Per and Polyfluoroalkyl Substances (PFAS) Release from Landfills

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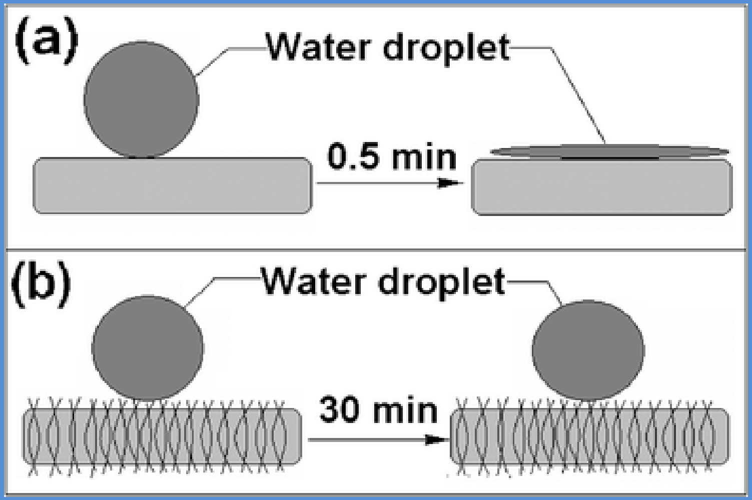
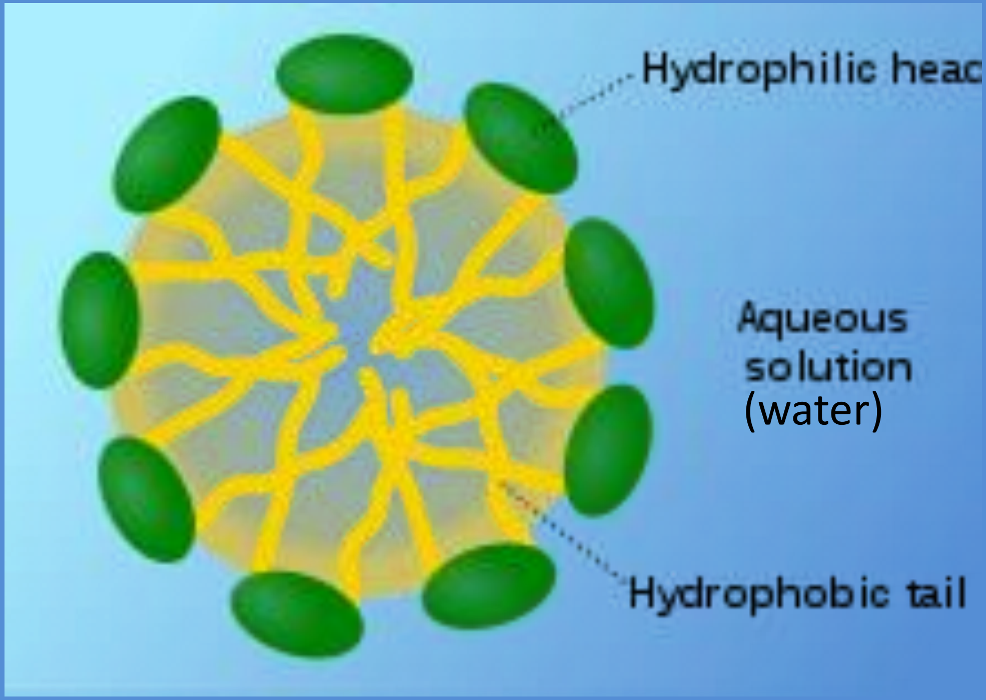
Disclaimer

- This research was completed as my PhD dissertation from North Carolina State University (NCSU).
- The information presented here does not represent the official views and policy of the US EPA.
- No part of this presentation should be considered an endorsement or recommendation by the USEPA.

PFASs

- Compounds with Carbon Fluorine Bonds
- Repel oil and water
- Hydrophilic head group likes water, but hydrophobic tail does not





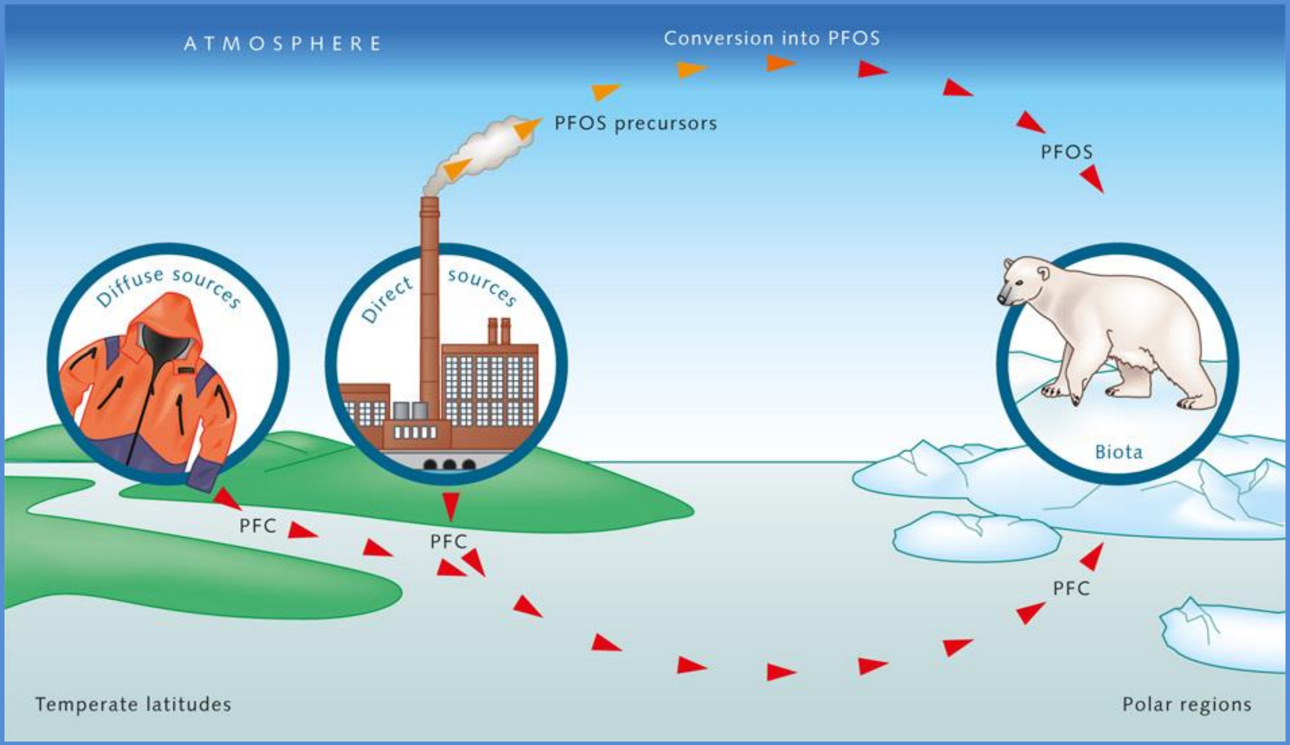
https://www.quora.com/How-do-non-stick-pans-work

PFASs

- Used in a wide range of applications, including clothing, carpet, upholstery, food packaging, fire fighting foam, and industrial applications

PFASs

- Nondegradable: The carbon fluorine (C-F) bond is extremely stable[1]
- Bioaccumulative: 98% of the US population blood



1 Smart, 1994

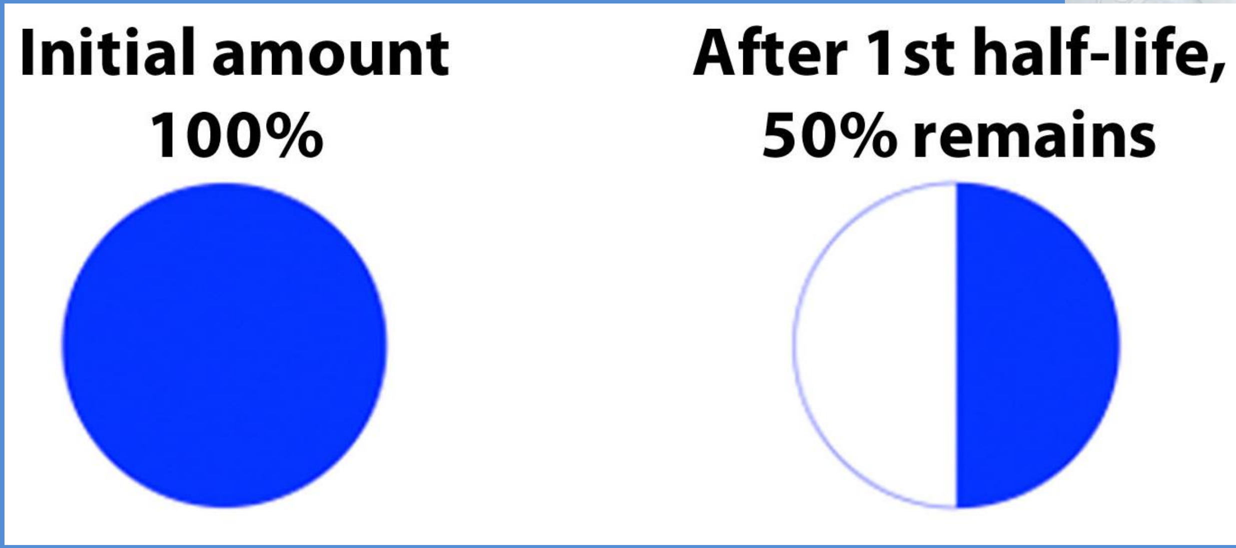
2 Health Effects Support Document for Perfluorooctanoic Acid (PFOA). EPA. May 2016

http://worldoceanreview.com/en/wor-1/pollution/organic-pollutants/2/

PFAS ½ Lives

Half-lives of PFASs in workers estimated through daily elimination (Fu et al. 2016)

- PFOS: 21.6 years
- PFHxS: 11.7 years
- PFOA: 4.0 years

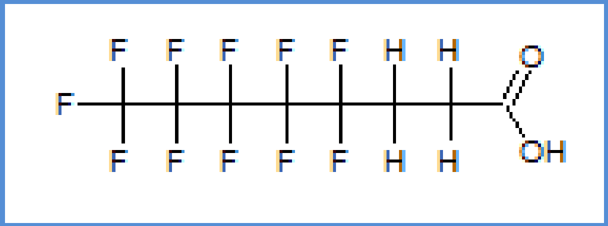
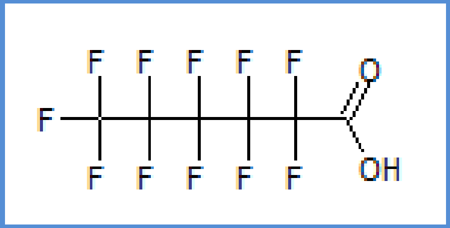
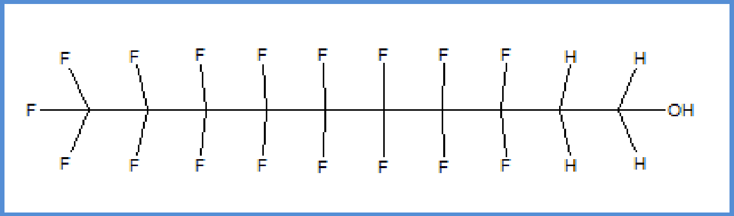
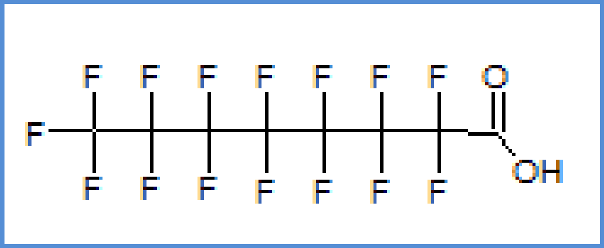


PFAS and Your Health

- The toxicology of PFOA and PFOS has been thoroughly researched, but there are hundreds of other PFASs being used on products and emitted as industrial waste with no toxicology data
- Human epidemiology PFOA Studies:
  - High cholesterol
  - Increased liver enzymes
  - Decreased vaccination response
  - Thyroid disorders
  - Pregnancy-induced hypertension and preeclampsia
  - Cancer (testicular and kidney)

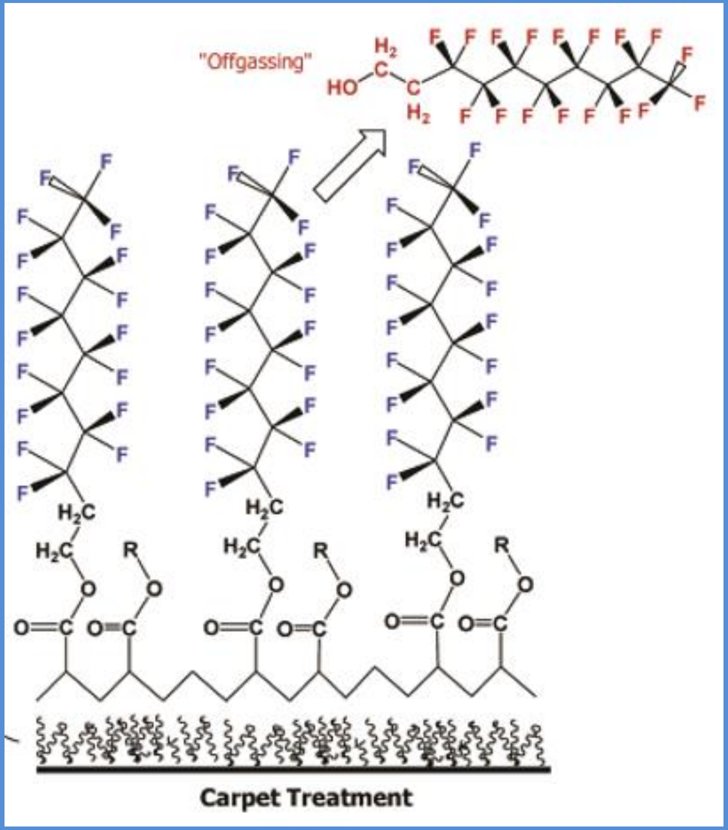
Chemistry and Acronyms of Monomers

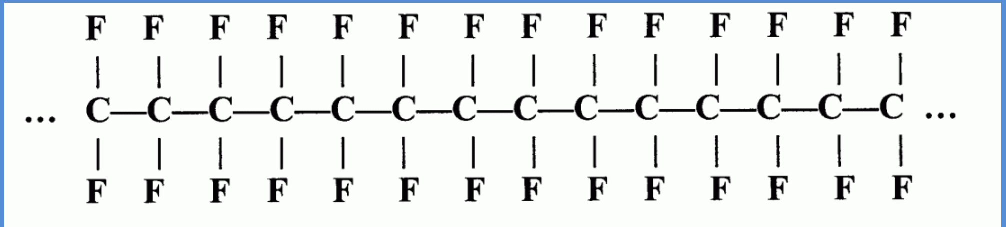
- Monomers: a single fluorinated carbon tail
- Fluorinated tail: Hydrophobic
- Head group: Hydrophilic

Polyfluoroalkyl Substances (degrades to perfluorinated substances)	**Perfluoroalkyl Substances** (non-degradable)
5:3 Fluorotelomer Carboxylic Acid	Perfluorohexanoic Acid (PFHxA – C6)
	
8:2 Fluorotelomer Alcohol	Perfluorooctanoic Acid (PFOA – C8)
	

PFASs on Products

- PFASs on products (i.e. carpet and non-stick pans) are fluoropolymers, not monomers
- Monomers can exist as a residual of manufacture
- Previous Major Unproven Assumption in Global Models: Fluoropolymers are considered recalcitrant and releases are zero (Wang et al. 2014)




TEFLON polymer (segment)

Dinglasan-Panlilio, M.A. And Mabury, S.A. Significant Residual Fluorinated Alcohols Present in Various Fluorinated Materials. ES&T 2006, 40, 1447-1453.

My Life

PFAS in Landfill Leachate

Chemours PFAS Contamination of Wilmington, NC Drinking Water

Unknown PFASs using MS-TOF

Rodent Toxicology

National Estimate of PFAS Release to U.S. Municipal Landfill Leachate

ES&T, 2017, *51* (4), pp 2197–2205

PFAS Mass Flow Equation

$$M_p = \overline{x_p} \times V$$

M_p = Mass flow of PFAS p (kg yr^{-1})
$\overline{x_p}$ = Average concentration of PFAS p (ng L^{-1})
V = Total Volume of leachate generated in 2013 (m^3)

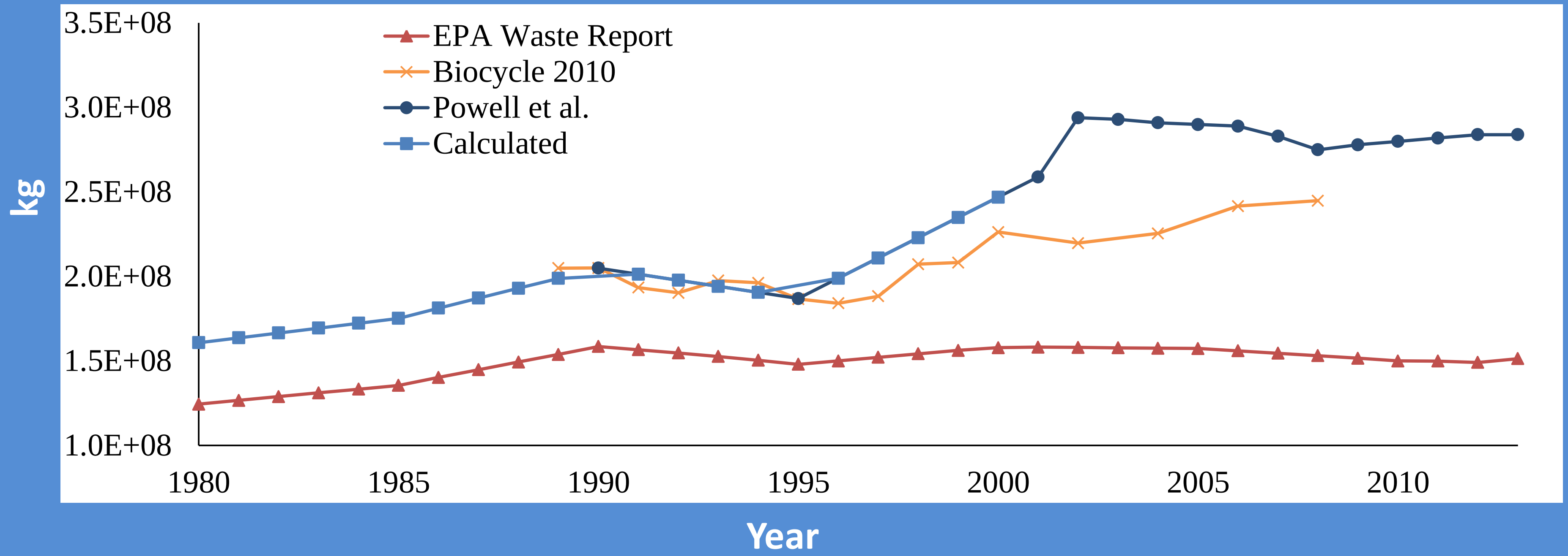
Equation repeated for wet, temperate and arid climates and for average waste ages >10 years and <10 years

PFAS Mass Flow Equation

$$M_p = \overline{x_p} \times WIP \times LG \;/\; SA$$

M_p = Mass flow of PFAS p (kg yr^{-1})
$\overline{x_p}$ = Average concentration of PFAS p (ng L^{-1})
WIP = Total mass of waste contained in Tg (1 Tg = 10^6 kg)
LG = Leachate generation rate (m^3/ha−day)
SA = Mass of waste per surface area (Tg ha^{-1})

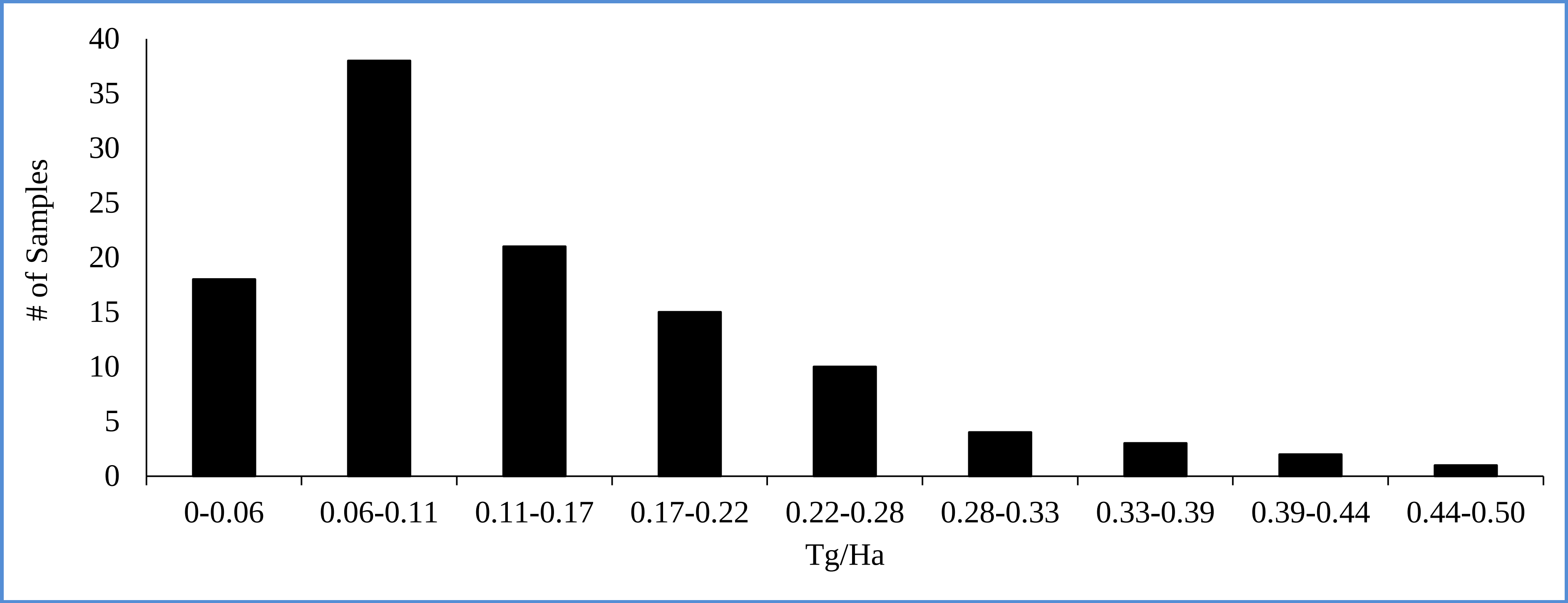
Waste in Place



WIP = Total Mass Buried 1980 to 2013

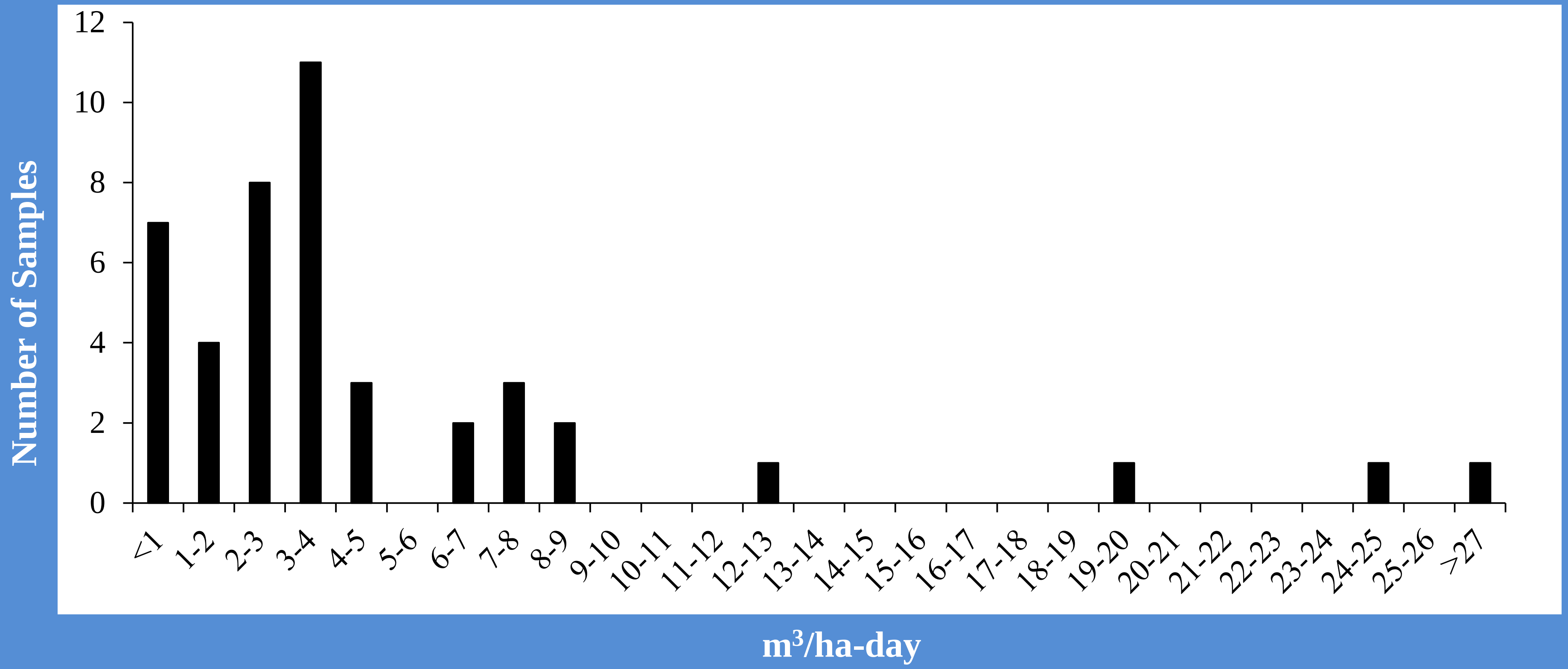
- EPA uses "top down" approach (material flow analysis)
- Biocycle and Powell et al. use surveys of solid waste management departments and landfill operators for the majority of the data

Mass of waste contained per landfill surface area



- Data obtained from state reports (n = 18) and a consulting engineer (n = 95)

Leachate Generation Rate in Wet Climates



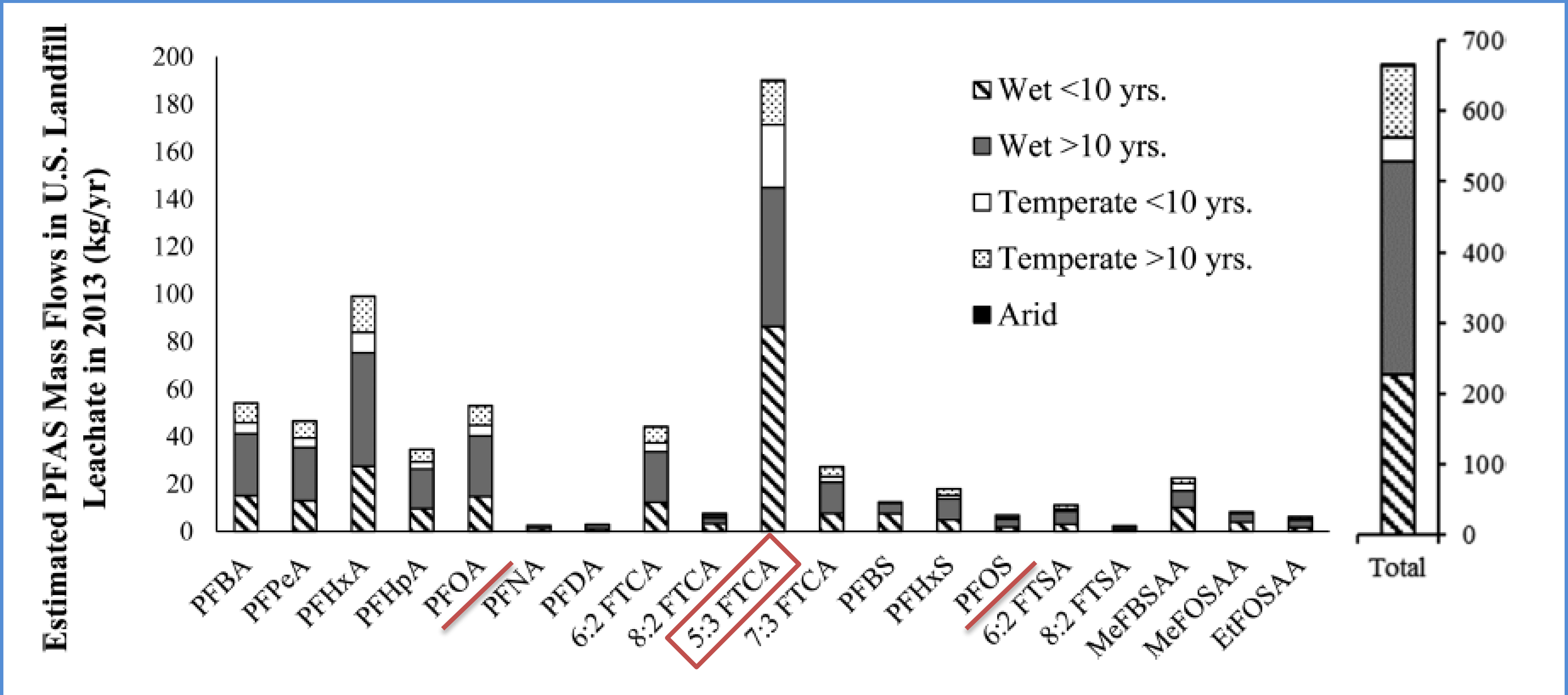
Data from annual landfill operating reports to state agencies (n = 27), published data (n = 12), landfills that participated in this study (n = 7) and a consulting engineer (n = 6)

Annual Landfill Leachate Generation Volume

$$M_p = \overline{x_p} \times WIP \times LG \; / \; SA$$

	Leachate Generation (m³/ha-day)	**Mass per Surface Area (Tg/ha)**	**Total Waste in Place[a] (Tg)**	**Volume of Leachate for 2013 (million m³/yr)**
Arid	0.04 ± 0.03	0.144 ± 0.098	1,492	0.1
Temperate	2.0 ± 3.0	0.144 ± 0.098	2,602	13.0
Wet	5.0 ± 14.0	0.144 ± 0.098	3,648	48.0
Total				**61.1**

PFAS Release from U.S. Landfills to WWTPs for waste landfilled in 2013



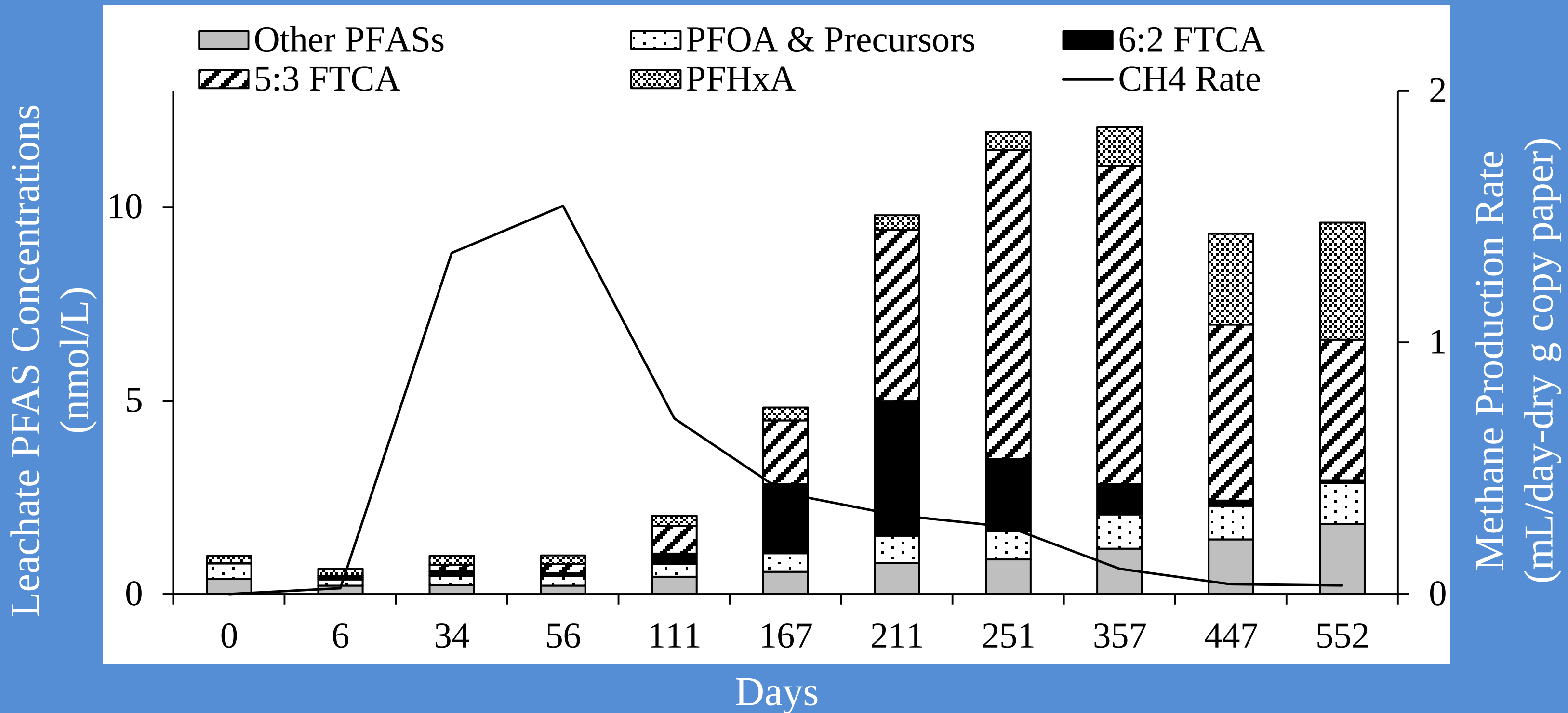
- Similar to carpet reactors, 5:3 FTCA a major component of total PFAS release in landfill leachate
- Total PFAS release for the US in 2013 is estimated at ~650 kg/yr

Physical and biological release of PFASs in laboratory-scale anaerobic bioreactors filled with carpet and clothing

ES&T 2016. 50, 5024−5032.

Objective: To measure aqueous phase concentrations of 70 PFASs released from carpet and clothing over time (>500 days)

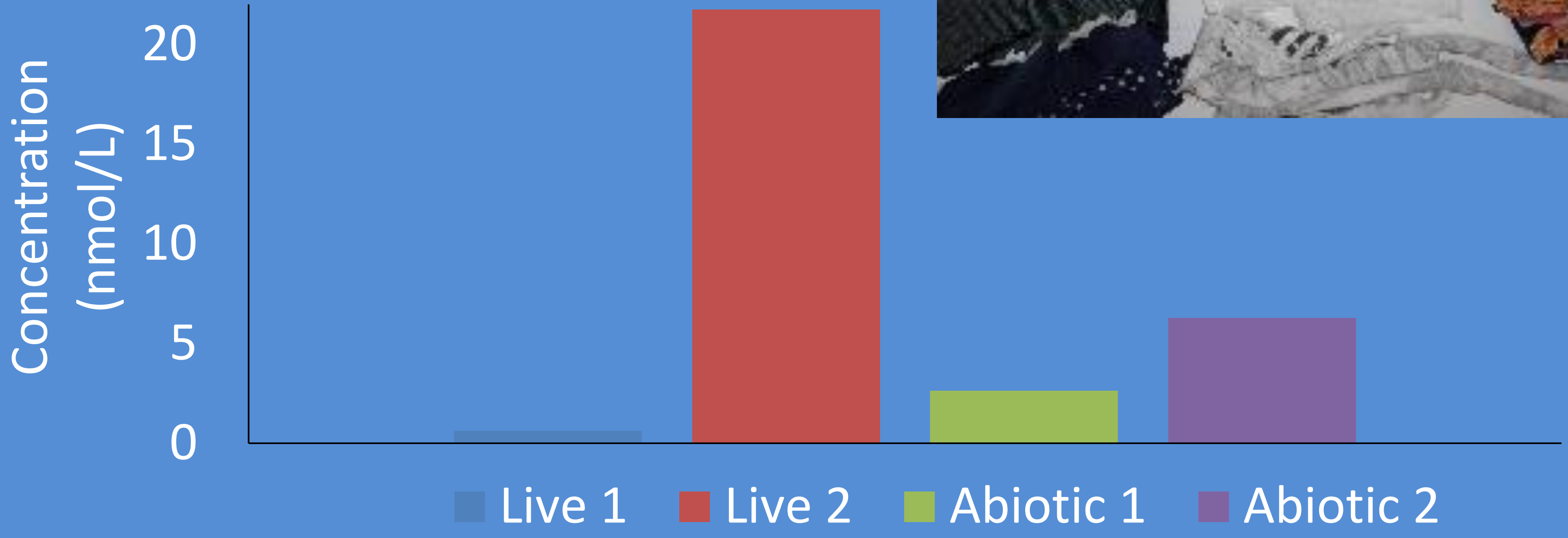
PFAS Release Live Carpet Reactor



- The lag period (>100 days) before the majority of PFAS release indicates the source of release may not be limited to residual monomers
- 5:3 flurotelomer carboxylic acids (FTCAs) are perfluoroalkyl precursors not commonly used on products

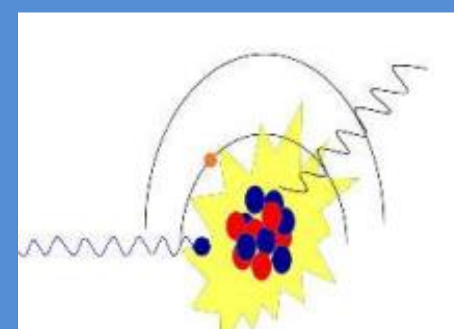
Clothing Reactors at the Final Time Point

High variability in total PFAS release due to sample variability (these red shorts)



Clothing Reactors

Particle Induced Gamma-ray Emission (PIGE)
Dr. Graham Peaslee, Notre Dame
Total Fluorine



Landfill Conclusions

- PFCA precursors contribute significantly to total PFAS release from landfilled carpet
- PFAS release from clothing is variable with large releases from some materials
- Release is Slow: The majority of PFAS release did not occur until >100 days of operation in model landfill reactors
- The mass of PFAS released yearly for a single year of municipal waste is small relative (~650 kg/yr) compared to industrial sources but may continue at low levels for many years

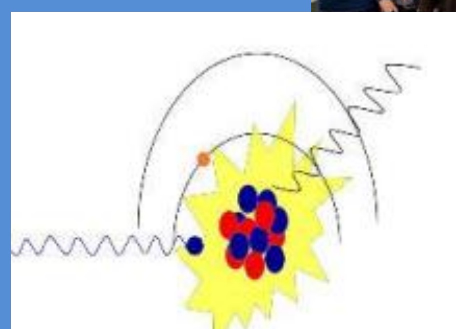
Mark Strynar, EPA, RTP, NC

- Mass spectrometry to quantify the concentrations of target compounds

- Mass spectrometry to identify unknown compounds

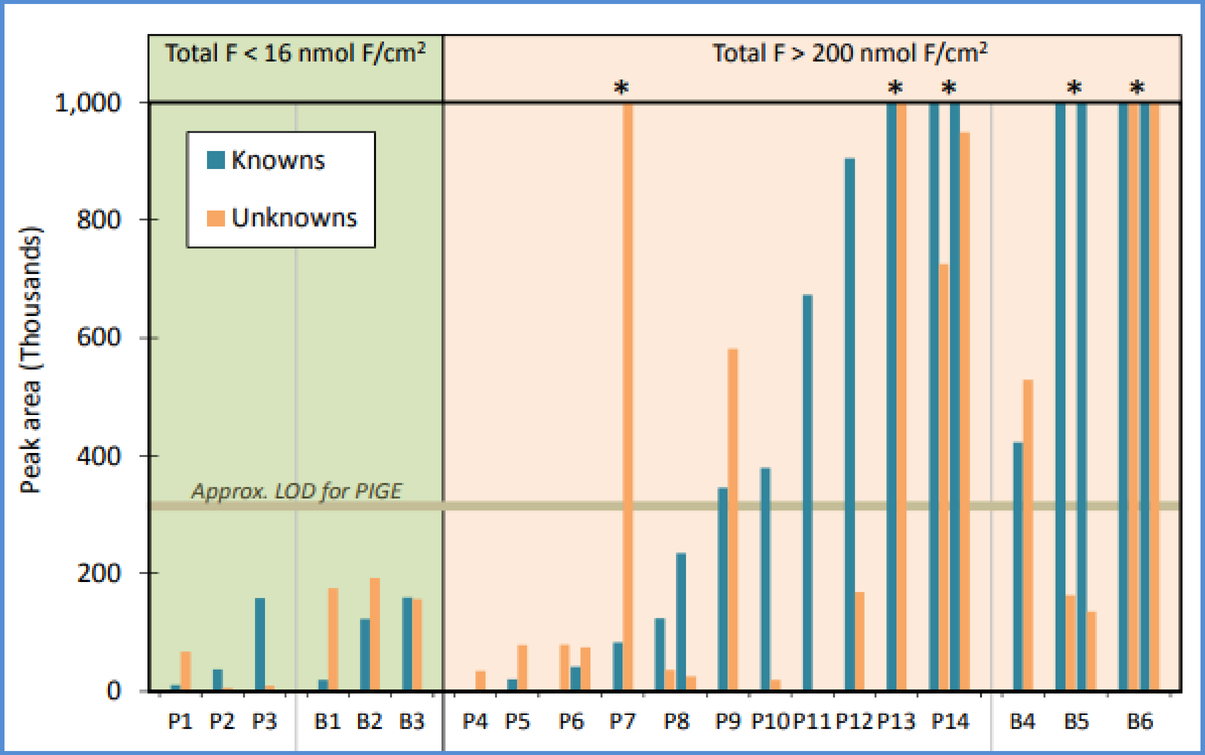
Fluorinated Compounds in U.S. Fast Food Packaging (ES&T Letters 2017)

Particle Induced Gamma-ray Emission (PIGE)
Total Fluorine on ~400 samples



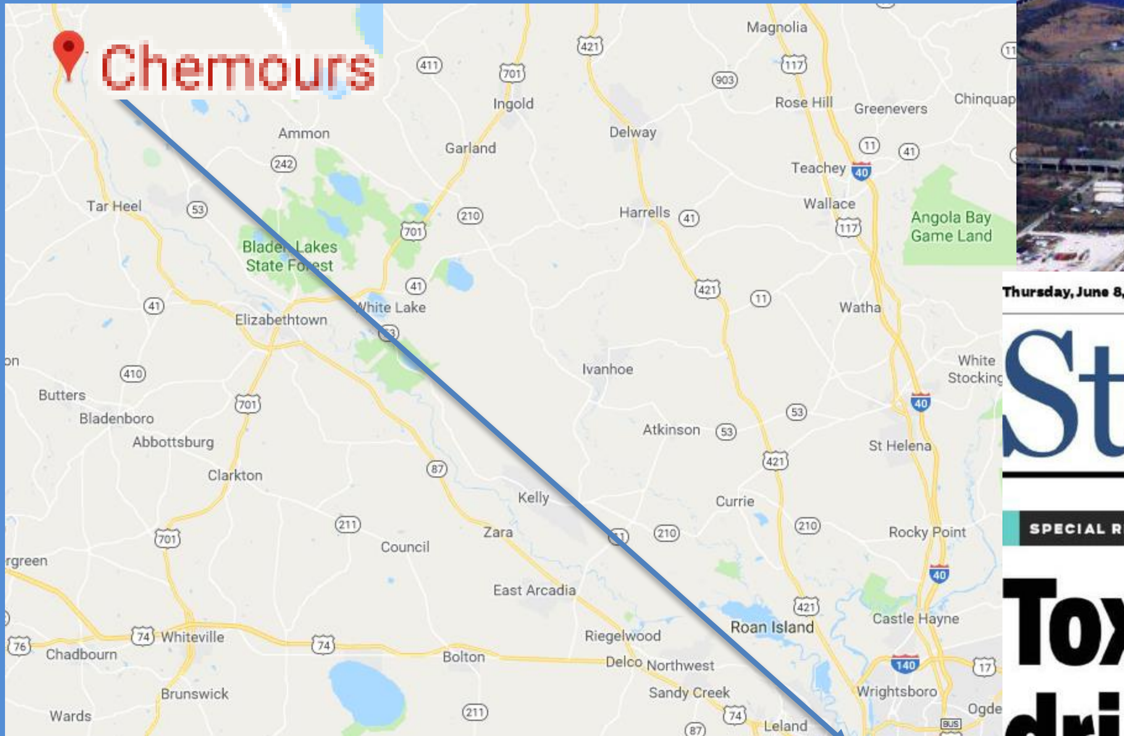
Time of Flight Mass Spectrometer (MS-TOF)
Presence/Absence and identification of PFASs on 20 samples

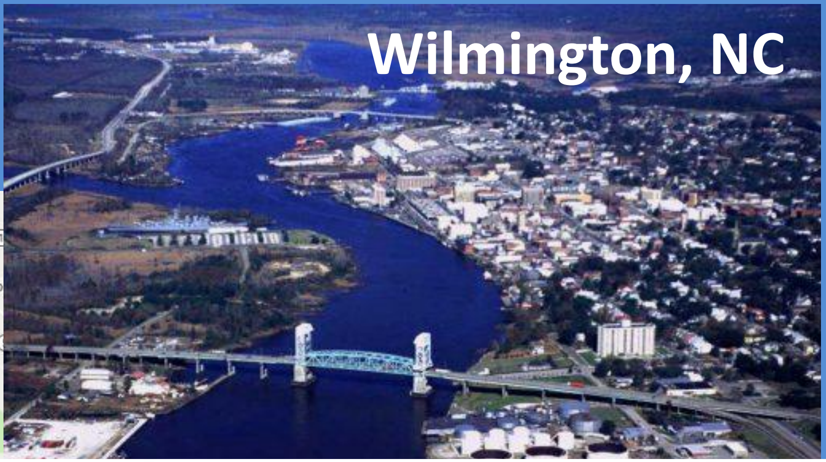
Fluorinated Compounds in U.S. Fast Food Packaging (ES&T Letters 2017)



- Use MS-TOF to show the present of unknown PFASs on food packaging
- Unknown fluorinated carbons were often at equal or greater peak areas compared to known PFASs (i.e. PFOA, PFOS)

GenX: PFOA alternative





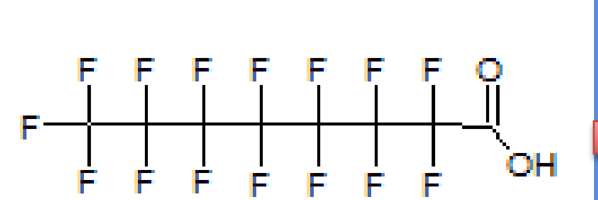

Thursday, June 8, 2017 @starnewsonline

WILMINGTON, N.C.

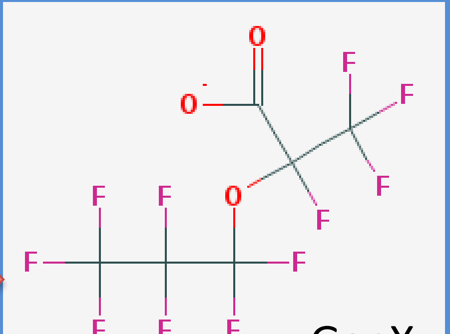
StarNews

SPECIAL REPORT: TOXIC TAP WATER

Toxin taints CFPUA drinking water



PFOA (C8)



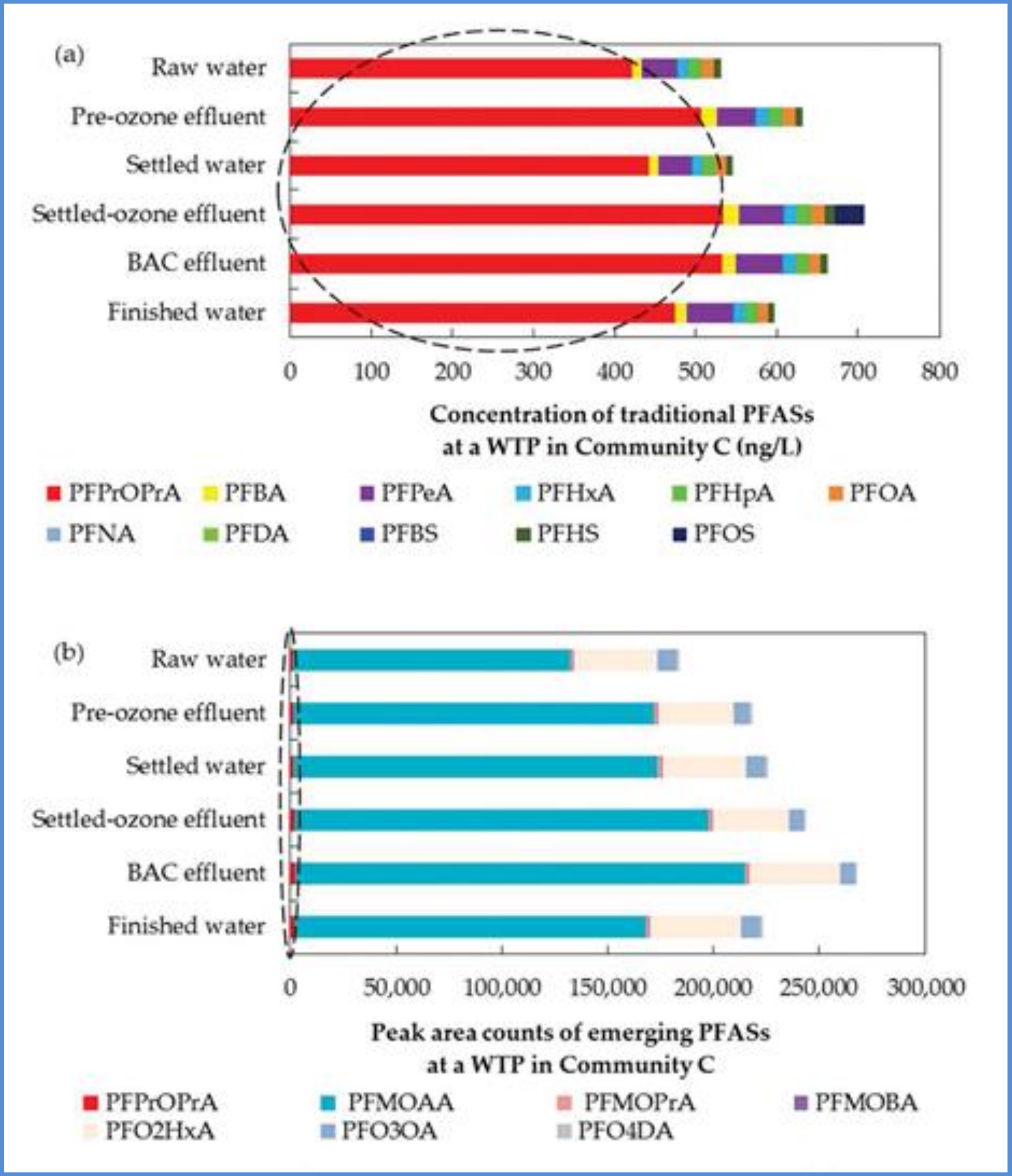
GenX

Timeline of Events in Wilmington NC

- **June 7, 2017** Star News publishes article on Sun et al. 2016 results that indicates GenX in Wilm. drinking water
- **June 20, 2017** Chemours announces they will stop emitting GenX to the Cape Fear River
- **July 14, 2017** NC DHHS issues a new Health Advisory Level for GenX of 140 ppt
- **July 21, 2017** NC Attorney General announces Criminal Investigative Demand into Chemours
- **September 6, 2017** NC DEQ sent Chemours a 60-day notice of violation of their NPDES permit and released data showing PFOA and GenX groundwater contamination
- **November 16, 2017** DEQ issued Chemours a Notice of Partial Suspension and 60-Day Notice of Intent to Partially Revoke their NPDES permit on November 30th

Major Roadblocks for NC Department of Environmental Quality (NCDEQ)

- Lack of toxicology data
- Lack of standards



- Red is GenX in both graphs

- The other compounds in the bottom graph are byproducts of manufacture without standards

Sun et al. 2016

Industrial Chemicals

Information on toxicology that can be used to set regulations

Industrial Chemicals

???

Standard Repository

United States Environmental Protection Agency
Environmental Science Center
701 Mapes Road
Fort Meade, MD 20755-5350
Pesticide_Standards@epa.gov

EPA National Pesticide Standard Repository Order Form

Information: (410) 305-2931 FAX: (410) 305-2999

- EPA's National Pesticide Standard Repository collects and maintains an inventory of analytical “standards” of pesticides:
  - Pure and/or technical grade active ingredients.
  - Regulated metabolites, degradates, and related compounds
- Standard Repository NOT required for industrial chemicals
  - Researchers can not determine toxicology
  - Analytical labs can not determine concentrations in water

Questions?