United States
Environmental Protection
Agency

Per- and Polyfluoroalkyl Substances (PFAS):

Source/Site Characterization and Treatment/Remediation

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EPA
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Overview

- **What the presentation doesn't cover:**
  - **Toxicology**
  - **Health research**

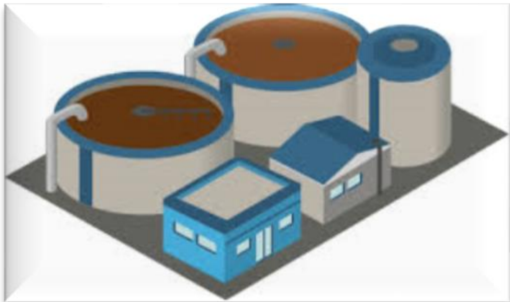
- **What this presentation does cover:**

Research to support…

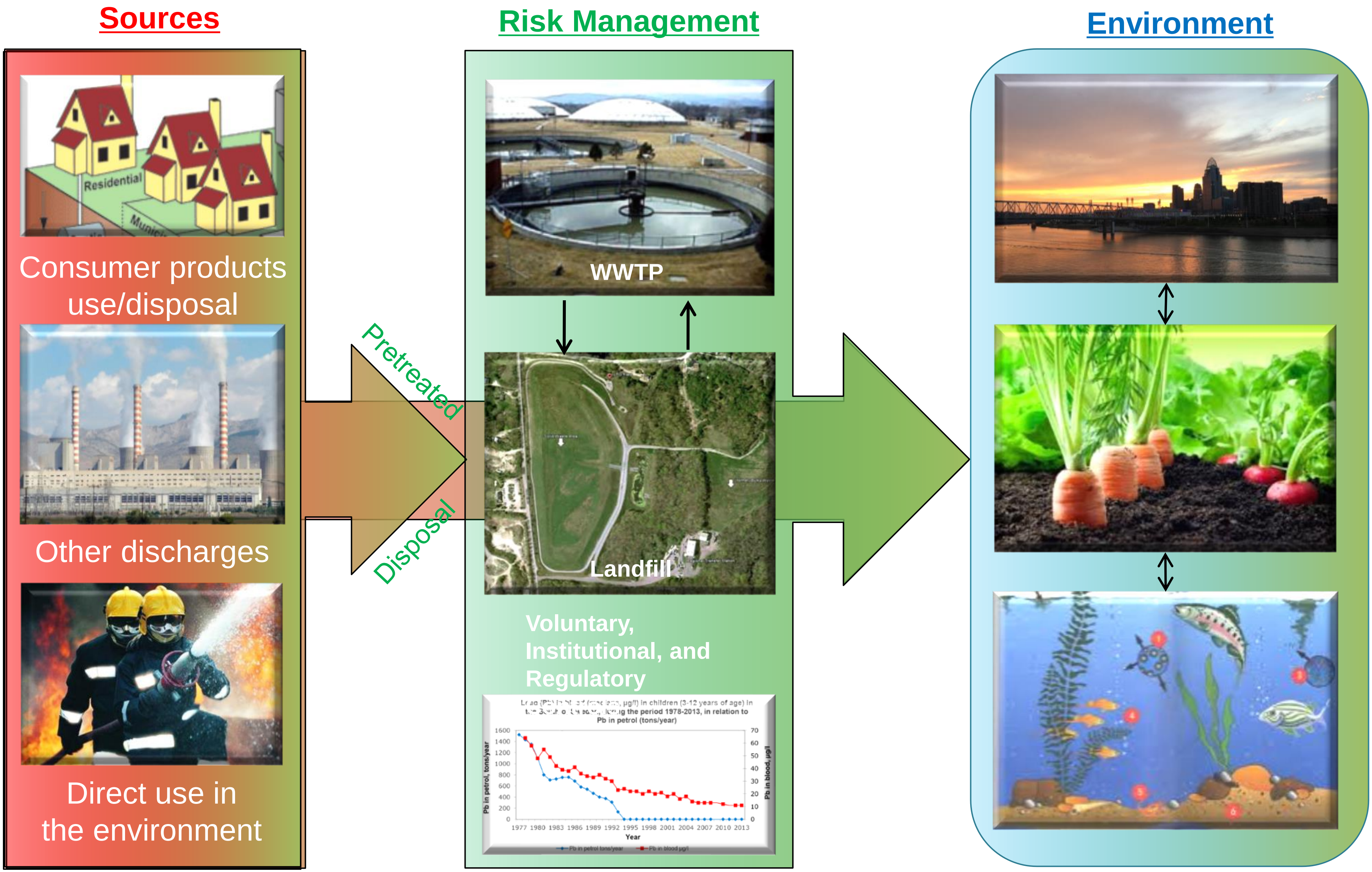
  - **Source and Site characterization**
    - **Analytical Methods for non-DW matrices**
    - **Sampling and analytical issues**
  - **Treatment**
  - **Site Remediation**

Brief regulatory update

CHEMICALS AT PFAS SITES….
PFOA/PFOS AND SO MUCH MORE!



PFASs enter the environment…



Sources

Consumer products use/disposal

Other discharges

Direct use in the environment

Pretreated

Disposal

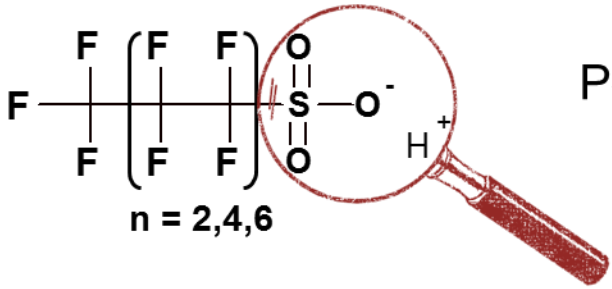
Risk Management

Voluntary, Institutional, and Regulatory

Environment

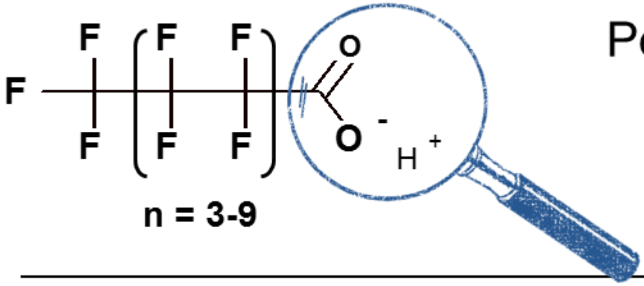
Photo Courtesy: USEPA, USGS, Artsyltech, West basin, Royer, DuPont

Common PFAS Structures



Perfluorosulfonic Acids

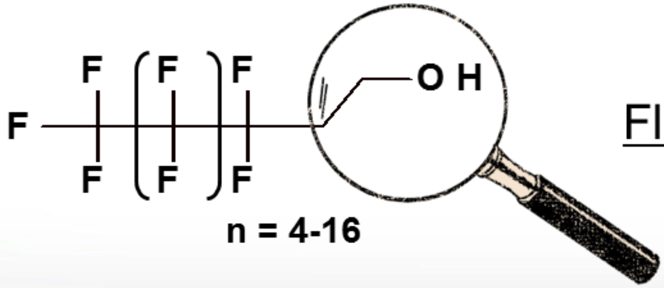
PFBS, PFHS, PFOS



Perfluorocarboxylic Acids

C_6 acid – C_{12} acid
PFOA C8 acid

Anionic at environmental pH, water soluble



Fluorotelomer Alcohols

6:2, 8:2 and 10:2

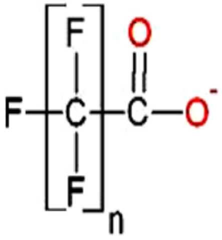
More volatile

More PFAS

Perfluoroalkyl Sulfonates

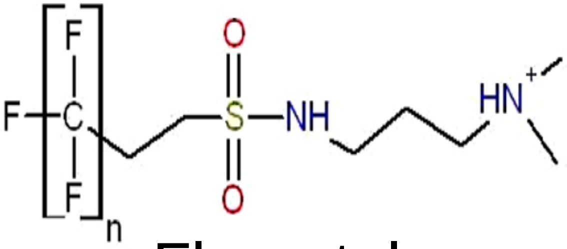
PFBS	n = 4	Qn
PFPeS *	n = 5	Ql
PFHxS	n = 6	Qn
PFHpS	n = 7	Qn
PFOS	n = 8	Qn
PFNS *	n = 9	Ql
PFDS	n = 10	Qn

Perfluoroalkyl Carboxylates



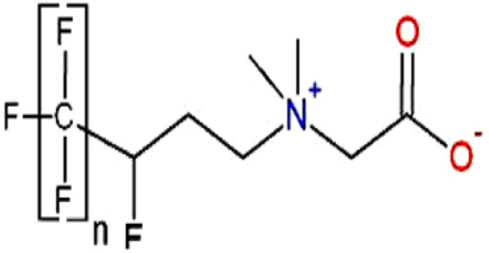
PFBA	n = 4	Qn
PFPeA	n = 5	Qn
PFHxA	n = 6	Qn
PFHpA	n = 7	Qn
PFOA	n = 8	Qn
PFNA	n = 9	Qn
PFDA	n = 10	Qn
PFUdA	n = 11	Qn
PFDoA	n = 12	Qn
PFTrA	n = 13	Qn
PFTeA	n = 14	Qn

Fluorotelomer Sulfonamide Amines

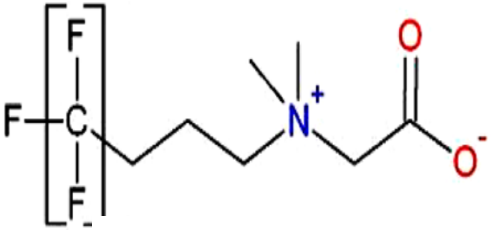


6:2 FtSaAm	n = 6	Sq
8:2 FtSaAm	n = 8	Ql

Fluorotelomer Betaines

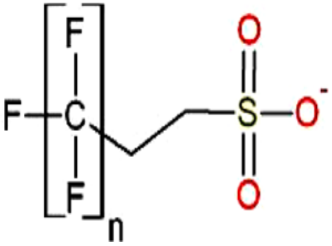


5:1:2 FtB	n = 5	Sq
7:1:2 FtB	n = 7	Sq
9:1:2 FtB	n = 9	Sq



5:3 FtB	n = 5	Sq
7:3 FtB	n = 7	Sq
9:3 FtB	n = 9	Sq

Fluorotelomer Sulfonates

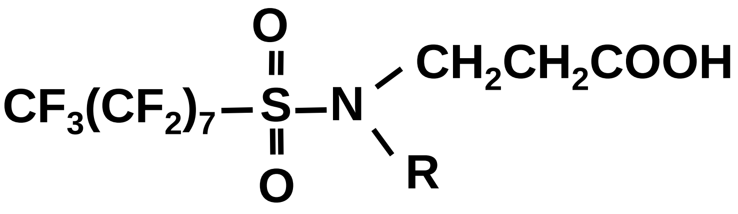


4:2 FtS	n = 4	Q
6:2 FtS	n = 6	Q
8:2 FtS	n = 8	Q

Backe et al. 2013 ES&T

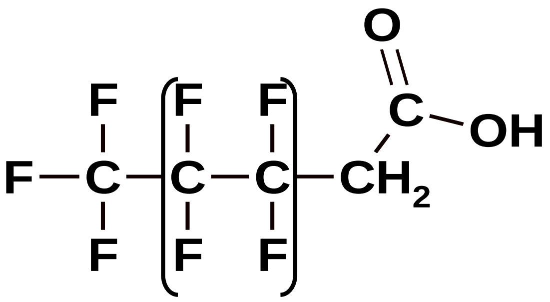
More PFAS Structures

Sulfonamides



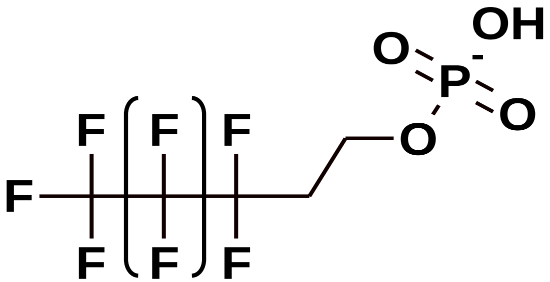
R = methyl, ethyl

Telomer Acids



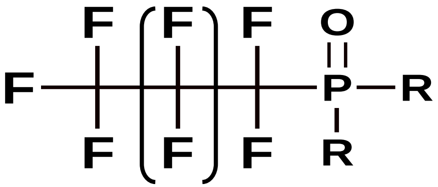
n = 4,6,8

Phosphate esters



n = 4,6,8

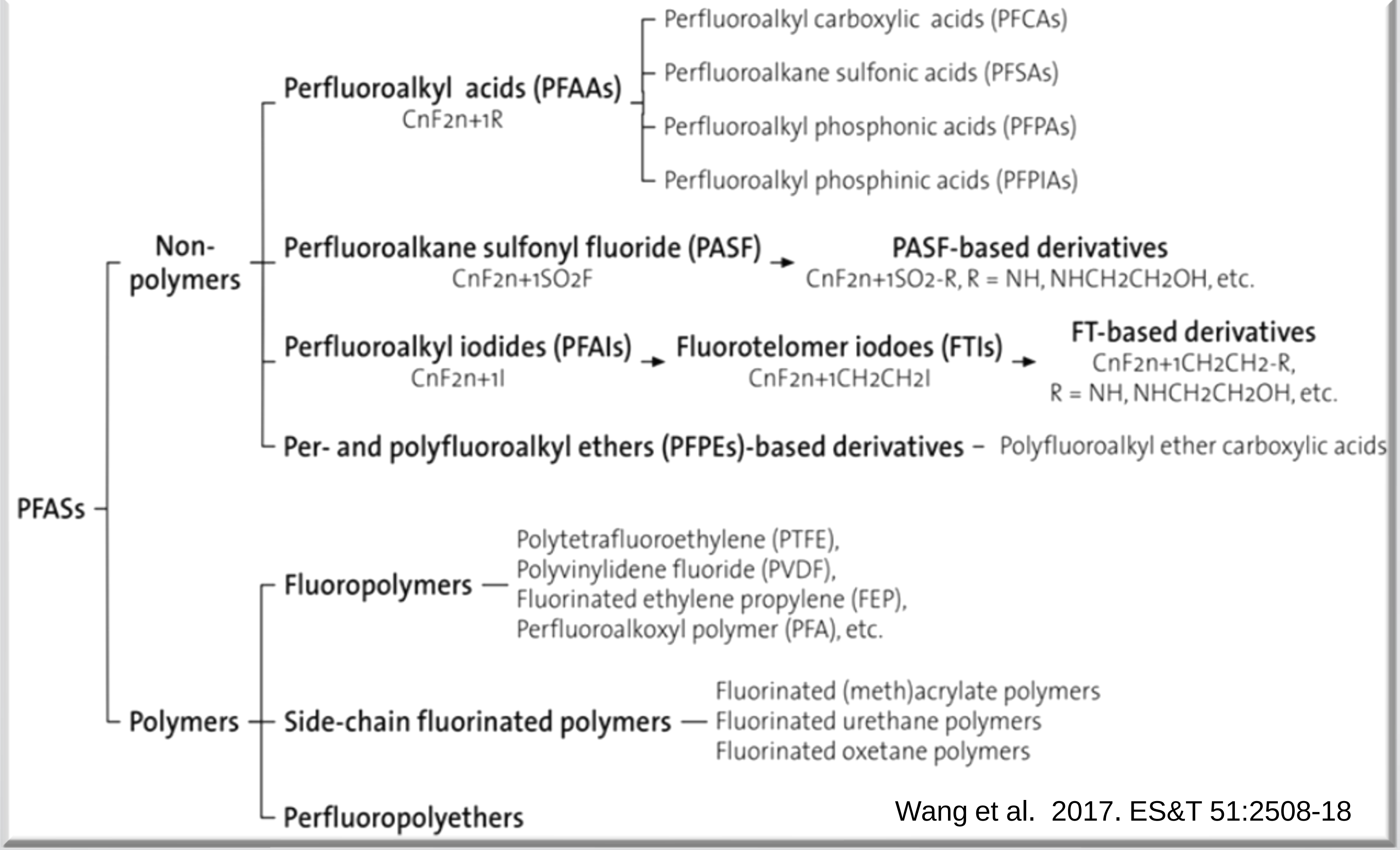
Phosphinic/phosphonic



R = OH, H

n = 2,4,6

PFASs … More than just PFOA and PFOS



- PFASs
  - Non-polymers
    - **Perfluoroalkyl acids (PFAAs)** $C_nF_{2n+1}R$
      - Perfluoroalkyl carboxylic acids (PFCAs)
      - Perfluoroalkane sulfonic acids (PFSAs)
      - Perfluoroalkyl phosphonic acids (PFPAs)
      - Perfluoroalkyl phosphinic acids (PFPIAs)
    - **Perfluoroalkane sulfonyl fluoride (PASF)** $C_nF_{2n+1}SO_2F$ → **PASF-based derivatives** $C_nF_{2n+1}SO_2\text{-}R$, R = NH, $NHCH_2CH_2OH$, etc.
    - **Perfluoroalkyl iodides (PFAIs)** $C_nF_{2n+1}I$ → **Fluorotelomer iodoes (FTIs)** $C_nF_{2n+1}CH_2CH_2I$ → **FT-based derivatives** $C_nF_{2n+1}CH_2CH_2\text{-}R$, R = NH, $NHCH_2CH_2OH$, etc.
    - **Per- and polyfluoroalkyl ethers (PFPEs)-based derivatives** – Polyfluoroalkyl ether carboxylic acids
  - Polymers
    - **Fluoropolymers** — Polytetrafluoroethylene (PTFE), Polyvinylidene fluoride (PVDF), Fluorinated ethylene propylene (FEP), Perfluoroalkoxyl polymer (PFA), etc.
    - **Side-chain fluorinated polymers** — Fluorinated (meth)acrylate polymers, Fluorinated urethane polymers, Fluorinated oxetane polymers
    - **Perfluoropolyethers**

Wang et al. 2017. ES&T 51:2508-18

PFAS Degradation & Stability: Fluorotelomer alcohol example

PFAS generally are produced with a non-fluorinated terminal functional group.

The C-F bond is very stable & tends not to degrade under environmental conditions.

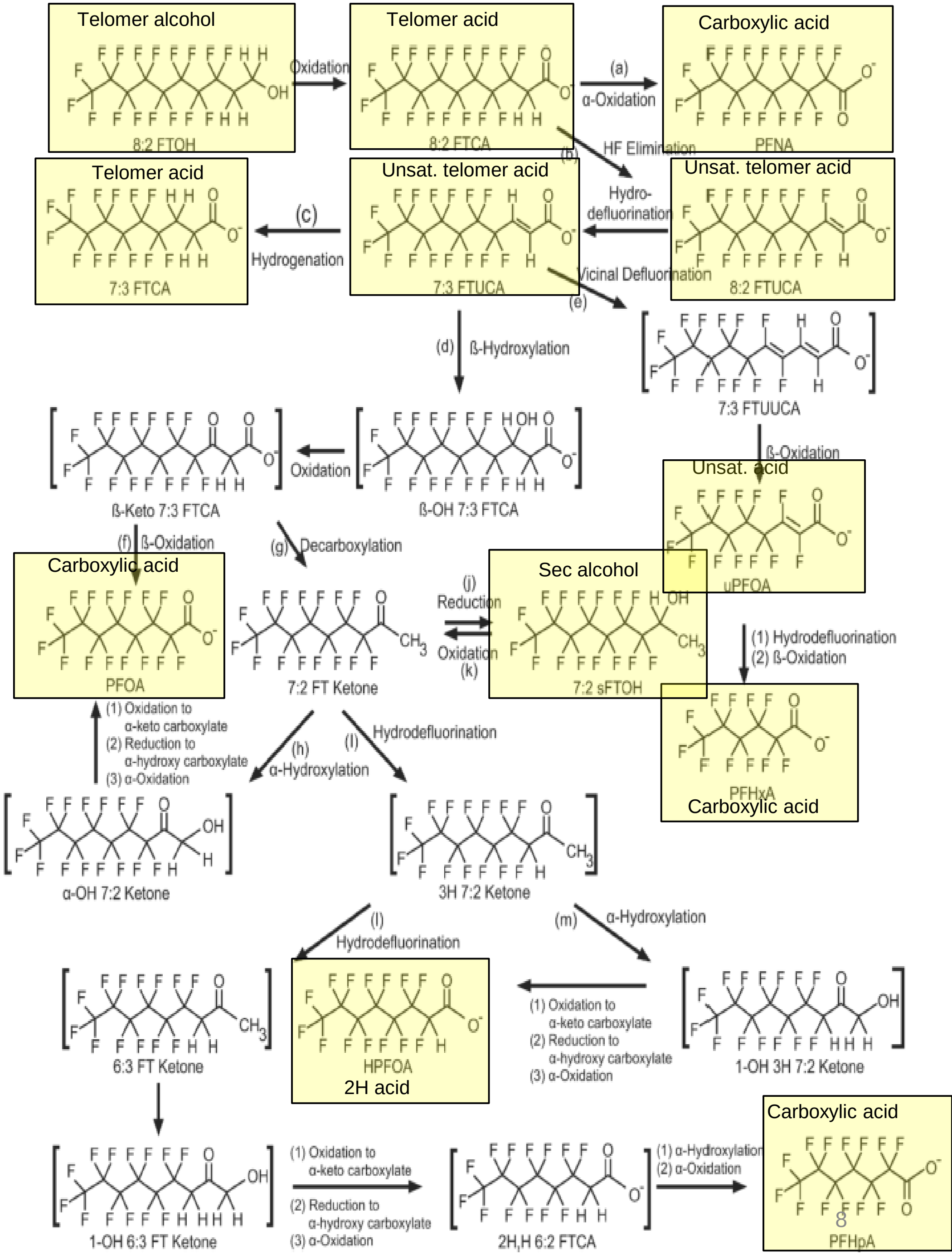
Consequently, PFAS transformation usually occurs at/near the non-fluorinated group.

Degradation mechanisms and pathways are complex & only partially understood with many unknowns.

Some transformation intermediates are very short-lived or even just inferred.

For this pathway, compounds which have been detected commonly in the environment are highlighted in yellow.

Other classes of PFAS (e.g. sulfonamides, PAPs have similarly complex and challenging transformation mechanisms and pathways.

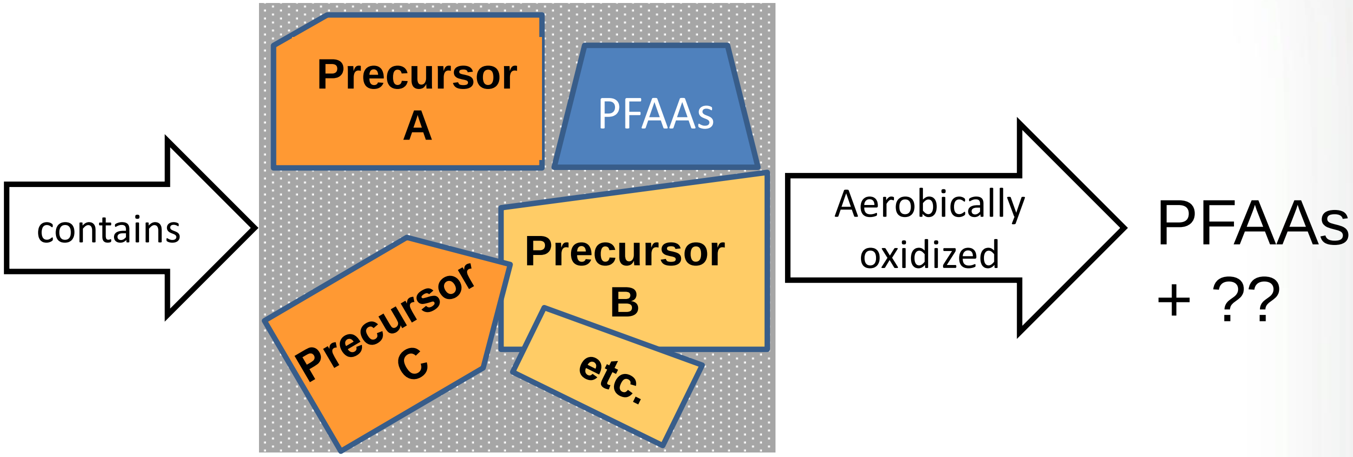


Co-contaminants at PFAS sites

- **Fire Training areas**
  - **BTEX**
  - **Chlorinated solvents**
  - **1,4 dioxane**
  - **Surfactants and AFFF components**
- **Manufacturing – production and secondary**
  - **PFAS Residuals from product formulation/production**
  - **Non-PFAS Surfactants, solvents**
- **Metal Plating**
  - **Metals**
  - **Solvents**

Precursors

PFAS Product
(e.g. AFFF)



contains

Precursor A

PFAAs

Precursor B

Precursor C

etc.

Aerobically oxidized

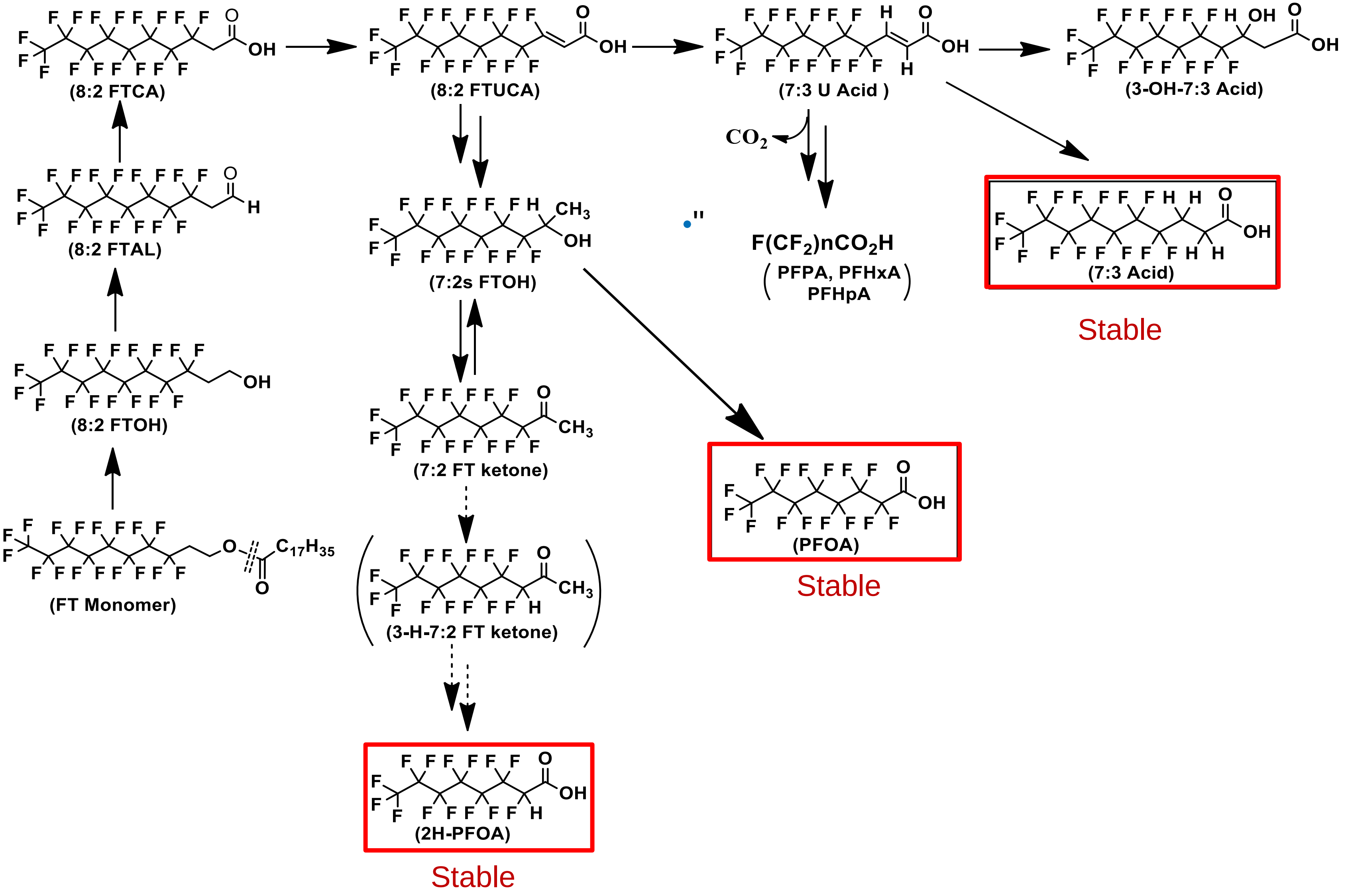
PFAAs
+ ??

PFAS = Per- & Polyfluoroalkyl Substances includes PFOA or PFOS <u>and</u> precursors

PFAAs = Perfluorinated alkyl acids includes PFOA and PFOS

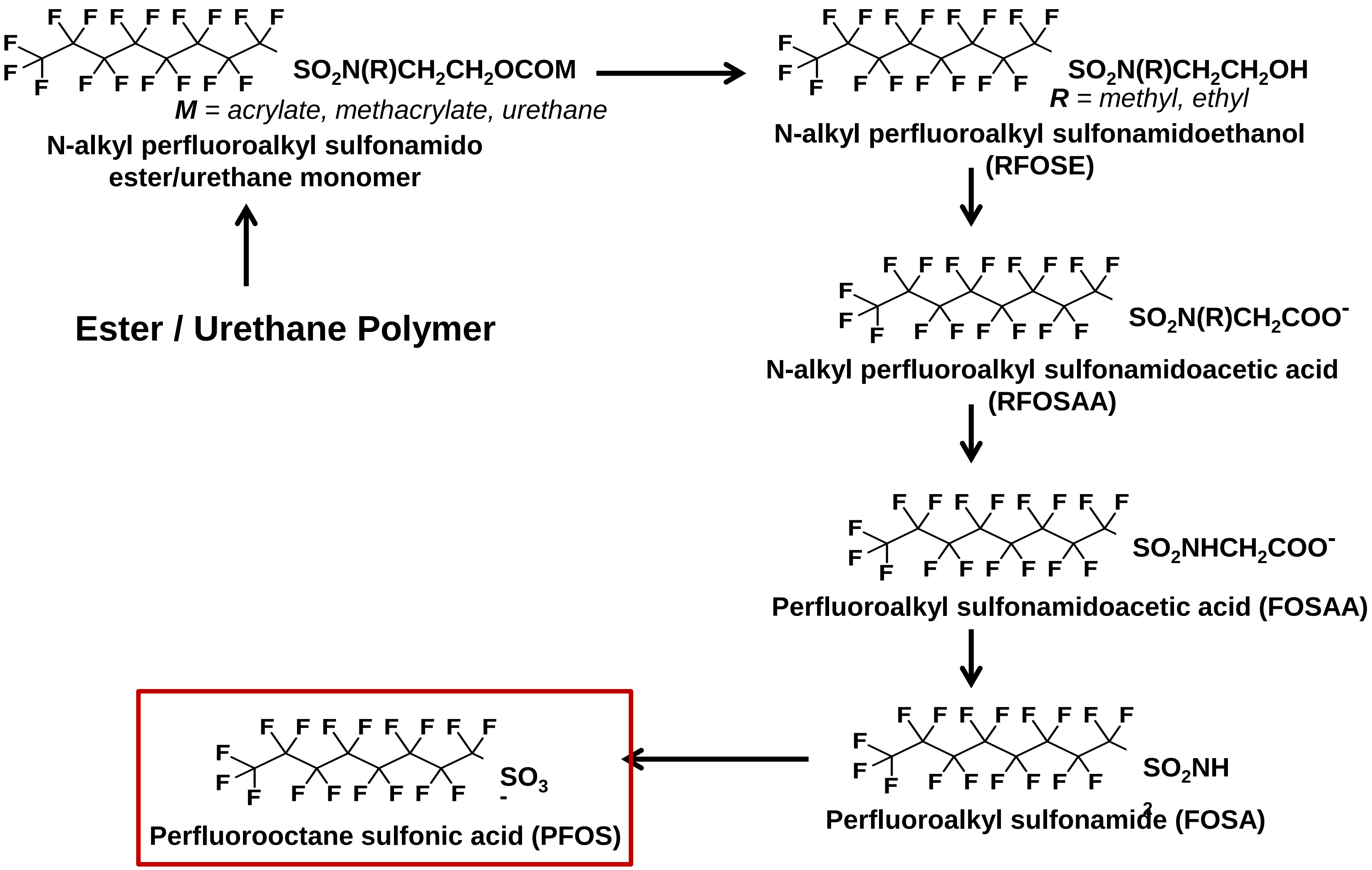
- PFAAs are more commonly measured
- Precursors mass may be substantial
- Air exposure and oxidative remediation for other chemicals may convert precursors to PFAAs over time or during treatment

Oxidative transformation to form PFOA



(Modified from Wang et al., 2009)

Oxidative Transformation to form PFOS



$SO_2N(R)CH_2CH_2OCOM$

M *= acrylate, methacrylate, urethane*

N-alkyl perfluoroalkyl sulfonamido ester/urethane monomer

Ester / Urethane Polymer

$SO_2N(R)CH_2CH_2OH$

R *= methyl, ethyl*

N-alkyl perfluoroalkyl sulfonamidoethanol (RFOSE)

$SO_2N(R)CH_2COO^-$

N-alkyl perfluoroalkyl sulfonamidoacetic acid (RFOSAA)

$SO_2NHCH_2COO^-$

Perfluoroalkyl sulfonamidoacetic acid (FOSAA)

SO_2NH_2

Perfluoroalkyl sulfonamide (FOSA)

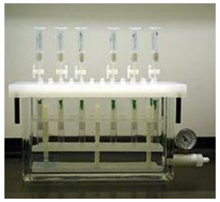
SO_3^-

Perfluorooctane sulfonic acid (PFOS)

Stable

Surrogates and Targets spiked

Effluent samples collected in Polypropylene bottles



Extraction using pre-conditioned WAX SPE cartridges

Elution of SPE cartridges using 1% NH_4OH in MTBE : MeOH (9:1)

Sample concentration using Turbo-Vap under N_2; reconstitution using mobile phase solvents and addition of internal standards

Analysis on UPLC/MS/MS
(equipped with PEEK™ tubing)

ANALYTICAL METHODS

EPA PFASs Analytical Methods

- **PFAAs Methods**

  Drinking Water: EPA Method 537 Version 1.1
  - Six (6) PFAS for the UCMR3 + 8 additional PFAS
  - <u>Finished (treated) drinking water samples… only</u>!

  Media other than drinking water:
  - **EPA OLEM, OW, and ORD currently conducting a multi-laboratory validation effort to establish an EPA method(s) for non-DW media**
  - **In the absence of EPA methods, contract labs have developed their own methods**
    - **Performance data is needed similar to that validating Method 537**
    - **Data from different labs (different methods) may not be comparable**
    - **QA/QC from 537 should be included regardless of the method along with prescreening supplies and QA controls is recommended**

- **PFAS precursors – EPA ORD, EPA Region 5, and others are developing methods in non-DW matrices (surface waters, groundwaters, wastewater, biosolids, soils, sediments, etc).**
- **PFAS unknowns from transformations, degradation, new formulations, etc– EPA ORD and others are developing methods to identify unknown PFAS in environmental samples**

EPA Method 537

- Drinking Water Only
- Solid phase extraction (SPE) followed by LC/MS/MS analysis
- 14 Target Analytes:
  - 9 PFCAs - PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTriA, and PFTreA
  - 3 PFSAs - PFBS, PFHxS, and PFOS
  - 2 precursors - N-EtFOSAA, and N-MeFOSAA

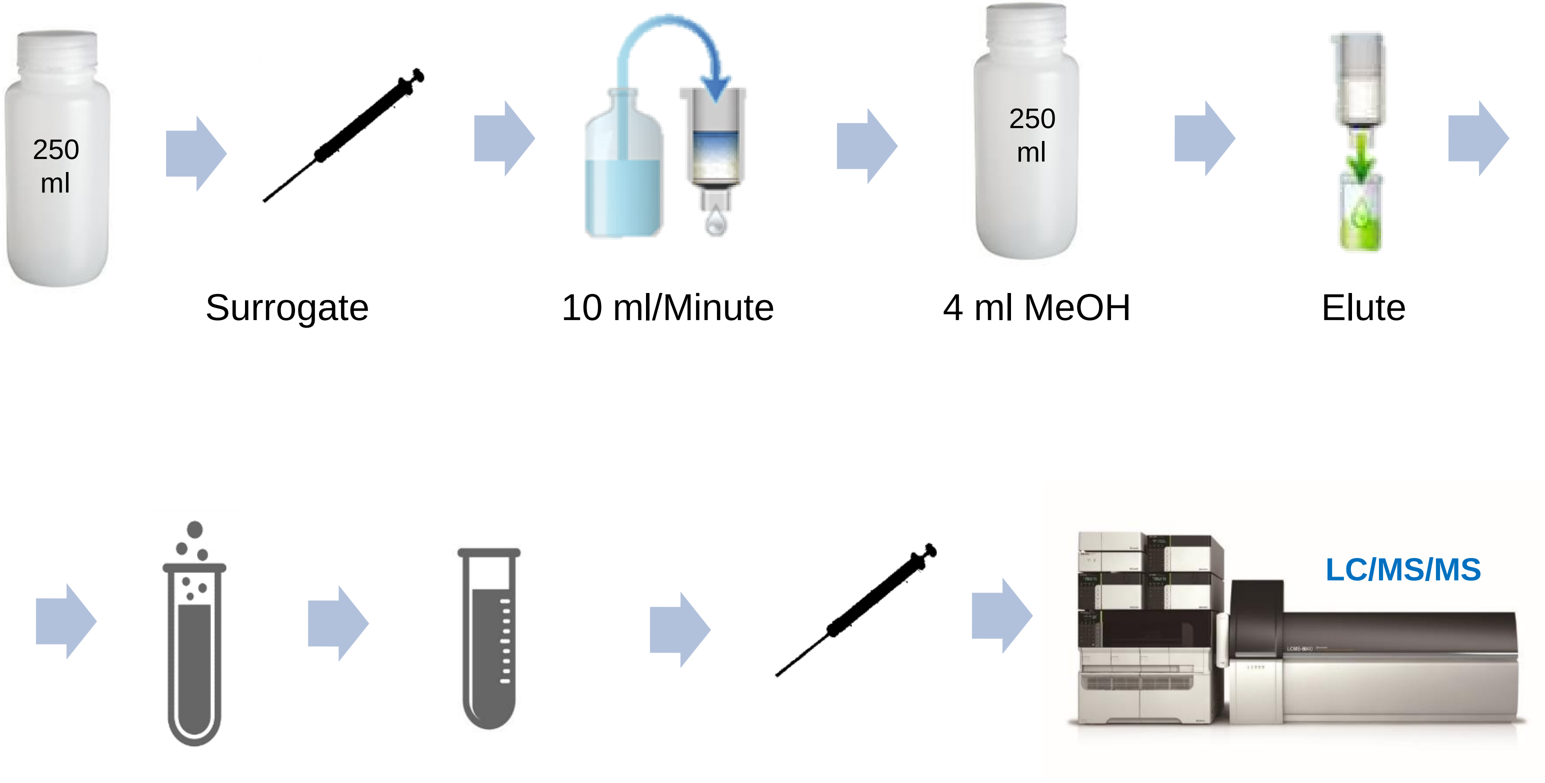
- 3 Surrogate Standards

  MPFHxA, MPFDA, MN-EtFOSAA

- 3 Internal standards

  ^{13}C-PFOA, ^{13}C-PFOS, d3-N-MeFOSAA

EPA Method 537 protocol



Surrogate

10 ml/Minute

4 ml MeOH

Elute

Evaporate

1 ml 96% MeOH

Internal Standard

Courtesy of William Lipps, Shimadzu

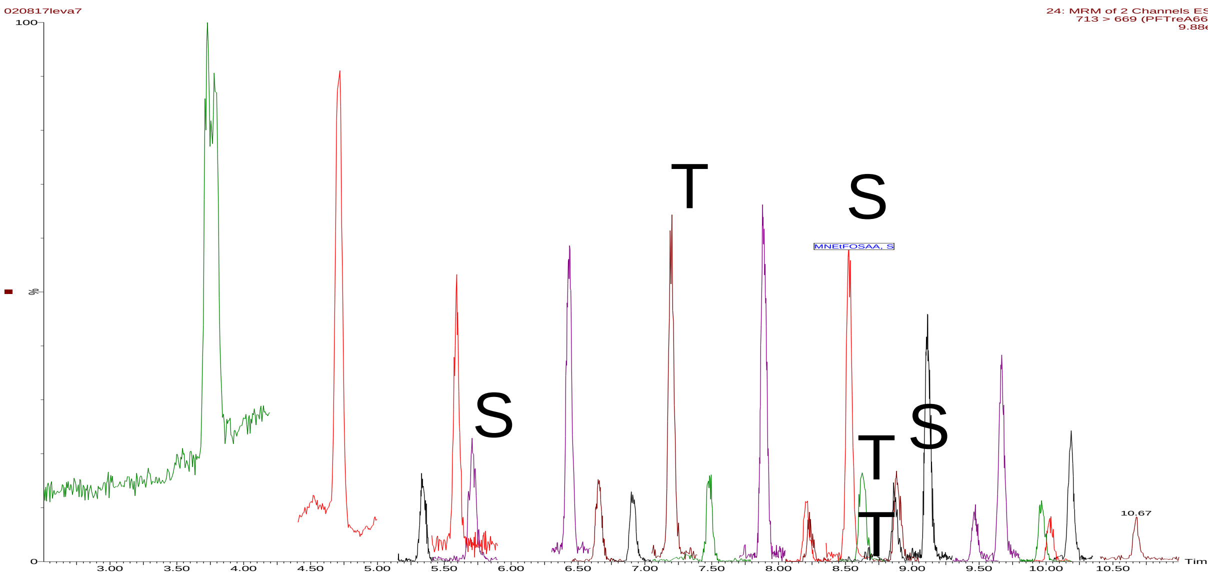
Method 537 Quantitation/Surrogates

Target compound (T) using internal standard quantitation

- Susceptible to matrix interference that affects the internal standards (IS)
- Generally less of a problem for drinking water
- Could be an issue for "dirtier" matrices

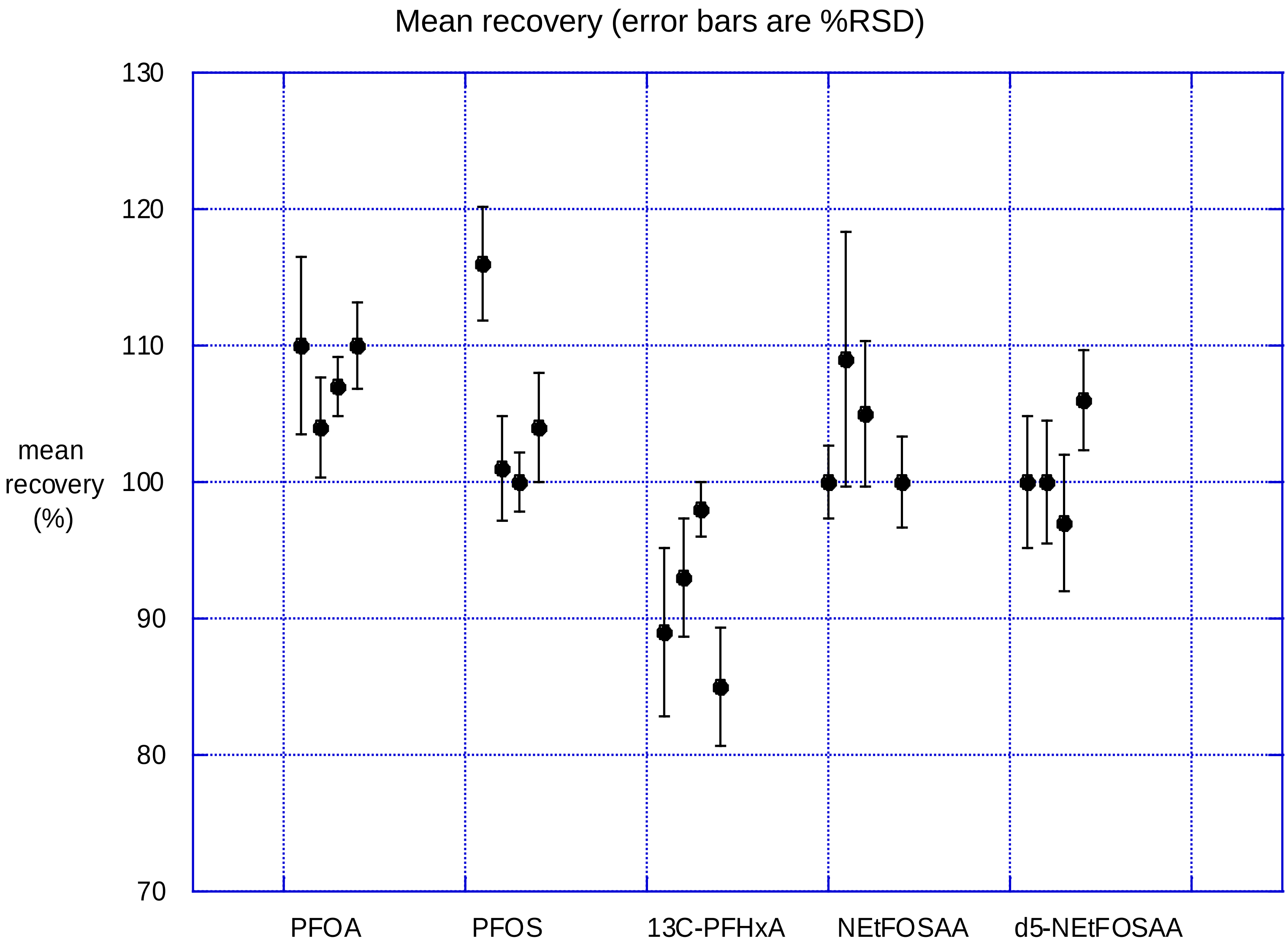
Surrogate standards (S)

- Used to monitor the analytical method
- Not used to "correct" concentration
- Compare target analyte recovery in matrix spikes to the surrogates.



Courtesy of Larry Zintek, EPA

Method 537 1.1 - Performance data



Four water matrices: Reagent water (low spike), Reagent water (high spike), Chlorinated groundwater, High TOC (5 mg/L) groundwater. 7 replicates of each matrix

Why not use EPA Method 537 for Matrices other than Drinking Water?

- Method 537 is a **drinking water method**!
  - Not demonstrated for other matrices
  - Co-contaminants can impact methods
- Quantitation is more difficult in dirtier matrices
  - Only monitor one SRM transition = less confidence in identification
  - Internal Standard signal suppression and enhancement can be an issue
- 537 requires Solid Phase Extraction
  - Challenging for all analytes of interest in one analysis
  - Pre-filter samples with particulates (Bias low results)
- Limited number of surrogates to mimic the extended analyte mix
- Concentration by evaporating to dryness
  - Lose volatile PFAS
  - Concentrates matrix interferences

EPA PFAS Methods Validation

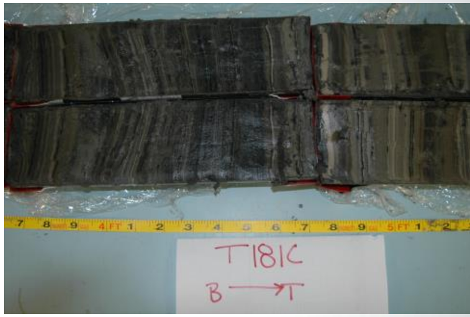
Method Validation for ground, surface, and wastewaters

- **24 PFASs** (including all target analytes in EPA Method 537)
- **Methods under consideration** (all using LC/MS/MS)
  - Direct injection
  - Solid phase extraction (with and without labeled internal standard correction)
- **Direct injection**
  - Similar to draft ASTM Method D7979 from EPA Reg 5
  - Targeting DL's in 10's ng/L
  - Phase 1: 5 internal (EPA) lab validation (Commenced in April 2017)
  - Phase 2: 5 external lab validation
- **Schedule:**
  - Assess methods through winter 2017
  - Publish draft method in spring 2018

EPA PFAS Methods Validation

Method Validation for solids (soil, sediment, sludge)

- Same 24 PFAS
- Commence in late 2017
- Working toward 2018 for draft methods
- Target DL's in the 0.1 - 2.5 ug/kg range



Sampling/Storage

- Holding time studies
- Sample vessel materials
- Standard operating procedures for field sampling

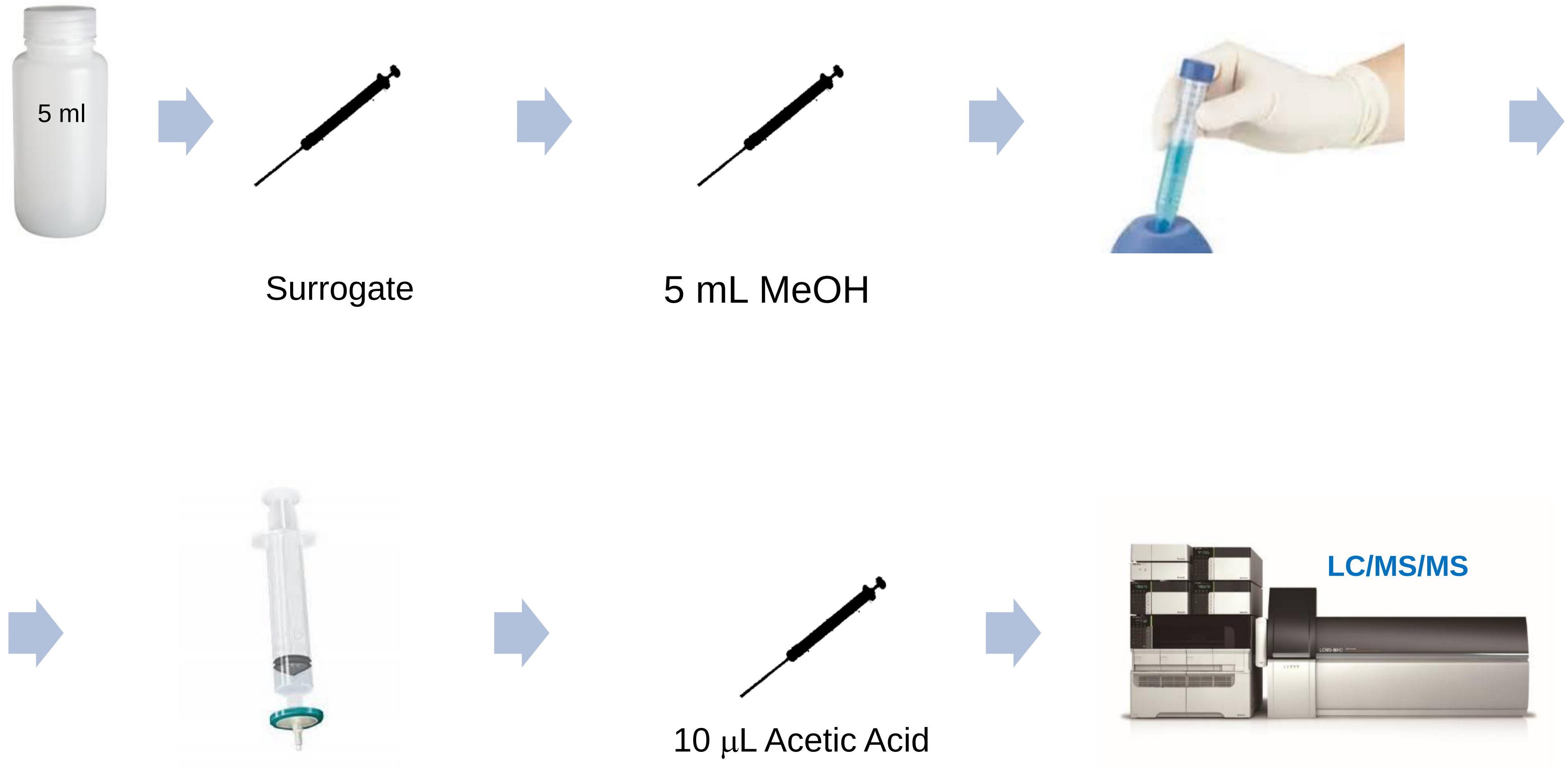
EPA Points of Contact:

OLEM	Schatzi Fitz-James	(fitzjames.schatzi@epa.gov)
Region 3	Cynthia Caporale	(caporale.cynthia@epa.gov)
ORD	Chris Impellitteri	(impellitteri.christopher@epa.gov)
Communications	Michelle Latham	(latham.michelle@epa.gov)

ASTM Method 7979-17

- Environmental Waters (not drinking water)
- Direct Injection analysis by LC/MS/MS is the first method evaluated by EPA workgroup
- 21 Target Analytes:
  - **11 PFCAs** - PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTriA, PFTreA
  - **3 PFSAs** - PFBS, PFHxS, PFOS
  - **6 precursors** - 6:2 FTCA, 6:2 FTUCA, 8:2 FTCA, 8:2 FTUCA, 10:2 FTCA, 7:3 FTCA
- Surrogate standards (isotopic-labeled target analytes):
  - **7 PFCAs** - MPFBA, MPFHxA, MPFOA, MPFNA, MPFDA, MPFUnA, MPFDoA
  - **2 PFSAs** - MPFHxS, MPFOS
  - Used to monitor analytical method, not used to “correct” the data
- Quantitation with 2 SRMs and ion ratios

ASTM 7979-17 Protocol



5 ml

Surrogate

5 mL MeOH

10 µL Acetic Acid

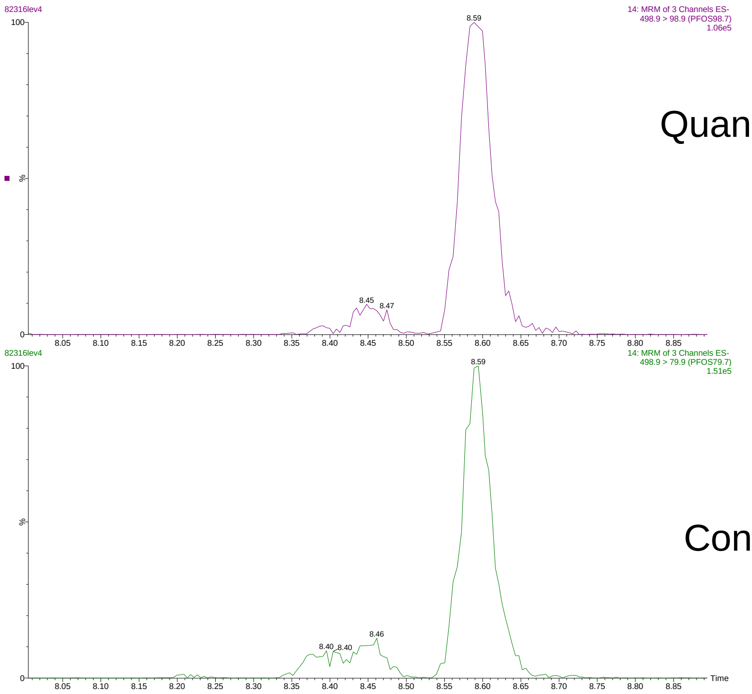
LC/MS/MS

Courtesy of William Lipps, Shimadzu

ASTM PFAS QUANTITATION

- Because of dirtier matrices – use 2 SRM transitions or MRM
  - Measure confirmatory transition and ion ratios
  - Example for PFOS, same samples. Ion Ratio Difference is 4.3% and within Tolerance

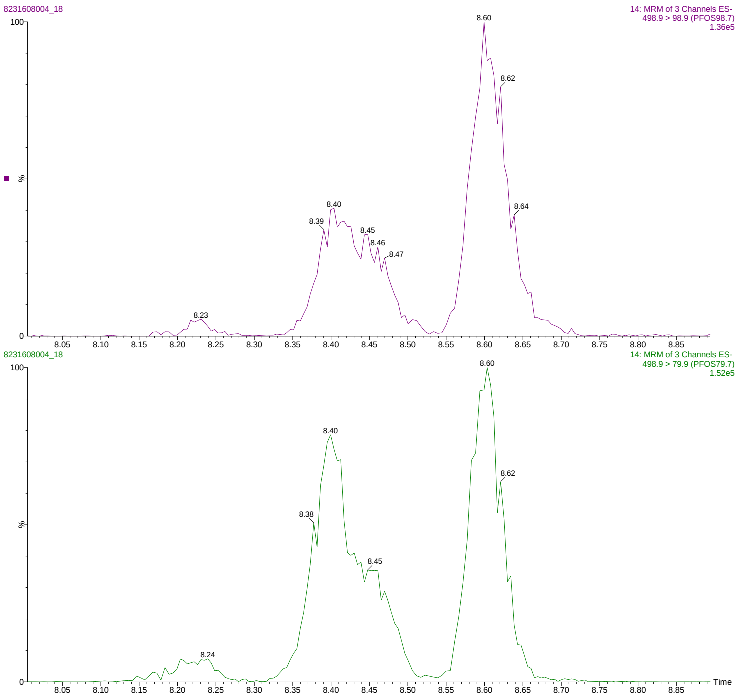
Calibration Ion Ratio-1.41



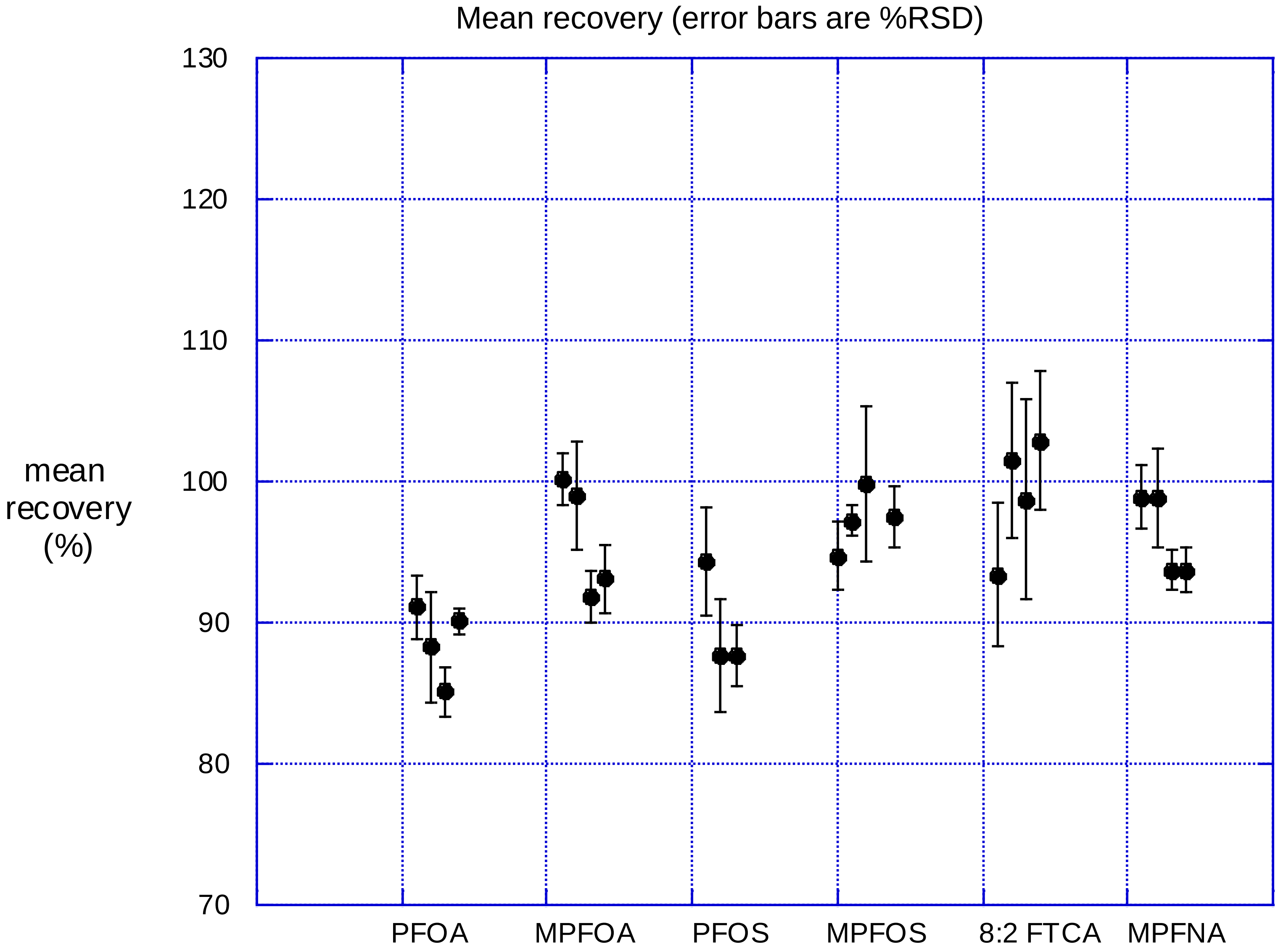
Quantitation Ion

Confirmation Ion

Sample Ion Ratio-1.35



ASTM 7979 Performance data



Four fortified matrices: Reagent water, River water, WWTP effluent, and WWTP influent*. 6 replicates of each matrix.

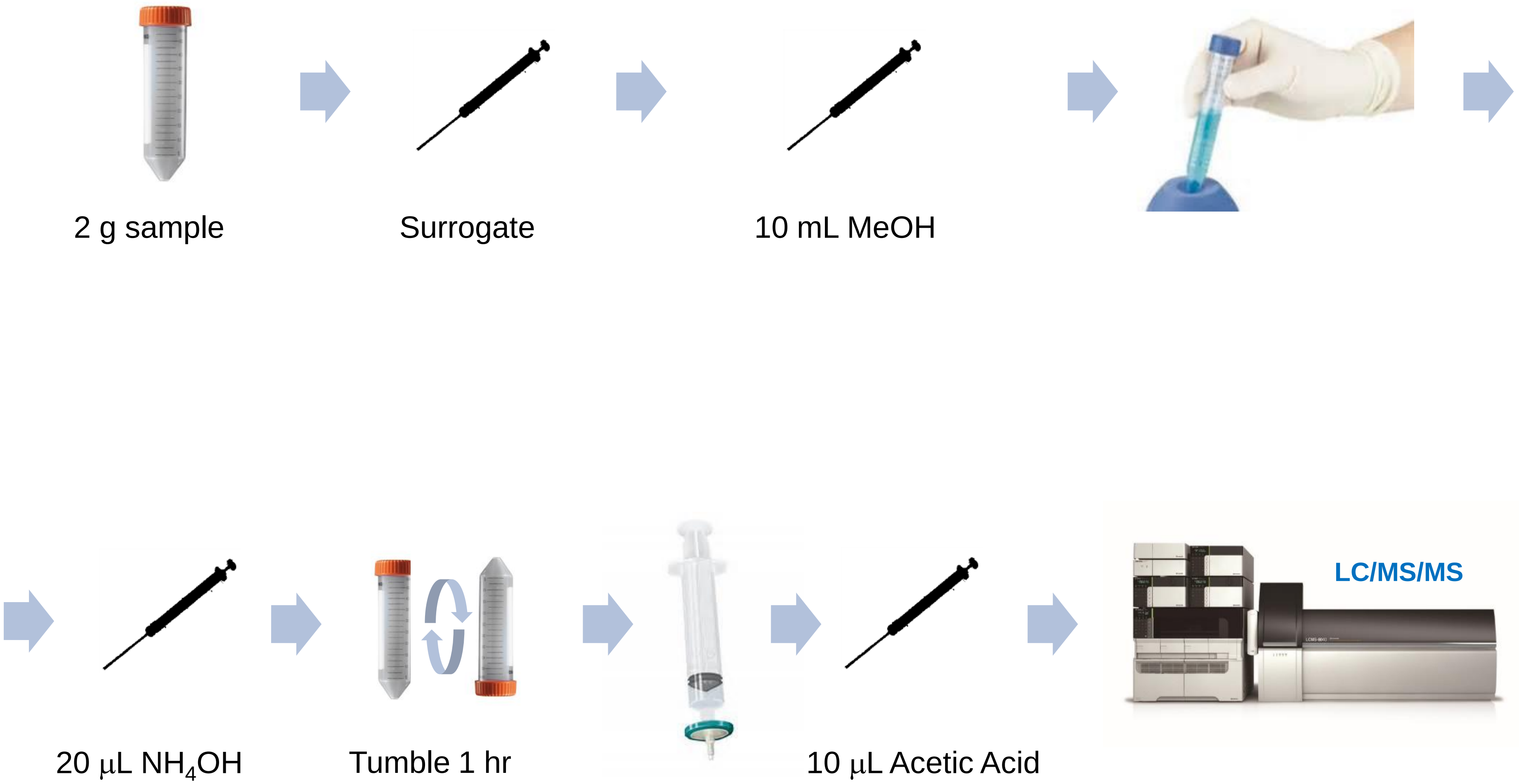
*PFOS not shown because the matrix had background concentration comparable to spike concentration

ASTM D7968

- Environmental solids: soil, sediment, sludge, etc

- Solvent extraction, analysis by LC/MS/MS
- 21 Target Analytes:
  - **11 PFCAs** - PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTriA, PFTreA
  - **3 PFSAs** - PFBS, PFHxS, PFOS
  - **6 precursors** - 6:2 FTCA, 6:2 FTUCA, 8:2 FTCA, 8:2 FTUCA, 10:2 FTCA, 7:3 FTCA
- Surrogate standards (isotopic-labeled target analytes):
  - **7 PFCAs** - MPFBA, MPFHxA, MPFOA, MPFNA, MPFDA, MPFUnA, MPFDoA
  - **2 PFSAs** - MPFHxS, MPFOS
  - Used to monitor analytical method, not used to “correct” the data
- Quantitation with 2 SRMs and ion ratios

ASTM D7968 protocol



2 g sample

Surrogate

10 mL MeOH

20 μL NH_4OH

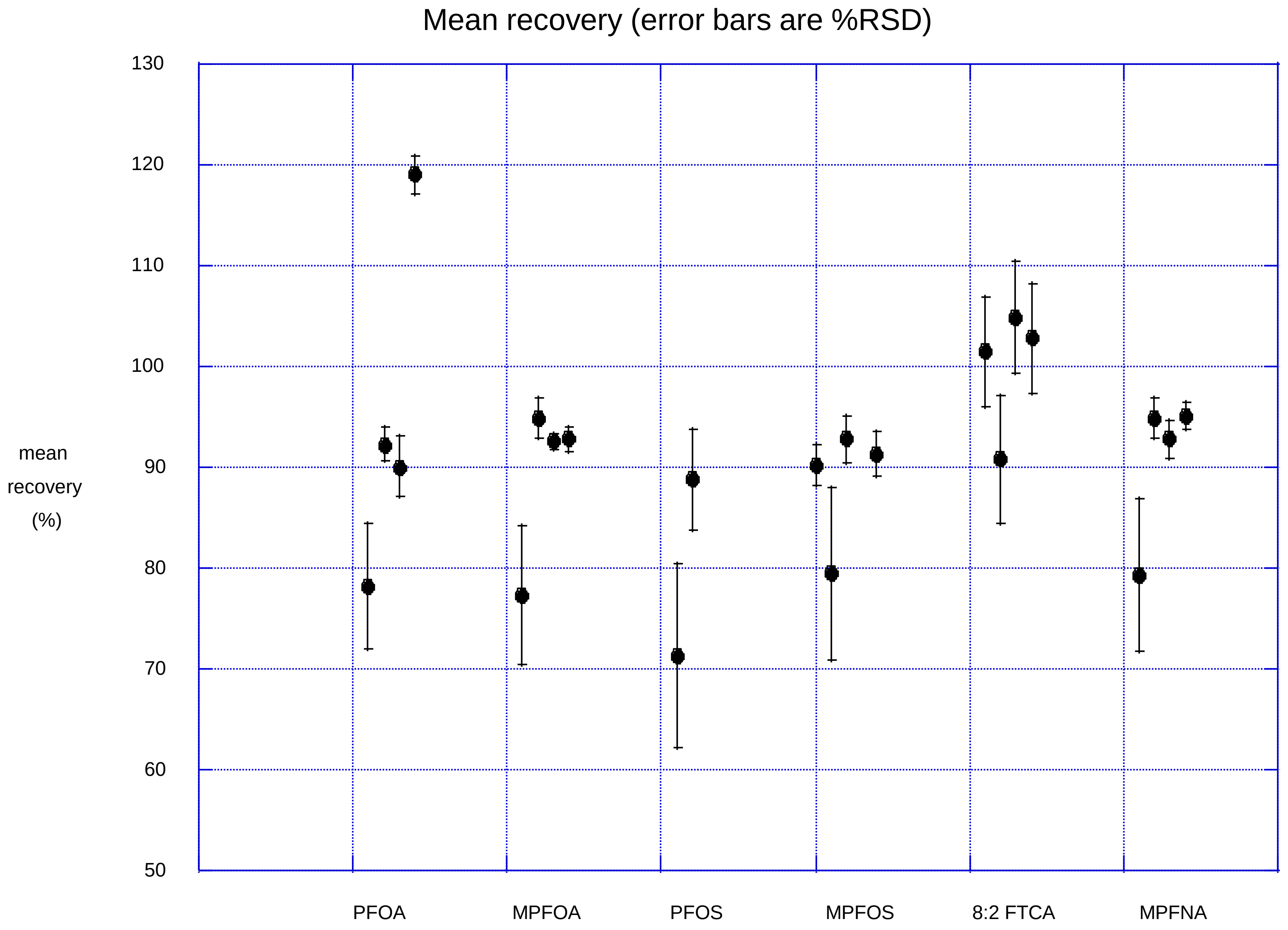
Tumble 1 hr

10 μL Acetic Acid

LC/MS/MS

Courtesy of William Lipps, Shimadzu

ASTM D7968 Performance Data



Four ASTM soil matrices: CL-1, CH-1, SP-1, and ML-1. 6 replicates of each matrix.

*PFOS not shown for SP-1 and ML-1 because the matrices had background concentration comparable to spike concentration.

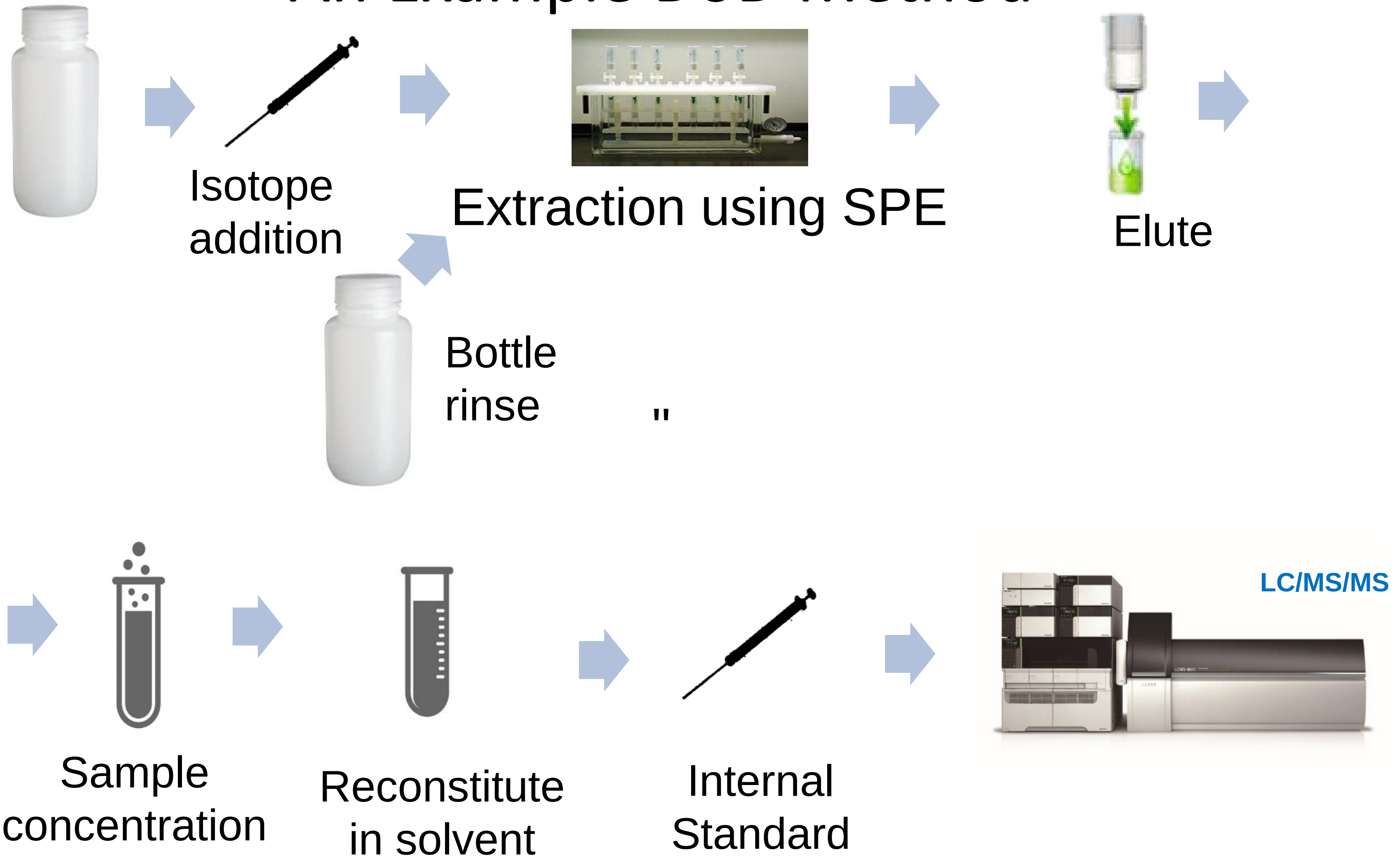
Research Methods

- ORD labs and other research groups have developed methods to analyze various matrices for various PFAS
- These methods may work for your study/site
- To decide:
  - Read the SOP
  - Review performance data and QA/QC

DoD Methods

- Often called “Modified Method 537”
  - This title is wrong
  - Modifications are not permitted by Method 537, section 1.6
  - No data to show modifications work
- SOPs:
  - Vary from contract lab to contract lab
  - Often claimed as confidential business information
- Contract Labs accredited by DoD
  - Not clear what information required for accreditation
  - Accreditation can be withdrawn – check if current

An Example DoD Method



Isotope addition

Extraction using SPE

Elute

Bottle rinse

"

Sample concentration

Reconstitute in solvent

Internal Standard

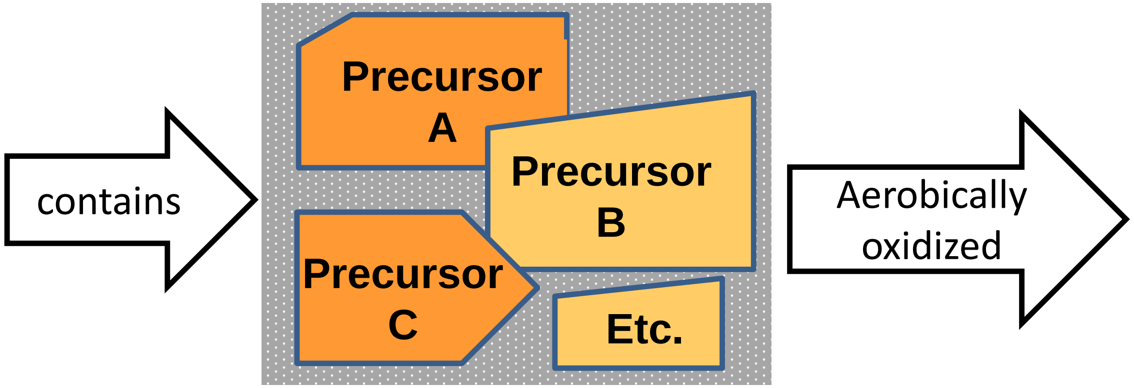
LC/MS/MS

DoD Methods

- Analyte concentrations are “corrected” for isotope recovery
  - If recovery < 100%, concentrations increase
  - If > 100%, concentrations decrease
  - Some labs “correct” with recoveries as low as 1%
- May or may not use confirmation ion and ion ratio – read the SOP
- Performance Data ?

Precursors

PFAS Product



contains

Precursor A

Precursor B

Precursor C

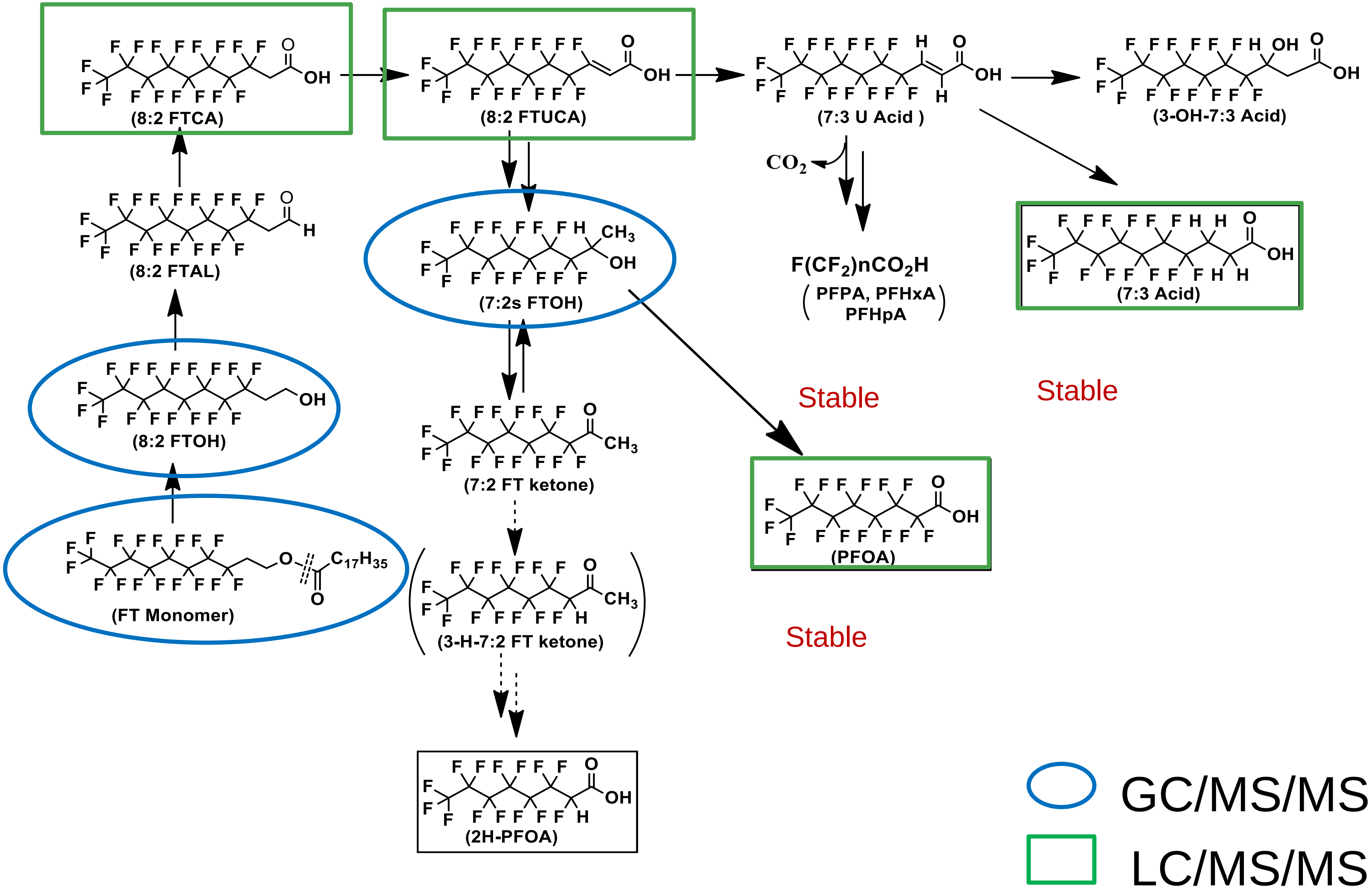
Etc.

Aerobically oxidized

PFAAs

- Precursors mass may be substantial
- No EPA or standard methods to measure precursors
- Individual labs have developed methods to analyze for precursor compounds
- Total Oxidizable Precursors (TOP) assay estimates precursor mass by measuring PFAAs before and after oxidation
- Particle Induced Gamma ray Emission (PIGE) measures total fluorine which can be used to estimate precursor and unknown PFAS in solid samples

Transformation to form PFOA



(Modified from Wang et al., 2009)

Analysis of Precursors

- NRMRL SOPs for Environmental Waters (not DW) and solids

- Methods
  - Water - SPE, analysis by GC/MS/MS
  - Solids – solvent extraction, analysis by GCMS/MS

- Analytes:
  - Fluorotelomer Alcohols(FTOHs)- 4:2, 6: 2, 8:2, 7:2s, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, and 11:1
  - Fluorotelomer monomers- 6:2 Fluorotelomer Acrylate (6:2 FTAc), 6:2 Fluorotelomer Methacrylate (6:2 FTMAc), 8:2 FTAc, 8:2 FTMac, 10:2 FTAc, and 10:2 FTMac
  - Perfluoro-1-octanesulfonamido-ethanol (FOSE)- 2-N-ethylFOSE (N-EtFOSE), and 2-N-MethylFOSE (N-MeFOSE)
- Surrogate standards- 8:2 MFTOH and d7-MeFOSE

- Quantitation similar to ASTM method – monitoring 2 SRMS and evaluating ion ratios ??

Total Oxidizable Precursors (TOP) assay

- Developed by Houtz and Sedlak
- Available from some contract labs
- No EPA method

→ Measure PFAA concentration (C1)

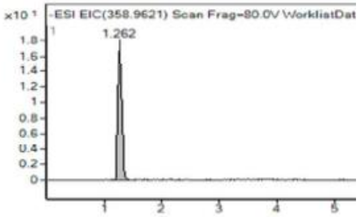
→ Persulfate
Hydroxide
Heat
6 hrs

→ Measure PFAA concentration (C2)

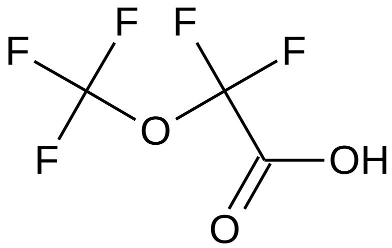
- Bulk Precursor amount can be estimated by C2 – C1
- Does not identify individual precursor compounds

Non-Targetted Methods

- Explore Unknown compounds using High resolution mass spectrometry
  - a peak in a chromatogram and to ultimately predict the identity of this unknown
- Initially, the mass spectrometer assigns a mass for each peak observed, for example 179.9846 Daltons (Da)



- Software then calculates the exact number and type of atoms that measured mass, example $C_3HF_5O_3$ (need this number and type of atoms to weigh this much)
- Software and fragmentation experiments allow determination of most likely structure:



Molecular Formula: $C_3HF_5O_3$
Monoisotopic Mass: 179.984585 Da
[M-H]-: 178.977308 Da

- With mass, formula, and structure determined, identity can be assigned by searching against databases of known compounds, example CAS number 674-13-5
- Search for standards from commercial sources to confirm identification if possible

SAMPLING GUIDANCE

Sampling and Laboratory Considerations

- Solvent contamination is source dependent, regular and/or sporadic
- Lab supplies
  - Polypropylene vials and centrifuge tubes (from mold release or cross contamination from other production processes)
  - LC vial caps and septa (e.g. PTFE/silicone)
  - LC and SPE pump equipment, pump head seals (graphitized Teflon)
  - PTFE tubing
  - Low binding pipette tips
- Use of PFAS-containing equipment (gloves, coats, collection gear, etc) also an issue
- Many common laboratory/field materials and sampling equipment contain PFAS
- Other chemicals which may be present
  - e.g., AFFF sites may have hydrocarbons, chlorinated solvents, glycols, and other AFFF components as well as residuals from previous remediation efforts
- Research should evaluate professional opinions:
  - Volatile PFAS may be lost depending on the sampling methods.
  - PFAS stratification?
  - PFAS may sorb to sampling equipment possibly distorting measured concentration

Sampling and Analytical issues

Observations from ORD Tech Support for current preliminary site investigations:

- **Many conducted by federal partners (limited input by EPA)**
- **Low sample density – heterogeneity unknown**
- **Sampling approach and equipment not evaluated for PFAS**
- **Co-contaminants not sampled at the same time**
- **Site characterization and source identification affected by:**
  - **Many PFAS-products used with varying formulations, chemistries, etc**
  - **Lengthy time in the environment could result in transformations**
  - **Co-contaminants present**
  - **Remediation technologies used to clean up other chemicals may impact PFASs concentrations and distributions**

Where to Sample?

- PFAS manufacturing sites
  - Primary – Sites preparing or generating PFAS products
  - Secondary – Sites treating textiles, plastics, paper, etc. with PFAS products
- AFFF related sites
  - Sites with fire retardant systems such as tanks farms
  - Fire training areas
  - Crash sites – aircraft, motor vehicles
  - Airports, rail yards
- Metal coating and plating facilities
- Landfills, Water treatment systems

PFAS Sampling

- Information is evolving – check for updates

- Sample integrity
  - The collected sample should represent the matrix sampled
  - Don’t add PFAS to your sample
  - Don’t remove PFAS from your sample

- Non-ideal situations
  - Historical wells may contain teflon or PTFE
  - Safety trade-offs with issues of cross contamination

Accurate PFAS Sampling
Cross Contamination

- Don’t add analytes to your sample

- PFAS found in many common field supplies and equipment
  - Teflon – equipment, seals, sample caps and bottles
  - Water proof paper and PPE
  - Personal care products
  - Surface treatment on food wrappers

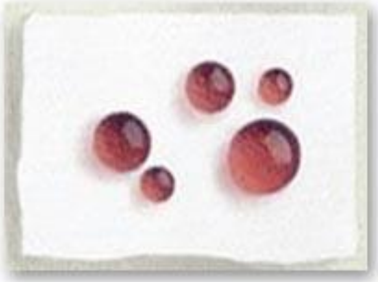
- Avoid using these items when possible

Sampling Procedure Precautions

Insect repellents and sunscreens

- PFAS detected in some sunscreens and repellants
- DEET not manufactured with PFAS but specific product may contain PFAS
- Some products have been labeled PFAS free:
  - but generally not effective
  - formulations may change without warning
- Use of engineering controls
  - Fans to reduce insect exposure
  - Removal of insect habitat
  - Canopies and protective clothing to reduce sun exposure

Sampling Procedure Precautions



PPE

- Preferred – well washed clothing
- Uncoated Tyvek ok, coated Tyvek contains PFAS
- Stain repellent clothing contains PFAS
- Water Repellent clothing
  - PFAS based treatments have many trade names such as Gore-tex, weatheredge, DWR, Omni-tech
  - Claims of “PFOS free” may contain C6 PFAS
  - Read labels and product descriptions carefully
  - Rubber, polyurethane, and PVC - ok

Sampling Procedure Precautions

Sampling Equipment and supplies

- No teflon or PTFE
- Fluoropolymers – generally no
- Aluminum foil may have PFAS surface treatment
- No Decon 90, sharpies, post-it notes, waterproof field papers or books
- Blue Ice

Ok

- HDPE, polypropylene, and silicone materials
- Alconox or Liquinox
- Ball point pens
- Water ice – double bag in polyethylene bags

Sampling Procedure Precautions

Other

- Food packaging may contain PFAS treatments – don’t eat on site, and wash hands before returning to site
- Frequent nitrile glove changes
- Collect field blanks
- Field spiked blanks used by some
- Avoid re-using equipment - previous use may have involved PFAS materials

Best practice

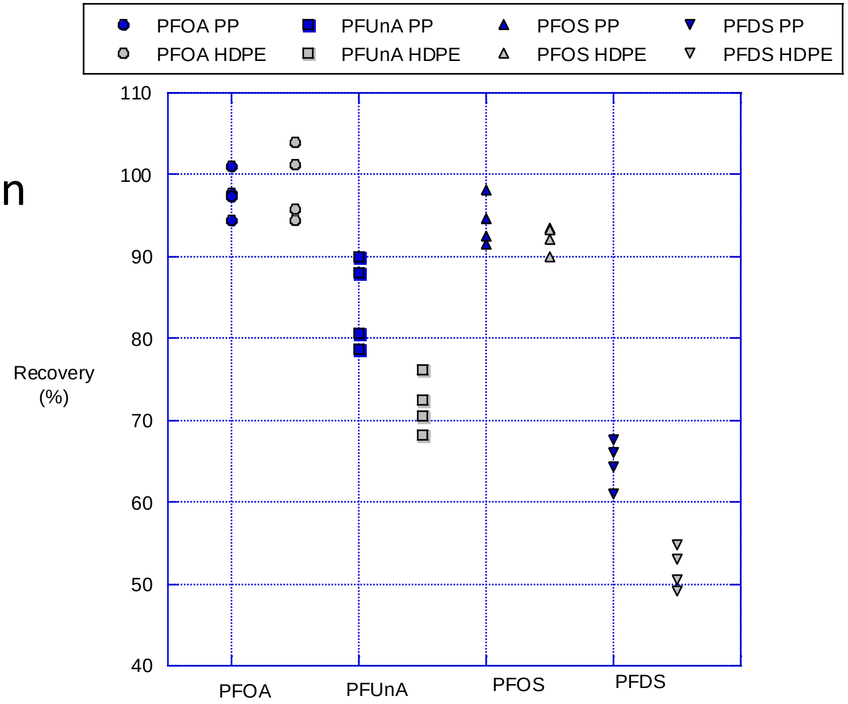
- Pretest materials and products for PFAS contamination
- Keep separate from “normal” sampling supplies

Accurate PFAS Sampling

- Don’t remove analytes from your sample = bias results low
- PFAS don’t like water so they sorb to surfaces
  - Possible to sorb PFAS to tubing during ground water extraction
  - Lose analytes during sample manipulation or sample transfers
- PFAS may be volatile
  - Possible to volatilize PFAS during collection or manipulation
- Information evolving

Example – PFAS loss in plastic vessels

- Subsamples removed from spiked bottles. Vessel types evaluated included:
  - Polypropylene (PP)
  - High Density Polyethylene (HDPE)
- Substantial losses observed depending on the analyte and material
- If entire sample is removed and vessel is solvent rinsed, recovery acceptable
- Take home messages
  - Don’t subsample water samples
  - PFAS may sorb to plastics and glass
  - Information evolving



Data from the time zero sample event is shown.

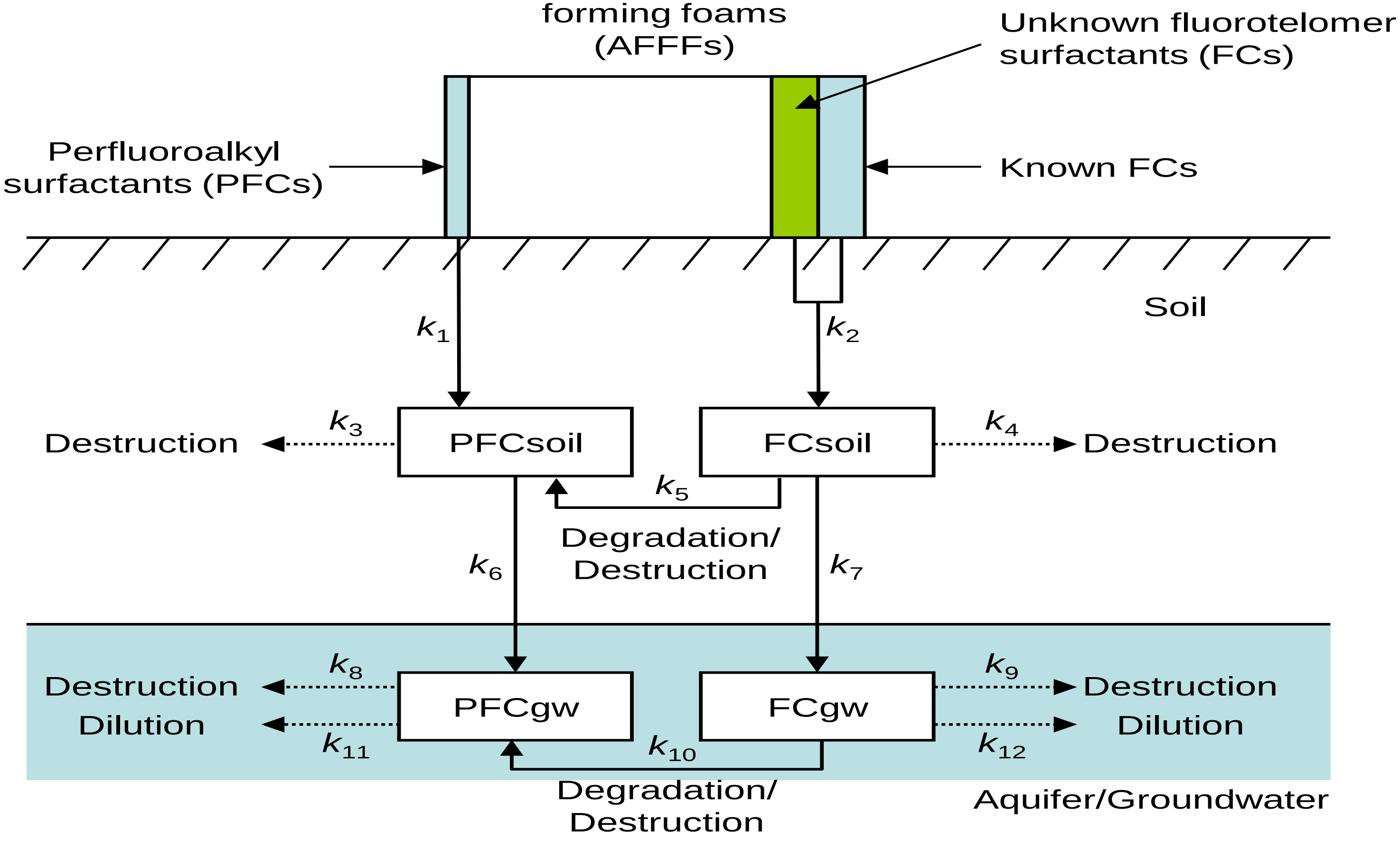
Data from Larry Zintek and Danielle Kleinmaier, Region 5, Chicago Regional Laboratory, US EPA

PFAS Sampling Guidance

- Cross-EPA workgroup
  - Generic SOP for groundwater sampling external review soon
  - SOPs for surface water, soil, etc to follow
- Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)Contaminated Sites Guidelines – Gov't of State of Western Australia
- US States
  - Department of Environmental Protection, Massachusetts
  - New Hampshire Department of Environmental Sciences

ENVIRONMENTAL FATE

www.offshore-technology.com/



Aqueous film forming foams (AFFFs)

Unknown fluorotelomer surfactants (FCs)

Perfluoroalkyl surfactants (PFCs)

Known FCs

Soil

k_1

k_2

Destruction k_3 PFCsoil

FCsoil k_4 Destruction

k_5

Degradation/ Destruction

k_6

k_7

Destruction k_8

Dilution k_{11}

PFCgw

FCgw

k_9 Destruction

k_{12} Dilution

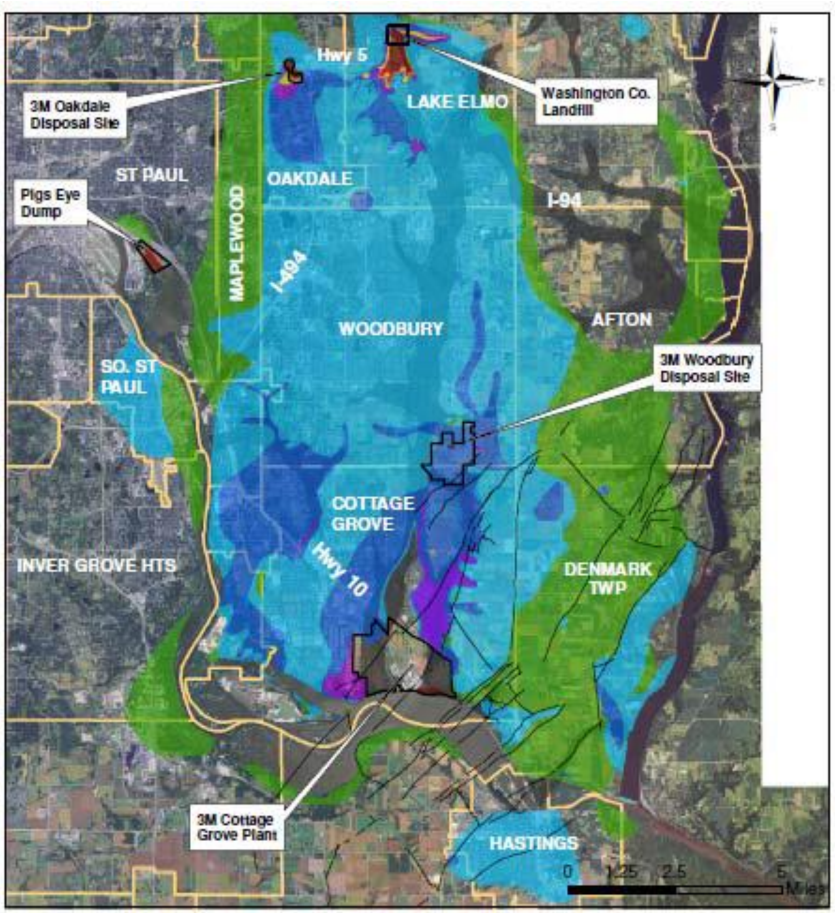
k_{10}

Degradation/ Destruction

Aquifer/Groundwater

Figure 2. Two-dimensional conceptual site model (CSM) showing fate/transport and remediation of fluoroalkylchemicals

Environmental Fate

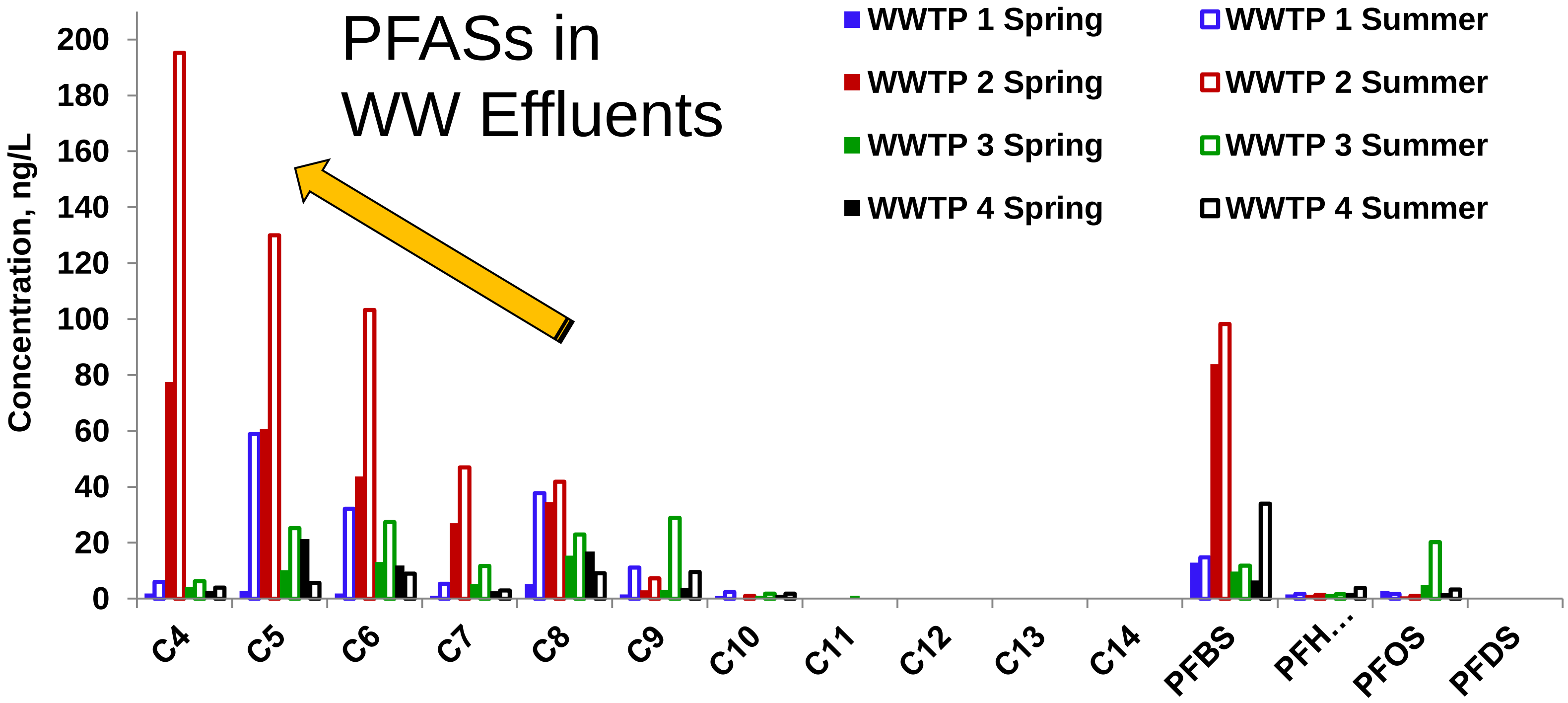


- PFASs groundwater plumes can be **<u>huge</u>**!
- For example, some Minnesota PFAS plumes in groundwater
  - 10+ miles long
  - cover over 100 mi^2

(MDH, 2012)

Changing targets with changing formulations

- Industry continues to modify their formulations to meet consumer needs and regulatory drivers.
- Changes include:
  - Shorter carbon chain lengths (<C6) – no longer just C8 chemistry
  - Use of polyfluorinated chemistries – not completely saturated with fluorines
  - Use of alternative chemistries for linkages – more ether and oxetane linkages to polymer

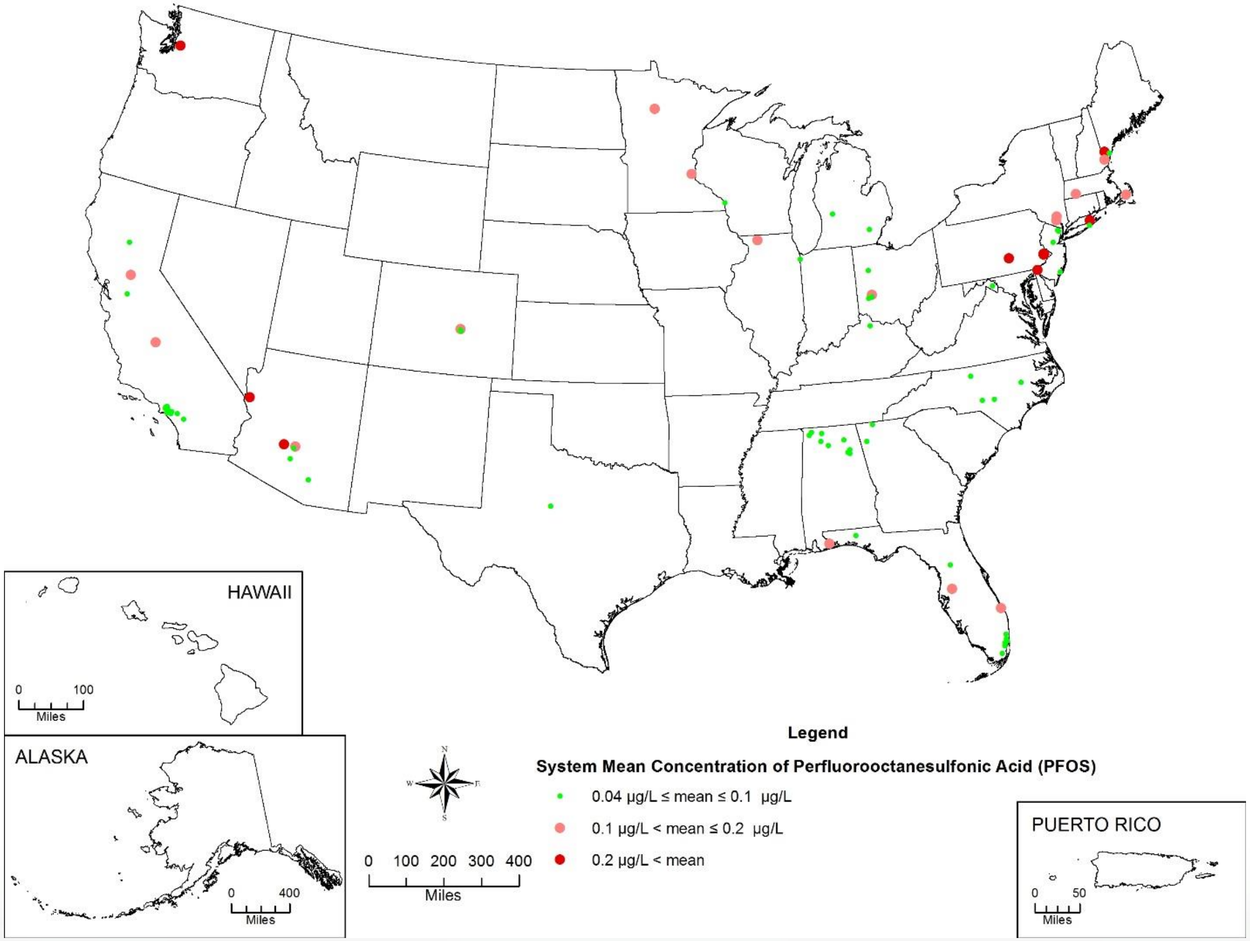


PFASs in WW Effluents

TREATMENT

UCMR3 PFOA Results

Mean Concentrations



Drinking Water Treatability Database

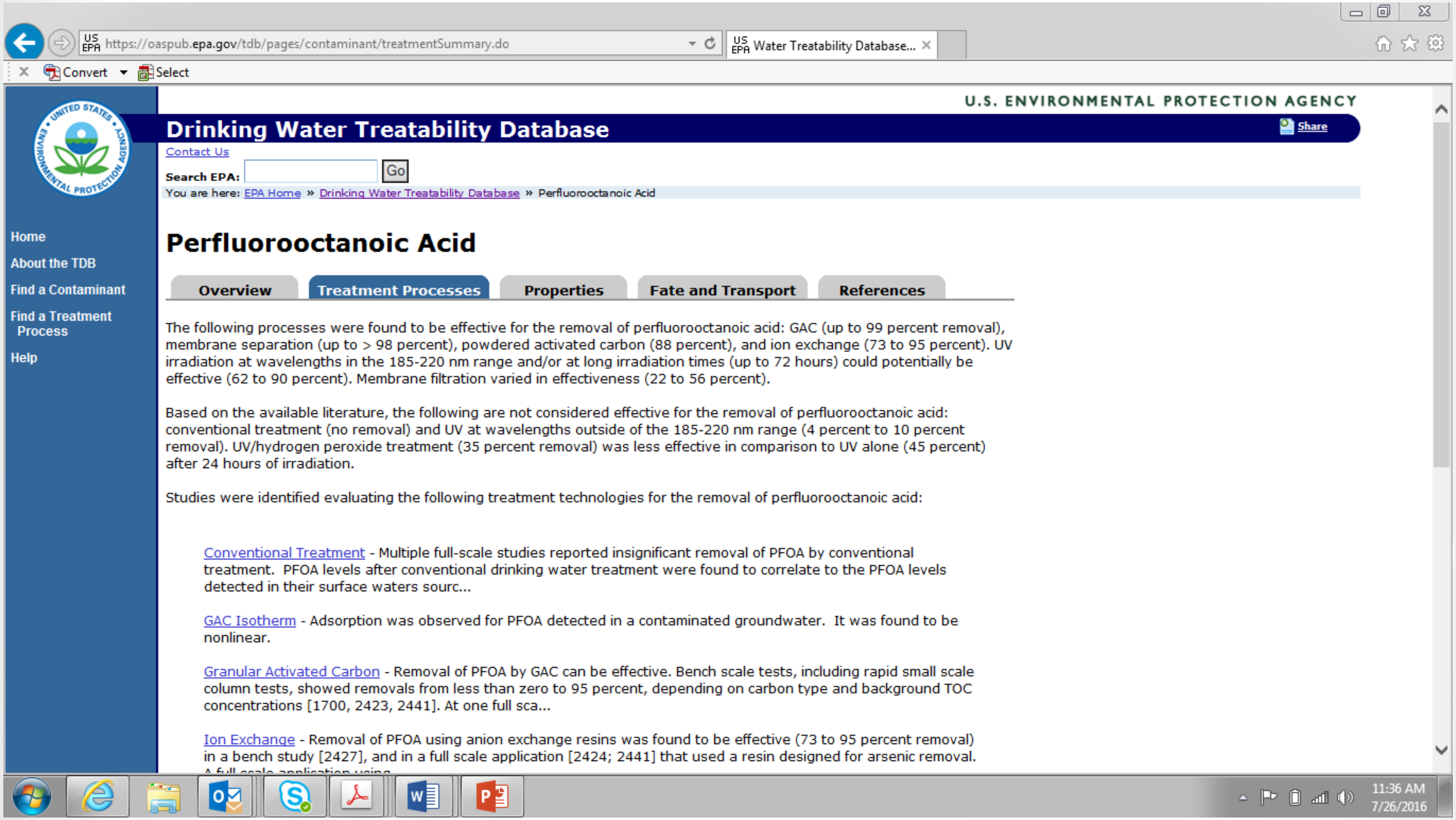
Publically Available Resource

- Interactive database that contains over 65 regulated and unregulated contaminants and covers 34 treatment processes commonly employed or known to be effective
- Referenced information gathered from thousands of literature sources assembled on one site
- Carbon tetrachloride, nitrate, 1,2,3-TCP, cis 1,2-DCE and Natural Organic Matter (NOM) added recently
- Updates to **PFOA, PFOS,** strontium and cyanide also added recently

http://iaspub.epa.gov/tdb/pages/general/home.do

Search: EPA TDB

Drinking Water Treatability Database



Drinking Water Treatability Database

Contact Us

Search EPA: Go

You are here: EPA Home » Drinking Water Treatability Database » Perfluorooctanoic Acid

Perfluorooctanoic Acid

Overview | Treatment Processes | Properties | Fate and Transport | References

The following processes were found to be effective for the removal of perfluorooctanoic acid: GAC (up to 99 percent removal), membrane separation (up to > 98 percent), powdered activated carbon (88 percent), and ion exchange (73 to 95 percent). UV irradiation at wavelengths in the 185-220 nm range and/or at long irradiation times (up to 72 hours) could potentially be effective (62 to 90 percent). Membrane filtration varied in effectiveness (22 to 56 percent).

Based on the available literature, the following are not considered effective for the removal of perfluorooctanoic acid: conventional treatment (no removal) and UV at wavelengths outside of the 185-220 nm range (4 percent to 10 percent removal). UV/hydrogen peroxide treatment (35 percent removal) was less effective in comparison to UV alone (45 percent) after 24 hours of irradiation.

Studies were identified evaluating the following treatment technologies for the removal of perfluorooctanoic acid:

Conventional Treatment - Multiple full-scale studies reported insignificant removal of PFOA by conventional treatment. PFOA levels after conventional drinking water treatment were found to correlate to the PFOA levels detected in their surface waters sourc...

GAC Isotherm - Adsorption was observed for PFOA detected in a contaminated groundwater. It was found to be nonlinear.

Granular Activated Carbon - Removal of PFOA by GAC can be effective. Bench scale tests, including rapid small scale column tests, showed removals from less than zero to 95 percent, depending on carbon type and background TOC concentrations [1700, 2423, 2441]. At one full sca...

Ion Exchange - Removal of PFOA using anion exchange resins was found to be effective (73 to 95 percent removal) in a bench study [2427], and in a full scale application [2424; 2441] that used a resin designed for arsenic removal. A full scale application using

PFOS Treatment: Ineffective

Treatment	Percent Removal
Conventional Treatment	0
Low Pressure Membranes	0 to 23
Biological Treatment (inc. slow sand)	0 to 15
Disinfection - Chloramines	0
Oxidation	
Permanganate	1 to 53 * #
Hydrogen Peroxide	0 to 2 *
Ozone	0 to 7
Advanced oxidation	
UV – TiO_2	15
UV – Ozone	0 *
Ozone – Peroxide	9

** All bench-scale data*

 # Up to 18 days of exposure

PFOS Treatment: Effective

Treatment	Percent Removal
Anion Exchange Resin *	90 to 99 @
High Pressure Membranes	93 to 99
Powdered Activated Carbon (PAC)	10 to 97 ^
Granular Activated Carbon (GAC) *	
Extended Run Time #	0 to 26
Frequent GAC Replacement	> 89 to > 98

* Non-steady state process

@ No bed volume fed data for cost analysis

^ Dose, water, and carbon dependent

Extended run time with no regeneration

PAC Dose to Achieve	
50% Removal	16 mg/l
90% Removal	>50 mg/L

Dudley et al., 2015

PFOA Treatment: Ineffective

Treatment	**Percent Removal**
Conventional Treatment	0
Low Pressure Membranes	2 to 56 ^
UV Disinfection	0 to 90 * #
Advanced Oxidation	
UV – Peroxide	11 to 35 *
UV – Iron	< 5 *
UV – Persulfate	5 to 87 *
UV – Periodate	9 to 87 *

^ One data point for high removal results (little information about plant)
** All bench-scale data*
 # Up to 72 hours of exposure

PFOA Treatment: Effective

Treatment	Percent Removal
Anion Exchange Resin *	73 to 95 @
High Pressure Membranes	> 98
Powdered Activated Carbon (PAC)	20 to 88 ^
Granular Activated Carbon (GAC) *	
Extended Run Time #	0
Frequent GAC Replacement	90 to > 99

PAC Dose to Achieve

50% Removal	28 mg/l
90% Removal	>50 mg/L

Dudley et al., 2015

* Non-steady state process

@ No bed volume fed data for cost analysis

^ Dose, water, and carbon dependent

Extended run time with no regeneration

EPA Drinking Water Treatment Cost Models

Uses

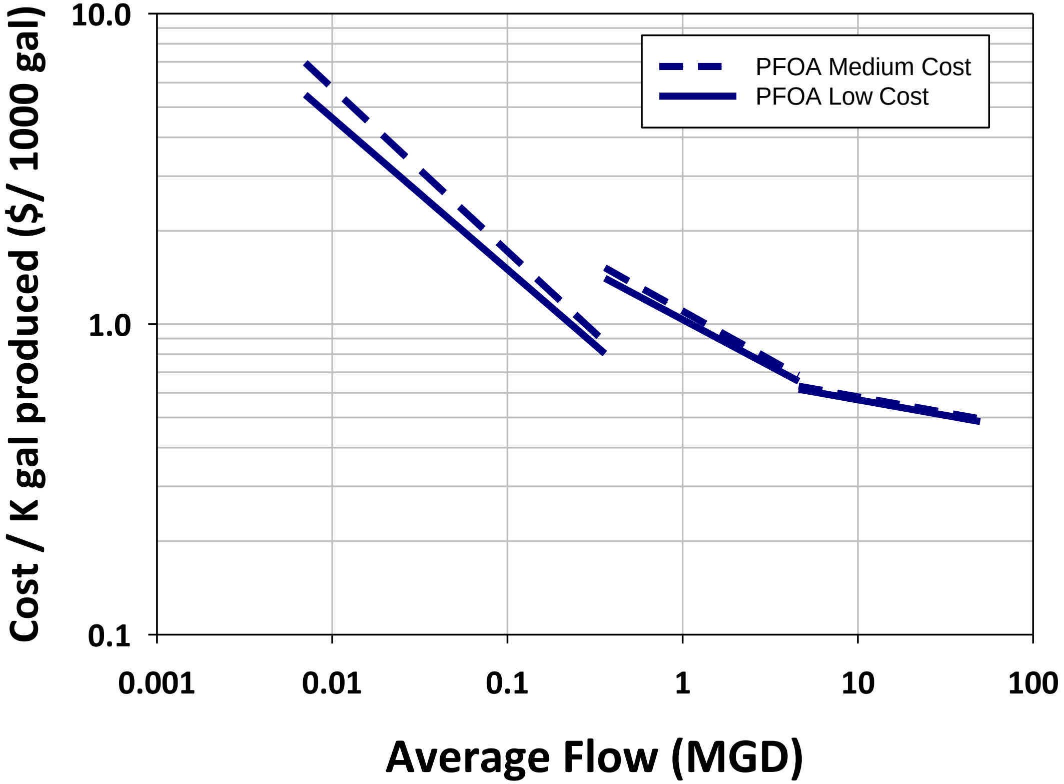
The cost models can be used by EPA to conduct benefit-cost analyses of a new drinking water regulation. Each model estimates the unit cost (capital and operating cost) of a specific drinking water process.

A treatment technology is broken down into discrete components that can be measured for the purpose of estimating costs

- Specific equipment (e.g., tanks, vessels, pipes, and instruments)
- Other identifiable cost elements (construction costs, and annual expenditures on labor, chemicals, and energy)

Cost /1000 gal: PFOA

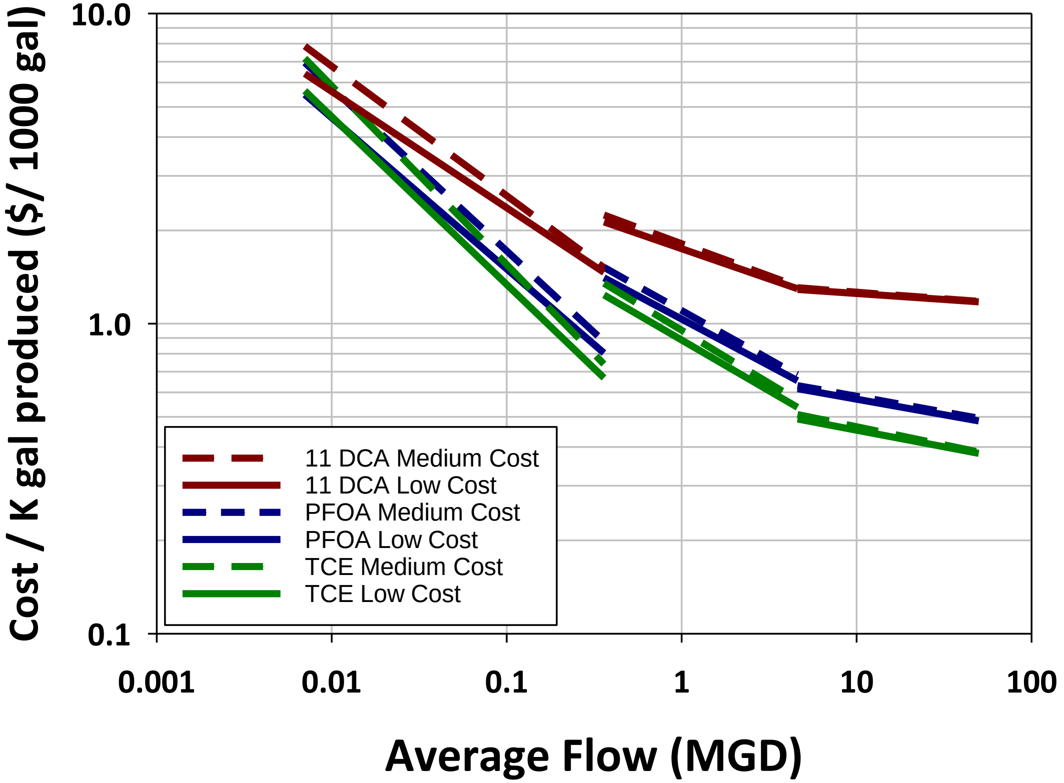
PFOA will break through before PFOS



- Full Scale
- 26 min EBCT
- Lead-Lag configuration
- F600 Calgon carbon
- 1.5 m^3/min flow
- Full automation
- POTW residual discharge
- Off site regeneration
- 70K bed volumes to breakthrough for PFOA

Cost / 1000 gal: PFOA, TCE, & 11 DCA

PFOA will break through before PFOS



- Full Scale
- 26 min EBCT
- Lead-Lag configuration
- F600 Calgon carbon
- 1.5 m^3/min flow
- Full automation
- POTW residual discharge
- Off site regeneration
- 135K, 70K, and 11K bed volumes to breakthrough for TCE, PFOA, and 11DCA, respectively.

TDB + Cost Model

Concept

To have a system where the treatment performance information feeds directly into the cost models.

Benefits

- A transparent system for costing of future regulations
- Reduces the effort needed to access treatment performance data and design criteria.
- Provides an opportunity to focus on contaminants of interest to small systems
- Enhances university stakeholder interactions through supplementing and using treatability data.

Water Treatment Technologies for PFAS

Varies by carbon chain length and functional groups, but generally:

Ineffective:

Coagulation
Sedimentation
Aeration
Microfiltration
Ultrafiltration
Ozone
Chlorine
Ultraviolet Photolysis
Advanced Oxidation Process

Partially Effective:

Anion Exchange
Granular Activated Carbon (GAC)

Effective:

Reverse Osmosis

[1] As presented to RITS 2016 (Remediation Innovative Technology Seminar) by John Kornuc, Ph.D., NAVFAC EXWC

[2] Research on remediation of PFAS is only starting, so information is evolving

[3] OW's Drinking Water treatability database for PFOS and PFOA

Treatment Technologies for PFAS by Media

Drinking Water [1]: GAC, RO, Anion Exchange

Research evolving for other media but currently based on professional opinion with some performance information

Groundwater: GAC

Soils, sediments, Concentrates

- **High Temperature Thermal Oxidation (>1100°F) [2]**
- **Excavation and offsite disposal**

---

[1] https://www.epa.gov/sites/production/files/2016-05/documents/pfoa_health_advisory_final_508.pdf

[2] As presented to RITS 2016 (Remediation Innovative Technology Seminar) by John Kornuc, Ph.D., NAVFAC EXWC

GAC Treatment Considerations

- **Only current practical treatment for contaminated groundwater (RO can be used in drinking water)**

- **Current GAC treatment may not effectively remove shorter-chain or replacement PFASs, which may be a future concern**
  - **Longer chain compounds are more effectively removed**
  - **Sulfonates removed better than carboxylates**

- **Elevated DOC decreases GAC performance**

- **Other treatment technologies (e.g., advanced oxidation) can change PFAS composition and may alter GAC performance**

GAC Treatment Considerations

- **Only current practical treatment for contaminated groundwater**
- **GAC treatment need to be designed to remove shorter-chain or replacement PFASs**
  - **Longer chain compounds are more effectively removed**
  - **Sulfonates removed better than carboxylates**
- **Other treatment units (e.g., advanced oxidation) can change PFAS mixture, should be considered in GAC design**
- **Elevated DOC decreases GAC performance – treatment trains may be effective and reduce costs**
- **Strong preference for in situ technologies - Permeable Reactive Barriers (PRBS) may be useful technology for field implementation**

Treatability: PFASs

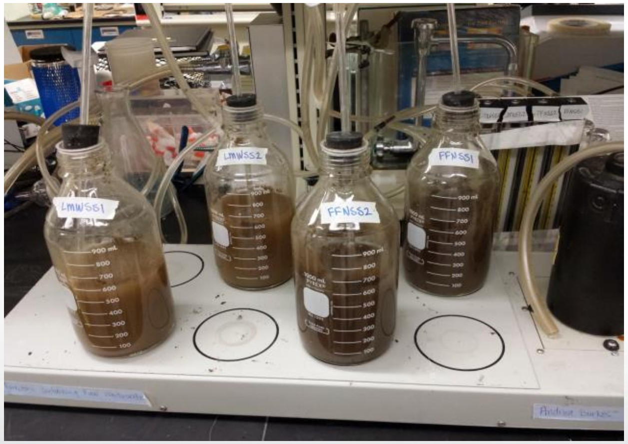
What is missing?

- Evaluate more that PFOA and PFOS
- A great deal of the treatment data is at concentrations higher than the level of the 2016 Health Advisory
- Although the general trends regarding the efficacy of various treatment technologies are known, certain technologies need additional pilot- or full-scale testing
  - GAC: Data needed to address adsorption kinetics and competitive adsorption for various carbons
  - Ion Exchange: A number of studies are needed to address the impact of water quality parameters, different resins, and the impact of regeneration conditions

Technologies exist to treat for PFOA and PFOS although pilot-scale data under a wider range of water quality conditions would be valuable

EPA Wastewater research overview

- **Surveys of occurrence and composition associated with wastewater treatment**
    - **Seasonal effects on treatment of PFASs through conventional WWT**
    - **Survey of biosolids for PFASs concentrations and composition**
    - **Transformation and sorption of PFAS using model wastewater reactors**
- **Land Application of biosolids**
    - **municipal biosolids applied to fescue field and monitored for 1 year**
    - **PFAS transformation and persistence observed**
- **Long-term monitoring of treatability of municipal WW for Direct Potable Reuse**



Homeland Security and Emergency Response - Background

Contamination incidents (terrorist attacks, natural disasters, industrial spills etc.) and response activities may produce large volumes of contaminated wash water. This water may require pre-treatment prior to disposal and may have adverse affects if it enters the collection system and reaches wastewater utilities.

Research Topics:

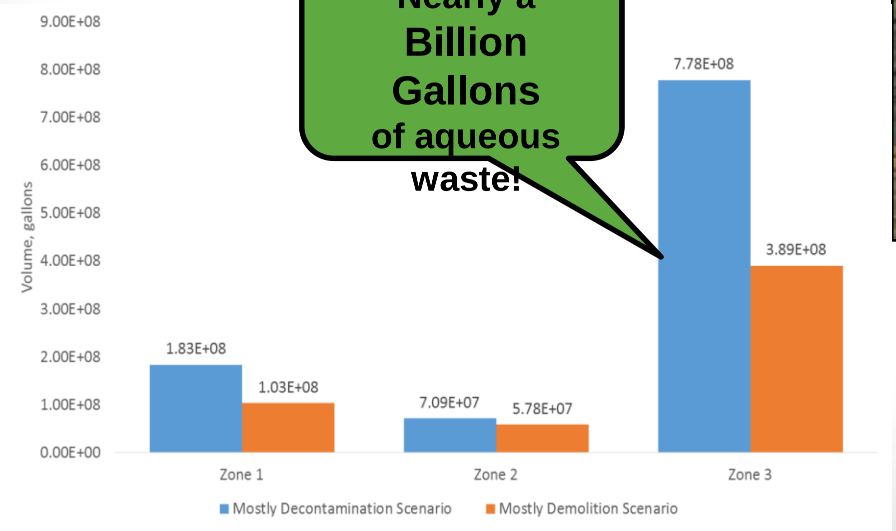
- Toolbox of Advance Oxidation Process (AOP) pre-treatment strategies for the disposal of large volumes of contaminated water and wash water, with resulting microbial toxicity.
- Treatment of perfluorinated compounds (PFCs), as may arise from AFFF firefighting activities, using AOPs and adsorption
- Rad: Integrated Wash-Aid, Treatment, and Emergency Reuse System (IWATERS) for mitigation of wash water with soluble and particulate contaminants

Quantity potentially needing treatment

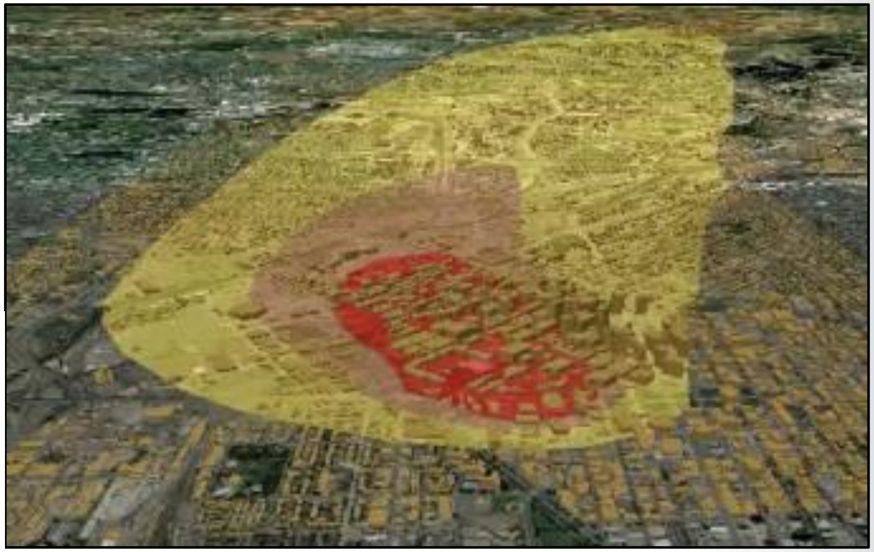
How much contaminated water is generated?

Aqueous waste estimation:

- Both scenarios (decontamination and demolition) generate significant volumes of contaminated wash water that may require special treatment or disposal.



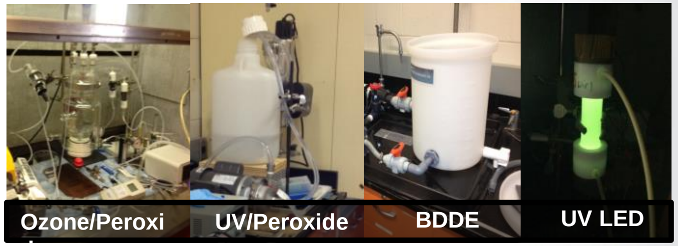
Nearly a Billion Gallons of aqueous waste!



AOP Research: Results

Toolbox of Advanced Oxidation Process (AOP)

Choice of AOP technology based on needs and goals



Comparison Criteria	AOP Technologies			
	Ozone/Peroxide	**UV/Peroxide**	**BDDE**	**UV LED**
Required Reagents	**Hydrogen Peroxide**	**Hydrogen Peroxide**	**Electrolyte**	**Hydrogen Peroxide**
Durability/ Transportability	**Fragile**	**Fragile/Mercury Concern**	**Durable**	**Durable**
Degradation Rate	**Fastest (<20 min.)**	**Fast (<90 min)**	**Slower**	
Contaminant Dependancy	**Little Dependancy**	**Some Dependancy**	**High Dependancy**	
Microbial Toxicity	**Low**	**Low**	**Moderate**	
Ease of Use	**Most Difficult**	**Easy**	**Easiest**	**Easy**

Soil remediation

- **Currently,**
  - **excavation and landfilling**
  - **excavation and thermal oxidation**

- **Research needed to evaluate or develop alternate methods such as soil solidification, and transformation/removal technologies**

Disclaimer

Acknowledgments

- OLEM
  - Schatzi Fitz-James
  - Linda Gaines
  - Jed Costanza
  - Terry Smith
- OW
  - Adrian Hanley
  - Paul Grimmett
- Regions
  - 3 – Cindy Caporale
  - 5 – Larry Zintek
- ORD
  - Christopher Impelliteri
  - NRMRL
    - Tom Speth
    - Carolyn Acheson
    - Gerard Henderson
  - NERL
    - Jody Shoemaker
    - Andrew Lindstrom
    - Mark Strynar

Laboratory Considerations

- Solvent contamination is source dependent, regular and/or sporadic
- Lab supplies
    - Polypropylene vials and centrifuge tubes (from mold release or cross contamination from other production processes)
    - LC vial caps and septa (e.g. PTFE/silicone)
    - LC and SPE pump equipment, pump head seals (graphitized Teflon)
    - PTFE tubing
    - Low binding pipette tips
- Use of PFAS-containing equipment (gloves, coats, collection gear, etc) also an issue
- Many common laboratory/field materials and sampling equipment contain PFAS

Sampling Considerations

- **Several professional opinions would benefit from research**
  - **Volatile PFAS may be lost depending on the sampling methods.**
  - **PFAS stratification in ground water and at interfaces**
  - **PFAS may sorb to sampling equipment possibly distorting measured concentration**

PFAS sampling

- Other chemicals which may be present
  - e.g., AFFF sites may have hydrocarbons, chlorinated solvents, glycols, and other AFFF components as well as residuals from previous remediation efforts
- Sampling for multiple analytes at the same time may require careful planning and execution due to cross contamination issues
  - PFAS sampling equipment should be free of exposure to PFAS containing materials
  - Other analytes may commonly be sampled using PFAS containing materials such as teflon or PTFE