PERFLUORINATED ALKYL SUBSTANCES IN PLASMA, LIVER, BRAIN AND EGGS OF GLAUCOUS GULLS (*LARUS HYPERBOREUS*) FROM THE NORWEGIAN ARCTIC

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Introduction

Recent environmental surveys have ascertained the widespread occurrence of perfluorinated alkyl substances (PFAS) in tissues of wildlife from the Arctic, including species occupying high trophic positions in the marine food web. The predominant PFAS reported in arctic biota has been perfluorooctane sulfonate (PFOS), while perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonamide (PFOSA), and 8 to 15 carbon-chain length perfluorocarboxylic acids (PFCAs) have also been reported. PFOS and other fluorochemicals retained in serum have been demonstrated to bind with high affinity to the protein albumin (1), which is one of the major circulating hormone (e.g., thyroid hormone thyroxin – T4) carrier proteins in birds. Recent experimental studies in which birds were exposed chronically to PFOS via the diet have shown slight adverse reproductive and developmental effects (2). At present, the distribution and levels of PFAS in top-predator avian species from the Arctic are poorly investigated, and nonexistent for birds from the Norwegian Arctic.

Aim of this study

To investigate the distribution and levels of a suite of PFAS in plasma, liver, brain, and egg samples collected from adult glaucous gulls (*Larus hyperboreus*), a marine scavenger-predator species breeding in the Norwegian Arctic.

Experimental Section

Species Studied and Sample Collection

The glaucous gull has previously been reported to accumulate some of the highest tissue/plasma levels of organohalogens of any arctic seabird species and populations. The seasonal/annual distribution of glaucous gulls is entirely within the North Atlantic region, suggesting the main pathway of contaminant exposure is via long-range atmospheric transport. Several adverse biological effects associated with organohalogen exposure have been documented in this species. In this study, samples of blood (plasma) (n = 20), liver (n = 9), brain (n = 8), and eggs (n = 10) were collected by the Norwegian Polar Institute during the breeding season of 2004 from an equal number of adult male and female glaucous gulls at Svalbard (ice edge) and Bear Island in the Norwegian Arctic (FIGURE I).

Chemical Analyses

Analyses of glaucous gull samples were carried out by two laboratories using different extraction and cleanup procedures based on methods by Hansen et al. (3) and Berger and Haukås (4). Instrumental quantification was performed using high-performance liquid chromatography-electrospray ionization (ESI)/tandem mass spectrometry (MS) (HPLC-ESI/MS/MS), or HPLC-time-of-flight-high-resolution MS with ESI in the negative ionization mode (HPLC-ESI-ToF-HRMS). An inter-laboratory test based on the analysis of a suite of PFAS in glaucous gull liver samples resulted in mean percentage deviation of compound concentrations ranging between 6% and 77%. Data comparison showed, e.g., a non-significant difference in mean PFOS liver concentrations between method A and method B, which was consistent with the other analytes determined. QA/QC included laboratory blanks, duplicate sample extraction, matrix spikes, and calibration standard injections for each block of 5 to 10 samples to monitor changes in instrument sensitivity, and to minimize matrix effects on ESI suppression/enhancement.

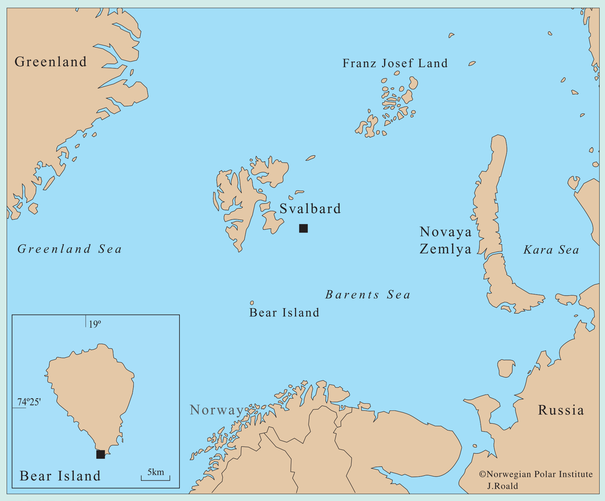

FIGURE I
Map of the Norwegian Arctic showing sampling locations [■] of glaucous gulls.

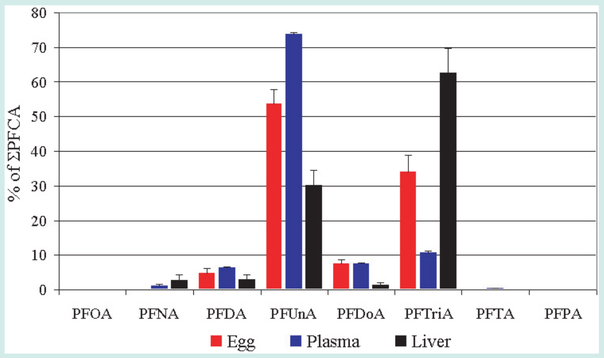

FIGURE II
Mean (+1 standard error) percentage contribution of individual perfluorocarboxylic acids (PFCAs) with carbon-chain lengths between 8 and 15 to sum (Σ) PFCA in glaucous gull egg, plasma, and liver samples.

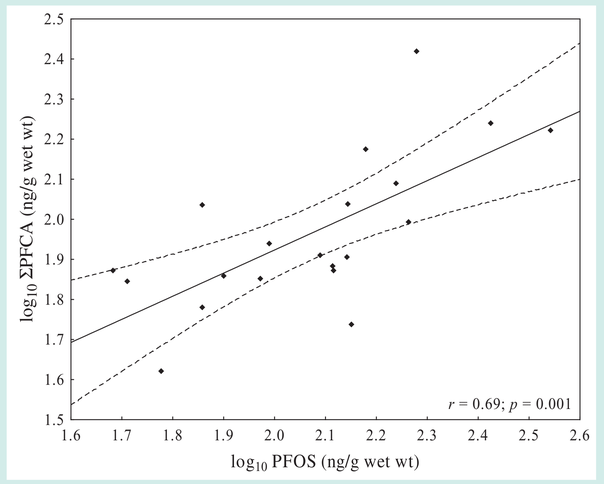

FIGURE III
Relationship with 95% confidence interval (stippled line) between $\log_{10}$ - transformed perfluorooctane sulfonate (PFOS) and sum (Σ) perfluorocarboxylic acid (ΣPFCA) concentrations (ng/g wet wt) in glaucous gull plasma.

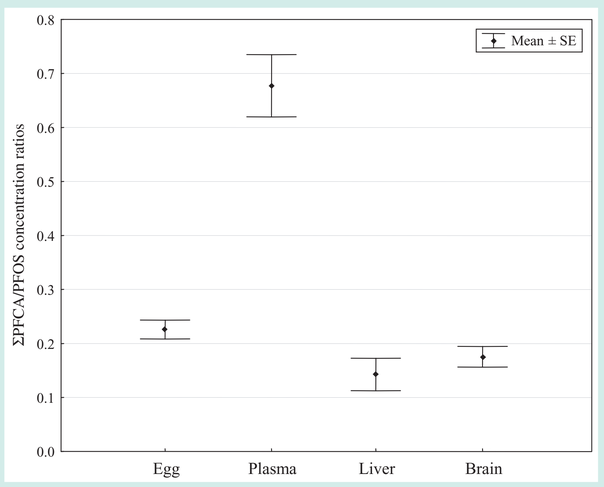

FIGURE IV
Mean (±1 standard error (SE)) concentration ratios of sum perfluorocarboxylic acid (ΣPFCA) to perfluorooctane sulfonate (PFOS) in glaucous gull egg, plasma, liver, and brain samples.

Main Findings

- PFAS concentrations were not significantly different between male and female glaucous gulls.
- PFOS was consistently the most prominent PFAS in samples.
- Among the body compartment/tissue samples analyzed, PFOS concentrations ranked as follows: plasma > liver ≈ egg > brain.
- PFOS concentrations in plasma, liver, and eggs were within a range comparable to those of the most recalcitrant neutral organochlorines determined in this species, e.g., *p,p'*-DDE and CB153.
- Regardless of factors influencing the degree of exposure among seabird species and populations (e.g., seasonal/annual spatial movements, habitat, and feeding ecology), PFOS levels measured in Norwegian arctic glaucous gulls are the highest reported thus far in any arctic seabirds.
- Perfluorobutanoic acid (PFBS), PFOSA, and four saturated (8:2 FTCA and 10:2 FTCA) or unsaturated (8:2 FTUCA and 10:2 FTUCA) fluorotelomer carboxylic acids were below the limits of detection in all samples.
- Sum (Σ) PFCA concentrations (sum of 8 to 15 carbon (C)-chain length PFCAs) were highest in plasma and decreased in the order egg > liver > brain.
- 5C- and 6C-chain length PFCAs (perfluoropentanoic acid (PFPeA) and perfluorohexanoic acid (PFHxA), respectively) were below the limits of detection in all samples.
- The accumulation profiles of PFCAs were characterized by high proportions of odd and long carbon-chain length compounds, namely perfluoroundecanoic acid (PFUnA; 11C) and perfluorotridecanoic acid (PFTriA; 13C). The individual contribution of PFUnA and PFTriA varied between the analytical matrices (FIGURE II).
- ΣPFCA concentrations co-varied positively with those of PFOS in plasma (FIGURE III), liver, brain, and egg samples.
- The ΣPFCA-to-PFOS concentration ratios in samples revealed plasma, weighed against tissues and eggs, retained substantially higher burdens of ΣPFCA proportionally to PFOS (FIGURE IV).
- Factors such as body compartment/ tissue specific carrier protein affinity may play a primary role in the accumulation/elimination dynamics of PFCAs versus PFOS in glaucous gulls.

		Egg (n = 10)			Plasma (n = 20)		
	Acronym	% of Samples >MDL	Mean ± SE	Range	% of Samples >MDL	Mean ± SE	Range
Perfluorosulfonic acids							
Perfluorohexane sulfonate	PFHxS	30	-	<0.27 – 1.23	100	1.12 ± 0.15	0.29 – 2.71
Perfluorooctane sulfonate	PFOS	100	104 ± 13.2	51.7 – 196	100	134 ± 16.6	48.1 – 349
Perfluorocarboxylic acids	PFCA						
Perfluorooctanoic acid	PFOA	0	-	<0.70	5	-	<0.70 – 0.74
Perfluorononanoic acid	PFNA	0	-	<2.33	40	-	<2.33 – 6.33
Perfluorodecanoic acid	PFDA	70	2.08 ± 0.46	<0.93 – 4.62	100	6.56 ± 0.82	3.07 – 15.1
Perfluoroundecanoic acid	PFUnA	100	21.4 ± 2.82	8.74 – 38.7	100	74.4 ± 8.06	32.0 – 184
Perfluorododecanoic acid	PFDoA	90	3.35 ± 0.62	<0.78 – 7.25	100	7.68 ± 1.04	2.90 – 23.9
Perfluorotridecanoic acid	PFTriA	100	15.1 ± 3.61	4.0 – 42.4	100	11.0 ± 1.29	3.63 – 30.2
Perfluorotetradecanoic acid	PFTA	0	-	<0.25	60	0.54 ± 0.14	<0.25 – 2.77
Perfluoropentadecanoic acid	PFPA	0	-	<0.25	5	-	<0.25 – 0.70
ΣPFCA		100	41.8 ± 5.27	14.7 – 63.4	100	102 ± 11.6	41.8 – 262

TABLE I
Mean concentration (ng/g wet wt), standard error (SE), and range of a suite of PFAS in egg and plasma samples of glaucous gulls from the Norwegian Arctic.

Conclusion

A suite of PFAS is retained in plasma, liver and brain of glaucous gulls from the Norwegian Arctic at concentrations varying to some extent between tissues/body compartments. A substantial burden of PFAS is transferred from mother to eggs at the time of ovogenesis. Because the toxicological effects mediated by PFAS exposure are largely unknown in apex avian wildlife and developing embryos, research is warranted to assess the implications of current high levels in glaucous gulls.

Acknowledgements

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