Perfluoroalkyl Contaminants in an Arctic Marine Food Web: Trophic Magnification and Wildlife Exposure

BARRY C. KELLY,[†] MICHAEL G. IKONOMOU,[*,‡] JOEL D. BLAIR,[†] BLAIR SURRIDGE,[§] DALE HOOVER,[§] RICHARD GRACE,[§] AND FRANK A. P. C. GOBAS[†]

School of Resource and Environmental Management, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6, Contaminant Sciences, Institute of Ocean Sciences, Fisheries and Oceans Canada (DFO), 9860 West Saanich Road, Sidney, British Columbia, Canada, V8L 4B2, AXYS Analytical Services Ltd, 2045 Mills Road, Sidney BC Canada, V8L 5X2

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To better understand the bioaccumulation behavior of perfluoroalkyl contaminants (PFCs), we conducted a comparative analysis of PFCs and lipophilic organohalogens in a Canadian Arctic marine food web. Concentrations of perfluorooctane sulfonic acid (PFOS), perfluorooctansulfoamide (PFOSA), and C_7-C_{14} perfluorocarboxylic acids (PFCAs) ranged between 0.01 and 0.1 ng·g^{-1} dry wt in sediments and 0.1 and 40 ng·g^{-1} wet wt in biota, which was equivalent to or higher than levels of PCBs, PBDEs, and organochlorine pesticides. In beluga whales, PFOS and PFCA concentrations were higher ($P < 0.05$) in protein-rich compartments (liver and blood), compared to other tissues/fluids (milk, blubber, muscle, and fetus). In the marine mammalian food web, concentrations of PFOSA and lipophilic organochlorines (ng·g^{-1} lipid equivalent) and proteinophilic substances (i.e., PFOS and C_8-C_{14} PFCAs, ng·g^{-1} protein) increased significantly ($P < 0.05$) with trophic level. Trophic magnification factors (TMFs) of organochlorines ranged between 5 and 14 and exhibited significant curvilinear relationships ($P < 0.05$) with octanol−water and octanol−air partition coefficients (K_{OW}, K_{OA}). TMFs of perfluorinated acids (PFAs) ranged between 2 and 11 and exhibited similar correlation ($P < 0.05$) with protein−water and protein−air partition coefficients (K_{PW}, K_{PA}). PFAs did not biomagnify in the aquatic piscivorous food web (TMF range: 0.3−2). This food web specific biomagnification behavior was attributed to the high aqueous solubility and low volatility of PFAs. Specifically, the anticipated phase-partitioning of these proteinophilic substances, represented by their protein−water (K_{PW}) and protein−air (K_{PA}) partition coefficients, likely results in efficient respiratory elimination in water-respiring organisms but very slow elimination and biomagnification in air-breathing animals. Lastly, the results indicate that PFOS exposure in nursing Hudson Bay beluga whale calves (CI_{95} range = 2.7×10^{-5} to 1.8×10^{-4} mg·kg bw^{-1}·d^{-1}), exceeds the oral reference dose for PFOS (7.5×10^{-5} mg·kg bw^{-1}·d^{-1}), which raises concern for potential biological effects in these and other sensitive Arctic marine wildlife species.

Introduction

Perfluoroalkyl chemicals (PFCs) are stable fluorinated compounds that exhibit both polar and apolar moieties. These amphipathic compounds, due to their ability to repel both water and oils, are commonly used in the production of commercial stain repellents, surface coatings, firefighting foams, insecticides, and cleaners. Perfluorinated acids (PFAs), including perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs), have been detected in blood and tissues of wildlife and humans, worldwide, including remote regions such as the Arctic (*1*−*9*). Perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$) and perfluorooctane sulfonic acid (PFOS, $C_8F_{17}SO$-) are the most extensively studied PFAs. PFA precursor compounds, including fluorotelomer alcohols (FTOHs) and perfluoroalkyl sulfonamide alcohols (PFASs), which are used in a variety of fluorochemical manufacturing processes, can degrade to PFAs through photolysis and/or biotransformation processes (*10, 11*). Bioaccumulation of PFAs in wildlife and humans is a concern as elevated exposure to those compounds can impact lipid metabolism, reproduction, and development (*12*).

In May 2000, 3 M voluntarily abandoned its long-standing perfluorooctanesulphonyl fluoride (POSF), C_8-based electrochemical fluorination (ECF) chemistry used to produce Scotchgard products. Other fluorochemical producers (e.g., Dupont), continue fluorotelomerization (FT) processing to manufacture fluorotelomer-based products. PFOS and PFOS precursors were proposed for international regulation under the Stockholm Convention in 2001 (*13*). In 2004, Environment Canada initiated a temporary ban on fluoropolymers containing FTOHs (*14*).

Toxicokinetic studies (*15*−*18*) indicate PFAs exhibit high dietary absorption efficiencies, possibly due to bilary enterohepatic recirculation (*15*), and have a high affinity for plasma proteins such as albumin (*16*). In contrast to lipophilic contaminants such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated (PBDEs), which are associated with organism lipids, PFAs are proteinophilic and tend to accumulate in blood, liver, and kidneys (*17*). Bioconcentration factors (BCFs) are relatively low for C_8-C_{11} PFAs (4.0−4900 L/kg), while BCFs of long-chain PFAs ($C_{12}-C_{14}$ PFCAs) are higher (18,000−40,000 L/kg) (*17*). Field studies report varying degrees of PFA bioaccumulation in freshwater and marine food webs (*5, 6, 9, 19, 20*). The current understanding is that PFOS and longer chain PFCAs (>C_8) bioaccumulate and persist in protein-rich compartments of fish, birds, and marine mammals (*21*).

Regulatory agencies identify bioaccumulative substances as liphophilic compounds exhibiting BCFs or bioaccumulation factors (BAFs) > 5,000 in aquatic organisms or exhibiting octanol−water partition coefficients (K_{OW}) > 10^5. This method can lead to misidentification of moderately lipophilic compounds with high octanol−air partition coefficient (K_{OA}), due to a corresponding low rate of aerial respiratory elimination and biomagnification in air-breathing animals (*22*). Chemical bioaccumulation in food webs is complex and undoubtedly includes large inter- and intraspecies variability in biological factors (feeding ecology, trophic status, growth) as well as chemical factors (exposure level, pharmacokinetics, and biotransformation rates), which can greatly affect tissue residue concentrations. An accurate and rigorous measure

* Corresponding author e-mail: IkonomouM@pac.dfo-mpo.gc.ca.
† Simon Fraser University.
‡ Fisheries and Oceans Canada.
§ AXYS Analytical Services Ltd.

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of chemical biomagnification potential is the trophic magnification factor (TMF), which represents the average concentration change over a defined trophic range of a food web (*23, 24*).

It is well established that stepwise increases of lipophilic contaminant concentrations with increasing trophic level (on a lipid weight basis), represent increases in chemical activity or fugacity in the food web (i.e., biomagnification). PFA biomagnification is commonly evaluated using wet weight based concentrations in blood, liver tissue, and/or whole organisms (*5, 6, 9, 19, 20*). Proteinophilic PFA concentrations exhibit positive correlation with protein content, rather than lipid content in organism tissues/fluids (*25*). Thus, PFA kinetics may be more accurately represented by protein−water and protein−air partition coefficients (K_{PW}, K_{PA}) and PFA biomagnification may best be evaluated by TMFs based on protein normalized concentrations in food web organisms.

The main objective of this study is to evaluate trophic magnification and wildlife exposure levels of PFCs in a Canadian Arctic marine food web. We measured concentrations of several PFCAs, PFSAs, and PFOSA in Arctic marine sediments and various organisms. PFC concentrations and observed TMFs were compared to those of persistent lipophilic organohalogens (PCBs, OCPs, and PBDEs) in this food web. We also investigated concentration differences between various tissues/fluids (i.e., blood, liver, muscle, blubber, milk, and fetus) in individual male and female beluga whales of different ages. The study provides new information regarding perfluoroalkyl contaminants including (i) the degree of trophic magnification, (ii) the influence of physical−chemical properties on bioaccumulation behavior, (iii) tissue distribution and exposure levels in Arctic marine wildlife, and (iv) human dietary exposure for indigenous Inuit people of northern Canada.

Materials and Methods

Samples. During the months of May to September between 1999 and 2003 marine sediments and tissues/fluids of Arctic marine organisms (macroalgae, bivalves, fish, seaducks, and marine mammals) were collected from the Hudson Bay region of northeastern Canada, (64° 15′ N 113° 07′ W), (Figure S1). Details regarding sample origin and handling procedures are reported elsewhere (*22, 26*) and provided in the Supporting Information (SI).

Extraction and Cleanup. Sediment and biological samples were extracted at the Institute of Ocean Sciences (IOS), Fisheries and Oceans Canada (DFO), Sidney, British Columbia, using modified versions of methods presented by Higgins et al. (*27*) and Tanyiashu et al. (*28*). Sediment samples (ca. 10 g wet wt) were added to 50-mL polypropylene centrifuge tubes and spiked with internal surrogate spiking solution (360 ng of $^{13}C_2$ PFOA, 120 ng of $^{13}C_2$ PFDA, 120 ng of $^{13}C_2$ PFDoA, and 120 ng of $^{13}C_4$ PFOS). After 20 min, 10 mL of 0.1% acetic acid in MeOH was added and samples were extracted on a shaker table for 16 h. Aliquots (1 mL) of the extracts were diluted with HPLC water to 100 mL prior to purification via solid-phase extraction (SPE). Biota samples (ca. 10 g of macroalgae; 2 g of muscle tissue; 2 g of liver tissue; 10 g of whole blood; 2 g of milk; 1 g of blubber) were homogenized, spiked with spiking standards, then extracted with 10 mL of 0.01 M KOH in MeOH on a shaker table for 16 h. Aliquots (1 mL) were diluted to 100 mL prior to SPE. SPE cartridges (OasisWAX, Milford, MA; 6 cc, 150 mg, 30 μm) were conditioned with 3 rinses of MeOH, followed by 3 mL of 0.1 M formic acid. After sample loading, SPE columns were washed with 3 mL of 50% MeOH 50% 0.1 M formic acid. SPE cartridges were then eluted with 2 mL of MeOH. Extracts were reduced to <1 mL and spiked with the recovery standard ($^{13}C_4$−PFOA) prior to analysis.

Quantification. PFC concentrations were analyzed by liquid chromatography tandem mass spectrometry (LC/MS/MS) at AXYS Analytical Services Ltd. in Sidney, British Columbia, Canada. Separations of the target analytes were achieved with a Waters 2795 Alliance HPLC using an Xtera C18 3.5 μm, 2.1 mm × 100 mm analytical column and a guard column (C18 1 mm opti-guard column). Mobile phases included 0.1% ammonium acetate/0.1% acetic acid in HPLC grade water (Solvent A) and 90% acetonitrile (Solvent B). Gradient elution consisted of 0−0.5 min, 40−70% B, 0.5−6.5 min, 70−100% B then a 1 min hold time followed by a 4 min re-equilibration to starting conditions. Injection volumes were 15 μL. A Micromass Quattro Ultima tandem quadrupole mass spectrometer (Manchester, UK), equipped with Z-spray electrospray (ESI) ion source operating in negative ion multiple reaction monitoring (MRM) mode was employed for sample analysis. Desolvation and cone gas (nitrogen) flows were set at 450 L/h and 80 L/h, respectively. Ion source temperature was 120 °C and the desolvation temperature was 400 °C. MRM transitions used for analyte quantification are shown in Table S1.

Calibration curves were constructed from the analysis of 7 calibration solutions (range 0.2−500 ng/mL). Analyte concentrations were determined with respect to the mass-labeled quantification and internal standards using isotope dilution method (Table S1). Recoveries of labeled surrogate standards ranged between 30 and 120%. Two procedural (or method) blanks were analyzed with every batch of 12 samples. Method detection limits (MDLs) were determined as 3 standard deviations (SD) above the mean blank levels. When analyte concentrations were nondetectable in blanks, the MDL was set equal to the instrument detection limit (IDL), determined from the analyte peak response with a signal-to-noise ratio of 3. When analyte concentrations were detected in blanks, sample concentrations were blank corrected. C_7−C_{14} PFCAs were occasionally observed in blanks, but at relatively low levels compared to extracted sample matrix.

Data Compilation and Treatment. Geometric means (GM, ng·g^{-1} wet wt), along with asymmetric SD and 95% confidence intervals (CI_{95}) were calculated when frequency of detection was >50% (Table S2). PCB, OCP, and PBDE concentrations were previously measured in these samples (*22, 26*). We compiled previously reported PFC data for Hudson Bay fish (*4*), ringed seals (*29*), and polar bears (*4, 7*). PFA concentrations were also expressed on a protein weight basis (ng·g^{-1} protein wt), using previously reported protein content (P_{TOTAL} %) values of biological tissues/fluids (see SI for details).

One-way Analysis of Variance (ANOVA) was used to assess concentration differences between different body tissues/fluids. Log-linear regressions were conducted between the logarithm ($\log_{10}$) of the chemical concentration in biota (C_B) and trophic level (TL), i.e., $\log C_B = (m \times TL) + b$, where m is slope and b is y-intercept. TMFs were determined as 10^m. TMFs of PFAs were determined using both wet weight concentrations (TMF_{WW}) and protein corrected concentrations (TMF_{PW}). TMFs of PFOSA and other lipophilic organohalogens were derived using lipid corrected concentrations (TMF_{LW}).

We compiled physical−chemical properties of PFCs, based on previous calculated values and empirical observations (Table S3). K_{OW} and K_{OA} for individual PFCs values ranged between 10^3−10^9 and 10^6−10^8, respectively. Corresponding K_{PW} and K_{PA} values, which were slightly lower than K_{OW} and K_{OA} values, were determined from a previously observed relationship between K_{OW} and K_{PW} during chemical partitioning experiments using bovine serum albumin (BSA) (*30*).

Lastly, dietary exposure estimates (mg·kg bw^{-1}·d^{-1}) for PFOS and PFOA, as well as PCBs and PBDEs in nursing beluga

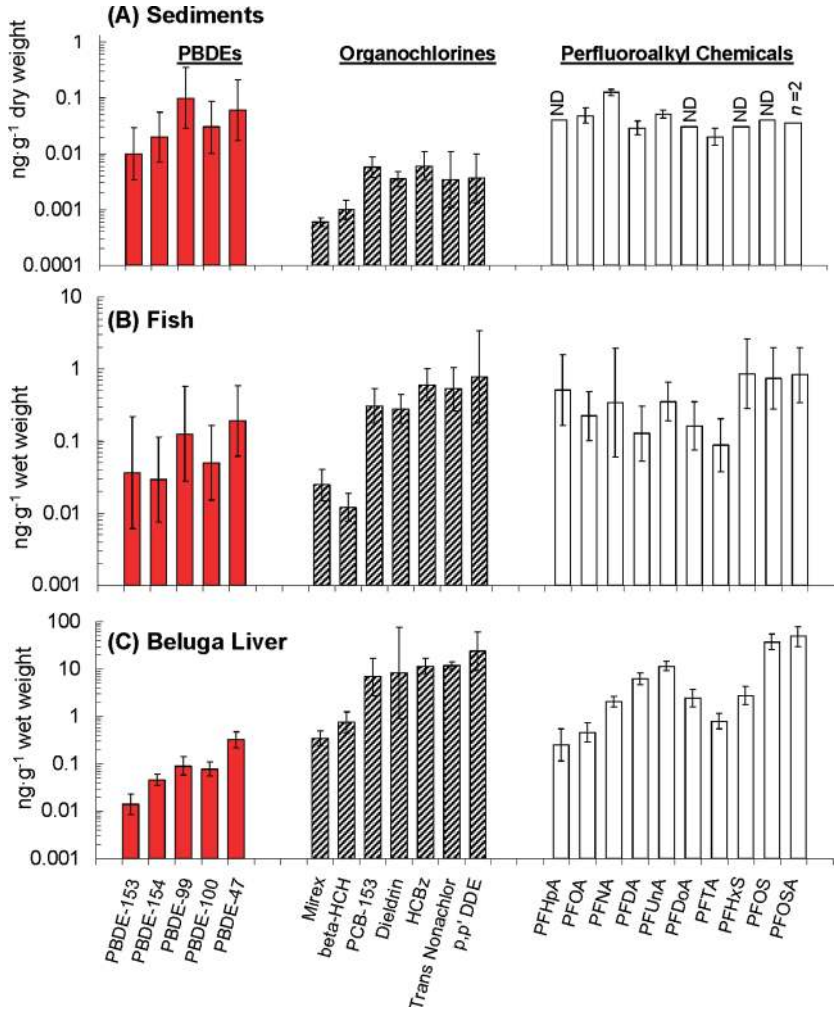

FIGURE 1. Concentrations (ng·g^{-1} wet wt) of selected lipophilic organohalogens and perfluoroalkyl contaminants in (a) sediments, (b) fish, and (c) beluga whale liver from E. Hudson Bay. Data are geometric means ± 1 SD.

whale calves and adult animals, were determined from mean and CI_{95} concentrations observed in beluga milk and Hudson Bay fish. Additional details regarding dietary exposure assessment are provided in the SI.

Results and Discussion

Concentrations of Perfluoroalkyl Contaminants in Arctic Marine Sediments and Biota. PFCAs, PFSAs, and PFOSA concentrations in sediments, macroalgae, and tissues/fluids of fish, seaducks, and beluga whales are shown in Table S4. PFOA, PFNA, PFDA, and PFUnA were commonly detected in sediments and macroalgae. PFOS and C_7−C_{14} PFCAs were routinely detected in fish, seaduck, and beluga whale samples. PFHxS and PFDS were occasionally detected in beluga whale samples. Levels of PFOA (mean = 0.05 ng·g^{-1} dry wt) and PFOS (<0.04 ng·g^{-1} dry wt) in sediments were lower than previous observations from more populated/urban locations (*27*) (e.g., San Francisco Bay sediments, range: 0.1 to 3.76 ng·g^{-1} dry wt). PFC concentrations in Hudson Bay biota were generally comparable to previous reports in Arctic species (*4, 6, 7, 19, 20, 29*). PFOS concentrations in E. Hudson Bay beluga whales (mean = 37.3 ng·g^{-1} wet wt, CI_{95} = 3.0−109 in male beluga liver) were similar to those observed in beluga whale livers sampled from nearby Baffin Island (12.6 ± 1.1 ng·g^{-1} wet wt) (*6*).

Detected levels of PFCs and PBDEs in sediments were an order of magnitude higher than concentrations of organochlorine contaminants (range: 0.001−0.006 ng·g^{-1} dry wt), (Figure 1a). Conversely, Figure 1b shows concentrations of PFCs, organochlorines, and PBDEs in fish muscle (ng·g^{-1} wet wt) are similar. Figure 1c shows PFC concentrations in beluga liver are generally equivalent to or higher than organochlorine concentrations, while PBDE concentrations are comparatively low.

PFCAs and PFOSA comprised >90% of ΣPFCs in sediments, macroalgae, and fish (Figure S2). PFOS comprised 75−85% of ΣPFCs in wildlife (seaduck, ringed seals, and polar bears), with the exception of beluga whales. In beluga whale liver, PFOSA and PFOS contributed 50% and 40%, respectively. Tomy et al. (*6*) and Hart et al. (*31*) reported similar findings of relatively high PFOSA residue burdens in beluga whales and melon-headed whales (*Peponocephala electra*), respectively. Comparatively high PFOSA burdens in beluga whales may be the result of divergent dietary exposures and/or biotransformation capacity, relative to other Arctic wildlife species (seaducks, ringed seals, polar bears).

Gender, Age, and Tissue Specific Accumulation Patterns in Arctic Beluga Whales. No significant correlations (P > 0.05) were observed between PFC concentration and gender or age of beluga whales (Table S4, Figure S3). Concentrations of PFCs in beluga fetus were generally lower than maternal blood and liver concentrations (Table S4). However, relatively high concentrations of PFUnA (range: 6.1−10.6 ng·g^{-1} wet wt) and PFOS (range: 9.1−12.1 ng·g^{-1} wet wt) were observed in beluga fetus samples. Concentrations of PFOS were relatively high in a beluga calf liver (158 ng·g^{-1} wet wt, n = 1), but this could not be fully validated due to limited sample size. A previous study of PFCs in Tucuxi Dolphins (*Sotalia*

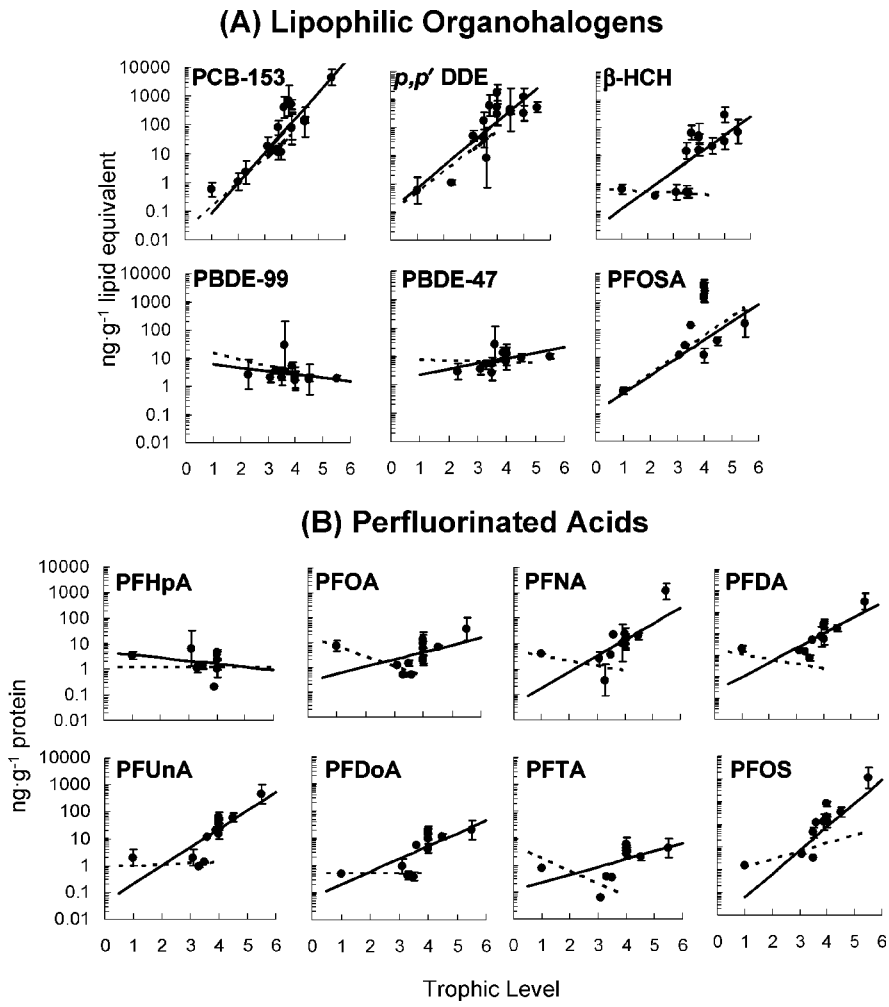

FIGURE 2. Chemical concentrations in organisms of the Arctic marine food web versus trophic level (TL) for (a) lipophilic organohalogens (ng·g^{-1} lipid equivalent) and (b) perfluorinated acids (ng·g^{-1} protein). Data are geometric means ± 1 SD. Data for E. Hudson Bay sculpin and polar bears are from references *4, 7,* and *37*. Solid lines represent log-linear regression of C_B−TL relationship over the entire food web. Dashed line represents those regressions using only data for the piscivorous food web.

guianensis) from Brazil showed elevated PFOS concentrations in liver of calves and fetus, compared to adult animals (*32*).

Wet weight concentrations of PFAs (ng·g^{-1} wet wt) were significantly higher ($P < 0.05$) in liver and blood compared to muscle, blubber, and milk (Figure S4), which is consistent with previous observations (*8*). Perfluoroalkyl chemicals (ΣPFCAs, ΣPFSAs, and PFOSA) represented 70−90% of the total organohalogen burden in blood and liver, but <3% in milk and blubber (Figure S5). Because PFAs are primarily retained in protein-rich compartments (blood and liver), organism- and compartment-specific protein turnover rates may influence the toxicokinetics of these compounds. Also, retention in these compartments may be toxicologically significant, due to potential interference with basic cellular processes such as fatty acid metabolism (*15*) and thyroid hormone transport (*33*).

Biomagnification Behavior. Wet weight concentrations of PFCs (ng·g^{-1} wet wt) increased significantly ($P < 0.05$) with increasing trophic level (Figure S6, Table S5). TMF_{WW} values ranged between 1.43 and 17.4. TMF_{WW} of PFOS (17.4) was substantially higher than that of PFOSA (5.09) and PFOA (3.28). A strong curvilinear relationship ($R^2 = 0.86$) was observed between TMF_{WW} and perfluoroalkyl chain length (Figure S7). Observed TMF_{WW} values were consistent with previously reported TMF values of PFCs (*6, 9, 19*). Tomy et al. (*6*) reported a TMF_{WW} of 3.1 for PFOS in an eastern Arctic (Baffin Island) marine food web. Houde et al. (*9*) investigated PFCs in bottlenose dolphin (*Tursiops truncatus*) food webs and reported TMF_{WW} values of 5.9, 4.9, and 13 for PFOSA, PFOS, and PFOA, respectively. Martin et al. (*5*) reported TMF_{WW} values ranging between 0.4 for PFOSA and 5.88 for PFOS in a piscivorous food web from Lake Ontario. The comparatively higher TMF_{WW} values of PFOSA and PFAs observed in the present study are likely due to the relatively broader trophic level range investigated in these analyses (i.e., macroalgae to polar bears, TL range: 1.0 −5.5).

Protein-corrected concentrations of PFOS and C_8−C_{12} PFCAs increased significantly ($P < 0.05$) with trophic level, while PFHpA and PFTA concentrations were similar ($P > 0.05$) across the food web (Figure 2, Table S6). TMF_{PW} values (range: 0.76−11.0) were slightly lower than corresponding TMF_{WW} values of PFAs, due to differences in sample protein content.

Figure 2 illustrates that lipid corrected concentrations of organochlorines (PCB-153, *p,p′* DDE, and *β*-HCH) increased significantly ($P<0.05$) with trophic level. PBDE-47 and PFOSA exhibited moderate concentration increases over the food web. PBDE-99 concentrations show significant declines ($P < 0.05$) with trophic level (trophic dilution), likely due to debromination and/or cytochrome P450 mediated metabolism (*26*).

We observed substantial differences between the TMFs of the piscivorous and marine mammalian food webs (Figure 2, Table S7). In the piscivorous food web, PCB-153 and *p,p′* DDE exhibited high degrees of biomagnification, while *β*-HCH and PFA biomagnification was negligible. In the

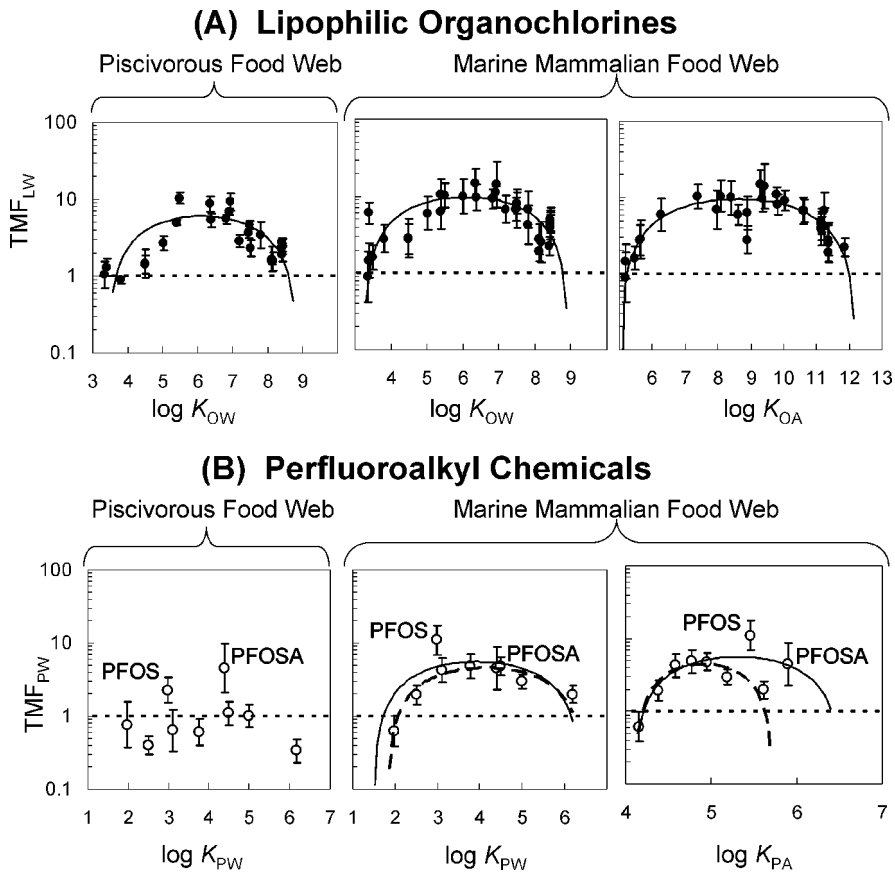

FIGURE 3. Plots showing relationship between observed TMF and logarithms of organic phase−water (log K_{OW}, log K_{PW}) and organic phase−air partition coefficients (log K_{OA}, log K_{PA}) for (a) lipophilic organochlorines and (b) perfluoroalkyl chemicals in the studied Arctic marine food webs. Error bars represent CI_{95} estimates. Curved solid lines represent quadratic regressions of all compounds plotted. Curved dashed lines represent quadratic regressions of only C_7−C_{14} PFCAs.

marine mammalian food web, PCB-153, *p,p′* DDE, and β-HCH, as well as several PFAs (PFNA, PFUnA, and PFOS) exhibited high degrees of biomagnification. Thus, unlike lipophilic persistent organic pollutants (POPs), which biomagnify in all food webs, proteinophilic PFAs and the moderately lipophilic β-HCH principally biomagnify in upper trophic level animals of the food web (i.e., seaducks, beluga whales, ringed seals, and polar bears).

Influence of Physical−Chemical Properties. Figure 3 illustrates curvilinear relationships between TMF_{LW} values of organochlorines versus log K_{OW} and log K_{OA} (a) and TMF_{PW} values of PFAs versus log K_{PW} and log K_{PA} (b). Regression results and quadratic equations are summarized in Table S8. TMF_{LW} values of organochlorines in the piscivorous food web increase from 1 to 10 between K_{OW}'s 10^3 and 10^7, with highest TMFs occurring between K_{OW} of 10^6 and 10^7. The observed drop in biomagnification potential for organochlorines with a $K_{OW} > 10^7$ is attributed to reduced dietary uptake efficiency of those highly lipophilic compounds (*22*). Similar relationships were observed between TMF_{LW} values and K_{OW} and K_{OA} in the marine mammalian food web. Similarly, TMF_{LW} values of organochlorines increase from 1 to 14 between K_{OA} of 10^5 and 10^{10} and drop with increasing K_{OA} when K_{OA} exceeds 10^{10}, which again is likely due to reduced dietary uptake efficiency, resulting from their high K_{OW} (*22*).

TMF_{PW} values of PFAs in the piscivorous food web (based on protein-corrected concentrations) were variable over the K_{PW} range 10^2 to 10^6 (Figure 3b). TMF_{PW} values of PFCAs were below 1, while PFOS exhibited a TMF_{PW} value of 2.2. PFOSA exhibited a relatively high TMF_{LW} value (4.53) in the piscivorous food web. In the marine mammalian food web, strong curvilinear relationships ($R^2 > 0.8$, $P < 0.01$) were observed between TMF_{PW} values of C_7−C_{14} PFCAs and K_{PW} and K_{PA}. TMFs of PFCAs increased from below 1 to 5 between K_{PW}'s 10^2 and 10^4, followed by declining TMFs above K_{PW} 10^4. Similar trends were observed between TMF_{PW} values of PFCs and K_{PA} (K_{PA} range: 10^4 to 10^6). In the marine mammalian food web, PFOS exhibited the highest TMF_{PW} value (11.0). PFOSA exhibited a TMF_{LW} of 4.46 in the marine mammalian food web. The low degree of biomagnification of PFHpA ($TMF_{PW} = 0.76$) and PFOA ($TMF_{PW} = 1.93$) may be due to elimination via respiration or urinary excretion of those highly water-soluble compounds (*15, 17*). The reduced biomagnification of PFTA ($TMF_{PW} = 1.43$) may be due to reduced bioavailability of this long-chain PFA, due to association with dissolved and colloidal organic matter, low dietary assimilation, and/or reduced permeation across gill membranes (*17*). Regardless, the observed TMFs indicate that PFAs, with K_{PW}'s between 10^3 and 10^5 and K_{PA}'s between $10^{4.5}$ and 10^6, exhibit a high degree of biomagnification in the Arctic marine mammalian food web. The corresponding K_{OW} and K_{OA} ranges of these bioaccumulative PFAs (PFOS and C_9−C_{12} PFCAs) are 10^4 to 10^7 and 10^7 to 10^9, respectively.

Biomagnification of lipophilic organochlorines (e.g., PCBs, DDTs) is explained by the fact these high K_{OW}−high K_{OA} compounds, which are generally resistant to metabolic transformation, exhibit high gastrointestinal uptake rates and slow respiratory elimination rates in aquatic water-respiring organisms (i.e., slow lipid−water transport), as well as air-breathing animals (i.e., slow lipid−air transport). β-HCH is moderately lipophilic but relatively nonvolatile and hence respiratory elimination of this recalcitrant low K_{OW}−high K_{OA} compound, which is relatively efficient for water-respiring organisms, is very slow in air-breathing animals, resulting in biomagnification in food webs containing air-breathers (*22*). 1,2,4,5-Tetrachlorobenzene and β-endosulfan are other low

K_{OW}−high K_{OA} chemicals that exhibit similar food web-specific bioaccumulation behavior (*22*).

PFOA, PFNA, and PFOS are characterized as low K_{OW}−high K_{OA} compounds ($K_{OW} < 10^5$, $K_{OA} > 10^6$) and were expected to only biomagnify in air-breathing wildlife (*22*). Dietary exposure studies with fish and rats indicate these compounds are readily absorbed from ingested food (*15*−*18*). In fish experiments (*17, 18*), PFOS and PFCAs exhibit a high degree of respiratory elimination to ambient water via gills, thereby reducing the bioaccumulation potential in those organisms (*17, 18*). In contrast, respiratory elimination of PFAs in air-breathing animals (birds, mammals) is anticipated to be negligible, due to low volatility and hence slow protein−air elimination. This is similar to the anticipated slow respiratory elimination and high degree of biomagnification of low K_{OW}−high K_{OA} substances in air-breathers (*22*).

Longer-chain PFCAs (PFDA, PFUnA, PFDoA, PFTA) are characterized as high K_{OW}−high K_{OA} compounds (K_{OW}'s > 10^5−10^9, K_{OA}'s > 10^6). These relatively lipophilic PFAs were expected to biomagnify in all food webs (similar to lipophilic organohalogens). These lipophilic PFAs are also readily absorbed from ingested food (*15, 18*). Experiments with fish show that, despite their anticipated hydrophobicity, these PFAs are also efficiently eliminated to water via respiration (*17, 18*). The efficient respiratory elimination of these PFAs in water-respiring organisms is attributed to the simultaneous hydrophilic nature of these compounds, due to presence of the carboxylate or sulfonate functional group. A high rate of respiratory elimination of PFAs in water-respiring organisms is likely facilitated by a considerable presence of PFA residues in circulating blood, coupled with extensive blood−water exchange at the gill lamellae during respiratory gas exchange.

PFOSA, a neutral lipophilic chemical (log $K_{OW} = 6.3$, log $K_{OA} = 8.4$), exhibited biomagnification in both food webs studied, which is consistent with the behavior of lipophilic POPs. Laboratory studies have shown in vitro biotransformation of *N*-EtPFOSA to PFOSA and subsequently PFOS (*11*). *N*-EtPFOSA and PFOSA have been detected in tissues of Arctic fish and marine mammals (*6*). Thus, PFOS residues in Arctic marine wildlife may, in part, be due to bioformation via the *N*-EtPFOSA → PFOSA→ PFOS biotransformation pathway.

The above analyses clearly highlight the problem of using a K_{OW} based (hydrophobicity) approach for evaluating bioaccumulation potential of PFAs. In particular, many PFAs have calculated K_{OW}'s < 10^5 (PFOS, PFOA, PFNA), yet clearly can biomagnify in food chains. Nevertheless, thermodynamics and equilibrium partitioning undoubtedly remains an important process affecting the bioaccumulation kinetics of PFAs. K_{PW}'s and K_{PA}'s, which delineate chemical exchange between protein−water and protein−air phases, respectively, may be useful parameters for evaluating PFA bioaccumulation.

Toxicological Implications. A PFOS exposure equal to 7.1×10^{-5} mg·kg bw^{-1}·d^{-1} ($CI_{95} = 2.7 \times 10^{-5}$ to 1.8×10^{-4}) was estimated for nursing beluga whale calves via milk consumption (Figure S8). This dose is low compared to the previously reported LOAEL of 0.15 mg·kg bw^{-1}·d^{-1} (*34*). However, the upper 95% confidence limit of PFOS exposure for beluga whale calves (1.8×10^{-4} mg·kg bw^{-1}·d^{-1}) was 7 times higher than the RfD of 7.5×10^{-5} mg·kg bw^{-1}·d^{-1} (*35*). For PCBs, exposure of Aroclor 1254 in newborn beluga whale calves (5.9×10^{-5} mg·kg bw^{-1}·d^{-1}, $CI_{95} = 2.0 \times 10^{-5}$ to 2.0×10^{-4}) exceeded the RfD (2.0×10^{-5} mg·kg bw^{-1}·d^{-1}). Conversely, estimated PFOA and PBDE-47 exposure levels were below RfD values reported for those compounds, 3×10^{-4} and 1.0×10^{-4}, respectively. The results show that biomagnification and persistence of PFOS residues in Arctic beluga whales and subsequent maternal transfer to nursing calves (via milk), results in an elevated risk of potential developmental impacts in those animals. Other Arctic wildlife species such as ringed seals and polar bears, which exhibit relatively high PFOS residue levels (100−6000 ng·g^{-1} in liver tissue) (*4, 29, 36*), may be susceptible to similar PFOS exposure and related biological impacts. The calculations also signal that legacy POPs (i.e., PCBs), banned nearly 40 years ago, remain a potential threat to wildlife, even in remote ecosystems. Recent studies have demonstrated relatively high PFOS exposure levels in nursing human newborns (*35*). PFOS and PFOA exposure to northern peoples (E. Hudson Bay Inuit population) via consumption of fish and beluga whale meat (i.e., muscle tissue) is seemingly low, due to negligible contamination of those traditional foods (Table S4).

Summary. PFOS and C_8−C_{14} PFCAs are highly bioaccumulative in this Arctic marine food web. However, unlike lipophilic POPs, PFAs exhibited no biomagnification in aquatic organisms of the food web. The observed food web-specific biomagnification of PFAs can be explained by the anticipated phase partitioning behavior of these recalcitrant proteinophilic compounds. Specifically, the high degree of PFA biomagnification in upper trophic level wildlife (seals, whales, and polar bears) is likely due to the combination of (i) efficient dietary assimilation, (ii) strong partitioning into organic-phase (i.e., retention in protein rich tissues/fluids), (iii) high resistance to metabolism, and (iv) low volatility of those compounds, which essentially relates to high gastrointestinal uptake and slow elimination rates in air-breathing animals. Conversely, the lack of PFA biomagnification in aquatic organisms is attributed to the relatively high aqueous solubility (>500 mg/L) and hydrophilic nature of those compounds, hence efficient respiratory elimination via gills in water-respiring organisms. Chemical K_{OW} is fundamentally problematic in assessing the bioaccumulation potential of these proteinophilic compounds. Protein−water and protein−air partition coefficients (K_{PW}, K_{PA}) may provide some utility for assessing uptake and elimination kinetics of these unique environmental contaminants. It is important to note that K_{PW}'s and K_{PA}'s of PFAs presented in this study are best estimates, based on quantitative structure−activity relationships (QSARs). Direct empirical measurements of partitioning behavior of specific PFAs (PFCAs vs PFSAs) in different proteins and organism tissues/compartments may elicit greater insight into PFA toxicokinetics.

In conclusion, the recent voluntary action taken by 3M to produce C_4- rather than C_8-based Scotchgard products is anticipated to greatly reduce PFOS emissions. Laboratory studies demonstrate perfluorobutansulfonic acid (PFBS), the replacement chemical used in 3M's new Scotchgard production, is not bioaccumulative due to efficient clearance of this compound (*17, 18*). However, continued manufacturing of PFA precursors such as FTOHs, *N*-EtPFOSA, and other perfluoroalkyl sulfonamide alcohols may result in further accumulation of PFOS and other PFA residues to natural environments, wildlife, and humans. Future investigations of environmental transport pathways, phase-partitioning, and biotransformation/bioformation kinetics of PFAs and PFA precursor compounds will aid future risk assessment initiatives of perfluoroalkyl contaminants.

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Supporting Information Available

Supplemental tables (Tables S1−S8) and supplemental figures (Figures S1−S8). This material is available free of charge via the Internet at http://pubs.acs.org.

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