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Fluorinated Organic Compounds in an Eastern Arctic Marine Food Web

GREGG T. TOMY,*,†,‡ WES BUDAKOWSKI,† THOR HALLDORSON,† PAUL A. HELM,† GARY A. STERN,† KEN FRIESEN,§ KAREN PEPPER,|| SHERYL A. TITTLEMIER,|| AND AARON T. FISK⊥

Department of Fisheries & Oceans Canada, 501 University Crescent, Winnipeg, Manitoba R3T 2N6, Canada, Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada, Department of Chemistry, University of Winnipeg, Winnipeg, Manitoba R3B 2E9, Canada, Food Research Division, Health Products and Food Branch, Health Canada, Ottawa, Ontario K1A 0L2, Canada, and Warnell School of Forest Resources, University of Georgia, Athens, Georgia 30602

An eastern Arctic marine food web was analyzed for perfluorooctanesulfonate (PFOS, $C_8F_{17}SO_3^-$), perfluorooctanoate (PFOA, $C_7F_{15}COO^-$), perfluorooctane sulfonamide (PFOSA, $C_8F_{17}SO_2NH_2$), and *N*-ethylperfluorooctane sulfonamide (*N*-EtPFOSA, $C_8F_{17}SO_2NHCH_2CH_3$) to examine the extent of bioaccumulation. PFOS was detected in all species analyzed, and mean concentrations ranged from 0.28 ± 0.09 ng/g (arithmetic mean ± 1 standard error, wet wt, whole body) in clams (*Mya truncata*) to 20.2 ± 3.9 ng/g (wet wt, liver) in glaucous gulls (*Larus hyperboreus*). PFOA was detected in approximately 40% of the samples analyzed at concentrations generally smaller than those found for PFOS; the greatest concentrations were observed in zooplankton (2.6 ± 0.3 ng/g, wet wt). *N*-EtPFOSA was detected in all species except redfish with mean concentrations ranging from 0.39 ± 0.07 ng/g (wet wt) in mixed zooplankton to 92.8 ± 41.9 ng/g (wet wt) in Arctic cod (*Boreogadus saida*). This is the first report of *N*-EtPFOSA in Arctic biota. PFOSA was only detected in livers of beluga (*Delphinapterus leucas*) (20.9 ± 7.9 ng/g, wet wt) and narwhal (*Monodon monoceros*) (6.2 ± 2.3 ng/g, wet wt), suggesting that *N*-EtPFOSA and other PFOSA-type precursors are likely present but are being biotransformed to PFOSA. A positive linear relationship was found between PFOS concentrations (wet wt) and trophic level (TL), based on $\delta^{15}N$ values, ($r^2 = 0.51$, $p < 0.0001$) resulting in a trophic magnification factor of 3.1. TL-corrected biomagnification factor estimates for PFOS ranged from 0.4 to 9. Both results indicate that PFOS biomagnifies in the Arctic marine food web when liver concentrations of PFOS are used for seabirds and marine mammals. However, transformation of *N*-EtPFOSA and PFOSA and potential other perfluorinated compounds to PFOS may contribute to PFOS levels in marine mammals and may inflate estimated biomagnification values. None of the other fluorinated compounds (*N*-EtPFOSA, PFOSA, and PFOA) were found to have a significant relationship with TL, but BMF_{TL} values of these compounds were often >1, suggesting potential for these compounds to biomagnify. The presence of perfluorinated compounds in seabirds and mammals provides evidence that trophic transfer is an important exposure route of these chemicals to Arctic biota.

Introduction

Fluorinated organic compounds constitute a diverse group of chemicals that are used in a variety of specialized consumer and industrial products. They are used as refrigerants, agrochemicals, chemical catalysts/reagents, and surfactants and in fire-fighting foams (*1*). The perfluorinated acids (PFAs) are the group of fluorinated organic compounds that have attracted most of the interest, and of these, perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3^-$) and perfluorooctanoate (PFOA, $C_7F_{15}COO^-$) have received the most attention.

The key ingredient in the 3M-made fabric protector Scotchgard is a neutral polymeric compound containing the PFOS base structure ($C_8F_{17}SO_2$), which has been valued for its ability to protect materials from stains because it repels both oil and water. Unlike PFOS, PFOA continues to be used today in the synthesis of fluoropolymers. The U.S. Environmental Protection Agency and Health Canada are currently performing risk assessments on PFOA and related compounds. Results of these are sure to raise public interest and questions about the safety of Teflon (and PFOA) and other fluoropolymers that rely on PFOA in their synthesis.

Much of the recent interest in PFAs can be attributed to the ubiquitous presence of PFOS and PFOA in environmental media. Both compounds have been detected in human sera (*2*), freshwater and marine biota (*3*−*6*), and surface water (*7*, *8*). The unique chemical and biological stability of PFOS and PFOA appears to preclude any degradation or metabolism and contributes to their bioaccumulation and persistence (*9*, *10*).

A recent study by Van de Vijver et al. (*11*) found a positive linear relationship between PFOS concentration in livers of harbor porpoises and nitrogen stable isotopes. However, because only top predators were examined in that study, biomagnification through the food web could not be determined.

To our knowledge, no attempts have been made to examine the extent of accumulation and transfer of PFAs in an aquatic food web. The objective of this study is to address this knowledge gap by examining PFOS and PFOA concentrations in an Arctic food web from eastern Canada. Stable isotopes of nitrogen were also used to assess the transfer of PFOS within the food web. The distribution of two neutral-PFOS precursors (*12*), *N*-ethylperfluorooctane sulfonamide (*N*-EtPFOSA, $C_8F_{17}SO_2NHCH_2CH_3$) and perfluorooctane sulfonamide (PFOSA, $C_8F_{17}SO_2NH_2$), in this food web was also examined.

Materials and Methods

Standards and Reagents. PFOA, the tetraethylammonium salt of PFOS, perfluorobutane sulfonate (PFBS), tetrabutylammonium (TBA) hydrogen sulfate, sodium hydroxide, and sodium carbonate were obtained from Sigma-Aldrich Canada Ltd. (Oakville, ON, Canada). *N*-EtPFOSA (85% purity) was

* Corresponding author telephone: (204)983-5167; fax: (204)984-2403; e-mail: tomyg@dfo-mpo.gc.ca.
† Department of Fisheries & Oceans Canada.
‡ University of Manitoba.
§ University of Winnipeg.
|| Health Canada.
⊥ University of Georgia.

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purchased from Interchim (Montlucon, France), and methyl perfluorotetradecanoate (MePFTeD) and methyl perfluorodecanoate (MePFD) were purchased from SynQuest Laboratories (Alachua, FL). PFOSA was provided by Griffin LLC. Optima grade methanol and water and reagent grade methyl *tert*-butyl ether (MTBE) were purchased from Caledon Laboratories Ltd. (Georgetown, ON, Canada).

Sample Collection

Fluorinated organic compounds were analyzed in liver tissues of beluga whale (*Delphinapterus leucas*), narwhal (*Monodon monoceros*), walrus (*Odobenus rosmarus*), deepwater redfish (*Sebastes mentella*), glaucous gulls (*Larus hyperboreus*), and black-legged kittiwake (*Rissa tridactyla*). Whole organism homogenates of Arctic cod (*Boreogadus saida*), shrimp (*Pandalus borealis; Hymenodora glacialis*), clams (*Mya truncata*; *Serripes groenlandica*), and mixed zooplankton were analyzed. Mammal samples were obtained through the Department of Fisheries and Oceans collection programs as part of subsistence hunts and sponsored by the Nunavut Wildlife Management Board. Seabirds were collected as part of the Northwater Polyna study (*13*). Archived mammal tissues were collected from Frobisher Bay near Iqaluit (beluga; 1996), from Cape Dorset (walrus; 1998), and from Grise Fiord (narwhal; 2000). Beluga (aged 3.5−10.5 yr) and narwhal were all males, while walrus samples consisted of both sexes. Fish and shrimp were collected from Davis Strait in October of 2000 and 2001 by trawling from the Greenland Institute of Natural Resources R/V *Paamiut*. Arctic cod were young of the year and 2 years of age, and deepwater redfish ranged in age from 4 to 7 yr. Clams and zooplankton samples were collected from Frobisher Bay in May 2002. Zooplankton samples consisted of bulk sieved mixed species (predominantly copepods with 5th stage *Calanus hyperboreus* removed) collected using 350 and 500 μm mesh nets. Clams were collected by a diver.

Extraction and Analyses of PFOS and PFOA. Extraction of PFOS and PFOA from samples was done in a manner similar to that described by Hansen et al. (*14*) with small modifications. Prior to extraction, samples and blanks were spiked with 500 pg (5 μL of a 100 pg/μL solution) of the recovery internal standard (RIS), PFBS, to monitor recovery efficiencies. PFOS and PFOA concentrations were recovery corrected based on the recovery of PFBS. PFBS was used as a RIS because it has the same functional groups as PFOS and was not present at detectable concentrations in solvent blanks. It is likely that PFBS is not an ideal surrogate for PFOA since it contains a shorter perfluoroalkyl chain as compared to the perfluorooctyl chain in PFOA, and this structural difference may affect recovery efficiencies. While perfluorononanoic acid (PFNA) or a similar compound with a larger perfluorinated chain would better approximate the behavior of PFOS and PFOA than PFBS, the presence of this and other perfluorinated acids in the samples led us to use PFBS as the RIS.

Extracts were chromatographed on a Supelcosil C_8 analytical column (5.0 cm × 2.1 mm i.d., 5 μm particle size; Supelco, Oakville, ON, Canada). The analytical and C_8 guard columns (Phenomenex, USA) were installed on an Agilent 1100 series HPLC system (Agilent Technologies, Palo Alto, CA) equipped with a vacuum degasser, binary pump, and autosampler. The mobile phase system used consisted of water (A) and methanol (B), both of which contained 2 mM ammonium acetate. Flow rate was 300 μL/min, and the injection volume was 3 μL. The gradient employed started at 20% B increasing to 95% B in 9.5 min and held for 2 min. Thereafter the mobile phase composition was returned to starting conditions in 5 min. The column was allowed to equilibrate for 5 min between runs.

Analyses were performed with a Sciex API 2000 triple quadrupole mass spectrometer (MDS Sciex, Ontario, Canada) in the negative ion ES mode using multiple reaction monitoring. The optimized parameters were ionspray voltage, −1200 V; curtain gas flow, 15.00 arbitrary units (au); sheath gas flow, 30.00 au; turbo gas flow, 35.00 au; temperature 525 °C; focusing potential, −360 V; and collision-assisted dissociation gas flow, 8 au. The reactions monitored and the corresponding ion kinetic energy (KE) were as follows: PFBS, 299 → 80 (KE = −51.00 eV), *299 → 99* (KE = −37 eV); PFOS, *499 → 80* (KE = −80 eV), 499 → 99 (KE = −63 eV); PFOA, 413 → 369 (KE = −9 eV), *413 → 169* (KE = −26 eV). Italicized ion transitions were used in the quantitation while the other transitions were used for confirmation.

Standards solutions of PFOS and PFOA in methanol were run with every 10−15 samples. A five-point calibration curve spanning concentrations from 10 to 300 pg/μL was used to quantify target analytes.

Extraction and Analysis of *N*-EtPFOSA and PFOSA. Extraction of *N*-EtPFOSA and PFOSA from samples was done according to the method described by Tittlemier et al. (*15*). In brief, approximately 5 g of sample was spiked with 5000 pg of the RIS, MePFTeD (10 μL of a 500 pg/μL solution), homogenized and extracted using hexane:acetone (2:1 v/v). Lipids were removed from the organic extract using concentrated sulfuric acid. Residual material from the lipid destruction step was removed by chromatography on a silica gel column containing both neutral and acidic (40% H_2SO_4 by weight) silica gel. MePFD instrument performance IS (5000 pg) was added to samples just prior to analysis by gas chromatography/positive chemical ionization/mass spectrometry in the selected ion monitoring mode. Analyses of samples, extraction blanks (run with each set of samples), and external standards were made on an Agilent 6890 GC coupled to a 5973N mass spectrometer.

Quality Control. The inherent problems associated with quantifying fluorinated organic compounds by LC/MS/MS in environmental samples, including high background signals of PFOA from injections of solvent (typically methanol and water), potential carryover between injections, and lack of appropriate isotopically labeled IS has been well-documented in the literature (*6*). Two types of blanks were employed in this study. Instrument blanks were injections of methanol run after every two samples and were used to monitor PFOA and PFOS contamination from the LC/MS/MS instrument. Extraction (or method) blanks consisted of Optima grade water and were extracted along with each sample species. Extraction blanks were used to monitor the potential for contamination to occur during extraction and workup of the sample.

In general, PFOA signals were similar between the instrument and method blanks, suggesting that sample contamination during extraction and workup was probably less important than from the instrument itself. The background signal of PFOA could be reduced appreciably (10×) by reducing the column equilibration time between sample injections. It appears that PFOA is continually leaching from the inner parts of the HPLC system and concentrating on the head of the analytical column. A similar finding was made by Martin et al. (*6*). For PFOS, extraction blanks always had higher signals than instrument blanks, suggesting that contamination during extraction and workup was more significant.

In addition to spiking every sample with PFBS, a test was done to check the recoveries of PFOS, PFOA, and PFBS by spiking a known amount of each into Optima grade water ($n = 4$) and extracting according to Hansen et al. (*14*). Average PFOS, PFOA, and PFBS recoveries were 93 ± 7 [arithmetic mean ± 1 standard error (SE)], 104 ± 6, and 78 ± 3%, respectively.

PFOS and PFOA concentrations in samples were blank corrected by subtracting the signal from extraction blanks (one for each sample species) from the sample signals. Average recoveries of PFBS were 101 ± 4% (see table in Supporting Information). Samples were corrected for recoveries of PFBS only when recoveries were less than 100%. Duplicate analyses were performed on Arctic cod to measure the repeatability of the method. In addition, after every 10−15 samples, the LC/MS/MS system was rinsed with methanol containing 75 mM ammonium acetate for several hours.

For *N*-EtPFOSA and PFOSA, one method blank (consisting of 5 mL of Milli-Q water) was extracted and worked up concurrently with each set of 12 samples. Concentrations of *N*-EtPFOSA and PFOSA in samples were blank corrected by subtracting the signal of the method blank from the sample signals. Average MePFTeD recoveries were 69 ± 2%, and all samples were recovery corrected.

Method Detection Limits (MDLs). Known amounts of PFOS and PFOA were spiked into extracts of clams ($n = 4$) that were previously analyzed and found to have nondetectable concentrations of PFOS and PFOA (i.e., response of PFOS and PFOA were not above the response from the extraction blanks). Five separate injections of the spiked extracts were then made. The ion signals obtained for both PFOS and PFOA were then adjusted to estimate concentrations that would give a signal-to-noise ratio of 3:1. In this manner, MDLs of PFOS and PFOA were estimated to be 0.06 and 0.2 ng/g, respectively. For calculation of mean concentrations, a concentration of half of the MDLs was assumed in those instances that PFOS and PFOA were below MDLs. MDLs for *N*-EtPFOSA and PFOSA were determined according to Winefordner and Long (*16*). Respective MDLs for *N*-EtPFOSA and PFOSA were 0.57 and 0.035 ng/g.

LC/MS/MS Matrix Effects. Extracts of clam ($n = 5$) that were previously analyzed and found to have nondetectable concentrations of PFOS and PFOA were spiked with accurate amounts of PFOS and PFOA to give concentrations of 10, 20, 30, 50, and 100 pg/μL. Injections were made each time PFOS and PFOA had been added to the extract. Separate to this, an injection of a methanol solution was made that contained the same concentrations of PFOS and PFOA that had been spiked into the clam extract. The ion signals of PFOS and PFOA from the spiked clam extracts were then compared to the signals obtained from the standard methanol solution.

Stable Isotope Determination. Prior to stable isotope analyses, all tissue samples were washed in distilled water and then freeze-dried, powdered, and treated with a 2:1 (by volume) chloroform:methanol solution to remove lipids. Stable-carbon and nitrogen isotope assays were performed on ~1 mg subsamples of homogenized materials by loading into tin cups and combusting at 1800 °C in a Robo-Prep elemental analyzer. Resultant CO_2 and N_2 gases were then analyzed using an interfaced Europa 20:20 continuous-flow isotope ratio mass spectrometer (CFIRMS) with every 5 unknowns separated by 2 laboratory standards. Stable isotope abundances were expressed in δ notation as the deviation from standards in parts per thousand (‰) according to the following equation:

$$\delta X = [(R_{sample}/R_{standard}) - 1] \times 1000 \quad (1)$$

where X is ^{13}C or ^{15}N and R is the corresponding ratio $^{13}C/^{12}C$ or $^{15}N/^{14}N$. The $R_{standard}$ values were based on the PeeDee Belemnite (PDB) for ^{13}C and atmospheric N_2 (AIR) for ^{15}N. Replicate measurements of internal laboratory standards (albumen) indicate measurement errors of ±0.3‰ for stable-nitrogen isotope measurements.

Food Web and Biomagnification Factor Calculations. Two measures of trophic transfer were calculated for PFOS in the studied food web. The first determined trophic magnification factors (TMFs) for the entire food web based on the relationship between $\delta^{15}N$ and contaminant concentration:

$$\ln \text{PFOS concentration (wet wt)} = a + (b \times \text{trophic level}) \quad (2)$$

Trophic levels (TLs) were determined using equations modified slightly from those reported in Fisk et al. (*13*). Trophic level was determined relative to the clam, which we assumed occupied trophic level 2 (i.e., primary herbivore). For each individual sample of zooplankton, fish, and marine mammal, trophic level was determining using the relationship:

$$TL_{consumer} = 2 + (\delta^{15}N_{consumer} - \delta^{15}N_{clam})/3.8 \quad (3)$$

where $TL_{consumer}$ is the trophic level of the organism, $\delta^{15}N_{clam}$ is equal to 7.99 ± 0.93 (mean ± 1 SE, $\delta^{15}N$ for *C. hyperboreus*), and 3.8 is the isotopic enrichment factor (*17*). Captive-rearing studies on birds suggest that a diet−tissue isotopic fractionation factor of +2.4‰ is appropriate for these taxa (*18*). Following the derivation outlined in Fisk et al. (*13*), we used the equation:

$$TL_{bird} = 3 + (\delta^{15}N_{bird} - (\delta^{15}N_{clam} + 2.4)/3.8) \quad (4)$$

The slope b of eq 1 was used to calculate TMF using:

$$TMF = e^b \quad (5)$$

TMFs between zero and 1 imply that the chemical is present throughout the food web but is not being biomagnified, whereas a TMF of >1 indicates that a chemical is biomagnifying (*13, 19*). Negative values indicate that a chemical is decreasing in concentration with each step in the food web, either because it is not accumulated or readily metabolized and eliminated at higher trophic levels.

The second method determined biomagnification factors (BMF_{TL}) for individual species, corrected for trophic level as outline in Fisk et al. (*13*), using:

$$BMF_{TL} = [\text{predator}]/[\text{prey}]/(TL_{pred}/TL_{prey}) \quad (6)$$

where [predator] and [prey] are the wet wt concentrations of analyte in the predator and prey species, respectively, and TL is the trophic level based on $\delta^{15}N$ for the predator and prey. Subscripts for whole organisms (w) and liver (l) are added as suffices to define the tissues being compared since different tissues were analyzed. For example, $BMF_{TL(w:l)}$ would be the ratio of the concentration in the whole organism of the predator to that of the concentration in the liver of the prey.

It should be stressed that liver tissues were used to determine PFOS concentrations in redfish, seabirds, and marine mammals. Liver is generally thought to have the highest concentrations of PFOS, and determination of trophic transfer using muscle tissue or whole body concentrations may yield lower values

Results

PFOS and PFOA. PFOS was detected in all the species analyzed. PFOS concentrations were generally greater than that of PFOA (Table 1) with the mean (calculated as the arithmetic mean ± 1 SE) PFOS concentrations ranging from 0.28 ± 0.09 ng/g in clams ($n = 5$) to 20.2 ± 3.0 ng/g in glaucous gulls ($n = 5$). PFOA concentrations in clam and black-legged kittiwake samples ($n = 5$) analyzed were below MDLs. Mean concentrations of PFOA in zooplankton ($n = 5$) were 2.6 ± 0.3 ng/g. PFOS was detected in 4 of the 5 shrimp samples

TABLE 1. Recovery and Blank-Corrected Mean Concentrations (arithmetic mean ± 1 SE, ng/g wet wt) of Fluorinated Organic Compounds in Eastern Arctic Food Web

species[a]	PFOS ng/g (wet wt)	PFOA ng/g (wet wt)	*N*-EtPFOSA ng/g (wet wt)	PFOSA ng/g (wet wt)
zooplankton	1.8 ± 0.3[b] (n = 5) 1.1−2.6[c]	2.6 ± 0.3 (n = 5) 1.7−3.4	0.39 ± 0.07 (n = 5) nd−0.65	nd[d] (n = 5)
clams	0.28 ± 0.09 (n = 5) 0.08−0.6	nd (n = 5)	20.1 ± 16.5 (n = 5) 1.9−85.9	nd (n = 5)
shrimp	0.35 ± 0.15 (n = 7) nd−0.9	0.17 ± 0.06 (n = 7) nd−0.5	10.4 ± 8.6 (n = 5) nd−44.8	nd (n = 5)
Arctic cod	1.3 ± 0.7 (n = 6) 0.3−4.7	0.16 ± 0.06 (n = 6) nd−0.5	92.8 ± 41.9 (n = 3)[e] 9.6−144.6	nd (n = 3)[e]
redfish	1.4 ± 0.9 (n = 7) nd−6.3	1.2 ± 0.8 (n = 7) nd−5.3	nd (n = 2)[f]	nd (n = 2)[f]
walrus	2.4 ± 0.4 (n = 5) 1.4−3.6	0.34 ± 0.09 (n = 5) nd−0.7	na[g]	na
narwhal	10.9 ± 2.3 (n = 5) 5.4−17.7	0.9 ± 0.1 (n = 5) 0.7−1.1	10.9 ± 7.1 (n = 5) 0.5−6.9	6.2 ± 2.3 (n = 5) 6.8−10.9
beluga	12.6 ± 1.1 (n = 5) 9.8−15.8	1.6 ± 0.3 (n = 5) 1.0−2.8	3.8 ± 2.2 (n = 5) 0.1−11.7	20.9 ± 7.9 (n = 5) 3.9−48.4
black-legged kittiwake	10.0 ± 4.6 (n = 4) 1.2−20	nd	n/a	n/a
glaucous gulls	20.2 ± 3.9 (n = 5) 9.9−33.2	0.14 ± 0.05 (n = 5) nd−0.3	n/a	n/a

[a] See text for tissues analyzed. [b] Arithmetic mean ± standard error. [c] Range. [d] Below MDLs. [e] Two samples consisted of pools of 2 individual organisms. [f] Pools of two livers of individual organisms. [g] Not analyzed.

analyzed at a mean concentration of 0.35 ± 0.15 ng/g; PFOA was detected in only 3 samples at a mean concentration of 0.17 ± 0.06 ng/g. PFOA was detected in only a single Arctic cod (0.47 ng/g) (n = 5) and was about 3 times smaller than average PFOS concentrations (1.3 ± 0.7 ng/g). Duplicates of Arctic cod, analyzed to check for reproducibility of the method, were within 80% of each other for PFOS. Unfortunately, a similar comparison could not be made for PFOA since it was not detected in the sample.

PFOS and PFOA concentrations were similar in the deepwater redfish (n = 5); however, PFOA was detected in only 2 of the samples while PFOS was detected in 4 of the samples analyzed. For the marine mammals, mean PFOS concentrations were statistically different ($p < 0.001$; two-tailed t-test) between beluga (12.6 ± 1.1 ng/g) (n = 5) and walrus (2.4 ± 0.4 ng/g) (n = 5) and between narwhal (10.9 ± 2.3 ng/g) (n = 5) and walrus ($p < 0.05$). However, there were no significant differences in mean PFOS concentrations between beluga and narwhal ($p > 0.1$). Statistical differences in the mean PFOA concentrations were observed between walrus (0.34 ± 0.09 ng/g) and narwhal (0.9 ± 0.1 ng/g; $p < 0.005$) and between walrus and beluga (1.6 ± 0.3 ng/g; $p < 0.05$).

Mean PFOS concentrations in black-legged kittiwake (10.0 ± 4.6 ng/g) were 2 times smaller than that found in the glaucous gulls (20.2 ± 3.9 ng/g). PFOA concentrations were below MDLs in all the black-legged kittiwake and were detected in only one of the glaucous gulls (0.33 ng/g).

***N*-EtPFOSA and PFOSA.** Due to the limited amount of sample material, *N*-EtPFOSA and PFOSA were not analyzed in walrus or sea-birds. *N*-EtPFOSA was detected in all the other species analyzed except for redfish, while PFOSA was detected only in beluga and narwhal (Table 1).

Mean *N*-EtPFOSA concentration ranged from below MDLs in the redfish to 92.8 ± 41.9 ng/g (wet wt) in Arctic cod. For the invertebrate species, mean *N*-EtPFOSA concentrations were highest in the clams (20.1 ± 16.5 ng/g) followed by shrimp (10.4 ± 8.6 ng/g) and zooplankton (0.39 ± 0.07 ng/g). There were also no statistically significant differences between mean *N*-EtPFOSA concentrations in beluga (3.8 ± 2.2 ng/g) and narwhal (10.9 ± 7.1 ng/g). Mean PFOSA concentrations were not statistically different ($p > 0.1$) between beluga (20.9 ± 7.9 ng/g) and narwhal (6.2 ± 2.3 ng/g).

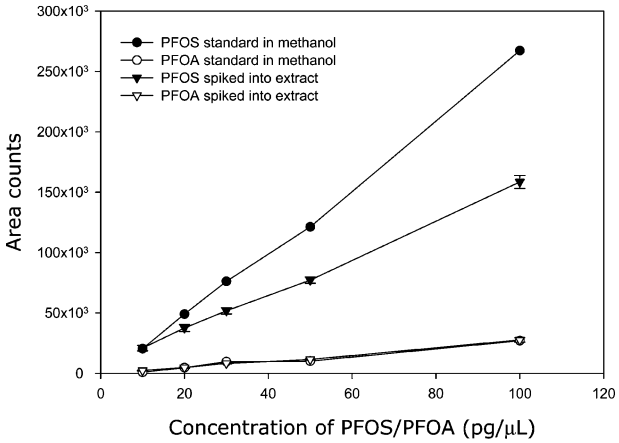

FIGURE 1. Effect of sample matrix on the ionization of PFOS and PFOA.

Matrix Effects. Differential suppression of ion signals as a result of matrix interferences has not been documented for PFAs. If we assume that clam extracts are suitable surrogates for other biotic extracts, then the results of our studies suggest that suppression of the PFOA ion signal caused by the matrix is negligible but suppression of the PFOS ion signal increases with increasing PFOS concentration (see Figure 1). Without isotopically labeled IS, possible ways to account for analyte ion suppression include standard addition, quantifying samples against spiked tissue extracts, or diluting the final volume of extracts that are injected. Future PFAs studies in our laboratory will compare these two approaches more closely.

Discussion

Concentrations. Perfluorinated compounds are now one of the more frequently detected class of organic contaminants found in Canadian Arctic biota (*20*). This study as well as recent studies (*3*, *6*) have found concentrations of PFOS and PFOA in Arctic seabirds and marine mammals to be in the range of legacy organochlorines (OCs), such as PCBs and DDT. For example, mean concentrations of PFOS in black-legged kittiwake livers (8 ng/g, wet wt) in this study were

only 3 times lower than that of total chlordane and PCB 153 in the same samples (*21*). Similar trends exist for glaucous gulls.

Concentrations of PFOS reported in this studied are slightly higher or in the range of concentrations reported for this compound in other Canadian Arctic biota. Martin et al. (*6*) reported low nanogram per gram concentrations of PFOS in livers of northern fulmar (*Fulmarus glacialis*) from Prince Leopold Island that were 8−20 times lower than that of the glaucous gulls and black-legged kittiwakes reported here. However, the seabird samples used by Martin et al. were collected in 1993, and concentrations of PFOS in ringed seals (*Phoca hispida*) collected in 1998 from the Canadian Arctic (*6*) were similar to those found in seabirds, beluga, and narwhal from this study. As well, interspecies differences in PFOS concentrations exist in seabirds and this may, along with spatial differences, may explain the differences observed between this study and Martin et al. (*6*). For example, PFOS concentrations in cormorant (*Phalacrocorax carbo*) livers (61 ng/g, wet wt) from the Mediterranean Sea were 3 times higher than that of glaucous gulls (*22*). These differences are likely related to their diet choices, migration habitats, exposure, and differences in metabolic capabilities, all of which have been shown to influence concentrations of organochlorines in seabirds (*21*, *23*, *24*).

It is not known why PFOS and PFOA concentrations are greater in zooplankton compared to clams and shrimp. The fact that clams and shrimp have a greater benthic association and lower PFOS and PFOA concentrations than zooplankton is suggestive that concentrations and exposure of PFOS and PFOA may be greater in the water column resulting in higher concentrations in zooplankton.

Bioaccumulation, Trophic Transfer, and Biomagnification. The pattern of bioaccumulation of the perfluorinated compounds examined in this study is complicated and varies among the different compounds. A major confounding factor is biotransformation, which is currently not well studied for perfluorinated compounds. In particular, the potential formation of PFOS from *N*-EtPFOSA and PFOSA and possible formation from other perfluorinated compounds not measured in this study make assessing the trophic transfer of PFOS difficult. A lack of correlation between body burdens of *N*-EtPFOSA, PFOSA, and PFOS was found but is not surprising considering that there may be numerous PFOSA and PFOS metabolic precursors. For example, the perfluorooctanesulfonamides are thought to degrade to PFOS via the PFOSA intermediate (*12*). The biotransformation of PFOSA from other precursor compounds is likely to confound any relationships between concentrations of PFOSA and PFOS. Biotransformation of one contaminant from a similar contaminant has been observed with PBDEs in fish (*25*, *26*), and biotransformation has also been shown to increase the estimated TMF and BMF of *p*,*p*′-DDE and heptachlor epoxide in Arctic biota (*13*). A better understanding of biotransformation rates, all formation pathways, and a full list of perfluorinated precursors would improve assessments of PFOS bioaccumulation.

Despite these difficulties, it is clear that PFOS biomagnifies through this Arctic marine food web. This is exemplified by the significant relationship between ln concentration of PFOS and TL based on δ^{15}N (Figure 2, $r^2 = 0.51$, $p < 0.0001$) and TL-adjusted BMFs calculated for various species (Table 2). Other studies have made similar conclusions about PFOS. Van de Vijver et al. (*11*) found a significant positive linear relationship between PFOS concentrations and δ^{15}N in livers of four species of marine mammals from the North Sea. Martin et al. (*6*) reported that concentrations of PFOS were greater in upper trophic level organisms. Neither study attempted to quantify the magnitude of biomagnification or trophic transfer.

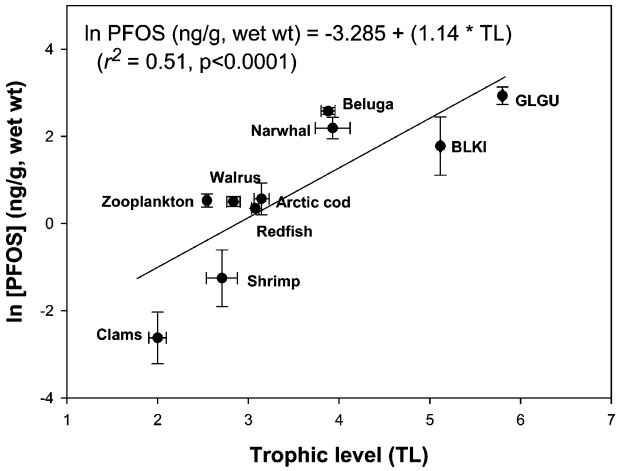

FIGURE 2. Mean (±1 SE) PFOS concentrations (ng/g, wet wt)—trophic level relationship for the eastern Arctic food web. Regression analysis: ln [PFOS] = −3.28 + 1.14 (TL) ($r^2 = 0.51$, $p < 0.0001$). BLKI = black-legged kittiwakes; GLGU = glaucous gulls.

TABLE 2. Trophic Level (TL) Biomagnification Factors (BMFs) for PFOS, PFOA, PFOSA, and *N*-EtPFOSA in the Eastern Arctic Food Web[a,b]

predator:prey	PFOS	PFOA[c]	PFOSA[c]	*N*-EtPFOSA[c]
$walrus_l$:$clam_w$	4.6	1.8		
$narwhal_l$:cod_w	7.2	1.6	347	0.1
$beluga_l$:cod_w	8.4	2.7	889	0.04
$beluga_l$:$redfish_l$	4.0	0.8	860	9.6
$BLKI_l$:cod_w	5.1	0.3		
$GLGU_l$:cod_w	9.0	0.6		
cod_w:$zooplankton_w$	0.4	0.04	0.7	238

[a] See text for details on calculation of BMF_{TL}. [b] Concentration data in redfish, seabird, and marine mammal data are for liver, but for cod and invertebrates, data are whole body. [c] Concentration of half of the MDL was assumed in those instances where concentrations were below MDLs

Differences in PFOS concentrations among tissues are an important issue that needs to be identified when assessing trophic transfer of PFOS-like compounds. PFOS accumulates preferentially in the blood and liver rather than in lipids (*10*). Greater concentrations in the liver as compared to muscle tissue is also observed for hydrophobic and lipophilic OCs, but this is dealt with by assuming that OCs are in equilibrium among the various tissues and by using lipid-based concentrations to calculate TMFs and BMF_{TL}s. The use of lipid based concentrations negates OC concentration differences among various tissues caused by differences in lipid content of the tissues. Since PFOS is not a lipophilic compound, the use of lipid based concentrations is not applicable to compensate for differences in PFOS concentrations among tissues. Thus, TMFs and BMF_{TL}s based on PFOS concentrations in muscle may be lower than those estimated using liver. Unfortunately, PFOS concentrations in muscle of seabirds and marine mammals were not determined for this study and differences in TMFs and BMF_{TL}s between tissues cannot be addressed. PFOS concentration in lower TL organisms (fish and invertebrate) were based on whole body, which is realistic since they would be consumed whole by seabirds and marine mammals. However, at this point it is necessary to identify that the BMFs and TMFs determined for PFOS and associated compounds are based on liver concentrations in seabirds and marine mammals.

TMFs have been used to describe the increase of OCs from one trophic level to the next and are usually derived from the slope of the regression between an organisms' lipid normalized OC concentrations and trophic position, as

determined by stable isotopes of nitrogen (*27*). Furthermore, TMFs represent the average increase in contaminant concentration in food webs rather than the variability shown between species and compounds in BMF_{TL} calculations, which represent only specific predators. The TMF for PFOS in this study was calculated to be 3.1. TMFs have been determined for a range of OCs (PCBs, chlordanes, DDTs) in a number of Arctic food webs (*13*, *28*, *29*) and are generally in the range of 2−15 (*24*). As stated above, it should be stressed that TMFs, and BMF_{TL}s, for PFOS are based on concentrations in the liver of seabirds and marine mammals. PFOS $BMF_{TL(l:w)}$ for black-legged kittiwake using Arctic cod as the prey item (= 5.1) was generally lower than for PCB congeners reported by Fisk et al. (*13*) but similar to *p*,*p*′-DDT for the same feeding relationship. The highest PFOS BMF_{TL} was seen for the glaucous gull using Arctic cod as the prey item ($BMF_{TL(l:w)}$ = 9.0) and was similar to that of some chlorinated biphenyls (CBs) (*13*). The high BMF in glaucous gull is likely due in part to the fact these gulls feed or scavenge on higher trophic level organisms (*30*). However, these TMFs and BMF_{TL}s estimated for OCs were based on lipid corrected concentrations. Since lipid levels generally increase with trophic level, calculation of TMFs and BMF_{TL}s for these OCs using wet wt concentrations will yield a greater value. Regardless, concentrations of PFOS increase across the eastern Arctic food web at a magnitude that is similar to legacy OCs.

BMF_{TL}s calculated for PFOS were fairly similar between seabird and marine mammal species but greater than those estimated for Arctic cod. Concentrations of PFOS in Arctic cod were based on whole bodies so higher concentrations, and BMF_{TL}s may have been found if the livers of Arctic cod had been used. As well, the higher BMF_{TL}s for the birds/mammals could also be due to a combination of greater biotransformation and feeding rates in these organisms. Higher concentrations and BMFs for OCs in mammals and birds have been shown to be related to greater feeding rates (*13*). Although information for perfluorinated compounds is lacking, it is generally assumed that mammals and birds have a greater ability to biotransform organic contaminants than lower level trophic organisms (*27*, *31*) and likely greater ability to biotransform PFOS precursors to PFOS.

Bioaccumulation of *N*-EtPFOSA and PFOSA was different from that of PFOS and PFOA. Unlike other hydrophobic halogenated organic compounds, concentrations of *N*-EtPFOSA and PFOSA do not correlate with lipid content of samples from various species. This may be related in part to their susceptibility to biotransformation. Mean *N*-EtPFOSA and PFOSA concentrations were highest in upper TL animals, and PFOSA was not detected in any species other than narwhal and beluga. If lower level organisms have lower metabolic capacities (differences in metabolic capabilities among different marine biota species has been observed for other organohalogen contaminants), then the transformation of *N*-EtPFOSA to PFOSA may be negligible and result in low PFOSA concentrations. Nondetectable concentrations of PFOSA in lower level organisms in this study are consistent with an explanation of low metabolic capacities. It is also possible that (i) PFOSA biomagnifies and concentrations in lower TL organisms are below detection limits, (ii) exchange of PFOSA between the water and the animals at lower TL is occurring, and (iii) use of whole bodies resulted in concentrations that were below detection limits. Conversely, mammals have less efficient water exchange mechanisms, and excretion is complication by the enterohepatic recirculation (*32*).

Although no relationship was found between concentrations of PFOS and *N*-EtPFOSA or PFOSA for beluga, there were differences in *N*-EtPFOSA and PFOSA concentrations. Mean *N*-EtPFOSA concentrations were 5-fold less than those of PFOSA. This is suggestive that belugas have a greater ability to biotransform *N*-EtPFOSA as compared to narwhal and the other biota examined in this study since beluga and narwhal feed at a similar trophic level and likely have similar exposure to these compounds. A variation in exposure would also be reflected in the body burdens of PFOSA; as with some other halogenated contaminants, beluga (and narwhal) are likely exposed to larger amounts of these PFOS precursors than other organisms because of their higher TL in the marine food web.

The high BMF_{TL} values for PFOSA in Table 2 should be treated with caution as the concentrations of PFOSA in the cod and redfish prey species were assumed to be half of the MDL (i.e., 0.017 ng/g). If other PFOSA-type compounds in addition to *N*-EtPFOSA are present at low concentrations and are being transferred through the food chain, metabolism to PFOSA by upper TL species would result in high PFOSA BMF_{TL} values. It is known that PFOSA is used as the chemical building block in the industrial synthesis of numerous other PFOSA-type compounds (*33*). For example, the perfluorooctanesulfonamidoethanols (PFOSEs), used in various surface treatment applications and detected in air samples from southern Ontario (*34*), are synthesized from PFOSA (*32*). *N*-Ethyl-*N*-(2-hydroxyethyl)perfluorooctanesulfonamide (*N*-EtPFOSE) has also recently been shown to biotransform to PFOS in experimental animals (*35*). The PFOSEs are in turn used to synthesize analogous acrylates, urethanes, and phosphate esters (*33*). None of these compounds were examined in this study but may be present in lower (and upper) TL organisms that may subsequently biotransform them to PFOSA.

A systematic study on the potential matrix effects (in particular biotic matrixes) on ion intensity of fluorinated organic compounds has not been investigated in detail. An attempt was made to do so in this study. Assuming that the clam matrix is a suitable surrogate for the other animals, then this suggests that our reported PFOS concentrations are perhaps underestimated but that PFOA concentrations are more accurate (assuming that it is recovered in a manner similar to PFBS). The effect of the ion suppression for PFOS is also more pronounced at higher concentrations. This in turn has implications on our calculated BMF_{TL}s (and TMFs). For example, if clams are a suitable matrix for glaucous gulls and Arctic cod, our "matrix-corrected" $BMF_{TL(l:w)}$ for this feeding relationship would be 12.7, which is 1.4 times higher than the "uncorrected" $BMF_{TL(l:w)}$. Future studies, especially on PFOS, should consider ion suppression arising as a result of the sample matrix.

Although analytical difficulties with perfluorinated compounds may influence the accuracy of reported concentrations, this does not diminish the importance of these findings. Perfluorinated compounds have been identified as chemicals of concern in the Arctic due to their unique toxicological properties (*20*). The concentrations reported here and in Martin et al. (*6*) provide additional evidence that these compounds require further study and monitoring in the Arctic.

Age, year of sampling, and geographical sampling location are some of the factors that influence intraspecies differences in concentrations of persistent organohalogens in biota. However, it is difficult to determine the extent to which these variables affect the concentration of the compounds investigated in this study since samples were not chosen to evaluate these factors. Past work suggests there is no correlation between PFOS concentrations and age—no significant associations between age and PFOS concentrations were found in livers of ringed (*Phoca hispida*) and gray seals (*Halichoerus grypus*) from the Baltic Sea (*36*) or in livers of bottlenose dolphin (*Tursiops truncatus*) from the coastal waters of Florida (*4*).

In conclusion, PFOS and PFOA are detected at low nanogram per gram concentrations in the eastern Arctic food web with PFOS concentrations consistently higher than those of PFOA. Bioaccumulation tendencies were different between PFOS and PFOA, especially in upper TL animals. PFOA did biomagnify between individual feeding relationships but not through the entire food web. TMFs for PFOS were slightly lower than those of other persistent organochlorines. Significant concentrations (ng/g, wet wt) of the neutral-PFOS compounds, *N*-EtPFOSA and PFOSA, were detected in many of aquatic organisms. Because of their susceptibility to metabolism, no correlation between lipid-corrected concentrations of PFOSA or *N*-EtPFOSA were observed in the animals. Further work is necessary to determine other neutral PFOSA precursors in biota, which may help to explain the trophodynamics of PFOS in food webs. Time-related changes in concentrations of fluorinated compounds in animals from the Arctic also warrants future research.

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Supporting Information Available

A table with information on the samples and concentrations of the fluorinated organic compounds analyzed in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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