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Circumpolar Stud erfluoroalkyl Contaminants in Bears (*Ursus maritimus*)

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Perfluoroalkyl substances were determined in liver tissues and blood of polar bears (*Ursus maritimus*) from five locations in the North American Arctic and two locations in the European Arctic. Concentrations of perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate, heptadecafluorooctane sulfonamide, and perfluoroalkyl carboxylates with C_8−C_{15} perfluorinated carbon chains were determined using liquid chromatography tandem mass spectrometry. PFOS concentrations were significantly correlated with age at four of seven sampling locations, while gender was not correlated to concentration for any compound measured. Populations in South Hudson Bay (2000−2730 ng/g wet wt), East Greenland (911−2140 ng/g wet wt), and Svalbard (756−1290 ng/g wet wt) had significantly ($P < 0.05$) higher PFOS concentrations than western populations such as the Chukchi Sea (435−729 ng/g wet wt). Concentrations of perfluorocarboxylic acids (PFCAs) with adjacent chain lengths (i.e., C_9:C_{10} and C_{10}:C_{11}) were significantly correlated ($P < 0.05$), suggesting PFCAs have a common source within a location, but there were differences in proportions of PFCAs between eastern and western location sources. Concentrations of PFOS in liver tissue at five locations were correlated with concentrations of four polychlorinated biphenyl congeners (180, 153, 138, and 99) in adipose tissue of bears in the same populations, suggesting similar transport pathways and source regions of PFOS or precursors.

Introduction

Concentrations and global distribution of perfluoroalkyl substances in wildlife have been described in recent publications (*1*, *2*). The U. S. Environmental Protection Agency has expressed concern over effects of these types of compounds, due to their potential for accumulation and toxicity to humans and wildlife (*3*). Perfluorocarboxylic acids (PFCAs) are peroxisome proliferators (*4*) as well as tumor promoters (*5*) and may inhibit gap junction intercellular communication at environmentally relevant concentrations (*5*).

Perfluoroalkyl substances can be divided into two major groups: perfluorinated acids (PFAs) and precursors. The perfluorinated acids can be further divided into perfluoroalkyl sulfonic acids (PFSAs) (e.g., perfluorooctane sulfonate (PFOS)) and perfluorocarboxylic acids (PFCAs) (e.g., perfluorooctanoic acid (PFOA)). PFAs with chain lengths greater than six or seven carbons have been found to bioconcentrate in fish (*2*, *6*). PFOS has been identified as the major perfluorinated acid in wildlife (*1*). PFOS has been found in liver tissue of animals worldwide, and there have been increasing reports of the presence of PFCAs with chain lengths from 8 to 15 carbons (*2*, *7*). The highest body burdens reported have been in top-level predators in the Arctic marine ecosystem such as polar bears (*2*, *8*). Concentrations reported for South Hudson Bay (*2*) populations were significantly greater than reported for Alaskan bears (*1*), possibly indicating a spatial trend within the Arctic.

The transport pathway for these chemicals to the Arctic remains unclear. They are used in fire-fighting foams, stain repellents, cleaners, and lubricants (*3*). PFAs have no natural source, and their chemical properties preclude long-range atmospheric transport, which makes their presence in remote locations such as the Arctic difficult to explain (*9*). Ellis et al. (*10*) have shown that fluorotelomer alcohols (FTOHs) degrade via hydroxyl-radical-initiated atmospheric processing to yield PFCAs, which would be removed through wet and dry deposition, and proposed that this may explain the presence of these perfluorinated acids in remote regions such as the Arctic. It has previously been shown that FTOHs can be metabolized to PFOA by rats and mixed microbial systems (*11*, *12*). The PFSAs also may be degradation products of neutral compounds such as *N*-methyl perfluorooctane sulfonamidoethanol and *N*-ethyl perfluorooctane sulfonamide (*13*). These latter compounds have been measured along

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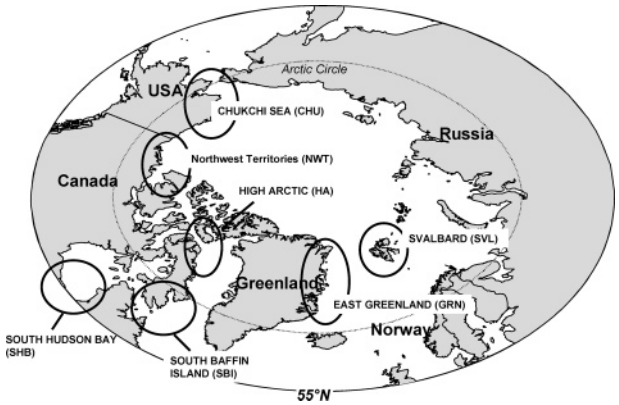

FIGURE 1. Map showing seven sampling locations of polar bear liver tissue: Chukchi Sea, Northwest Territories, South Baffin Island, High Arctic, South Hudson Bay, East Greenland, and Svalbard, Norway.

with FTOHs in urban and rural air samples in North America (*14*, *15*).

Polychlorinated biphenyl (PCB) contamination and distribution in polar bear populations has been well documented over the past 30 years (*16*−*20*). The currently accepted hypothesis is that atmospheric transport and ocean currents bring these chemicals to the Arctic marine food webs, resulting in a distinctive distribution pattern of contamination in polar bear tissues (*18*−*25*): Polar bears from East Greenland, Svalbard, and the Kara Sea in Russia have the highest concentrations of PCBs, with a decreasing westward trend to the lowest concentrations in the Chukchi and Bering Sea regions. Similar contamination patterns for PFAs would support the hypothesis that Eastern North America and Western Europe are the primary source regions of these compounds (*22*, *24*, *25*). In this study, we examined PFAs in polar bear liver tissue from five locations in North America and two in the European Arctic. Age and gender effects are examined as well as spatial trends. Correlations between PFCAs and between PFOS and four PCB congeners, measured in many of the same bears by Verreault et al. (*25*), were examined to identify potential pathways and source regions.

Materials and Methods

Chemicals. The 3M Company (St. Paul, MN) provided standards of perfluorohexane sulfonate (PFHxS, 99.9%), perfluorooctane sulfonamide (PFOSA, 99.9%), and potassium PFOS (86.4%). Standards of perfluoroheptanoic acid (PFHpA, 99%), PFOA (98%), perfluorononanoic acid (PFNA, 97%), perfluorodecanoic acid (PFDA, 98%), perfluoroundecanoic acid (PFUA, 95%), perfluorododecanoic acid (PFDoA, 95%), and perfluorotetradecanoic acid (PFTA, 97%) were purchased from Sigma-Aldrich (Oakville, ON, Canada). Ammonium acetate (98%) and tetrabutylammonium hydrogen sulfate were purchased from Sigma-Aldrich, anhydrous sodium carbonate (99.8%) was purchased from J. T. Baker (Phillipsburg, NJ), and methyl-*tert*-butyl ether (MTBE, 99.5%) was purchased from VWR Canlab (Mississauga, ON, Canada).

Samples. Local hunters in Nunavut, Northwest Territories (NWT), Northwestern Alaska, and Eastern Greenland collected tissue samples, including liver, from bears killed during the annual hunt (Figure 1). Hunters were provided with sampling kits and returned the samples to community wildlife officers. Livers were collected within 12 h post mortem and stored in individual Zip Lock bags. All samples were kept at −20 °C or at lower temperature before sample preparation and extraction. Gender and kill location in degrees of latitude and longitude were also recorded, and a vestigial premolar tooth was extracted for age determination.

Eastern Greenland liver samples were collected between January 1999 and September 2001 in the area of Scoresby Sound. Twenty-nine samples were selected for analysis to give an even distribution of age and approximately equal number of males and females. Nunavut samples (n = 26) were collected between February and May 2002. The Nunavut samples were divided into two groups to reflect geographic separation; bears killed in Pangnirtung, Qikiqtarjuaq, Iqaluit, and Kimmirut are referred to as the South Baffin Island population, and bears killed in the area of Resolute, Grise Fjord, and Pond Inlet are referred to as the High Arctic samples. NWT (n = 7) and Alaskan (n = 10) bears were sampled in 2001. Samples from Alaska were taken in the regions of the Chukchi and Bering Seas and are referred to as the Chukchi Sea samples in this study. South Hudson Bay samples were collected in 2002, in the vicinity of Sanikiluaq. Liver tissues were shipped to the Canada Center for Inland Waters (Burlington, ON) and stored at −20 °C.

Samples from Svalbard were collected from free-ranging bears tranquilized for research purposes (*25*). Blood samples were collected from the vena femoralis. Heparinized blood was collected in vacutainers, and plasma was separated by centrifugation for 10 min. All samples were kept in NUC Cryo vials at −20 °C until analysis.

Age Estimation. Age determination was carried out by counting the tooth cementum growth layer groups of the lower incisor (I_3) after decalcification, thin sectioning (14 μm), and staining (toluidine blue) using the method described by Hensel and Sorensen (*26*) and Dietz et al. (*27*). When necessary, the individuals were categorized as subadults, adult males, and adult females by the criteria adult males ≥ 6 years, adult females ≥ 5 years, and others as subadults. Svalbard bears were aged using a vestigal premolar tooth (P1) after method described by Calvert and Ramsay (*28*).

Chemical Analysis. Samples were prepared following methods developed by Hansen et al. (*29*) and described by Smithwick et al. (*8*). In brief, approximately 0.2 g of liver tissue was extracted using MTBE and an ion-pairing agent. The MTBE was evaporated off, and the samples were reconstituted in 1 mL of methanol and filtered through 0.2-μm nylon filters into plastic vials.

Instrumental analysis was performed by liquid chromatography tandem mass spectrometry (LC-MS/MS) following previously described conditions (*7*, *8*). A 10 μL aliquot of sample was injected on a Luna 3-μm C8 column (50 mm × 2.0 mm) (Phenomenex, Inc., Torrance, CA).

PFA recoveries were examined by spiking liver tissue (n = 3) at 500 ng/g with all analytes. The standard contained all compounds examined in this study with the exception of perfluoropentadecanoic acid (PFPA) and perfluorotridecanoic acid (PFTriA), for which standards were not available. The standard was spiked into the homogenate and was in contact with the tissue for 2 min prior to extraction. Unspiked liver tissue from the same bear was also analyzed, and background PFA concentrations were subtracted from the spiked sample concentrations. Results were expressed as a percentage of the initial spike concentration.

Quantification was performed relative to PFHpA by using a standard curve of known concentrations that had been extracted in a manner similar to the samples. Polar bear liver tissue had previously been shown not to contain background PFHpA (*2*). PFHpA has similar chemical properties to the compounds of interest, making it an appropriate internal standard. Injections of standards were made every 10 samples to monitor changes in sensitivity. All standards and samples were blank-subtracted prior to quantification. The instrument detection limit (IDL) was defined as the value corresponding to the peak with a signal-to-noise ratio of 3. Background concentrations of PFNA (average 0.5 ng/g) and PFOA (0.5−1 ng/g) in the blanks resulted in method detection limits

TABLE 1. Acronym, Structure, Monitored Transition, and Method Detection Limit (ng/g wet wt) of Perfluorinated Acids Found in Polar Bear Liver Samples

compound	acronym	structure	ion transition monitored by LC-MS/MS	method detection limit (ng/g wet wt)
		Perfluorocarboxylates		
perfluoroheptanoate	PFHpA	$CF_3(CF_2)_5COO^-$	363 → 219	*a*
perfluorooctanoate	PFOA	$CF_3(CF_2)_6COO^-$	413 → 369	2.3
perfluorononanoate	PFNA	$CF_3(CF_2)_7COO^-$	463 → 419	1.6
perfluorodecanoate	PFDA	$CF_3(CF_2)_8COO^-$	513 → 469	0.3
perfluoroundecanoate	PFUA	$CF_3(CF_2)_9COO^-$	563 → 519	0.63
perfluorododecanoate	PFDoA	$CF_3(CF_2)_{10}COO^-$	613 → 569	0.6
perfluorotridecanoate	PFTriA	$CF_3(CF_2)_{11}COO^-$	663 → 619	*b*
perfluorotetradecanoate	PFTA	$CF_3(CF_2)_{12}COO^-$	713 → 669	0.6
perfluoropentadecanoate	PFPA	$CF_3(CF_2)_{13}COO^-$	763 → 719	*b*
perfluorooctane sulfonate	PFOS	$CF_3(CF_2)_7SOO^-$	499 → 99	2.2
perfluorohexane sulfonate	PFHxS	$CF_3(CF_2)_5SOO^-$	399 → 99	3.2
perfluorooctane sulfonamide	PFOSA	$CF_3(CF_2)_7SO_2NH_2$	498 → 78	1.7

[a] Perfluoroheptanoic acid is used as an internal standard. All samples and blanks are spiked with 25 ng/g. [b] Detection parameters were not determined for these compounds due to lack of authentic standards.

TABLE 2. Geometric Means (ng/g wet wt) and Ranges in Concentration of Perfluorinated Compounds in Liver Tissue from Polar Bears Collected at Seven Locations in the North American and European Arctic[a]

location[b]	concn	PFOS	%	PFHxS	%	PFOSA	%	PFOA	%	PFNA	%	PFDA	%	PFUA	%	PFDoA	%	PFTriA	%	PFTA	%	PFPA	%
CHU	mean	729	100	129	90.0	2.55	90	2.40	80	214	100	33.2	100	26.7	100	1.44	40	1.54	40	1.21	100	<0.6	0
	min	435		35.2		<1.7		<2.3		123		19		14.6		<0.6		<0.6		0.63			
	max	1480		325		8.7		9.04		398		98.5		70		26.0		9.55		3.07			
NWT	mean	1320	100	44.8	71.4	<1.7	0	16.3	100	405	100	103	100	101	100	3.09	100	3.87	87.5	<0.6	14.3	<0.6	0
	min	982		<3.2				10.2		331		73.2		77.9		0.75		<0.6		<0.6			
	max	2160		261				33.3		540		155		146		5.71		8.34		1.86			
HA	mean	1170	100	35.9	77.8	<1.7	44.4	18.6	100	182	100	58.5	100	34.5	100	1.77	44.4	1.62	87.5	<0.6	11.1	<0.6	0
	min	263		<3.2		<1.7		8.64		12.2		9.32		6.39		<0.6		<0.6		<0.6			
	max	2410		263		10		31.8		431		117		81.8		2.7		3.15		1.08			
SBI	mean	1390	100	71.4	87.5	5.75	100	36	100	182	100	43.3	100	45.2	100	2.82	87.5	3.32	100	2.37	75	<0.6	0
	min	977		<3.2		1.9		20		85.8		14.4		17.4		<0.6		0.75		<0.6			
	max	2100		417		13.1		55.8		317		124		162		11.4		25.3		17.53			
SHB	mean	2730	100	62.3	90.0	6.23	83.3	24.9	100	277	100	77.1	100	114	100	4.99	100	10.6	100	1.05	66.7	<0.6	0
	min	2000		<3.2		<1.7		18.6		195		53.3		108		3.47		7.37		<0.6			
	max	3770		321		65		31.2		360		111		120		6.59		14.6		2.94			
GRN	mean	2140	100	80.2	100	8.46	85.7	9	75.0	191	100	72.1	100	104	100	7.86	100	18.6	100	3.27	96.4	1.44	28.6
	min	911		4.39		<1.7		<2.3		64.5		17		39.8		3.7		7.87		<0.6		<0.6	
	max	6340		544		71.5		57.1		513		209		179		16.6		46.9		16.19		16.3	
SVL	mean	1290	100	2940	100	3.82	64.3	20.6	100	102	100	42.9	100	112	100	14.8	100	22.4	100	<0.6	0	6.35	100
	min	756		2260		<1.7		11.9		75.7		23.4		82.6		10.3		17.2				3.64	
	max	1990		4430		11		37.5		153		71.8		161		19.8		35				9.5	

[a] Percent columns indicate percent of samples above MDL. [b] Location acronyms are defined in Figure 1.

(MDLs) of 1.6 and 2.3 ng/g, respectively. The MDLs were determined as the IDL plus 3 times the standard deviations of the blanks, unless blank values were below detection limit, wherein a value of 3 times the standard deviation of the lowest standard was used. Values ranged from 0.3 for PFDA to 3.2 ng/g wet wt for PFHxS (Table 1).

Data Analysis. Statistical analyses were performed with SYSTAT (Point Richmond, CA) for Windows (version 10) at a significance level of $\alpha = 0.05$, except where stated otherwise. The contaminant data were log-transformed prior to the statistical analysis to meet the assumption of normality and homogeneity of the variance. Samples with concentrations less than the MDL were assigned a value equal to one-tenth of the MDL. This allowed the log transformations and the calculation of geometric means without significantly raising the mean values.

A single-factor one-way ANOVA was used to investigate differences of age-adjusted means of PFAs among locations. Significant differences were investigated among locations using Tukey's post hoc test.

The plasma to liver conversion factor was determined by dividing the average liver concentration by the average plasma concentration in bears from the same geographic location (Alaska), using data generously provided by J. Giesy (Michigan State University) (*1*). The plasma to liver conversion factor for the samples was generated with only PFOS data but was used to convert all PFA values.

Results and Discussion

PFOS, PFHxS, and PFCAs with chain lengths C_8 through C_{13} were detected at concentrations above the MDL at all locations. PFOSA was not detected in the NWT samples, and PFTA was not detected in the Svalbard samples. PFPA was only detected above the MDL in the Greenland and Svalbard samples (Table 2).

The percent recoveries for PFOS, PFHxS, and PFCAs (C_8 through C_{14}) ranged from 53 ± 10% to 130 ± 16% and were similar to those found in spike and recovery of Greenland polar bear liver samples by Smithwick et al. (*8*). Recoveries for PFTA averaged 53% while recovery of PFPA was not deter-

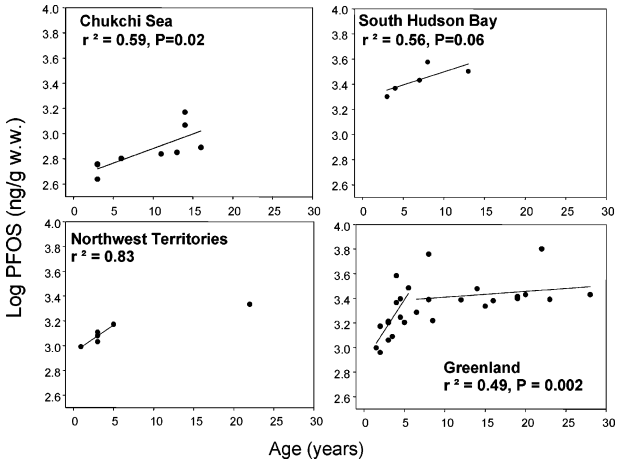

FIGURE 2. Linear correlations between concentrations (ng/g wet wt) of PFOS and age (years) in polar bear liver tissue from four sampling locations in the North American and European Arctic. Trend lines represent linear regressions. The Greenland panel has one regression line for juvenile bears (<6 years) and one for adults.

mined. The assumption was made that PFPA recovery would be similar to PFTA recovery; therefore PFTA and PFPA values were recovery-compensated prior to statistical analysis.

Sex and Age Differences. The sample group consisted of 40 males aged from 0.9 to 28 years and 43 females aged from 2 to 25 years. There were no significant differences attributable to gender for any PFA; therefore the samples were treated as one group. This trend is consistent with the hypothesis that PFAs are retained via enterohepatic recirculation, a process that is similar to both males and females (*30*). Also, because PFAs are lipophobic, they would not be expected to accumulate in fatty tissues or be excreted via lactation, processes which, in part, result in gender differences observed for PCBs in polar bears (*18*, *19*). There may also be differences in the metabolism and urinary excretion rates between males and females, and lactation and/or gestation may also affect these rates in females. PFOS showed a significant increase with age at four of the seven locations sampled (Figure 2). The South Baffin Island, Svalbard, and High Arctic groups showed no significant age trends for any compound, while South Hudson Bay bears showed age trends for PFOS and PFUA. We have previously reported that polar bears from East Greenland also showed significant increases in concentration with age in juvenile male bears for PFOS, PFNA, and PFCAs C_{10}–C_{14} (*8*). One outlying sample in the NWT group was not used in the linear regression, which resulted in a sampling group of bears age 5 or less. The lack of trends at other locations may be attributable to limited sample size; however, metabolism or regional differences in diet and habitat may also affect concentrations. The correlation with age implies that PFA excretion is slow in polar bears, resulting in a long time to approach steady-state concentrations. Similar observations have been reported for PCBs in polar bears (*25*).

Geographic Trends. PFOS was the major contaminant in all samples, having concentrations at least a factor of 10 higher than all other PFAs. There was a significant geographic trend for PFOS, with South Hudson Bay and East Greenland having significantly greater concentrations than Svalbard, High Arctic, and Western NWT and all having significantly greater concentrations ($P < 0.05$) than the Chukchi Sea samples (Figure 3).

The greater concentrations measured in bears from East Greenland and the South Hudson Bay are possibly due to proximity to sources in Europe and Eastern North America, respectively. Only blood plasma was available from the Svalbard bears, and the PFOS concentrations after conversion

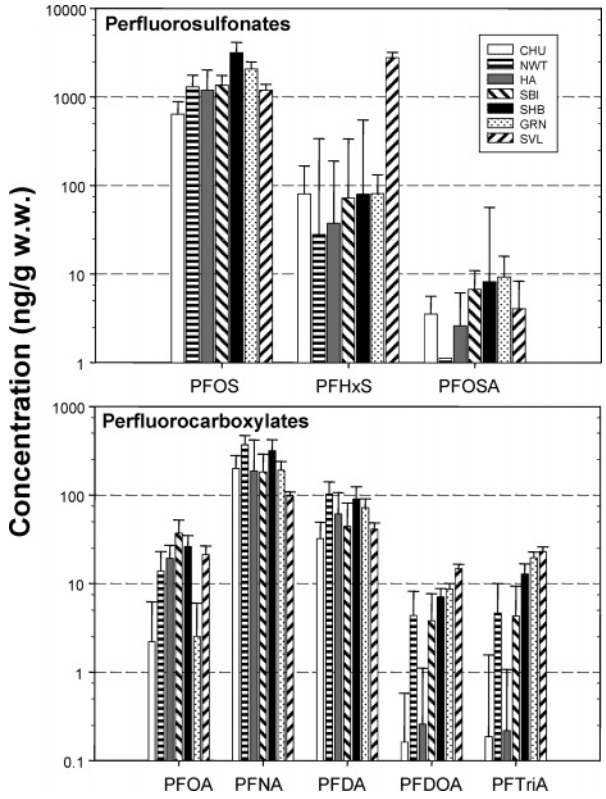

FIGURE 3. Concentrations (ng/g wet wt) of various perfluorinated organics in polar bear liver tissue at seven sampling locations across the North American and European Arctic. PFOS, PFDoA, and PFTriA show a trend of increasing from west to east, while PFNA decreases over the same area. Error bars represent 95% confidence intervals.

were lower compared to the East Greenland bear livers. However, the plasma to liver conversion factor used on the Svalbard samples was based on the Alaskan samples (*1*), and there is uncertainty in the extrapolation to other regions.

PFUA (excepting NWT), PFDoA, PFTriA, and PFPA showed similar geographic trends to PFOS. The only PFPA values above MDL were measured in bears from Svalbard and Greenland. The remaining PFAs did not show distinguishable geographic trends (Figure 3). PFOS and PFCAs with chain lengths greater than 10 carbons had similar geographic distributions, while PFOA, PFNA, PFDA, PFHxS, and PFOSA are more evenly distributed or showed higher concentrations in the Western North American Arctic. The plasma PFCA values for Svalbard were adjusted using the PFOS plasma to liver ratio for Alaskan bears, and thus actual liver values are uncertain, particularly for the longer chain length, more lipophilic PFCAs.

Statistically significant correlations were found among concentrations of some PFCAs ($r^2 > 0.5$, $P < 0.05$) within location (Figure 4, Table 3), and the strongest correlation was, in general, between PFDA and PFUA. These correlations suggest a common source at each location. Concentrations of PFOS, PFOSA, PFHxS, and PFOA were not correlated with any other PFA. Atmospheric degradation experiments by Ellis et al. (*10*) indicated that FTOHs degrade through reaction with a hydroxyl radical to yield a homologous series of PFCAs. According to Ellis et al. (*10*), 10:2 FTOH is a potential source of both PFDA and PFUA. The strong correlation shown here suggests a common source and therefore supports this hypothesis. However, 8:2 FTOH should be a source of both PFOA and PFNA (*10*), but the present study did not find a significant correlation between these two contaminants. Metabolism of 8:2 FTOH to PFOA has been documented in

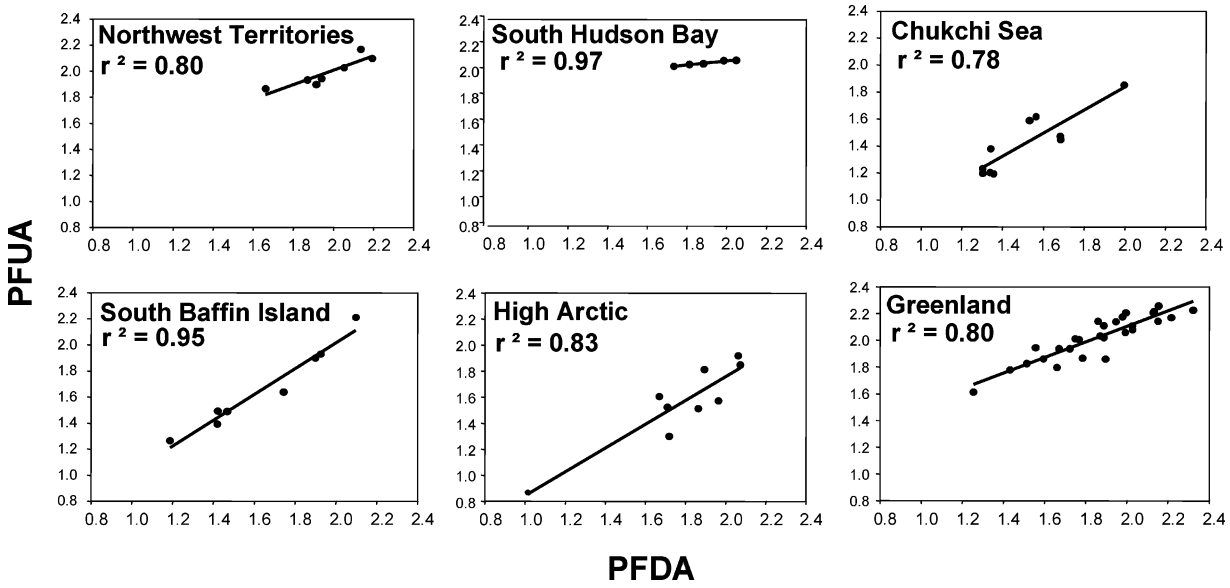

FIGURE 4. Linear correlations between concentrations (ng/g wet wt) of PFDA and PFUA acid from polar bear liver tissue samples from locations in the North American and European Arctic. Similar correlations exist between other adjacent-chain-length pairs at all locations (Table 3). Coefficients of variation (r^2) are shown (all $P < 0.05$, Table 3).

TABLE 3. Coefficient of Correlation (r^2) of Linear Regression of Adjacent-Chain-Length Perfluorocarboxylic Acids at Seven Locations in the North American and European Arctic

	chain length							
	9:10		10:11		12:13		9:11	
location[a]	r^2	P	r^2	P	r^2	P	r^2	P
CHU	0.65	<0.01	0.78	<0.01	0.38	0.06	0.28	0.12
NWT	0.88	<0.01	0.80	0.01	0.81	0.01	0.57	0.08
HA	0.98	<0.01	0.83	<0.01	0.83	<0.01	0.78	<0.05
SBI	0.66	<0.01	0.95	<0.01	0.62	0.02	0.57	0.03
SHB	0.76	0.03	0.97	<0.01	0.38	0.38	0.72	0.07
GRN	0.90	<0.01	0.75	<0.01	0.55	<0.01	0.79	<0.01
SVL	0.77	<0.01	0.71	<0.01	0.30	0.56	0.37	0.02

[a] Location acronyms are defined in Figure 1.

rats and mixed microbial systems (*11*, *12*) and could be a source in the marine food web. Lack of bioaccumulation of PFOA or additional sources of PFNA could further obscure this relationship.

De Silva and Mabury reported that a high proportion of linear isomers of PFOA was present in bears from the Canadian Arctic and >99% linear isomers of PFNA and PFTriA were found, suggesting that FTOHs were the ultimate source (*31*).

To address the question of sources at different locations, the ratios of adjacent-chain-length PFA concentrations were calculated, and the arithmetic means and 95% confidence intervals were determined (Figure 5). Chukchi Sea samples had a much higher proportion of PFNA to PFOS than those in the eastern sampling locations (Figure 5a). Similar relationships existed between PFUA to PFDA, PFDA to PFNA, and PFDoA to PFUA (Figures 5c, 5e, and 5f). The proportion of PFNA was much greater than PFOA in the Chukchi Sea samples but lower in the eastern sampling areas (Figure 5b). PFTriA and PFDoA were present at similar concentrations within all locations (Figure 5d). The resulting patterns could be explained by different geographic sources of PFAs for the eastern and western locations.

The local atmospheric processes or chemistry are unlikely to be significantly different between the sampling locations. It is similarly unlikely that there are major differences in metabolic processes or transformations at some stage of the food chain. If PFAs (and/or precursors) are being transported via wind and/or ocean currents, then the prevailing pathways suggest that the source of the PFAs in the European Arctic and eastern Greenland would be attributable to transport from Western Europe and eastern North America, while the Western North American Arctic would be influenced mainly by East Asian sources (*24*). No regional use or emission data are available at this time, but similar geographical source patterns have been presented for PCBs (*24, 25*). In contrast, PFHxS and PFNA had a geographic distribution more similar to that of hexachlorocyclohexane isomers in polar bears, which are thought to have an East Asian source (*25*).

Concentration Relative to PCB Congeners. The geometric mean (ng/g wet wt ± 95% confidence intervals) of concentrations for PFOS in liver and four PCB congeners in fat were determined for five sampling locations. PCB concentrations were not available for South Hudson Bay, and the Svalbard data were not used due to the uncertainty in the plasma to liver conversion factor as described above. While the same individuals were not analyzed for both groups of compounds, the animals were collected from the same location at the same time. Full analysis of PCB concentrations in the same populations utilized in the present study is available in Verreault et al. (*25*). The geographic means of PFOS and PCBs were plotted against one another, and linear regressions were carried out (Figure 6). The geographic trend of PFOS concentrations was positively correlated with PCB 180 ($r^2 = 0.81$, $P = 0.04$) and showed marginal significance with PCB congeners 153, 138, and 99 (Figure 6). This suggests that PFAs and PCBs may have common transport and bioaccumulation pathways, particularly with higher congeners. Tomy et al. (*32*) have shown that PFOS biomagnifies in the arctic marine food chain. As atmospheric circulation and ocean currents are currently thought to be responsible for the distribution of PCBs (*24*, *25*, *33*), this supports an atmospheric and oceanic distribution model for PFAs and/or their precursors. Taniyasu et al. (*34*) have recently reported higher concentrations of PFSAs and PFCAs in the North Atlantic compared to those in the North Pacific Ocean. Although they did not investigate PFAs in Arctic waters, their results are consistent with the geographical trends observed in this study with the North Atlantic influencing the European Arctic Ocean, while flow from the Pacific Ocean influences the Chukchi and Beaufort Seas in the Western North American Arctic.

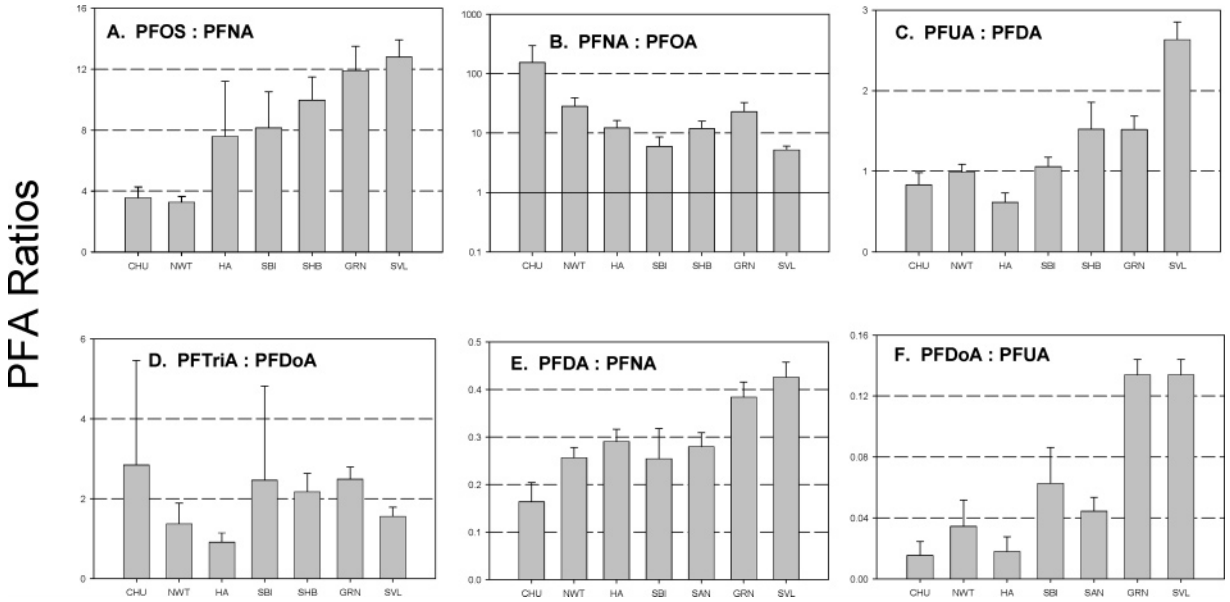

FIGURE 5. Arithmetic means with 95% confidence intervals of ratios of concentration (ng/g wet wt) of adjacent-chain-length PFCAs in polar bear liver tissue at individual sampling locations across the North American and European Arctic.

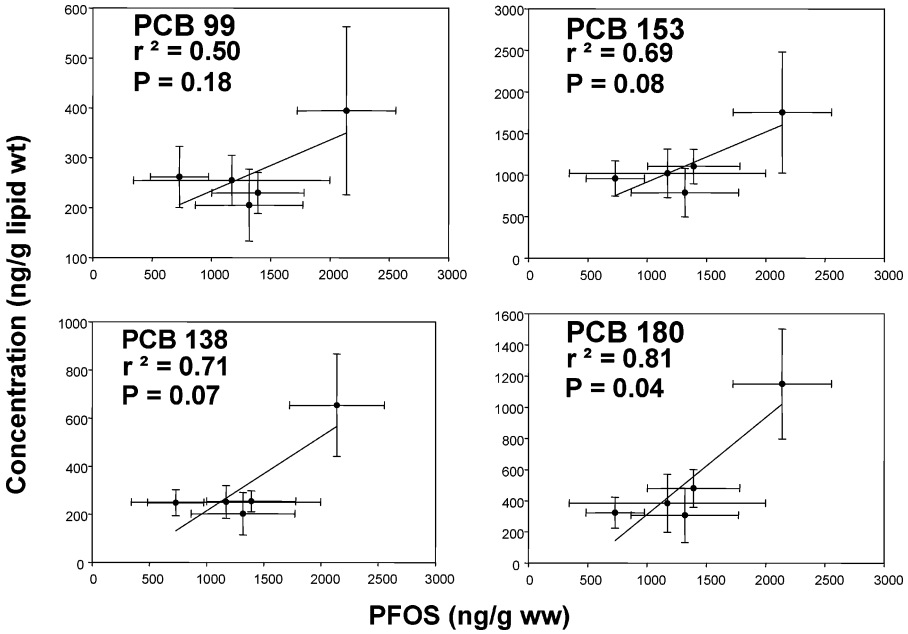

FIGURE 6. Linear correlations with 95% confidence intervals between PCB congener concentrations (ng/g wet wt) and PFOS concentrations (ng/g wet wt) in polar bear liver tissue from sampling locations in the North American and European Arctic.

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