Understanding Per- and Polyfluoroalkyl Substances (PFAS) in Air

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Presentation Overview

- General Background

- Air Research
  - Methods Development
  - Dispersion Modeling
  - Thermal Treatment

- Planned Products
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.
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.
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

Fluoropolymer manufacturing, using, or treatment facility

Air emissions

Wet Scavenging

Runoff

Migration

Well

River

Dry deposition

Wind transport

Adapted from:
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

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](https://www.epa.gov/hw-sw846/sw-846-test-method-0010-modified-method-5-sampling-train)
- **Volatile**s – Modified TO-15 using SUMMA canisters, GC/MS targeted and non-targeted analysis. See [https://www3.epa.gov/ttnamti1/airtox.html](https://www3.epa.gov/ttnamti1/airtox.html) for methods.
- **Surrogate Indicators** – Measure PFAS as a class, e.g., Total Organic Fluorine (TOF)
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. C₃HF₅O₃
• Software and fragmentation inform most likely structure
• With mass, formula, structure known, potential identities determined by database search

Molecular Formula: C₃HF₅O₃
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 CF₄ requires 1,440 °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
  • CF₂ 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)?
• Explore minimum conditions (temperature, time, fuel H₂) 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 H₂) 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**

- 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

**PFAS Fluorotelomer Alcohols Tested:**

- FTOH source (2 L min⁻¹)
- Humidified nitrogen (1.75 L min⁻¹)
- Sorbent tubes
- Thermocouple
- Tube furnace (200 - 800 °C)
- CaO

**Experimental Setup Diagram:**

- Compressed lab air (0.5 L min⁻¹)
- FTOH source
- Tube furnace (200 - 800 °C)
- CaO
- Thermocouple
- Sorbent tubes
- Overflow
- Humidified nitrogen
- TD-GC/MS (2 L min⁻¹)
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 °C, and >1000 °C 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
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

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