Bioaccumulation of Perfluorinated Organic Chemicals in Canadian Arctic Beluga Whales

(Delphinapterus leucas)

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Background

• Persistent, bioaccumulative, potentially toxic chemicals classified as Persistent Organic Pollutants (POPs)

• Legacy POPs such as PCBs and OC Pesticides in the Arctic marine wildlife stable in recent years

• Increasing levels of perfluorinated compounds (PFCs) in Arctic marine wildlife (ionic, water soluble compounds)

• PFOS Hazardous Substance under Health Canada Risk Assessment

• PFOS voluntarily removed from production

• Bioaccumulation behaviour and toxicokinetics of PFCs not fully understood

This study presents data of perfluorinated carboxylates, sulfonates, sulfonamides bioaccumulation in Arctic beluga whales and their habitat
Roles and Acknowledgements

Simon Fraser University
- Field collections, Data Interpretation

Canadian Department of Fisheries and Oceans (Institute of Ocean Sciences)
- Sample Extractions and Purification
- Analysis of PCBs, OC Pesticides, PBDEs

AXYS Analytical Services
- PFC Method Development
- LC/ESI-MS-MS analysis of PFC compounds
- QA/QC
Sampling Locations

Field work: Village of Umiujaq / Nastapoka River Estuary
Trophic Level (TL)

Water column

Bottom Sediment

Tidal Ecozone

Atmospheric Input

Macro-algae

Micro-algae

Pelagic amphipods

Benthic amphipods

Bivalves

Eider duck

Sculpin

Arctic cod

Capelin

Ringed seals

Beluga

Human (Inuit)

Wolves

Caribou

Lichen

Polar bears

Capelin

Micro-algae

Macro-algae

Scoter

Salmon

Salmon

Sculpin

Beluga

Capelin

Micro-algae
Sample Collections: E. Hudson Bay

- Sediment samples (n = 8) petit ponar grabs
- Macro-algae (n = 6)
- Harvested beluga whales (n=25); 12 females, 12 males, 1 calf - liver, blubber, blood, milk
- Fish: capelin, arctic cod, sculpin, salmon (n = 6 per species)

Chemical analysis:

- Previous Work: PCBs, PBDEs, OC Pesticides
- Current Study: PFCs (Carboxylates, Sulfonates, Sulfonamides)
# 21 PFC Compound Target List

<table>
<thead>
<tr>
<th>Carboxylates</th>
<th>Sulfonates</th>
<th>Sulfonamides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorobutanoic acid</td>
<td>Perfluorobutansulfonic acid</td>
<td>Perfluorooctansulfoamide</td>
</tr>
<tr>
<td>Perfluoropentanoic acid</td>
<td>Perfluorohexansulfonic acid</td>
<td>N-Me-perfluorooctansulfonamide</td>
</tr>
<tr>
<td>Perfluorohexanoic acid</td>
<td>Perfluoroocitansulfonic acid</td>
<td>N-Et-perfluorooctansulfonamide</td>
</tr>
<tr>
<td>Perfluoroheptanoic acid</td>
<td>Perfluorodecansulfonic acid</td>
<td>2-(N-Me-perfluorooctansulfonamido) ethanol</td>
</tr>
<tr>
<td>Perfluoroctanoic acid</td>
<td></td>
<td>2-(N-Et-perfluorooctansulfonamido) ethanol</td>
</tr>
<tr>
<td>Perfluorononanoic acid</td>
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<td>Perfluorodecanoic acid</td>
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<td>Perfluoroundecanoic acid</td>
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<tr>
<td>Telomer acids</td>
<td>Telomer acids</td>
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<tr>
<td>Fluoroctaunsaturatedethanoic acid</td>
<td>Fluoroctaunsaturatedethanoic acid</td>
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<td>Fluorohexaunsaturatedethanoic acid</td>
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<td></td>
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<tr>
<td>Mass Labelled Internal Standards</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluorooctanoic acid</td>
<td>13C2-PFOA</td>
<td></td>
</tr>
<tr>
<td>Perfluorodecanoic acid</td>
<td>13C2-PFDA</td>
<td></td>
</tr>
<tr>
<td>Perfluorododecanoic acid</td>
<td>13C2-PFDoA</td>
<td></td>
</tr>
<tr>
<td>Fluoroctaunsaturatedethanoic acid</td>
<td>13C2-FOUEA</td>
<td></td>
</tr>
<tr>
<td>Perfluorooctansulfonic acid</td>
<td>13C4-PFOS</td>
<td></td>
</tr>
</tbody>
</table>
PFC Analysis

Extraction of PFC's


1) Addition of mass labeled internal standards to allow for recovery correction in quantification

2) KOH/MeOH extraction (Base digestion)

3) WAX-SPE sample purification (collection of one fraction only)

4) Add Recovery standard (13C4-PFOA)

5) Analysis by LC/ESI-MS/MS (Waters 2795 - Quattro Ultima)

Sediments - Extraction based on methodology in Higgins, C. et.al., Environ. Sci. Technol. 2005, 39, 3946-3956 with modifications as described below

Extraction with 0.1% acetic acid (aq) then further extract with basic methanol. Purification by WAX-SPE
QC Protocols for PFC Analysis

Method validation (as per CFR 40, Part 136, Appendix B)

Batch QC

- Method blanks, sample duplicates, and sample matrix spikes were prepared and run with each batch (min. 5 QC per 20)
- 9 pt initial calibration curve run with every sample batch
- Continuing calibration verification (10 samples)
- Use of five 13C-labeled PFC’s
- Sample specific evaluation of instrument matrix suppression — 13C4-PFOA spiked before instrument analysis. If significant suppression samples were diluted and re-run
PFC Analysis – Method Limitations

• In General QC was good but some issues noted

• Low % recoveries of me/etFOSA’s (0 - 50%) and me/etFOSE’s (20- 80%) in some matrix spikes (blowdown vs. detection limits?)

• Low % recoveries for 13C2-PFDoA (10-80%) for lipid rich samples

• N-Et-FOSA LC/ESI-MS/MS DL < than reported for GC/MS (Tomy et al and Martin et al.ES&T, 2004)

• High chemical noise for PFBA – results need confirmation (re-injection with different LC column and gradient conditions), matrix spikes good
<table>
<thead>
<tr>
<th>Sample</th>
<th>Carboxylates</th>
<th>Sulfonates</th>
<th>Sulfonamides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macroalgae</td>
<td>0.01-0.07</td>
<td>0.02-0.4</td>
<td>0.3-20</td>
</tr>
<tr>
<td>Sediments</td>
<td>0.01-0.07</td>
<td>0.02-0.3</td>
<td>0.06-0.7</td>
</tr>
<tr>
<td>Fish</td>
<td>0.01-1</td>
<td>0.1-6</td>
<td>0.1-20</td>
</tr>
<tr>
<td>Blood</td>
<td>0.04-1</td>
<td>0.1-5</td>
<td>1-23</td>
</tr>
<tr>
<td>Blubber</td>
<td>0.1-2</td>
<td>0.3-7</td>
<td>0.1-32</td>
</tr>
<tr>
<td>Milk</td>
<td>0.2-1</td>
<td>0.01-2</td>
<td>0.1-15</td>
</tr>
<tr>
<td>Liver</td>
<td>0.02-0.8</td>
<td>0.2-5</td>
<td>0.05-30</td>
</tr>
</tbody>
</table>
RESULTS

Levels and Patterns of PFCs
PFCs in Sediments and Macroalgae

- PFBA (C4)
- PFPeA (C5)
- PFHxA (C6)
- PFHpA (C7)
- PFOA (C8)
- PFNA (C9)
- PFDA (C10)
- PFUnA (C11)
- PFDoA (C12)
- PFTA (C13)

Sediments

- PFBS
- PFHxS
- PFOS
- PFDS

Macroalgae

- PFOSA
- N-MeFOSA
- N-EtFOSA
- N-MeFOSE
- N-EtFOSE

ng.g⁻¹ dry wt.
PFCs in Fish and Beluga Liver

- PFBA (C4)
- PFPeA (C5)
- PFHxA (C6)
- PFHpA (C7)
- PFOA (C8)
- PFNA (C9)
- PFDA (C10)
- PFUnA (C11)
- PFDoA (C12)
- PFTA (C13)

Fish
Male Beluga

* P < 0.01
Trophic Magnification Factors (TMFs)

PCB153

\[ \text{TMF} = 11.5 \]

p,p' DDE

\[ \text{TMF} = 10.3 \]

PFOS

\[ \text{TMF} = 8.0 \]

This study

Tomy et al and Martin et al. (ES&T, 2004)
**PFC Levels in Female Beluga Tissues and Milk**

- **Blood**
- **Liver**
- **Milk**
- *P < 0.01

Bar charts showing ng·g⁻¹ dry wt. of various PFCs in different tissues. The bars are color-coded by tissue type, with * indicating statistical significance (P < 0.01).
PFC Levels in Male Beluga Tissues

* * P < 0.01
Tissue Distribution of PFCs in Beluga Whales

Female Beluga

Male Beluga

% Composition

Female Liver Female Blood Milk Male Liver Male Blood Blubber

Σ Sulfonamides Σ Sulfonates Σ Carboxylates
PFCs versus other Organohalogens

ng g\(^{-1}\) dry wt.

- **Sediments**
- **Macro-algae**
- **Capelin**
- **Cod**
- **Salmon**
- **Beluga Liver**

- **PCBs**
- **OC Pest.**
- **PBDEs**
- **PFCs**

Beluga Liver

= PCBs
= OC Pest.
= PBDEs
= PFCs
Maternal Transfer

**Milk Diet**
- 2.8 kg milk /day
- $\sum$ PFC Milk Flux = 45 ug.d\(^{-1}\)
- $\sum$ PCB Milk Flux = 300 ug.d\(^{-1}\)
- $\sum$ PBDEs Milk Flux = 15 ug.d\(^{-1}\)

**Fish Diet**
- 27.7 kg /day
- $\sum$ PFCs Food Flux = 610 ug.d\(^{-1}\)
- $\sum$ PCBs Food Flux = 25.2 ug.d\(^{-1}\)
- $\sum$ PBDEs Food Flux = 2.6 ug.d\(^{-1}\)

**Calf**
- $\sum$ PFCs 950 ng/g dw
- $\sum$ PCB 107 ng/g dw
- $\sum$ BDE 4ng/g dw

**Mother**
- $\sum$ PFCs 370 ng/g dw
- $\sum$ PCB 93 ng/g dw
- $\sum$ BDE 3 ng/g dw
Summary

- Individual PFC levels: 0.01 – 30 ng/g dry wt. in sediments and fish
  1 - 300 ng/g dry wt. beluga whale tissues

- PFOSA > PFOS in beluga tissues

- PFOSA by LC/MS-MS comparable to GC/MS data (Tomy et al., 2004)

- PFC levels in blood and liver were comparable,
  (and were 50 times higher than PFCs in blubber & milk)

- Levels and Food web magnification of PFCs comparable to PCBs, DDTs

- PFOS in Arctic beluga whales: 100 times below LOAEL in lab tests
  (<< 0.1 mgPFOS/kg/d)

- ΣPFCs: 50-80% Total Organohalogen burden in sediments and fish
  30-60% Total Organohalogen burden in beluga whale tissues
Future Work

• Resolve method limitations
• Evaluate data ranges within species and matrices
• Dietary uptake and toxicokinetic studies
• Blood-Tissue Partition Coefficients
• Physicochemical properties
• Development of PFC bioaccumulation models
• Temporal trends in Arctic biota
Questions?