Aerosol Composition

Instrument Teams

GOTHAAM, AEROMMA, Ground Sites, EPCAPE

Online and offline measurements of organic and inorganic aerosols at NYC-METS: ACSM, OFR, LC-TOF, SMPS, BC/BrC

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Graduate Researcher
Yale

Jo Machesky
Graduate Researcher
Yale

Taekyu Joo
Postdoctoral Researcher
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Mitchell Rogers
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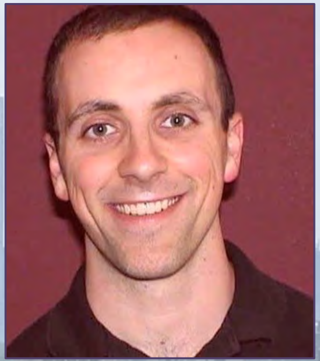
Yale

Ben Nault
Instrument PI
Aerodyne

Phil Croteau
Instrument PI
Aerodyne

Manjula Canagaratna
Instrument PI
Aerodyne



Andrew Lambe
NYC-METS PI
Aerodyne

Contact: drew.gentner@yale.edu;
lambe@aerodyne.com

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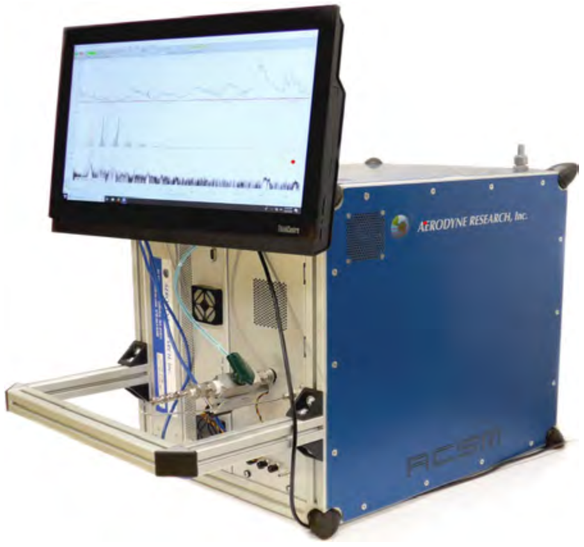
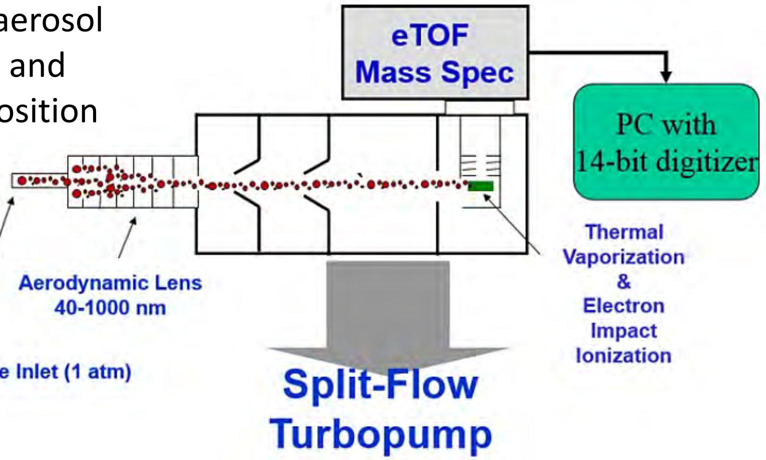
Online Measurements of Aerosol Chemical & Physical Properties



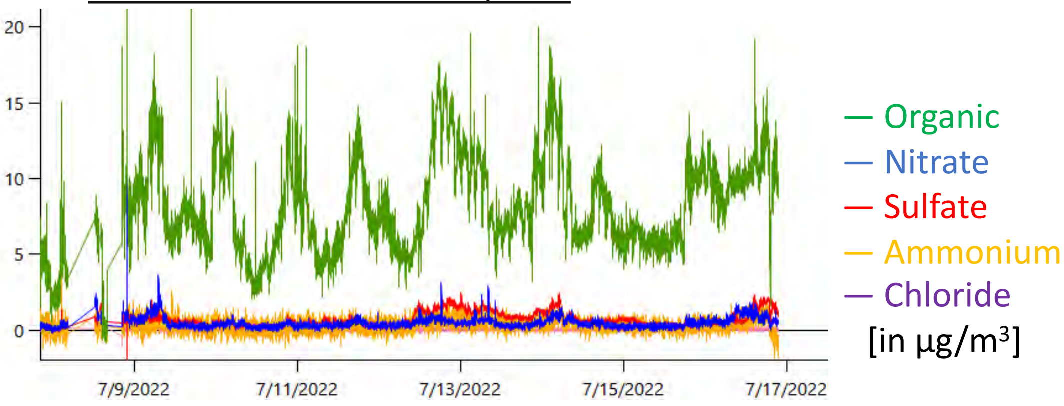
Aerodyne Aerosol Chemical Speciation Monitor (TOF-ACSM) at NYC and Coastal CT sites

Measures real-time, non-refractory aerosol particle mass and chemical composition



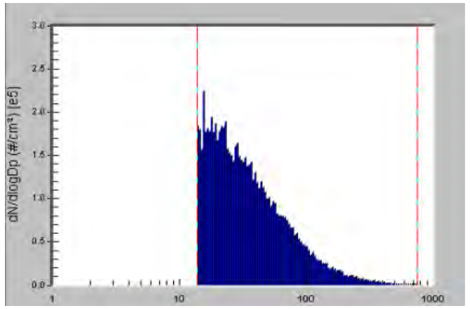
- Aerosol size range: 40 nm to 1 µm
- Averaging time (NYC): 40 seconds
- Sample flow: 85 cc/min
- LOD (@ 10 min, 3σ)
    - Organic: 0.17 µg/m^3
    - Sulfate: 0.02 µg/m^3
    - Nitrate: 0.04 µg/m^3
    - Ammonium: 0.17 µg/m^3
    - Chloride: 0.02 µg/m^3

Manhattan 2022 Data Snapshot



TSI SMPS (at NYC site) (Scanning Mobility Particle Sizer)

- Aerosol size range: up to 800 nm
- Scan rate (NYC): 135 s
- Measures particle number concentrations in ambient air and OFR effluent



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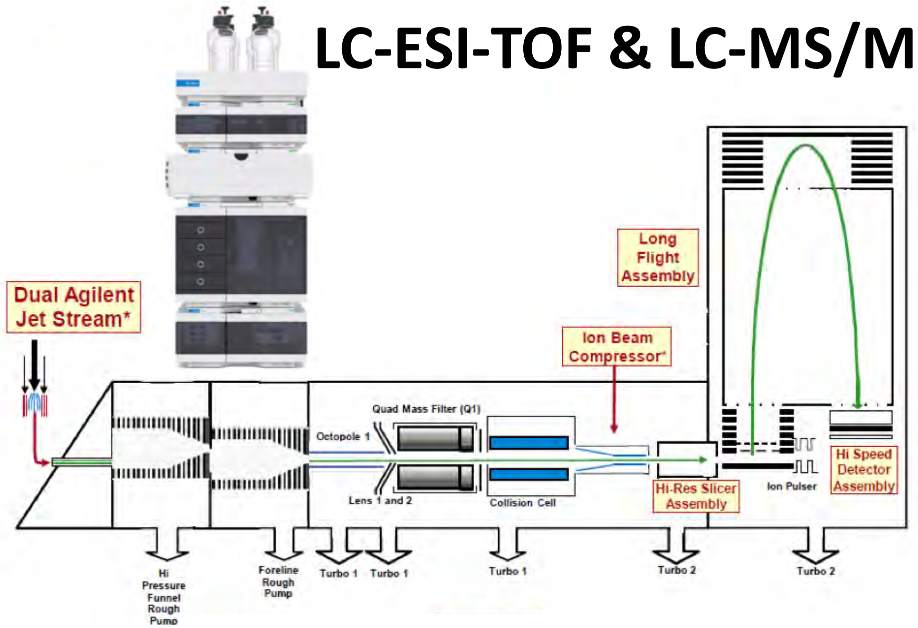
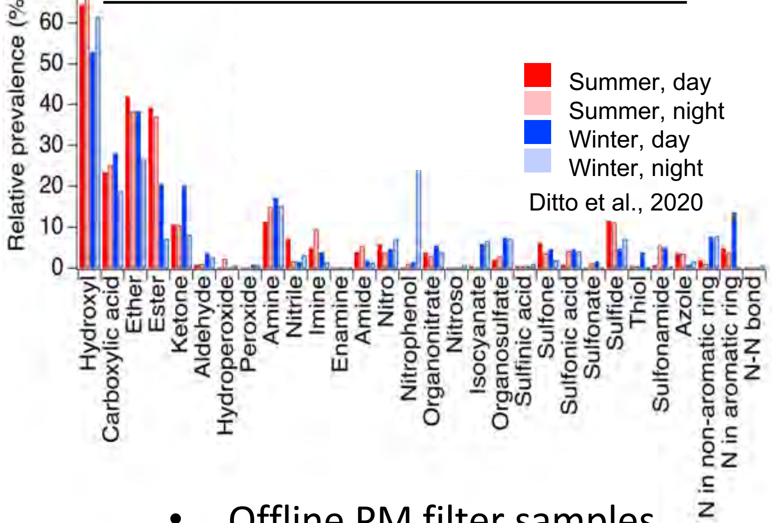
Offline LC-TOF & MS/MS and Online Black/Brown Carbon

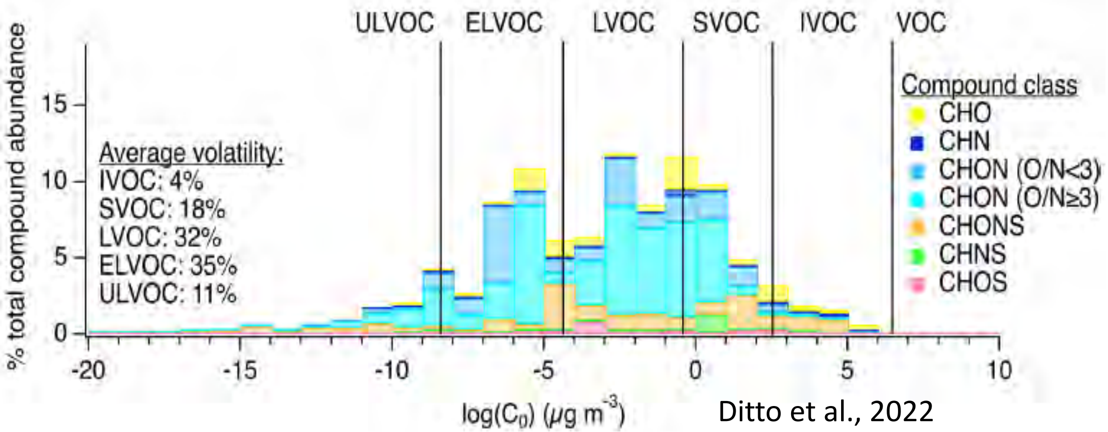
LC-ESI-TOF & LC-MS/MS



Observed functional group distributions at Coastal CT Site



Functionalized OA at Coastal CT Site



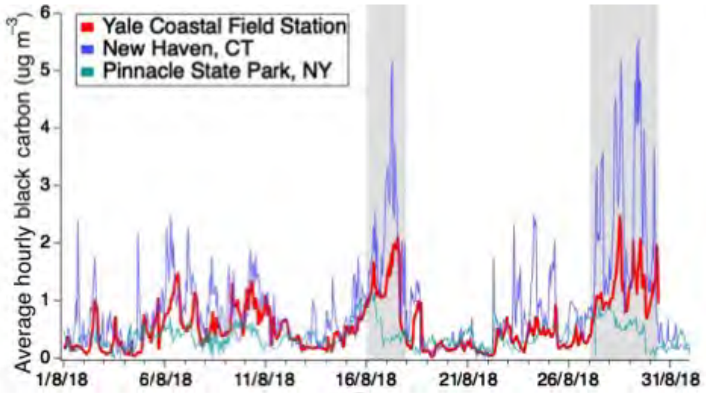
Ditto et al., 2022

- Offline PM filter samples analyzed at Yale via LC-TOF and LC-MS/MS
- At both NYC and Coastal CT sites
- Agilent 6550 LC-Q-TOF:
  - Measurement range: VOCs-ULVOCs
  - Mass accuracy: 1 ppm
  - Mass resolution: 25,000-40,000 m/Δm

Magee Aethalometer for BC/BrC (Model AE33) at Manhattan and Coastal CT sites

- Time resolution: 1 min
- Wavelengths: 370, 470, 520, 590, 660. 880, 950 nm
- Sensitivity: 0.03 μg/m3 at 1 min

Long-distance biomass burning influence in BC data at the Coastal CT site (Rogers et al. 2020)



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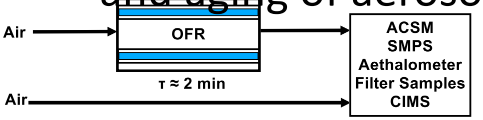
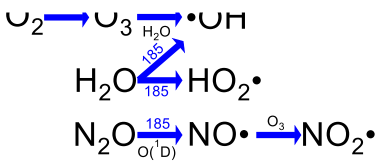
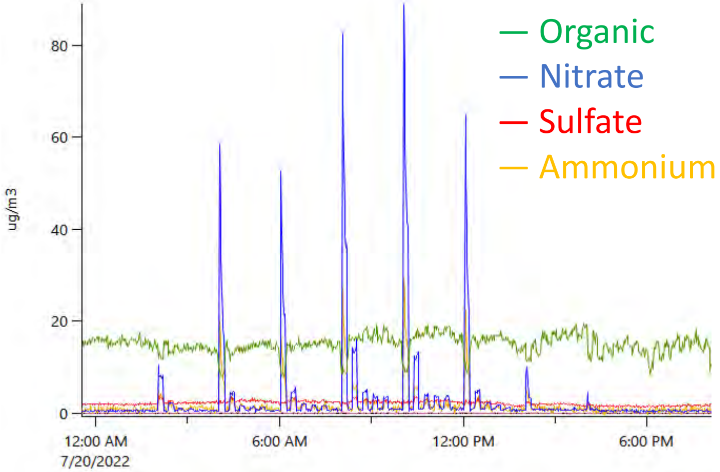
in situ oxidation flow reactor (OFR) studies

Routine (i.e., 10 min) switching between ambient air and OFR effluent with varying photochemical aging timescales to examine *in situ* formation and aging of aerosols and OVOCs





Preliminary NYC rooftop data



https://sites.google.com/site/pamwiki/home?authuser=0

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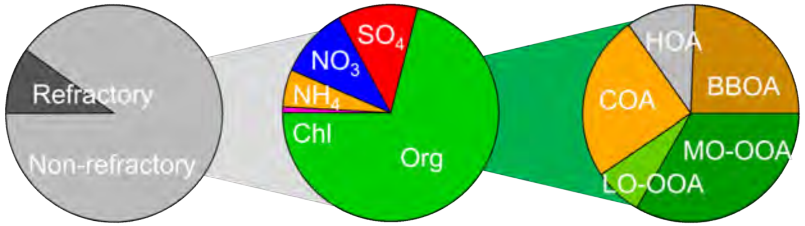
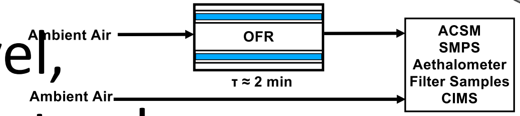
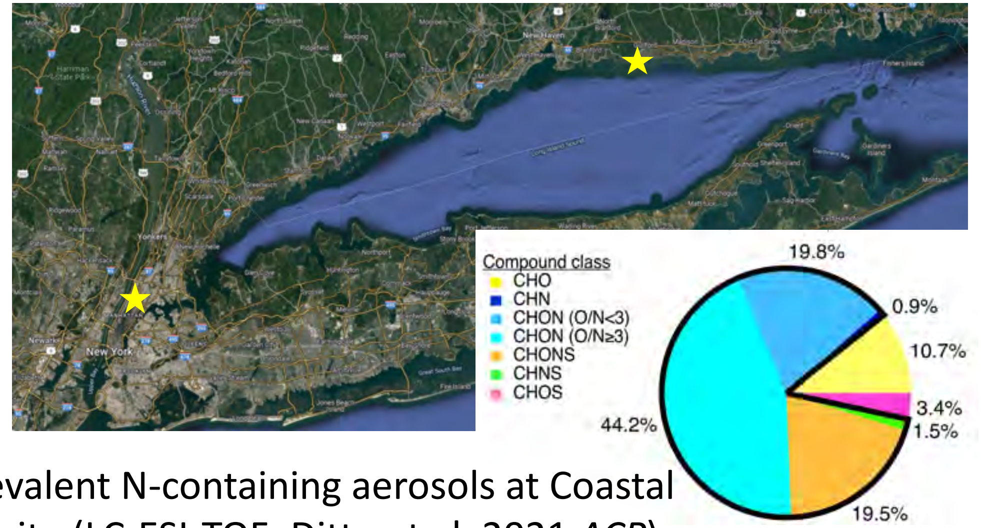
Overview of Science Goals and Foci

- Aerosol source apportionment in NYC and Coastal CT with variations in environmental conditions
- Aerosol composition: Online/offline speciation spanning from the bulk to molecular level, including functional group analysis using tandem mass spectrometry (MS/MS)
- Evaluate secondary aerosol formation potential in NYC and downwind using ambient measurements and *in situ* OFR perturbation studies
  - Dual ACSM and offline aerosol speciation at NYC and Coastal CT sites (Also Ng/Thornton FIGAERO-CIMS's at NYC/Coastal CT)
- Intercomparisons with chemistry and regional transport models



ACSM-based source apportionment in Atlanta (Joo et al. 2021)





Prevalent N-containing aerosols at Coastal CT site (LC-ESI-TOF; Ditto et al. 2021 *ACP*)

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Yale ENVIRONMENTAL ENGINEERING

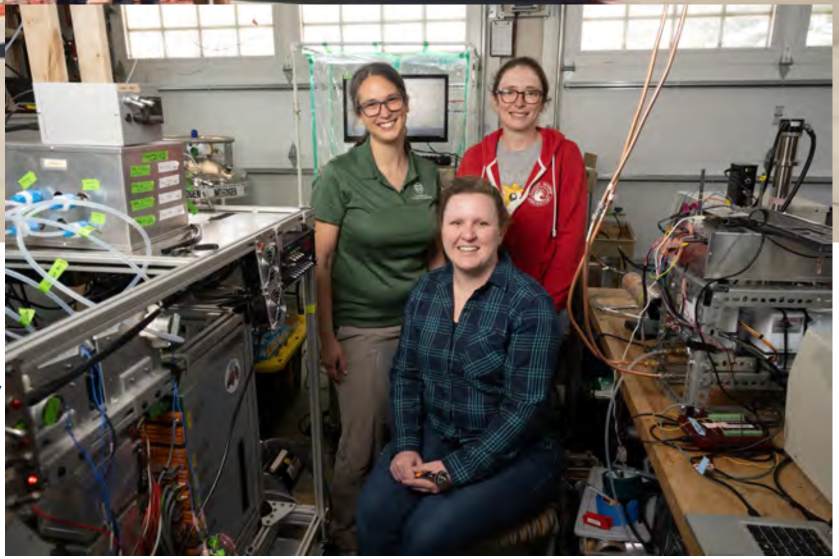
GOTHAAM Submicron Aerosol Composition

Delphine Farmer & Lauren Garofalo
Department of Chemistry, Colorado State University

GOTHAAM: Sub-micron Aerosol Composition (CSU)

Goals:

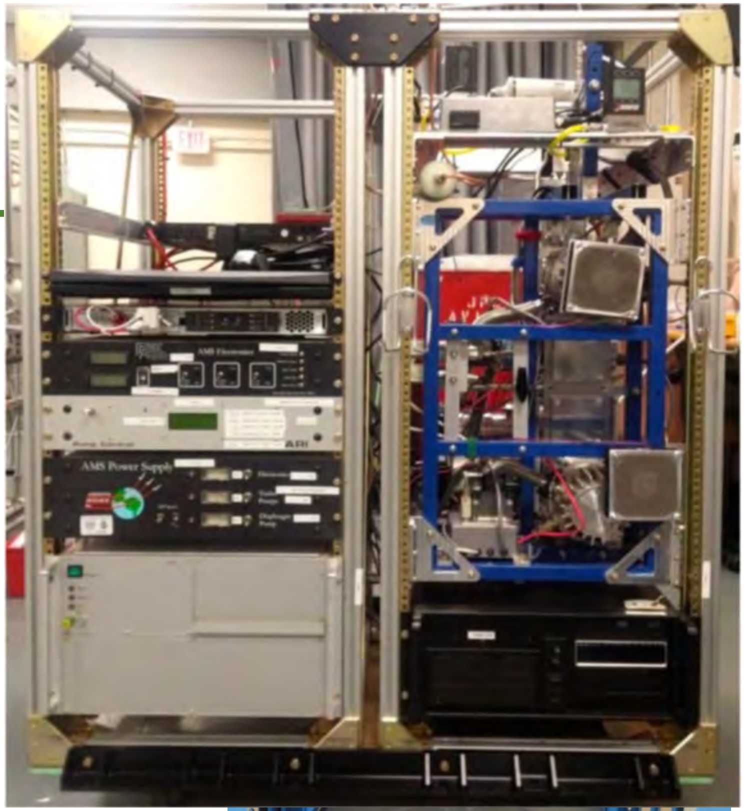
- To understand the chemical evolution of organic aerosol and aerosol composition budget in the urban plume
- To quantify the contributions of different sources to aerosol during day vs night
- To investigate the extent to which measured VOCs explain observed SOA



Research Team

Dr. Delphine Farmer, Dr. Lauren Garofalo, graduate student TBD + help from Dr. Kathryn Mayer and others

GOTHAAM: Sub-micron Aerosol Composition (CSU)



- Quantitative size-resolved sub-micron non-refractory aerosol composition by High Resolution Aerosol Mass Spectrometry
  - pOrg, pNO_3, pSO_4, pCl, pNH_4
  - O:C, H:C, OM:OC
  - PM_1
  - *Organic N is a research product – we will see how well various approaches work…*

- Size-resolved black carbon measurements by Single Particle Soot Photometry (SP2)
  - Can provide insight on coating thickness, which we may be able to link to evolution of organic aerosol in urban plume

University of Michigan Aircraft Aerosol Time-of-Flight Mass Spectrometer (A-ATOFMS) on the NCAR C-130 measuring individual aerosol particles

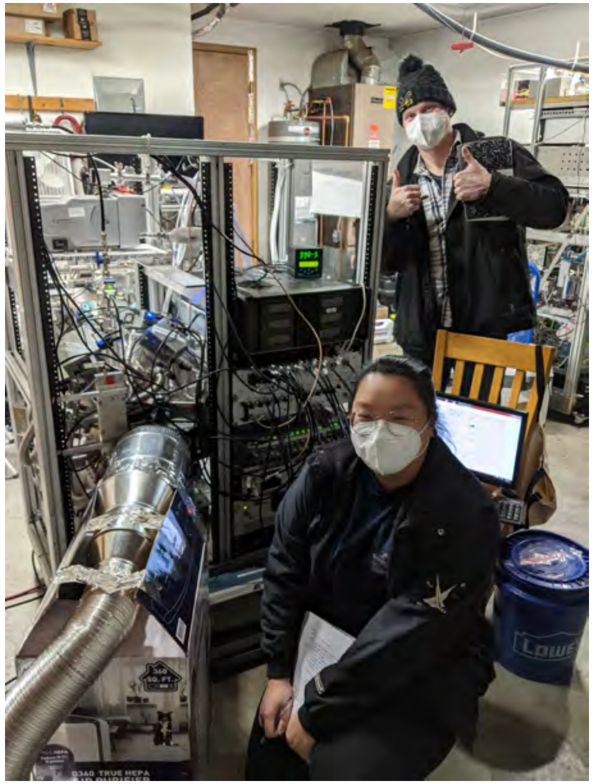
LSA CHEMISTRY
UNIVERSITY OF MICHIGAN

GREATER NEW YORK OXIDANT TRACE GAS HALOGEN AND AEROSOL AIRBORNE MISSION
GOTHAAM
SUMMER 2023

PI Kerri Pratt
prattka@umich.edu

Andrew Holen,
PhD Student

Michigan A-ATOFMS on the NCAR C-130 measuring individual aerosol particles

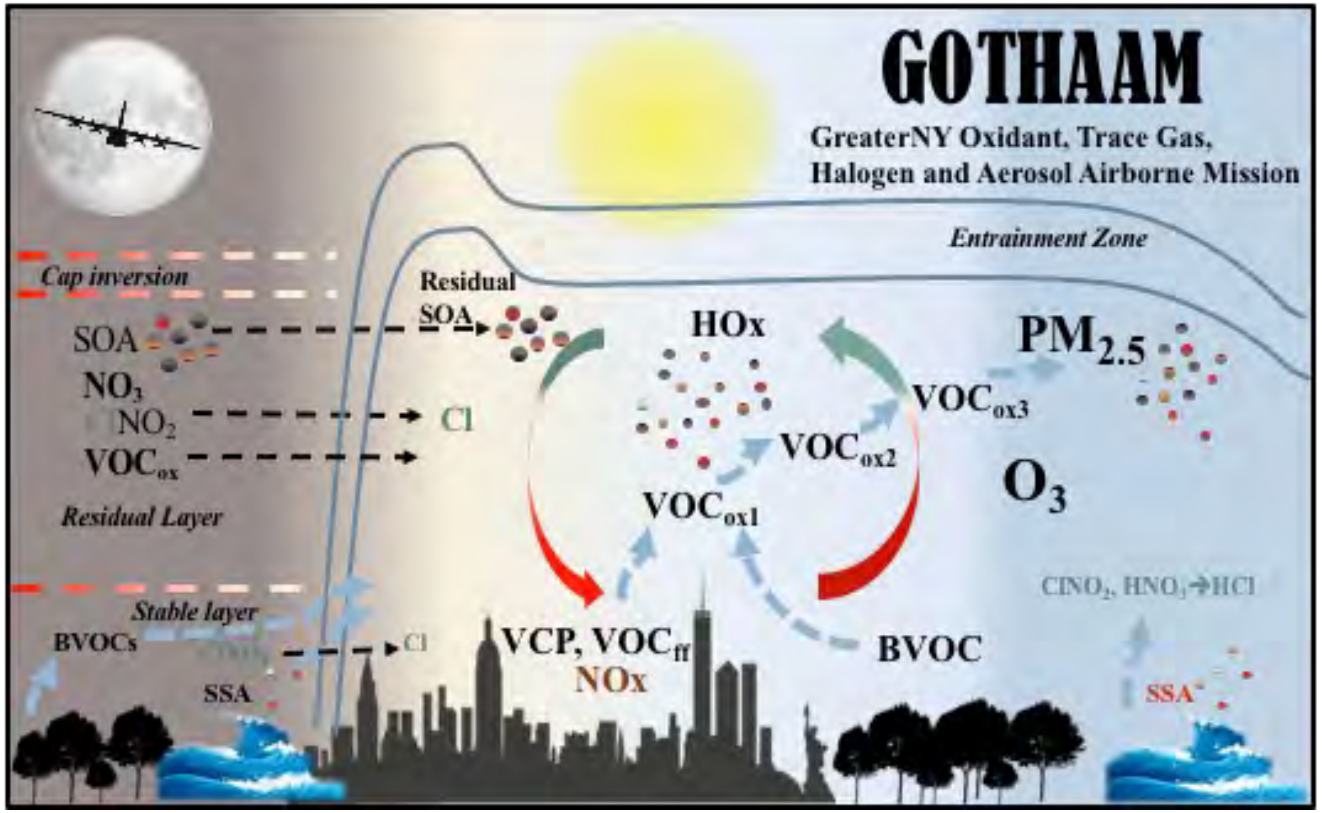


Real-time measurement of the size and chemical composition of individual particles

- ~0.09-1.5 µm, vacuum aerodynamic diameter
- Up to ~10 Hz single-particle chemical analysis
- Instrument components: aerodynamic lens, 488 nm & 408 nm scattering lasers, 266 nm triggered desorption/ionization laser, dual-polarity TOF
- Both refractory (eg., soot, sea salt, dust) & non-refractory material (e.g., organics, sulfate, nitrate, ammonium)
- Particle source/type size distributions, as well as number & mass concentrations, by calibrating with aerosol sizing instrumentation

References: Pratt et al. 2009, *Analytical Chem.*
Gunsch et al. 2017, *Atmos. Chem. Phys.*

Science Goals & Foci

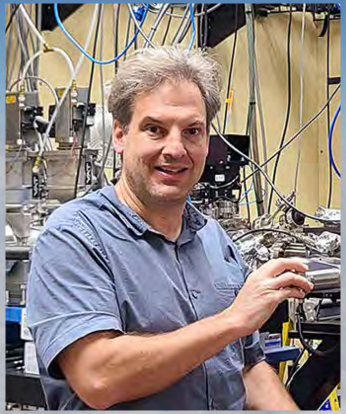


Integrating understanding of single-particle composition with modeling of heterogeneous chemistry (e.g. McNamara et al. 2020, *ACS Central Sci.*)

- What are the contributions of primary sources of aerosols?
  - Sea spray aerosol
  - Fossil fuel soot
- What is the distribution of various chemical species across the aerosol population (i.e. mixing state)?
  - Secondary organic aerosol – biogenic and anthropogenic
  - Chloride (for $ClNO_2$ formation)
- How do particle sources and mixing state change during transit from upwind to downwind of NYC?

Micro-Spectroscopic Analyses of Aircraft-Collected Aerosol Particles

Alexander Laskin
Instrument PI
Purdue University



Daniel Knopf
Instrument co-PI
Stony Brook University

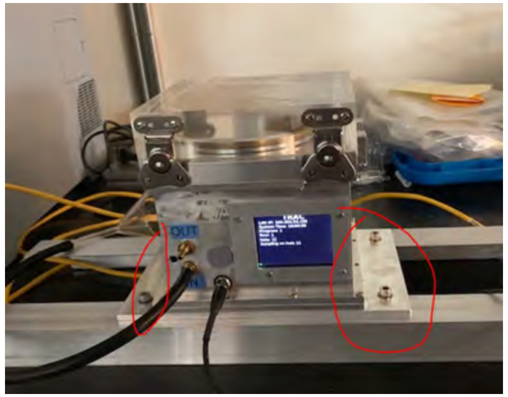
?

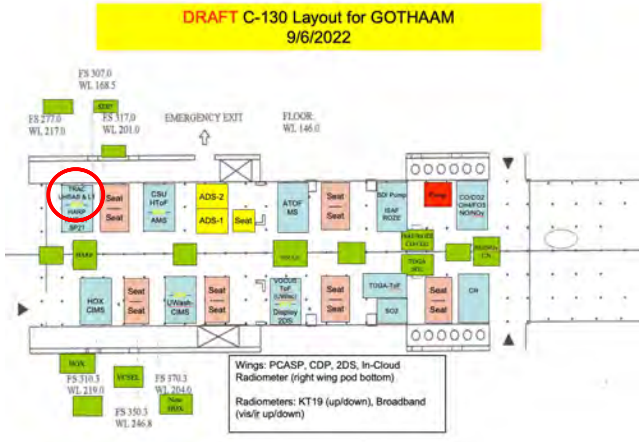
Graduate Student
TBD

Complementary offline single particle analyses to examine SOA evolution.

Micro-Spectroscopic Analyses of Aircraft-Collected Aerosol Particles

- **Employ TRAC** – Time Resolved Aerosol Collector





- Deposit particles on various substrate types for micro-spectroscopic single particle analysis:

Instrument specifications:

- Outer Dimensions: 7"x6.5"x5.5"
- Weight: ~10 lbs
- Input Voltage: 100-240VAC
- Power Supply Current Requirement: 1.5A
- Samples at 1 L min^{-1}
- Particle size range: cutoff size ($D_{50\%}$) of 0.36um. Typically collects particle in sizes between 0.1 to 5 μm
- 160 substrates mounted per disc
- Sampling time per substrate 5-10 min (depending on flight and aerosol concentrations)

Key publications:

Laskin et al, *JGR*, 117, D15302, ***2012***
Tomlin et al, *ACP*, 21, 18123–18146, **2021**

PURDUE UNIVERSITY

Stony Brook University
School *of* Marine and Atmospheric Sciences

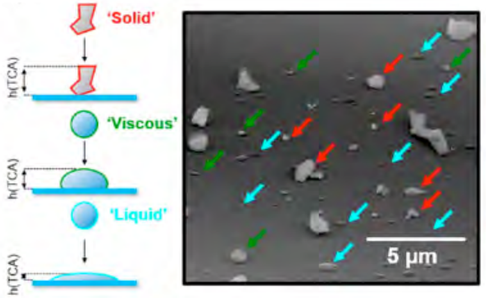
Micro-Spectroscopic Analyses of Aircraft-Collected Aerosol Particles

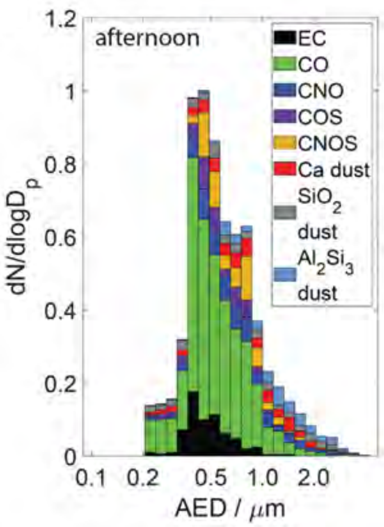
Science Goals:

Quantifying mixing state metrics of aged SOA. How well do speciation and quantification of VOC together with laboratory-based SOA yields explain evolution of SOA as the urban plume evolves downwind?

CCSEM/EDX:

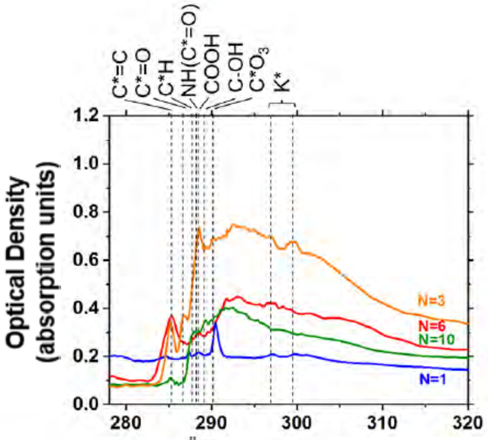
- Elemental composition
- Viscosity
- Identify particle-type classes

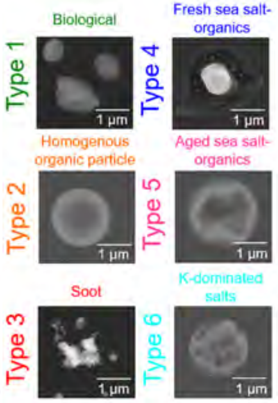


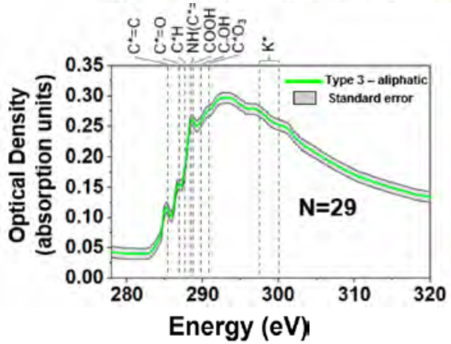


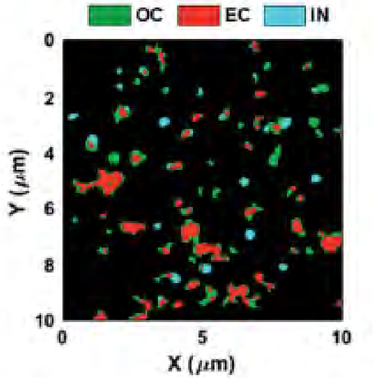
STXM/NEXAFS:

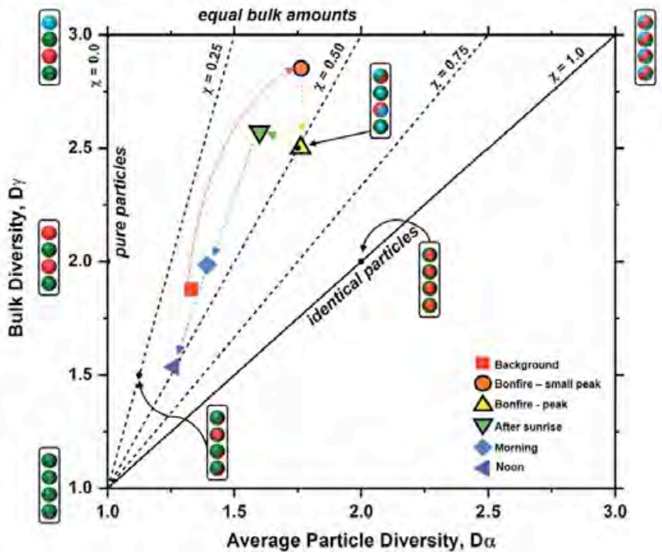
- Organic speciation
- Particle mixing state











AEROMMA PILS Measurements

Amy P. Sullivan
PI

Rodney J. Weber
co-PI

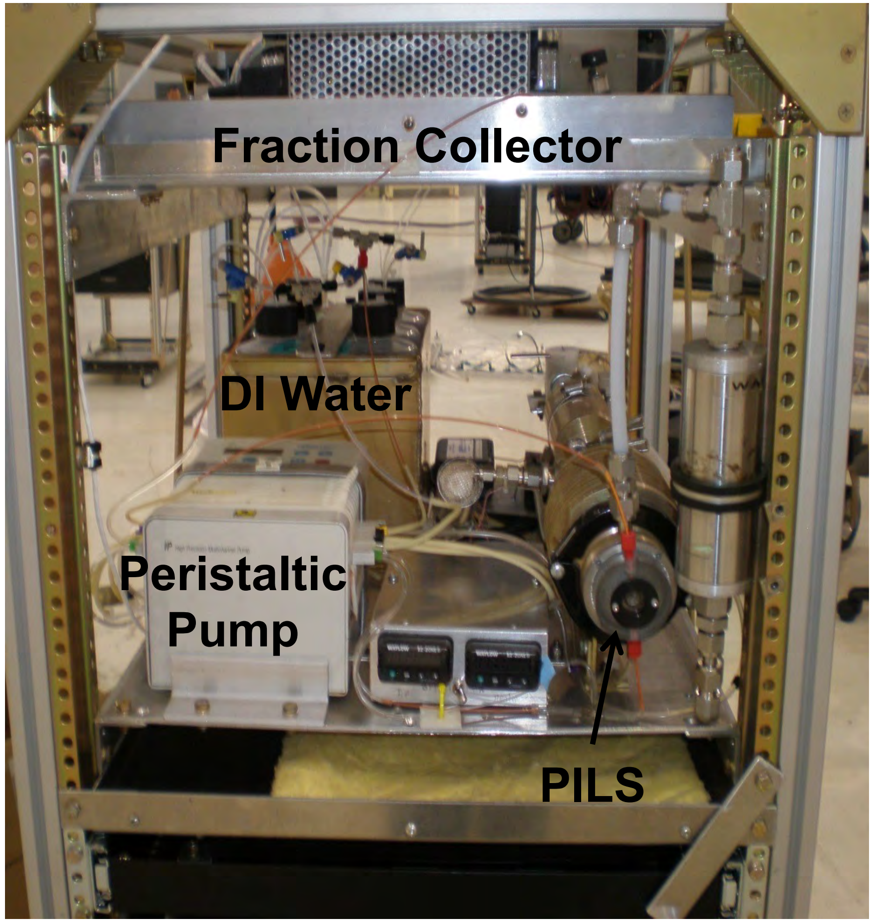
Magesh Kumaran Mohan
Graduate Student

Colorado State University

Georgia Tech

PILS with Fraction Collector

PILS | **Fraction Collector**



-Collect ~1.2 mL of liquid sample per vial every 2 min across entire flight

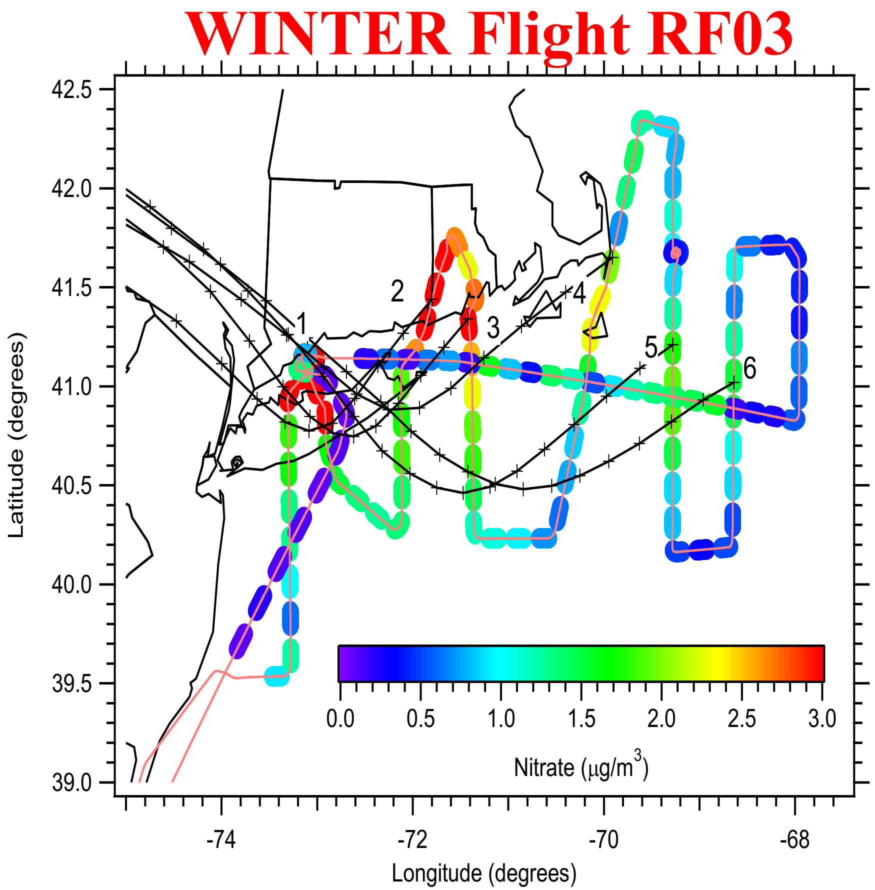
-Analyze samples using variety of ion chromatography techniques

Research Questions

1. What are the differences in the type of sulfur observed in urban vs. marine emissions?

2. What is the contribution of biomass burning in the study regions? How does it compare to winter?

3. What is the pH of the aerosol in the study regions in summer? How does it compare to winter?



-Colored by PILS nitrate

-Backtrajectories indicate followed urban plume from NYC downwind

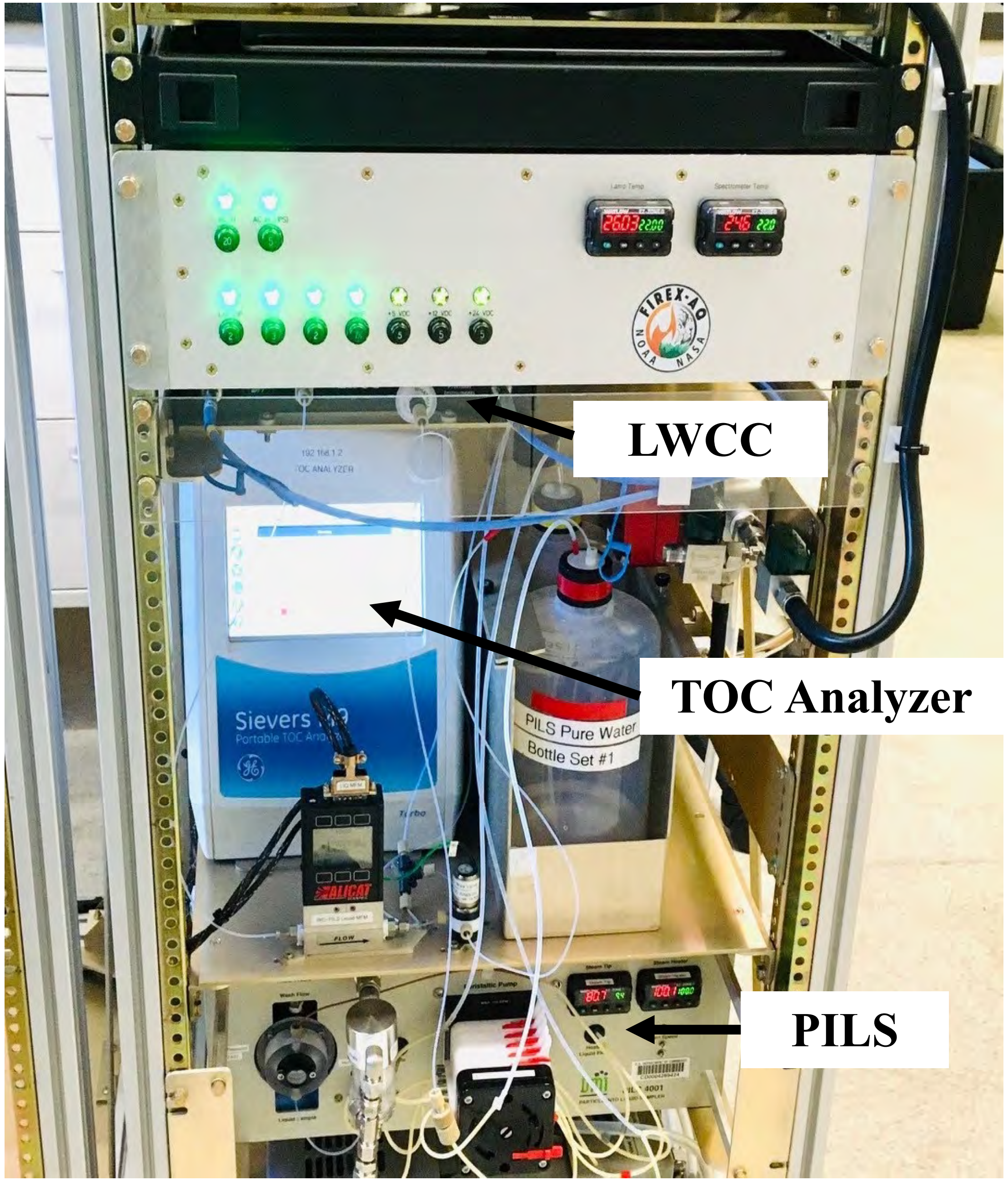
PILS-LWCC-TOC

-Additionally has Liquid Waveguide Capillary Cell (LWCC)

-Provides measurement of absorbance from 300 -700 nm

-Abs 365 = “Brown Carbon”

-Provides 3 s integrated measurement of Water-Soluble Organic Carbon (WSOC)



Potential Ideas for Data Analysis

- Assessment of BrC during study periods and contrast to other studies

- Combine WSOC and organic aerosol PMF factors from AMS to construct budget for BrC

- Compare BrC and its sources in Eastern vs. Western U.S.

- Examine impact of aqueous processing on BrC and WSOC

- Connect BrC and WSOC with biomass burning and pH analysis already planning

NOAA HR-AMS on NASA DC8 Measuring Aerosol Composition

Ann Middlebrook
Team Lead
NOAA CSL

Alison Piasecki
Instrument PI
CIRES/NOAA CSL

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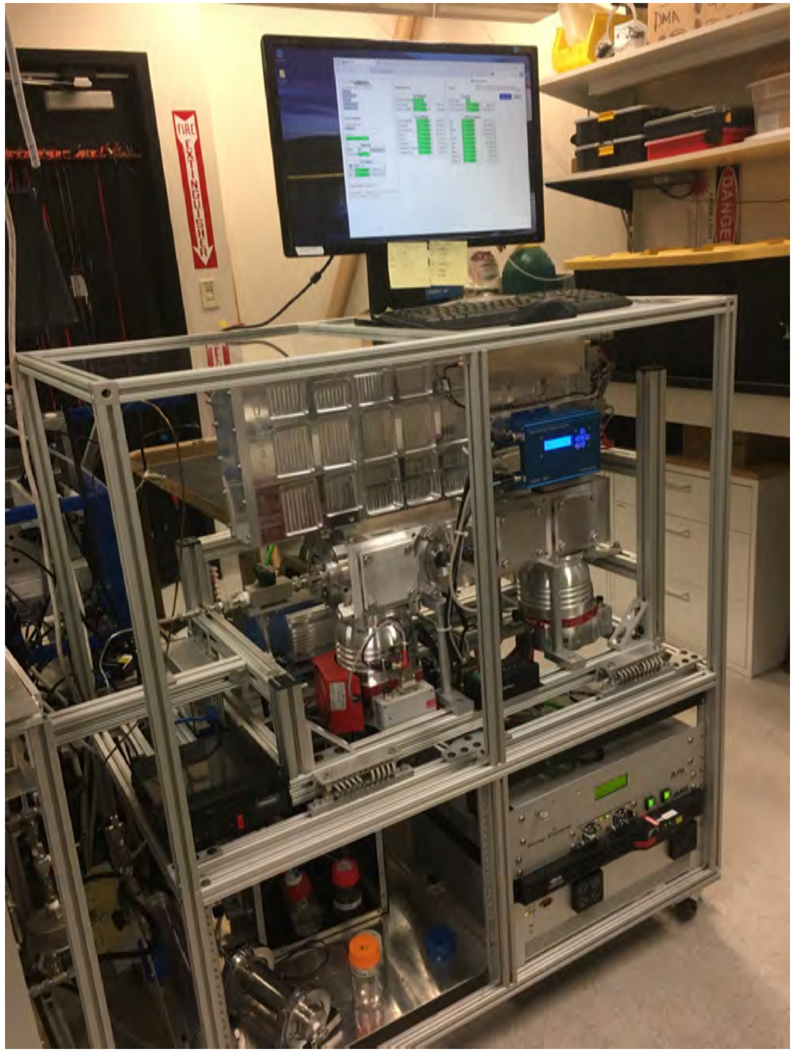
NOAA CHEMICAL SCIENCES LABORATORY

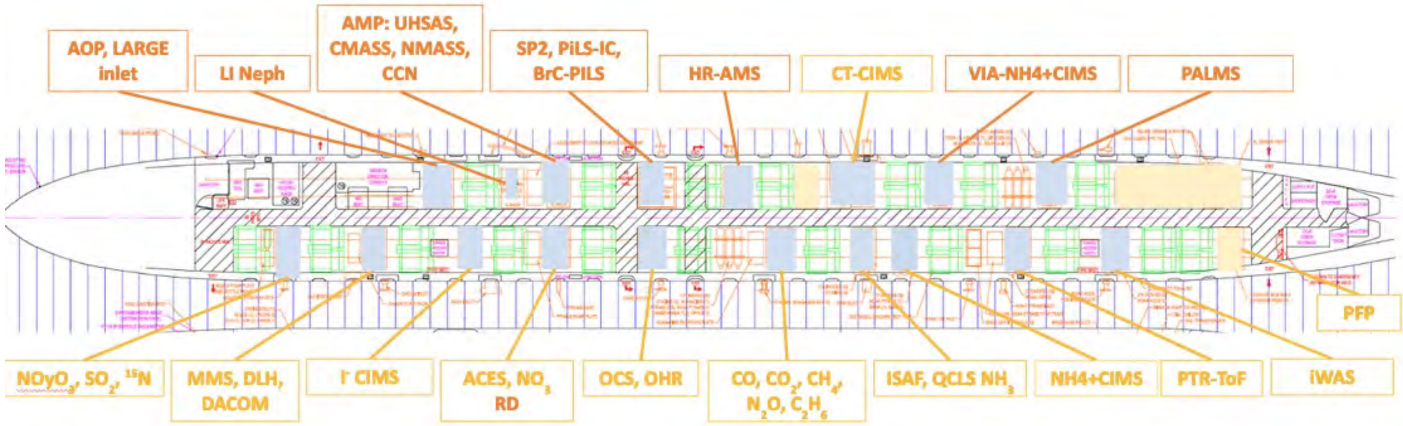
CIRES

NOAA HR-AMS on NASA DC8 Measuring Aerosol Composition

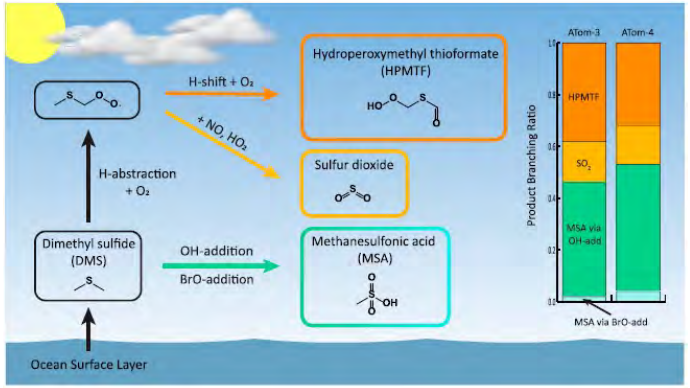


Non-refractory Aerosol Chemical Composition

- Sulfate (0.11 μg sm^{-3},1 Hz DL), Nitrate (0.21), Ammonium (0.09), Chloride (0.11), and Organic Species (1.64)
- Bulk Measurements and Speciated Mass Distributions
- Oxidation State of Aerosol Carbon
- Other components if possible (e. g. sulfur species)
- Submicron/$PM_{2.5}$ Inlet Lens
- Uncertainty ± 30%



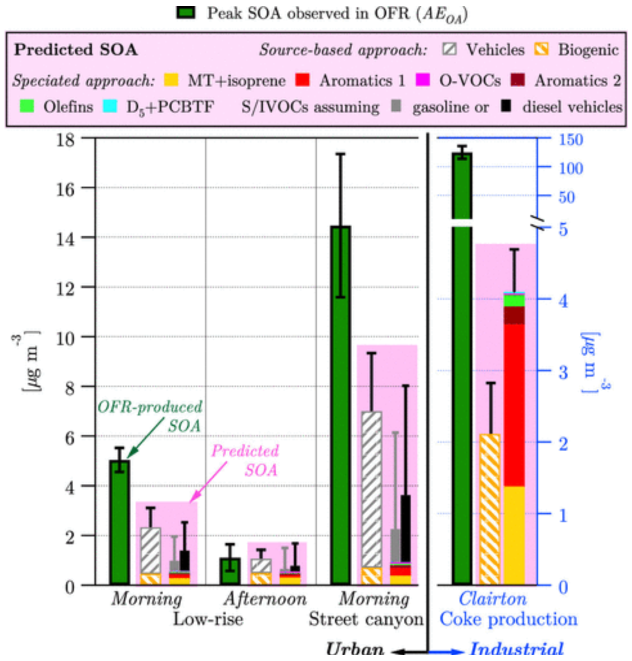
Science Goals and Foci



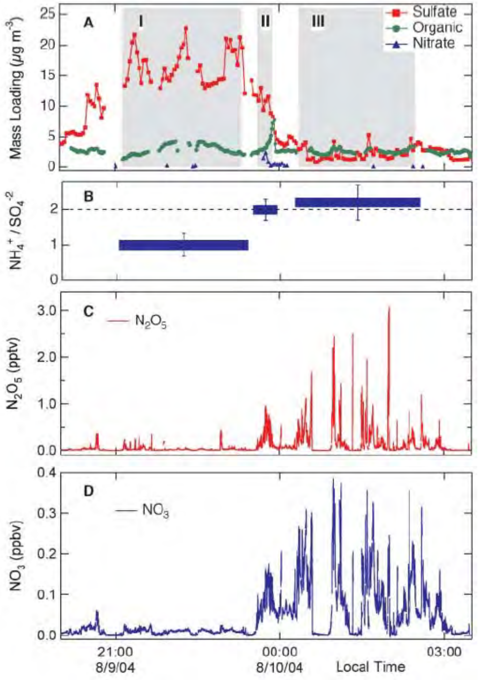
Veres et al. 2020

Use measurements to examine marine sulfur oxidation

Work with modeling groups to evaluate SOA production from a variety of sources



Shah et al. 2020



Brown et al. 2006

Compare aerosol composition with historical trends and affect on chemistry

NOAA NH_4^+ CIMS on NASA DC8
In-situ measurement of gas and aerosol composition





Chelsea Stockwell
Instrument PI
CIRES/NOAA

Lu Xu
Instrument PI
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Georgios Gkatzelis
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Julich

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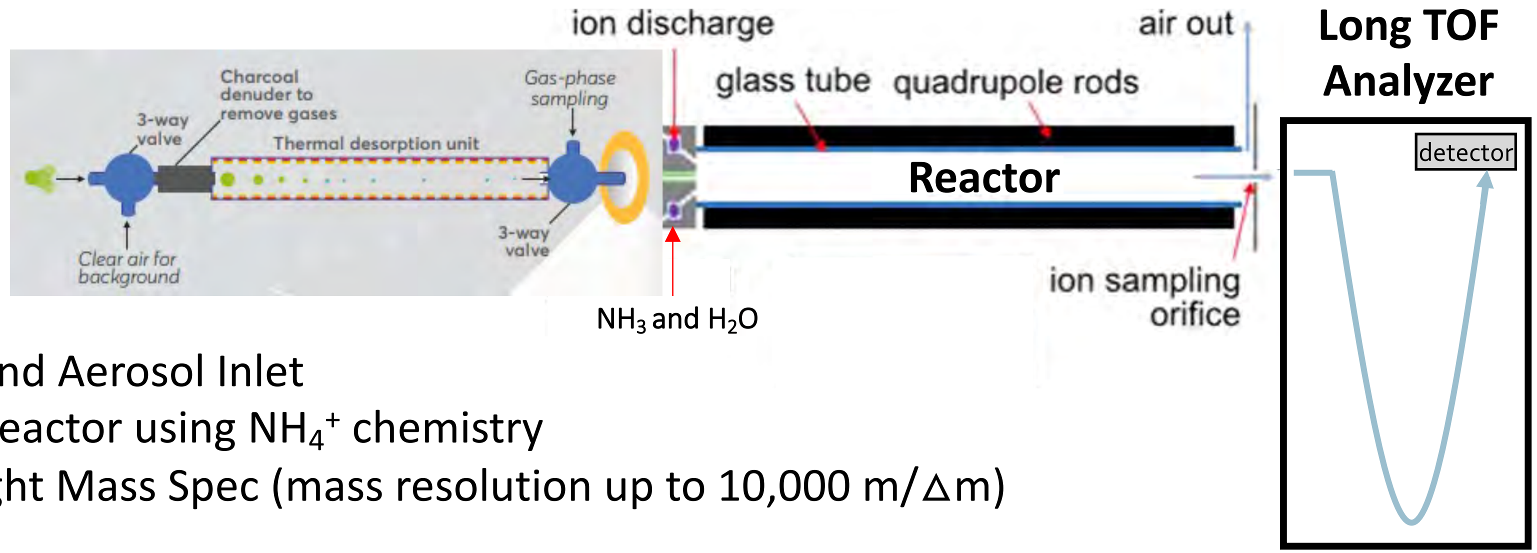
Contact: lu.xu@noaa.gov

CSL NOAA CHEMICAL SCIENCES LABORATORY

CIRES

NOAA NH_4^+ CIMS on NASA DC8 measuring gas and aerosol composition



- Switchable Gas and Aerosol Inlet
- Tofwerk VOCUS reactor using NH_4^+ chemistry
- Long Time-of-Flight Mass Spec (mass resolution up to 10,000 m/∆m)

Gas Measurement Performance
Targeted Species: Ketones, Aldehydes, Alcohols
Feature: Minimal fragmentation
Detection limits: < 100 ppt for 1s
Accuracy: 30-100%

Particle Measurement Performance
Detection limits: < 5 ng m^{-3}
Size Range: 60 – 1000 nm
Targeted Species: Semi-volatile oxygenated organic compounds

Key reference: Xu et al. (2022), AMTD, doi.org/10.5194/amt-2022-228

Science Goals and Foci

- Quantify fluxes of oxygenated organic species from ocean
- Measure aerosol chemical composition over urban area
- Utilize aerosol composition to conduct source apportionment of urban organic aerosol
- Evaluate the life cycle of urban aerosol and evaluate model performance in simulating organic aerosol

PURDUE UNIVERSITY | Department of Earth, Atmospheric, and Planetary Sciences

PALMS-NG: a new airborne single particle mass spectrometer

Purdue University: Daniel Cziczo (PI), Justin Jacquot, Xiaoli Shen

NOAA: Daniel Murphy, Gregory Schill, Michael Lawler, Maya About-Ghanem

CIRES / Air Innova: Karl Froyd

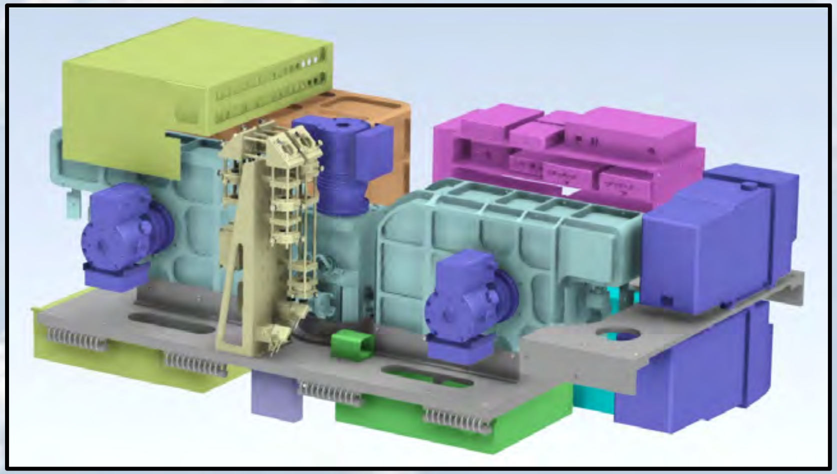
Original Code Consulting: David Thomson

DCOTSS
NASA Earth Venture Suborbital 3
Dynamics and Chemistry of the Summer Stratosphere

ACCLIP
Asian Summer Monsoon Chemical and Climate Impact Project

NASA ER-2

NASA WB-57



CAD drawing of PALMS-NG

Photo credit: NASA ER-2 pilot Timothy L Williams on June 3rd, 2022

PALMS-NG: Bipolar time-of-flight mass spectrometer

Particle **A**nalysis by **L**aser **M**ass **S**pectrometry – **N**ext **G**eneration:

- Size measurement
- Chemical composition

Particle detection:

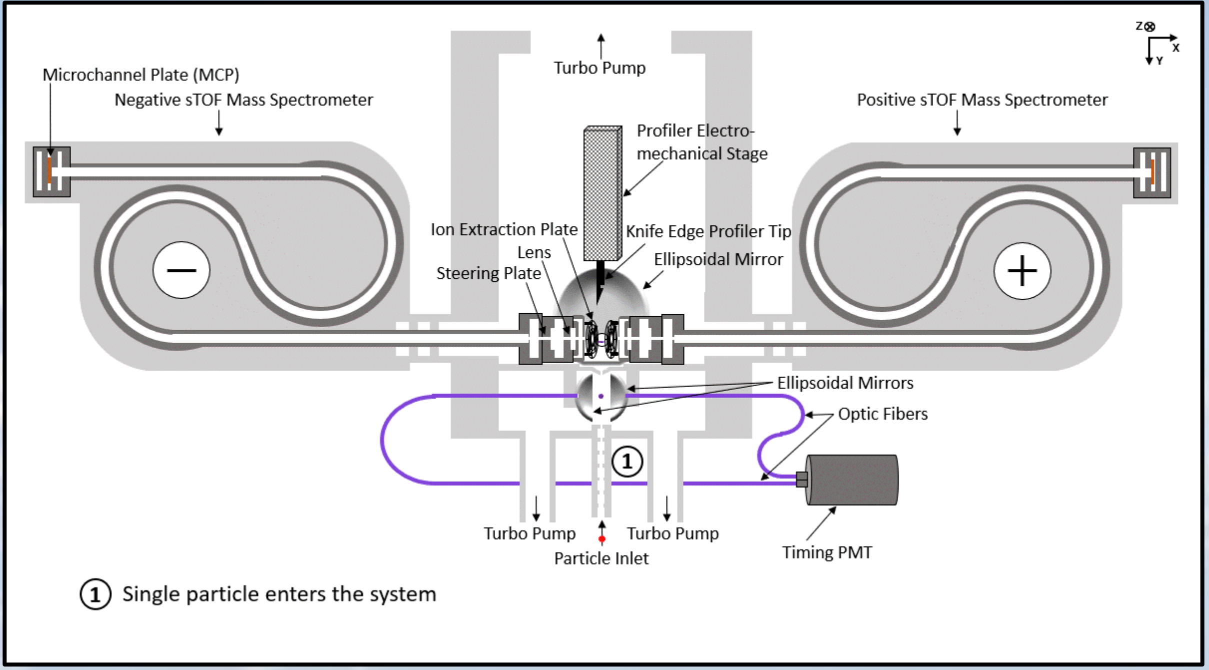
- Size range: 100 nm to >3 µm
- Detection rate: up to 20 Hz
- Detection efficiency: 1-4 orders of magnitude higher than older PALMS

S-shape TOF Mass Spectrometer:

- Compact shape – bipolar spectra (*Murphy, JASMS 2017*)
- Ion transmission: close to 100%
- Mass resolution: 5x better than older PALMS

Operation:

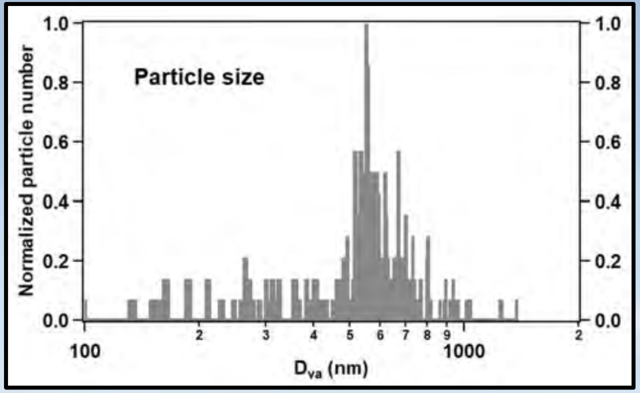
- 2 switches (Power + Run)
- Full control from the ground via satellite communication



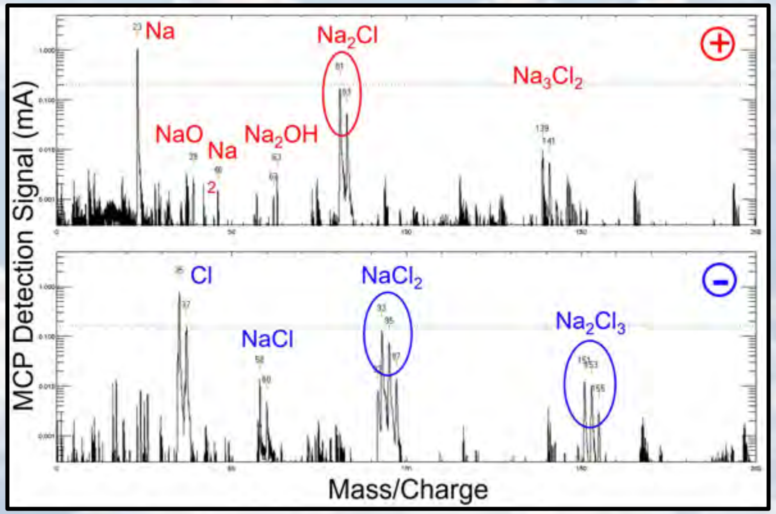
PALMS-NG particle detection and ion path

PALMS-NG: Data product

1. Particle size distribution

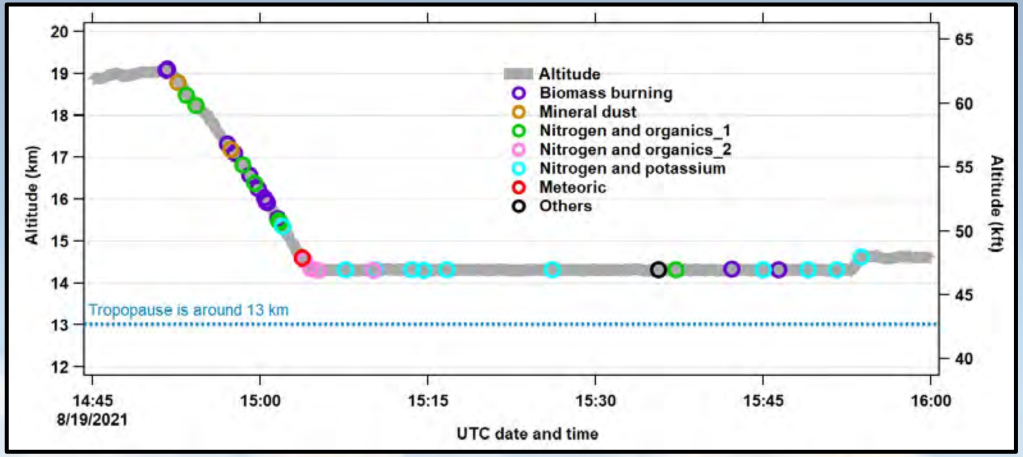


2. Bipolar spectra of single particles



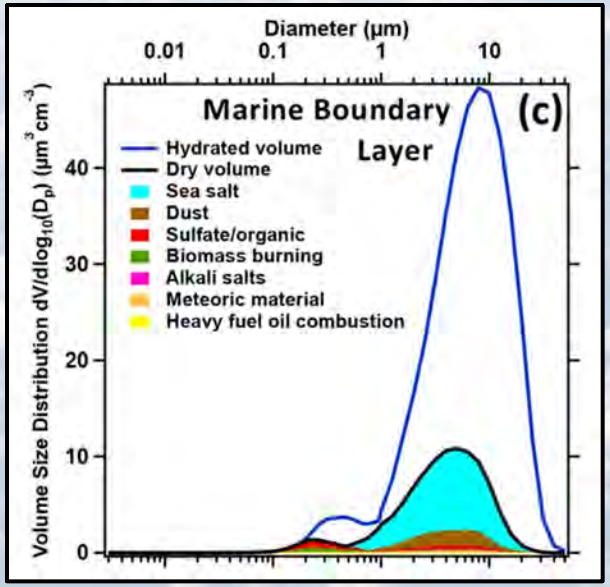
Sodium Chloride: NaCl

3. Time-series of particle type



Example of RF11 from DCOTSS #1

4. Volume of particles of different aerosol as a function of diameter



Example of average composition-dependent size distribution of the aerosol from ATom deployment (Fig.11 (c), Brock & al 2021)

Size resolved aerosol mixing state and composition at NYC-METS ground site

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CEE

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Chemistry

Yao Xiao
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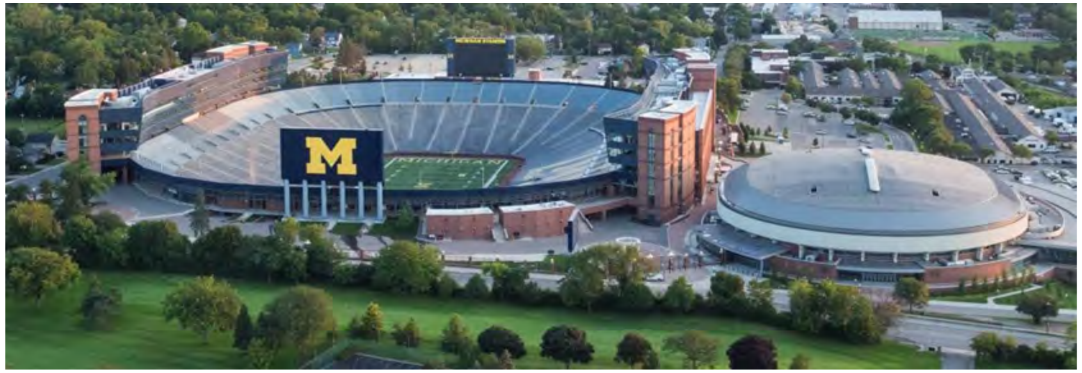

Impactor sampling NYC-METs

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- NYC – CCNY ASRC
  - Low Flow Impactor 1 - (mini-MOUDI)
  - MOUDI 1 - (O'Brien)
  - MediumVol - (Ault/Pratt)
  - Spot Sampler (DMA size select)
    - Microscopy substrates - ultrafines
- Yale
  - Low Flow Impactor 2 - MPS or mini-MOUDI or Slot Impactor
  - MOUDI 2 - (Ault)
- Location To Be Determined
  - Brechtel sampler
  - Picarro (NH_3, H_2O, CO_2)
  - APS

Time resolution: ½ days to days (impactors)
Analytical methods: SEM/EDX, OPT-IR, offline-AMS, FT-ICR, IC
Substrates: TEM grids, silicon, quartz, Teflon filters, Aluminum foil

Science goals + analysis

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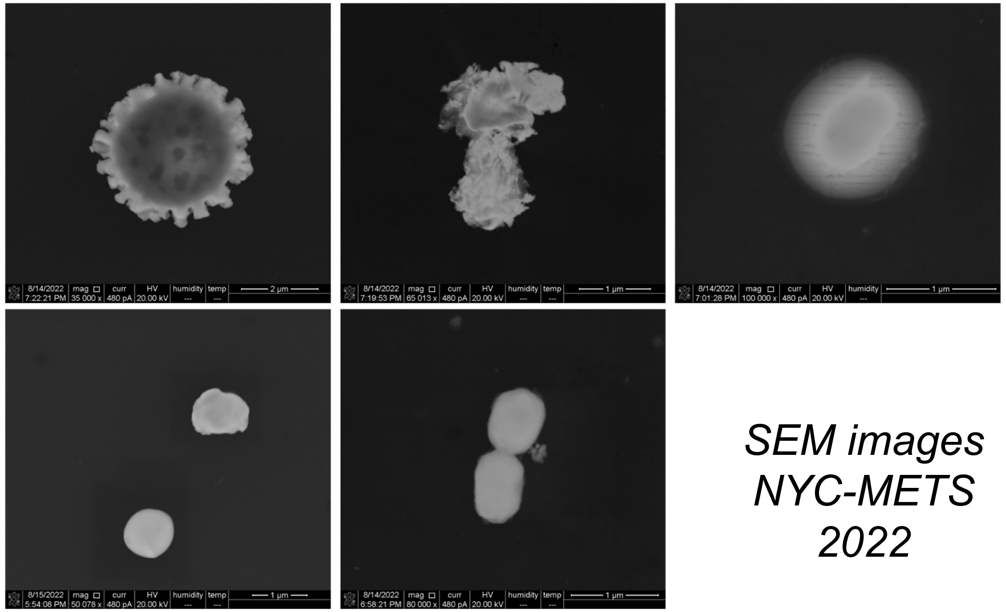
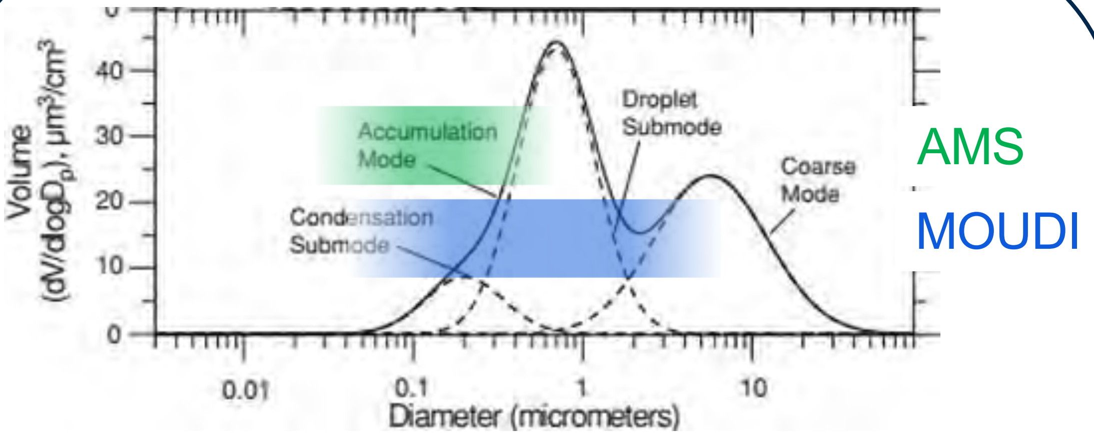
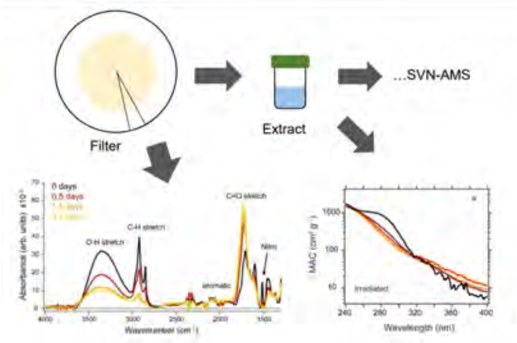


SEM images NYC-METS 2022

Aerosol mixing state/morphology → understand how this relates to VCP emissions



Aerosol composition (size resolved)

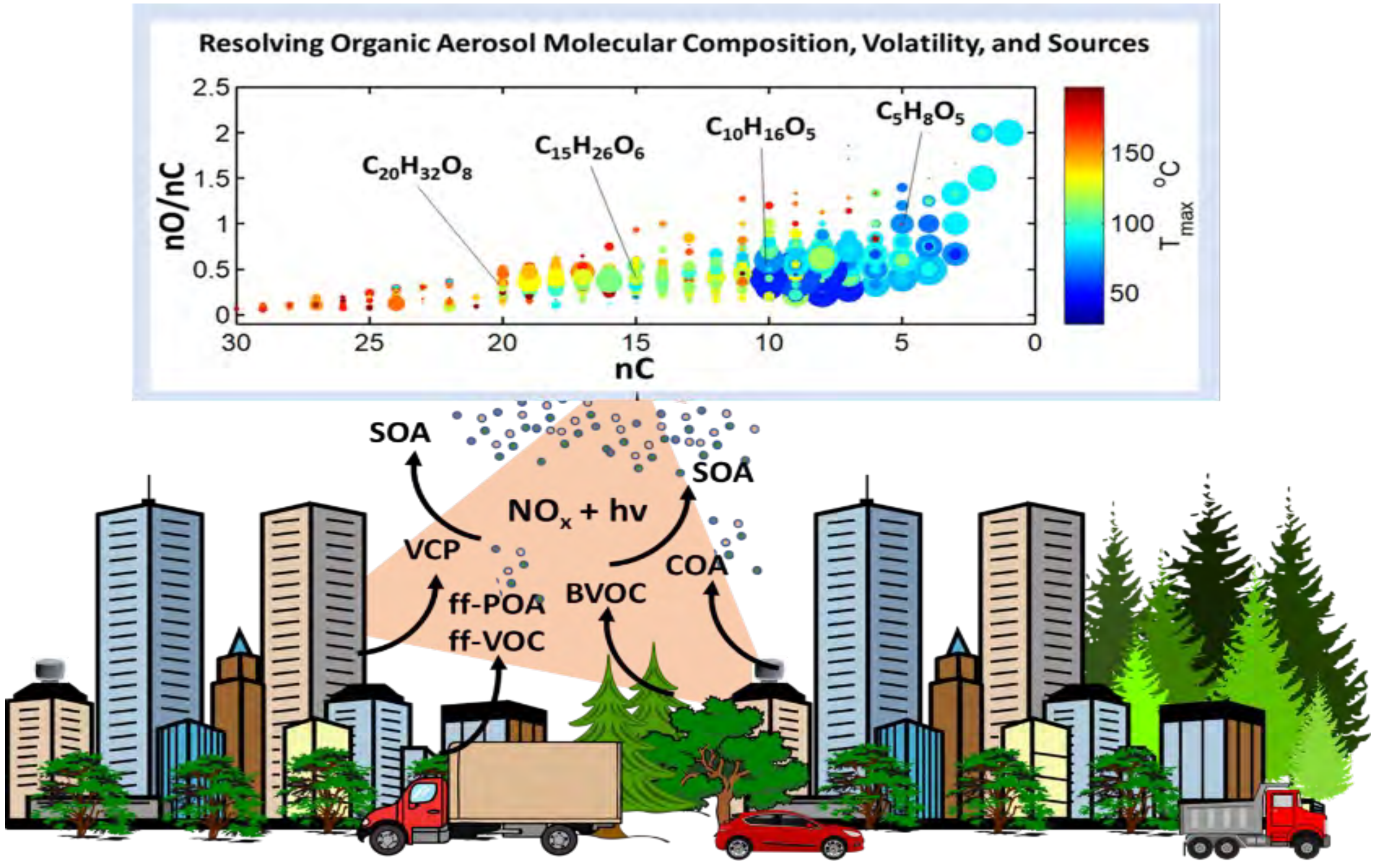


Marine emissions + aerosol transport/aging

Molecular-level Source Apportionment of Ambient Particulate Matter in a Coastal Mega-City

PI Joel Thornton (UW), Co-PI Sally Ng (Gatech)

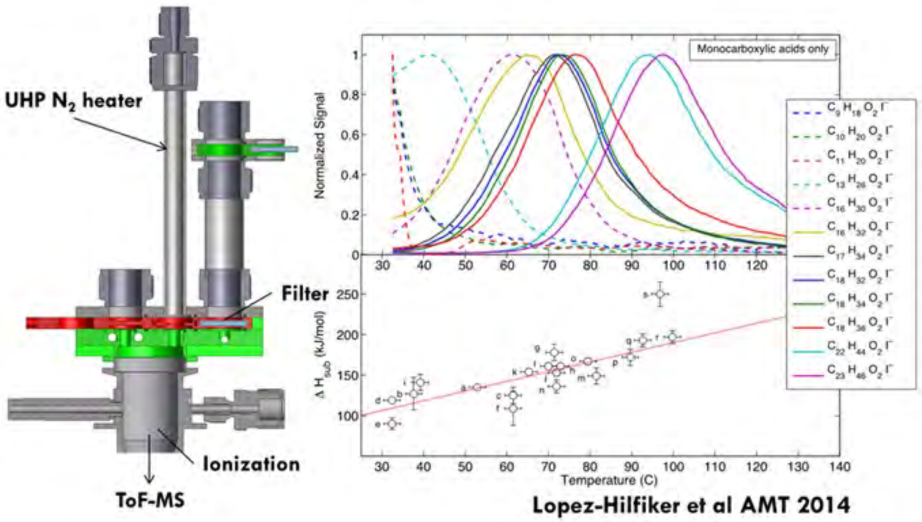
NOAA AC4 NA21OAR4310130

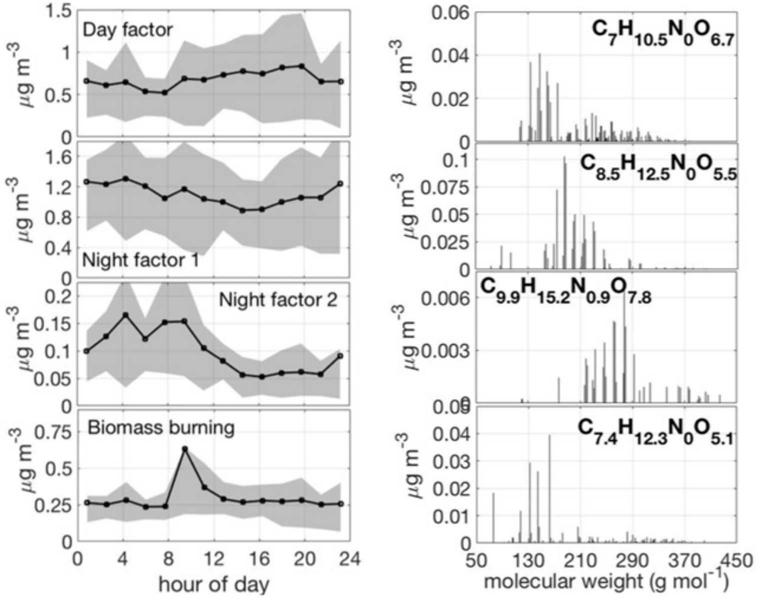


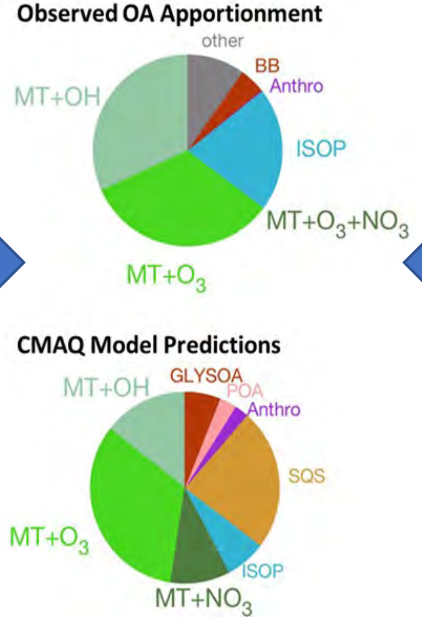
Objectives and Methods

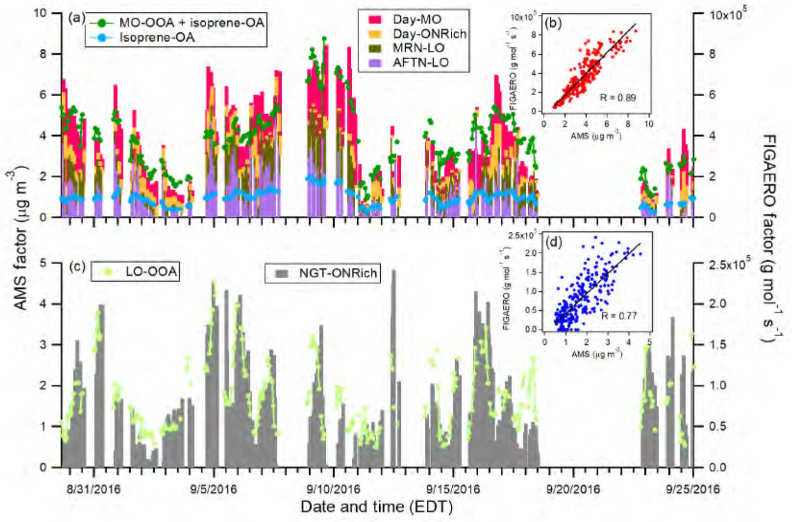
- ***Conduct online and near real-time molecular-level measurements of gas and particle composition using FIGAERO-HRToF-CIMS in two NYC area locations***

- ***Use hourly molecular information to conduct quantitative and detailed source apportionment of the OA fraction of PM1 into important primary and secondary OA sources, pathways, and properties (e.g. volatility)***







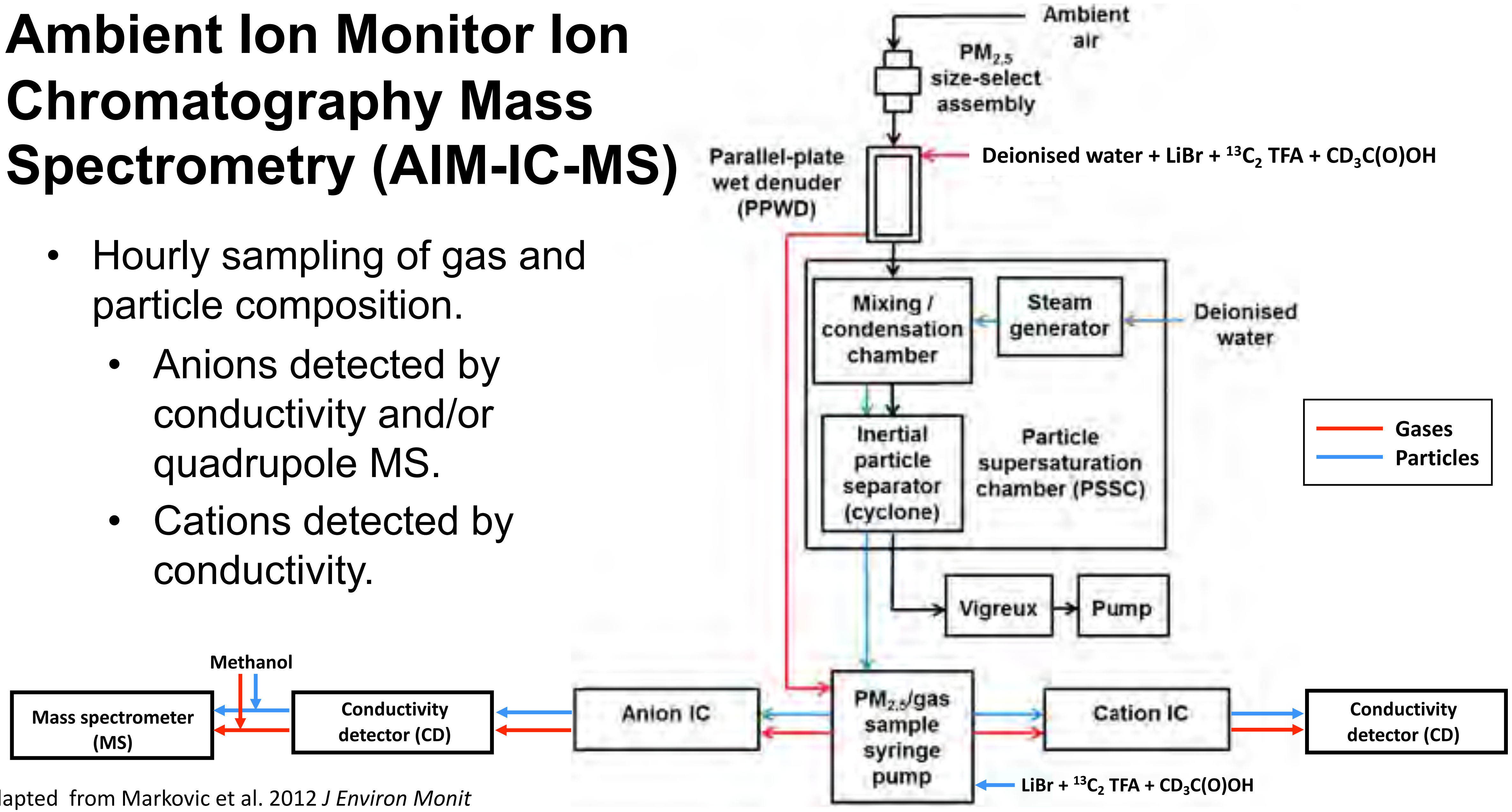


Deployment Plans and Opportunities for Collaboration

- Locate a FIGAERO HRToF-CIMS at CUNY ASRC and another at Yale Coastal Field-site
- Prioritize overlap with AGES NYC activities (e.g., July 2023)
- Locations and measurements will produce data useful for reactive nitrogen partitioning, halogen activation, marine emissions and chemistry (e.g. DMS)
- We are happy to share data for these and other studies, please reach out.
  - joelt@uw.edu and/or ng@chbe.gatech.edu

Ambient Ion Monitor Ion Chromatography Mass Spectrometry (AIM-IC-MS)

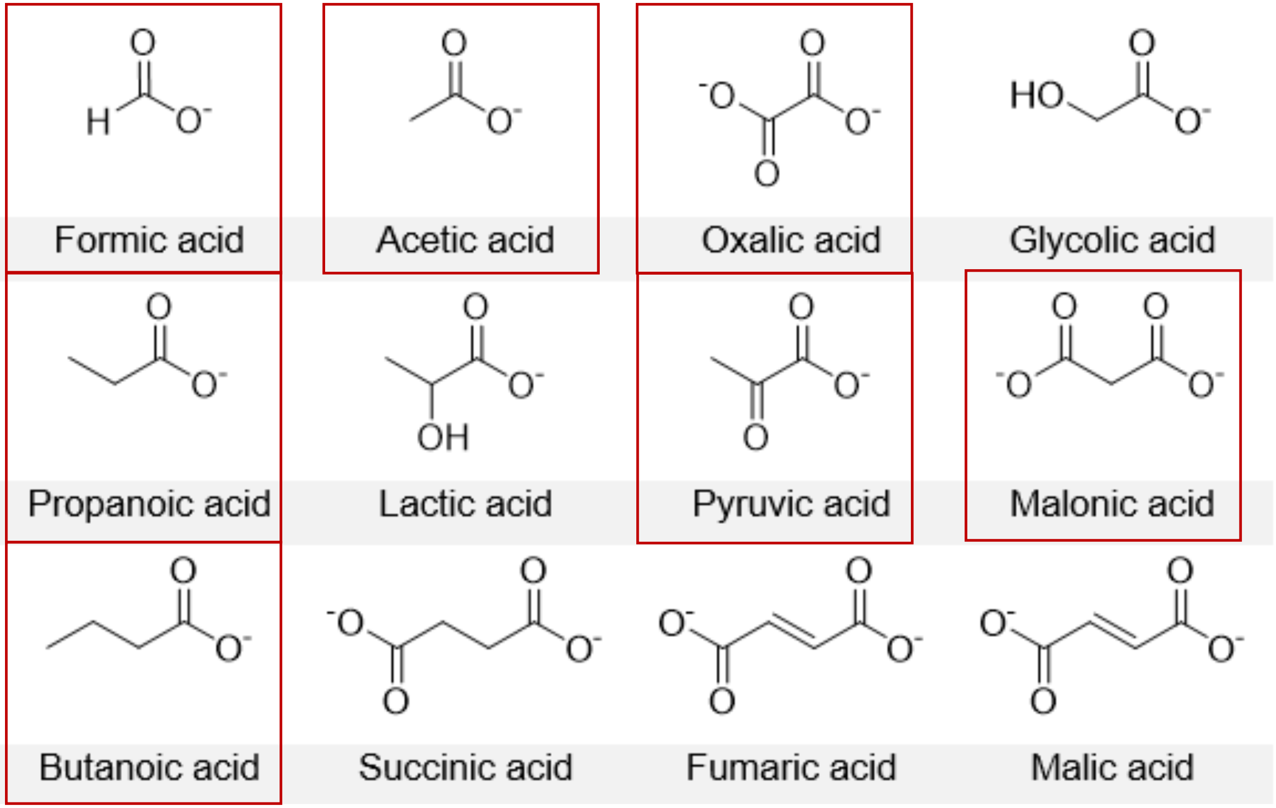
- Hourly sampling of gas and particle composition.
  - Anions detected by conductivity and/or quadrupole MS.
  - Cations detected by conductivity.

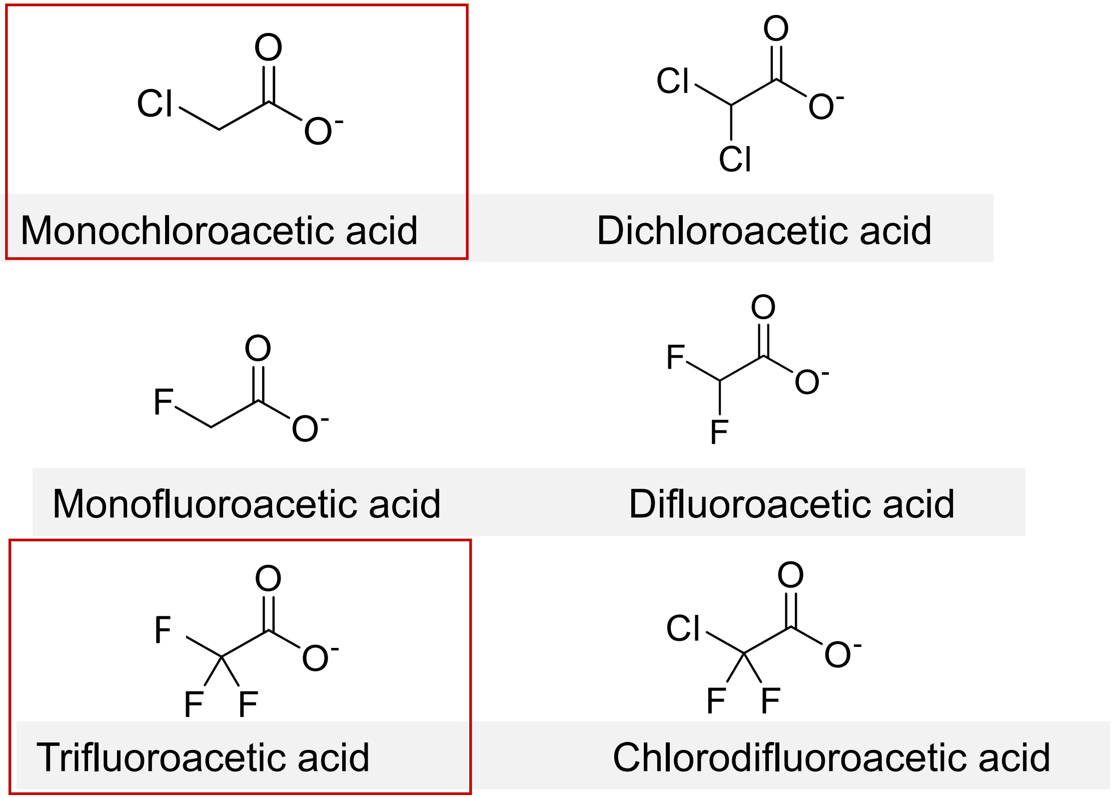


Adapted from Markovic et al. 2012 *J Environ Monit*

AIM-IC-MS Targets

- Cations: NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}
- Anions (conductivity): F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}
- Anions (MS):





Science Goals

Halogens

- HCl intercomparison
- Particle chloride measurement

Contaminants

- Contaminant abundance and gas-particle partitioning

Inorganics

- PM2.5 composition and gaseous HNO_3, SO_2 for gas-particle partitioning

FALCON: Fluxes of AerosoL Continuous Observing Network (EPCAPE Deployment)

<u>Goal:</u> To quantify size-resolved particle fluxes at multiple sites over different surfaces to investigate underlying processes of particle deposition

- Portable Optical Particle Sizer (POPS) measures particles 140 – 3000 nm
- Eddy covariance / wavelet flux analysis
- Scripps Pier: Spring 2023 – 2024+
- Measure particle emission deposition over coastal water

<u>Research Team</u>

Dr. Delphine Farmer (PI, CSU), Dr. Ethan Emerson (coPI, CSU), Dr. Ruthambara Joshi (CSU), Mr. Ricky Peña (CSU) + technical support from DOE ARM