Per- and Poly-Fluoroalkyl Substances and Temporal Trends and in Relation to Diet in Polar Bears From Hudson Bay

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Introduction

An array of persistent organic pollutants (POPs) are know to be present in the Arctic and bioaccumulate in biota and wildlife. Recently emerged and emerging POPs include per-/poly-fluoroalkyl substances (PFASs). PFASs end up directly in the Arctic region by long range oceanic transport, but along with their more volatile precursors, can also be transported by atmospheric processes [*1,2,3*].

The polar bear (*Ursus maritimus*) is the apex predator of the arctic marine ecosystem and food web. Bioaccumulative PFASs such as PFOS and other perfluorinated sulfonic acids (PFSAs), and perfluorinated carboxylic acids (PFCAs), are well-known in Arctic biota including in the tissues (mainly in liver) of bears from circumpolar subpopulations in Hudson Bay (Canada) and East Greenland [*1,2,4,5,6*]. The increasing complexity of (known) POP exposure (including PFASs) in polar bears poses an increase in health risks to polar bears, especially bears from Hudson Bay, which have been shown to be a `hot spot` with respect to high and /or changing tissue levels of POPs, and/or greater temperature changes due to Arctic warming [*6,7,8,9*].

Stable isotope (SI) ratios of carbon and nitrogen are routinely used as ecological tracers of food web primary production and trophic level, respectively. They can be used to assess the influence over time of shifting diet and food web structure on contaminant levels in the tissues of exposed wildlife [*10*].

Study Objectives:

1) **To determine the most recent 7-year temporal trends (2007-2014) of bioaccumulative PFASs in polar bears from southern and western Hudson Bay subpopulations of polar bears.**
2) **To preliminarily examine the influence of polar bear diet shifts on PFAS temporal trends using stable isotope ratios of carbon and nitrogen.**

Results

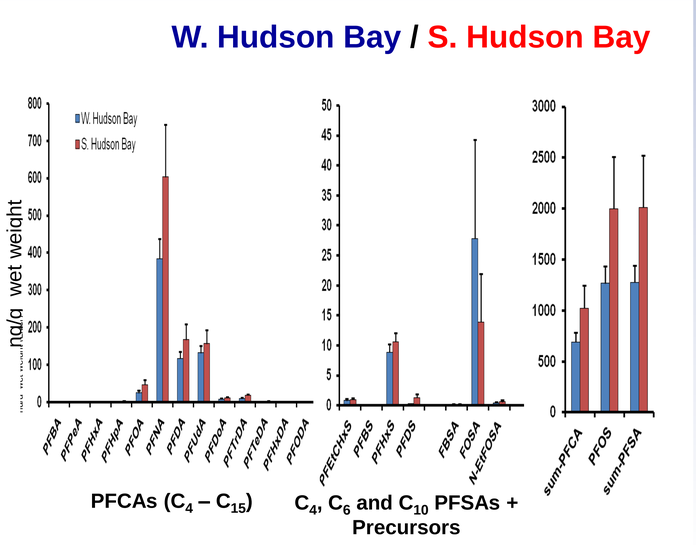


Figure 1. Mean concentrations of perfluoroalkyl acids and precursors in 2013 samples (n=12 WHB and n=12 SHB) (R. Letcher, unpublished). Error bars are SDs. Data not corrected for sex, age or diet.

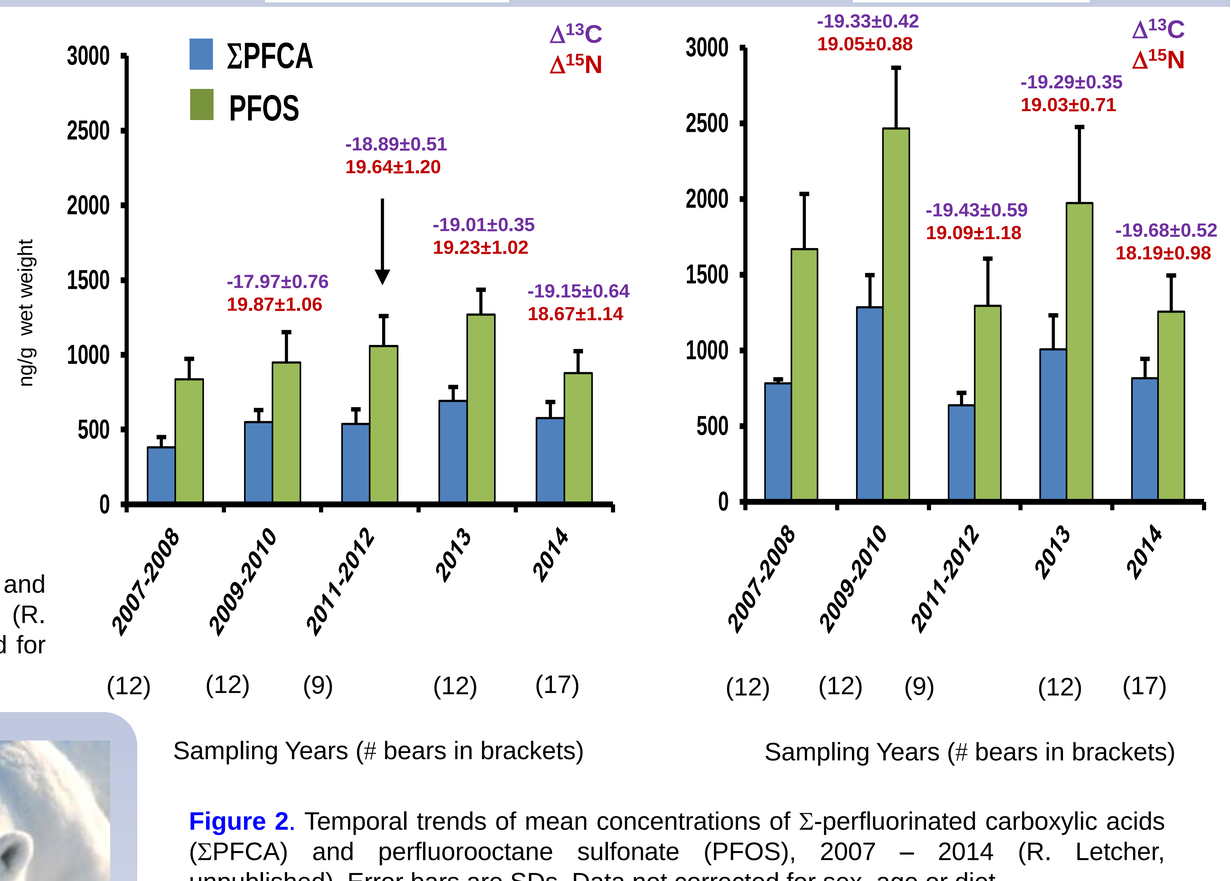
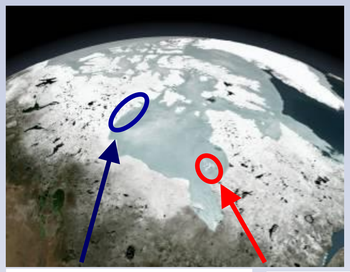


Figure 2. Temporal trends of mean concentrations of Σ-perfluorinated carboxylic acids (ΣPFCA) and perfluorooctane sulfonate (PFOS), 2007 – 2014 (R. Letcher, unpublished). Error bars are SDs. Data not corrected for sex, age or diet.

Methods [*9*]



S. Hudson Bay

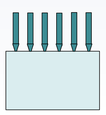
Collection : 2007 - 2014
All Adult Males and Females
(> 5 years of age)

Hudson Bay (subpopulations circled on map) → Free roaming animal → Hunted By local hunters → Harvested → Shipped frozen

0.3 – 0.5 g

3 mL 0.2% Formic acid in Acetonitrile → Homogenized 1 minute → Centrifuged 5000 rpm, 5 minutes (2x) → Extract supernatant

Stable Isotopes (U.W., GLIER)
δ13C – primary production
δ15N – trophic level (TL)



Internal Standards :

- Mass-labelled PFCAs and PFASs solution/mixture, MPFAC-MXA.
- Perfluoro-1-[$^{13}C_8$]-octanesulfonamide, (M8FOSA), N-methyl-d_3-perfluoro-1-octanesulfonamide, (d-N-MeFOSA)
- N-ethyl-d_5-perfluoro-1-octanesulfonamide, d-N-EtFOSA

Quantification:
PFAS using internal Standard Method

LC- or 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-4-ethylcyclohexane sulfonic acid	(PFEtCHxS)
Perfluoro-n-nonanoic acid	(PFNA)
Perfluoro-n-decanoic acid	(PFDA)
Perfluoro-n-undecanoic acid	(PFUdA)
Perfluoro-n-dodecanoic acid	(PFDoA)
Perfluoro-n-tridecanoic acid	(PFTrDA)
Perfluoro-n-tetradecanoic acid	(PFTeDA)
Perfluoro-n-hexadecanoic acid	(PFHxDA)
Perfluoro-n-octadecanoic acid	(PFODA)
Perfluoro-perfluoro-1-butanesulfonic acid	(PFBS)
Perfluoro-perfluoro-1-hexanesulfonic acid	(PFHxS)
Perfluoro-perfluoro-1-octanesulfonic acid	(PFOS)
Perfluoro-perfluoro-1-decanesulfonic acid	(PFDS)
Perfluoro-1-butanesulfonamide	(FBSA)
Perfluoro-1-octanesulfonamide	(FOSA)
N-methylperfluoro-1-octanesulfonamide	(N-Me-FOSA)
N-ethylperfluoro-1-octanesulfonamide	(N-Et-FOSA)

Conclusions

- 2013-collected liver samples showed that PFCAs were mostly C_9-C_{11} with PFNA (C_9) dominating (Fig. 1). PFBA was measureable at low ppb levels with almost 100% frequency in all bear livers.
- In addition to high PFOS levels, C_6 PFSA and several “Pre-FOS” precursors were quantifiable at low levels e.g. N-Et-FOSA and FOSA (Fig. 1). Low concentrations of the C_4 FBSA were detected, although no corresponding PFBS was detectable in any sample. The cyclic analogue of PFOS, PFEtCHxS was quantifiable in all samples.
- Even though the concentrations were uncorrected for e.g. age, sex and diet, ΣPFCAs appear not to have decreased, whereas PFOS concentrations may have decreased slightly in Hudson Bay bears over the period of 2007-2014 (Fig. 2).
- Preliminary C + N SI comparative analysis indicates no shift in bear diet (trophic level and primary production) between 2009 and 2014, and thus diet appears to have little influence on ΣPFCA and PFOS temporal trends over this 5-year period (Fig. 2).
- Regardless of e.g. phase-outs of C8 fluoroalkyl chemistry in 2002 and increasing regulation, marginal changes of both PFCA and PFOS conc. in Hudson Bay bears (2007-2014), and thus other PFCA and PFSA sources and precursor degradation are important.

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