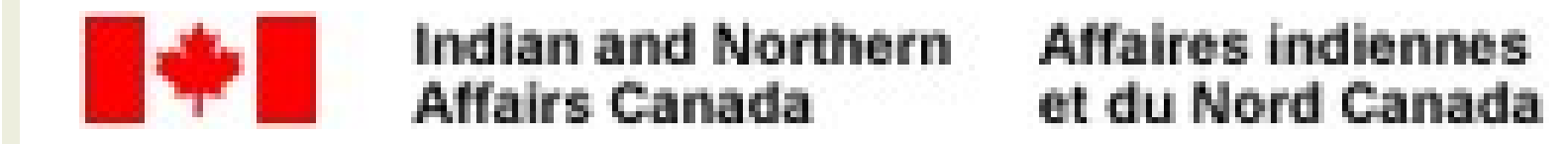


Perfluorinated Sulfonic and Carboxylic Acids and Precursors in East Greenland and Compared to Subpopulations of Polar Bears From Hudson Bay, Canada



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Introduction

Perfluoroalkyl substances (PFASs) are a wide category of chemicals that include perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSA). These PFASs are not naturally occurring and are anthropogenic in origin [1]. However, because of their large scale production, PFSA and PFCAs are ubiquitous all around the world, and notably in the Arctic. PFCAs and PFSA can be formed by transformations of precursors such as fluorotelomer alcohols (FTOHs) [2,3]. Also, part of the concern is their ability to biomagnify through food chains [4,5,6]. The C8 PFSA, perfluorooctane sulfonate (PFOS), have been replaced by shorter versions, such as : perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS) and perfluoroheptane sulfonate (PFHpS) to reduce their bioaccumulation and biomagnification potential [4,5]. There are also other new replacement PFASs that have not been reported yet in Arctic biota including perfluoroethylcyclohexyl sulfonic acid (PFEtCHxS).

PFASs can travel by long-range oceanic transport to the Arctic, while their volatile precursors can travel by long-range atmospheric transport [7]. PFASs are known to biomagnify through the marine foodweb of the Arctic and end up in the apex predator, the polar bear (*Ursus maritimus*) [6]. One of the main concerns of PFASs is the fact that the exposure and levels are not necessarily decreasing over the years in the tissues of e.g. East Greenland and Hudson Bay polar bears [9, 10].

If fact, East Greenland and Hudson Bay are two contamination "hotspots" regarding PFASs in polar bears, with PFOS levels comparable to e.g. ΣPCBs [9,10].

Study Objective :
To compare concentrations of legacy and new, bioaccumulative PFASs in polar bear subpopulations from two different contamination "hotspots", East Greenland and Hudson Bay.

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Results

Table 1. Concentration of a suite of PFASs (ng/g wet weight) in polar bear livers from East Greenland (n=10) and Hudson Bay (n=19)

		Carboxylic Acids														Sulfonic Acids					Non-Acids			Total		
		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUDA	PFDoA	PFTeDA	PFTrDA	PFTeDA	PFHxDA	PFODA	Sum PFCA	PFBS	PFHxS	PFEtCHxS	PFOS	PFDS	Sum PFSA	FBSA		FOSA	N-Me-FOSA
East Greenland	Mean (ng/g ww)	36	NQ	0.5	0.3	17	364	165	249	24	61	7.0	0.2	0.3	924	0.7	18	3.1	2583	5.7	2610	0.4	9.5	NQ	1.5	3546
	± SE	4.9		0.1	0.1	2.6	28	13	17	1.5	3.0	0.4	0.0	0.0	71	0.1	1.6	0.1	199	1.1	202	0.1	1.4		0.4	275
	Range (ng/g ww)	14		0.2	0.0	12	248	112	174	16	37	3.8	0.1	0.2		0.3	7.2	2.3	1500	2.6		0.1	2.4		0.2	
Hudson Bay	Mean (ng/g ww)			NQ	NQ	27	274	137	147	13	12	NQ			610	NQ	7.6		1176	NQ	1184		31	NQ		1825
	± SE					3.3	20	9.7	10	1.1				45		0.6		115		115					168	
	Range (ng/g ww)					5.2	127	57	73	5.2	5.5						3.7		549				0.0			
						59	447	213	245	22	23						13		2411				92			

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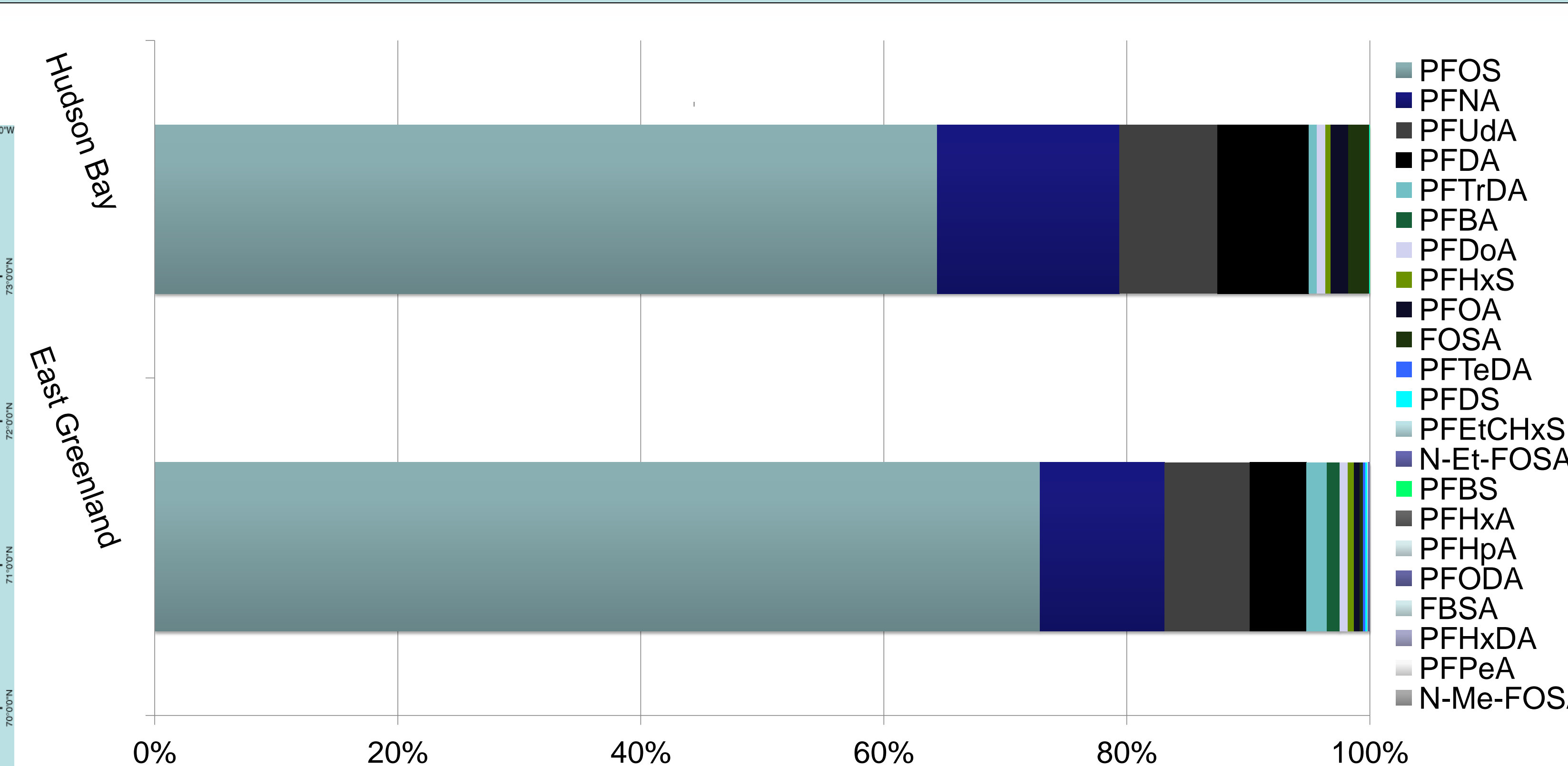
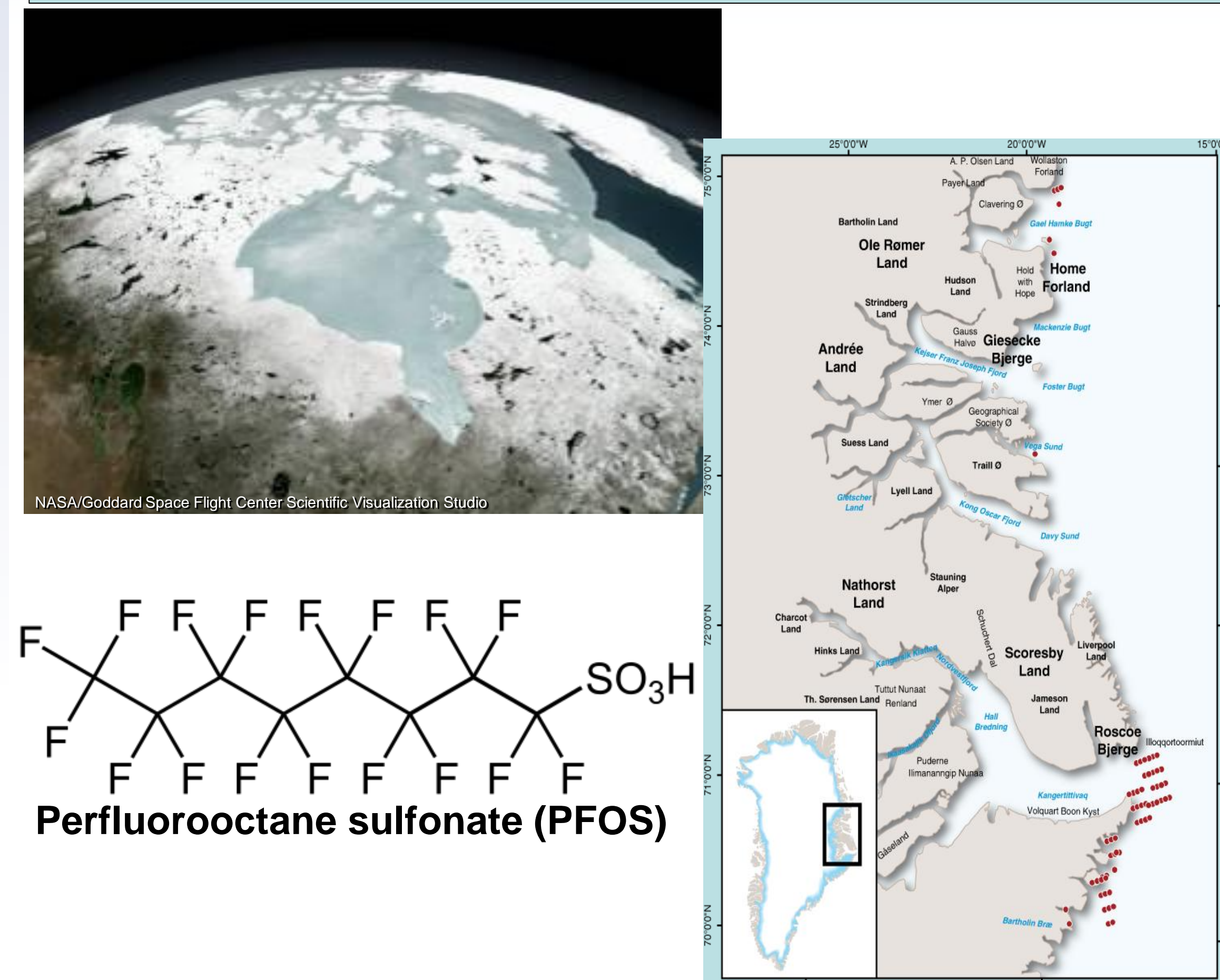


Figure 1. Bioaccumulation pattern of a suite of PFASs in polar bear livers from East Greenland (n=10) and Hudson Bay (n=19).

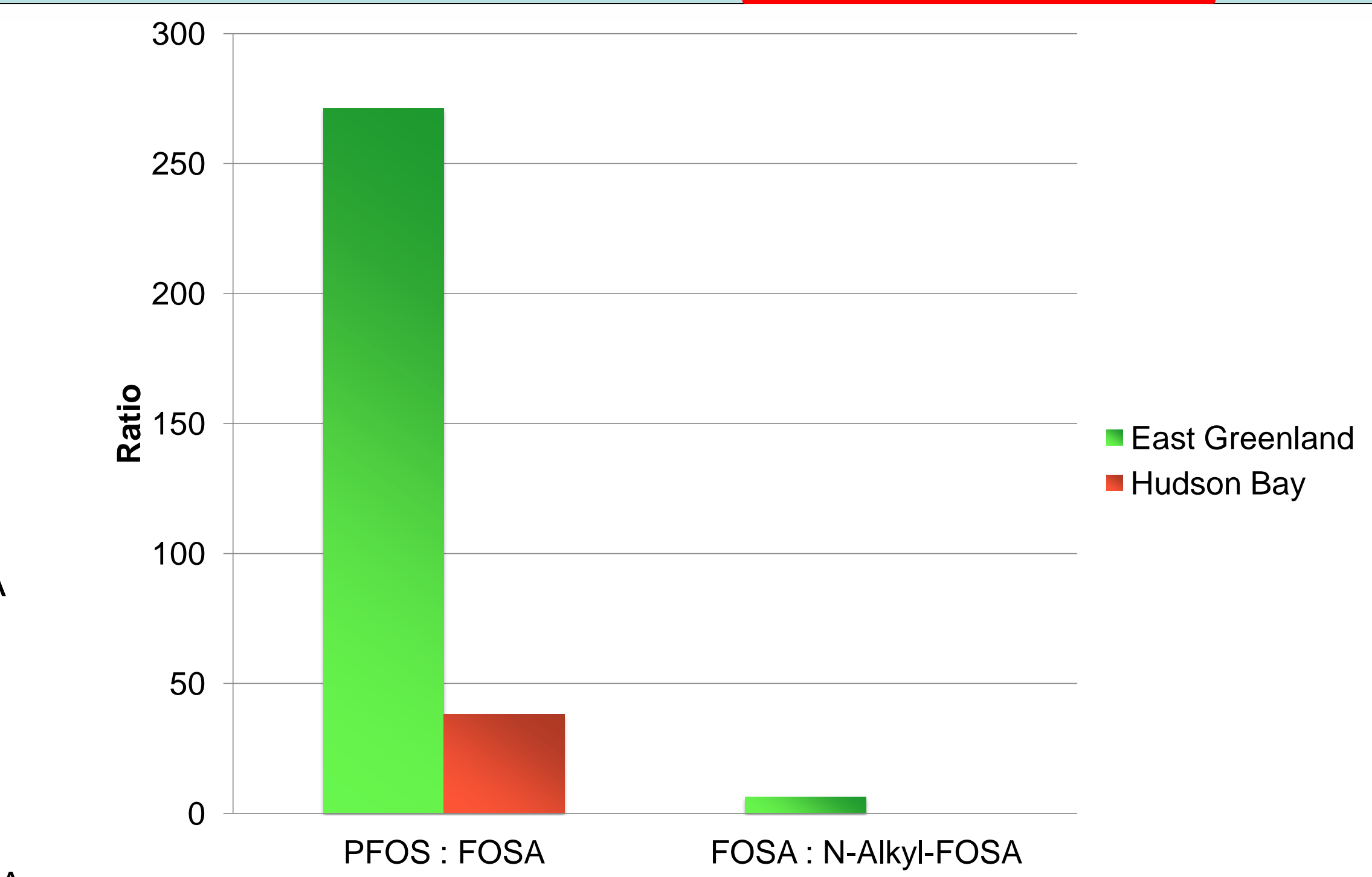
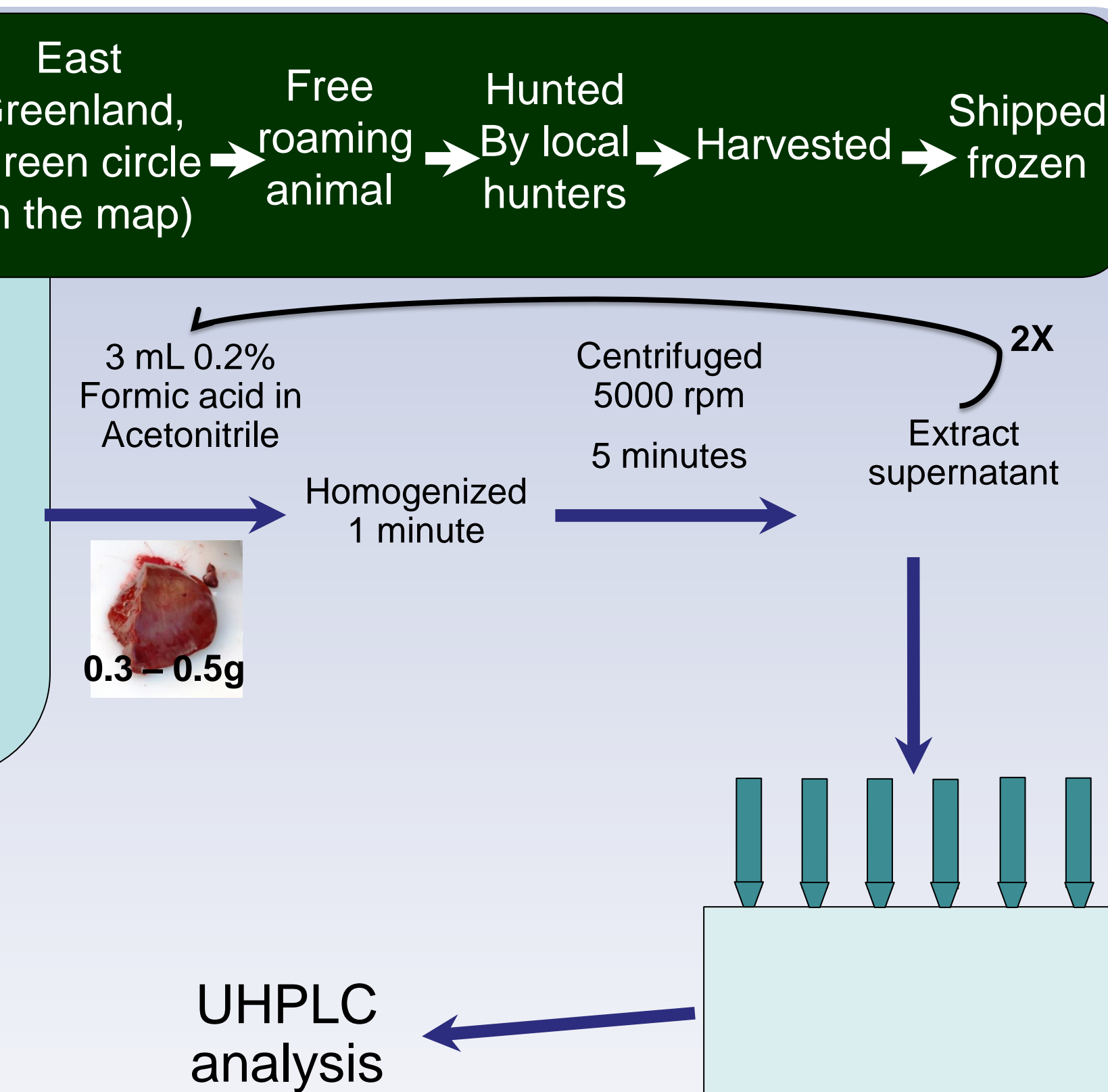


Figure 2. Ratio of PFOS to its precursor (FOSA) and ratio of FOSA to its precursors N-Et-FOSA + N-Me-FOSA in polar bear livers from East Greenland (n=10) and Hudson Bay (n=19).

Methods

Hudson Bay :
Collection : Nov. 2011 - Jan. 2012
14 males, 5 females
Ages : Yearling-Adult

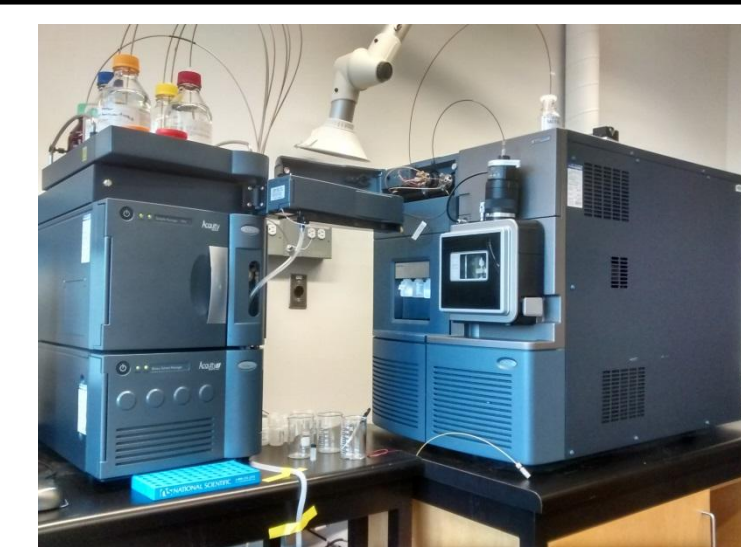
East Greenland :
Collection : Feb. -March 2011
5 males, 5 females
Ages : 2-10 years



Internal Standards :
- Mass-labelled PFCAs and PFASs solution/mixture, MPFAC-MXA.
- Perfluoro-1-[¹³C₈]-octanesulfonamide, (M8FOSA), N-methyl-d₃-perfluoro-1-octanesulfonamide, (d-N-MeFOSA)
- N-ethyl-d₃-perfluoro-1-octanesulfonamide, d-N-EtFOSA

Quantification:
PFAS using internal Standard Method

UHPLC-ESI(-)MS/MS



- List of Target PFASs :**
- Perfluoro-n-butanoic acid (PFBA)
 - Perfluoro-n-pentanoic acid (PFPeA)
 - Perfluoro-n-hexanoic acid (PFHxA)
 - Perfluoro-n-heptanoic acid (PFHpA)
 - Perfluoro-n-octanoic acid (PFOA)
 - Perfluoro-n-nonanoic acid (PFNA)
 - Perfluoro-n-decanoic acid (PFDA)
 - Perfluoro-n-undecanoic acid (PFUDA)
 - Perfluoro-n-dodecanoic acid (PFDoA)
 - Perfluoro-n-tridecanoic acid (PFTeDA)
 - Perfluoro-n-tetradecanoic acid (PFTrDA)
 - Perfluoro-n-hexadecanoic acid (PFHxDA)
 - Perfluoro-n-octadecanoic acid (PFODA)
 - Perfluoro-perfluoro-1-butanedisulfonic acid (PFBS)
 - Perfluoro-perfluoro-1-hexanedisulfonic acid (PFHxS)
 - Perfluoro-perfluoro-1-octanedisulfonic acid (PFOS)
 - Perfluoro-perfluoro-1-decanedisulfonic acid (PFDA)
 - Perfluoro-1-butanedisulfonamide (PFBA)
 - Perfluoro-1-octanedisulfonamide (PFOA)
 - N-methylperfluoro-1-octanedisulfonamide (N-Me-FOSA)
 - N-ethylperfluoro-1-octanedisulfonamide (N-Et-FOSA)

Conclusions

- Results showed that the East Greenland bears are generally more contaminated than Hudson Bay bears (Table 1). Which may be due to differences in PFASs sources and/or diet for the two subpopulations.
- Bioaccumulation patterns of PFAS between the two subpopulations were similar. However, Hudson Bay bears contained less PFOS and more FOSA, PFNA, PFDA and PFUDA than East Greenland bears (Fig. 1).
- The ratio of PFOS to its' precursor FOSA was very different between the subpopulations, as the East Greenland polar bears had a huge concentration of PFOS compared to its precursor (Fig. 2). This suggests that exposure to FOSA is greater and exposure to PFOS is lower for Hudson Bay bears than for East Greenland bears, and/or FOSA to PFOS metabolism is greater for East Greenland bears.



Photo: R. Dietz

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