Understanding Per- and Polyfluoroalkyl Substances (PFAS) in Air

Environmental Measurement Symposium / National Environmental Monitoring Conference – August 4, 2020

Lara P. Phelps
Director, Air Methods and Characterization Division, Center for Environmental Measurement and Modeling
US EPA Office of Research and Development

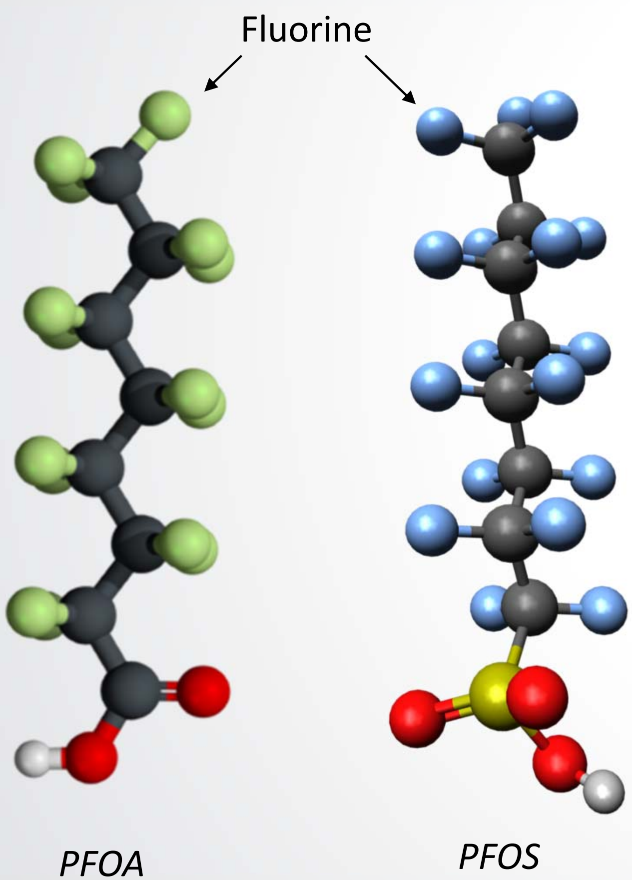
Presentation Overview

- General Background
- Air Research
  - Methods Development
  - Dispersion Modeling
  - Thermal Treatment
- Planned Products

General Background

- Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that have been in use since the 1940s, found in a wide array of consumer products and facilities
- Most people have been exposed to PFAS. Some PFAS chemicals can accumulate and stay in the human body for long periods of time
- There is evidence that exposure to certain PFAS may lead to adverse health effects
- PFAS is an issue of high and growing concern for EPA customers and the public, and so EPA is committed to taking action to address public concerns

Per- & Polyfluoroalkyl Substances (PFAS)



- **A class of man-made chemicals**
  - **Chains** of carbon (C) atoms surrounded by fluorine (F) atoms, with different terminal ends
  - **Complicated chemistry** – thousands of different variations exist in commerce
  - **Widely used** in industrial processes and in consumer products
  - **Some** PFAS are known to be **PBT**:
    - **Persistent** in the environment
    - **Bioaccumulative** in organisms
    - **Toxic** at relatively low (ppt) levels

Thousands of chemicals can become air sources during production, use, and disposal of PFAS-contaminated materials

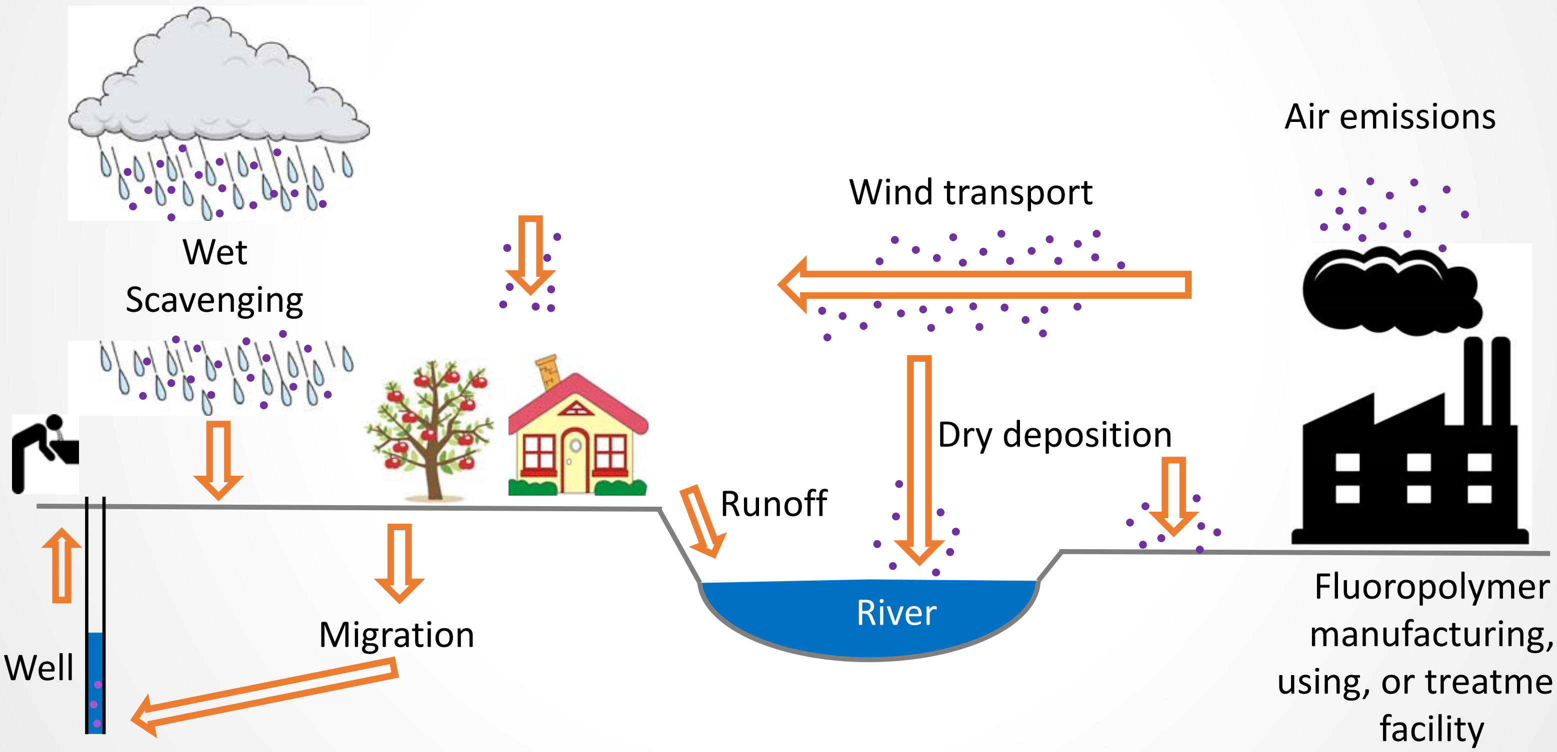
PFAS

- **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** $C_nF_{2n+1}SO_2$-R, R = NH, $NHCH_2CH_2OH$, etc.
  - **Perfluoroalkyl iodides (PFAIs)** $C_nF_{2n+1}I$
    - → **Fluorotelomer iodides (FTIs)** $C_nF_{2n+1}CH_2CH_2I$
      - → **FT-based derivatives** $C_nF_{2n+1}CH_2CH_2$-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)
    - Others
  - **Side-chain fluorinated polymers**
    - Fluorinated (meth)acrylate polymers
    - Fluorinated urethane polymers
    - Fluorinated oxetane polymers
  - **Perfluoropolyethers**

Known Sources of PFAS in the Environment

- Direct release of PFAS or PFAS products into the environment
  - Use of aqueous film forming foam (AFFF) in training and emergency response
  - Industrial facilities
  - Incineration/thermal treatment facilities
- Landfills and leachates from disposal of consumer and industrial products containing PFAS
- Wastewater treatment effluent and land application of biosolids

Air Emissions Contribute to PFAS Concentrations



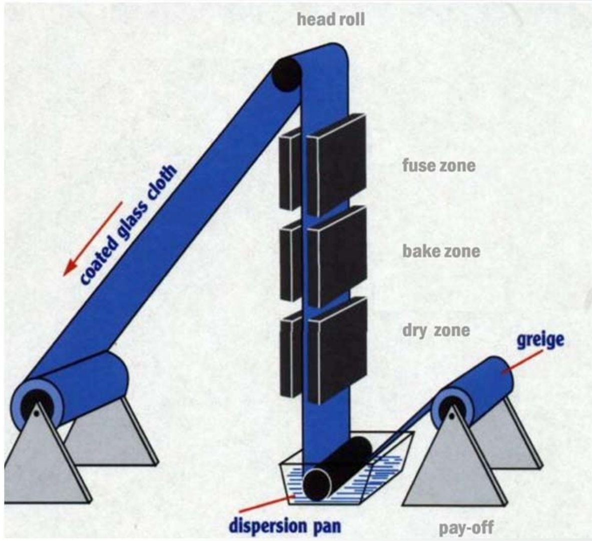
Adapted from:
Davis, K. et al. Chemosphere, 2007.

EPA PFAS Air-Related Research

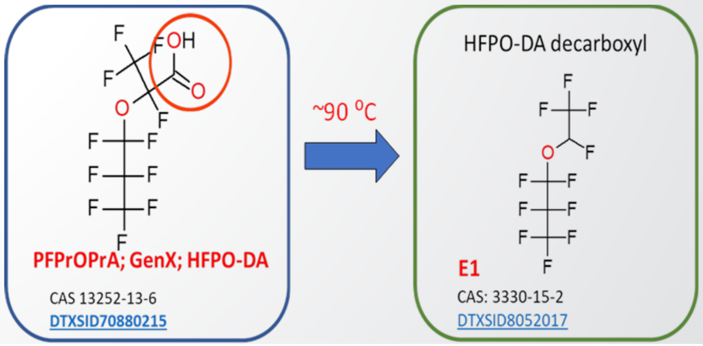
- **Analytical Methods** to detect, identify, quantify PFAS in emissions and ambient air
- **Dispersion Modeling** to predict air transport and deposition associated with air sources
- **Effectiveness of Thermal Treatments** for destroying PFAS materials

Emission Measurement Considerations

- Emission sources are diverse:
  - PFAS chemical manufacturers
  - PFAS used in commercial applications
  - PFAS emitted during thermal treatment of waste (e.g., AFFF, biosolids, municipal)
  - Products of Incomplete Combustion (PICs)
- Process can alter emission composition
- Validated source and ambient air methods for PFAS do not exist, but some research methods are available
- Current emissions tests often target only a small number of PFAS compounds for analysis while significantly more may be present
- Emissions measurements are needed for source characterization
- Emissions measurements are needed for control technology evaluation



Example Coating Process

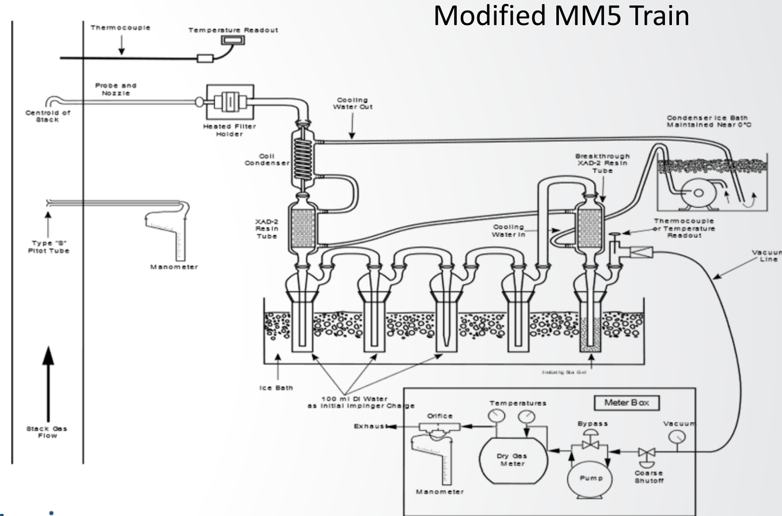


Source Methods Development

No Validated (Only Research) Methods for PFAS Emissions

- Considering both sampling and analysis methods, targeted and non-targeted
- Diverse sources – chemical manufacturers, commercial applications, thermal treatment incineration processes
- Methods needed for source characterization and for control technology evaluation

Modified MM5 Train



Method Development Details

- **Semi/Non-Volatiles** – Performance-based, Modified Method 5 train (i.e., Other Test Method [OTM] 45) approach using isotope dilution, GC/MS targeted and non-targeted analysis. For Modified Method 5, see: https://www.epa.gov/hw-sw846/sw-846-test-method-0010-modified-method-5-sampling-train
- **Volatiles** – Modified TO-15 using SUMMA canisters, GC/MS targeted and non-targeted analysis. See https://www3.epa.gov/ttnamti1/airtox.html for methods.
- **Surrogate Indicators** – Measure PFAS as a class, e.g., Total Organic Fluorine (TOF)

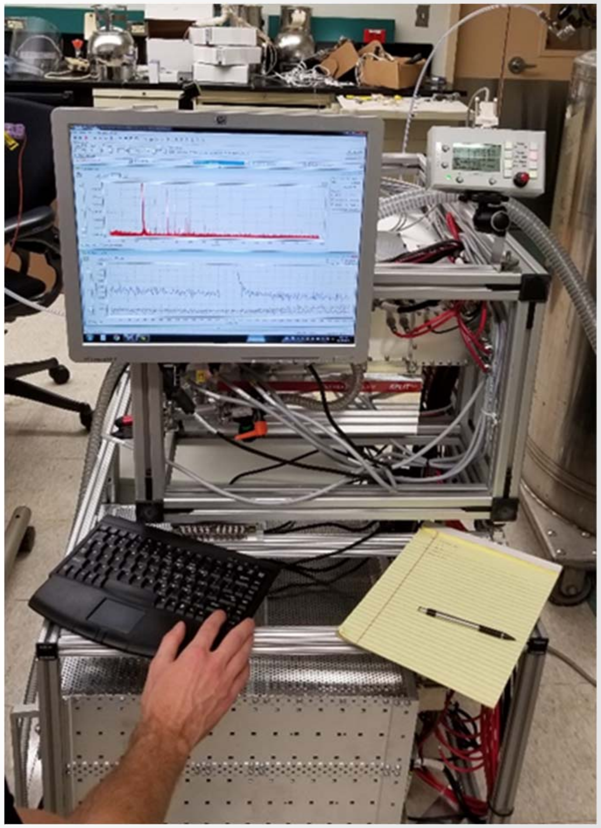
Ambient Methods Development

No Validated (Only Research) Methods for Ambient Air

- Considering both sampling and analysis methods, targeted, and non-targeted
- Applications include fenceline monitoring for fugitive emissions, deposition, and receptor exposure

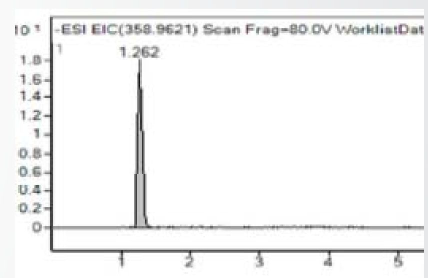
Method Development Details

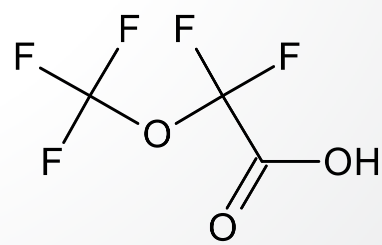
- **Ambient/Near-Source** – Field deployable Time of Flight/Chemical Ionization Mass Spectrometer for real time detection/measurement
- **Semivolatile PFAS –** Performance Based following guidance in EPA TO-13a
- **Volatile PFAS –** SUMMA canisters, sorbent traps, GC/MS targeted, and non-targeted analysis



Non-targeted Analysis

- High resolution mass spectrometry
- Software calculates exact number and type of atoms needed to achieve measured mass, e.g. $C_3HF_5O_3$
- Software and fragmentation inform most likely structure
- With mass, formula, structure known, potential identities determined by database search





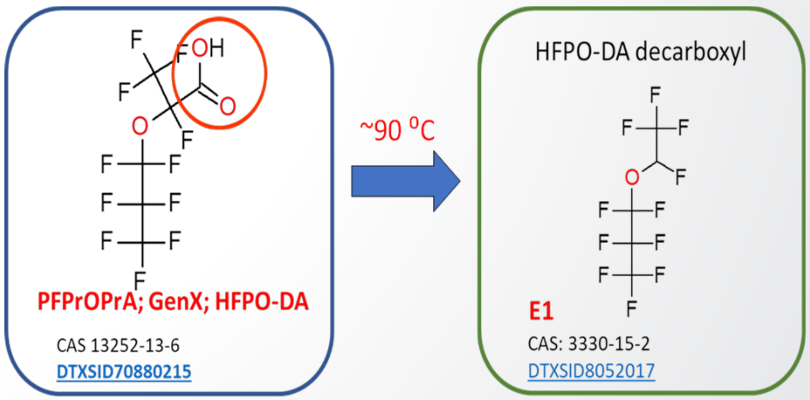
Molecular Formula: $C_3HF_5O_3$
Monoisotopic Mass: 179.984585 Da
[M-H]-: 178.977308 Da

Source: Strynar et al. 2015; Sun et al. 2016

Thermal Treatment of PFAS

- Highly electronegative fluorine makes C-F bonds particularly strong, require high temperatures for destruction
  - Unimolecular thermal destruction calculations suggest that CF_4 requires 1,440 ^{o}C for >1 second to achieve 99.99% destruction (Tsang et al., 1998)
  - Sufficient temperatures, times, and turbulence are required

- Functional group relatively easy to remove/oxidize
  - Low temperature decarboxylation is an example
  - Information regarding potential products of incomplete combustion (PICs) is lacking



Products of Incomplete Combustion (PICs)

- When formed in flames, F radicals quickly terminate chain branching reactions to act as an extremely efficient flame retardant, inhibiting flame propagation
- PICs are more likely formed with F radicals than other halogens such as Cl
- PICs may be larger or smaller than the original fluorinated Principal Organic Hazardous Constituents (POHC) of concern
  - CF_2 radicals preferred and relatively stable, suggesting the possibility of reforming fluorinated alkyl chains
  - Remaining C-F fragments may recombine to produce a wide variety of fluorinated PICs with no analytical method or calibration standards
  - May result in adequate PFAS destruction but unmeasured and unquantified PICs
- Very little information is published on PFAS destruction
  - Fluorine chemistry sufficiently different than Cl that we cannot extrapolate
  - Analytical methods and PFAS standards are lacking
  - Measurements focusing on POHC destruction may miss the formation of PICs
- Hazardous waste incinerators and cement kilns may well be effective, but what about municipal waste combustors and sewage sludge incinerators (i.e., lower temperatures)?

Incinerability & Mitigation Research

- Explore minimum conditions (temperature, time, fuel H_2) for adequate PFAS destruction

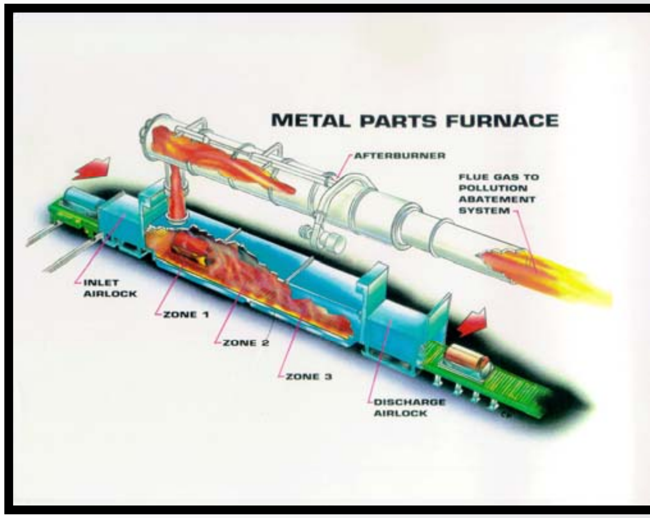
- Investigate relative difficulties in removing PFAS functional groups (POHC destruction) vs. full defluorination (PIC destruction)

- Effects of incineration conditions (temperature, time, and H_2) on PIC emissions

- Examine relative differences in the incinerability of fluorinated and well studied corresponding chlorinated alkyl species

CFS Software for EPA

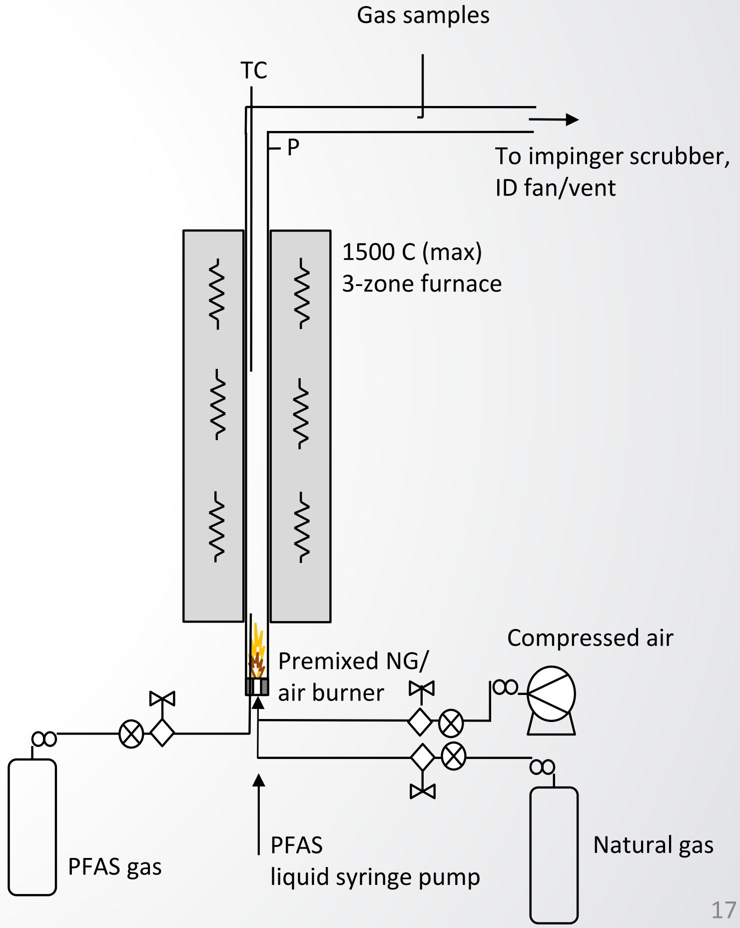
Reaction Engineering International (REI)



- The Configured Fireside Simulator (CFS)
  - Developed for the Department of Defense to evaluate operations of the chemical demilitarization incinerators processing the US chemical warfare agent stockpile
- Destruction kinetics developed
- Adapted to provide for the ability to run "what if" scenarios of waste streams contaminated with chemical and biological warfare agents
  - EPA's pilot-scale Rotary Kiln Incinerator Simulator (RKIS)
  - Three commercial incinerators based on design criteria for actual operating facilities
    - Medical/Pathological Waste Incinerator
    - Hazardous Waste Burning Rotary Kiln
    - Waste-to-Energy Stoker type combustor
- CFS uses chemical kinetic data for destruction derived from bench- and pilot-scale experiments at EPA's Research Triangle Park, NC facility

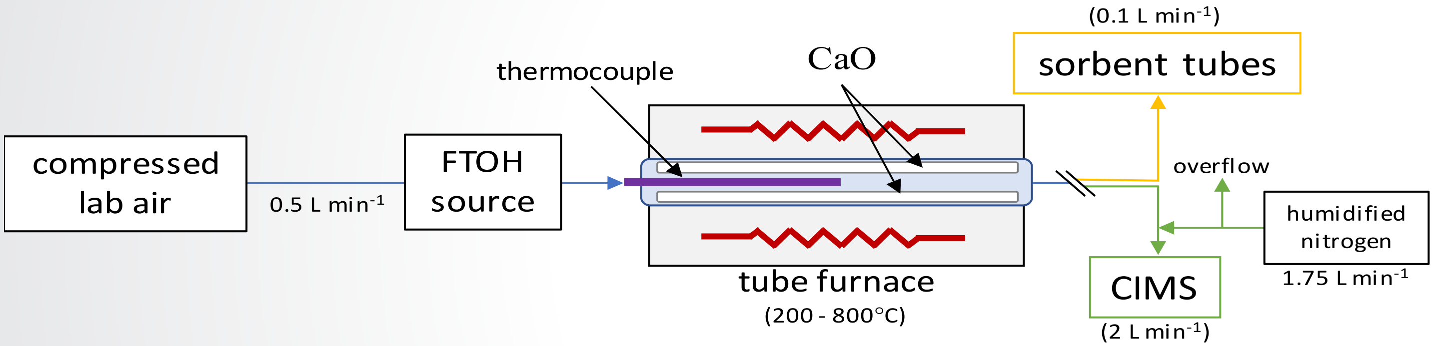
Bench-scale Incineration Experiments

- Repurpose existing equipment (i.e., formerly used for oxy-coal)
- Small scale (L/min & g/min)
- Full control of post-flame temperature & time (2-3 sec)
- Able to add either gas or liquid PFAS through or bypassing flame
- Premixed or diffusion flames possible
- Platform for measurement methods development (e.g., SUMMA, sorbent, total F, GC/ECD, real-time instruments)

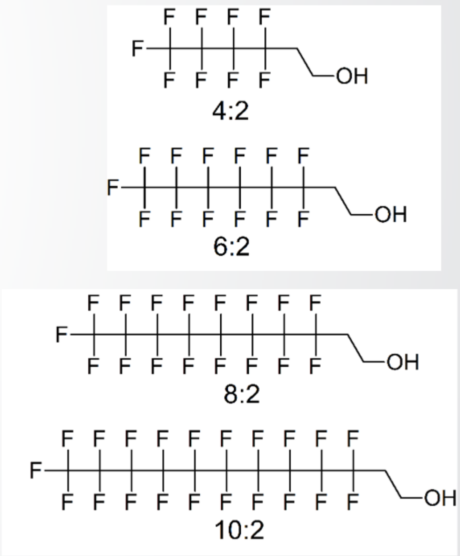


Tube Furnace Experiments

Experimental Setup



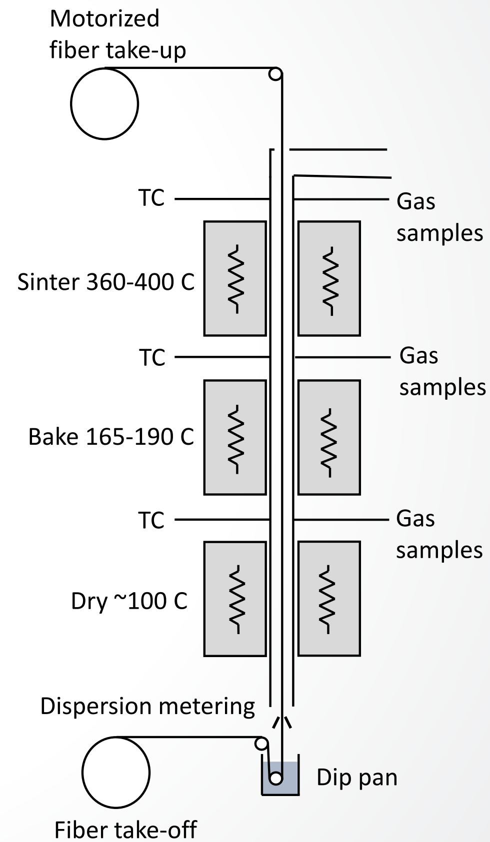
PFAS Fluorotelomer Alcohols Tested:

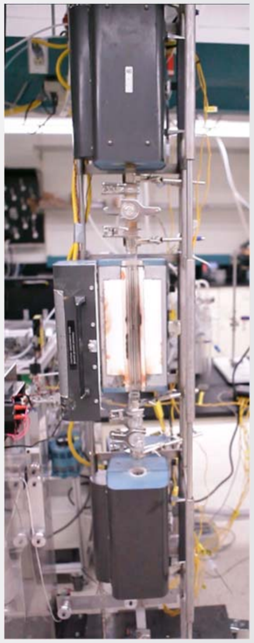


- Thermal treatment with calcium oxide (CaO) from 250 to 800 °C
- Observe destruction of parent compound using two techniques: CIMS and sorbent tube analysis by TD-GC/MS
- TD-GC/MS analyses show the presence of degradation products from FTOH destruction

String Reactor Experiments

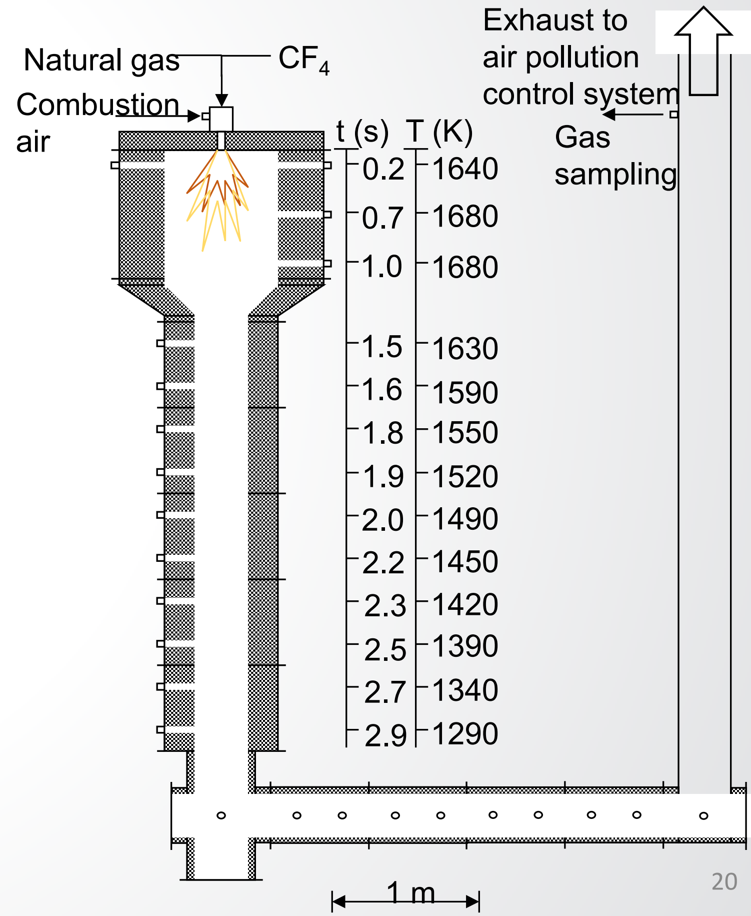
- **New experiment that simulates industrial PFAS coating facilities**
  - Built from 3 existing furnaces
  - Applies commercial dispersions to fiber (string)
  - Full control of flows, times, temperatures, application rates
  - Small scale (L/min & g/min)
  - Located in lab w/ real-time instruments
- **Investigates key research questions:**
  - What PFAS & additives are present in different commercial dispersions?
  - What PFAS (and other species) are vaporized during application processes?
  - How do vapor phase PFAS emissions compare to dispersion compositions?
    - Are surfactants (GenX, telomer alcohols) included in the vapor emissions?
  - Are processing temperatures sufficient to transform PFAS?
    - Cleave functional groups to produce new PFAS?
    - Are processing temperatures sufficient to cleave C-F bonds and produce F2 and HF?
  - How do processing temperatures and times affect vapor and aerosol emissions (mass and composition)?





Pilot-scale Incineration Experiments

- 65 kW refractory lined furnace (aka Rainbow Furnace) with peak temperatures at ~1400 ⁰C, and >1000 ⁰C for ~3 sec
- Combustor connected to facility air pollution controls
  - Afterburner, baghouse, NaOH scrubber
- Introduce C1 and C2 fluorinated compounds with fuel, air, post flame to measure POHC destruction and PIC formation
  - FTIR and other real-time and extractive methods
- Add modeling component using REI's Configured Fireside Simulator (CFS) CFD/kinetic model to include C1 & C2
  - F chemistry from literature (Burgess et al. [1996])



Field-scale Incineration Experiments

- Evaluating a variety of technologies and approaches for the thermal destruction of PFAS
- Collection of replicate samples using different systems
  - Modified SW-846 Method 0010 Train (MM5) to collect polar and nonpolar, semivolatile and nonvolatile PFAS compounds
  - Modified Method 18 PFAS sampling train developed by Test America to collect polar, volatile PFAS
  - EPA-ORD's SUMMA canister sampling method to collect nonpolar, volatile PFAS
- Analysis includes targeted (known analytes) and non-targeted (high resolution mass spectrometry for unknown PFAS) , and a proof-of-concept test for a Total Organic Fluorine (TOF) method

- **(OPTION)** Surrogate testing using carbon tetrafluoride (CF4) or hexafluoroethane (C2F6) as a surrogate for PFAS
  - CF4 in particular has a very strong C-F bond which would give confidence in the thermal destruction of C-F bonds in PFAS (note CF4 is used as refrigerant and is a GHG)
  - Advantage of using a surrogate is that the test would be for a short duration (~1hr)
  - FTIR used to continuously monitor emissions

PFAS Innovative Treatment Team (PITT)

- Full-time team that brings together a multi-disciplined research staff
- Charge: How to remove, destroy, and test PFAS-contaminated media and waste
- Goals:
  - Assess current and emerging destruction methods being explored by EPA, universities, other research organizations, and industry
  - Explore the efficacy of methods while considering by-products to avoid creating new environmental hazards
  - Evaluate methods' feasibility, performance, and costs to validate potential solutions
- Expected Results: States, tribes, and local governments will be able to select the approach that best fits their needs, leading to greater confidence in clean-up operations and safer communities
- Deadline: Later this year

Non-Incineration Technologies Reviewed

- Chemical
- Biological
- Plasma
- Mechanochemical
- Sonolysis
- Ebeam
- UV
- Supercritical water oxidation
- Deep well injection
- Sorption/stabilization
- Electrochemical
- Landfill
- Land application

Assessment Factors:
- Technology readiness
- Applicability
- Cost
- Required development remaining
- Risk/reward of technology adoption

Innovative technologies selected for further investigation.

Planned Products

- **ORD Products on Fundamental Understanding of Thermal Treatment**
  - TGA/MS Thermal Destruction Temperature Points with Off Gas Measurements on Potential Defluorination
  - PFAS Model Incorporation of Published C1 and C2 Fluorocarbon Kinetics to Predict Simple PFAS Behavior in Incineration Environments
  - Low Temperature Interactions of PFAS with Sorbents from Bench-Scale Experiments
  - Thermal Destruction of PFAS from Pilot-Scale Experiments
- **ORD Measurement Methods for PFAS**
  - Quantitative Assessment of Modified Method 5 Train for Targeted PFAS
  - PFAS Method OTM 45
  - Total Organic Fluorine Methods
  - Non-targeted Measurement Approaches to Identify PFAS
- **Other Contributions**
  - Supporting Incineration Guidance as part of the National Defense Authorization Act

EPA's PFAS Research

- The EPA is rapidly investigating PFAS to prioritize risk and needs
- This research is organized around:
  - identifying **analytical methods**
  - understanding **toxicity**
  - understanding **exposure**
  - identifying effective **treatment and remediation** actions
- Visit EPA's website – Research on Per- and Polyfluoroalkyl Substances (PFAS):

  https://www.epa.gov/chemical-research/research-and-polyfluoroalkyl-substances-pfas

Questions

Lara P. Phelps, Director
Air Methods and Characterization Division,
Center for Environmental Measurement and Modeling
US EPA Office of Research and Development

phelps.lara@epa.gov
(919) 541-5544 – Office
(984) 287-0594 – Cell

The views expressed in this presentation are those of the individual author and do not necessarily reflect the views and policies of the US EPA