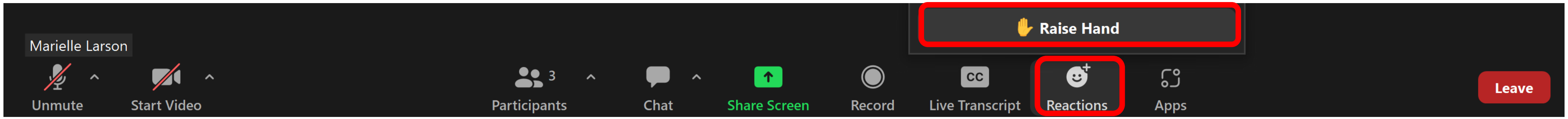
Navigating the Symposium

Welcome! While we wait, please:

- Update your name to include your pronouns and organization
- Message Marielle with any access needs
- Introduce yourself in the chat. We've muted participants to minimize technical issues, so we encourage you to use the chat to say hello instead

Questions or Comments?

- Add them to the chat
- Raise your hand and we'll unmute you



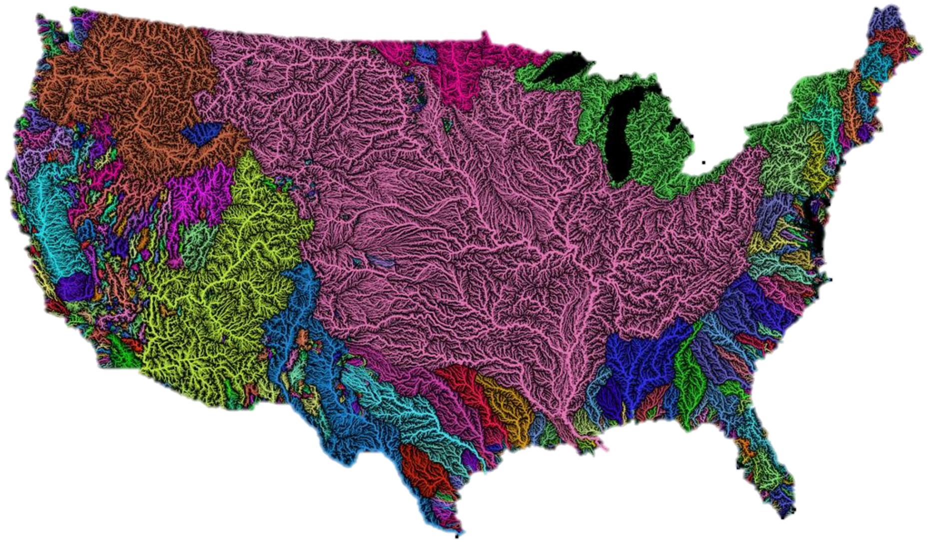
The slides and recording will be available on [Puget Sound Institute's website]

PCB Symposiums

Cross Program Contaminant Working Group

BACKGROUND:

- Many estuaries (and river systems) are dealing with anthropogenic contaminants. Face similar challenges in this work.
- Share information on programs, projects, and best practices across regions to improve the effectiveness by which toxics contaminants are managed, controlled, and remediated.
- Initial focus on PCBs. Then poll those who are involved in contaminant management, and address the topics that are of interest

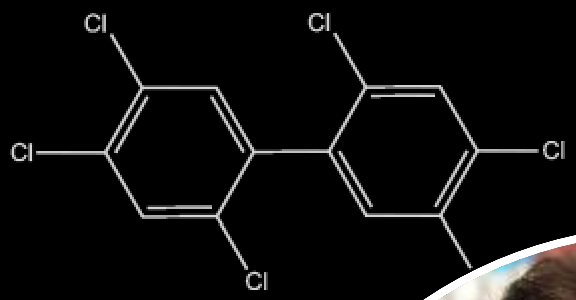


Map from Grasshopper Geography

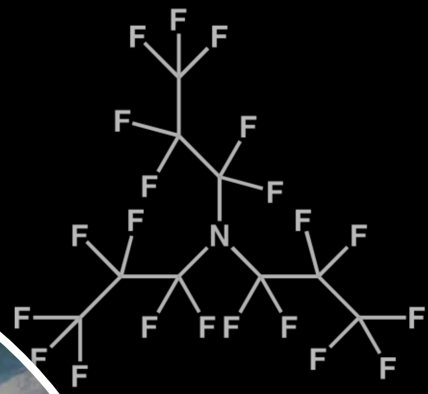
Previous Symposiums

Learn More

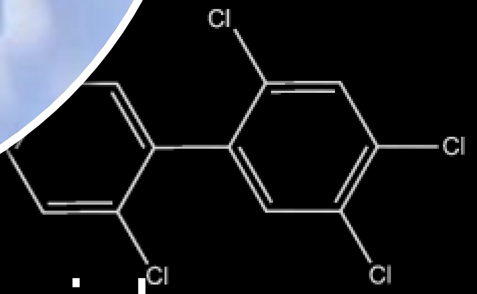
www.pugetsoundinstitute.org/about/cross-program-contaminant-working-group/



From PCBs to PFAS

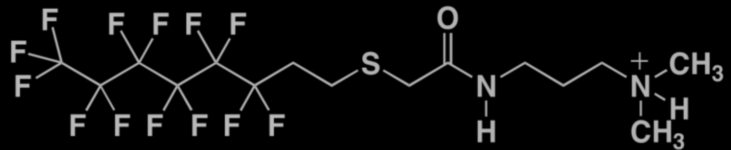


May 9, 2024



Dr. Steven Eisenreich

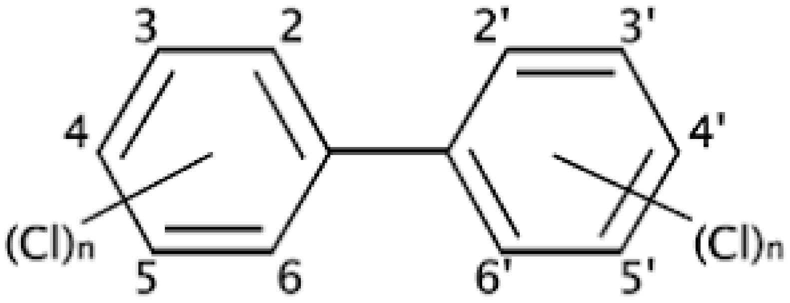
Dr. Scott Mabury



WATER & CLIMATE
DEPARTMENT

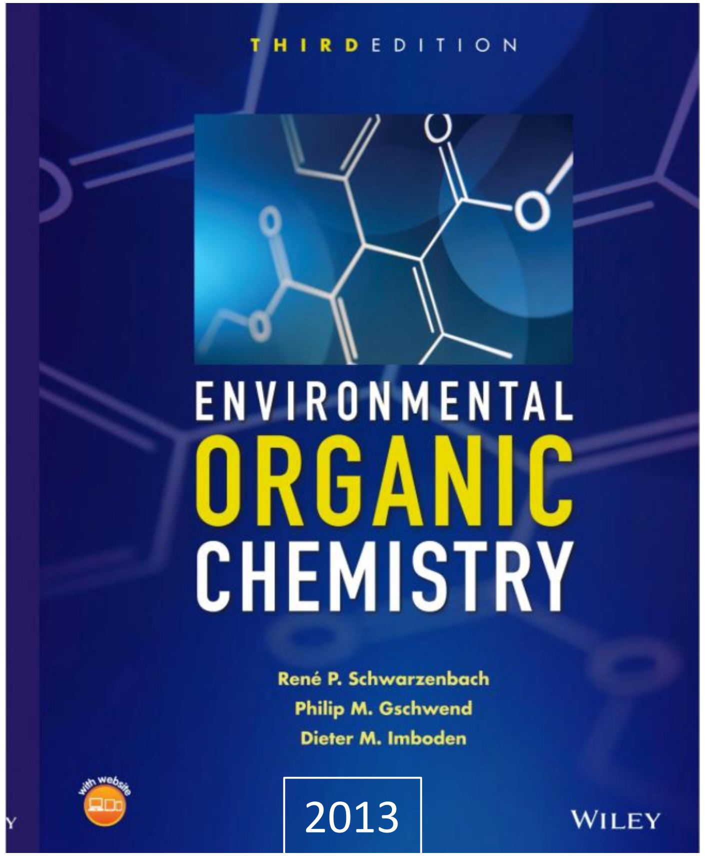
PCBs: what we know and lessons learned

Physical -Chemical Properties
Environmental Processing controls
PCBs fate in aquatic systems



Steven Eisenreich

Polychlorinated biphenyls PCBs)



2013

Rene Schwarzenbach
Phillip Gschwend
Dieter Imboden

Deb Swackhamer, 2021
Uof MN

Ron Hites, 2024
Indiana U

Don Mackay, 2024
U of Toronto

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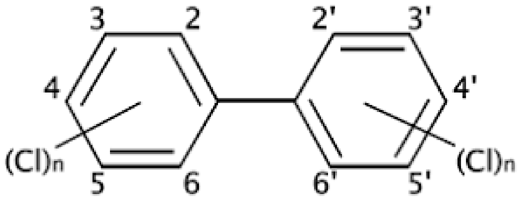
Why do we care?



Biomagnification of PCBs in the Aquatic Foodweb

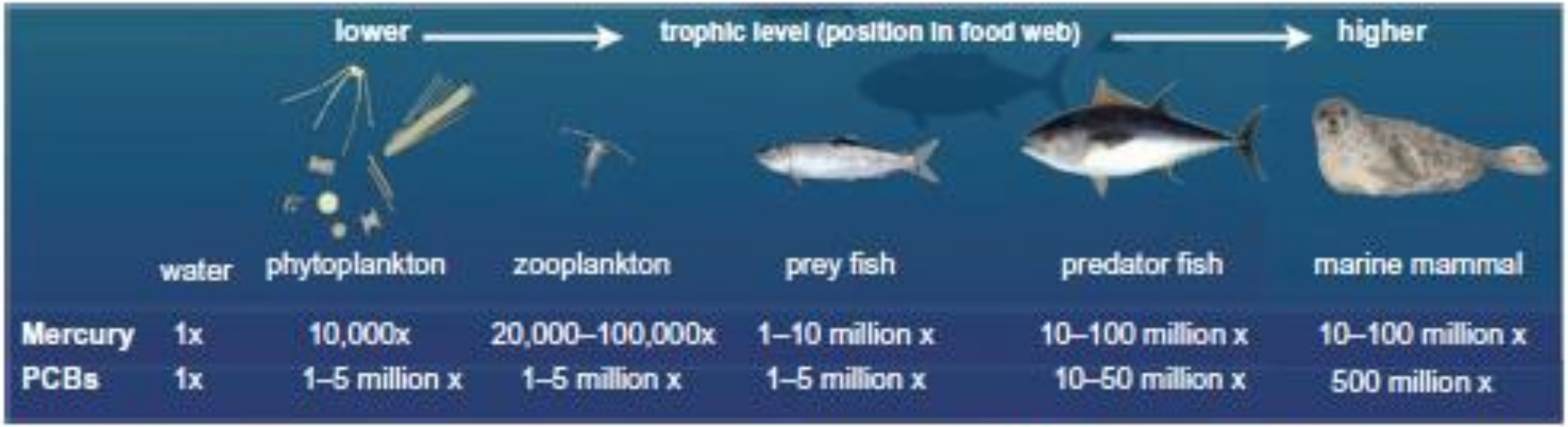


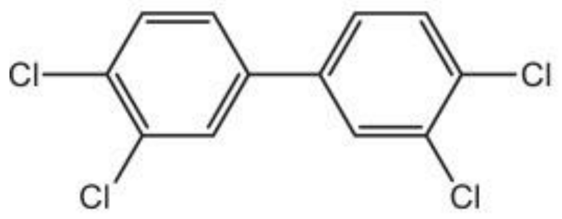
FIG. 13.5 Biomagnification in marine food webs. *Adapted from Chen CY, Driscoll CT, Lambert KF, et al.: Sources to seafood: Mercury pollution in the marine environment, Hanover, NH, 2012, Dartmouth College.*

Chen et al., Chemical Pollution of the Ocean,

Oceans and Human Health https://doi.org/10.1016/B978-0-323-95227-9.00001-4

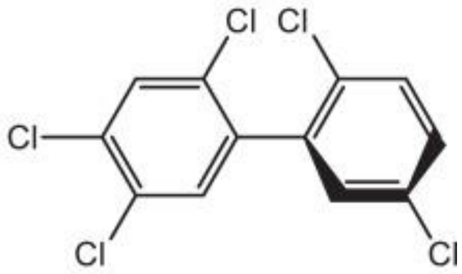
What are PCBs and how used

(a)



Dioxin-like PCBs
(Planar structure)

(b)



Non-dioxin-like PCBs
(Non-planar structure)

209 possible PCB congeners
~130 congeners in commercial mixtures

- Co-planar PCBs
  12 PCB congeners in this pool
  (dioxin-like)
- Non-planar PCBs

Coolants and lubricants in transformers, capacitors, and other electrical equipment.
Electrical, heat transfer and hydraulic equipment. ***Plasticizers in paints, plastics and rubber products.***
Hydraulic fluids, …

- Last decade has shown aquatic and air presence of ‘non-Arochor PCB’ – PCB 11 (di-Cl) produced as incidental by-products in pain pigment, cabinet sealing, and silicone rubber production …
- PCB congeners 47,51, 68 found in CA and Europe atmosphere related to silicone rubber and polyester production.
- Aroclor PCBs still dominate but unintentional by-products could be 10% of atmospheric burden in CA.
- ‘Legal’ production today in manufacturing as incidental could approach Aroclor production peak.
- Check out: K. Hornbuckle, F. Wania, K. Hombrecher, L. Rodenberg

Advances in PCB tools
allowing high specificty and sensitive congener-specific analyses

Glass Capilary Gas Chromatography columns with coatings – 1960s-1970s
→ Congener-specific analysis (e,g., vs % Arochlor)

Electron Capture Detector **(ECD)** invented in 1958 by Lovelock
(senstive to halogenated (here, Chlorinated) organics

‘Inexpensive’ Desktop GC-Mass Spectrometers

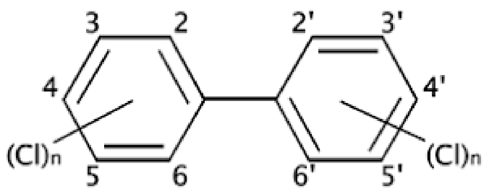
High Resoltuion GC- High Resolution MS(-MS)

GC-MS-MS

Improved and sustainable sample extraction/cleanup techniques

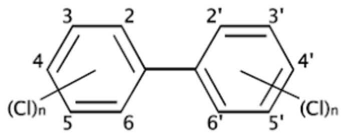
Stable-isotope labelled internal and external standards

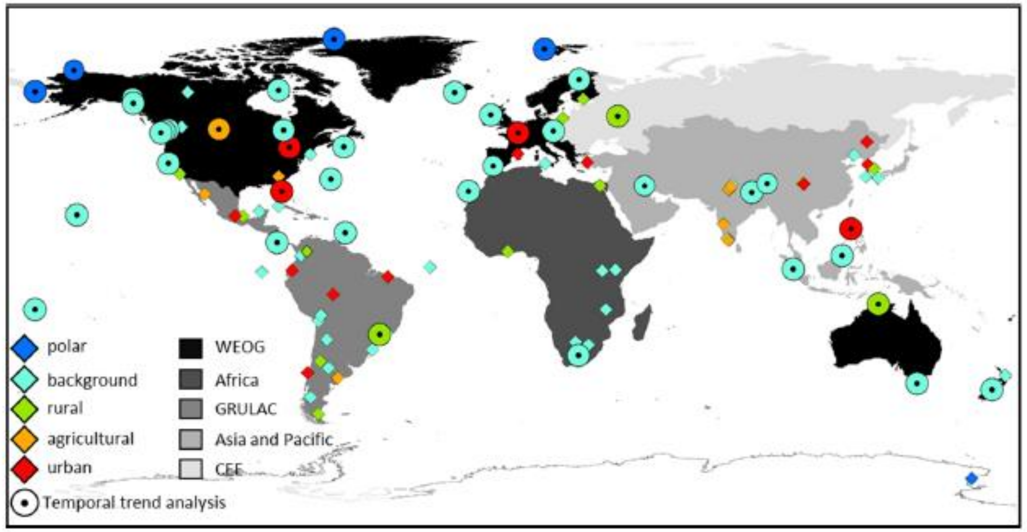
Passive sampling for Air and Water (spatial and temporal trends)

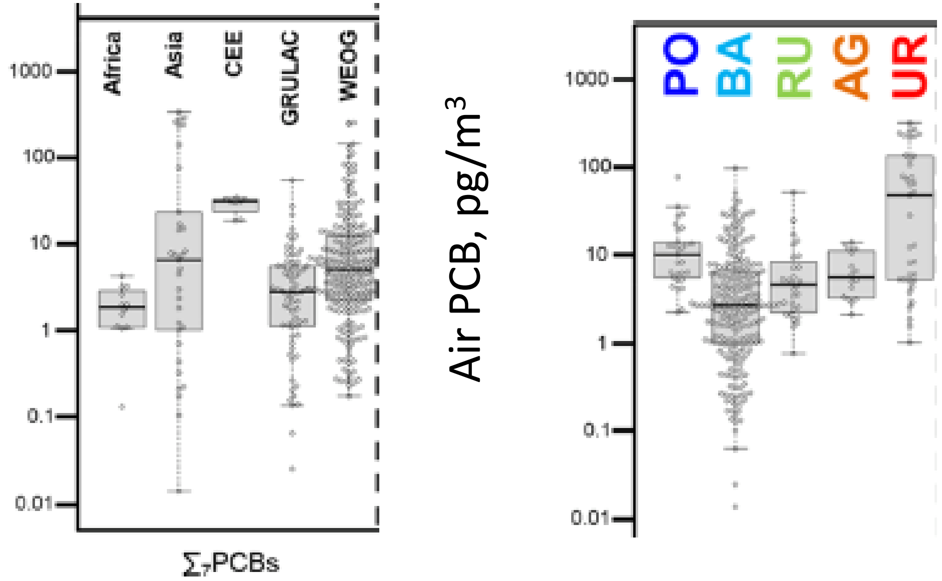


Tracking POPs in Global Air from the First 10 Years of the GAPS Network (2005 to 2014)

Schuster et al., ES&T, 2023

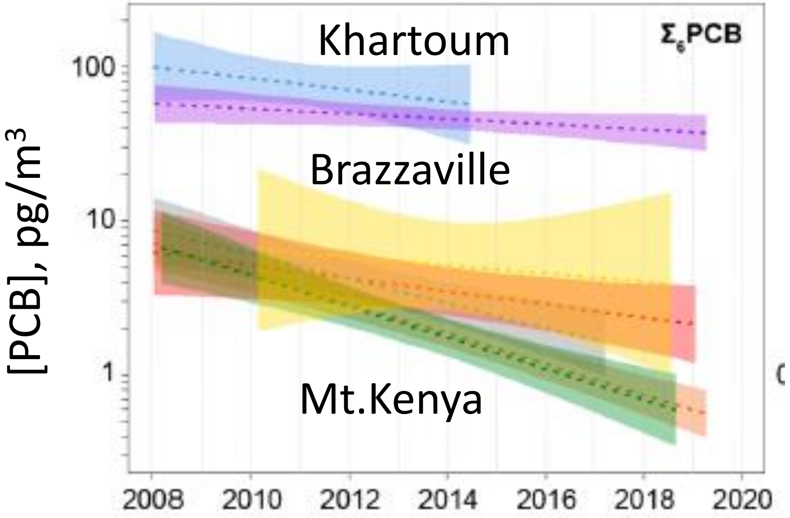






Temporal Trends of PCBs across Africa after a Decade of MONET Passive Air Sampling

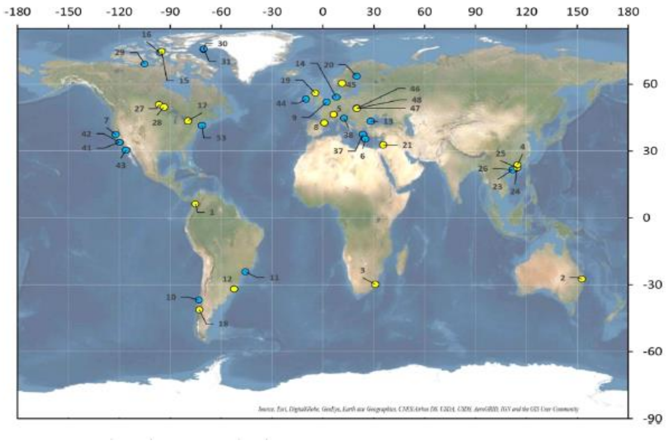
White et al., ES&T,2024

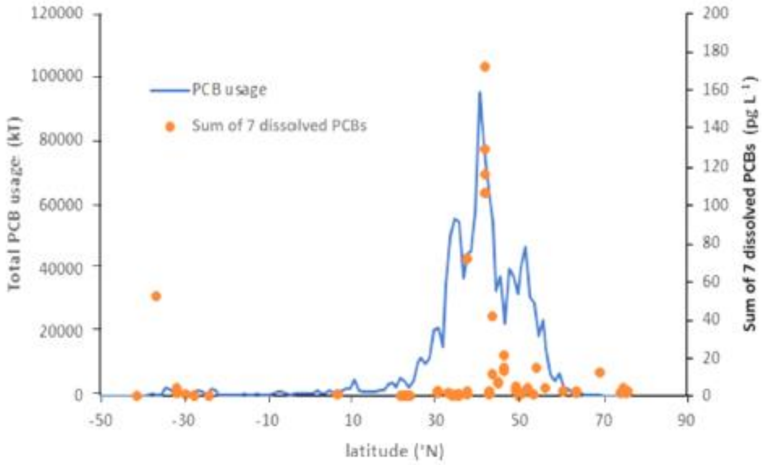


Polychlorinated biphenyls PCBs)

Passive-Sampler-Derived PCB and OCP Concentrations in the Waters of the World First Results from the AQUA-GAPS/MONET Network

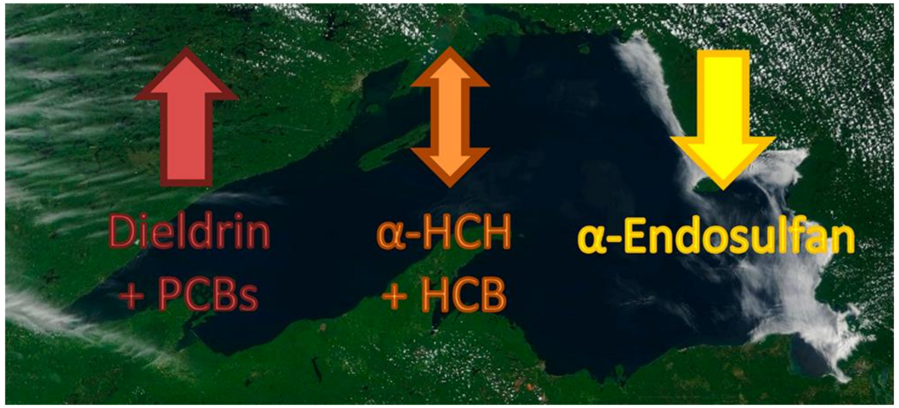
Lohmann, et al., ES&T, 2023





Concentrations, Trends, and Air–Water Exchange of PCBs and Organochlorine Pesticides Derived from Passive Samplers in Lake Superior in 2011

Ruge et al., ES&T, 2023



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PCB Congeners analyzed in air, water, and sediment samples

90 congeners

$\Sigma 1_{90}$PCB

43 congeners

$\Sigma 1_{43}$PCB

30 congeners

$\Sigma 1_{30}$PCB

12 congeners

$\Sigma 1_{12}$PCB

22 congeners

17	151
18	149
28	118
31	153
33	132/105
49	138
52	187
49	183
99/101	128
110	177
82	171/156
	180

Σ_{22}PCB

18 congeners

8
18
28
44
52
66
101
105
118
128
138
153
170
180
187
195
206
209

Σ_{18}PCB

7 congeners
(ICES 'Indicator' PCBs)

28 - tri
52 - tetra
101- penta
118 - penta
138 - hexa
153 - hexa
180 - hepta

Log Kow = 5.67 – 7.36

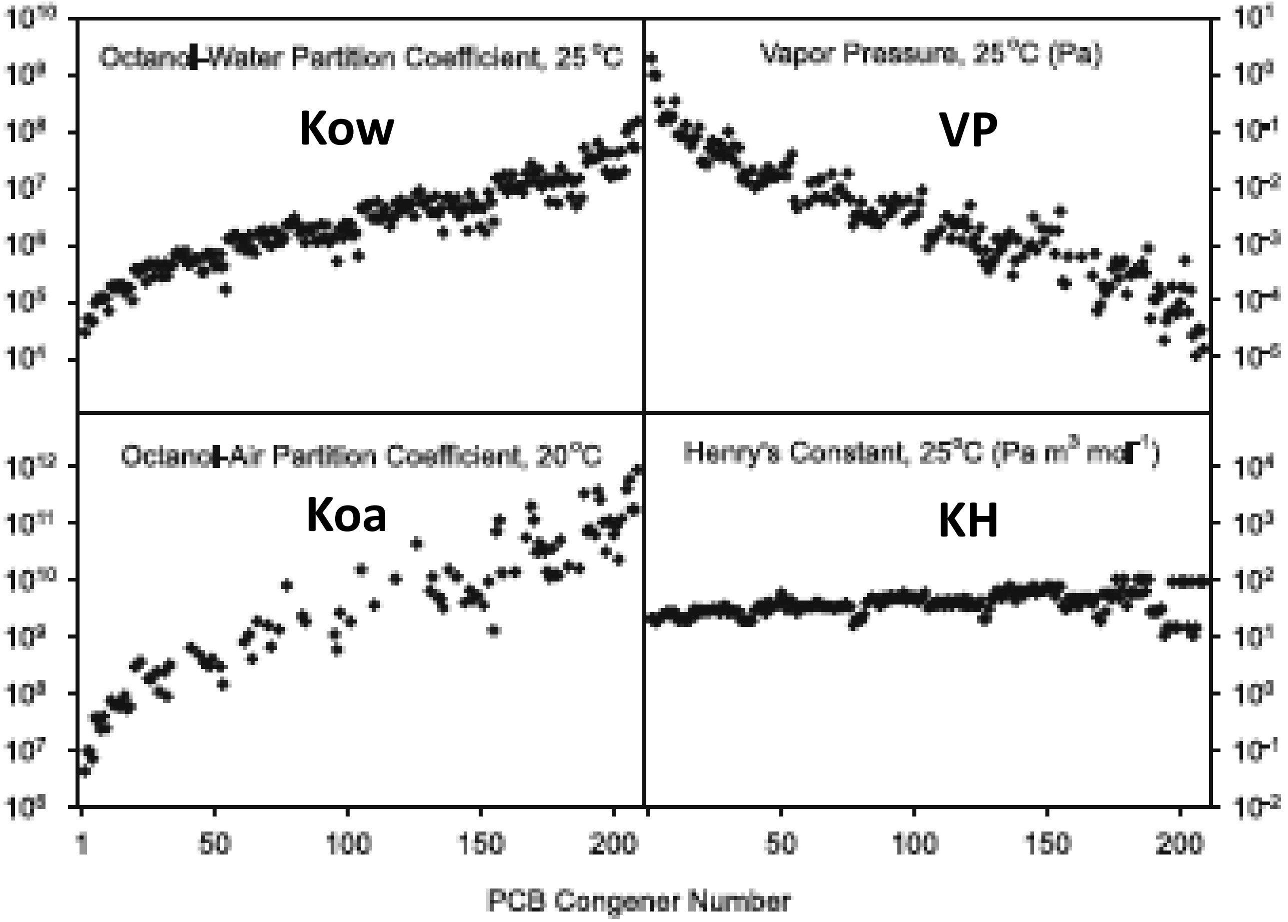
Σ_7PCB

We have a problem!

Polychlorinated biphenyls (PCBs)

Partitions preferentially ot living and dead OM

Partition behavior to Atmospheric particles and vegetation



- Low MW PCBs preferentially transported over mid- and high MW PCBs.
- VP ∝ 1/T

KH is ~ constant across PCB congeners

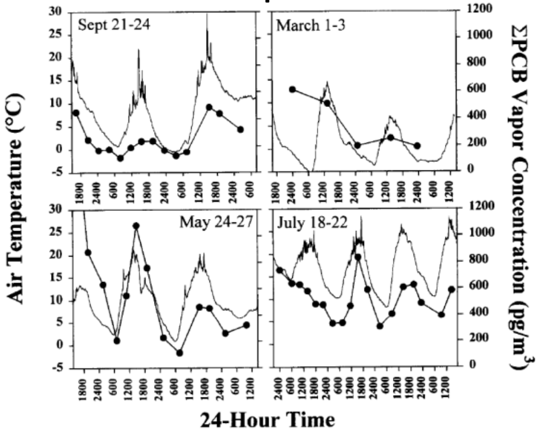
Physical-Chemical Properties of PCB congeners

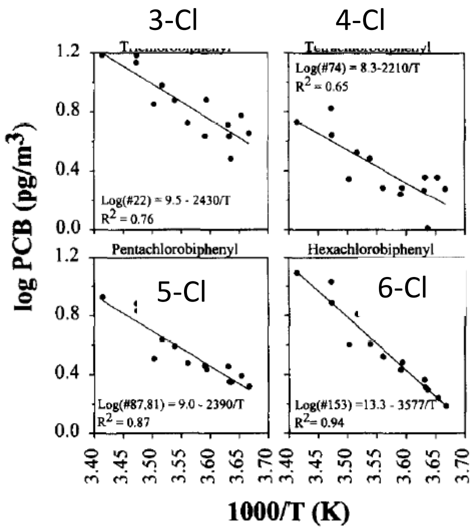
Classified as PBTs, Hydrophobic, Moderate VP, Fate linked to C Cycle in aquatic systems, High Volume Production, Globally Distributed (LRAT & Oceanic) , Banned for > 50 years

Hornbuckle at el. 2006. PCBs in the Great Lakes. Handbook of Environ. Chem. Vol.5. Part N, 1-70.

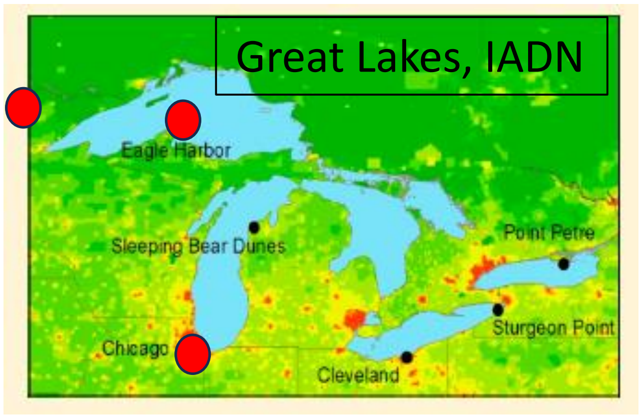
Vapor Pressure

Diurnal PCB concentrations in an Ombrotrophic wetland

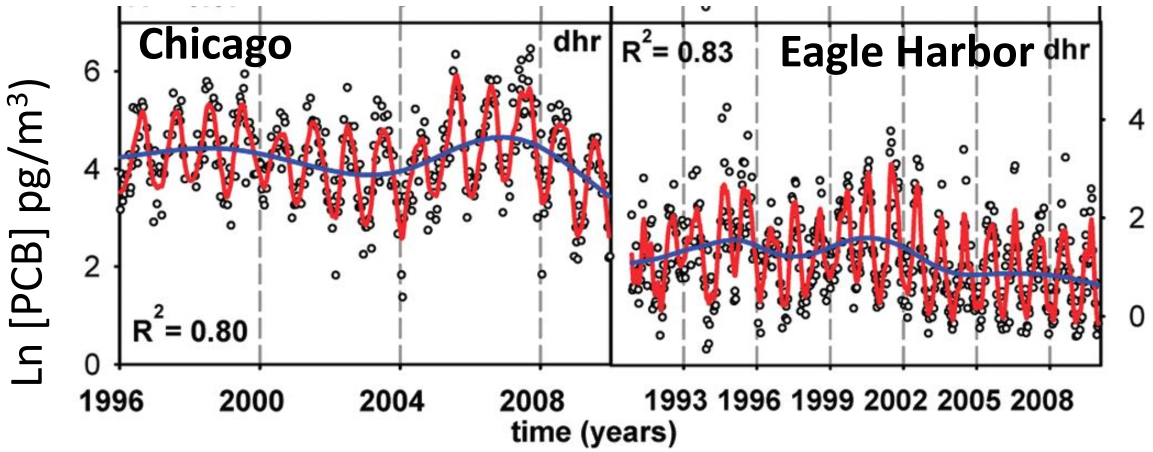




Hornbuckle et al., 1996

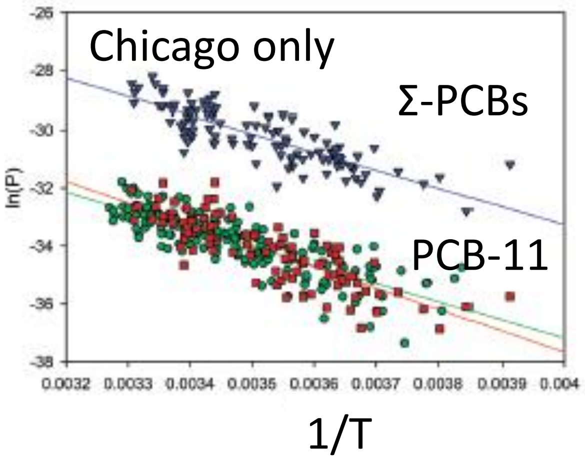


Monthly PCB concentrations at IADN, NA Great Lakes



Venier et al., EST, 2024

Black – Conc, Red – fit seasonal cycle, Blue - trends

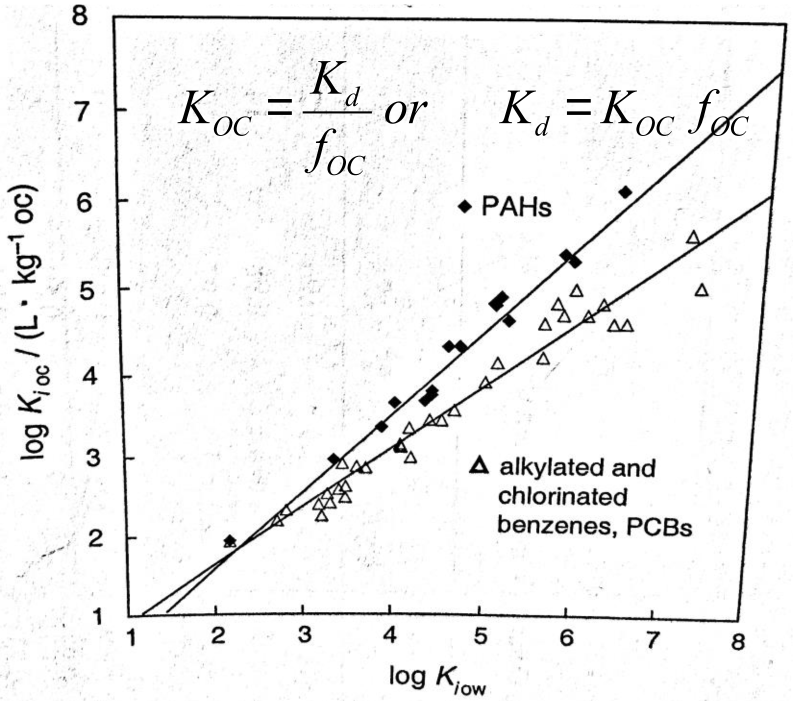


Salamova et al., ES&T, 2015

PCB Sorption/Partitioning of PCBs to Aquatic OM/OC

Sorption Coefficients of PCBs to Natural Organic Matter

log Koc vs log Kow



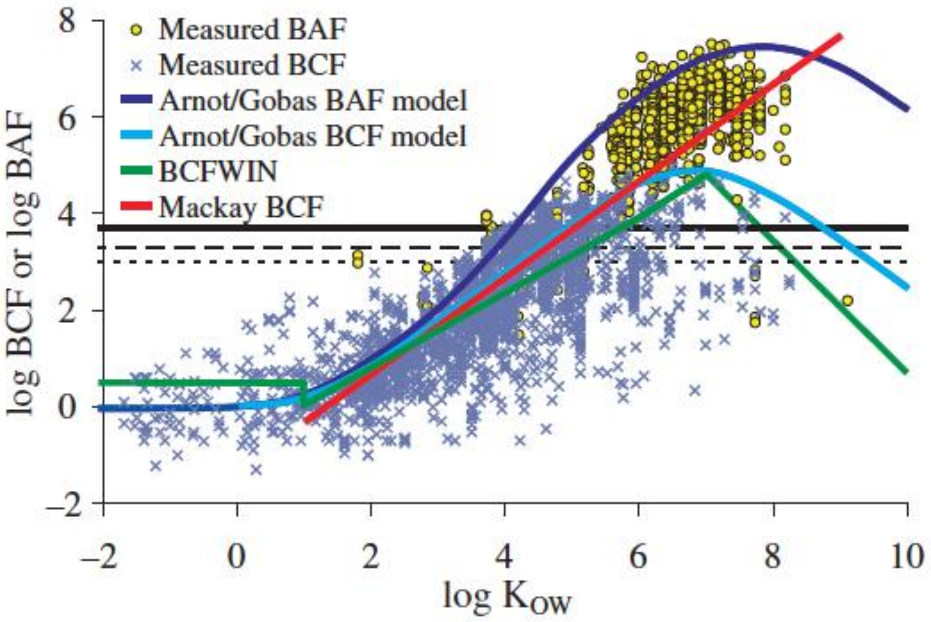
$$K_{ioc} = \frac{K_{id}}{f_{oc}}$$

$F_{diss,\ part}$ = function (Kow, TSS, *f*oc)

Schwarzenbach et al., 2013

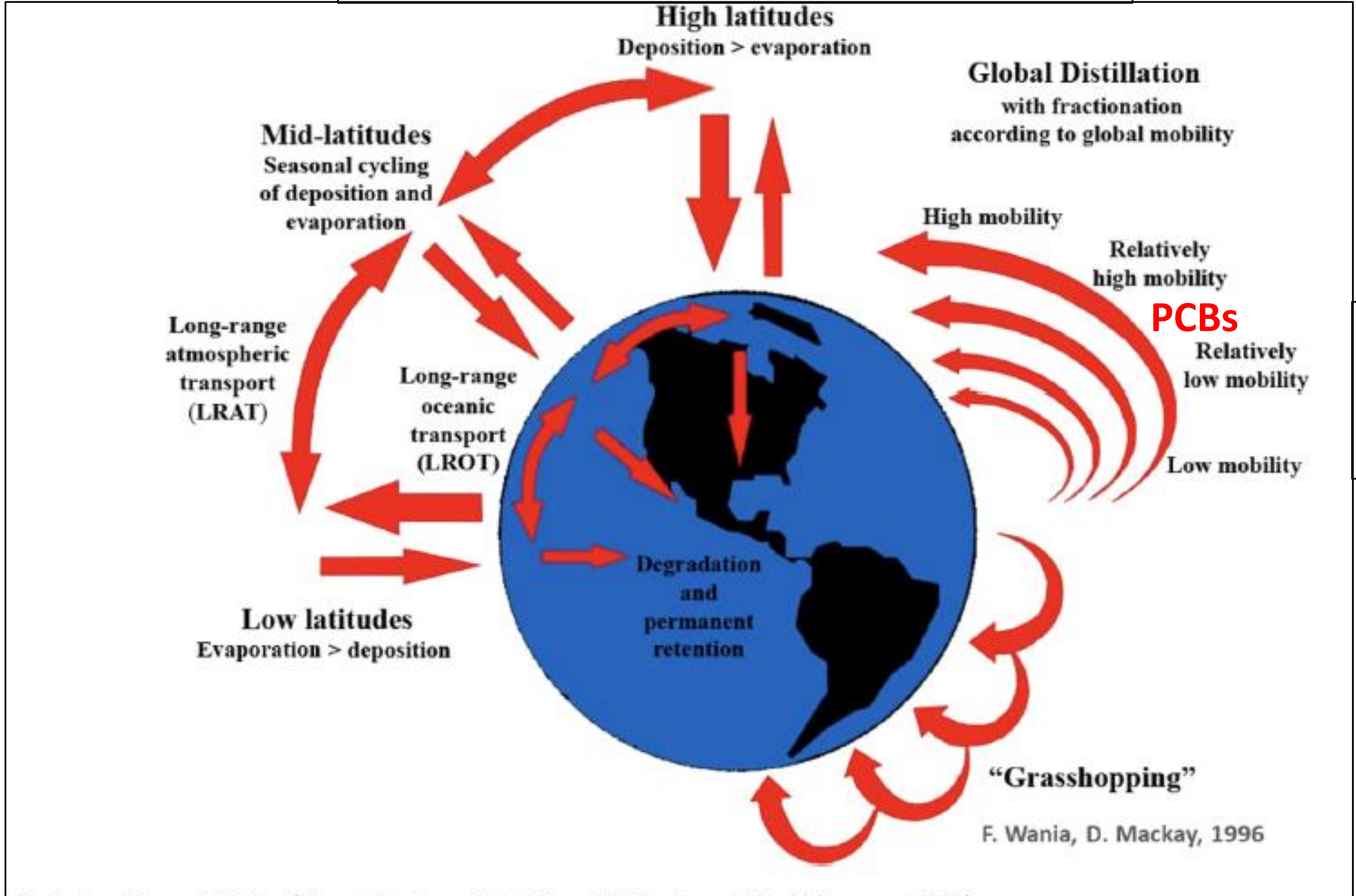
Bioaccumulation and Bioconcentration Factors for PCBs (measured and modeled)

log BCF or BAF vs Kow



Environ. Rev. 14: 257–297 (2006)

The Global Distribution of PCBs



Global cycling of POPs (after Wania and Mackay 1996, adapted by Schuster, 2008).

PCB Characteristic
Travel Atmospheric Distances
100's – 1000's kms

"don't travel far"

PCBs are emitted in the mid-latitudes where it is warm or seasonally warm and are transported and deposited in regions where it is cold or seasonally cold.

K.C. Jones. Persistent Organic Pollutants (POPs) and Related Chemicals in the Global Environment: Some Personal Reflections. Environ. Sci. Technol. 2021, 55, 9400−9412

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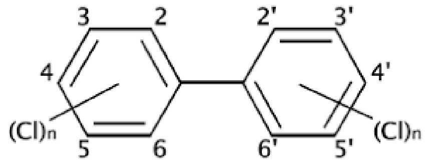
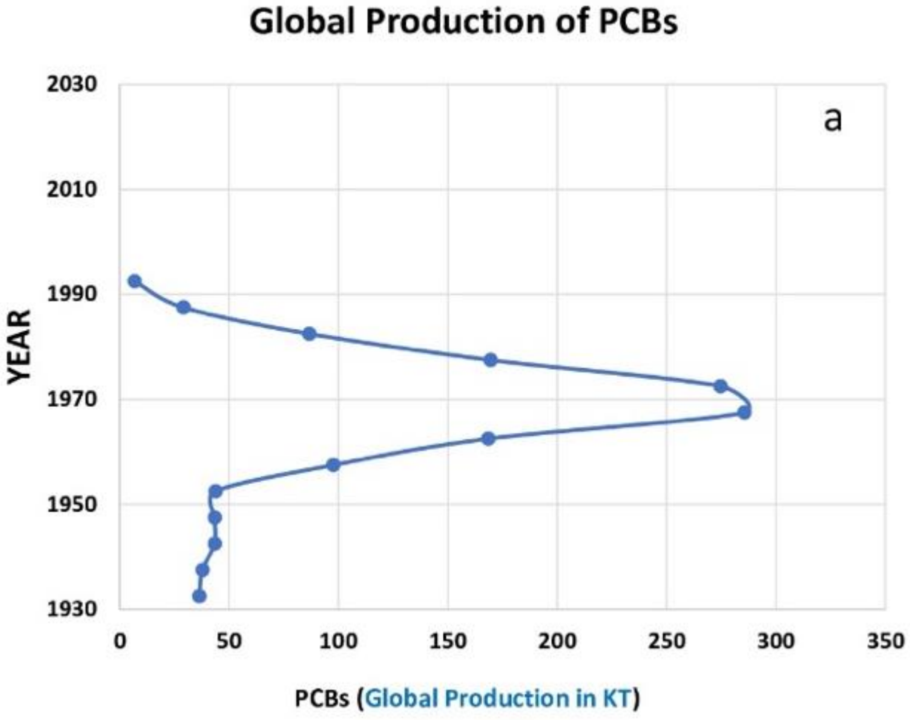
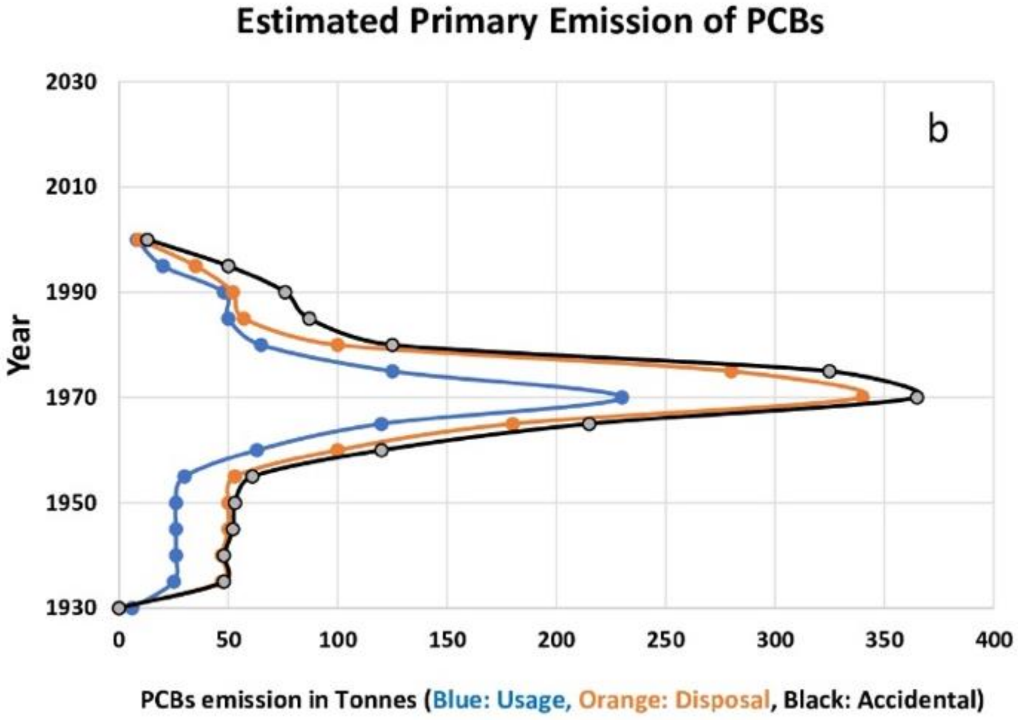
Global Production Polychlorinated biphenyls PCBs)





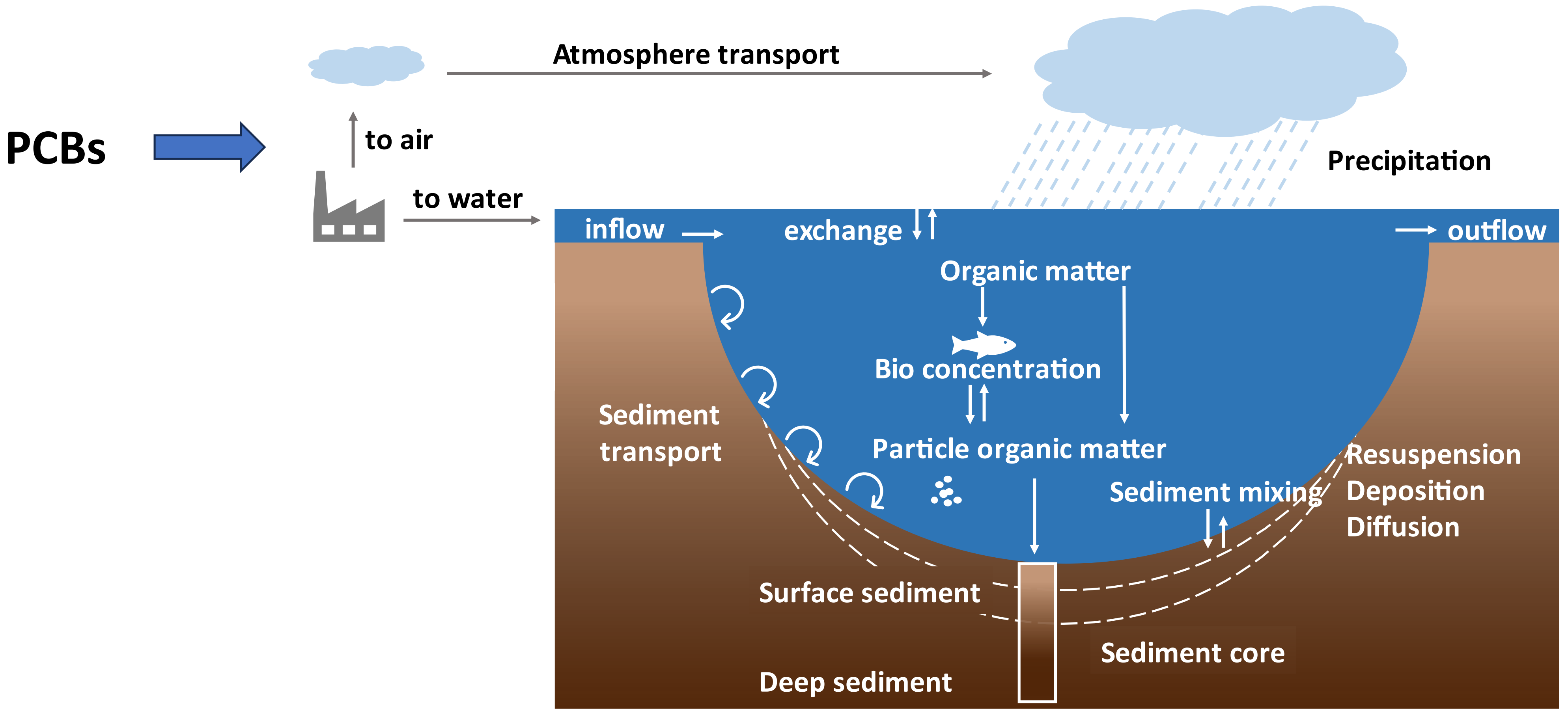


(a) Global production of PCBs (Breivik et al., 2002a,b) and

(b) Estimated Primary Emission of PCBs due to usage, disposal, and accidental release (Breivik et al., 2002b).

Global production and use = 1 312 Mt
96% in Northern Hemisphere
Onset in early 1930's; Peak production in ~ 1970
Banned from open systems – 1974; general ban 1979
~ 1-3% of global PCB production in global environment (uncertain)

Lakes as Biogeochemical Reactors



Once PCBs enter the water column, partition/sorb to OC-rich particles and settle / deposit / accumulate in bottom sediments.

Environmental processes and P-C properties linked to the C Cycle Control the Fate of PCBs in aquatic systems

2015)

ROLE OF THE ATMOSPHERE

Accumulation of PCBs in Lake Superior sediments: atmospheric deposition
Eisenreich, et al., ES&T, 1979, 13:569-573

Airborne organic contaminants in the Great Lakes ecosystem.
Eisenreich, et al., ES&T , 1981, 15:30-38

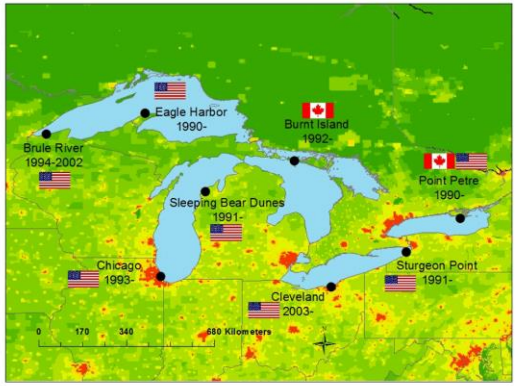
.

Strachan, W.M. & Eisenreich, S.J. (1988). ***Mass Balancing of Toxic Chemicals in the Great Lakes: the role of atmospheric Deposition.*** International Joint Commission. https://scholar.uwindsor.cs.ijcarchive/374

Atmospheric deposition accounted for 90, 58 and 63% of Direct PCB inputs to Lakes Superior, Michigan and Huron.
Strachan and Eisenreich, (1988)

US Clean Air Act Amendments (1990):
GREAT Waters Program

..”to identify and assess the extent of atmospheric deposition of air pollutants on the Great Lakes, the Chesapeake Bay, Lake Champlain, etc.



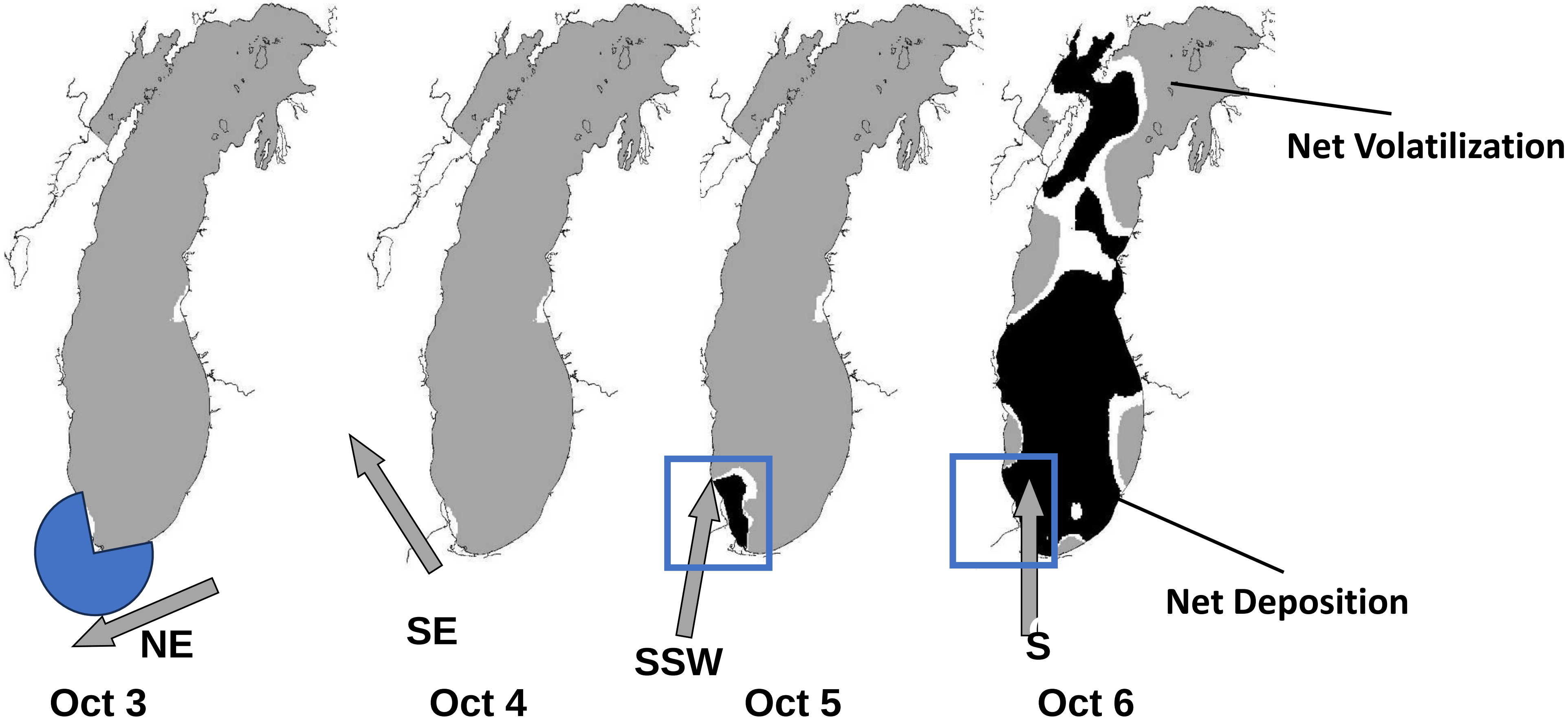
International Great Lakes Atmospheric Deposition Network (IADN)
1991 - present

AEOLOS – Atmospheric Exchange over Lakes and Oceans
LMMB – Lake Michigan Mass Balance (PCBs, ecosystem approach)

Major cities are large sources of PCBs to neighboring Great Waters

AEOLOS (Atmospheric Exchange over Lakes and Oceans)
LMMB (Lake Michigan Mass Balance)

Chicago



Chicago Metropolis

- **[PCB]$_{air}$ in Chicago > ~10 - > 100x regional [PCB]$_{air}$**
- **~25% of Annual PCB loading to Lake Michigan comes from Emissions from Chicago area.**

Courtesy – K. Hornbuckle

PCB Concentration Decreases in Lake Superior Water

Where did the PCBs go?

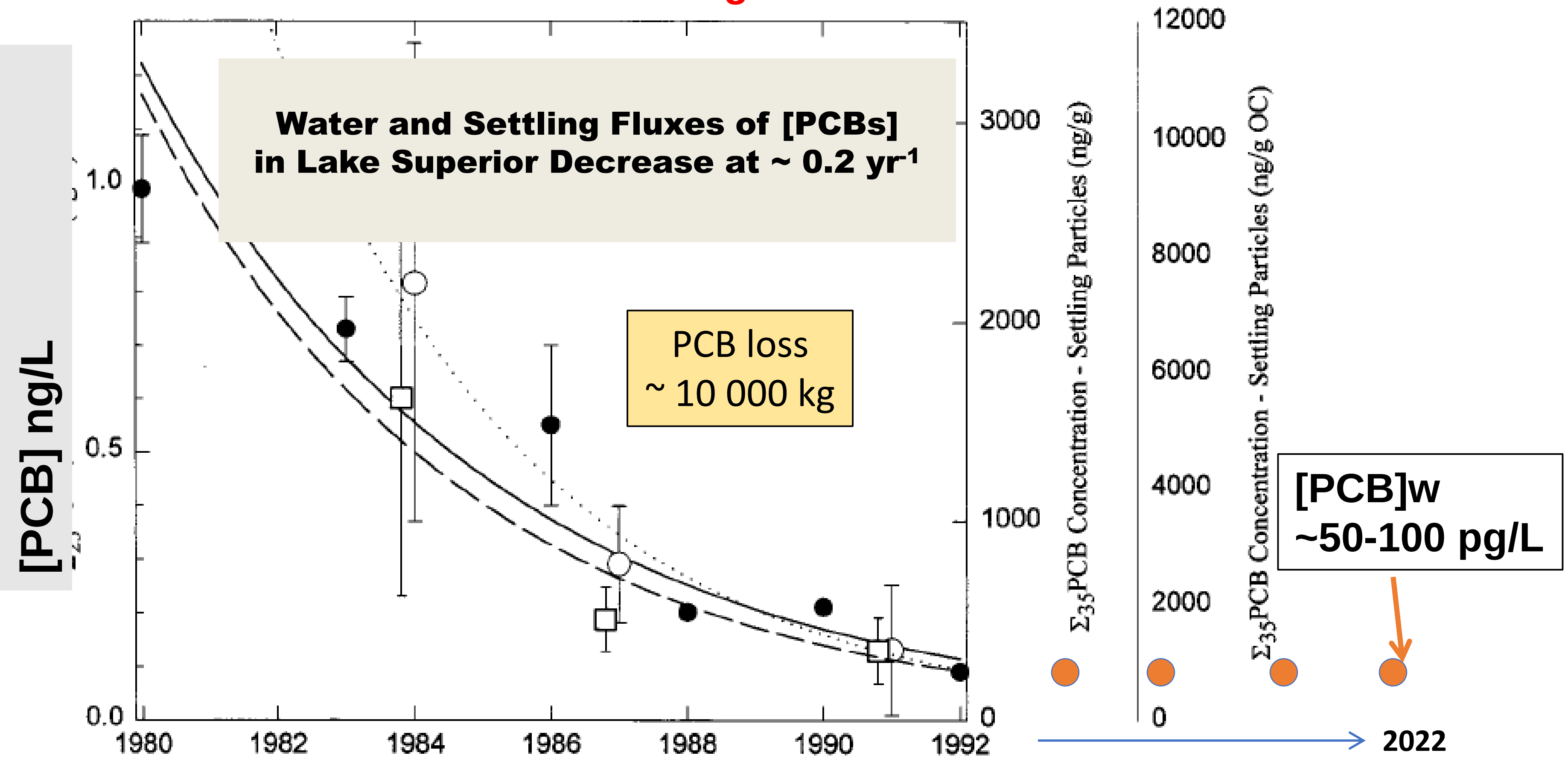
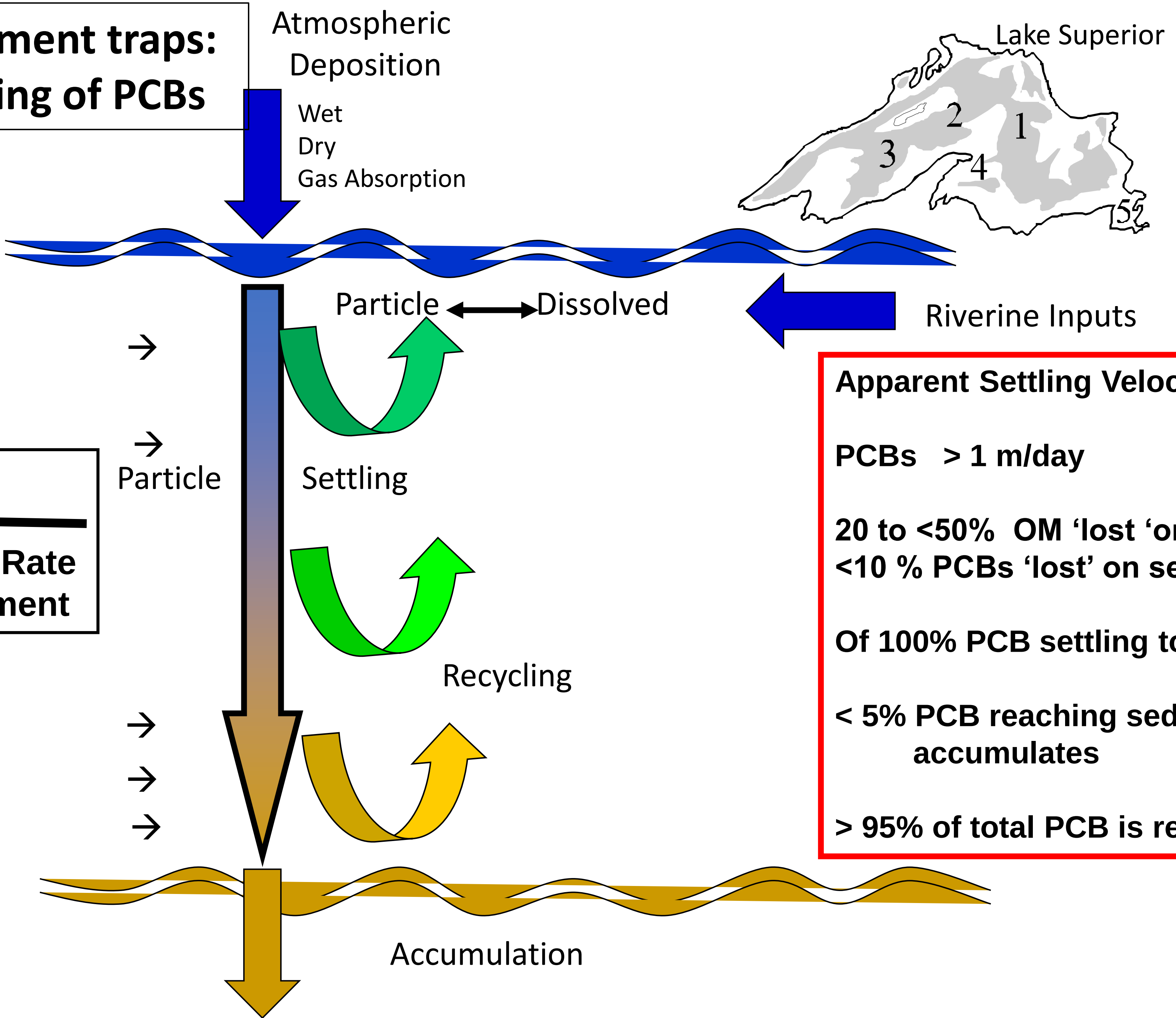


FIGURE 1. First-order PCB decrease in Lake Superior water (ref *20*; 25 congeners) and settling solids (35 congeners) collected from surface traps.

THUS → **$[PCB]_w$ ~100 pg/L; $[PCB]_a$ ~ 100 pg /m^3 : → Ratio ~ 10^{-3} → K_H 10^{-3}**
Water in near equilibrium with atmosphere PCB concentration (TODAY)

Jeremiason et al, *Environ. Sci. Technol.* **1998**, *32*, 3249−3256

Depolyment of sediment traps: Sedimentary Recycling of PCBs



$$RR = \frac{\text{Vertical Flux}}{\text{Accumulation Rate Surface Sediment}}$$

Apparent Settling Velocity(m/d)

PCBs > 1 m/day

20 to <50% OM 'lost 'on settling
<10 % PCBs 'lost' on settling

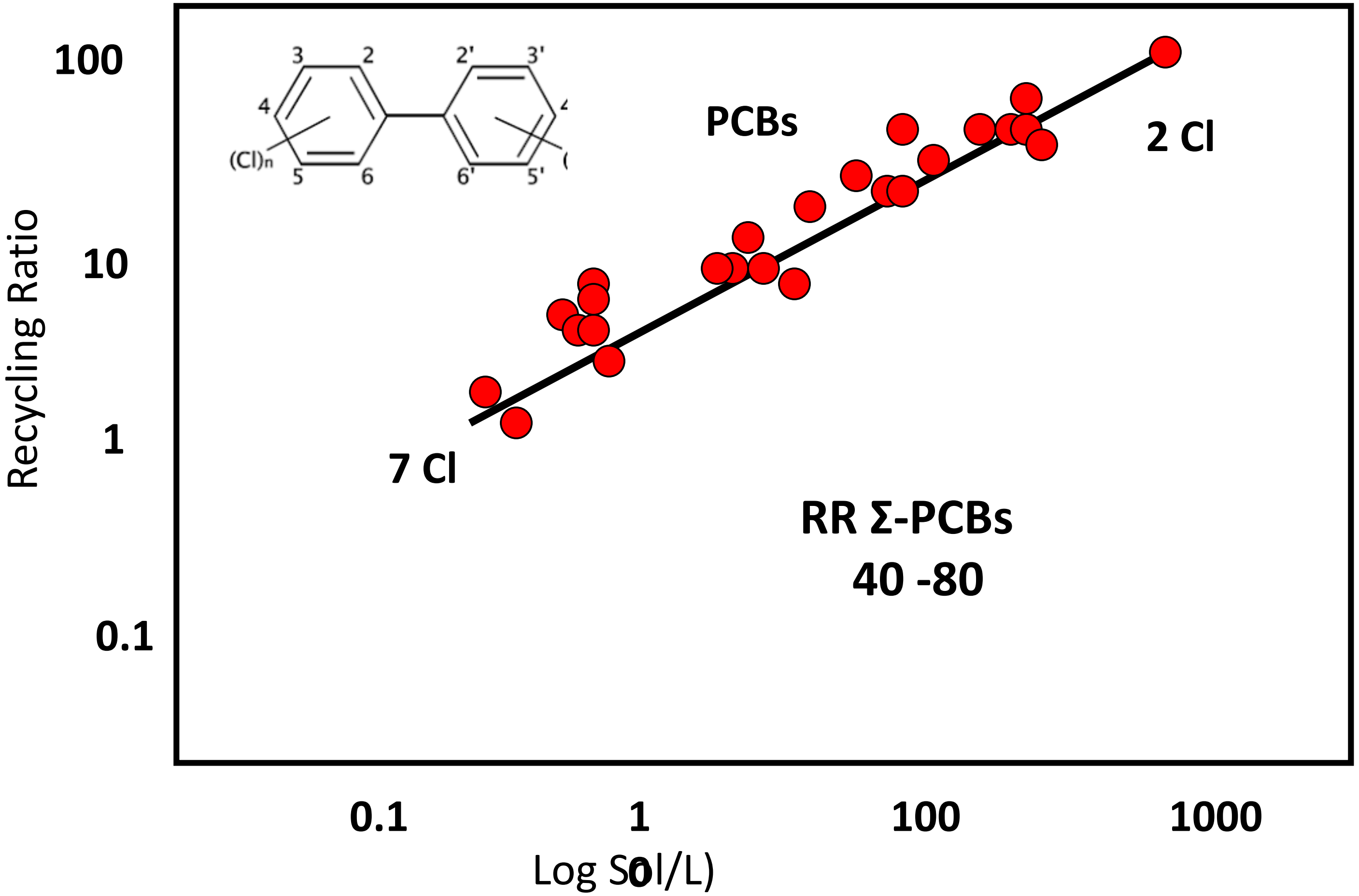
Of 100% PCB settling to sediment,

< 5% PCB reaching sediment accumulates

> 95% of total PCB is recycled

Recycling Ratio of PCBs and PAHs in Lake Superior

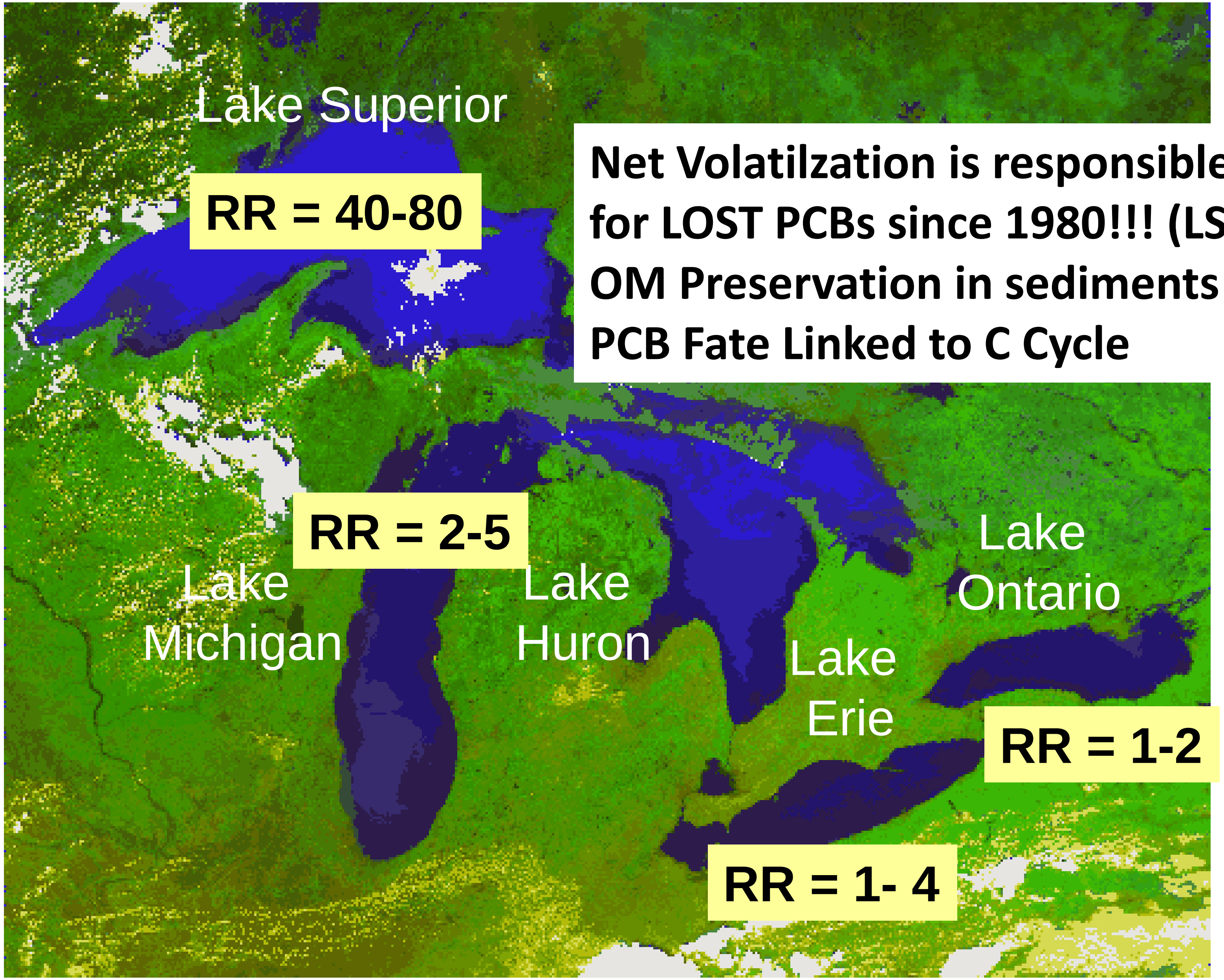
$$RR = F_{settling}/Accum_{sed}$$



Low Solubility

Baker et al., 1991
Jeremiason et al., 1998

Recycling Ratios of PCBs in Great Lakes Sediments

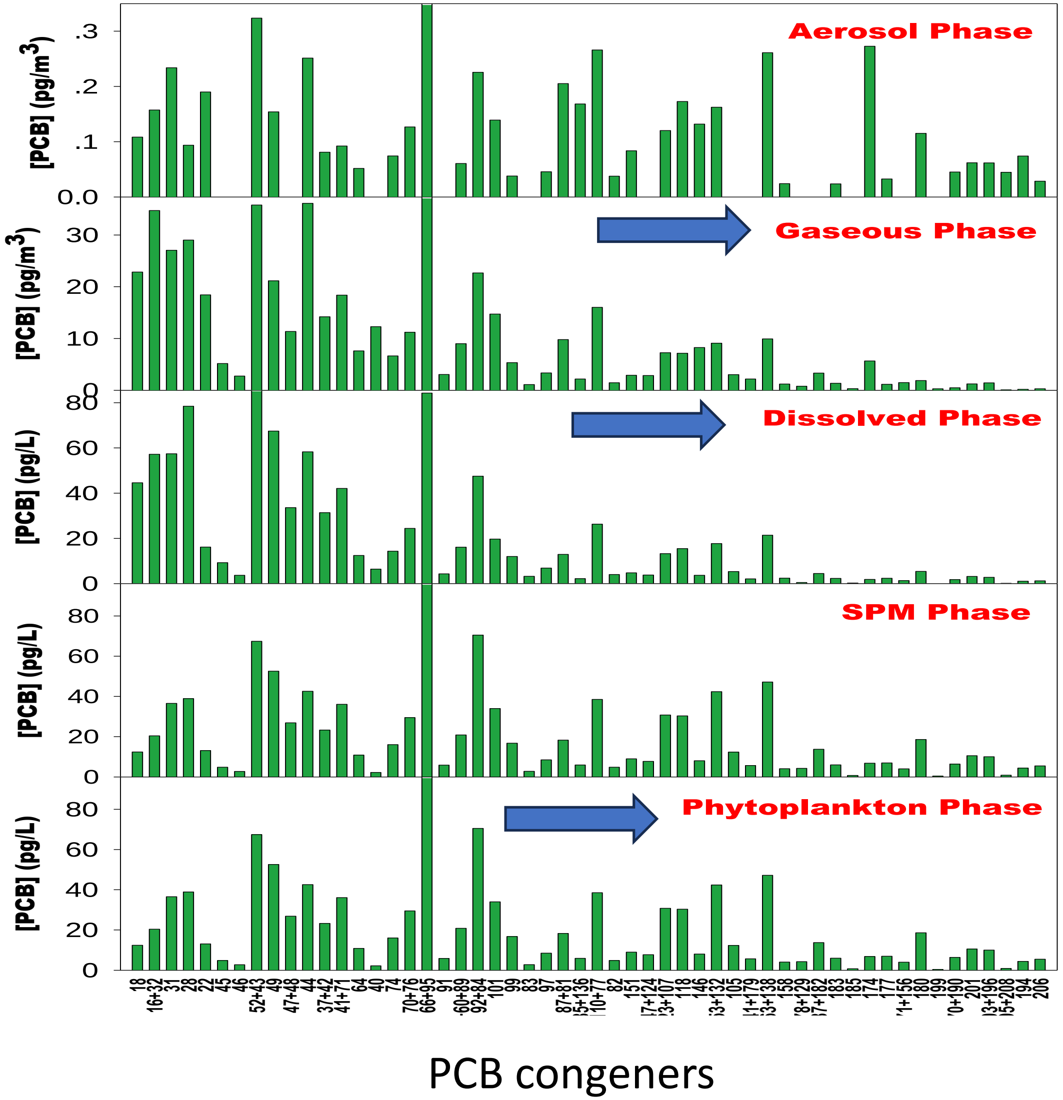


Net Volatilzation is responsible for LOST PCBs since 1980!!! (LS)
OM Preservation in sediments
PCB Fate Linked to C Cycle

Critical Observation:

Field Observation of PCBs in atmosphere above water, in dissolved phase and in phytoplankton

Example: Evidence for Gas-Phase Driven Phytoplankton accumulation of PCBs



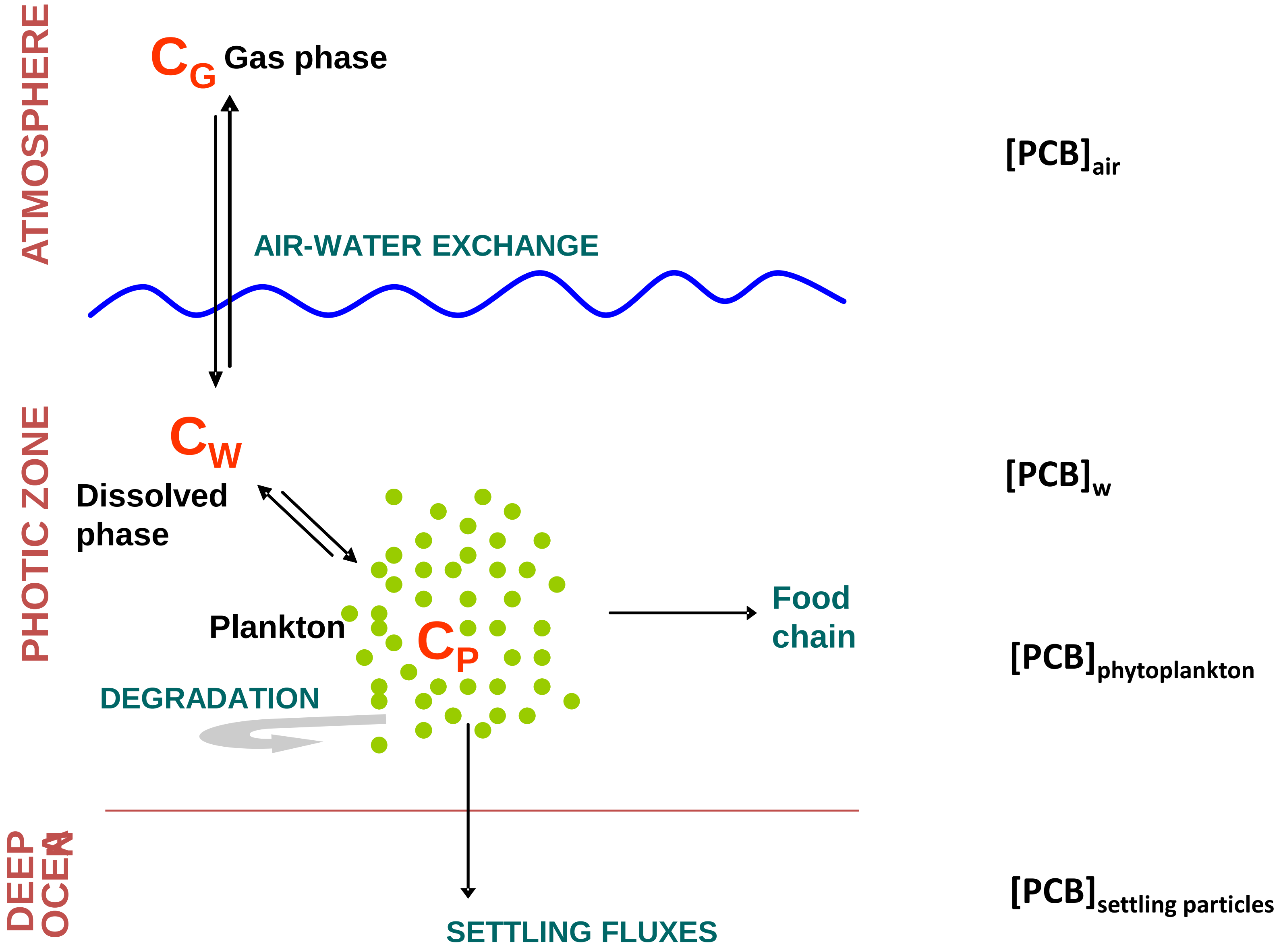
un-correlated

Correlated: $R^2 = 0.90$

Correlated: $R^2 = 0.70$

Correlated: $R^2 = 0.96$

Biological Carbon and PCB Pump
Air – Water - Phytoplankon



Air-Water-Phytoplankton Exchange of POPs

C_A

Air-water exchange

Implications:

- ***The biological PCB pump is responsible for entry of PCBs into <u>aquatic food chain</u> in world's oceans and many freshwaters.***
- ***The biological PCB pump is a main process for <u>loading and transport</u> atmospheric PCBs into the world's oceans and many freshwater systems.***
- ***The biological PCB pump (and subsequent ' particle settlng') controls the ecosystem Residence Time and delivery of PCBs to deep ocean waters and sediments***
- ***Primary Emissions vs Secondary emissions – need to greater focus on bio-physical-geo-chemical transfer processes as we transition from primary source emissions (global production) to secondary emissions***

$$k_{Sink} = F_{OM} \frac{k_u}{k_d + k_G}$$

At steady state, $F_{AW} = F_{WP} = F_{sink}$

J. Dachs, S.J. Eisenreich, J.E. Baker, F.C. Ko, J.D. Jeremiason. Coupling of phytoplankton uptake and air-wáter Exchange of POPs. 1999. *Environ. Sci. Technol*. 33, 3653-3660,.

J. Dachs, R. Lohmann, W. A. Ockenden, L. Méjanelle, S. J. Eisenreich and K. C. Jones. Oceanic biogeochemical controls on global dynamics of POPs., 2002, *Environ. Sci. Technol*. 36 :4229 –4237 .

Sediment cores from lakes, rivers and estuaries reveal temporal PCB inputs at basin and hemispheric scales

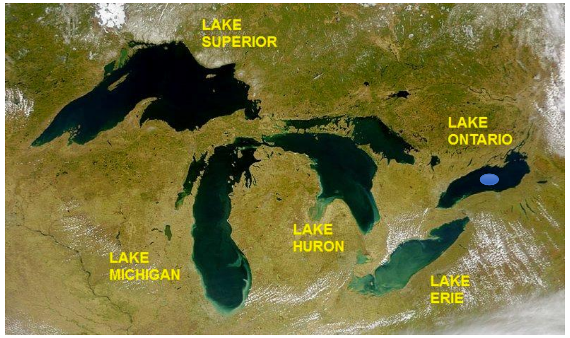
Locations of global aquatic sediment cores revealing temporal PCB profiles and comparison to production and emissions

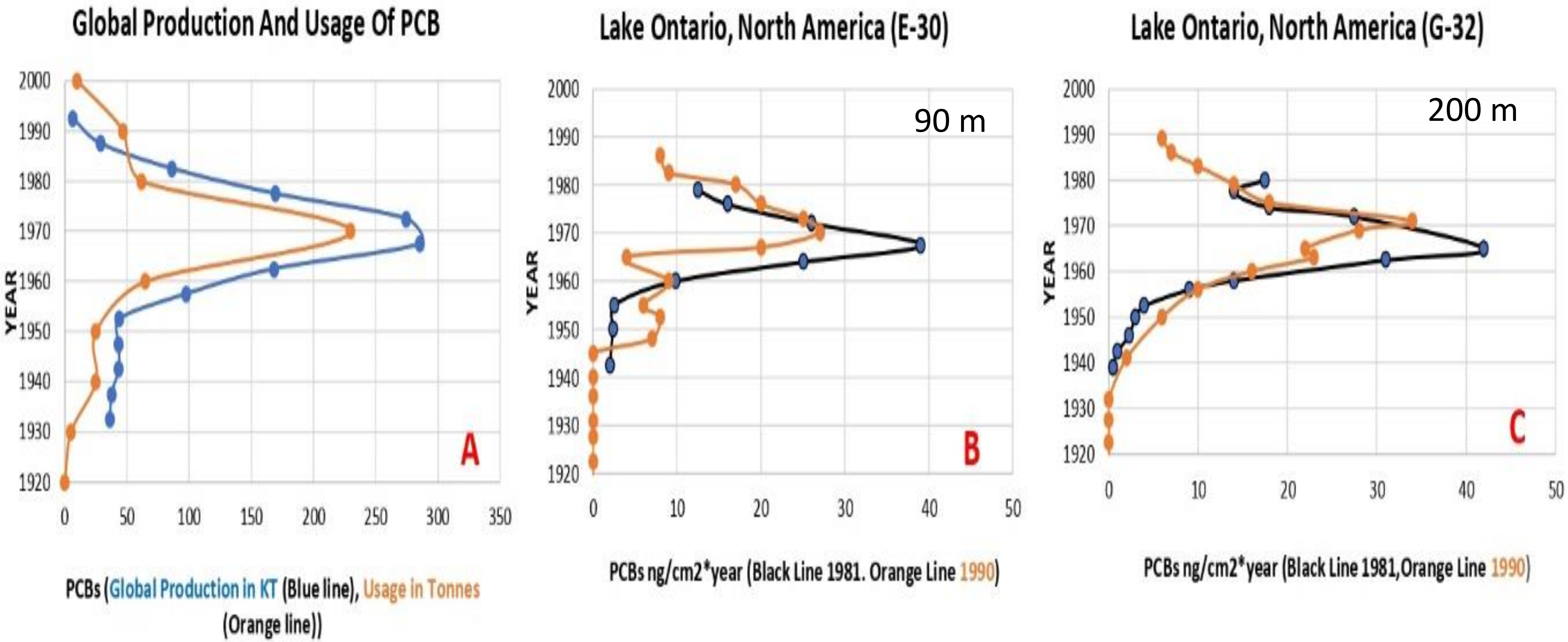
Majunder & Eisenreich, 2024

Criteria for core selection

1. Were the collections and sectioning of sediment cores described appropriately?
2. Were PCBs in sediment cores extracted and analyzed by the most appropriate analytical methodology?
3. Were the sediment cores dated with ^{210}Pb and/or ^{137}Cs?
4. Were PCB sediment profiles consistent with onset, peak and decrease in global PCB production/use/regulation?

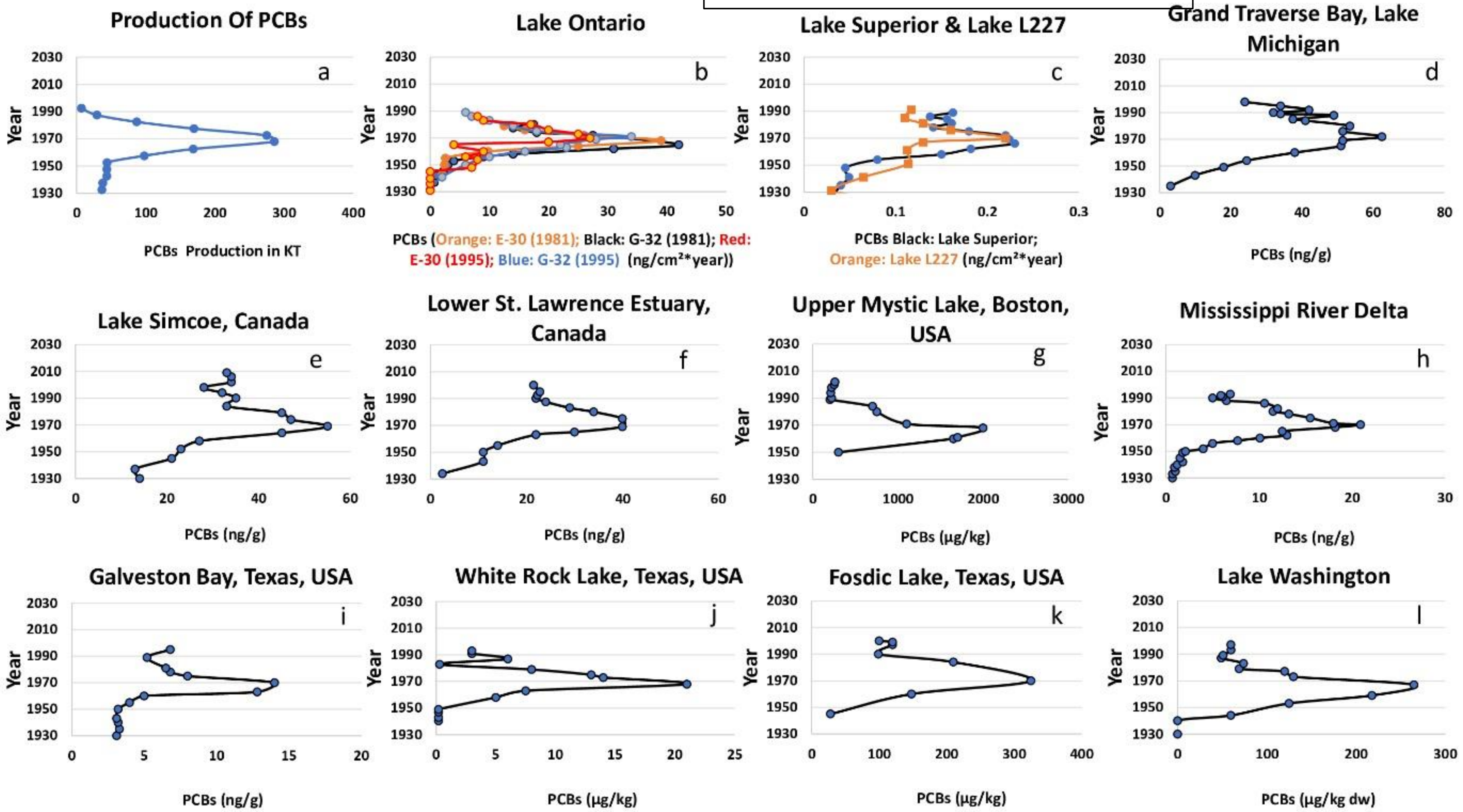
Our sediment story begins!



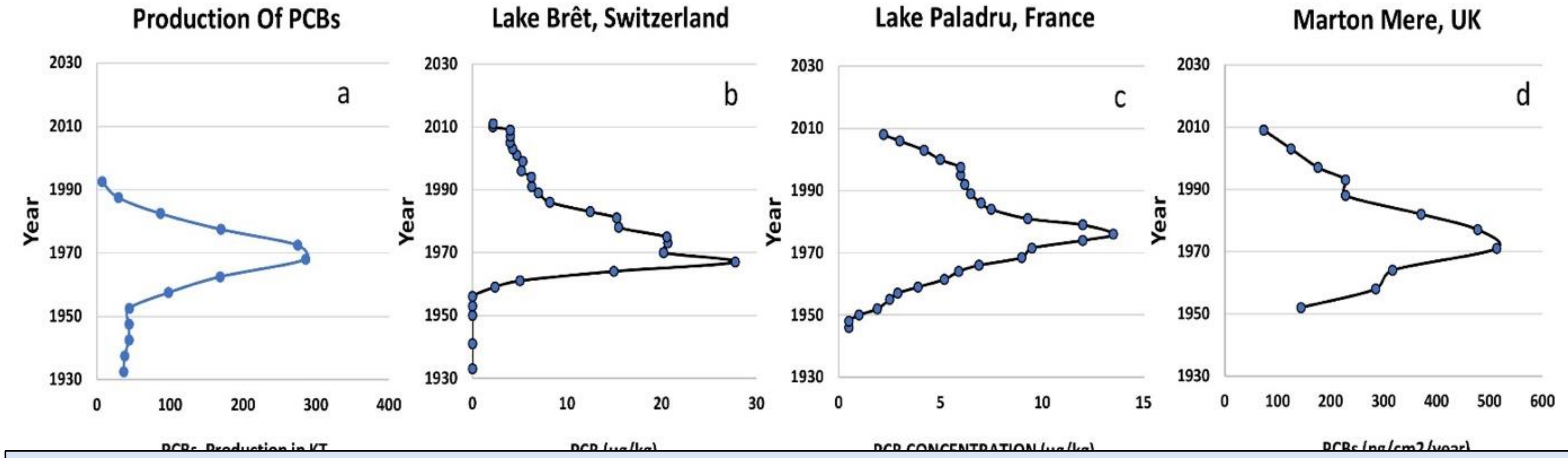


(A) Production/Use of PCBs (Breivik et al., 2002 a,b) and (B, C) sediment box cores from Lake Ontario (Eisenreich et al., 1989; Wong et al., 1995).

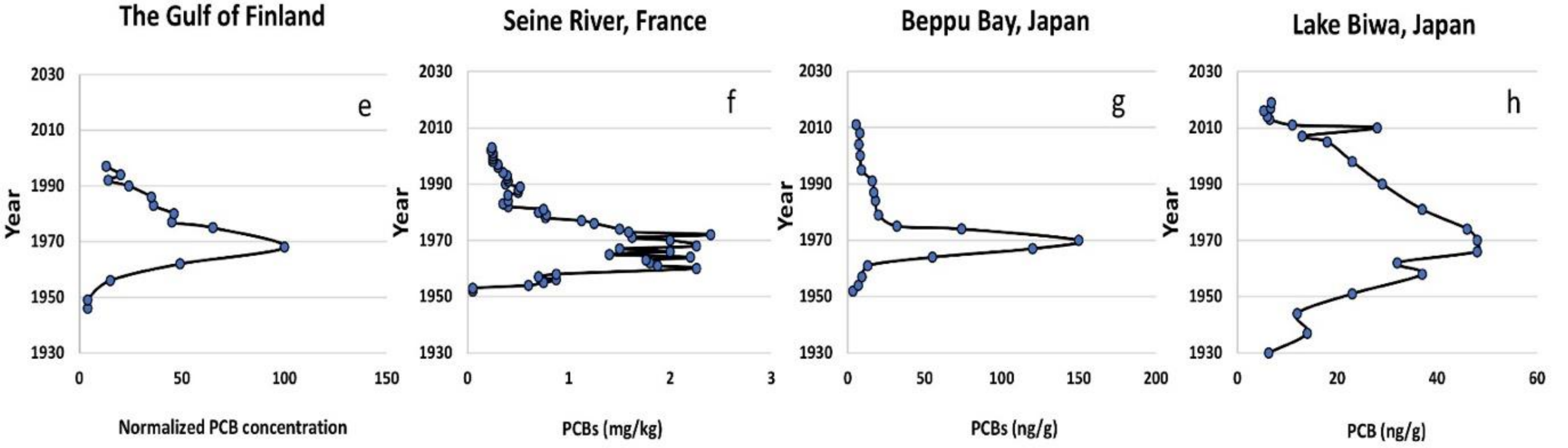
Candidate atmospheric signal



Synchronous signals of global Production of PCBs and PCBs in aquatic sediment cores from North America.

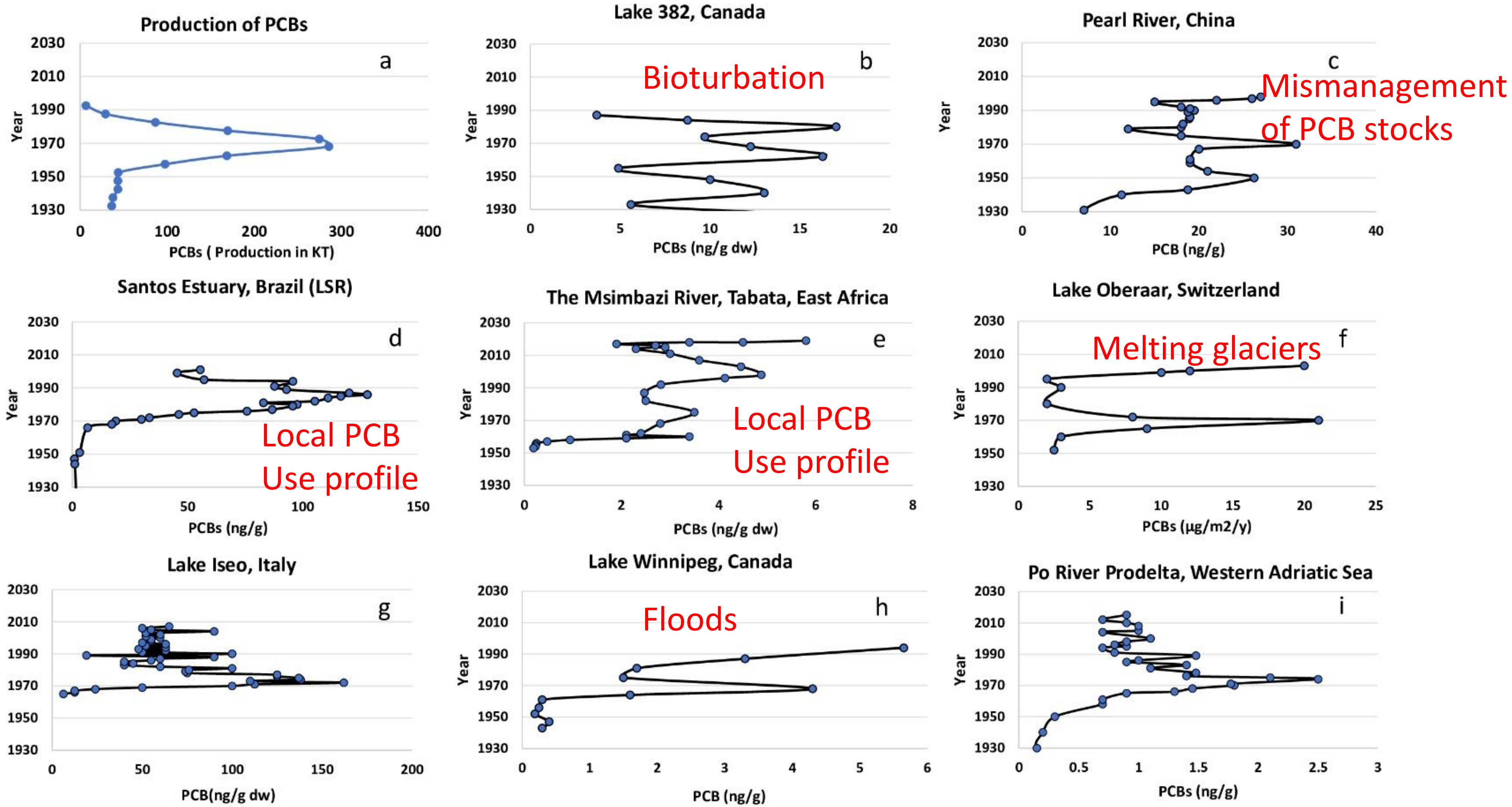


Sediment core profiles of PCBs reflect the temporal signal of global PCB production



Comparison of global production/use of PCBs and time-dependent PCB signals in selected aquatic sediment cores from Europe and beyond

Examples: Sediment Cores That Deviated From Production/Emission Profiles



Comparison between the production of PCBs and 'deviating' cores (a) Production of PCBs (Breivik et al., 2002a) (b) Lake 382, Canada (Derek C. G. Muir et al., 1996) ; (c) Pearl River Delta, China (Mai et al., 2005b); (d) Santos Estuary, Brazil (de Souza et al., 2018); (e) The Msimbazi River, Tabata, East Africa (Nipen et al., 2022); (f) Lake Oberaar, Switzerland (Bogdal et al., 2009); (g) Lake Iseo, Italy (Roberta Bettinetti et al., 2011); (h) Lake Winnipeg, Canada (Rawn et al., 2000b); (i) Po River Pro-delta, Western Adriatic Sea (Combi et al., 2020).

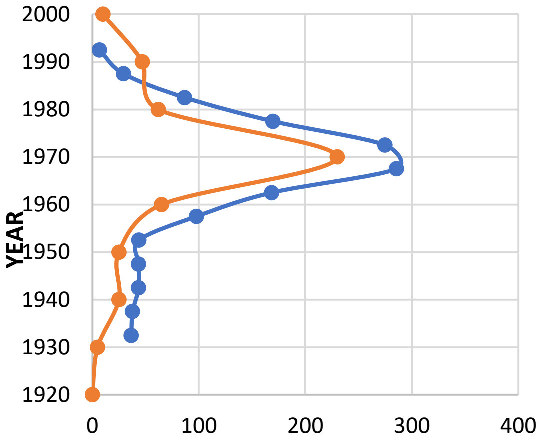
Examples: Sediment Cores That Deviated From Production/Emission

What we really need is an atmospheric signal of PCB input

<u>Some reasons for Deviation:</u>

- Non depositional area
- Bioturbation/internal mobilization
- Glacial melting
- River Basin Floods
- Mismanagement of PCBs (leakage)
- Illegal discharges
- Different (later) 'local' use & emission pattern

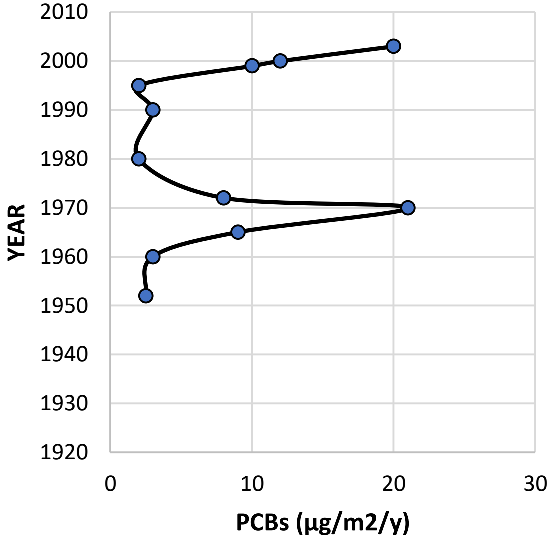
Global Production And Primary Emission Of PCB



PCBs (Global Production in KT (Blue line), Primary Emission in Tonnes (Orange line))

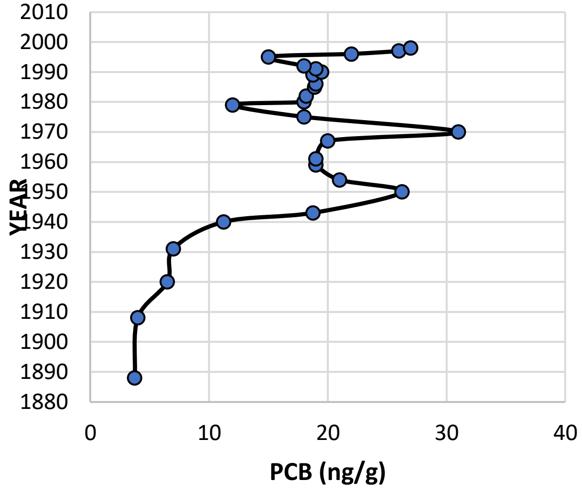
Melting of Glaciers under warming climate

Lake Oberaar, Switzerland



...nagement and Leakage of PCB Stocks

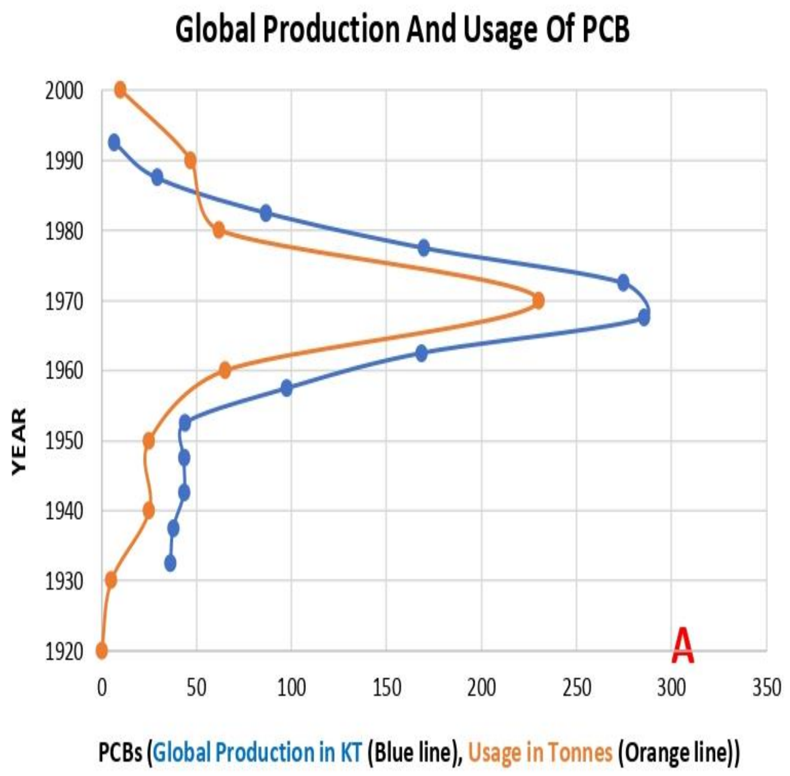
Pearl River, China



Lake Oberaar, Switzerland
Oberaarsee, near Grimsel

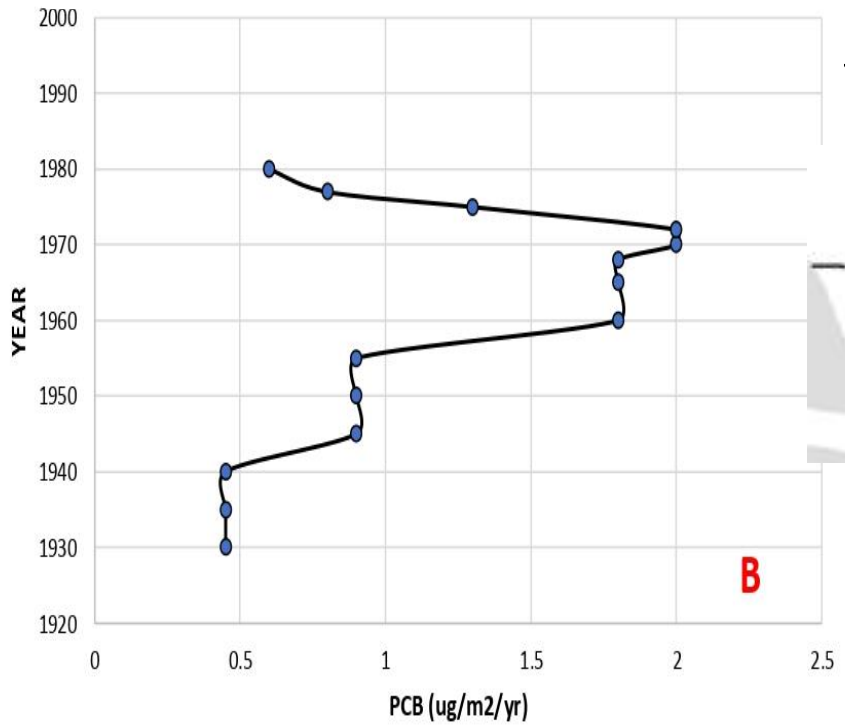
(Bogdal et al., 2009; Huo et al., 2017)

Primary Sources



Secondary Sources
- mobilisation from sources, soils and water bodies -

Ombrotrophic bogs – Atmospheric signal
(Rapaport & Eisenreich, 1988)



Wetlands across northern Great Lakes

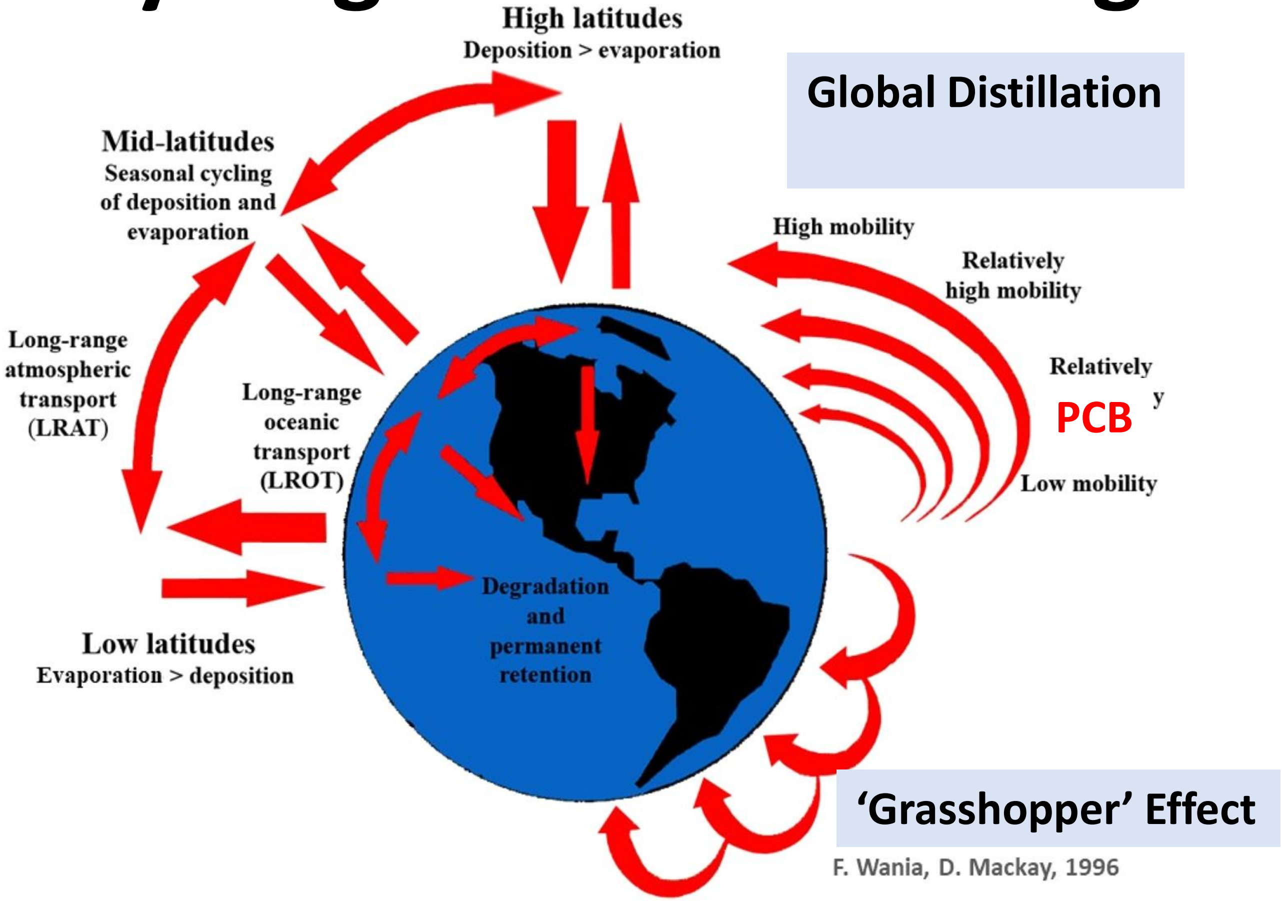
Mitsch and Hernandez, 2013

PCB Global production and primary emissions have synchronous sediment and peat (atmospheric) profile

Global PCB Production – Lake Sediment cores – ombrotrophic (atmospheric) signals are synchronous!

Onset – acceleration in 1950's – peak at ~ 1970 – decrease to low present-day

Global Cycling of Persistant Organic Pollutants



Global cycling of POPs (after Wania and Mackay 1996, adapted by Schuster, 2008).

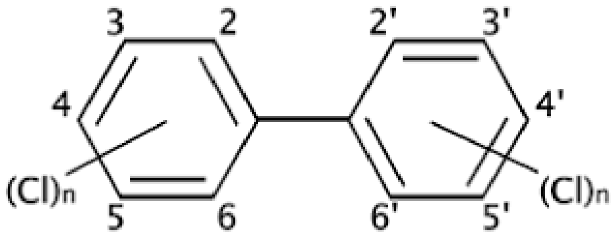
Production → Use → Emission → Transport → Deposition → Accumulation

is *remarkably fast and efficient* in distributing PCBs

10's -100's kms distance → primary emissions

100's –1000 kms/elevations → secondary emissions (remobilization of PCBs from environmental reservoirs)

Key Messages on on PCBs - what we know



A *must* read: K.C. Jones. Persistent Organic Pollutants (POPs) and Related Chemicals in the Global Environment: Some Personal Reflections. Environ. Sci. Technol. 2021, 55, 9400–9412.

Knowledge of P-C Properties and Environmental Processes are critical to understanding PCB cycling in environment.

Time from PCB production → emission → transport → deposition →accumulation in environment is 'fast'.

Aquatic Cycle of PCBs is intimately lined to the C Cycle (role of trophic interactions).
(OM preservation in sediments is a requirement of PCB retention in water bodies).

PCB concentrations are decreasing worldwide at ~ 10-20% per year in atmosphere and aquatic systems.

Air –water – phytoplankton exchange is a major or dominant global process. A-W Exchange is major transport process.

Atmospheric PCBs are near 'equilibrium' with marine systems and many inland water bodies.

Present-day PCB emissions are still dominated by primary emissions (use, disposal, accidents).

PCB emissions are largely linked to urban-industrial areas (primary emissions).

Global reservoirs: 75% in ocean sediments; 6% in ocean reservoirs; 3% in terrestrial reservoir; 13% - degradation (ocean, atm)

Transition of PCB emissions from primary to secondary sources requires focus on bio-physical-geo-chemical processes.

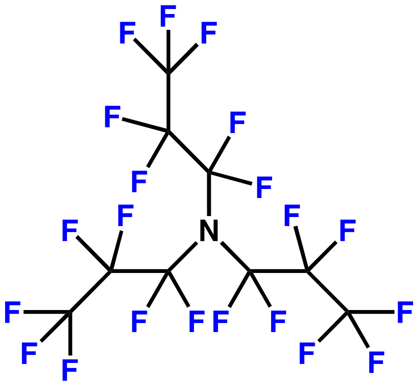
Anthropogenic climate change likely mobilizes PCB deposits from soils and water (e.g., Increased T, floods, melting glaciers)

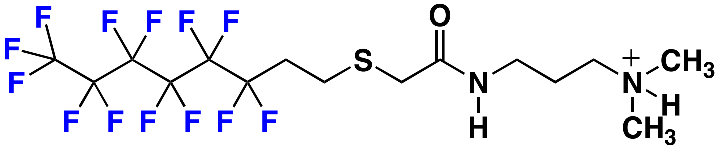
'Non-Aroclor' PCB emissions today are high and implications not well known.

Thank you!

Σας ευχαριστώ!

“PFAS Today …What Have We Learned So Far?”





Scott Mabury
Department of Chemistry
University of Toronto

"Small Polyfluorinated Organics"

Anthropogenic 'small organofluorines'

Aluminum Production: CF_4 (82), CF_3CF_3 (3) [0.75 and 0.11 kg/ton of Al]
Freons: $CFCl_3$ (267), CF_2Cl_2 (535), $CF_2ClCFCl_2$ (85)
HCFC: CF_3CFH_2 (12), CHF_2Cl (145), CH_3CF_2Cl (15)
HFCs: CF_3CHFCF_3, $CF_3CHFCHFCF_2CF_3$, $CH_2FCF_2CHF_2$

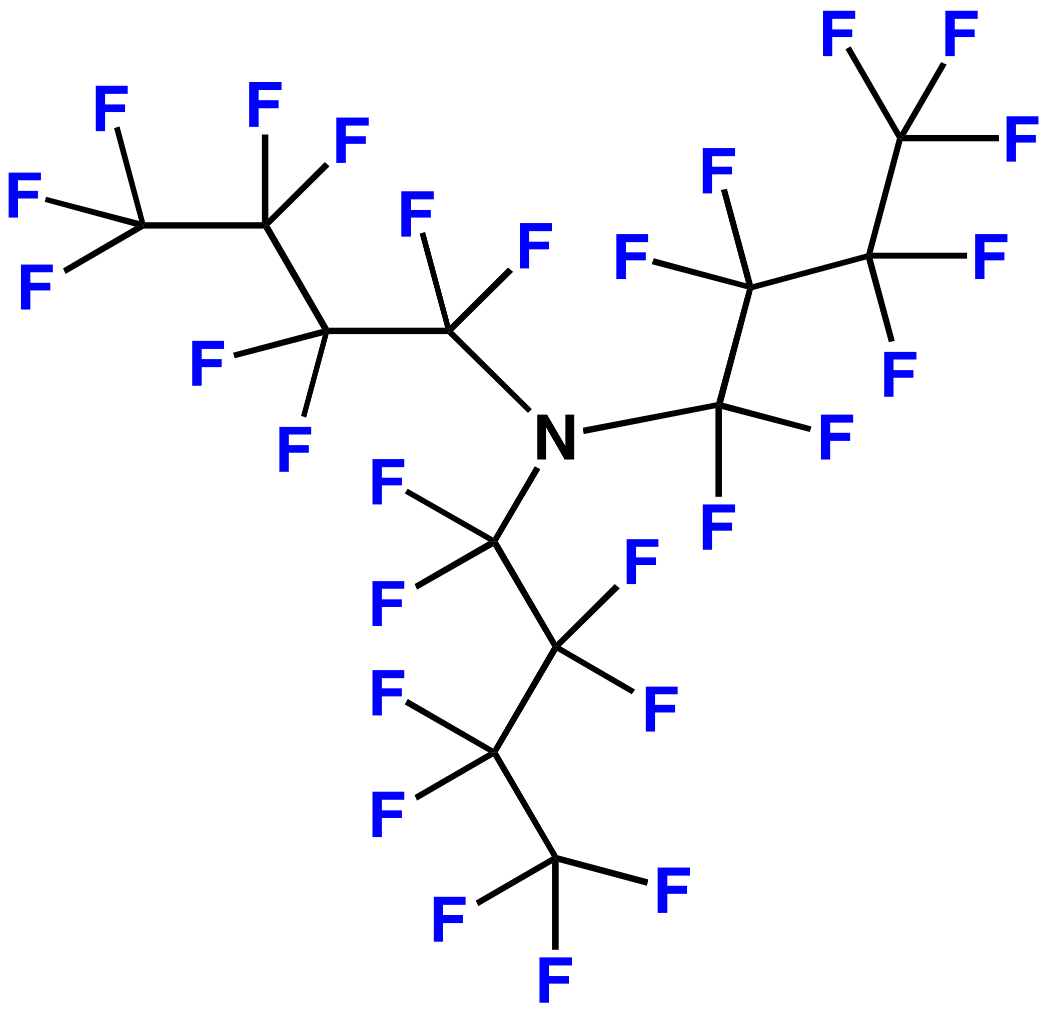
Note: numbers in (x) reflect atmospheric concentration pptv;

IPCC Climate Change 2001: The Scientific Basis

Natural Sources as well?

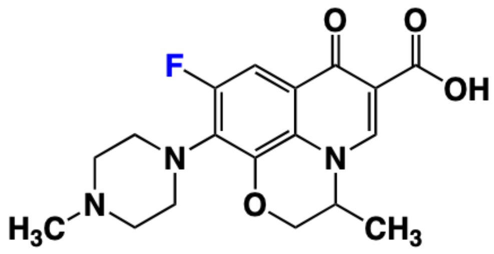
CF_4, CF_2Cl_2, $CFCl_3$, CF_3Cl, CHF_3, $CF_2{=}CF_2$ (fluorite)[1]....
$CFCl_3$, CF_2Cl_2, $CF_2{=}CF_2$, CHF_2Cl, $CHFCl_2$, CCl_2FCClF_2 (volcanoes)[2]...
CF_3COOH ....estimate of 268 million tons in the world's oceans[3]; (ocean vents[4])

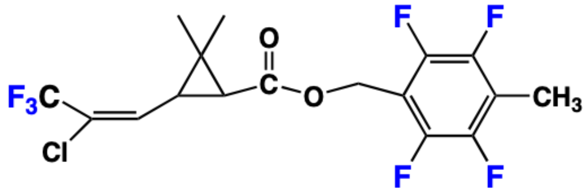
1) Harnisch & Eisenhauer, 1998; Harnischs et al, 2000.
2) Isidorov et al 1990; Isidorov, 1990.
3) Frank et al, 2002
4) Scott et al, 2005

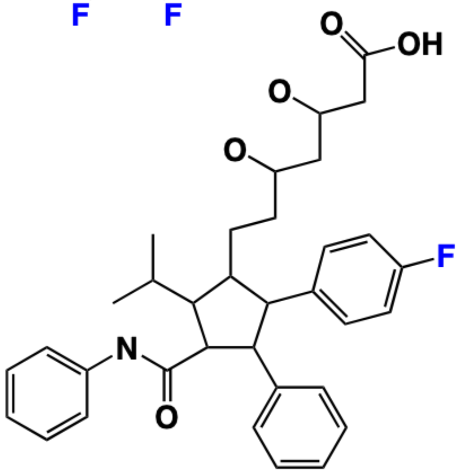


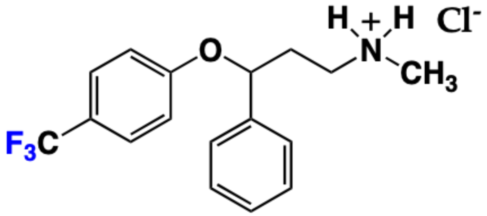
Hong, AC, CJ Young, MD Hurley, TJ Wallington, & SA Mabury. 2013. Perfluorobutyl amine: A Novel Long-Lived Greenhouse Gas. *Geophys Res Letters.* **40:6010-6015.**

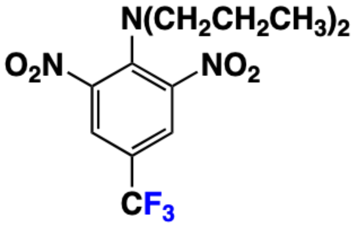
Pesticides and Pharmaceuticals…

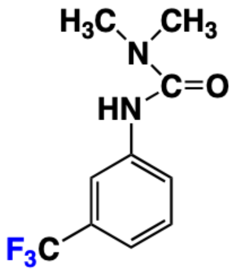


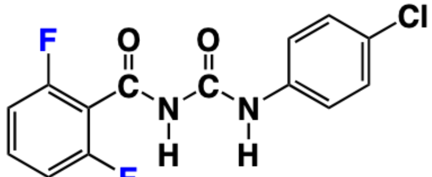


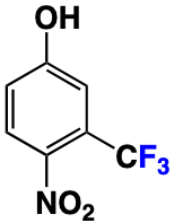


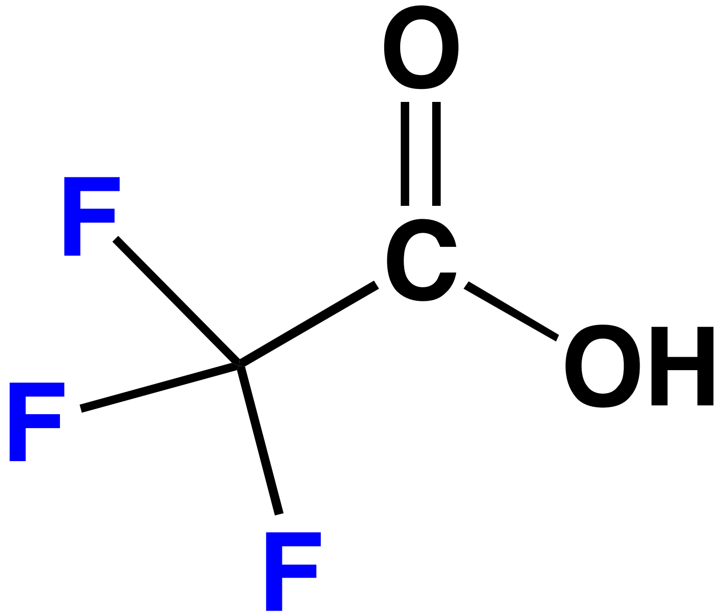








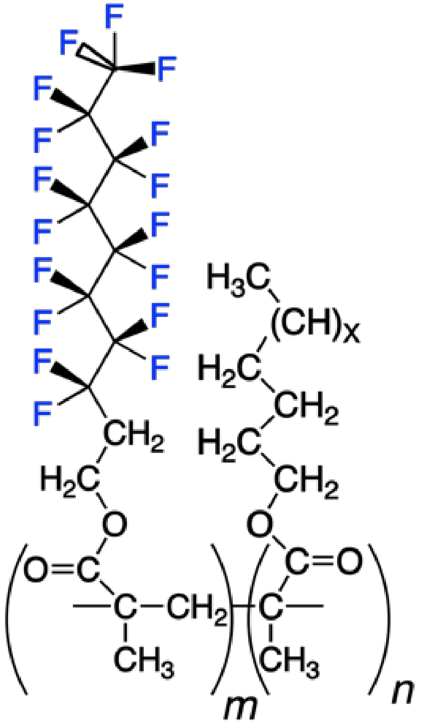




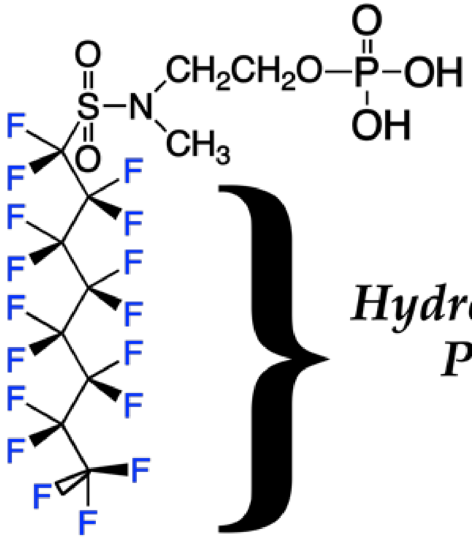
TFA

Do these "common" fluorinated polymers & surfactants contribute?

Hydro & Lipo-Phobic



Polymer (Ester)



Hydro & Lipo-Phobic

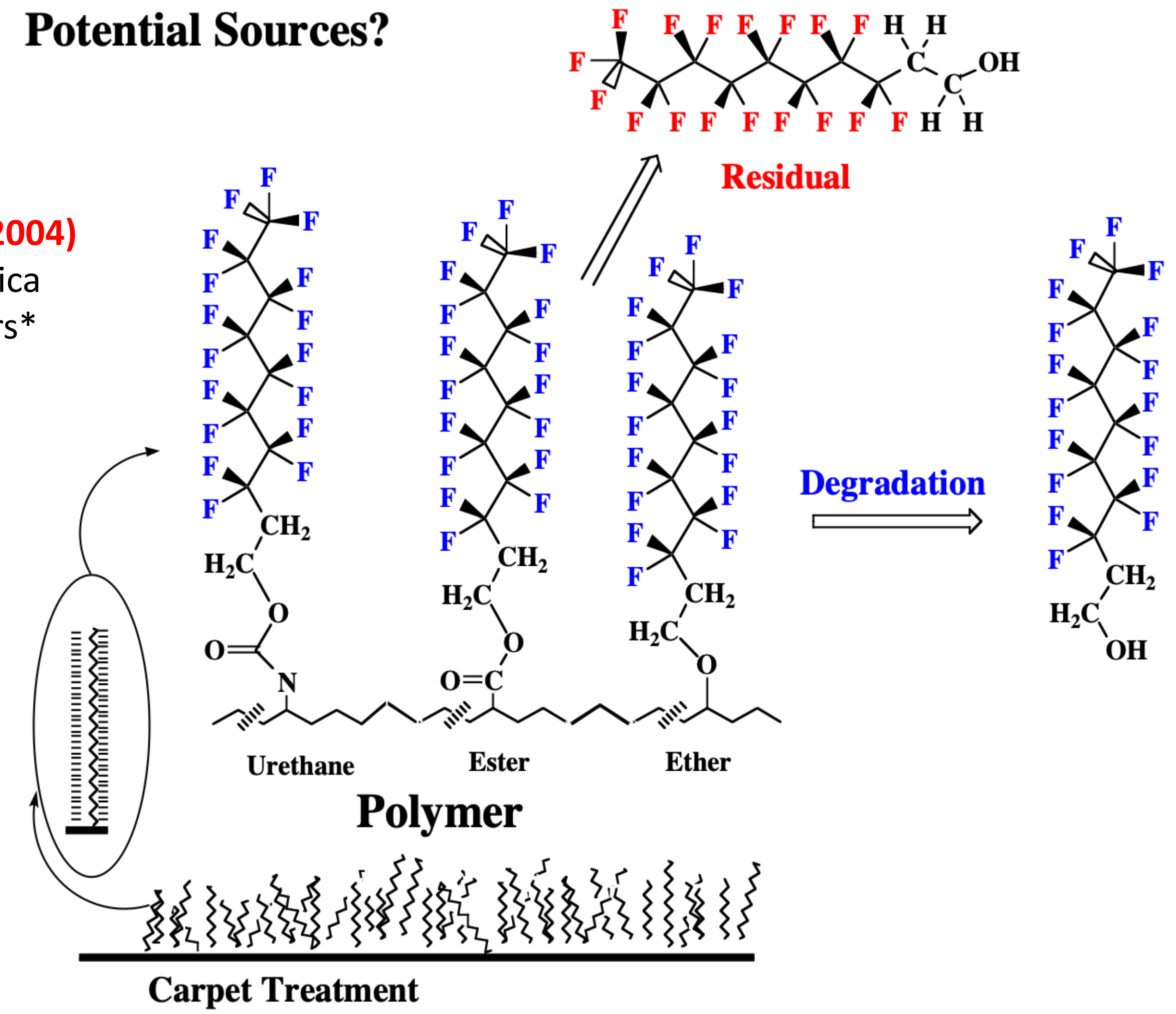
Surfactants (Phosphate)

Fluoro alcohols ~ Fugitive Emissions from Residual Material OR Does the Linkage Chemistry Break?

11 to 14 x10⁶ kg/yr (2004)

40% in North America

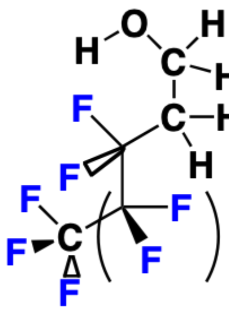
80% are in polymers*



*Dupont Presentation to
USEPA OPPT. Jan 31, 2005
US Public Docket AR226-1914

Residuals could be important source of fluoroalcohols
...to the atmosphere

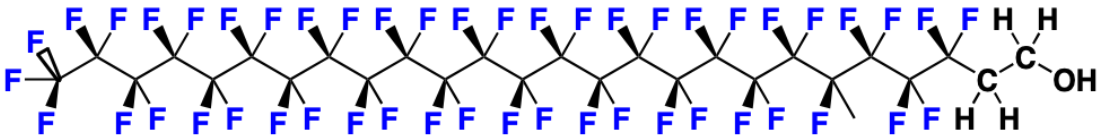
Fluorinated Material	Dry Weight % Residual
Polyfox-L-Diol	0.11 (0.03)
Teflon™ Advance	0.34 (0.20)
Zonyl™ FSO 100	1.03 (0.61)
Zonyl™ FSE	3.80 (1.09)
8:2 Methacrylate Monomer	0.04 (0.01)
Motomaster™ Windshield Washer Fluid w/ Teflon	0.36 (0.01)
Scotchgard™ Rug and Carpet Protector*	0.39 (0.06)



FTOH

n=3 or 6

Dinglasan, MJA and SA Mabury. 2005. *Environ. Sci. Technol.* **In review**

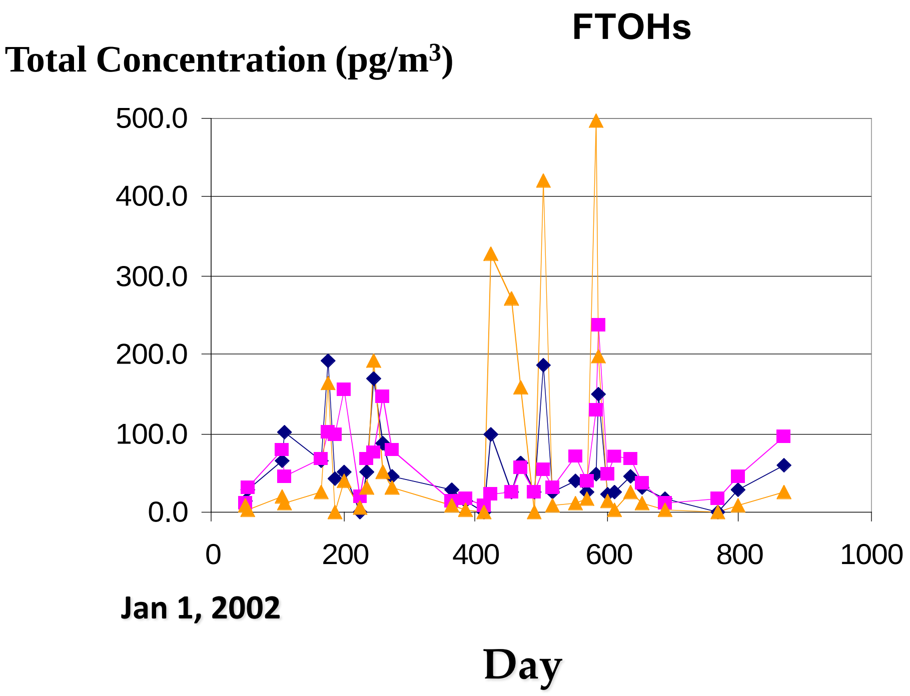


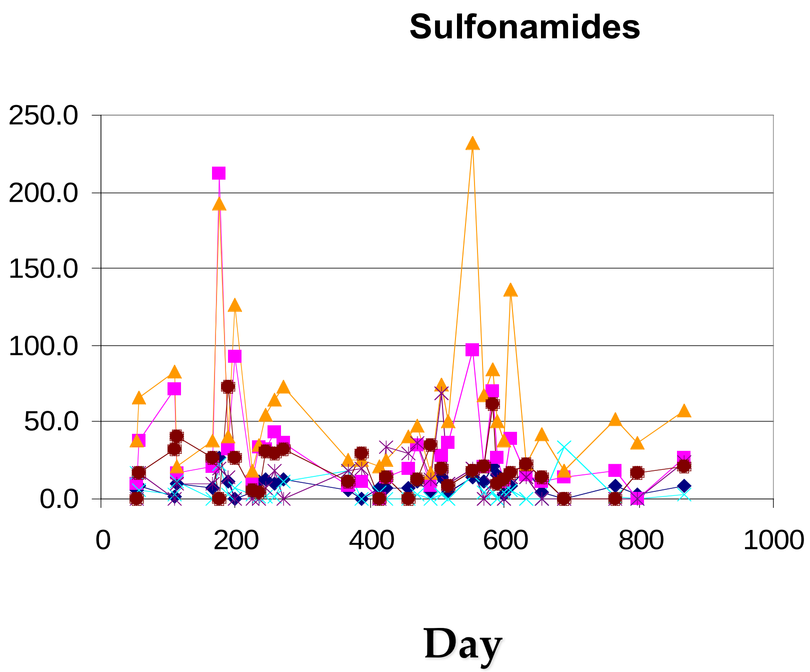
24:2 FTOH
"49 Fluorines"

Tentatively identified in a telomer phosphate mixture via GC/MS;

Are Fluorinated Precursors in the Air?

Fluoroalcohol Trends in Toronto ~ long term monitoring





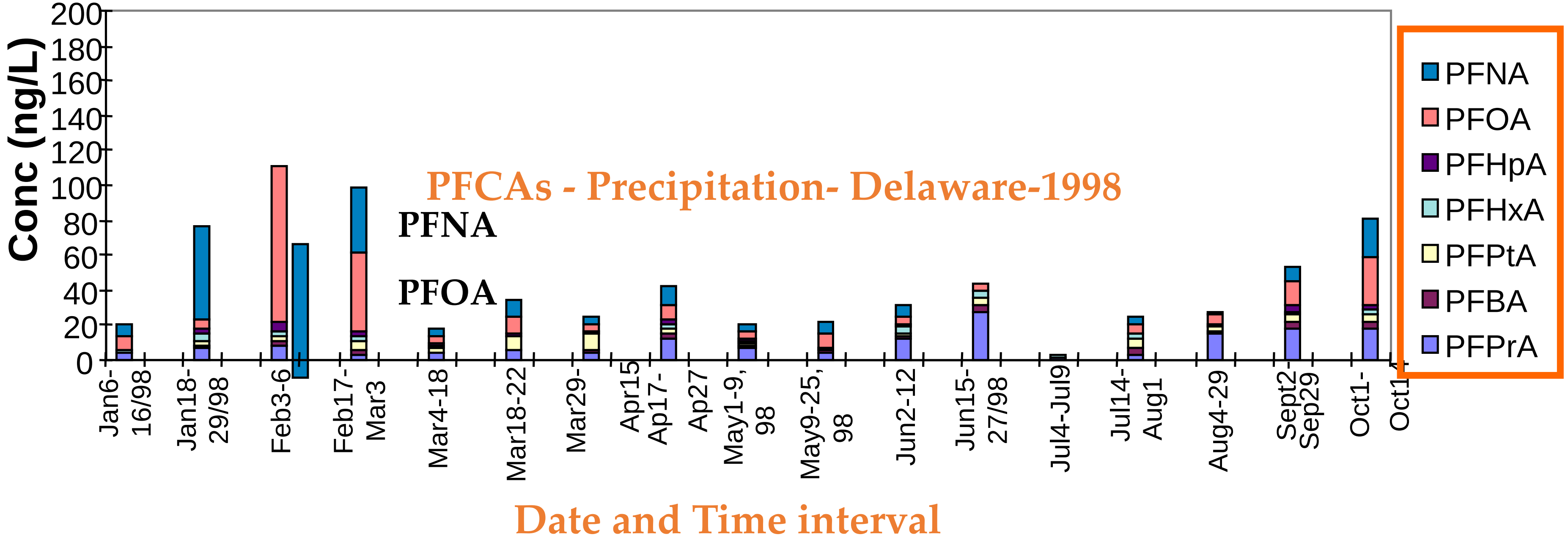
Published data, May-June/Nov 2001 air samples: FTOHs 100 to 350 pg/m^3;
Sulfonamidoethanols: 30 to 500 pg/m^3

Martin, JW., D.C.G. Muir, W.C. Kwan, C.A. Moody, K.R. Solomon, and S.A. Mabury. 2002. Collection of Airborne Fluorinated Organics and Analysis by Gas Chromatography-Chemical Ionization-Mass Spectrometry. *Anal. Chem.* . **74:**584-590**.**

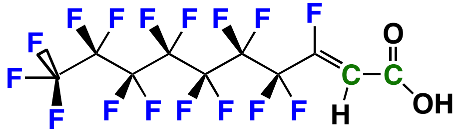
Stock, NL, FK Lau, DA Ellis, JW Martin, DCG Muir, and SA Mabury. 2004. Polyfluorinated Alcohols and Amides in the North American Troposphere. *Envion. Sci. Technol.* **38**:991-996.

Are PFCAs in Rain?

1 ng/L = 250 t across Northern Hemisphere
Equivalent to annual industrial production of PFOA



Also observed FTCA & FTUCAs



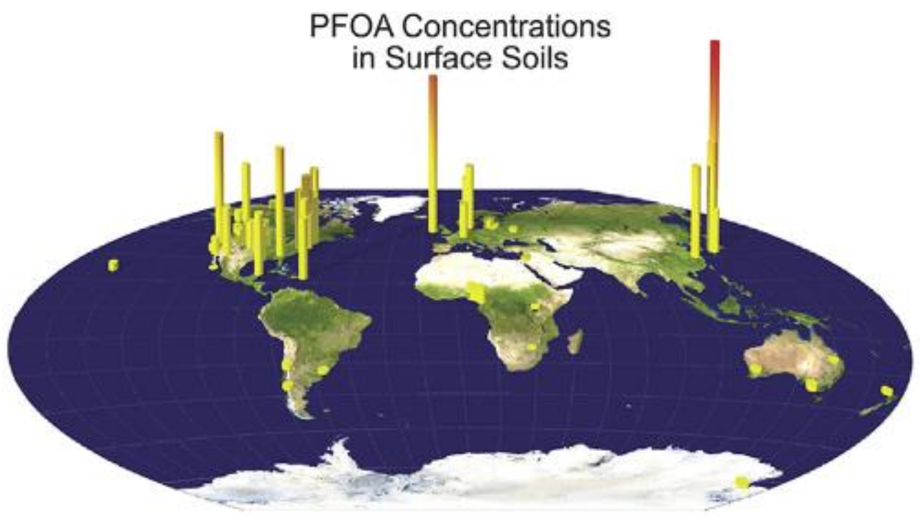
Scott, BF, C. Spencer, SA Mabury, DCG Muir. **2006**. Per and Polyfluorinated Acids in the North American Atmosphere. *Environ. Sci. Technol.* **40:**7167-7174.

Background PFAS in soils

Table 1
Continental PFAS concentration ranges in pg/g dry weight with the continental geometric mean in parentheses.

Continent	ΣPFCA	ΣPFSA
North America (NA) (n = 33)[a]	145–6080 (1820)	35–1990 (410)
Europe (EU) (n = 10)	55–3640 (1000)	<LOD-3270 (808)
Asia (AS) (n = 6)	129–14300 (4710)	79–421 (183)
Africa (AF) (n = 5)	124–1490 (548)	<LOD-144 (67)
Australia (AU) (n = 4)	79–1260 (673)	44–297 (154)
South America (SA) (n = 3)	29–319 (138)	26–48 (36)
Antarctica (AN) (n = 1)	191	7

[a] Includes a sample from Waimea, Hawaii (NA19).



Rankin, K., Mabury, S. A., Jenkins, T. M. & Washington, J. W. A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence. Chemosphere 161, 333–341 (2016).

Biosolid Results – Detected

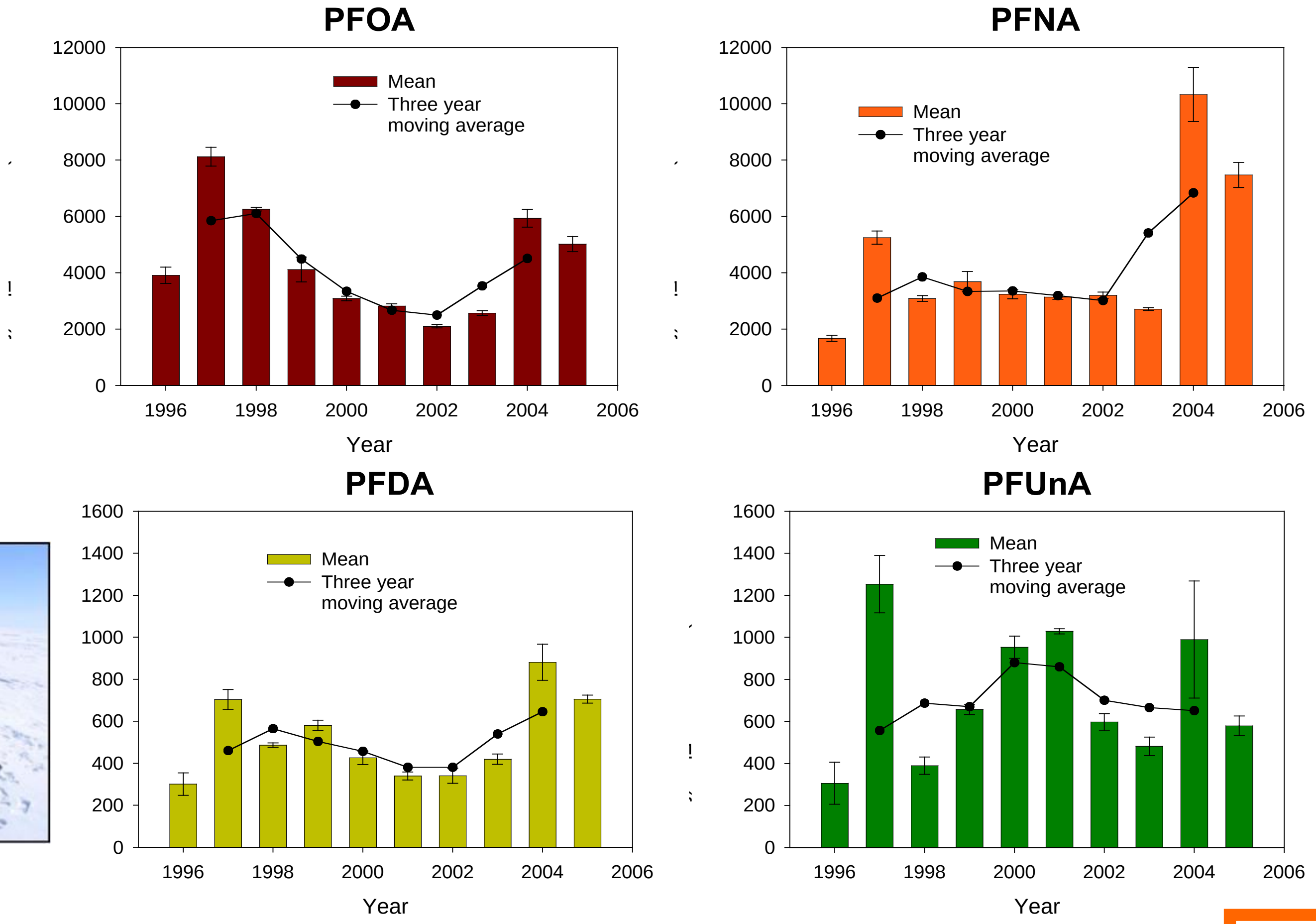
	LOD (ng/g biosolid)	LOQ (ng/g biosolid)	**Biosolid Amended Soil (ng/g)**	**Not-Biosolid Ammended Soil (ng/g)**	Rankin, et al. (2016). **NA Background Soils** (Range) (ng/g)	Gerwurtz, Bradley et al. (2018) **Canadian Great Lakes Precipitation,** (Median) (ng/g)
PFBA	0.067	0.224	<LOD - 2.76	<LOD - 1.79	N/A	0.00093
PFPeA	0.131	0.438	<LOD - LOQ	<LOD	N/A	<RL
PFHxA	0.124	0.414	<LOD - <LOQ	<LOD - <LOQ	0.0323 - 1.986	0.00023
PFOA	0.056	0.186	0.37 - 0.94	0.26 - 0.62	0.0217 - 1.838	0.00046
PFNA	0.091	0.304	<LOD - 0.32	<LOD - <LOQ	0.0148 - 1.000	0.00030
PFDA	0.158	0.528	<LOD - <LOQ	<LOD	0.0047 - 0.8804	0.00015
PFOS	0.096	0.323	<LOD - 1.41	<LOD - 1.84	0.0181 - 1.956	0.00039
6:2FTS	0.022	0.075	<LOD - 0.17	<LOD - 0.268	N/A	N/A

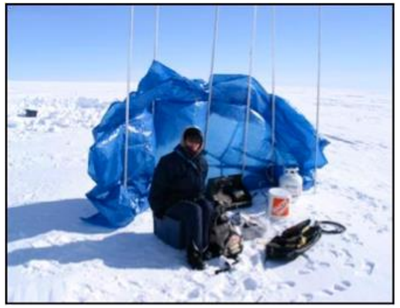
* <RL is reported for non-detectable concentrations.

The LOD represents the lowest concentration of the chemical that can be detected by the method. The LOQ represents the lowest concentration that can be quantified with confidence by the method.

PFA Flux to Arctic (Devon Ice Cap)

Flux
ng/cm²



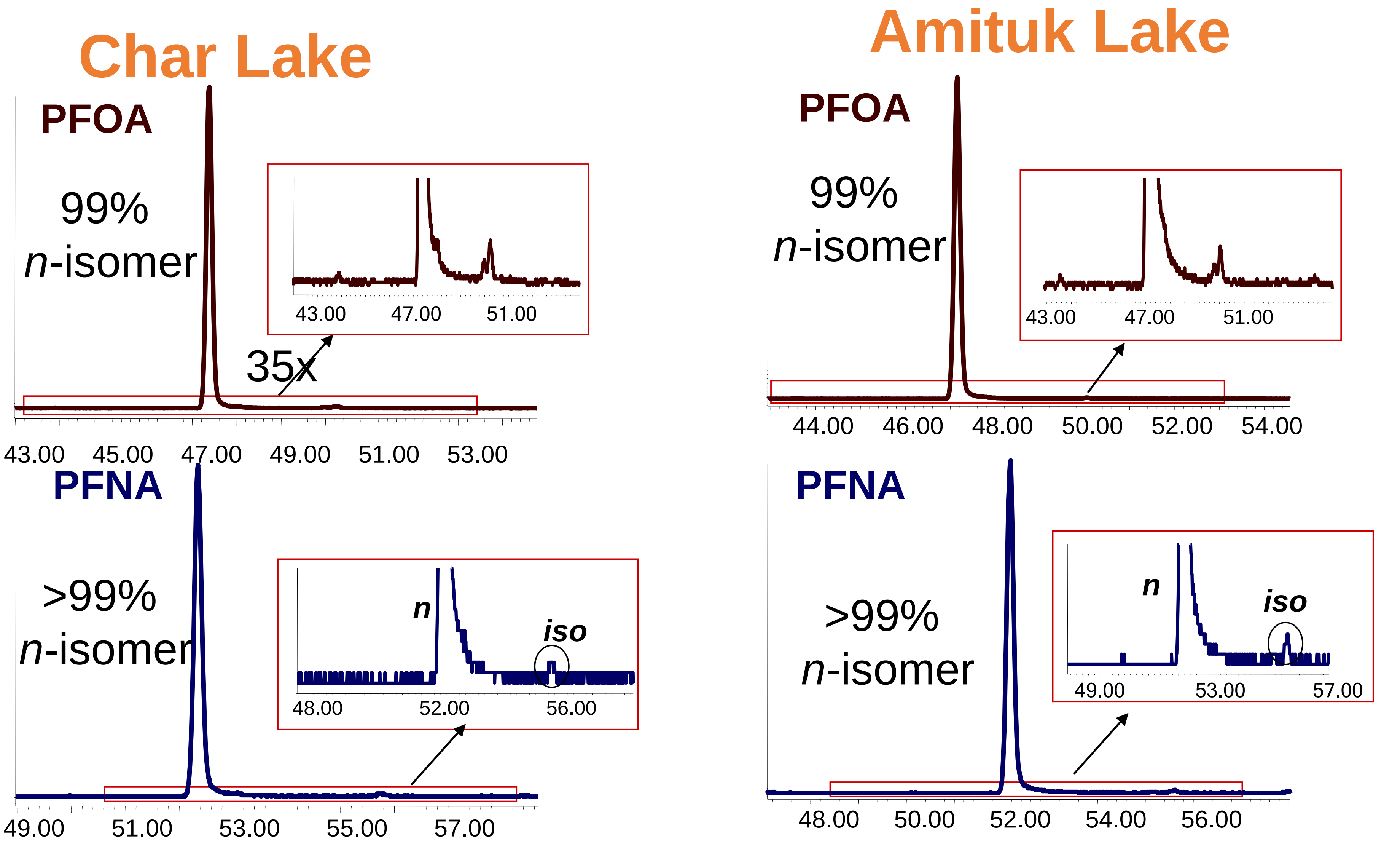


Young, Furdui, Franklin, Koerner, **Muir**, and Mabury. **2007**. Perfluorinated Acids in Arctic Snow: New Evidence for Atmospheric Formation. *Environ. Sci. Technol.* **41**:3455-3461 **[Citations 285]**

PFOA flux to Arctic:
Measured: 114 to 586 kg/yr
Model Prediction: 400 kg/yr

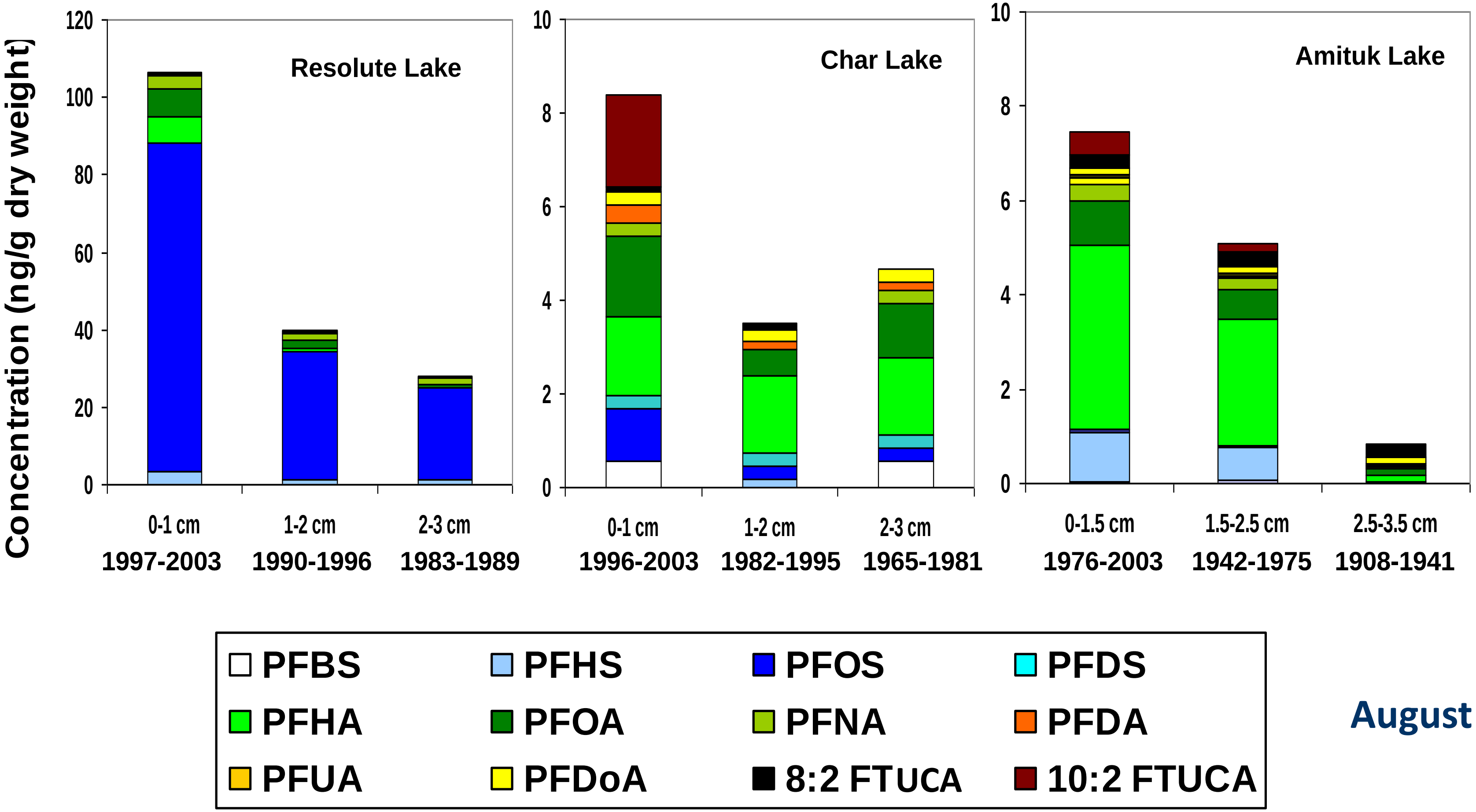
Wallington, TJ, MD Hurley, J Xia, DJ Wuebbles, S Sillman, A Ito, JE Penner, DA Ellis, SA Mabury, OJ Nielsen, MP Sulbaek Andersen. **2006**. *Environ. Sci Technol*. .**40:924-930.**

Arctic Surface Water



De Silva, AO, DCG Muir, and SA Mabury. 2009. Distribution of Perfluorinated Carboxylated Isomers in the North American Environment. *Env. Tox. Chem.* **28:**1801-1814. [Citations 60]

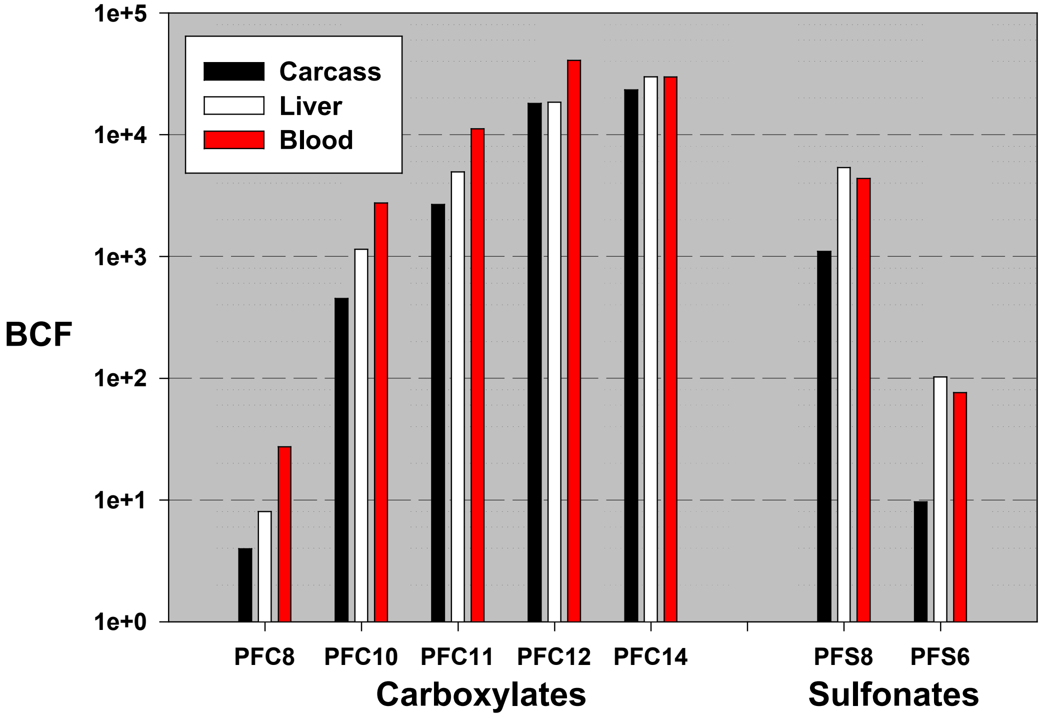
PFSAs/PFCAs and FTUCAs IN ARCTIC SEDIMENT



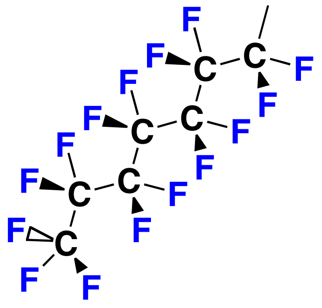
August 2003

Stock, NA, V. Furdui, DCG Muir, and SA Mabury. 2007. Perfluoroalky Contaminants in the Canadian Arctic: Evidence of Atmospheric Transport and Local Contamination. *Environ. Sci. Technol.* **41**:3529-3536. [Citations 171]

BCF/BAF in Carcass, Liver, and Blood of Rainbows



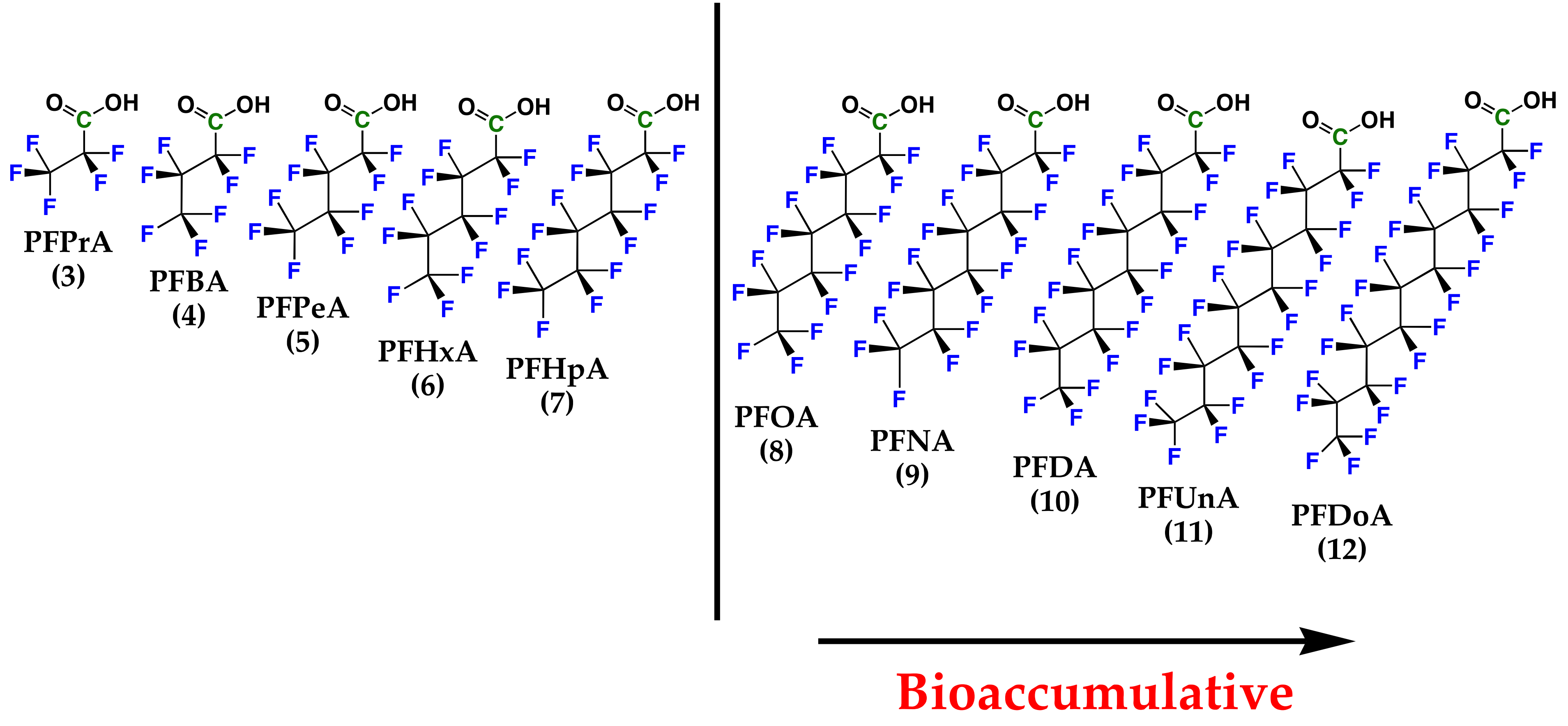
$$BCF = k_u/k_d$$



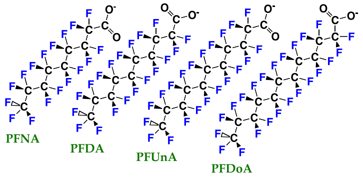
Additional CF_2 results in a ~7x increase in the BCF.

Martin, J., S.A. Mabury, K.S. Solomon, D.C.G. **Muir.** **2003** Bioconcentration and Tissue Distribution of Perfluorinated Acids in Rainbow Trout (*Oncorhynchus mykiss* Environ. Tox. Chem. **22: 189-195.** **[Citations 698]**

Martin, J., S.A. Mabury, K.S. Solomon, D.C.G. **Muir. 2003** Dietary Accumulation of Perfluorinated Acids in Rainbow Trout (*Oncorhynchus mykiss*. Environ. Tox. Chem. **22L 196-204.** **[Citations 378]**


PFPrA
(3)
PFBA
(4)
PFPeA
(5)
PFHxA
(6)
PFHpA
(7)
PFOA
(8)
PFNA
(9)
PFDA
(10)
PFUnA
(11)
PFDoA
(12)
Bioaccumulative

Discovery of Long Chain PFCAs



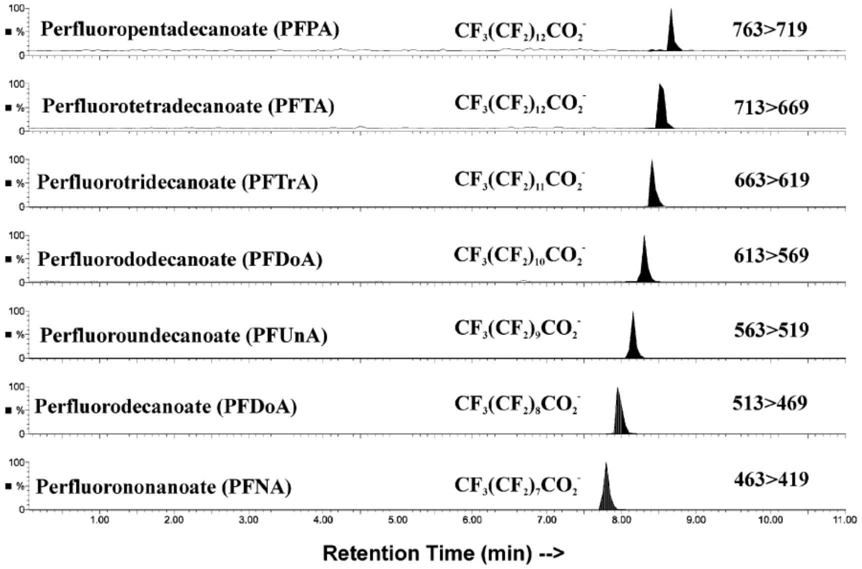


FIGURE 2. Tandem mass spectrometry chromatogram of polar bear extract showing the homologous series of PFCAs detected and later confirmed.

Confirm

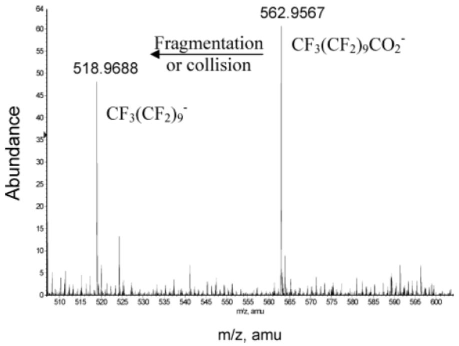
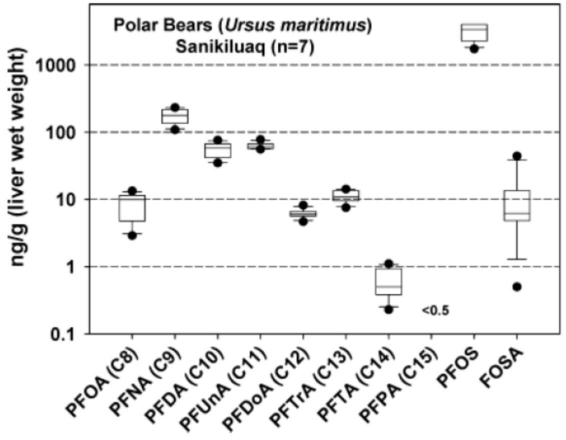


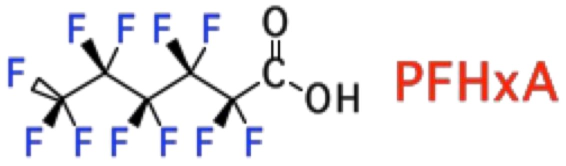
FIGURE 3. Full scan high-resolution mass spectrum for a polar bear extract showing the accurate mass associated with the negative molecular ion of PFUnA (*m/z* 562.9567) and of its characteristic fragment or daughter ion (*m/z* 518.9688).

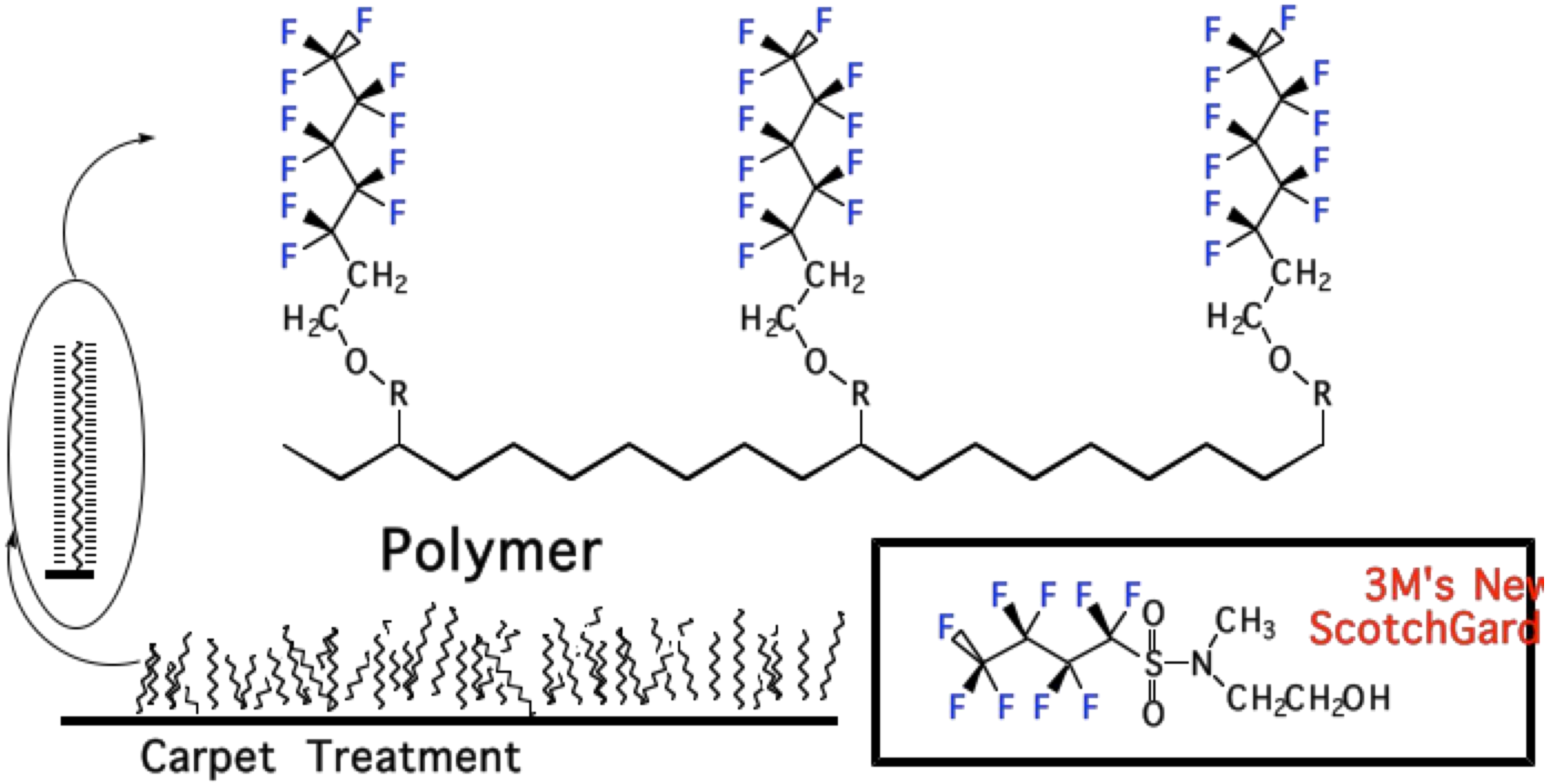


even:odd ratios
Where does this come from?

Martin, J.W., M.M. Smithwick, B. Braune, P.F. Hoekstra, D.C.G. Muir, S.A. Mabury. **2004**. Identification of Long-Chain Perfluorinated Acids in Biota from the Canadian Arctic. *Environ. Sci Technol.* **38**:373-380. [Citations 580]

What to do? ~ 2) Shorten the perfluorochains~ 6 or less carbons as resulting PFCAs are not expected to bioaccumulate.





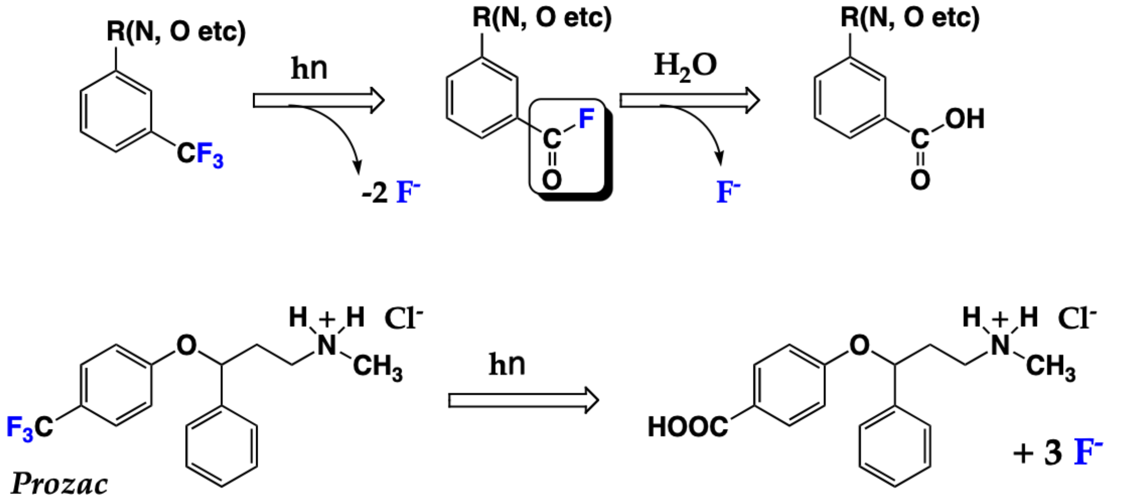
Bruce E. Smart of Dupont in C&EN Feb 14, 2005 p 36 *"It's possible, with the right design, that some of these materials can be lightly fluorinated and still express the surface activity of the long-chain surfactants."*

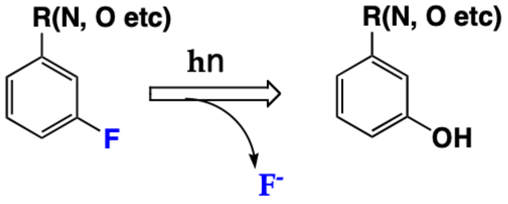
C-F bond breakage & the ”F” word….

Can you break a C-F bond?

Only in special cases or conditions

Photolysis in Natural Waters





Br>Cl>F

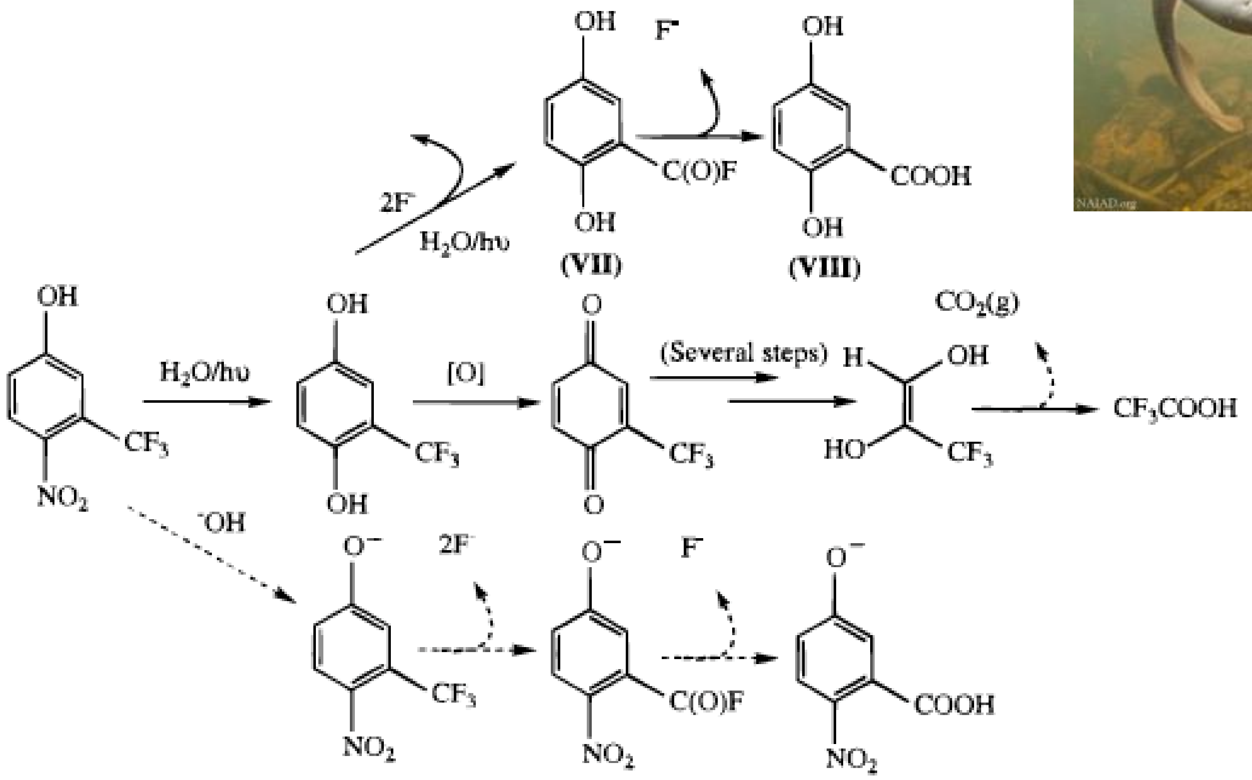
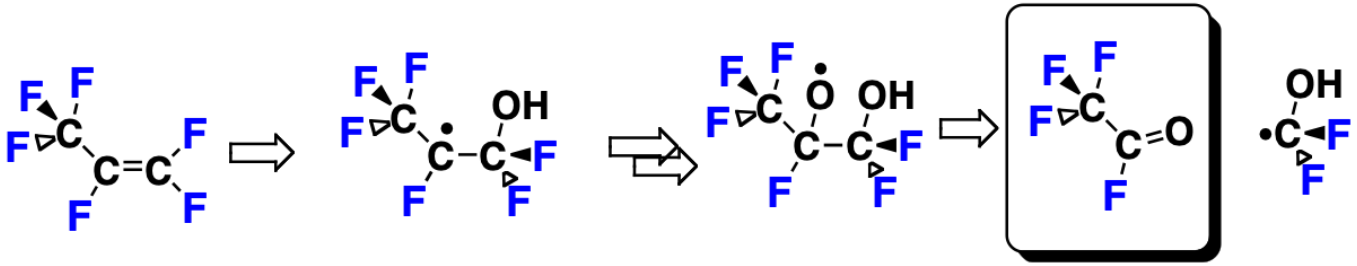
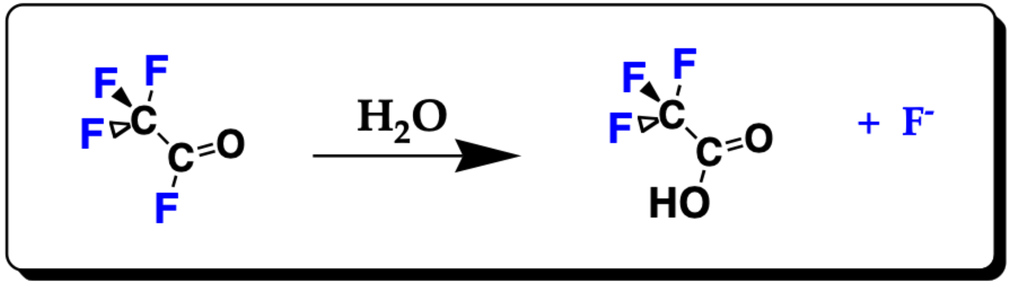


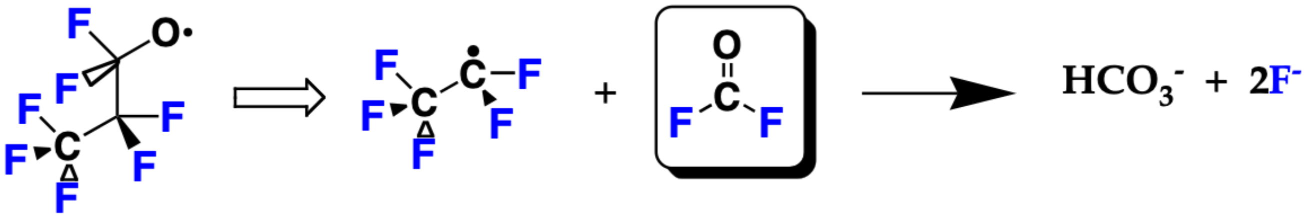
FIGURE 7. Proposed mechanism for the production of TFA from TFM (I). The alternate pathways for the degradation of TFM are also indicated.

Ellis & Mabury, 2000. ES&T 34:632-637

Fluoride is a terrible leaving group:
Except in special cases…where F^- is pushed!

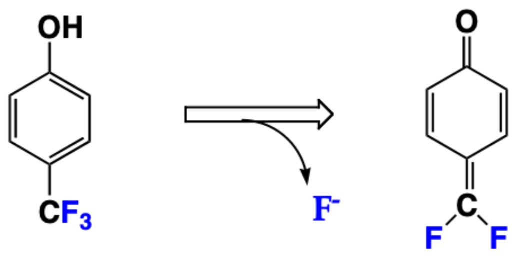






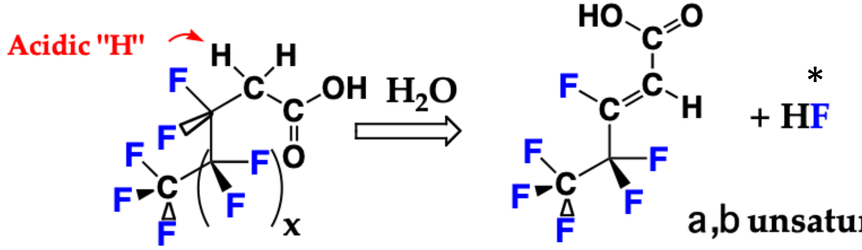
If the right 'architecture' then ELIMINATE?

Elimination



Stable

b-Elimination



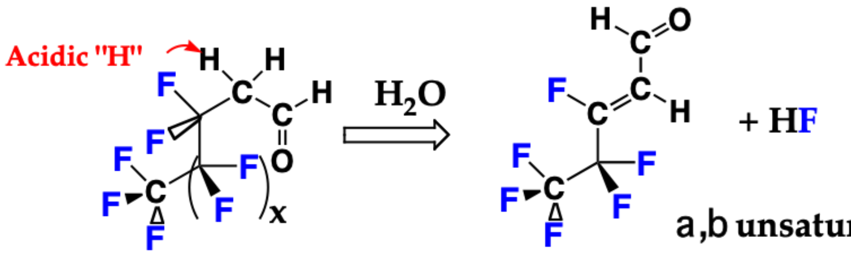
Telomer Acids

a,b unsaturated acids

abiotic; x=6, pH 7, T=23C
~35 days

biotic (bacteria); x=6, pH 7, T=23C
~14 days

biotic (rats); x=6, pH 7.2, T=23C
~very fast

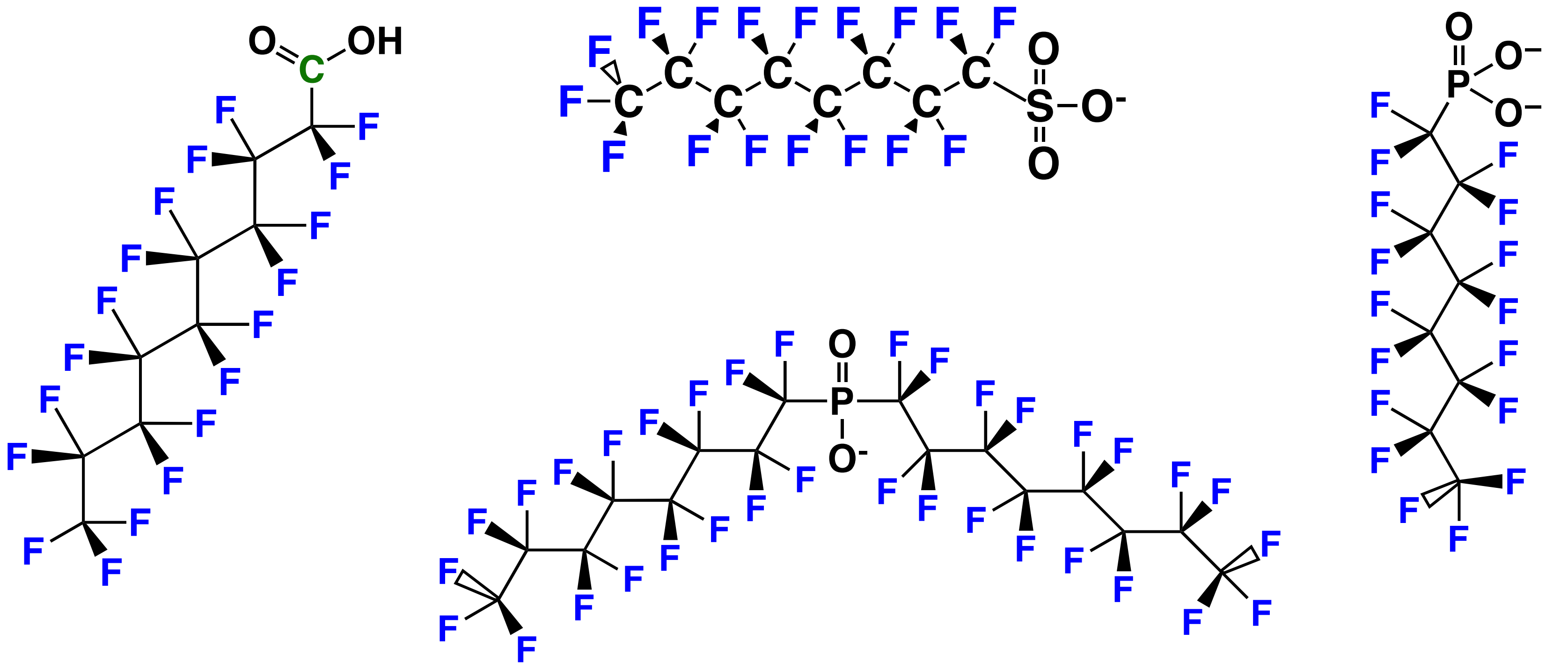


Telomer Aldehyde

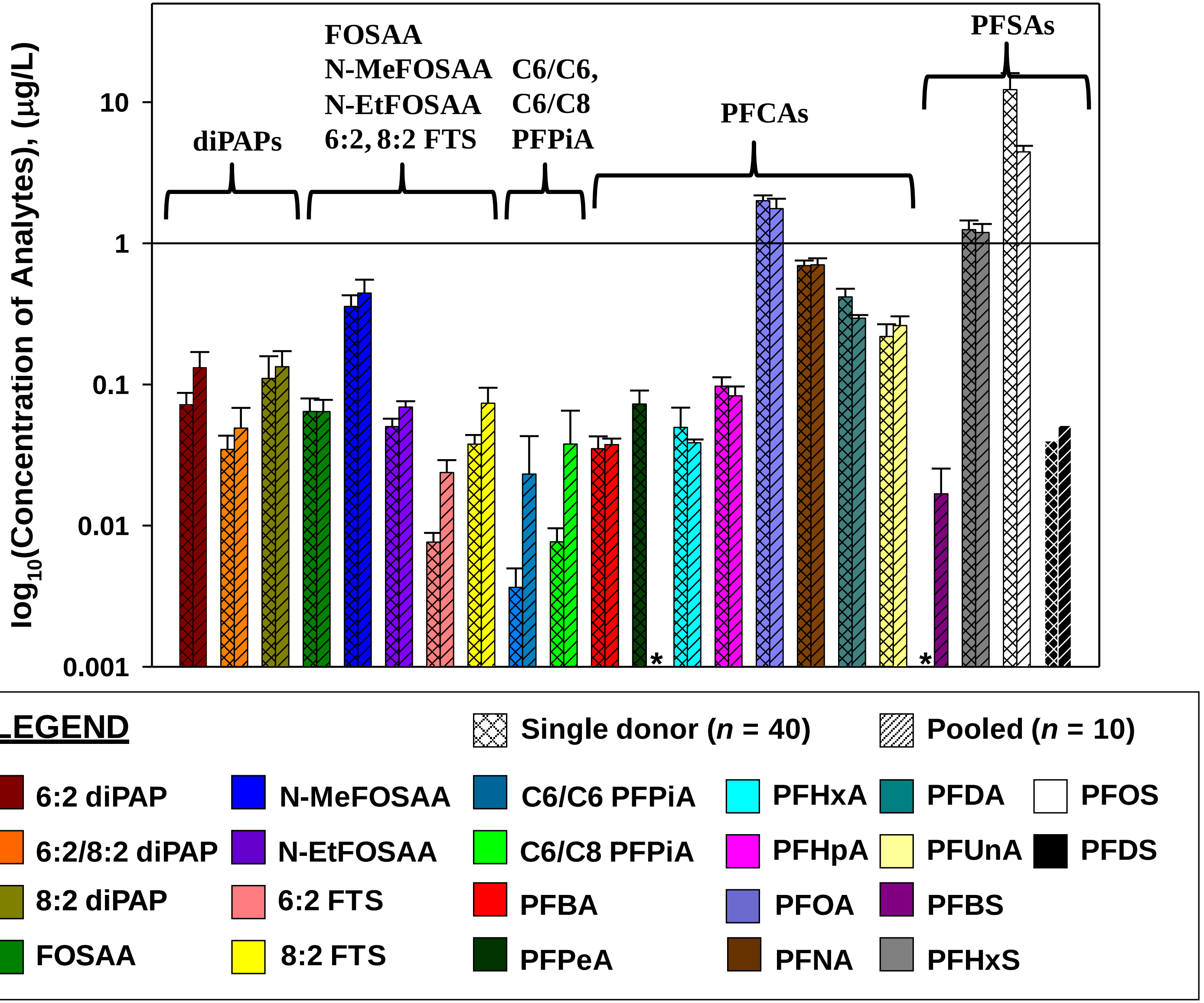
a,b unsaturated aldehydes

Biotic & Abiotic are much Faster

Perfluorinated Acids…. “extremely persistent”….?



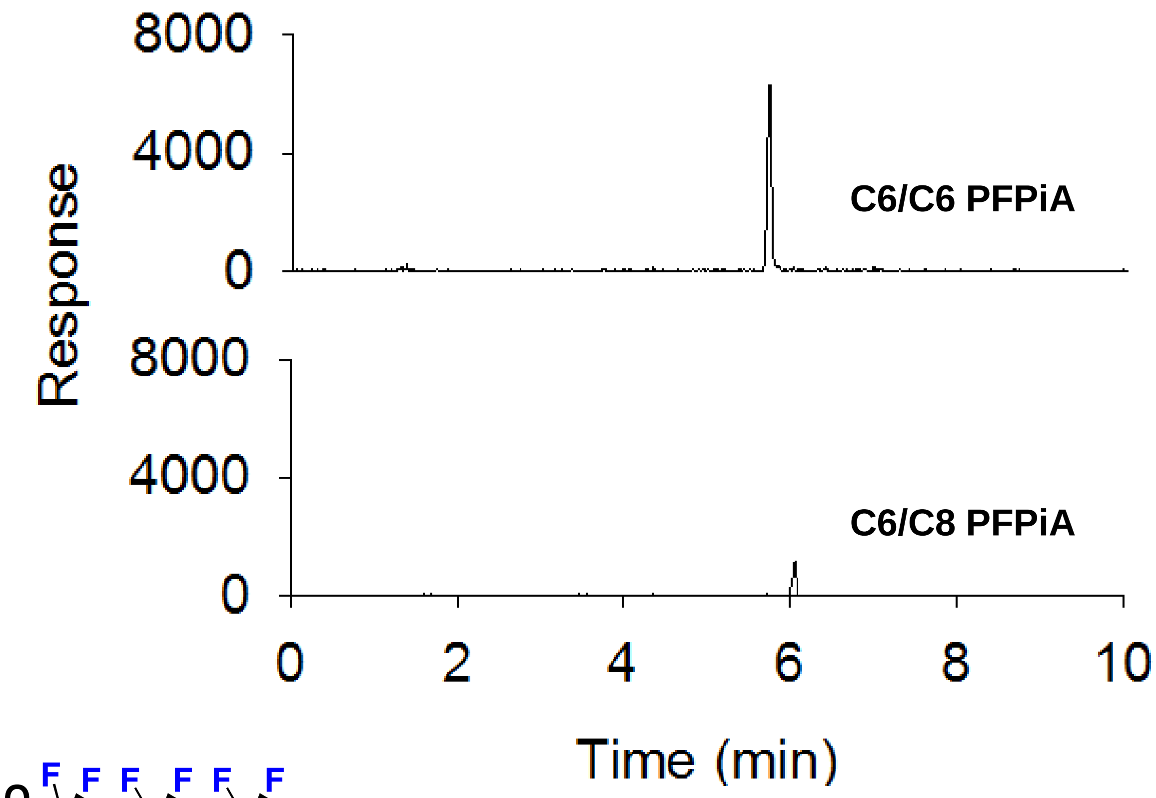
Human Contamination of Fluorinated Chemicals

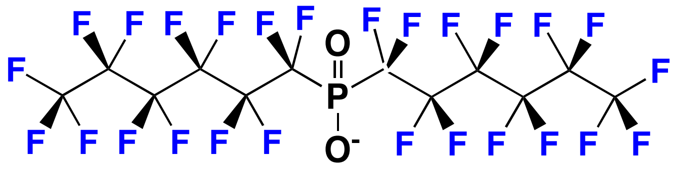


Lee and Mabury, **2011**, *Environ. Sci. Technol.* **45:8067-8074**

Yes detection of the perfluorophosphinates as well

NIST WWTP sludge standard reference material at 2 ng/g

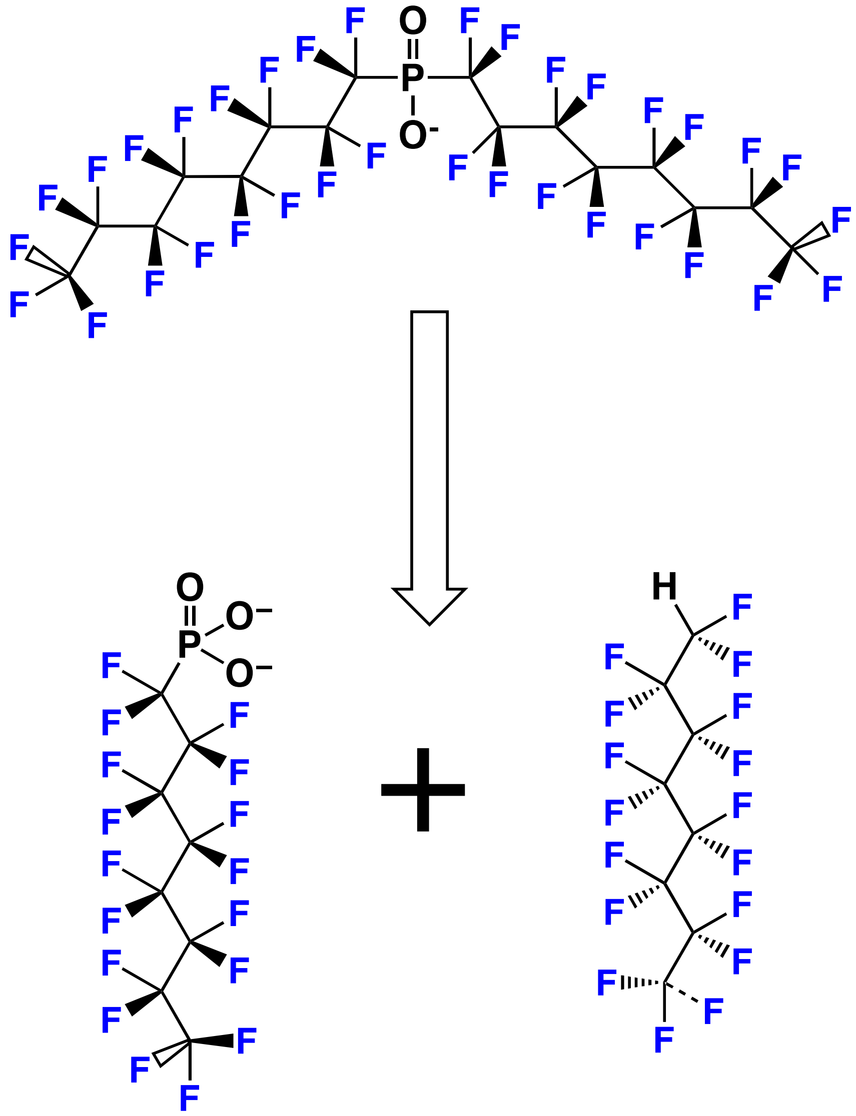




C6/C6-PFPiA

D'eon, JP and SA Mabury. **2010**. Uptake and Elimination of Perfluorinated Phosphonic Acids in the Rat. *Env. Tox. Chem.* . **29:1319-1329.**

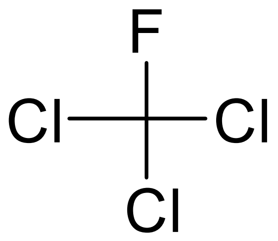
Overall…



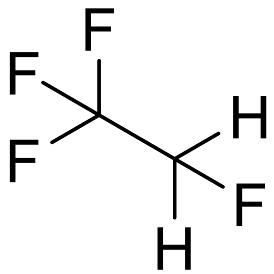
Lee, De Silva, & Mabury. *Environ. Sci. Technol.* **2012**, *46*, 3489

Joudan, S and SA Mabury, 2017, *Environ. Health Persp* **125**:DOI 10.1289/EHP1841

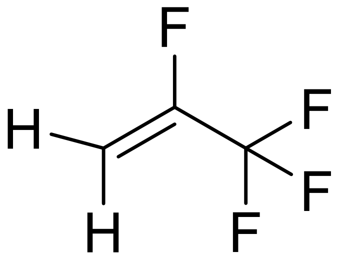
Ozone Depletion…Global Warming



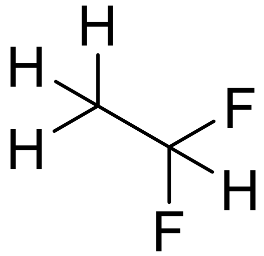
CFC-11



HFC-134a



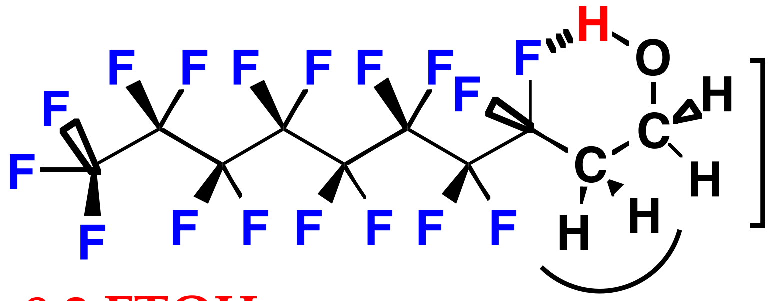
HFC-1234yf



HFC-152a

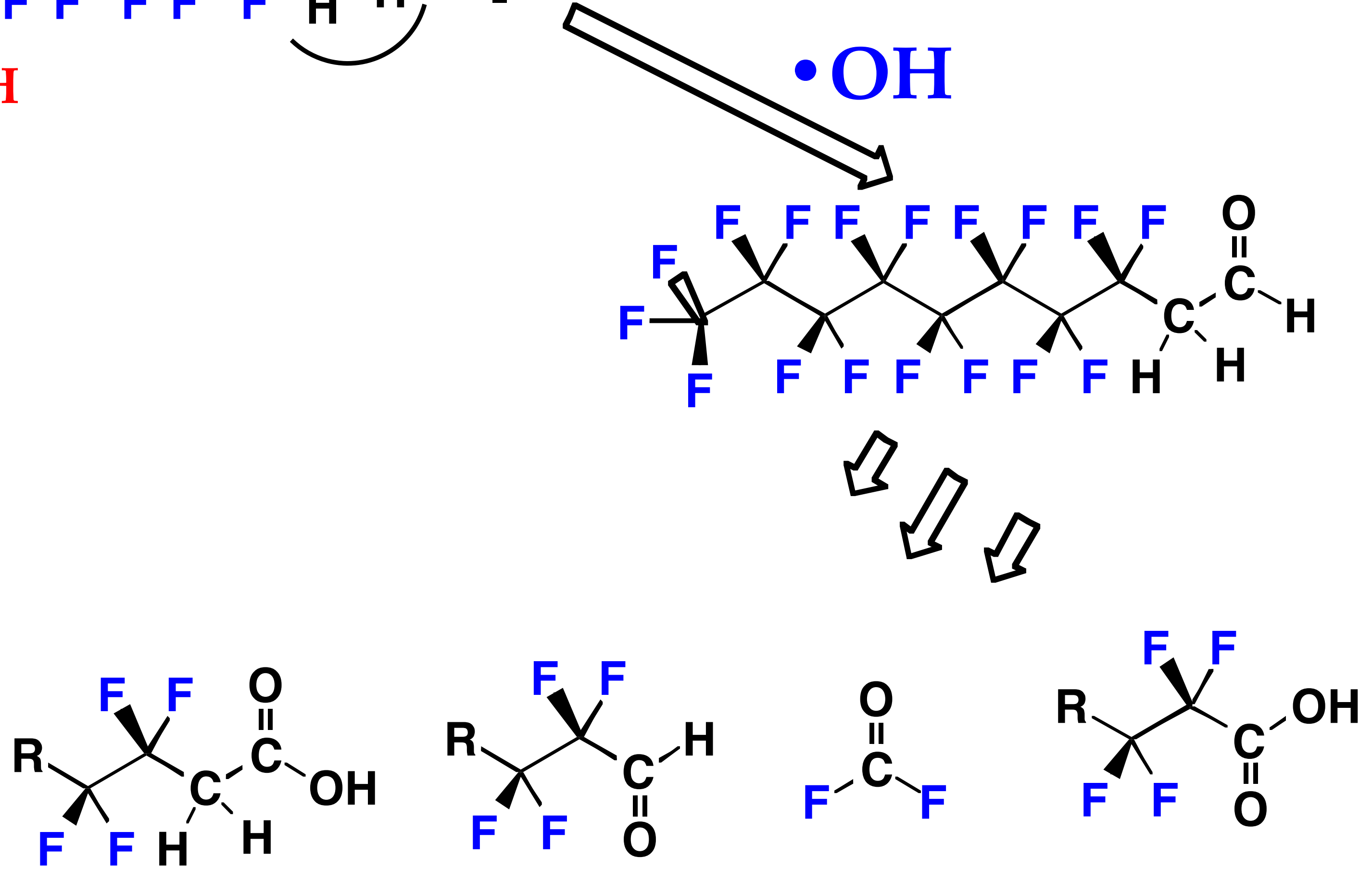
Atmo Fate

Reaction Products from OH Rxn w/ FTOHs

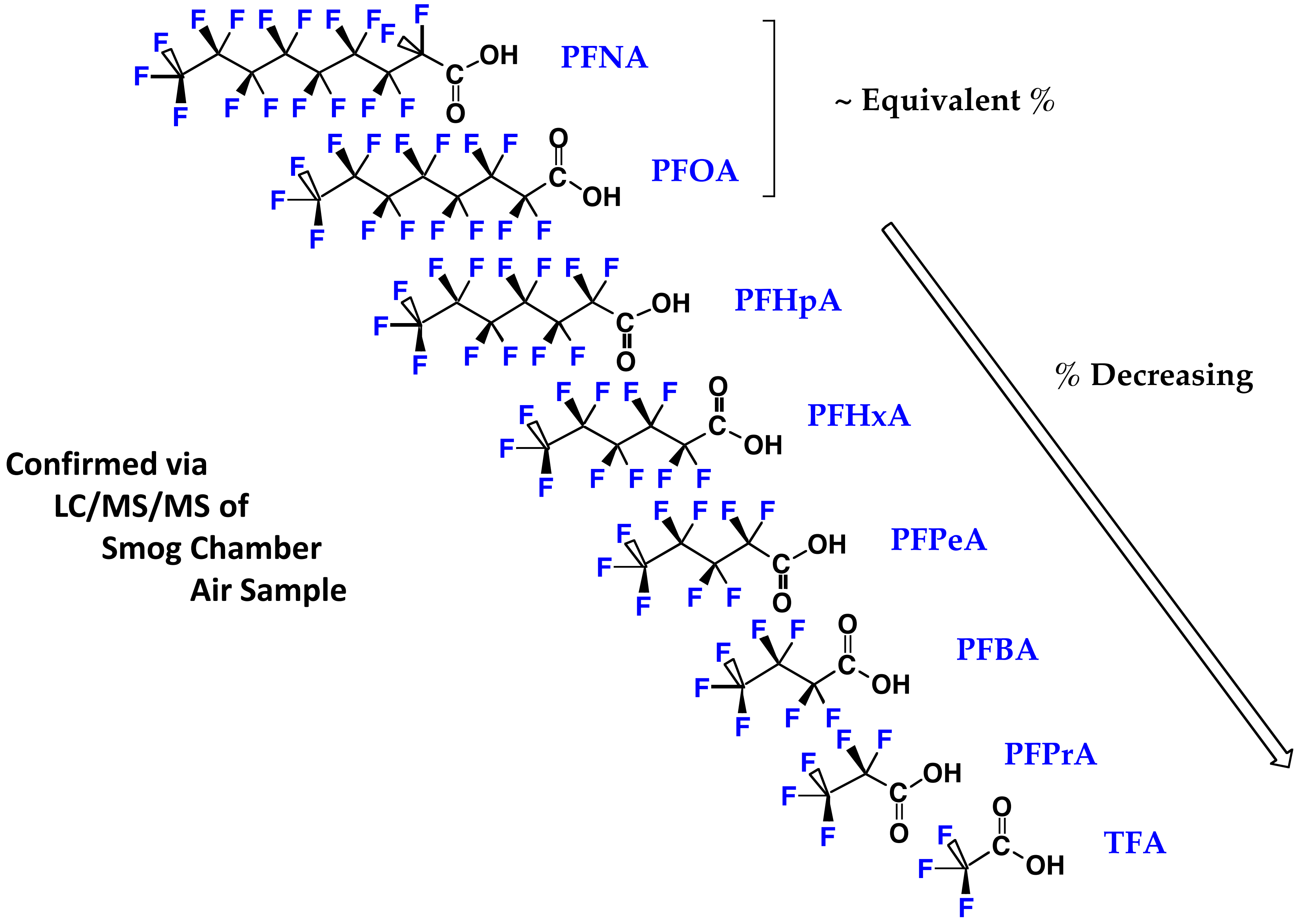


8:2 FTOH

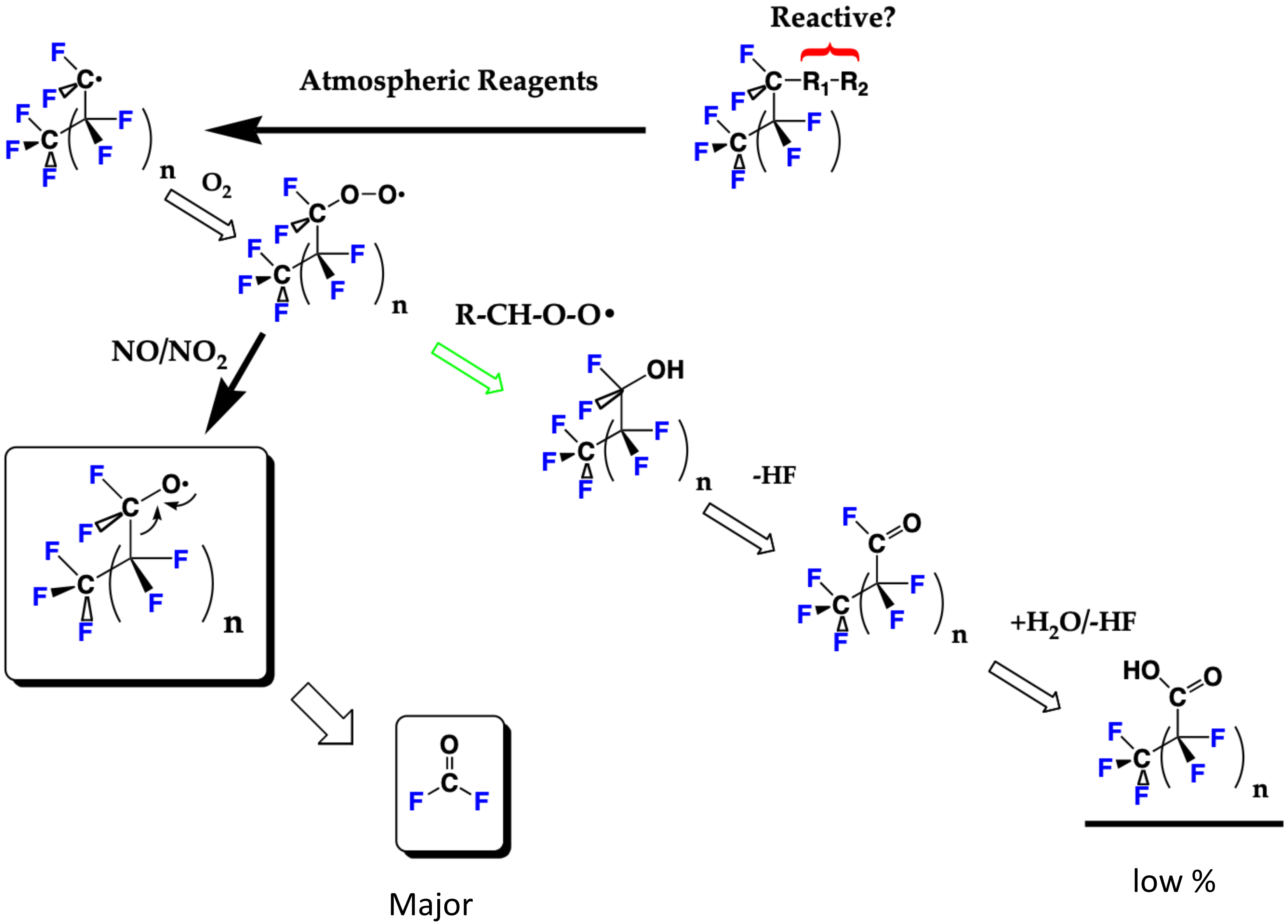
>90% Attack on
α hydrogens; H-Bond
deactivates OH abstraction



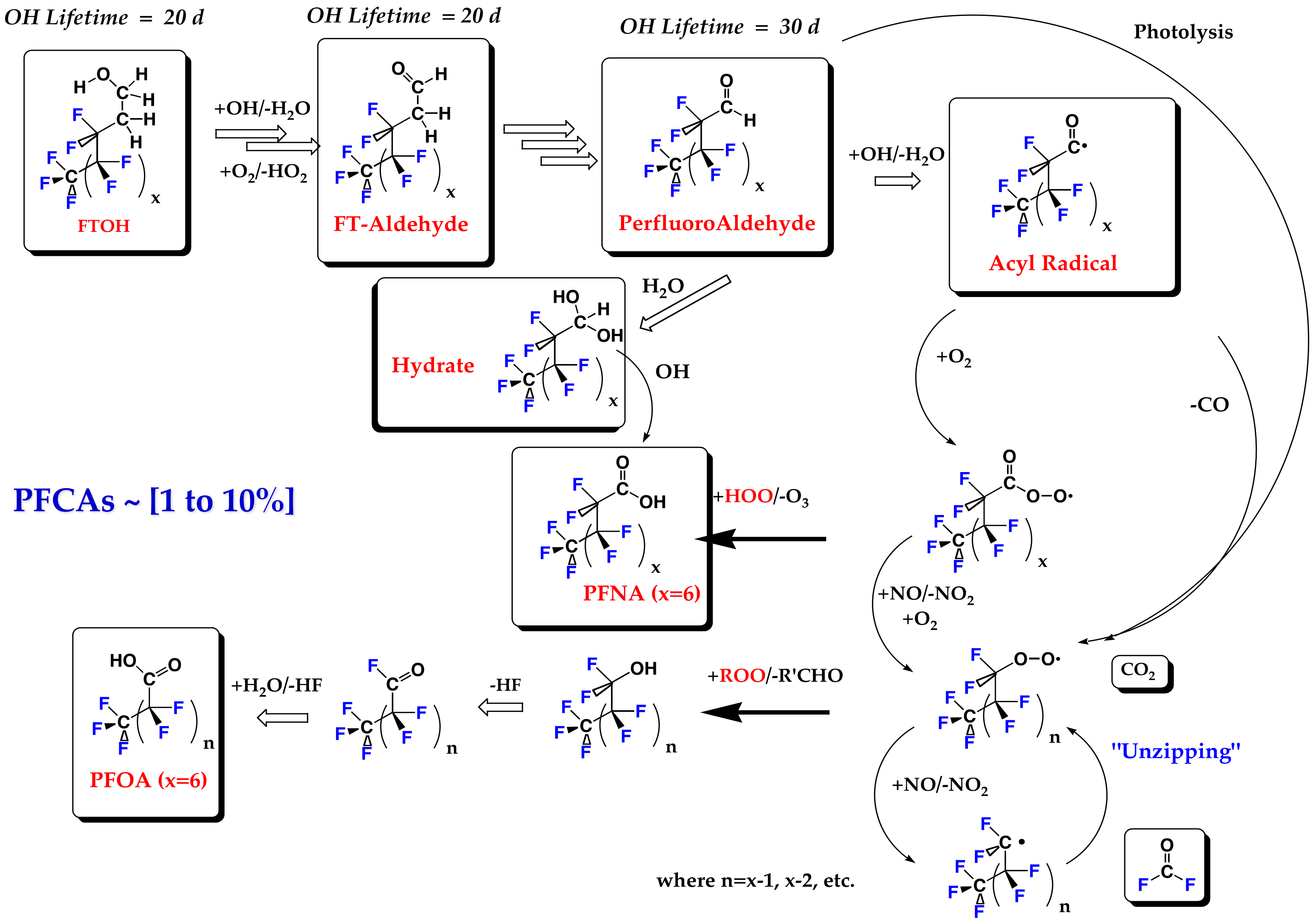
David Ellis
Jon Martin
Jessica D'eon
Cora Young
Tim Wallington
Mike Hurley
Mads Sulbaek Andersen
Scott Mabury


PFNA
PFOA
~ Equivalent %
PFHpA
PFHxA
% Decreasing
PFPeA
PFBA
PFPrA
TFA
Confirmed via
LC/MS/MS of
Smog Chamber
Air Sample

Fate of Perfluorocarbon Radicals

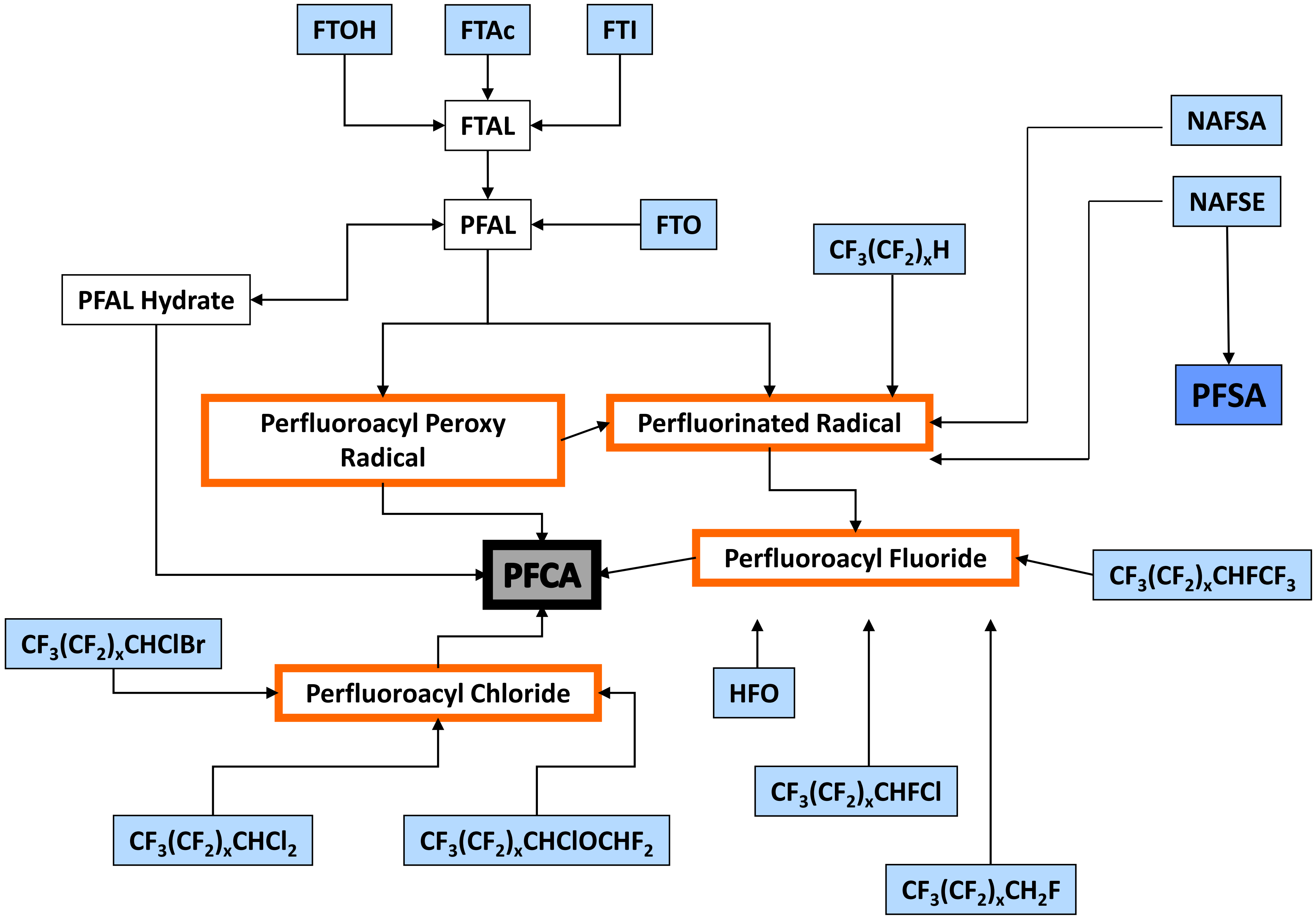


Overall Atmospheric Chemistry of FTOHs



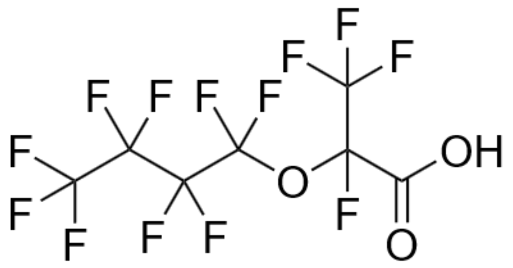
PFCAs ~ [1 to 10%]

Overall Big Picture of Atmospheric Pathways of Precursors

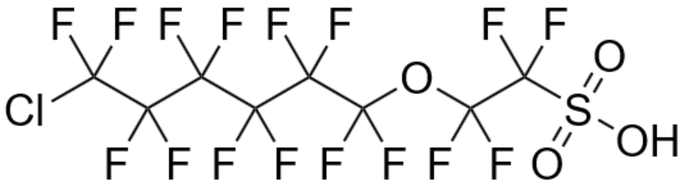


Young & Mabury. **2010.** Atmospheric PFCA Precursors ~ A Review; *Rev Env Contam Tox* **208:1-109.**

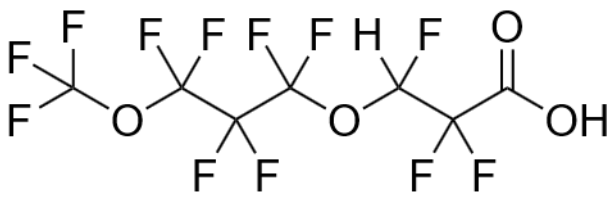
Evolution….?



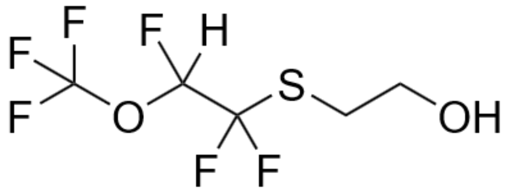
HFPO-DA
(GenX)



F53B; 6:2 Cl-PFESA



ADONA



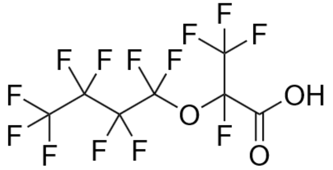
MeFESOH*

Next-generation replacement*

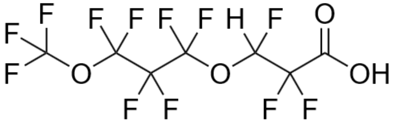
Folkerson, AP and SA Mabury. 2024. [A Comparative Biodegradation Study to Assess the Ultimate Fate of Novel Highly Functionalized Hydrofluoroether Alcohols in Wastewater Treatment Plant Microcosms and Surface Waters](). Env Tox Chem. DOI: 10.1003/etc.5815

Folkerson, AP, SR Schenider, JPD Abbatt and SA Mabury. 2023. [Avoiding Regrettable Replacements: Can the Introduction of Novel Functional Groups Move PFAS from Recalcitrant to Reactive?]() Env Sci Technol. 57:17032-17041.

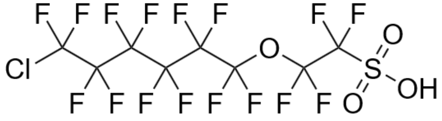
Legacy Replacements



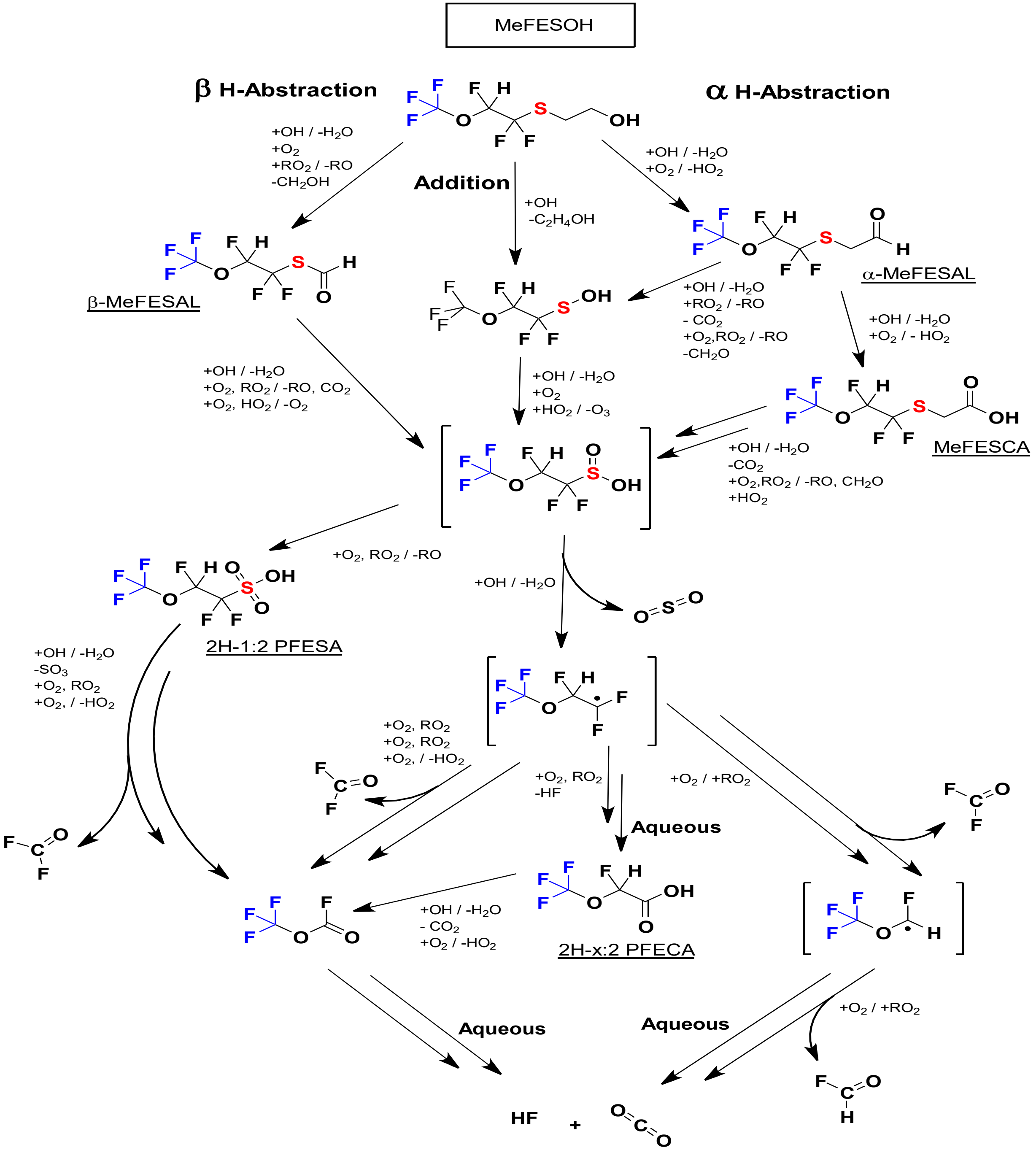
HFPO-DA (GenX)



ADONA



F53B



Trends

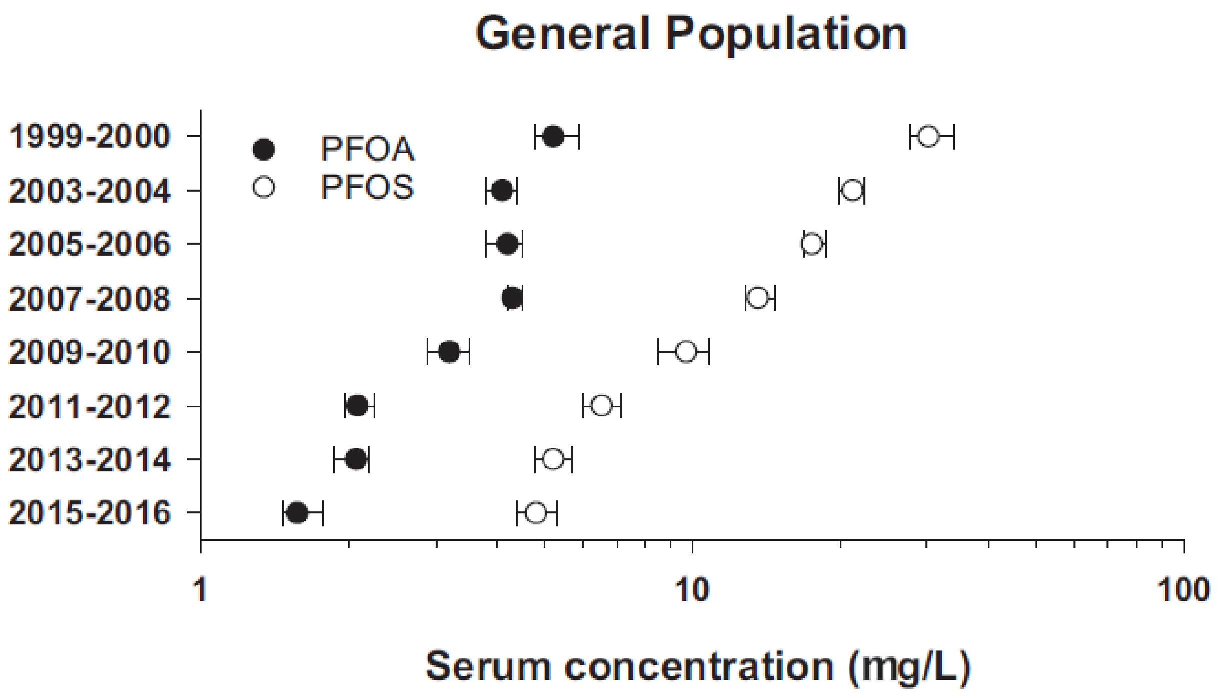
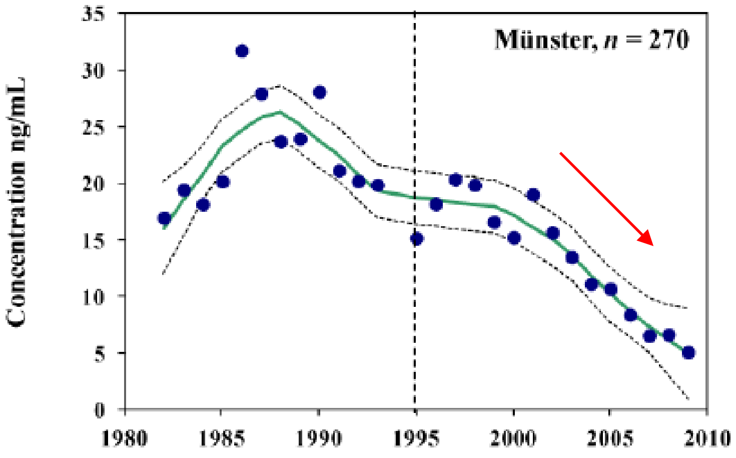


Fig. 1. Median serum concentrations with 95% confidence intervals for PFOA and PFOS among the general US population.

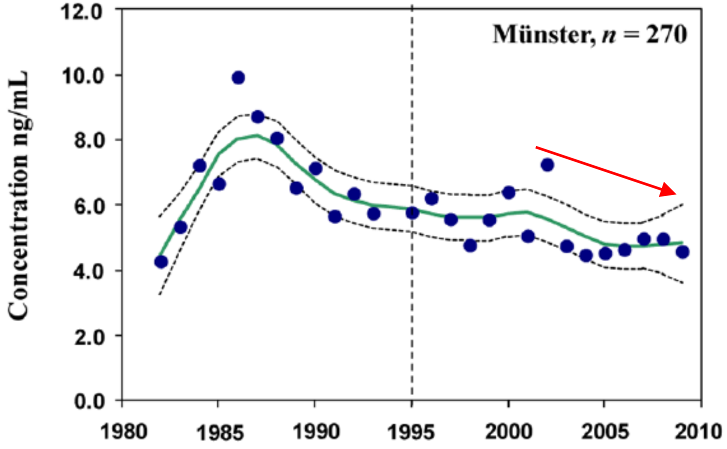
Garnick et al, 2021. Sci Tot Env 761:144107

Are humans exposed to lower amounts of PFAS?

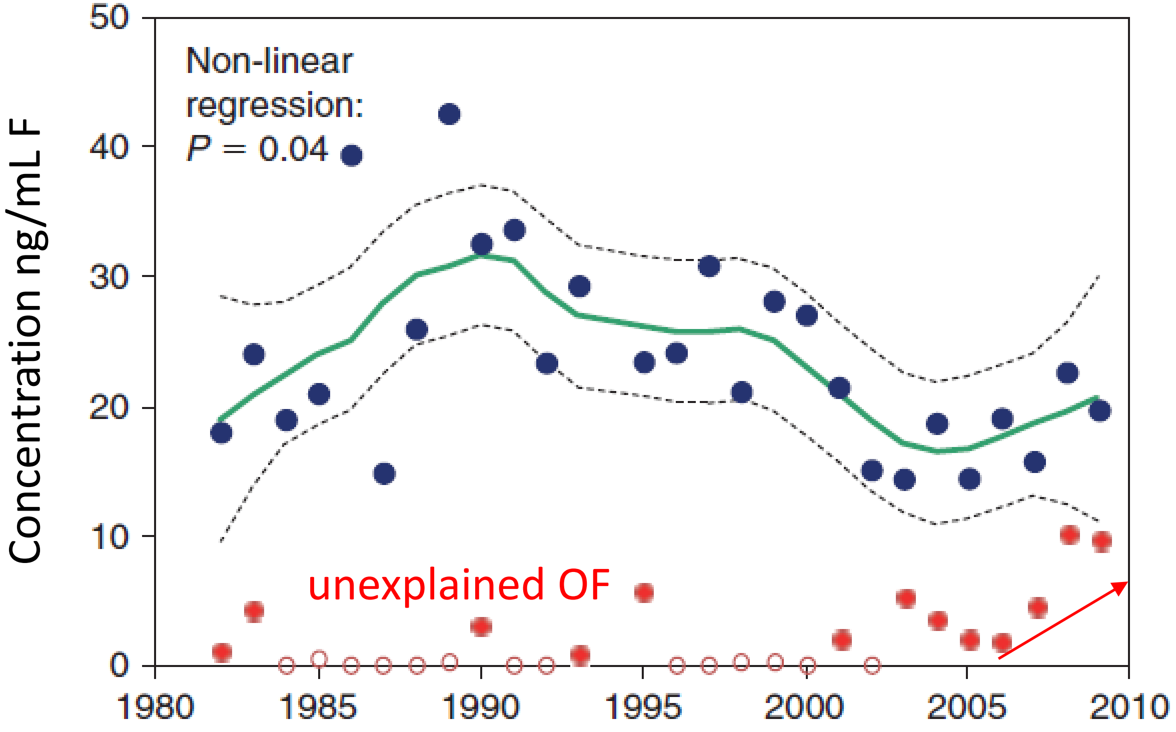
PFOS



PFOA

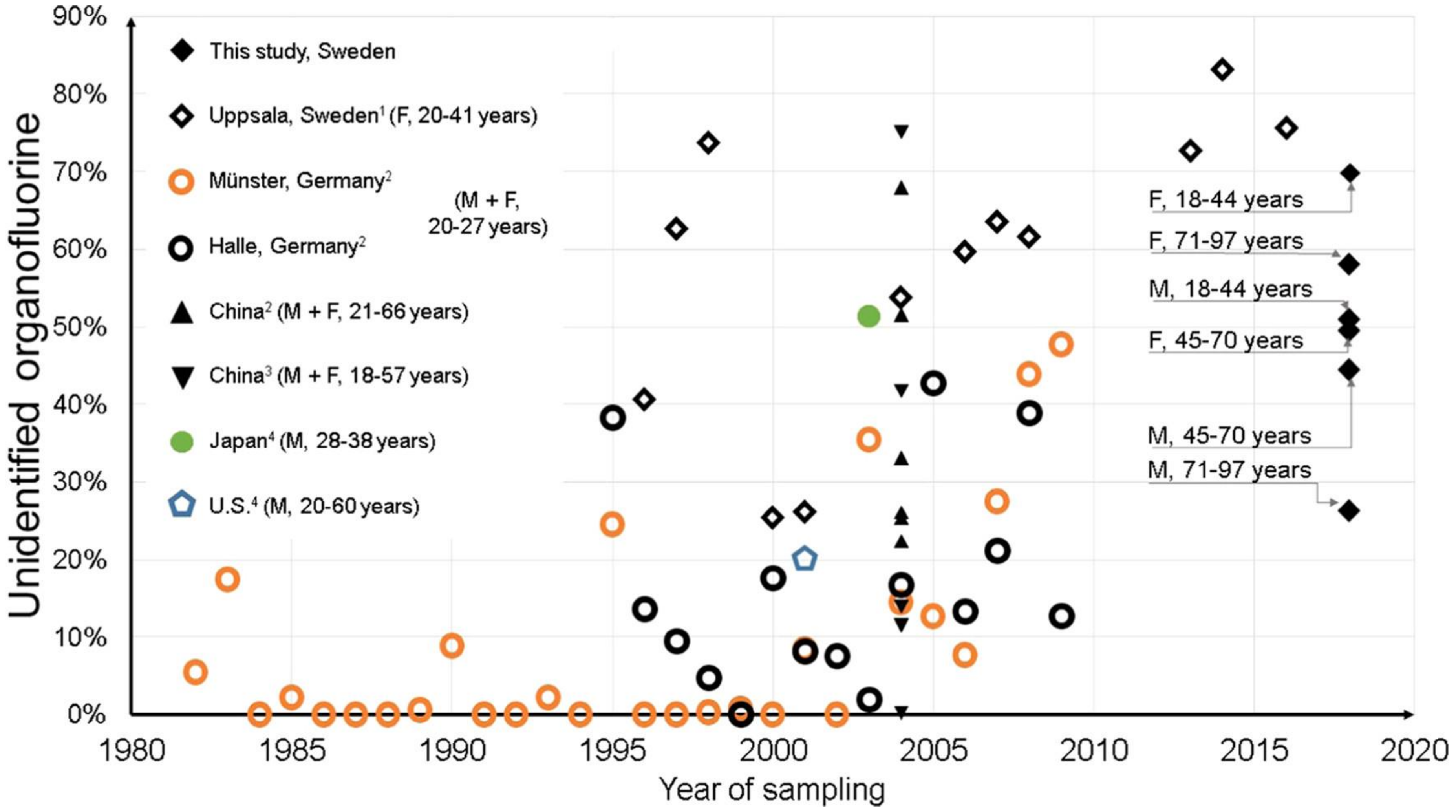


EOF



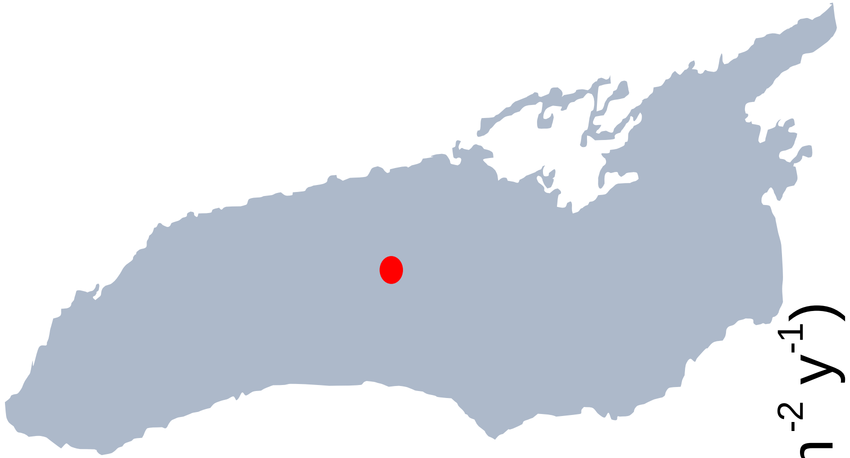
Environmental Science & Technology 2013, 47, 8, 3865-3874
Environmental Science & Technology 2013, 47, 8, 3875-

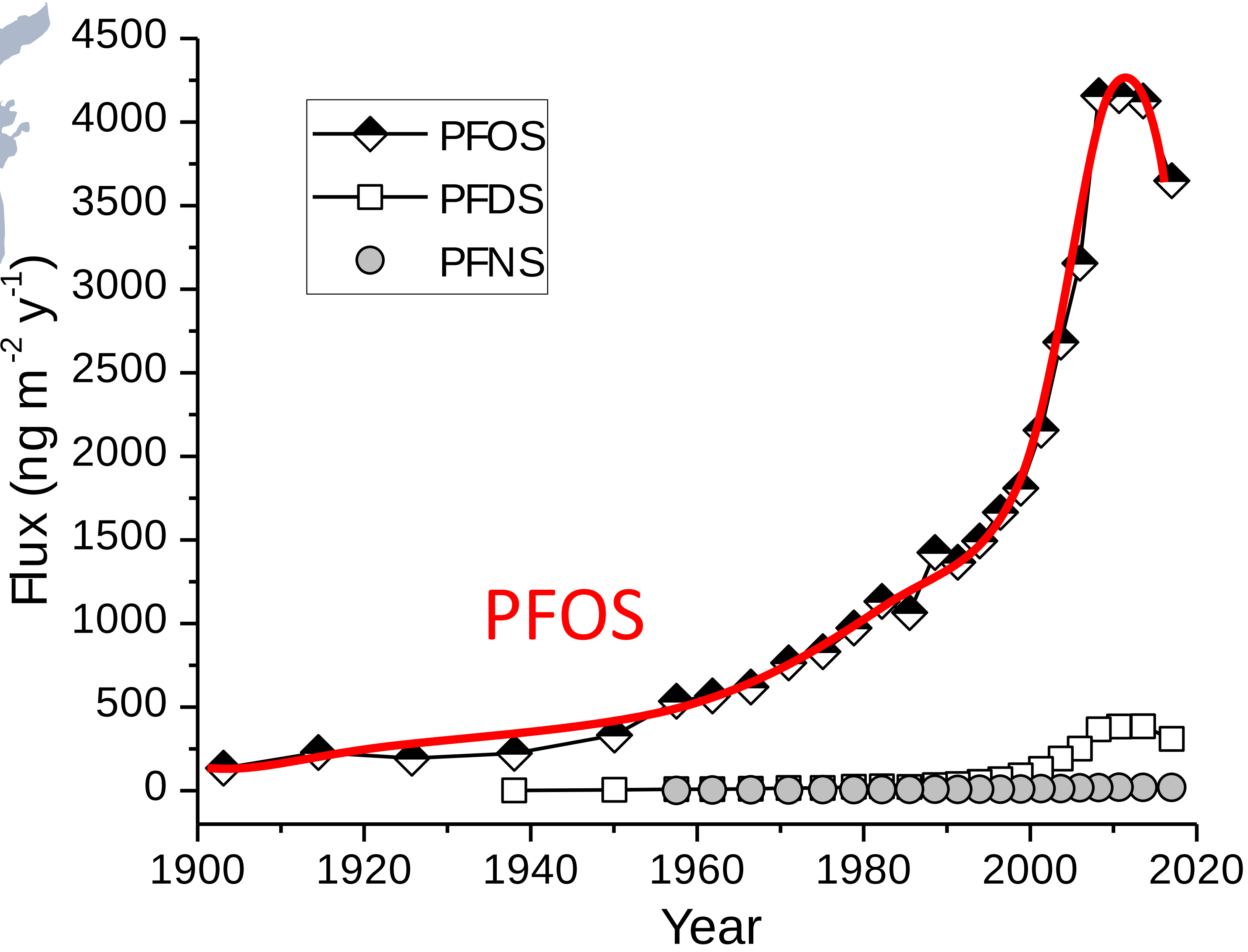
Are humans exposed to lower amounts of PFAS?



Environ. Sci. Technol. 2021, 55, 19, 13142–13151

PFAS Trends in Lake Ontario sediment core

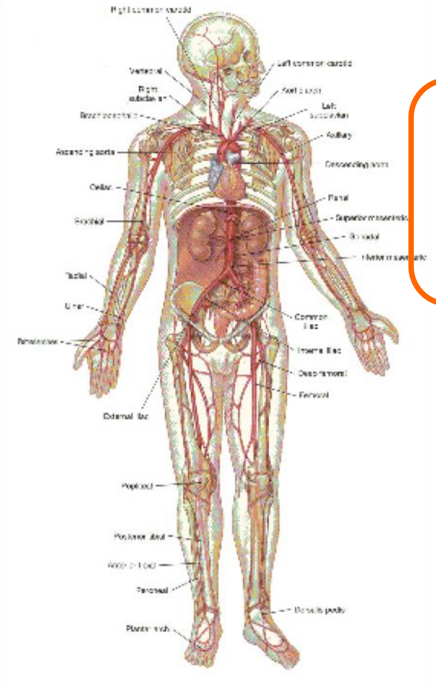




- Similar to trends in trout, PFOS has declined since the 2000s
- In sediment, PFOS has the highest concentration of the other PFAAs

Human exposure etc

Motivation: Polar Bears & Human Contamination



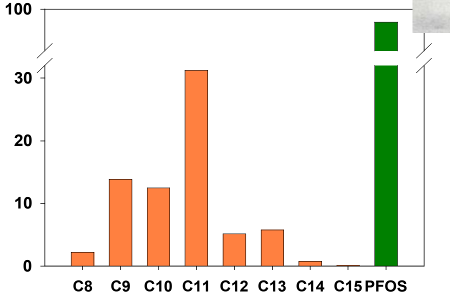
Taves, D.R. 1968.
"*Evidence for Two Forms of Fluoride in Human Serum.*"
Nature, 217:1050-1051

	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFOS
Falandysz, 2006 Poland	3.0	0.56	0.18	0.09	0.018	13
Karrman, 2006 Sweden	4.8	0.6	0.2	0.2		32
Calafat, 2006 USA	3.7	0.56				21
Kuklenyik, 2004 GA	4.9	2.6	0.51	0.68	0.14	56
Guruge, 2004 Sri Lanka	6.4	0.39	0.19	0.25	0.022	36
De Silva, 2006 USA	4.4	0.77	0.17	0.06		

DeSilva, AO and S.A. Mabury. **2004**. Isolating Isomers of Perfluorocarboxylates in Polar Bears (*Ursus maritumus*) from Two Geographical Locations. *Environ. Sci. Technol*. **38**:6538-6545.

DeSilva, A.O, and S.A. Mabury. **2006**. Isomer Distribution of Perfluorinated carboxylates in Human Blood – Potential Correlation to Source. *Environ. Sci. Technol.* **40**: 2903-2909.

What is the Question and Why are we interested?



Arctic Critters

Homo sapiens

Interest: Significant [PFOS] & [PFCAs]

Question: How did they get there?

…two main ideas: Direct & Indirect

PFOA
0, 0.3, 1, 30, 70 mg/L

PFOS
0, 0.3, 3, 10, 30 mg/L

"PFCs are extremely toxic chemicals…"
Keen Shoe ad
Globe & Mail
April 22, 2021

Aquatic invertebrates…e.g. *Daphnia Magna* – the Canary

Table 2
Summary of comparative results ($mg\,L^{-1}$) and detectability ($\Delta = 0 - 1$)

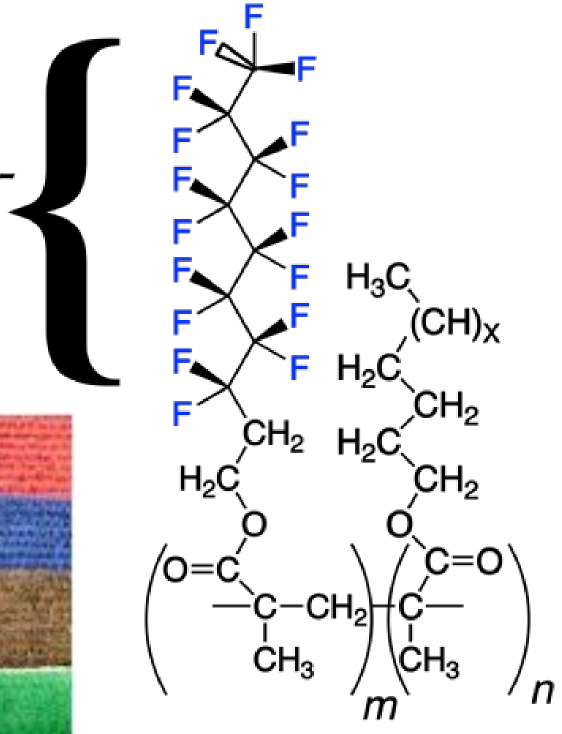
Design	PFOS $LOEC_{community}$	Mean Δ	PFOA $LOEC_{community}$	Mean Δ
Laboratory	13–50 (D. pulicaria)	0.01	No data	No data
30-L indoor	1–10	0.21 and 0.39	30–70	0.15 and 0.83
12,000-L outdoor	10–30	0.63 and 0.99	30–70	0.57 and 0.99

Sanderson *et al*, 2004. Ecotox & Env Saf; **58**:68-76

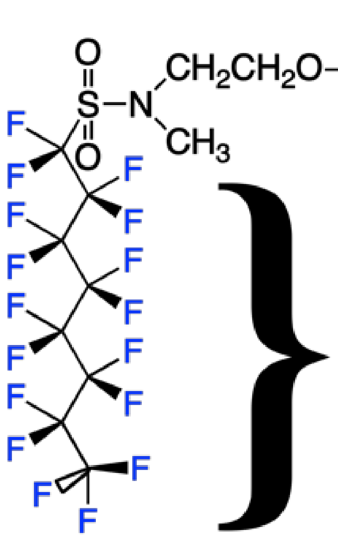
US EPA Health Advisory in Drinking Water: 0.00004 mg/L (4 ng/L)
or 750,000 x below the LOEC for PFOA

Do these "common" fluorinated polymers & surfactants contribute?

Hydro & Lipo-Phobic



Polymer (Ester)



Hydro & Lipo-Phobic

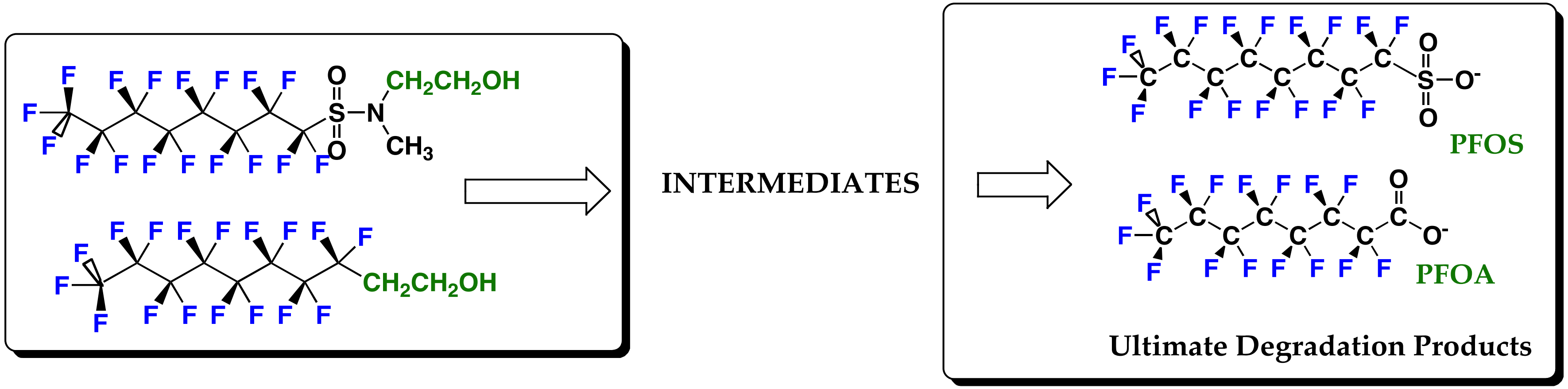
Surfactants (Phosphate)

Two hypotheses:

Direct: ***Release of PFOS and PFOA/PFNA from industrial, commercial, or consumer uses has been significant and has resulted in global contamination, including the Arctic and humans.***[1,2]

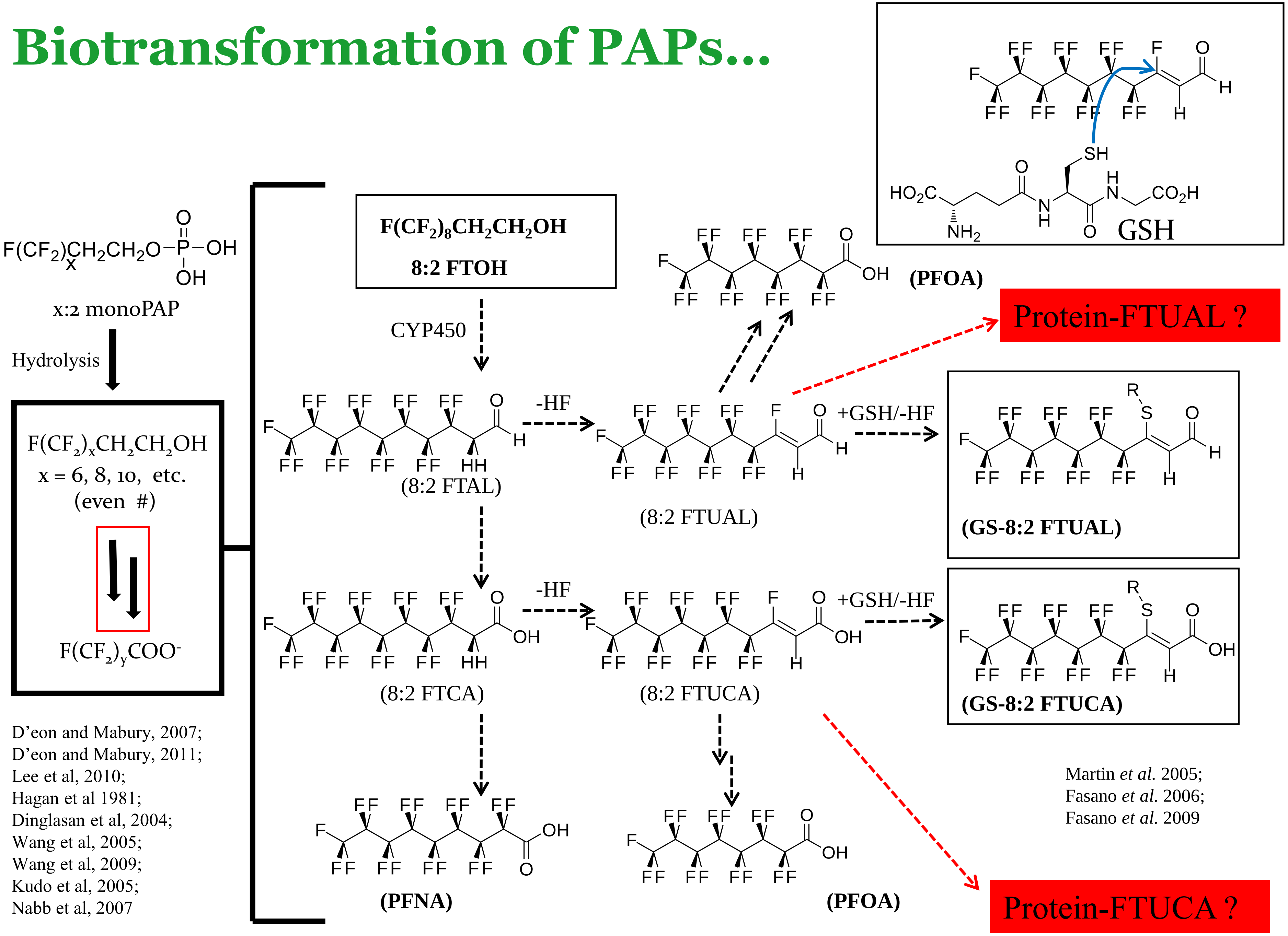
- *Thousands of tons of PFOA alone emitted from fluoropolymer manufacture*
- *major releases to surface waters (58,000 lbs of PFOA in '99/W.Va);*
- *major fate is to the oceans;*
- *ppm 'residual' in products;*

Indirect: ***Fluorinated precursors (FPs) are degraded atmospherically and metabolically to yield PFCAs. FPs are released from industrial sources and from 'in use' consumer products.***[3,4,5,6]



[1]Prevederous et al 2005; [2]Armitage et al 2006; [3]Martin et al, 2002; [4]Ellis et al 2003/2004; [5]Hurley et al 2004; [6]Desilva & Mabury 2006

Biotransformation of PAPs…



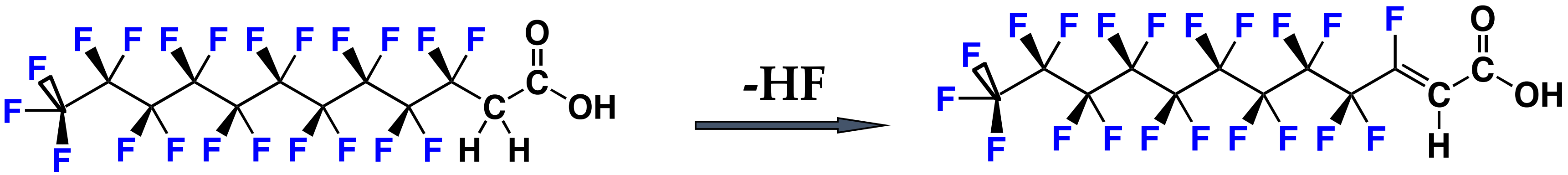
D'eon and Mabury, 2007;
D'eon and Mabury, 2011;
Lee et al, 2010;
Hagan et al 1981;
Dinglasan et al, 2004;
Wang et al, 2005;
Wang et al, 2009;
Kudo et al, 2005;
Nabb et al, 2007

Martin *et al.* 2005;
Fasano *et al.* 2006;
Fasano *et al.* 2009

FTCAs and FTUCAs Toxicity

MacDonald et al. found:

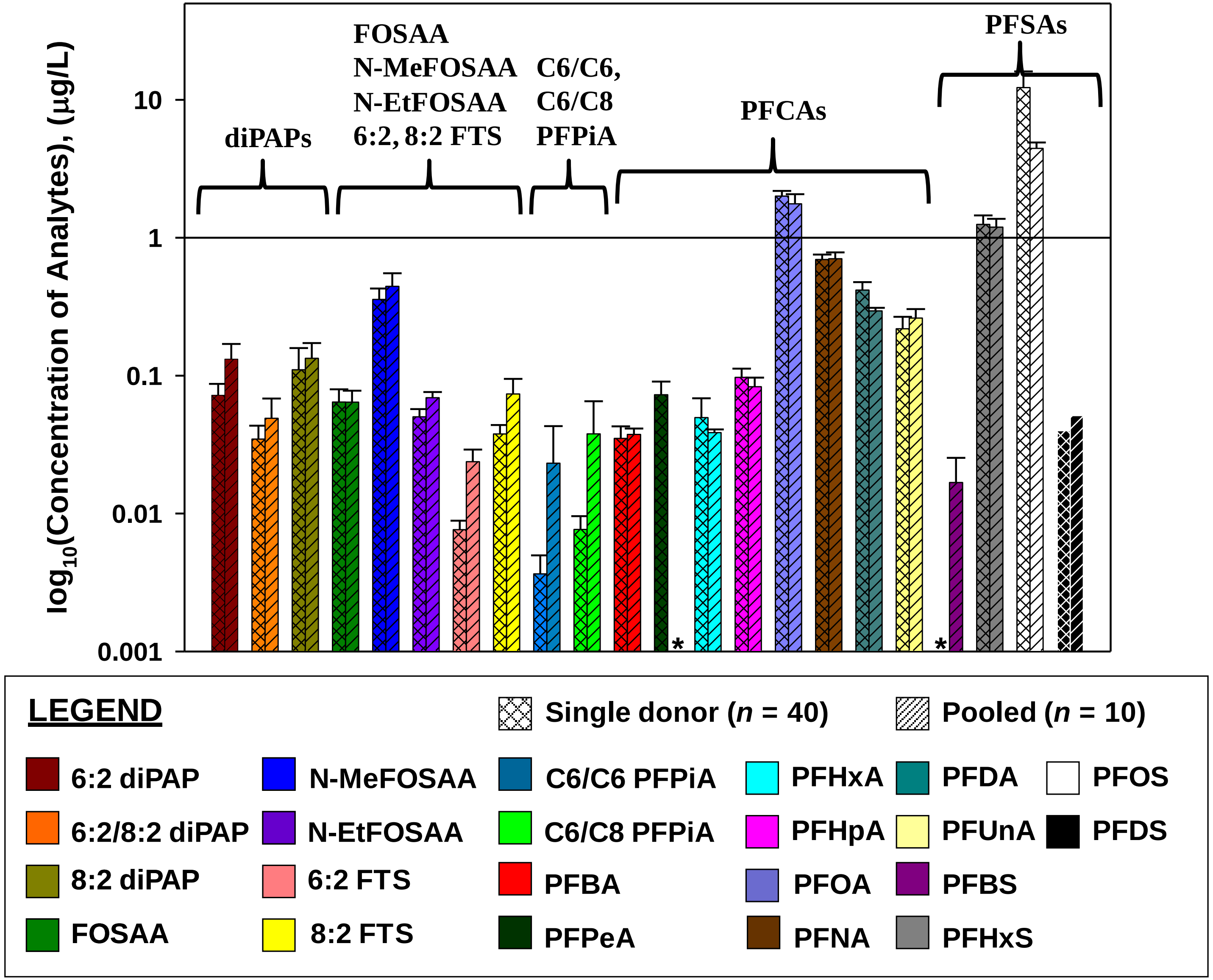
- 8:2 and 10:2 FTCAs and FTUCAs are up to **10,000 times** more toxic than PFCAs in freshwater species
- *Daphnia magna* particularly sensitive to telomer acids with a carbon chain length 8 and greater
  - Longer chain length → greater hydrophobicity → greater bioaccumulation
  - Compared with 8:2 telomer acids
    - 10:2 FTUCA 10x more toxic (EC50=0.28ppm)
    - 10:2 FTCA 100x more toxic (EC50=0.03ppm)
- FTCAs particularly toxic; idea why?



10:2 FTCA **10:2 FTUCA**

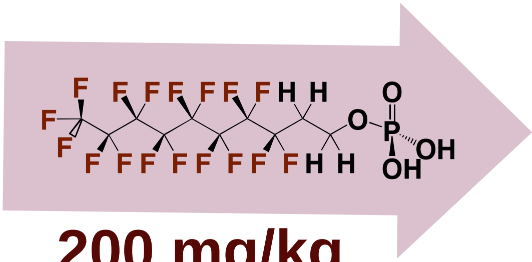
Phillips, MM et al., *Environ. Sci. Technol.*, **2007**, 41: 7159-7163 (Sibley/Mabury). **As of 5/1/24: 103 citations**

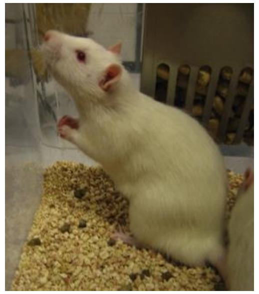
Human Contamination of Fluorinated Chemicals

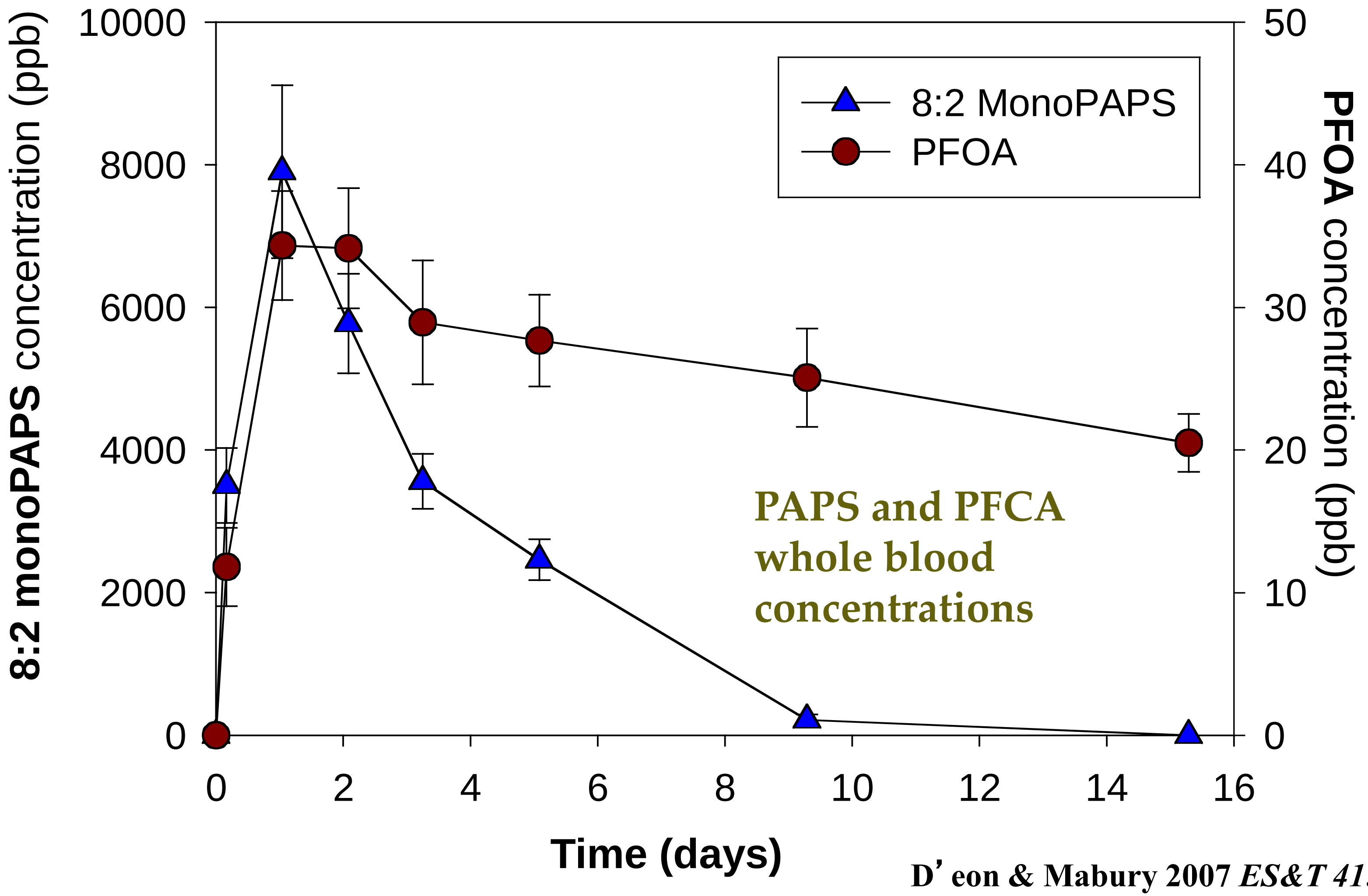


Lee and Mabury, **2011**, *Environ. Sci. Technol.* **45:8067-8074**

Metabolism of PAPs

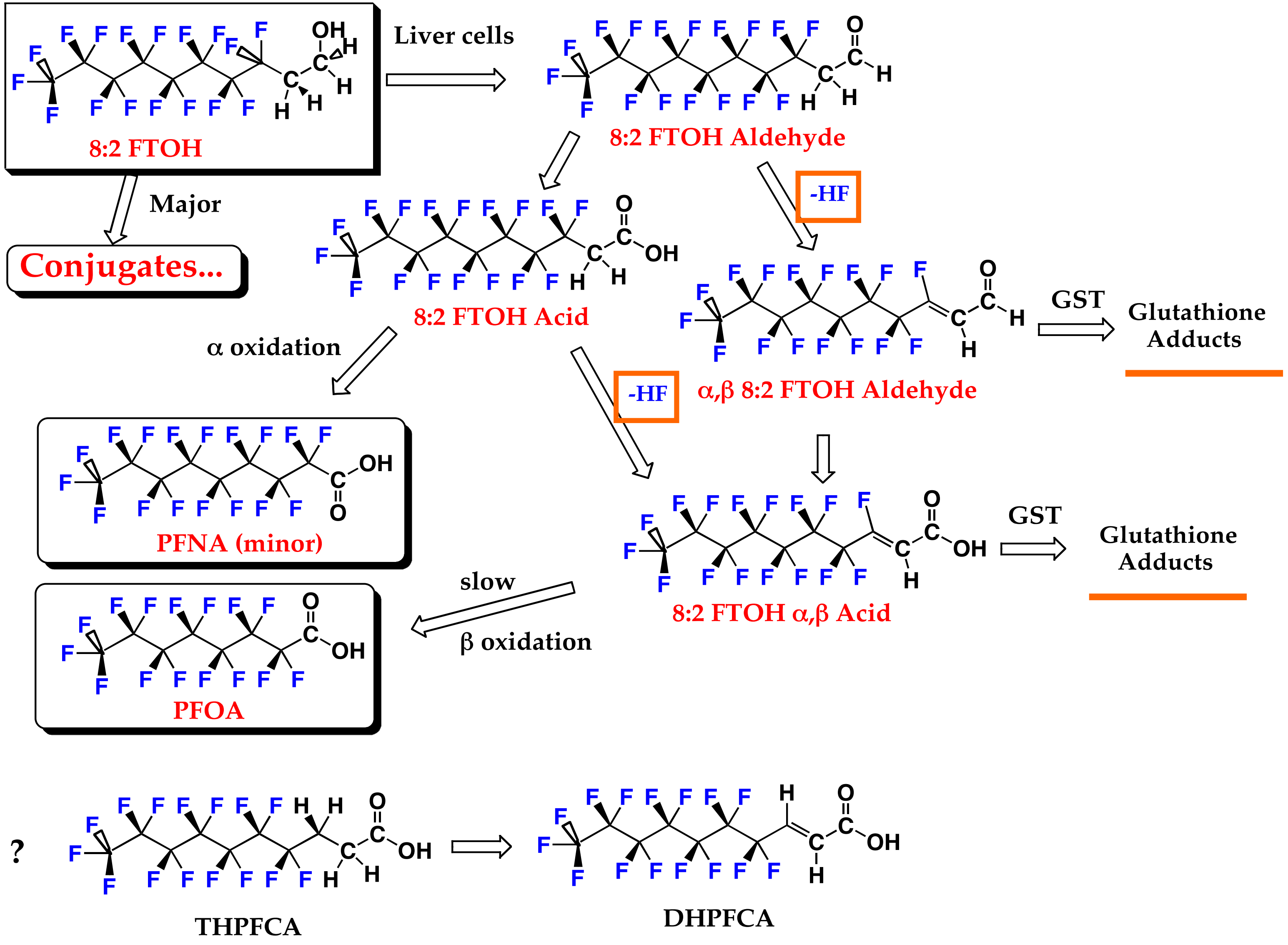






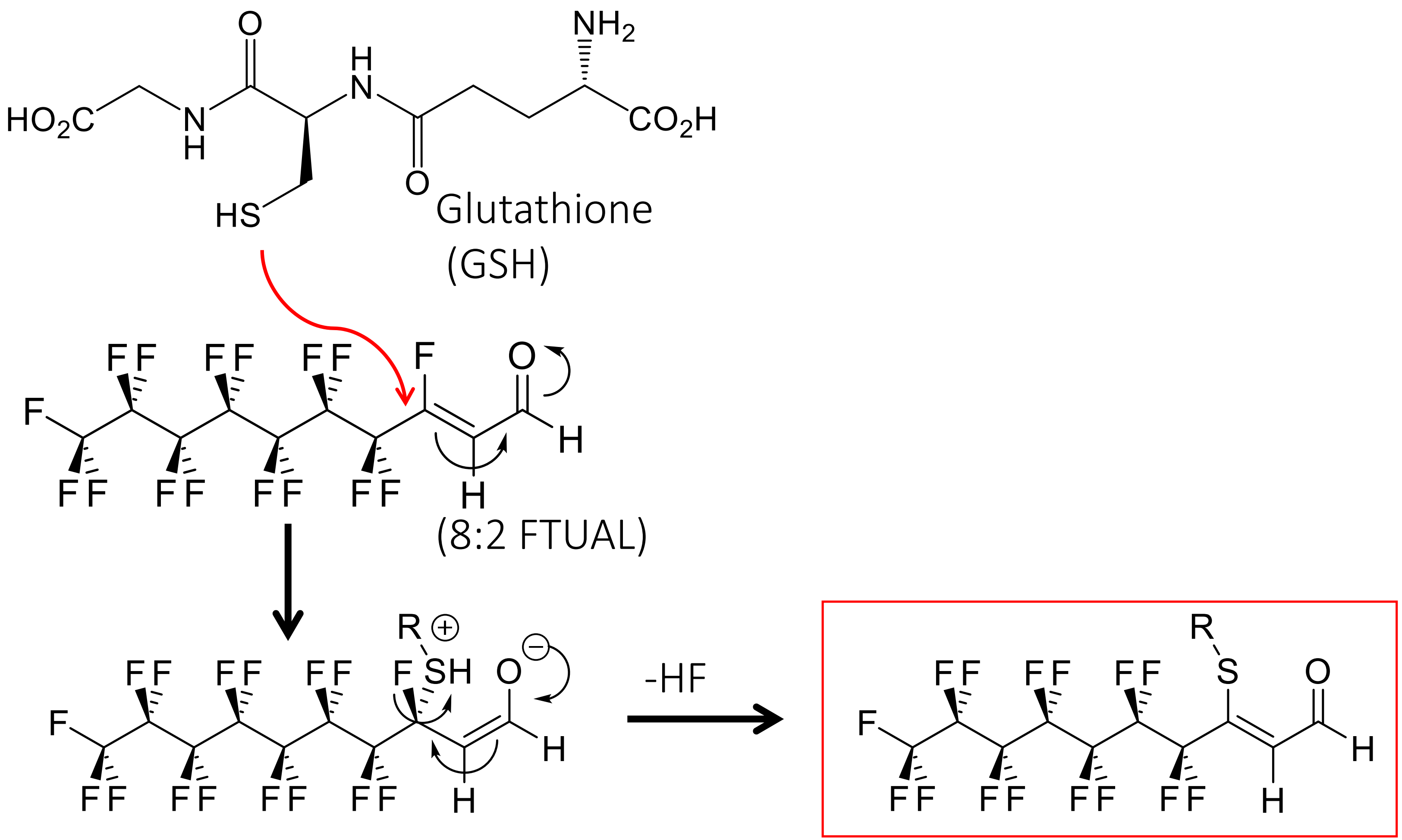
D' eon & Mabury 2007 *ES&T 41:4799-4805*

It matters because of mammalian metabolism (rat)



Hagen, Belisle, et al, 1981. Anal Biochem. 118:336-343; Martin, JW, SA Mabury, and PJ O'Brien. **2005**. *Chemico-Biological Inter*. **155**:165-180. Fasano et al 2006, Tox Sci 91:341-355.

Glutathione reactivity with fluorinated aldehydes

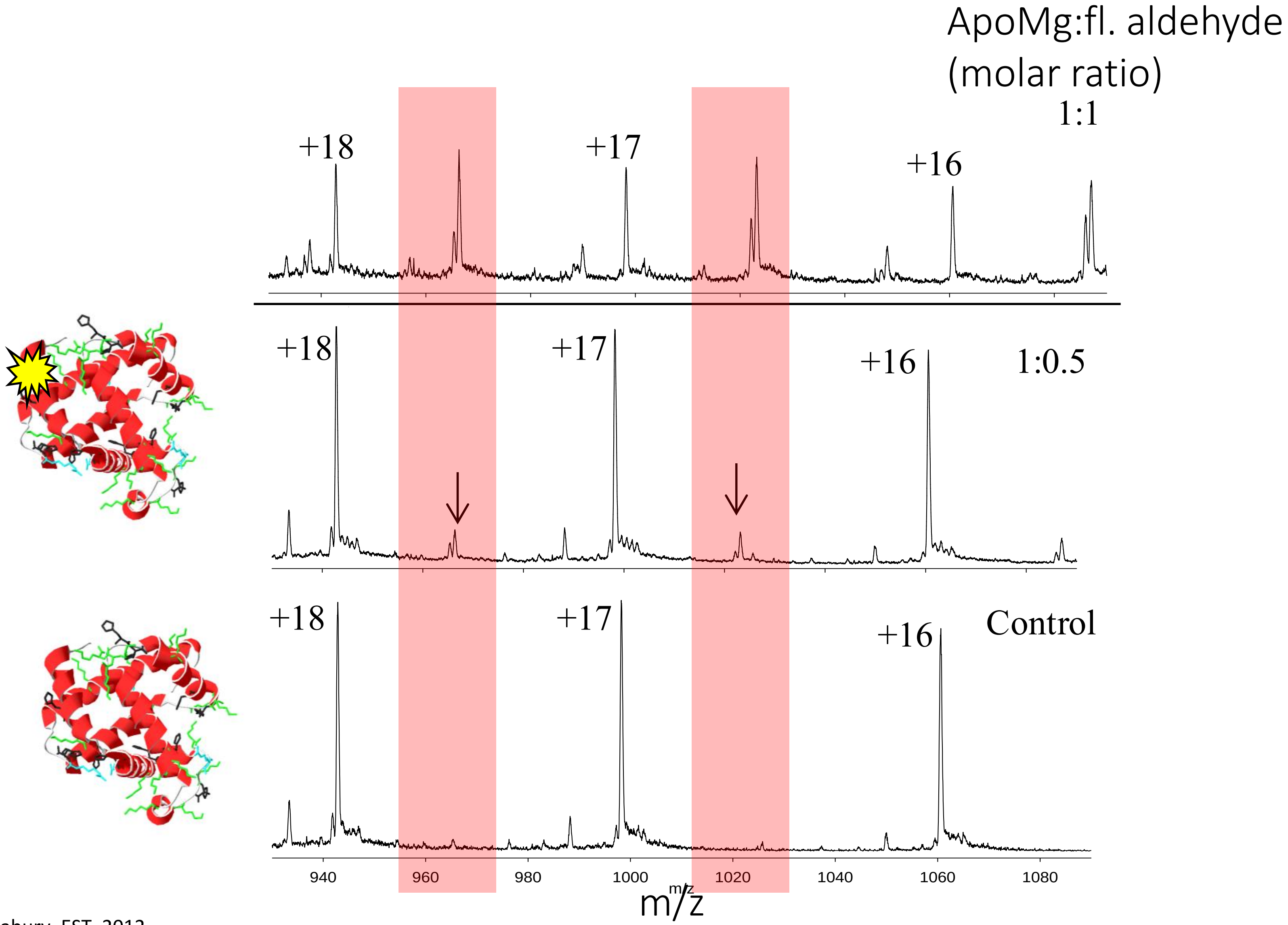


1,4 – Michael Addition

Protein binding?

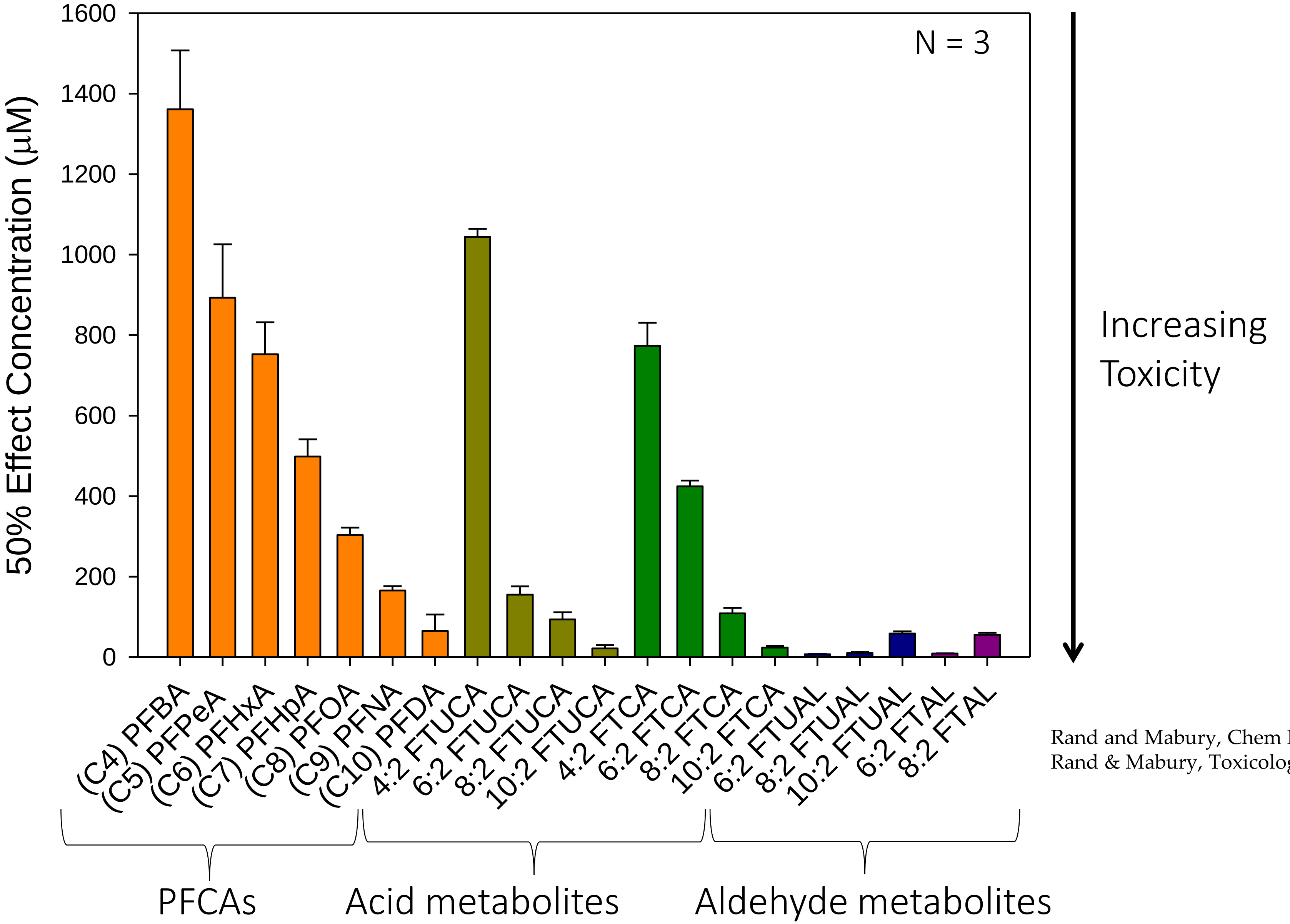
Nabb et al, 2007; Martin et al, 2005; Martin et al, 2009; Fasano et al, 2006; Fasano et al 2006

Fluorinated aldehyde adduct formation with ApoMg

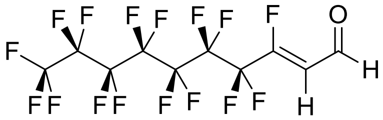


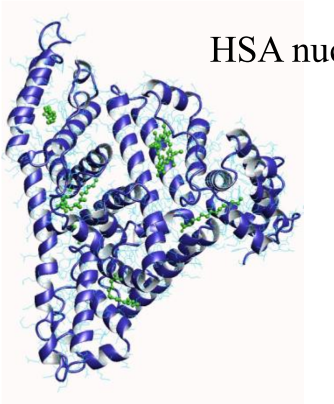
Rand and Mabury, EST, 2012

Cell survival and toxicity



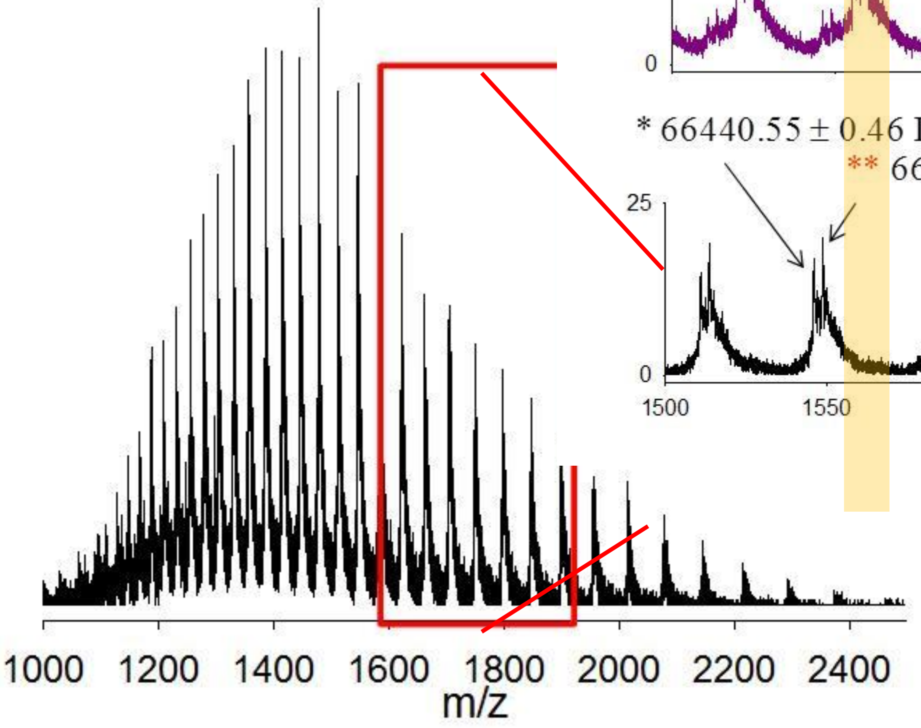
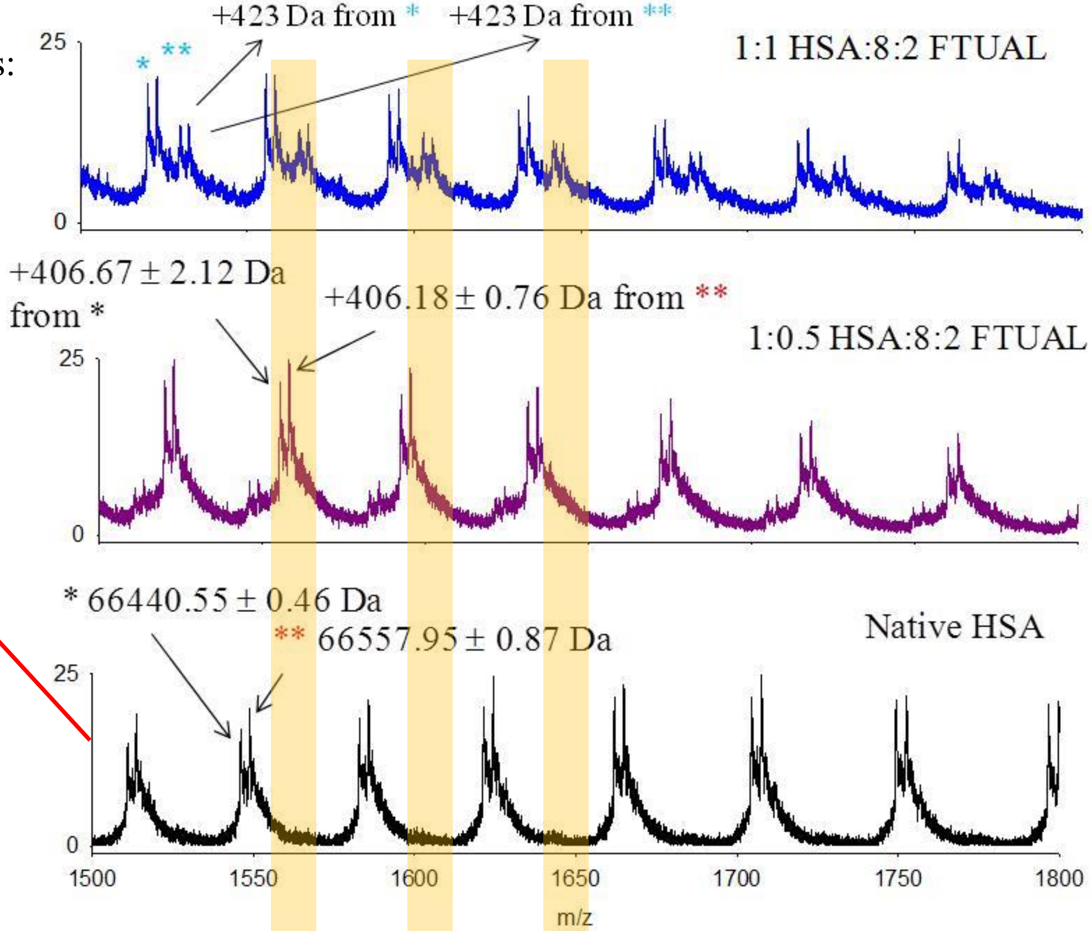
Rand and Mabury, Chem Res Toxicol, 2014. 27:42-50
Rand & Mabury, Toxicology 2017. 375:28-36

Human Serum Albumin (HSA) +  ⟶ HSA adducts



HSA nucleophilic amino acids:

23 Arg
58 Lys
15 His
1 Cys

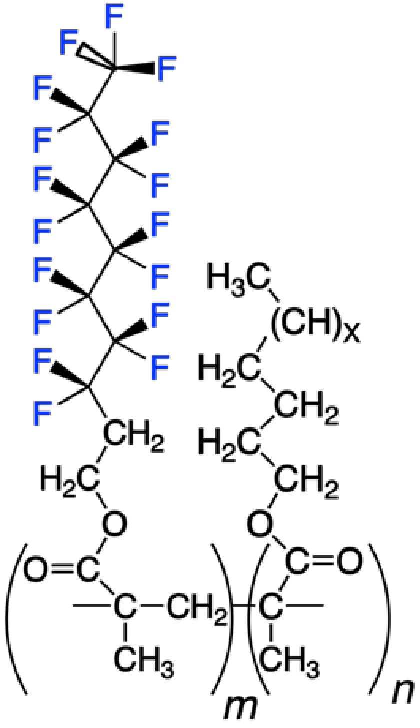



Rand A.A., Mabury S.A. Protein binding associated with exposure to fluorotelomer alcohols (FTOHs) and polyfluoroalkyl phosphate esters (PAPs) in rats. *Environmental Science and Technology*. 2014, *48*, 2421-2429

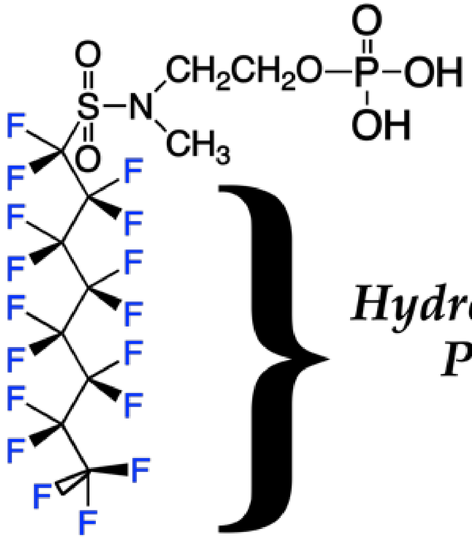
polymers

Do these "common" fluorinated polymers & surfactants contribute?

Hydro & Lipo-Phobic



Polymer (Ester)

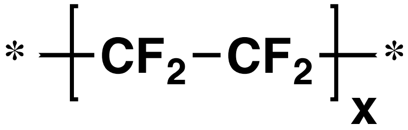


Hydro & Lipo-Phobic

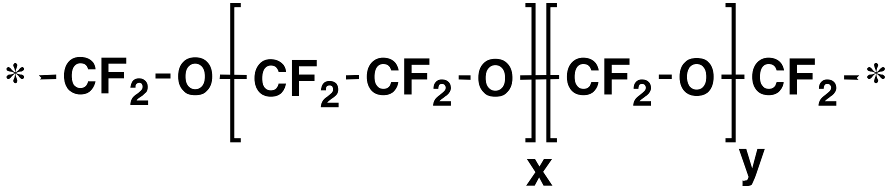
Surfactants (Phosphate)

Fluorinated Polymers

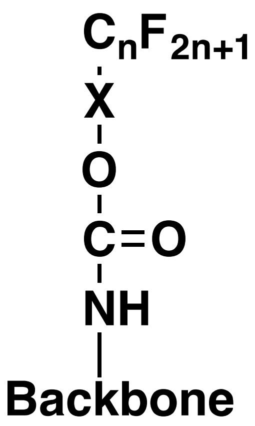
Fluoropolymers (eg. PTFE)



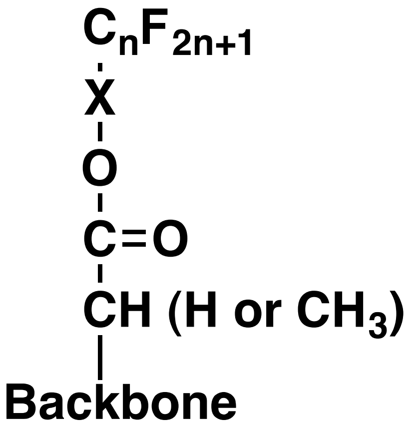
Perfluoropolyethers (PFPEs)



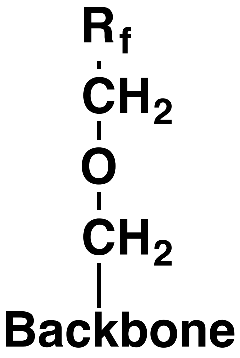
Side-Chain Fluorinated Polymers



Urethane



Acrylate and Methacrylate



Oxetane

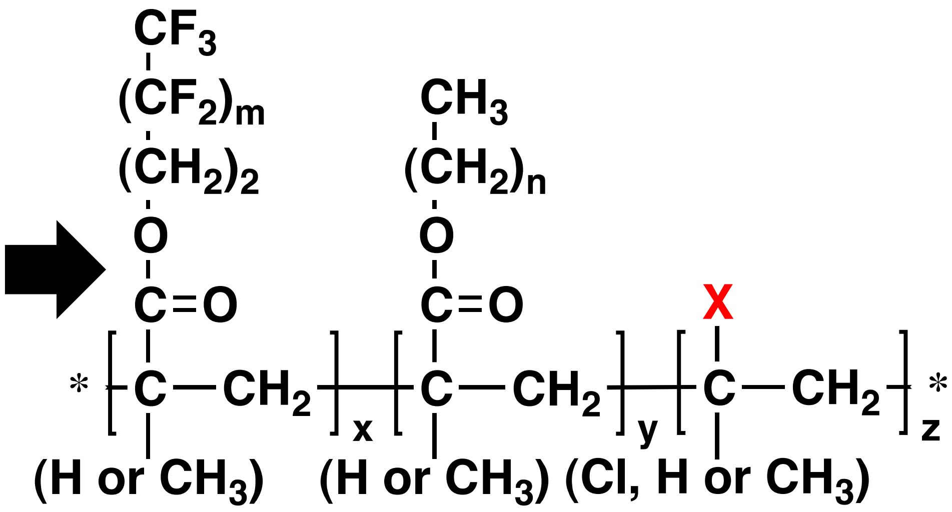
FTACPs

- Fluorotelomer-based acrylate polymers (FTACPs) are copolymers prepared fluorinated and non-fluorinated monomers
- Extremely effective surface protectants in carpet, textile and upholstery industries[1]
- Largests fraction of commercial fluorotelomer products constituting >80% of all fluorotelomer-based raw material produced[2,3]

Do FTACPs biodegrade?

How labile is the ester moiety?

What analytical techniques are suitable to study FTACP biodegradation?

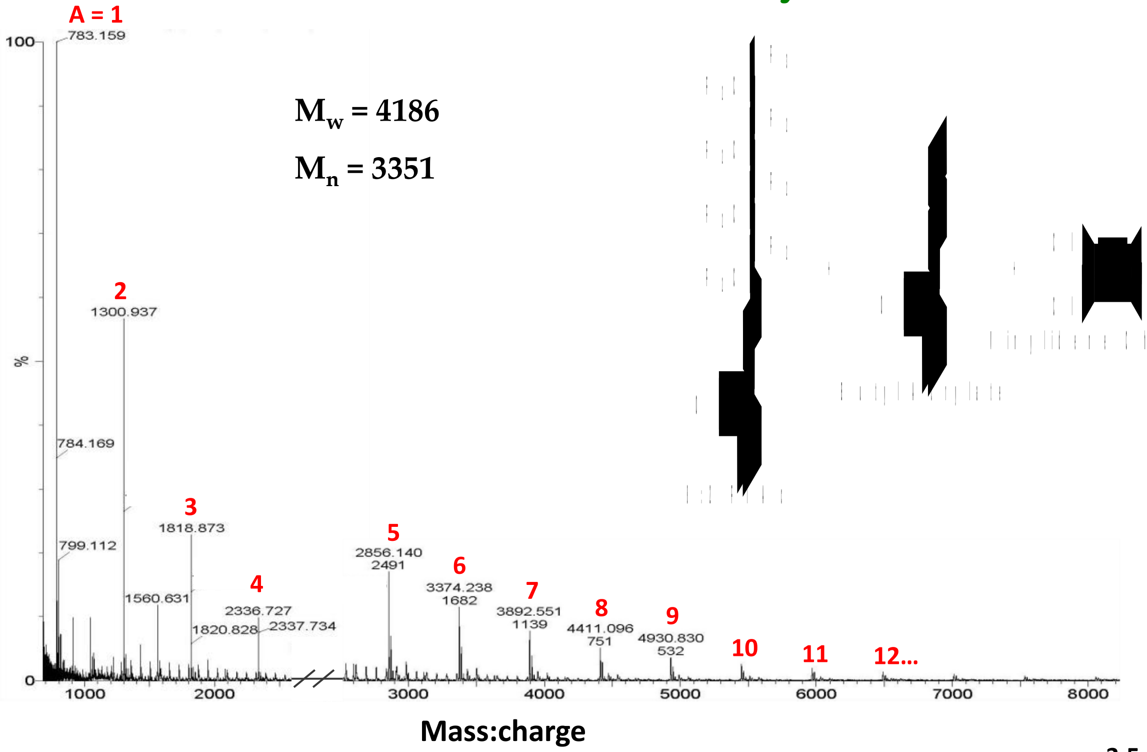


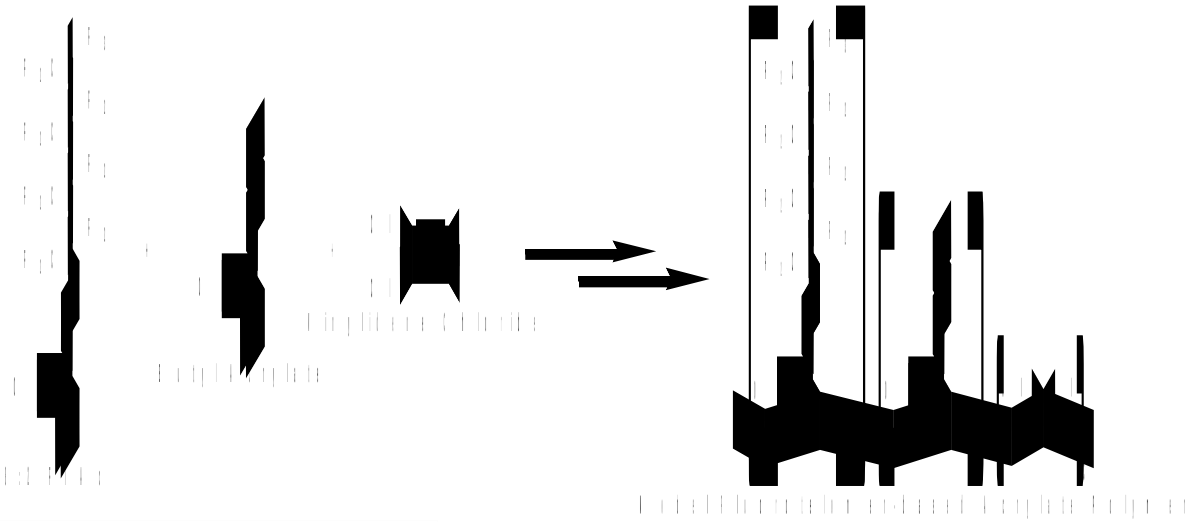
m = 5-13 and n=1-17

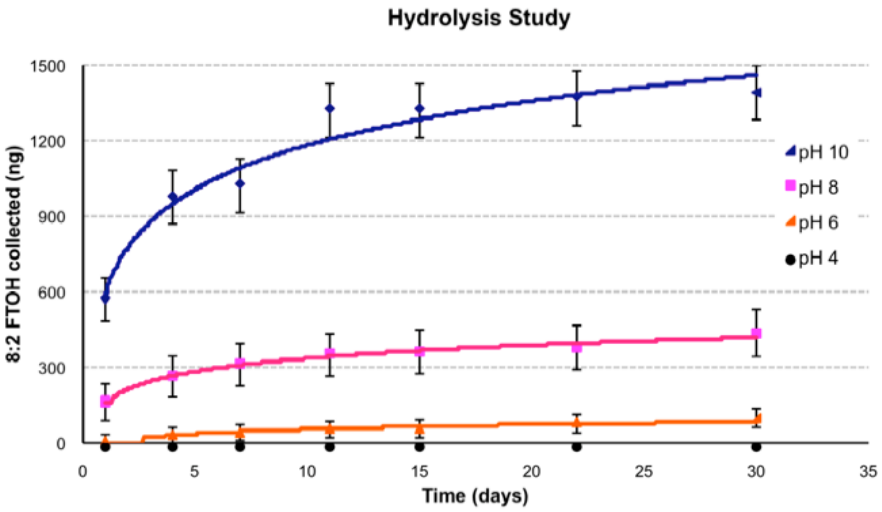
x = variety of non-fluorinated monomers

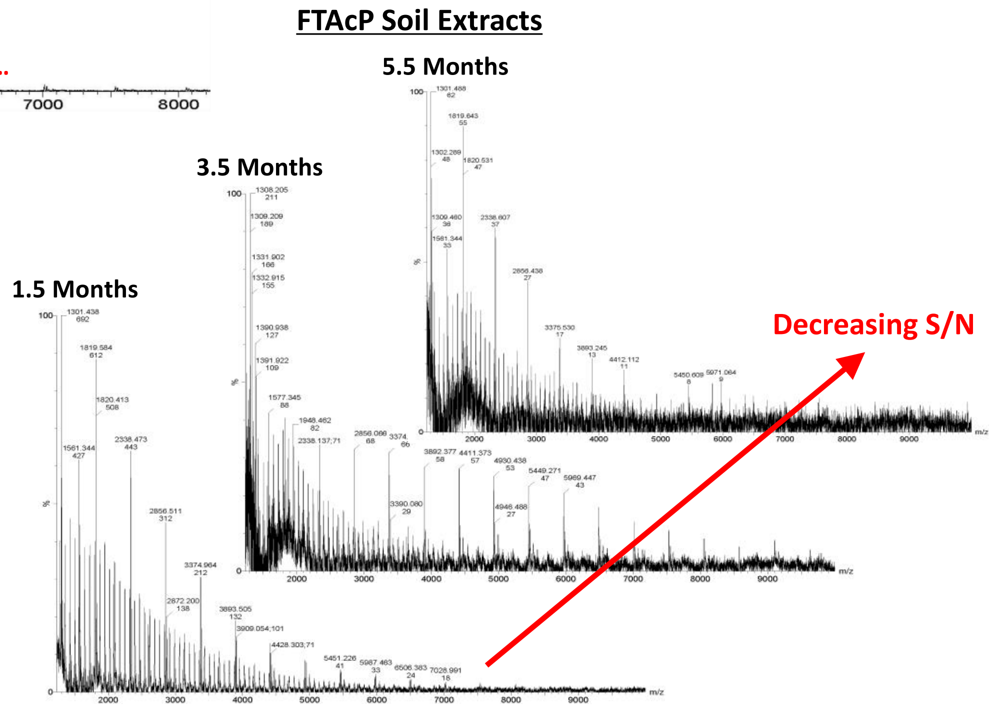
1. Rao *et al*. Organofluorine Chemistry (**1994**) 321-336.
2. USEPA Docket AR-226-1141 (**2002**) 1-48.
3. Prevederous *et al*. *Environ. Sci. Technol. 40* (**2006**) 32-44.

Our “New Model Polymer”









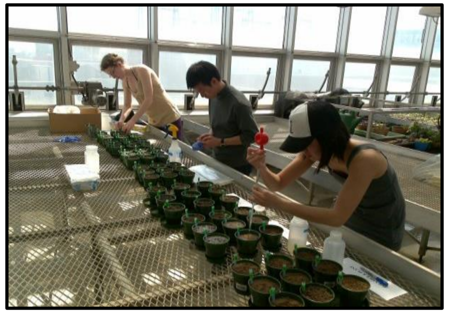
Fate of that Polymer in an Agrocosm?

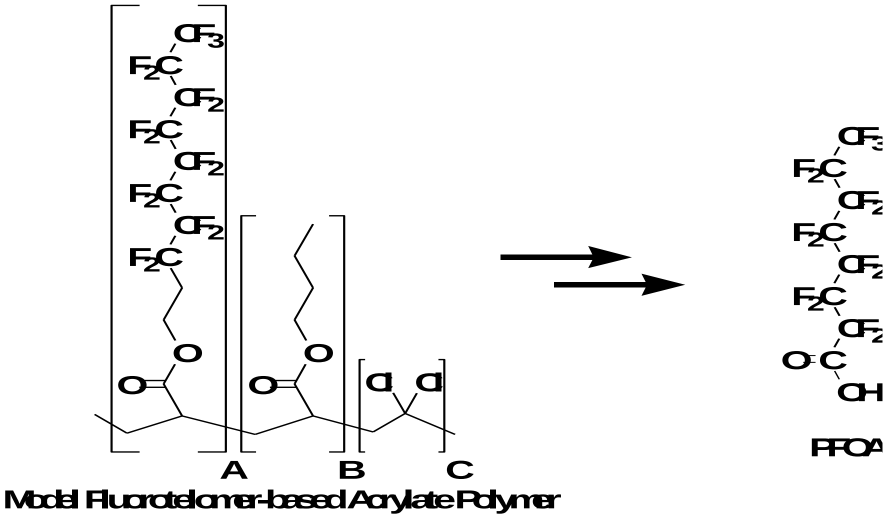
Sandy loam soil

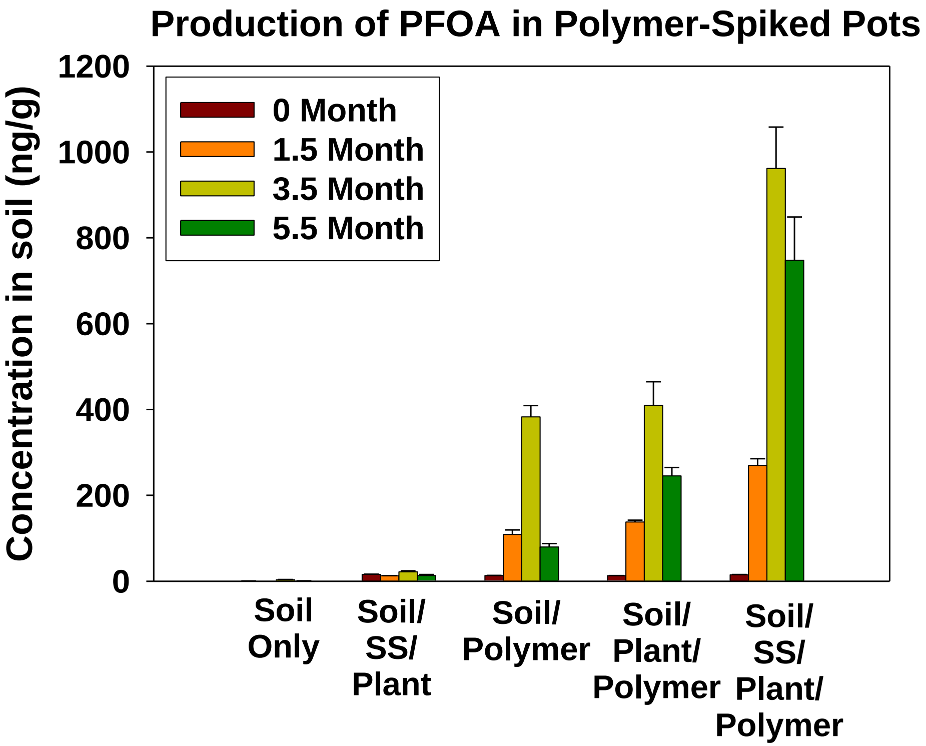
Medicago truncatula

Sinorhizobium meliloti (innoculum)

Sewage Sludge (16g/1000g soil)



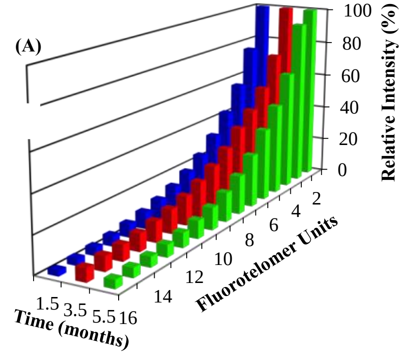


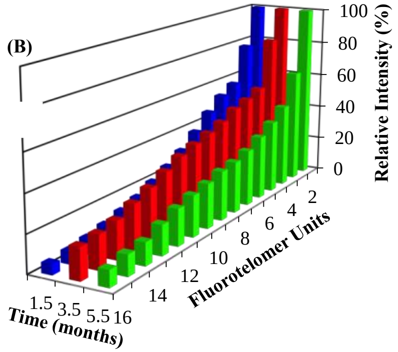


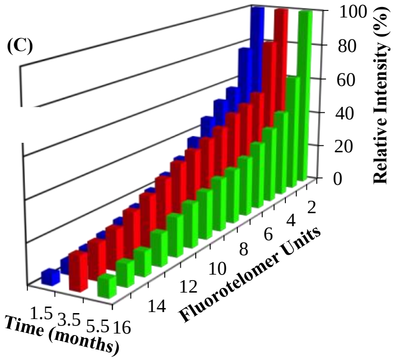
FTACP Biodegradation

Direct Analysis (MALDI-TOF)

FTACP/Soil



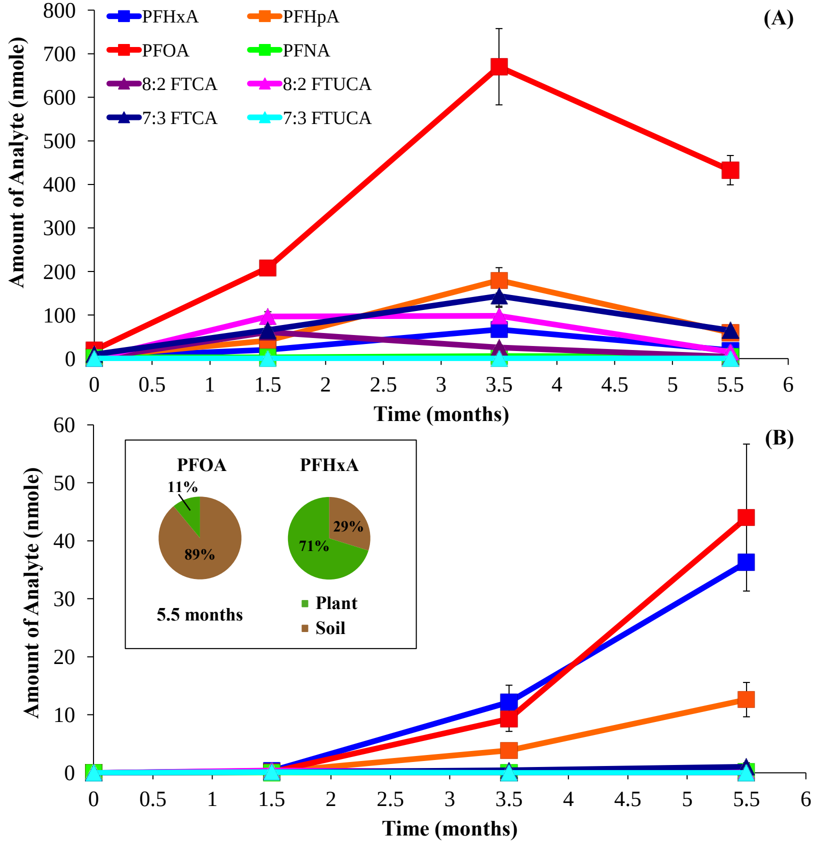




FTACP/Plant

FTACP/Plant/Bio solids

Indirect Analysis (LC-MS/MS)



Analytes measured in soil (A) and plant (B) for FTACP/Plant pots.

Rankin, K. H Lee, PJ Tseng, & SA Mabury 2014. Investigating the Biodegradability of a Fluorotelomer-Based Acrylate Polymer in a Soil-Plant Microcosm by Indirect and Direct Analysis. Env Sci Technol. **48:12783-12790.**

^{19}F NMR

Detailed analysis of Lake Niapenco

- NMR can identify additional fluorinated compounds in this sample compared with MS/MS measurements

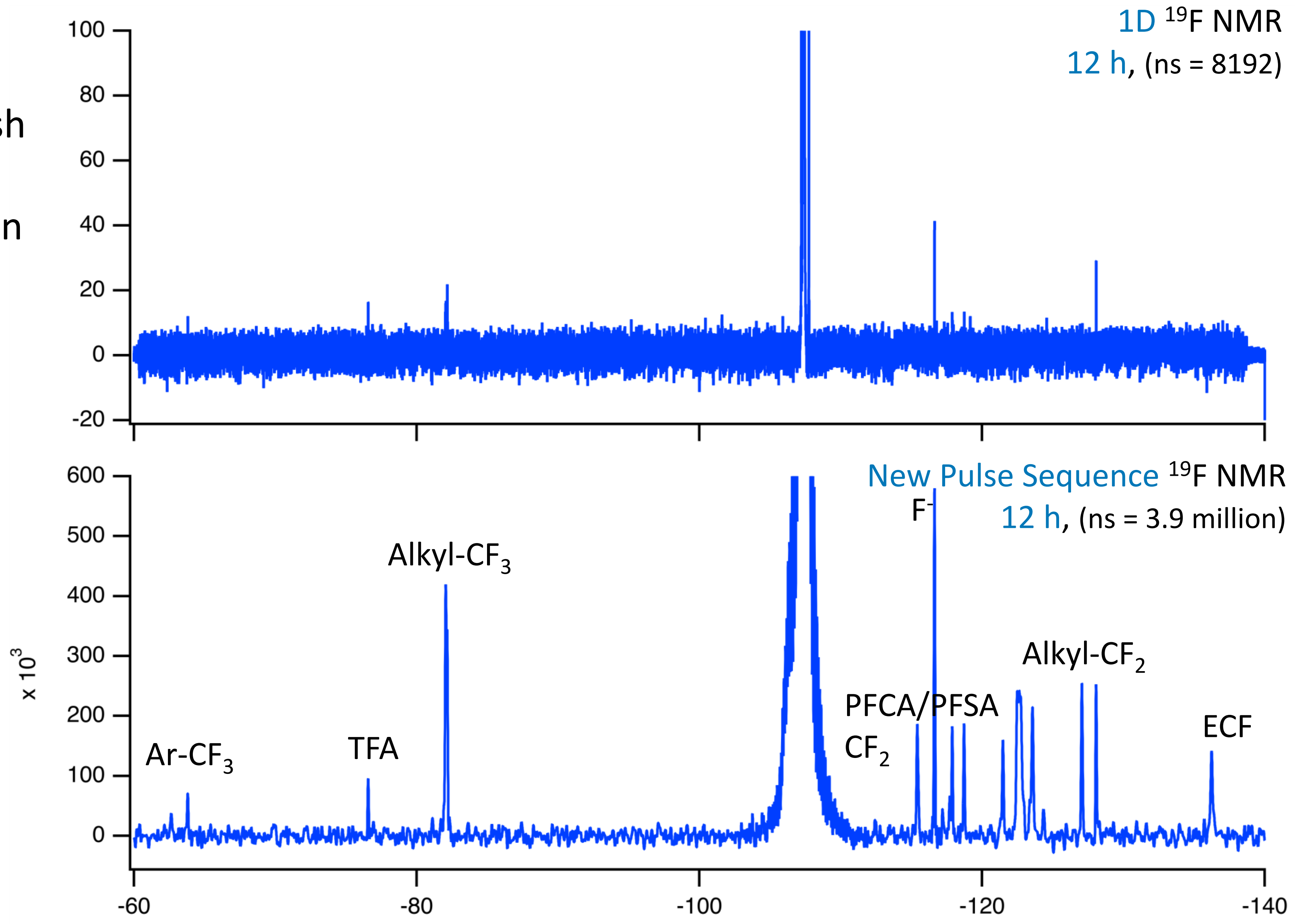
	^{19}F NMR	MS/MS	CIC-TOF
Total Fluorine	**65.7 µM**	**20.1 µM**	**66.9 µM**
TFA	0.437 µM	0.433 µM	?
PFCAs	19 µM	18.5 µM	?
PFSAs	1.87 µM	0.321 µM	?
Aromatic CF_3	12.8 µM	0.178 µM	?
Fluoride	22.8 µM	?	?
Others	8.79 µM	?	?

Towards the future of 19F NMR

- New pulse sequences push the capability of NMR. Revealing more detail than ever before

Sample Preparation

- 100 mg Polar Bear Liver
- Homogenize in d4 MeOH, centrifuge



Summary thoughts

- we've learned a lot;
- Chain length matters;
- Not all C-F bonds are recalcitrant/persistent…but some 'chemical architecture' does define persistence;
- Many of the original longer chain PFAS (PFOS/PFOA etc) seem to be declining in humans….;
- Shorter chain PFAS appear to be more widely used;
- Quite a few areas of inquiry have relatively paltry activity in the scientific community – polymers, reactive intermediates, atmospheric;
- Analyte list often is quite traditional and unimpressive;
- 19F NMR is very complementary to mass spec etc;
- Some progress towards 'greener use of F in chemical architecture'….need more creativity applied to the problem

Acknowledgements
- All the talented students who produced this work
- NSERC Funding

Cross Program Contaminant Working Group

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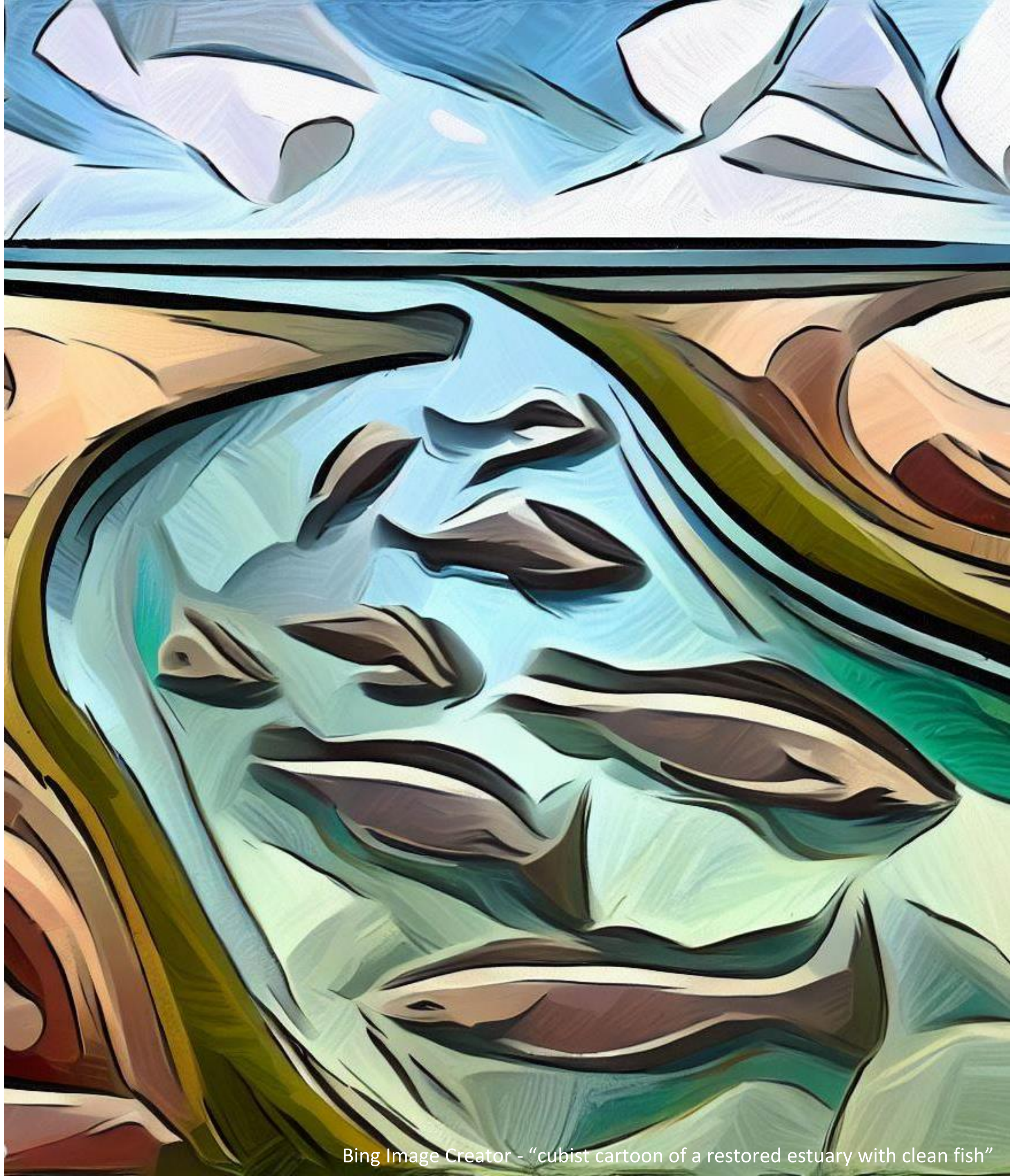
www.pugetsoundinstitute.org/collaboration/cross-program-contaminant-working-group/



Bing Image Creator - "cubist cartoon of a restored estuary with clean fish"