SBM State Bar of Michigan | ENVIRONMENTAL LAW SECTION

A Legal Perspective on PFOS/PFAS Contamination Issues

July 10, 2018

Noon-1:00 p.m.

Email questions to: parks.maryanne@gmail.com or use the question option on your screen

Participants

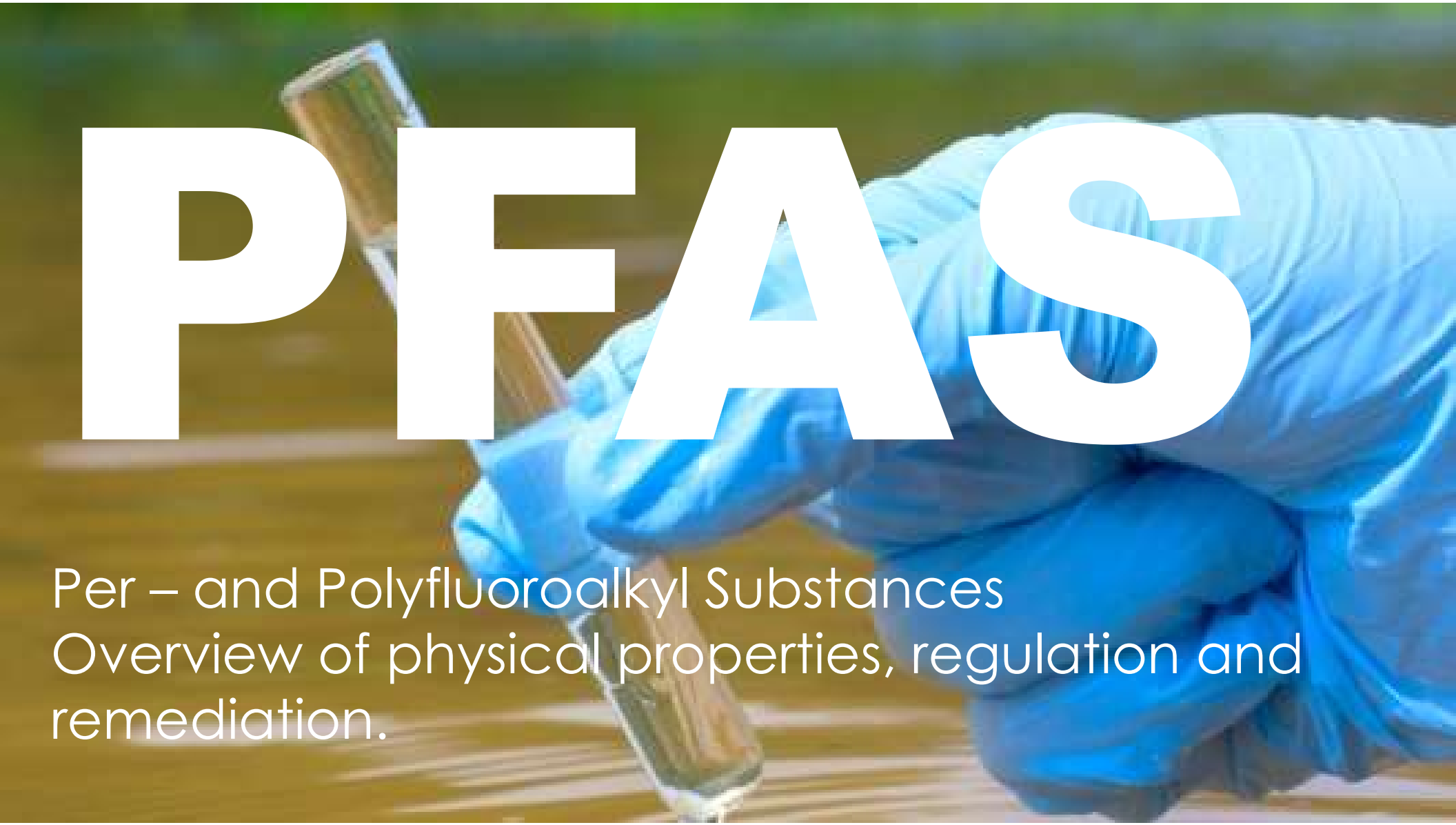
Moderator: **Tammy Helminski**
Barnes & Thornburg LLP

Panelists: Benjamn Fruchey, Foley Baron Metzger & Juip PLLC
Taryn McKnight, Product Manager at Test America
Ryan Thomas, Environmental Scientist at GHD

Ben Fruchey, B.S., M.S., J.D.
Foley, Baron, Metzger & Juip, PLLC

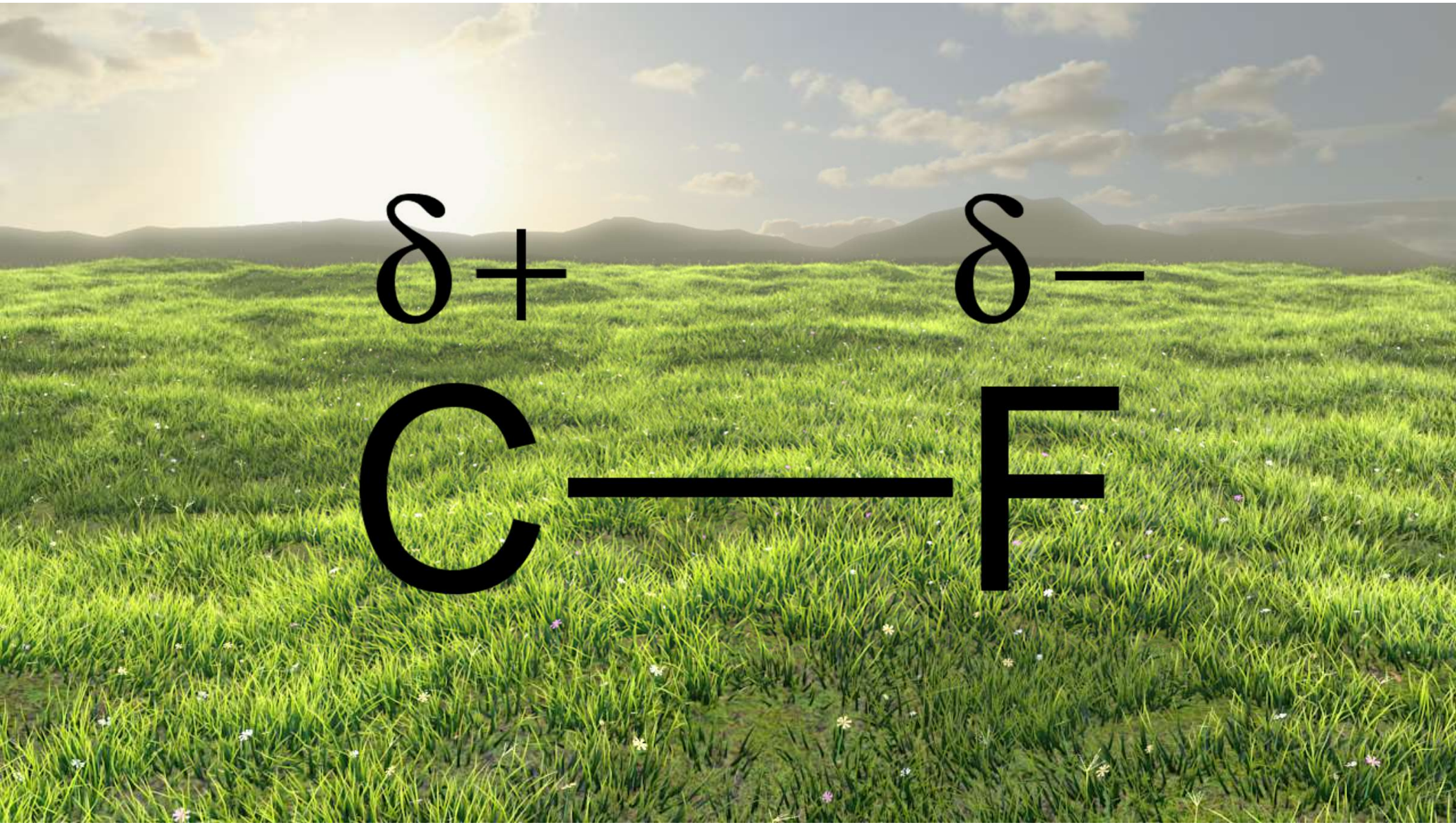
Taryn McKnight, Product Manager
TestAmerica Laboratories, Inc.

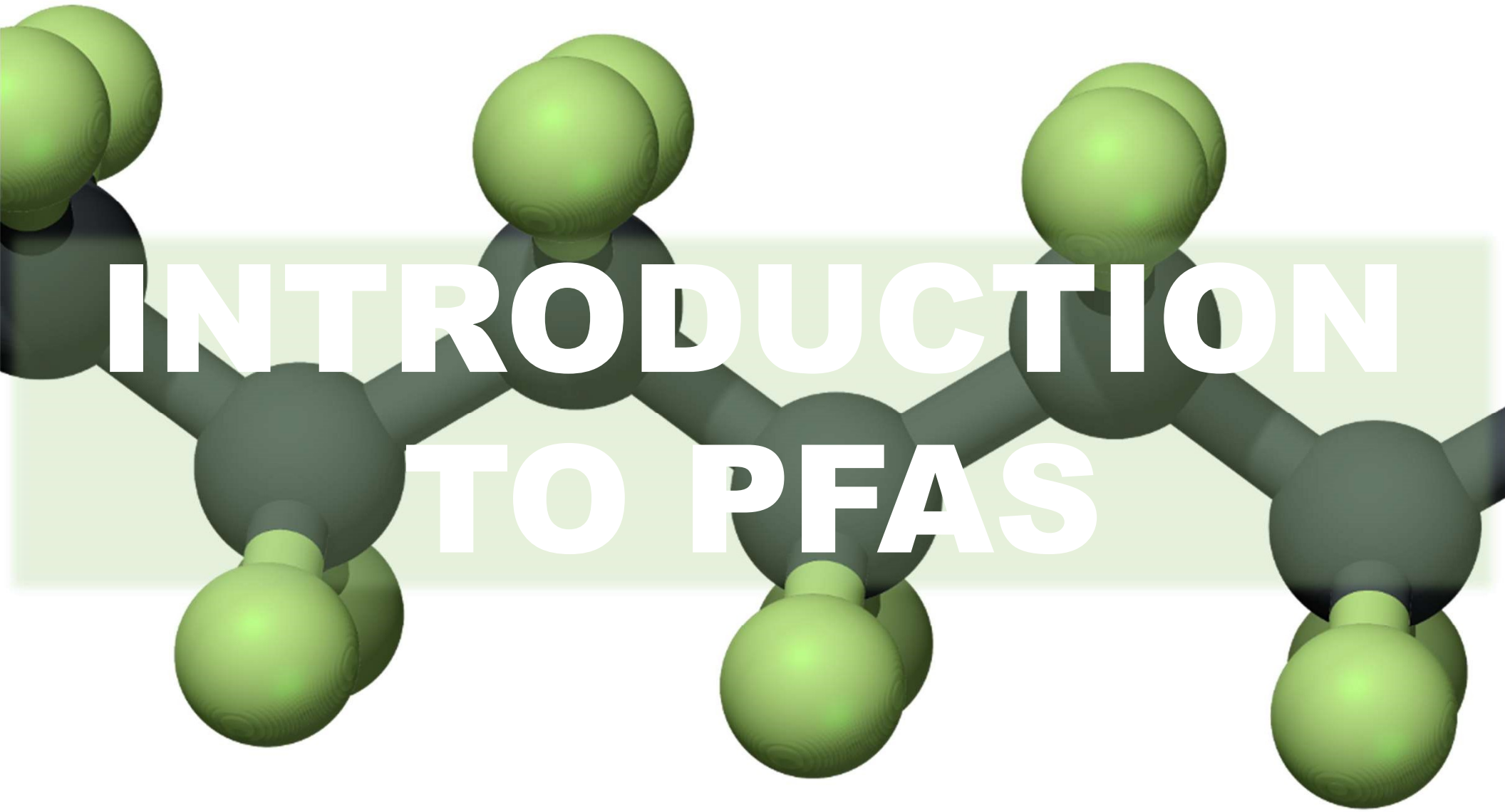
Ryan Thomas, B.S., Ph.D. Environmental Scientist
GHD



PFAS

Per – and Polyfluoroalkyl Substances
Overview of physical properties, regulation and remediation.

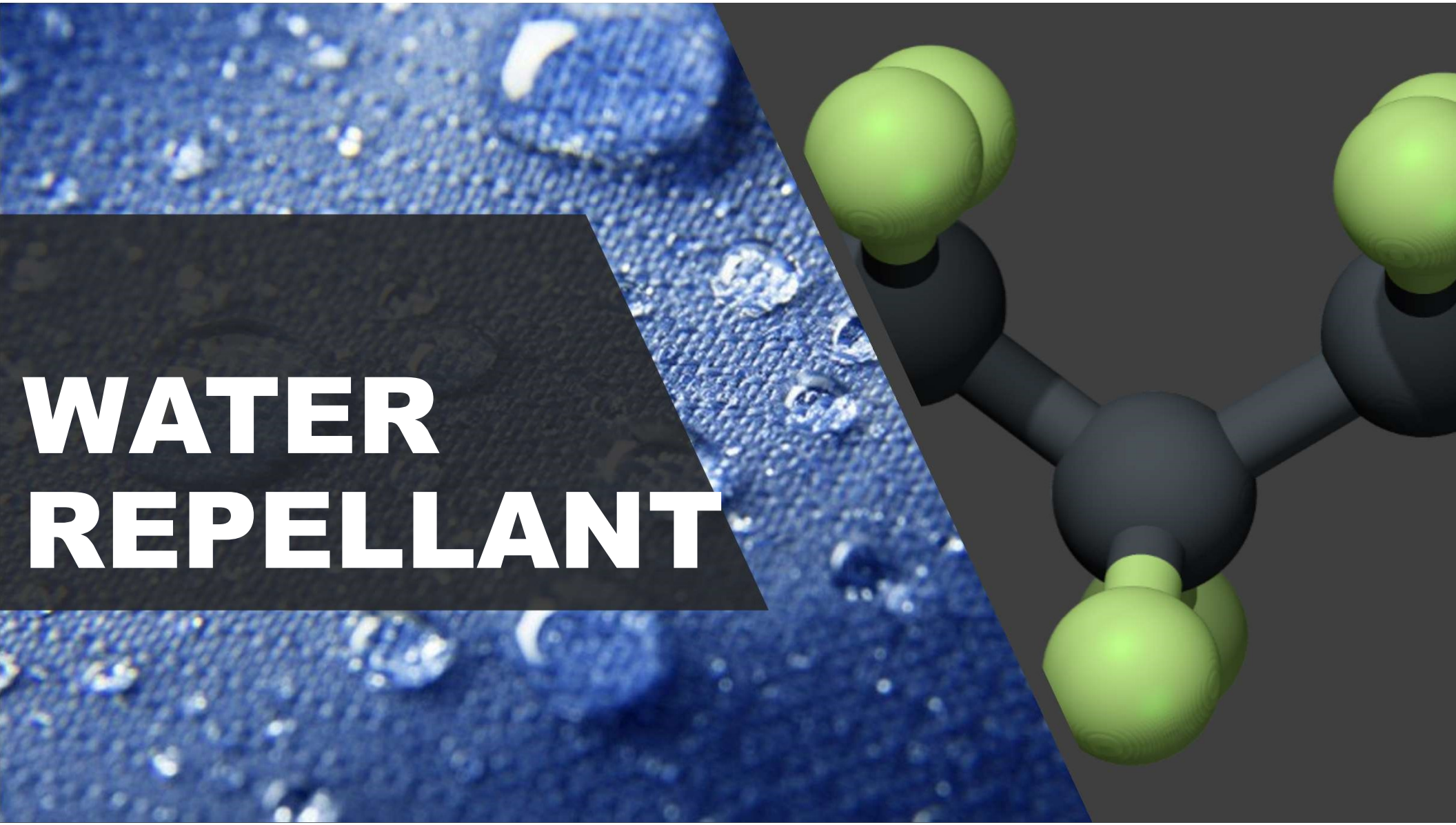

δ+
δ−
C—F



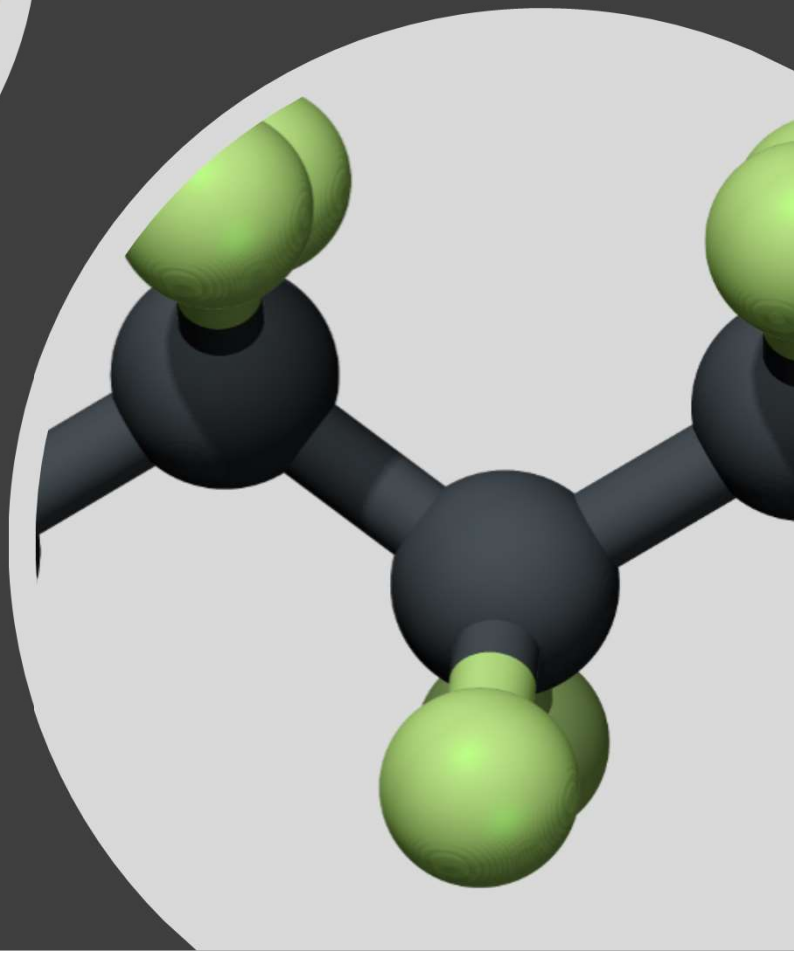
INTRODUCTION TO PFAS

HISTORICAL USES


HEAT
RESISTANT


WATER
REPELLANT

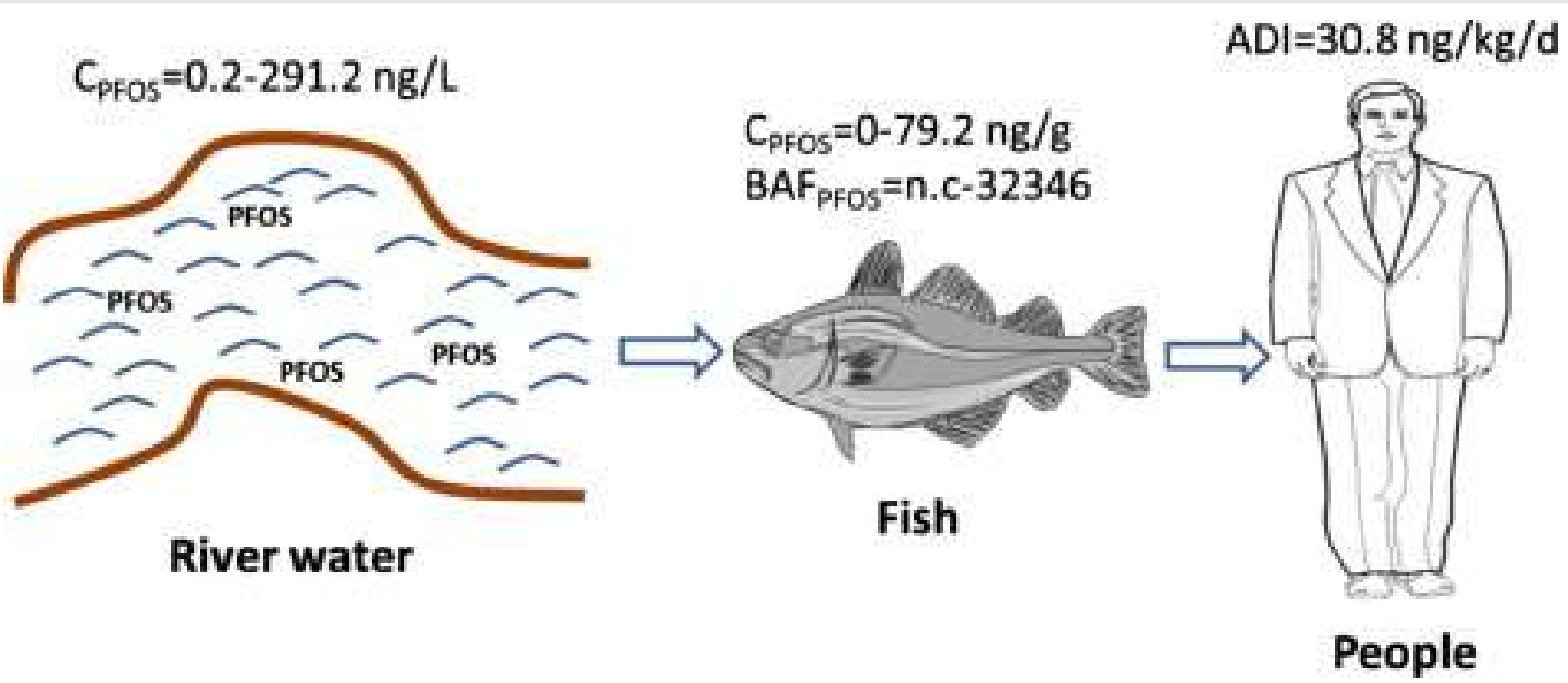
STAIN RESISTANT



Long-Chain Perfluorinated Chemicals (PFCs) Action Plan

Table 1. Comparative Rates of Elimination*

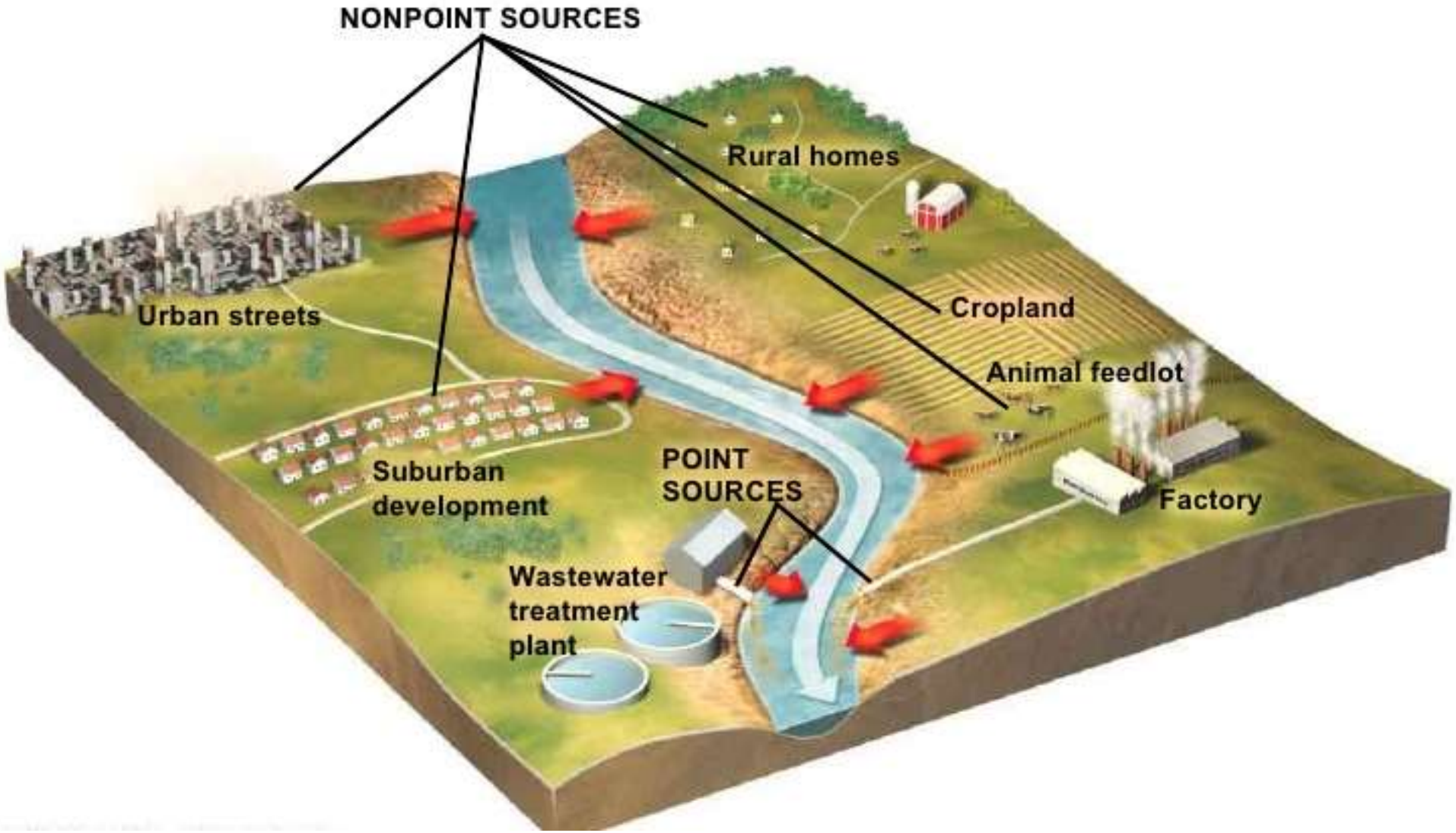
Serum Half-life	PFHxS (C6)	PFOS (C8)	PFOA (C8)	PFNA (C9)	PFDA (C10)
. . . .					
Human	8.5 years	5.4 years	2.3-3.8 years		



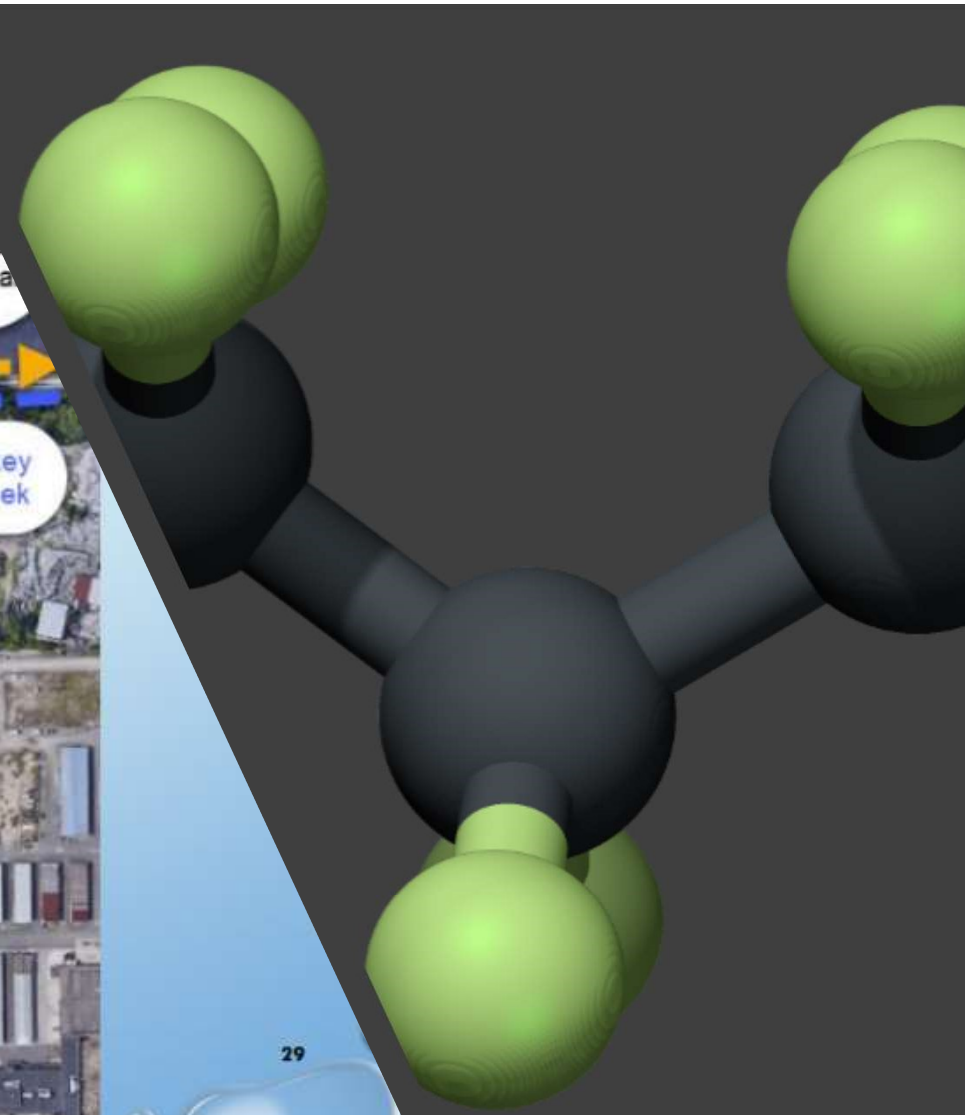
BIOACCUMULATION


PFAS ACTION
RESPONSE
TEAM

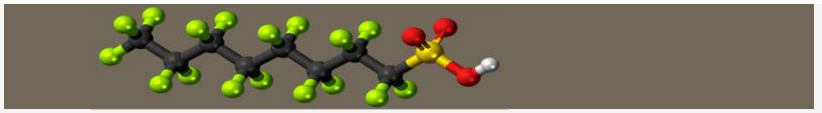
INDUSTRIAL PRETREATMENT PROGRAM INITIATIVE


NONPOINT SOURCES
Rural homes
Urban streets
Cropland
Animal feedlot
Suburban development
POINT SOURCES
Factory
Wastewater treatment plant

Gilkey Creek

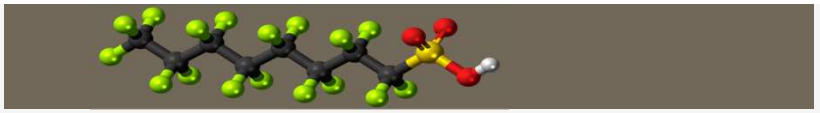



CHROME
PLATING



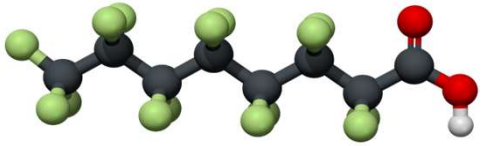
Chemistry & Analysis of PFAS

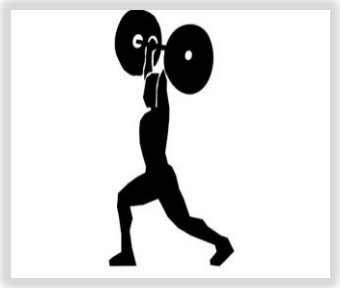
Taryn McKnight
TestAmerica Laboratories, Inc.



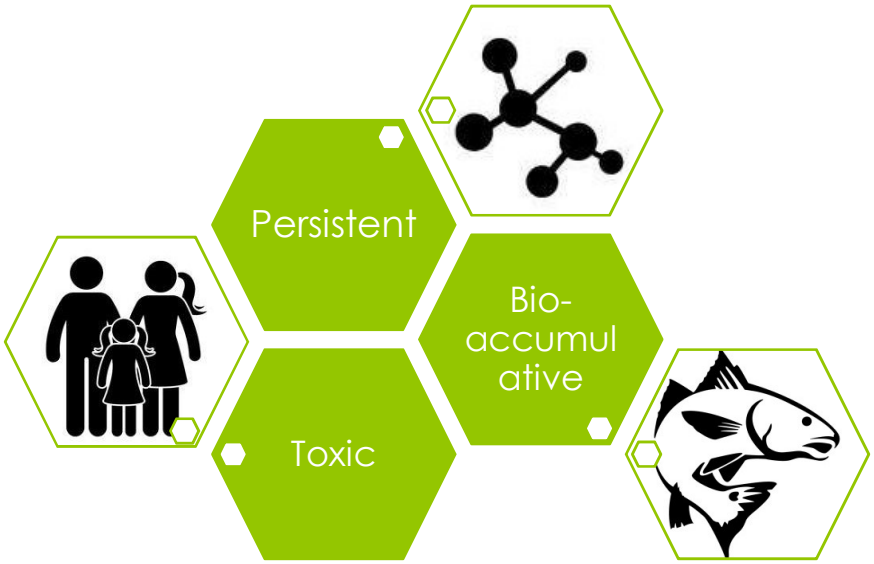
Briefly - What are PFASs?

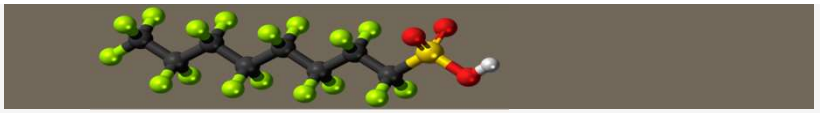
Class of synthetic compounds containing thousands of chemicals formed from **carbon** chains with **fluorine** attached



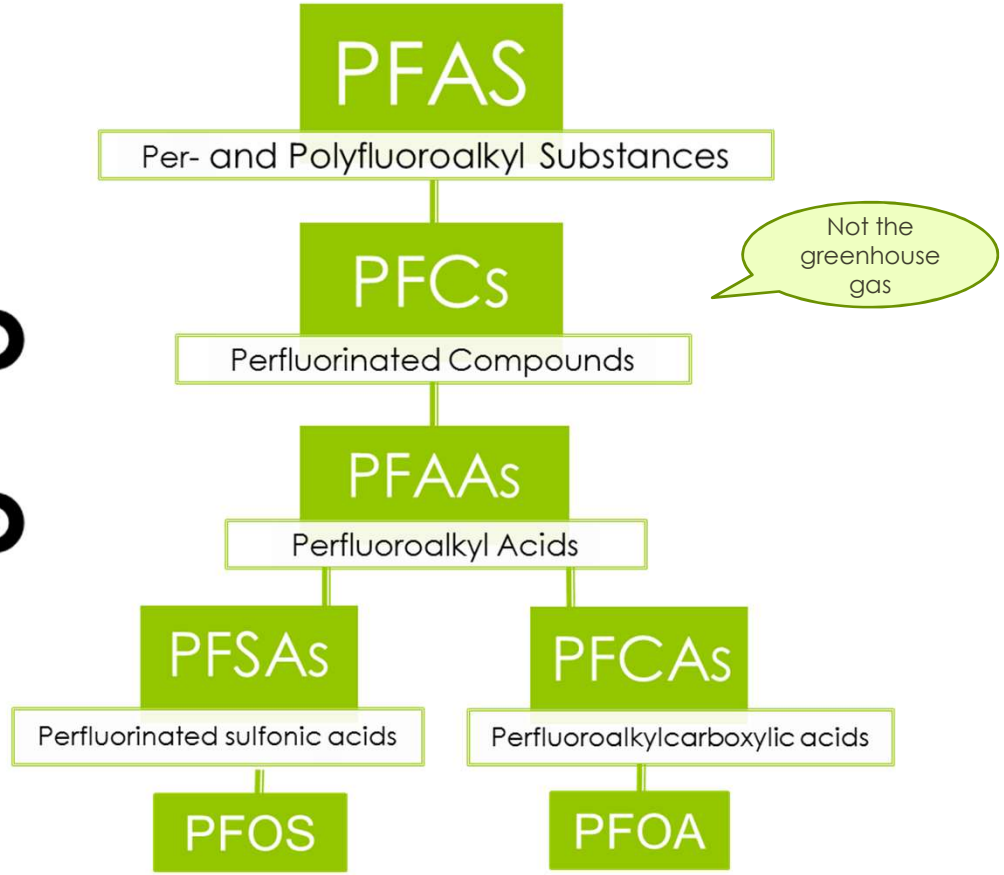


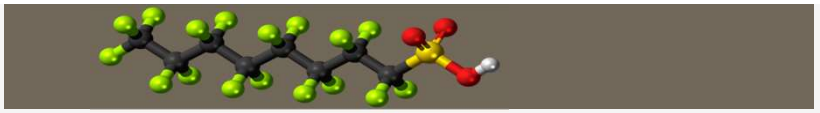
The **C-F bond** is one of the shortest and strongest in nature



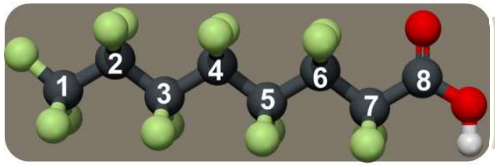


Nomenclature

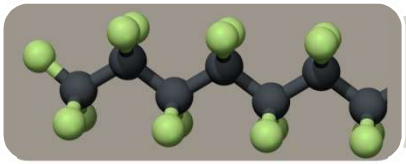




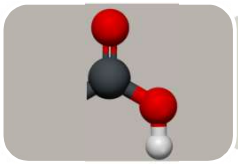
Chemical Structure



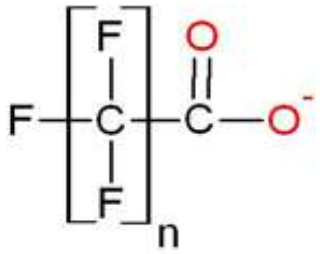
- **Chain Length**

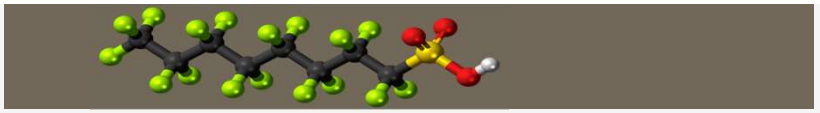


- Carbon Backbone



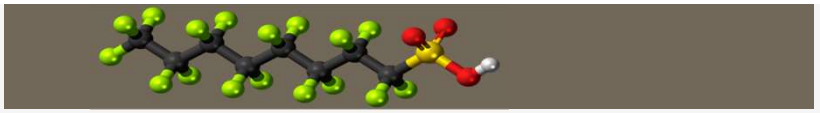
- Functional Group





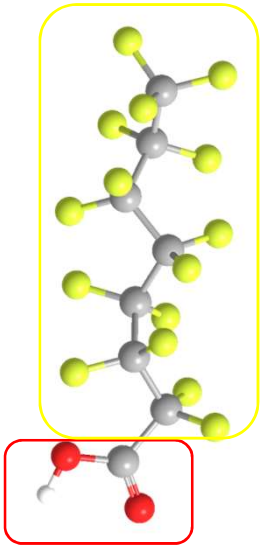
Carbon Chain Nomenclature

Acronym	Compound Name	Carbon Chain Length
PFUnA	Perfluoro**undeca**noic acid	C11
PFDA	Perfluoro**deca**noic acid	C10
PFNA	Perfluoro**nona**noic acid	C9
PFOA	Perfluoro**octa**noic acid	C8
PFHpS	Perfluoro**hepta**nesulfonic acid	C7
PFHxS	Perfluoro**hexa**nesulfonic acid	C6
PFBS	Perfluoro**buta**nesulfonic acid	C4

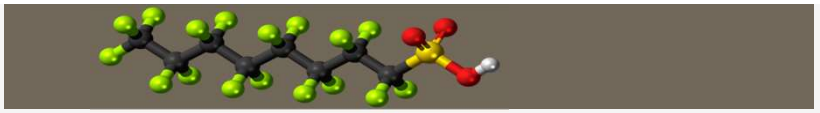


Properties

Fluorocarbon "Tail" = Hydrophobic and Oleophobic

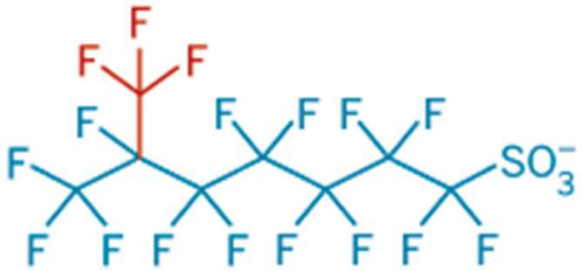


Functional Group "Head" = Hydrophilic

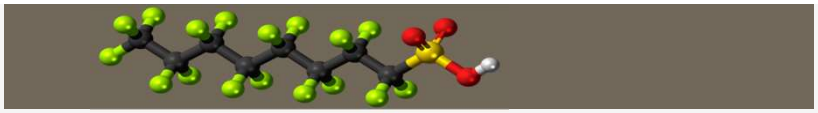


Branched & Linear Isomers

PFOS linear isomer

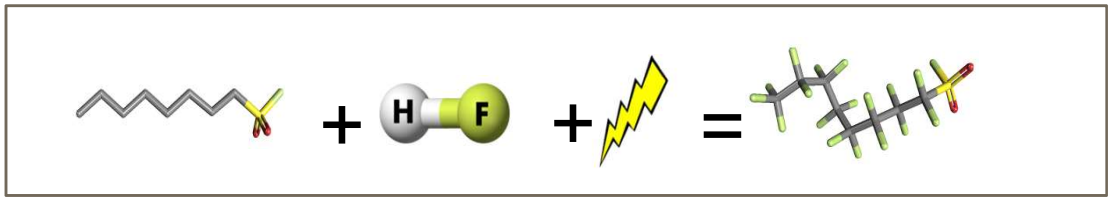


PFOS branched isomer

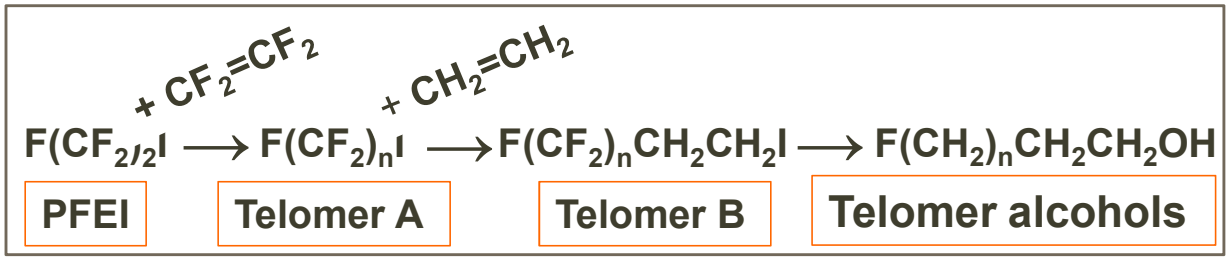


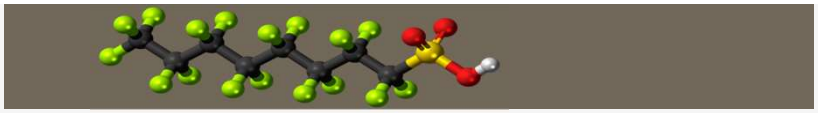
PFAS Formation

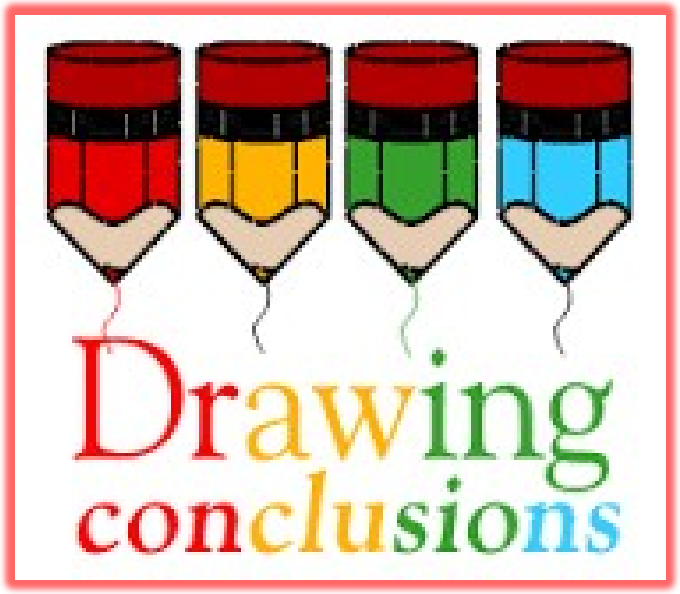
ECF Reaction = B&L & Unintended Byproducts



Telomer Reaction: Unintended Byproducts

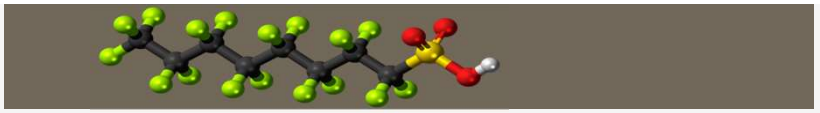






A lesson ...

... in jumping to CONCLUSIONS



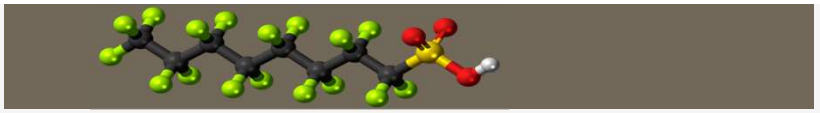
Precursors

PFAA Precursors → Biotransformation → PFAA → PFOA, PFOS

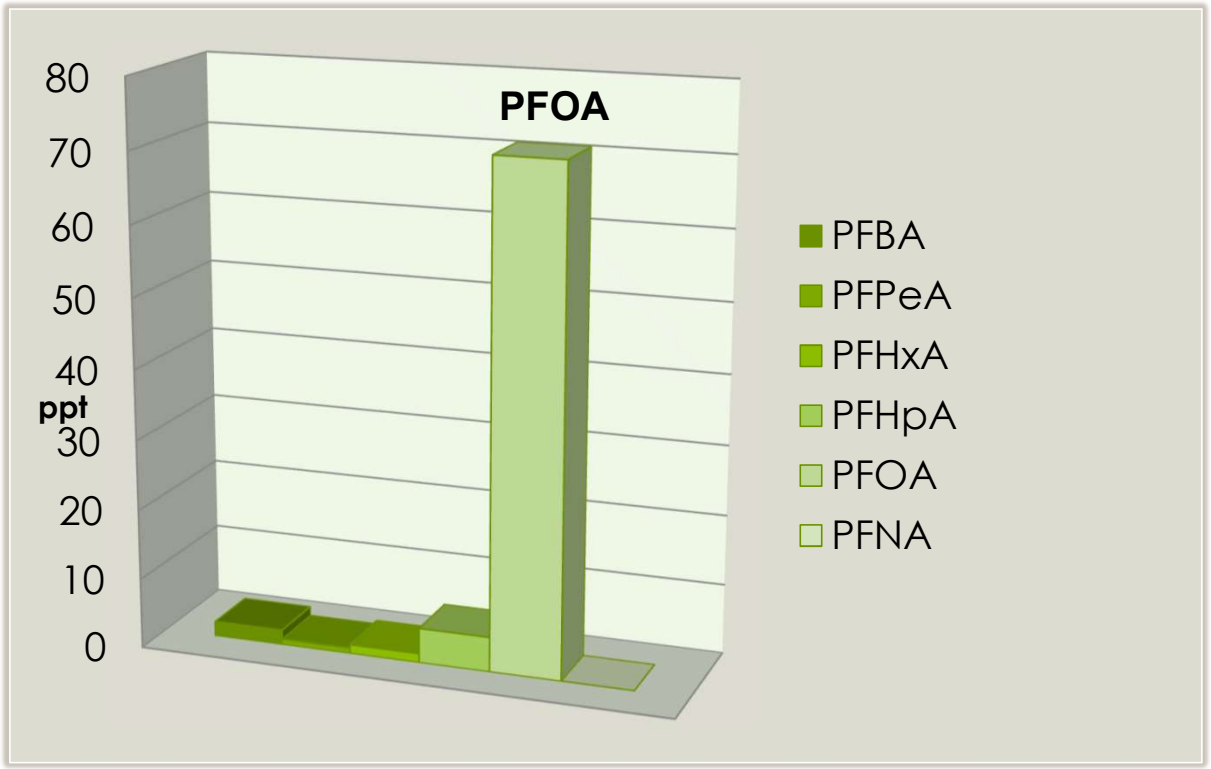
Oxidation via TOP Assay

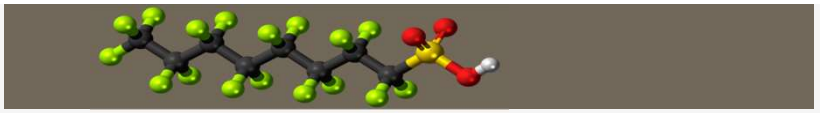
Precursors → 

→ PFAAs



PFCA Pattern – MeFOSA Precursor



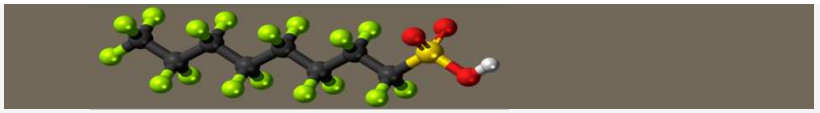


PFAS – Regulatory Timeline

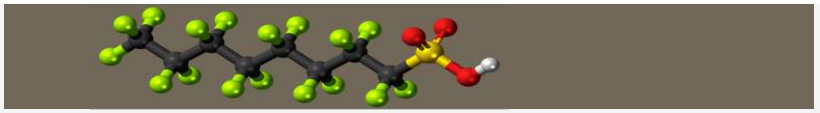
When	Who	What Happened
2002	US EPA	Initiated voluntary phase out of PFOS
2002	3M	Voluntarily discontinued making PFOS (7 other makers complied)
2006	US EPA	PFOA Stewardship Program initiated
2008	Canada	Regulated and prohibited PFOS imports to Canada
2009	UN	Stockholm Convention - adds PFOS to Annex B
2010	US EPA	PFOA Stewardship Program - PFOA reduced by 95%
2015	US EPA	Eliminate the use of PFOA by December 31, 2015
May 2016	US EPA	PFOS and PFOA lifetime health advisory limits reduced to 70 ppt combined

STOCKHOLM CONVENTION

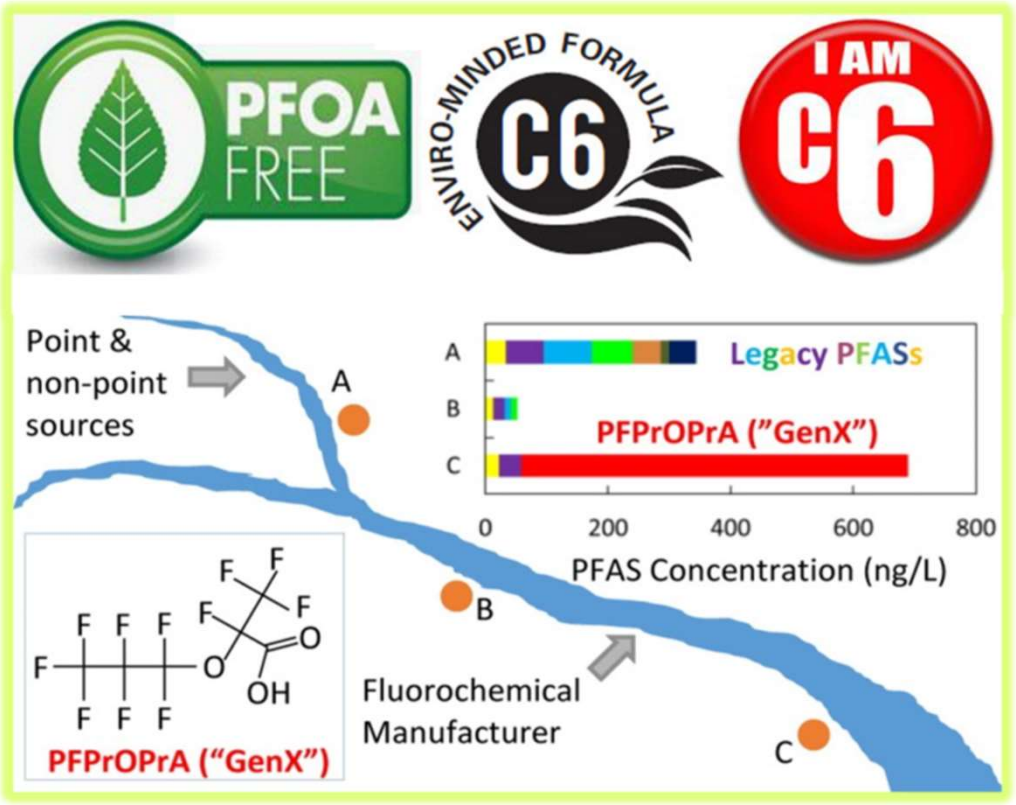
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

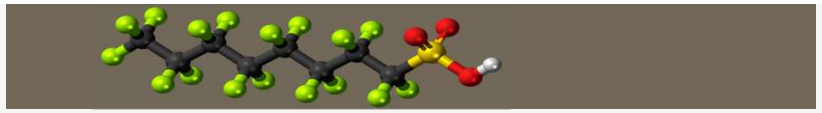


State	PFOA ppt	PFOS ppt	Comments
California	Prop 65	Prop 65	
Washington	NA	TBD	Listed PFOS as PBT
Oregon	24000	300000	PFHpA, PFNA, PFOSA
North Carolina	2000	NA	“GenX” 140 ppt
Alaska	400	400	
Texas	290	560	PCLs for 16 PFCs
Illinois	400	200	
Kentucky	400	200	
Ohio	400	200	
Alabama	70	70	
Connecticut	70	70	PFNA, PFHxA, PFPeA, PFHpA
Delaware	70	70	
Georgia	70	70	Proposed
Iowa	70	70	
Maine	70	70	
Maryland	70	70	
Michigan	**70**	**70**	**5ppt TDL**
New Hampshire	70	70	
New York	70	70	
Rhode Island	70	70	
Pennsylvania	70	70	May lower to 6ppt
Minnesota	35	27	
Vermont	20	20	
New Jersey	14	TBD	PFNA 13 ppt

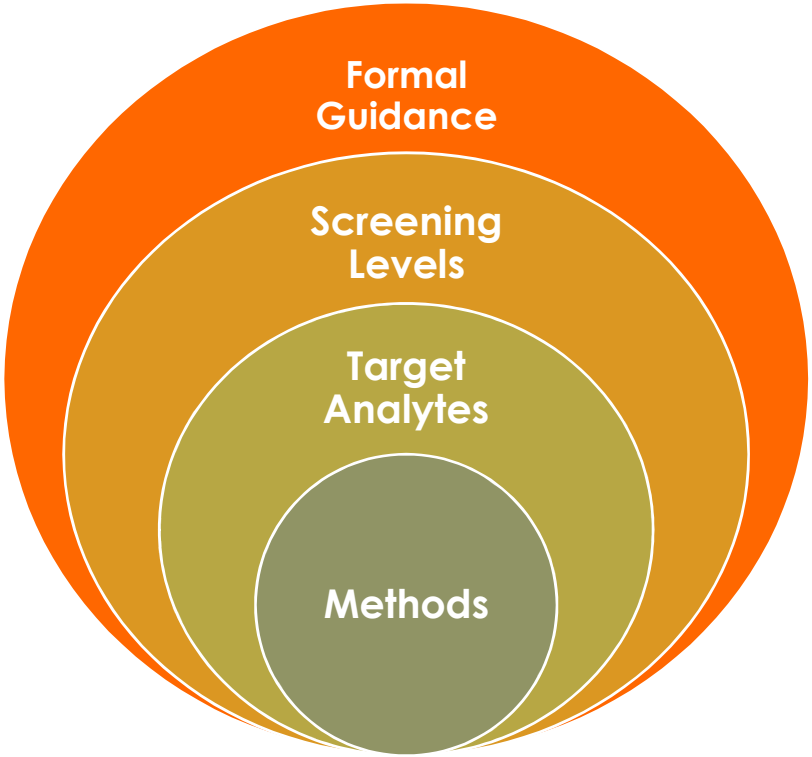


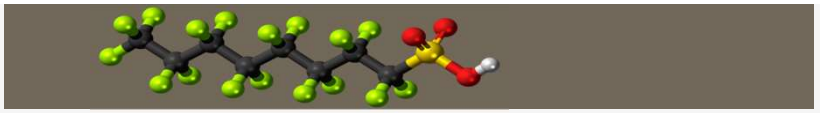
Replacement Chemicals





Regulatory Challenges

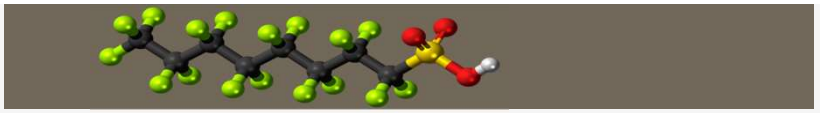




EPA Method 537

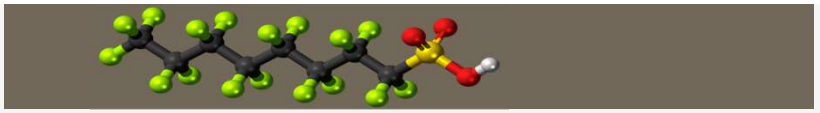
"A Finished Drinking Water Method"

The Only Approved EPA Method for PFAS

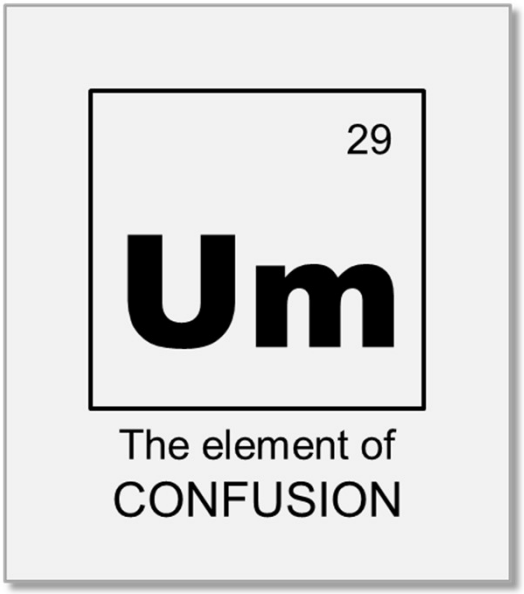


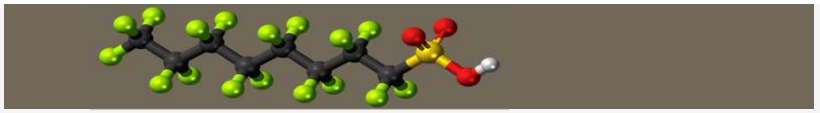
Groundwater, Soil, Tissue?

What method do we use for non-potable water matrices?

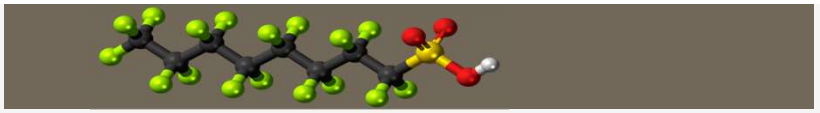


537 “Modified”



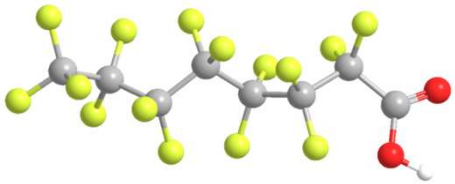


Reducing Variability

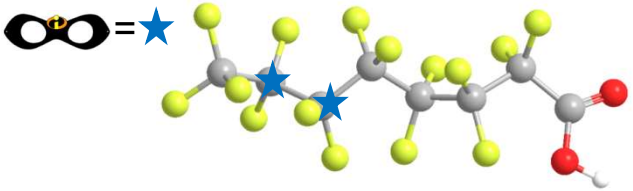


Labeled Analogues

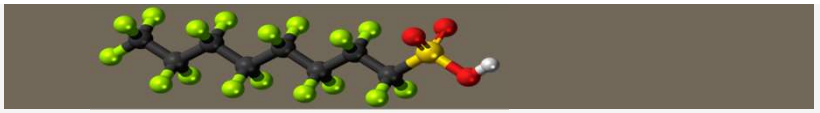
The Parr Family = Native PFOS



The Incredible Family = Labeled PFOS



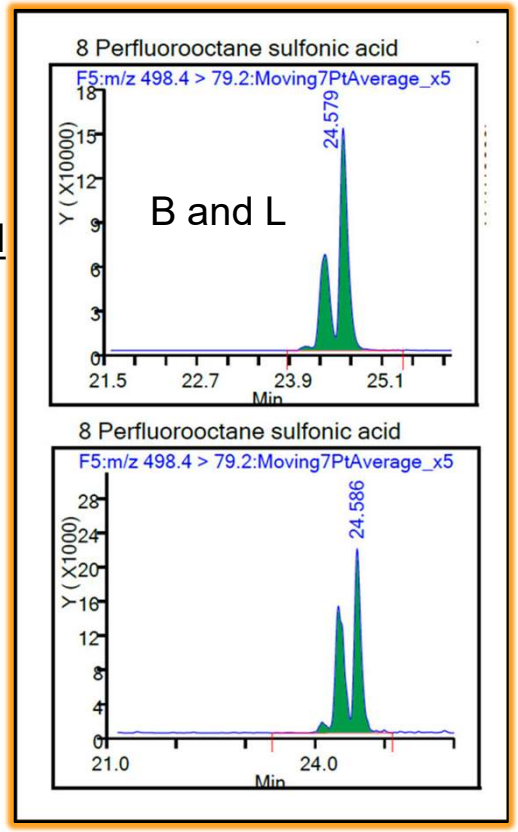
★ = ^{13}C

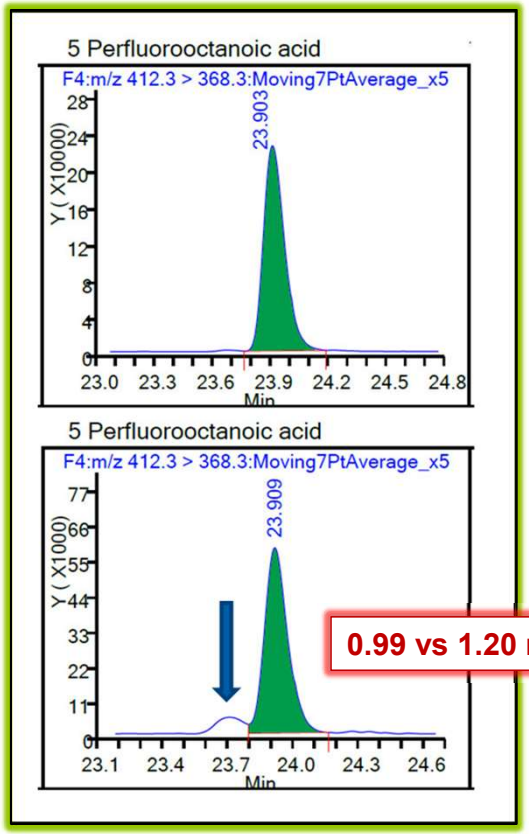


Branched and Linear Error

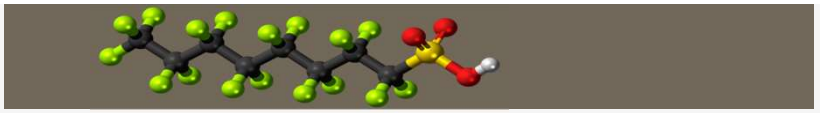
Standard

Sample





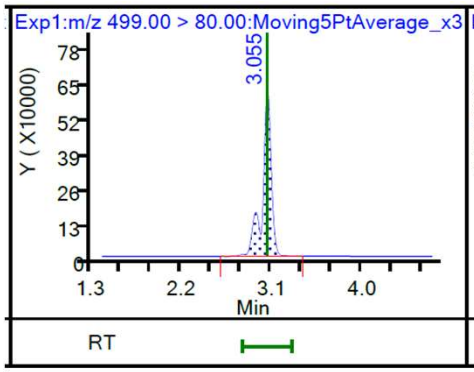
0.99 vs 1.20 ng/ml



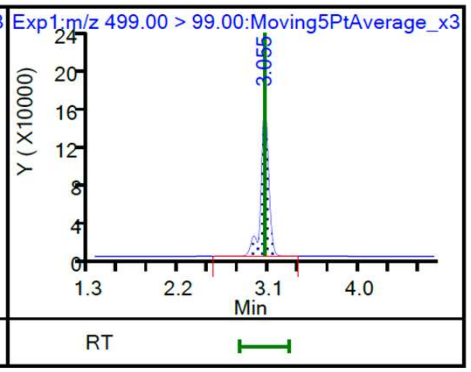
Secondary Ion Transition - PFOS

Standard

Primary Ion Transition

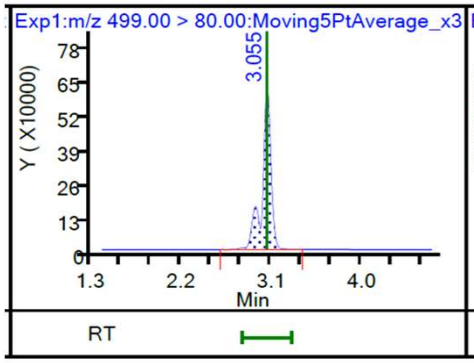


Secondary Ion Transition

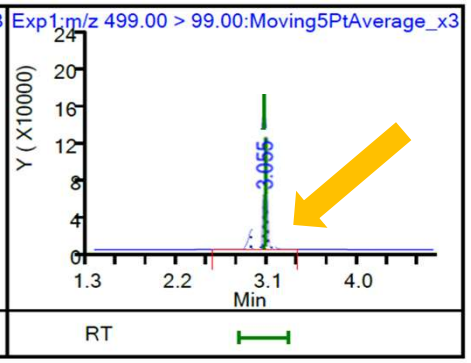


Sample

Primary Ion Transition



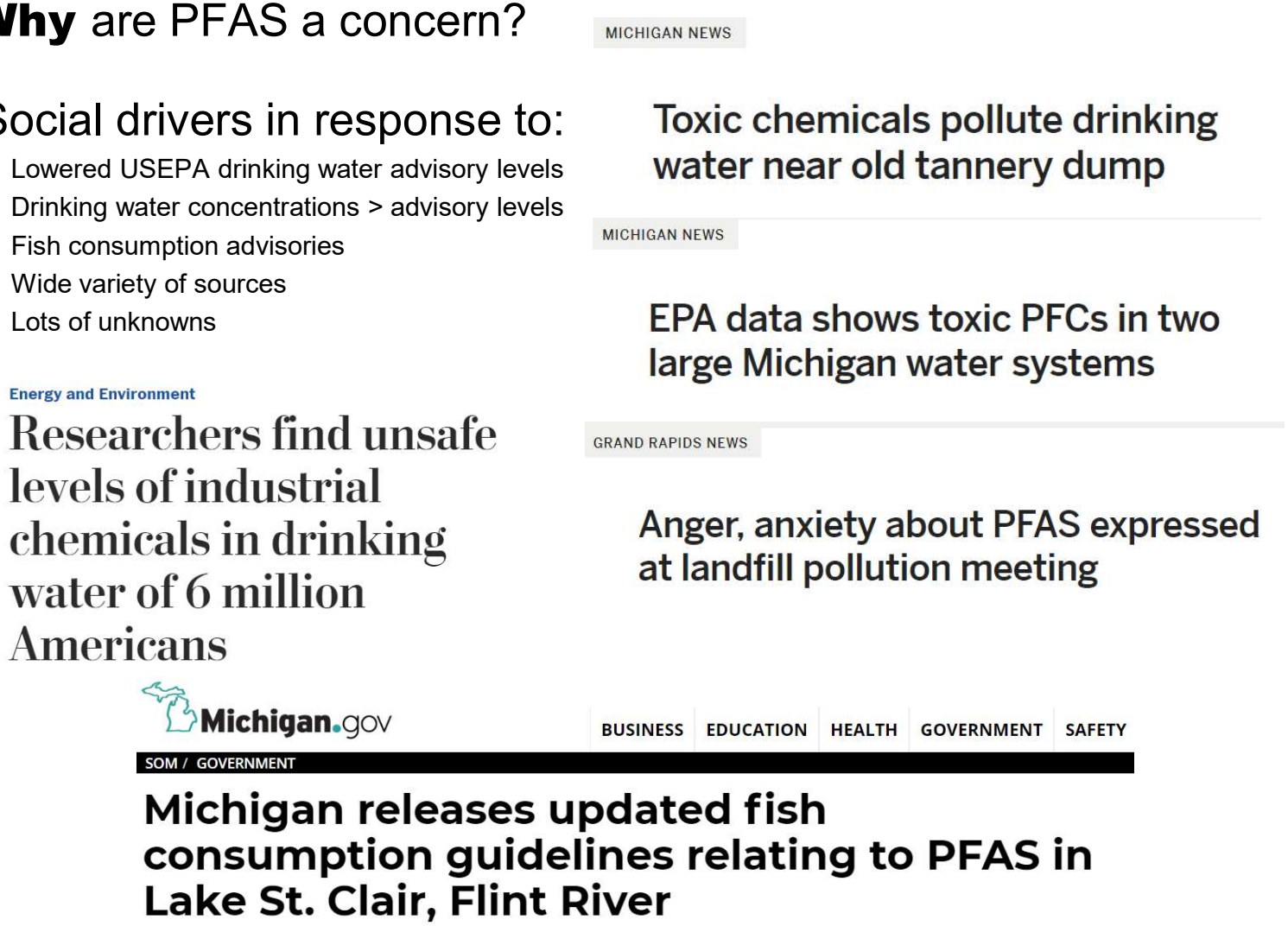
Secondary Ion Transition



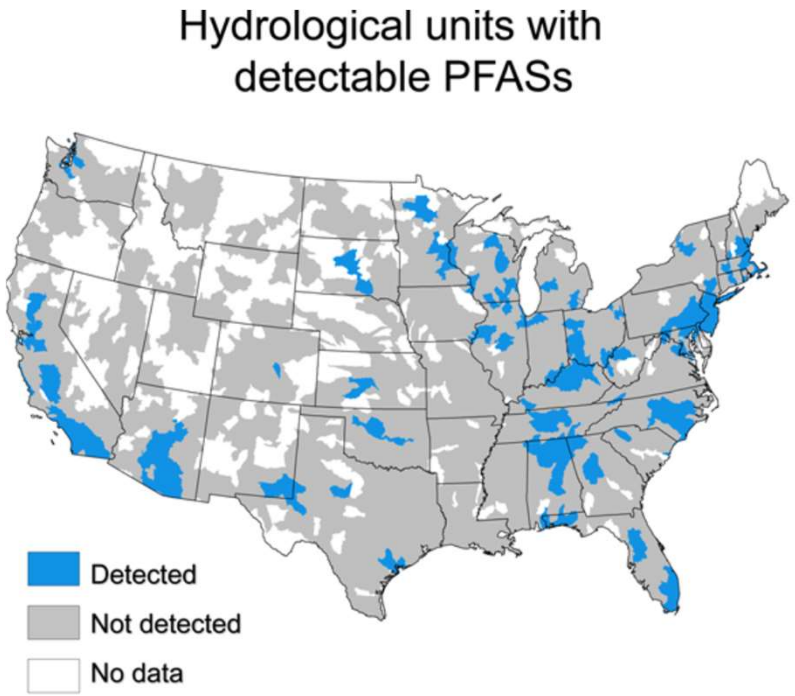
Proficiency Testing

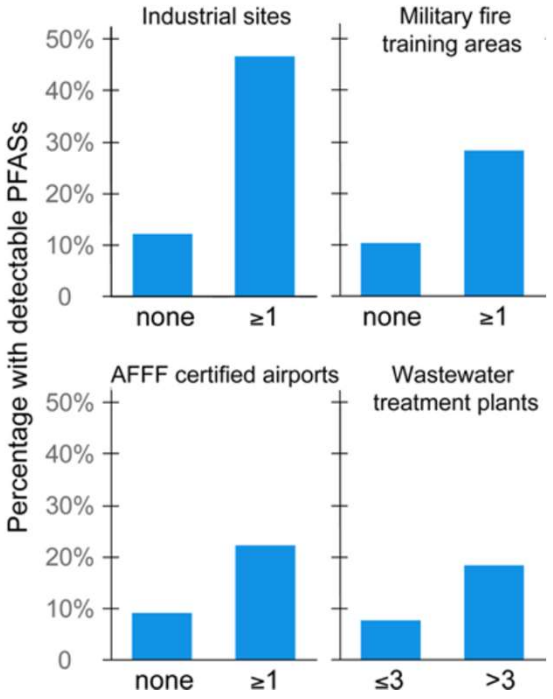
Why are PFAS a concern?

- Social drivers in response to:
  - Lowered USEPA drinking water advisory levels
  - Drinking water concentrations > advisory levels
  - Fish consumption advisories
  - Wide variety of sources
  - Lots of unknowns



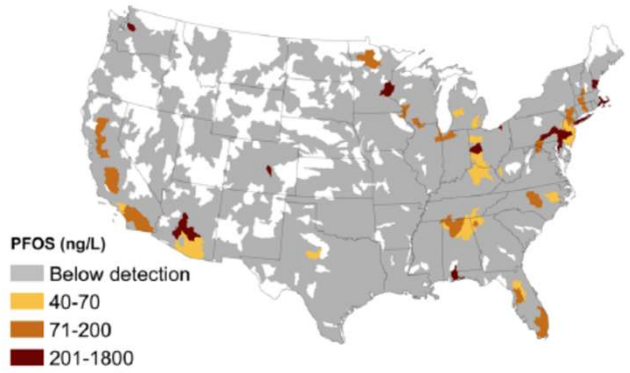
Potential Exposure Pathways – Drinking Water

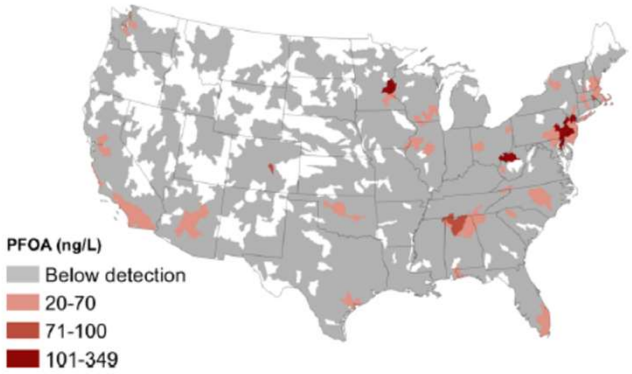




SOURCE: Hu, Xindi C., et al. "Detection of poly-and perfluoroalkyl substances (PFASs) in US drinking water linked to industrial sites, military fire training areas, and wastewater treatment plants." *Environmental science & technology letters* 3.10 (2016): 344.

Potential Exposure Pathways – Drinking Water





US EPA's Health Advisory is 70 ng/L

Figure 1. Hydrologic unit codes (eight-digit HUCs) used as a proxy for watersheds with detectable PFOA and PFOS in drinking water measured in the US EPA's UCMR3 program (2013–2015). Blank areas represent regions where no data are available.

SOURCE: Hu, Xindi C., et al. "Detection of poly-and perfluoroalkyl substances (PFASs) in US drinking water linked to industrial sites, military fire training areas, and wastewater treatment plants." *Environmental science & technology letters* 3.10 (2016): 344.

Potential Exposure Pathways – Consumption Fish and PFOS

Region	County	Waterbody	Type of Fish	Size of Fish	Michigan (MI) Servings Per Month*
Northeast	Iosco	Allen Lake	All Other Species (other than Bluegill, Largemouth/Smallmouth Bass, and Sunfish)	Any	Do not eat**
		Au Sable River (downstream of Foote Dam; includes Van Etten Creek)	Carp	Any	Do not eat**
			Largemouth Bass	Any	Do not eat**
			Rock Bass[1]	Any	Do not eat**
			Smallmouth Bass	Any	Do not eat**
			Suckers	Any	Do not eat**
			All Other Species (other than Brown Trout, Chinook Salmon, Coho Salmon, Rainbow Trout, Steelhead, or Walleye)	Any	Do not eat**
		Clark's Marsh	Bluegill	Any	Do not eat**
			Sunfish	Any	Do not eat**
			All Other Species (other than Bluegill and Sunfish)	Any	Do not eat**
Southwest	Berrien	St. Joseph River (downstream of the Berrien Springs Dam)	Rock Bass	Any	1
	Kent	Rogue River (upstream of Rockford Dam)	Suckers[1]	Any	4
Southeast	Bay	Saginaw River	Bluegill	Any	4
			Largemouth Bass[2]	Under 18"	2
			Smallmouth Bass[2]	Under 18"	2
			Sunfish	Any	4
	Genesee	Flint River (downstream of Mott Dam)	Largemouth Bass	Any	6 per year
			Smallmouth Bass	Any	6 per year
	Saginaw	Saginaw River	Bluegill	Any	4
			Largemouth Bass[2]	Under 18"	2
			Smallmouth Bass[2]	Under 18"	2
			Sunfish	Any	4
		Flint River (downstream of Mott Dam)	Largemouth Bass	Any	6 per year
			Smallmouth Bass	Any	6 per year
			Rock Bass	Any	1

Note: PFOS can't be reduced by trimming and cooking.

*MI Serving Size:

Weight of Person	MI Serving Size
45 pounds	2 ounces
90 pounds	4 ounces
180 pounds	8 ounces

** No one should eat fish listed as do not eat, regardless of age or health. When these fish were tested, MDHHS found very high levels of chemicals. Eating even one meal of these fish could possibly lead to health problems in the future, regardless of age or health.

[1] In addition to PFOS, the guideline also includes mercury

[2] In addition to PFOS, the guideline also includes mercury and PCBs

Source: http://www.michigan.gov/mdhhs/0,5885,7-339-71548_54783_54784_54785_58671-296074--,00.html.

SOURCE: US EPA. 2016. Fish and Shellfish Program Newsletter

Potential Exposure Pathways – Commercial and Consumer Products

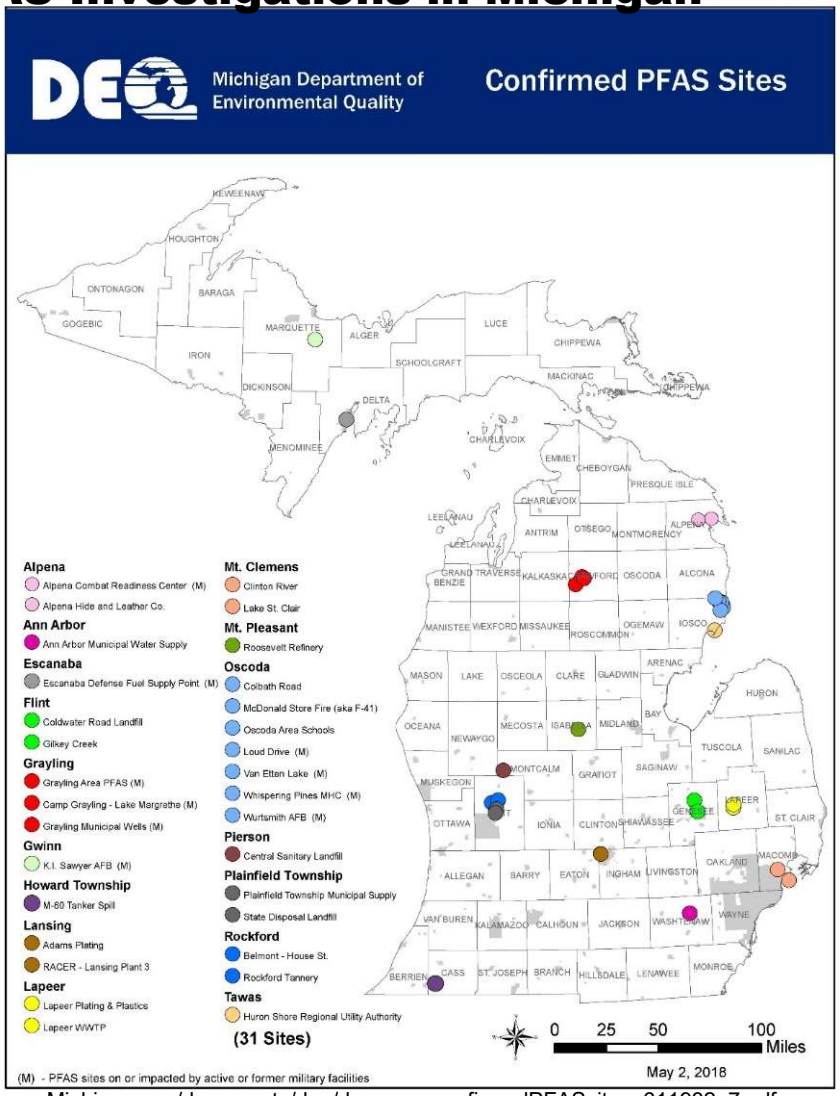
Commercial and Consumer Products Containing PFAS:

- paper and packaging
- clothing and carpets
- outdoor textiles and sporting equipment
- ski and snowboard waxes
- non-stick cookware
- cleaning agents and fabric softeners
- polishes and waxes, and latex paints
- pesticides and herbicides
- hydraulic fluids
- windshield wipers
- paints, varnishes, dyes, and inks
- adhesives
- medical products
- personal care products (for example, shampoo, hair conditioners, sunscreen, cosmetics, toothpaste, dental floss)

SOURCE: www.atsdr.cdc.gov/pfas

SOURCE: ITRC – History and Use of PFAS Fact Sheet 2017

Status of PFAS Investigations in Michigan



SOURCE: www.Michigan.gov/documents/deq/deq-map-confirmedPFASsites_611932_7.pdf

Status of PFAS Investigations in Michigan

Michigan Department of Environmental Quality
News Release

May 18, 2018

For More Information:
DEQ Media Office, deq-assist@michigan.gov, 517-284-9278

Michigan embarks on statewide study of PFAS in water supplies

SOURCE: MDEQ: https://www.michigan.gov/deq/0,4561,7-135--468979--,00.html

Sampling Challenges – PFAS

- PFAS are ubiquitous
- Can be on samplers clothing, gloves, sampling equipment
- Waterproof field note books
- Glass bottles can cause loss of analyte
- Water for blanks (must be certified-PFAS free)
- Clean hands / Dirty hands

Sampling Challenges – PFAS

Prohibited Items	Acceptable Items
Field Equipment	
Teflon® containing materials (tubing, bladders, o-rings, caps)	High-density polyethylene (HDPE) materials
Low density polyethylene (LDPE) materials	Acetate Liners
	Silicon Tubing
Waterproof field books	Loose paper (non-waterproof)
Plastic clipboards, binders, or spiral hard cover notebooks	Metal field clipboards or with Masonite
Post-It Notes®, Sharpies®	Ball point pens
Chemical (blue) ice packs	Regular ice
Field Clothing and PPE	
New cotton clothing or synthetic water resistant, waterproof, or stain-treated clothing, clothing containing Gore-Tex™	Well-laundered clothing made of natural fibers (preferable cotton) washed at least 6 times since purchase
Clothing laundered using fabric softener	No fabric softener
Boots containing Gore-Tex™	Boots made with polyurethane and PVC (PVC over boots over leather steel-toe safety boots are acceptable*)
Tyvek®	Powder-free nitrile gloves
No cosmetics, moisturizers, hand cream, or other related products as part of personal cleaning/showering routine on the morning of sampling	**Sunscreens** - Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my face, Baby sunscreens that are “free” or “natural” **Insect Repellents** - Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellant, Herbal Armor, California Baby Natural Bug Spray, BabyGanics **Sunscreen and insect repellant -** Avon Skin So Soft Bug Guard Plus – SPF 30 Lotion

Remediation Challenges – PFAS

Field Demonstrated Treatment Technologies for Liquids

- Extraction and sorption with granular activated carbon or anion exchange resin
- Extraction and membrane filtration/reverse osmosis
- Extraction and precipitation/flocculation

Field-Demonstrated Treatment Technologies for PFAS in Solids

- Excavation and off-site landfilling or incineration
- Sorption/stabilization through ex situ soil mixing
- Ex situ thermal desorption and off-gas destruction

SOURCE: ITRC's Remediation Technologies and Methods for PFAS – Fact Sheet

Remediation Challenges – PFAS

Biodegradation

- Very limited research to date showing biodegradation of Per-PFAS
- Evidence of transformations of Poly-PFAS
- Ability to treat to the proposed standards?

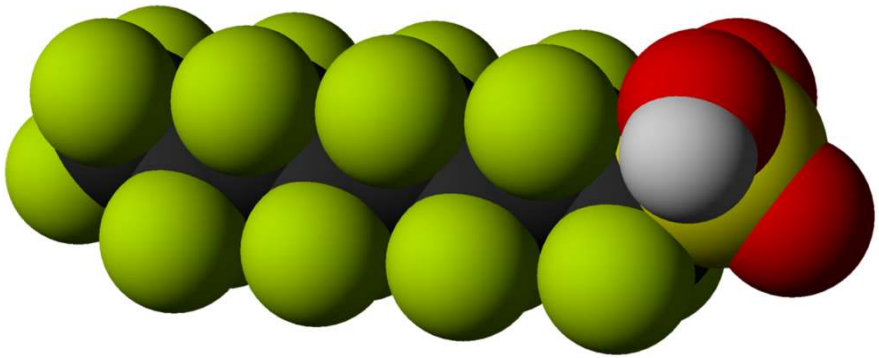
Oxidative / Reductive Technologies

- Requires high energy and/or diverse reactive species – complex chemistry
- Several bench studies and few pilots performed showing destruction of PFAS
- Research is ongoing to treat precursors

SOURCE: XDD Environmental – PFAS Remediation Webinar – Part 1

Remediation Challenges – PFAS

Extremely recalcitrant to degradation or destruction



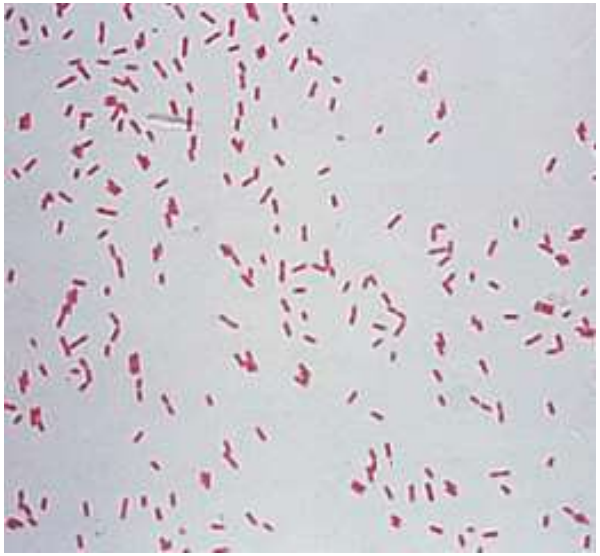
Technologies under investigation:

- Biodegradation
- Flocculation
- Sorption

Remediation Challenges – PFAS

Biodegradation

- Biodegradation of PFOS under aerobic conditions in wastewater treatment sludge has been observed
- Organism identified as Pseudomonas aeruginosa strain HJ4
- 67% of PFOS was biologically decomposed
- Research is ongoing

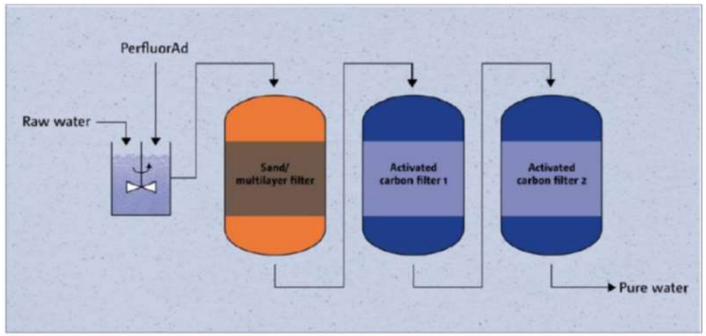


SOURCE: Chemosphere 109 (2014) 221 – 225

Remediation Challenges – PFAS

Flocculation

- PerfluorAd®
- Surface active liquid reagent
- Non-toxic and biodegradable
- Causes flocculation and precipitation of PFAS from water
- Approximately 95% removal of PFAS
- Mobile treatment system is available



SOURCE: tersusenv.com

Remediation Challenges – PFAS

Sorption

- Activated Carbon or RemBind®
- RemBind recently used in Australia to treat 1,000 tonnes of soil impacted with PFAS
- Mixing soil with 5% RemBind® decreased leaching of PFAS from soil to below the analytical detection limit

SOURCE: tersusenv.com


QUESTIONS?