Perfluorinated Alkyl Substances in Eggs of Herring Gulls from Northern Norway: Spatial and Temporal Trends

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1. Preface

The principal objective of the present study was to investigate the accumulation profiles and temporal trends of perfluorinated alkyl substances in eggs of herring gulls (*Larus argentatus*) collected from two major colonies along the coast of Northern Norway in 1983, 1993 and 2003. Companion studies from our research group have recently reported the spatial and temporal trends of brominated flame retardants, cyclododeca-1,5,9-triene and mercury in the same herring gull egg samples (Knudsen et al., 2005: http://www.sft.no/publikasjoner/overvaking/2134/ta2134.pdf; Knudsen et al., 2006: http://www.sft.no/publikasjoner/overvaking/2175/ta2175.pdf).

This project involved the collaboration between the Norwegian Polar Institute and the Stockholm University (Department of Applied Environmental Science (ITM)). Financial support was provided by the Norwegian Pollution Control Authority (SFT) and the Ecotoxicology Programme of the Norwegian Polar Institute.

Tromsø, November 2006

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Cover page photo
Herring gulls (Rob Barrett, Tromsø University Museum)

2. Table of Contents

3. Sammendrag

Formålet med dette studiet var å kartlegge nivåer, sammensetning av forbindelser og tidstrend (1983, 1993 og 2003) av perfluoralkylstoffer (PFAS) i egg (n = 30) av gråmåker (*Larus argentatus*) fra to hekkekolonier i Nord-Norge. Disse koloniene ble valgt basert på den sørlige og nordlige geografiske plassering av gråmåker som hekker i Nord-Norge. Perfluoroktanylsulfonat (PFOS) var den av PFAS som ble funnet i høyest konsentrasjon i eggprøvene. Blant de andre perfluorosulfonater (PFSs) analysert ble ikke perfluorobutansulfonat (PFBS) påvist i noen av eggene. Perfluoroheksansulfonat (PFHxS) og perfluorodekansulfonat (PFDcS) ble funnet i svært lave konsentrasjoner. De var flere ganger lavere enn PFOS. Perfluorokarboksylater (PFCAs) med 8 til 15 karbon (C)-atomer ble analysert i egg av gråmåker. Akkumulasjonsmønsteret av PFCAs var karakterisert av en høy andel av oddetall og lang karbonkjedete forbindelser. Blant PFCAs var perfluoroundekanoate (PFUnA) (11 C) og perfluorotridekanoate (PFTriA) (13 C) de mest dominerende. 6:2 fluorotelomersulfonate (6:2 FTS) ble ikke funnet i noen av prøvene. Perfluorooktanesulfonamide (PFOSA) ble funnet i meget lave nivåer. Konsentrasjoner av PFAS-forbindelsene i egg av gråmåker var ikke signifikant forskjellige i de to hekkekoloniene når innsamlingsår (1983, 1993 og 2003) ble analysert i en felles gruppe. Unntaket var perfluorooktanoate (PFOA) (8 C-PFCA) som var høyest i den sørligste kolonien. Imidlertid var sammensetningen (angitt i %) av individuell PFCA forbindelser (8 til 15 C) i sum PFCA (ΣPFCA) generelt forskjellig mellom koloniene når innsamlingsår ble analysert hvert for seg. I begge koloniene ble PFOS nivåer i egg nær doblet mellom 1983 og 1993, etterfulgt av et stabilt nivå frem til 2003. Til sammenlikning var økning i ΣPFCA konsentrasjoner mellom 1983 og 1993 sammenlignbar med PFOS. Den var etterfulgt av en svak, men ikke signifikant økning av nivåer, mellom 1993 og 2003. PFAS konsentrasjoner i egg fra gråmåker fra Nord-Norge indikerer at disse forbindelsene er bioakkumulerende hos denne arten. PFAS akkumulert i egg av gråmåker må sees på som en del av en sammensatt miljøgift ”cocktail” med potensielt toksisitet i voksne og unge individer av sjøfugler.

4. Summary

The present study reports on concentrations, patterns and temporal trends (1983, 1993 and 2003) of perfluorinated alkyl substances (PFAS) in eggs (n = 30) of herring gulls (*Larus argentatus*) from two colonies in Northern Norway. The colonies selected encompass the southern and northern distribution range of herring gulls breeding in Northern Norway. Perfluorooctane sulfonate (PFOS) was the predominant PFAS in all egg samples. Among the other perfluorosulfonates (PFSs) monitored, perfluorobutane sulfonate (PFBS) was not detected in any eggs, while perfluorohexane sulfonate (PFHxS) and perfluorodecane sulfonate (PFDcS) were found at concentrations several orders of magnitude lower than PFOS. The perfluorocarboxylates (PFCAs) with 8 to 15 carbon (C) atoms were quantified in herring gull eggs. The accumulation profiles of PFCAs were characterized by consistently high proportions of odd and long carbon-chain length compounds, in which perfluoroundecanoate (PFUnA) (11 C) and perfluorotridecanoate (PFTriA) (13 C) dominated. The 6:2 fluorotelomer sulfonate (6:2 FTS) was not detected in any samples and perfluorooctane sulfonamide (PFOSA) was found at very low concentrations. Concentrations of the present PFAS compounds analyzed in herring gull eggs did not differ between the two colonies when the three sampling years were combined, with the exception of perfluorooctanoate (PFOA) (8 C-PFCA) that was highest in the southernmost colony. Nonetheless, the percentage composition of individual PFCAs (8 to 15 C) to the sum PFCA (ΣPFCA) generally differed between the colonies when sampling years were investigated separately. In both colonies PFOS concentrations in eggs showed a nearly 2-fold increase from 1983 to 1993, followed by a leveling off up to 2003. By comparison, the ΣPFCA concentrations also showed a marked and comparable increase during 1983–1993, but a weak although non-significant increase between 1993 and 2003. Current PFAS concentrations suggest bioaccumulation potential in herring gull eggs from Northern Norway. The accumulated PFAS in herring gulls and their eggs need to be assessed as part of a broad organohalogen contaminant cocktail with potential for mediating biological processes in this species.

5. Background

The perfluorinated alkyl substances (PFAS) are used in a multitude of industrial and commercial products such as various stain repellents, fire-fighting foams and impregnation agents for textiles (see also: http://www.sft.no/tema____3338.aspx). Due to their unique chemical and biological stability with respect to abiotic and biotic degradation, PFAS exhibit a high propensity for persistence and bioaccumulation in humans and animals. The worldwide surveys of PFAS have ascertained their ubiquitous presence in human populations and wildlife species from urban and remote locations. The wildlife species studied include a growing number of mammals and seabirds occupying high trophic positions in the marine food web. The predominant PFAS reported has been consistently the perfluorooctane sulfonate (PFOS). Perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonamide (PFOSA) and 8 to 15 carbon-chain length perfluorocarboxylates (PFCAs) also have been reported.

The pattern of PFAS contamination in wildlife has been shown to vary greatly among species and geographical locations suggesting multiple emission sources (Houde et al., 2006). Temporal trend studies using archived seabird (egg) and marine mammal samples have indicated that exposure to PFAS has increased significantly over the last decades (e.g., Bossi et al., 2005; Holmstrom et al., 2005; Smithwick et al., 2006). In bird laboratory studies, chronic exposure to PFOS and analogous PFAS (e.g., PFOA) was shown to cause subtle toxicological and reproductive endpoints in northern bobwhite quails (*Colinus virginianus*) and mallard ducks (*Anas platyrhynchos*) (Newsted et al., 2005, 2006), adverse effects on alanine aminotransferase, cholesterol, triglyceride and relative liver weight in great (*Parus major*) and blue tit nestlings (*Parus caeruleus*) (Hoff et al., 2005), and reduced hatchability and pathological changes in the liver of white leghorn chickens (*Gallus domesticus*) (Molina et al., 2006).

In the present study, we investigated the concentrations and patterns of a suite of PFAS in eggs of herring gulls (*Larus argentatus*) from two geographically-isolated colonies along the coast of Northern Norway. These colonies encompass the southern and northern distribution range of herring gulls breeding in Northern Norway. Further, temporal variations of PFAS concentrations were examined for herring gull eggs collected during 1983, 1993 and 2003. The herring gull is a widespread seabird species in Norway and exhibits a typical scavenger-predator diet composed of mainly fish, crustaceans, seabird chicks and eggs (Anker-Nilssen et al., 2000). In the context of contaminant monitoring, the herring gull has been identified as key sentinel species of freshwater basin contamination in densely populated and industrialized regions such as in the North American Great-Lakes (Hebert et al., 1999).

6. Materials and Methods

6.1. Sampling

A total of 30 freshly-laid eggs of herring gulls were collected randomly in 1983, 1993 and 2003 from major breeding colonies along the coast of Northern Norway (Hornøya, Røst and Hekkingen). Hornøya is located in the northernmost part of Northern Norway, whereas Røst and Hekkingen (both colonies hereafter referred to as Røst only) are situated in the southern part (FIGURE 1). The eggs were wrapped in aluminium foil and stored frozen until laboratory analyses.

FIGURE 1. Map of Northern Norway showing the sampling locations (Hornøya, Røst and Hekkingen) of herring gull eggs in 1983, 1993 and 2003.

6.2. Chemical Analyses

Chemical analyses of herring gull egg samples were carried out in the laboratory of Dr. U. Berger (Department of Applied Environmental Science (ITM), Stockholm University (Stockholm, Sweden) in August-September 2006.

6.2.1. Sample Preparation

A 1 g aliquot of homogenized whole egg samples was transferred to a PP-centrifuge tube, and spiked with the internal standard $^{13}C_4$-perfluorooctanoate ($^{13}C_4$-PFOA). Egg homogenate aliquots were extracted twice with 5 mL of acetonitrile in an ultrasonic bath. Following centrifugation, the supernatant extract was removed and the combined acetonitrile phases were concentrated to 1 mL under a stream of nitrogen. The concentrated extract underwent dispersive clean-up on graphitized carbon and acetic acid. Approximately 0.5 mL of the cleaned-up extract was added 0.5 mL of aqueous ammonium acetate. Precipitation occurred and the extract was centrifuged before the clear supernatant was transferred to an autoinjector vial for instrumental analysis. Finally, the volume standard 7H-perfluoroheptanoate was added.

6.2.2. Instrumental Analysis

Aliquots of the final extracts were injected automatically on a high performance liquid chromatography system coupled to high resolution mass spectrometry (HPLC-HRMS for sulfonates (PFSs)) or tandem mass spectrometry (HPLC-MS-MS for carboxylates (PFCAs)). The instrumental setup for the HPLC-HRMS was: Acquity Ultra Performance LC (Waters) and Q-ToF Premier (Micromass). For HPLC-MS-MS, an Alliance 2695 pump (Waters) was coupled to a Quattro II triple quadrupole MS (Micromass). Compound separation for the PFSs was achieved on an Ace 3 C18 column (Advanced Chromatography Technologies), whereas this was achieved on a Discovery HS C18 column (Supelco) with a binary gradient of buffered (4 mM ammonium acetate) methanol and water for the PFCAs. Quantification was performed in high resolution mass chromatograms (PFSs) or selected reaction monitoring chromatograms (PFCAs) using the internal standard method.

6.2.3. Quality Control

Method detection limits (MDLs) for all compounds were determined on the basis of four blank extraction experiments. A complete list of the compound acronyms and specific MDLs can be found in TABLE 1. The stable isotope mass-labelled internal standard ($^{13}C_4$-PFOA) was used as surrogate standard for the PFSs and PFCAs. Recovery rates for the internal standard were on an average (± 1 standard error) 70 ± 1.3% (n = 34; including 4 method blank samples). A fish tissue sample used in an international inter-laboratory comparison (ILC) study in 2005 was analyzed along with the egg samples. The obtained concentrations deviated from the median concentration in the ILC by 67% for PFOSA, 37% for PFDoA and less than 22% for all other compounds.

TABLE 1. Acronyms and compound-specific method detection limits (MDLs) (pg/g wet weight) of perfluorinated alkyl substances in herring gull eggs.

	Acronyms	MDLs
6:2 Fluorotelomer sulfonate	6:2 FTS	161
Perfluorooctane sulfonamide	PFOSA	53
Perfluorosulfonates	*PFSs*	
Perfluorobutane sulfonate	PFBS	9
Perfluorohexane sulfonate	PFHxS	12
Perfluorooctane sulfonate	PFOS	51
Perfluorodecane sulfonate	PFDcS	21
Perfluorocarboxylates	*PFCAs*	
Perfluorohexanoate	PFHxA	215
Perfluoroheptanoate	PFHpA	167
Perfluorooctanoate	PFOA	91
Perfluorononanoate	PFNA	64
Perfluorodecanoate	PFDcA	49
Perfluoroundecanoate	PFUnA	30
Perfluorododecanoate	PFDoA	62
Perfluorotridecanoate	PFTriA	52
Perfluorotetradecanoate	PFTeA	128
Perfluoropentadecanoate	PFPeDA	88

6.3. Data Analyses

The differences in compound patterns (PFCAs) in eggs of herring gulls between the sampling sites (Hornøya and Røst) and collection years (1983, 1993 and 2003) were investigated using principal component analysis on the correlation matrix. This was done by extracting principal components (PCs) from the relative proportions of PFCA compounds (PFOA, PFNA, PFDcA, PFUnA, PFDoA, PFTriA, PFTeA and PFPeDA) detected in 60% or more of the egg samples (for each year and colony groups) to the sum PFCA concentrations (ΣPFCA). For the PFCAs detectable in 60% or more of the samples, the samples with concentrations below the MDLs were assigned a randomly-generated value between 0 (zero) and the compound-specific MDLs (TABLE 1). Relative concentration proportions were arcsin-transformed prior to the principal component analysis. The PCs with eigenvalues above 1 (one) were considered to account for a significant contribution to the total variance according to the latent root criterion. Compounds with correlation coefficients in the principal component analysis (i.e., PC loadings) greater than ± 0.65 on any PCs were considered significant. The differences between sampling sites and collection years in compound concentrations (log_{10}-transformed) and patterns (i.e., arcsin-transformed PFCA proportions to ΣPFCA) were investigated using the analysis of variance (ANOVA), followed by the Fisher *post-hoc*

test. Correlations between two variables were expressed using the Pearson coefficient *r*. The statistical package utilized was Statistica® (StatSoft, Tulsa, OK, U.S.A.) and α was set at 0.05.

7. Results and Discussion

7.1. Concentrations and Patterns

Herring gull egg samples were monitored for 6:2 FTS, PFOSA, four perfluorosulfonates (PFSs) and ten perfluorocarboxylates (PFCAs) with chain lengths between 6 and 15 carbons (C). The applied analytical method and instrumentation allowed detection of most PFAS at very low concentrations (see TABLE 1 for MDLs). This hampers direct comparison of the number of PFAS detected in egg samples reported in the few studies available in the literature (Holmstrom et al., 2005; Verreault et al., 2005), which are based on generally higher MDLs. The colony (Hornøya and Røst) and year (1983, 1993 and 2003)-specific concentrations in egg samples for individual compounds and sums are listed in TABLE 2.

TABLE 2. Mean (± 1 standard error)* concentrations (pg/g wet weight) of individual perfluorinated alkyl substances and sums (Σ) in eggs of herring gulls from northern (Hornøya) and southern (Røst) colonies of Northern Norway in 1983, 1993 and 2003.

	1983		**1993**		**2003**	
	Hornøya (*n* = 5)	**Røst (Hekkingen) (*n* = 5)**	**Hornøya (*n* = 5)**	**Røst (*n* = 5)**	**Hornøya (*n* = 5)**	**Røst (*n* = 5)**
6:2 FTS	<161	<161	<161	<161	<161	<161
PFOSA	<53	88 ± 8	226 ± 23	56 ± 14	342 ± 34	202 ± 35
Perfluorosulfonates						
PFBS	<9	<9	<9	<9	<9	<9
PFHxS	222 ± 39	314 ± 49	305 ± 51	802 ± 57	1,069 ± 96	970 ± 257
PFOS	21,435 ± 4,732	22,108 ± 5,018	39,527 ± 4,287	41,670 ± 4,111	36,973 ± 4,897	42,206 ± 3,552
PFDcS	38 ± 9	36 ± 8	85 ± 11	92 ± 12	172 ± 28	210 ± 32
ΣPFS	21,695 ± 4,764	22,457 ± 5,064	39,917 ± 4,319	42,564 ± 4,111	38,214 ± 5,010	43,386 ± 3,481
Perfluorocarboxylates						
PFHxA	<215	<215	<215	<215	<215	<215
PFHpA	<167	<167	<167	<167	<167	<167
PFOA	125 ± 35	167 ± 15	<91 – 126	642 ± 75	146 ± 37	652 ± 119
PFNA	158 ± 18	228 ± 49	304 ± 27	940 ± 84	1,052 ± 92	1,110 ± 80
PFDcA	341 ± 45	285 ± 63	898 ± 106	707 ± 73	1,299 ± 173	978 ± 104
PFUnA	1,033 ± 252	1,341 ± 350	3,376 ± 415	1,615 ± 208	4,161 ± 622	2,623 ± 364
PFDoA	228 ± 52	260 ± 52	640 ± 89	576 ± 70	707 ± 109	782 ± 119
PFTriA	768 ± 142	1,124 ± 200	2,252 ± 263	2,809 ± 477	2,535 ± 473	1,965 ± 69
PFTeA	<128 – 153	<128 –142	274 ± 55	509 ± 90	176 ± 28	277 ± 66
PFPeDA	<88 – 142	<88 –171	157 ± 46	340 ± 114	170 ± 25	<88 – 169

ΣPFCA	2,712 ± 533	3,493 ± 735	7,945 ± 943	8,139 ± 945	10,245 ± 1,447	8,452 ± 399

** Individual compound means for each of the colonies in 1983, 1993 and 2003 were generated if 60% or more of the egg samples had detectable concentrations of the given compound. If this criterion was not respected, a range concentration (<MDL – max) was reported. For these compounds detectable in 60% or more of the samples, the samples with concentrations below the MDLs were assigned a randomly-generated value between 0 (zero) and the compound-specific MDLs. A complete list of the compound-specific MDLs can be found in TABLE 1.*

The perfluorosulfonate PFOS was consistently and by far the most prominent compound in herring gull eggs. Such large domination of PFOS was in good agreement with other investigations conducted in seabird eggs from the northern European region, e.g., common guillemots (*Uria algaa*) (Holmstrom et al., 2005) from the Baltic Sea and glaucous gulls (*Larus hyperboreus*) from Svalbard, Arctic Norway (Verreault et al., 2005). Mean concentrations of PFOS in herring gull eggs from Hornøya (2003) were nearly 3-fold lower compared to eggs of Svalbard glaucous gulls collected in 2004 (n = 10; mean: 104 ± 13.2 ng/g wet weight) (Verreault et al., 2005). Likewise to the herring gull, the glaucous gull is an opportunistic predator-scavenger in the marine environment and exhibits a generally comparable feeding ecology, and thus potentially comparable exposure to contaminants, to that of herring gulls. However, comparisons between gull populations and species in terms of dietary exposure to contaminants should be made with great caution as some populations/species have shown specialization on certain food items (fish vs. seabird chicks and eggs). Moreover, PFOS levels in herring gull eggs (2003) were roughly 10 times higher compared to that determined in liver (mean: 3.4 ± 2.2 ng/g wet weight) of northern fulmars (*Fulmarus glacialis*) collected from Svalbard in 2003 (Gabrielsen et al., 2005). Among the other PFSs analyzed, PFBS was not detected in any egg samples, while PFHxS and PFDcS were found at concentrations several orders of magnitude lower than PFOS. By comparison to concentrations of polybrominated diphenyl ethers (PBDEs) (sum of eight PBDE congeners) (e.g., Hornøya, 2003: 56.6 ± 11.3 ng/g wet weight) in the same herring gull eggs (Knudsen et al., 2005), the ΣPFS concentrations were approximately 30% lower.

The generally detectable concentrations of PFOSA in herring gull eggs suggest this intermediate compound has not been fully metabolized and degraded to, e.g., PFOS in the environment and/or in biota. Metabolism of PFOSA can potentially occur in herring gulls and/or in lower organisms of the food web, as for example shown in fish (Tomy et al., 2004). The fluorotelomer 6:2 FTS was below the established MDL in virtually all egg samples.

The profiles of PFCAs in herring gull eggs were characterized by high proportions of odd and long carbon-chain length compounds, in which the PFUnA (11 C) and PFTriA (13 C) were the most dominant (e.g., all Hornøya samples: FIGURE 2). This is a typical PFCA pattern also found in other marine mammal and bird species, also including eggs of Svalbard glaucous gulls (Verreault et al., 2005) and Svalbard polar bears (plasma)

(Smithwick et al., 2005). The origin of this pattern is still not known as almost exclusively PFOA and PFNA were/are produced industrially. However, the production of PFOA and PFNA was shown to generate long carbon-chain impurities, which may explain their ubiquitous presence in wildlife and human samples. The shorter carbon-chain compounds PFHxA (6 C) and PFHpA (7 C) were not detected in herring gull egg samples. This may suggest a high depuration and excretion rate for these compounds, and perhaps also low bioavailability, bioaccumulation potential and exposure, as a result of low environmental concentrations in Northern Norway. However, it should also be considered that the compound-specific MDLs for PFHxA and PFHpA were higher compared to the other PFCAs with longer carbon chain length. Concentrations of ΣPFCA in herring gull egg samples co-varied positively with those of ΣPFS ($n = 30$; $r^2 = 0.81$; $p < 0.0001$). However, current ΣPFCA concentrations were roughly 75-85% lower compared to ΣPFS.

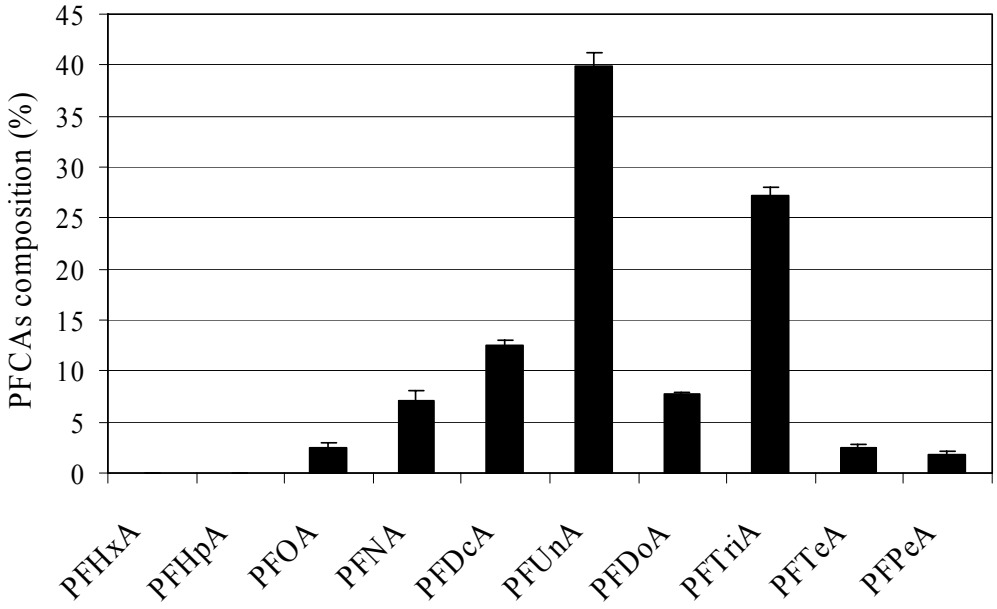

FIGURE 2: Mean (+ 1 standard error) percentage composition of individual perfluorocarboxylates (PFCAs) with chain lengths between 6 and 15 carbons to the sum PFCA (ΣPFCA) concentrations in herring gull eggs from Hornøya (1983, 1993 and 2003 samples combined; $n = 15$).

7.2. Spatial Trends

Concentrations of the individual PFAS compounds in herring gull eggs did not differ between the two colonies investigated when the three sampling years were combined, with the exception of PFOA. In fact, PFOA concentrations were highest ($p = 0.0002$) in the southernmost colony (Røst), relative to Hornøya. This suggests that based on egg measurements, total PFAS concentrations are relatively uniformly distributed in Northern Norway. The absence of a south-north gradient also was reported for PBDE congeners determined in the same herring gull eggs (with the exception of the PBDE-153 congener that was highest in Røst) (Knudsen et al., 2005). However, it could not be completely

disregarded that herring gull eggs collected from a wider geographical range in Norway would have yielded a different spatial distribution. In contrast, a different scenario was obtained when the proportions of closely-related compounds (PFCAs) to the sum of these compounds (ΣPFCA) was compared between the colonies when the sampling years were investigated separately. The PFCA patterns among herring gull eggs were compared by examining the structure in the relationships between the proportions of the eight PFCAs (8 to 15 C) to the ΣPFCA concentrations using the first two PCs, PC 1 and PC 2 (FIGURE 3). Egg samples from Hornøya were distinguished by higher proportions of PFDcA (10 C) and PFUnA (11 C), and lower proportions of PFTeA (14 C) and PFPeA (15 C). No pattern difference was found between the sampling years in Hornøya samples. However, eggs from Røst showed highly variable PFCA proportions between the sampling years comparatively to Hornøya. For example, eggs from Røst sampled in 2003 were characterized by higher proportions of PFNA (9 C), whereas eggs from the same colony collected in 1993 differed by higher proportions of PFTeA and PFPeA and lower proportions of PFDcA and PFUnA. One factor that could explain this marked variation in PFCA makeup among the Røst eggs sampled at 10-year intervals is a change in feeding ecology, i.e., a shift in dietary preference for herring gulls breeding in this region. Also, it cannot be completely disregarded that PFCAs with different carbon-chain lengths may have distinct transport pathways or fate in the environment. Herring gulls may also have been exposed to different local and/or remote sources of PFCAs in their ecosystem.

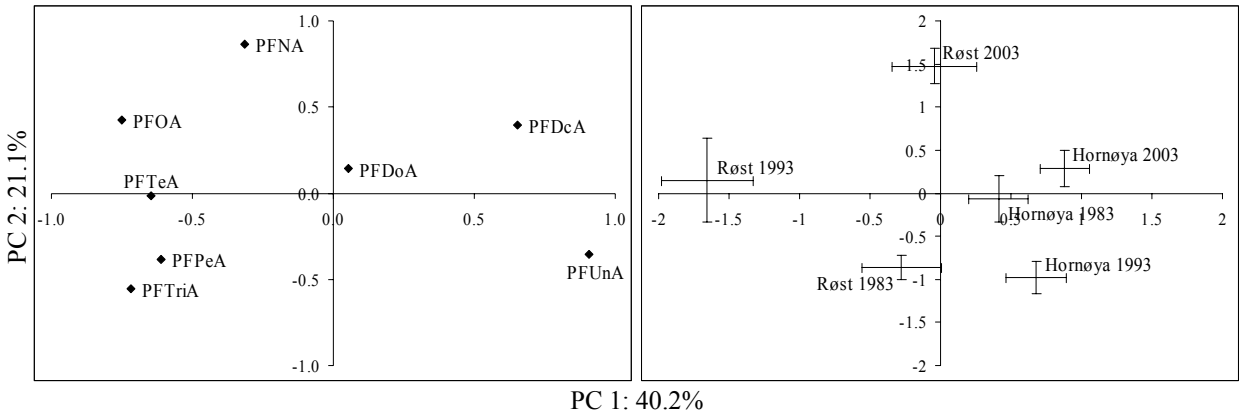

FIGURE 3: Proportions of eight individual perfluorocarboxylate (PFCA) compounds (8 to 15 carbon-chain lengths) to the sum PFCA (ΣPFCA) concentrations plotted using the two first principal components (PCs), PC 1 and PC 2. Mean (± 1 standard error) factor scores (right biplot) are showed for individual sampling sites and collection years of herring gull eggs (n = 30) from Northern Norway. The percent variability explained by PC 1 and PC 2 is provided.

7.3. Temporal Trends

Temporal trends of PFOS and ΣPFCA concentrations in herring gull eggs collected between 1983–2003 are presented in FIGURE 4 (A and B). In both colonies PFOS concentrations showed a nearly 2-fold increase from 1983 to 1993, followed by a leveling

off up to 2003. By comparison, the ΣPFCA concentrations also showed a marked and comparable increase during 1983–1993, but a weak although non-significant increase between 1993 and 2003. This pattern could be reflective of the phase-out of PFOS-based chemicals by the main producer (3M, U.S.A.) in 2000-2002, and the ongoing and large volume production of PFCAs (i.e., PFOA and PFNA products). The present trends of PFOS and PFCAs in herring gull eggs are in general agreement with those reported in eggs of common guillemots from the Baltic Sea collected between 1968 and 2003 (Holmstrom et al., 2005). In this particular study, a sharp peak in PFOS concentrations was observed in 1997, followed by decreasing levels up to 2002. However, these authors concluded that the decrease in PFOS in common guillemot eggs could not be linked to the PFOS phase-out, which occurred at the end of this period.

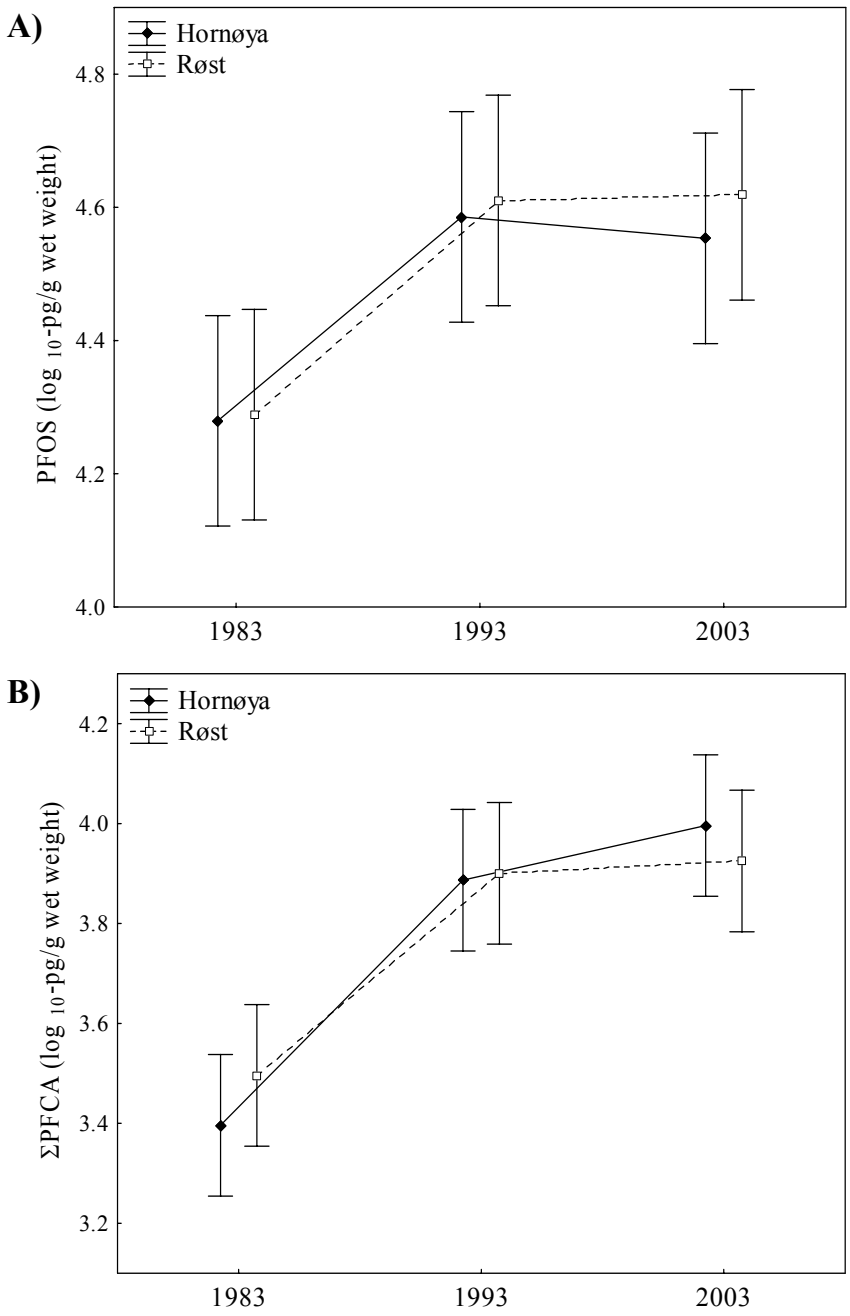

FIGURE 4: Temporal trends (1983–2003) of PFOS (**A**) and sum perfluorocarboxylate (ΣPFCA) (**B**) concentrations (pg/g wet weight; log_{10}-transformed) in eggs of herring gulls from Hornøya and Røst, Northern Norway. PFOS and ΣPFCA concentration means are shown with ± 95% confidence intervals as vertical bars. The sample size for each sampling sites and collection years can be found in TABLE 2.

7.4. Toxicological Implications

Recently, experimental exposure studies of PFOS in mallard ducks and northern bobwhite quails has led to calculation of protective screening-level concentrations of

PFOS (Beach et al., 2006). In this study, egg yolk-based benchmarks were determined as 1.7 µg PFOS/mL yolk, which is roughly 40-45 times higher than PFOS levels in whole eggs of herring gulls from Northern Norway (comparison based on 2003 samples from both colonies). Therefore, from a toxicological standpoint, and assuming the potency/sensitivity described in mallard ducks and northern bobwhite quails also applies to herring gulls, current concentrations in eggs suggest that PFOS alone would pose a minimal risk to herring gulls. Nonetheless, PFOS and other accumulated fluorochemicals in herring gulls, particularly in developing embryos, need to be assessed as part of a broad organohalogen contaminant cocktail with potential for mediating biological processes. Because the toxicological effect studies of PFOS in developing avian embryos are limited (Beach et al., 2006; Molina et al., 2006), more research is warranted to assess the implications of current levels in herring gull eggs.

8. Acknowledgments

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Tittel - norsk og engelsk
"Perfluoralkylstoffer i Egg av Gråmåker fra Nord Norge: Geografisk- og Tidstrend"

"Perfluorinated Alkyl Substances in Eggs of Herring Gulls from Northern Norway: Spatial and Temporal Trends"

Sammendrag – summary
Formålet med dette studiet var å kartlegge nivåer, sammensetning av forbindelser og tidstrend (1983, 1993 og 2003) av perfluoralkylstoffer i egg av gråmåker fra to hekkekolonier i Nord-Norge. Konsentrasjoner av forbindelsene var ikke signifikant forskjellige i de to hekkekoloniene. I begge koloniene ble konsentrasjoner av perfluoroktanylsulfonat og perfluorokarboksylater i egg nær doblet mellom 1983 og 1993. Konsentrasjoner av disse forbindelsene var nokså stabilt mellom 1993 og 2003.

The present study reports on concentrations, patterns and temporal trends (1983, 1993 and 2003) of perfluorinated alkyl substances in eggs of herring gulls from two colonies in Northern Norway. No difference in total compound concentrations was found between the two colonies. In both colonies, concentrations of perfluorooctane sulfonate and perfluorocarboxylate compounds in eggs showed a nearly 2-fold increase from 1983 to 1993. Concentrations of these compounds from 1993 and up to 2003 did not change significantly.

4 emneord Perfluoralkylstoffer; tidstrend; gråmåke; egg	4 subject words Perfluorinated alkyl substances; temporal trend; herring gull; egg