Pilot-scale thermal treatment of PFAS-laden materials

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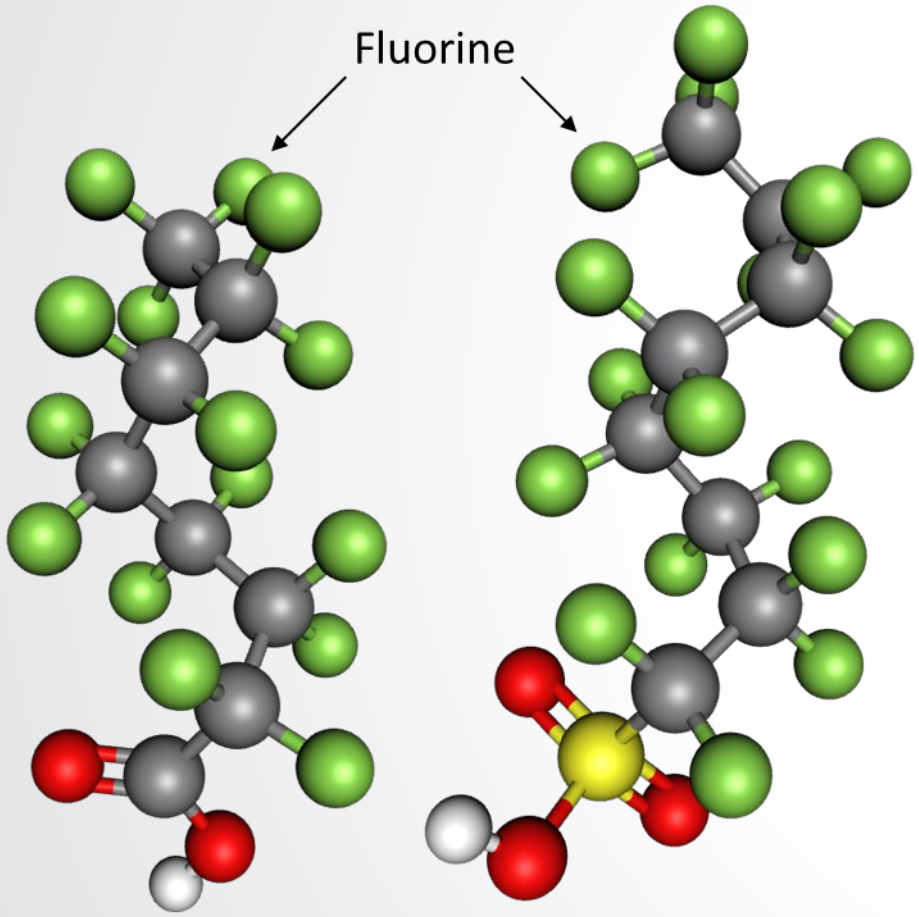
Outline

- Background
- Sampling & analytical for PFAS emissions
- Fate of PFAS during pilot-scale biosolids incineration
- Fate of PFAS during pilot-scale GAC regeneration

Per- and Polyfluoroalkyl Substances (PFAS)



Perfluorooctanoic acid (PFOA)

Perfluorooctanesulfonic acid (PFOS)

A large class of synthetic chemicals

- Features chains of carbon atoms surrounded by fluorine atoms
- Wide variety of chemical structures, from single molecules to polymers

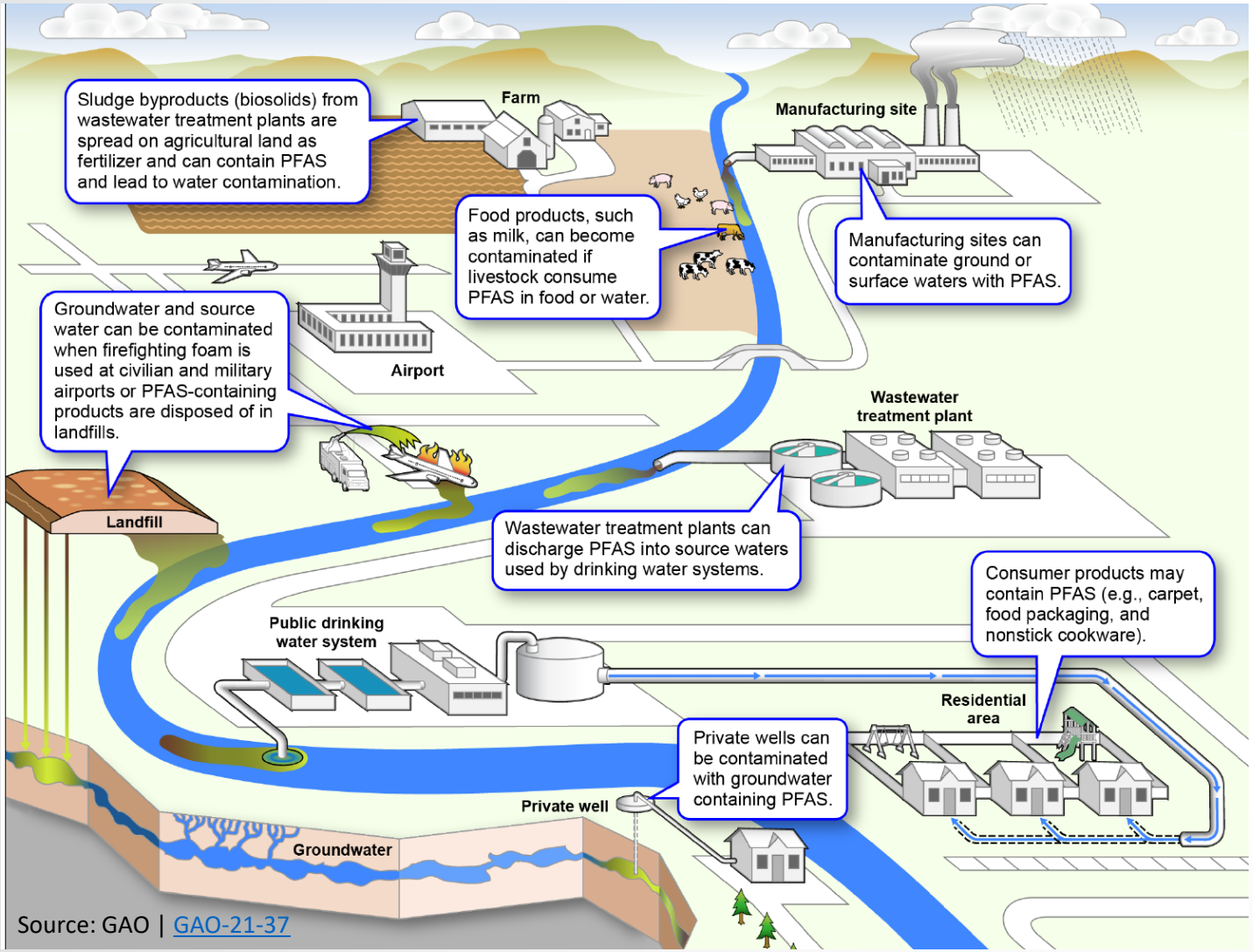
Used in homes, businesses and industry since the 1940s

- Have been detected in soil, water and air samples
- Most people have been exposed to PFAS

Some PFAS are known to be PBT

- P = Persistent in environment and through treatment
- B = Bioaccumulative in organisms
- T = Toxic at relatively low levels (ppt)

Sources of PFAS in the Environment



Source: GAO | GAO-21-37

- Direct release into the environment
  - Use of aqueous film-forming foam (AFFF) in training and emergency response
  - Consumer product use
  - Release from industrial facility
- Landfills and leachates from PFAS-containing products
- Wastewater treatment discharge and biosolids
- PFAS are found in air, soils, plants, biota, water, and sediments

Destruction & Disposal

Data Gap: Knowledge regarding end-of-life management and ultimate disposal of PFAS-containing materials

Actions:

- Characterize end-of-life PFAS disposal streams (e.g., municipal, industrial, manufacturing, recycled waste streams)
- Evaluate efficacy of disposal/destruction technologies (e.g., landfilling, incineration, *in situ* stabilization) to manage end-of-life disposal
- Evaluate possibility of products of incomplete combustion/destruction

Research Products:

- PFAS presence in different waste streams
- PFAS behavior in thermal treatment systems
- Thermal treatment of PFAS-contaminated biosolids

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

Products of Incomplete Combustion (PICs)

- **<u>PFAS are easily transformed, but not destroyed</u>**
- Alternately: Products of Incomplete Destruction (PIDs)
- PICs are generally chemicals beyond the typical list of targeted PFAS analytes
  - Shorter chain PFAS, partially fluorinated PFAS, defunctionalized perfluorinated carbon chains, etc.
- Nature and amount of PICs depend on:
  - Temperature
  - Oxygen availability
  - Residence time at higher temperatures
  - Physical state of the product

CHF_2

C_2F_6 CF_3

CF_3COOH

CH_2F

EPA-ORD's Rainbow Furnace

Pilot-Scale Thermal Destruction of Per- and Polyfluoroalkyl Substances in a Legacy Aqueous Film Forming Foam

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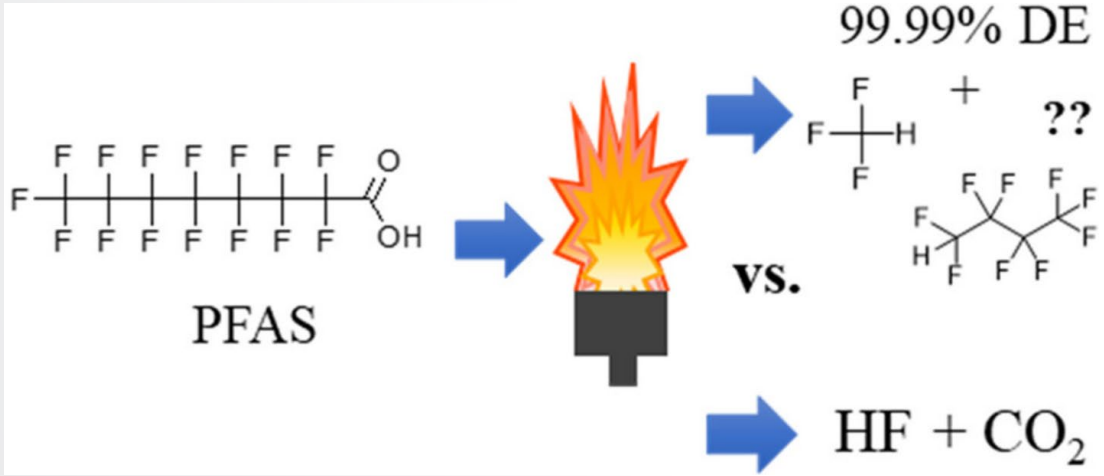
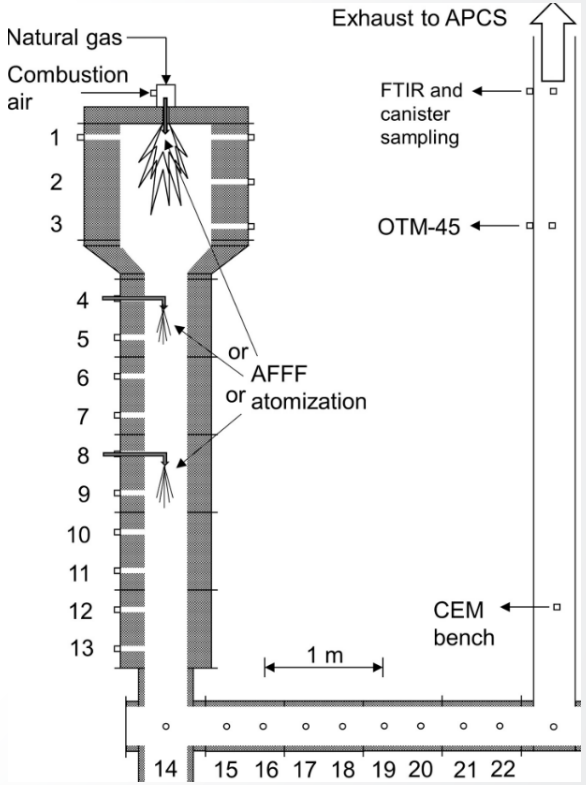




- **High Destruction & Removal Efficiency (DRE) does not necessarily mean full destruction (mineralization) of PFAS**

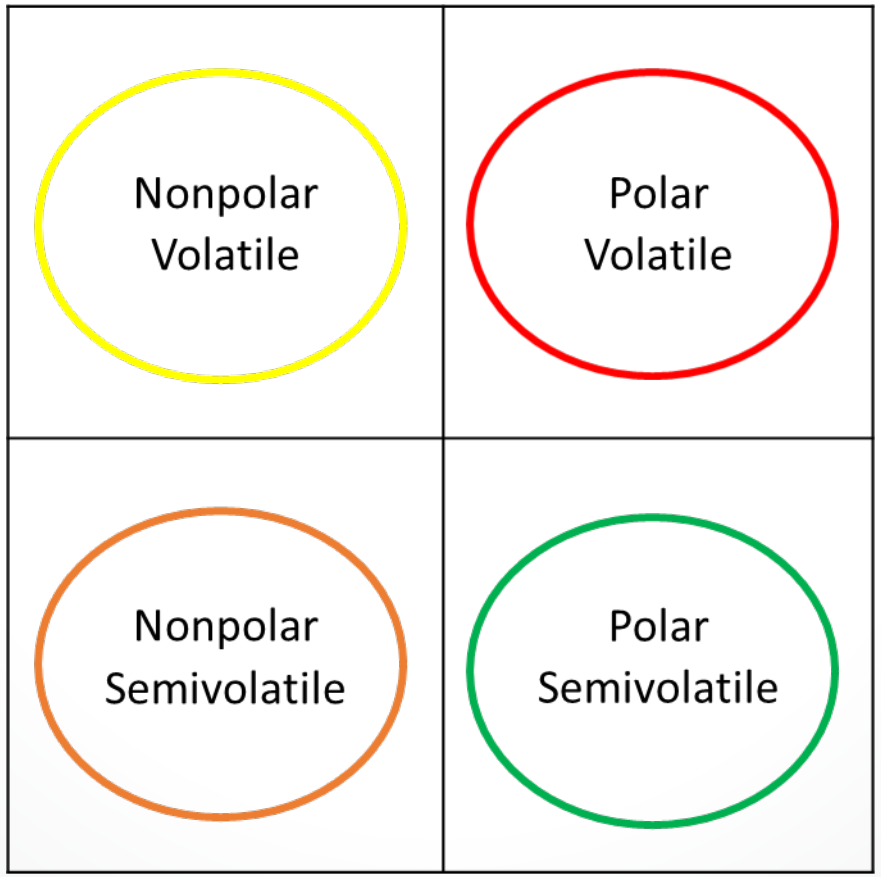
Shields et al. ACS ES&T Engineering Article ASAP DOI: 10.1021/acsestengg.3c00098

Sampling and Analytical Method Development

PFAS Sampling & Analysis – Air Emissions

- **Canister sampling (OTM-50) with GC/MS analysis**
- Currently limited to 30 targeted C1-C8 PFAS
- Primarily known PICs, some industrial PFAS

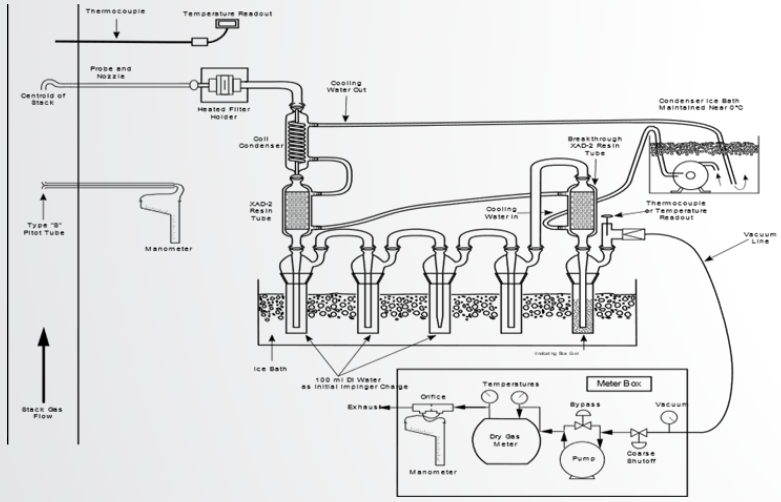
- **Method 0010 sampling with GC/MS analysis (OTM-55)**
- Targeted analysis for FTOHs, select 8270 compounds and potential PICs
- Includes potential compounds of concern



- Impinger sampling?
- LC analysis?
- Limited number of PFAS in this class

- **OTM-45 sampling with LC/MS analysis**
- Currently includes >50 targeted PFAS (C4 and larger)
- Analysis (and standards) largely related to drinking water methods 533 & 537.1, 1633

Air Sampling Methods

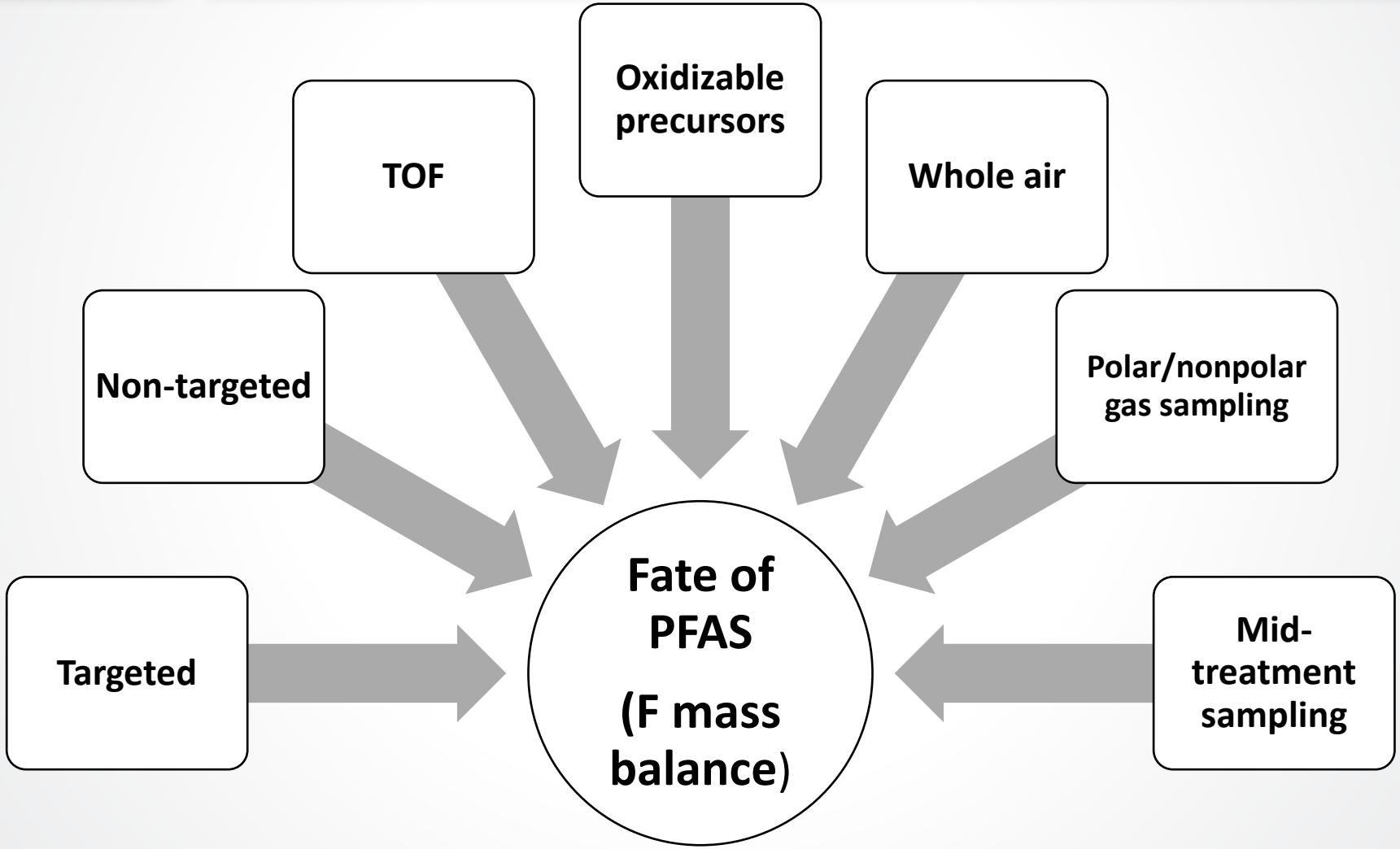


OTM-45 Diagram

OTM-45 in use at incinerator stack

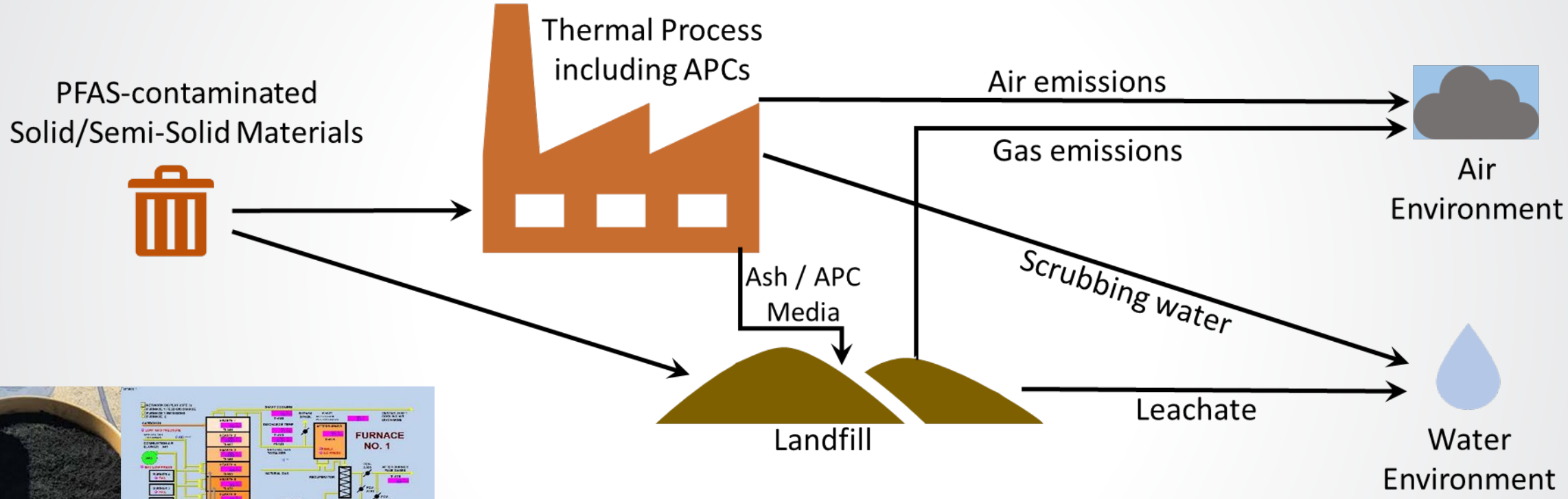
OTM-50 in use at incinerator stack

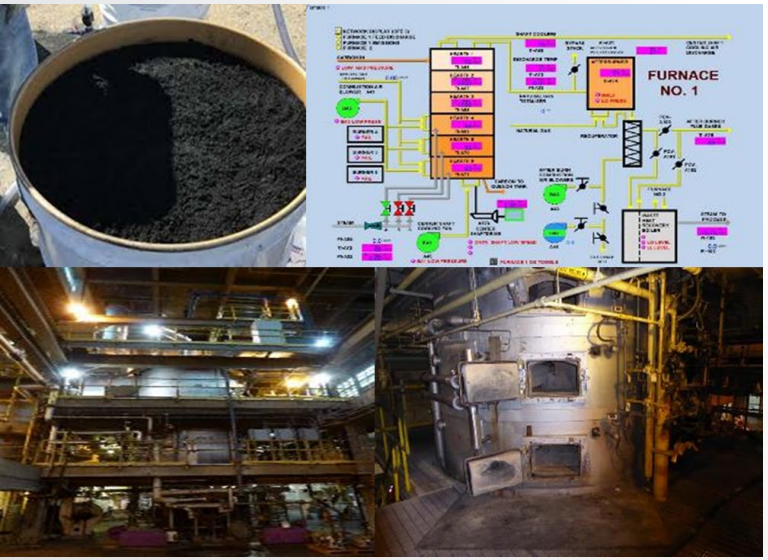
Sampling/Analytical Approach



Pilot-scale Thermal Treatment

Thermal Treatment





PFAS Waste Destruction and Disposal

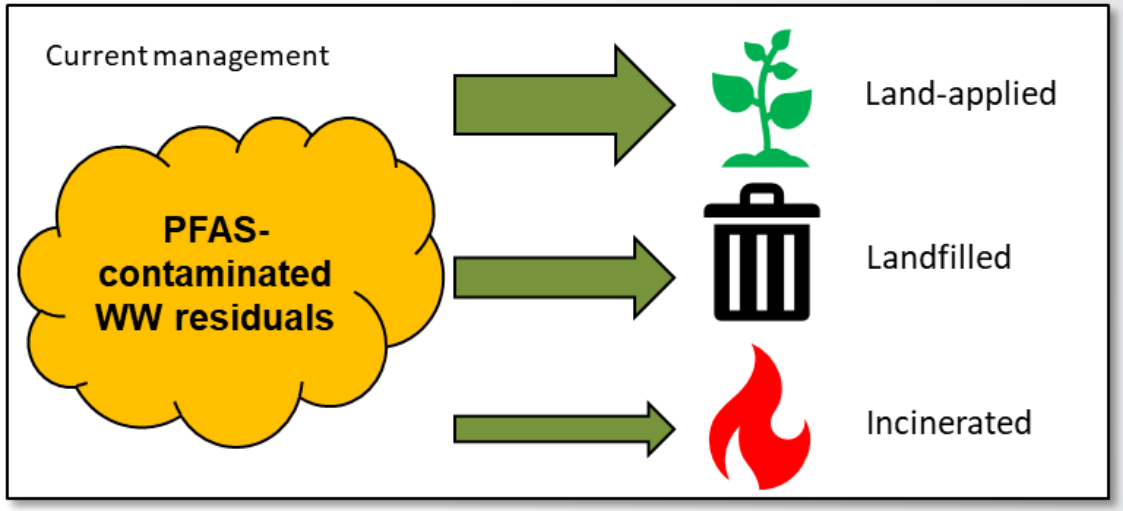
There is a data gap regarding how the end-of-life management and ultimate disposal of PFAS-containing materials can impact PFAS concentrations in the environment.

Treatment Residuals

PFAS are found in ash, scrubbing waters, and subsequent leachates

Changing Fate of Treatment Residuals

- Biosolids
  - Increased concern over PFAS in re-entering the environment through land application or landfilling may lead to increased focus on potentially destructive technologies like incineration



- Granular Activated Carbon (GAC)
  - Excellent technology for PFAS removal from drinking water, but reactivation is most cost-effective path

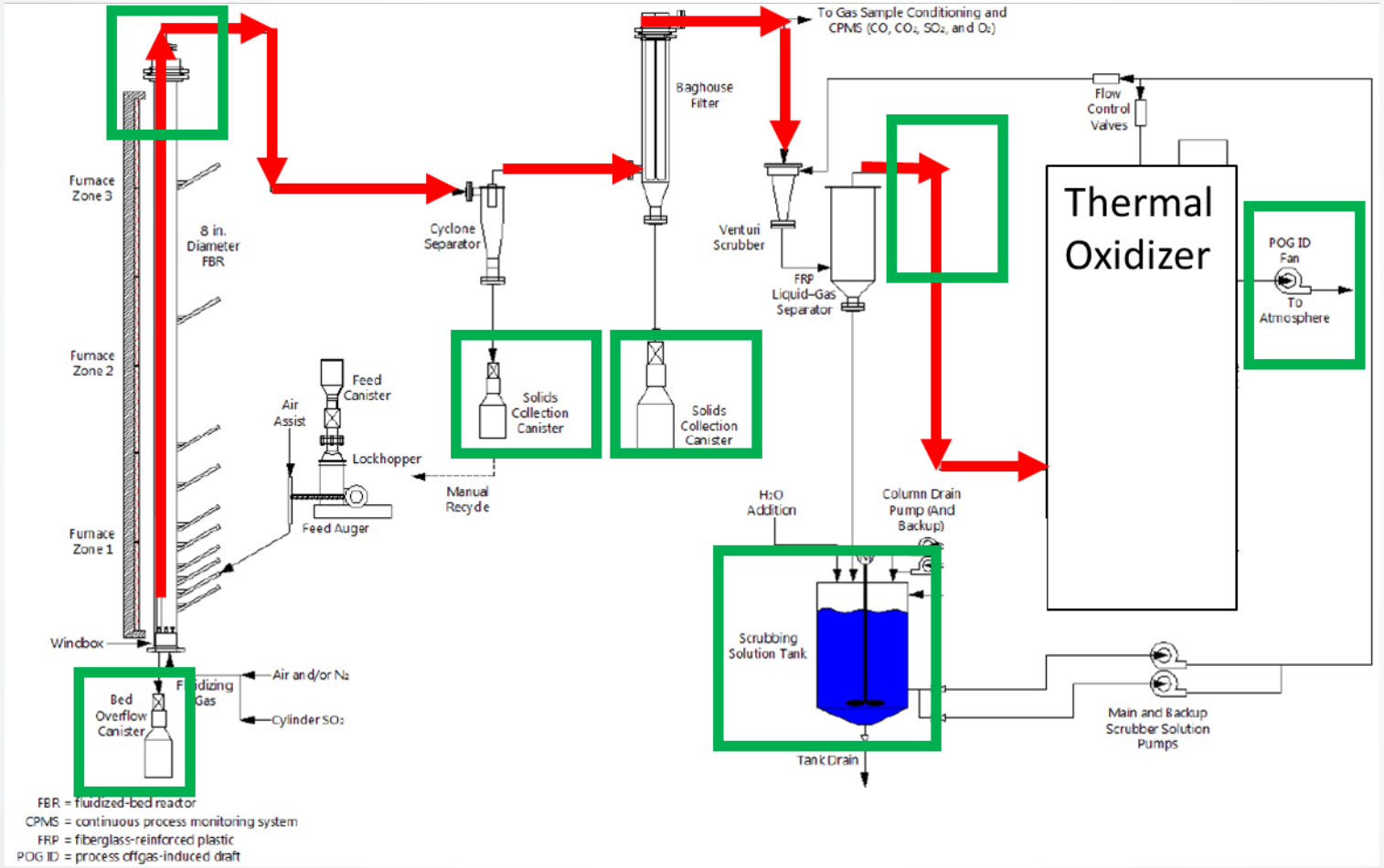
Thermal treatment – Hazen Research Inc.

- Hazen Research Inc.
  - Private lab with pilot-scale thermal systems
- Maximized our time with this system by performing sequential experiments for both biosolids incineration and GAC reactivation
  - Biosolids from POTW with no on-site thermal treatment
  - GAC from a groundwater remediation site

Operating Parameters

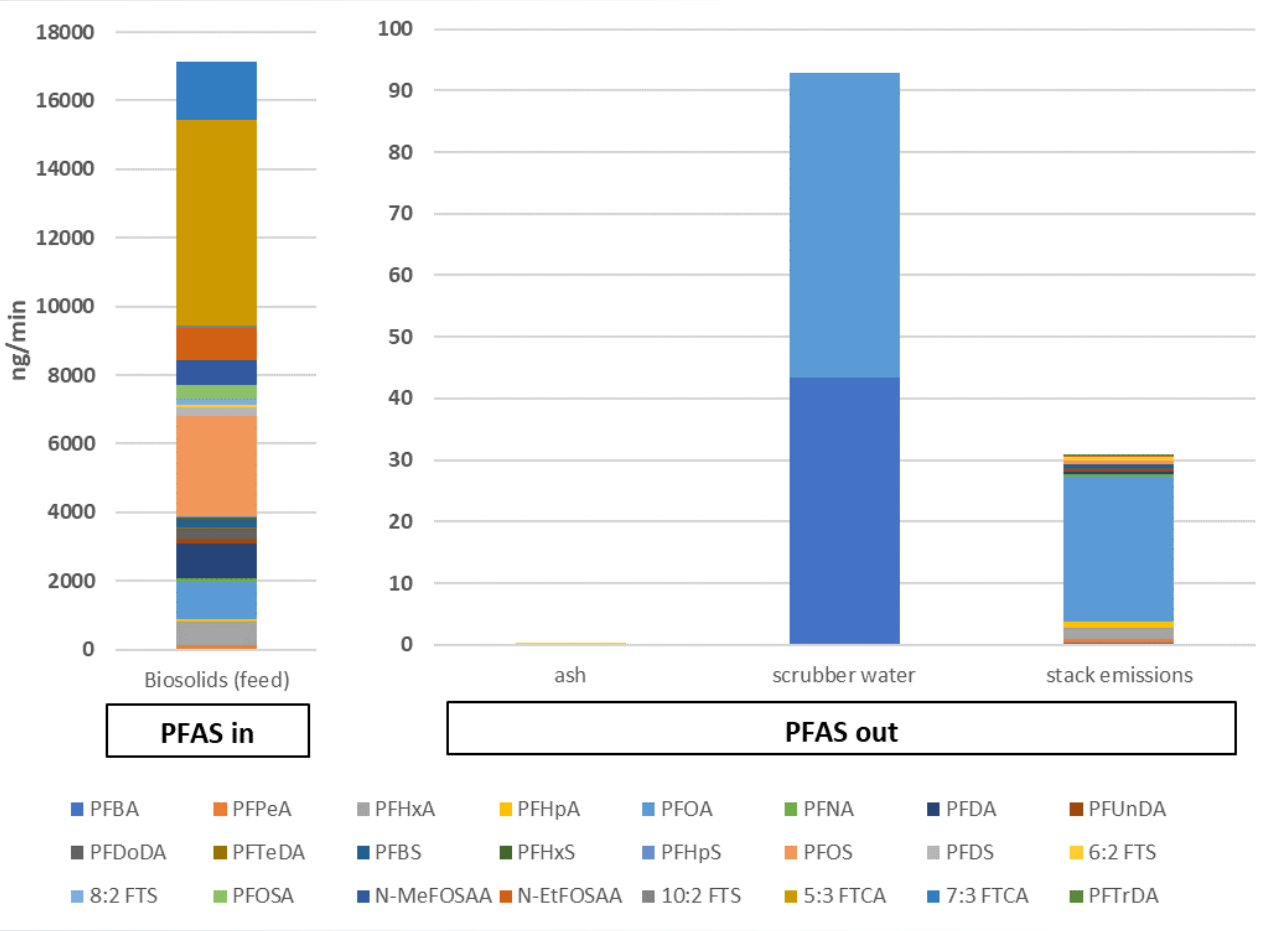
Feed	Fluidizing gas	Bed temperature	Freeboard temperature	Air Pollution Control Systems (APCs)
Biosolids	Air	700 C 1300 F	850 C 1550 F	Cyclone separator, Baghouse, Venturi scrubber
GAC	Nitrogen	800 C 1450 F	850 C 1550 F	Cyclone separator, Baghouse, Venturi scrubber, Thermal oxidizer (1100 C, 2000 F)

Pilot-Scale Fluidized Bed Reactor



- Emissions sampled at reactor outlet (all runs), venturi outlet (sludge incineration runs), and thermal oxidizer (not pictured, GAC reactivation runs)

Biosolid incineration results



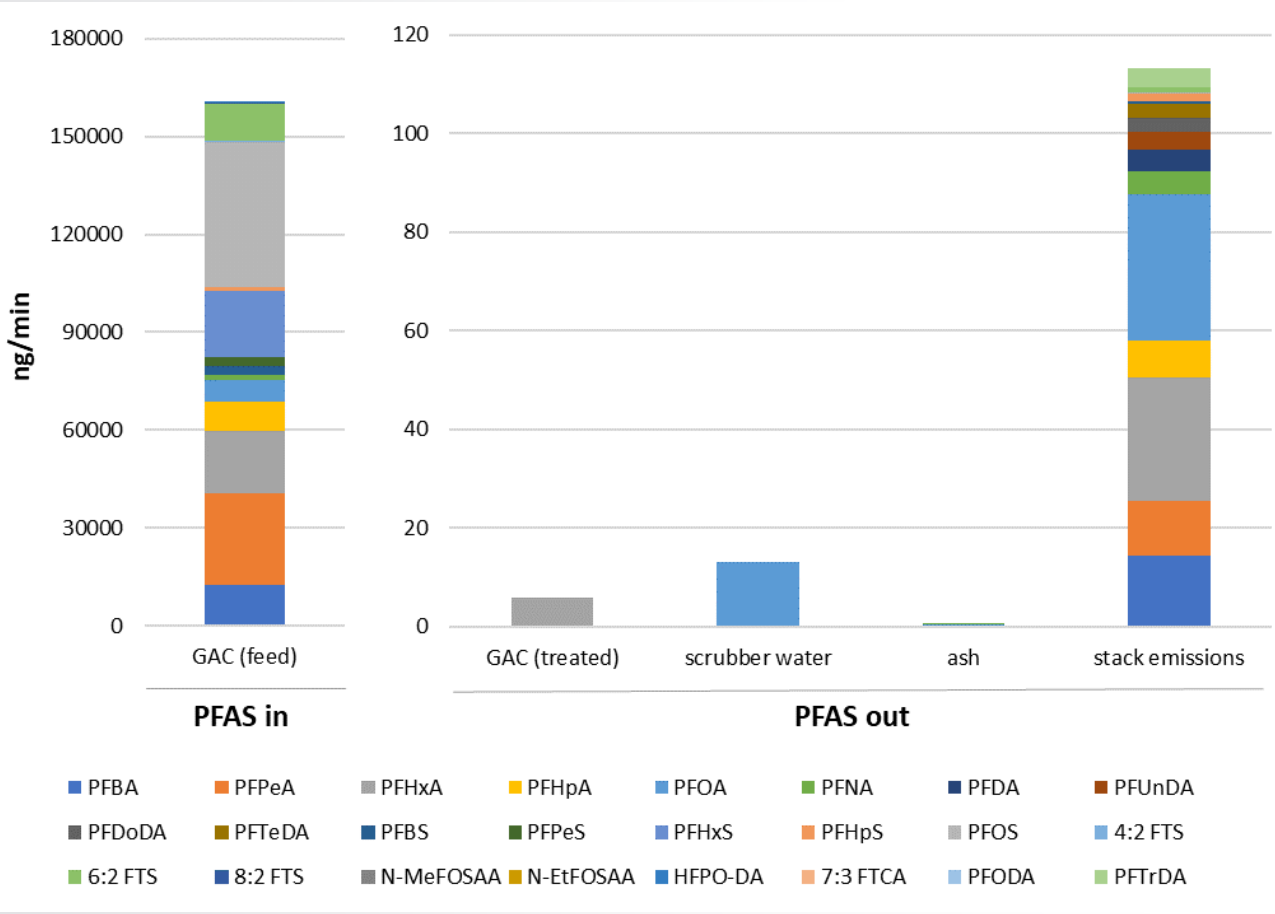
- >99.3% DRE for exhaust + residuals
- Likely transformation of precursors (FTCAs and FOSAAs) to PFCAs (PFOA)
  - Precursors make up ~50% of targeted PFAS in biosolids feed, not detected in exhaust + residuals

PICs?

- Analysis of the M0010 impinger train for Tentatively Identified Compounds (TICs) showed only one fluorinated potential PIC: 2-Fluorobiphenyl
  - 2-Fluorobiphenyl was only detected in the combustion blank run prior to the biosolids incineration runs
  - Biosolids had been introduced to the fluidized bed reactor during preliminary testing to determine feed and flow rates, conditions were not steady state, leading to the formation of this PIC

- 2-Fluorobiphenyl was not detected during any other sampling run, indicating the temperature ramps and combustion blank runs sufficiently cleaned the reactor between biosolid experiments and GAC experiments

GAC regeneration results

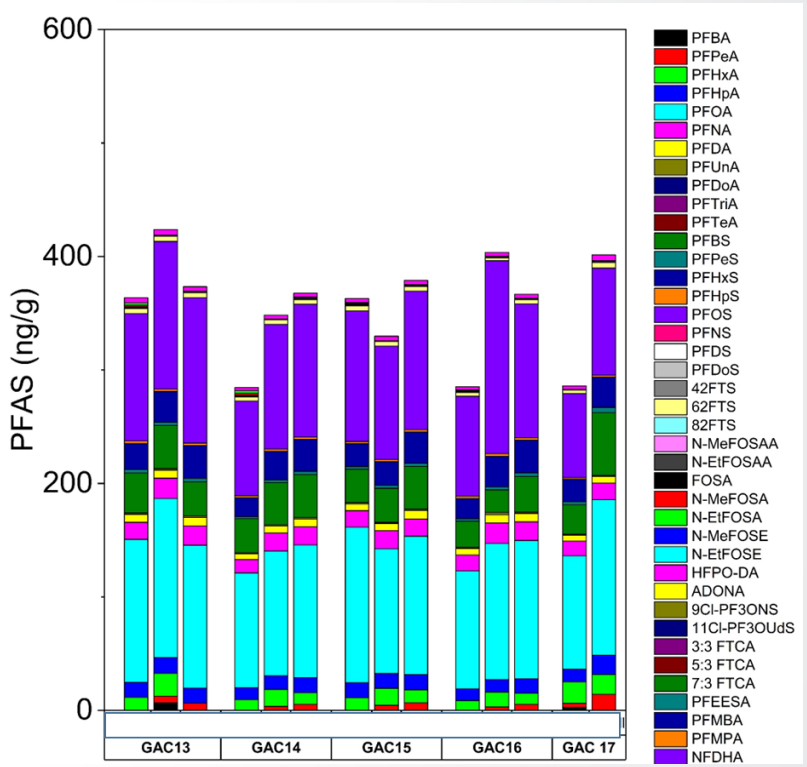


- >99.99% DRE for treated GAC
- >99.9% DRE for exhaust + residuals

- Formation of long chain PFAS (≥ C9) including PFTrDA and PFTeDA only detected after the thermal oxidizer, likely condensation of chain fragments from other PFAS

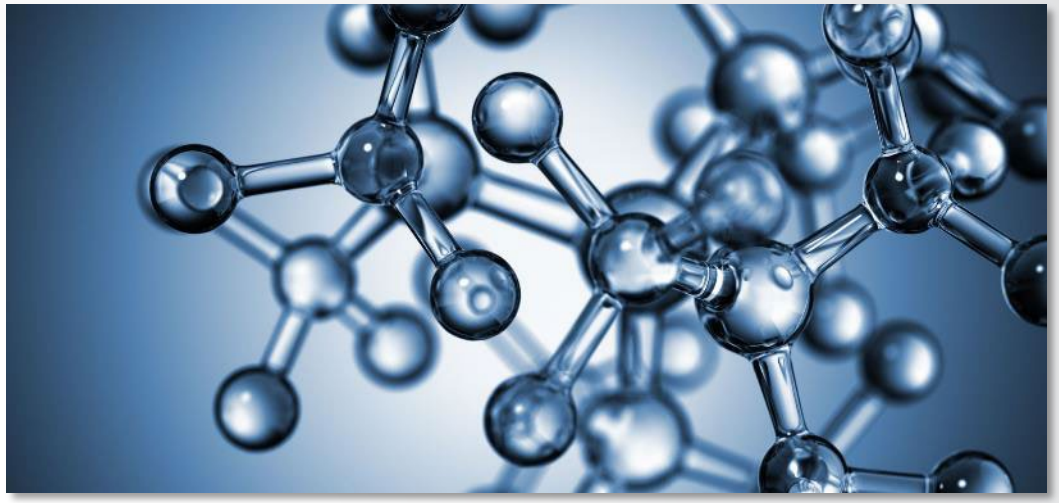
Granular Activated Carbon (GAC) Reactivation – Drinking Water Treatment Plant

- Drinking water POTW performing on-site GAC reactivation in a multiple hearth furnace
- Multiple hearth furnace equipped with thermal oxidizer, venturi scrubber, and tray scrubber
- Sampling event completed
  - Emissions sampling with OTM-45, MM0010, M26A (HF), and OTM-50 (canister)
  - Spent GAC, reactivated GAC, scrubber water, and other inputs collected



PFAS concentrations on spent GAC feed

Questions?



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EPA PFAS Activities – www.epa.gov/pfas

PFAS Research and Development – www.epa.gov/chemical-research/research-and-polyfluoroalkyl-substances-pfas