AR226 - 3606

Environmental fate of Fluorotelomer Based Substances

Derek Muir
Aquatic Ecosystem Protection Research Division
Water Science and Technology Directorate
Science and Technology Branch
Environment Canada
Burlington ON

Environment Canada Environnement Canada

Outline

1) Conversion of 'fluorotelomer alcohols' to PFCAs

- Atmospheric degradation of "Residual FTOHs"
- Atmospheric measurements (air, precipitation)
- Biological degradation of FTOHs
- Biodegradation of fluorotelomer polymers?

2) Persistence and bioaccumulation of FTOHs and PFCAs

- Effect of chain length on bioaccumulation
- Bioaccumulation & magnification of PFCAs in food webs

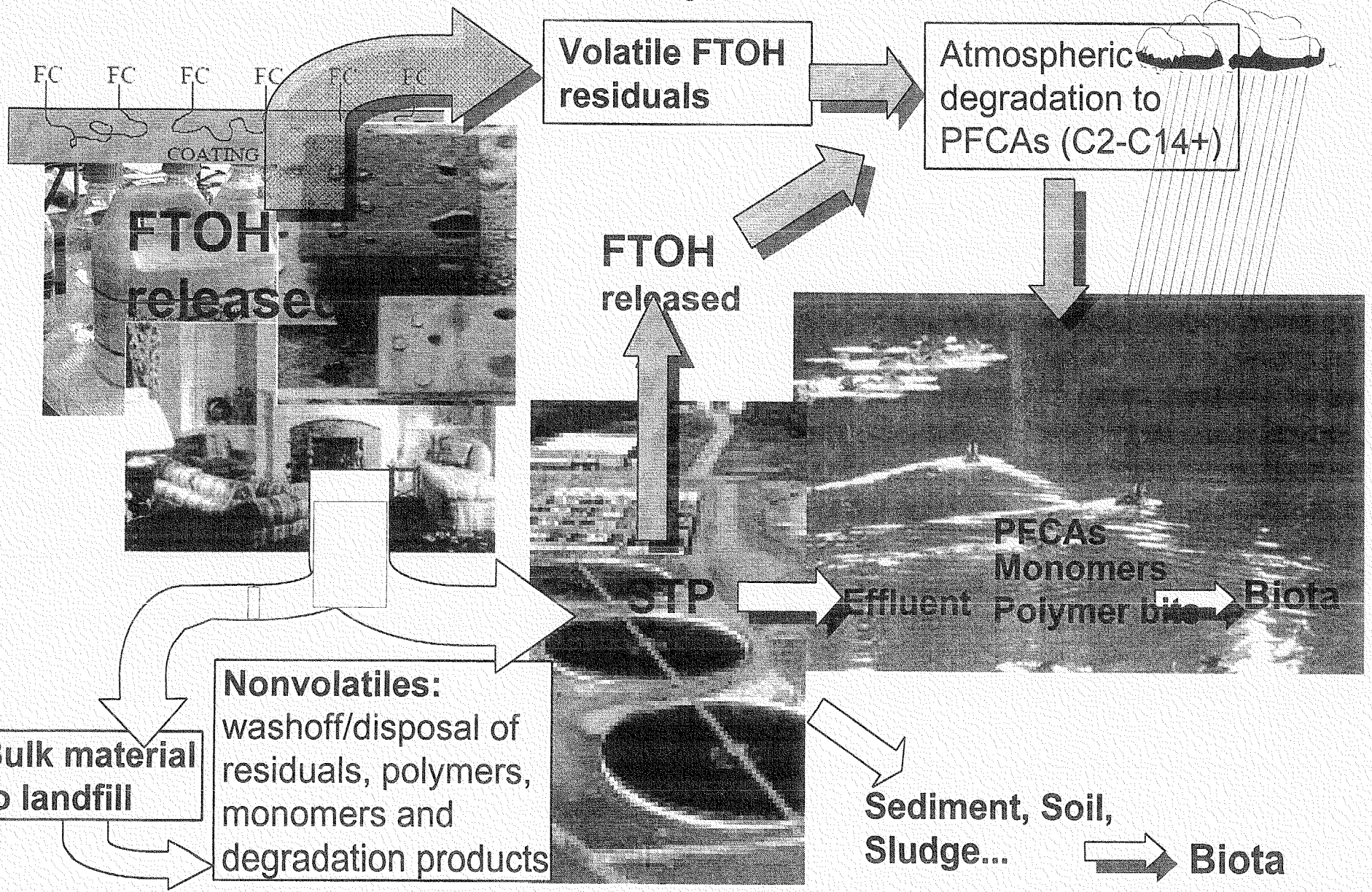
3) Toxicology and risk assessment of PFCAs

- mammalian; aquatic

4) Trends of PFCAs in the environment

- Geographical and temporal trends of PFCAs
- PFCA (C8-C15) chain length patterns
- Investigations of branched chain PFCA isomers

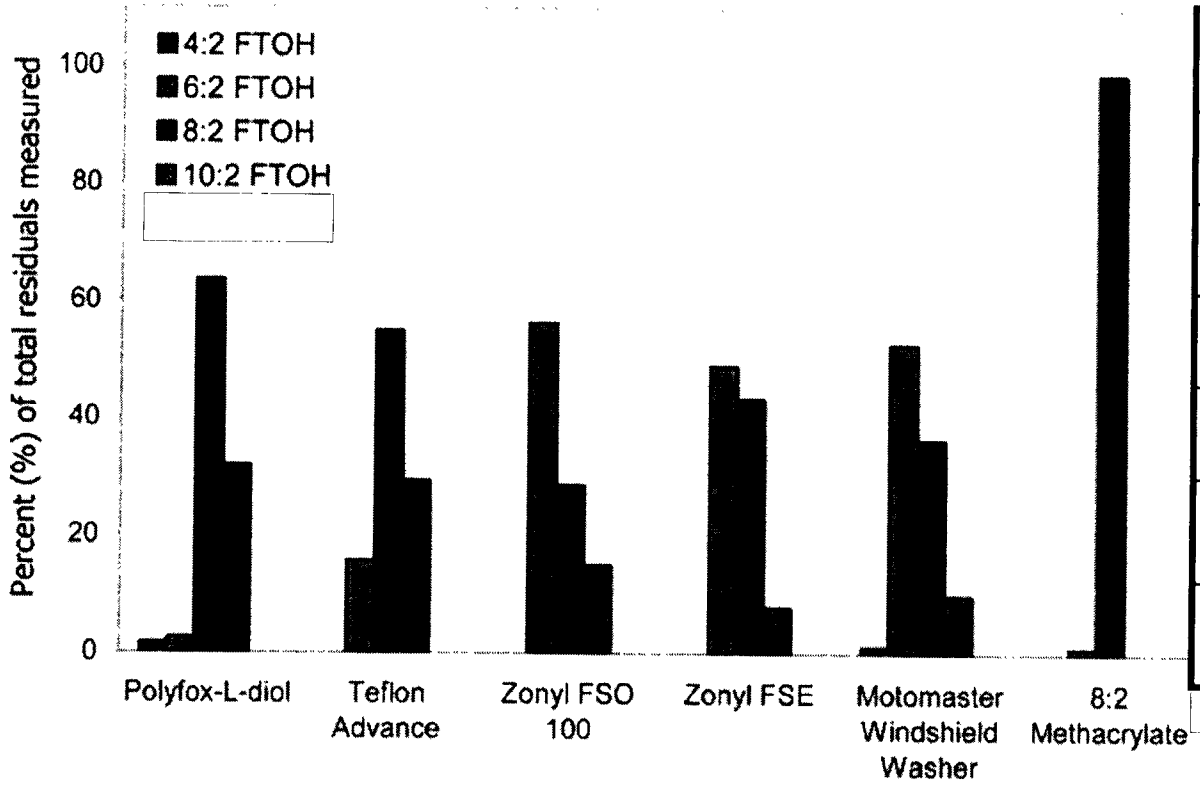
Overview of the Environmental fate pathways of the fluorotelomer polymers and residuals



1) Conversion of 'fluorotelomer alcohols (FTOHs)' to PFCAs

Profiles of residual unbound fluorotelomer alcohols (FTOHs) detected in 6 materials that include fluorotelomer based polymers or monomers (Dinglasan and Mabury ES&T In press)

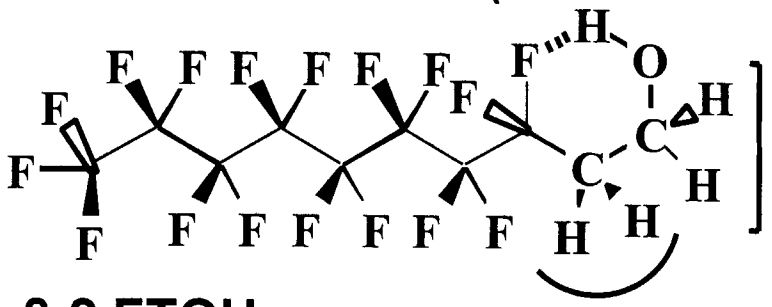
Values are expressed as percent of total residuals measured.



Fluorinated Material	% of dry weight
Polyfox-L-Diol	0.11 ± 0.03
Teflon™ Advance	0.34 ± 0.20
Zonyl™ FSO 100	1.03 ± 0.61
Zonyl™ FSE	**3.80 ± 1.09**
8:2 Methacrylate Monomer	**0.04 ± 0.01**
Motomaster™ Windshield Washer	0.36 ± 0.01

Atmospheric degradation of the FTOHs:

Reaction with OH radicals yields aldehydes and acids and can "unzip" the perfluorinated chain (Ellis et al. 2003; Hurley et al. 2004)



8:2 FTOH

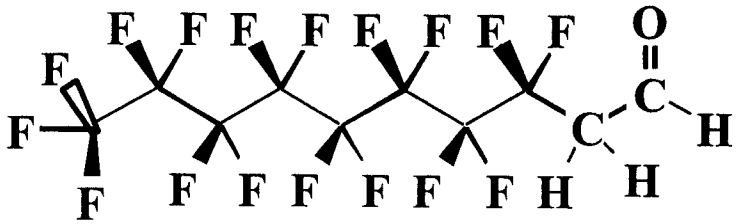
Atmospheric Lifetime = 20 d

>90% Attack on α hydrogens; H-Bond deactivates OH abstraction

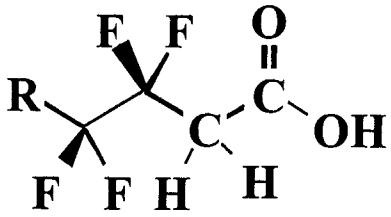
•OH

FT-Aldehyde

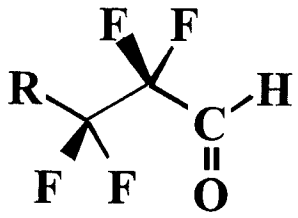
Lifetime = 20 d



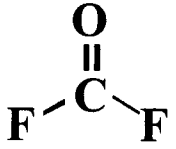
FT unsaturated acids



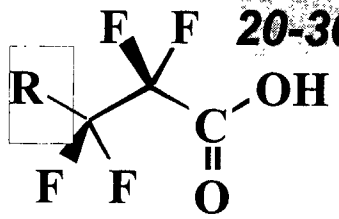
Perfluoro aldehyde



Carbonyl fluoride



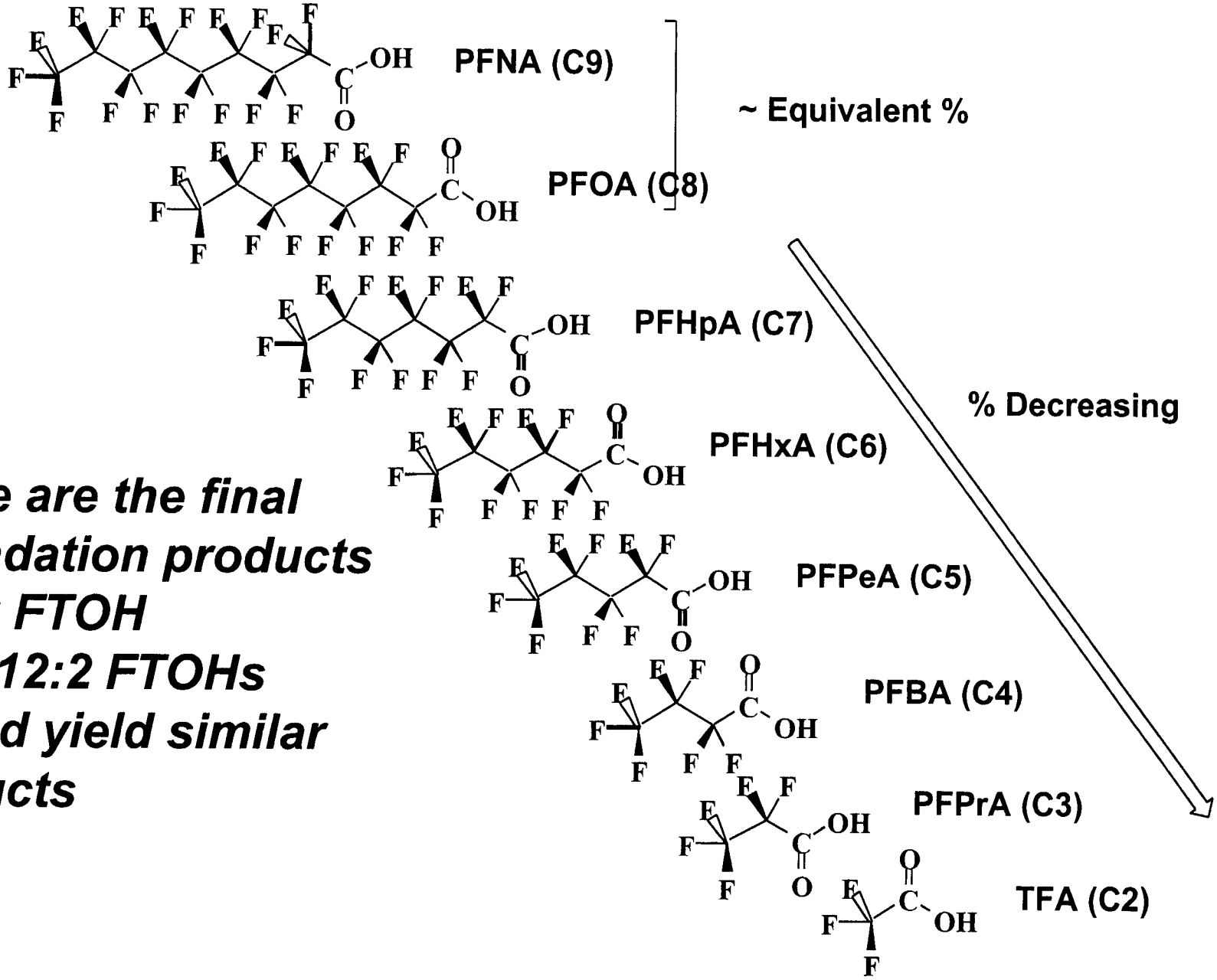
PFCAs



PFOA Atmospheric Lifetime = 20-30 d

10:2 and 12:2 FTOHs should yield similar products

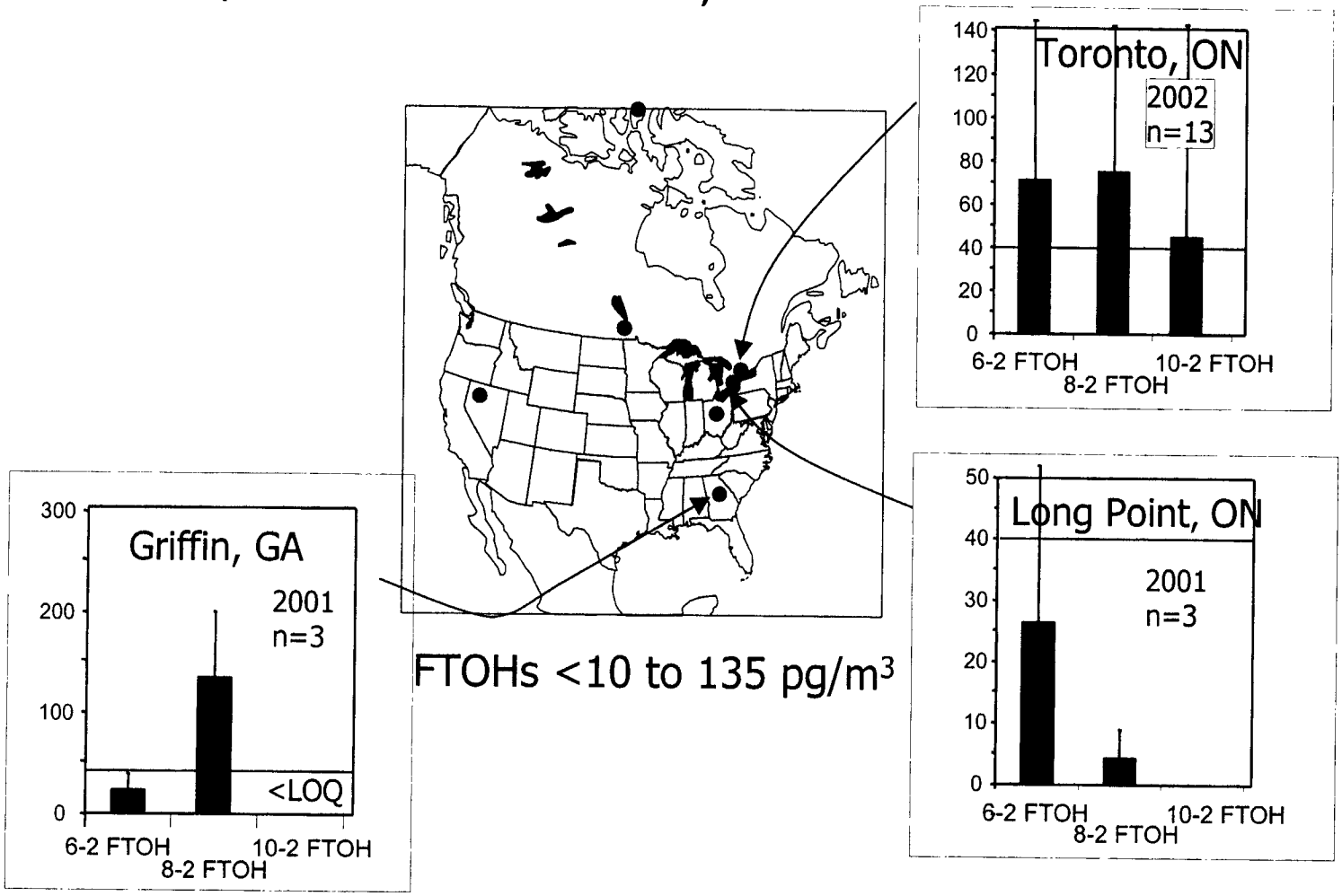
p.6



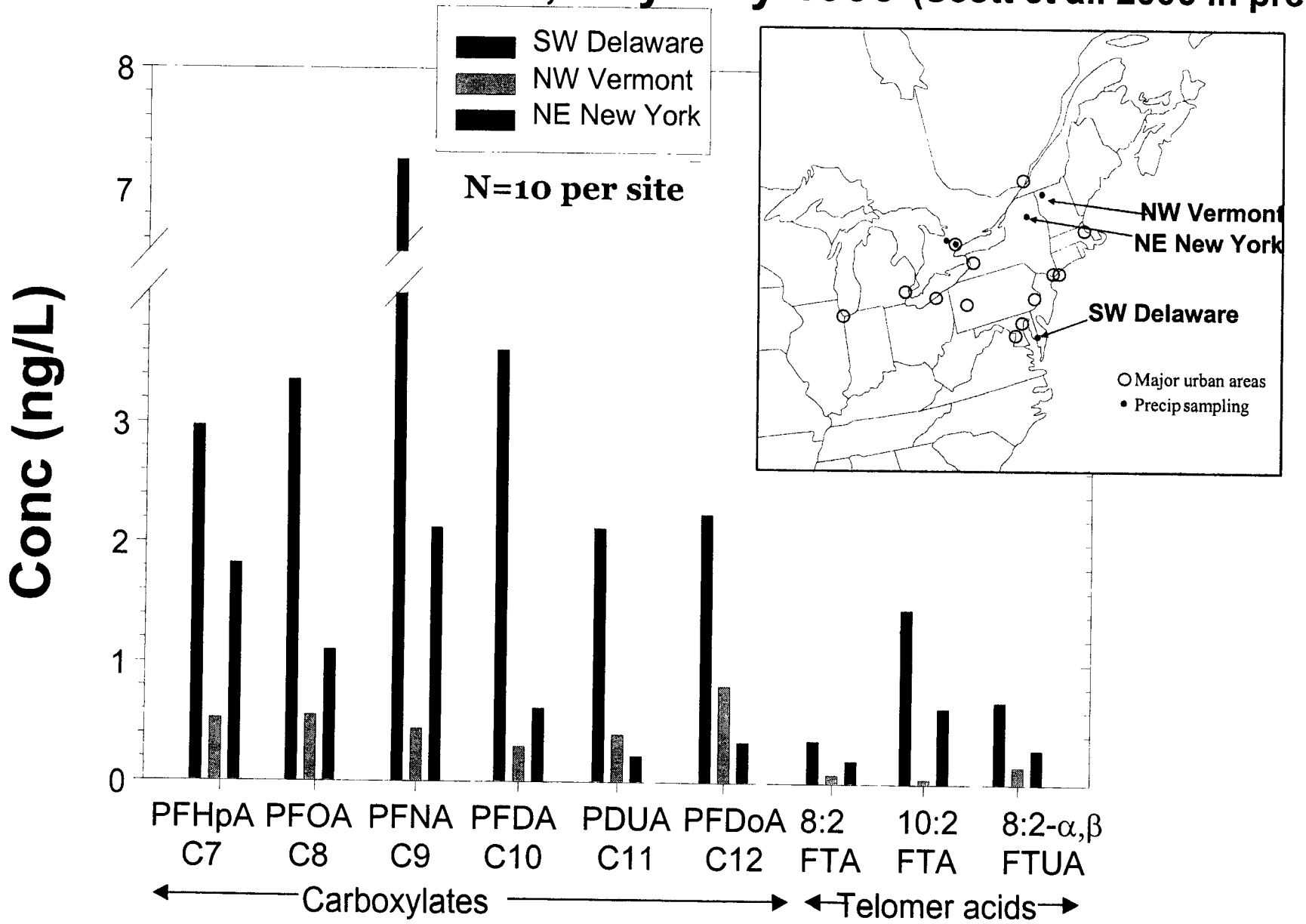
These are the final degradation products of 8:2 FTOH
10:2, 12:2 FTOHs should yield similar products

Atmospheric concentrations of FTOHs
(Stock et al. 2004; Stock 2006 unpublished)

Implies emissions of 100-1000 tonnes/yr of FTOHs - which in reasonable agreement with estimated FTOH residuals in FTpolymers (Prevedouros et al 2006)

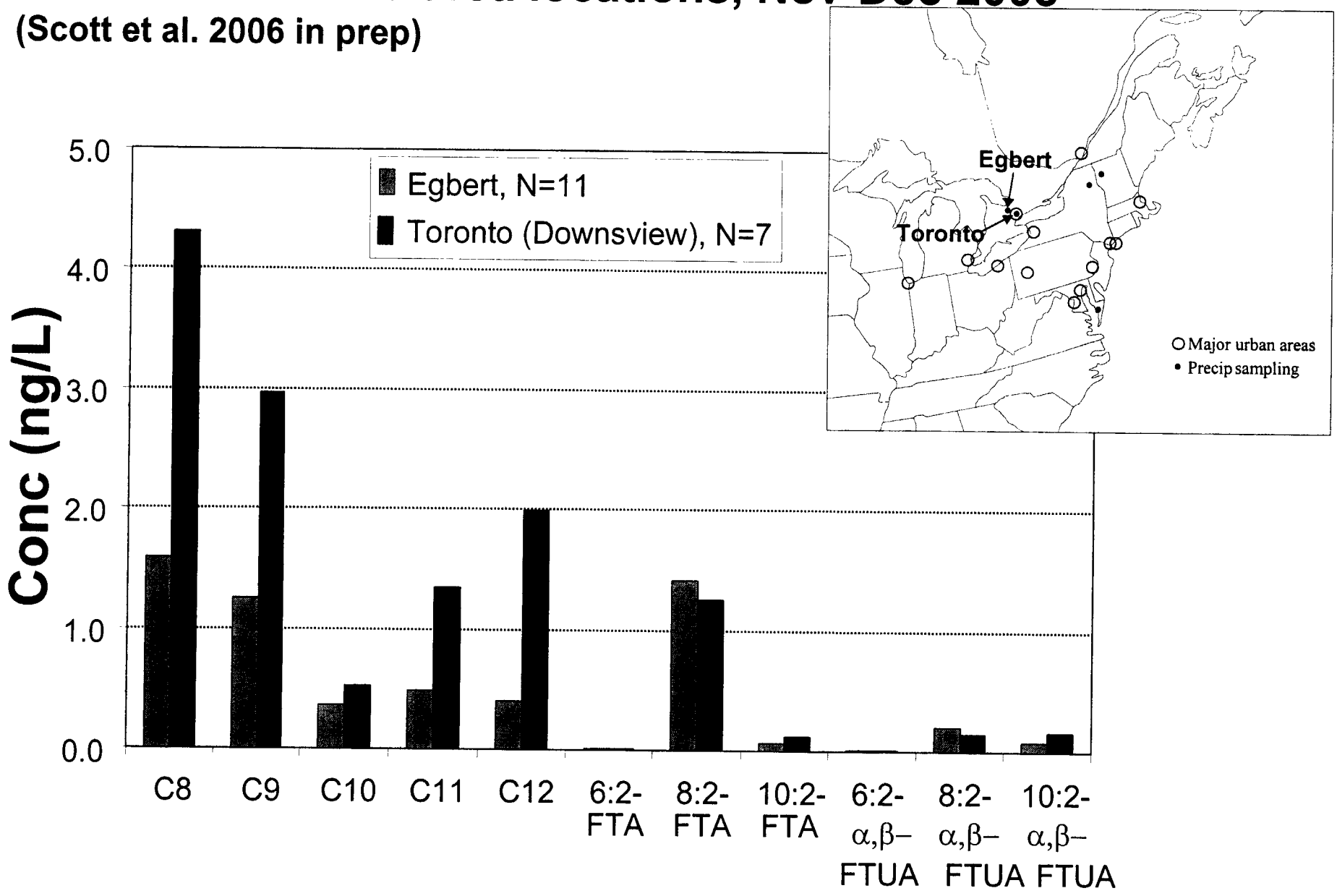


Evidence of PFCAs & Fluorotelomer Acids in Rainwater from Three Locations, May-July 1999 (Scott et al. 2006 in prep)



PFCAs & Fluorotelomer Acids in Rainwater from Two Toronto area locations, Nov-Dec 2003

(Scott et al. 2006 in prep)



Global modelling of the degradation and transport of FTOHs
(Wallington et al. ES&T 2006)

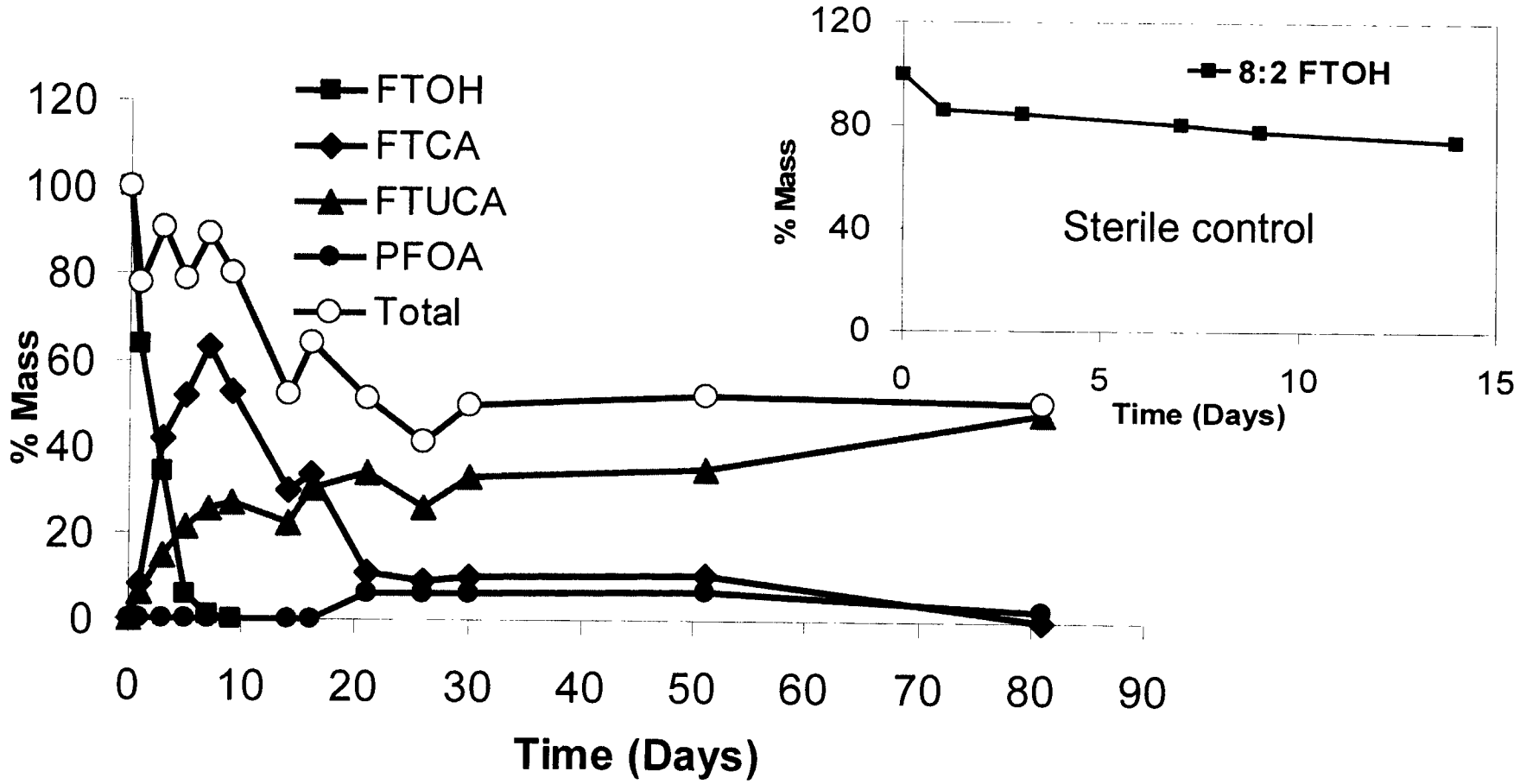
Summed concentration of 8:2 FTOH and all of its degradation products at 50 m in altitude for (a) January and (b) July.

Concentration of PFOA (in molecule cm^{-3}) at 50 m in altitude for (a) January and (b) July.

Graphics copied directly from Wallington et al. omitted to make the file smaller. Please see the original paper Figures 2-5.

Biodegradation of 8:2-FTOH by a mixed microbial system

Dinglasan et al ES&T 2004

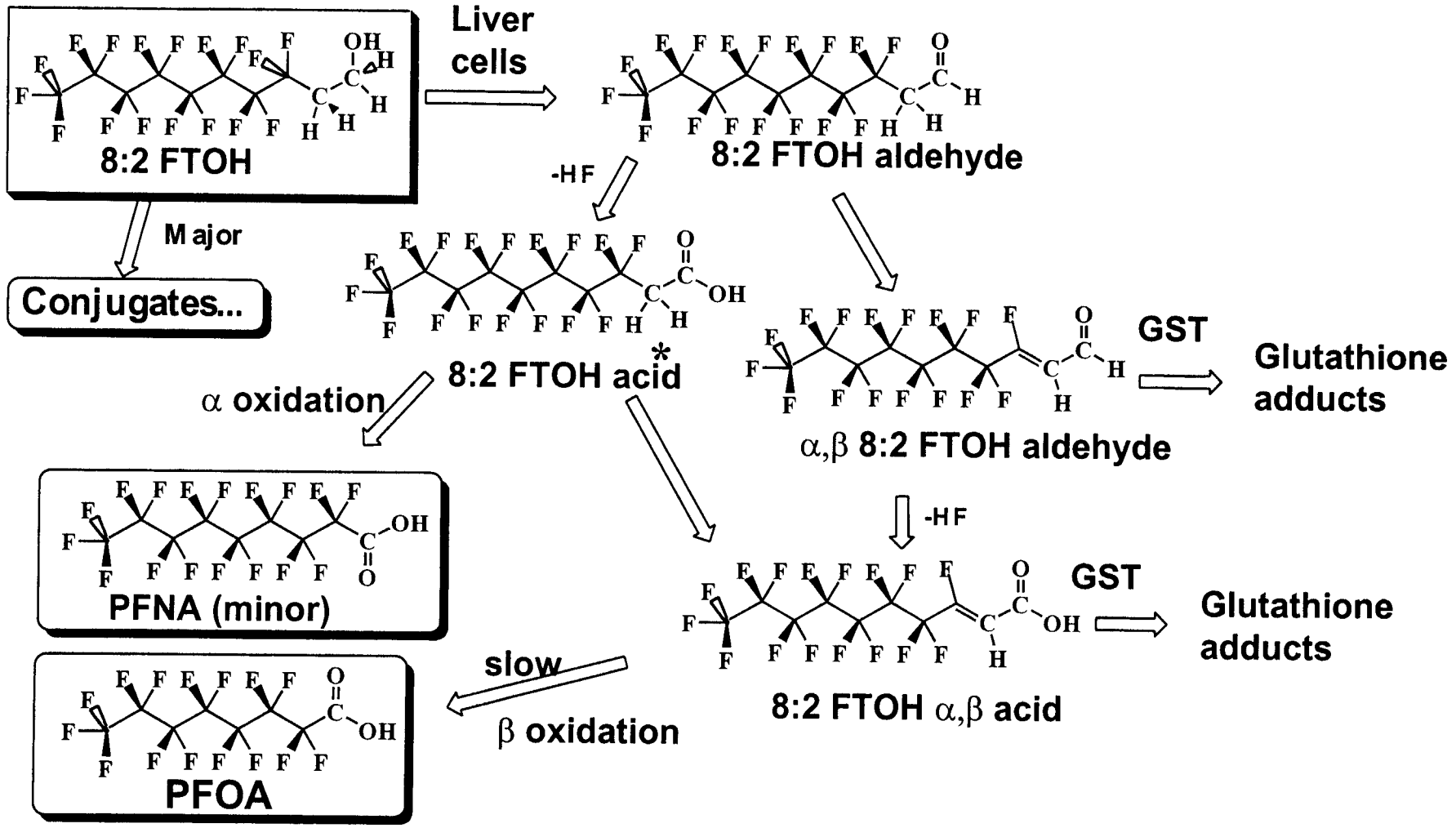


Degradation of 8:2 FTOH (Days 1-81). Fluorotelomer unsaturated acid (FTUCA) is major product.

Wang et al ES&T 2005 a,b have also shown biodegradation of 8:2FTOH using 14C-labelled chemical – which allowed more products to be identified

Rat Liver Metabolism Pathway of 8:2 FTOH yields PFOA and adducts of FT unsaturated aldehydes and acids

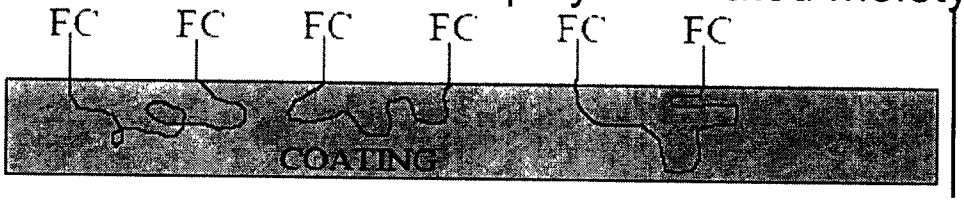
(Martin et al 2005)



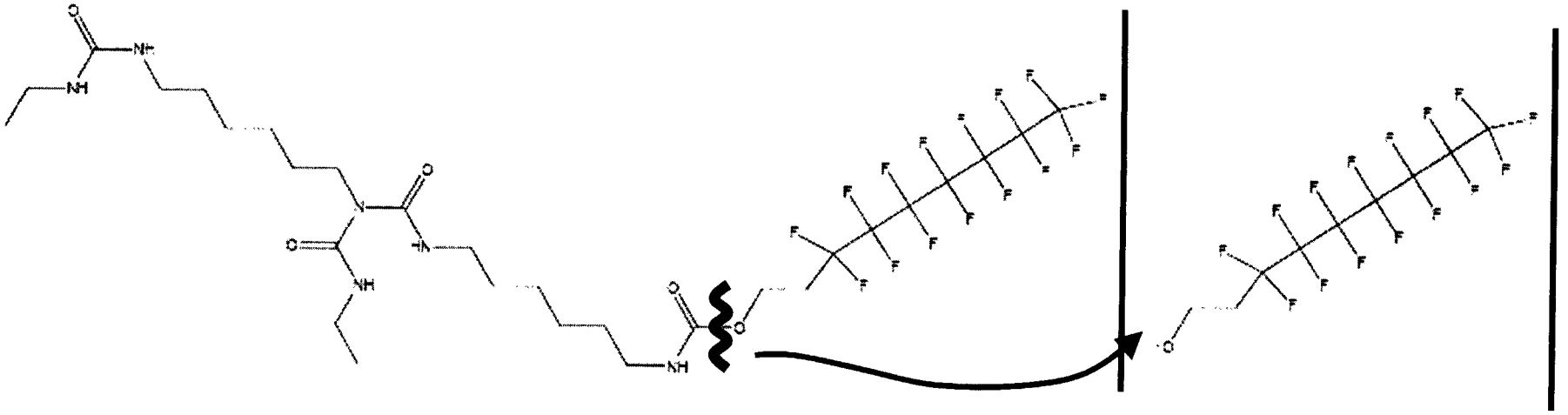
Note: important that PFNA (C9) is, at most, a minor component. indicating that oxidation at the α-carbon is slow

Do fluorotelomer based polymers degrade?

- surface exposure of the polyfluoro chain which gives stain/water repellency is expected to encourage the degradation and release of the polyfluorinated moiety.



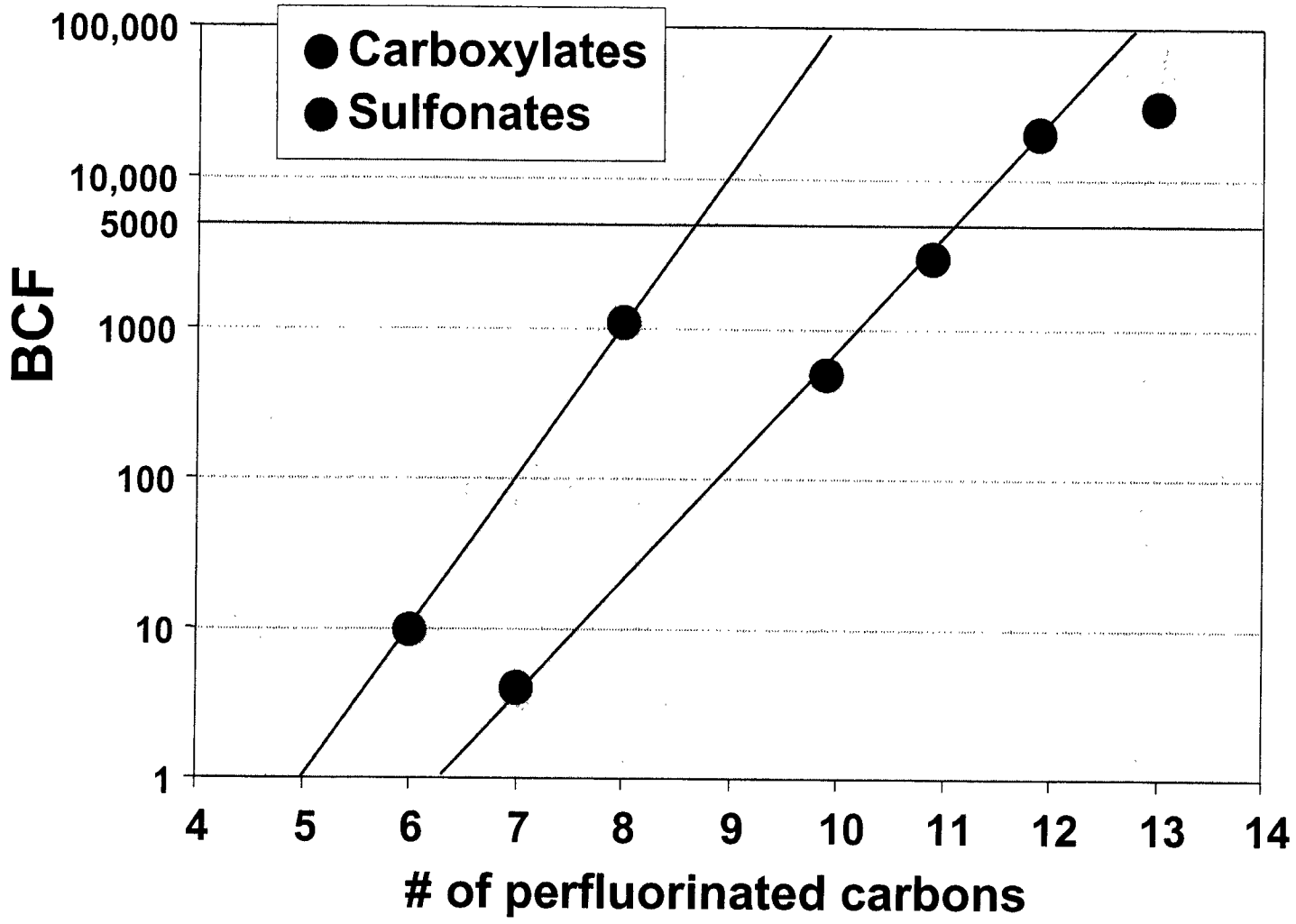
- Degradation of a fluorotelomer based polymer at the urethane linkage was observed in an *in vitro* study using cholesterol esterase (Jahangir et al. 2003)



- Degradation of the fluorotelomer based polymer above is predicted to occur at the urethane linkage by various QSAR models e.g. CATABOL, yielding an FTOH

Persistence and bioaccumulation of FTOHs and PFCAs

Bioconcentration factors (BCF) for PFCAs in juvenile rainbow trout increase with Chain Length

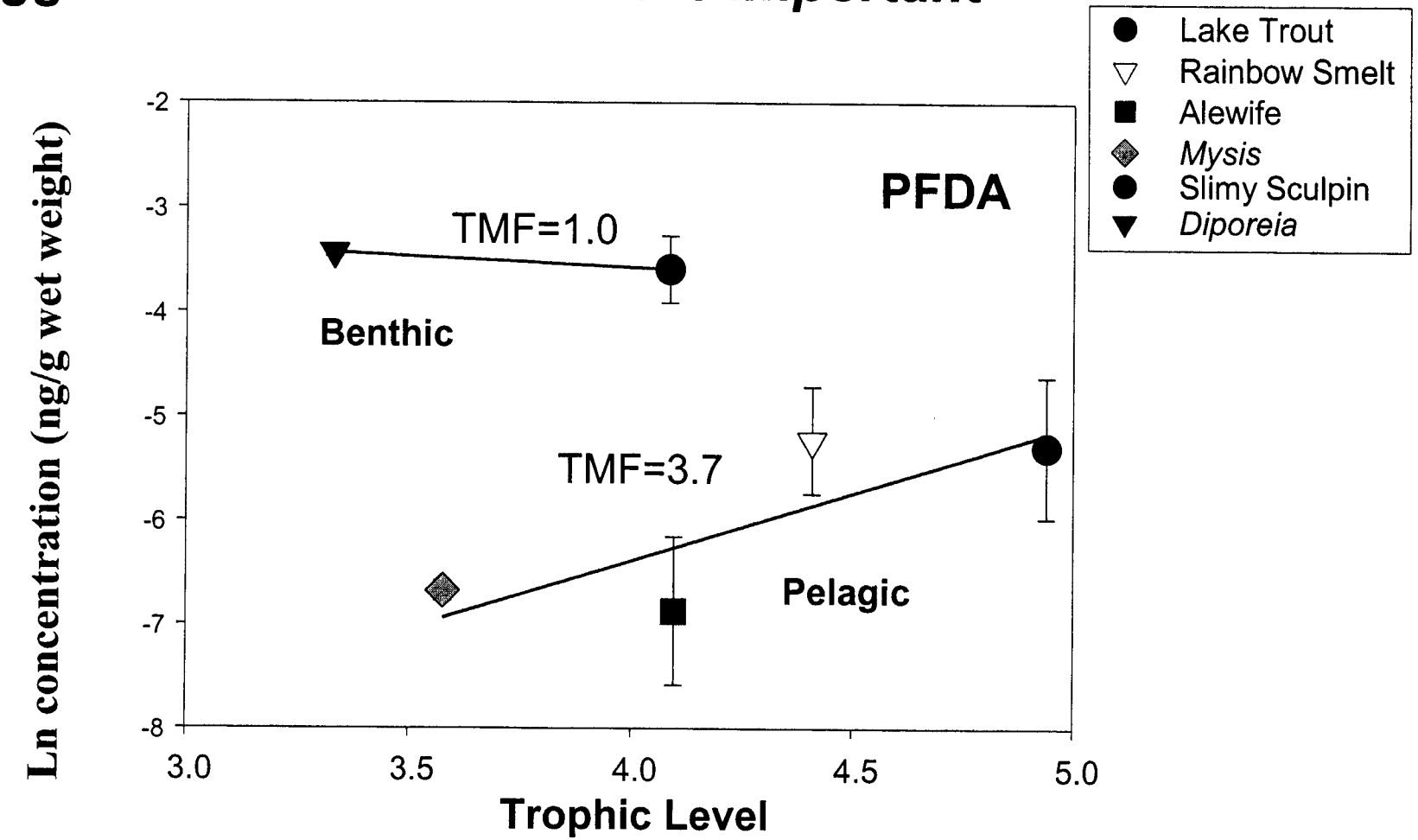


Additional CF_2 results in a **~7x** increase in the BCF.

even:odd pattern ~ expect PFNA higher than PFOA; PFUnA > PFDA, etc IF delivered in similar quantities.

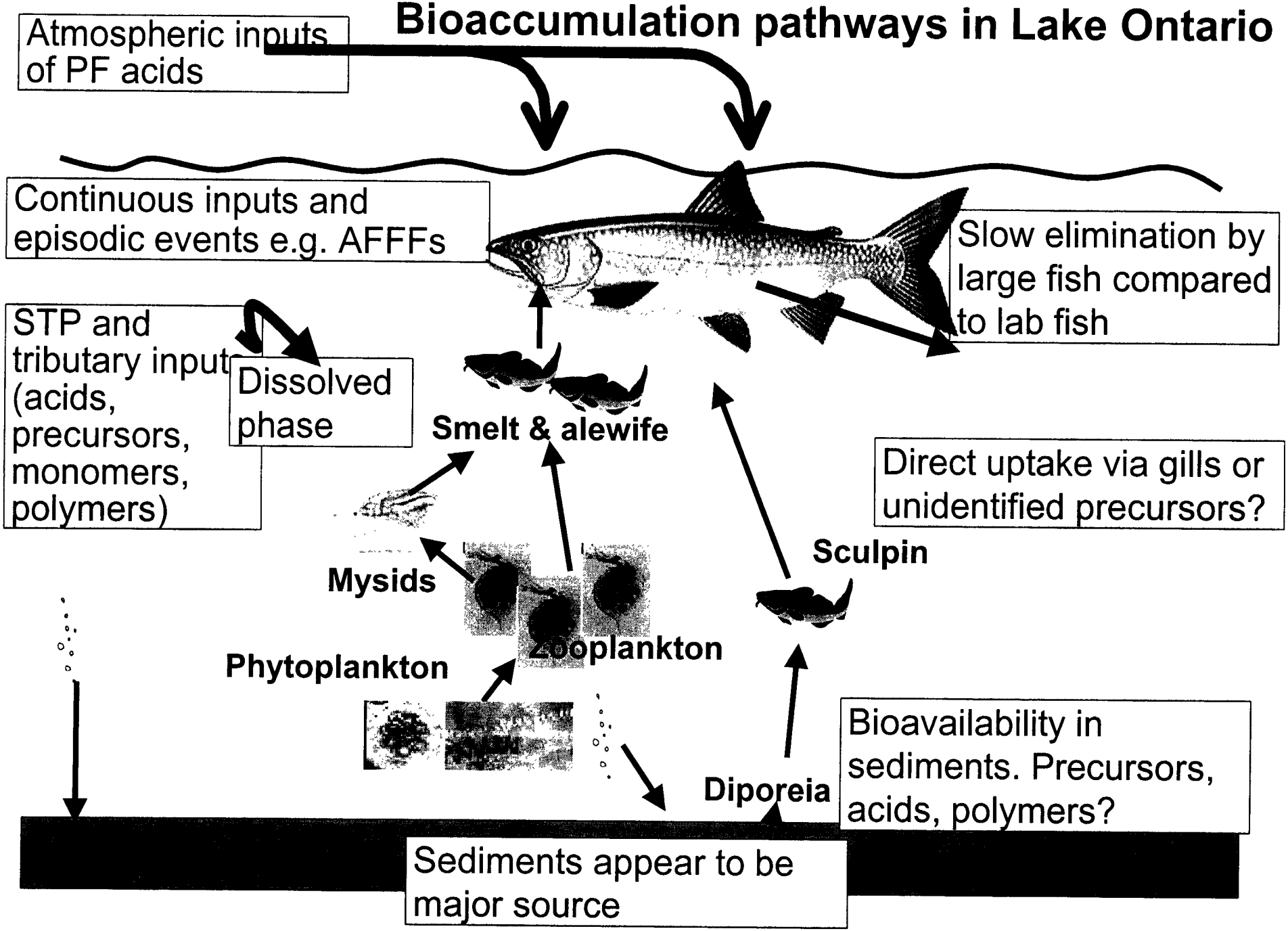
Bioaccumulation of PFCAs in the Lake Ontario Food Web

...suggests benthic sources are important



Martin, JW, DM Whittle, DCG Muir and SA Mabury. 2004. Perfluoroalkyl Contaminants in a Food Web From Lake Ontario. *Environ. Sci. Technol.* **38**:5379-5385.

Bioaccumulation pathways in Lake Ontario



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

PFA	Lake trout (Martin et al. 2004) + water (Furdui et al)	Lake trout (Furdui et al. 2006)	Various species (Houde et al. 2006)	Various species of marine fish (Kallenborn et al. 2004)	Lab BCF (Martin et al. 2003)
	Lake Ontario	4 Great Lakes (C8-C10) & Lake Ont (C11-C12)	Charleston SC harbor	Iceland, Denmark, Swedish Baltic coast, Faroe Is	Based on Lake trout carcass
PFOA	270	1260 ± 160	95	180	4
PFNA	4,530	3980 ± 330	560	9,500	-
PFDA	13,780	7940 ± 610	1,500	-	450
PFUnA	55,300	10,900	2,200	-	2,700
PFDoA	8,680	1,560	>7,700	-	18,000

PFCA biomagnification factors in freshwater and marine food webs

Predator	Prey	PFOA	PFNA	PFDA	PFUnA	PFDoA	Reference
Lab BMFs >>>		**0.038**	**-**	**0.23**	**0.28**	**0.43**	
fish/invertebrates							
Arctic Cod	Zooplankton	0.04	-	-	-	-	Tomy et al 2004
sculpin	Diporeia	0.5	0.6	0.9	1.0	1.0	Martin et al 2004
Sea trout	pinfish	7.2	1.5	3.7	0.9	0.1	Houde et al. 2006
lake trout	alewife	0.6	5.3	4.4	6.4	1.9	Martin et al 2004
lake trout (diet weighted)	prey	0.4	2.3	2.7	3.4	1.6	Martin et al 2004
Mammals - fish							
Dolphin (whole)	Pinfish	13	3.2	8.8	2.4	0.1	Houde et al. 2006
Dolphin (whole)	seatrout	1.8	2.1	2.4	2.5	0.6	Houde et al. 2006
Beluga (liver)	Cod	2.7	-	-	-	-	Tomy et al. 2004
Polar bear (liver)	Ringed seal (liver)	7.9	14	4.5	2.6	0.8	Martin et al. 2004

Toxicology and Human risk assessment

- Health Canada's hazard evaluation based on the hypothesis of ultimate breakdown of the notified substances and residual materials.
- These breakdown products will ultimately be PFCAs of various chain lengths - primarily 8 carbons and greater.
- Most toxicological studies on laboratory animals have been on PFOA (C8)

PFOA and its salts;

- produce moderate to high oral toxicity in rodents and monkeys
- mortality at very low doses in monkeys (20/30 mg kg^{-1} d^{-1}); very narrow range between appearance of toxicity and death
- cause tumours in rats and immunotoxic effects in mice;
- display reproductive/developmental effects in rodents
- Science Advisory Board to the US EPA recommends 'likely human carcinogen' classification

Longer chain PFCAs;

- PFCAs (>C8) are reasonably expected to be of greater concern than PFOA as a result of their known slower clearance rates and higher bioaccumulation potential

Exposure

- evidence is equivocal on whether PFOA levels in humans are rising, not enough data yet
- Many perfluoro compounds are being detected in human blood in Canada and other countries
- found in foodstuffs including beans, apples; household dust particles (in Canada),
- Biomonitoring data for Canada indicate PFCAs found in breast milk, blood, fetal cord blood

Uncertainties

Areas of uncertainty for human risk assessment of PFCAs include;

- large elimination/excretion differences between species
- for example, remarkable differences in clearance rates of PFOA
- Rodent half- life - hours (sex-related differences too)
- Monkey half- life - days
- Human half- life - years

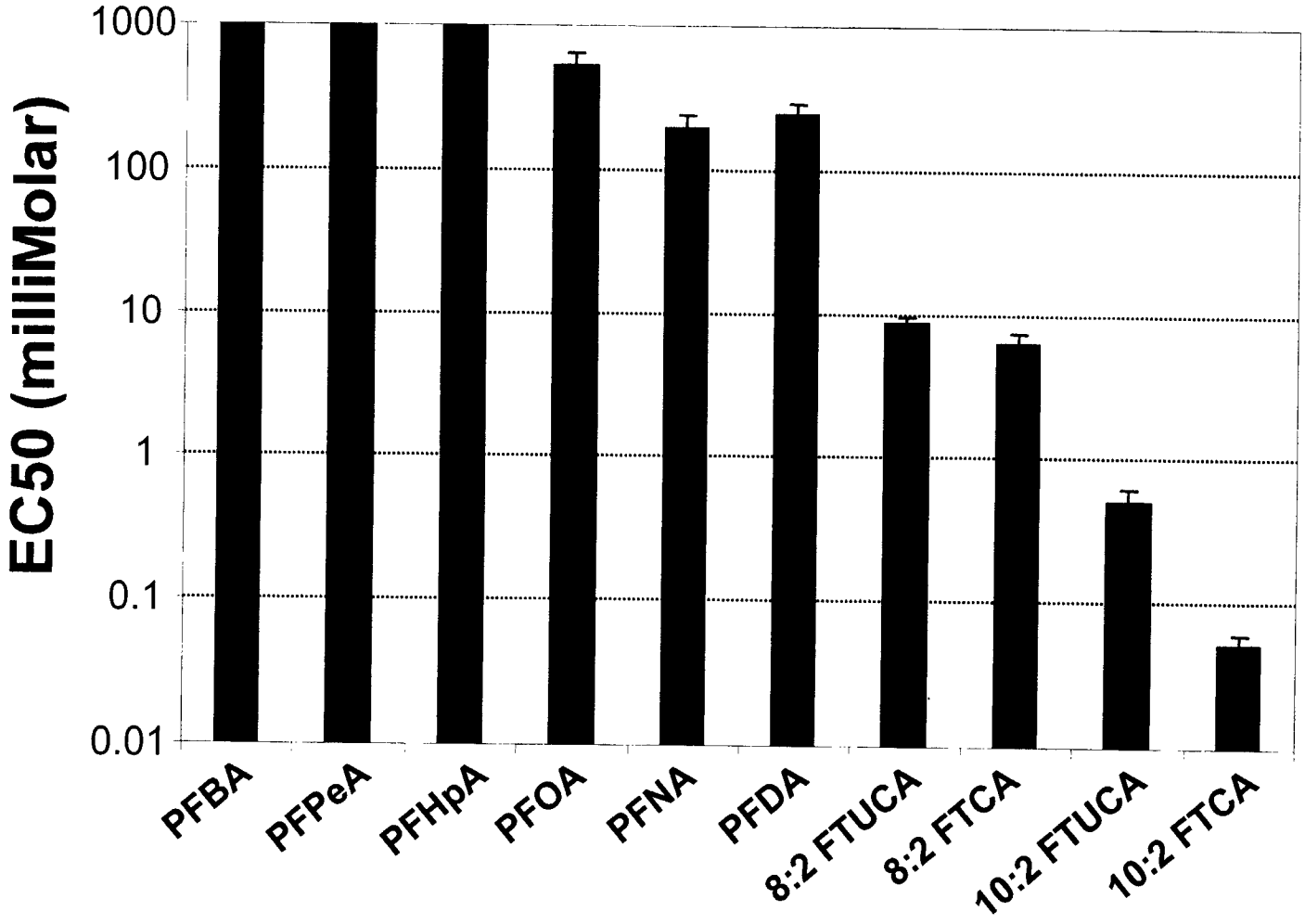
Data gaps

- trends of human body burdens?
- mechanism of action of PFOA and other PFCAs
- Understanding the laboratory species differences and relevance to humans
- Effects on susceptible groups (fetus, infants and elderly)

Acute toxicity of PFCAs to the water flea, *Daphnia magna*

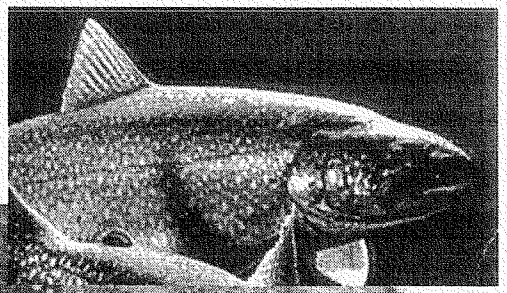
(Macdonald et al. 2006; Boudreau et al. 2004)

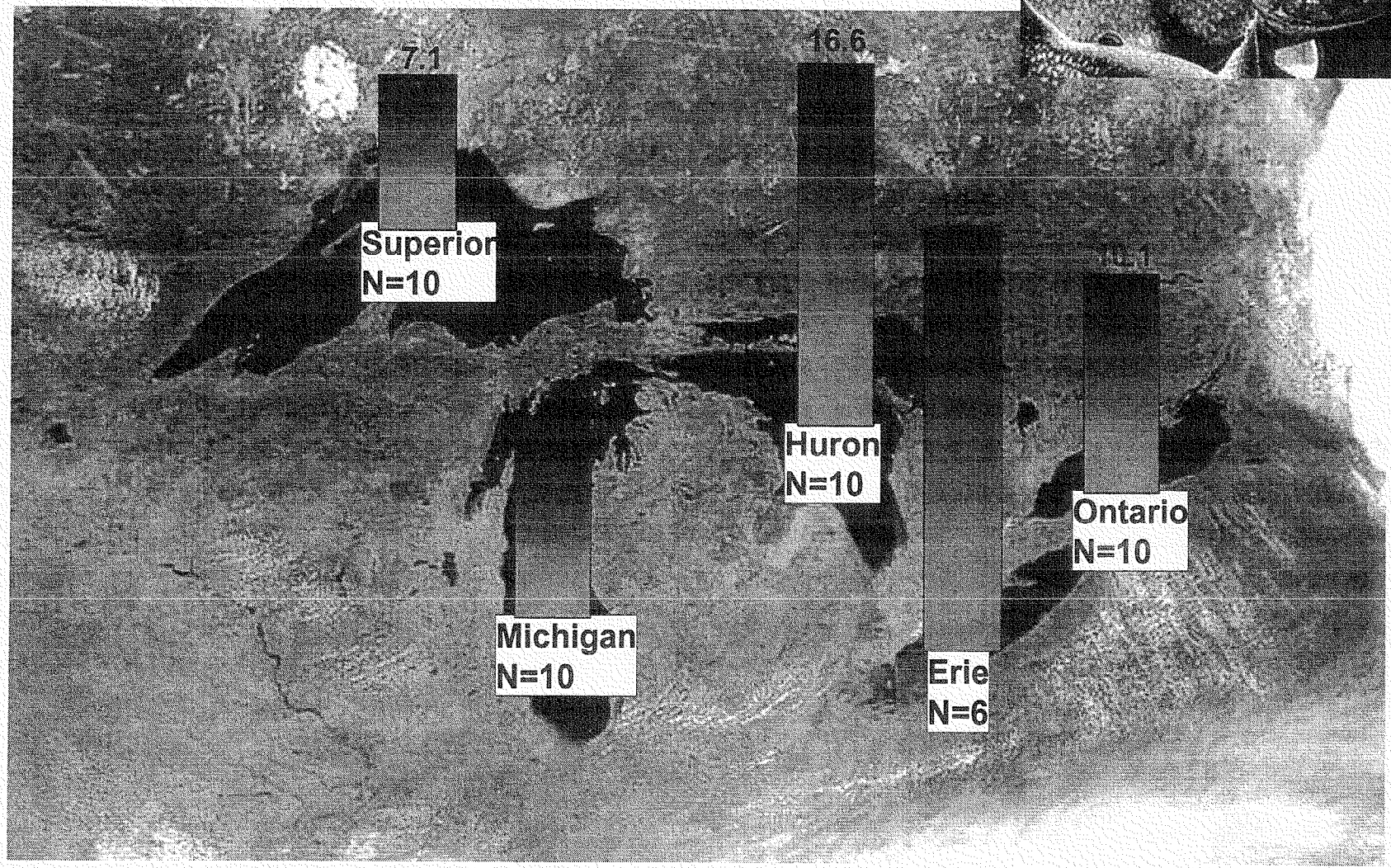
10:2 FTCA is ~10,000x more toxic to *D. Magna* than PFDA. **Environmental risk Quotients** for 10:2 FTCA >100 assuming water concentration <1 ng/L



4. Trends of PFCAs in the environment:

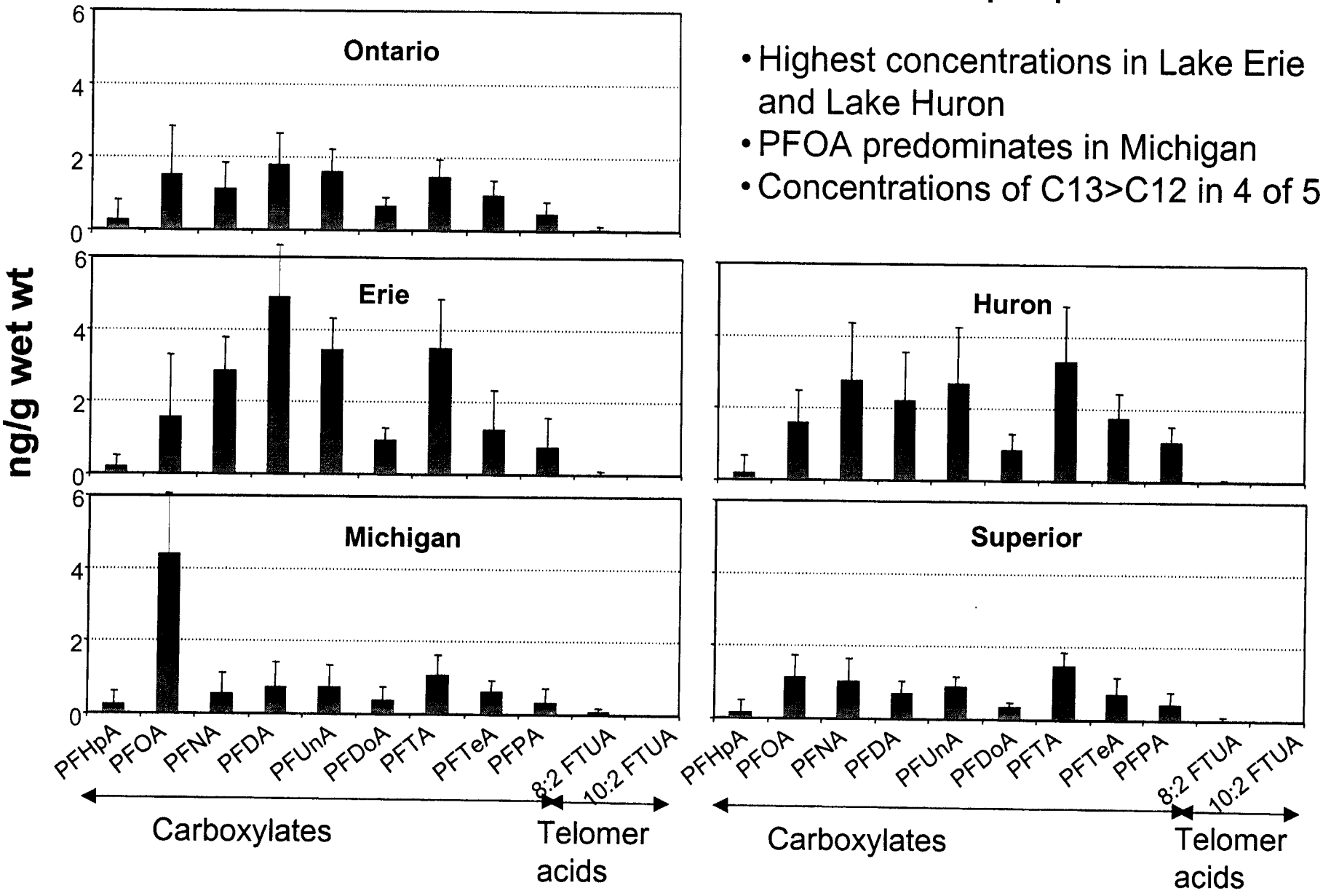
Total PFCAs (ng/g wet wt) in Great Lakes lake trout (whole fish; age = 4 yrs)
Furdui et al. 2006 in prep





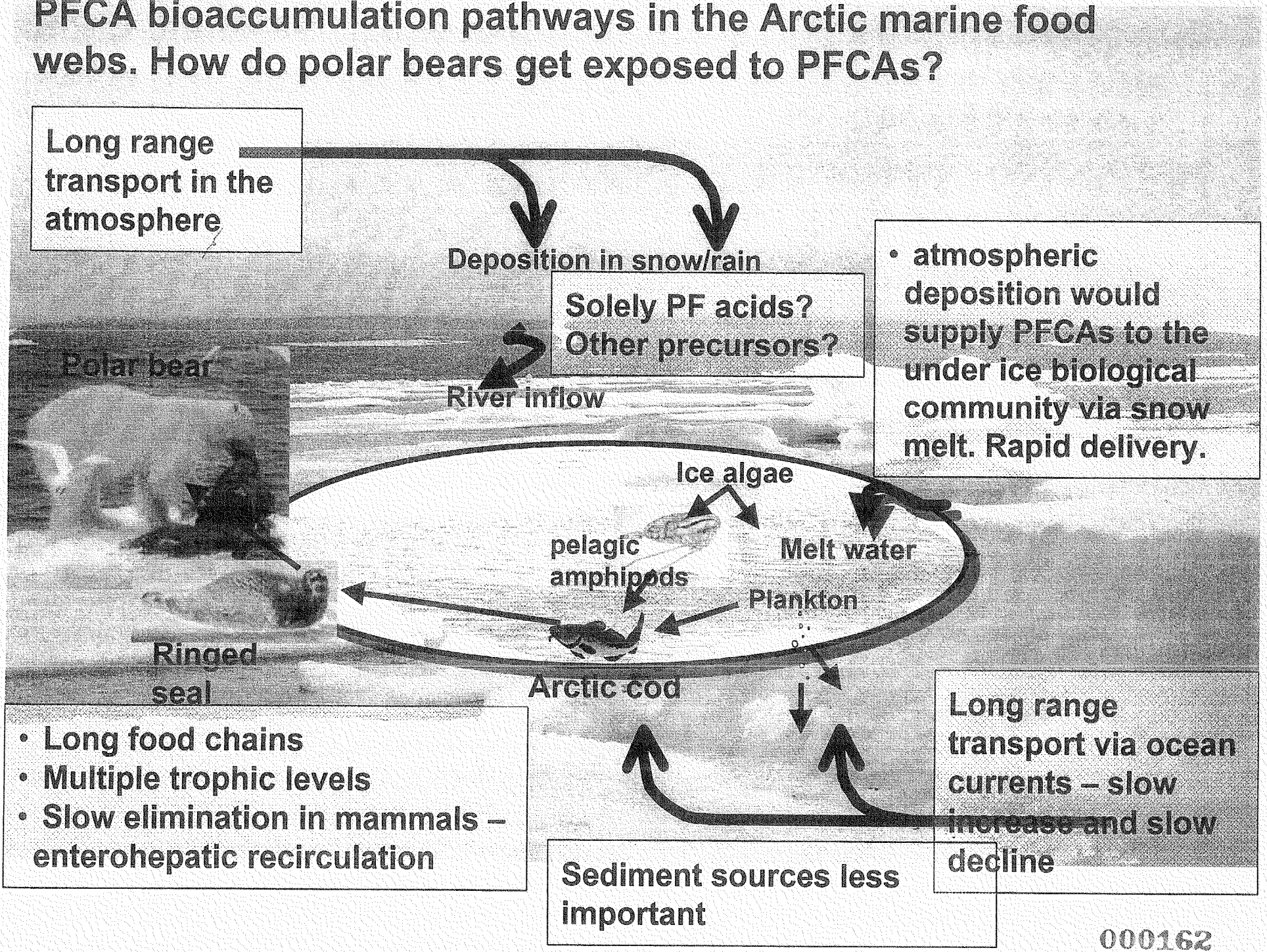
Individual PFCAs (ng/g wet wt) in Great Lakes lake trout

(whole fish; age = 4 yrs); Furdui et al. 2006 in prep

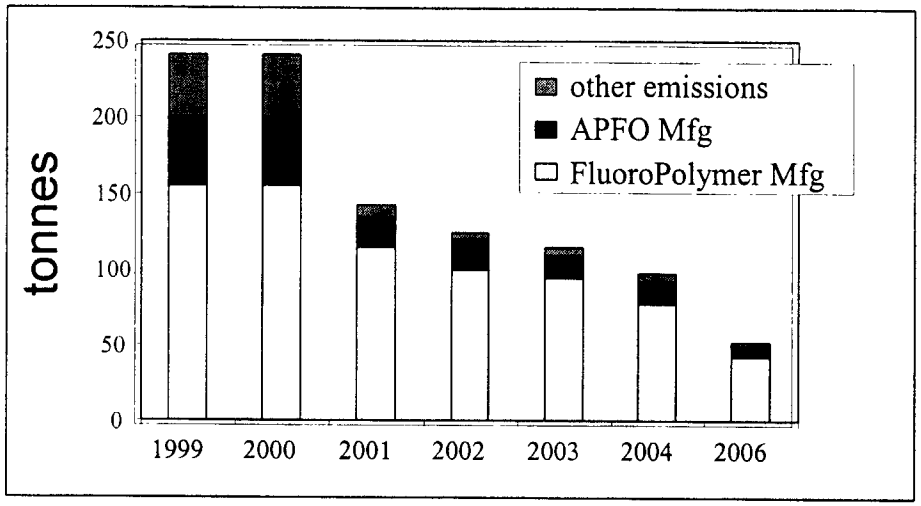


- Highest concentrations in Lake Erie and Lake Huron
- PFOA predominates in Michigan
- Concentrations of C13>C12 in 4 of 5

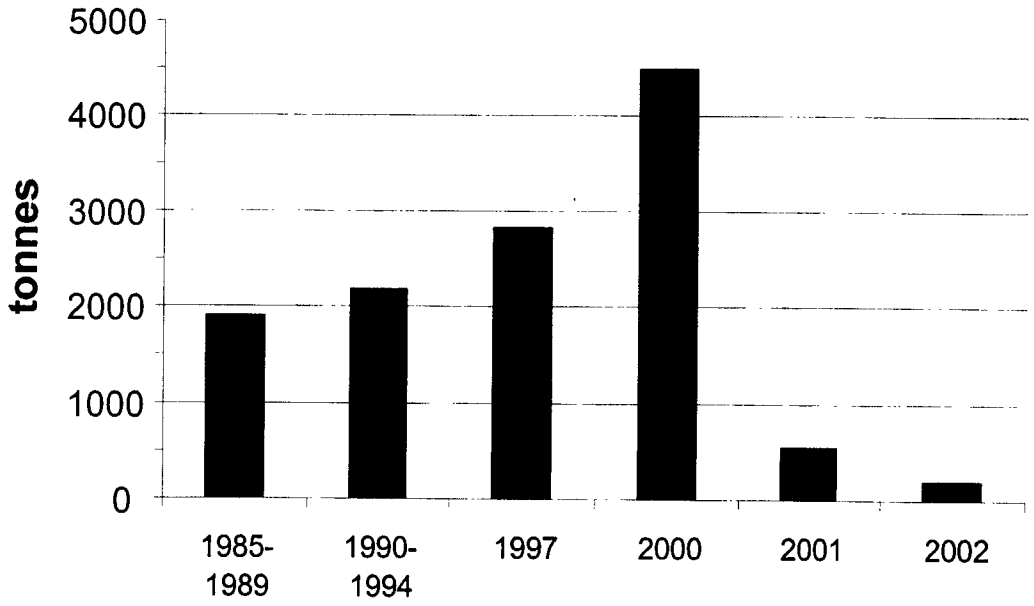
PFCA bioaccumulation pathways in the Arctic marine food webs. How do polar bears get exposed to PFCAs?



Comparison of recent historical trend of PFOA emissions from all sources from 1999-2006 (Prevedouros et al. 2006) suggests PFCAs should be declining

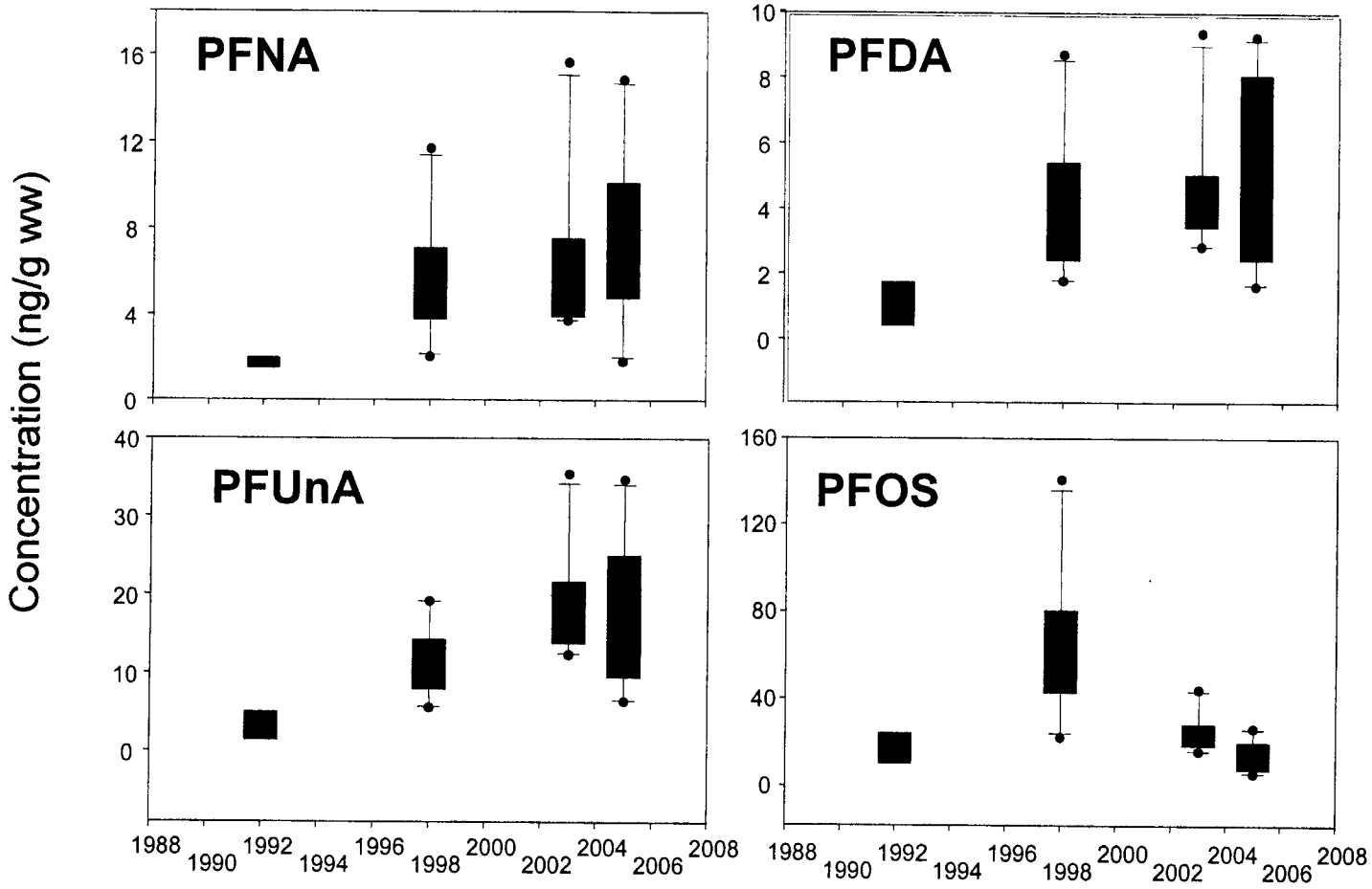


Production of perfluorooctane sulfonyl fluoride (PFOSF) had a DT = ~11 yrs (Smithwick et al 2006) which is similar to observed increase of PFOS in seals and polar bears. With the withdrawl of this product post-2000 emissions should be declining sharply.



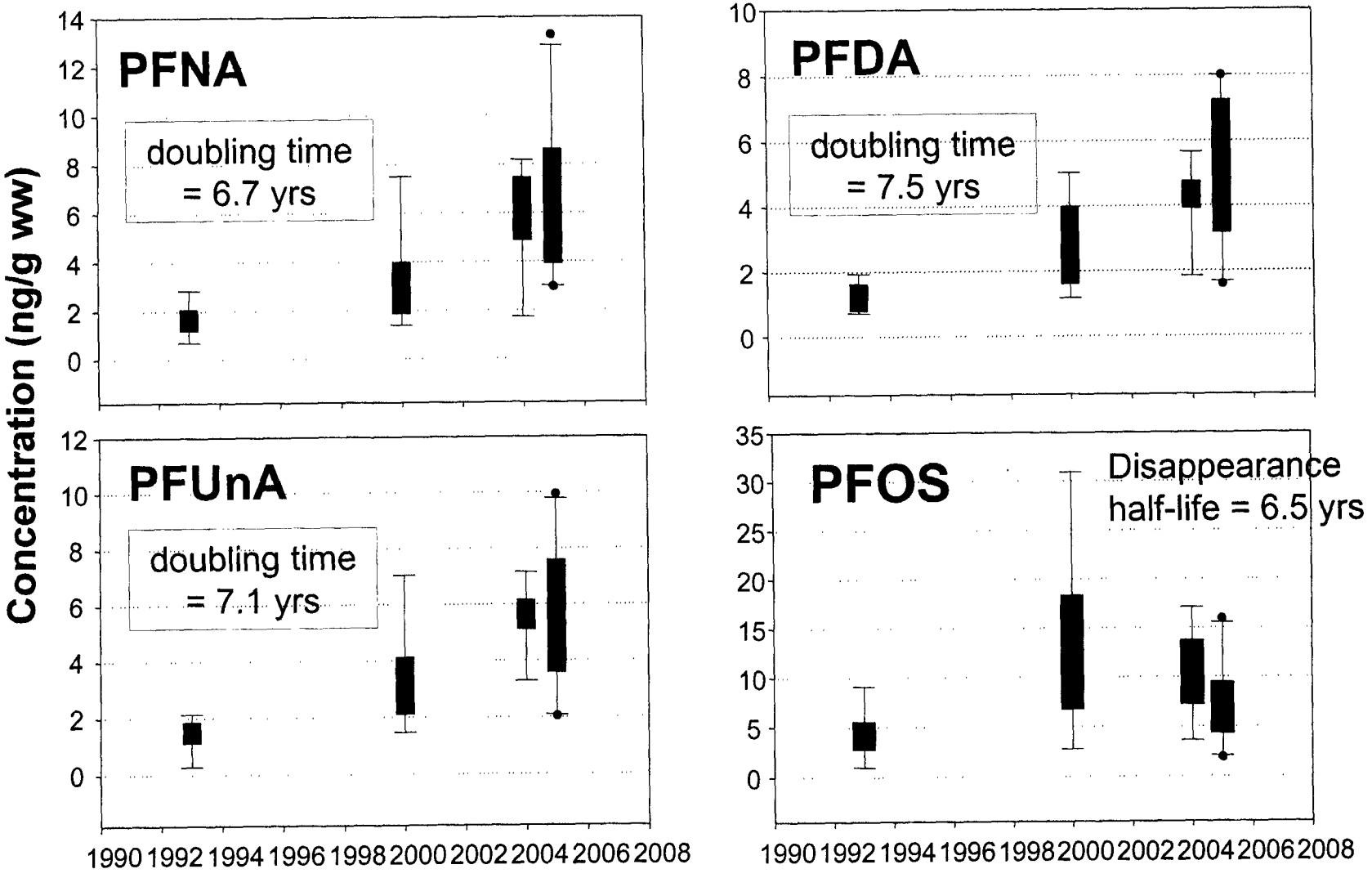
PFCAs and PFOS in liver of ringed seals at Arviat NU - Increasing trend for PFCAs, decline for PFOS post-1998

(Butt et al. in prep)



PFCAs and PFOS in ringed seals from Resolute NU – increase for PFCAs, decline post-2000 for PFOS

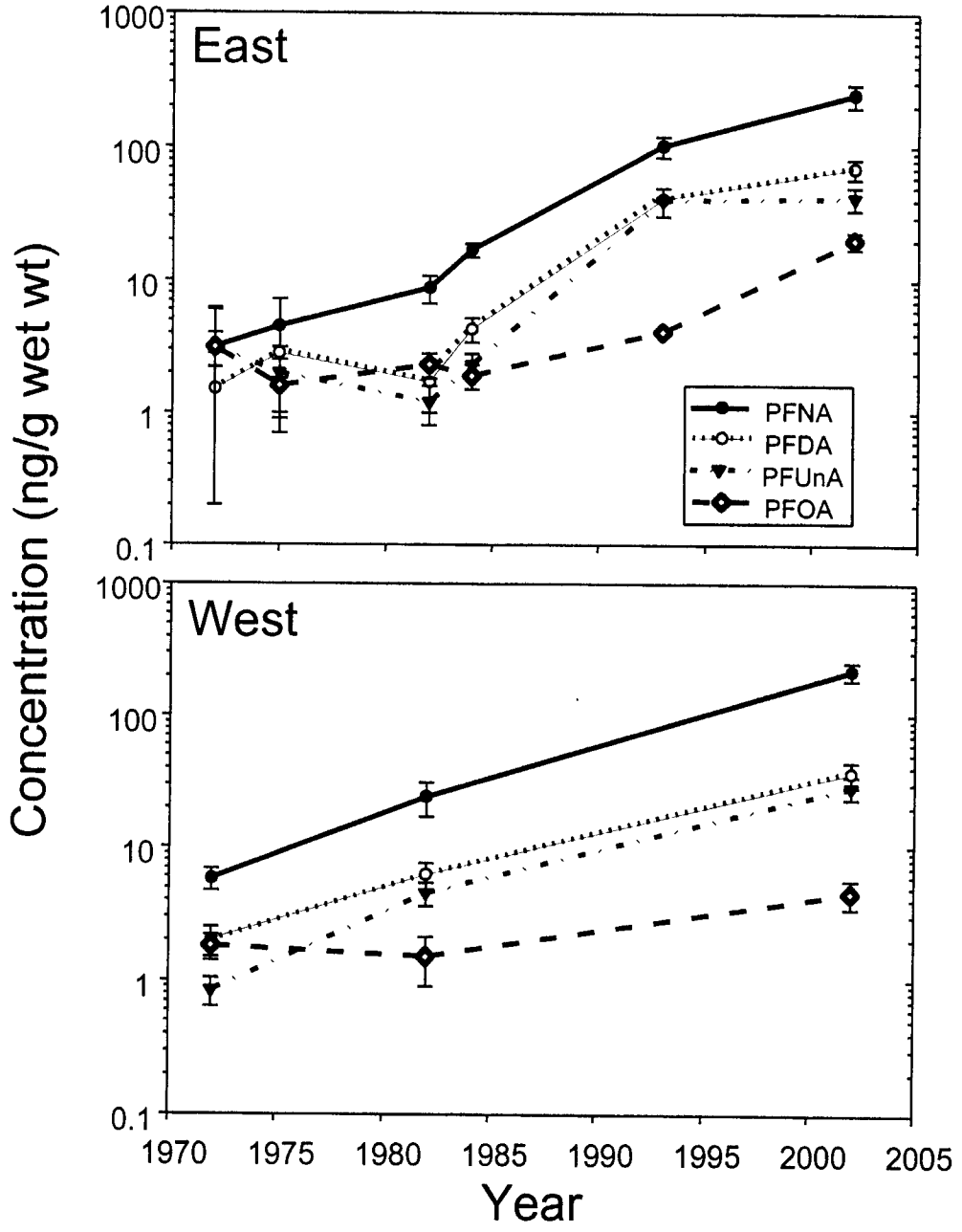
(Butt et al. Fluoros 2006 - updated)



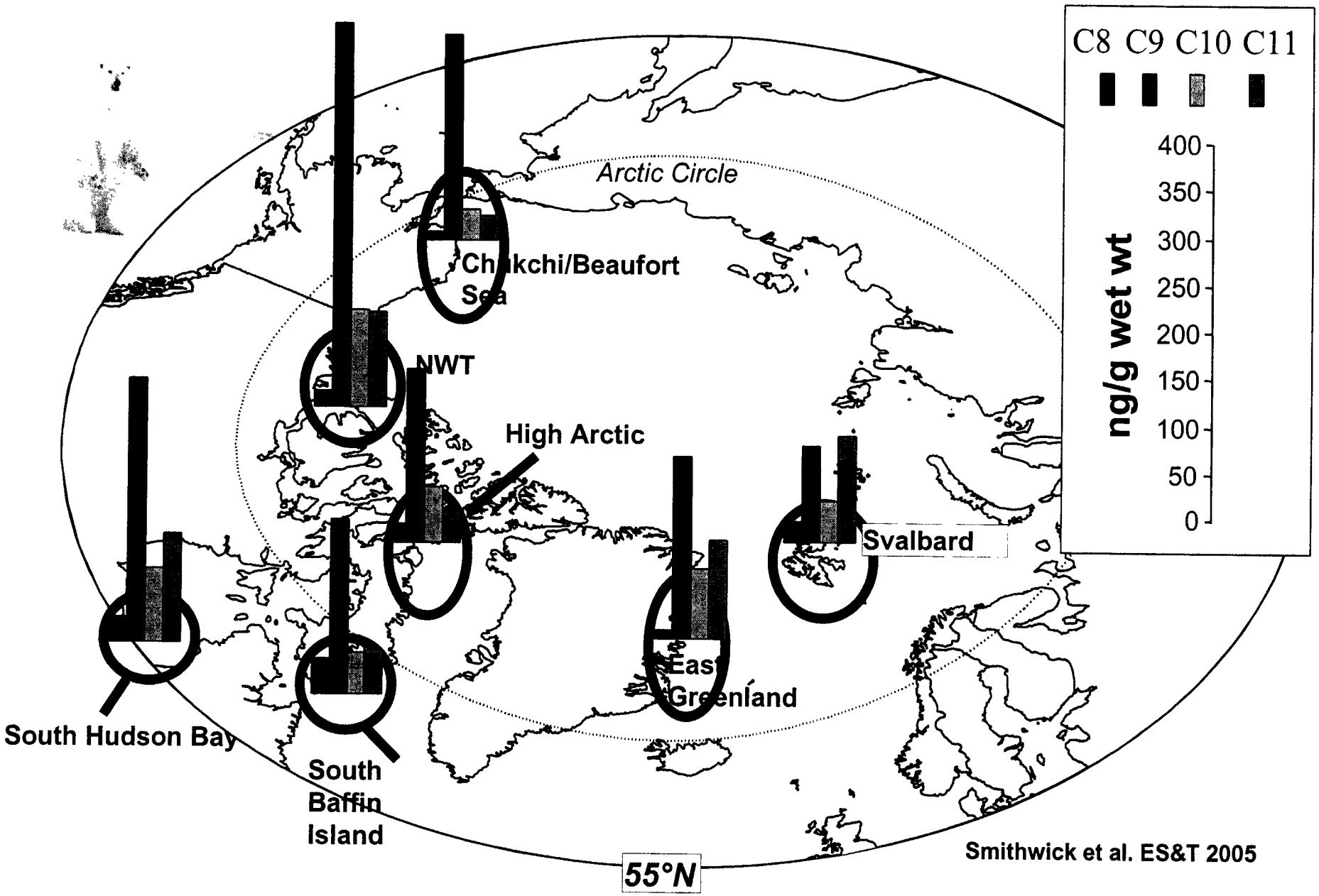
Temporal trends of PFCAs in polar bears
(Smithwick et al ES&T 2006)

Doubling time (years)

	East		
Chemical	**R^2**	**P**	**DT**
PFOS	0.35	<0.001	9.8±5.1
PFOA	0.48	<0.001	7.3±2.8
PFNA	0.69	<0.001	3.6±0.9
PFDA	0.72	<0.001	4.2±1.0
PFUA	0.57	<0.001	4.1±1.4
PFDoA	0.02	0.405	nd
		West	
PFOS	0.66	<0.001	13±4.0
PFOA	0.14	0.055	14±14
PFNA	0.87	<0.001	5.6±0.9
PFDA	0.72	<0.001	6.7±1.7
PFUA	0.85	<0.001	6.1±1.1
PFDoA	0.05	0.276	nd

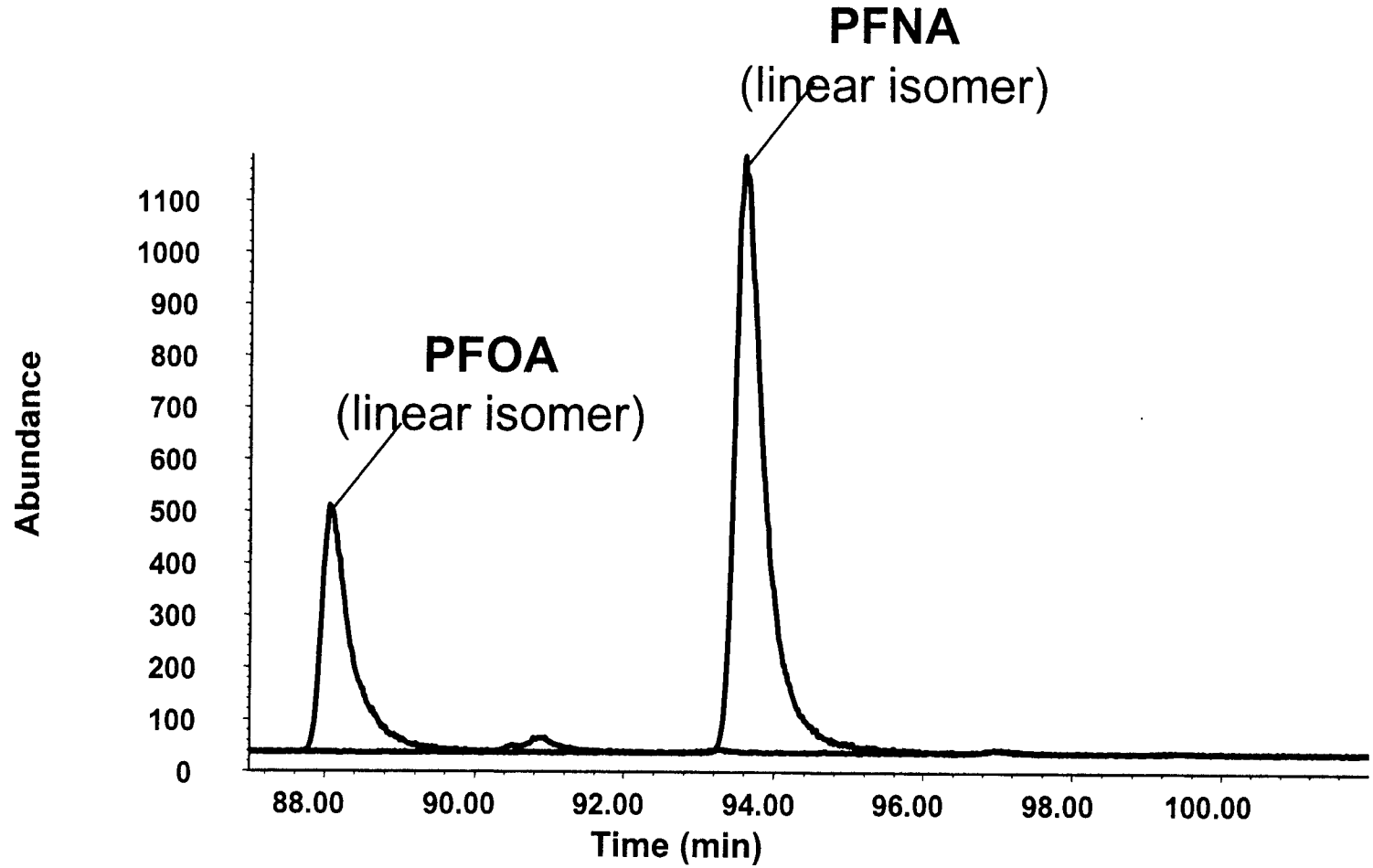


Trends of Perfluorinated carboxylic acids in polar bear liver (ng/g wet wt) (Smithwick et al. 2005)



Smithwick et al. ES&T 2005

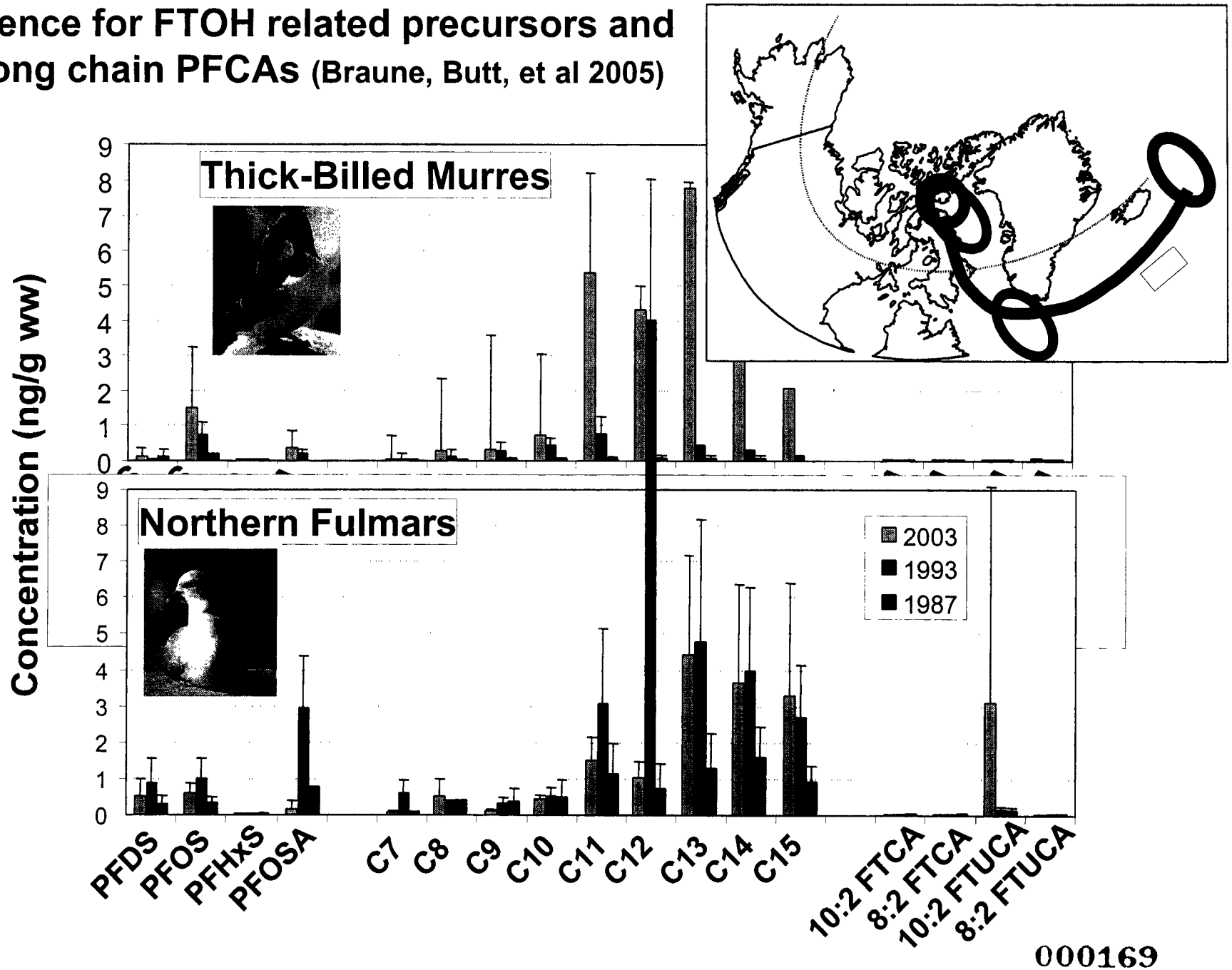
PFOA in polar bears mostly 'straight' but some (~10%) branched chains; PFNA 'straight' only implying FTOH source



A.O. DeSilva & SA Mabury, 2004. Isolating Isomers of PFACs in Polar Bears. *Environ. Sci. Technol.* **38**:6538-6545.

PFA profiles and temporal trends in Arctic seabird livers

Evidence for FTOH related precursors and for long chain PFCAs (Braune, Butt, et al 2005)



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Uncertainties in overall assessment of fluorotelomer polymers

Biodegradation rates of the polymers

- Rate of degradation and actual release of FTOHs from polymers has not been demonstrated

Environmental levels:

- Contribution of C10-C13 PFCAs from non-fluorotelomer materials (e.g. see Prevedouros et al. 2006)
- Very limited air measurements of FTOHs
- Limited measurements of FTOHs in wildlife – only as acids
- Limited measurements of C14 PFCAs (and up) – these should be solely from fluoro telomers

Bioaccumulation

- C14 PFCAs (and up) could be very P but not B

Toxicology

- remarkable differences in clearance rates among species
- Understanding the laboratory species differences and relevance to humans

Conclusions

- Fluorotelomer-based polymers are expected to release FTOHs into the environment as residual alcohol or through degradation of the polymer;
  - Biodegradation and metabolism studies demonstrate production of persistent PFCAs
- FTOHs are volatile and have long predicted atmospheric half-lives
  - They can undergo long-range transport
  - Strong evidence exists for their transformation to PFCAs via OH-radical reaction
- The properties of longer carbon-fluorine chain length PFCAs (≥C9) include high persistence, bioaccumulation (lab and field data)
- Adverse effects of PFOA in laboratory mice, rats and monkeys; including high subchronic oral toxicity, tumorigenicity, and immunological toxicity.
- PFCAs (>C8) are reasonably expected to be of greater concern than PFOA as a result of their known slower clearance rates and higher bioaccumulation potential
- PFCAs are widespread throughout Arctic and Great Lakes biota and evidence indicates that concentrations in wildlife tissues are increasing over time