Perfluorinated Carboxylates and Sulfonates and Precursor Compounds in Herring Gull Eggs from Colonies Spanning the Laurentian Great Lakes of North America

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Environmentally important perfluorinated carboxylates and sulfonates, as well as per- and polyfluorinated precursor compounds including several sulfonamides, telomer acids, and alcohols were determined in individual herring gull (*Larus argentatus*) eggs collected (in 2007) from 15 colonies located at Canadian and some American sites across the Laurentian Great Lakes of North America. The pattern of perfluorosulfonates (PFSAs; C_6, C_8, C_{10} chain lengths) was dominated by PFOS (>90% of ΣPFSA concentration) regardless of collection location. Concentrations of ΣPFSA were significantly ($p < 0.03$) higher in eggs from Middle Island (western Lake Erie; 507 ± 47 ng/g ww), Toronto Harbour (484 ± 49 ng/g ww), and Strachan Island (486 ± 59 ng/g ww) (Lake Ontario) compared to eggs from colonies on Lakes Superior, Michigan, and Huron. Perfluorocarboxylic acids (PFCAs) ranging in chain length from C_8 to C_{15} were detected in the eggs, with PFUnA and PFTrA being the dominant compounds. PFOA and PFNA were more abundant in the ΣPFCA in eggs from Lake Superior and Michigan colonies, and PFUnA and longer chain PFCAs were more abundant in the ΣPFCA in eggs from Lake Erie and Ontario colonies. In contrast to ΣPFSA, the highest concentrations of ΣPFCA were found in eggs from Double Island, Lake Huron (113 ± 12 ng/g ww) followed by eggs from colonies on Lakes Erie and Ontario. Among the PFOS or PFCA precursor compounds assessed (6:2, 8:2, and 10:2 fluorotelomer alcohols and acids and PFOSA), none were detectable in eggs from any sampling location. The exception was PFOSA (average concentration <1 ng/g ww), which suggests that PFOS in the gulls and subsequently in their eggs may be due, in part, to biotransformation of PFOSA to PFOS in the gull and/or in their diet and food web. The accumulation of PFSA and PFCA from mainly aquatic dietary sources was suggested, and were highly lake- and/or colony-dependent, especially showing a northwest and southeast spatial trend and with higher concentrations in eggs from colonies in close proximity to highly urbanized and industrialized sites in Lakes Erie and Ontario.

Introduction

Various perfluorinated compounds and their polyfluorinated precursor compounds (PFCs) have been industrially manufactured for over 50 years with global production currently reported to be on the order of thousands of tons per year (*1, 2*). PFCs are used in various industrial and consumer products such as fluorinated polymers, surfactants, insecticides, and aqueous fire-fighting foams. The presence of PFCs that are terminal products with respect to degradation and shown to be bioaccumulative environmental contaminants has become a global issue. Specifically, perfluorinated sulfonates (PFSAs), carboxylic acids (PFCAs), and the perfluorooctanesulfonate (PFOS) precursor, perfluoro-1-octanesulfonamide (PFOSA), have been reported in tissues or eggs of various fish, birds, and mammals (*3, 4*).

Besides atmospheric transport of PFCAs and PFSAs (*5*), atmospheric transport of the more volatile PFC precursors is believed to be an additional source of PFOS and PFCAs. Degradation of fluorotelomer alcohols (FTOHs), fluorotelomer unsaturated acids (FTUCAs), and perfluorosulfonamides (FOSAs; especially PFOSA) has been found to be an additional precursor source of terminal PFOS and PFCAs in biota (*6, 7*). However, some of these compounds, i.e., FTUCAs, have only been found at low concentrations, specifically in fish (*8*). PFCAs and PFSAs have bioaccumulative properties and biomagnify in the aquatic food web, resulting in the highest exposure in top predator species (*9, 10*). Over the last decades, concentrations of PFOS and PFCAs have been increasing in higher trophic level wildlife species such as Norwegian herring gulls (*Larus argentatus*) (*11*), and in the only report from fish in the Great Lakes, in lake trout (*Salvelinus namaycush*) from Lake Ontario (*9, 12*).

Recent studies of spatial trends, mainly of PFOS and PFCAs, have shown differences in concentrations in environmental samples collected from urban versus more nonurbanized areas. For example, guillemot (*Uria aalge*) eggs collected in northwest Europe (*13*), skipjack tuna (*Katsuwonus pelamis*) collected off-shore and in open-ocean in eastern Asia (*14*), and bottlenose dolphins (*Tursuops truncatus*) collected in South Carolina (*15*) all showed higher concentrations of PFCs in the samples that were collected closer to industrialized/urban areas.

To our knowledge, there is only one study that has investigated the spatial trend of any PFC in biota from the Laurentian Great Lakes of North America. Furdui et al. (*8*) determined the spatial trend of PFSAs, PFCAs, and precursors (PFOSA and 8:2 and 10:2 FTUCAs) in lake trout collected in all five Great Lakes. Overall, the highest concentrations of ΣPFCA (C_8−C_{15}), ΣPFSA (C_6, C_8, C_{10}), and PFOSA were found in trout collected from Lake Erie, followed by those from Lakes Ontario and Huron. These areas represent some of the more populated and industrialized parts of the Great Lakes. The lowest concentrations of ΣPFCA and ΣPFSA were found in trout from Lake Superior and Lake Michigan; especially Lake Superior is more remote with respect to urban areas and PFC and precursor sources. The pattern of PFCA (C_8−C_{15}) in lake trout from Lake Michigan was dominated by PFOA when compared to fish from the other lakes. It was suggested that this was related to 8:2 FTUCA, which was detected in the trout and is a possible precursor of PFOA.

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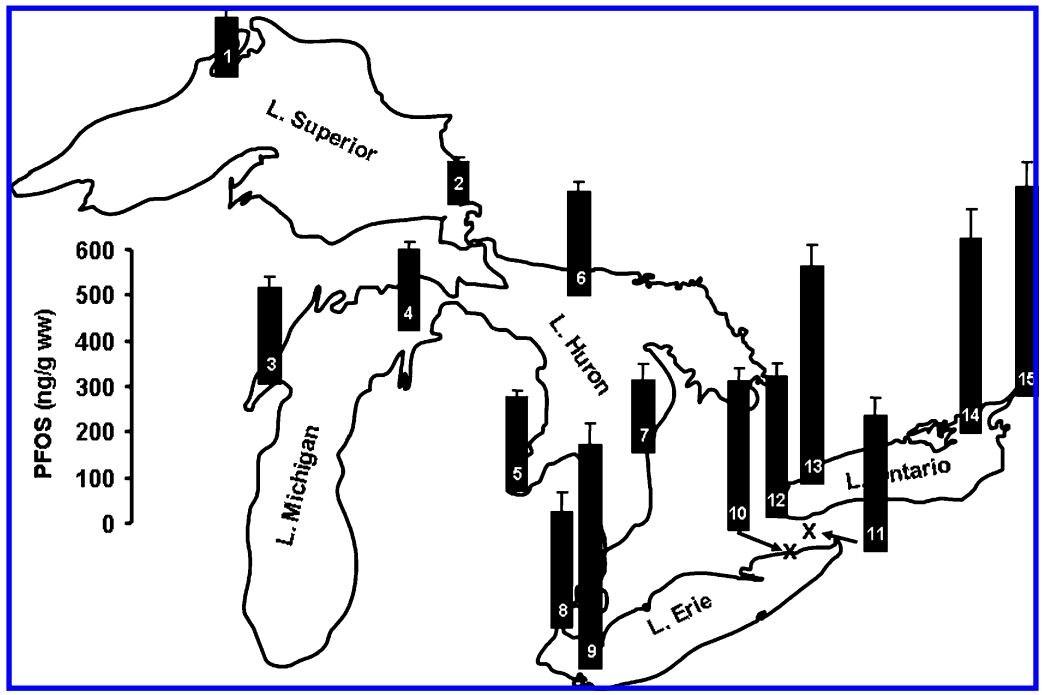

FIGURE 1. Arithmetic mean PFOS concentrations (ng/g ww ± SE) in individual herring gull eggs (n = 13) collected in 2007 from 15 colonies in the Laurentian Great Lakes: (1) Granite Island, (2) Agawa Rocks, (3) Big Sister Island, (4) Gull Island, (5) Channel-Shelter Island, (6) Double Island, (7) Chantry Island, (8) Fighting Island, (9) Middle Island, (10) Port Colborne, (11) Niagara River, (12) Hamilton Harbour, (13) Toronto Harbour, (14) Snake Island, and (15) Strachan Island.

The Canadian Wildlife Service (CWS) annually collects herring gull eggs from 15 colonies (as part of Environment Canada's Great Lakes Herring Gull Monitoring Program) that are used to monitor environmental contaminants such as PCBs and organochlorine (OC) pesticides (*16, 17*), and more recently, polybrominated diphenyl ether (PBDE) and other (brominated) flame retardants (*18, 19*) in the Great Lakes ecosystem. The herring gull, an avian top predator, is exposed to environmental contaminants via its diet which primarily consists of prey associated with aquatic food webs. Thus, it is an ideal species for biomonitoring of contaminants. The objectives of the present study were to characterize PFSAs, PFCAs, PFOSAs, FTUCAs, and FTOHs in herring gull eggs (collected in 2007) from the Laurentian Great Lakes, and examine the fate, sources, and trends of detected PFCs among eggs from 15 colonies spanning all 5 Great Lakes.

Experimental Section

Standards and Chemicals. The perfluorosulfonate standards (PFBS, PFHxS, PFOS, PFDS), perfluorocaboxylic acid standards (PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA), fluorotelomer unsaturated acids (6:2, 8:2, 10:2 FTUCA) and fluorotelomer alcohols (6:2, 8:2, 10:2 FTOH), perfluorosulfonamides (PFOSA, N-Me-FOSA), and all internal standards (see Supporting Information (SI) Table S1 (all chemical structures listed as well)) were obtained from Wellington Laboratories (Guelph, ON, Canada). All solvents used were HPLC grade and purchased from Fisher Scientific (Ottawa, Canada).

Sample Preparation. Individual herring gull eggs were collected in late April to early May 2007 at fifteen colonies in the Laurentian Great Lakes (Figure 1) (*16*). For each site, n = 13 individual eggs were homogenized and stored at −40 °C at Environment Canada's National Wildlife Specimen Bank (EC-NWSB) prior to chemical analysis. The extraction and cleanup was based on Taniyasu et al. (*20*) and Chu and Letcher (*21*). Briefly, approximately 1 g of homogenate was spiked with labeled internal standards and extracted with 10 mM KOH acetonitrile/water. The cleanup and fractionation of the overall PFC extract was performed using Waters Oasis WAX cartridges. The first fraction contained the neutral FTOHs and FOSAs, the second fraction contained the acidic PFSAs, PFCAs, and FTUCAs. More details are provided in the SI.

Instrumental Analysis. Separation of the target compounds in both fractions was carried out on a Waters 2695 HPLC coupled with a Waters Quattro Ultima triple quadrupole mass spectrometer (Waters, Milford, MA). Details on HPLC and LC-MS/MS parameters are provided in the SI. Quantification was performed using an internal standard approach. The calibration curve of PFTeA was used for PFPA quantification since PFPA standard was unavailable at the time of this study. Where no labeled standards were available, labeled ISs with the closest retention time were used. The recovery efficiency of all the internal standards was generally greater than 70% (Table S1). For every block of 10 samples, an NWRC in-house reference material of double-crested cormorant egg pool (based on eggs collected in 2003) was analyzed to assess reproducibility of the method. For ΣPFSA (C_6, C_8, C_{10}), good reproducibility was seen with a RSD of 11% (n = 23); analysis of ΣPFCA (C_8−C_{15}) showed a RSD of 9%. NWRC laboratories also participated in two PFC QA/QC exercises in 2007. For several PFCAs, PFSAs, and PFOSA, NIST SRM 1945 analysis results were within 10% of the interlab mean values as reported in the 2007 NIST/NOAA Interlaboratory Comparison Exercise Program for Organic Contaminants in Marine Mammal Tissues. Similar results were achieved on a ringed seal liver SRM as part of an interlab QA/QC exercise in the 2007 phase III exercise as part of the Northern Contaminants Program (NCP, Department of Indian and Northern Affairs Canada).

Data Analysis. Arithmetic mean concentrations were calculated only for samples with >60% detection of individual PFCs in the eggs for a given colony, and a Shapiro−Wilk's W test indicated a normal distribution for the majority of individual PFCAs and PFSAs. Differences in the pattern of

TABLE 1. Arithmetic Mean Concentrations of ΣPFSA and ΣPFCA (ng/g Wet Weight) in Individual Herring Gull Eggs Collected from 15 Colonies in the Great Lakes in 2007 (n = 13 Per Colony)

colony	lake/river	ΣPFSA[a] (±SE)	ΣPFCA[b] (±SE)	correlations of ΣPFCA versus ΣPFSA[c]		
				slope	r	p
Granite Is.	L. Superior	127 ± 20	46 ± 6	2.47	0.744	0.001
Agawa Rocks	L. Superior	91 ± 13	72 ± 5	0.89	0.335	0.22
Big Sister Is.	L. Michigan	212 ± 26	63 ± 9	2.52	0.834	<0.0001
Gull Is.	L. Michigan	178 ± 18	30 ± 5	2.86	0.845	<0.0001
Channel-Shelter Is.	L. Huron	227 ± 16	41 ± 4	3.06	0.808	0.0003
Double Is.	L. Huron	227 ± 24	113 ± 12	0.40	0.197	0.48
Chantry Is.	L. Huron	160 ± 37	32 ± 7	5.07	0.959	<0.0001
Fighting Is.	Detroit River	264 ± 47	58 ± 9	5.06	0.972	<0.0001
Middle Is.	L. Erie	507 ± 47	94 ± 9	5.30	0.959	<0.0001
Port Colborne	L. Erie	328 ± 32	51 ± 6	5.47	0.949	<0.0001
Niagara River	Niagara River	301 ± 40	64 ± 8	4.94	0.965	<0.0001
Hamilton Harbour	L. Ontario	319 ± 32	56 ± 8	3.43	0.832	<0.0001
Toronto Harbour	L. Ontario	484 ± 49	70 ± 6	6.71	0.849	<0.0001
Snake Is.	L. Ontario	427 ± 67	73 ± 12	5.32	0.985	<0.0001
Strachan Is.	St. Lawrence River	486 ± 59	66 ± 9	6.12	0.956	<0.0001

[a] ΣPFSA = PFHxS, PFOS, PFDS. [b] ΣPFCA = PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA, PFPA. [c] See Figure S3 for the correlative plots and linear regression lines for colonies in each of the lakes.

PFCAs and PFSAs in the eggs collected from the 15 colonies were investigated using principal components (PC) analysis using correlation matrices. PC analysis was conducted on percent composition data for the concentration of individual PFCAs (C_8−C_{15}) relative to the ΣPFCA concentrations, and individual PFSAs (C_6, C_8, C_{10}) relative to ΣPFSA concentrations. Concentrations that did not approximate the normal distribution using the Shapiro−Wilk's W test required $\log_{10}$-transformation. Thus, all PFCA and PFSA concentrations were $\log_{10}$-transformed to meet the assumptions of the statistical tests. For samples with PFC concentrations less than method limits of quantitation (< MLOQs), a randomly generated value was assigned between zero and MLOQ for statistical purposes. The differences in patterns and sum concentrations ($\log_{10}$ transformed) in the eggs from the 15 colonies were analyzed using a single factor analysis of variance (ANOVA), followed by a Tukey's *post hoc* test. A general linear model (GLM) was used to determine the significance and Pearson's coefficient of the ΣPFSA/ΣPFCA ratio. The statistical package utilized was Statistica (StatSoft, Tulsa, OK) and α was set at 0.05.

Results and Discussion

PFSAs and Spatial Distribution. The C_6, C_8, and C_{10} PFSAs were detected but dominated by PFOS (C_8), which comprised 91−99% of the ΣPFSA concentrations depending on the colony. This finding is consistent with a recent report for Lake Ontario fish including major aquatic prey fish of herring gulls such as alewife (*Alosa pseudoharengus*) and rainbow smelt (*Osmerus mordax*), where the PFSA pattern was also shown to be dominated by PFOS (>83%) (*8, 9*). A similar result was reported for the contribution of PFOS to ΣPFSA concentrations in the eggs and liver of glaucous gulls (*Larus hyperboreus*) from the Norwegian Arctic and herring gull eggs from northern Norway (>97%) (*11, 22*).

The proportion of PFOS in ΣPFSA in gull eggs collected at Channel-Shelter Island was significantly lower (p < 0.0001) when compared to the other colonies. The contribution of PFOS to ΣPFSA was significantly greater (p < 0.05) in eggs from Granite, Double, Chantry, and Snake Islands and Port Colborne compared to the Channel-Shelter, Fighting, and Strachan Islands and Hamilton Harbour. The proportion of PFHxS at the Toronto Harbour colony was significantly (p < 0.02) higher compared to Gull, Big Sister, Channel-Shelter, Middle Island, Port Colborne, and Niagara River colonies (Figure S1). Channel-Shelter Island had a significantly (p < 0.0001) higher proportion of PFDS relative to the other colonies. Degradation of precursors could be one of the factors influencing the observed PFSA patterns among the colonies (as discussed later).

A northwest to southeast spatial trend was observed for arithmetic mean ΣPFSA concentrations in eggs, where concentrations were lower for the more remote colonies on Lakes Superior, Michigan, and Huron compared to colonies on the populated Lakes Erie and Ontario, indicating that local sources play a key role in the spatial distribution of PFSAs in herring gull eggs (Table 1, Figure 1). Arithmetic mean concentrations of ΣPFSA for Middle Island, Toronto Harbour, and Strachan Island were significantly (p < 0.03) higher compared to colonies on Lakes Superior, Michigan, and Huron and also the Fighting Island colony in the Detroit River. Gauthier et al. recently reported that for ΣPBDE concentrations in herring gull egg pools (collected in 2006) from seven Great Lakes sites, the highest concentrations were from Gull Is. (northern Lake Michigan) (*18*). It was argued that this was likely due to higher PBDE exposures, at least from some eggs making up this pool, as a result of postbreeding migration to southern Lake Michigan, which is not known to freeze over in the winter thus giving gulls access to aquatic foods year-round (*23*). Southerly migration has been shown for gulls from colonies on Lakes Superior, Michigan, and northern Lake Huron (*23*); the ice coverage of these lakes was even greater during the 2006/07 winter compared to the 2005/06 winter (*24*), but this does not appear to be a substantial explanatory factor for PFOS or mean ΣPFSA concentrations in the 2007 gull eggs analyzed here. Mean concentrations at northern colonies were significantly lower compared to those in eggs from colonies on Lake Erie and Lake Ontario (Figure 1).

PFOSA in Relation to PFOS. PFOSA is a known precursor to PFOS and was measurable in all herring gull eggs except some from the Granite Is. colony (Table 2). On average, the concentrations of PFOSA were <1 ng/g ww, with the highest concentrations at Port Colborne and Hamilton Harbour, although only the Hamilton Harbour colony was significantly (p < 0.05) higher compared to Agawa Rocks, Gull Is., Channel-Shelter Is., Chantry Is., Fighting Is. and Strachan Is. The degradation of PFOSA to PFOS has been observed in in vitro studies using rainbow trout hepatocytes (*6*). Whether metabolic degradation of PFOSA to PFOS by the gulls could affect the observed spatial distribution of PFOS (Figure 1) is unclear. However, the presence of PFOSA in herring gull fish prey has been studied in Lake Ontario (*9*), where the PFOS to PFOSA

TABLE 2. Arithmetic Mean Concentrations of PFOSA (ng/g Wet Weight) and the PFOS to PFOSA Concentration Ratio in Individual Herring Gull Eggs Collected from 15 Colonies in the Great Lakes in 2007 (n = 13 Per Colony)

colony	PFOSA (±SE)	PFOS to PFOSA conc. ratio
Granite Is.	<0.005 − 0.14[a]	
Agawa Rocks	0.06 ± 0.01	1752 ± 229
Big Sister Is.	0.28 ± 0.05	954 ± 106
Gull Is.	0.10 ± 0.01	2063 ± 258
Channel-Shelter Is.	0.08 ± 0.02	5020 ± 1723
Double Is.	0.19 ± 0.03	1395 ± 207
Chantry Is.	0.03 ± 0.01	5035 ± 1223
Fighting Is.	0.12 ± 0.02	2664 ± 506
Middle Is.	0.21 ± 0.02	2624 ± 288
Port Colborne	0.43 ± 0.30	2923 ± 400
Niagara River	0.17 ± 0.03	3116 ± 827
Hamilton Harbour	0.54 ± 0.13	741 ± 85
Toronto Harbour	0.26 ± 0.03	2191 ± 323
Snake Is.	0.13 ± 0.02	3811 ± 620
Strachan Is.	0.09 ± 0.01	7664 ± 2677

[a] Detection of PFOSA was <60% in individual eggs, and thus the range of concentrations is given.

ratios in alewife and rainbow smelt were found to be at least 2 orders of magnitude lower compared to the ratio in the present herring gull eggs (Table 2). PFOS to PFOSA ratios in the eggs analyzed here are comparable to those in the livers of herring gulls (collected in 2004) (Gebbink et al. NWRC, Environment Canada, Ottawa, ON. Unpublished data, 2009) (Table 2). This suggested that there was no discrimination between PFOSA or PFOS transfer from the maternal gulls to their eggs, and that the egg is reflective of the residual accumulated and nonmetabolized PFOSA and PFOS in the adult female. A significant (r = 0.42; p < 0.0001) positive correlation between PFOSA and PFOS concentration in individual eggs was also found (Figure S2). Collectively, these findings suggest that biotransformation of accumulated PFOSA to PFOS occurs in the gulls, although further study is warranted.

The PFOS to PFOSA ratio in the eggs from Hamilton Harbour were significantly (p < 0.03) lower compared to the other colonies except at the Agawa Rocks, Big Sister Is., and Double Is. colonies (Table 2). The highest ratio was found at the Strachan Is. colony, which was significantly (p < 0.04) higher than the other colonies except the Channel-Shelter, Chantry, Middle, and Snake Is. colonies. To our knowledge, there are no available data on the spatial distribution of PFOSA (and thus PFOSA to PFOS ratios) in herring gull prey fish in the Great Lakes. Furdui et al. (*8*) showed interlake variation of the ratio of PFOS to PFOSA in lake trout, with ratios in fish from Lake Erie and Lake Ontario being higher compared to the other lakes; whether this could affect the spatial trend of PFOS was not mentioned. However, the ratios in lake trout were greater overall compared to those in alewife and smelt. The presence of PFOSA in herring gulls and possible subsequent biotransformation appears to be an additional source of PFOS.

PFCAs and Spatial Distribution. PFCAs of chain length C_8−C_{15} were measurable in the herring gull eggs, and PFUnA and PFTrA dominated ΣPFCA, at 26% and 28%, respectively for eggs from all 15 colonies (Tables 1 and S4). Studies investigating the PFCA pattern in birds in North America are limited to the northern fulmar (*Fulmarus glacialis*) and the thick-billed murre (*Uria lomvia*) from the Canadian Arctic where the C_9, C_{11}, and C_{12} PFCA dominated the pattern (*4, 25*). This is likely an indication of differences in PFCA exposure in the Arctic versus the Great Lakes. Norwegian herring gull and glaucous gull egg PFCA patterns were comparable to the present egg PFCA patterns suggesting similar exposure to PFCAs of various chain lengths (*11, 22*). The PFCA pattern in water birds from different locations in Asia were dominated by PFUnA, although the concentrations of PFCA > C_{13} were not reported (*26, 27*).

The PFCA pattern for various fish species from the Great Lakes, including prey species for the herring gulls such as alewife and rainbow smelt, have been reported (*8, 9*). Relative to alewife and rainbow smelt, the shorter chain length PFCAs, i.e., PFOA, PFNA, and PFDA, were less abundant in herring gull eggs. This suggests that pharmacokinetics of the C_8−C_{15} PFCA differ in these fish relative to herring gulls; and/or there is selective PFCA transfer from female gulls to their eggs. In fact, we have recently determined that, in comparing PFSAs and PFCAs in egg and liver for Lake Ontario gulls (collected in 2004), C_{11}−C_{15} PFCAs appear to be highly enriched in eggs relative to the liver (Gebbink et al. NWRC, Environment Canada, Ottawa, ON. Unpublished results, 2009). This was also observed in the common guillemot (*28*). This would suggest that the PFCA pattern in adult gulls is similar to that of their fish prey (i.e, the greater proportion of shorter chain length PFCAs). Furthermore, enrichment on longer chain PFCAs in the gull eggs may be related to the binding of selective PFCAs to proteins that are part of *in ovo* transport, which is consistent with findings that PFCAs are known to bind to fatty acid binding proteins (FABPs), lipoproteins, and albumin in the liver (*29, 30*).

On closer examination by PCA of the PFCA pattern in the herring gull eggs among colonies, there were small but significant differences. The proportion of PFOA and PFNA in the ΣPFCA from eggs collected from the colonies on Lake Superior, Lake Michigan, and Lake Huron were greater compared to the eggs collected on Lake Erie and Lake Ontario (Figure 2). The amount of PFOA in the eggs from Granite Is., Big Sister Is., Double Is., and Chantry Is. was significantly greater (p < 0.005) compared to the other colonies. PFNA was more abundant in the eggs collected on Granite Is., Agawa Rocks, and Double Is. (p < 0.02). For the longer chain length PFCAs, the amount of PFUnA in the eggs collected from Snake Is. and Strachan Is. was significantly higher (p < 0.03) when compared to the other colonies except for the Channel-Shelter Is. colony (Figure 2). For PFDoA and PFTeA, significantly higher (p < 0.04) contributions to the ΣPFCA concentration were found at Fighting Is., and Hamilton and Toronto Harbours relative to the other colonies, with the exception of Big Sister and Middle Is. for PFDoA. At Chantry Is. the amount of PFTrA was significantly higher (p < 0.001) compared to the other 14 colonies among the lakes. These differences in the PFCA patterns could be related to several factors, e.g., differences in the diet among the colonies, accumulation of precursors, and subsequent biotransformation. The greater abundance of the shorter chain length PFCAs in the northern lakes and the greater abundance of the longer chain PFCAs around Lake Erie and Ontario has also been reported in the spatial trend study of PFCAs in lake trout (*8*). For example, high amounts of PFOA were detected in lake trout from Lake Michigan, which the authors linked to the presence of the 8:2 FTUCA, a precursor to PFOA. Thus, differences in the observed PFCA pattern in herring gull eggs could be related to the degradation of more volatile precursors; although the FTUCAs and FTOHs were below the detection limit in the eggs from all the colonies. Laying female gulls may have not been exposed to accumulated precursor FTUCAs and FTOHs and these may have been rapidly metabolized rapidly by the gulls. If accumulated, rapid metabolism of FTUCA and FTOH would have had to occur (in the liver). In livers of herring gull collected from Lake Ontario in 2004, we failed to detect the same FTUCAs (LOD ~0.01 ng/g) and FTOHs (LOD ~0.5 ng/g) (Gebbink et al.

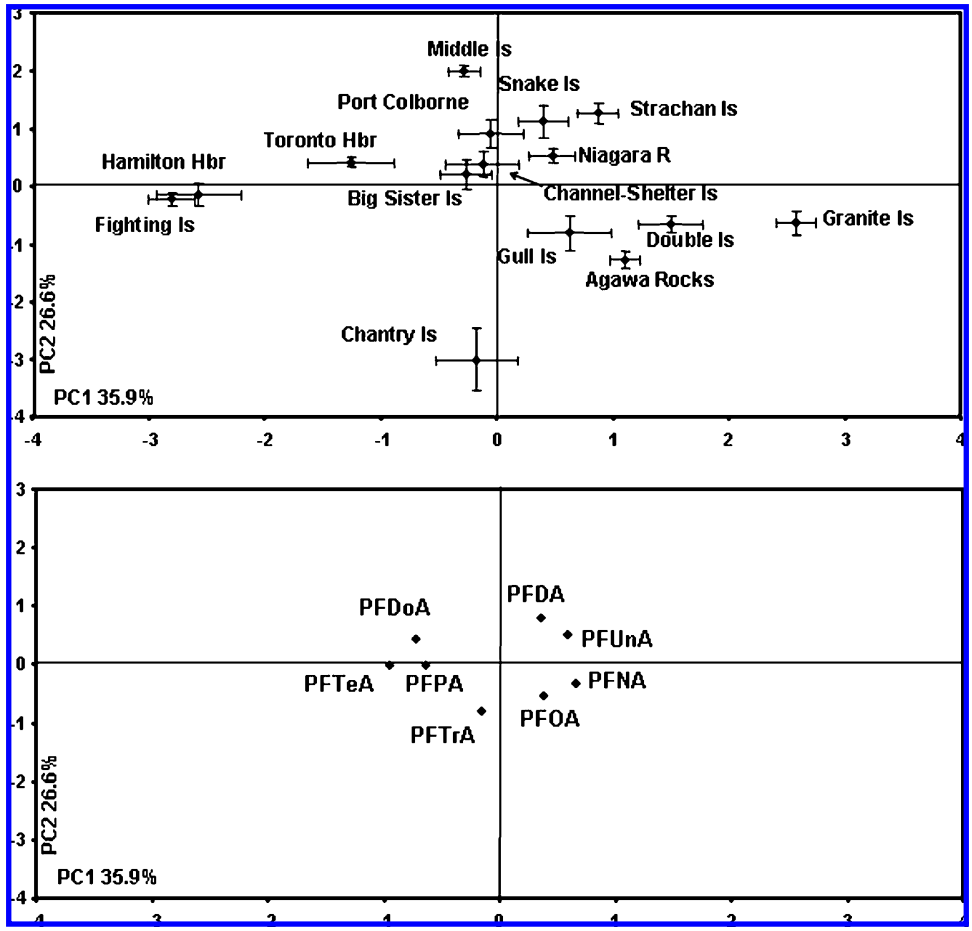

FIGURE 2. Proportions of C_8−C_{15} to ΣPFCA concentrations plotted using the first two principal components (PCs), PC1 and PC2. Mean (±SE) factor scores (top biplot) are shown for the 15 colonies. The percent variability explained by PC1 and PC2 is provided.

NWRC, Environment Canada, Ottawa, ON. Unpublished work, 2009).

The highest ΣPFCA concentrations were found in eggs from the Double Is. colony followed by the Middle Is. colony (Table 1). Double Is. had significantly higher ($p < 0.05$) concentrations in the eggs compared to the Granite Is., Big Sister Is., Gull Is., Channel-Shelter Is., Chantry Is., Fighting Is., Port Colborne, and the Hamilton Harbour colonies. The highest concentrations found at colonies on Lake Huron (Double Is.) and Lake Erie (Middle Is.) are consistent with results reported for lake trout by Furdui et al. (*8*), where they reported that the highest ΣPFCA concentrations were found in fish from Lake Erie followed by Lake Huron. As discussed for PFSAs, postbreeding migration of herring gulls from Double Is. to Lake Ontario (*23*) may affect exposure to environmental contaminants. Alternatively, there may be a unique (e.g., terrestrial) local source that could explain the high concentrations at Double Is. This explanation appears to be plausible since gull egg pools from Double Is. have been reported to have among the lowest concentrations of PCBs, organochlorine pesticides, and PBDEs compared to other colony sites (*17, 31*). Similarly, we found that the arithmetic mean ΣPFSA concentration for eggs from Double Is. was not among the most highly contaminated colonies (Figure 1, Table 1).

ΣPFSA versus ΣPFCA Accumulation. The concentrations of ΣPFCA and ΣPFSA were positively and significantly correlated for individual eggs from each of the 15 colonies, with the exception of Agawa Rocks and Double Is. (Table 1, Figure S3). However, the slopes of the linear regressions varied considerably, which suggested covariant but different dietary sources (aquatic and/or terrestrial) of PFCAs and PFSAs depending on the colony. The slopes of these linear relationships of ΣPFCA and ΣPFSA concentration were compared to those previously reported for lake trout for each lake (*8*), and in the case of Lake Ontario also for alewife and rainbow smelt (*9*). Slopes describing the relationship between concentrations of ΣPFCA and ΣPFSA are similar for lake trout and herring gulls from Lake Michigan, and to a lesser degree, Lake Superior (Figure S3). Slopes were also similar between lake trout and gulls from Channel-Shelter Island on Lake Huron but less so between trout and gulls at Chantry Island (Figure S3). Even more different were the slopes for lake trout and herring gull eggs from the Double Is. colony on Lake Huron (Figure S3). As has been discussed, this further suggests the contrasting sources for PFSAs and PFCAs for Double Is., which was reflected in lack of a statistically significant relationship between ΣPFSAs and ΣPFCAs ($p = 0.40$) unlike all other colonies except Agawa Rocks (Table 1). This may be a function of contrasting terrestrial and aquatic PFCA and PFSA dietary exposure among the Double Is. birds. For all the gull colonies on Lakes Erie and Ontario, the slope of the linear relationships between ΣPFCA and ΣPFSA concentrations was similar to lake trout and/or alewife and rainbow smelt (*8, 9*) (Table 1, Figure S3). This suggests that the source of both PFCAs and PFSAs is mainly aquatic food webs.

Sources of PFC Exposure in Herring Gulls. The differences observed in the patterns of PFCAs, PFSAs, and PFOSA and sum concentrations among the breeding colonies are most likely due to differences in PFC patterns and concentrations in the gull diet. The gull diet consists mainly of prey fish, although a decline in trophic position in recent years indicates an increasing reliance on terrestrial food sources (*32*). For other POPs, i.e. PCBs, a decline in egg concentrations was linked to changes in trophic position. Greater proportions

of terrestrial food in the gull diet result in lower exposure to PCBs highlighting the importance of aquatic food as the predominant source of these compounds (*33*). Whether this is the case for PFCAs, PFSAs, and PFOSA cannot be completely ascertained here. However, dietary source inputs are possible using tracers such as stable carbon and nitrogen isotope ratios and fatty acid profiles. Hebert et al. (*32*) recently showed that there is a difference in trophic position of the gulls from the 15 different colonies in the Great Lakes basin based on stable carbon and nitrogen isotope data on egg pools from 2005. To illustrate the importance of diet in regulating concentrations of PFCs in gull eggs, we examined individual herring eggs ($n = 15$) collected (in 2001−2002) from Strachan Is. (St. Lawrence River). Trophic position of individual female gulls was inferred from stable nitrogen isotope values in their eggs. ΣPFCA and ΣPFSA concentrations in eggs were significantly ($p < 0.02$ for ΣPFCA and $p < 0.009$ for ΣPFSA) correlated with trophic position (Figure S4). A similar analysis conducted using eggs ($n = 17$) collected in 2005 from Scotch Bonnet Island (Lake Ontario) found a similar positive but nonsignificant relationship between trophic position and concentrations of ΣPFCA ($r = 0.408$; $p = 0.10$) and ΣPFSA ($r = 0.472$; $p = 0.06$) (Gebbink et al. NWRC, Environment Canada, Ottawa, ON. Unpublished data, 2009). These data highlight the importance of diet as a major factor regulating the exposure of PFCs and further suggest that aquatic prey may be the main source of accumulation of PFCAs and PFSAs to herring gulls, and that any terrestrial inputs to the gull diet are not significant. In contrast, the observed spatial and temporal differences in ΣPBDEs in pools of gull egg from several (of the same) sites were attributed to differences or changes in PBDE exposure through the herring gull food web, which includes terrestrial (including human garbage, but also terrestrial invertebrates, small mammals, and passerine birds) as well as aquatic inputs (*34*). Hebert et al. (*35*) showed that the composition of the herring gull diet varies among the Great Lakes, including terrestrial foods.

Using the PFC data of the alewife and smelt from Martin et al. (*9*) as representative of the aquatic component of the gull's diet, biomagnification factors (BMFs) were calculated for the herring gulls from Strachan Is. (collected in 2001−2002). Biomagnification of PFSAs and PFCAs was suggested as the BMFs of ΣPFSA were estimated at 9.5 and 2.6 based on the alewife and smelt as prey fish. The ΣPFCA BMF we estimated at 6.0 and 1.8 using these prey fish. Regardless of the diet, it is unlikely that there are gull differences in PFC uptake and selectivity of *in ovo* transport during egg development. PFCAs and PFSAs are not lipophilic, but rather are protein-associated, and any PFC−protein complex formation and transfer to eggs would be PFC selective rather than bird selective.

The present findings suggest mainly aquatic sources of PFSA and PFCA accumulated in gulls and with subsequent transport to their eggs, either uptake from an aquatic (fish) diet and/or via metabolism of precursors. These dietary sources of accumulation were highly colony dependent, especially showing a northwest and southeast spatial trend and with higher concentrations in eggs from colonies in closer proximity to urban areas. To our knowledge, this is the first report on PFCAs and PFSAs and spatial trends in Great Lakes wildlife other than fish. The exposure and effects ramifications to herring gulls and perhaps other fish-easting bird species in the Great Lakes are unclear. There is extremely limited information on the effects of individual C_8−C_{15} PFCAs and C_4−C_8 PFSAs or mixtures in any bird species. In a rare recent example, chicken eggs injected with PFOS showed a decline in hatchability and decreased embryo pippability at PFOS concentrations in the μg/g range (measured in the liver) (*36, 37*). O'Brien et al. (*37*) showed that declines in embryo pippability of chicken eggs injected with PFOS were at concentrations comparable to what we presently report in the eggs of herring gulls from the highest contaminated colonies, i.e., in the μg/g ww concentration range.

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Note Added after ASAP Publication

This article was released ASAP on August 28, 2009, with a minor error in the text. The correct version was posted September 2, 2009.

Supporting Information Available

Details on chemical structures, internal standards used, % recovery, mobile phase gradients, and C_8−C_{15} PFCAs concentrations (Tables S1−S4); PCA of the C_6, C_8, C_{10} fraction of ΣPFSA, PFOS−PFOSA relationship, plots of ΣPFSA to ΣPFCA ratio per colony, ΣPFSA and ΣPFCA versus trophic position (Figures S1−S4). This material is available free of change via the Internet at http://pubs.acs.org.

Literature Cited

(1) Key, B. D.; Howell, R. D.; Criddle, C. S. Fluorinated organics in the biosphere. *Environ. Sci. Technol.* **1997**, *31*, 2445–2454.
(2) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40*, 32–44.
(3) Giesy, J. P.; Kannan, K. Global distribution of perfluorooctane sulfonate in wildlife. *Environ. Sci. Technol.* **2001**, *35*, 1339–1342.
(4) Houde, M.; Martin, J. W.; Letcher, R. J.; Solomon, K. R.; Muir, D. C. G. Biological monitoring of polyfluoroalkyl substances: A review. *Environ. Sci. Technol.* **2006**, *40*, 3463–3473.
(5) Barber, J. L.; Berger, U.; Chaemfa, C.; Huber, S.; Jahnke, A.; Temme, C.; Jones, K. C. Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. *J. Environ. Monit.* **2007**, *9*, 530–541.
(6) Tomy, G. T.; Tittlemier, S. A.; Palace, V. P.; Budakowski, W. R.; Braekevelt, E.; Brinkworth, L.; Friesen, K. Biotransformation of *N*-ethyl perfluorooctanesulfonamide by rainbow trout (*Onchorhynchus mykiss*) liver microsomes. *Environ. Sci. Technol.* **2004**, *38*, 758–762.
(7) Martin, J. W.; Mabury, S. A.; O'Brien, P. J. Metabolic products and pathways of fluorotelomer alcohols in isolated rat hepatocytes. *Chem. Biol. Interact.* **2005**, *155*, 165–180.
(8) Furdui, V. I.; Stock, N. L.; Ellis, D. A.; Butt, C. M.; Whittle, D. M.; Crozier, P. W.; Reiner, E. J.; Muir, D. C. G.; Mabury, S. A. Spatial distribution of perfluoroalkyl contaminants in lake trout from the Great Lakes. *Environ. Sci. Technol.* **2007**, *41*, 1554–1559.
(9) Martin, J. W.; Whittle, D. M.; Muir, D. C. G.; Mabury, S. A. Perfluoroalkyl contaminants in a food web from lake Ontario. *Environ. Sci. Technol.* **2004**, *38*, 5379–5385.
(10) Haukås, M.; Berger, U.; Hop, H.; Gulliksen, B.; Gabrielsen, G. W. Bioaccumulation of per- and polyfluorinated alkyl substances (PFAS) in selected species from the Barents Sea food web. *Environ. Pollut.* **2007**, *148*, 360–371.
(11) Verreault, J.; Berger, U.; Gabrielsen, G. W. Trends of perfluorinated alkyl substances in herring gull eggs from two coastal colonies in nothern Norway: 1983−2003. *Environ. Sci. Technol.* **2007**, *41*, 6671–6677.
(12) Furdui, V. I.; Helm, P. A.; Crozier, P. W.; Lucaciu, C.; Reiner, E. J.; Marvin, C. H.; Whittle, D. M.; Mabury, S. A.; Tomy, G. T. Temporal trends of perfluoroalkyl compounds with isomer analysis in lake trout from Lake Ontario (1979−2004). *Environ. Sci. Technol.* **2008**, *42*, 4739–4744.
(13) Löfstrand, K.; Jörundsdóttir, H.; Tomy, G. T.; Svavarsson, J.; Weihe, P.; Nygård, T.; Bergman, Å. Spatial trends of polyfluorinated compounds in guillemot (*Uria aalge*) eggs from North-Western Europe. *Chemosphere* **2009**, *72*, 1475–1480.
(14) Hart, K.; Kannan, K.; Tao, L.; Takahashi, S.; Tanabe, S. Skipjack tuna as a bioindicator of contamination by perfluorinated

compounds in the oceans. *Sci. Total Environ.* **2008**, *403*, 215–221.
(15) Adams, J.; Houde, M.; Muir, D. C. G.; Speakman, T.; Bossart, G. D.; Fair, P. A. Land use and the spatial distribution of perfluoroalkyl compounds as measured in the plasma of bottlenose dolphins (*Tursiops truncatus*). *Mar. Environ. Res.* **2008**, *66*, 430–437.
(16) Hebert, C. E.; Norstrom, R. J.; Weseloh, D. V. A quarter century of environmental surveillance: The Canadian Wildlife Service's Great Lakes Herring Gull Monitoring Program. *Environ. Rev.* **1999**, *7*, 147–166.
(17) Weseloh, D. V. C.; Pekarik, C.; De Solla, S. R. Spatial patterns and rankings of contaminant concentrations in Herring Gull eggs from 15 sites in the Great Lakes and connecting channels, 1998−2002. *Environ. Monit. Assess.* **2006**, *113*, 265–284.
(18) Gauthier, L. T.; Hebert, C. E.; Weseloh, D. V.; Letcher, R. J. Dramatic changes in the temporal trends of polybrominated diphenyl ethers (PBDEs) in herring gull eggs from the Laurentian Great Lakes: 1982−2006. *Environ. Sci. Technol.* **2008**, *42*, 1524–1530.
(19) Gauthier, L. T.; Potter, D.; Hebert, C. E.; Letcher, R. J. Temporal trends and spatial distribution of non-polybrominated diphenyl ether flame retardants in the eggs of colonial populations of Great Lakes herring gulls. *Environ. Sci. Technol.* **2009**, *43*, 312–317.
(20) Taniyasu, S.; Kannan, K.; So, M. K.; Gulkowska, A.; Sinclair, E.; Okazawa, T.; Yamashita, N. Analysis of fluorotelomer alcohols, fluorotelorner acids, and short- and long-chain perfluorinated acids in water and biota. *J. Chromatogr., A* **2005**, *1093*, 89–97.
(21) Chu, S. G.; Letcher, R. J. Analysis of fluorotelomer alcohols and perfluorinated sulfonamides in biotic samples by liquid chromatography-atmospheric pressure photoionization mass spectrometry. *J. Chromatogr., A* **2008**, *1215*, 92–99.
(22) Verreault, J.; Houde, M.; Gabrielsen, G. W.; Berger, U.; Haukås, M.; Letcher, R. J.; Muir, D. C. G. Perfluorinated alkyl substances in plasma, liver, brain, and eggs of glaucous gulls (*Larus hyperboreus*) from the Norwegian Arctic. *Environ. Sci. Technol.* **2005**, *39*, 7439–7445.
(23) Hebert, C. E. Winter severity affects migration and contaminant accumulation in northern Great Lakes Herring Gulls. *Ecol. Appl.* **1998**, *8*, 669–679.
(24) Canadian Ice Service, Environment Canada. *Latest, Past & Future Ice Conditions -Great Lakes*;http://ice-glaces.ec.gc.ca/App/WsvPageDsp.cfm?Lang=eng&lnid=37&ScndLvl=no&ID=11890.
(25) Butt, C. M.; Stock, N. L.; Mabury, S. A.; Muir, D. C. G.; Braune, B. M. Spatial and temporal trends of perfluoroalkyl substances in ringed seals and seabirds (Northern flumar and thick-billed murre) from the Canadian Arctic. Presented at FLUOROS, Toronto, ON, Aug. 19−20, 2005.
(26) Yoo, H.; Kannan, K.; Kim, S. K.; Lee, K. T.; Newsted, J. L.; Giesy, J. P. Perfluoroalkyl acids in the egg yolk of birds from Lake Shihwa, Korea. *Environ. Sci. Technol.* **2008**, *42*, 5821–5827.
(27) Wang, Y.; Yeung, L. W. Y.; Taniyasu, S.; Yamashita, N.; Lam, J. C. W.; Lam, P. K. S. Perfluorooctane sulfonate and other fluorochemicals in waterbird eggs from south China. *Environ. Sci. Technol.* **2008**, *42*, 8146–8151.
(28) Holmström, K. E.; Berger, U. Tissue distribution of perfluorinated surfactants in common guillemot (*Uria aalge*) from the Baltic Sea. *Environ. Sci. Technol.* **2008**, *42*, 5879–5884.
(29) Jones, P. D.; Hu, W.; De Coen, W.; Newsted, J. L.; Giesy, J. P. Binding of perfluorinated fatty acids to serum proteins. *Environ. Toxicol. Chem.* **2003**, *22*, 2639–2649.
(30) Luebker, D. J.; Hansen, K. J.; Bass, N. M.; Butenhoff, J. L.; Seacat, A. M. Interactions of flurochemicals with rat liver fatty acid-binding protein. *Toxicology* **2002**, *176*, 175–185.
(31) Norstrom, R. J.; Simon, M.; Moisey, J.; Wakeford, B.; Weseloh, D. V. C. Geographical distribution (2000) and temporal trends (1981−2000) of brominated diphenyl ethers in Great Lakes herring gull eggs. *Environ. Sci. Technol.* **2002**, *36*, 4783–4789.
(32) Hebert, C. E.; Weseloh, D. V. C.; Idrissi, A.; Arts, M. T.; O'Gorman, R.; Gorman, O. T.; Locke, B.; Madenjian, C. P.; Roseman, E. F. Restoring piscivorous fish populations in the Laurentian Great Lakes causes seabird dietary change. *Ecology* **2008**, *89*, 891–897.
(33) Hebert, C. E.; Shutt, J. L.; Norstrom, R. J. Dietary changes cause temporal fluctuations in polychlorinated biphenyl levels in herring gull eggs from Lake Ontario. *Environ. Sci. Technol.* **1997**, *31*, 1012–1017.
(34) Hebert, C. E.; Weseloh, D. V. C.; Gauthier, L. T.; Arts, M. T.; Letcher, R. J. Biochemical tracers reveal intra-specific differences in the food webs utilized by individual seabirds. *Oecologia* **2009**, *160*, 15–23.
(35) Hebert, C. E.; Arts, M. T.; Weseloh, D. V. C. Ecological tracers can quantify food web structure and change. *Environ. Sci. Technol.* **2006**, *40*, 5618–5623.
(36) Molina, E. D.; Balander, R.; Fitzgerald, S. D.; Giesy, J. P.; Kannan, K.; Mitchell, R.; Bursian, S. J. Effects of air cell injection of perfluorooctane sulfonate before incubation on development of the white leghorn chicken (*Gallus domesticus*) embryo. *Environ. Toxicol. Chem.* **2006**, *25*, 227–232.
(37) O'Brien, J. M.; Carew, A. C.; Chu, S. G.; Letcher, R. J.; Kennedy, S. W. Perfluorooctane sulfonate (PFOS) toxicity in domestic chicken (*Gallus domesticus*) embryos in the absence of effects on peroxisome proliferator activated receptor alpha (PPARα)-regulated genes. *Comp. Biochem. Physiol. C* **2009**, *149*, 524–530.

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