Leveraging the High-Resolution Time-of-Flight Aerosol Mass Spectrometer to Measure PFAS Aerosols

Adam M. Deitsch[1,2], Jie Zhang[2], Alexandra M. Catena[2], Margaret J. Schwab[2], James J. Schwab[2], Sara M. Lance[2]

[1]NOAA Cooperative Science Center in Atmospheric Sciences and Meteorology
[2]University at Albany Atmospheric Sciences Research Center (ASRC)



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Background

- Per- and Polyfluoroalkyl Substances (PFAS)
  - C – H Partially or Totally Replaced by C – F
  - Extensive Class (n ≈ 15,000) of Compounds Ranging in Chemical Properties
    - e.g., Solubility, Volatility
  - Present in a Multitude of Environmental Compartments
    - Air, Landfills, Precipitation, Surface and Waste Waters [1 – 5]
      - Aqueous, Gas and Particle Phases [5]
      - Lagging Info on Atmospheric Loading and Transport

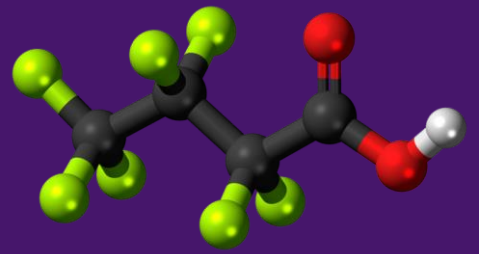
[1]Ahrens et al., *Environ. Sci. Technol.* **2011**, (45), 8098–8105.
[2]Galloway et al., *Environ. Sci. Technol.* **2020**, (54),7175–7184.
[3]Pétré et al., *Environ. Sci. Technol.* **2021**, (55),5848–5856.
[4]Pfotenhauer et al., *Atmos. Environ.* **2022**, (291), 119368.
[5]Li et al., *Environ. Sci. Technol.* ***2024,*** (58), 9283–9291.

Background

- Important Emerging Pollutant
  - Known Impacts to Human Health[6]
- We Previously Investigated PFAS Concentrations in Cloud Water and Precipitation at Whiteface Mountain (NY)[7–8]
  - Very Different from PFAS in the Current Study
    - e.g., *Much* Smaller Molecular Weight Compounds Targeted in Cloud Water Study
      - Volatile and Water Soluble
      - In Contrast to Nanoplastic PFAS Particles Used in the Current Study



Butanoic Acid[9]



Perfluorobutanoic Acid (PFBA)[10]

[6]Fenton et al., *Environ. Toxicol. Chem.* **2021**, *40*, 606
[7]Deitsch et al., *NADP Fall Meeting.* **2023**.
[8]Deitsch et al., *AMS 104th Annual Meeting.* ***2024.***
[9]https://en.wikipedia.org/wiki/Butyric_acid
[10]https://en.wikipedia.org/wiki/Perfluorobutanoic_acid

Background

- High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) Debuted About 20 Years Ago[11]
  - Chemical Analysis via Mass/Charge (m/z) Ratio of Molecular Fragments
  - Now Commonly Used Worldwide to Characterize Aerosol Composition
  - Little Evidence of Previous Use for Ambient PFAS Aerosol Sampling

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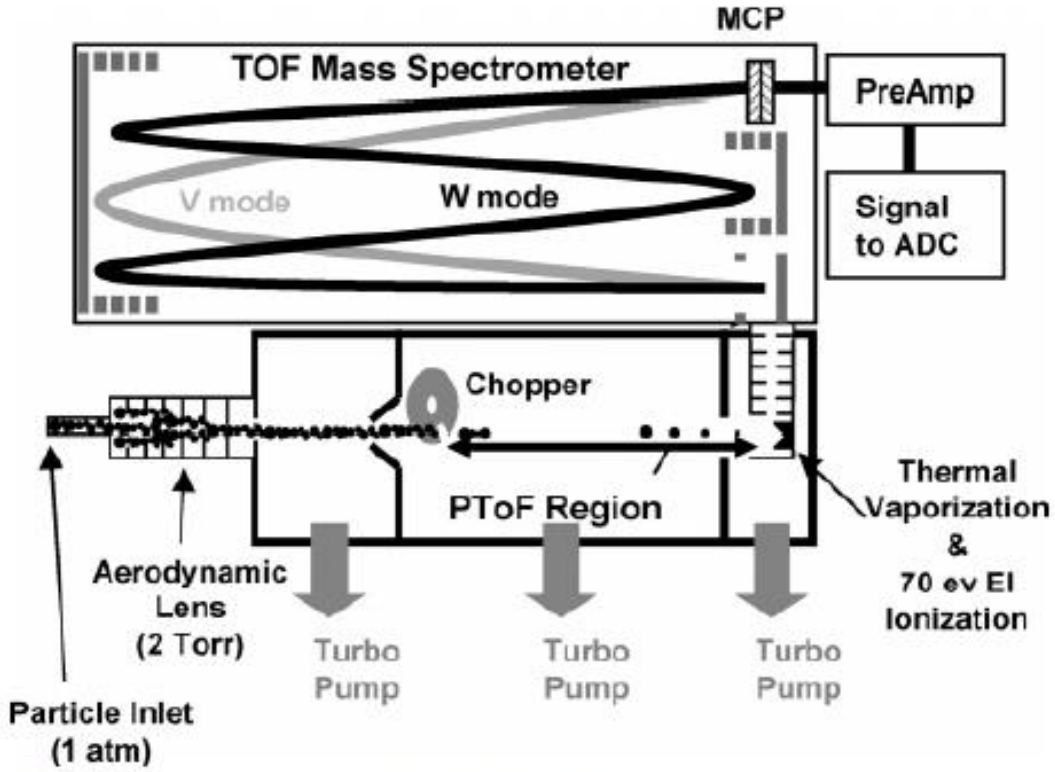


Figure 1. Schematic of the HR-ToF-AMS showing its two ion optical modes.

[11]DeCarlo et al., *Anal. Chem.* **2006** *78* (24), 8281-8289.

Background

[12]Shilling. *8th AMS Users Meeting*. **2007**.
[13]Shilling. *10th AMS Users Meeting*. **2009**.
[14]Marcolli et al., *Atmos. Chem. Phys.* **2006**, (6), 5649–5666.

- Measurement of Some PFAS Aerosols *is* Known to be Possible with AMS
  - Used in Calibration Beyond 200 m/z [12 – 13]
    - Perfluorotetracosane ($C_{24}F_{50}$)
      - Reported as “Crystalline” Particles
      - Likely Much Different From a Polymer
        - e.g., Much Lower Molecular Weight
  - Picked up as Background Noise on Field Study [14]
    - Attributed to Exhaust from Mechanical Pumps Using Fluorinated Hydrocarbon Oil

Background

- Marcolli et al (2006)[14]
  - Ship-based Measurements
    - New England 2002
  - Quadrupole AMS, with Unit Mass Resolution (UMR)
    - Lower Mass Spectral Resolution than a HR-ToF-AMS

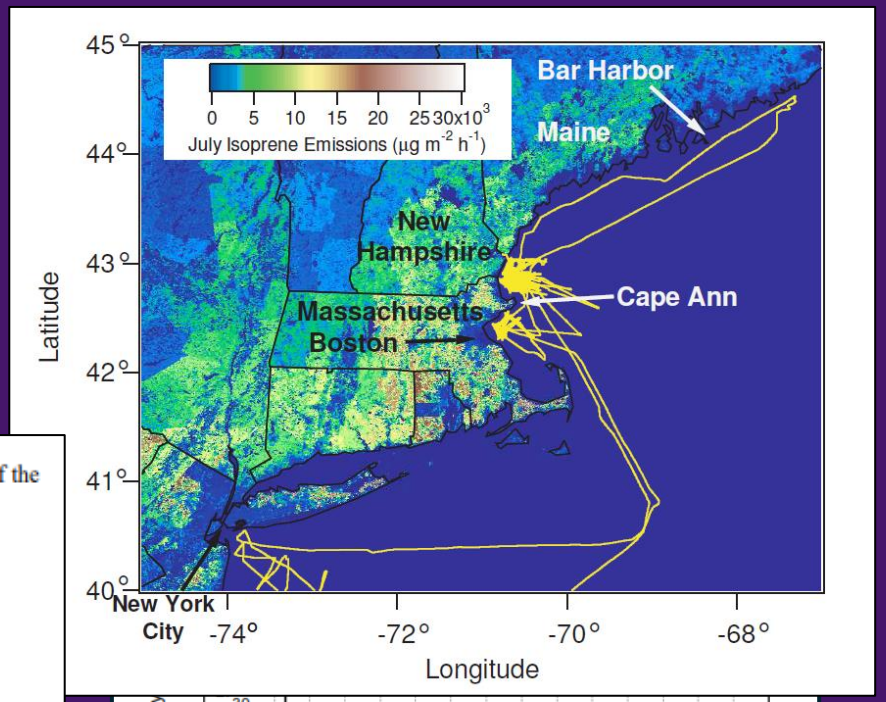


Table 1. Assignment of fragments for the most intense m/z of the investigated mass spectra.

m/z	Fragments
26	CN^+, $CHCH^+$
27	CH_2CH^+
29	$CH_3CH_2^+$, CHO^+, CH_3N^+
30	NO^+, CH_2O^+, CH_4N^+
31	CH_3O^+
41	$CH_2CHCH_2^+$ and isomers
42	$CH_2CH_2CH_2^+$, CH_2CO^+
43	$CH_3CH_2CH_2^+$, CH_2CHO^+, CH_3CO^+
44	CO_2^+
55	$CH_2CHCH_2CH_2^+$, CH_2CHCO^+ and isomers
57	$CH_3CH_2CH_2CH_2^+$, $CH_2CHCH_2O^+$ $CH_3CH_2CO^+$ and isomers
67	$CH_2(CH)_2CH_2^+$ and others
69	CF_3^+ and others
119	$CF_3CF_2^+$ and others
169	$CF_3CF_2CF_2^+$ and others

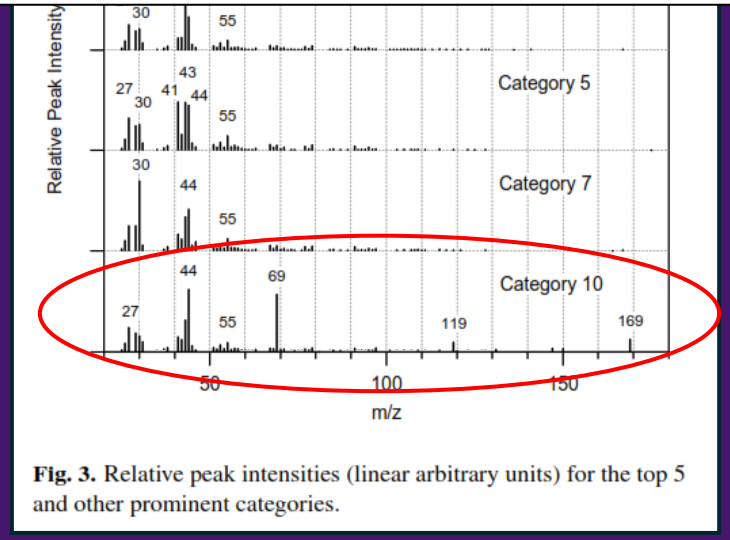


Fig. 3. Relative peak intensities (linear arbitrary units) for the top 5 and other prominent categories.

[14]Marcolli et al., *Atmos. Chem. Phys.* **2006**, (6), 5649–5666.

Lab Methods

- 3-D Printed PRIZE (PRinted fluidIZed bed gEnerator) [15]
  - Formlabs Form 2 Printer
    - PFAS-free Resin
      - (Formlabs Clear Resin V4)
  - Post-printing Processing Handled with Isopropanol

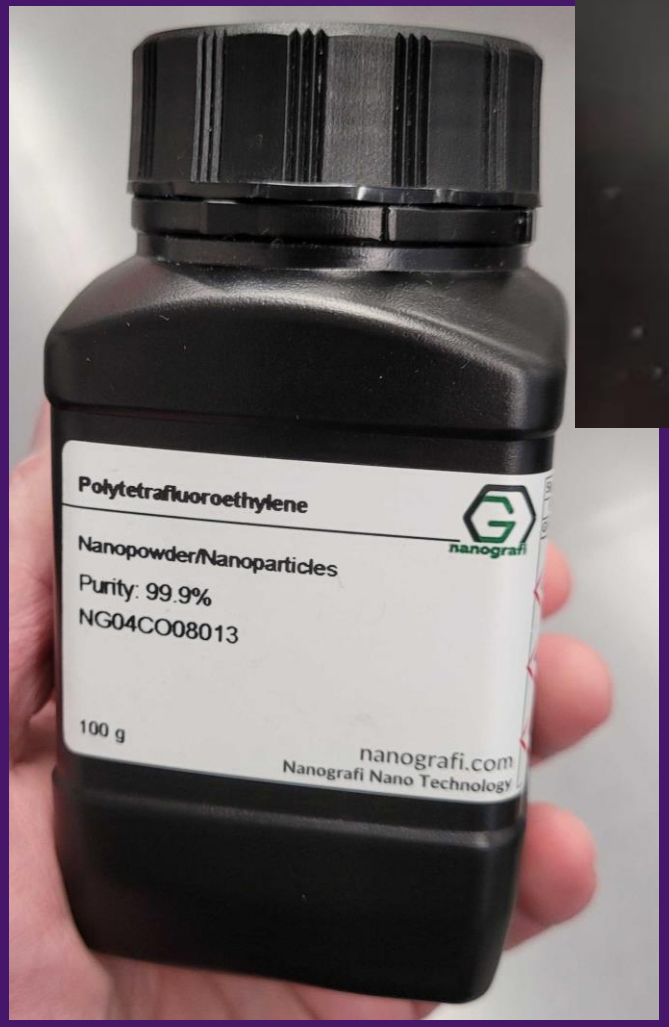


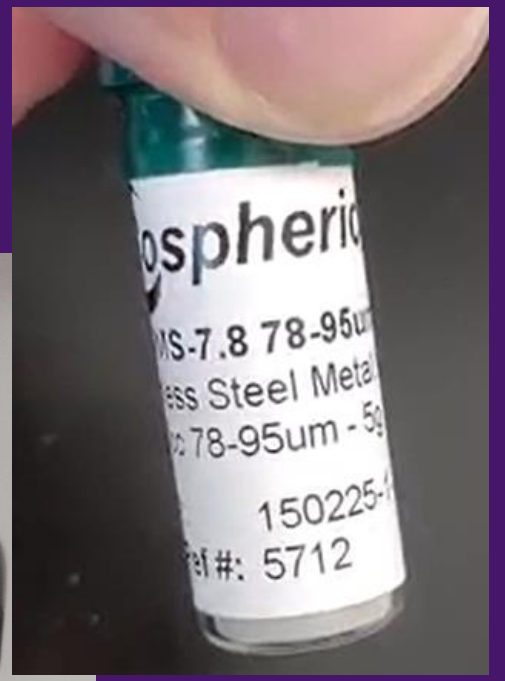
[15]Roesch et al., *Atmos. Meas. Tech.* **2017**, (10), 1999–2007

Lab Methods

- Stainless Steel Mesh Screen (76.2 μm pores)
- Stainless Steel Tube (25mm diameter, 1.5mm wall)
- Stainless Steel Beads (78 – 95 μm)
- Stainless Steel Wire (28 gauge) for Grounding
- PTFE ($[C_2F_4]_n$) Nanospheres (dry powder)

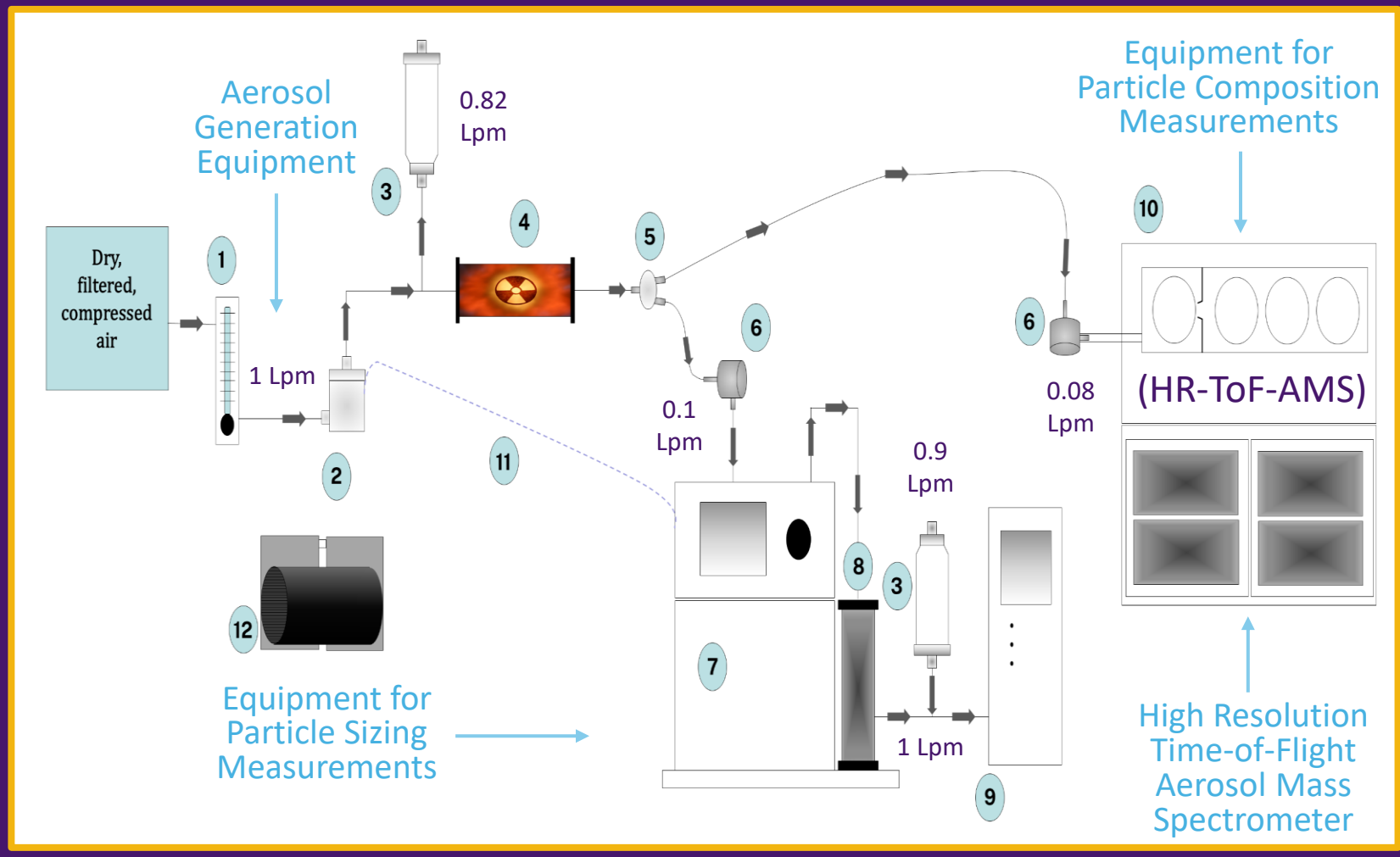
  ($\overline{D}_p \approx 100nm,\ \rho \approx 2.2\ \frac{g}{cm^3}$)





Lab Methods

1. Airflow Regulator
2. PRinted fluidIZed bed gEnerator (PRIZE)
3. HEPA Filter
4. Kr-85 Aerosol Neutralizer
5. Flow Splitter
6. Impactors (0.0457cm orifice)
7. Electrostatic Classifier
8. Nano DMA
9. Condensation Particle Counter
10. HR-ToF-AMS
11. Stainless Steel Wire (for Ground)
12. Diaphragm Pump (for Vibration)



Lab Methods

- HR-ToF-AMS Operated in V-Mode
  - ≈10x More Sensitive Compared to W-Mode[11]
  - V-Mode was Used in 2021 ASRC Mobile Lab Study
- While Much Higher Mass Spectral Resolution, W-Mode Likely Not Feasible for Detection of Trace Compounds Like PFAS Due to the 1/10th Sensitivity

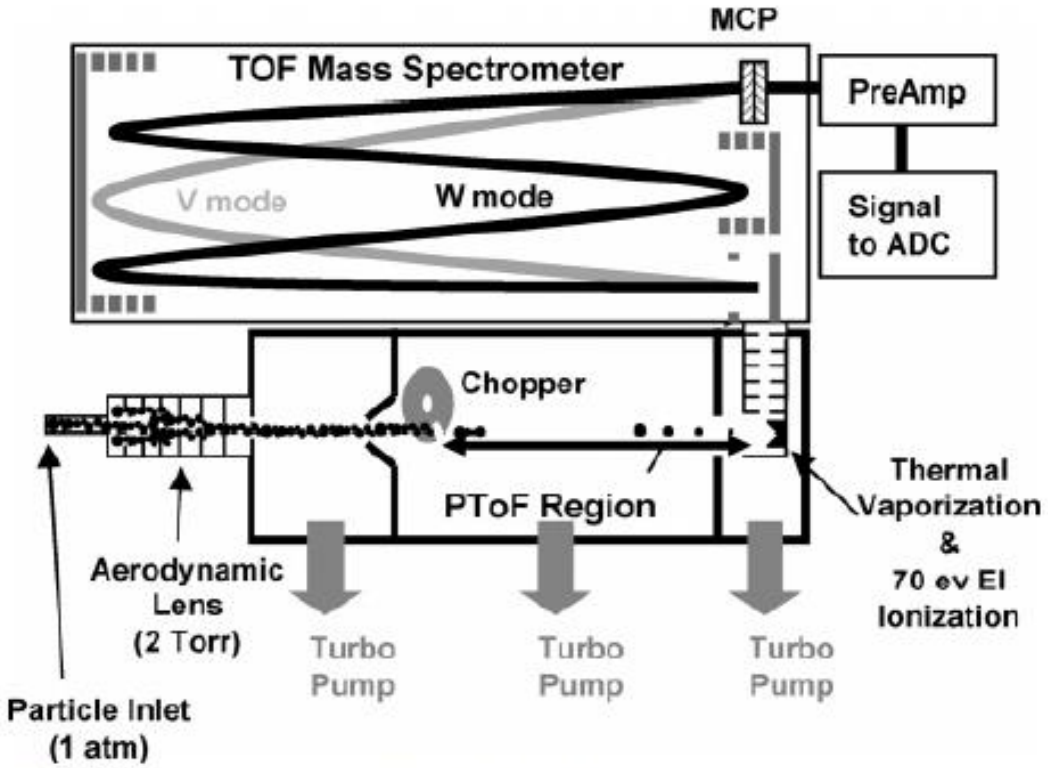


Figure 1. Schematic of the HR-ToF-AMS showing its two ion optical modes.

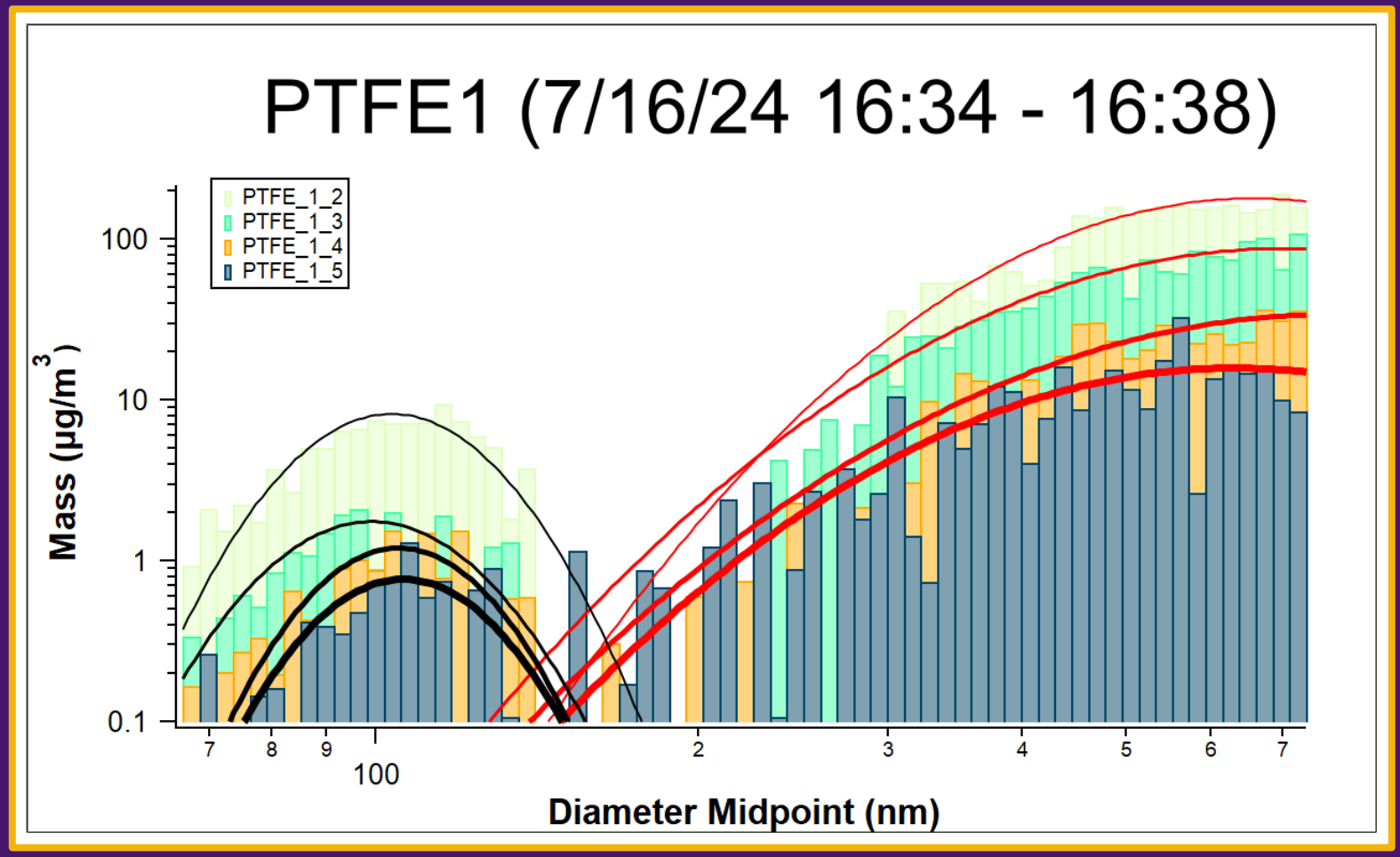
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[11]DeCarlo et al., *Anal. Chem.* **2006** *78* (24), 8281-8289.

PTFE Nanosphere Calibration Aerosol Size Distribution Data

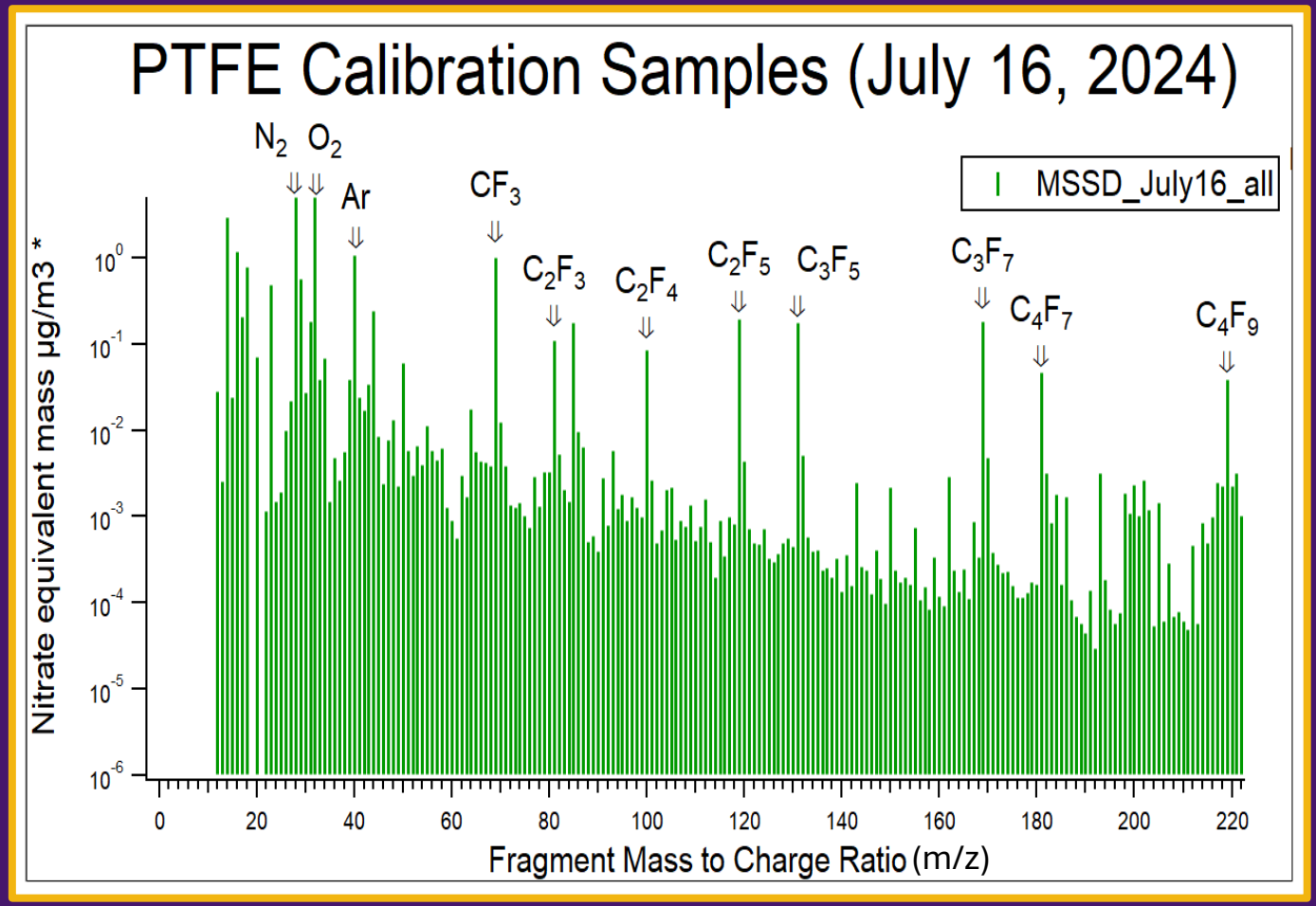
Somewhat “Reproducible”:

- Bi-modal Size Distributions
  - Likely Due to Coagulation of 100nm PTFE Nanospheres
- Rapidly Decreasing Sample Efficiency
  - Likely Due to Static Charge and Particle Losses to Tubing Walls

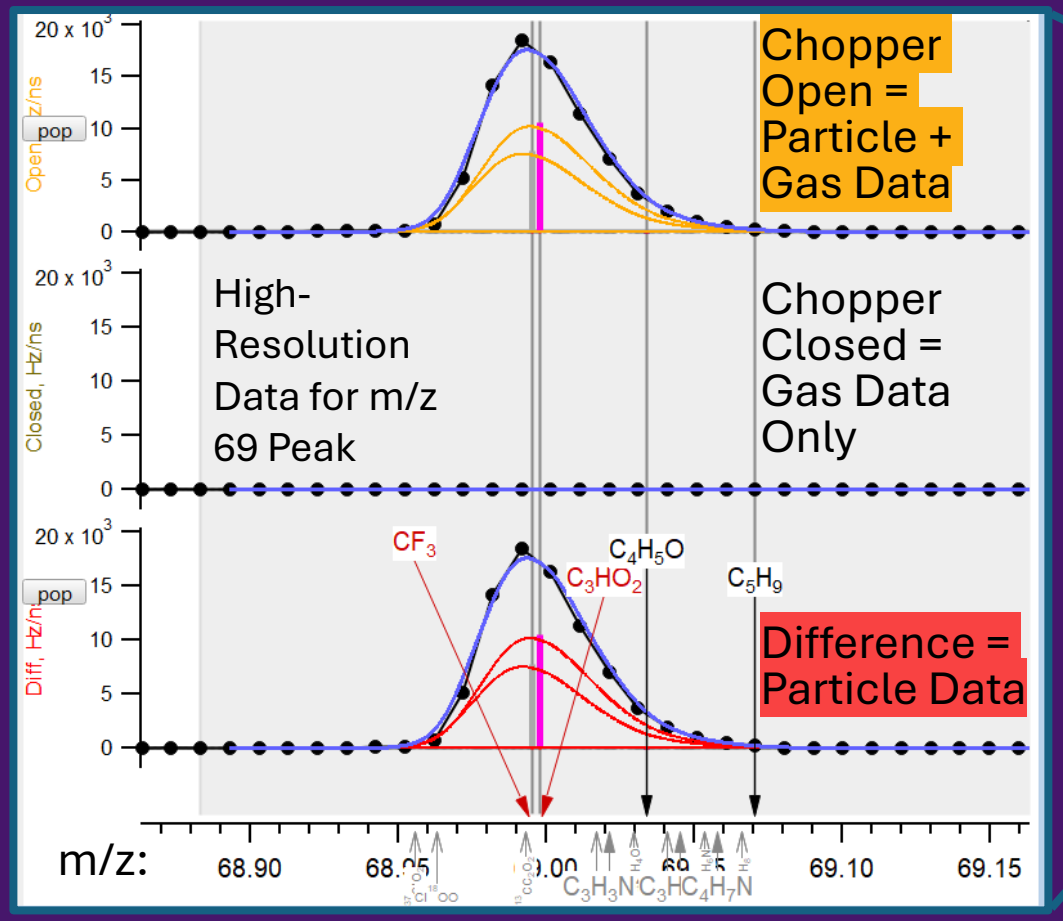


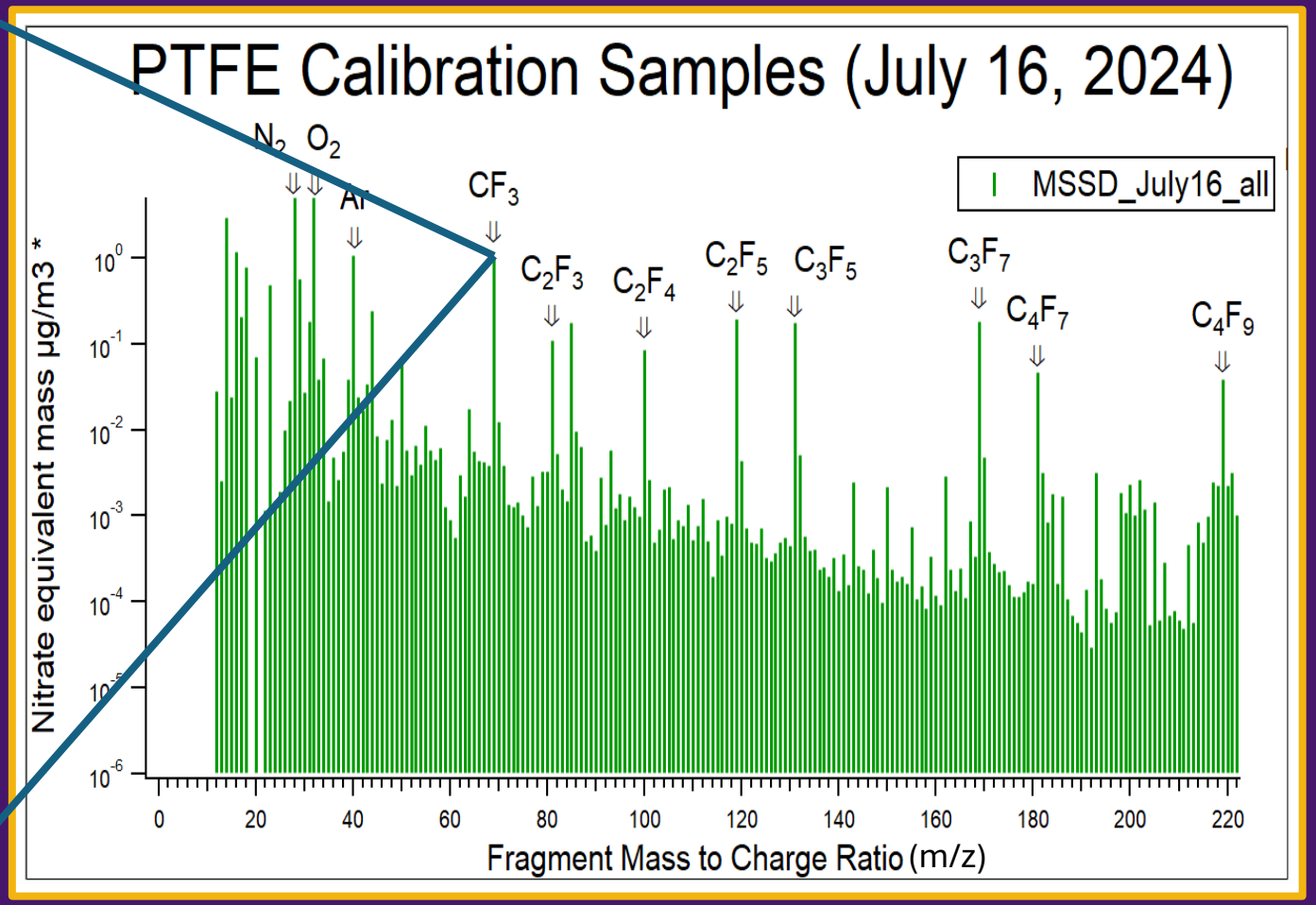
PTFE Nanosphere Calibration Chemical Composition with HR-ToF-AMS

- Clearly Visible Fluorocarbon Peaks
  - 10 to 10^3 Times Above Other m/z
- Evidence of
  - PTFE Plastic Beads Vaporizing, Ionizing Within HR-AMS
- Confirms Potential Viability of AMS Use for Measurements of Ambient PFAS Aerosols



PTFE Nanosphere Calibration Chemical Composition with HR-ToF-AMS





Overlap in CF_3 and C_3HO_2 Fragment Fits for These Pure PTFE Calibrations

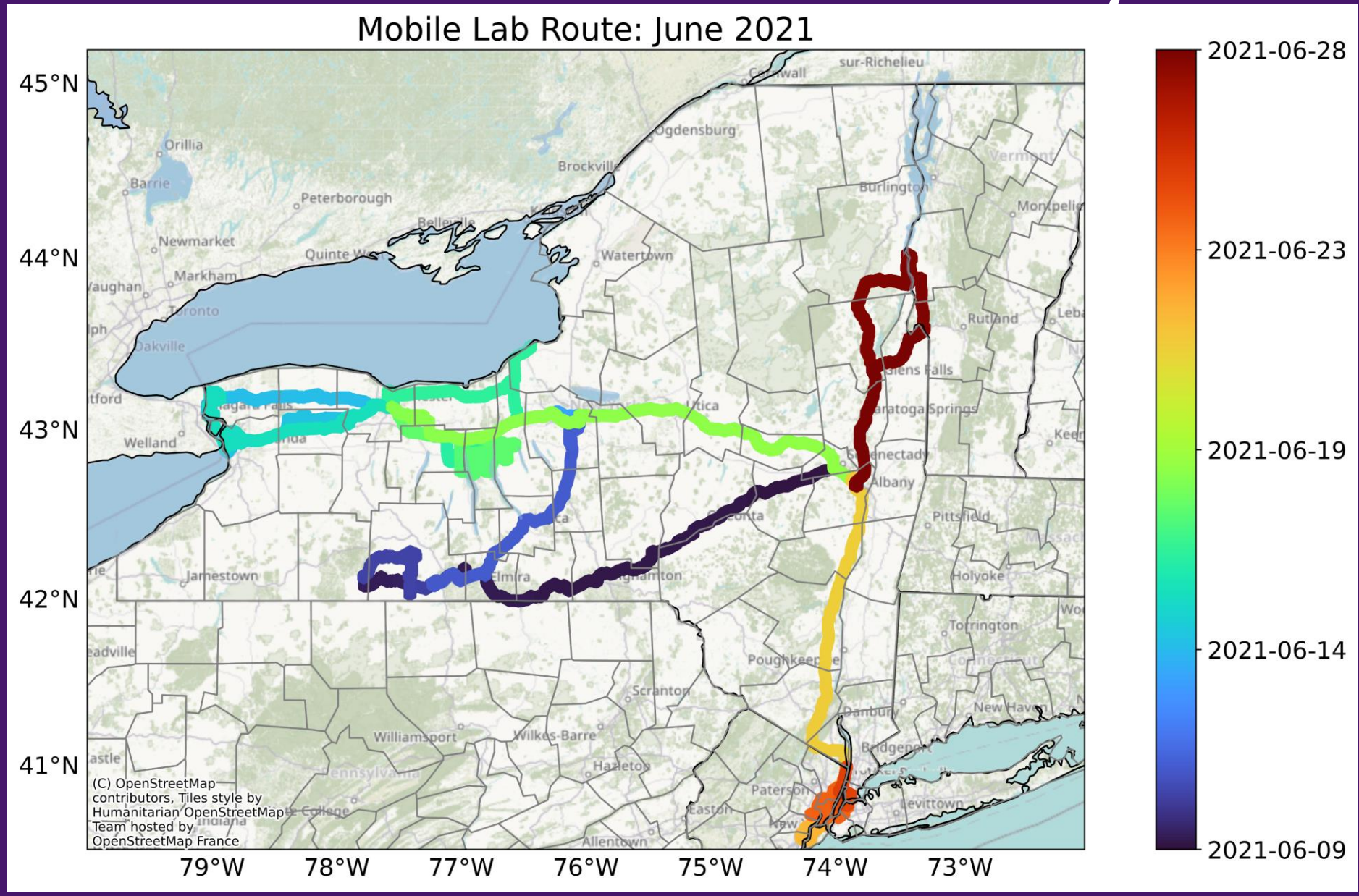
Future Work: Field Data Analysis

- ASRC Mobile Lab Study (June 2021)
  - Not Focused on PFAS or Aerosol Chemistry
  - Potentially Fruitful Dataset for PFAS
    - Wide Breadth of Sample Sites
      - Landfills, Wastewater Treatment Plants, Roadways, Urban Areas
        - Potential PFAS Sources [1 – 3]



[1]Ahrens et al., *Environ. Sci. Technol.* **2011**, (45), 8098–8105.
[2]Galloway et al., *Environ. Sci. Technol.* **2020**, (54),7175–7184.
[3]Pétré et al., *Environ. Sci. Technol.* **2021**, (55),5848–5856.

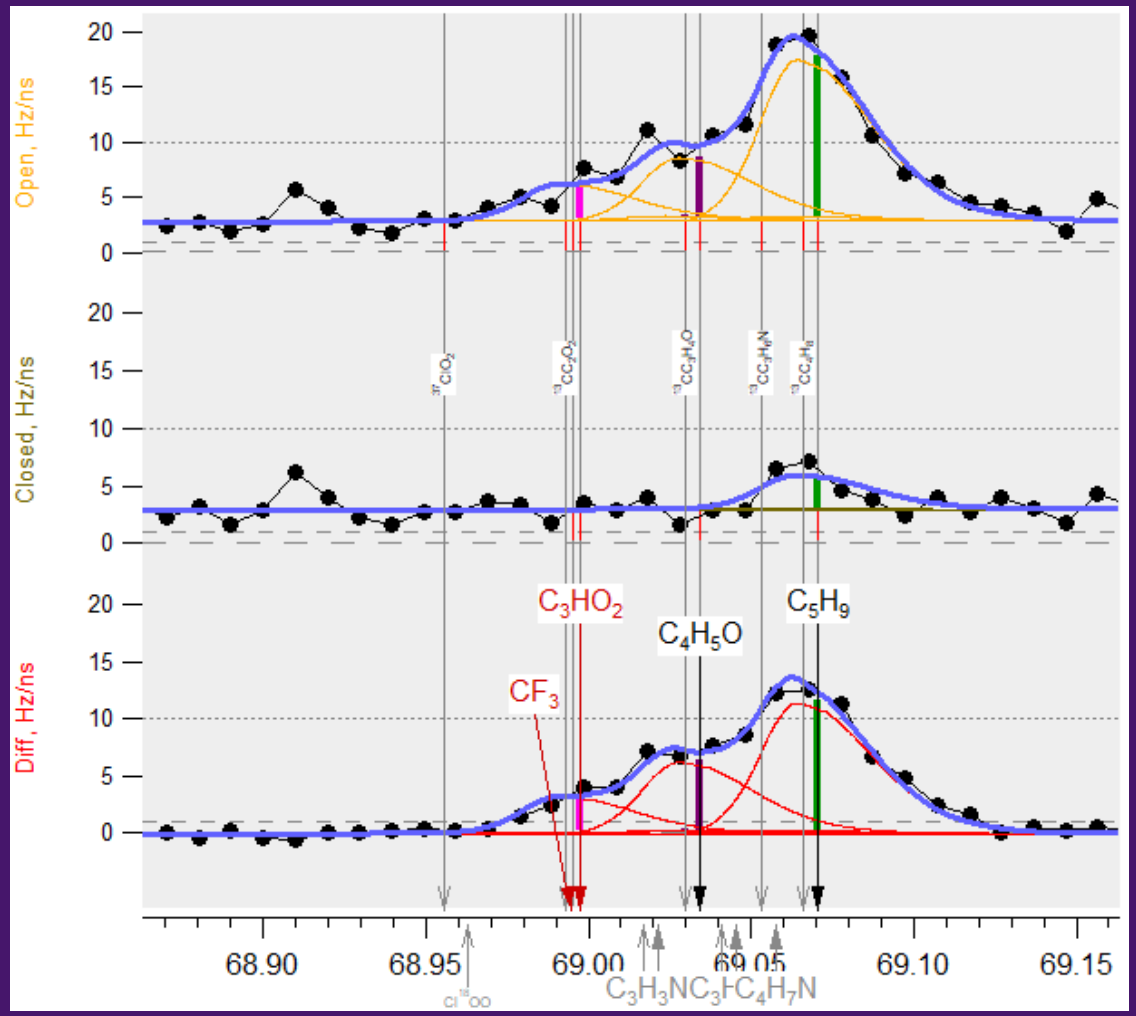
Future Studies: Field Data Analysis



Future Studies: Field Data Analysis

- Peak Near 69 m/z is Relatively Repeatable Across Parts of Field Data
- Starting to Utilize SoFi and ME-2 Engine to More Closely Explore Data
  - Implement Positive Matrix Factorization (PMF)
    - Pull PFAS Fragment "Needles" Out of Organic Aerosol "Haystack" in Ambient Air
    - Separate e.g. CF_3^+ and $C_3HO_2^+$ Based on their Temporal Variance

HR-ToF-AMS Field Data from ASRC Mobile Lab (June 18, 2021)



Summary Conclusion

[5]Li et al., *Environ. Sci. Technol.* ***2024,*** (58), 9283–9291.
[6]Fenton et al., *Environ. Toxicol. Chem.* **2021**, *40*, 606
[7]Deitsch et al., *NADP Fall Meeting.* **2023**.
[8]Deitsch et al., *AMS 104th Annual Meeting.* ***2024.***
[14]Marcolli et al., *Atmos. Chem. Phys.* **2006**, (6), 5649–5666.

- PFAS is a Set of Emerging Pollutants with Human Health Implications[6]
- Limited Measurements of Ambient PFAS in Gas[5], Aqueous[5, 7 – 8] and Dry Particle[5,14] Phases

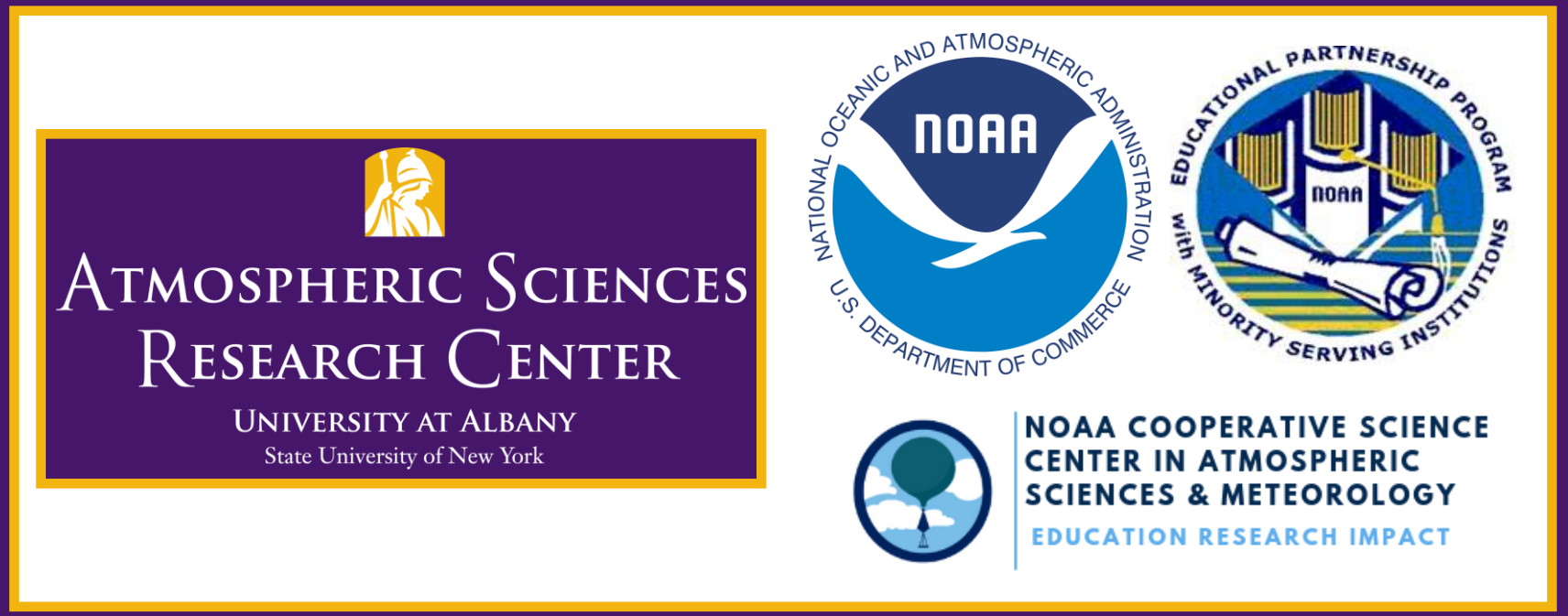
In the Current Study:

- PTFE (Teflon) Nanoplastic Particles Shown to Vaporize and Ionize Within a HR-ToF-AMS, with Distinct PFAS Signatures in V-Mode
- High-Resolution Data Show Peaks Associated with PFAS Aerosols in 2021 NYS Field Data
- Overlapping Peaks and Trace Concentrations Pose Challenges to Isolating PFAS Signals in Ambient Samples
  - Wide Range of Organic Molecules in Ambient Samples, Many With High Concentrations

Future Work:

- Plan to Use PMF to Isolate Covarying PFAS “Family” from Ambient Organic Aerosol

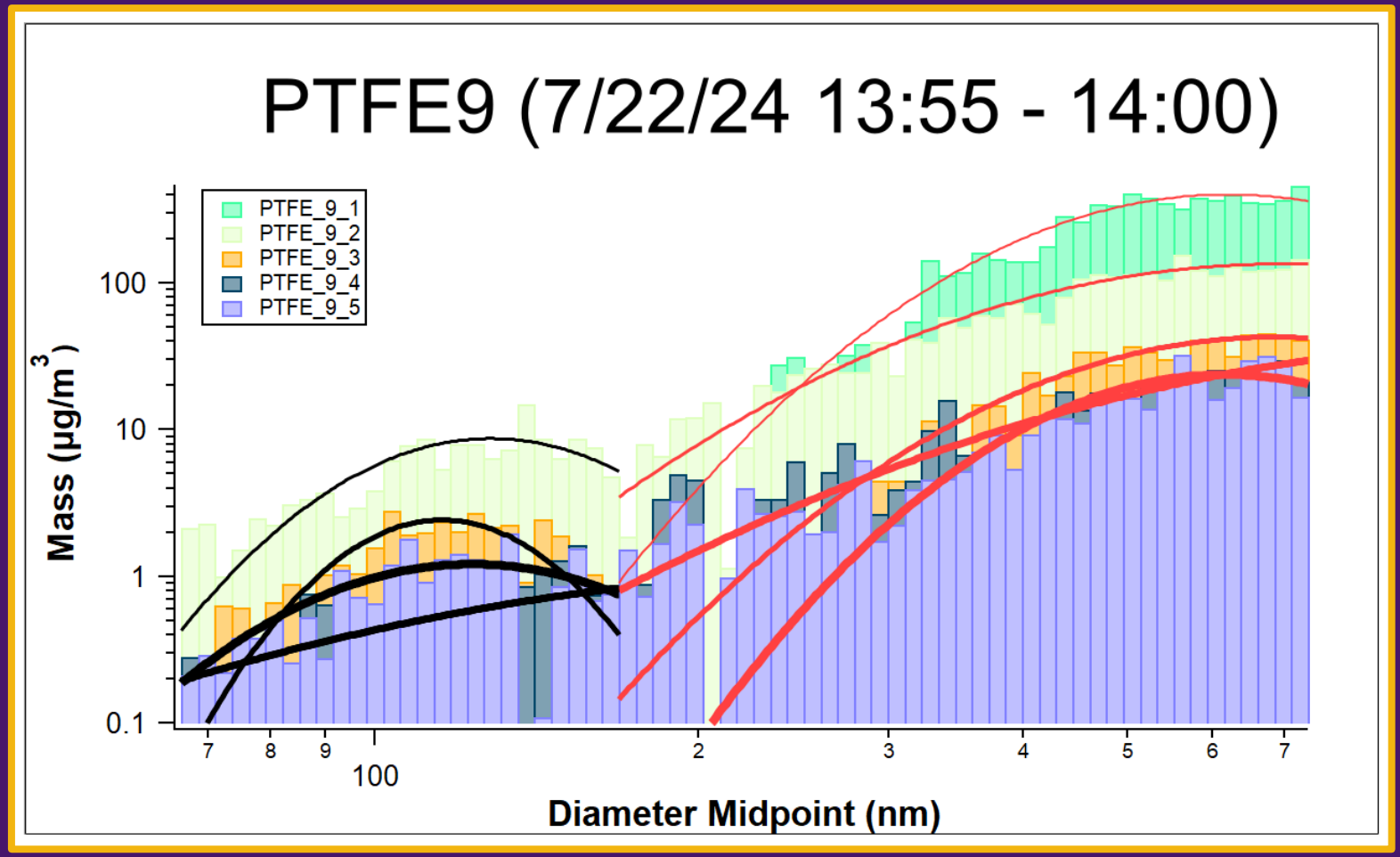
Acknowledgements



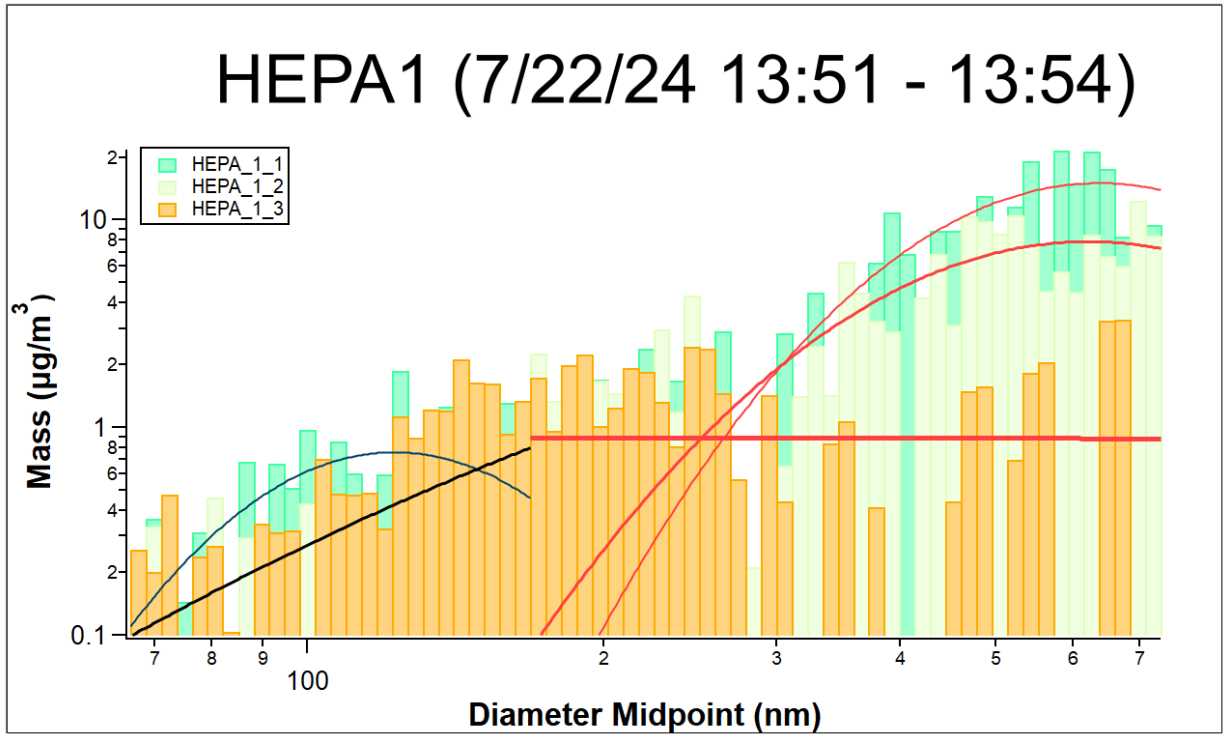
This research is based on work supported by the U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Educational Partnership Program under Agreement No. NA22SEC4810015.

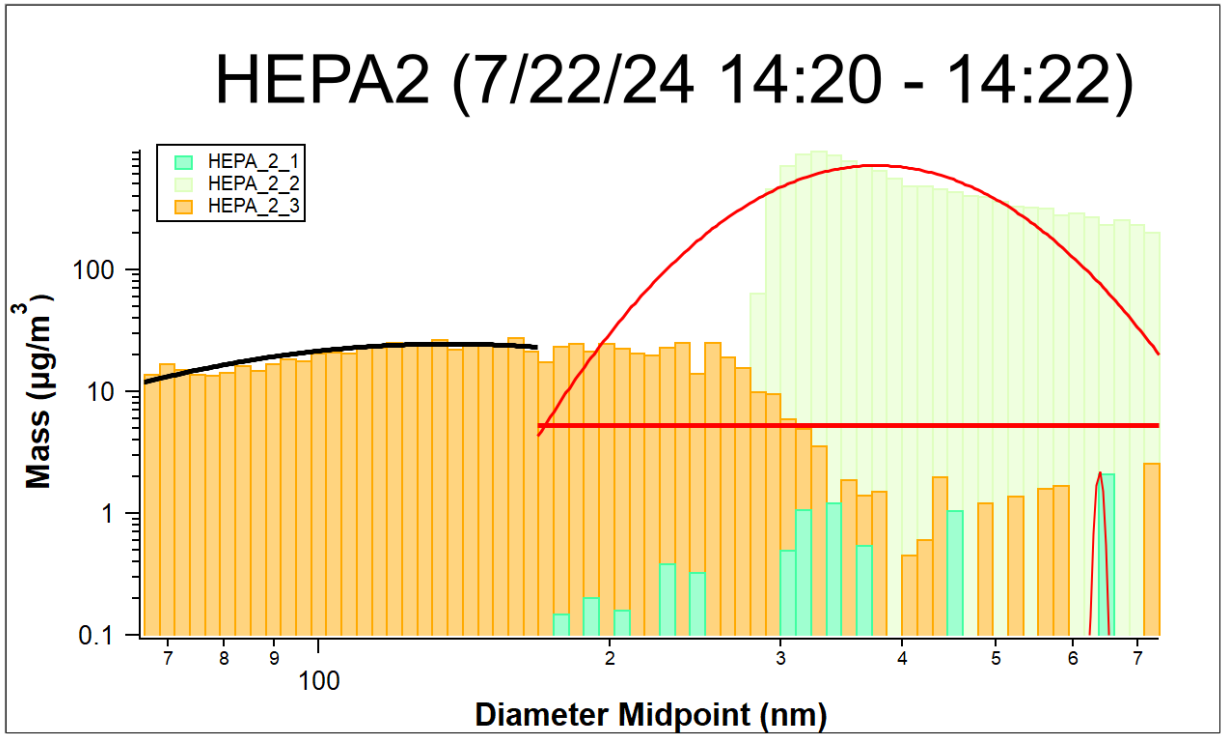
Extras

- “Reproducible”
  - Bi-modal
  - Efficiency Deterioration
  - Non-steady Aerosol Sampling State
- Likely Loss of Mass Due to Agglomerates Not Passing Impactor

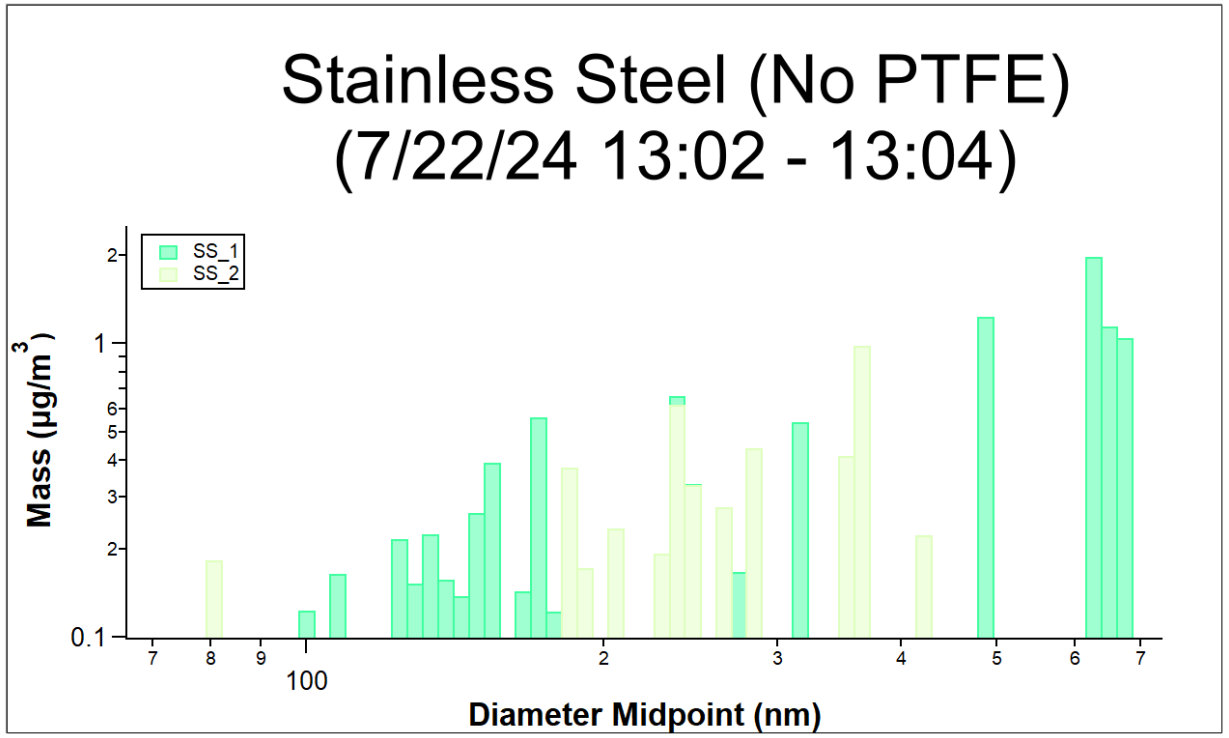


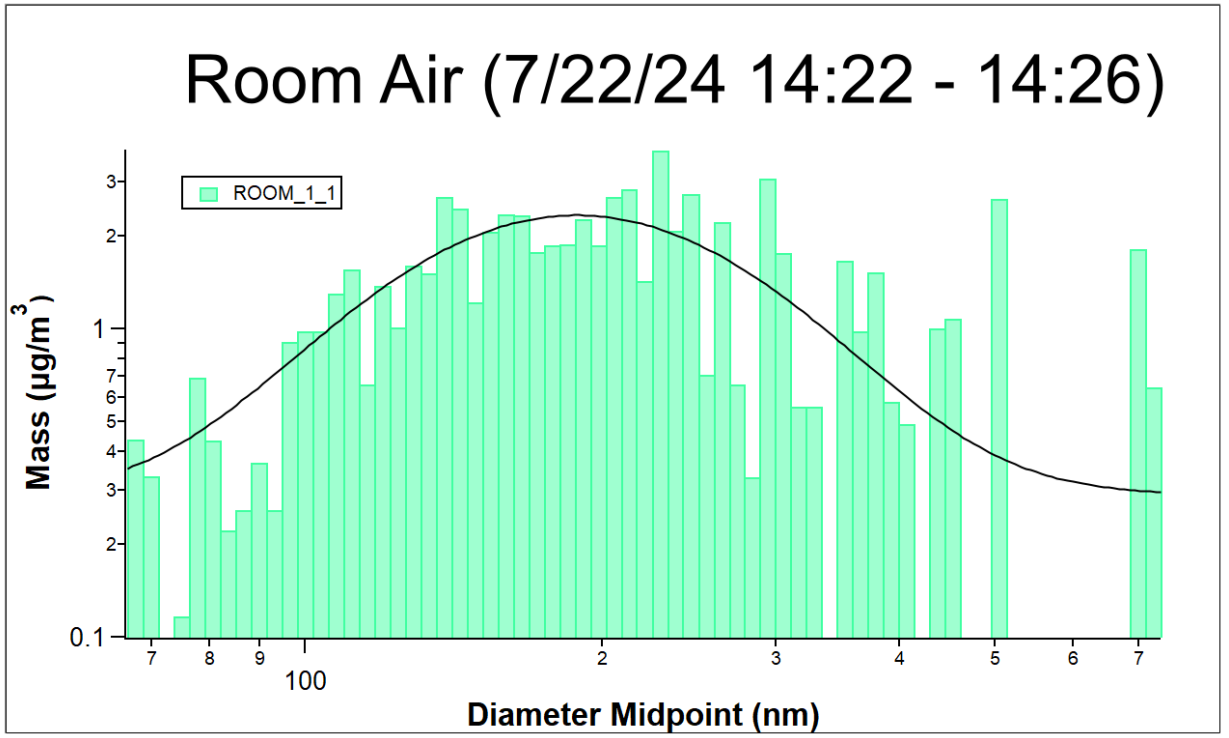
Extras


HEPA1 (7/22/24 13:51 - 13:54)
HEPA_1_1
HEPA_1_2
HEPA_1_3
Mass (µg/m3)
Diameter Midpoint (nm)


HEPA2 (7/22/24 14:20 - 14:22)
HEPA_2_1
HEPA_2_2
HEPA_2_3
Mass (µg/m3)
Diameter Midpoint (nm)

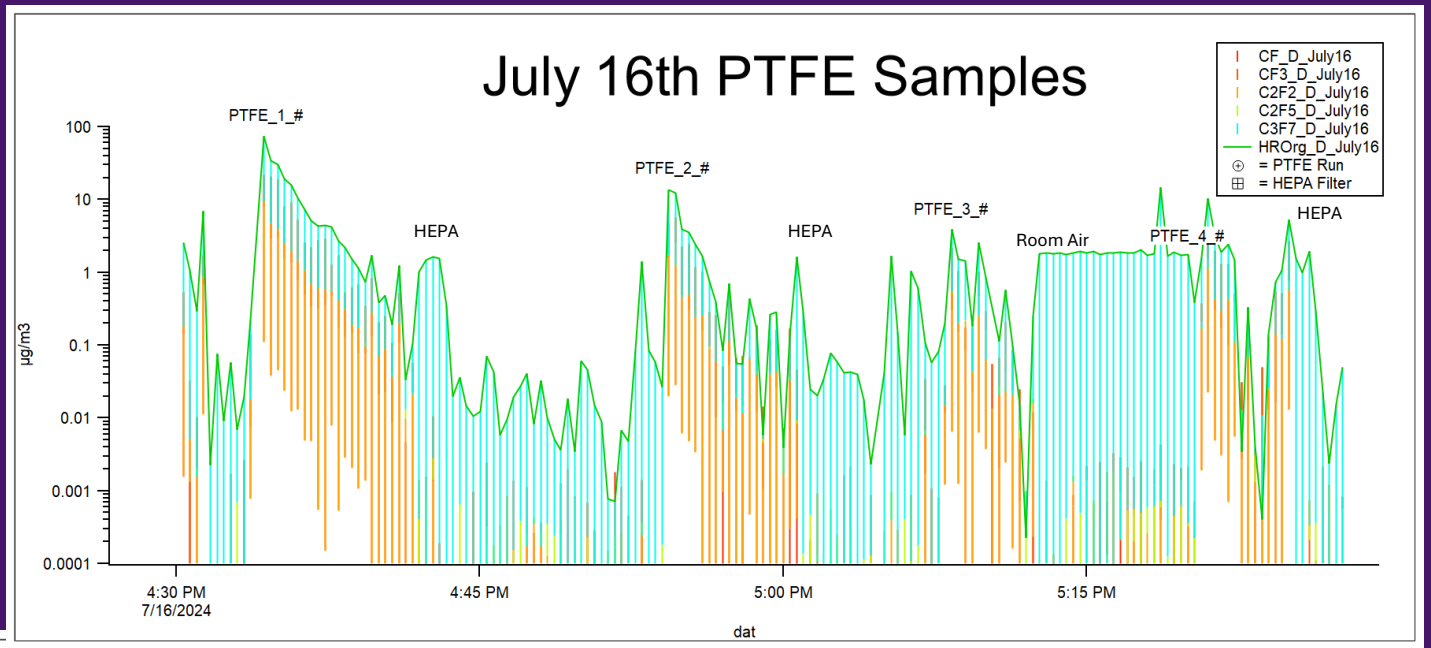
Extras

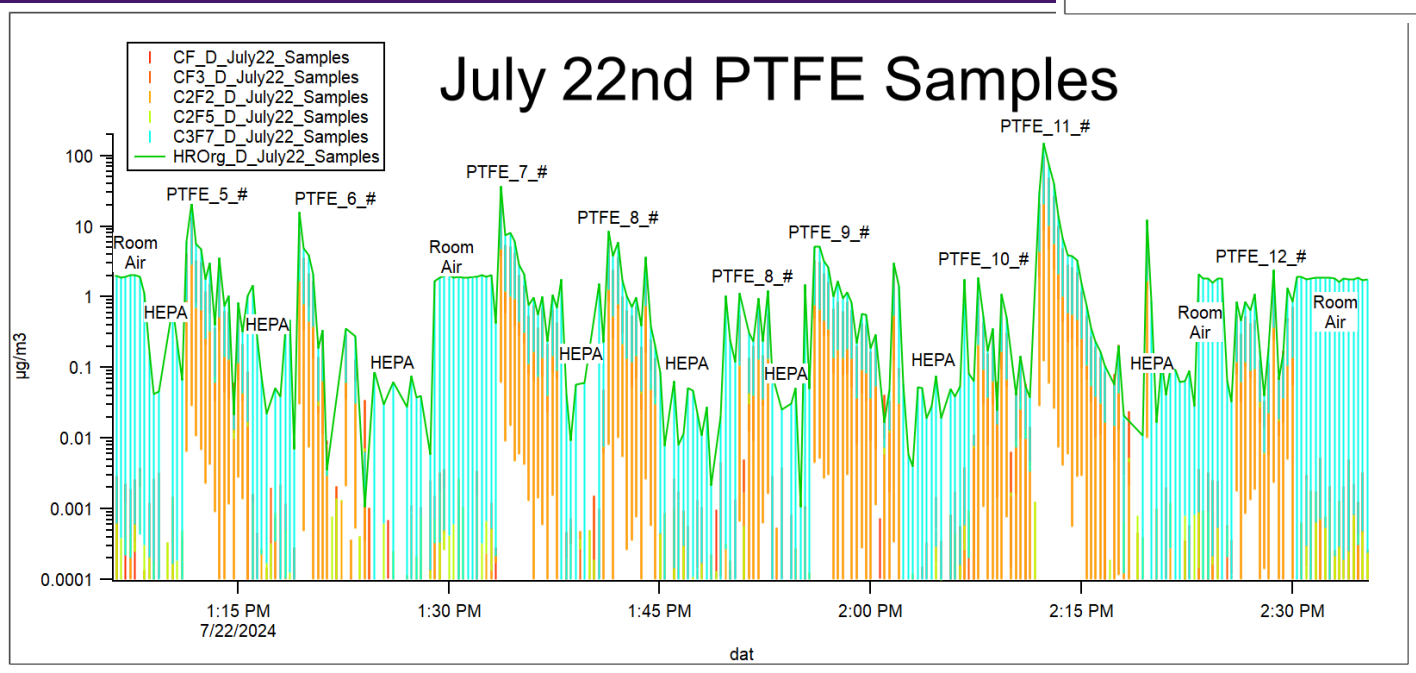

Stainless Steel (No PTFE)
(7/22/24 13:02 - 13:04)
SS_1
SS_2
Mass (µg/m3)
Diameter Midpoint (nm)


Room Air (7/22/24 14:22 - 14:26)
ROOM_1_1
Mass (µg/m3)
Diameter Midpoint (nm)

Extras

- Efficiency deterioration reflected in AMS data





- Supports conglomeration/clogging