BACWA PFAS Presentation

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PFAS: Analytical Challenges and Best Practices

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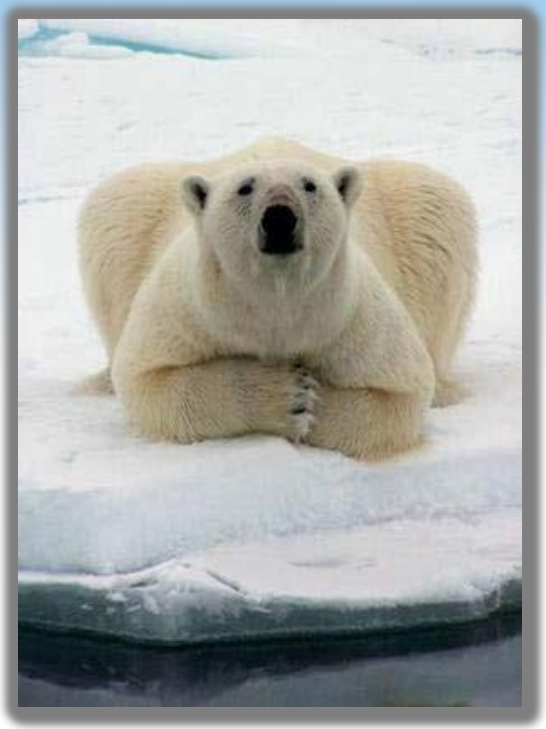
PFAS - Outline

Introduction:

- What are PFAS?
- Exposure, Toxicity and Risk
- Formation, Chemistry
- Sources, Exposure Routes
- Regulatory Progress

Sampling & Analytical Challenges:

- Which Method Do I Need?
- What is Isotope Dilution?
- Branched and Linear Isomers
- What is the TOP Assay?
- Replacement Chemicals
- Field Screening
- What's Next?



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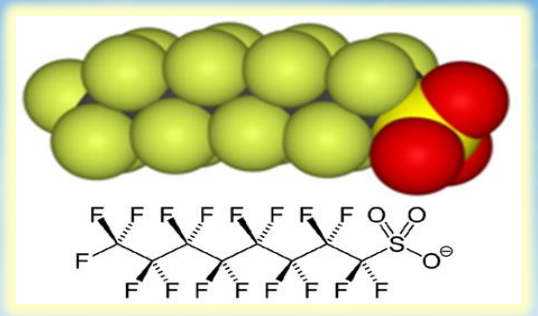
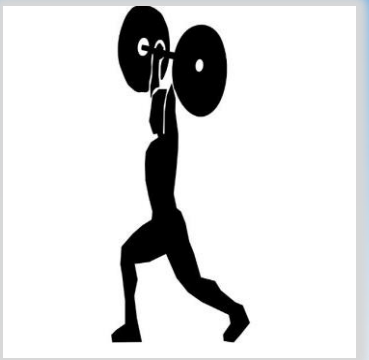
Briefly - What are PFASs?

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



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



PFOS and PFOA are fully fluorinated and the most common perfluorinated chemicals (PFCs).

Persistent and resistant to degradation
Found in soil, air and groundwater..

Exposure, Toxicity and Risk

Human exposure is primarily from:

- **food (fish) and air**

Exposure continues beyond phase out:

- **due to persistence**

Half-lives in humans:

- **2 to 9 years**

PFOA associated with:

- **liver, pancreatic, testicular, mammary gland tumors in animals.**

PFOS associated with:

- **liver and thyroid cancer in rats.**

PFOA and PFOS associated with:

- **cancers in humans; toxicology still being studied**

PFAS Formation

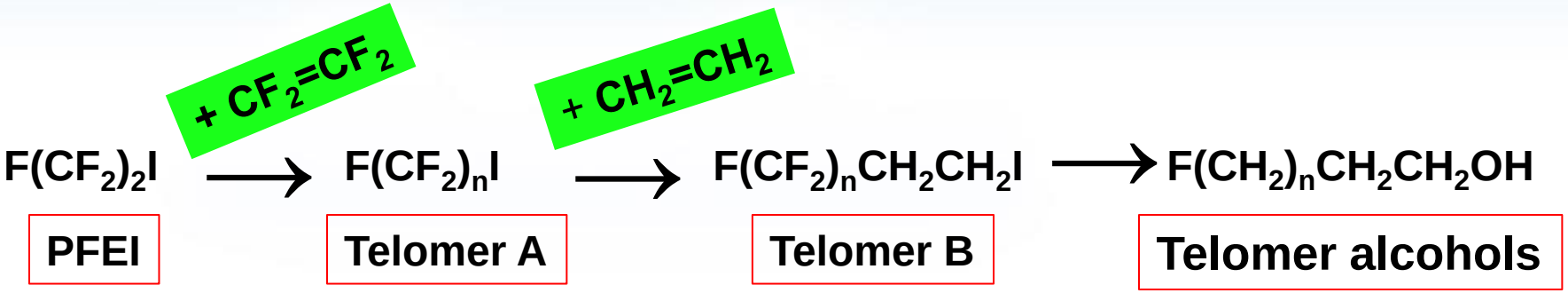
- **ECF Reaction:** Process yields a mixture of B/L isomers

(5 volts)

$$C_8H_{17}SO_2F + 34HF \rightarrow C_8F_{17}SO_2F + 17H_2 \text{ (POSF)}$$

- **Telomer Reaction:** Process yields 100% linear isomers

(Synthesis of building blocks leading to fluorotelomer alcohols)



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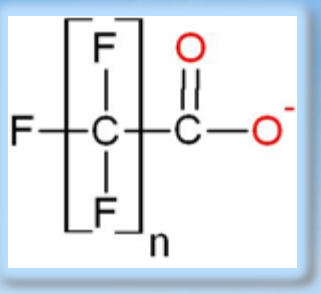
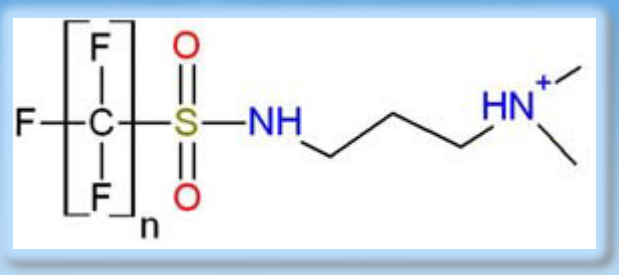
Chemical Structure Why is it Important?



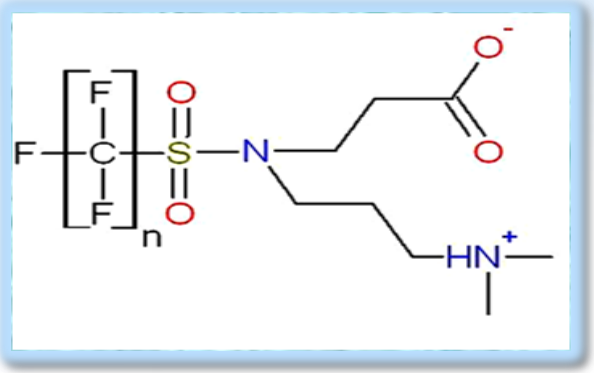
Perfluoroalkyl Carboxylate

Perfluoroalkyl Sulfonate



Perfluoroalkyl Sulfonamido Amines

Fluorotelomer Sulfonates



Perfluoroalkyl Sulfonamido acetic acid amine

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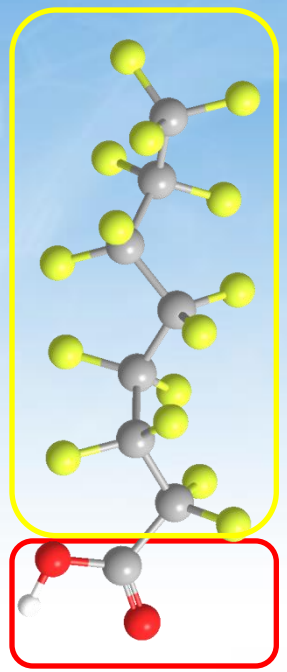
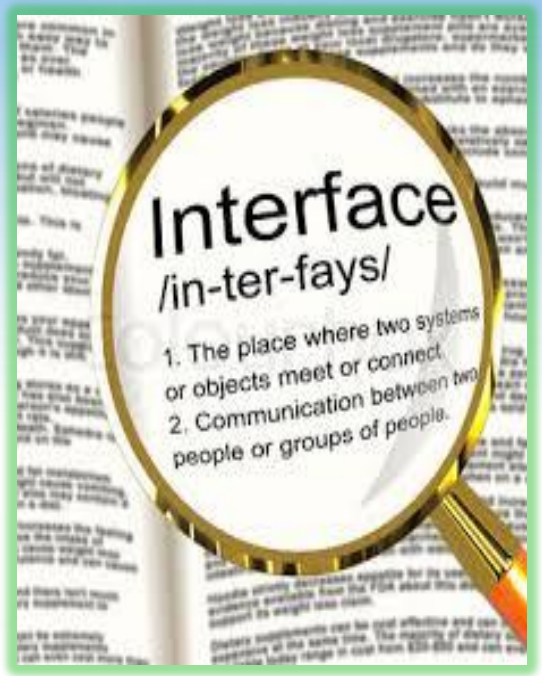
3 Unique Chemical Properties

Hydrophobic and Lipophobic



Interfacial Behaviors



Hydrophilic and Electrostatic

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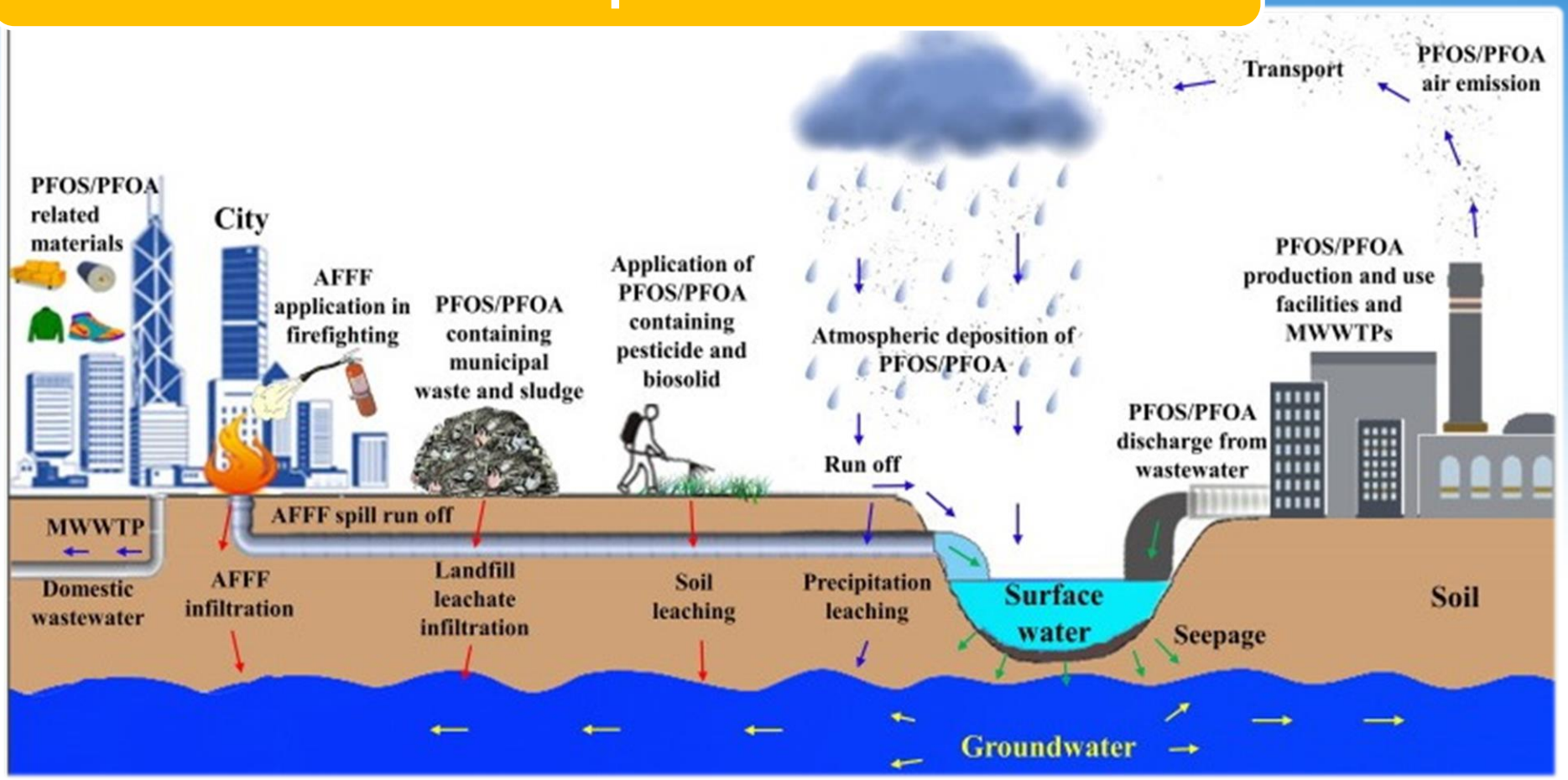
Major Sources to the Environment

- Industrial Sites – Manufacturing and secondary industries
- Any locations where AFFF was stored or used
- Landfills – lined and unlined. Leachates
- WWTP and Biosolids used as agricultural amendments
- Many non-point sources

How are we exposed to them?



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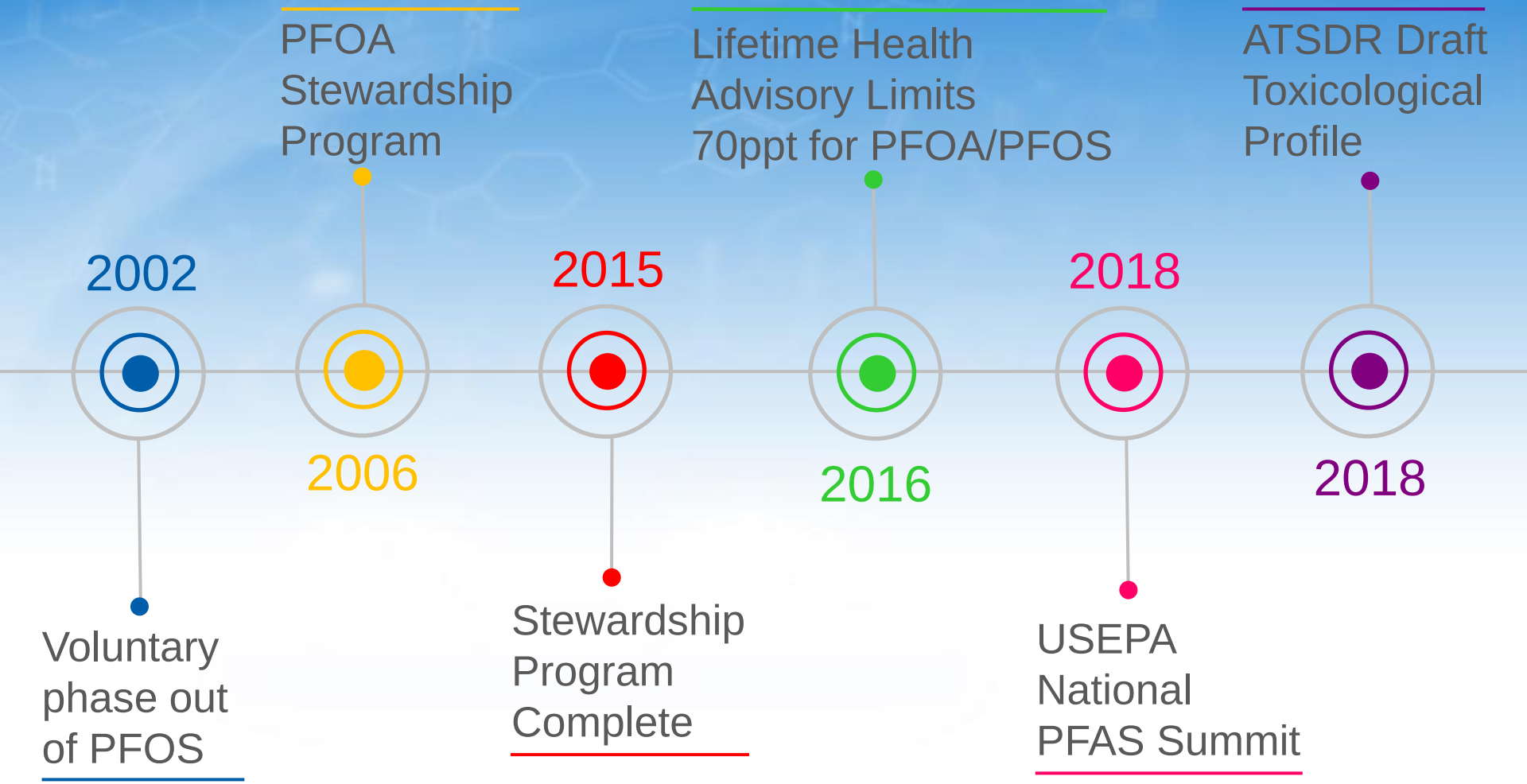
What have we done about it?



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Regulatory Challenges and New Developments

- Lack of regulatory guidance for most matrices and most PFAS compounds
- Wide variety of detection limits and analyte lists
- Lack of published method – expect multi-lab validated methods in 2019
- DoD QSM 5.2 published – changes are significant

State Drinking Water Limits

State	PFOA ppt	PFOS ppt	Ratified Y/N	Comments
North Carolina	NA	NA	N	“GenX” 140 ppt
Nevada	667	667	N	
AZ, AL, CO, ME, MI, RI,WV	70	70	Varies	Adopted HAL from 2016
CT & MA	70	70	N	PFNA, PFHxA, PFHpA
Alaska	70	70	N	PFBS, PFNA, PFHxA, PFHpA
Minnesota	35	27	N	
New Hampshire	38	70	N	PFNA 23ppt PFHxS 85ppt
Vermont	20	20	Y	PFNA, PFHxA, PFHpA
California	14	13	N	Interim Notification Levels
New Jersey	14	13	N/Y	PFNA 13 ppt
New York	10	10	N	

USEPA Health Advisory Limit = 70 ppt

https://pfas-1.itrcweb.org/fact-sheets/

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State GW/SW Limits

State	PFOA ppt	PFOS ppt	Comments
Oregon	24,000	300,000	SW; PFNA, PFHpA, PFOSA
North Carolina	2,000	NA	
Texas	290	560	PCLs for 16 PFCs
Maine	130	560	
PA, RI, DE, IA, NH	70	70	
Connecticut	70	70	PFNA, PFHxA, PFHpA
Alaska	70	70	PFNA, PFHxA, PFHpA, PFBS
Minnesota	35	27	
New Hampshire	38	70	PFNA, PFHxS
Vermont	20	20	PFNA, PFHxA, PFHpA
Michigan	420	11	SW; 70ppt GW
New Jersey	10	10	13 ppt for PFNA

https://pfas-1.itrcweb.org/fact-sheets/

LOOKING BACK

2018

LOOKING AHEAD

2019

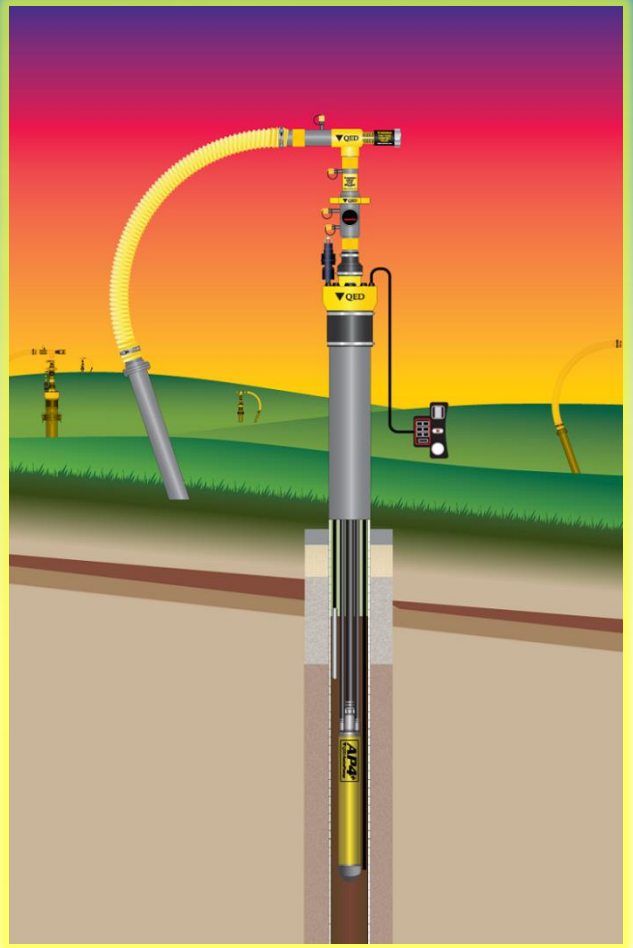
Additional state limits
Method 537.1
QSM 5.2
Published standardized methods
Target analyte list
ATSDR toxicology report finalized?
EPA draft toxicology report finalized?
Groundwater Cleanup Criteria?
Hazardous Substance Designation?
Formal Guidance?

Why are PFAS an Analytical Challenge?

- Globally distributed
- Present at low concentrations and high
- Contamination and analyte loss at all stages of collection and analysis
- Lack of authentic standards
- Unusual physical and chemical properties
- Lack of consensus “best” method for non-DW

Sampling – Manage Artifacts

- Collected in HDPE bottles fitted with unlined polyethylene screw caps.
- The field crew – personnel hygiene, clothing, food products, sunscreens and insect repellants.
- Sampling equipment – avoid fluoropolymer bailers, pump bladders, tubing, valves etc.
- Sample collection – wash hands, wear nitrile gloves, do not filter samples, add field QC samples routinely
- Avoid food or drink on-site
- Limit visitors during sample collection

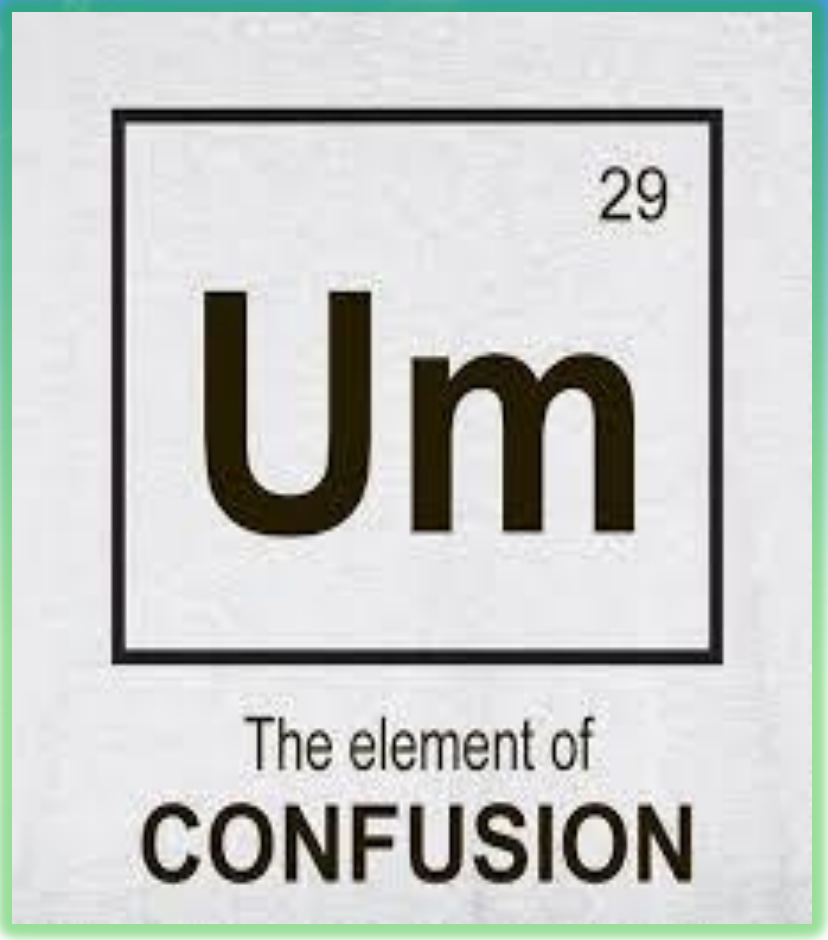


Managing Loss/Adsorption

- Many PFAS are surface active, which cause them to stratify, adsorb to surfaces
- Extraction type – whole bottle or subsample play a more significant role then material type
- PFAS can adsorb to the filtration equipment. PFAS in the dissolved phase can also adsorb to the filter material
- Unless the samples are analyzed immediately adsorption to glass vials may occur

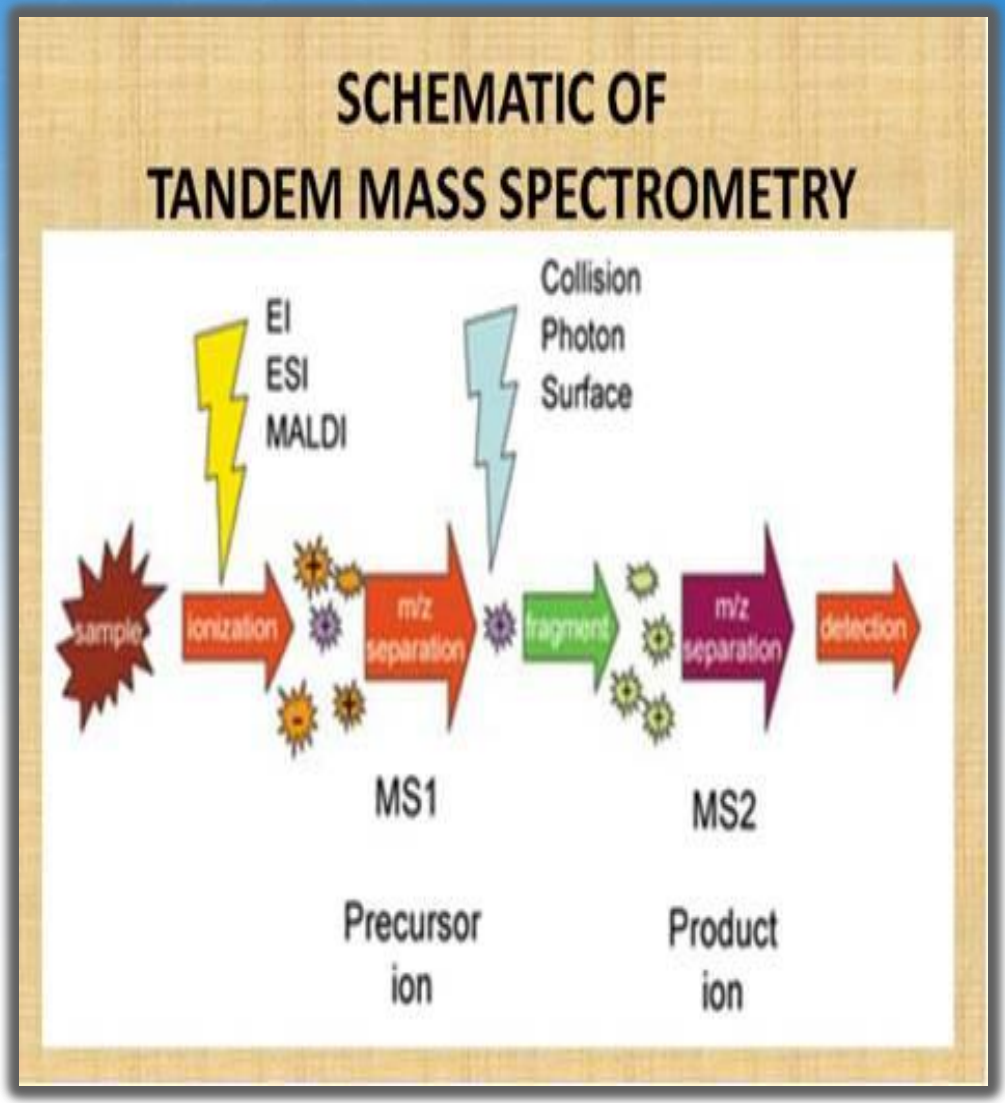
PFAS Analytical Methods

- **Manufacturer's methods were adopted by the environmental industry – SW-846 Method 8321**
- EPA expanded manufacturer's method for drinking water-Method 537 – Labs commercialized 537
- **Labs had to modify Method 537 in order to meet client needs**
- Then ASTM Methods published-not widely adopted by industry
- **EPA Published Method 537.1**
- DoD QSM 5.1 addresses PFAS – then 5.2



LC/MS/MS – Electrospray Ionization

Step 1 - Separation chemistry occurs in the LC column
Step 2 – Excess solvent is removed and ions are formed.
Step 3 – Ions travel through the first quadrupole and ion selection occurs
Step 4- Selected ions travel through the second quadrupole where selection occurs again
Hence, tandem MS
Step 5 – A response is measured and reported



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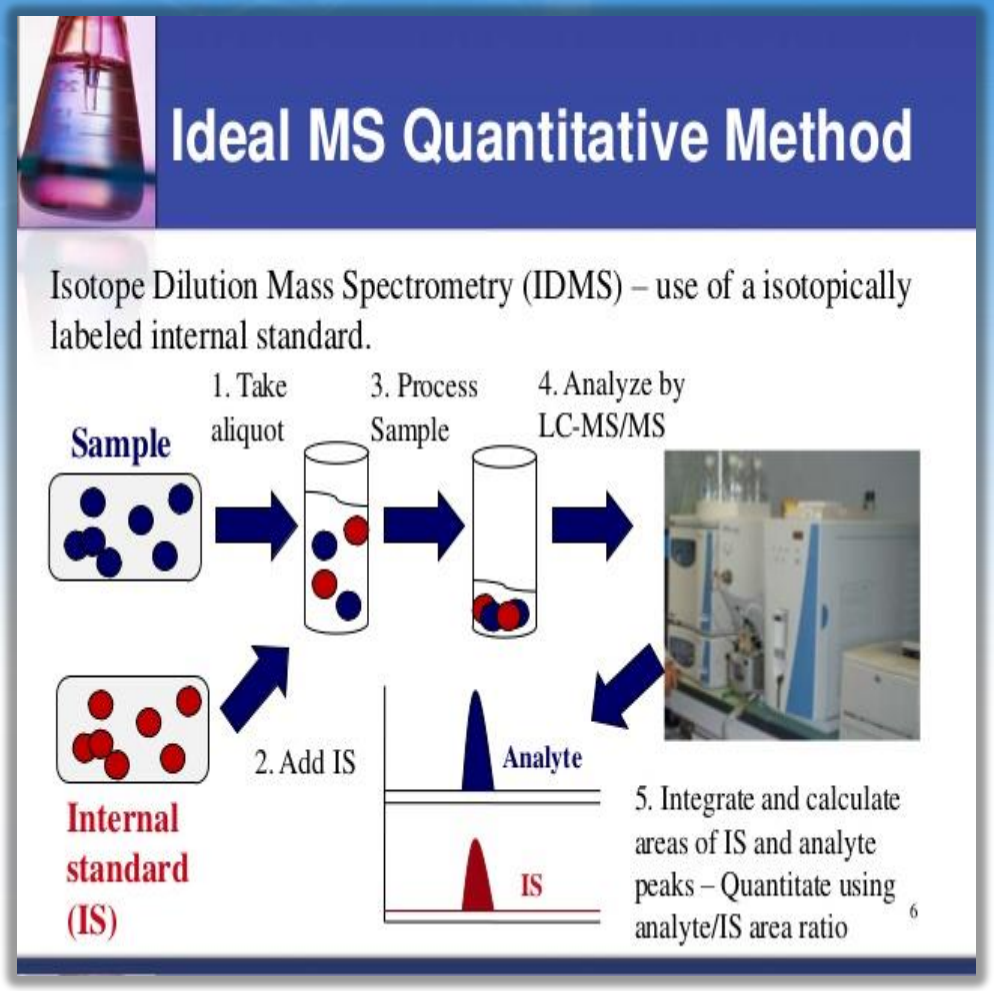
What is Isotope Dilution?

- Most accurate and precise calibration method available
- Partial loss of analyte during preparation is compensated for since chemical interferences are not an issue
- Allows for matrix recovery correction – what affects the native analyte will equally affect the isotope
- Correction for signal drift
- Improved qualitative identification – RT shifts



Extraction by Method 537 Mod – Aqueous and Solid Matrices

1. Sample collection and shipment to the lab chilled in HDPE bottles with DW preservative if appropriate.

2. Measure 250 mls of sample and spike with isotopically labeled target analytes.

3. Prepare SPE, load sample and elute PFAS off the cartridge with an ammonium hydroxide/methanol solution. In line SPE is available.

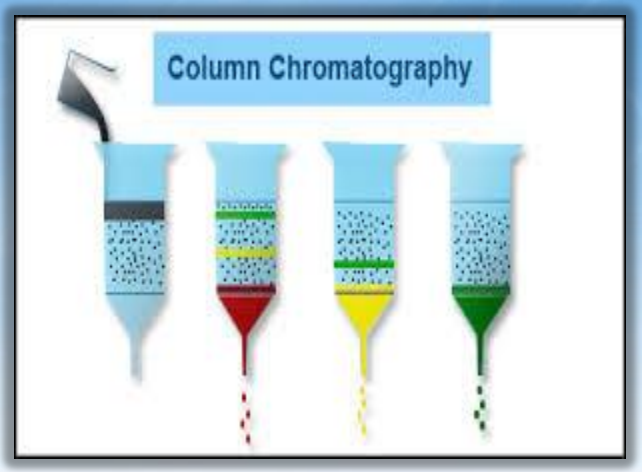
1. Sample collection and shipment to the lab chilled in HDPE bottles.

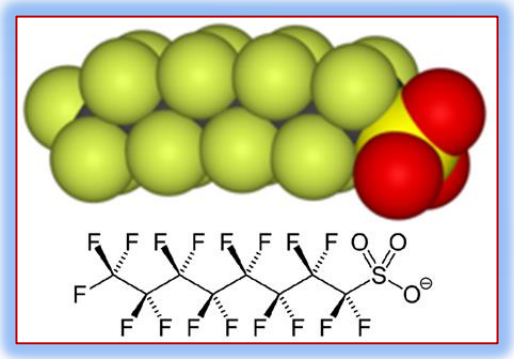
2. Measure 5 g of sample and spike with isotopically labeled target analytes. Extract with KOH/MeOH. Shake for 3 hours and sonicate for 12 hours

3. Prepare SPE, load sample and elute PFAS off the cartridge with an ammonium hydroxide/methanol solution.

Move on to the Analysis

Analysis by Method 537 Mod – Aqueous and Solid Matrices





4. Concentrate PFAS extract to dryness. Add methanol to each, soak and vortex to mix well. Then add water to final composition of 80:20 methanol:water

5. Analyze by LCMSMS using a C18 column with a gradient program using 20 mM ammonium acetate/water and methanol. Mass spec is operated in (ESI) negative ion mode.

6. Process and review data. Assess QC elements, narrate anomalies and send report to client.

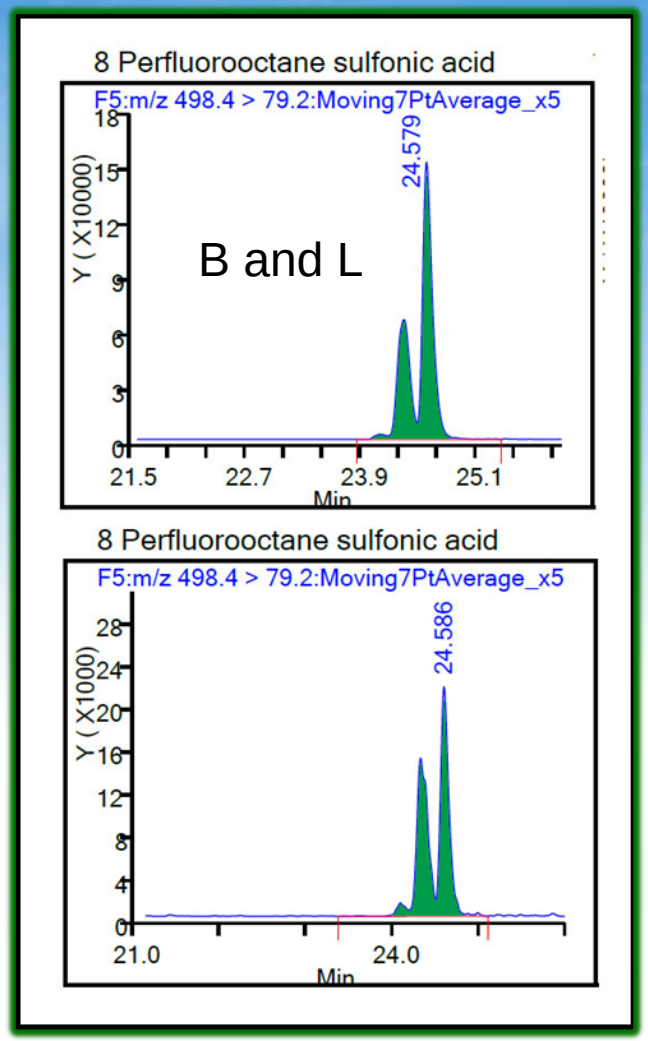
Branched and Linear Error

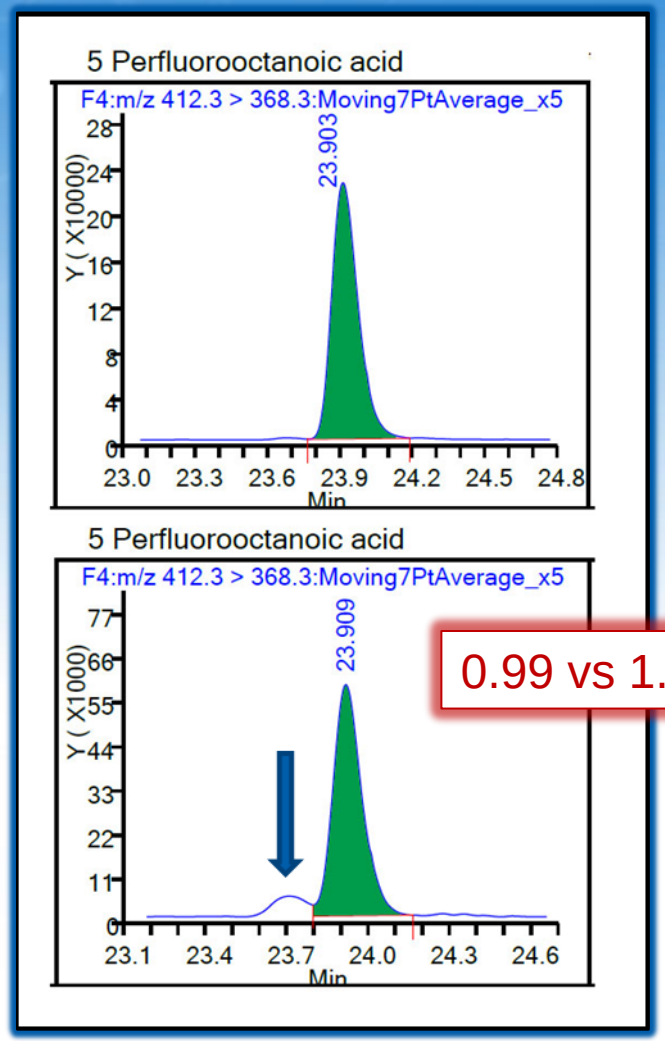
PFOS

PFOA

Standard

Sample





0.99 vs 1.20 ng/ml

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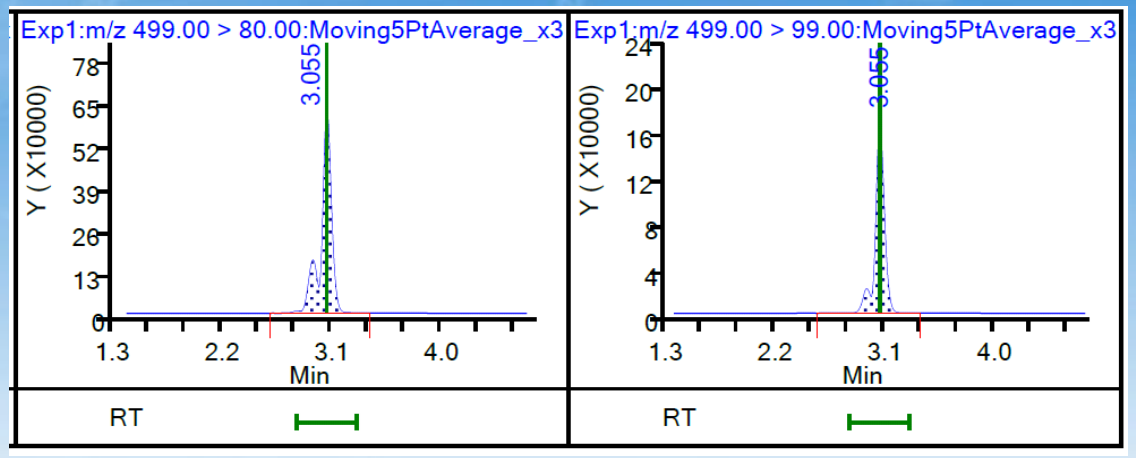
Secondary Ion Transition - PFOS

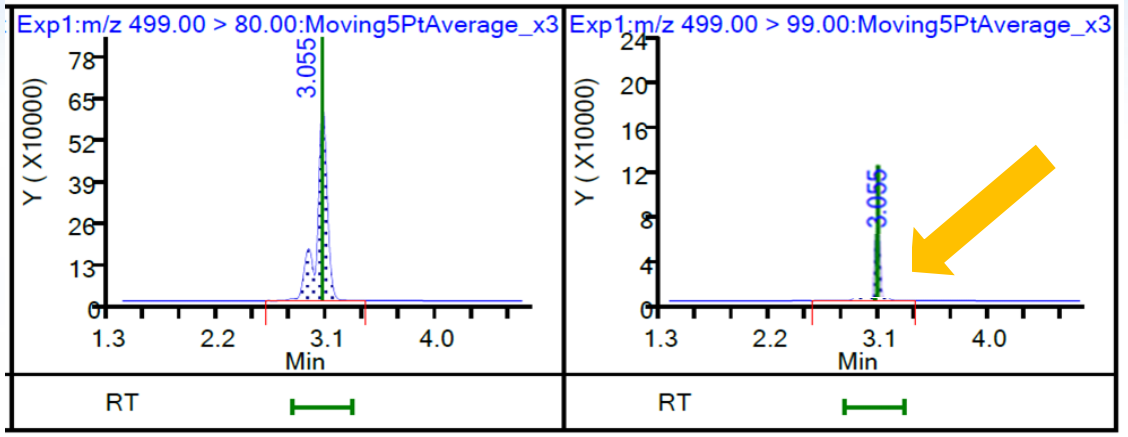
Primary Ion Transition | Secondary Ion Transition

Standard



Primary Ion Transition | Secondary Ion Transition

Sample



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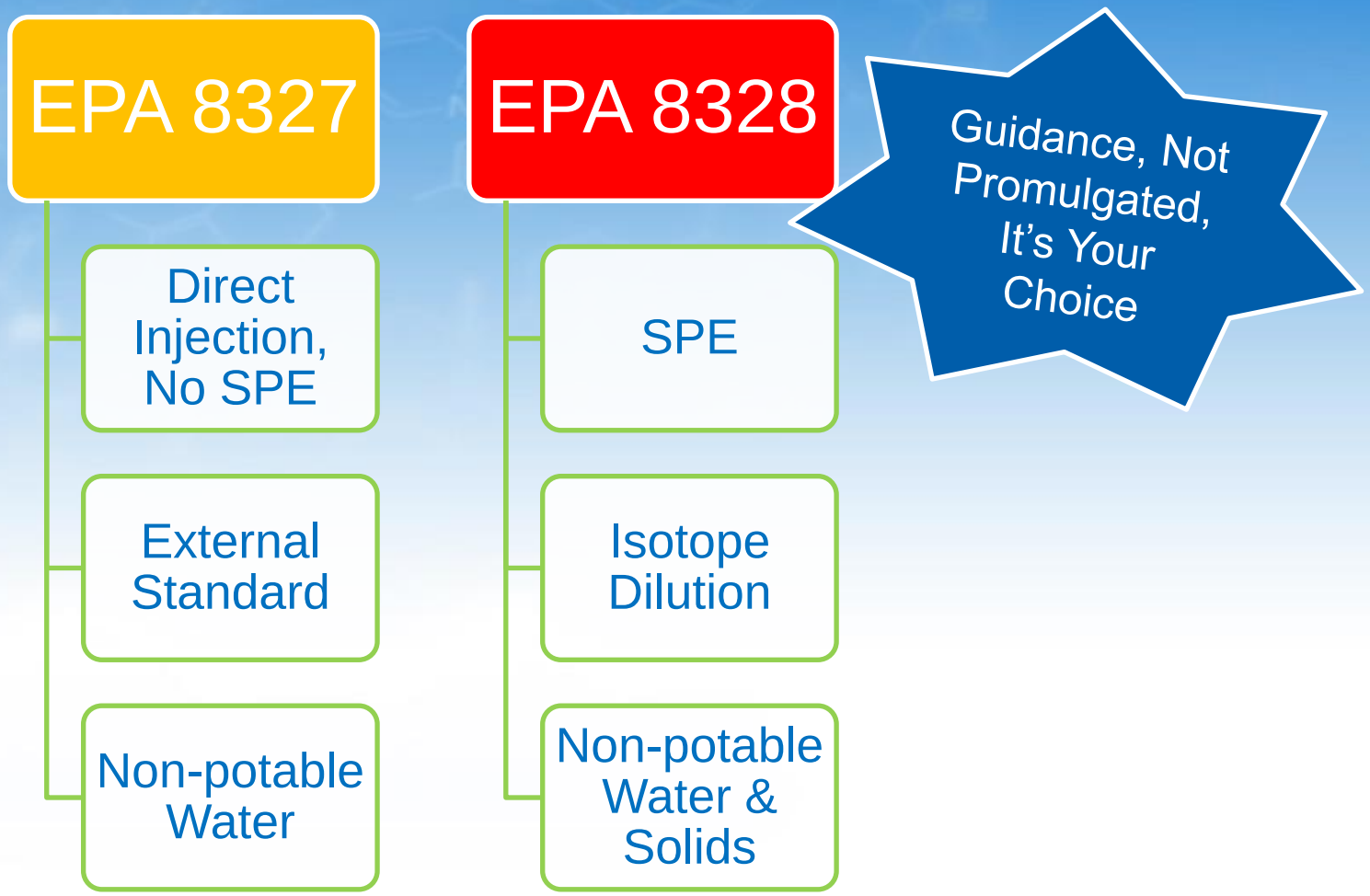
SW-846 Methods



537 vs ASTM vs 537M

PFAS Method Comparison Table for Aqueous Matrix				
Features	**Method 537**	**ASTM D7979-17**	**TestAmerica Sacramento Method 537M Manual SPE[1]**	**TestAmerica Sacramento Method 537M In-line SPE**
Sample size	250 mls	Any are allowed (5 mls used in validation)	Same as 537	1 ml
Holding times	14 days for extraction	28 days for analysis	Same as 537	28 days for analysis
Matrices	Drinking Water	All aqueous matrices, no DW	All aqueous matrices	All aqueous matrices
Aqueous Extraction	SPE SDVB	DAI	SPE Waters WAX	DAI
Analysis	LCMSMS - no confirmation ion	LCMSMS with confirmation ion, if available	LCMSMS with confirmation ion, if available	LCMSMS with confirmation ion, if available
Mass Spec	ESI Negative ion mode	Same as 537	Same as 537	Same as 537
Result includes Branched and Linear isomers	Yes, for available standards	Same as 537	Same as 537	Same as 537
Quantitation	Internal standard	External standard	Isotope dilution	Isotope dilution
Reporting Limits	(2 ppt - 40 ppt)	(10ppt - 8000ppt)	(2ppt - 20ppt)	(2ppt - 20ppt)
Isotope Recovery Correction	No	No	Yes	Yes
LCS recovery limits	70-130	Default to 70-130 until a multi-lab validation study can be done or lab statistical limits are determined.	70 to 130 for DW, Statistical limits for others	70 to 130 for DW, Statistical limits for others

[1] - **Please note that TestAmerica Sacramento's manual SPE method is DoD QSM 5.1 Table B-15 compliant.**

Method 537M – In Line SPE (ASTM – Like)

- **What is it?**
  - Dilute a water sample with methanol and inject a large volume onto a modified UPLC
- **What are the advantages?**
  - Simplicity – reduced sample manipulation
  - Reduced sample volume (5 mls)
  - Speed, reduced TAT
  - Increased capacity
  - Reduced risk of laboratory background artifacts

Complex Matrices – Biphasic (Leachates, Biosolids, etc.)

Do you want results for the whole sample or the dissolved fraction?

- If whole sample then spike IDAs prior to sample manipulation
- Limited SPE capacity?
- If yes proceed with complex extraction option
- Complex option includes centrifuge and filter. Extraction of both fractions and recombine

- If only dissolved fraction
- Then centrifuge to remove particulate fraction
- Decant aqueous fraction
- Spike with IDAs
- Determine aqueous fraction by LCMSMS

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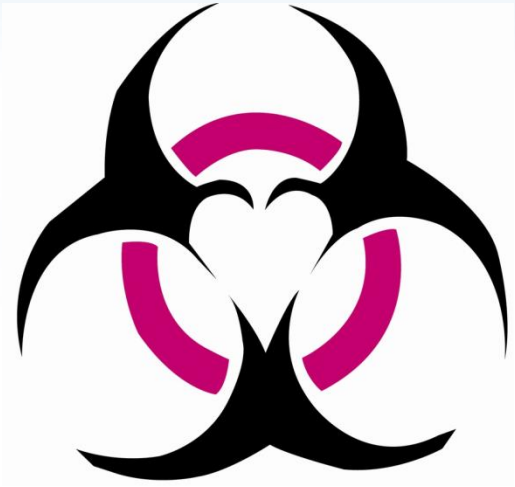
What are Precursors and Why Do We Care?

- Thousands of precursors used in industrial and consumer products
- Some biotransform to make PFAAs
- Some are fluorotelomers
- Most are ionic, either positive, negative or both
- Fate and transport – complex process



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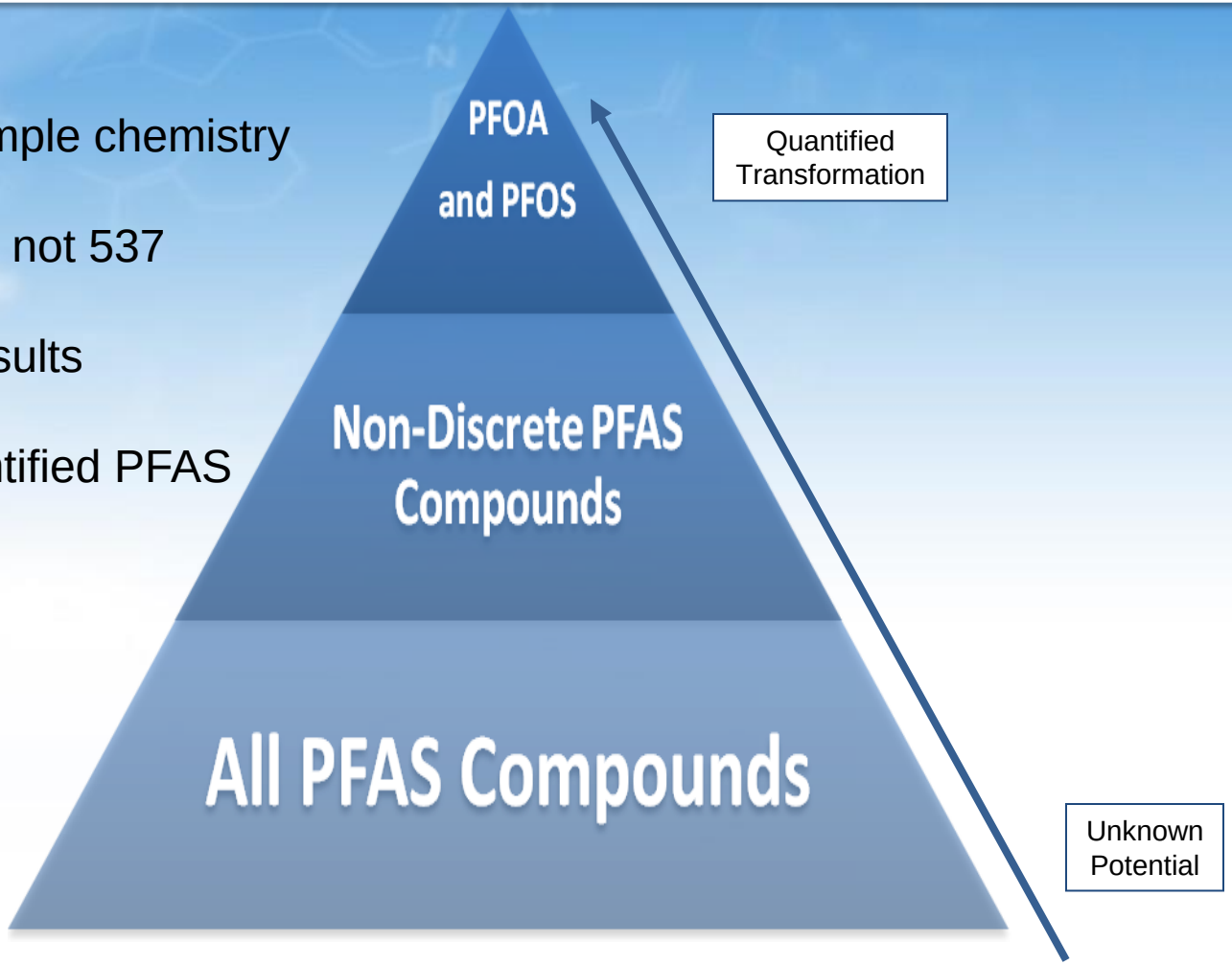
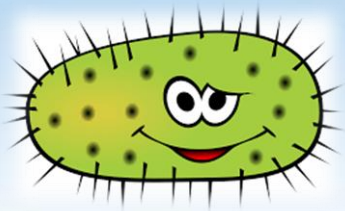
What is the TOP Assay?

A new PFAS sample preparation technique

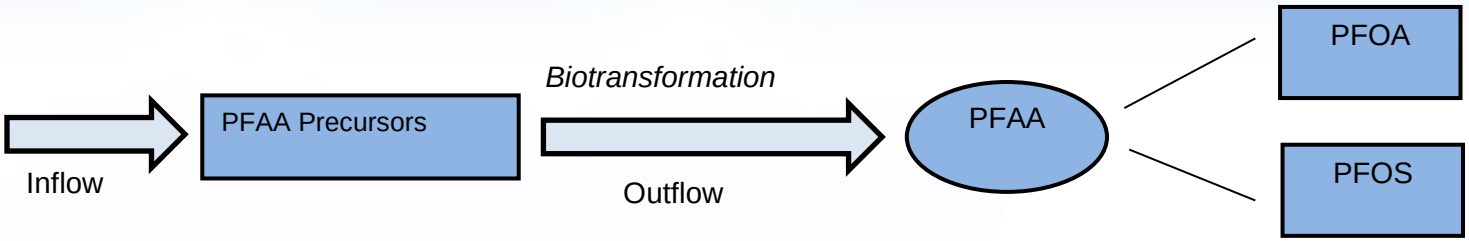
- Conceptually simple chemistry
- Used with 537M not 537
- Pre and Post results
- Indicates unidentified PFAS



How Does it Work in the Environment?



Give me an example:



Low levels of discrete compounds are detected

High levels of discrete compounds are detected, which can include PFOA and PFOS

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TOP – How Does it Work in the Laboratory?

PFAA Precursors + OH• OH• OH• 85°C = PFOA + other PFCAs

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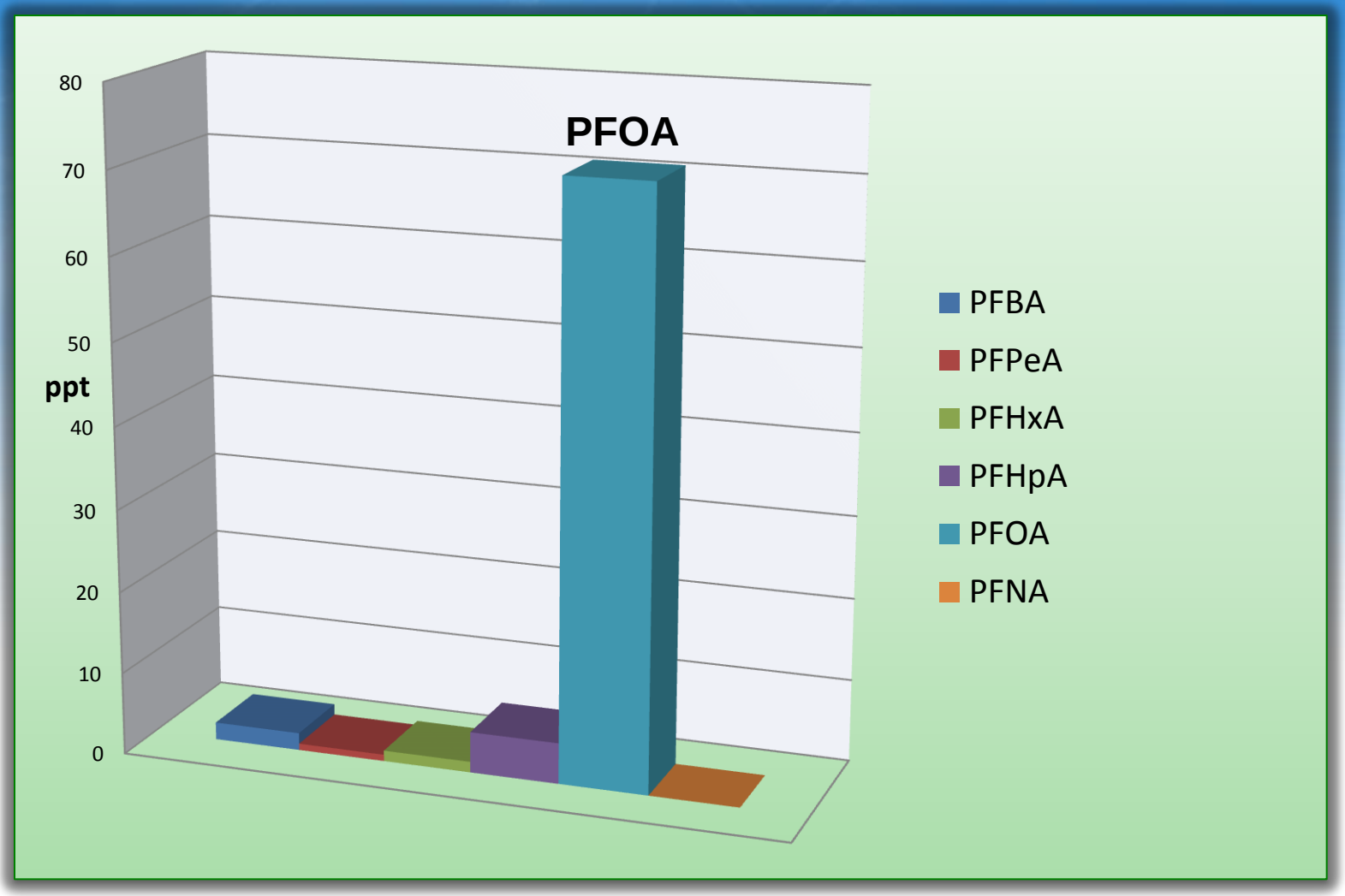
PFCA Pattern – Me-FOSA Precursor



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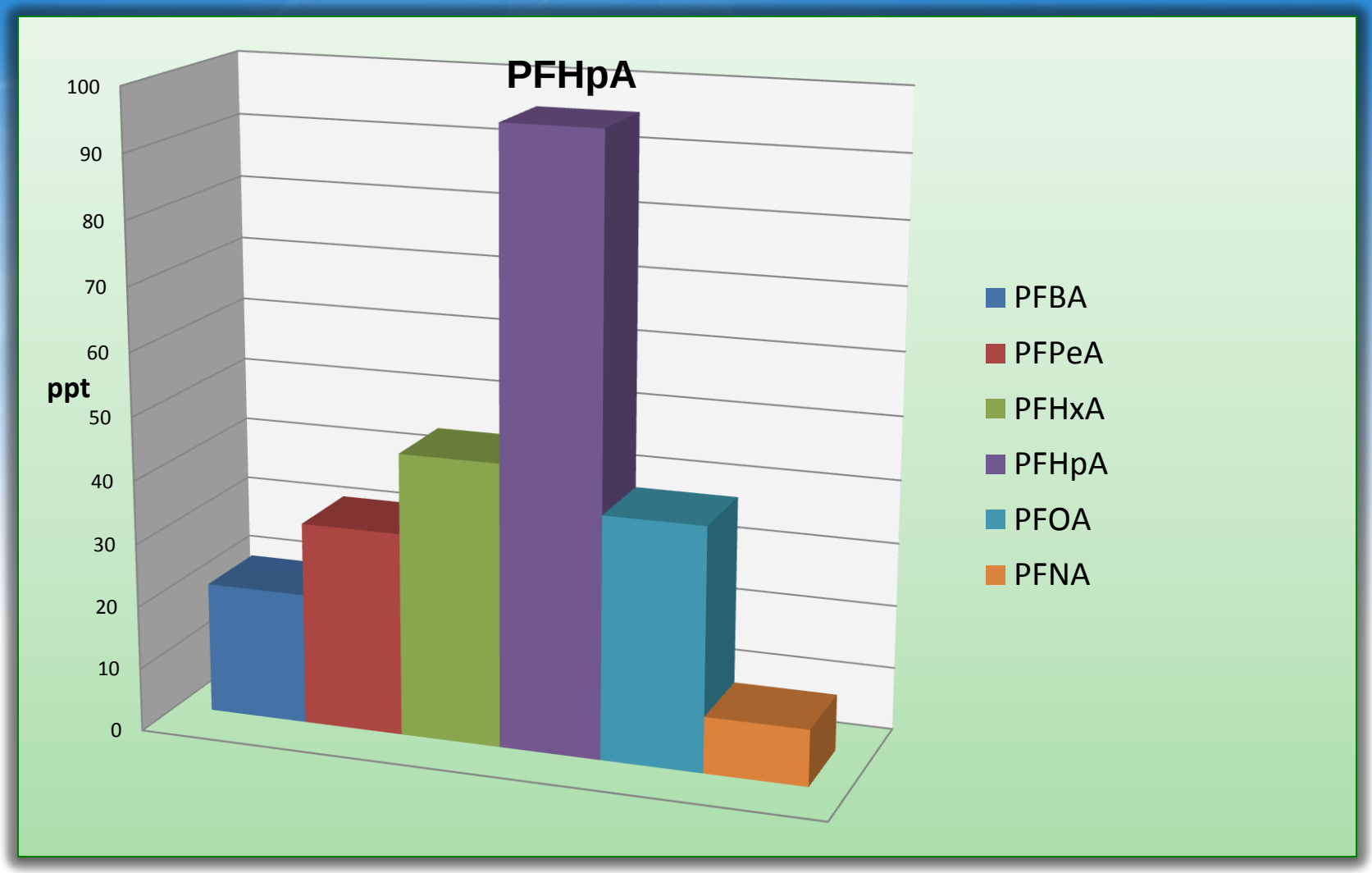
PFCA Pattern – 8:2 FTS



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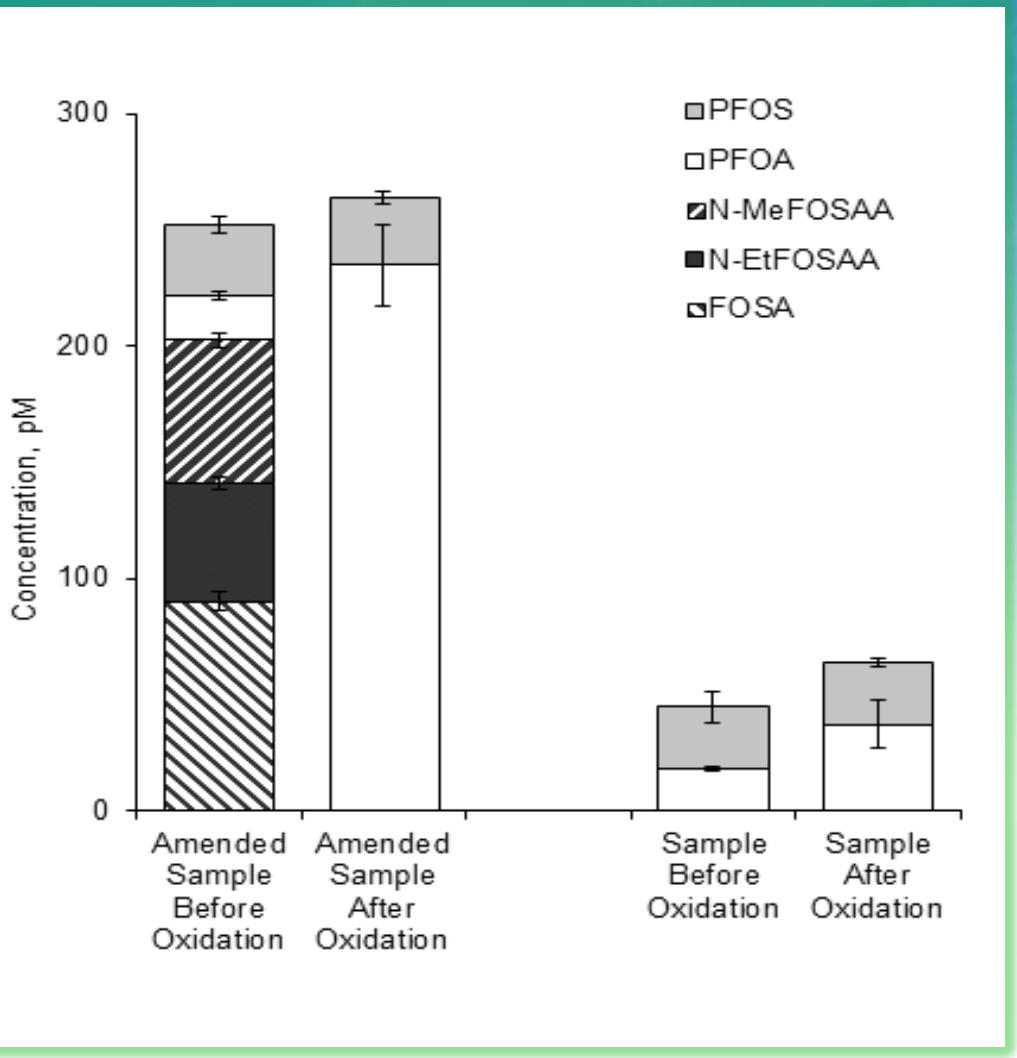
Urban Runoff – San Jose, CA



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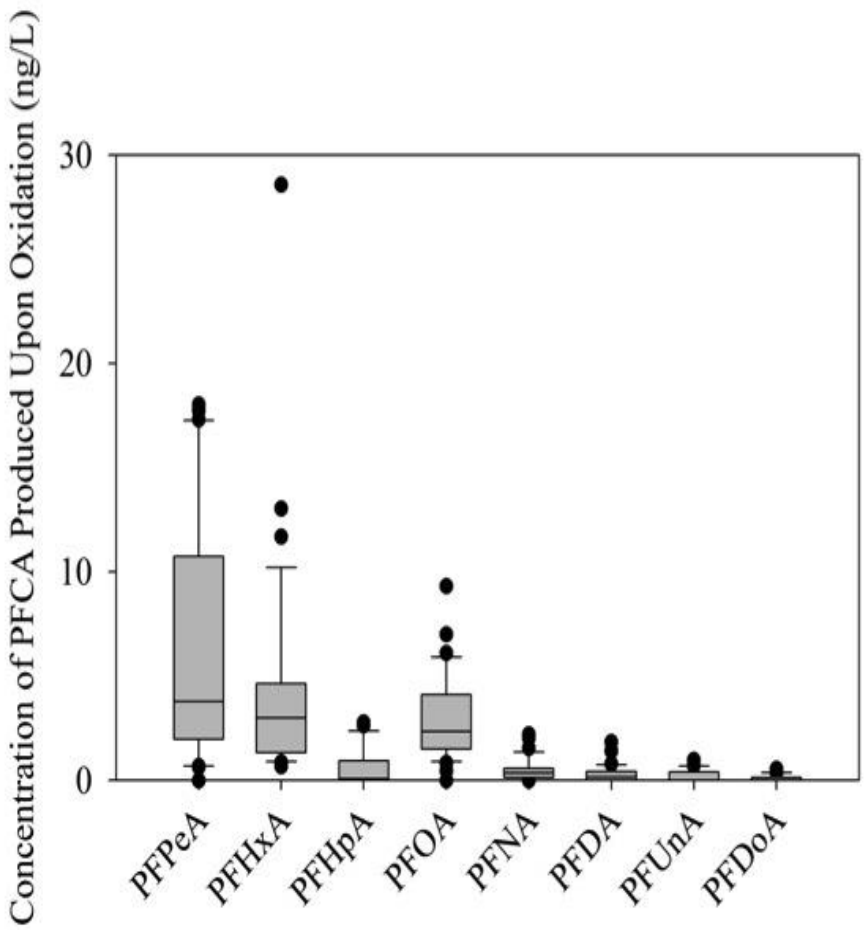
Erika F. Houtz and David L. Sedlak, "Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff," Environmental Science and Technology 46, no. 17 (2012): 9342-49.

Urban Runoff from SF Bay Area



Erika F. Houtz and David L. Sedlak, "Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff," Environmental Science and Technology 46, no. 17 (2012): 9342-49.

Fluorinated Replacement Chemicals

- Since 2000, on-going industrial transition to replace LC PFCAs, PFSAs and precursors
- Many alternative chemicals are in use – below regulatory radar
- Unclear whether they are safe for humans or the environment
- DuPont developed patented GenX technology - enables them to make fluoropolymers without PFOA
- GenX is not a chemical it is a process

Emerging Field Screening Methods

- Methylene blue active substance (MBAS) anionic surfactant detection kit
- Fluorous membrane ion-selective electrode (ISE)
- Particle-induced gamma ray emissions (PIGE) spectroscopy
- Adsorbable organic fluorine (AOF)

Conclusions and Future Concerns

- PFAS include thousands of compounds, used in many industries
- Regulations developing in ppt
- Many secondary sources
- Sampling, analysis and data interpretation requires experience
- Remediation can be challenging and conventional approaches can make a site worse
- We need a consensus “best” method
- Analyte lists are growing for discrete methods and may lead to forensics
- Need effective field screening techniques

Experience

- 20 Years of Experience
- Significant Investment in Method Development

Capabilities

- Nations Largest LCMSMS Capacity
- Extensive Analyte List, TOP Assay & Replacement Chemicals

Ease of Use

- Consistent and Defensible Data
- Seamless Data Deliverable
- Nationwide Coverage

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