

US EPA's Research on PFAS: Managing PFAS End-of-Life Issues

Recycling , Landfills, Land Applications, and Incineration

Presentation overview

- Introduction to PFAS end-of-life issues
- Materials management
- Wastewater/Biosolids/Soil treatment
- Thermal treatment/Incineration
- Cross Agency technical support and collaboration

RCRA Waste Management Facilities:

Problem: Lack of knowledge regarding end-of-life management of PFAS-containing consumer and industrial products

Action:

- Develop appropriate methods for appropriate media (e.g. liquids, solids, air/soil sampling)
- Characterize end-of-life PFAS recycle and disposal streams (e.g. municipal, industrial, manufacturing, recycled waste streams)
- Evaluate efficacy of materials management and remediation technologies (e.g. recycling, land application, landfilling, incineration, carbon regeneration) to manage end-of-life disposal
- Evaluate performance and cost data with collaborators to manage these materials and manage environmental PFAS releases

Results: Development/assessment of technologies, data and tools to manage end-of-life streams

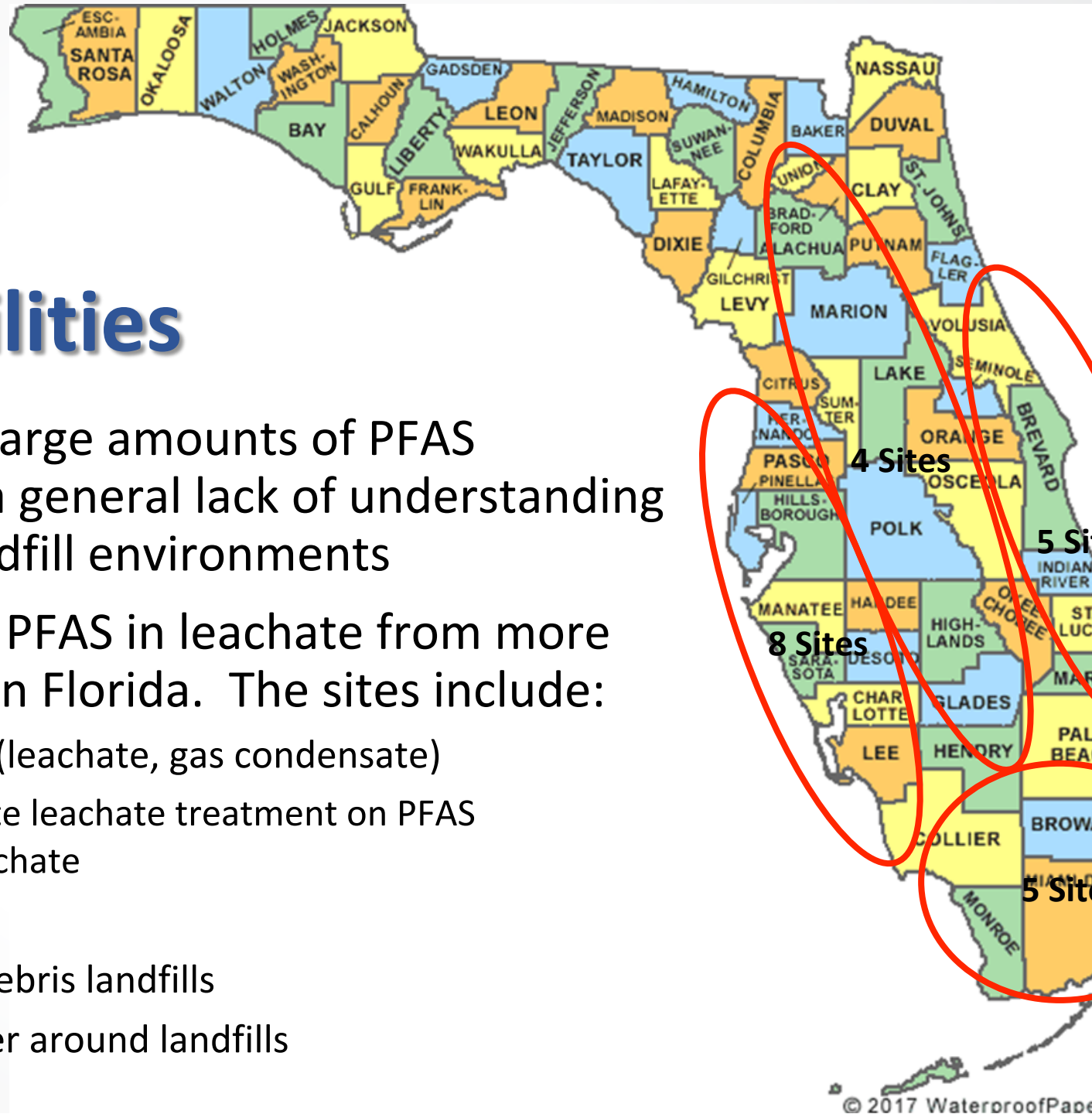
Impact: Responsible officials will be able to manage effectively end-of-life disposal of PFAS-containing products

RCRA Waste Facilities

Problem: Landfills receive large amounts of PFAS containing waste, there is a general lack of understanding of fate and transport in landfill environments

Action: collect and analyze PFAS in leachate from more than 20 RCRA landfill sites in Florida. The sites include:

- Municipal solid waste landfills (leachate, gas condensate)
 - Examine the impact of onsite leachate treatment on PFAS concentration in landfill leachate
- Ash monofills (Leachate)
- Construction and demolition debris landfills
- Groundwater and surface water around landfills



Future Work: RCRA Waste

achate sampling to expand to other regions of the United States.

- In discussion with Waste Management Inc and The Solid Waste Association of North America (SWANA) to provide site access for sample collection
- Include total oxidizable precursors analysis

ate, transport, and transformation of PFAS
simulated landfill environments

PFAS transport through earthen and
an-made liners

PFAS concentration in MSW ash and flue gas

PFAS flow and concentrations through
the MSW recycling processes including
composting



Wastewater and Land Application of Biosolids/Wastes

Wastewater treatment and Land Application of Biosolids/Wastes

Problem: Lack of knowledge regarding end-of-life management of PFAS-containing consumer and industrial products in wastewater

Action:

- Characterize wastewater and relate discharge streams (e.g. municipal and industrial wastewater, land applied waste streams)
- Evaluate efficacy of existing management technologies to manage end-of-life disposal (e.g. land application of biosolids)
- Evaluate performance and cost data to manage these waste streams and environmental PFAS releases

Results: Provide technologies, data, and tools to manage wastewater streams

Impact: Responsible officials will be able to manage PFAS-containing waste streams

PFAS in Biosolids

	PFOA (ng/g dry wt)	PFOS (ng/g dry wt)
Navarro, 2016	1 - 14	4 - 84
Sepulvado, 2011	8-68	80-219
Venkatesan, 2013	12-70	308-618
Washington et al, 2010, 2011	50-320	30-410
Mills, Dasu (in prep)	10-60	30-102

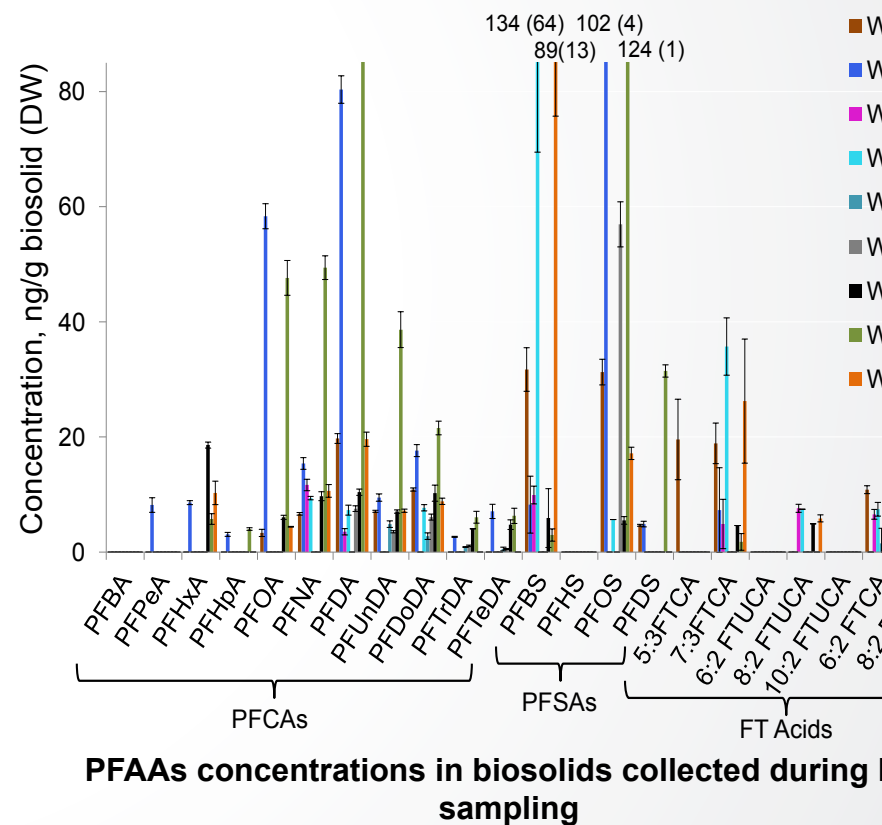
- Does not include other PFAS and precursors that can be degraded over time to more stable PFAAs
- PFAAs end products do not degrade and do bioaccumulate
- Many more PFAS compounds present and more being introduced
- Lindstrom et al, 2011 found there may be a relationship between land applied biosolids and contamination in wells in Decatur, AL

Conjunction with Region 6

Action: Nine wastewater treatment plants were sampled seasonally

- The solids treatment included anaerobic digestion and aerobic digestion
- Solid residuals and effluent were analyzed for PFAAs, precursors, and transformation products.

Results: PFAS and PFAS precursors of varying distributions were found



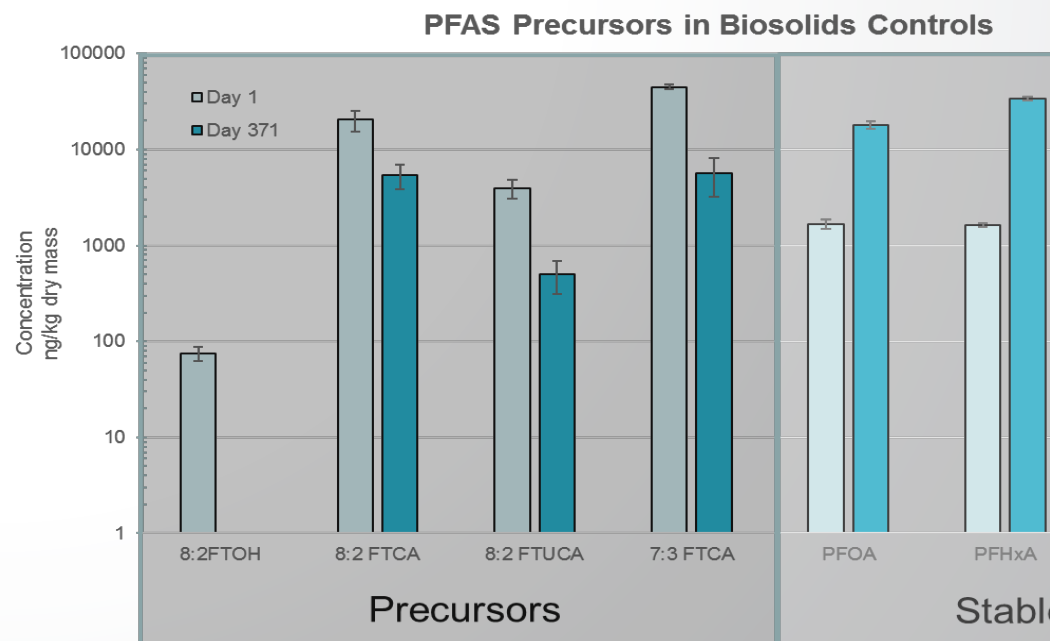
Land Application of Biosolids

Evaluate application methods for liquid and solid biosolids and measure the natural attenuation for various analytes including PFAS

Precursor concentrations were similar to PFAA concentrations

Precursor concentrations decreased with time

Stable PFAAs increased over 371 days commensurate to the expected metabolic pathways from precursor material



Land Application of Biosolids: PFAS uptake into edible plants

Conjunction with Region 5

Method: A variety of food crops were grown in soil amended with biosolids.

The biosolids contained PFAAs

PFAS concentrations in edible portion of the plant were measured.

Results

The edible portion had measurable levels of PFOA, among other PFAS

Further research needed to characterize uptake in more crops under varying conditions

Research needed to assess plant uptake as a route of human and ecological exposure

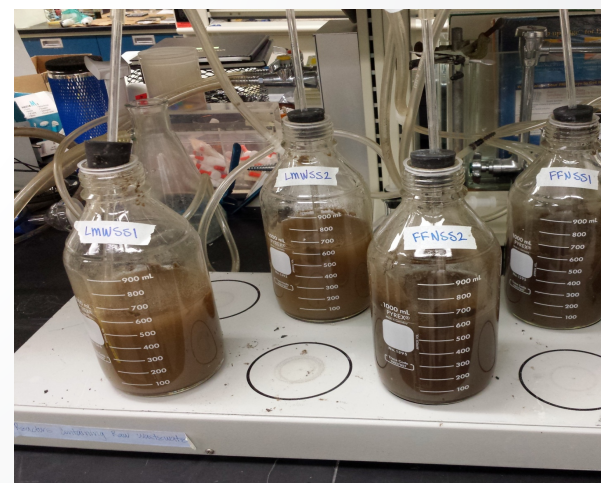


- Blaine, et al (2013). ES&T 47(24): 1
- Blaine, et al (2014). ES&T 48(14): 7

Problem: Wastewater Treatment Plants are a source of PFAS

Goal: Develop research to support:

- More robust and expanded analytical methods
- Bioassays to better understand if treatments are effective and to identify risks
- Evaluation of WWTP conventional and advanced unit operations to manage PFAS
- Evaluate air emissions from unit operations (e.g. activated sludge, biosolids drying, sewage sludge incineration)
- Evaluate biosolids treatment (e.g. land application under wide range of soil types, biosolids, and management strategies).
- Evaluate pretreatment technologies to address “sources” to wastewater as a more cost effective approach



Immobilization Technologies for PFAS-Contaminated Soils

Existing technologies have limitations

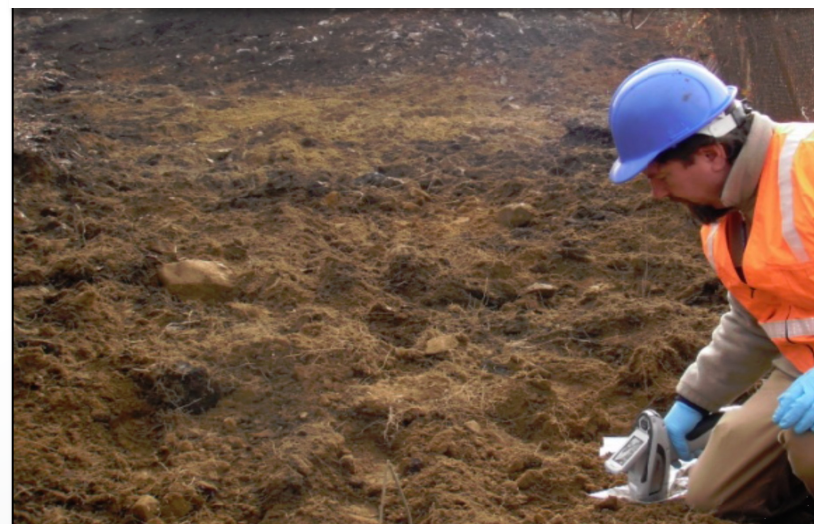
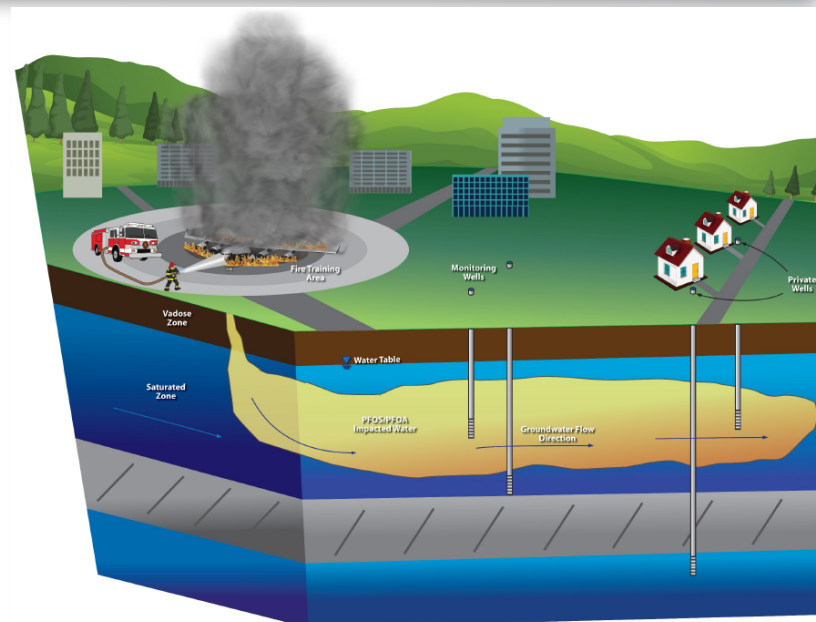
- Excavation and thermal treatment
- Capping

In-situ strategies

- Treatment
- Stabilization/Immobilization

There has been limited research on PFAS immobilization

- Stabilization well studied for some legacy contaminants
- No comparable data available for PFAS



Thermal treatment

Thermal treatment of PFAS

The strength of the C-F bonds require temperatures above 1,000 °C for greater than 1 second.

For example, CF_4 requires 1400 °C
Information is lacking in the literature and in practice
Its decomposition product, HF, is easily monitored

Products of Incomplete Combustion (PICs) are more likely formed with F radicals than other halogens such as Cl

Sufficient temperatures, times, and turbulence are necessary to ensure destruction
PIC data from incineration studies are lacking
The effect of mixed halogens in the waste stream introduces more unknowns
Measurement methods for PICs are under development at ORD

Initiating collaborative projects with DoD and industry partners to evaluate existing technologies:

Thermal treatment system for PFAS contaminated soils in Alaska
Fate of PFAS during GAC reactivation from treatment systems

Future work: Thermal treatment

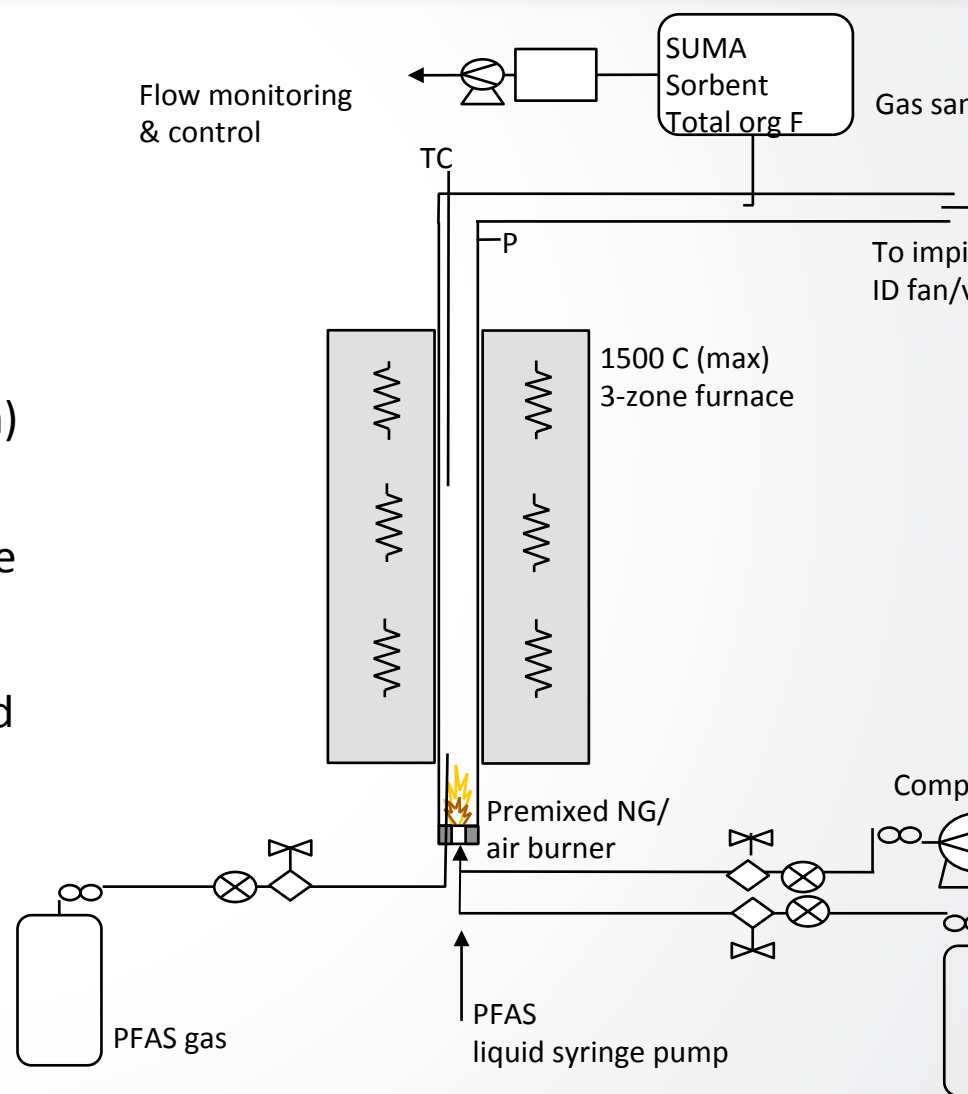
Problem: There are many sources of materials that may need to be incinerated

- Manufacturing wastes
- Biosolid sludges
- Municipal waste
- Obsolete flame retardants
- Spent water treatment sorbents (resins/activated carbon)

What minimum conditions (temperature, time) are needed to completely destroy PFAS and what are the products of incomplete combustion?

Objective: Conduct bench- and full-scale incineration studies and modeling to evaluate:

- Impact of source material
- Impact of temperature on degree of destruction
- Impact of calcium
- PFAS releases from incineration systems



Technical Support

has knowledge and expertise related to the analysis and management of PFAS for various medias. As more interest is placed on PFAS, ORD is a resource for states, Program Offices, Regions, Tribes, and Communities as they face these challenges.

Examples:

Underground and Engineering Technical Support Centers providing technical input to a variety of Superfund sites regarding PFAS issues

Assisting States in stack sampling to evaluate emissions from PFAS manufacturing facilities

Providing technical assistance regarding QA and data analysis for Federal facilities sites characterizing PFAS contamination.

Supporting the science synthesis of sampling techniques for sampling substituted AFFF foams from groundwater migration to surface waters





EPA actively partnering with Federal, State, Tribes, and Communities

- EPA serves on their technical advisory group that oversees DoD's PFAS research
- DoD and EPA developing analytical methods for characterizing PFAS exposure and site characterization
- Partnering with industry to evaluate thermal treatment systems for managing contaminated soil and reactivation of GAC
- EPA cost and performance models are being adapted with DoD for site remediation and cleanup
- Evaluating treatment technologies for site remediation and managing emergency response waste streams

A and FDA

- Initiated cross agency workgroups to focus on analytical methods, charactering exposure, and treatment/remediation
- Joint project with academia to evaluate E-beam treatment of PFAS in water

es/Tribes/Communities

- Stack sampling of emissions from manufacturing facilities
- State workgroups to assess drinking water and contaminated sites



For More Information

Speth – *Drinking water treatment, GAC regeneration*

McMills – *Remediation, analytical methods*

Di Impellitteri – *Analytical methods, biosolids*

Robert Tolaymat – *Landfills, materials management*

John Acheson – *Biosolids*

John Linak - *Incineration, thermal treatment*

Andrew Gillespie, Ph. D.

Associate Director,

National Exposure Research Laboratory

Executive Lead for PFAS R&D

EPA Office of Research and Development

gillespie.andrew@epa.gov

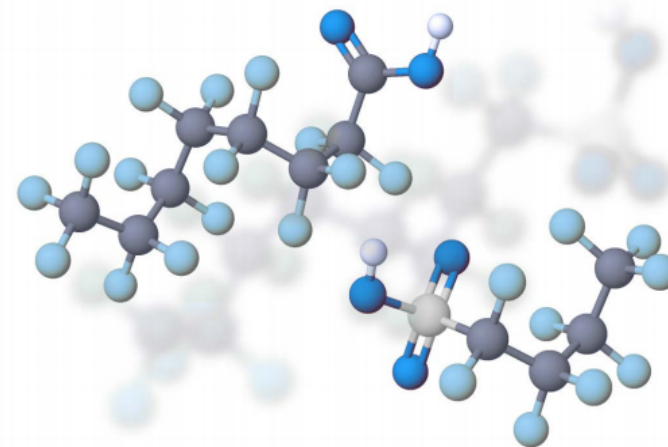
(202) 541-3655

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EPA's Per- and Polyfluoroalkyl Substances (PFAS) Action Plan



U.S. Environmental Protection Agency

Methods for detecting, identifying PFAS different end-of-life materials:

Precursors, Degradates, and Terminal PFAS



Non-Drinking Water Methods: *SW-846 Method 8327—Direct Injection*

AS target analytes

Inclusive of target analytes in EPA Method 537

Commercially available standards (“neat” and isotopically labeled)

Injection method based on EPA Region 5 SOP

Similar to ASTM Method D7979

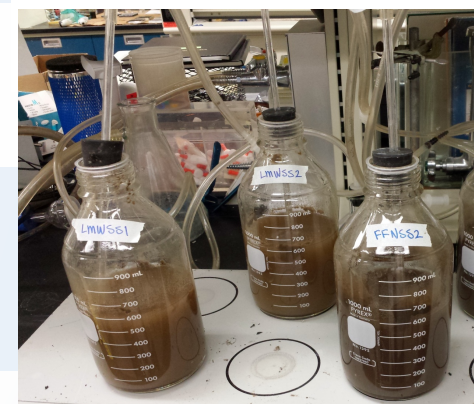
Multi-laboratory validation study completed in 2018

Method is currently available for comment through 23 Aug 2019

drinking water matrices

Cleaner matrices e.g surface water, groundwater, wastewater effluents

Quantitation Limits: 10 nanogram/L





Non-Drinking Water and Solids Method *Isotope Dilution*

More complex method relative to direct injection

More robust and accounts for complex matrices through isotopically labelled standard recoveries;

Meets DoD requirements, which are optional at non-DoD affiliated sites.

24 PFAS analytes plus GenX chemical (HFPO-DA) with 10 ng/L MDLs

Non-drinking water and solid matrices

Non-drinking waters (e.g. surface water, groundwater, wastewater, landfill leachate).

Solids (e.g. soils, sediments, biosolids, tissues).

Laboratory internal validation started, ten lab external validation study planned

ORD has internally demonstrated the method on limited matrices.

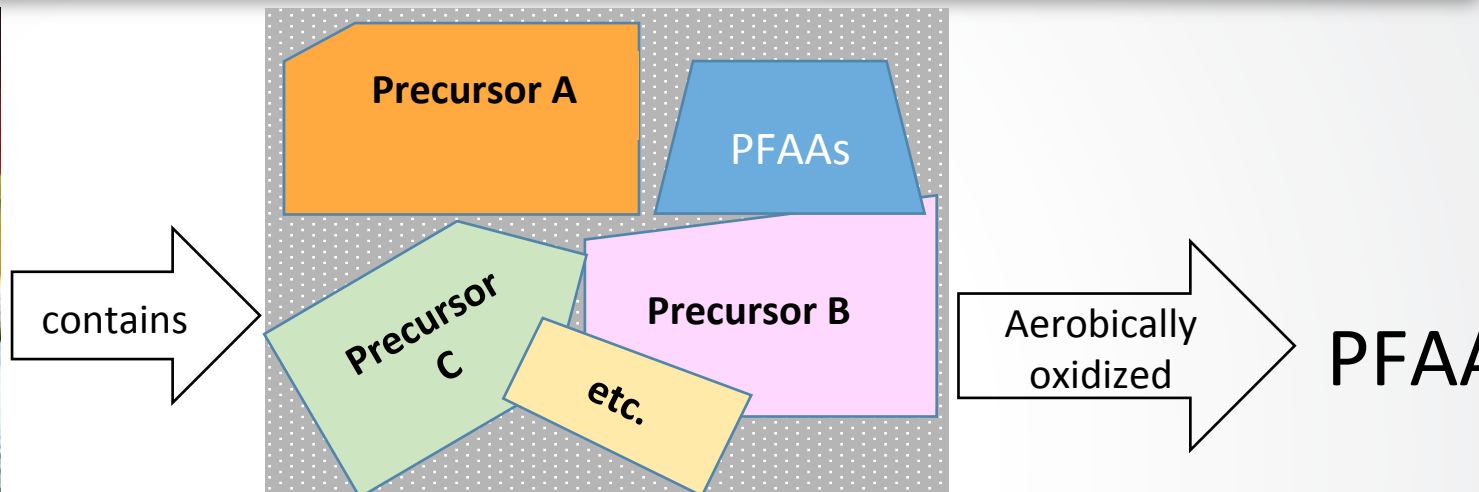
DoD is funding single and multilaboratory validation studies with input from EPA.

Goal is to submit the results of the methods studies to OW 1600 series and OLEM SW846 series.

PFAS Precursors



PFAS Product
(e.g. AFFF)



How to measure Precursors

PFAS products are often broad mixtures of PFAS

Highly stable & persistent PFAAs (e.g. PFOS) are most commonly identified

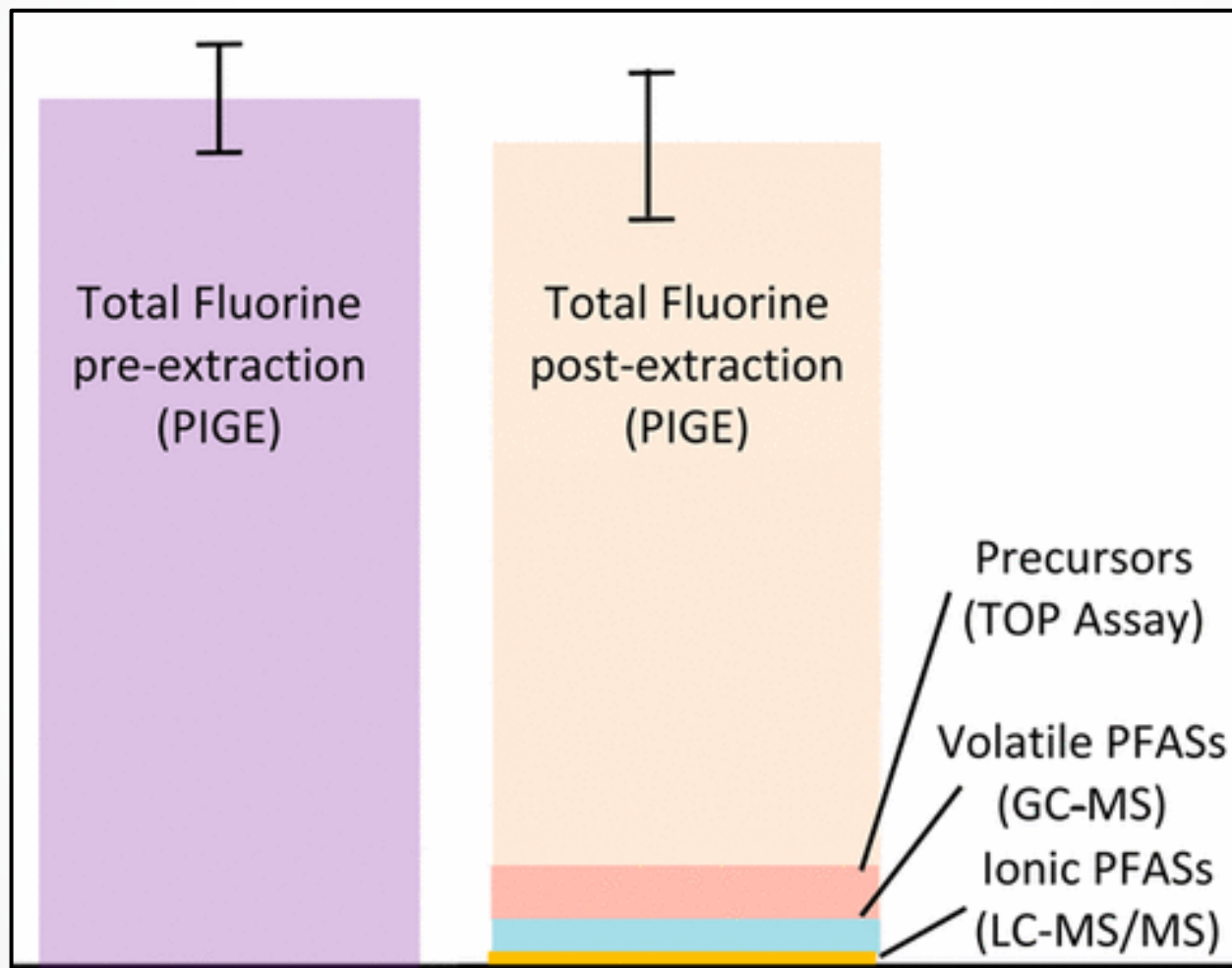
Precursor mass may be substantial component of the total product mass

Precursors degraded to PFAAs over time naturally or during oxidative treatment

How do we measure/account

- Total oxidizable Precursor Assay (TOP Assay)
- Total Organofluorine analysis using combustion ion chromatography (TOF-CIC)
- Particle induced gamma ray emission (PIGE)

For example... a mass balance for PFAS



Mass balance based on total fluorine in textiles and papers.