Biomonitoring of perfluoroalkyl acids: An overview of the global and temporal trend data

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Outline

- **Biomonitoring of PFAs – pros and cons**
- **Overview of measurements of PFAs in biota and humans**
  - **Geographical trends within Species or similar species**
  - **New temporal trends results**
- **Comparison of lab and field biomagnification/bioaccumulation**
  - Are calculate BMFs using plasma or liver appropriate?
  - Bioaccumulation pathways?
- **Conclusions**
  - What is the biomonitoring data telling us?

Biomonitoring of PFAs – pros and cons

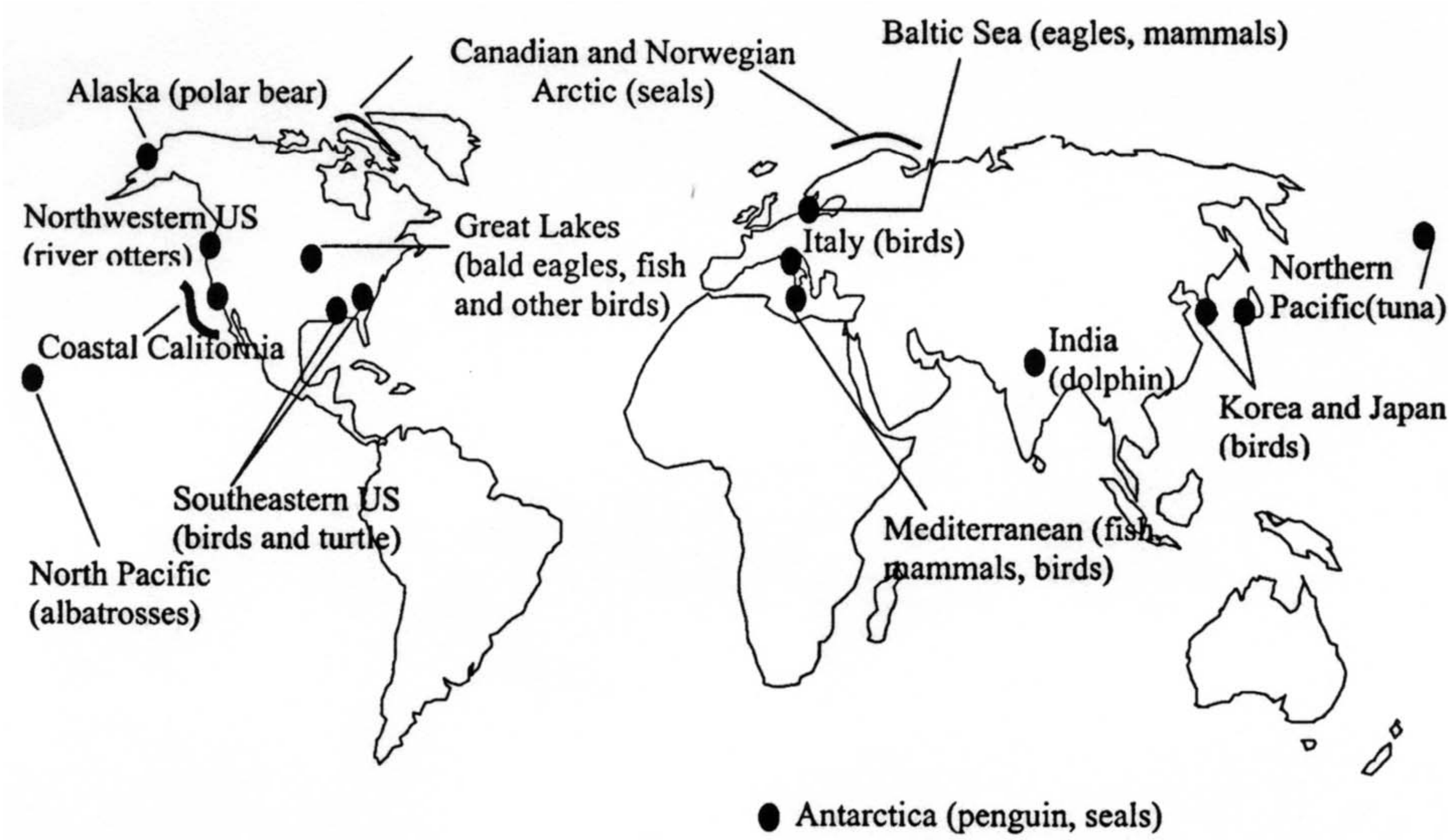
- Biota integrate exposures via water, sediment, soil and food webs
  - address the "so what" question re contaminants especially in remote environments
- Use of biota provides information on wildlife and human exposure, bioaccumulation potential, global distribution, temporal trends
- Great stability of PFAs (at least PFOS, PFCAs) allows for simple sample handling and storage and use of archived samples

Challenges

- Precursors generally have not been determined – are they important? Are they stable during sample storage?
- Contamination especially for PFCAs due to storage or handling with PTFE products could yield false positives
- Are liver or plasma data appropriate for assessing biomagnification?
- Effects of age, sex, feeding and migratory habits need to be considered

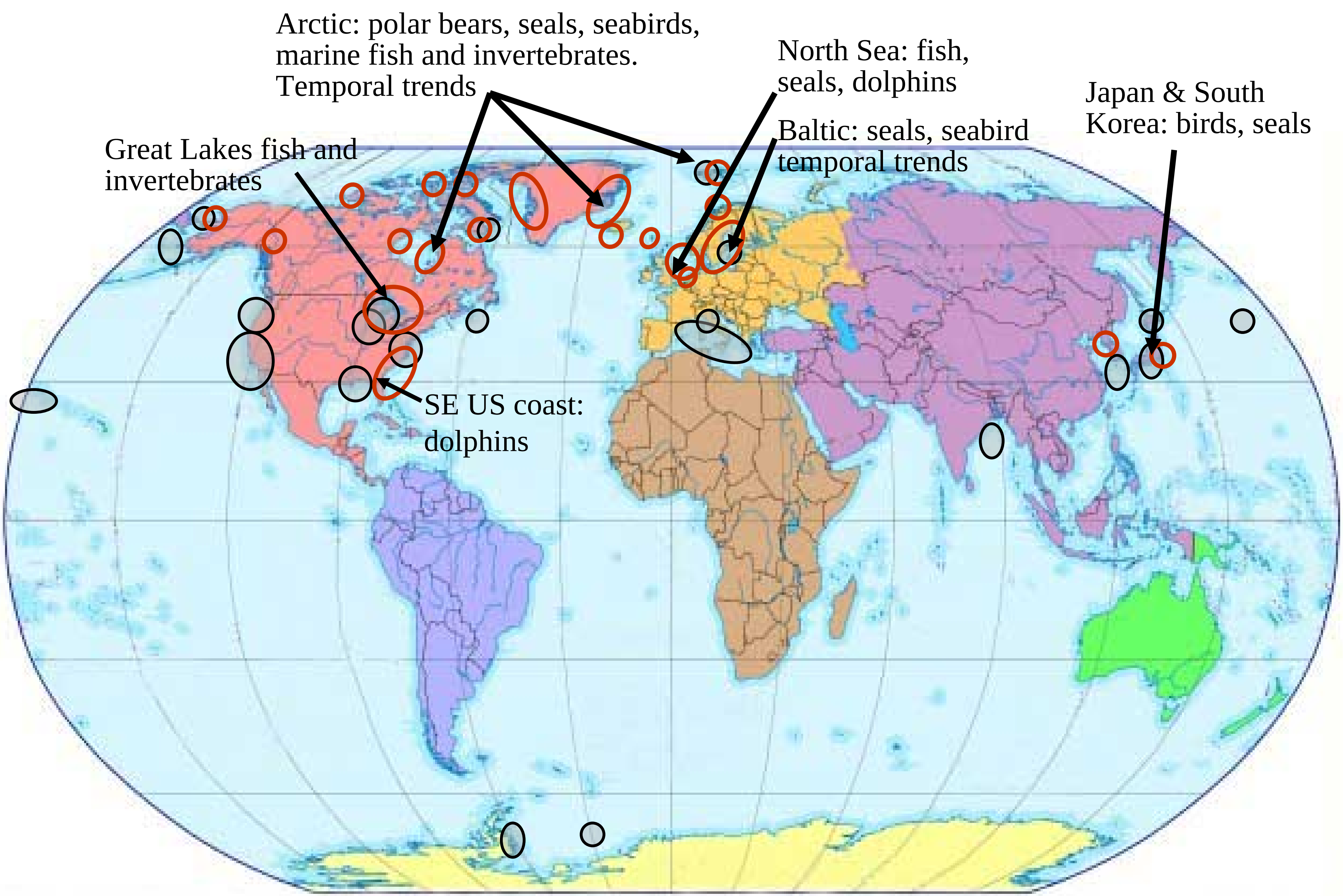
New era of biomonitoring of PFAs begins

(Giesy & Kannan ES&T, 35:139, 2001)

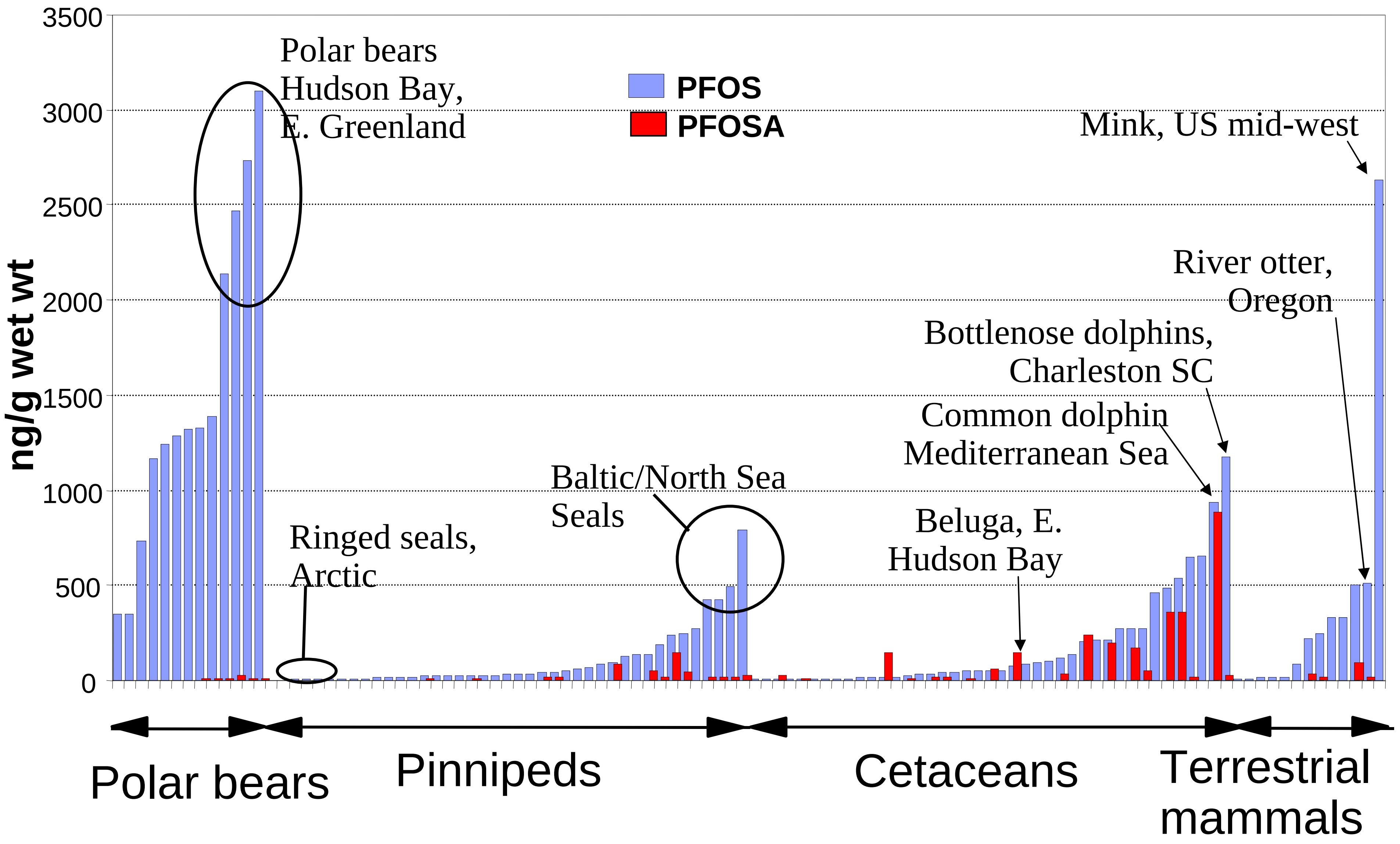


Global distribution of PFC measurements in fish and wildlife (to mid-2005)

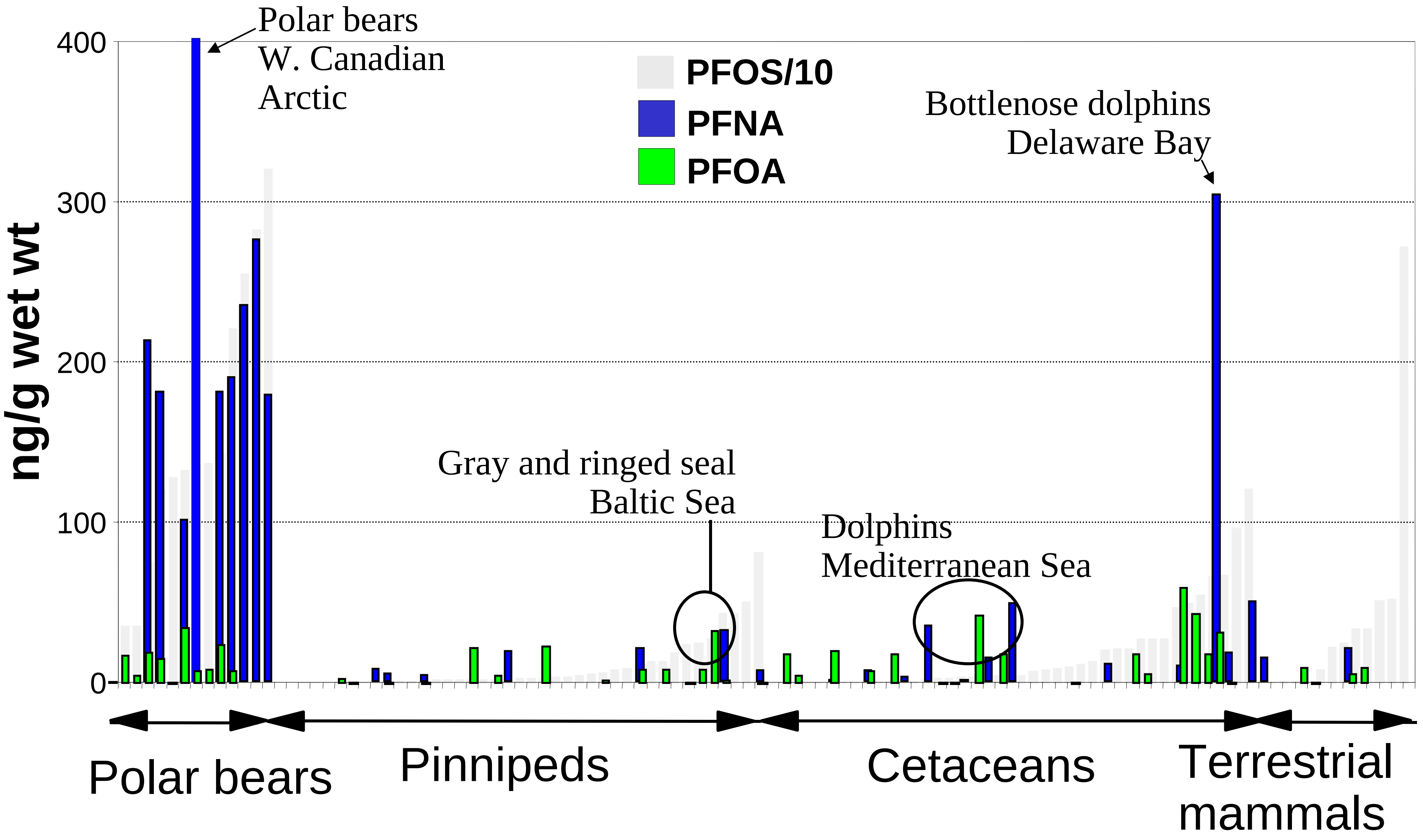
Geisy & Kannan; Kannan et al ⬭ Others ⬯



PFOS and PFOSA in marine and terrestrial mammals (liver, kidney, plasma) – 17 studies, 16 with PFOSA+PFOS

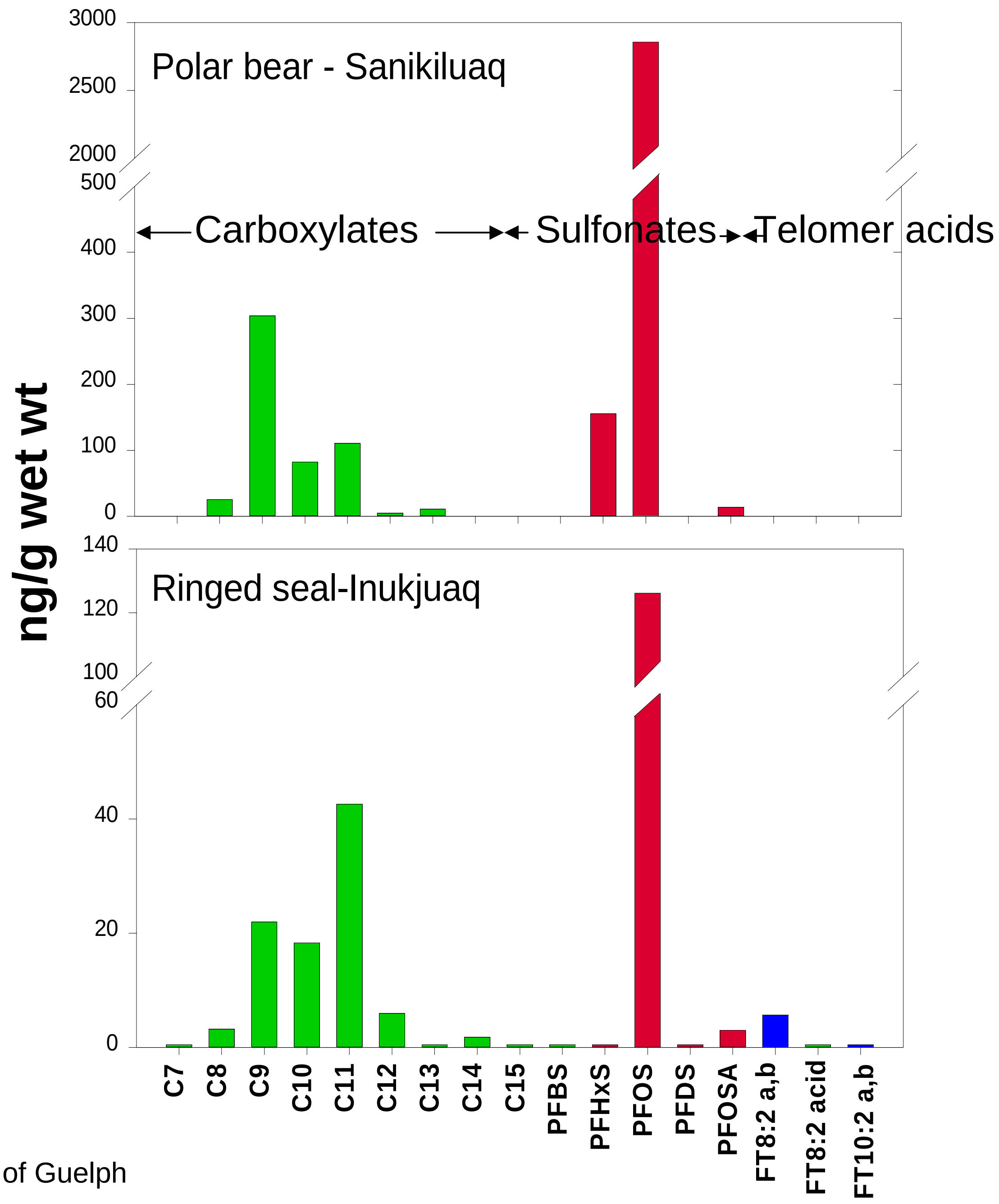


PFNA and PFOA in marine and terrestrial mammals (liver, kidney, plasma) – 10 studies with PFNA+PFOA and 13 with PFOA only



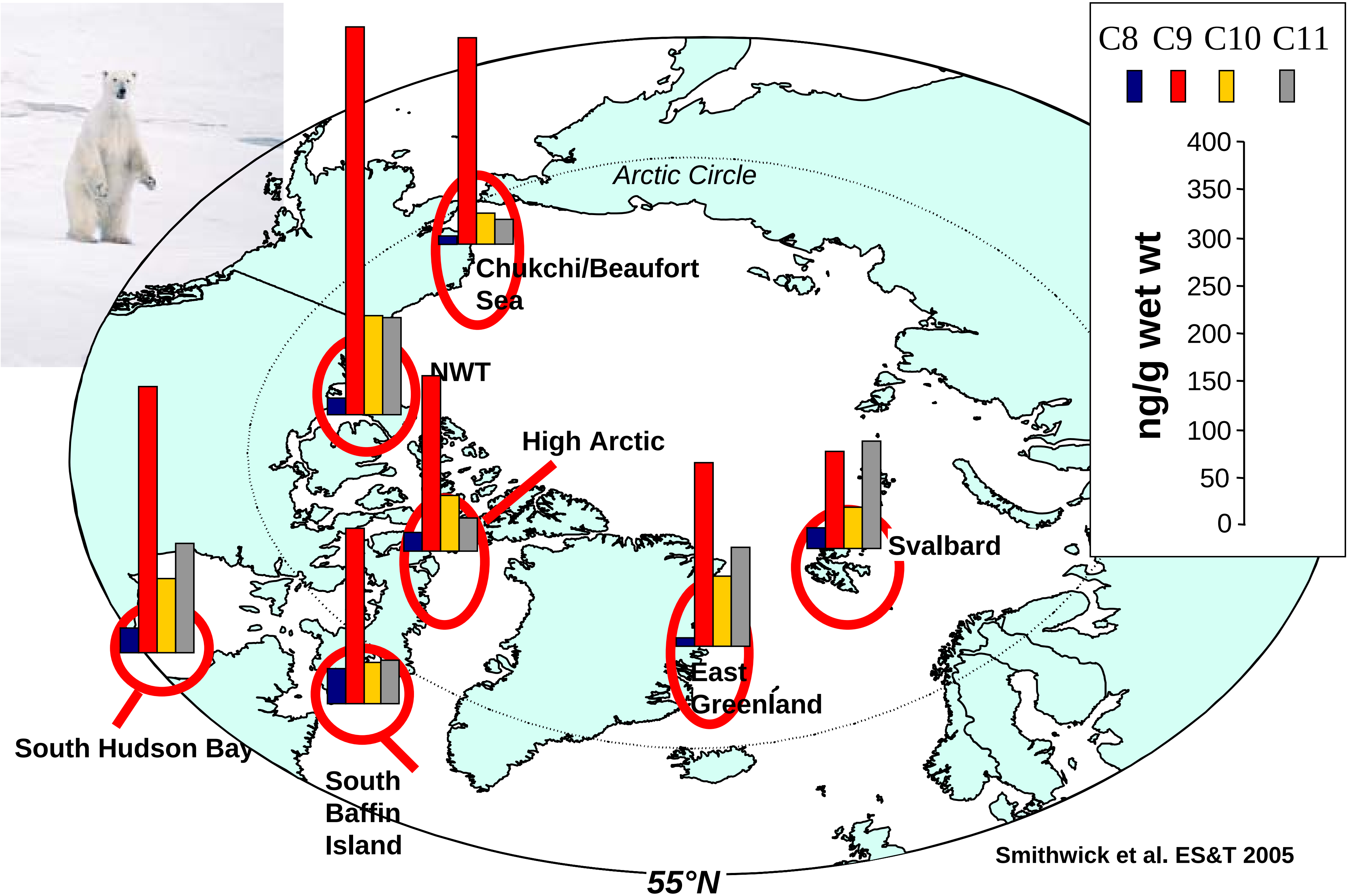
Pattern of perfluoro acids in polar bear and ringed seal livers (E. Hudson Bay)

PFA	Seal to Bear
C7	1
C8	8
C9	14
C10	4
C11	3
C12	1
C13	22
C14	0.4
C15	1
PFBS	1
PFHxS	310
PFOS	23
PFDS	1
PFOSA	5

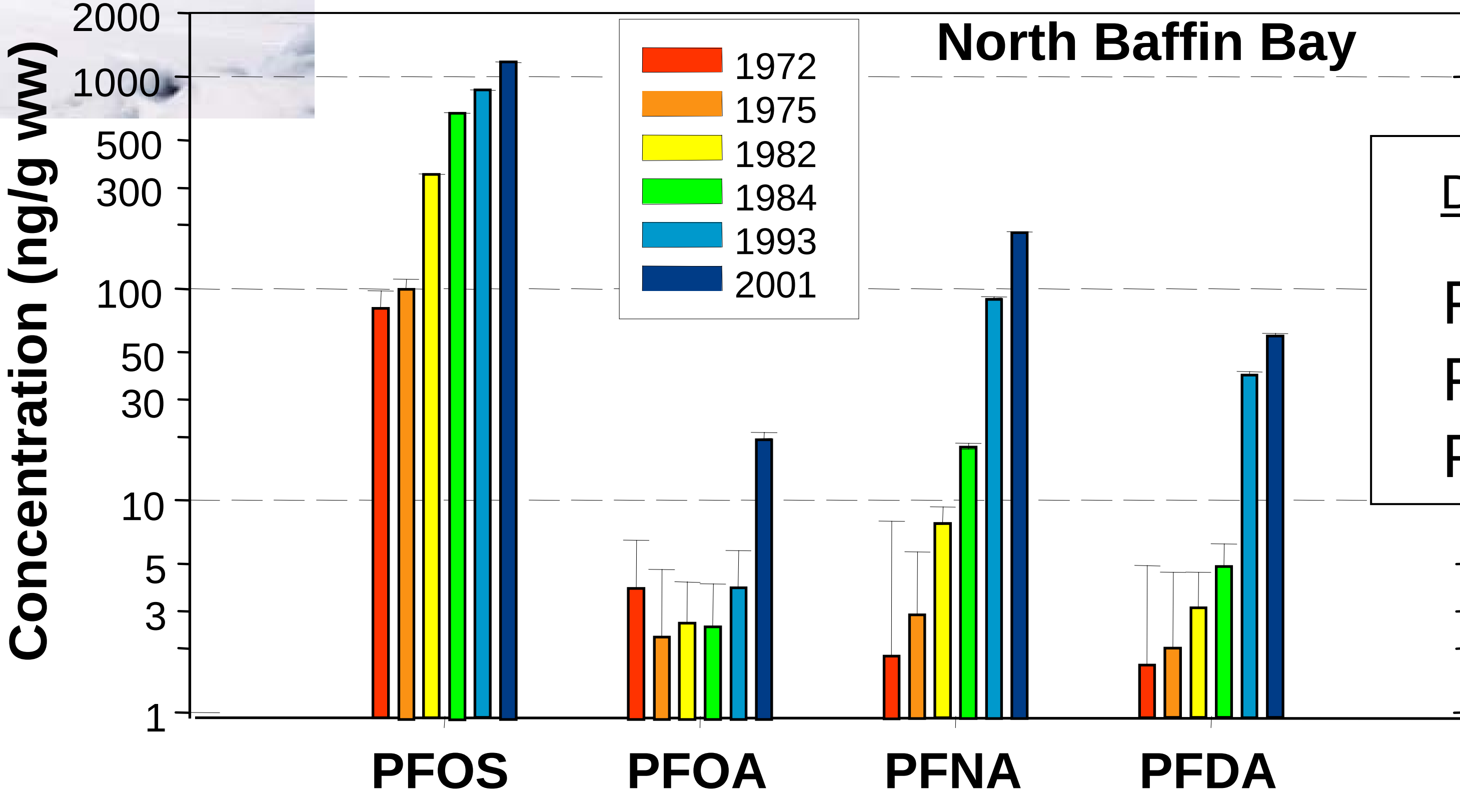


C. Butt, U of Toronto and M. Smithwick, U of Guelph
Unpublished results 2004

Trends of Perfluorinated carboxylic acidsin polar bear liver (ng/g wet wt) (Smithwick et al. 2005)



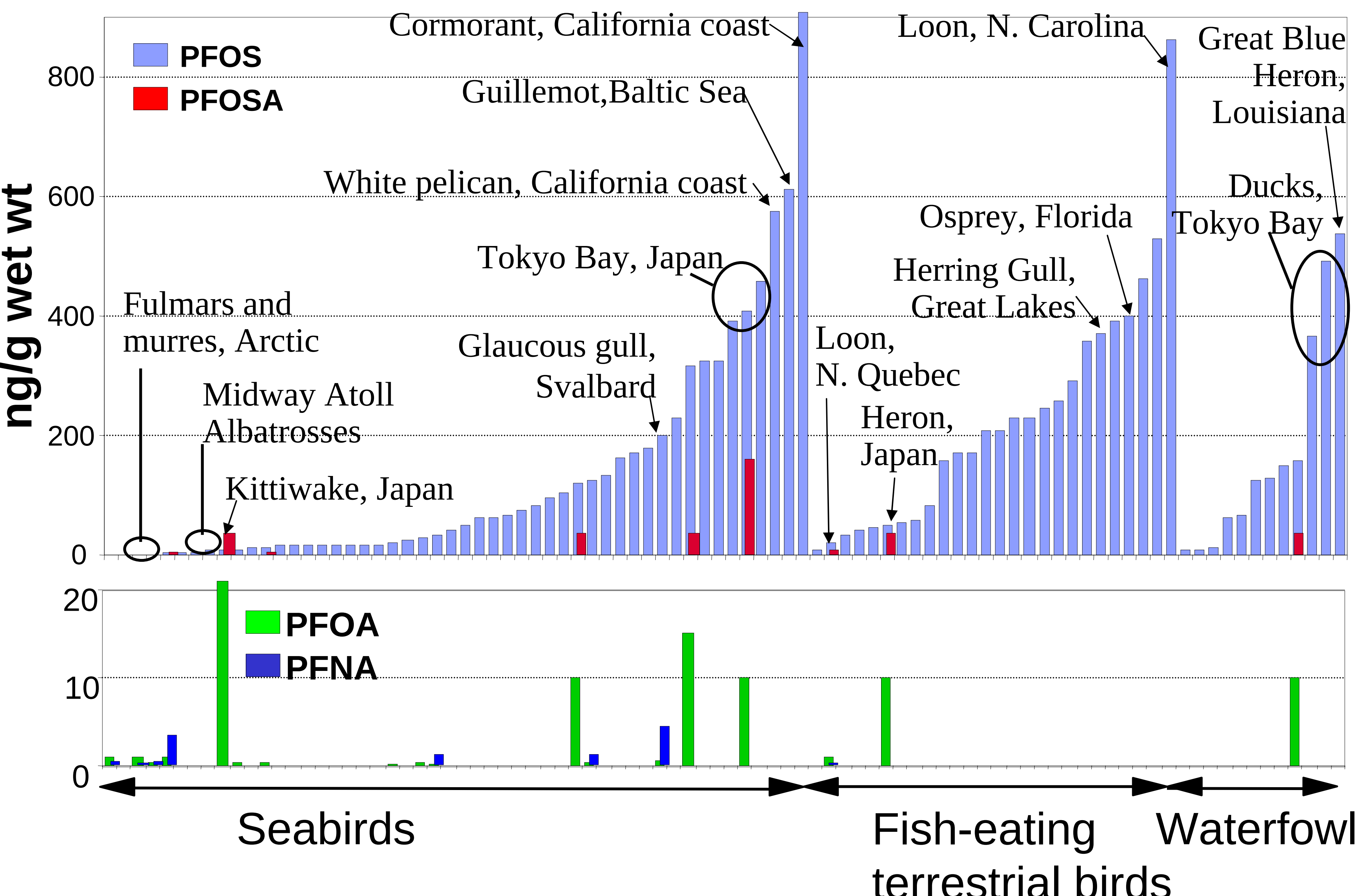
PFOS and major PFCAs increased in polar bear liver during the 1990s (Smithwick et al. submitted)



Doubling time (years)

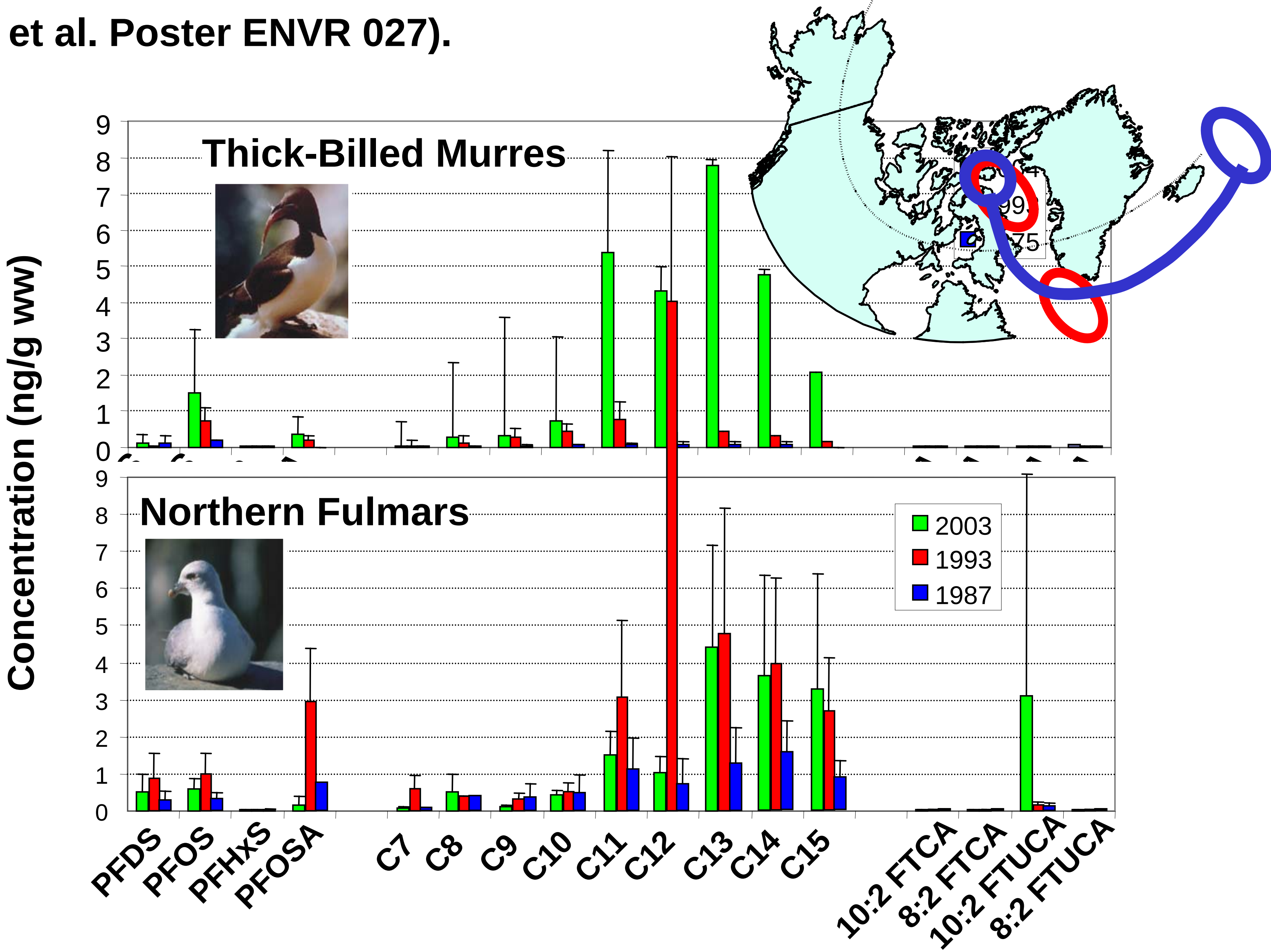
PFOS	10
PFNA	3.6
PFDA	4.2

PFCs in marine and terrestrial birds (liver, eggs, plasma)

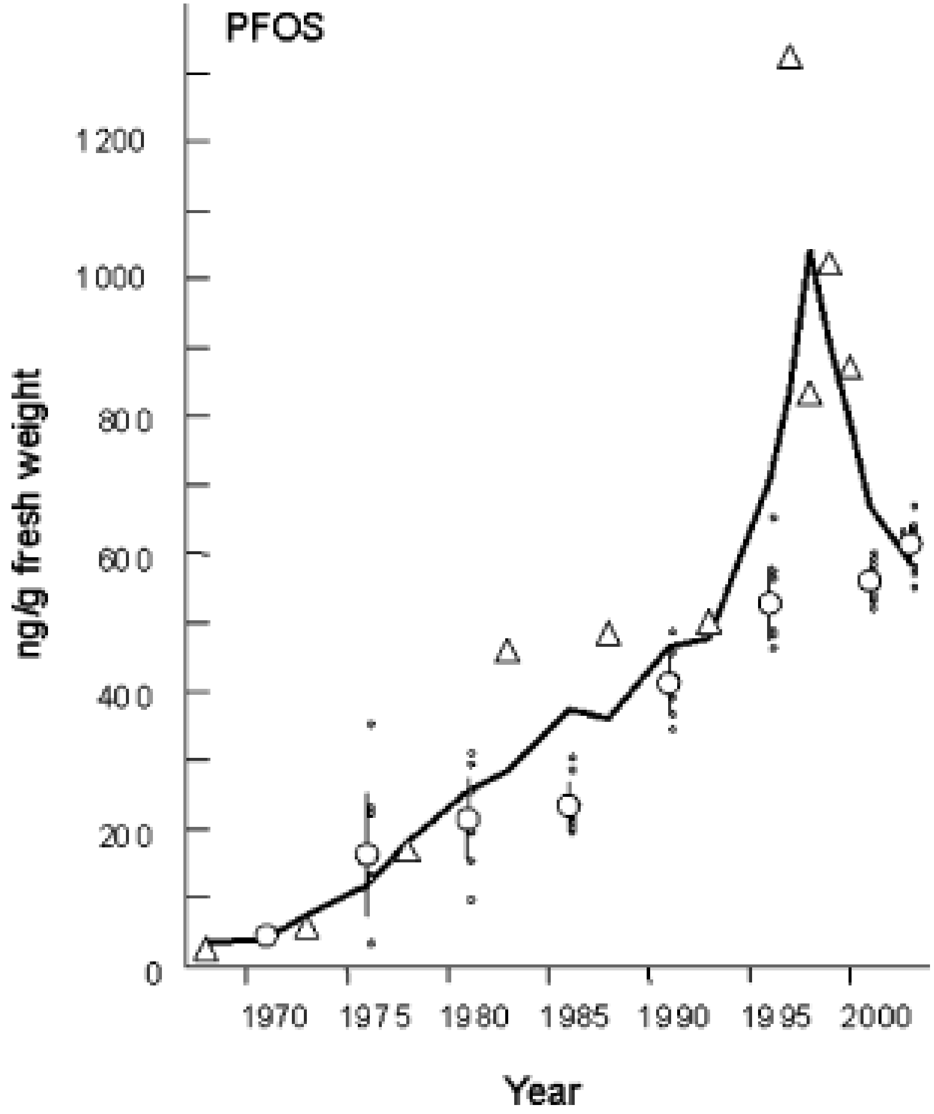


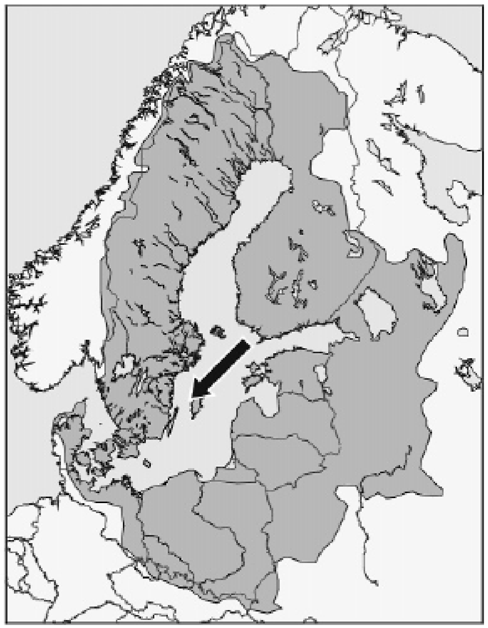
PFA profiles and temporal trends in Arctic seabird livers

(Butt et al. Poster ENVR 027).

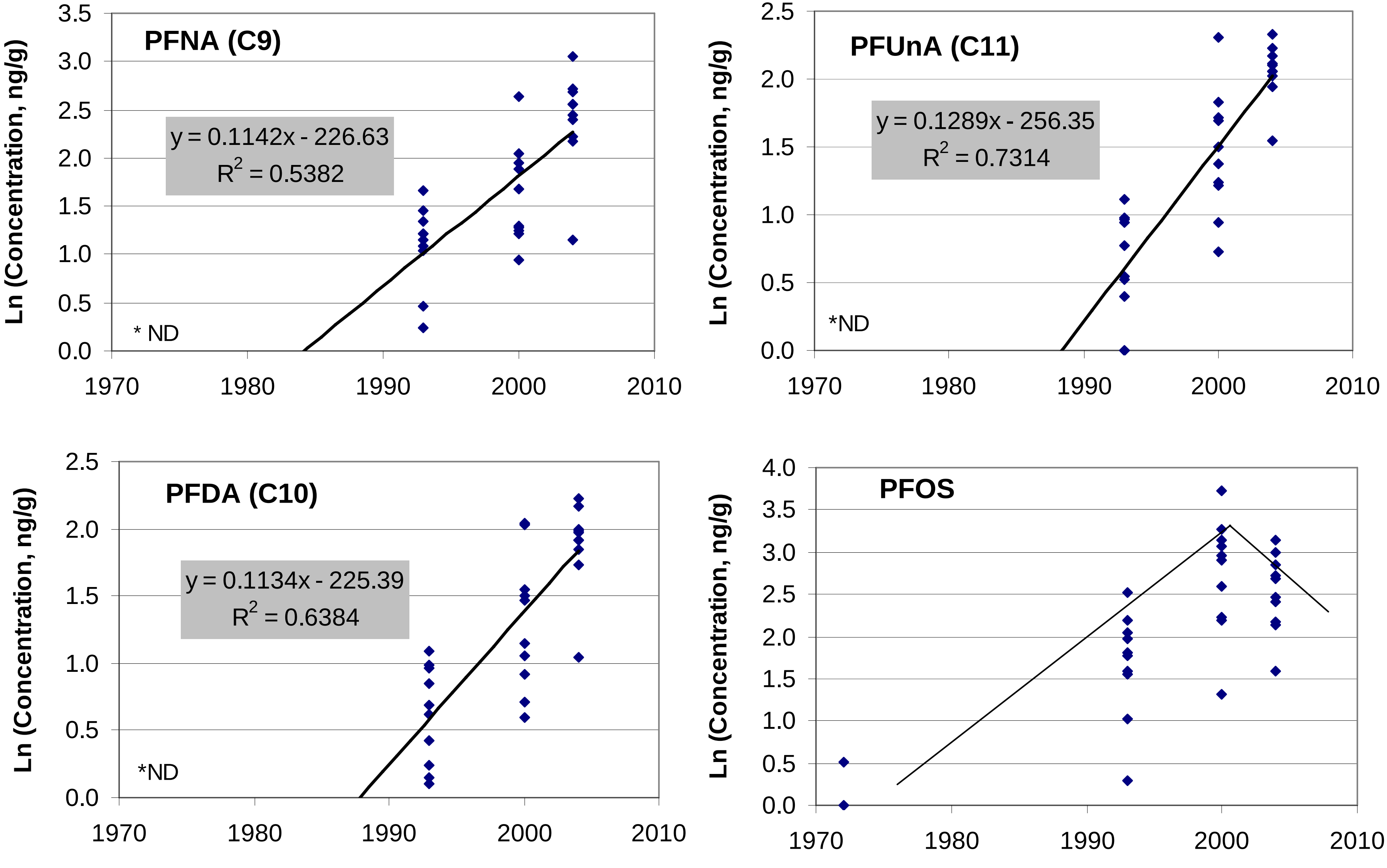


Trends of PFOS in guillemot eggs from the Baltic Sea (1968-2003) show overall doubling time of 7-10 yrs with possible maximum in late 1990s (Holmström et al ES&T 2005)

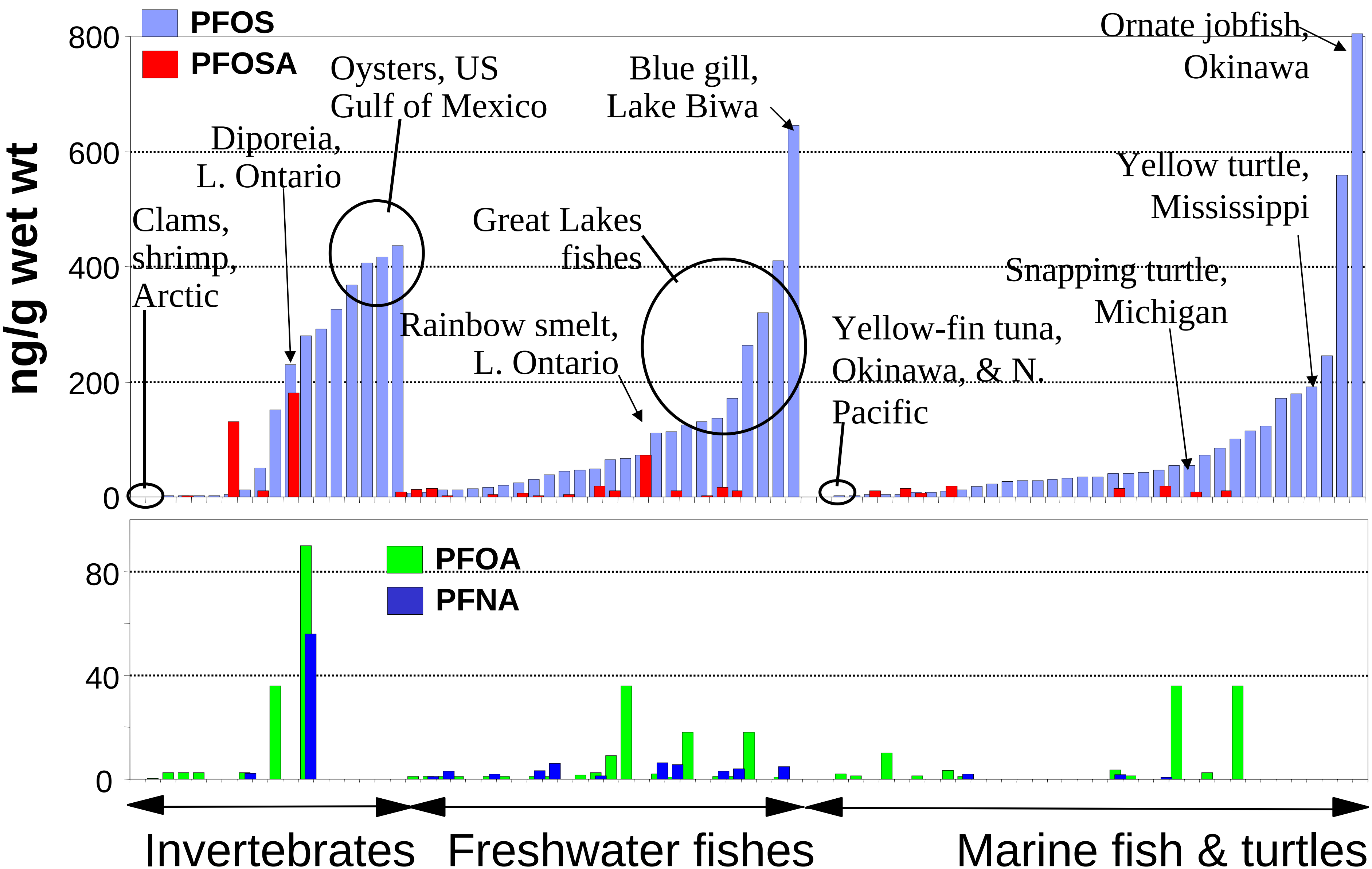




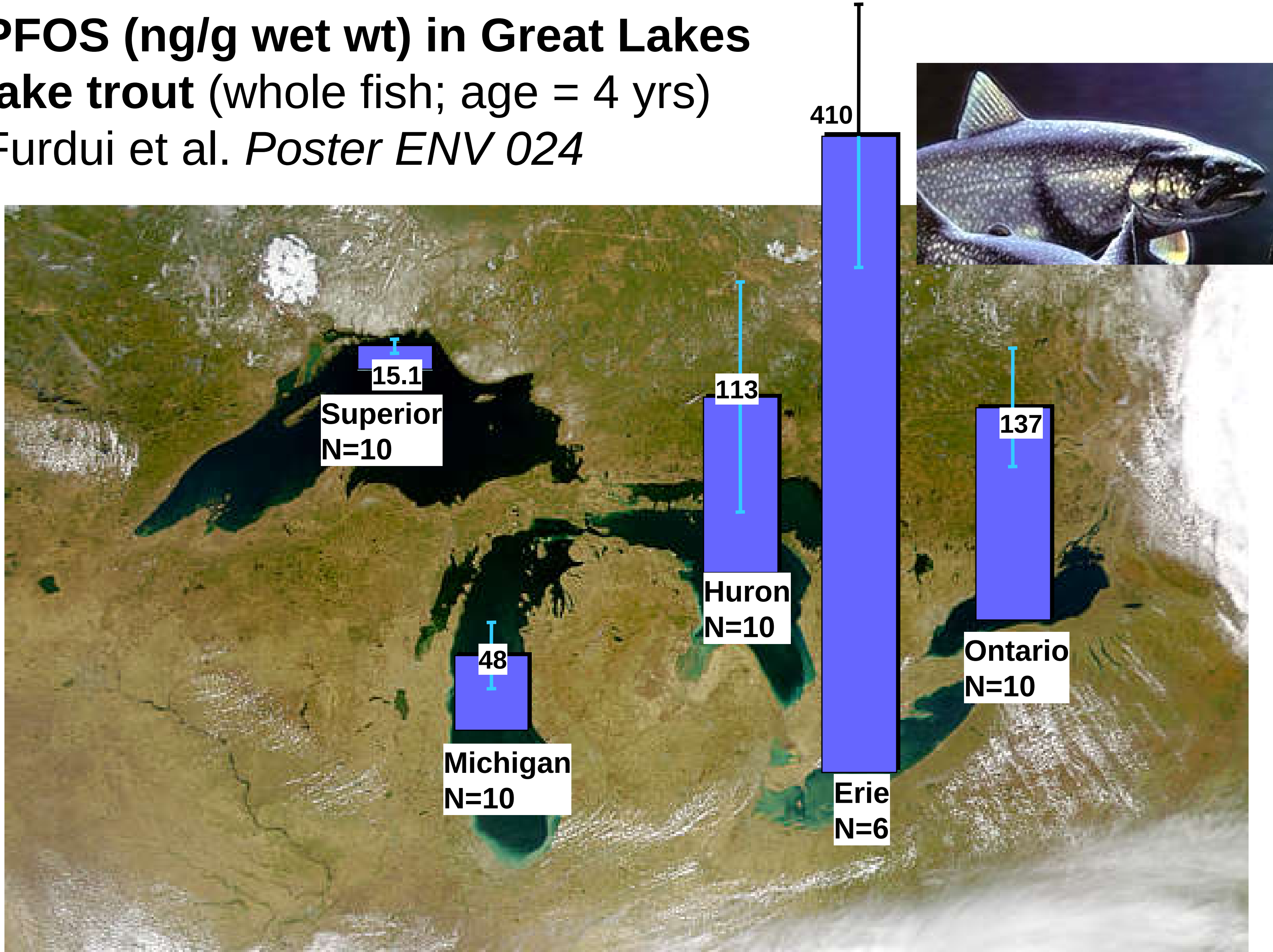
Temporal Trends –Ringed Seals in the Canadian Arctic (Butt et al. poster ENV 027)



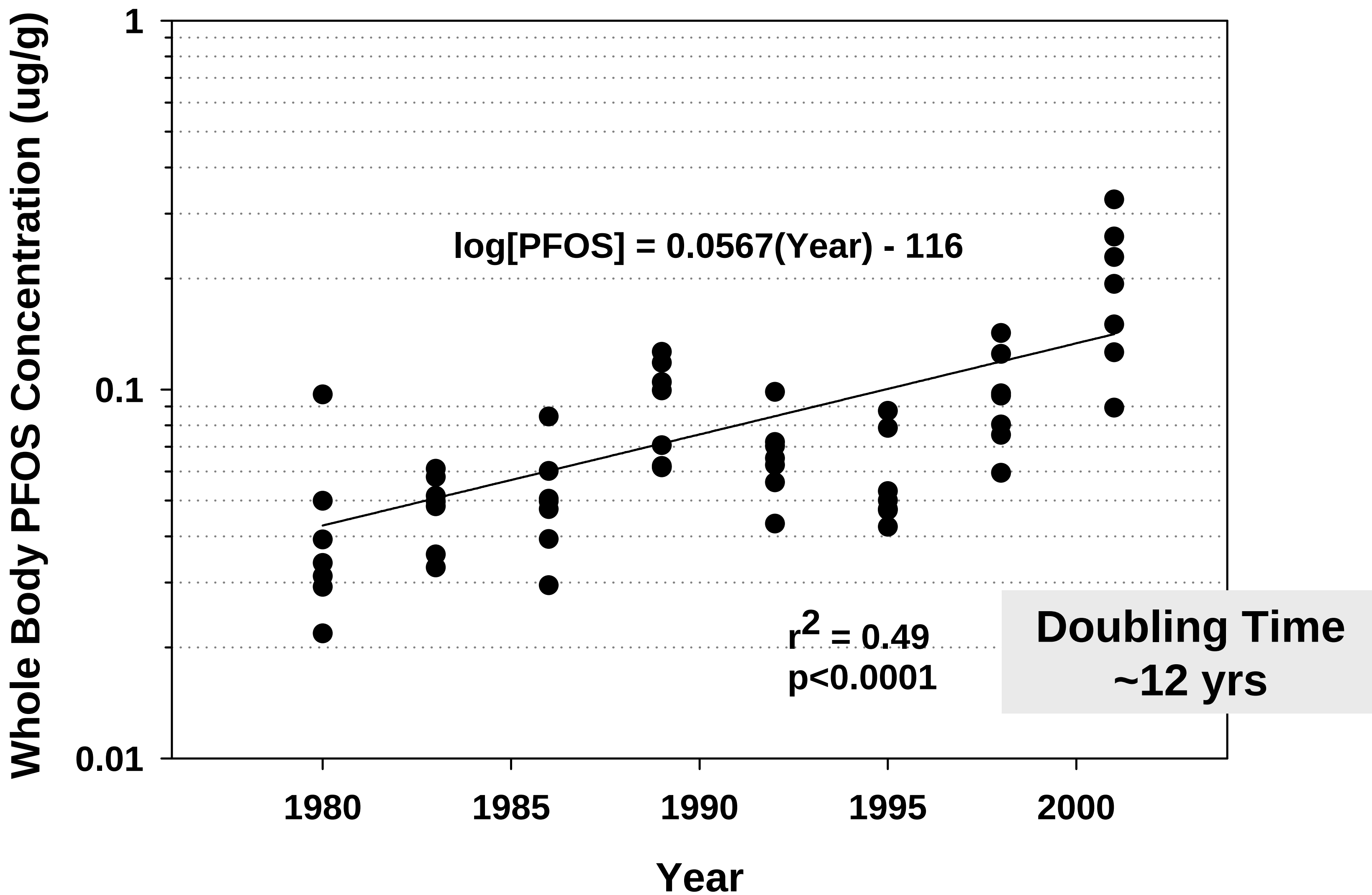
PFCs in invertebrates and freshwater and marine fish and turtles



PFOS (ng/g wet wt) in Great Lakes lake trout (whole fish; age = 4 yrs)
Furdui et al. *Poster ENV 024*

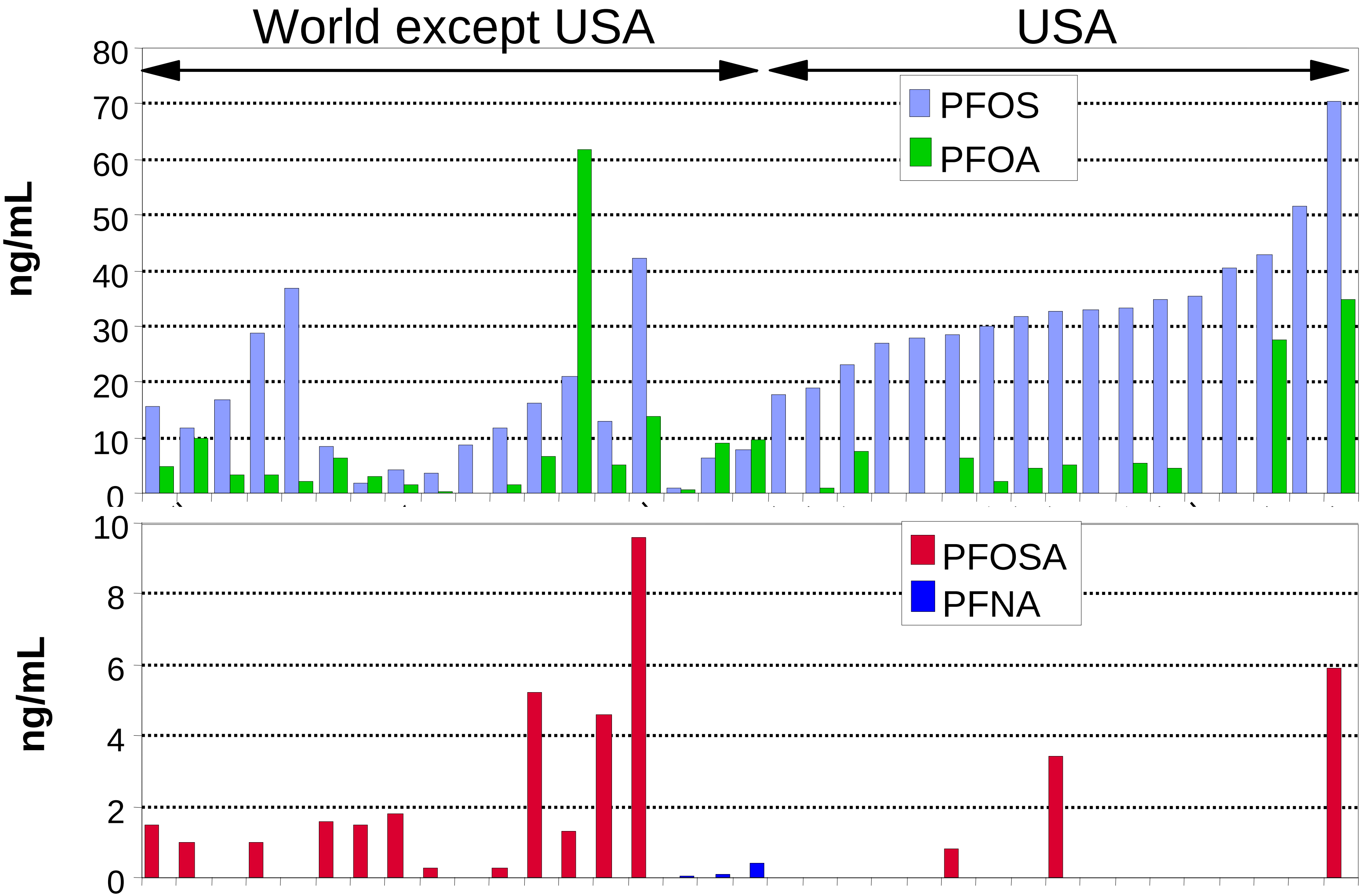


PFOS Trend in Archived Lake Trout (whole fish) from Lake Ontario (1980-2001) *(Martin et al ES&T 2004)*

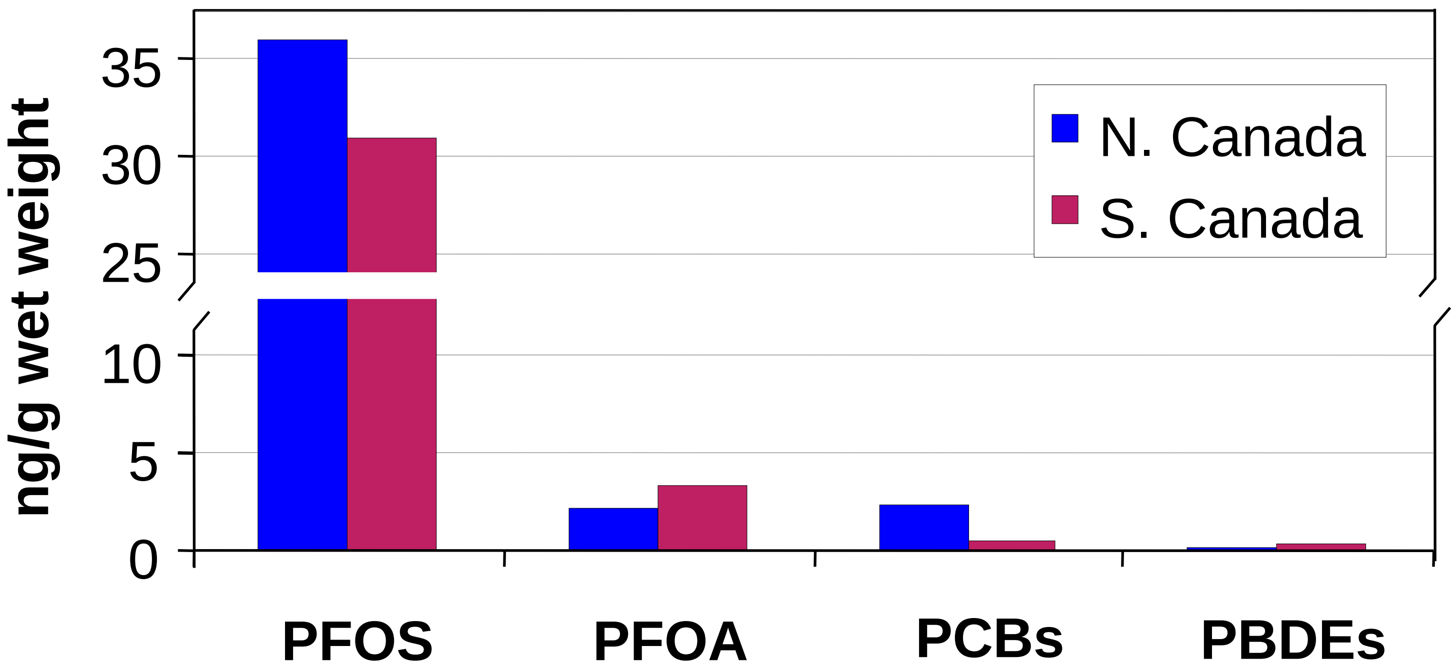


PFCs in human whole blood, plasma or serum

(see also ANA 019, 026, 033, 037, 043)

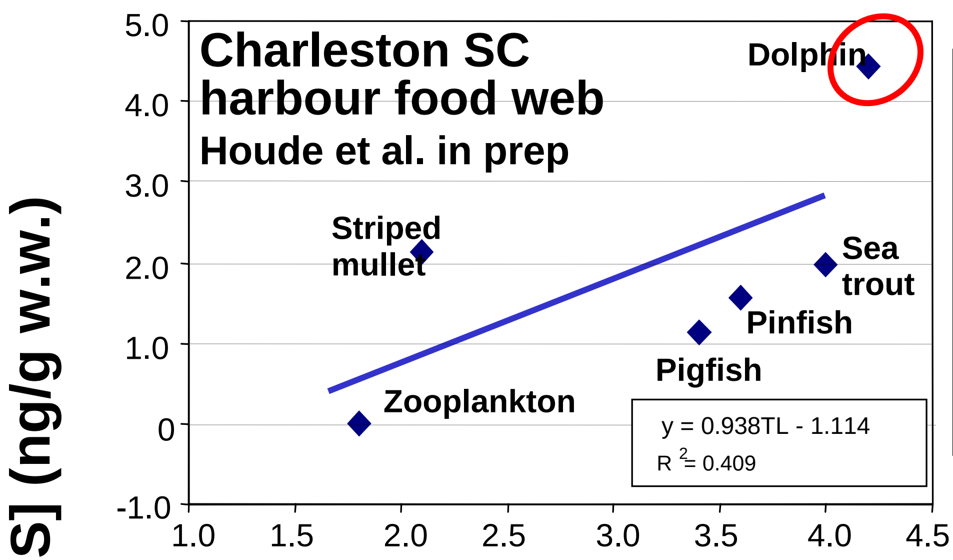


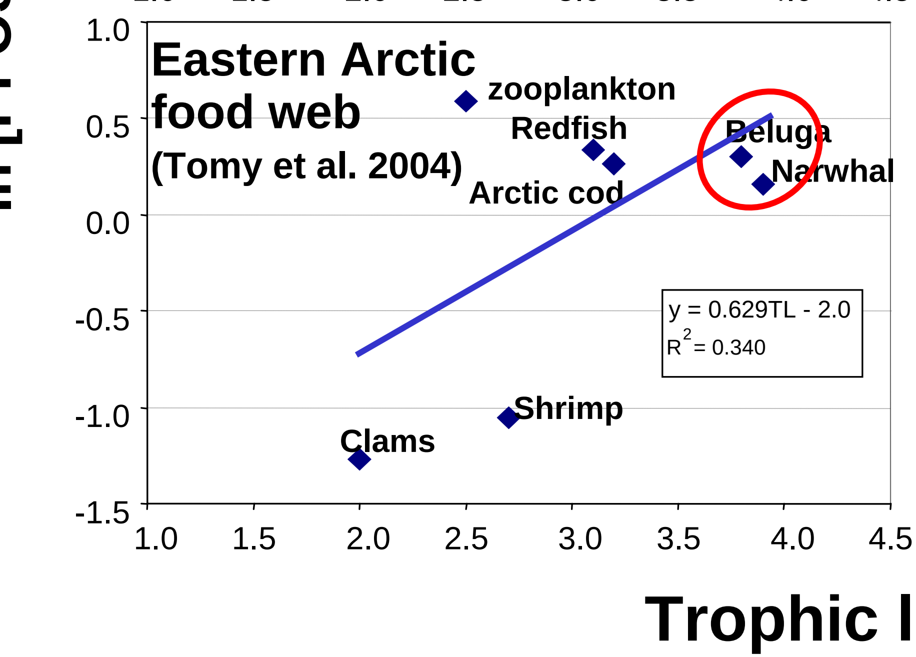
Northern Canadians have similar concentrations of PFOS and PFOA in maternal blood plasma as southern Canadians See also Posters ANA 036 and ANA 041



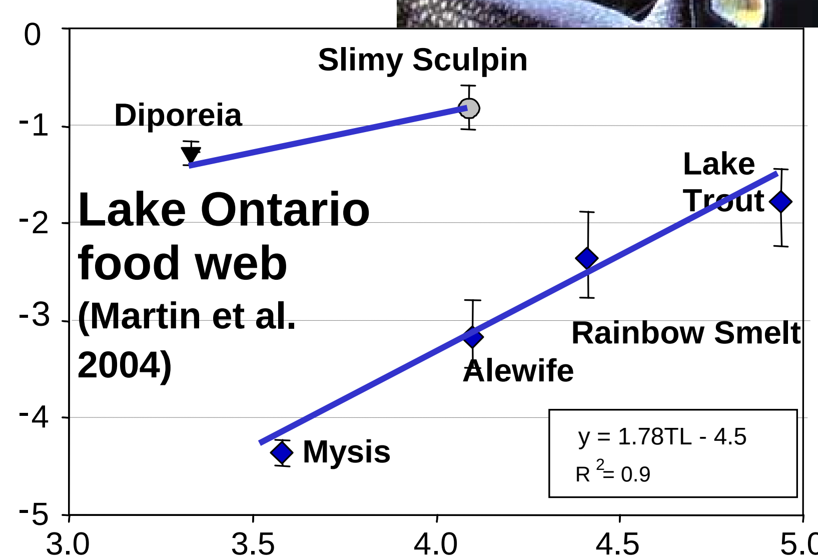
Tittlemeir and Ryan, Health Canada 2004

PFOS trophic magnification factors (TMFs)– using whole body concentrations in top predators (see also Poster ANA016)



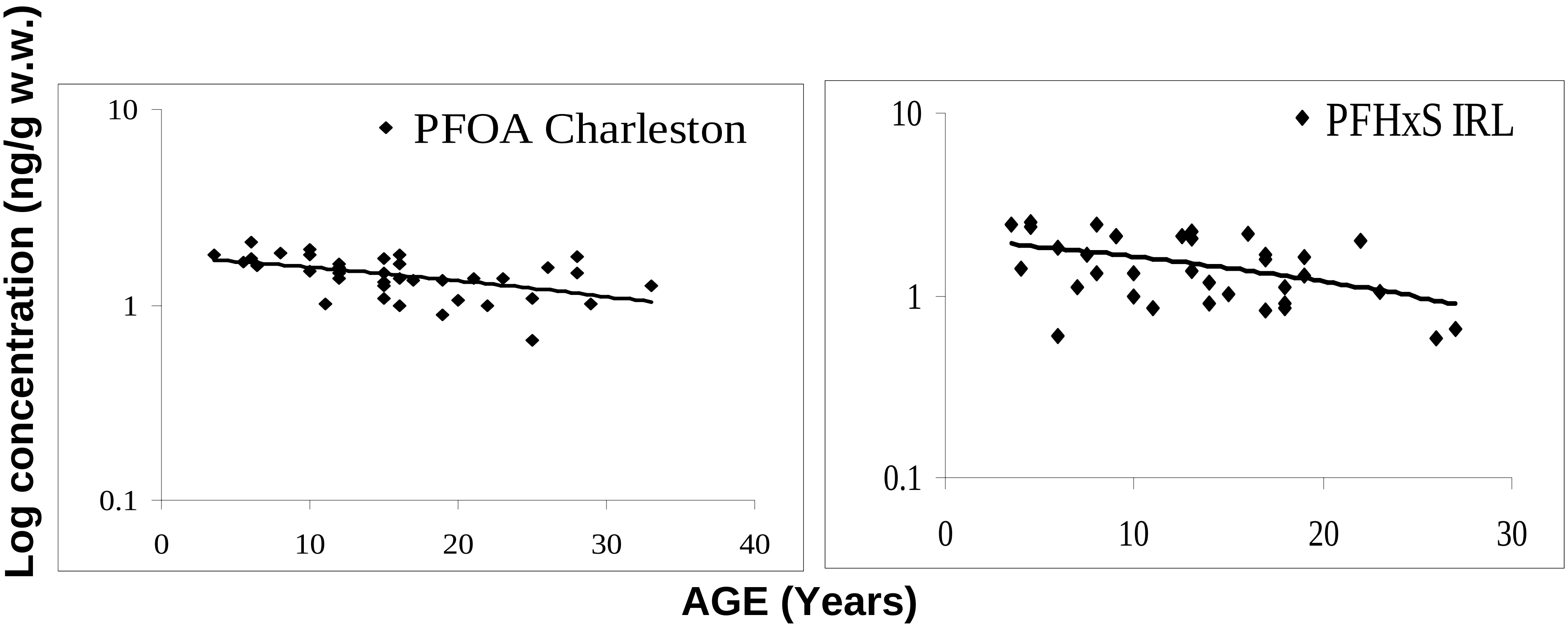


TMFs				
Study	**Food web**	**PFOS**	**PFOA**	**PFDA**
Martin et al	Pelagic - fish	5.9	0.6	3.7
Houde et al	Whole body	2.6	1.0	1.4
Tomy et al	Whole body	1.9	0.6	-
Tomy et al	With liver	3.1	1.2	-



PFAs vs age and gender in bottlenose dolphins (Houde et al. 2005; Poster ANA 14)

- No correlations between concentrations of PFAs in plasma and gender
- Significant <u>negative</u> correlations between AGE - PFOA and AGE - PFHxS



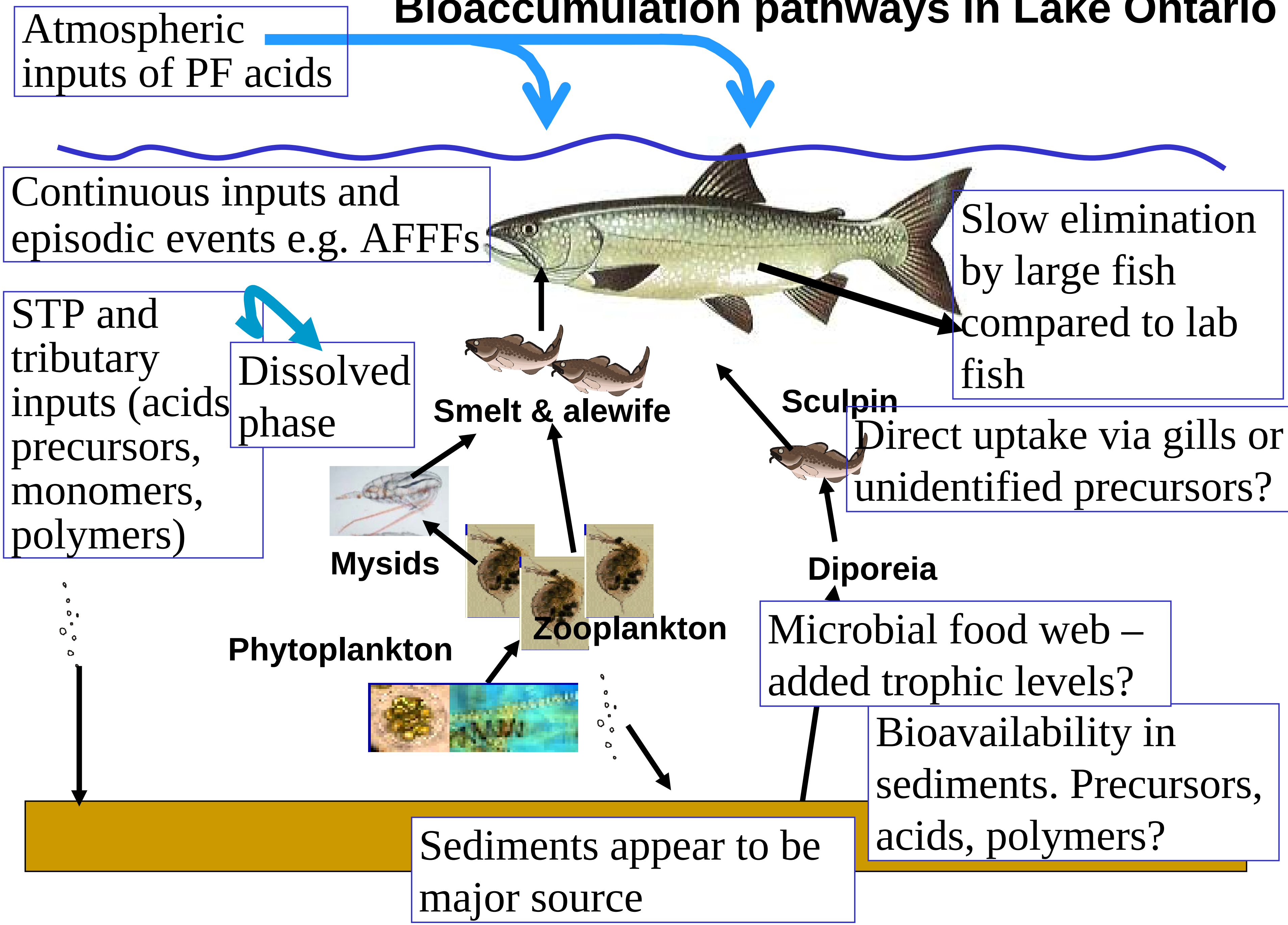
Bioaccumulation factors for PFAs in freshwater and marine fishes based on coinciding fish and water measurements

PFA	**Lake trout (Martin et al. 2004)**	**Various species (Taniyasu et al. 2003)**	**Various species of marine fish (Taniyasu et al. 2003)**	**Various species of marine fish (Kallenborn et al. 2004)**	**Lab BCF (Martin et al. 2003)**
	Lake Ontario	**Lake Biwa, Japan**	**Tokyo Bay, Osaka Bay and other urban centers**	**Iceland, Denmark, Swedish Baltic coast, Faroe Is**	**Based on Lake trout liver**
PFOS	34,000	67,000	8400	102,000	5,400
PFOA	208			180	8
PFNA	4,900			9,500	-
PFDA	>122,000				1100
PFUnA	>166,000				4900

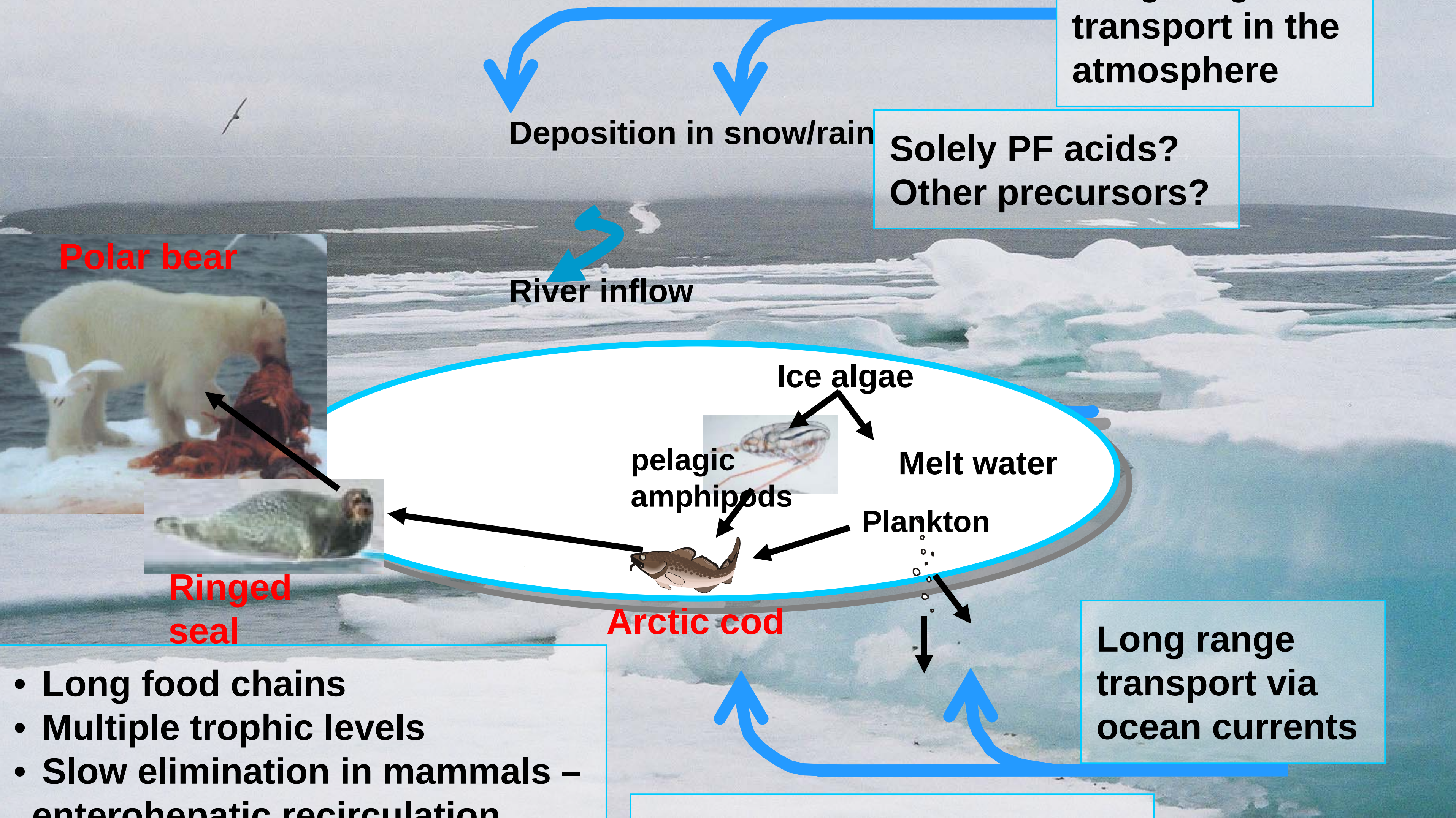
PFA biomagnification factors in freshwater and marine food webs

Predator	Prey	PFOS	N-EtFOSA	PFOA	PFNA	PFDA	Reference
P	**Lab BMFs >>>**	**0.32**	**-**	**0.038**	**-**	**0.23**	
Arctic Cod	Zooplankton	0.4	238	0.04			Tomy et al 2004
Smallmouth bass, R. gobies	Algae, Cray fish	10 to 20					Kannan et al 2005
Chinook salmon	Round Gobies	10 to 20					Kannan et al 2005
lake trout	alewife	3.7		0.6	5.3	4.4	Martin et al
lake trout	sculpin	0.4		0.02	0.1	0.2	Martin et al
lake trout (diet weighted)	prey	2.9		0.4	2.3	2.7	Martin et al
Mammals/birds - fish							
Dolphin (whole)	Pigfish	27		2.3	21	25	Houde et al. in prep
Beluga	Cod	8.4	0.004	2.7			Tomy et al. 2004
Mink	Chinook salmon	5 to 10					Kannan et al 2005

Bioaccumulation pathways in Lake Ontario



PFA bioaccumulation pathways in the Arctic marine food webs?



Long range transport in the atmosphere

Solely PF acids?
Other precursors?

Long range transport via ocean currents

- Long food chains
- Multiple trophic levels
- Slow elimination in mammals – enterohepatic recirculation

Sediment sources less important

Observations from the overview of biomonitoring results

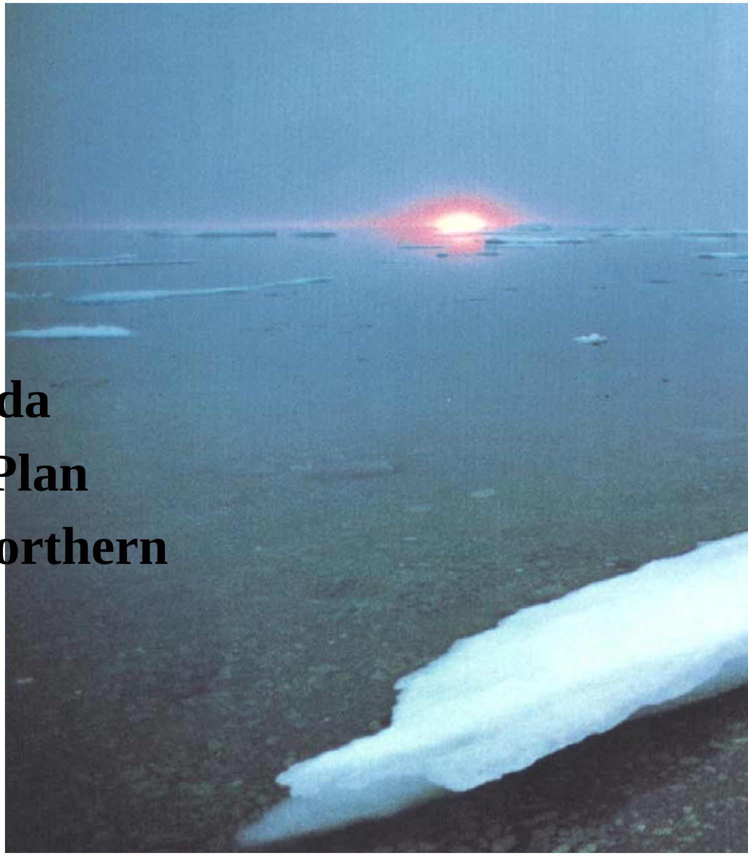
- PFOS is present at highest concentrations of all PFCs followed by PFOSA
- PFNA is generally the most prominent widely monitored PFCA
- Top predators have highest PFC concentrations e.g. polar bears – apex predator
- Fish eating mammals generally higher than fish eating birds
- Higher concentrations in fish, mammals and birds near urban areas e.g. CA, Tokyo, Baltic, North Sea, US SE coastal waters
- Filter/particle feeding invertebrates (Diporea, oysters) in near field sites have elevated amounts
- Humans have much different ratios of PFOS/PFOA than fish or wildlife

Conclusions

- Despite large dataset, global coverage of PFAs in biota is poor
- Plasma, liver and bird eggs all used effectively in biomonitoring and temporal trend studies
  - Limited whole body measurements for top predators
- General lack of correlation with age/sex in wildlife implies elimination via urine and feces is important and half-lives are relatively short in some biota
  - implies prevailing concentrations sustained by continuous inputs not legacy residues
- Lack of agreement between lab and field BAFs and BMFs for PFAs
  - implies multiple sources – precursors not monitored
  - organism size is important and difficult to mimic in the lab
  - unmonitored trophic levels e.g. microbial food webs could boost BMFs

Acknowledgements

- **New Substances Branch, Environment Canada**
- **Existing Substances Branch, Environment Canada**
- **Environment Canada Great Lakes 2020 Action Plan**
- **Northern Contaminants Program, Indian and Northern Affairs Canada**



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