 ± 0.87	<0.1	<0.1	16.2 ± 4.43	0.05 ± 0.05
	2007	15 (5)	27.5 ± 2.33	<0.1	<0.1	18.3 ± 4.49	<0.2
	2008	15 (5)	37.1 ± 1.49	<0.1	0.20 ± 0.03	36.0 ± 1.15	1.64 ± 0.10
	2009	15 (5)	31.4 ± 2.64	<0.1	0.21 ± 0.01	37.1 ± 5.18	0.20 ± 0.05
	2010	15 (5)	27.3 ± 1.29	<0.1	0.05 ± 0.03	27.4 ± 1.72	0.04 ± 0.04
	2011	15 (5)	23.6 ± 2.69	0.57 ± 0.46[b]	<0.1	19.8 ± 1.67	<0.2
thick-billed murre	1975	8 (3)[c]	<0.1	<0.1	<0.1	22.4 ± 12.3	<0.2
	1987	9 (3)	0.81 ± 0.20	<0.1	<0.1	28.8 ± 1.74	<0.2
	1993	12 (4)	2.15 ± 0.49	<0.1	<0.1	20.3 ± 2.0	<0.2
	1998	15 (5)	4.12 ± 0.34	<0.1	<0.1	25.4 ± 1.47	<0.2
	2003	15 (5)	11.8 ± 0.67	<0.1	<0.1	24.3 ± 3.79	<0.2
	2006	15 (5)	12.3 ± 1.12	<0.1	<0.1	6.53 ± 0.55	0.20 ± 0.14
	2007	15 (5)	12.4 ± 0.51	<0.1	<0.1	15.9 ± 3.53	<0.2
	2008	15 (5)	12.2 ± 0.77	<0.1	0.13 ± 0.06	30.7 ± 1.51	0.06 ± 0.06
	2009	15 (5)	16.3 ± 0.62	<0.1	0.09 ± 0.06	29.1 ± 2.58	0.26 ± 0.11
	2010	15 (5)	17.0 ± 0.45	0.04 ± 0.02	0.13 ± 0.03	24.7 ± 0.59	<0.2
	2011	15 (5)	16.5 ± 0.45	0.07 ± 0.05	<0.1	23.8 ± 1.29	<0.2

[a]Samples were analyzed in pools of 3 eggs. The number of eggs (*n*) is given with the number of egg pools shown in brackets. [b]One outlier was removed because it was more than an order of magnitude higher than the mean of the other values for that year. Therefore *n* = 12 (4). [c]One pool was comprised of only two eggs.

Table 2. Mean Concentrations (ng g^{-1} ww ± standard error) of Perfluorinated Carboxylates and Sulfonates As Well As Mean Ratios of ΣPFCA:PFOS (± standard error) in Eggs of Five Species of Seabirds Collected from Prince Leopold Island, Nunavut, Canada, in 2008

species	black guillemot	thick-billed murre	northern fulmar	glaucous gull	black-legged kittiwake
n (# pools)[a]	9 (3)	15 (5)	15 (5)	9 (3)	15 (5)
ΣPFCA	7.59 ± 1.15	12.2 ± 0.77	37.1 ± 1.49	24.2 ± 0.71	9.71 ± 1.93
PFBS (C_4)	<0.1	<0.1	<0.1	<0.1	<0.1
PFHxS (C_6)	0.11 ± 0.11	0.13 ± 0.06	0.20 ± 0.03	0.39 ± 0.04	<0.1
PFOS (C_8)	39.8 ± 8.09	30.7 ± 1.51	36.0 ± 1.15	20.0 ± 1.13	9.58 ± 0.96
PFDS (C_{10})	0.60 ± 0.60	0.06 ± 0.06	1.64 ± 0.10	1.75 ± 0.06	<0.2
ΣPFCA:PFOS	0.20 ± 0.02	0.40 ± 0.03	1.03 ± 0.05	1.21 ± 0.03	1.07 ± 0.27

[a]Samples were analyzed in pools of 3 eggs. The number of eggs (*n*) is given with the number of egg pools shown in brackets.

Martin et al.[22] first screened livers of northern fulmars (*Fulmarus glacialis*) and black guillemots (*Cepphus grylle*) sampled from Prince Leopold Island in 1993 for the presence of PFASs and found relatively low concentrations of both the PFCAs and PFOS in both species. In the present study, we examine temporal trends and compositional profiles of major bioaccumulative PFASs (PFSAs, PFCAs) as well as their precursors [FTOHs, fluorotelomer unsaturated acids (FTUCAs), perfluorosulfonamides (FOSAs)], in eggs of two species of seabirds, the thick-billed murre (*Uria lomvia*) and northern fulmar, from Prince Leopold Island in the Canadian Arctic. We also compare concentrations and compositional profiles of PFASs in eggs of five species of seabirds, the thick-billed murre, northern fulmar, black-legged kittiwake (*Rissa tridactyla*), black guillemot, and glaucous gull (*Larus hyperboreus*), collected from Prince Leopold Island in 2008.

MATERIALS AND METHODS

Sample Collection. For each of 11 years during the period from 1975 to 2011 (see Table 1 for sampling years), eggs were collected from each of two species of seabirds (northern fulmar, thick-billed murre) from Prince Leopold Island (74°02′N, 90°05′W) in Lancaster Sound (Figure S1). In 2008, eggs were also collected for three additional species (black-legged kittiwake, black guillemot, glaucous gull) from Prince Leopold Island for comparison. All eggs were randomly collected on the basis of one egg per nest to maintain independence among samples. Eggs were kept cool in the field and shipped to the National Wildlife Research Centre (NWRC) where egg contents were homogenized and stored frozen at −40 °C. Archived samples from 1975 to 2006 were retrieved from the National Wildlife Specimen Bank for analysis, whereas samples from 2007 to 2011 were analyzed within six months of collection. Egg homogenates were analyzed as pooled (composite) samples with each pool consisting of three

individual egg samples with one exception (see Table 1). Sample sizes are given in Tables 1 and 2.

Standards and Chemicals. Nonisotope enriched (or nonlabeled) standards for the PFSAs [C_4 (PFBS), C_6 (PFHxS), C_8 (PFOS), C_{10} (PFDS)], PFCAs (C_6–C_{15} chain lengths: PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA, and PFPA, respectively), 6:2, 8:2, and 10:2 FTUCAs, 6:2, 8:2, and 10:2 FTOHs, and two FOSAs [perfluorooctanesulfonamide (PFOSA), methylated perfluorooctanesulfonamide (N-Me-FOSA)] as well as all internal ^{13}C- or ^{18}O-enriched standards were obtained from Wellington Laboratories (Guelph, ON, Canada). See Table S1 for a complete listing of all of the above PFASs as well as the ^{13}C- or ^{18}O-enriched internal standards used. All solvents used were HPLC grade and purchased from Fisher Scientific (Ottawa, Canada).

Analytical Determination. The PFAS extraction of eggs and subsequent cleanup and analysis have been described in detail elsewhere.[27,33−36] Briefly, approximately 1 g of egg homogenate was spiked with labeled internal standards (see Table S1) and extracted with 10 mM KOH acetonitrile/water. The cleanup and fractionation of the overall PFAS extract was performed using Waters Oasis WAX solid phase extraction (SPE) cartridges. The first fraction contained FTOHs and FOSAs; the second fraction contained PFSAs, PFCAs, and FTUCAs. The separation of the target compounds in both fractions was carried out on a Waters 2695 HPLC equipped with an ACE 3 C_{18} analytical column (50 mm × 2.1 mm I.D., 3 μm particle size, Advance Chromatography Technologies, Aberdeen, UK) coupled to a Waters Quattro Ultima triple quadrupole mass spectrometer (Waters, Milford, MA, USA). Analysis of PFCAs, PFSAs, and FTUCAs was done using negative electrospray ionization (ESI^-), and the FTOHs and FOSAs were analyzed by negative atmospheric pressure photoionization ($APPI^-$). Quantification was performed using an internal standard approach. The calibration curve for PFTeA was used for PFPA quantification since a PFPA standard was unavailable at the time of this study. Where no labeled standards were available, labeled internal standards with the closest retention time were used. Since an isotope dilution quantification approach was used, concentrations were inherently recovery-corrected. Recoveries of the FTOH and FOSA internal standards averaged 70%, and, for the PFCAs, PFSAs, and FTUCAs, recoveries averaged 81%. For every block of 6−12 samples, a blank sample and a NWRC in-house reference material was analyzed. See Table S1 for limits of detection (LODs) and method quantification limits (MQLs) for the measured PFASs.

Data Treatment. All statistical tests were performed using Statistica for Windows Version 7.0 (StatSoft Inc., Tulsa, OK) with a significance level of $p < 0.05$. Since PFCAs and PFSAs are known to bind to proteins rather than partition into lipid,[6] concentrations were not lipid-normalized. Only those compounds for which >90% of the samples had detectable concentrations for a given species were statistically analyzed. Nondetect values were set to one-half the detection limit for purposes of statistical analyses but were set to zero for calculation of ΣPFCA and reported annual means. To account for any potential influence of change in trophic position over time, temporal trends were analyzed by backward stepwise regression analysis, with year and $\delta^{15}N$ (see Supporting Information and Table S2) as regressors, to select the best model. Regression analyses were performed for concentrations of ΣPFCA (sum of C_6–C_{15}), the individual longer-chained PFCAs (C_9–C_{15}), and PFOS. Residuals from the regression analyses were tested for normality using the Shapiro-Wilks' W test. Changes in percent contributions of PFCAs (C_6–C_{15}) to the total PFCA profile over time were analyzed using the Spearman Rank Correlation. Kruskal–Wallis analysis of variance by ranks was used to test for differences in ΣPFCA and PFOS concentrations among species. The tabulated data are presented as arithmetic means in concentration units of ng g^{-1} wet weight (ww).

RESULTS

Temporal Trends. ΣPFCA concentrations increased significantly from 1975 to 2011 in eggs of both northern fulmars ($n = 52$, $r = 0.86$, $p < 0.0001$) and thick-billed murres ($n = 50$, $r = 0.90$, $p < 0.0001$) at an average annual rate of 0.91 and 0.56 ng g^{-1} ww, respectively (Figure 1A), whereas PFOS concentrations did not change significantly ($p > 0.05$) (Figure 1B). The ratio of ΣPFCA:PFOS (Figure 1C) clearly shows the increasing concentrations of ΣPFCA relative to PFOS from 1975 to 2006, followed by a decrease in the ratio to 2008−2009 reflecting the increase in PFOS levels during those two years. ΣPFCA concentrations were approximately 2-fold higher than PFOS concentrations in 2006.

PFOS was the major PFSA measured (Table 1) and was detected in all fulmar and murre eggs sampled from 1975 to 2011. PFOSA was detected at very low concentrations (<0.7 ng g^{-1} ww) in only a few samples, and N-Me-FOSA was not detected in any of the samples (<0.2 ng g^{-1} ww). No fluorotelomer alcohols (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) were detected (<0.6 ng g^{-1} ww, <0.6 ng g^{-1} ww, and <0.5 ng g^{-1} ww, respectively) in any of the samples, and fluorotelomer unsaturated acids (6:2 FTUCA, 8:2 FTUCA, 10:2 FTUCA) were detected in a few samples but could not be quantified (<0.1 ng g^{-1} ww).

Temporal Changes in Composition of PFCA Profile. Significant increases ($p < 0.02$) in concentrations of all of the longer-chained PFCAs (C_9–C_{15}) contributed to the increasing ΣPFCA concentrations in the murres and the fulmars. PFUnA (C_{11}) and PFTrA (C_{13}) were the predominant PFCAs measured in eggs of both species (Figure 2). These two PFCAs together constituted >60% of ΣPFCA in all years, with PFTrA dominating the fulmar PFCA profile (except in 1975) and PFUnA generally dominating the murre PFCA profile. PFOA (C_8) was detected (>0.08 ng g^{-1} ww) in eggs of both species only since 2008 (Table S3) and comprises <3% of the PFCA profile. PFHpA (C_7) was not detected (<0.1 ng g^{-1} ww) in eggs of either species in any year. There was no significant change in the percent contribution of the longer-chained PFCAs (C_{11}–C_{15}) to the fulmar PFCA profile over the years, although shorter-chained PFCAs, such as PFHxA (C_6), PFOA (C_8), PFNA (C_9), and PFDA (C_{10}), increasingly appeared in the profile (Figure 2). In the murre eggs, there was a significant decrease in the contribution of PFUnA (C_{11}) and PFTrA (C_{13}) to the PFCA profile as PFHxA (C_6), PFOA (C_8), PFNA (C_9), PFDA (C_{10}), PFTeA (C_{14}), and PFPA (C_{15}) increasingly appeared in the profile (Figure 2). In 2011, the fulmar PFCA profile showed a stronger presence of the longer-chained PFCAs (C_{10}–C_{15}) which comprised >90% of ΣPFCA, whereas in the murres, the profile was dominated (>90%) by the C_9–C_{13} PFCAs.

Interspecies Comparison. Concentrations of PFCAs and PFSAs were determined in eggs of five species of seabirds

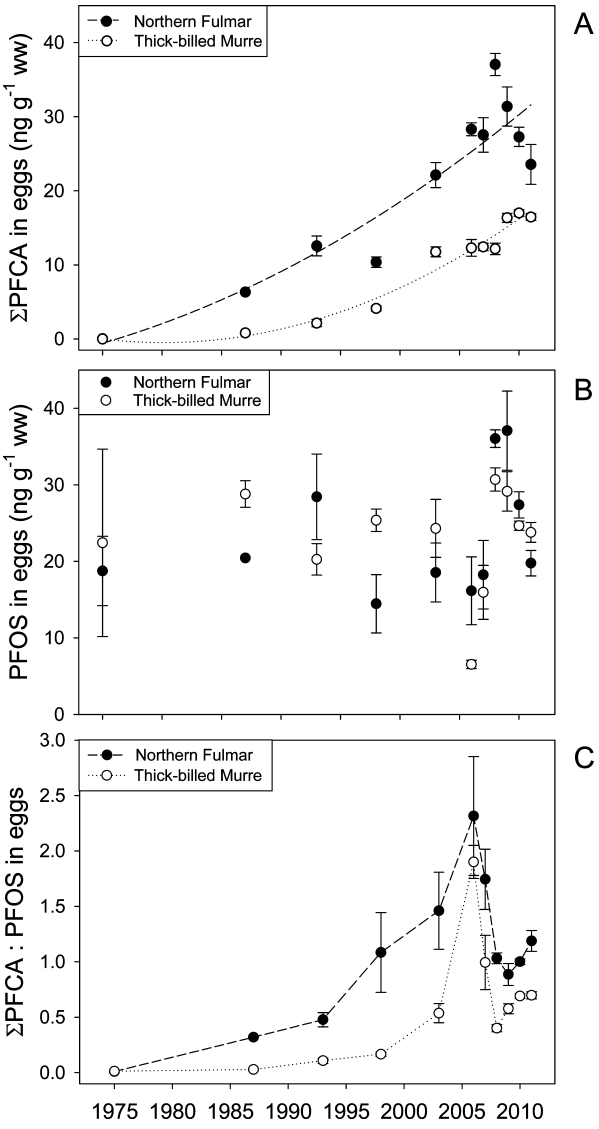

Figure 1. Mean annual concentrations (±standard error) of (A) ΣPFCA and (B) PFOS as well as (C) mean annual ratios of ΣPFCA:PFOS (±standard error) in eggs of northern fulmars and thick-billed murres from Prince Leopold Island, Nunavut, Canada, 1975–2011. ΣPFCA = sum of PFHxA (C_6), PFHpA (C_7), PFOA (C_8), PFNA (C_9), PFDA (C_{10}), PFUnA (C_{11}), PFDoA ($_{12}$), PFTrA (C_{13}), PFTeA (C_{14}), and PFPA (C_{15}).

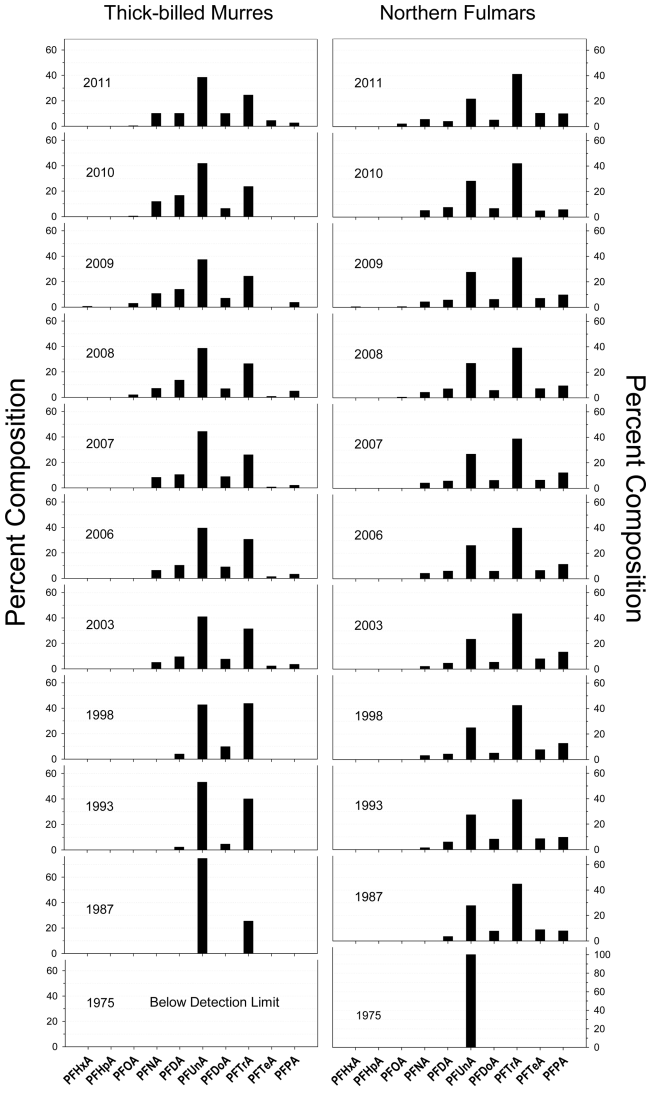

Figure 2. Mean contributions (%) of PFHxA (C_6), PFHpA (C_7), PFOA (C_8), PFNA (C_9), PFDA (C_{10}), PFUnA (C_{11}), PFDoA ($_{12}$), PFTrA (C_{13}), PFTeA (C_{14}), and PFPA (C_{15}) to ΣPFCA in eggs of thick-billed murres and northern fulmars from Prince Leopold Island, Nunavut, Canada, 1975–2011.

sampled at Prince Leopold Island in 2008 (Tables 2 and S4). PFOS was the major PFSA measured (Table 2) and was detected in all eggs analyzed. PFOSA and N-Me-FOSA were not detected in any of the samples (<0.03 ng g^{-1} ww and <0.2 ng g^{-1} ww, respectively). No fluorotelomer alcohols (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) were detected (<0.6 ng g^{-1} ww, <0.6 ng g^{-1} ww, and <0.5 ng g^{-1} ww, respectively) in any of the samples, and fluorotelomer unsaturated acids (6:2 FTUCA, 8:2 FTUCA, 10:2 FTUCA) were detected in a few samples but could not be quantified (<0.1 ng g^{-1} ww).

Significant interspecies differences were found for concentrations of ΣPFCA (p = 0.0023) and PFOS (p = 0.0028) in eggs of the five seabird species. Black guillemots had the highest PFOS levels and the lowest ΣPFCA levels (Table 2, Figure S2). Northern fulmars had the highest ΣPFCA levels, and black-legged kittiwakes had the lowest PFOS levels. The ratio of ΣPFCA:PFOS concentrations was close to unity in the northern fulmars, black-legged kittiwakes, and glaucous gulls, whereas the ratio was skewed toward higher PFOS concentrations in the black guillemots and thick-billed murres (Table 2, Figure S2). PFUnA (C_{11}) and PFTrA (C_{13}) were the predominant PFCAs measured in eggs of all species except for the black guillemot where PFDA (C_{10}) contributed almost equally with PFTrA (C_{13}) to the PFCA profile (Figure 3). The fulmars and kittiwakes had a higher proportion of PFTeA (C_{14}) and PFPA (C_{15}) in the PFCA profile compared with the other species (Figure 3). PFOA (C_8) was not detected (<0.08 ng g^{-1} ww) in any eggs of the kittiwakes, glaucous gulls, or black guillemots, PFHxA (C_6) was detected (>0.1 ng g^{-1} ww) in only one pool of murre eggs, and PFHpA (C_7) was not detected (<0.1 ng g^{-1} ww) in any of the samples.

DISCUSSION

PFOS Levels and Trends. In most wildlife, PFOS generally dominates the PFAS profile.[3,4,6] This was also true for the black guillemots and thick-billed murre eggs we sampled in 2008.

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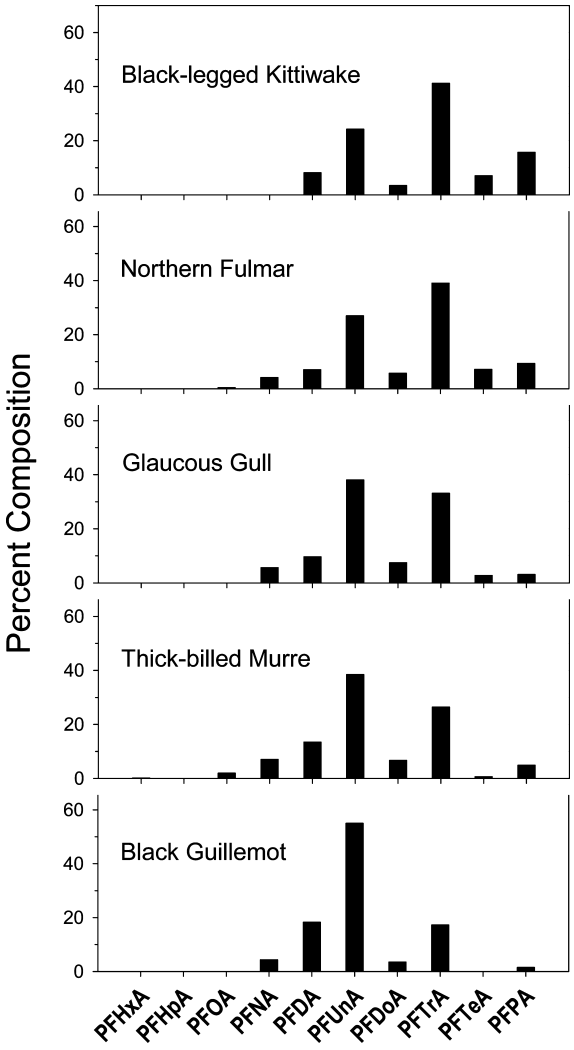

Figure 3. Mean contributions (%) of PFHxA (C_6), PFHpA (C_7), PFOA (C_8), PFNA (C_9), PFDA (C_{10}), PFUnA (C_{11}), PFDoA ($_{12}$), PFTrA (C_{13}), PFTeA (C_{14}), and PFPA (C_{15}) to ΣPFCA in eggs of black guillemots, thick-billed murres, northern fulmars, glaucous gulls, and black-legged kittiwakes sampled from Prince Leopold Island, Nunavut, Canada, 2008.

However, PFOS concentrations did not dominate the PFAS profile in the northern fulmars, glaucous gulls, and black-legged kittiwakes. PFOS concentrations in those three species were similar to ΣPFCA or even slightly lower (Table 2, Figure S2). These interspecies differences may be due to different feeding strategies[37] or different overwintering areas, which could account for varying exposures to these compounds. Samples collected from the Barents Sea in 2004 showed that PFOS constituted 80% and 94% of total PFASs in livers of black guillemots and glaucous gulls, respectively,[18] and 71% of total PFASs in eggs of glaucous gulls.[38] In the Canadian Arctic, PFOS constituted 83% and 43% of PFASs in eggs of black guillemots and glaucous gulls, respectively, in 2008. Black guillemots and thick-billed murres, which had the highest proportions of PFOS (82% and 71% of total PFASs, respectively) in our study, have overlapping wintering grounds and are both deep-diving species capable of feeding on both pelagic and benthic fish and invertebrates.[39,40] Glaucous gulls are both scavengers and predators utilizing a wide range of food items depending on location and season[41] which may explain the difference in the PFOS proportion between the European and Canadian Arctic. Proximity to different source regions may also play a role as illustrated by a spatial study of guillemot (*Uria aalge*) eggs from Iceland, the Faroe Islands, Norway, and Sweden where PFOS ranged from 14% to 80% of total PFASs.[42] Alternatively, as shown in Figure 1C, PFOS dominated the PFAS profile in the fulmar and murre eggs from Prince Leopold Island from the 1970s to the 1990s, but as the ΣPFCA concentrations increased relative to the PFOS concentrations, the proportional composition of the PFAS profile changed. The ratio of ΣPFCA:PFOS dropped dramatically after 2005 for both the murres and fulmars and has only started to increase again in recent years. The ΣPFCA:PFOS ratio clearly depends on the year sampled, at least for the murres and fulmars, and likely other species, as well.

PFOS concentrations in the eggs of Canadian Arctic seabirds in 2008 were relatively low compared with eggs of glaucous gulls sampled in 2004 from the Norwegian Arctic,[38] ivory gulls (*Pagophila eburnea*) sampled in 2006−2007 from the Norwegian and Russian Arctic,[43] guillemots (common murre − *Uria aalge*) sampled in 2003 from the Baltic Sea,[29] and herring gulls (*Larus argentatus*) sampled in 2007 and 2010 from the Great Lakes.[27,36] PFOS concentrations in herring gull and Brünnich's guillemot (a.k.a. thick-billed murre) eggs sampled in 2003 and 2007 from northern Norway and Svalbard[32,44] were within the same range as those in eggs of Canadian Arctic seabirds.

PFOS concentrations showed no significant change between 1975 and 2011 in the fulmar and murre eggs from Prince Leopold Island which is consistent with the findings of Butt et al.[45] for PFOS in livers of fulmars and murres from Prince Leopold Island between 1975 and 2003/2004. PFOS concentrations in common murres from the Baltic Sea increased almost 30-fold between 1968 and 2003,[29] whereas PFOS in Brünnich's guillemot eggs from northern Norway and Svalbard decreased between 1983 and 2007[44] as did PFOS in eggs of herring gulls from the Great Lakes between 1990 and 2010.[33] Concentrations of PFOS in herring gulls from northern Norway, however, increased from 1983 to 1993 followed by a leveling off between 1993 and 2003.[32] PFOS concentrations increased from 1972 to 2002 in the livers of polar bears (*Ursus maritimus*) from Alaska and Baffin Island in the North American Arctic,[46] whereas Butt et al.[47] showed that PFOS in ringed seals (*Phoca hispida*) from the Canadian Arctic increased from 1992 to 1998 at Arviat and from 1972 to 2000 at Resolute Bay followed by declines to 2005.

PFOS, its salts, and precursors are not manufactured in Canada. The 3M Company voluntarily phased out its perfluorooctane sulfonyl fluoride (POSF)-based products including PFOS and its precursors between 2000 and 2002. However, minor PFOS production continued in Europe and China (<42−82 t in Europe and <50 t in China in 2003), and by 2006 China had increased its POSF production to 200 t.[6,48,49] Butt et al.[47] suggested that phase-out accounted for the decline in PFOS concentrations observed in the seals between 1998/2000 and 2005, although we did not see a similar response in the PFOS concentrations in the fulmar and murre eggs (Figure 1B) suggesting that the increased production of PFOS in China may have offset the 3M phase-out with respect to exposure of some arctic biota. Armitage et al.[50] have proposed that the differing PFOS trends observed in biota may be attributed to the relative importance of various exposure

pathways; i.e. (1) uptake of PFOS emitted directly from source regions and transported to other regions, (2) uptake of PFOS derived from the atmospheric degradation of precursor compounds, and (3) *in vivo* transformation of precursor compounds to PFOS. Therefore, the inconsistency in PFOS temporal trends in biota among regions may represent not only differences in emissions from source regions[6,50] but also differences in exposure pathways.[50]

PFCA Levels, Trends, and Profile. ΣPFCA significantly increased between 1975 and 2011 in the fulmar and murre eggs from Prince Leopold Island, which is consistent with the findings of Butt et al.[45] for PFCAs in livers of fulmars and murres from Prince Leopold Island between 1975 and 2003/2004. PFCAs also increased in herring gull eggs from the Great Lakes between 1990 and 2010,[33] in herring gull eggs from northern Norway between 1983 and 2003,[32] and PFUnA and PFTrA increased in Brünnich's guillemot eggs from northern Norway and Svalbard from 1993 to 2003 followed by a leveling off of PFUnA and a decrease in PFTrA between 2003 and 2007.[44] PFCAs also increased in polar bears from Alaska and Baffin Island in the North American Arctic between 1972 and 2002,[46] in ringed seals from the Canadian Arctic between 1992/93 and 2005,[47] and in beluga whales (*Delphinapterus leucas*) from Alaska between 1989 and 2006.[51]

PFOA is the most studied of the PFCAs.[6] However, PFOA, along with other shorter-chain length PFCAs, are typically not detected or are found only at low concentrations in arctic biota.[4,6] This is likely because bioaccumulation potential increases with increasing perfluoroalkyl chain length.[52] As well, there is evidence for the preferential accumulation of longer-chain length PFCAs in the egg yolk.[27] Indeed, PFOA was detected at low concentrations only in the murre and fulmar eggs and only in more recent years (2008 onward, see Table S3) despite the fact that PFOA was included in the 3M Company's phase-out of POSF-based products. This supports the contention that historical electrochemical fluorination (ECF)-based emissions are the major source of PFOA to the oceans where residence times are long[12] and, therefore, that PFOA levels in Arctic Ocean waters are predicted to increase until 2030 and then only slowly decline.[13,53]

It has been proposed that biotic concentrations of C_8, C_9, C_{11}, and C_{13} predominantly reflect atmospheric and oceanic transport of direct sources (i.e., manufacturing and use), whereas C_{10} and C_{12} reflect indirect sources (i.e., atmospheric degradation of FTOHs).[54] Further, it has been hypothesized that the odd-chain length PFCAs are more bioaccumulative than the even-chain length PFCAs in wildlife.[8,52] In seabirds, PFUnA and PFTrA dominate the PFCA profile as shown in this study and others,[22,27,28,32−34,36,38,42−45,55] whereas PFNA and PFUnA appear to predominate in marine mammals.[22,51,56−58] This specific odd−even PFCA pattern supports the hypothesis of atmospheric FTOH degradation as a source of PFCAs followed by selective bioaccumulation[8,59] although the reason for the pattern difference between seabirds and marine mammals is not clear. Sturm and Ahrens[59] have suggested that seabirds may have a higher biomagnification potential for PFCAs than marine mammals.

Precursors. Of all the analyzed precursors for PFOS and PFCAs, only PFOSA was quantifiable in two pools of fulmar eggs, one from 1975 (0.35 ng g^{-1} ww) and one from 1993 (0.17 ng g^{-1} ww). This result for PFOSA is consistent with other recent reports for birds. In a temporal trend study (1990−2010) of herring gull eggs sampled from seven colonies in the Great Lakes,[33] PFOSA was also detected at low concentrations (<1.7 ng g^{-1} ww) from 1990 to 2006. However, after 2006, egg concentrations of PFOSA were below the detection limit.[33] PFOSA was detected (<0.43 ng g^{-1} ww) in herring gull eggs from northern Norway in 2003[32] and Gebbink et al.[36] reported very low concentrations (averaging <1 ng g^{-1} ww) for herring gull eggs collected in 2007 from 15 colonies across the Great Lakes. In eggs collected in 2008 from four gull species [glaucous-winged (*Larus glaucescens*), California (*L. californicus*), ring-billed (*L. delawarensis*) and herring gull] from 15 marine and freshwater colonies across Canada, PFOSA was detected in eggs from only eight colonies with averages ranging from 0.05 to 0.29 ng g^{-1} ww.[34]

FTUCAs were not detected in glaucous gull eggs from the Norwegian Arctic,[38] nor were FTOHs or FTUCAs detected in herring gulls from the Great Lakes.[27,33,36] However, Butt et al.[45] detected the 8:2 and 10:2 FTUCAs at very low concentrations in some livers of northern fulmars and thick-billed murres from Prince Leopold Island as was also the case for the fulmar and murre eggs in our study. Although volatile precursors have been measured in the Canadian Arctic atmosphere[60,61] as well as snow and ice,[62] the absence of measurable concentrations in the seabird eggs supports the view that these precursor compounds are readily oxidized and degraded to PFOS and PFCAs.[8,61−64]

Toxicological Implications. The effects of PFASs on wildlife are not well-known, in particular for Arctic biota.[6] Although the toxicities of PFOS and PFOA have been extensively studied, there is a lack of information for many of the PFASs including the long-chain PFCAs.[65] However, it has recently been shown that 11- and 12-carbon PFCAs are equally potent inducers of stress response genes relative to PFOS and PFNA and that the gene expression responses (oxidative damage, DNA damage, general cell lesions, membrane damage) were higher for the PFSAs than for the PFCAs although the effect of chain length is more important than the functional group.[66] Further, it seems that the PFCA precursors are more toxic than the PFCAs themselves.[67]

Laboratory studies have shown that PFOS is toxic to birds with effects ranging from decreased weight gain and increased liver mass[68,69] to higher mortality, reduced hatchability, and liver histopathological changes.[70] Estimated LD_{50} values for PFOS in eggs of domestic chickens (*Gallus gallus*) ranged from 4.9 $\mu g\ g^{-1}$,[70] to 93 $\mu g\ g^{-1}$.[71] Based on reduced hatchability, Molina et al.[70] estimated a lowest-observed-adverse-effect level (LOAEL) of 0.1 $\mu g\ g^{-1}$ for PFOS in eggs. Newsted et al.[68] estimated a toxicity reference value of 1.7 $\mu g\ mL^{-1}$ and a predicted no effect concentration of 1 $\mu g\ mL^{-1}$ for PFOS in eggs (1 mL egg corresponds to approximately 1 g[28]). Based on egg injection studies, Strömqvist et al.[72] have suggested that PFOA is a more potent embryotoxicant than PFOS. A slight but significant increase in mortality was seen in chicken embryos exposed to PFOA at a dose of approximately 20 $\mu g\ g^{-1}$.[72] PFOA, PFUnA, and PFDS had no effect on pipping success at concentrations up to 10 $\mu g\ g^{-1}$ in chicken embryos.[73] Based on the toxicity threshold levels found in the literature, the low PFOA levels found in seabird eggs from the Canadian Arctic are not of toxicological concern, and PFOS levels in the seabird eggs were orders of magnitude below most of the threshold levels cited. The LOAEL estimated by Molina et al.,[70] however, was only about 3- to 5-fold higher than PFOS concentrations in eggs of some species. It is important that we continue to monitor PFASs in arctic biota as our understanding

of the pharmacokinetics and behavior of this class of compounds improves.

■ ASSOCIATED CONTENT

Supporting Information

Description of stable-nitrogen isotope analysis, listing of complete PFAS names, abbreviations, LODs and MQLs, as well as additional tables and figures. 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.

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