

Examination of dietary exposure to polyfluorinated compounds via consumption of traditional foods

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Introduction

Recent work has described levels of certain perfluorinated compounds (PFCs) in human sera collected from donors in a large number of countries¹ including southern² and northern Canada³. The routes of human exposure to these perfluorinated compounds have not been well-characterized. One possible route is the consumption of foods containing PFCs. Past work on PFCs in Arctic biota^{4,5} demonstrates that these compounds are present in the Arctic environment and in some traditional foods consumed by northern populations. This initial study was performed to examine the dietary exposure of traditional food consumers to PFCs. Portions of liver consumed as traditional food were analyzed for five perfluorinated carboxylates (PFCAs), one perfluorinated sulfonate, three perfluorooctanesulfonamides (PFOSAs), three fluorinated telomer carboxylates (FTCAs), and three unsaturated fluorinated telomer carboxylates (FTUCAs).

Materials and Methods

Liver samples (20 in total) from Arctic char, burbot, caribou, loche, ringed seal, and walrus were collected from various locations in Nunavut between 1997 and 1999 (Table 1). Samples were stored at -20°C prior to analysis.

The samples were extracted using a newly developed solvent extraction method and analyzed using LC-MS/MS⁶. A 0.2 g portion of liver was spiked with recovery internal standards (¹³C₂-PFDA, 4H-PFOS, ¹³C₂-6:2 FTUCA, ¹³C₂-10:2 FTUCA, and d₅-NEtPFOSA) homogenized with 4 mL Optima grade methanol and centrifuged (10 min at 3600 x g) to obtain supernatant. The extraction was repeated twice with 2 mL volumes of methanol, and the supernatants were combined and reduced in volume at 37°C to 250 mL using N₂. Aliquots of methanol taken through the procedure were used as method blanks. Instrument performance internal standards were added (¹³C₂-PFOA, ¹³C₂-8:2 FTUCA, and d₃-NMePFOSA), and the final solution was centrifuged at 14 000 x g for 10 min. A portion of the final solution was transferred to a polypropylene autosampler vial prior to injection on the LC-MS/MS. All PFCs were quantitated using external standard solutions made up in methanol. Method detection limits were estimated to be 0.3 ng/g for PFOA and PFNA, 0.1 ng/g for PFDA, 0.03 ng/g for PFUA, 0.04 ng/g for PFDoDA, 0.02 ng/g for PFOS and 2 and 36 pg/g for PFOSA and N-EtPFOSA, respectively.

Results and Discussion

Table 1 lists concentrations of PFCs observed in the liver samples. The ringed seal liver contains the greatest amount of PFCs, followed by walrus, caribou, and fish livers. This rank order in sigmaPFA concentrations is driven by PFOS concentrations, which are approximately 2 to 10 times higher in ringed seal liver compared to samples from other species. PFCAs were also frequently detected, and were found at the highest levels in caribou and walrus, followed by ringed seal, and then fish. PFOSAs (only perfluorooctanesulfonamide in all but one instance) were only detected in walrus, ringed seal, and the one Arctic char liver sample. FTUCA/FTCAs were not detected in any of the 20 liver samples.

The PFC concentrations observed in this study are generally similar to what has been reported for liver in other ringed seal, walrus, and fish sampled in the Canadian Arctic. Previous work examining PFCs in Arctic biota also found that PFOS was present at higher concentrations than all individual PFCAs in ringed seal⁴, walrus⁵, and various species of fish^{4,5}.

Relative concentrations of the PFCA homologues in this limited number of traditional food samples analyzed are different than those observed in the plasma of traditional food consumers (Table 2). PFOS and PFNA are the two most abundant PFCs found in the traditional food samples analyzed in this pilot study (PFOS the most abundant in ringed seal, some walrus and loche; PFNA the most abundant in caribou and some burbot). However, in the plasma pools of donors identified as Dene, Metis, or Inuit, PFOS and PFOA were the most abundant PFCs, followed by PFHpA and then PFNA. PFCAs with perfluoroalkyl chains longer than C₉ were not observed in the human plasma³, but were observed in almost all of the traditional food samples analyzed.

The results of this pilot study indicate that consumers of liver are exposed to PFCAs, PFOS, and some PFOSAs. Consumption of ringed seal liver will lead to the greatest dietary exposure to PFCs, followed by caribou and walrus liver. However, since liver is not one of the main traditional food items consumed, a wider variety of food items must be analyzed to obtain a better picture of the dietary exposure of traditional food consumers to PFCs. An expanded survey of traditional food items for PFCs will also provide data to assess whether or not PFC concentrations observed in northerners are correlated to PFC concentrations in food.

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References

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Table 1. Liver perfluorinated sulfonate, carboxylate, and sulfonamide concentrations (ng/g, wet weight).

Species	Community	Preparation	PFOA	PFNA	PFOS	PFDA	PFUA	PFDoDA	ΣPFAs	ΣPFOSAs
Arctic char	Kugluktuk	Raw	nd ^a	nd	5.4	nd	nd	nd	5.4	152.6
Burbot	Aklavik	Raw	26.5	29.2	2.7	10.2	nd	nd	68.6	nd
Burbot	Aklavik	Raw	nd	nd	15.4	nd	nd	nd	15.4	nd
Caribou	Pond Inlet	Raw	8.9	26.3	19.8	12.8	7.6	10.8	86.3	nd
Caribou	pooled	Baked	2.1	24.6	19.7	7.8	4.9	6.4	65.5	nd
Caribou	Hopedale	Raw	12.2	17.8	24.4	14.5	11.6	nd	80.5	nd
Caribou	Pond Inlet	Raw	5.9	15.5	15.2	4.5	3.9	6.2	51.3	nd
Caribou	Pond Inlet	Raw	3.7	7.7	23.2	nd	10.7	nd	45.3	nd
Caribou	Kugluktuk	Raw	nd	nd	3.8	3.2	5.9	nd	12.9	nd
Loche	Aklavik-Jackfish Creek	Raw	2.7	nd	6.7	5.6	24.3	nd	39.3	nd
Loche	Aklavik	Raw	nd	nd	18.3	nd	nd	nd	18.3	nd
Ringed seal	Iglolik	Raw	nd	25.2	86.7	4.4	5.6	2.9	124.7	nd
Ringed seal	Iglolik	Raw	8.7	6.2	74.3	4.2	9.0	nd	102.5	0.4
Ringed seal	Qikiqtarjuaq	Raw	nd	7.1	152.8	3.3	4.9	7.5	175.6	1.6
Ringed seal	Iglolik	Raw	2.3	nd	291.7	0.7	4.6	13.6	312.9	0.2
Ringed seal	Iglolik	Raw	nd	9.0	197.9	7.1	nd	nd	214.1	2.8
Walrus	Iglolik	Raw	5.8	18.0	27.7	6.4	3.8	11.1	72.6	3.1
Walrus	Iglolik	Raw	0.3	22.3	38.6	2.7	1.8	4.7	70.6	3.3
Walrus	Iglolik	Raw	4.5	34.9	8.1	3.5	4.7	4.5	60.2	0.6
Walrus	Iglolik	Raw	nd	11.1	14.6	nd	4.8	8.8	39.3	1.1

^anot detected above method detection limits

Table 2. Average and range (in parentheses) of relative concentrations of selected perfluorocarboxylates and perfluorooctane sulfonate in liver traditional food samples and archived maternal and cord plasma collected from donors residing in the North.

Samples	PFOA/PFNA	PFOA/PFOS
Metis, Dene, Inuit plasma ^a	7.9	0.35
(n=9)	(0.2 – 32)	(0.04 – 1.54)
fish liver	0.9	2
(n=5)	(undefined – 0.9)	(0 – 10)
caribou liver	0.4	0.2
(n=6)	(undefined – 0.7)	(0 – 0.5)
ringed seal liver	0.4	0.03
(n=5)	(undefined – 1.4)	(0 – 0.1)
walrus liver	0.1	0.2
(n=4)	(0 – 0.3)	(0 – 0.5)

^adata is from Tittlemier et al.³