EPA PFAS Air Emission Measurements: Activities and Research

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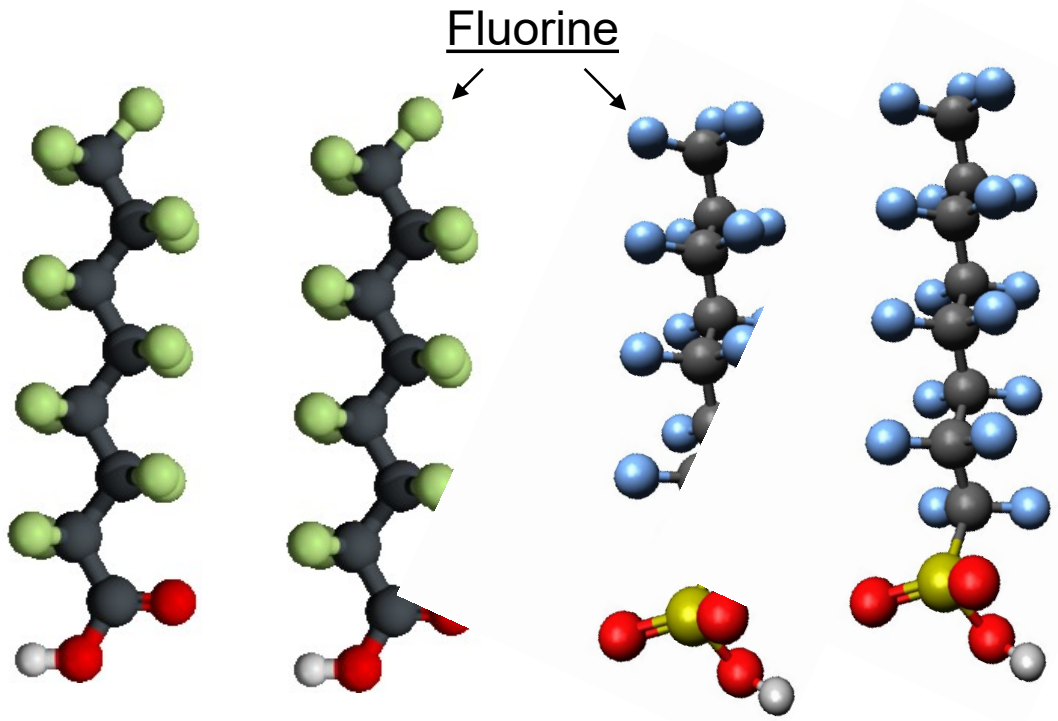
Presentation Overview …

- 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)

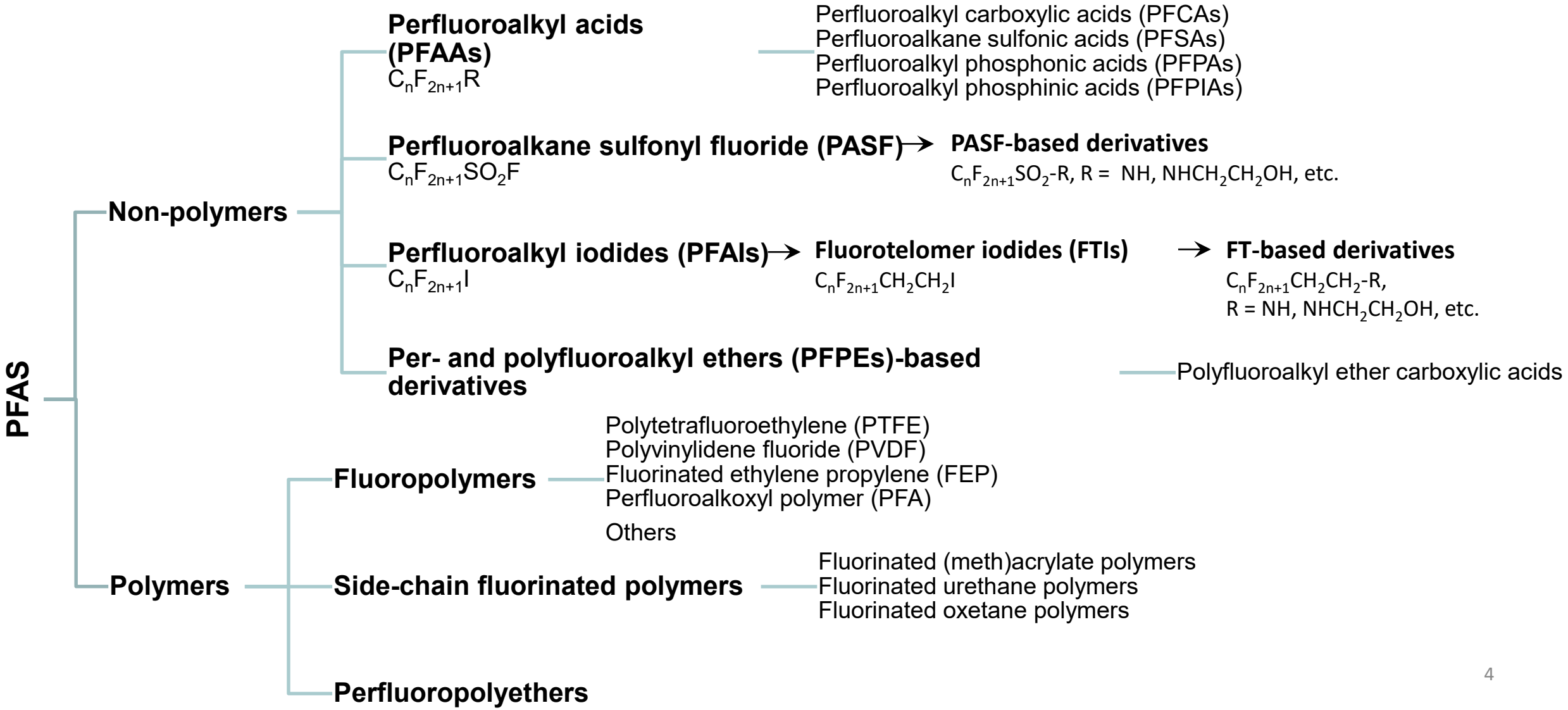


Perfluorooctanoic acid (PFOA)

Perfluorooctanesulfonic acid (PFOS)

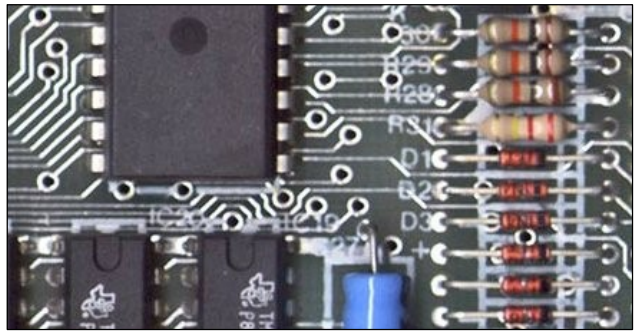
- **A class of man-made chemicals used for multiple purposes**
  - Chains of carbon (C) atoms surrounded by fluorine (F) atoms
    - Stable C-F bond
    - Many include a polar end
  - Some are persistent, bioaccumulative, and toxic

Thousands of chemicals that can become air sources during production and use of products



Used in Homes, Businesses, & Industry

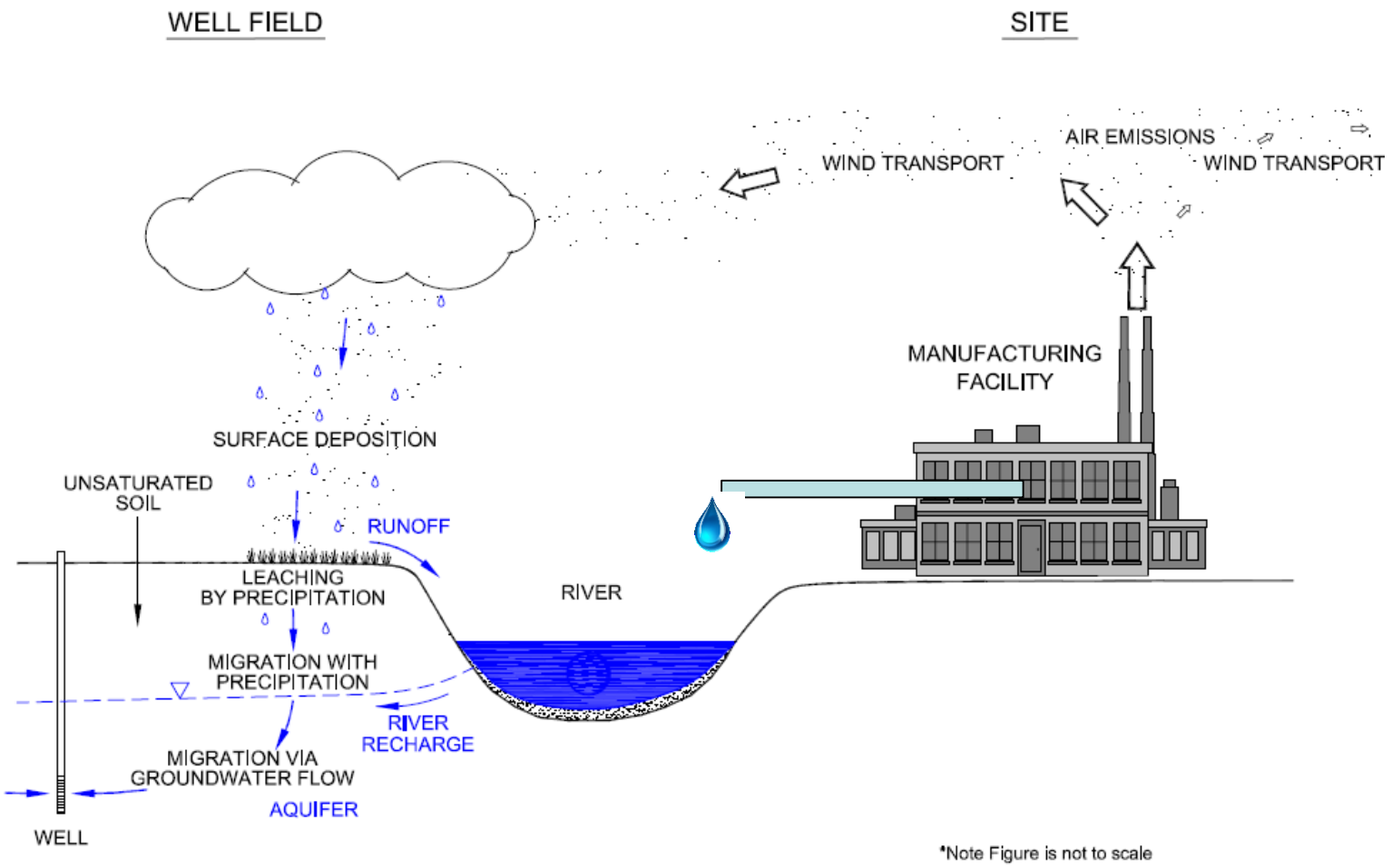
- Food contact surfaces such as cookware, pizza boxes, fast food wrappers, popcorn bags, etc.
- Polishes, waxes, and paints
- Stain repellants for carpets, clothing, upholstered furniture, etc.
- Cleaning products
- Dust suppression for chrome plating
- Electronics manufacturing
- Oil and mining for enhanced recovery
- Performance chemicals such as hydraulic fluid, fuel additives, etc.



Known Sources of PFAS in the Environment

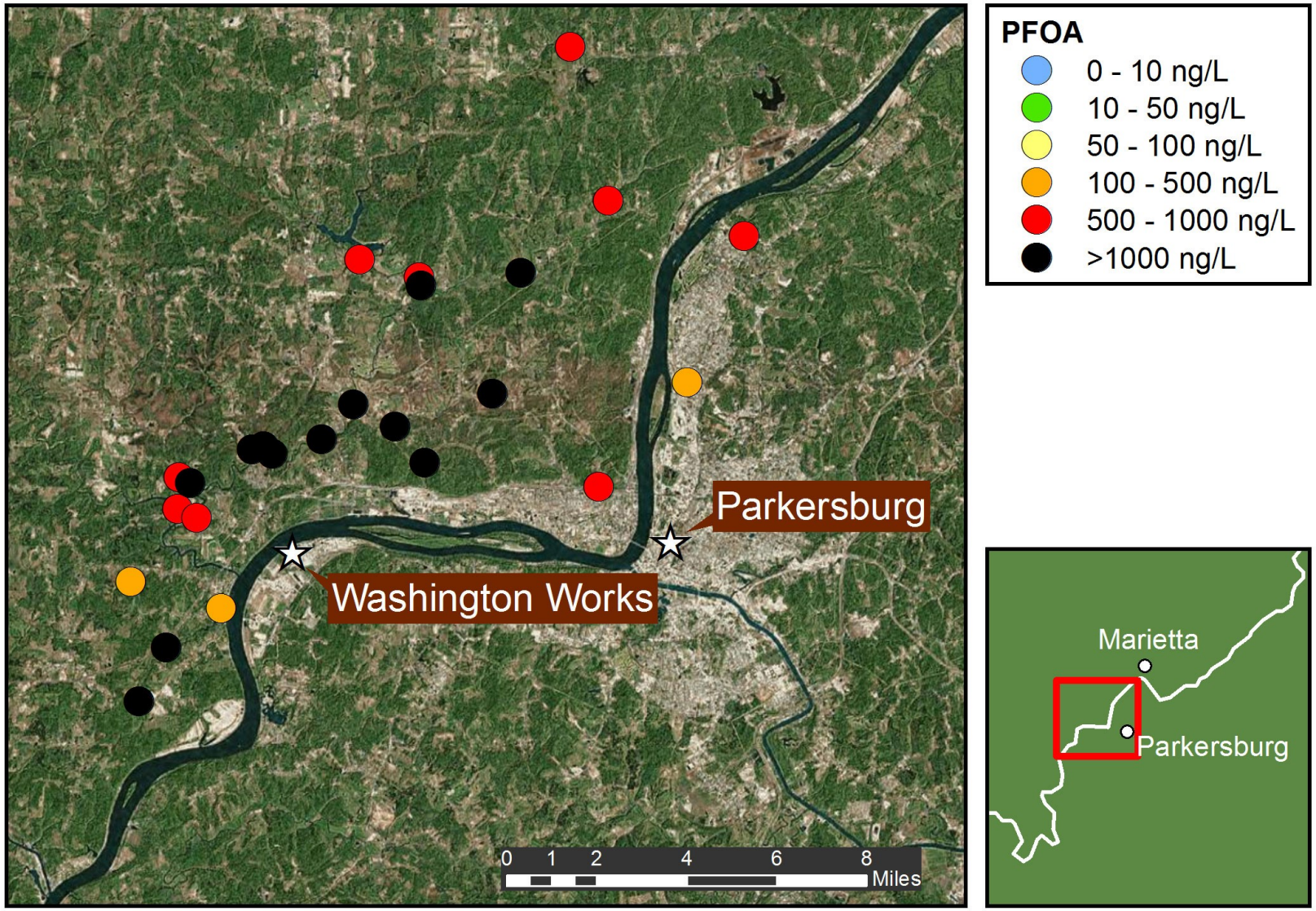
- Direct release of PFAS or PFAS products into the environment
  - Use of aqueous film forming foam (AFFF) in training and emergency response
  - Industrial facilities
- Landfills and leachates from disposal of consumer and industrial products containing PFAS
- Wastewater treatment effluent and land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

PFAS – Air is a Significant Source



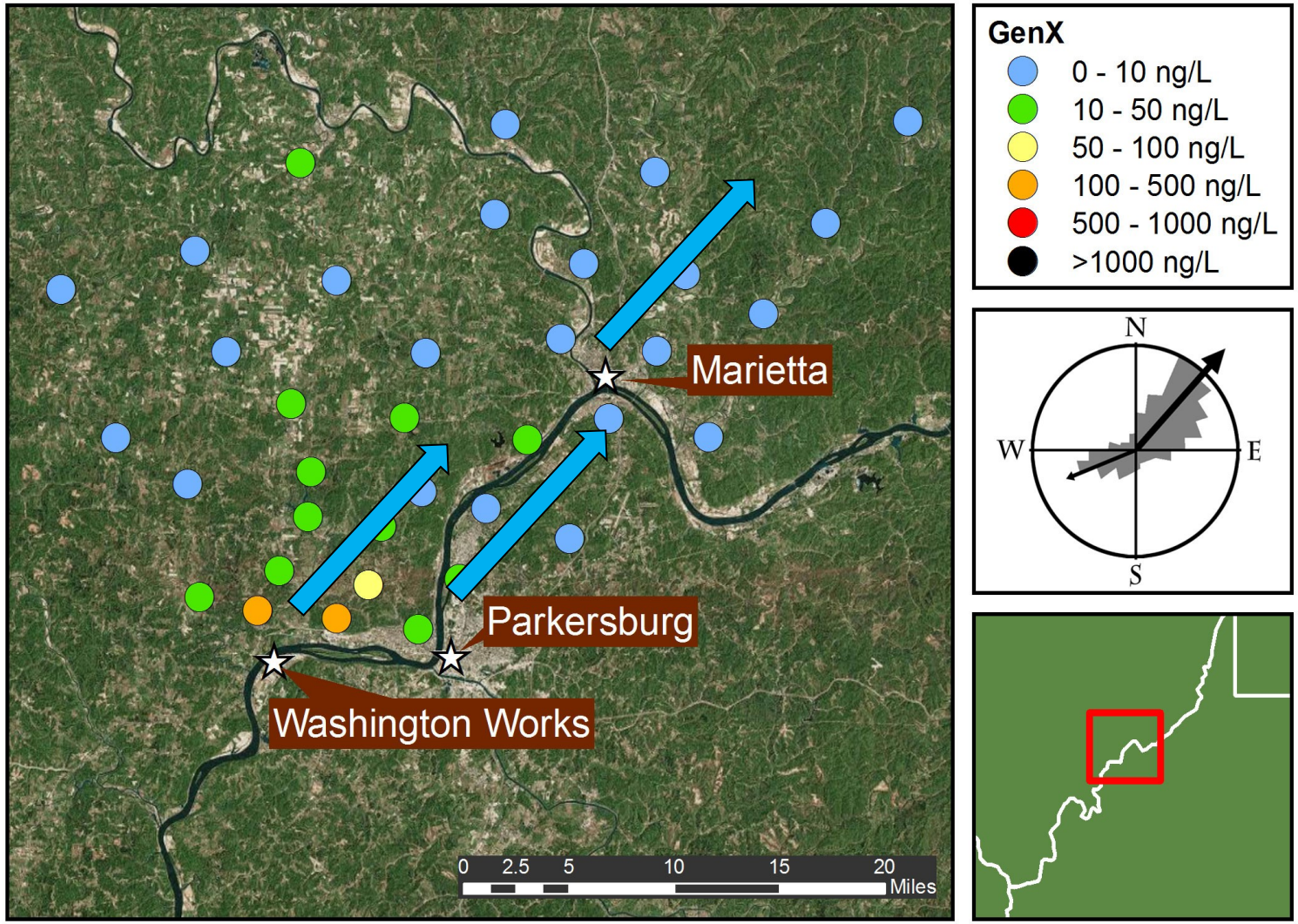
Davis et al. Chemosphere 67 (2007) 2011–2019

Evidence of PFAS Air Pathway: PFOA



Source: Ohio State University

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**

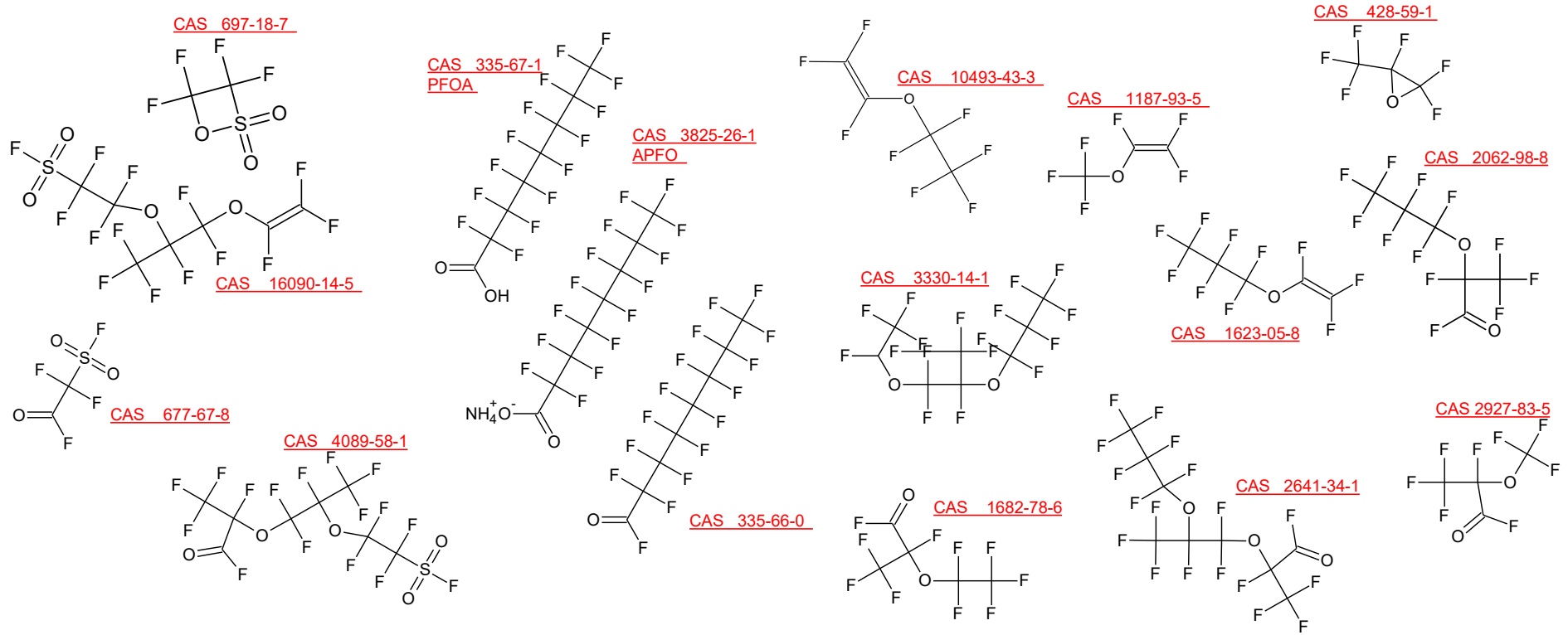
- The discovery of GenX at many of the collection sites suggests the replacement PFAS is contaminating the local environment via air deposition as well

PFAS (GenX) in Rainwater

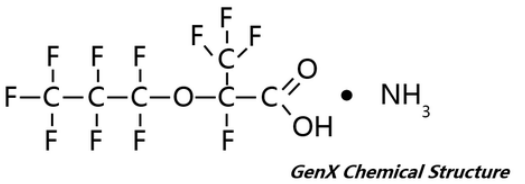
DAQ Rainwater Collection and Analysis
Concentrations in part per trillion (ppt)
January 28-29, & February 4-5, 2018 Rain Events

Source: NCDAQ

So Many PFAS Compounds!

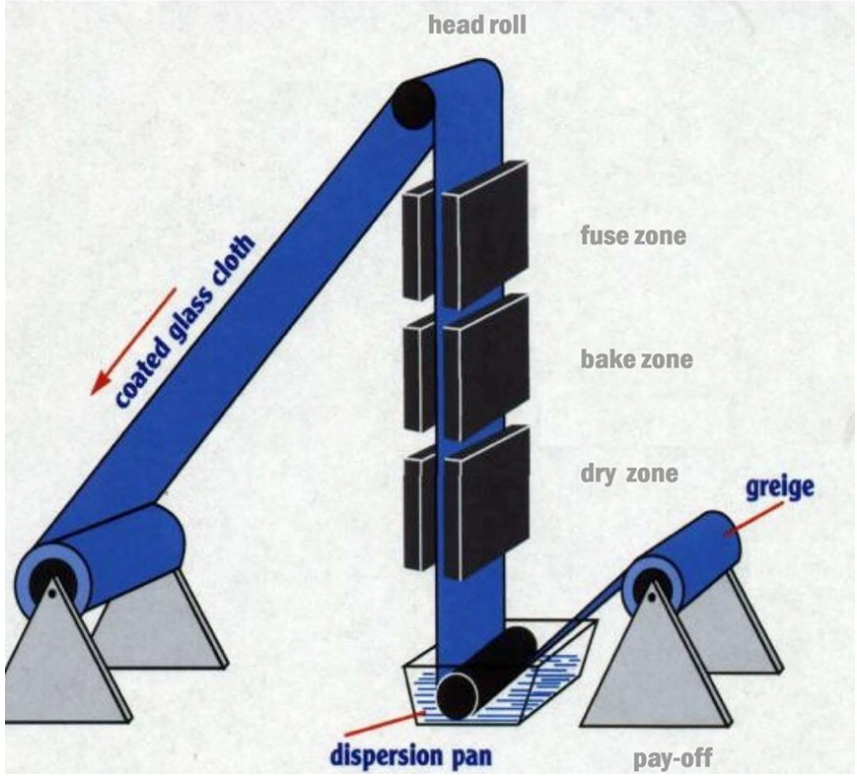


So how do we measure them?



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



Current Emissions Measurement Approaches

- 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!

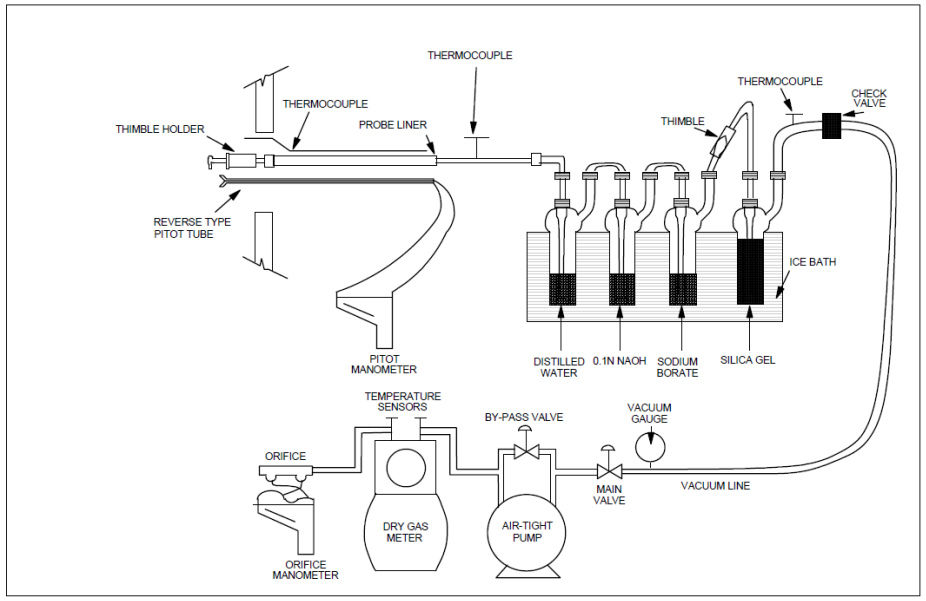
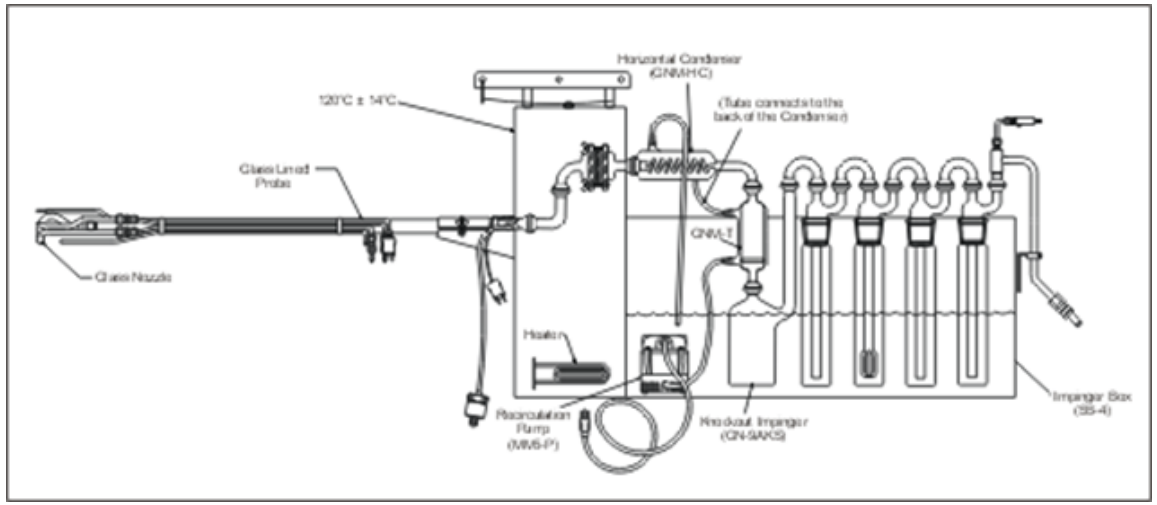


FIGURE 3-1
MODIFIED EPA METHOD 5
PFOA SAMPLING TRAIN



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

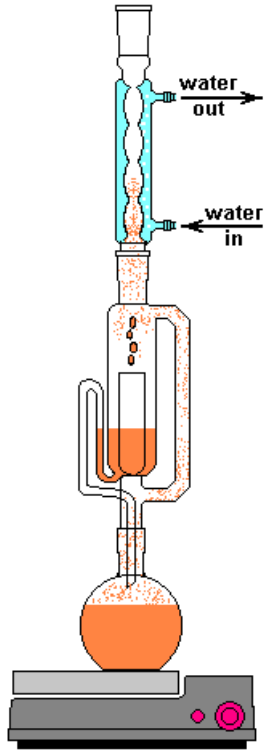
- Formal measurement methods to inform/support policy/regulatory decisions (long-term)
- Comprehensive emission characterizations
- Control technology evaluations
- Treatment technology evaluations

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**

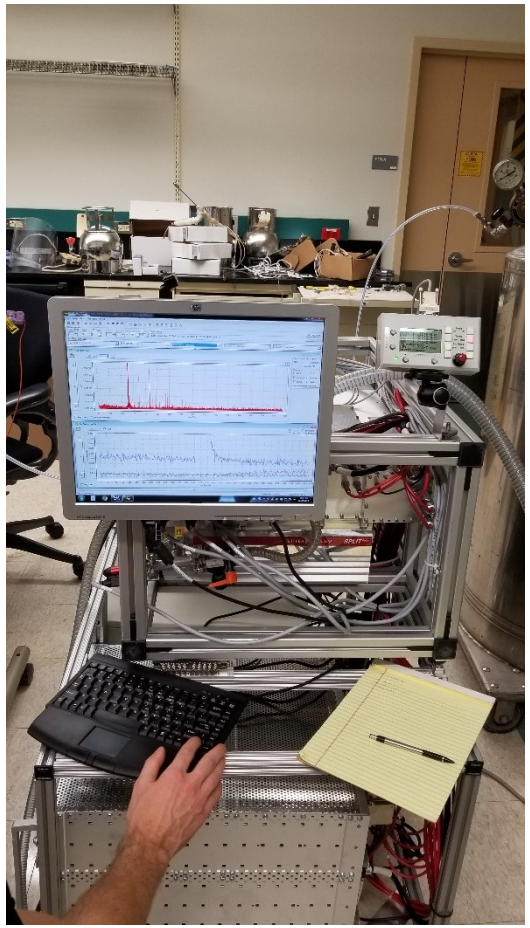


ORD Emissions Methods Development Research

- Volatiles:
  - 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?

Innovative Measurements Research

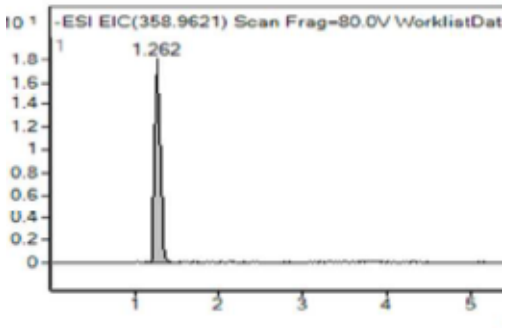
Online Chemical Analysis: Field Deployable, Time of Flight - Chemical Ionization Mass Spectrometer (ToF–CIMS)

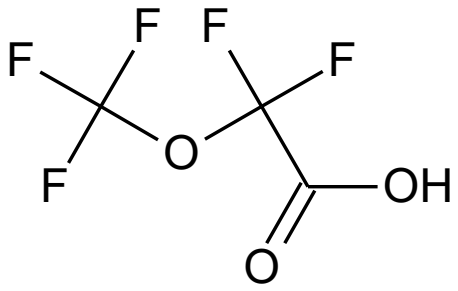


- Real-time measurement of PFAS and FTOHs
- Chemical specificity
  (Observe only polar compounds that ionize w/ reagent gas)
- High resolution for accurate mass determination
  (MS resolution of ~3000)
- Super sensitive (ppt measurement levels)
- High time resolution (e.g., seconds)
- Used to analyze 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. $C_3HF_5O_3$
- 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

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

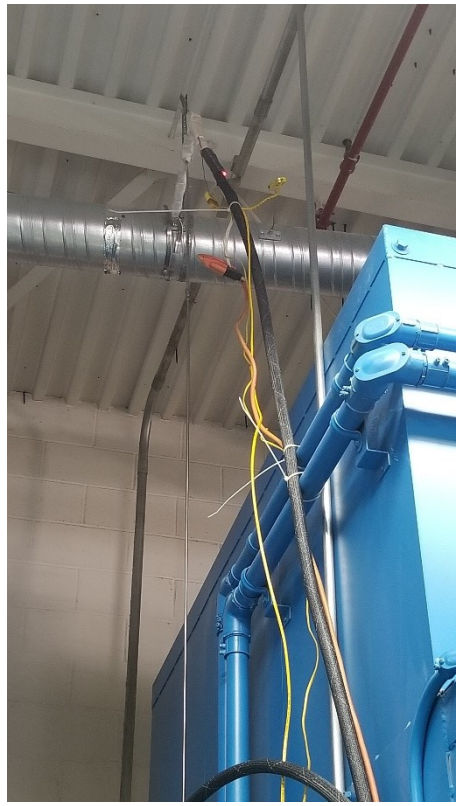
- Provided guidance to Region 1 and NHDEQ on emission methods to comprehensively characterize emissions from an industrial coating source using and emitting PFAS, including control technology evaluation
- Developed and provided NHDEQ with a method for measuring volatile PFAS emissions, including analyzing 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 ……

Clothing	**Building Materials**	**Food Related**	**Consumer Products**
Outdoor Gear	Teflon	Popcorn Bags	Cosmetics
Lab Coats	Carpets	Cookware	Dental Floss
Aprons	Paints	Cutting Boards	Boat Sails
Shirts	Window Coverings	Grille Mats	Umbrellas
Pants	Wall Coverings	Food Wraps	Dryer Sheets
Shoes	Pipe Sealants	Pizza Boxes	Whiteboards
Swimwear	Furniture	…	Car Wax
Beekeeper Suits	Stadium Roofs		Pool Tables
…	Airport Roofs		…
	Awnings		
	…		