EPA PFAS Air Emission Measurements: Activities and Research

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Presentation Overview ...

- What are PFAS?
- Why are they an air issue?
- What are the measurement factors?
- What are we doing?
- Wrap-up
Per- and Polyfluoroalkyl Substances (PFAS)

- A class of man-made chemicals used for multiple purposes
  - Chains of carbon (C) atoms surrounded by fluorine (F) atoms
    - Stable C-F bond
    - Many include a polar end
  - Some are persistent, bioaccumulative, and toxic

*Perfluorooctanoic acid (PFOA)*  *Perfluorooctanesulfonic acid (PFOS)*
Thousands of chemicals that can become air sources during production and use of products

Non-polymers

PFAS

Polymers

Side-chain fluorinated polymers

Fluoropolymers

Perfluoroalkyl acids (PFAAs)

Perfluorooalkane sulfonyl fluoride (PASF)

Perfluoroalkyl iodides (PFAs)

Per- and polyfluoroalkyl ethers (PFPEs)-based derivatives

Fluoropolymers

Polytetrafluoroethylene (PTFE)
Polyvinylidene fluoride (PVDF)
Fluorinated ethylene propylene (FEP)
Perfluoroalkoxyl polymer (PFA)
Others

Fluorinated (meth)acrylate polymers
Fluorinated urethane polymers
Fluorinated oxetane polymers

Perfluoroalkyl carboxylic acids (PFCAs)
Perfluorooalkane sulfonic acids (PFSAs)
Perfluoroalkyl phosphonic acids (PFPAs)
Perfluoroalkyl phosphinic acids (PFPIAs)

C_{n}F_{2n+1}SO_{2}F

C_{n}F_{2n+1}SO_{2}F-R, R = NH, NHCH_{2}CH_{2}OH, etc.

C_{n}F_{2n+1}^{I}

C_{n}F_{2n+1}CH_{2}CH_{2}I

C_{n}F_{2n+1}CH_{2}CH_{2}I-R, R = NH, NHCH_{2}CH_{2}OH, etc.

Polyfluoroalkyl ether carboxylic acids

Fluorotelomer iodides (FTIs)

C_{n}F_{2n+1}CH_{2}CH_{2}I

C_{n}F_{2n+1}CH_{2}CH_{2}I-R, R = NH, NHCH_{2}CH_{2}OH, etc.
Used in Homes, Businesses, & Industry

- Food contact surfaces such as cookware, pizza boxes, fast food wrappers, popcorn bags, etc.
- Polishes, waxes, and paints
- Stain repellants for carpets, clothing, upholstered furniture, etc.
- Cleaning products
- Dust suppression for chrome plating
- Electronics manufacturing
- Oil and mining for enhanced recovery
- Performance chemicals such as hydraulic fluid, fuel additives, etc.
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
- Landfills and leachates from disposal of consumer and industrial products containing PFAS
- Wastewater treatment effluent and land application of biosolids
PFAS – Air is a Significant Source

*Note Figure is not to scale*
Evidence of PFAS Air Pathway: PFOA
Evidence of PFAS Air Pathway: GenX

Source: Ohio State University
Ohio State University Conclusions

- The presence of significant levels of PFOA (>100 ng/L) in surface water more than 15 miles upstream from the facility and quantifiable levels (>10 ng/L) more than 25 miles away suggests contamination pathway via air deposition.

- The discovery of GenX at many of the collection sites suggests the replacement PFAS is contaminating the local environment via air deposition as well.
PFAS (GenX) in Rainwater

DAQ Rainwater Collection and Analysis
Concentrations in part per trillion (ppt)
January 28-29, & February 4-5, 2018 Rain Events

Source: NCDAQ
So Many PFAS Compounds!

How do we measure them?
Emissions Measurement Considerations/Challenges

- Industrial emission sources are diverse:
  - PFAS chemical manufacturers
  - PFAS used in commercial applications
  - Process can alter emission composition
- PFAS incineration sources
  - PFAS wastes (e.g., AFFF)
  - Products of Incomplete Combustion (PICs)
- Accepted source and ambient air methods for PFAS do NOT exist
- 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
PFAS emissions measurements have focused solely on PFAS targeted by water analysis methods or individual compounds.

What about other compounds?
- What about non-polars?
- What about volatiles?

What about data quality!
ORD PFAS Emissions Measurement Activities

• Supporting multiple State emissions testing campaigns
  – States and Regions are those most concerned and looking to EPA for guidance
    • OAQPS also highly interested
  – ORD collaborating to provide technical guidance and measurement assistance
  – Providing options for more comprehensive emissions characterizations
  – Analysis of industrial emissions samples for non-targeted PFAS compounds
  – Actively participating or leading field emissions tests

• Supporting Program Offices
• Methods development research
• Developing a more comprehensive analyte list
• Seeking to better understand industrial source processes, emission profiles, and control options
Methods Development Research Needs

- Formal measurement methods to inform/support policy/regulatory decisions (long-term)
- Comprehensive emission characterizations
- Control technology evaluations
- Treatment technology evaluations
Methods Development Research Needs

• What compounds to measure?
  – Legacy targets?
  – “new” designer chemicals?
  – Telomer alcohols?
  – PFAS precursors?
  – Thermal degradation products?
  – PFAS wastes and PICs?
  – HAPs?

• What kind of methods are needed?
  – Non/semi-volatiles
  – Volatiles

• Performance-based methods to assess measurement performance and data quality
ORD Emissions Methods Development Research

• Non-Volatiles:
  • Focusing on Modified Method 5 (MM5) Train-based approaches that are amenable to performance-based measurements
    • Isotope dilution
    • Use of internal and presampling surrogate standards (limited by availability of labeled standards)
  • MM5 train sample extraction/concentration recovery studies
    • Solvents
    • Extraction approach
    • Concentration approach
    • Sample stability
  • Looking at legacy PFAS to start, but also examining functional group properties for potential surrogates representative of multiple PFAS
  • Needs to be applicable to multiple sources and applications
  • Need access to field samples/conduct field tests
  • Initial goal is to develop draft Other Test Method (OTM) for OAQPS
ORD Emissions Methods Development Research

- **Volatile:**
  - Modified TO-15 for targeted and non-targeted compounds
  - Using SUMMA canisters
  - Limiting sample volume to avoid moisture condensation
  - GC/MS analysis for targeted and non-targeted compounds
    - TO-15 targets
    - Additional compounds of interest:
      - E1, E2
      - TFE
      - HFP
      - HFPO
  - On-Line Mass Spec for polar compounds
    - FTOHs
    - PFCAs?
Online Chemical Analysis: Field Deployable, Time of Flight - Chemical Ionization Mass Spectrometer (ToF–CIMS)

- Real-time measurement of PFAS and FTOHs
- Chemical specificity
  (Observe only polar compounds that ionize w/ reagent gas)
- High resolution for accurate mass determination
  (MS resolution of ~3000)
- Super sensitive (ppt measurement levels)
- High time resolution (e.g., seconds)
- Used to analyze SUMMA samples
- Currently being evaluated as a process emissions analyzer
Non-Targeted Analysis

- High resolution mass spectrometry
- Software calculates exact number and type of atoms needed to achieve measured mass, e.g. C$_3$HF$_5$O$_3$
- Software and fragmentation inform most likely structure
- With mass, formula, structure known, potential identities determined by database search

Source: Strynar et al. 2015; Sun et al. 2016
ORD Ambient Methods Development Research

- Currently in the early stages
- Mainly communications with other groups
- XAD-2/PUF extraction and analysis the main issue
- What we learn from MM5 XAD-2 extractions is likely to be applicable
- Holding ISO Ambient Measurement Workgroup kick-off meeting at EPA in May ’19
- CIMS for fence-line monitoring?
States Requesting PFAS Air Support from ORD

New Hampshire
New York
North Carolina
West Virginia
New Hampshire Support

• Provided guidance to Region 1 and NHDEQ on emission methods to comprehensively characterize emissions from an industrial coating source using and emitting PFAS, including control technology evaluation
• Developed and provided NHDEQ with a method for measuring volatile PFAS emissions, including analyzing samples by multiple MS techniques
• NHDEQ facilitated obtaining non-volatile (MM5-like) emissions samples for EPA’s methods development use
• Performing targeted and non-targeted analysis of volatile and non-volatile PFAS present in emissions
• Performing non-targeted analysis on various ancillary samples (dispersions, sumps, char, etc)
North Carolina Support

- Providing measurement guidance to Region 4 and NCDEQ
- High visibility industrial chemical manufacturing source
- Test plan and data report review and discussion
- Providing non-targeted PFAS analyses of split source emission samples
- Potential for future methods development opportunities
New York Support

- Joint ORD/NYSDEC study
- Providing emissions measurement guidance to Region 2 and NYSDEC
- Industrial PTFE sintering facility source
- ORD to perform on-site sampling for PFAS and PTFE thermal degradation products
- ORD to use on-line mass spec for real-time process characterization
- ORD to perform non-targeted PFAS analyses
West Virginia Support

• Providing measurement guidance to Region 3 and WVDEP
• High visibility industrial chemical manufacturing source
• Test plan and data report review and discussion
• Providing non-targeted PFAS analyses of split source emission samples
• Excellent methods development opportunity
ORD Research Team

Andrew Gillespie - ORD Executive Lead for PFAS R&D

ORD Experts

- Jeff Ryan
- Ingrid George
- Ken Krebs
- Dennis Tabor
- CW Lee
- Bill Linak
- Brian Gullet
- John Offenberg
- Mark Strynar
- Andy Lindstrom
- Theran Riedel
- John Washington
- James McCord
Take Home Messages

• Reliable PFAS and PFAS-related emissions measurement methods are needed for multiple purposes
• Targeted volatile and non-volatile PFAS emissions measurements of known and acceptable quality by formal performance-based methods is the ultimate goal
• **What compounds need to be targeted for measurement is the hard part**
• ORD is seeking to be responsive to States/Regions and Program Office needs
• ORD collaboration/partnership is integral
• It’s complicated!
Questions …
Thousands of **products** that become air sources

Emitted into the air during chemical production and product manufacturing, and present everywhere in our homes, schools, workplaces, hospitals …

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<th>Building Materials</th>
<th>Food Related</th>
<th>Consumer Products</th>
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