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Time trends and concentrations of PFAS in Arctic/sub-Arctic biota

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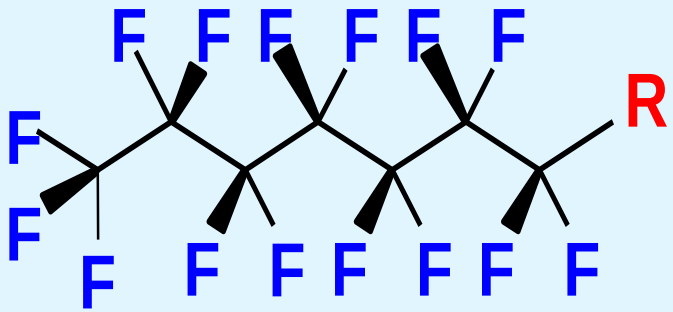
Per- and polyfluoroalkyl substances (PFAS)



SO_3- sulfonate - PFOS

CO_2- carboxylate - PFOA

CH_2CH_2OH alcohol - 8:2 FTOH

SO_2NH_2 amide - FOSA

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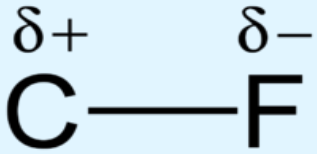
Chemical and physical properties

- The C-F bond makes these compounds very stable to heat, acids and microbial degradation



- Acids (e.g. PFOS) have low volatility, while the alcohols are relatively volatile

- Both hydrophobic and oleophobic (surfactants properties)

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Release to the environment

Sources

Direct emission of a specific PFAS (from e.g. manufacturing, use or disposal

Indirect: transformation from a precursor compound in the environment (e.g. PFOA from FTOH)

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Environmental fate

- Very stable because of the strong C-F bond
- Readily adsorbed by living organisms
- Bound to proteins (e.g. serum albumine)
- Bioaccumulate in the food chain (as the others halogenated POPs)
- Transported to remote regions
- Globally distributed

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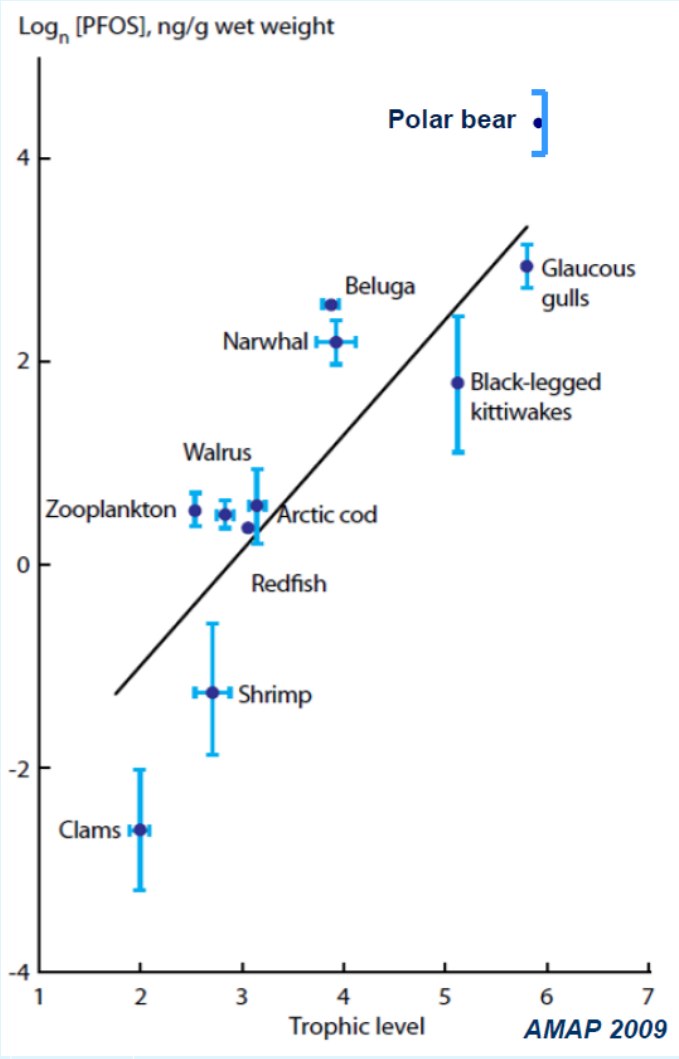
Biomagnification



PFOS in a Arctic food chain

Biomagnification factor
Polar bear / ringed seal
East Greenland

› PFOS: ~ 30

› PCB: 7,4
DDT/DDE: 0,5
Chlordanes: 6,1
HCH: 3,3

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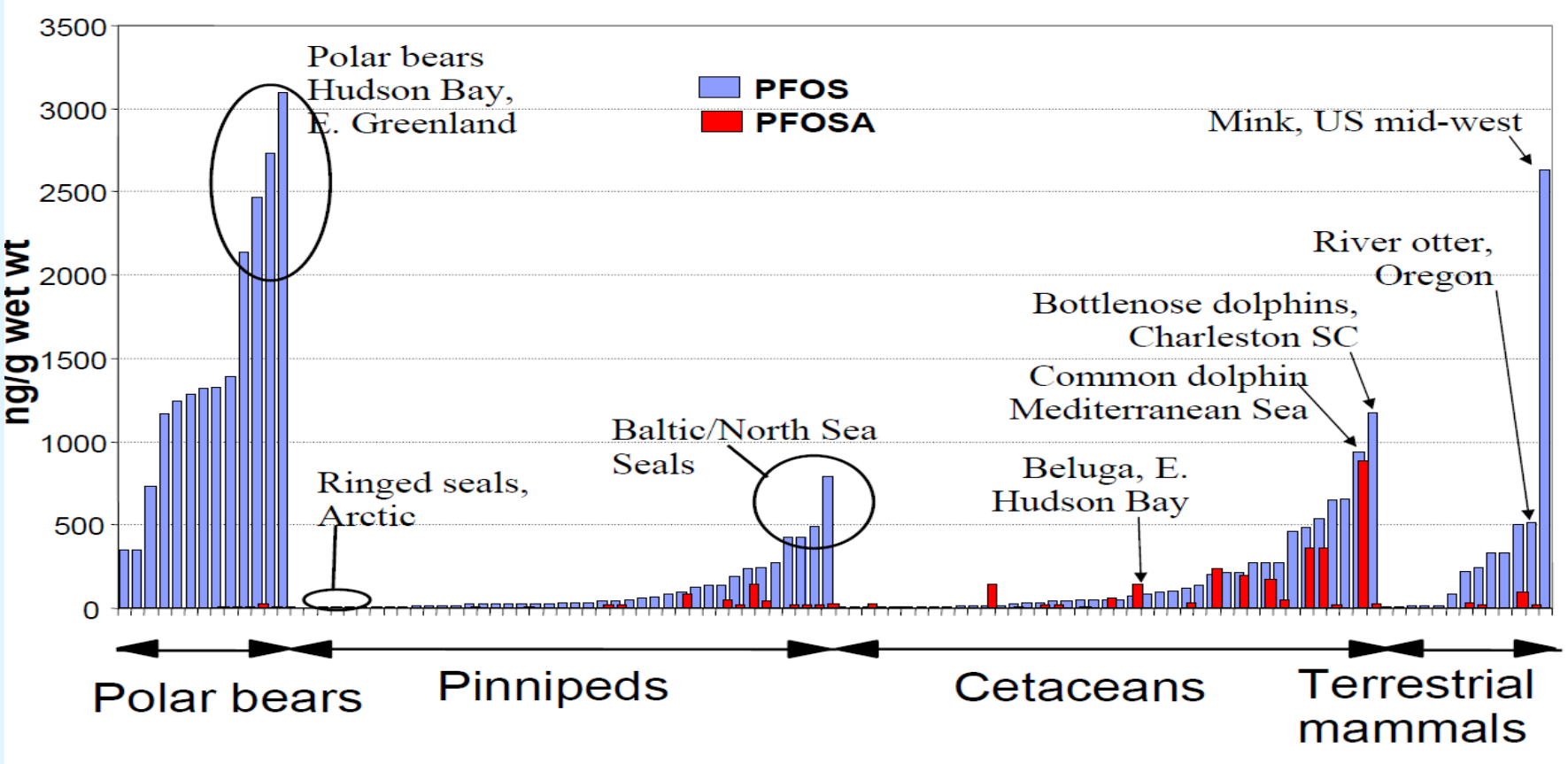
Bioaccumulation



› The highest concentrations are observed close to emission sources and in animals at high trophic levels, also long distances from sources.

Industrial production -PFOS

- Before phasing out PFOS and POSF production between 2000 and 2002, 3M (USA) was responsible for 80% of the global POSF production
- Minor production continued until 2006 in Europe and China (42-82 t/year in Europe and less than 50 t in China)
- By 2006 China has ramped up its POSF production to 200 t/year
- About half of the Chinese production is exported to Europe, Japan and Brazil

Industrial production -PFCAs

- Produced mainly by 3M until 2002 as processing aid for manufacturing of Teflon (production phased out by 3 m in 2002)
- In 2006, eight major PFCA, fluoropolymer and fluorotelomer manufacturers joined the global US EPA 2010/15 Stewardship Program (US EPA, 2006) to work toward the elimination of long-chain PFCAs and their precursors
- The production of PFCAs and their precursors has shifted to the emerging economies in continental Asia (e.g. China and India)

Legislation - PFOS

- EU Directive 2006/122: restriction in use of PFOS and its salts only in products at concentrations 0.005-0.1%
- Stockholm Convention on Persistent Organic Pollutants (2009): inclusion of PFOS and POSF in the Annex B, which restricts the use of these compounds with many exemptions (e.g. textile treatment and food packaging)

Legislation - PFOS

› US EPA (2010): has proposed actions to be taken in 2012 under the Toxic Substances Control Act to ban or restrict the manufacture (including import), processing, and use of long-chain perfluorinated chemicals. The rule will address both perfluoroalkyl sulfonate chemicals (from C_6) and perfluoroalkyl carboxylate chemicals (from C_8)

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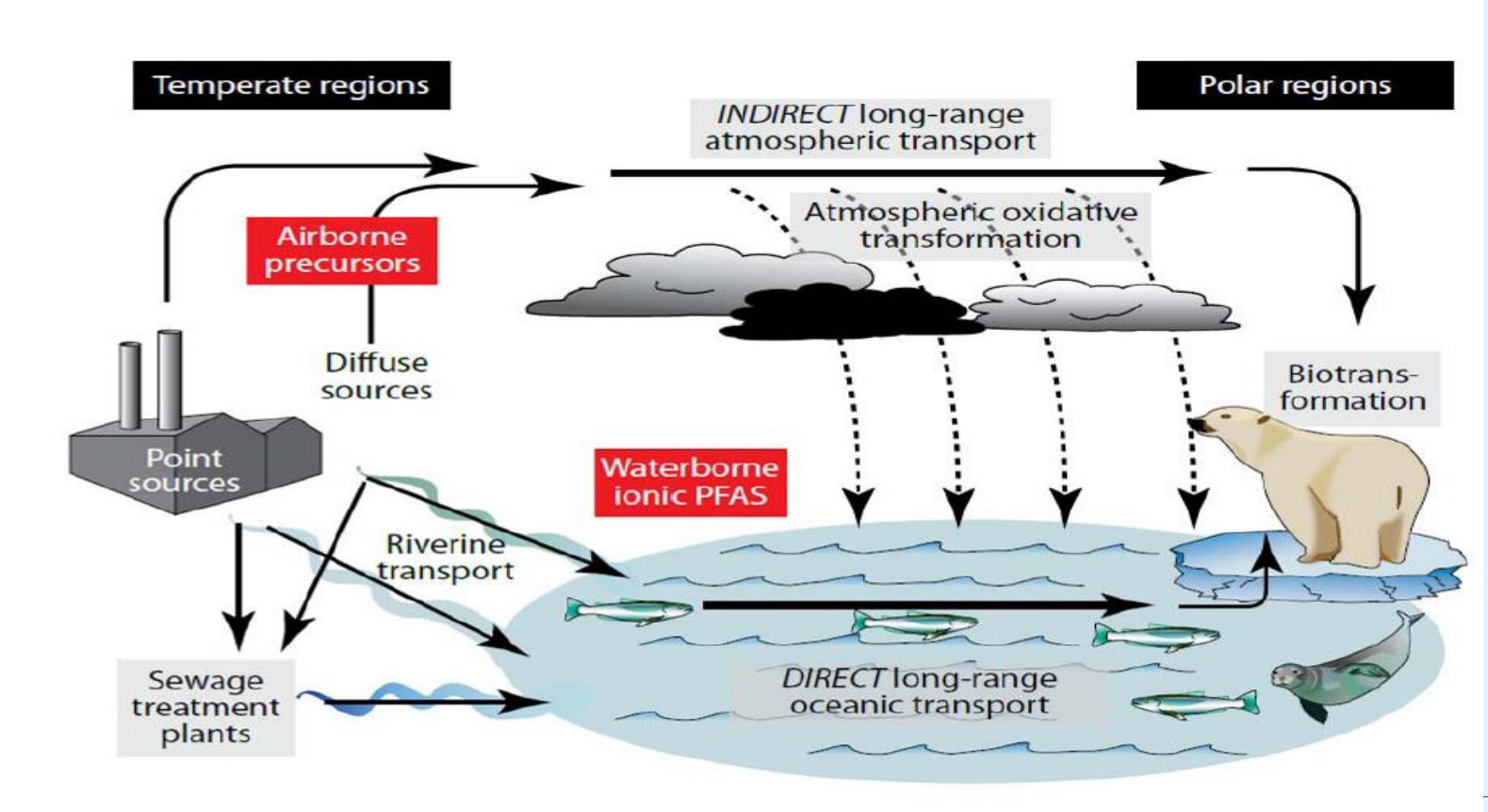
Transport paths to the Arctic



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Other sources of PFAS?

Microplastics released by melting arctic sea ice may be a potential source of e.g. fluorotelomer products

Obbard et al., Earth's Future, 2014

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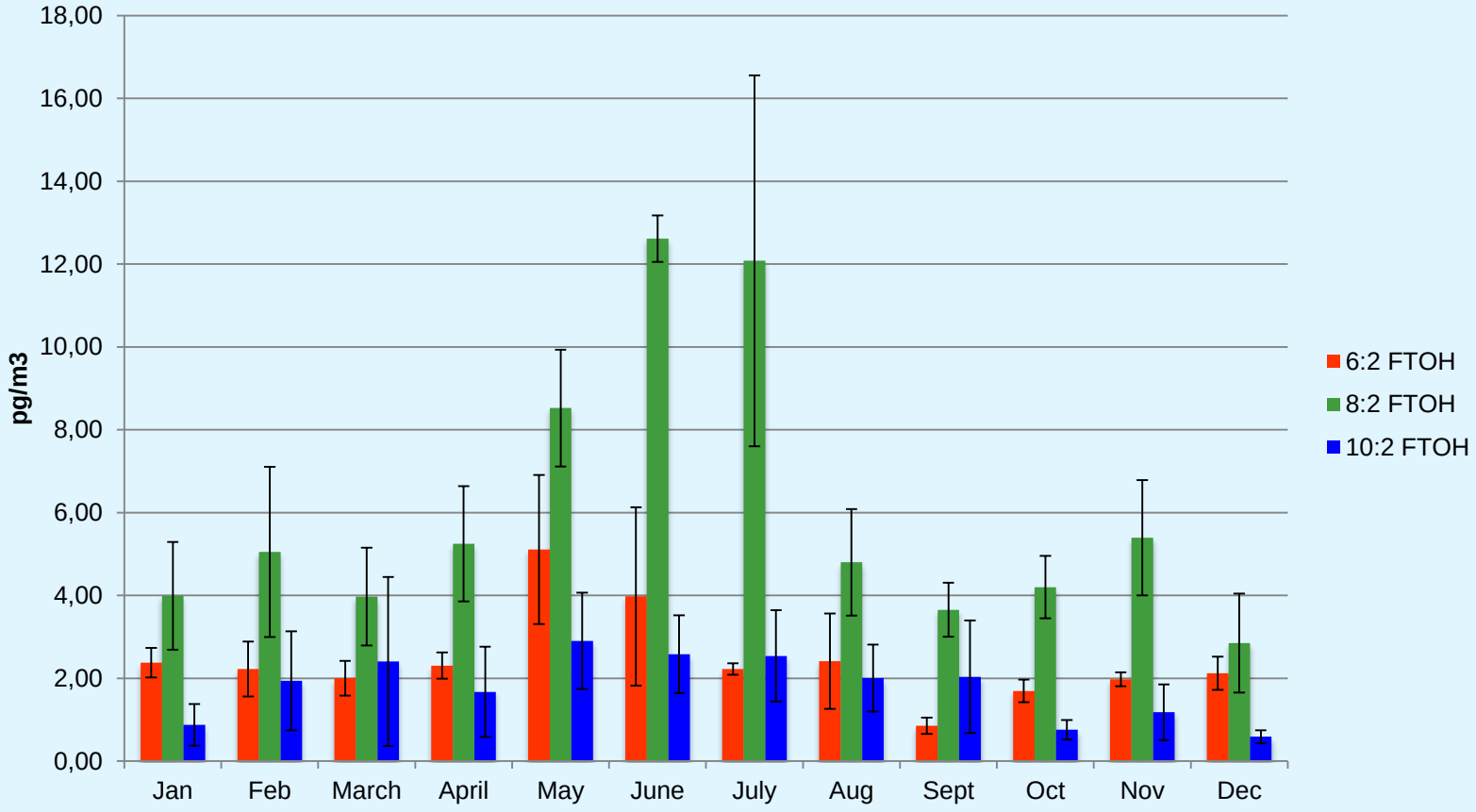
FTOH in the atmosphere- Greenland (2008-2013)



Bossi et al., Environ. Poll. 2016

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Atmospheric concentrations of ionic PFAS

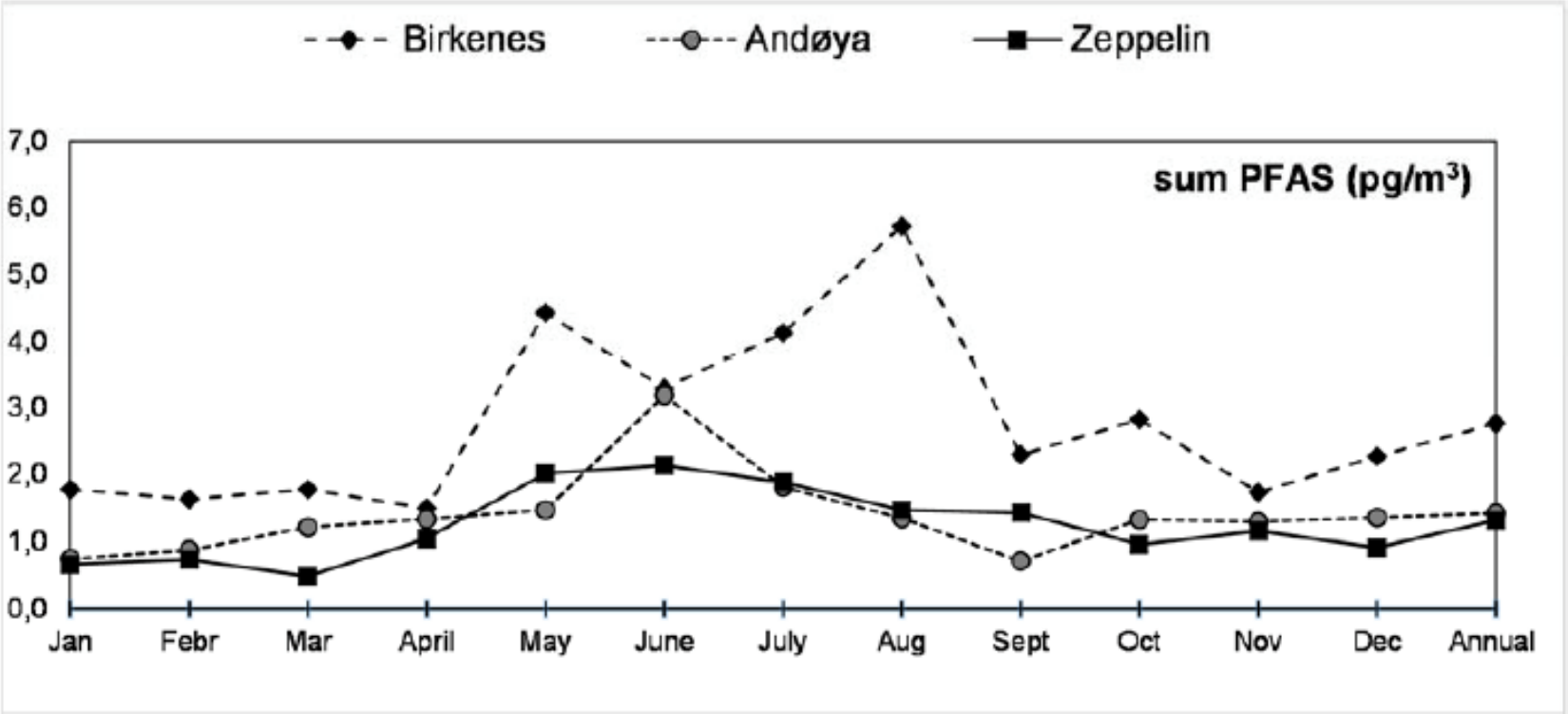

Figure 3.19: Monthly and annual mean concentrations (pg/m³) of sum PFAS in air for 2014.

Bohlin-Nizzetto et al., NILU, 2015

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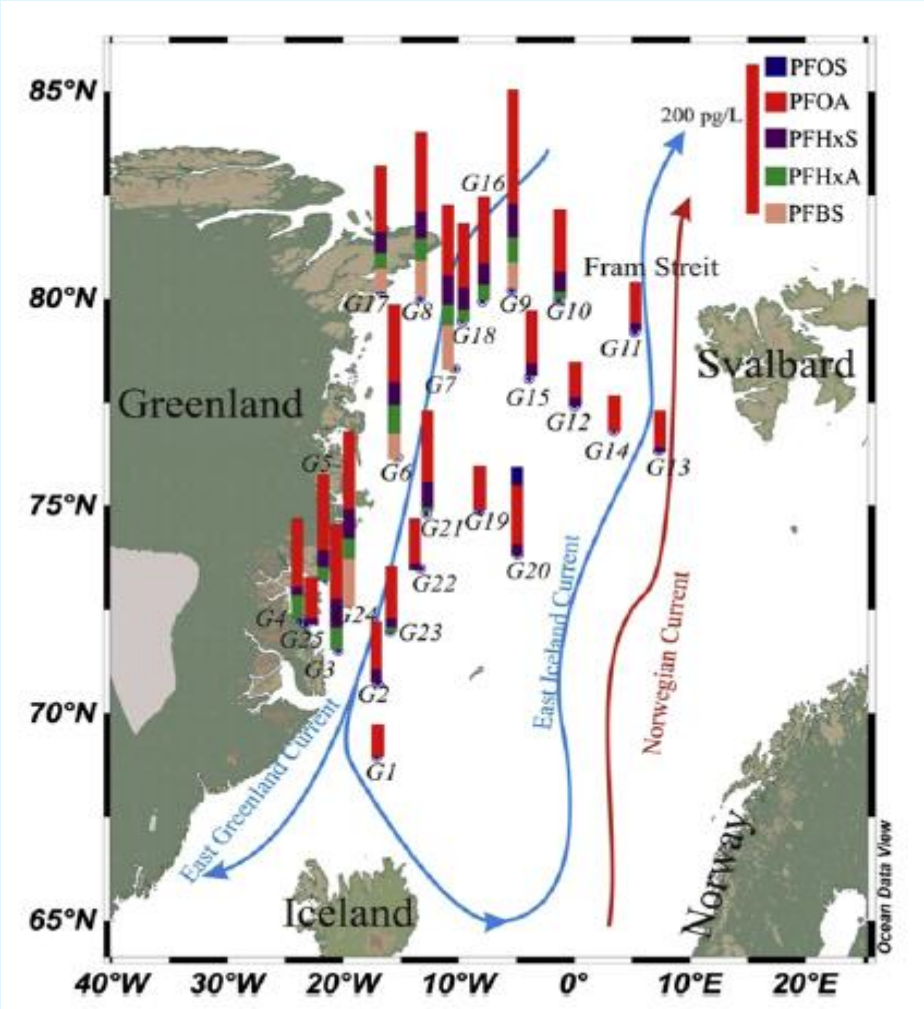
PFAS in Arctic ocean water



Ionic PFAS have been measured in the Greenland Sea in the concentration range 45-280 pg/L (Sum of PFAS)

Zhao et al., Environ. Poll.,2012

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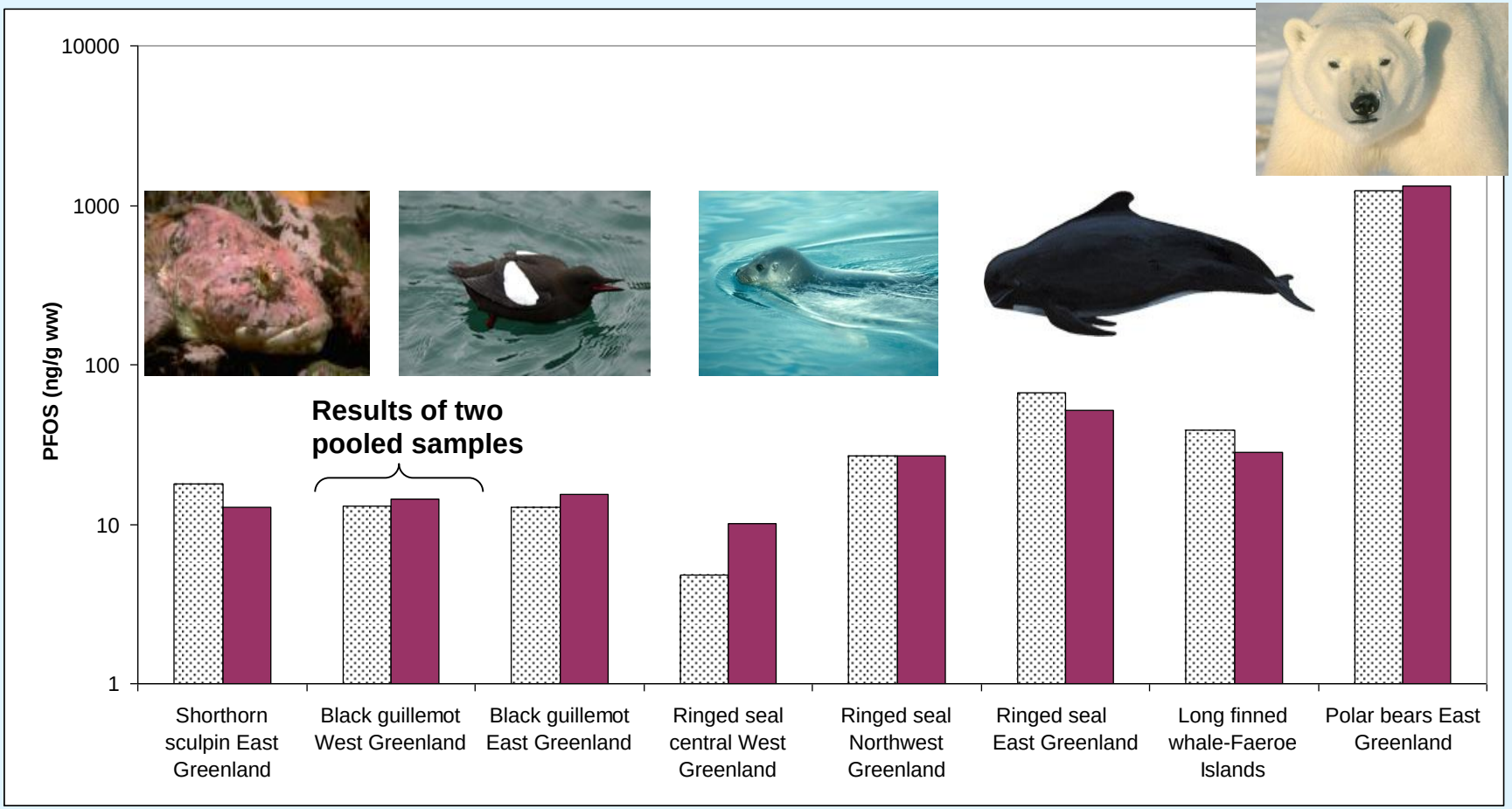
PFAS screening in marine Arctic biota (2002)



Bossi et al., Environmental Pollution (2005)

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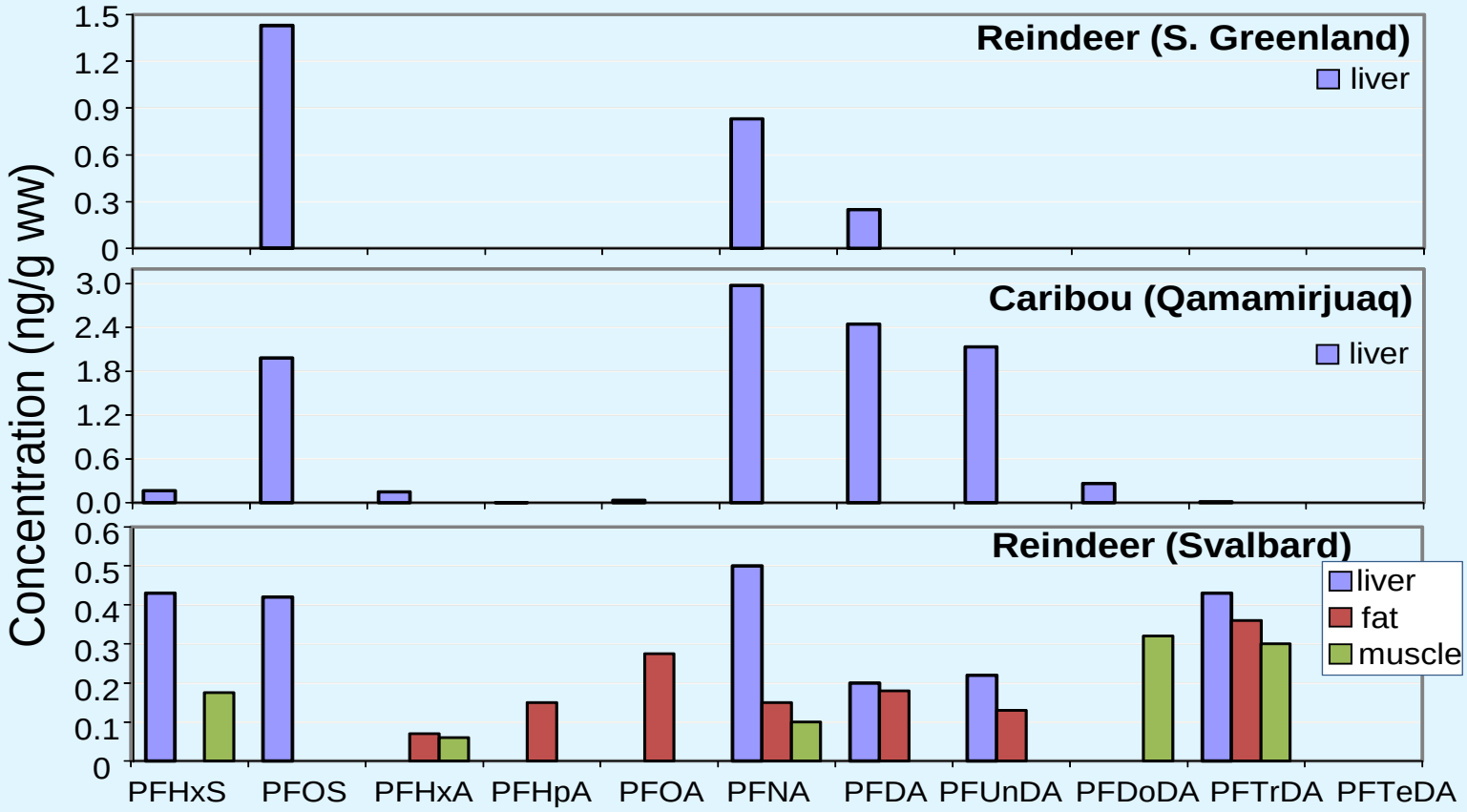
PFAS in terrestrial mammals



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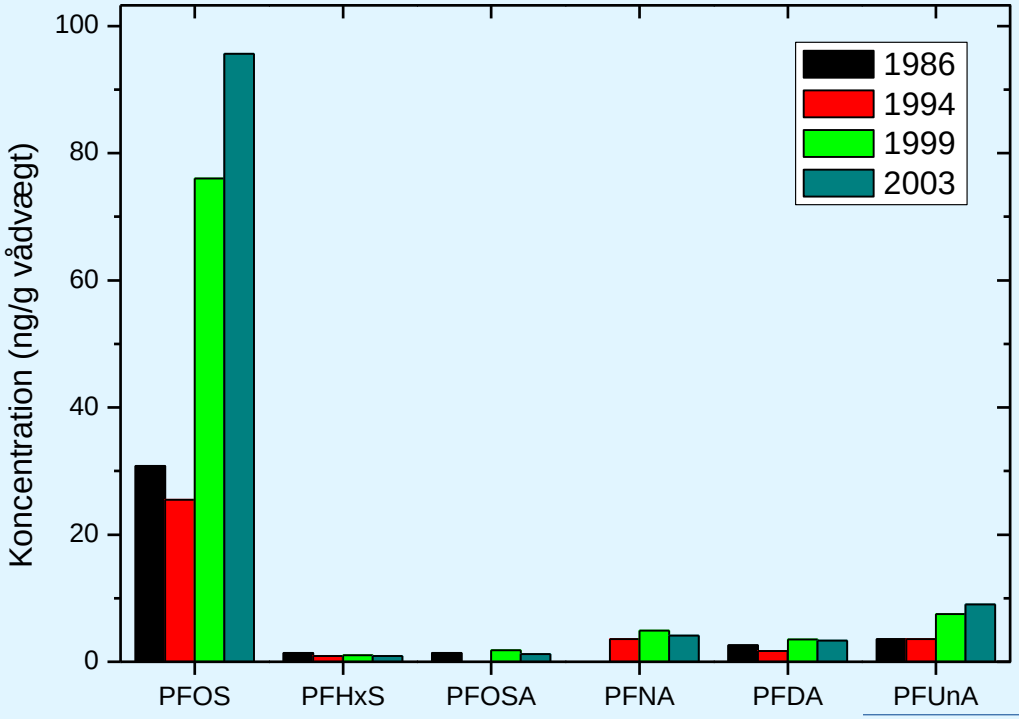
Time trend – Ringed seals

PFAS in liver from ringed seals, East Greenland (1986-2003)



- PFAS concentrations increase from 1986 to 2003
- Similar trend has been observed in polar bears

Bossi et al. (2005). Environ. Sci. Technol. 39, 74

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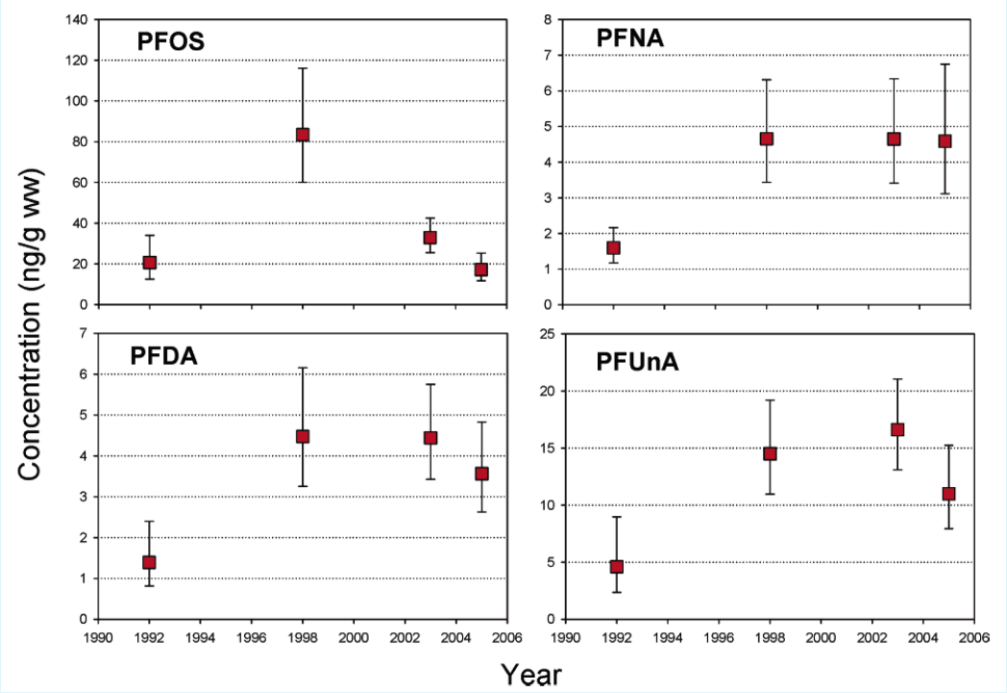
Time trend – Ringed seals

PFAS in liver from ringed seals, Canadian Arctic (1992-2005)



› PFOS concentrations decrease after 2002 (3M voluntary stop of PFOS-based production in North America)

Butt et al., Environ. Sci. & Technol., 2007

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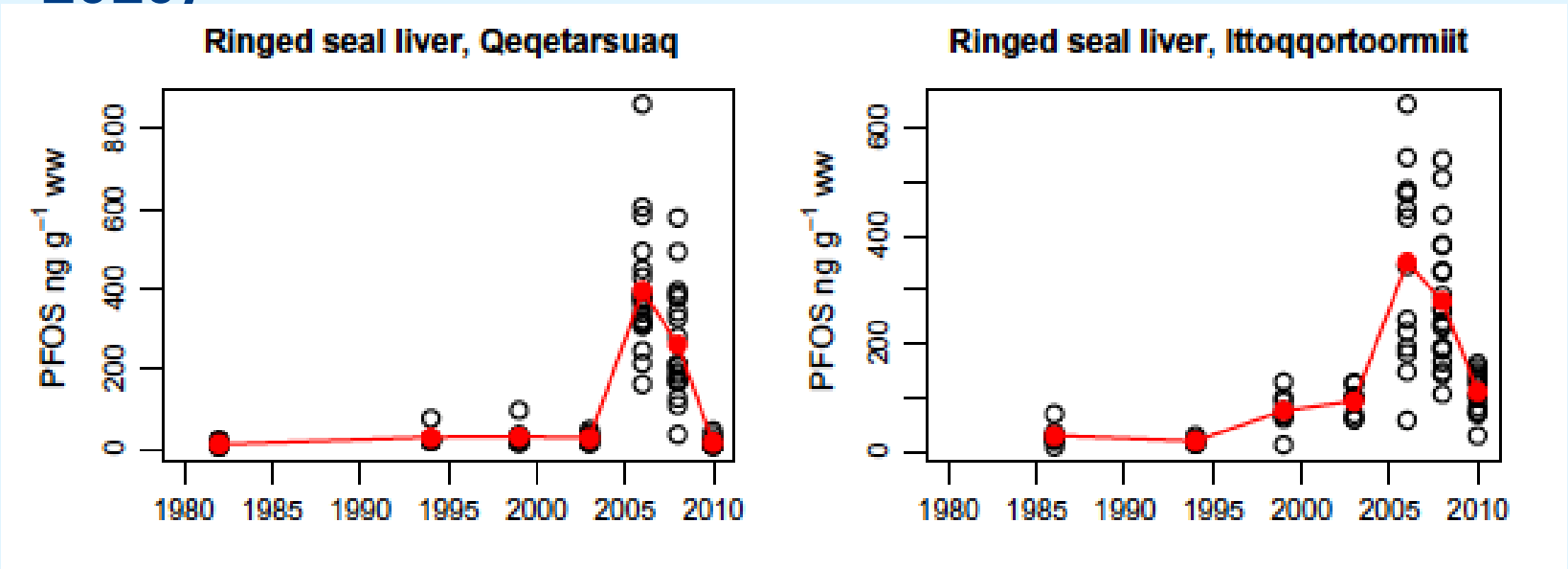
Time trend – Ringed seals

PFOS in liver from ringed seals, East & West Greenland (1986-2010)



Riget et al., Chemosphere, 2013

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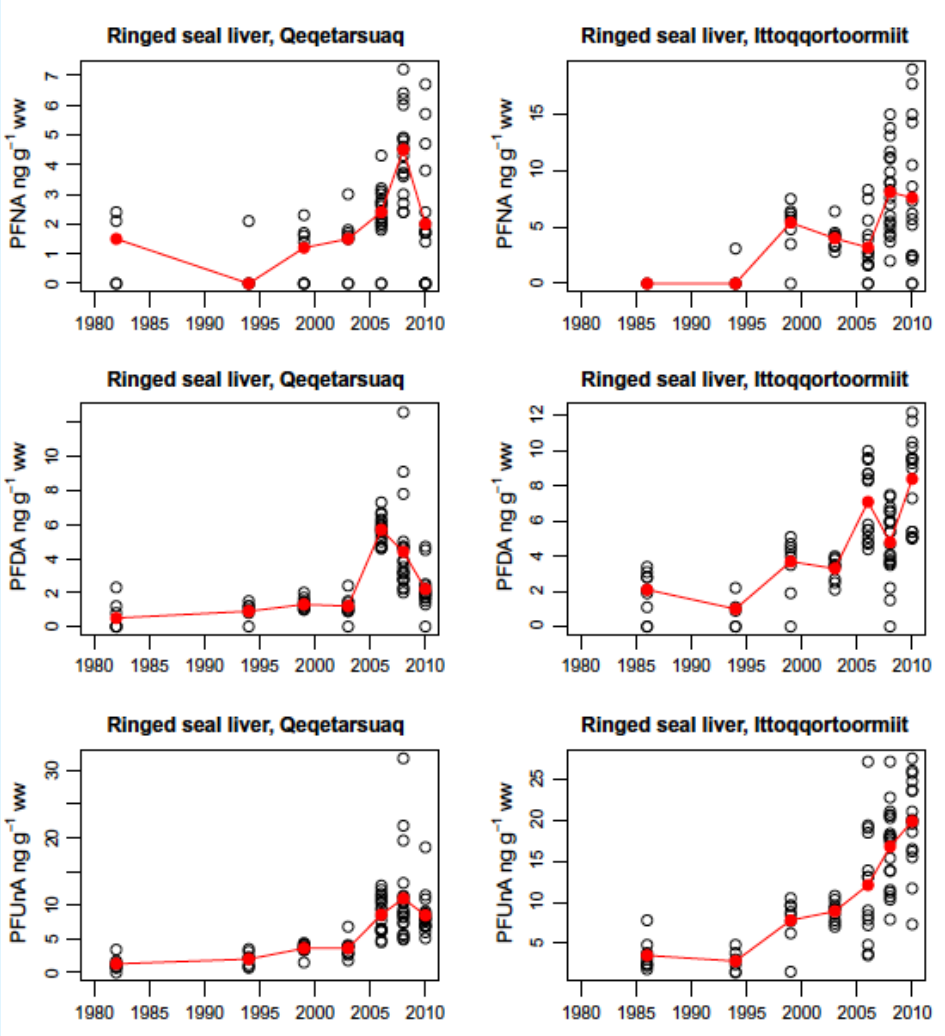
Time trend – Ringed seals



PFCAs in liver from ringed seals, East & West Greenland (1986-2010)

Riget et al., Chemosphere, 2013

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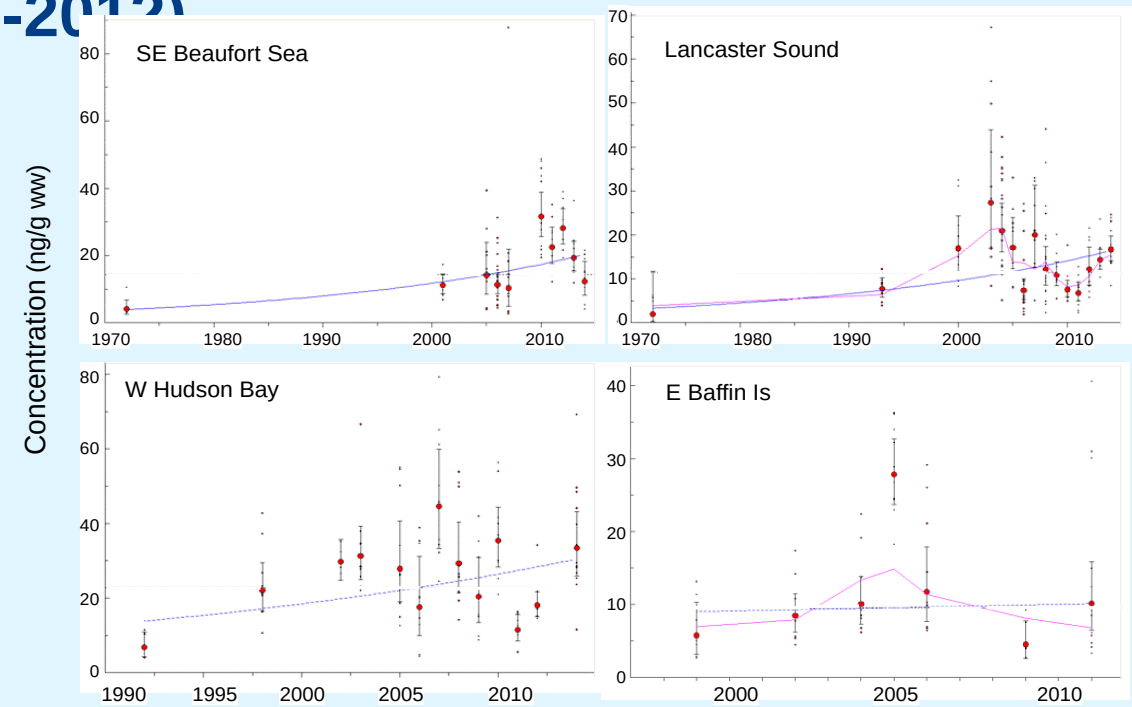
Time trend – Ringed seals

C7 to C14 PFCAs in liver from ringed seals, Canadian Arctic (1990-2012)



Muir et al., Aboriginal Affairs and Northern Development Canada, 2014

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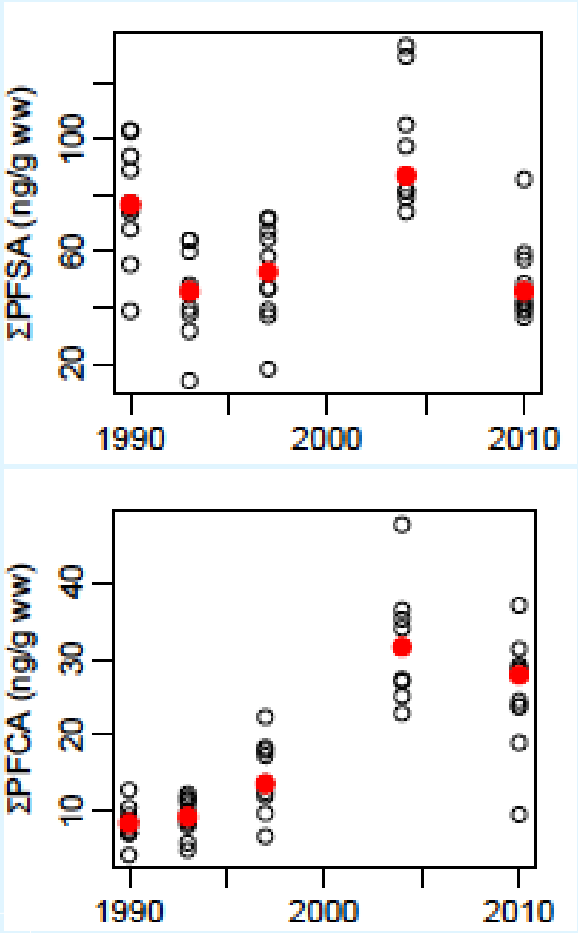
Time trend – Ringed seals



PFSAs and PFCAs in ringed seals from Svalbard (2002-2010)

Routti et al., Environ. Poll., 2016

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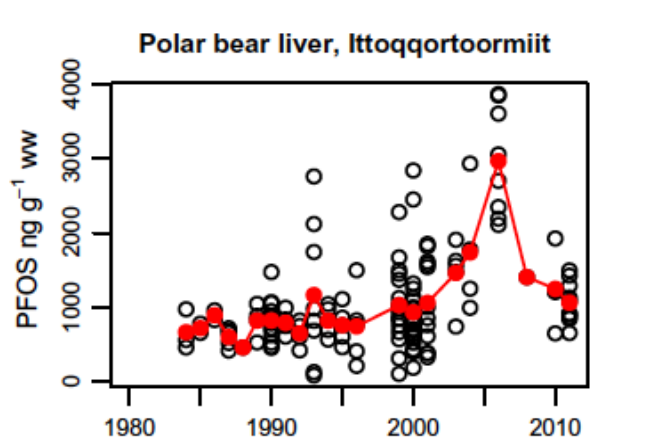
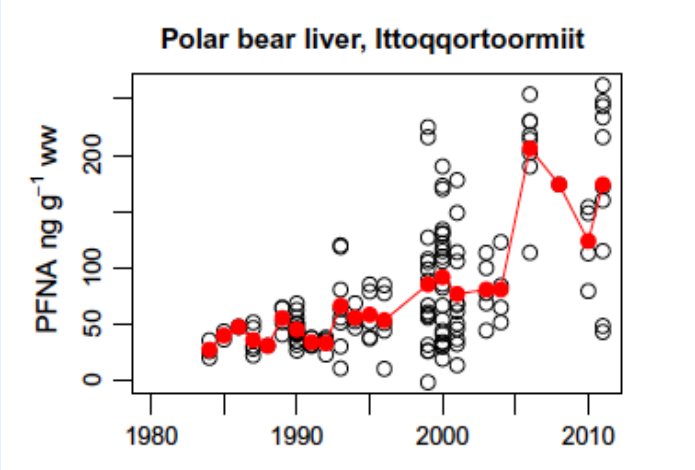
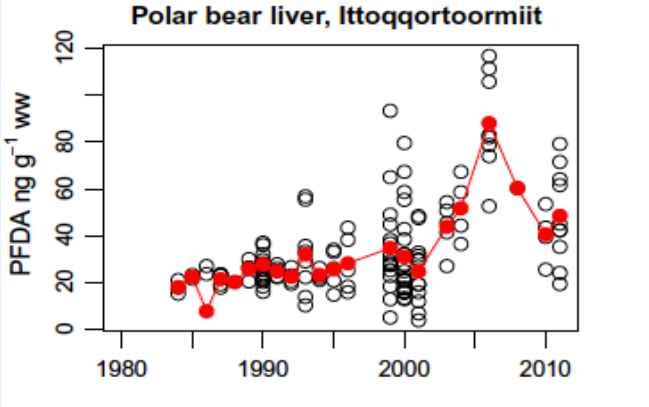
Time trend – Polar bears

PFAS in liver from polar bears, East Greenland (1980-2010)







Riget et al., Chemosphere, 2013

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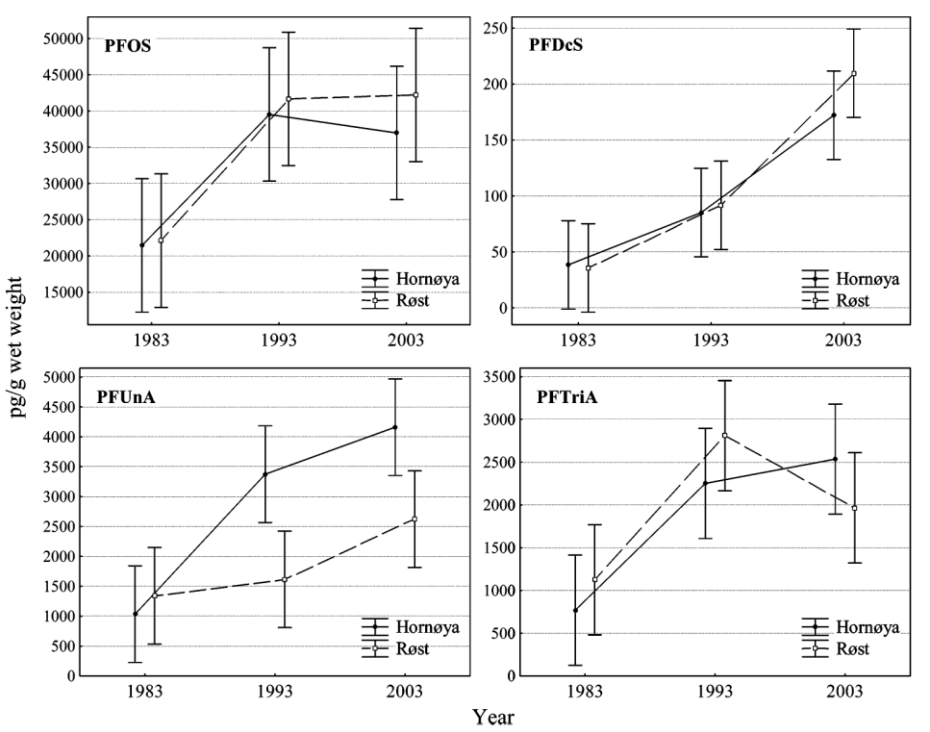
Time trend – Seabirds

PFAS in liver from herring gull, Norwegian Arctic (1983-2003)



- PFOS concentrations slightly decrease in 2003
- PFCAs concentrations increase after 1993

Verreault et al., Environ. Sci. & Technol., 200

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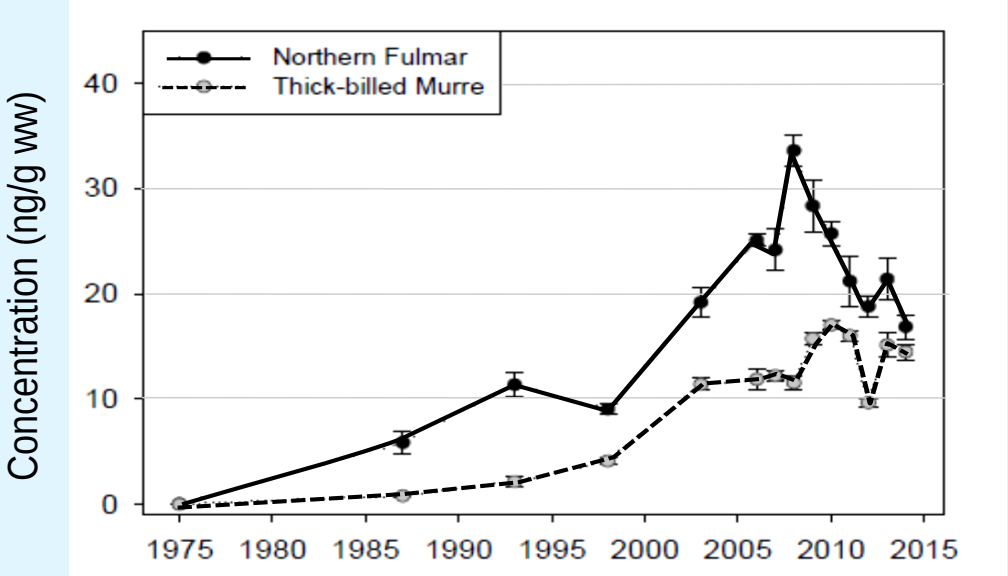
Time trend – Seabirds

C6 to C14 PFCAs in liver from northern fulmar and thick-billed murre, Canadian Arctic (1975-2015)



Braune, Aboriginal Affairs and Northern Development Canada, 2015

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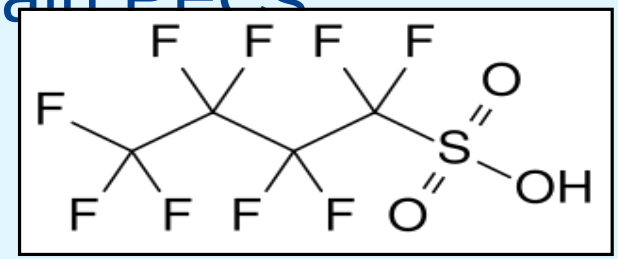
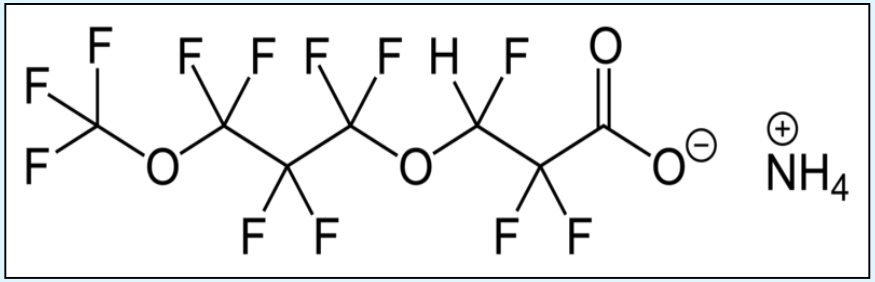
New PFASs

› The tendency is to produce shorter chain PFASs (e.g. perfluorobutane sulfonate) or oxygen-containing PFASs as substitutes for the longer chain PFCs

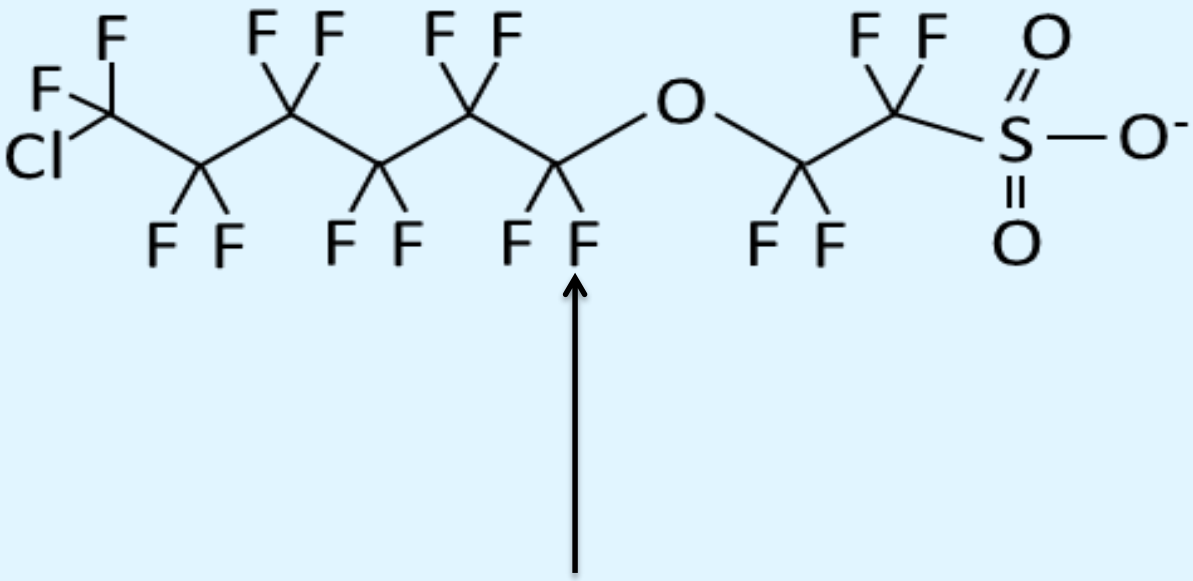


Perfluorobutane sulfonate (PFBS)



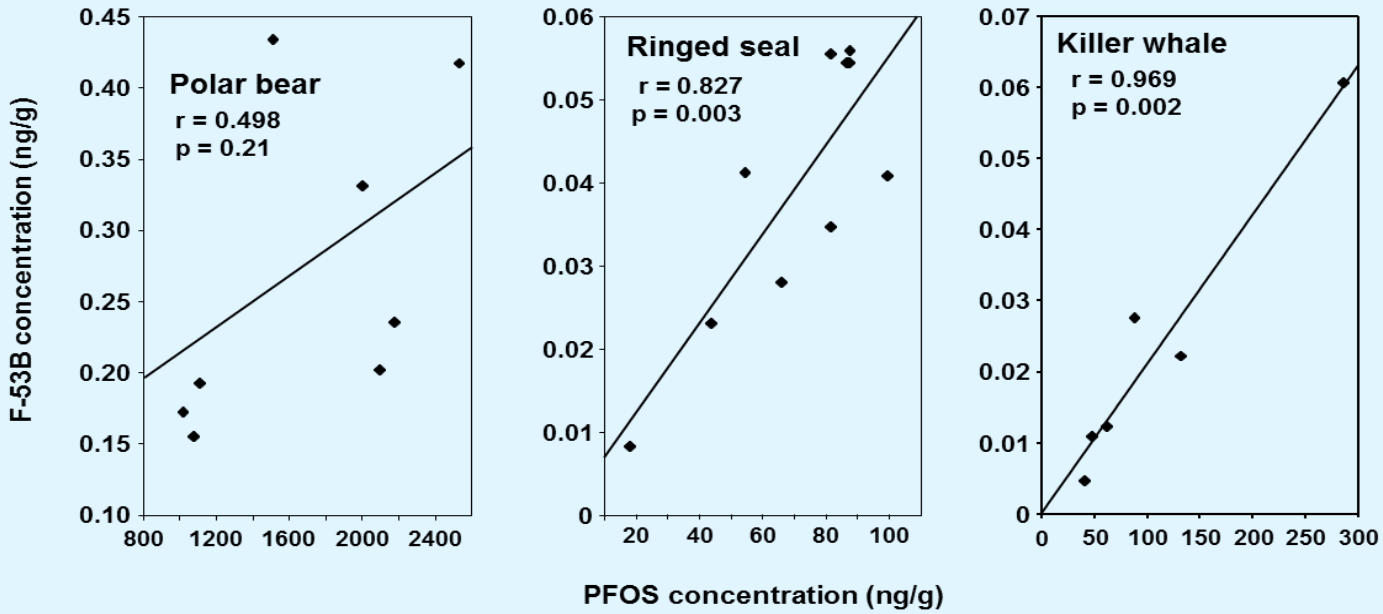
ADONA™ (ammonium 4,8-dioxa-3H-perfluorononanoate)

F-53B - AN ALTERNATIVE TO PFOS



Presence of oxygen in the C-F chain

F-53B /PFOS CORRELATION



Gebbink et al., Chemosphere 2016

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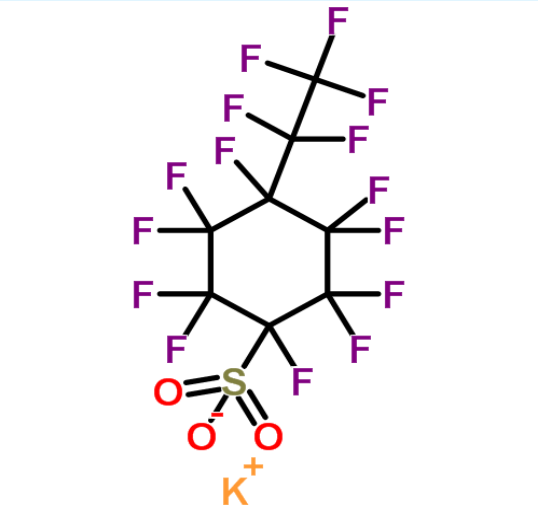
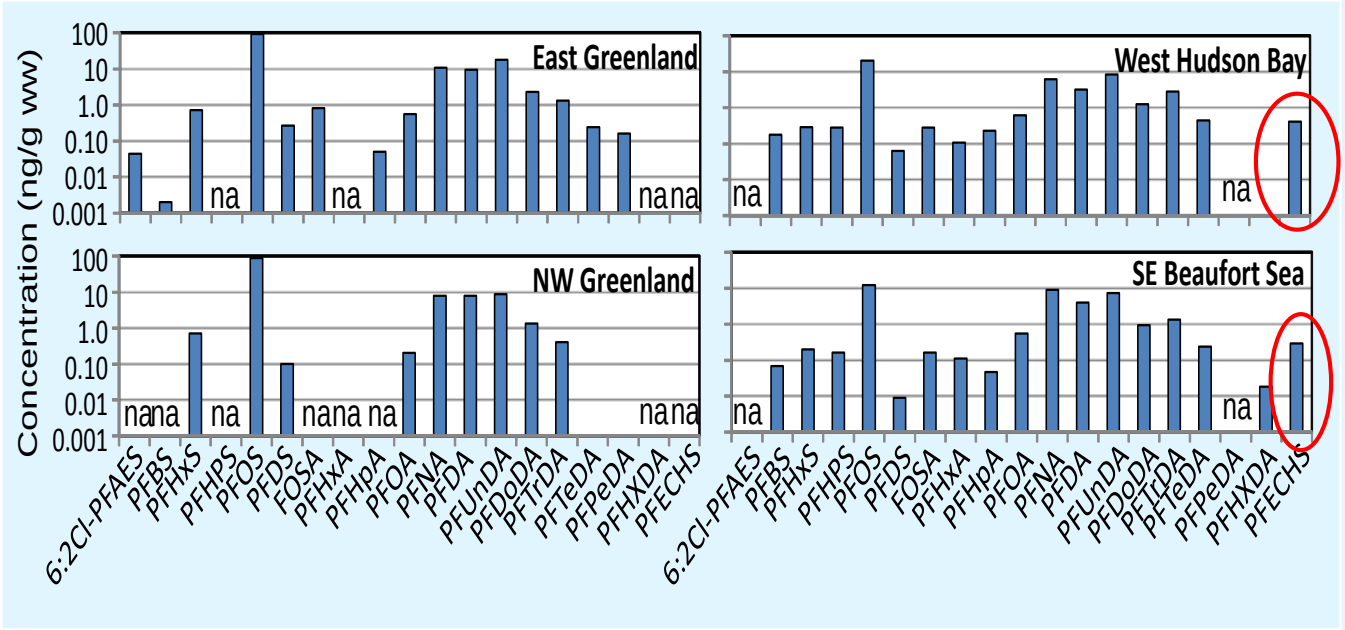
Perfluoroethylcyclohexanesulfonate (PFECHS)





PFECHS is found in ring seal liver from northern Canada

Muir et al., unpublished

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Conclusions

- PFOS concentrations are decreasing as a consequence of international regulations
- PFCAs temporal trends vary across the North American Arctic and between East and West Greenland
- PFCAs concentrations seems to be increasing after 2010 where a slight decline was observed
- Increasing PFCAS concentrations have been explained by continuing emissions of long-chain PFCAs and/or their precursors
- New PFAS have to be included in monitoring programs

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Acknowledgments

› Danish Environmental Protection Agency (DANCEA funds for environmental support to the Arctic Region) for financial support (AMAP Core project)