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Biomagnification of Perfluorinated Compounds in a Remote Terrestrial Food Chain: Lichen−Caribou−Wolf

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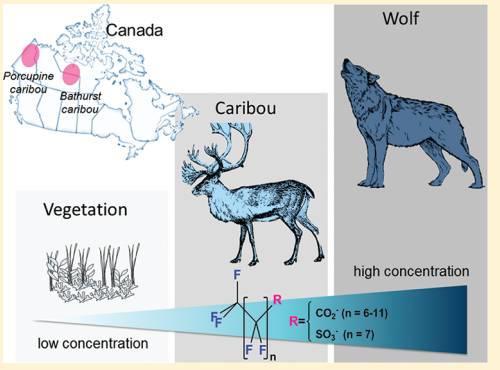
Supporting Information

ABSTRACT: The biomagnification behavior of perfluorinated carboxylates (PFCAs) and perfluorinated sulfonates (PFSAs) was studied in terrestrial food webs consisting of lichen and plants, caribou, and wolves from two remote northern areas in Canada. Six PFCAs with eight to thirteen carbons and perfluorooctane sulfonate (PFOS) were regularly detected in all species. Lowest concentrations were found for vegetation (0.02−0.26 ng/g wet weight (ww) sum (Σ) PFCAs and 0.002−0.038 ng/g ww PFOS). Wolf liver showed highest concentrations (10−18 ng/g ww ΣPFCAs and 1.4−1.7 ng/g ww PFOS) followed by caribou liver (6−10 ng/g ww ΣPFCAs and 0.7−2.2 ng/g ww PFOS). Biomagnification factors were highly tissue and substance specific. Therefore, individual whole body concentrations were calculated and used for biomagnification and trophic magnification assessment. Trophic magnification factors (TMF) were highest for PFCAs with nine to eleven carbons (TMF = 2.2−2.9) as well as PFOS (TMF = 2.3−2.6) and all but perfluorooctanoate were significantly biomagnified. The relationship of PFCA and PFSA TMFs with the chain length in the terrestrial food chain was similar to previous studies for Arctic marine mammal food web, but the absolute values of TMFs were around two times lower for this study than in the marine environment. This study demonstrates that challenges remain for applying the TMF approach to studies of biomagnification of PFCAs and PFSAs, especially for terrestrial animals.



INTRODUCTION

Perfluorinated compounds (PFCs) including perfluorinated carboxylates (PFCAs) and perfluorinated sulfonates (PFSAs) and their precursors, are a group of anthropogenic substances ubiquitously found in the environment, in industrialized regions as well as remote areas.[1−7] Although they have been produced since the 1950s for industrial applications and consumer products, their environmental presence was discovered only recently, in the early millennium.[7] Since then, PFCs have been found in all environmental compartments, as well as in humans from around the world.[1−7] PFCAs and PFSAs are environmentally recalcitrant and have a bioaccumulation and long-range transport (LRT) potential similar to other persistent organic pollutants (POPs).

The PFCAs and PFSAs are ionic substances and nonvolatile and therefore, their transport behavior differs from many classical POPs. Atmospheric LRT as anions is considered less significant compared with two alternative LRT processes: (i) transport by oceanic currents[8−10] or (ii) distribution of volatile precursor substances such as fluorotelomer alcohols (FTOHs) and perfluorosulfonamides via the atmosphere with subsequent degradation to PFCAs and PFSAs.[11−13] The relative importance of these two processes is still under debate. However, for remote terrestrial environments atmospheric transport of precursors is more likely. PFCAs with eight to twelve carbons and PFSAs bioaccumulate and biomagnify in aquatic food webs, as has been shown in several marine food web studies.[1−3,14−17] These anionic PFCs are proteinophilic and generally found at highest concentrations in blood and liver in contrast to lipophilic pollutants such as polychlorinated biphenyls (PCBs), which enrich mainly in lipid tissue. Some of the highest concentrations

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of PFCs in wildlife have been found for perfluorooctane sulfonate (PFOS) in polar bear liver (up to 3100 ng/g wet weight, ww).[4] Terrestrial animals from remote locations have also considerable PFOS concentrations, for example, the arctic fox, an opportunistic feeder, had liver concentrations of 250 ng/g ww while the herbivorous caribou had liver concentrations around 3 ng/g ww.[4,18]

While poorly metabolized chemicals with high octanol air partition coefficients K_{OA} ($\geq 10^6$) and medium octanol–water partition coefficients K_{OW} ($10^{10} \geq K_{OW} \geq 10^2$) are expected to biomagnify in air-breathers in terrestrial food webs,[19,20] little is known about accumulation of proteinophilic compounds in the same food webs. Therefore, to address this question we investigated the biomagnification of PFCs in terrestrial food webs in two areas in the Canadian Arctic in this study. These food webs included vegetation (plants and lichens), barren ground caribou (*rangifer tarandus groenlandicus*) and wolves (*canis lupus*). Investigation of this remote, terrestrial food chain has certain advantages: First of all, the lichen–caribou–wolf food chain is well documented and in particular caribou have been studied intensively due to their economic and social importance for indigenous people in the Canadian Arctic.[21] It is relatively simple, as caribou feed mostly on lichen (in summer the diet also consists of willow, sedges and grasses) and wolves living near barren-ground caribou herds almost exclusively feed on them. It is therefore potentially easier to assess diet-consumer relationships than for more complex aquatic food webs. A further advantage is that the PFC input into this remote environment is solely via the atmosphere and that local sources are absent.

The objectives of this study were therefore to (i) assess the input of PFCAs and PFSAs in the arctic terrestrial environment, (ii) study their biomagnification potential in terrestrial mammals and (iii) compare aquatic, marine mammalian and terrestrial biomagnification. To our knowledge, this is the first study on PFC biomagnification in a remote terrestrial food chain.

MATERIALS AND METHODS

Chemicals. Information on chemicals (standards of PFCAs, PFSAs, and isotopically labeled surrogates as well as reagents) is summarized in the Supporting Information SI.

Samples. Liver, muscle, and kidney samples from two caribou herds were collected; from the Porcupine herd in northern Yukon Territory and the Bathurst herd in the Northwest Territories (NWT)/western Nunavut (see map in SI Figure S1). Wolf, lichen (*cladonia mitis/rangiferina* and *flavocetraria nivalis/cucullata*), and plant samples were collected in the same region as the caribou. Plant samples included cottongrass (*eriophorum vaginatum*), aquatic sedge (*carex aquatilis*), willow (*salix pulchra*), moss (*rythidium rugosum*), and mushrooms (unknown species). Liver and muscle samples were collected from the sampled wolves. The sampling procedure, time, storage, and sample types are described in more detail in the SI.

Extraction and Cleanup. Vegetation samples were analyzed using a method similar to that described in Powley et al. (details see SI).[22] In brief, plant matter was extracted three times with methanol, the combined extract was concentrated and subjected to further clean up with a carbon solid phase extraction (SPE) cartridge.

The liver, kidney, and muscle samples were analyzed according to a modified method from Powley et al.[22] The homogenized tissue was extracted twice with methanol or with acetonitrile and the combined extract was concentrated to dryness. The reconstituted extract (in methanol) was then cleaned with a carbon cartridge.

Instrumental Analysis. All samples were analyzed for PFCAs from perfluorohexanoate PFHxA to perfluorotetradecanoate PFTeA, as well as the PFSAs, perfluorohexane sulfonate PFHxS, and PFOS. The analyses were performed by liquid chromatography with negative electrospray tandem mass spectrometry (LC-MS/MS). Analytes were detected using an API 4000 Q Trap (Applied Biosystems, Carlsbad, CA) after chromatographic separation with an Agilent 1100 LC (injection volume = 40 μL, flow rate = 300 μL/min). Chromatography was performed using an ACE C18 column (50 mm × 2.1 mm, 3 μm particle size, Aberdeen, U.K.), preceded by a C18 guard column (4.0 × 2.0 mm, Phenomenex, Torrance, CA) and the column oven was set to 30 °C. Samples were quantified with a six point calibration curve and isotopic dilution method.

Quality Assurance/Quality Control (QA/QC). Reproducibility of the analytical method was assessed by triplicate analysis of a sample of every species. Reproducibility was between 3 and 15% for all species and substances except for perfluorotridecanoate (PFTrA) which had relative standard deviation of up to 50%, due to very low concentrations. Recoveries were determined with spike and recovery, as well as by internal standard comparisons, and ranged from 26% to 46% for plants and from 65%–129% for all other sample types (see SI Table S3). PFTeA showed very high recovery (170%) for wolf liver, probably because of matrix enhancement. PFTeA results were therefore not reported. Method blanks were conducted for every batch of six to ten samples. All samples were blank-subtracted. The method detection limit (MDL) was defined as either as three times the standard deviation of the blank samples or, if the blanks had no detectable contamination, as the instrumental detection limit (IDL). MDLs and average blank levels are shown in the SI (Table S4 and Table S5).

Stable Isotope Analysis. Determination of carbon and nitrogen stable isotope ratios (δ^{13}C and δ^{15}N) were conducted for all species studied here to investigate the diet relationship in this food chain. Further information is provided in the SI.

Biomagnification and Trophic Magnification Factor Calculations. Biomagnification factors (BMF = $C_{consumer}/C_{diet}$) were calculated based on two different approaches: (i) on single tissue concentrations and (ii) on an estimated whole body concentration for caribou and wolf (see eq 1).

$$C_{\text{whole body}} = \sum_{n=1} C_{\text{tissue } n} \times f_{\text{tissue } n} \quad (1)$$

C_{Tissue} is the concentration of the specific tissue and f_{Tissue} is the mass fraction of this tissue in the whole body. Tissue fractions were obtained from post-mortem examinations of selected investigated animals. Every individual animal was calculated separately on the basis of the specific tissue concentration. Animals with only one tissue were excluded from this calculation. Concentrations of tissues, which were not measured here, were estimated on the basis of literature values.[1] It was assumed that the PFCA and PFSA concentration in blood and lungs were half that of liver and the carcass was assumed to have half the concentration found in muscle tissue. Bones were excluded from the whole body calculation because PFCs are assumed to not enrich in this media and bones are not part of the diet of wolves. When average concentrations were below MDL, they were substituted with MDL/2 in order to get numerical values for

whole body estimates. Tissue fractions for caribou and wolf are listed in SI Table S6. Average concentrations were used for BMF calculations.

Trophic magnification factor (TMF) was calculated according to Jardine et al.[23] The TMF provides information on the average change in contaminant concentration per relative trophic level and is calculated using the natural logarithm of the concentration (C_{ww}) of individual organisms versus their trophic level (TL):

$$\ln C_{ww} = a + (b \times \mathrm{TL}) \quad (2)$$

a is the intercept and b the slope of the linear equation. Two alternate calculation methods were tested: C_{ww} for the second and third trophic level was either the concentration in a specific tissue (liver or muscle) or the whole body concentration from eq 1. Additionally, lichen alone or all vegetation samples were used as the primary producer.

The trophic level can be derived from the stable isotope ratio of nitrogen $\delta^{15}N$ for the consumer (wolf or caribou) and first trophic level lichen with the relationship

$$\mathrm{TL} = 1 + (\delta^{15}N_{\mathrm{consumer}} - \delta^{15}N_{\mathrm{lichen}})/\Delta^{15}N \quad (3)$$

where 1 is the assumed trophic level of lichen and $\Delta^{15}N$ is the trophic enrichment factor constant. [24] Generally a factor of 3.4 ‰ is assumed for biomagnification assessments. For this study however, a factor of 3.8 ‰ was chosen, because caribou have been shown to have higher enrichment factors. This is based on earlier observations of Ben-David et al., who reported an enrichment of 3.8 ‰ and higher for barren ground caribou.[25]

The TMF can then be calculated based on the slope b of eq 2.

$$\mathrm{TMF} = e^{b} \quad (4)$$

Statistical Analysis. All statistical tests were done using SYSTAT (version 10, SPSS Inc.). The two tailed t test was used to test for differences in concentrations between species and locations. Slopes of TMF regressions were tested for significance at $P = 0.05$. Additionally, correlations between age and concentrations of caribou and wolf samples (both muscle and liver) were tested.

RESULTS AND DISCUSSION

Concentrations and Profiles of PFCs. An overview of PFCA and PFOS concentrations in both food chains, the Porcupine herd food chain in Yukon and the Bathurst herd food chain in NWT, can be found in Table 1 (more information in SI Table S7). Of the 11 PFCs analyzed in this study only PFCAs with eight to thirteen carbons and PFOS were regularly detected. Highest concentrations were measured in wolf liver (10 and 18 ng/g ww sum (Σ) PFCAs for Yukon and NWT, respectively), followed by caribou liver (6 and 10 ng/g ww ΣPFCAs, respectively). Considerably lower concentrations were found in vegetation samples, often close to the MDL.

Vegetation. Lowest average concentrations were found in cottongrass in Yukon (e.g., from <MDL for tridecanoate (PFTrA) to 0.013 ± 0.009 ng/g ww for perfluorooctanoate (PFOA)). Higher concentrations were found in lichen (e.g., 0.08 ± 0.01 and 0.10 ± 0.02 ng/g ww for perfluorononanoate (PFNA) in Yukon and NWT, respectively), willow (e.g., 0.19 ± 0.10 ng/g ww PFOA in Yukon), and mushroom (e.g., 0.19 ± 0.08 ng/g ww PFOA). While all concentrations are very low, the PFCA congener composition differed among types of vegetation (Figure 1). All plants (grass, sedge, willow, and moss) are dominated by PFOA, while both lichen species showed a dominance of the odd carbon chain lengths (C8 < C9 and C12 < C13, C10 < C11 only for lichen in Yukon). A weaker version of this pattern can also be seen in cottongrass and willow from NWT (C10 < C11, C12 < C13), but not in Yukon. This is most likely due to the fact that the vegetation samples had generally lower concentrations in Yukon and PFCs were more often below detection limits. PFOS concentrations in all vegetation samples are lower than for PFCAs, from <MDL to 0.062 ng/g.

The difference in PFOA concentrations between plants and lichen could possibly be explained by the different uptake mechanisms: Plants such as willows and cotton grass obtain nutrients and water via root systems in the soil. Lichen, on the other hand, do not have roots but absorb nutrients directly from precipitation. Therefore, PFCA levels in lichen should represent the direct input from the atmosphere. Uptake from soil is a more indirect pathway, where different discrimination mechanisms can play a role (preferential soil adsorption of longer chain PFCs,[26] possible preferential root permeation of shorter PFCs), leading to a PFCA composition different from the atmosphere.

In general, the source of atmospheric PFCAs and PFSAs is uncertain. In urban areas, precipitation samples often have high value of PFOS and PFOA, in more remote areas, this dominance seems to be weakened.[27,28] Measurements of PFCs in rain collected at Snare Rapids (NWT), a sampling site west of the Bathurst herd range, showed relatively high PFNA concentrations followed by PFOA (see Figure 1; details in SI Table S11).[29] The other odd chain PFCAs are, however, very low (C10 > C11, C12 > C13). Precipitation and particulate air samples from more northern locations in the Arctic show a pattern with strong dominance of PFOA and low contribution of odd chain PFCAs.[30,31] Furthermore, PFOS concentrations are much higher than PFOA or PFNA in these Arctic samples, whereas rain from the Bathurst region and the lichen samples have a low contribution of PFOS to total PFCs (a set of literature values are presented in SI Table S11).

Caribou. Highest PFC liver concentrations were found for PFNA (2.2 ± 0.2 and 3.2 ± 0.4 ng/g ww for the Porcupine and Bathurst herds, respectively) followed by perfluorodecanoate (PFDA, 1.9 ± 0.1 and 2.2 ± 0.2 ng/g ww) and perfluoroundecanoate (PFUnA, 1.7 ± 0.1 and 3.2 ± 0.2 ng/g ww). Similar to the vegetation results, the PFOS content was lower (0.67 ± 0.13 ng/g ww) in the Porcupine caribou. The Bathurst caribou on the other hand had PFOS concentrations (2.2 ± 0.3 ng/g ww) similar to that corresponding to the most prominent PFCAs. These results are in agreement with those reported in a study of PFCs in caribou from several communities in Nunavut in which PFCA and PFOS liver concentrations were in the same range (PFNA 2.0 ± 1.7 and PFOS 2.7 ± 2.3 ng/g ww).[18] Mean PFC concentrations in caribou were higher in the Bathurst samples, however this difference was statistically significant ($p < 0.05$) in liver only for PFOS, PFNA, and PFUnA (SI Figure S4). This might be due to differences in distance from source regions in North America. The study area in northern Yukon is more remote from these source regions than the Bathurst area in the NWT.

In comparison to liver, PFC concentrations in muscle and kidney were 10 to 20 times lower, which shows the extreme preference of PFCAs and PFSAs for liver. PFCAs and PFOS bind preferentially to certain proteins in the blood and liver, leading to enrichment in these tissues.[32−34] However, when the respective

Table 1. Overview of Sample Type, Size, Year of Collection, and Mean Concentration ± Standard Error (ng/g ww) of PFCAs and PFOS for the Porcupine (Northern Yukon) and Bathurst (Northwest Territories/Nunavut) Caribou Herd Food Chains

				concentration ± SE (ng/g ww)								
sample	herd	*n*	year	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTrA	PFOS	Σ PFCAs	Σ PFCs
						vegetation						
lichen (Fla)[a]	Porcupine	10	2008	0.023 ± 0.009	0.056 ± 0.018	0.025 ± 0.013	0.038 ± 0.014	0.016 ± 0.008	0.014 ± 0.010	0.014 ± 0.008	0.17 ± 0.07	0.19
lichen (Cla)[a]	Porcupine	8	2008	0.025 ± 0.010	0.083 ± 0.010	0.021 ± 0.010	0.049 ± 0.010	0.010 ± 0.010	0.018 ± 0.010	0.013 ± 0.006	0.21 ± 0.06	0.22
willow	Porcupine	7	2008	0.19 ± 0.10	0.056 ± 0.021	0.010 ± 0.010	0.003 ± 0.002	0.003 ± 0.004	<0.004	0.062 ± 0.029	0.26 ± 0.14	0.33
cotton grass	Porcupine	10	2008	0.013 ± 0.009	<0.004	0.003 ± 0.003	0.003 ± 0.002	0.005 ± 0.002	<0.004	0.002 ± 0.002	0.02 ± 0.02	0.03
lichen (Cla)[a]	Bathurst	9	2009	<0.003	0.099 ± 0.017	0.067 ± 0.039	0.041 ± 0.005	0.006 ± 0.001	0.010 ± 0.003	0.021 ± 0.003	0.22 ± 0.07	0.24
willow	Bathurst	3	2009	0.034 ± 0.005	0.021 ± 0.001	0.005 ± 0.001	0.013 ± 0.002	<0.002	0.008 ± 0.002	0.018 ± 0.003	0.08 ± 0.01	0.10
cotton grass	Bathurst	3	2009	0.047 ± 0.015	0.038 ± 0.012	0.005 ± 0.003	0.020 ± 0.004	0.002 ± 0.002	0.009 ± 0.001	0.014 ± 0.007	0.12 ± 0.04	0.13
moss	Bathurst	5	2009	0.024 ± 0.004	0.058 ± 0.018	0.006 ± 0.002	0.020 ± 0.009	0.004 ± 0.001	0.010 ± 0.003	0.008 ± 0.002	0.12 ± 0.04	0.13
mushrooms	Bathurst	3	2009	0.19 ± 0.08	0.012 ± 0.007	<0.005	0.008 ± 0.003	0.016 ± 0.008	<0.005	0.038 ± 0.006	0.22 ± 0.09	0.26
						caribou						
muscle	Porcupine	7	2007	0.022 ± 0.008	0.064 ± 0.008	0.033 ± 0.007	0.070 ± 0.010	<0.01	0.031 ± 0.008	0.028 ± 0.023	0.22 ± 0.04	0.25
liver	Porcupine	10	2007	<0.5	2.2 ± 0.2	1.9 ± 0.1	1.7 ± 0.1	<0.5	<0.5	0.67 ± 0.13	5.8 ± 0.4	6.5
kidney	Porcupine	10	2007	<0.01	0.10 ± 0.02	0.02 ± 0.01	0.02 ± 0.01	<0.01	<0.01	0.020 ± 0.003	0.15 ± 0.03	0.17
muscle	Bathurst	9	2008	0.024 ± 0.006	0.093 ± 0.009	0.075 ± 0.009	0.18 ± 0.01	0.031 ± 0.015	0.052 ± 0.006	0.076 ± 0.019	0.45 ± 0.06	0.53
liver	Bathurst	7	2008	0.11 ± 0.01	3.2 ± 0.4	2.2 ± 0.2	3.2 ± 0.2	0.66 ± 0.05	0.49 ± 0.03	2.2 ± 0.3	9.8 ± 0.9	12
						wolf						
muscle	Porcupine	6	2010	0.083 ± 0.013	0.44 ± 0.06	0.11 ± 0.02	0.15 ± 0.02	0.017 ± 0.003	0.005 ± 0.003	0.13 ± 0.02	0.8 ± 0.1	0.93
liver	Porcupine	6	2010	0.23 ± 0.08	4.7 ± 0.9	2.0 ± 0.2	2.5 ± 0.4	0.42 ± 0.05	0.35 ± 0.04	1.4 ± 0.3	10 ± 1.7	12
muscle	Bathurst	10	2007	0.06 ± 0.01	1.1 ± 0.1	0.21 ± 0.03	0.57 ± 0.14	0.039 ± 0.021	0.26 ± 0.15	0.14 ± 0.02	2.3 ± 0.5	2.4
liver	Bathurst	5	2007	0.10 ± 0.03	7.4 ± 1.3	3.2 ± 0.2	6.4 ± 1.2	0.72 ± 0.14	0.55 ± 0.10	1.7 ± 0.1	18 ± 2.9	20

[a] Fla: *flavocetratia*. Cla: *cladonia*

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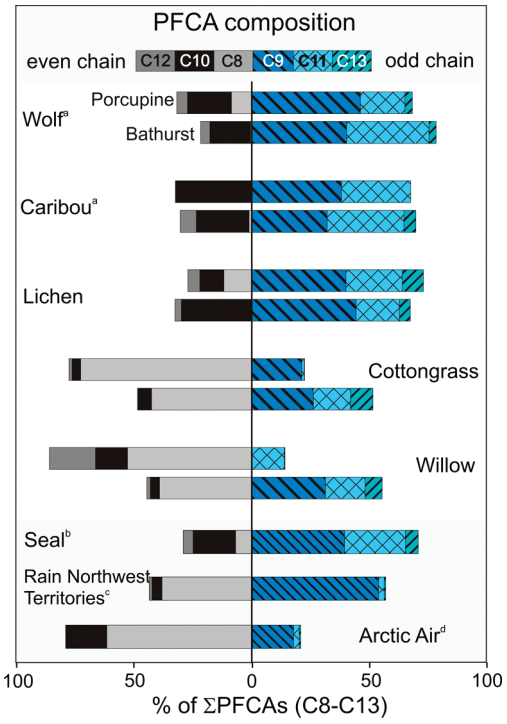

Figure 1. PFCA homologue composition of species studied here and selected comparisons from literature sources. (a) Wolf and caribou homologue distribution shown here are from muscle samples. Reference values are form (b) Martin et al.,[4] (c) Scott et al.,[29] and (d) Stock et al.[31]

body fractions of the tissues are considered, the distribution changes dramatically. Muscle tissue contains 60−90% of the body burden (concentration tissue × tissue fraction on total body weight, see SI Figure S3). Liver has only a minor contribution and kidney loses importance with less than 1% of the total burden. This shows that studying only liver concentration for biomagnification will greatly alter results, as muscle (and other) tissues are equally important dietary items for wolves.

Concentrations of PFCs in caribou muscle and liver were not significantly correlated with age except for PFOA in Bathurst caribou muscle (SI Table S8). Weak or nonsignificant correlations of PFCs with age have also been found in ringed seals[35] and dolphins.[1]

Wolf. The top predator of this food chain, the wolf, displayed a similar PFC distribution as caribou. The PFCA and PFSA concentrations present in wolf liver were 5 to 15 times higher compared to muscle and the contribution of liver to the whole body burden was about 10 to 40%. Highest concentrations were observed in PFNA (4.7 ± 0.9 and 7.4 ± 1.3 ng/g ww for Yukon and Bathurst, respectively) and PFUnA (2.5 ± 0.4 and 6.4 ± 1.2 ng/g ww, respectively). Again, concentrations were higher for the Bathurst wolves, however, this was significant only for PFDA and PFUnA. Concentrations of PFCs in Porcupine wolf liver and muscle were not significantly correlated ($P > 0.05$) with age, though a slight increase with age was seen for some PFCs (SI Table S9). To more thoroughly investigate the relationship between age and concentration, more individuals would be needed for both wolves and caribou.

In comparison to other predators, the PFC concentrations found in wolf are relatively low. Concentrations of up to 250 ng/g PFOS and 22 ng/g for PFNA were found in Arctic fox.[4] This terrestrial animal is an opportunistic predator and its diet can contain also marine animals, which could lead to higher contaminant levels. Wolves on the other hand mainly feed on herbivorous animals such as caribou, moose and sometimes smaller animals. In polar bear livers, PFOS concentrations up to 3100 ng/g ww and PFNA levels up to 190 ng/g ww have been found.[3] These much higher levels can be partially explained by the longer food chain (polar bears are on trophic level four/five) hence the biomagnification pathway is longer. Additionally, there is more PFC input into the marine food web, from atmospheric, as well as oceanic transport.

Looking at all species studied here two observations become apparent: (i) PFC concentrations in tissues increase with tropic level (see Table 1). For most PFCs, levels are highest in wolf, followed by caribou and then vegetation. (ii) The PFCA homologue pattern for lichen, caribou, and wolf are very similar (see Figure 1) with a dominance of the odd carbon chain PFCAs. Cotton grass, willow, and other plant have a dominance of PFOA.

Stable Isotopes and Food Web Structure. The stable isotope analyses were conducted for all species studied here to investigate the dietary relationship in this food chain. An overview of the $\delta^{13}C$ and $\delta^{15}N$ results of this study is shown in the SI (Figure S2). $\delta^{13}C$ vary widely in photosynthetic organisms and ^{13}C is only moderately enriched along the food chain (1−2‰).[23] Lichen, caribou, and wolf had similar $\delta^{13}C$ values implying that the caribou were mainly feeding on lichen and the wolves mainly on caribou. On the other hand, the $\delta^{15}N$ difference between lichen and caribou is rather large (7−8‰) compared to usually assumed $\Delta^{15}N$ of 3.4−3.8‰. It is however known that there are much larger $\Delta^{15}N$ values for herbivores feeding on a nitrogen poor diet.[25,36] For example, a controlled feed study on white tailed deer showed high shifts of 4.93 ± 0.74‰.[36] Additionally, the isotope composition can change seasonally with diet supply, for example, fasting in winter can increase the $\delta^{15}N$.[37]

A linear combination of food sources was calculated for caribou with the use of the IsoSource model from Phillips et al.[38] The results indicated that lichen, cotton grass, and mushroom are the main food sources (see SI Table S12). However, this analysis also showed that all plant samples had basically too low $\delta^{13}C$ values (more than 2‰ lower than caribou) and numerical results could only be obtained when an enrichment of 2‰ was assumed. It is therefore possible that these plants did not play a major role in the caribou diet. We analyzed most of the major plants that are thought to contribute to the diet but cannot rule out the possibility that some other plant or mushroom species are important. It has to be mentioned that vegetation and animal species were collected in different seasons, which may introduce additional variation and hamper food source interpretation. Both lichen and all vegetation were thus used for magnification factor calculations to study the potential influences of vegetation other than lichen. For BMF calculations, combined vegetation concentrations were calculated based on the food source contribution results of the IsoSource model.

Biomagnification Factors. Biomagnification factors (BMFs) were calculated to evaluate the biomagnification behavior between diet and consumer. Usually, the lipid normalized concentrations are used for these calculations to eliminate lipid content variability between organs/organisms. This is however not possible for PFCs, because they are rather proteinophilic than lipophilic. In literature, different approaches have been taken to calculate representative BMFs for PFCs: using either specific tissue concentrations (mostly blood or liver),[17] whole body concentrations,[1]

Table 2. Biomagnification Factors (BMFs) and Trophic Magnification Factors (TMFs) for PFCs for this Study and Reference Studies[a]

		PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTrA	PFOS
					biomagnification factors (BMFs)			
$caribou_{muscle}$/lichen	Porcupine	0.9 ± 0.4	1.2 ± 0.3	1.3 ± 0.6	1.9 ± 0.4	1.9 ± 0.9	2.1 ± 0.9	2.0 ± 1.8
	Bathurst		0.9 ± 0.2	1.1 ± 0.7	4.3 ± 0.6	5.2 ± 2.8	5.0 ± 1.7	3.6 ± 1.0
$caribou_{liver}$/lichen	Porcupine		40 ± 12	75 ± 25	46 ± 12	16 ± 4.9	17 ± 7	4.0 ± 3.7
	Bathurst	11 ± 1.2	32 ± 7.0	33 ± 19	78 ± 11	110 ± 28	47 ± 15	3.1 ± 0.9
$wolf_{muscle}$/$caribou_{muscle}$	Porcupine	3.8 ± 1.5	6.9 ± 1.2	3.3 ± 0.8	2.1 ± 0.4			4.5 ± 3.8
	Bathurst	2.6 ± 0.8	12.4 ± 1.7	2.8 ± 0.6	3.2 ± 0.8	1.2 ± 0.9	4.9 ± 2.9	1.8 ± 0.5
$wolf_{liver}$/$caribou_{liver}$	Porcupine	0.0	2.1 ± 0.5	1.0 ± 0.1	1.4 ± 0.3			2.1 ± 0.6
	Bathurst	0.9 ± 0.3	2.3 ± 0.5	1.4 ± 0.1	2.0 ± 0.4	1.1 ± 0.2	1.1 ± 0.2	0.8 ± 0.1
$caribou_{whole}$/lichen	**Porcupine**	**1.4 ± 0.4**	**2.8 ± 0.7**	**6.1 ± 2.2**	**3.8 ± 0.9**	**2.9 ± 1.1**	**2.4 ± 1.0**	**4.8 ± 2.3**
	Bathurst	**2.6 ± 0.5**	**2.7 ± 0.6**	**2.9 ± 1.7**	**8.2 ± 1.1**	**11 ± 3**	**6.9 ± 2.2**	**9.1 ± 1.6**
$caribou_{whole}$/vegetation	**Porcupine**	**1.8 ± 0.7**	**8.5 ± 2.6**	**12.4 ± 5.5**	**9.8 ± 3.2**	**4.5 ± 1.7**	**7.1 ± 4.7**	**9.1 ± 4.9**
	Bathurst	**0.3 ± 0.1**	**5.3 ± 1.0**	**7.2 ± 3.8**	**14.5 ± 1.8**	**8 ± 3**	**9.0 ± 2.5**	**7.9 ± 1.6**
$wolf_{whole}$/$caribou_{whole}$	**Porcupine**	**2.4 ± 0.6**	**3.8 ± 0.6**	**1.7 ± 0.2**	**2.0 ± 0.3**	**1.2 ± 0.1**	**0.8 ± 0.2**	**3.3 ± 1.1**
	Bathurst	**2.1 ± 0.5**	**5.4 ± 0.8**	**2.1 ± 0.2**	**2.8 ± 0.5**	**1.4 ± 0.4**	**3.2 ± 1.5**	**1.2 ± 0.2**
$dolphin_{whole}$/$seatrout_{whole}$	Houde et al.[1]	1.8	2.1	2.4	2.5	0.6		0.9
$seatrout_{whole}$/$pinfish_{whole}$	Houde et al.[1]	7.2	1.5	3.7	0.9	0.1		4.6
laketrout/prey	Martin et al.[3]	0.4	2.3	2.7	3.4	1.6	2.5	2.9
polar $bear_{liver}$/ $seal_{liver}$	Martin et al.[4]	8.6	33	22	18	10	14	177
					trophic magnification factors (TMFs)			
$wolf_{liver}$/$caribou_{liver}$/lichen	Porcupine	2.4 ± 0.1	6.7 ± 0.5	7.1 ± 0.4	6.6 ± 0.4	4.1 ± 0.1	3.7 ± 0.1	6.7 ± 0.3
	Bathurst	2.2 ± 0.1	4.5 ± 0.2	5.1 ± 0.3	6.1 ± 0.3	5.2 ± 0.3	4.2 ± 0.3	5.2 ± 0.4
$wolf_{whole}$/$caribou_{whole}$/lichen	**Porcupine**	**1.3 ± 0.1**	**2.7 ± 0.2**	**2.6 ± 0.1**	**2.5 ± 0.1**	**1.4 ± 0.1**	**1.4 ± 0.1**	**2.6 ± 0.1**
	Bathurst	**1.3 ± 0.1**	**2.2 ± 0.1**	**2.3 ± 0.1**	**2.8 ± 0.1**	**2.2 ± 0.1**	**2.0 ± 0.1**	**2.4 ± 0.1**
$wolf_{whole}$/$caribou_{whole}$/vegetation	**Porcupine**	**1.1 ± 0.1**	**2.0 ± 0.2**	**2.3 ± 0.1**	**2.2 ± 0.2**	**1.3 ± 0.0**	**1.4 ± 0.0**	**2.2 ± 0.1**
	Bathurst	**1.3 ± 0.1**	**1.9 ± 0.1**	**2.3 ± 0.2**	**2.9 ± 0.3**	**2.0 ± 0.1**	**1.8 ± 0.1**	**2.3 ± 0.1**
piscivorous food web	Kelly et al.[15]	0.4	0.6	0.6	1.1	1.0	0.4	0.5
arctic marine mammalian food web	Kelly et al.[15]	2	4	5	5	3	2	11
dolphin food web	Houde et al.[1]	6	2	2	2	1		2

[a] BMF ± standard error; TMF ± 95% confidence interval (CI). Upper and lower CI did not differ after rounding to one decimal place.

or normalize to protein content of the tissue.[15] We tested the first two approaches.

Tissue specific BMFs varied considerably (see Table 2 and SI Table S13); highest values were found for lichen to caribou liver BMFs from 11 for PFOA to 110 for perfluorododecanoate PFDoA (Bathurst caribou). PFCs are only moderately magnified in muscle tissue of caribou from 0.9 to 2.4 for PFOA to 1.9 to 5.2 for PFDoA. In general, biomagnification seemed to be dependent on fluorinated alkyl chain length: BMFs were highest for PFNA/PFOS to PFUnA for caribou liver, whereas PFUnA to PFTrA had highest biomagnifications for caribou muscle. This shows that single compartment BMFs can obscure the true biomagnification behavoiur. The difference between these two tissues might be explained with different protein compositions. Additionally, the different metabolic rate of muscle and liver could have an influence. Liver tissue has a faster turnover rate than muscle tissue and liver concentrations could therefore represent a shorter term contaminant situation.

As tissue specific BMFs differ considerably, BMFs on whole body provide a more realistic estimate of biomagnification behavior (see Table 2). Lichen to caribou BMFs range from 1.4 ± 0.1 (PFOA) to 6.1 ± 2.2 (PFDA) for the Porcupine caribou and from 2.6 ± 0.5 (PFOA) to 11 ± 3 (PFDoA) for the Bathurst caribou. It can be seen that the BMFs differ considerably between the two caribou herds. However, if combined vegetation based on weighted species average is used as diet for the caribou, then the two herds are more uniform. BMFs were lowest for PFOA with 0.3 to 1.8 and highest for PFDA and PFUnA with 12.4 and 14.5, respectively. In late fall/early winter, caribou are thought to consume also shrubs and mushroom, and the animals studied here were all collected in this period. The studied willow and also cotton grass showed higher long-chain PFCA concentrations in the Bathurst than in Porcupine region, which could explain the difference in BMFs.

Wolves seem to biomagnify all investigated PFCs. Caribou to wolf BMFs (whole body) are highest for PFNA (3.8 ± 0.6 and 5.4 ± 0.8) but also PFOA has a BMF above one (2.4 ± 0.6 and 2.1 ± 0.5). There are two BMF values which do not follow the general trend. PFOS BMF was low for the Bathurst food chain with 1.2 ± 0.2 and PFTrA BMF was high with 3.2 ± 1.5. The high PFTrA BMF is probably because concentrations are rather low for both species and tissues and the error is consequently rather high. The low PFOS BMF is reflective of PFOS concentrations being in the same range for Bathurst wolf and caribou. Except for PFOA, caribou seem to biomagnify PFCs to a greater extent than wolves. PFNA to PFTrA values are two to four times

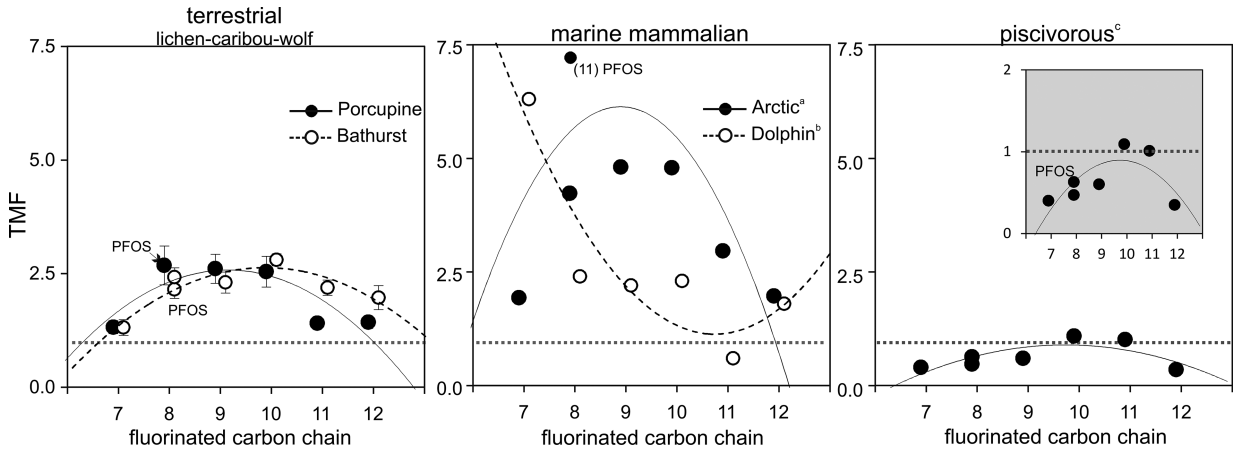

Figure 2. TMF values ± standard errors for the Porcupine herd (black dots) and the Bathurst herd (white dots) food chain are shown on the left. The two plots on the right show literature TMFs for (a) an arctic marine mammal,[15] (b) a dolphin,[1] and (c) a piscivorous food web.[15] Fluorinated carbon chain length 7 equals PFOA, 8 equals PFNA and PFOS, 9 equals PFDA etc.

higher for caribou, which might be explained by higher food assimilation efficiency of caribou.

Previous (aquatic) food web studies have found that biomagnification is dependent on the chain length of PFCAs and PFSAs: highest BMFs are mostly found for PFNA to PFUnA and PFOS, but the magnitude of BMF varies (see Table 2). The only other published mammal to mammal BMF is for seal to polar bear on a liver concentration basis.[4] About 10 times higher BMFs were observed for this food chain but this comparison is limited since PFC body distribution might vary for the organisms. A whole body BMF comparison would be more significant. Dolphin from the Charleston SC area had BMFs (seatrout as the diet) with similar magnitude (∼2) and chain length dependence (maximum BMF for PFNA to PFUnA) as did wolves from this study. Piscivorous food webs do not show consistent BMFs. Lake trout magnify all PFCAs and PFOS but not PFOA,[3] which could mean that the less proteinophilic PFCA[39,40] is not enriched in the water breathing organisms in contrast to the air breathing mammals.

In general, it can be said that PFCAs from PFNA to PFDoA, as well as PFOS, biomagnify in the lichen−caribou−wolf food chain and that PFOA shows only moderate enrichment for caribou. The comparison of wolf−caribou and caribou−lichen BMFs shows that the biomagnification for these two species has different chain length dependence demonstrating that PFC biomagnification is highly species-specific and may be dependent on many factors including protein composition. [33,39,41] Calculation of whole body concentrations may help to understand biomagnification of PFCs. However, there are certain disadvantages to this method: it is very complex and laborious to obtain all information needed to calculate whole body concentrations for larger animals. Additionally, concentrations or body composition have to estimated, when not all information is available, which introduces uncertainties.

Trophic Magnification. Determining the biomagnification of PFCs in a whole food web with TMFs is equally as challenging as determining BMFs as it is not possible to use lipid normalized concentrations. In this study, the estimated whole body concentration in caribou and wolf was used for TMF calculation and the first trophic level was assumed to be lichen or all vegetation (Table 2). Additionally, a separate TMF calculation was done using liver. Statistically significant relationships between trophic level and logarithmic concentrations (ng/g ww) were found for PFOS and almost all PFCAs, except PFOA (see SI Table S14). TMFs ranged between 1 and 3 for both food chains with highest values for PFNA to PFUnA. PFOS had very similar TMF values compared to its carboxylate counterpart PFNA (e.g., 2.7 ± 0.2 for PFNA and 2.6 ± 0.1 for PFOS for the Porcupine herd). This indicates that the biomagnification process is mainly dependent on the fluorinated chain and not on the functional group. Both food webs show very similar TMFs, the only major difference can be seen for PFDoA and PFTrA. The Bathurst food web has higher TMFs (2.2 ± 0.1for PFDoA and 2.0 ± 0.1 for PFTrA, respectively) than the Porcupine herd (1.4 for both PFDoA and PFTrA). This is because PFCA levels are slightly higher for caribou in the Bathurst herd. Other vegetation could potentially influence this difference (e.g., higher concentrations of PFDoA/PFTrA in plants from the Porcupine herd range compared to the Bathurst range). The incorporation of all other vegetation into TMF calculation does, however, not change the TMF dramatically. All values are in the same range as with lichen only.

Not surprisingly, when liver is used as the basis of TMF calculations, higher concentrations in caribou and wolf liver give rise to a greater slope for the linear regression of concentration versus trophic level. TMFs are consistently two to three times higher and the overall trend remains with highest enrichment for PFNA to PFUnA. This shows that liver-based TMFs will overestimate the biomagnification and that whole body calculations can help to more accurately approximate actual biomagnification behavior. This is particularly important for PFOA, because according to its whole body TMF, it is not statistically biomagnified, whereas liver TMFs would indicate that PFOA is bioaccumulative.

A similar relationship with the chain length can be observed for TMFs from the Arctic marine mammal food web, but the absolute values are around two times lower for this study (Figure 2).[15] PFOS shows a much stronger biomagnification behavior in the marine food web. Studies of the lake trout food web in Lake Ontario show a range of TMFs for PFOS from around 1−3.8.[3,42] Respiratory elimination of PFCs is important in water breathing organisms, as PFCAs and PFOS are relatively water-soluble and hydrophilic.[15] Air breathing animals cannot eliminate anionic PFCs over the lungs, as these PFCs are not volatile. Especially in food webs near source regions, nonvolatile precursors such as perfluoroalkyl phosphates may play an

additional role. These precursors enter the surface waters via wastewater treatment plants and could be metabolized by higher organisms, thereby increasing the concentration of PFCAs and PFSAs in higher trophic levels and leading to overestimates of BMF and TMF in source areas.[43] On the other hand, it is possible that semivolatile precursors of PFOS, such as the perfluorosulfonamido alcohols, which have been detected in Arctic air,[31,44] as well as nonvolatile precursors such as perfluoroalkyl phosphates transported on particles, could be present in vegetation and then metabolized by caribou. However, no measurements of these precursors in vegetation have been made to our knowledge. It is therefore difficult to draw a clear conclusion on whether terrestrial/marine mammalian differs from piscivorous magnification.

Overall Implications. This study shows that even in remote areas PFCs are present in terrestrial animals and vegetation because of atmospheric transport and deposition. PFCAs and PFOS have clear biomagnification potential similar to marine mammalian food webs. This study also shows that challenges remain for applying the TMF approach to studies of terrestrial biomagnification of PFCAs and PFSAs and indeed other persistent and bioaccumulative organics. Seasonal variation in $\delta^{13}C$ and $\delta^{15}N$ in vegetation will be important in temperate and arctic climates as will dietary variation in herbivores. Selection of the species used to calculate trophic levels and of the appropriate trophic enrichment factor are important factors which need further study in terrestrial food webs.

■ ASSOCIATED CONTENT

Supporting Information. More information on analytical methods, sampling locations, standard chemicals, data sets on all concentrations, TMF calculations, and further details are shown in Figures S1−S6 and Tables S1−S14.This material is available free of charge via the Internet at http://pubs.acs.org.

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