Infrared Analysis of IMPROVE filters the Depth and Breadth of what this provides

Ann M. Dillner
Associate Director of Analytical Research
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University of California, Davis

IMPROVE Steering Committee Meeting (virtual)
November 18, 2025

IMPROVE CESU funding for FT-IR

- Fourier Transform – Infrared spectroscopy
  - Uses infrared light to probe chemical bonds in particles
  - Non-destructive to samples so that gravimetric mass, XRF, HIPS and FTIR can analyze the same filters
- Cooperative agreement (CESU) funding supports the FTIR analysis of Teflon filters collected at a subset of IMPROVE sites
  - 20+ sites used to calibrate FTIR spectra to TOR OC and TOR EC
    - Used to measure OC and EC at international sites operated by SPARTAN and NASA/MAIA
    - Smaller research projects – impact of smoke on the growth of plants
  - Sites collocated with the new ASCENT network
  - Sites to support DOE-funded organic hygroscopicity research

IMPROVE
40 YEARS OF IMPROVING VISIBILITY
1985 - 2025

US EPA
Chemical Speciation Network

SPARTAN
Global Particulate Matter Network

US and Global Aerosol Speciation Monitoring Networks: Successes and Opportunities

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MAIA
Multi-Angle Imager for Aerosols

AEESP AAAR Plenary Presentation
October 16, 2025

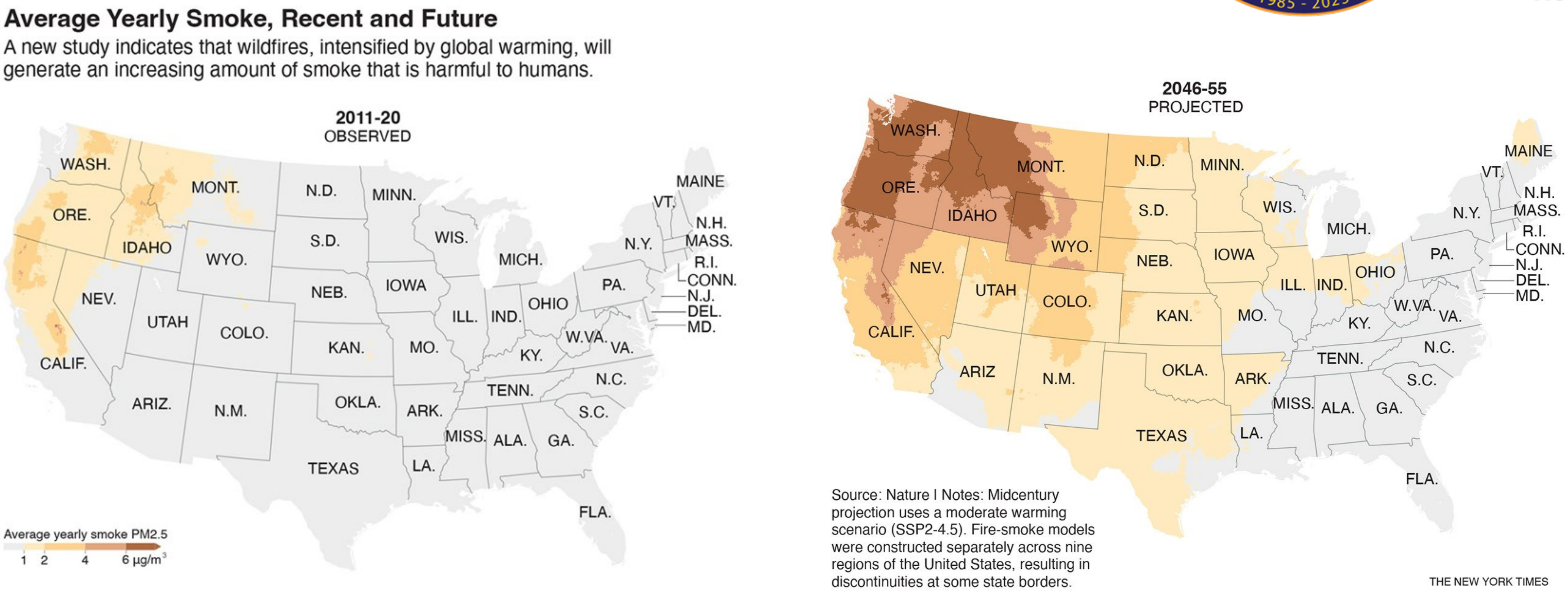
ASCENT
Atmospheric Science and Chemistry mEasurement NeTwork

AAAR Plenary on Monitoring Networks

Increased Mortality in US due to Wildfire Smoke – NY Times

US EPA

Chemical Speciation Network



- IMPROVE and CSN data with GEOS-CHEM and satellite AOD used to estimate monthly PM2.5 (van Donkelaar et al., 2021), PM2.5 smoke estimated by machine learning model (Childs et al., 2022)
- Increased wildfire smoke due to global warming will kill 70,000 Americans/year by 2050
- Network data allows us to identify impact of climate change and the resulting impact on human health

Quit et al., Nature, 2025, Accelerated Article Preview. Figure from The New York Times.

Los Angeles Urban Wildfires in January 2025

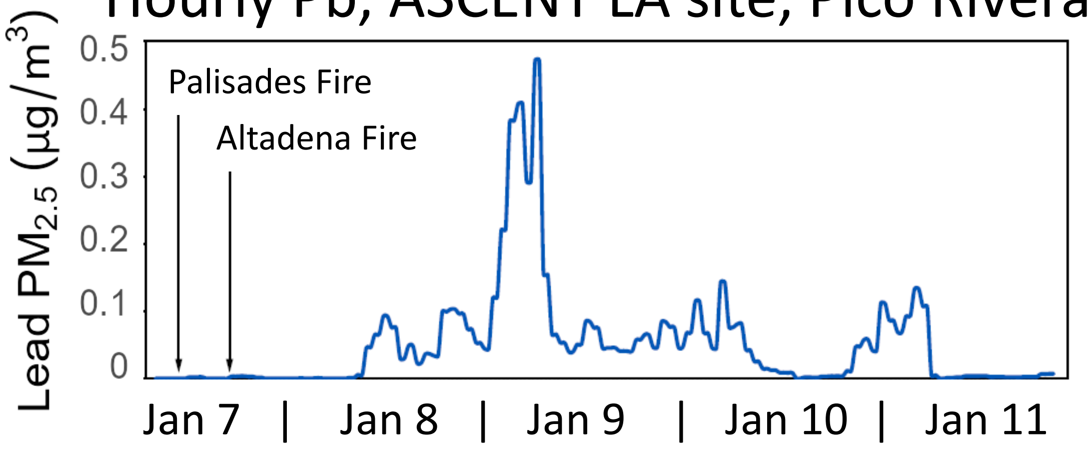
US EPA Chemical Speciation Network

ASCENT Atmospheric Science and Chemistry mEasurement NeTwork

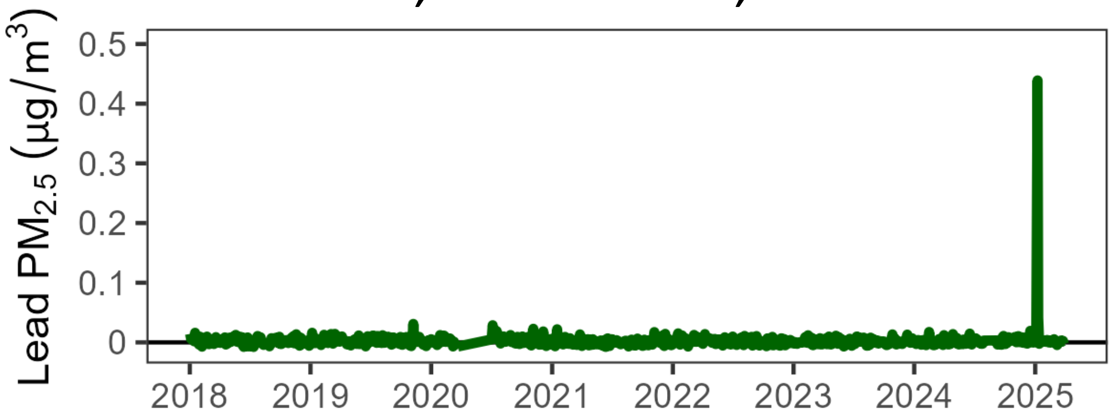
ASCENT in Jan 20th NY Times article

Researchers used a new network of sensors to track chemicals in the Los Angeles air in real time. Credit: Loren Elliott for The New York Times

Hourly Pb, ASCENT LA site, Pico Rivera



24-hour Pb, CSN LA site, North Main



American Association for Aerosol Research



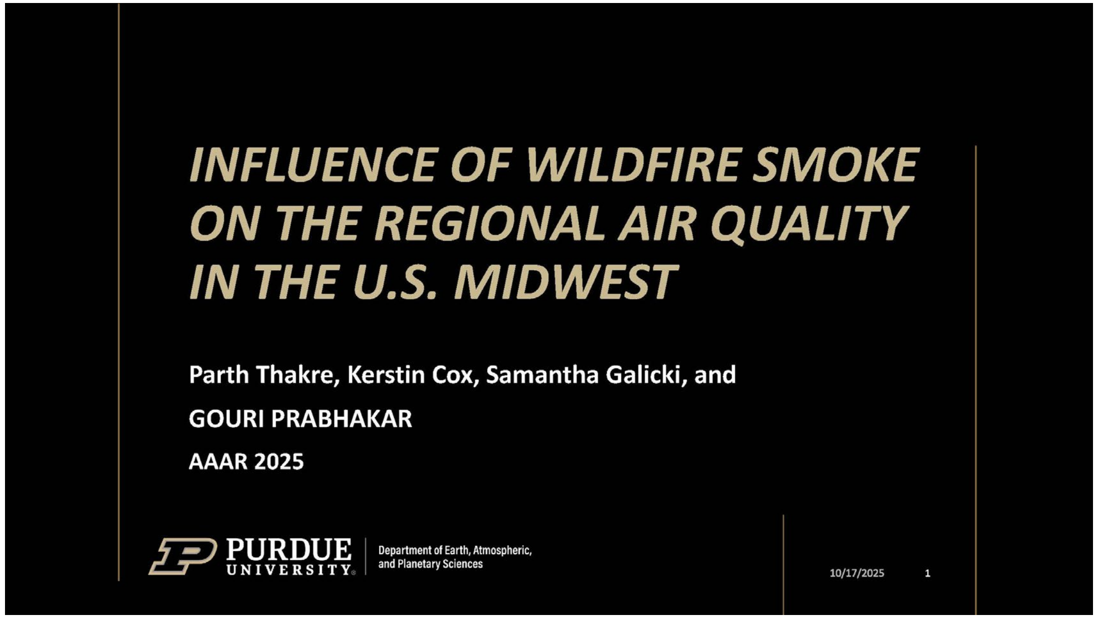


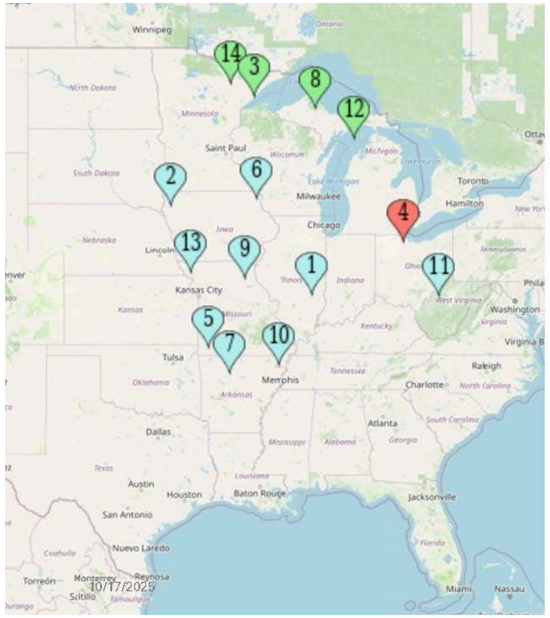






AAAR presentation using IMPROVE data





DATA

- IMPROVE Network - Longest ground observations of speciated aerosol in the U.S.
- Eight states – IN, IL, IA, MI, WI, MN, OH, MS
- Only sites with **at least 10 years** of data included → 14 sites

10/17/2025 7

From Purdue Professor that gave this talk: I have used this data to guide undergraduate research and to teach data-sharing principles in our introductory Atmospheric Sciences course.

Topics for this talk

- Estimating hygroscopicity of organics in wildfire samples at Yosemite, Sequoia and PMRF IMPROVE sites
- Measuring organic functional groups in high time resolution with an ACSM instrument – method developed using FTIR spectra and ACSM data at IMPROVE Atlanta, Ga site
- Using 20+ sites to calibrate FTIR spectra to TOR OC and TOR EC
    - Used to measure OC and EC at international sites operated by SPARTAN and NASA/MAIA
    - Smaller research projects – impact of smoke on the growth of plants

Hygroscopicity of Organic Aerosol from Wildfire Emissions

Nagendra Raparthi, Anthony S. Wexler, Ann M. Dillner

Air Quality Research Center
UC Davis

Submitted to Nature Communications on November 12, 2025

Why Study Wildfire Emissions & Hygroscopicity

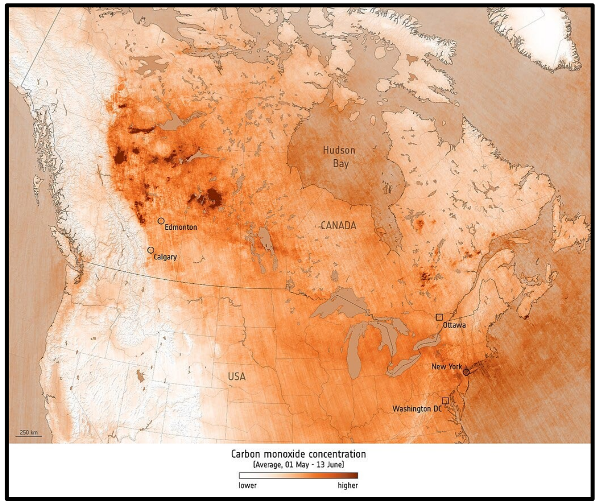
- **Chemical composition** – different from other aerosol sources
  - Heavily dominated by organics
  - Varies by fuel properties, combustion conditions (flaming vs smoldering), fire size and intensity
  - Meteorology and Topography

- **Hygroscopicity depends on chemical composition**
  - Organic hygroscopicity not well understood

- **Hygroscopicity impacts**
  - Particle size
  - Aqueous phase chemical reactions
  - Cloud condensation nuclei (CCN)
  - Influence Earth's radiation balance
  - Particle lifetime

Pika Fire in Yosemite National Park on July 15, 2023.

Garnet Fire in Sierra National Forest on Sep 10, 2025.



Canadian wildfire in the year 2023.

Research Gaps & Objectives

Research Gaps

- Limited knowledge of the hygroscopicity of organic matter (OM)
  - Developed a method to measure water uptake on Teflon filters (Raparthi et al., AMT, 2025)
  - First used on laboratory-generated organic chemical filter samples (Raparthi et al., ES&T Air, in press)

- Dependence of wildfire $PM_{2.5}$ hygroscopicity on chemical composition remains largely unexplored.

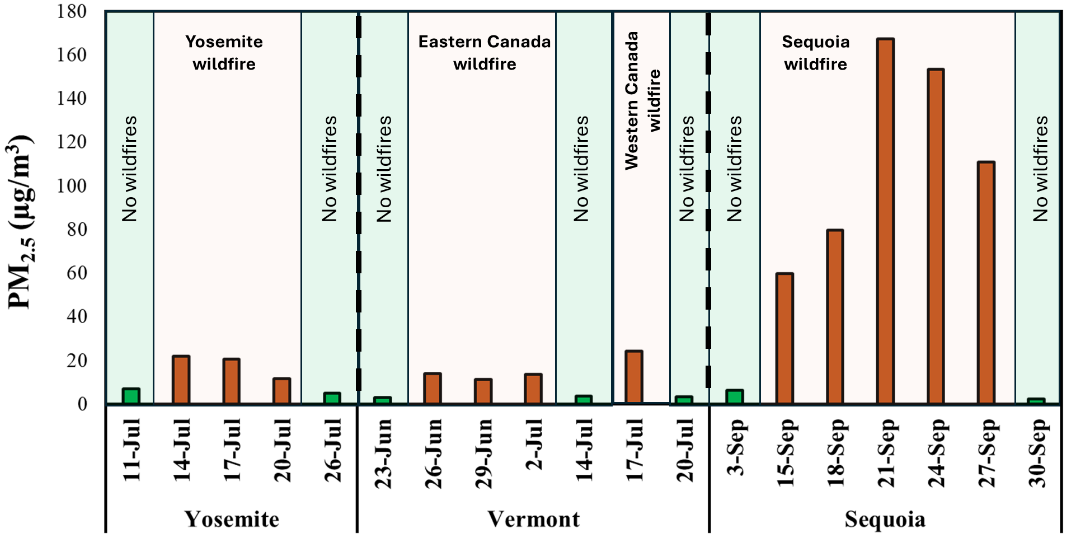
Objectives of this Study

- Measure hygroscopicity of $PM_{2.5}$ from local and long-range transported wildfires
- Derive organic matter hygroscopicity in local and long-range wildfire
- Model hygroscopicity from chemical composition of wildfire samples

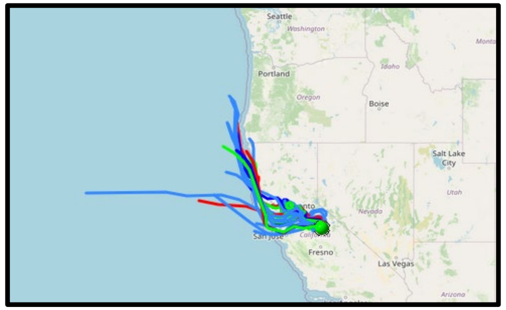
Study Area: Identifying Local and Long-range Transported Smoke

- **Three IMPROVE sites**
  - YOSE: Yosemite National Park
  - PMRF: rural Vermont
  - SEQU: Sequoia National Park

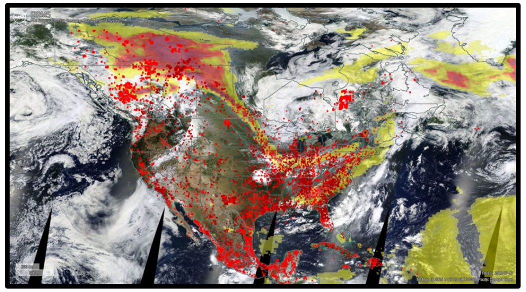
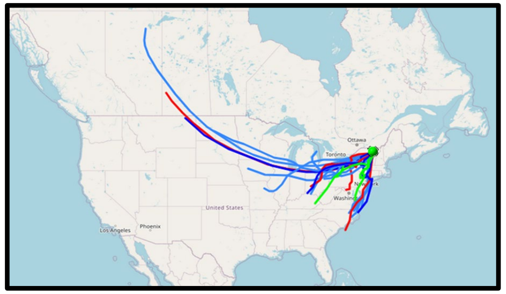
- **Wildfire day selection (in 2023):**
  - Satellite-based active fire detection (NASA FIRMS)
  - 72-hr backward air mass trajectories (NOAA HYSPLIT)
  - $PM_{2.5}$ concentration – IMPROVE network



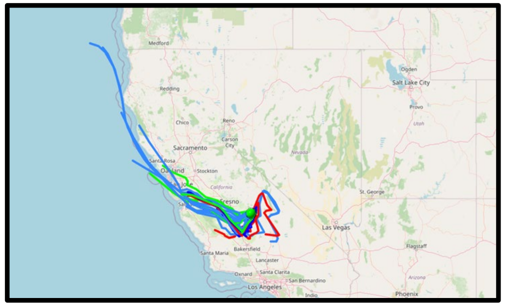
Local smoke - ***Yosemite***

Long-range transported smoke - ***Vermont***

Local smoke - ***Sequoia***

NASA FIRMS

HYSPLIT Backward Trajectory

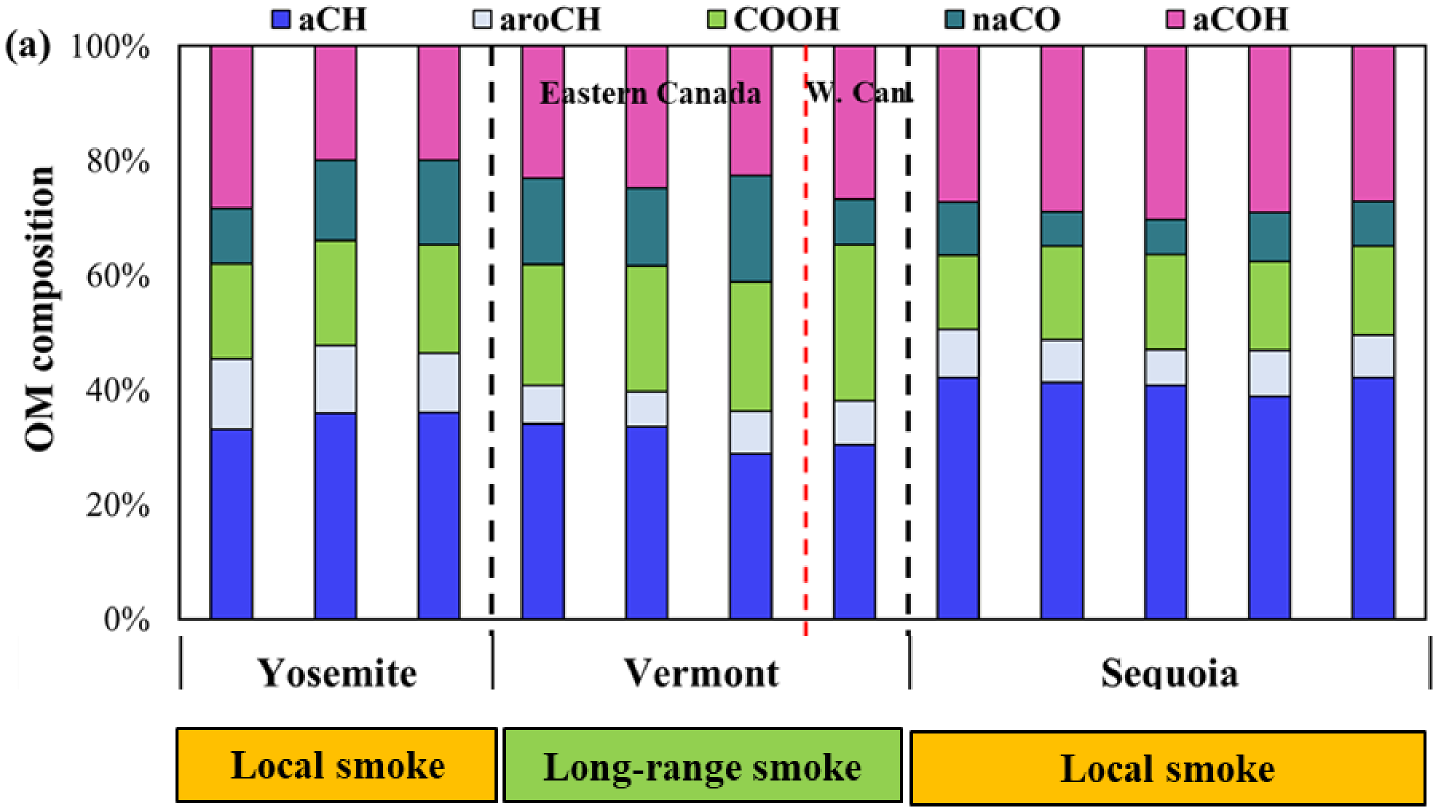
Methodology: Chemical Composition and Hygroscopicity

Chemical composition (IMPROVE)

- **Quartz**
  - **TOR –** *Elemental Carbon & Organic Carbon*
- **Nylon**
  - **Ion Chromatography** *- Inorganic ions: Sulfate Nitrate Chloride*
- **Teflon**
  - **$PM_{2.5}$ mass**
  - **XRF -** *Elements*
  - **FT-IR –** Organic Matter (OM): *aliphatic CH, aromatic CH, alcohol OH, non-acid carbonyl, carboxylic acid*
  - **Water uptake at** 84%, 90%, 97% RH

    (Raparthi et al., 2025)

Results: Organic Matter (OM) Composition from FT-IR



Local smoke – Yosemite and Sequoia

- **Yosemite:**
  - ~50% of OM is oxygenated

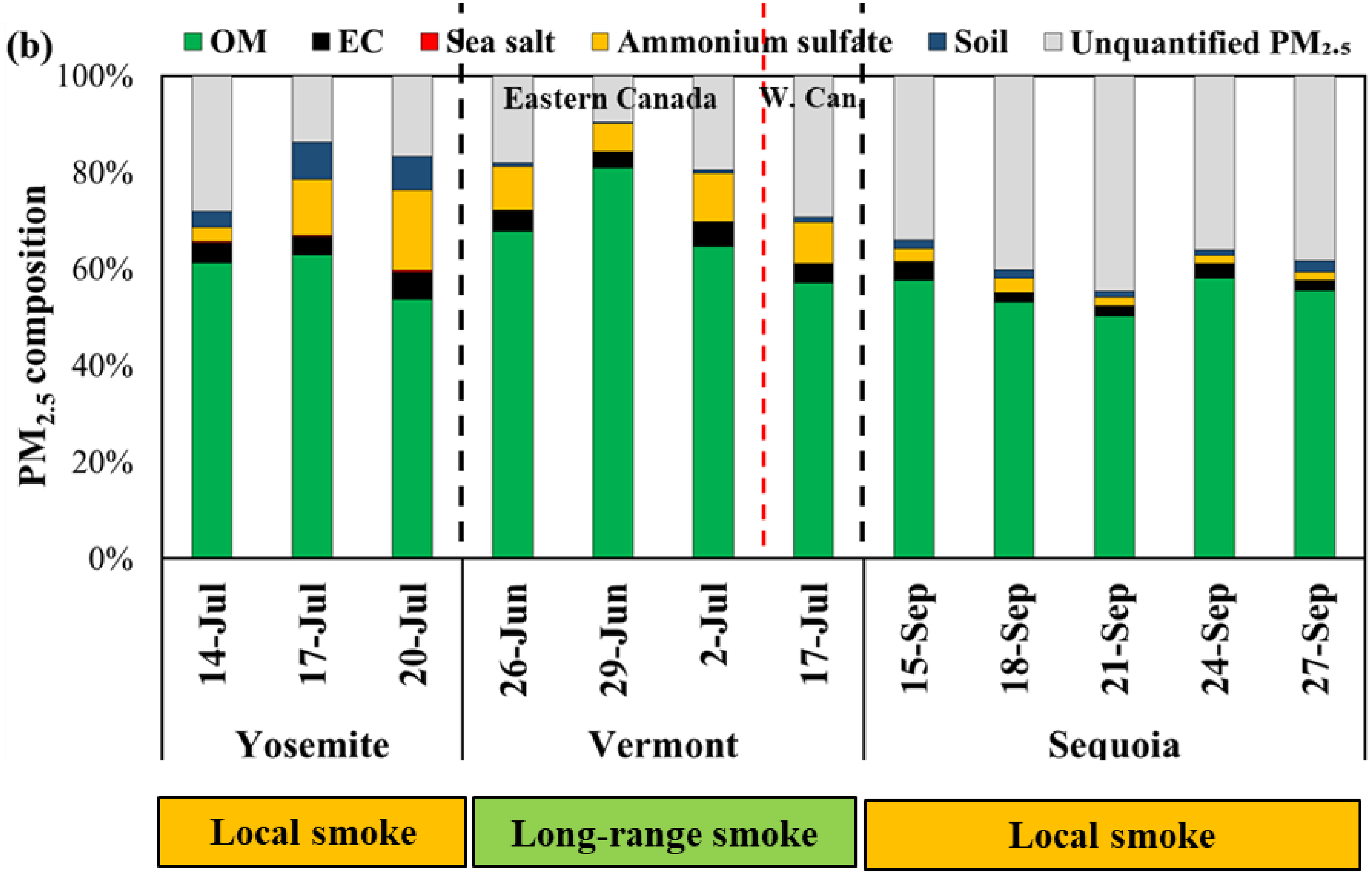
Long-range smoke to Vermont -

- **Eastern and Western Canada smoke:**
  - ~60% of OM is oxygenated
- **Western Canada smoke:**
  - High COOH

Oxygenated functional groups = sum(COOH, naCO, aCOH)

Non-oxygenated functional groups = sum(aCH, aroCH)

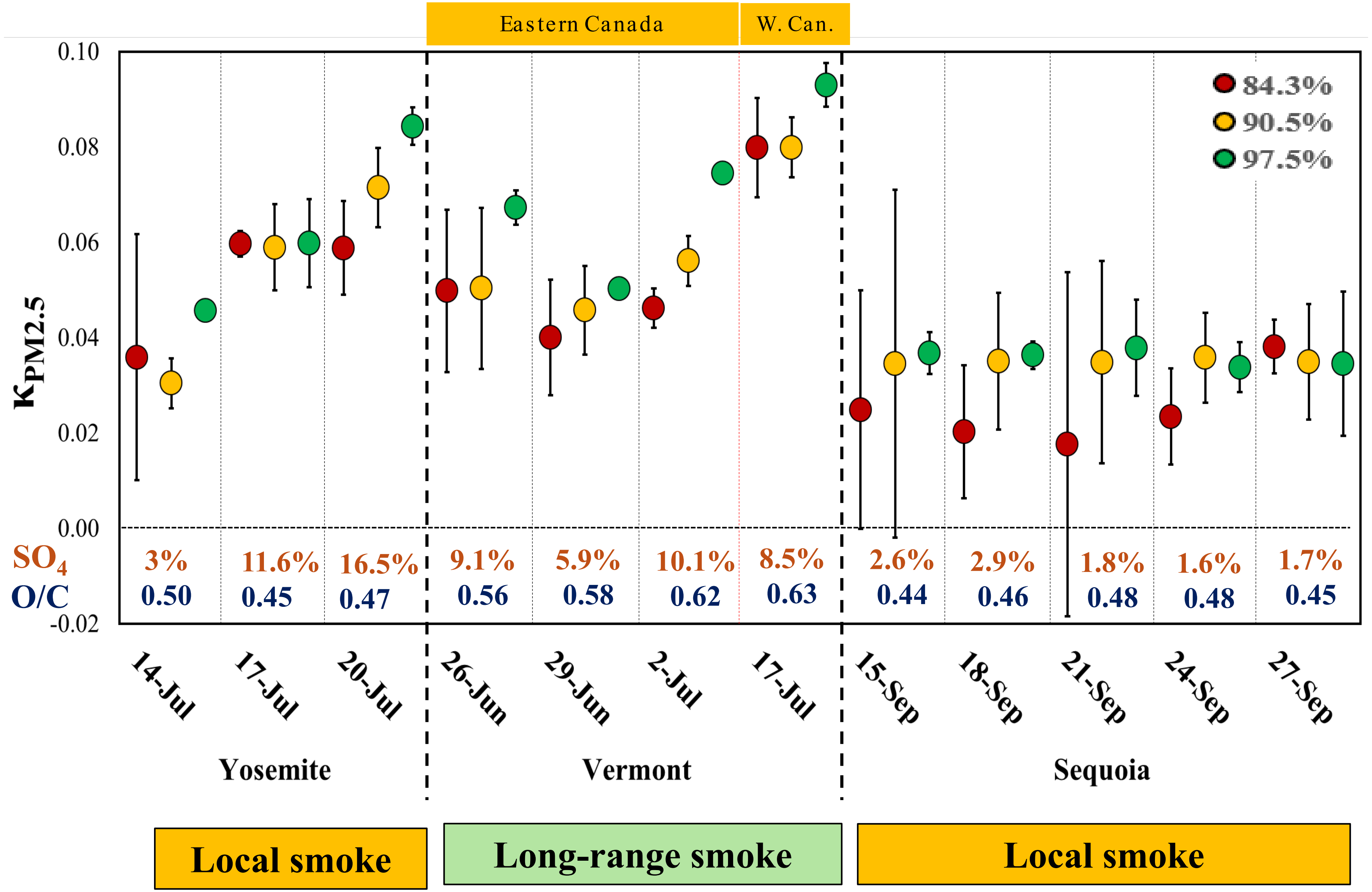
Results: $PM_{2.5}$ Chemical Composition



- OM dominates
  - 50 to 81% of $PM_{2.5}$
- Amm. Sulfate
  - 2 to 17% of $PM_{2.5}$

- Unaccounted fraction –
  - **Yosemite:** 20%
  - **Vermont:** 19%
  - **Sequoia:** 39%
  - Possibly due to different sampling times of nylon and quartz at Sequoia
  - Also due to missing C-O-C bonds for all samples

Results: Hygroscopicity of $PM_{2.5}$ - $\kappa_{PM2.5}$



- Hygroscopicity of PM2.5 typically dominated by sulfate
- Local smoke -
  - Sequoia –
    - Low sulfate
    - Moderate $\kappa_{PM2.5}$
  - Yosemite
    - sulfate increased over time
    - $\kappa_{PM2.5}$ increased over time
- Long-range transport
  - High sulfate
    - High $\kappa_{PM2.5}$
  - Western Canada
    - Highest $\kappa_{PM2.5}$

κ – single hygroscopic parameter - kappa

Deriving Hygroscopicity of Organic Matter (κ_{OM})

Zdanovskii-Stokes-Robinson (ZSR) mixing rule:

$$k_{OM,q} = \frac{k_{PM2.5} - k_{AS}\varepsilon_{AS} - k_{SS}\varepsilon_{SS} - k_{soil}\varepsilon_{Soil} - k_{EC}\varepsilon_{EC}}{\varepsilon_{OM}}$$

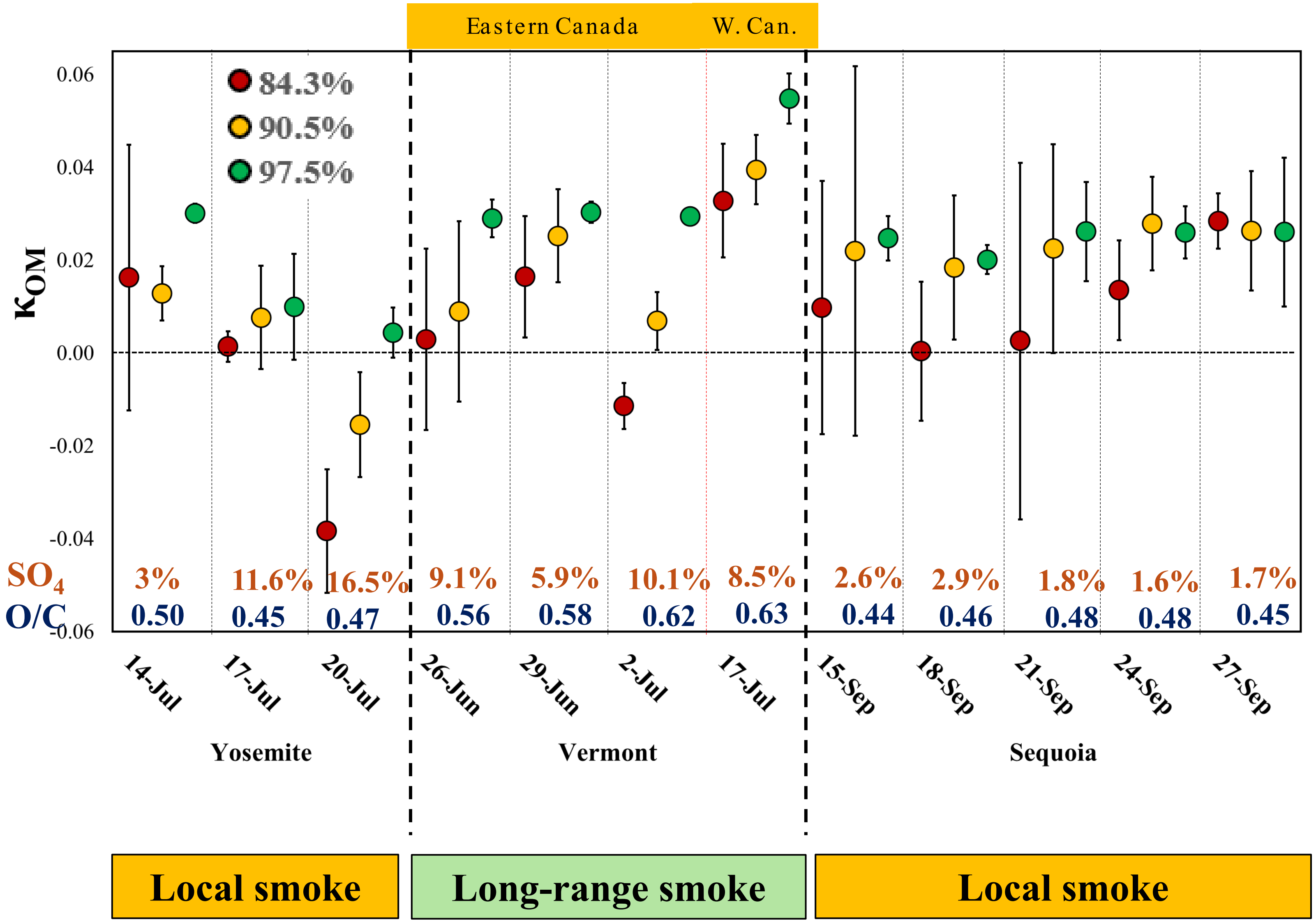
Measured
Modeled
Known

$k_{PM2.5} = (kappaPM2.5)$
$k_{soil} = 0$
$k_{EC} = 0$
k_{AS} & k_{AS} *from* **E-AIM** model
$\varepsilon = volume\ fraction$, *measured by IMPROVE and FTIR*

Simplified mixing rule:

$$k_{OM,q} = \frac{k_{PM2.5} - k_{AS}\varepsilon_{AS} - k_{SS}\varepsilon_{SS}}{\varepsilon_{OM}}$$

Results: Organic Matter Hygroscopicity (κ_{OM}) using Quantified PM



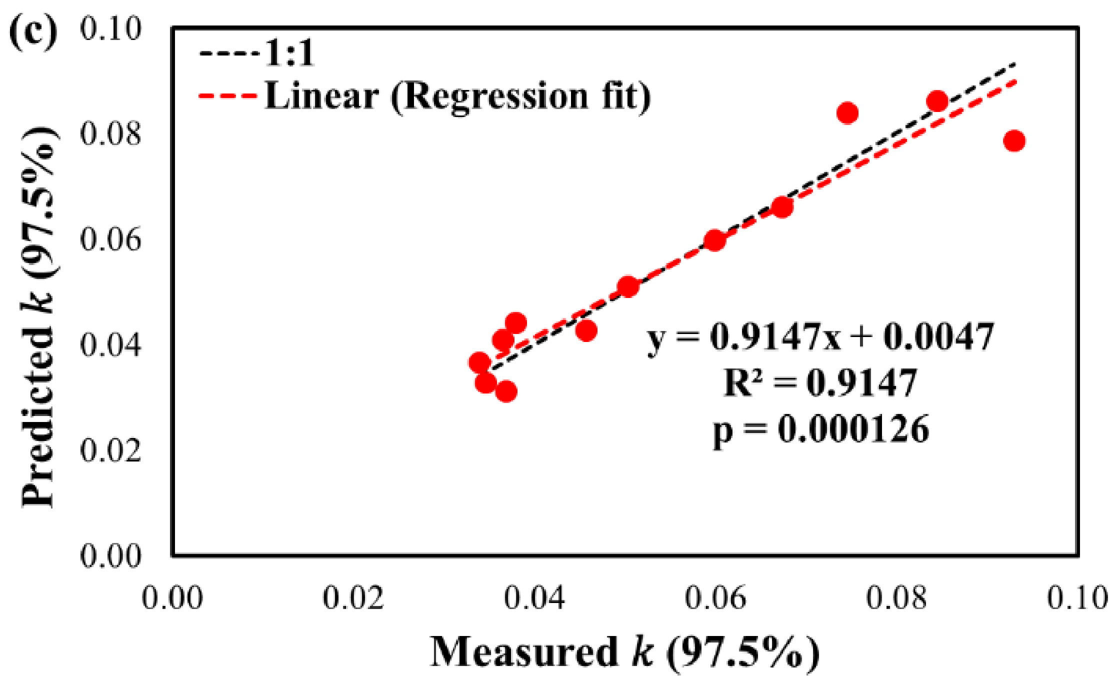
Local smoke –

- **Sequoia**
  - 50% oxygenated functional groups
  - Moderate $\kappa_{OM,SEQU}$
- **Yosemite**
  - 50% oxygenated functional groups, high sulfate
  - Moderate $\kappa_{OM,\ YOSE}$
- **Long-range transported**
  - 60% oxygenated functional groups (O/C)
  - **Western Canada**
    - High O/C, $\kappa_{OM,\ Vermont}$

Modeling $\kappa_{PM2.5}$ as a function of organic and inorganic composition

- Stepwise Multiple Linear Regression to obtain statistically significant predictors
  - $\kappa_{PM2.5}$ 97.5% RH
  - $PM_{2.5}$ species mass fractions – Ammonium sulfate, oxygenated (COH + CO+ COOH) and non-oxygenated (aliphatic and aromatic CH)

$$k_{PM2.5} = 0.29 * \frac{AS}{PM2.5} + 0.1 * \frac{Oxygenated\ OM}{PM2.5} - 0.33 * \frac{Non\text{-}oxygenated\ OM}{PM2.5} + 0.09$$



Conclusions

- **First study** quantifying wildfire $PM_{2.5}$ & OM hygroscopicity (Teflon filters).
- **Hygroscopicity varies** – depending on chemical composition which is dependent on fuel, aging, particle size (not considered here)
- **OM hygroscopicity varies** - depending on functional groups (oxygenated or non-oxygenated)
- **Modeled hygroscopicity** of smoke dominated samples in IMPROVE network

Enhancing Organic Characterization from ACSM Mass Spectra Using Collocated Functional Groups Measurements at IMPROVE/ASCENT Site in Atlanta

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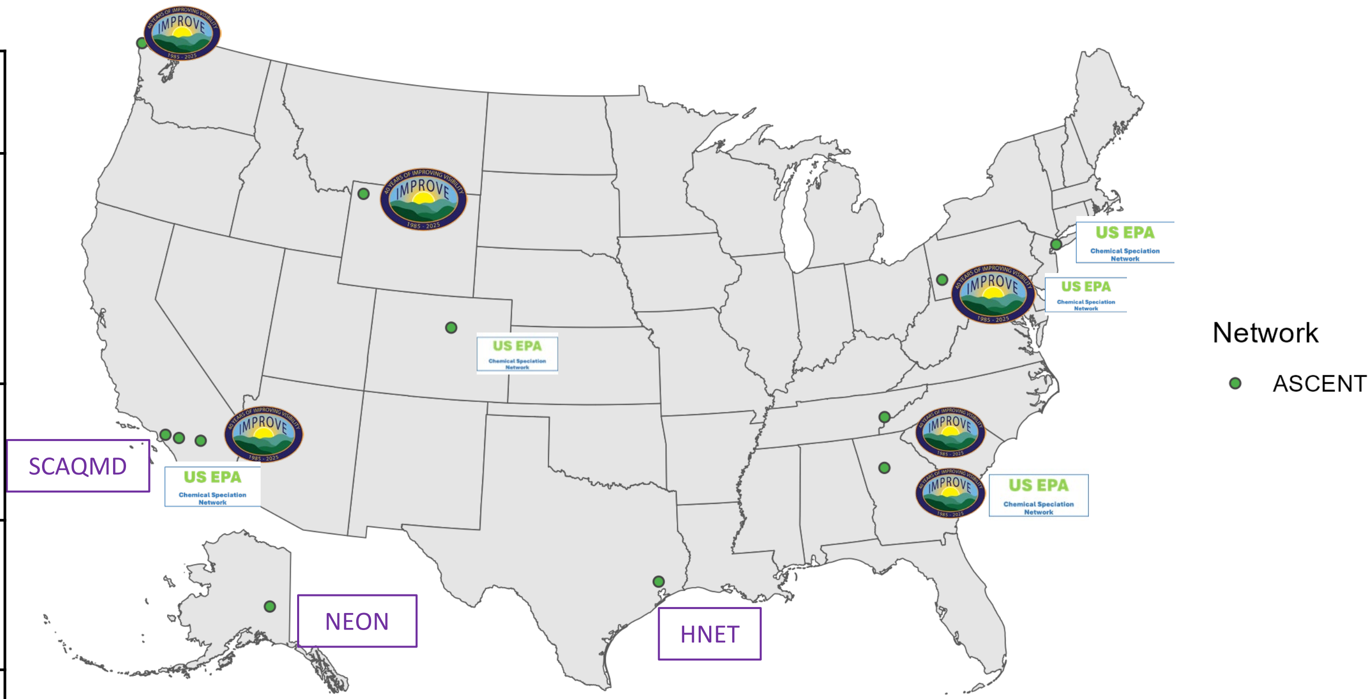
Atmospheric Science and Chemistry Measurement Network (ASCENT)

High-Time, Real-Time, All-the-Time

Infrastructure Funded Oct. 2021, Sampling May 2024, Operations Funded Sept. 2025

Instrument	Model and Manufacturer	Measurements
Aerosol Chemical Speciation Monitor (ACSM), $PM_{2.5}$	ToF-ACSM, Aerodyne Research	Organics, sulfate, nitrate, ammonium, chloride
Xact, $PM_{2.5}$	625i, Cooper Environmental	Trace metals
Aethalometer, $PM_{2.5}$	AE33, Magee Scientific	black and brown carbon
Scanning Mobility Particle Sizer, PM_1	3938W89, TSI	Particle number size distribution, number concentration



Motivation

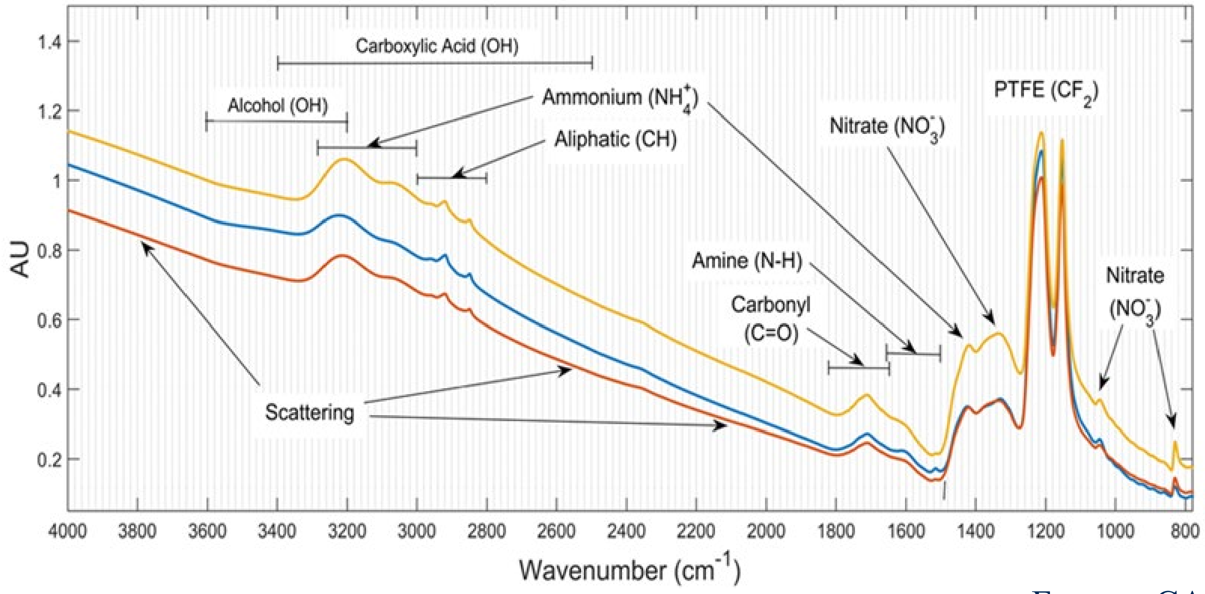
- Aerosol mass spectrometer/Aerosol chemical speciation monitor (AMS/ACSM) fragment ions lack chemical specificity
- Fourier Transform Infrared Spectroscopy (FTIR) analysis provides chemical specificity through functional groups
- Challenges in measuring functional groups from ACSM include:
    - ACSM responds differently to same functionality
    - FTIR spectral interferences
    - Time resolution differences between the ACSM and FTIR measurements

Goals

- Enhance chemical resolution of ACSM spectra using parallel FTIR functional groups
- Develop parameterizations to predict functional groups from ACSM spectra

Functional group measurements

- 24-hour filters are collected every third day by IMPROVE in Atlanta
- Analyzed by FTIR
- Non-destructive FTIR analysis takes 5 minutes per sample
- Measure five functional groups
  - Carbonyl (CO)
    - Carboxylic acid (COOH)
    - Nonacid carbonyl (naCO)
  - Alcohol (aOH)
  - Alkane (aCH)

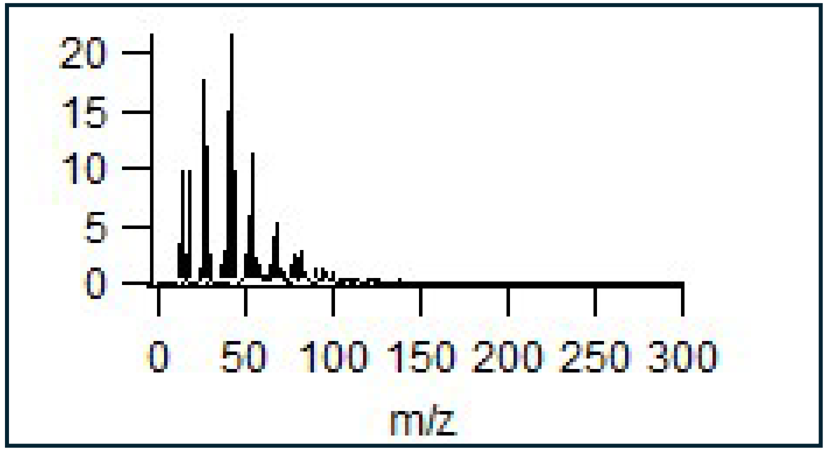


Fresno, CA

ACSM organic fragment ions

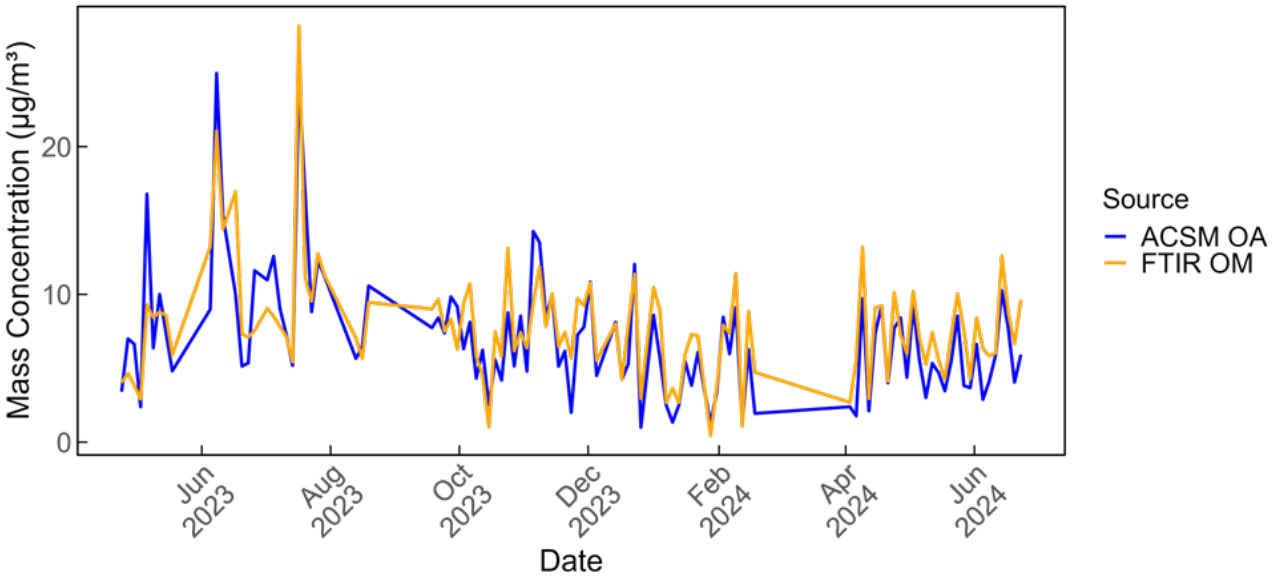
- Hourly organic fragment data from ACSM at Atlanta site
  - Number of ions at each mass/charge (m/z)
- Average to 24-hours to match FTIR spectra

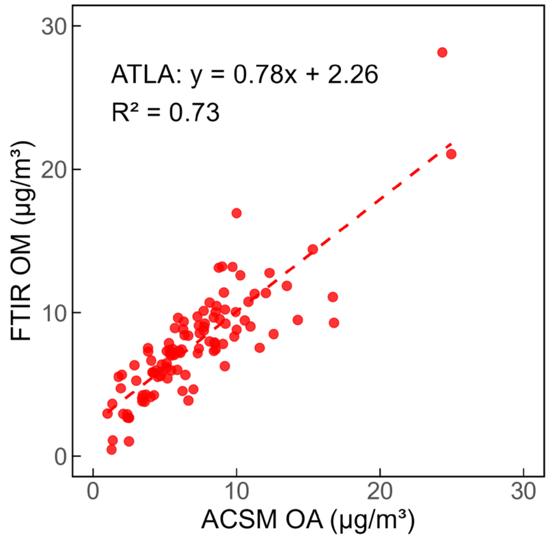
Mass Spectra



m/z	Ion Identity	Related functional groups
29	CHO^+/ $C_2H_5^+$	Alcohol, alkane
43	$C_2H_3O^+$ / $C_3H_7^+$	Carbonyl, alkane
44	CO_2^+	Carboxylic acid
55	$C_4H_7^+$ or $C_3H_3O^+$	Alkane
57	$C_4H_9^+$	Alkane
60	$C_2H_4O_2^+$	Alcohol
69	$C_5H_9^+$	Alkane
71	$C_5H_{11}^+$	Alkane
73	$C_3H_5O_2^+$ or $C_4H_9O^+$	Carbonyl, alcohol, carboxylic acid

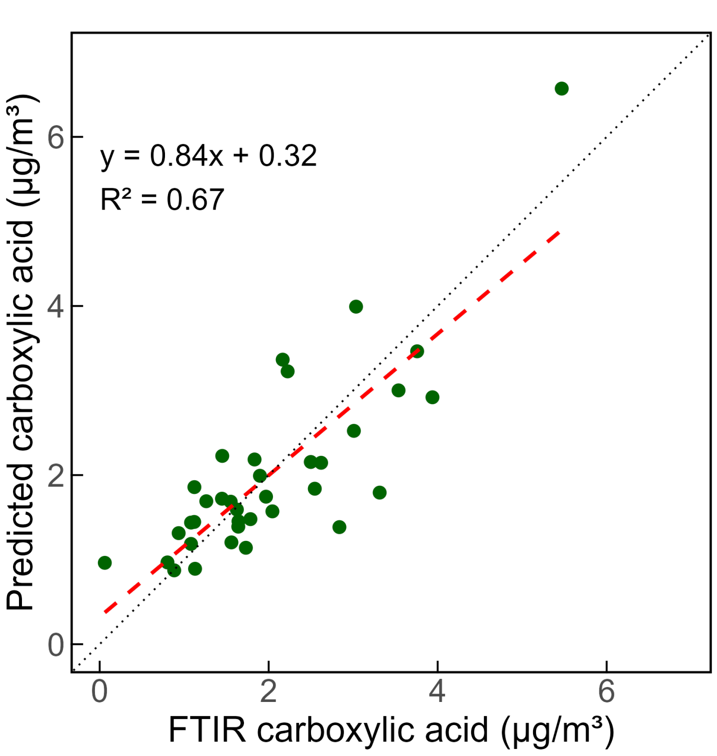
FTIR OM and ACSM OA comparisons

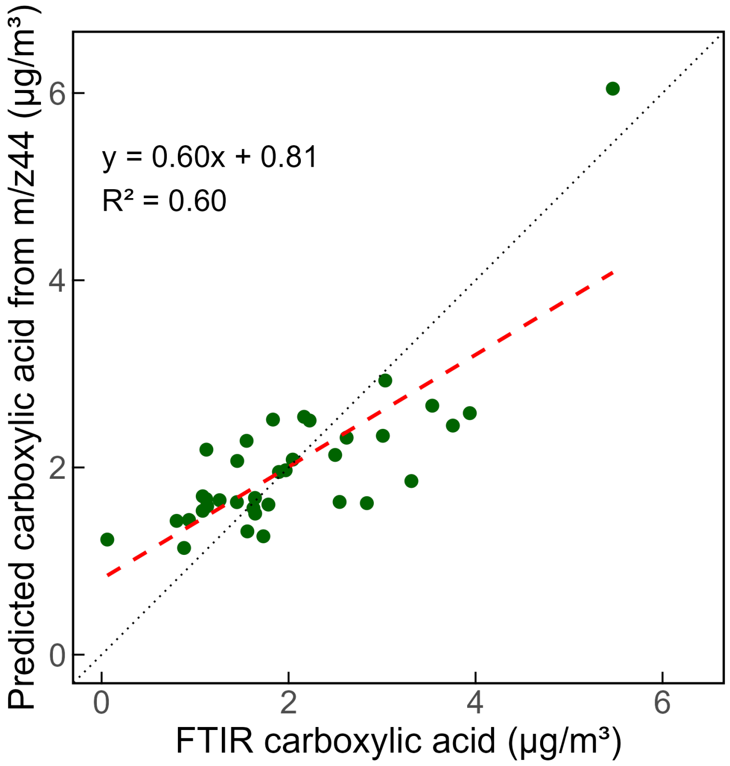




- Time series shows similar pattern
- Atlanta ASCENT site:
  - FTIR OM=0.78*ACSM OA+2.26, R^2=0.73
- Primary and aged chamber aerosols (Yazdani et al,2022)
  - FTIR OM=1.3*AMS OA+9.7, R^2=0.92
- Gives confidence for further model development

Carboxylic acid (COOH)

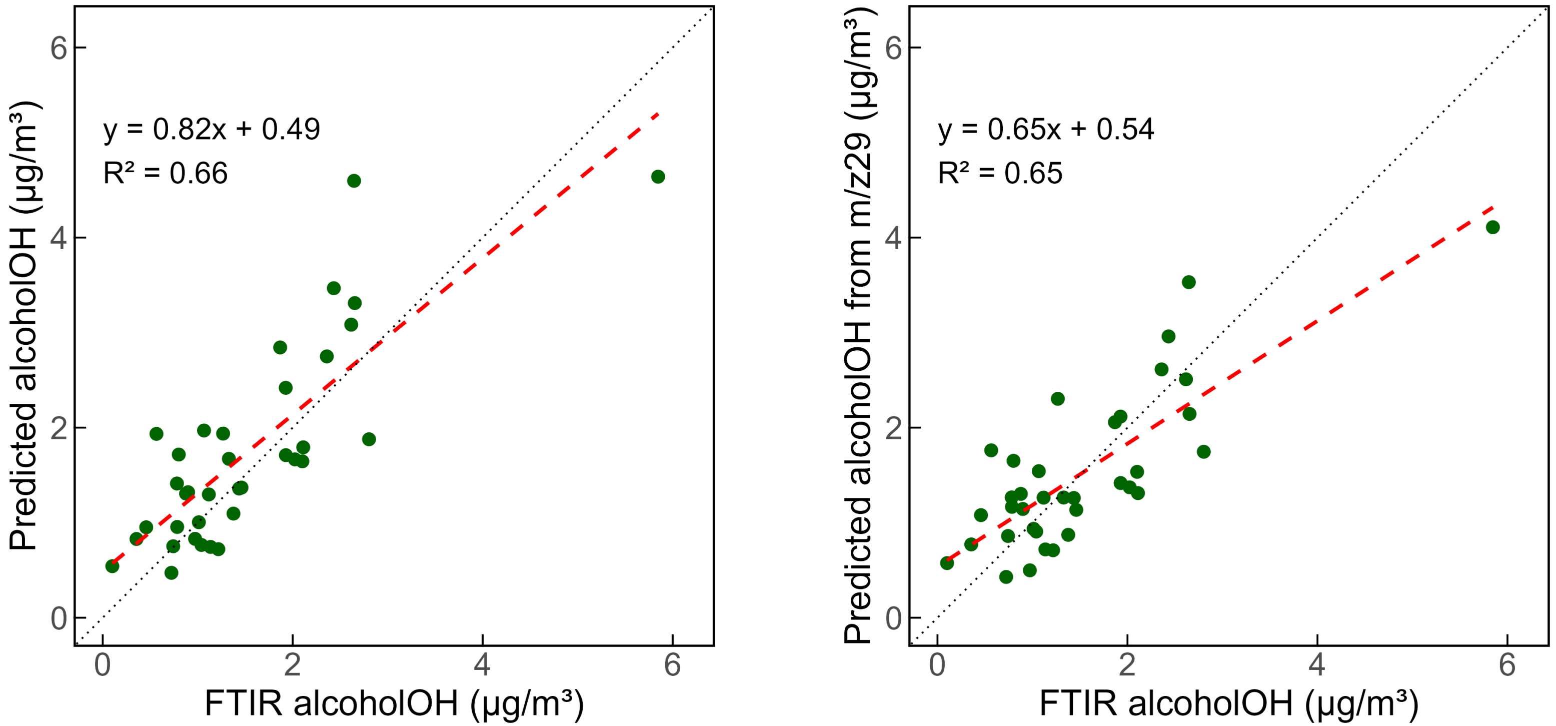




- COOH well predicted using FTIR to calibrate mzs
- Multiple mzs give better prediction than only one

FG model type	Predictors	Calibration equation
Carboxylic acid EN	mz29, mz43, mz44, mz55, mz57, mz60, mz69, mz71, mz73	y = -2.53*mz29 + 1.28*mz43 + 2*mz44 + 0.87*mz55 -17.95*mz57 + 87.28*mz60 -12.44*mz69 + 62.27*mz71 -188.91*mz73 + 0.8093
Carboxylic acid linear	mz44	y = 1.06*mz44 + 1.01

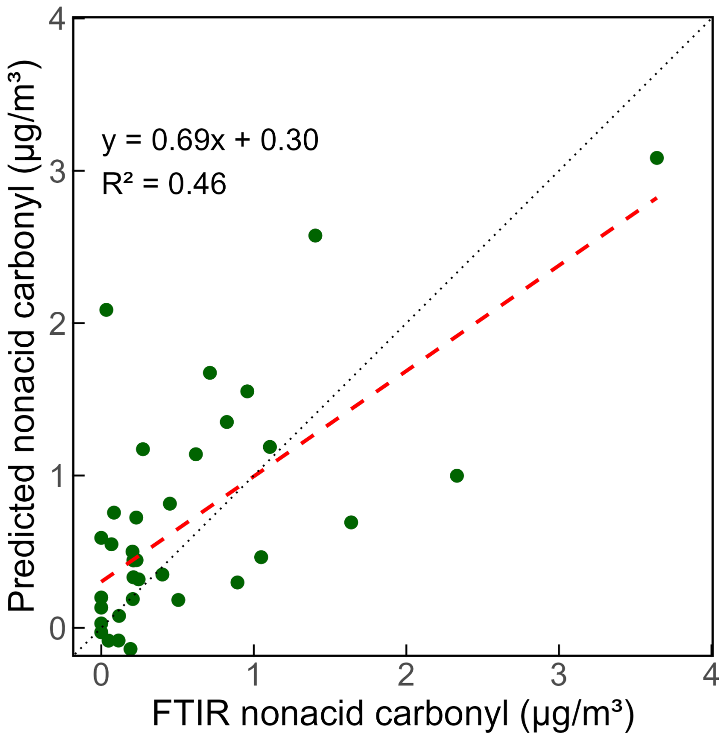
Alcohol (aOH)

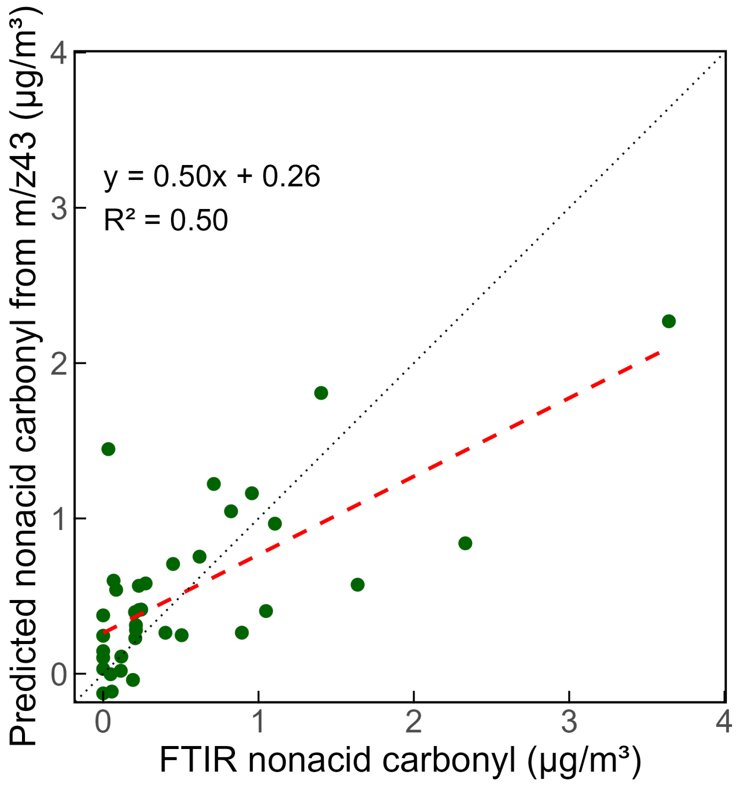


- aOH well predicted using FTIR to calibrate mzs
- Multiple mzs give better prediction than only one

FG model type	Predictors	Calibration equation
AlcoholOH EN	mz29, mz60, mz73	y = 1.86*mz29 + 2.54*mz60 + 33.93*mz73 + 0.2
AlcoholOH linear	mz29	y = 4.19*mz29 + 0.18

Non-acid carbonyl (naCO)

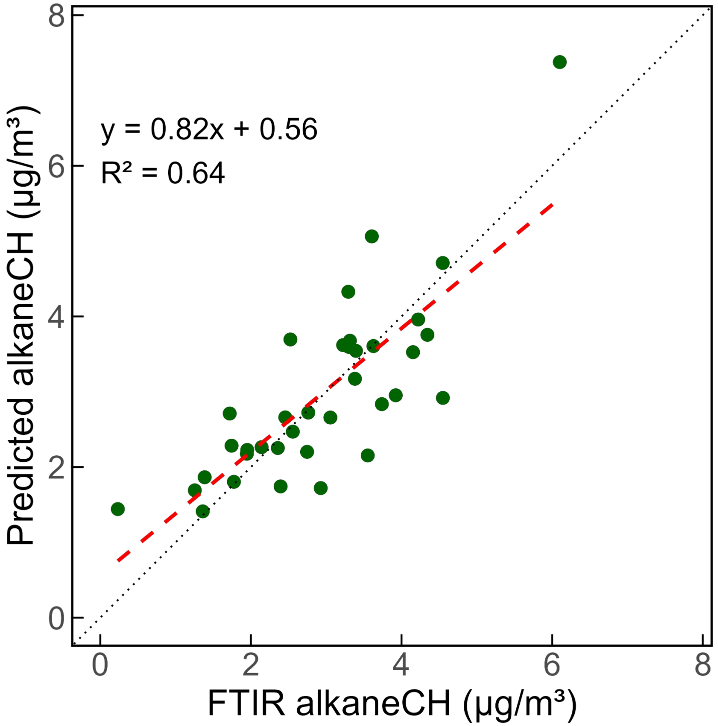


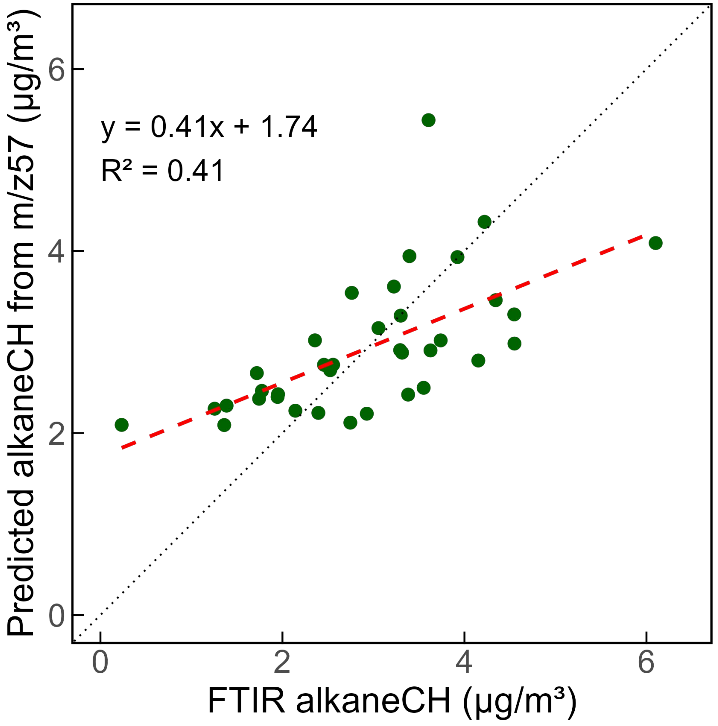


- naCO not very well predicted
- Concentrations are low in Atlanta
- A data set with higher concentrations

FG model type	Predictors	Calibration equation
Nonacid carbonyl EN	mz43, mz55, mz73	y = 1.88*mz43 -1.02*mz55 + 15.69*mz73 -0.4685
Nonacid carbonyl linear	mz43	y=1.51*mz43 - 0.27

aCH

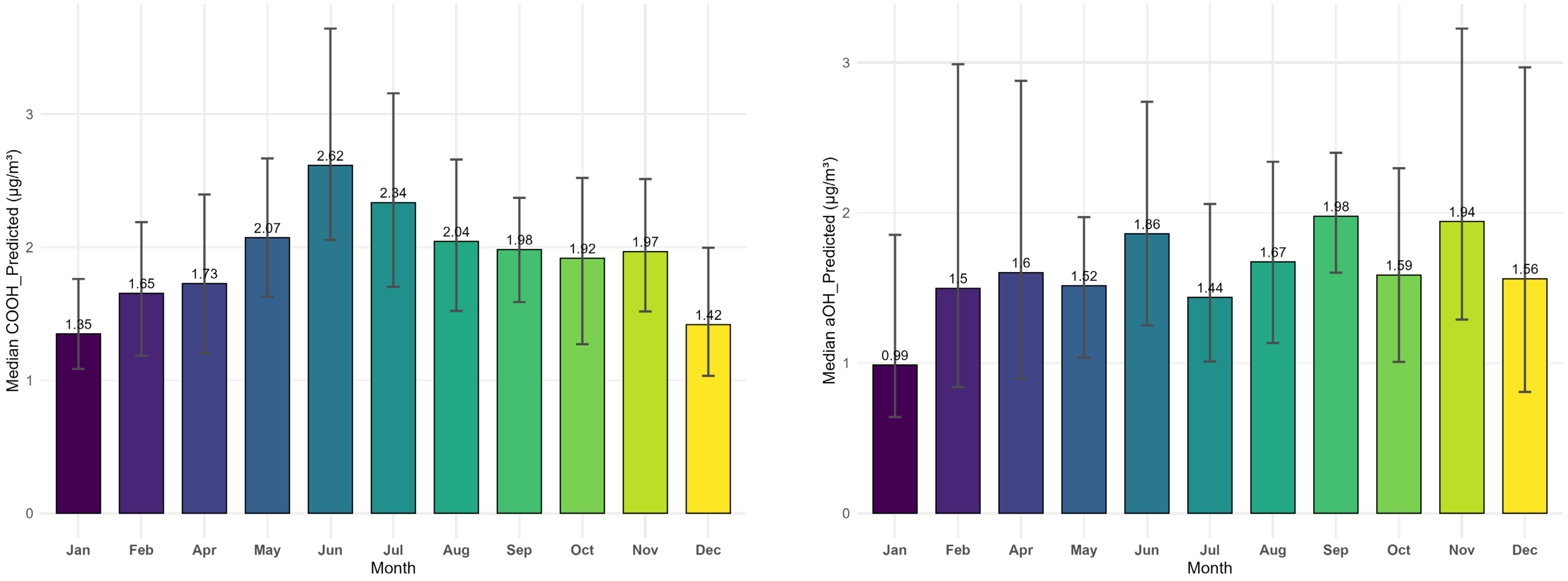




- aCH well predicted using FTIR to calibrate mzs
- Multiple mzs give much better prediction than only one

FG model type	Predictors	Calibration equation
AlkaneCH EN	mz29, mz43, mz44, mz57, mz60, mz73	y = -2.92*mz29 + 3.3*mz43 + 1.43*mz44 + 2.51*mz57 + 58.42*mz60 + -116.99*mz73 + 1.22
AlkaneCH linear	mz57	y = 6.52*mz57 + 1.96

Seasonal variations in Atlanta



Predicted COOH is high in summer and low in winter, whereas aOH is not show seasonal pattern

Summary of functional group predictions from ACSM using FTIR data from IMPROVE

- Functional groups can be predicted by ACSM fragment ions in Atlanta
  - COOH, CO, aOH, and aCH are well predicted
  - naCO is not well predicted due to low concentration
- Predicted COOH shows seasonal variation
- Next Steps
  - Diurnal variability of functional groups
  - Apply/try at other IMPROVE/ASCENT sites

International Speciated PM2.5 Monitoring

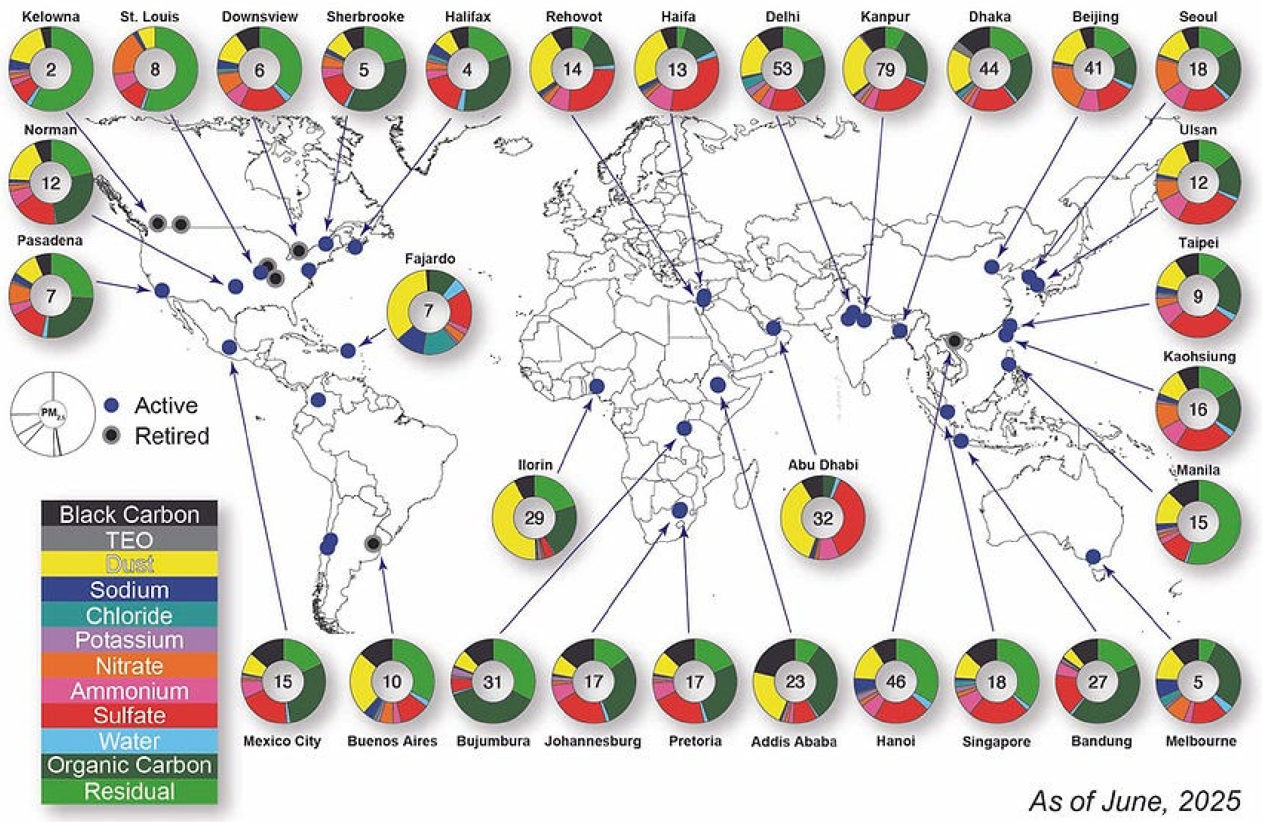
SPARTAN
Global Particulate Matter Network

MAIA
Multi-Angle Imager
for Aerosols

Surface PARTiculate mAtter Network (1 of 2)

SPARTAN
Global Particulate Matter Network

- Began 2012
- Low- and Middle-Income Countries
    - ~29 sites
    - Dense urban areas
    - High pollution
    - Little to no monitoring data
- Objectives: Evaluate and enhance satellite estimates of PM2.5 and resulting health impacts
- Optical: Nephelometers and Collocated AERONET Sunphotometers

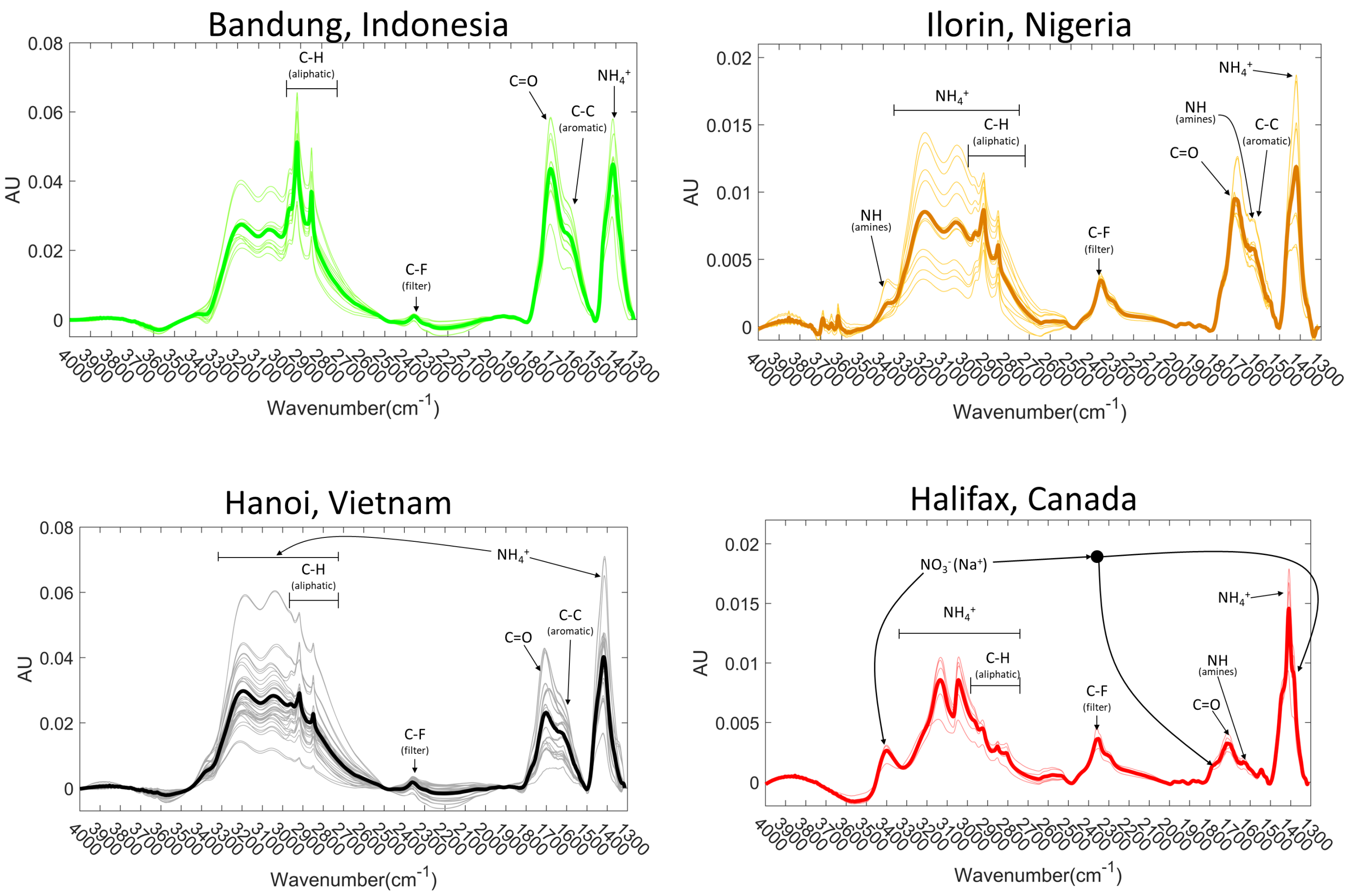


Data publicly available https://www.spartan-network.org/

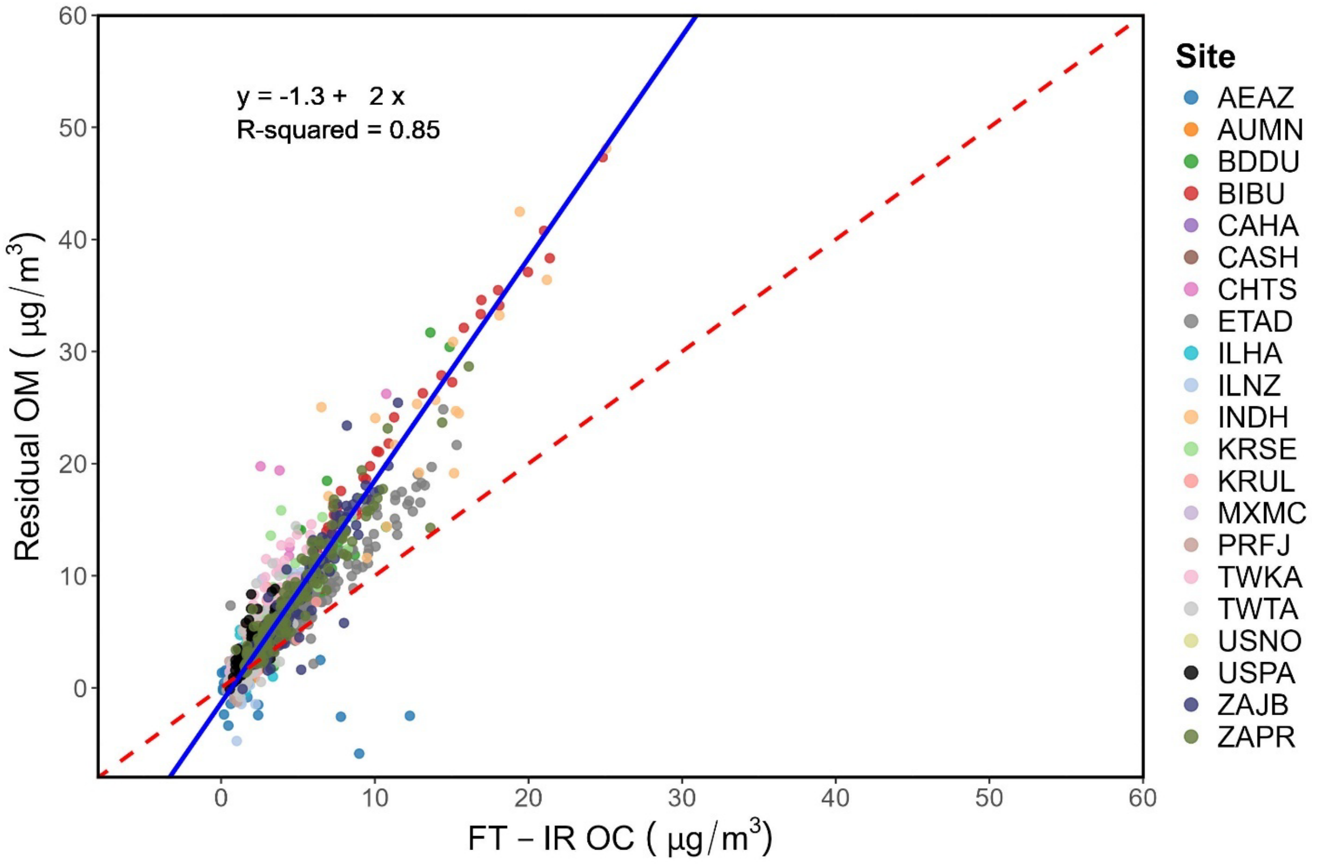
Surface PARTiculate mAtter Network (2 of 2)

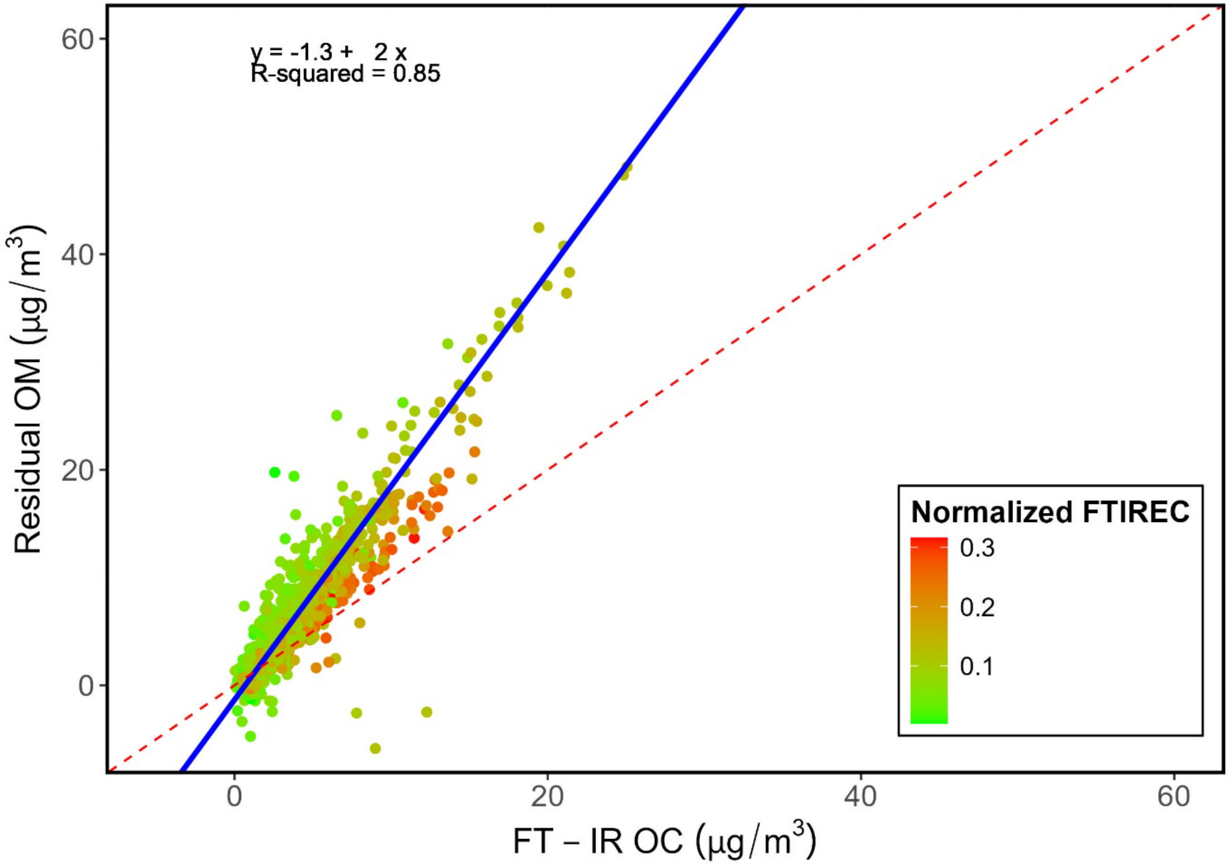
SPARTAN Global Particulate Matter Network

- Teflon filter samples:
  - 24 hour PM2.5 samples
  - Collected 1 in 3 days (9 am to 9 am) or 9 days (on and off)
  - Species
    - Gravimetric mass (Wash U)
    - Organic and elemental carbon (UC Davis)
    - Soil and trace elements (Wash U)
    - Anions and cations (Wash U)
  - OC and EC measured using FTIR
    - Calibrations developed from FTIR spectra of IMPROVE Teflon filters and IMPROVE TOR OC and EC at AQRC, UC Davis



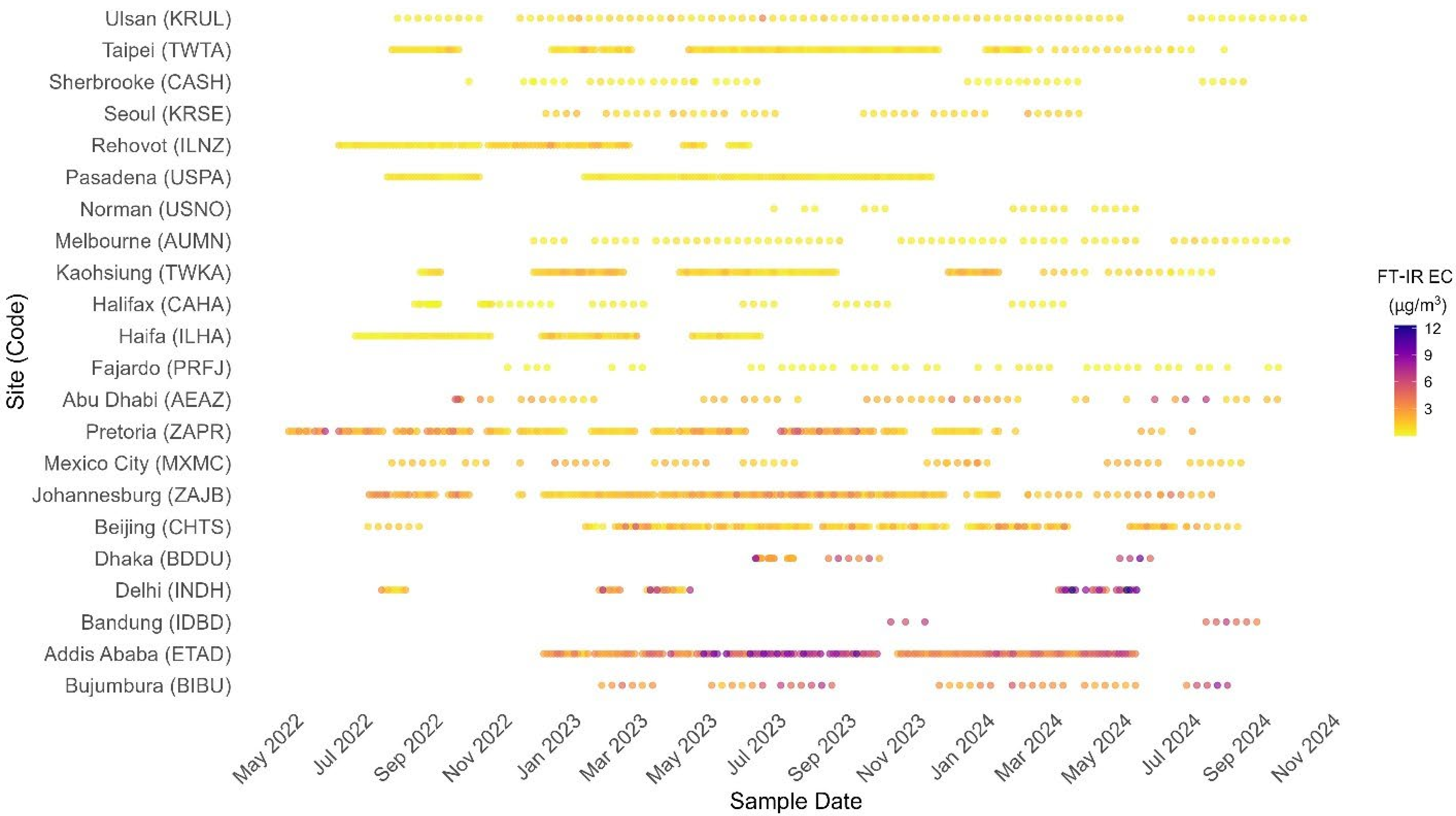
FT-IR OC Data Quality





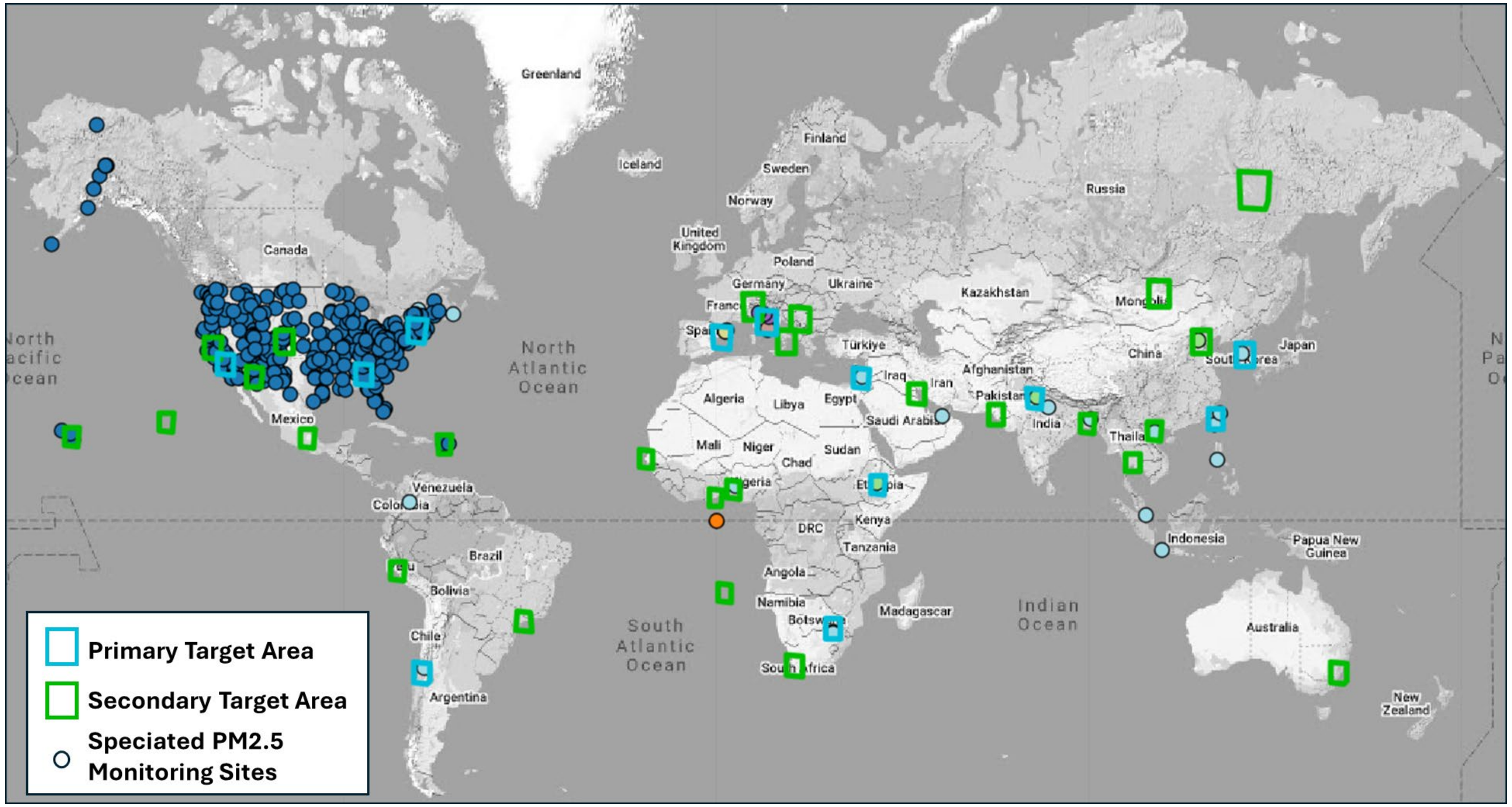
n = 1390; sampling duration: May 2022 to Nov 2024

FT-IR EC Concentrations for SPARTAN data



UCDAVIS

Mission to Earth: Multi-Angle Imager for Aerosols (MAIA) Satellite



- Satellite to measure aerosol composition in a set of globally-distributed target areas
- Expected to launch no earlier than 2026, surface monitoring operational now
- Objective: Understand the health impacts of aerosol species in globally-distributed target areas
- Data: international sources

SPARTAN Global Particulate Matter Network | Colorado State University | IMPROVE 40 Years of Improving Visibility 1985 - 2025 | US EPA Chemical Speciation Network | AETHLABS

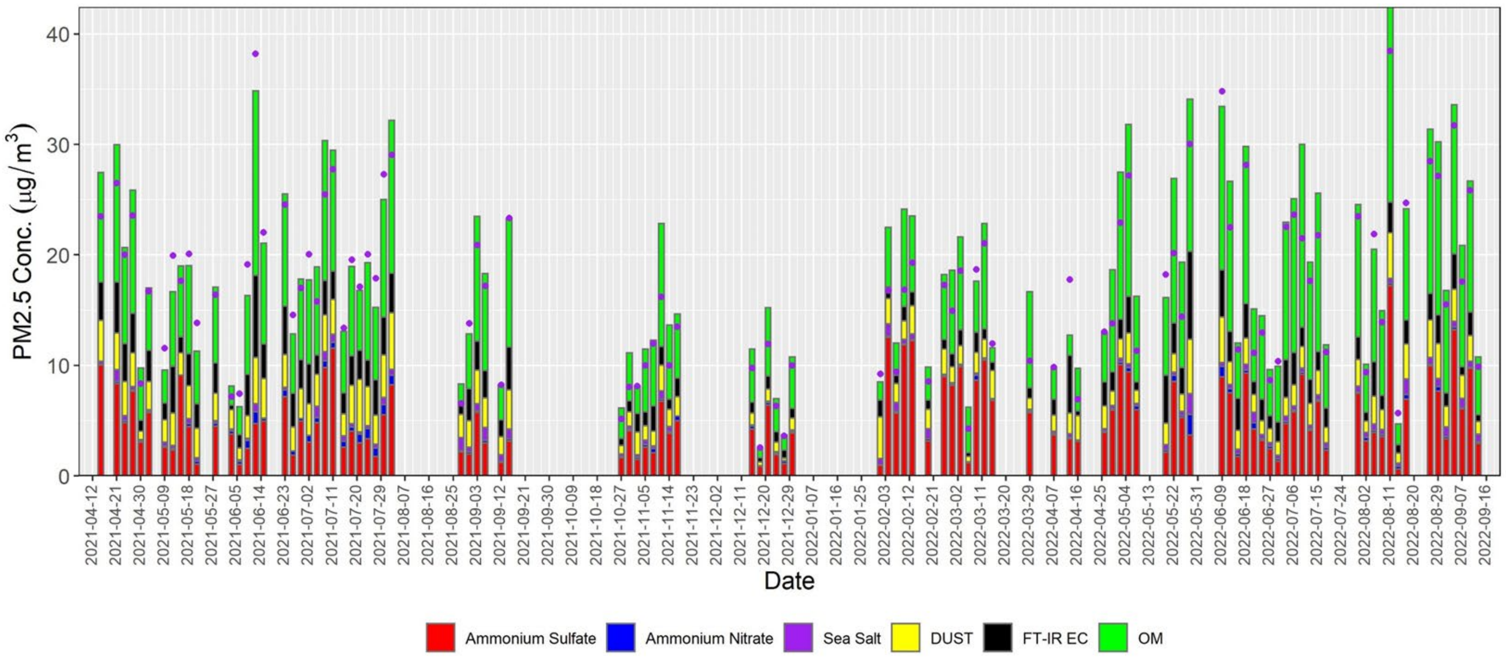
PM2.5 composition and organic matter sources in Pretoria, South Africa

Anwar M. N., Takahama S., C.R. Oxford, Martin R. V., Li Y. , Igel A. L., Hasheminassab, S., Raffuse S.M., Naidoo M. , Garland R. M., Dillner A. M.

Submitted May, 2, 2025 *Aerosol and Air Quality Research*. *(Under Review)*

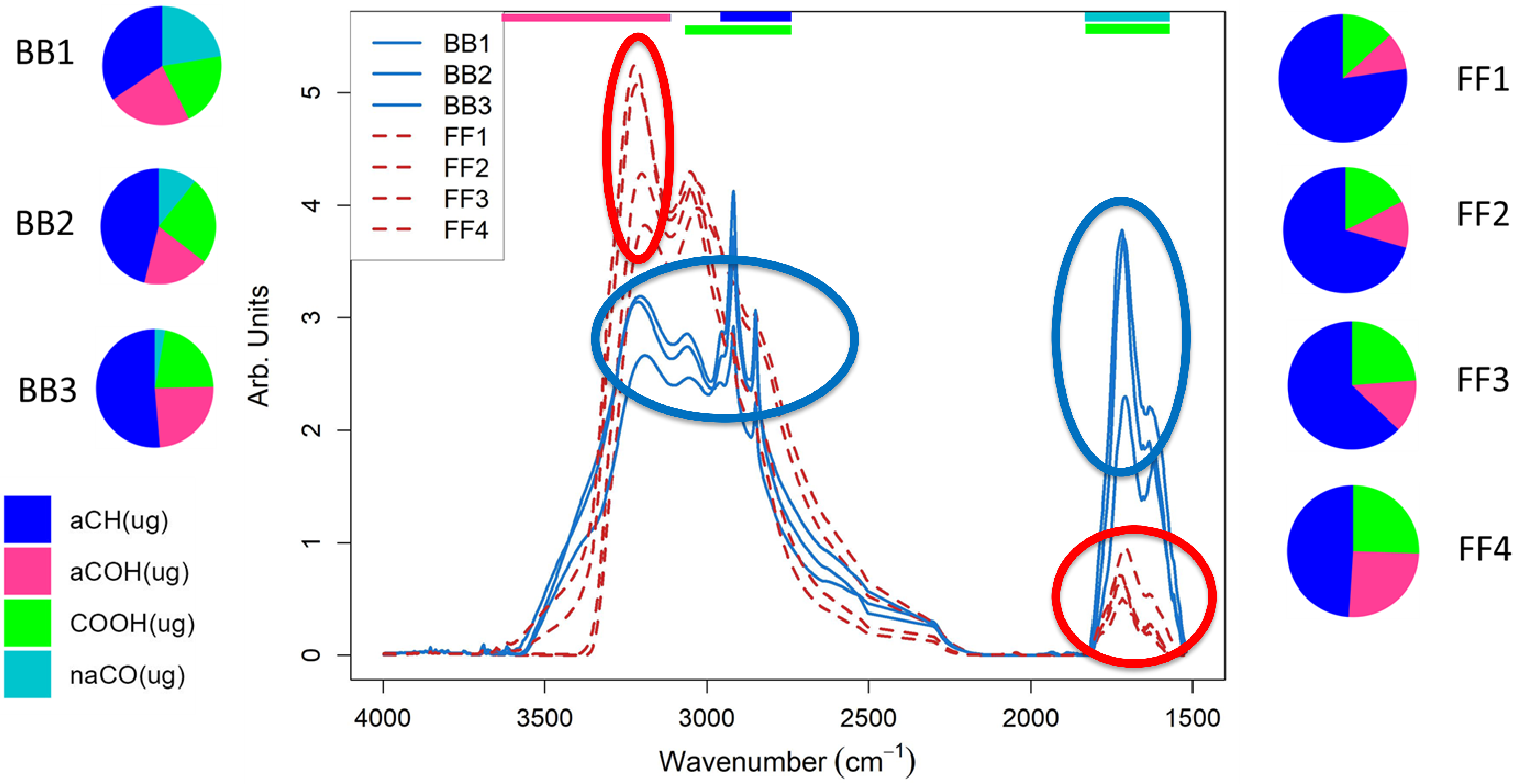
Pretoria, South Africa

- 3.3 million people
- Middle income country
- Data from 4/21 to 9/22
- Sampling 1 in 3 days



- Fairly complete data set
- Sulfate and OM dominated

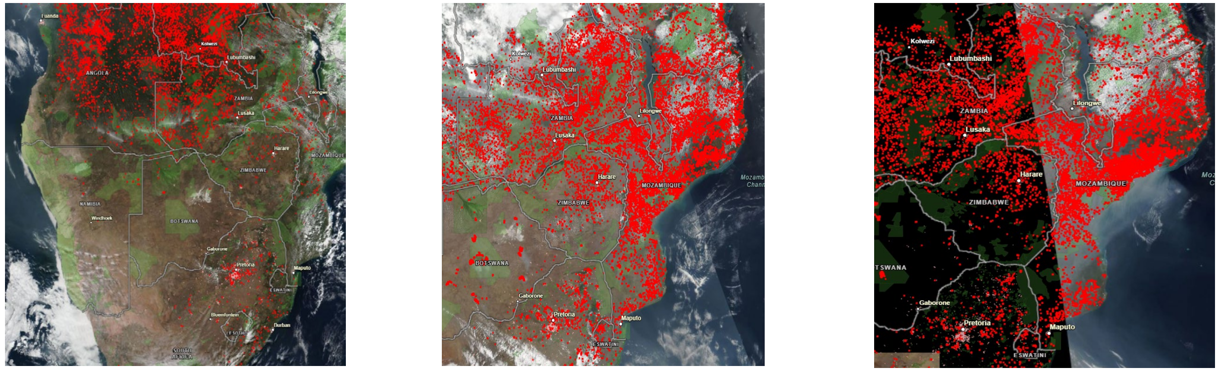
OM Source Apportionment employing PMF with FT-IR Spectra



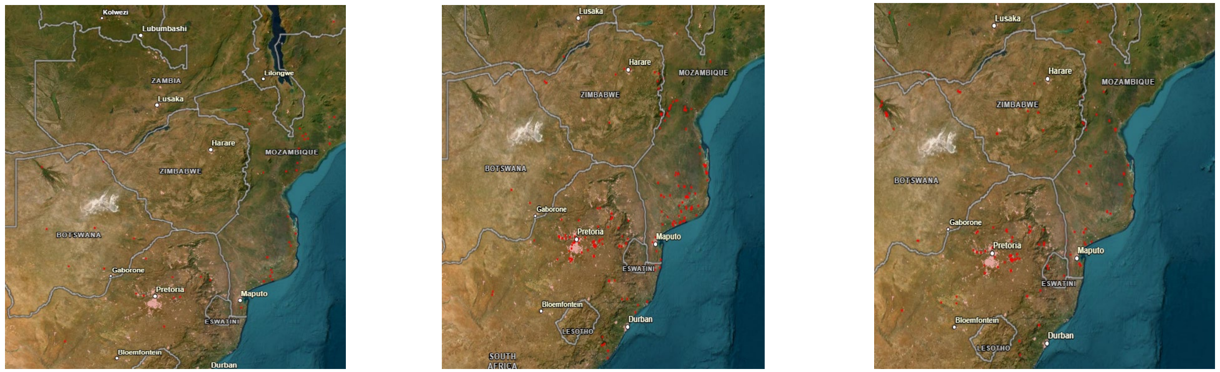
Separation of Sources in the BB/biogenic SOA and FFC

- ❑MODIS fire product imageries
- ❑Correlation with the chemical speciation
    - ❑K, naCO for biomass burning
    - ❑Heavy metals for industrial
- ❑ Timeline of occurrence

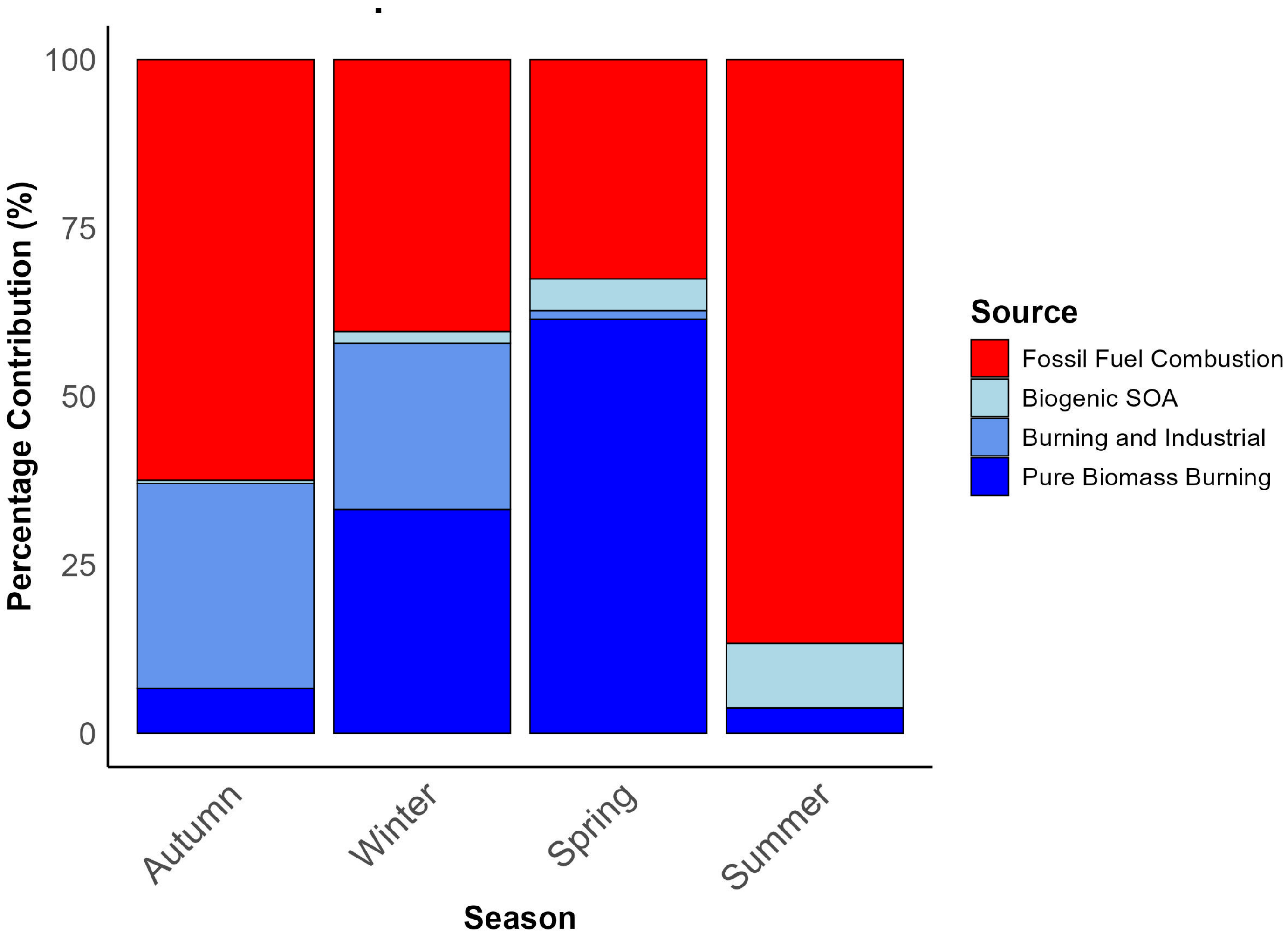
Days with highest fraction of BB/Biogenic SOA



Days with lowest fraction of BB/Biogenic SOA



OM Sources by Season in Pretoria, South Africa



Pretoria Summary

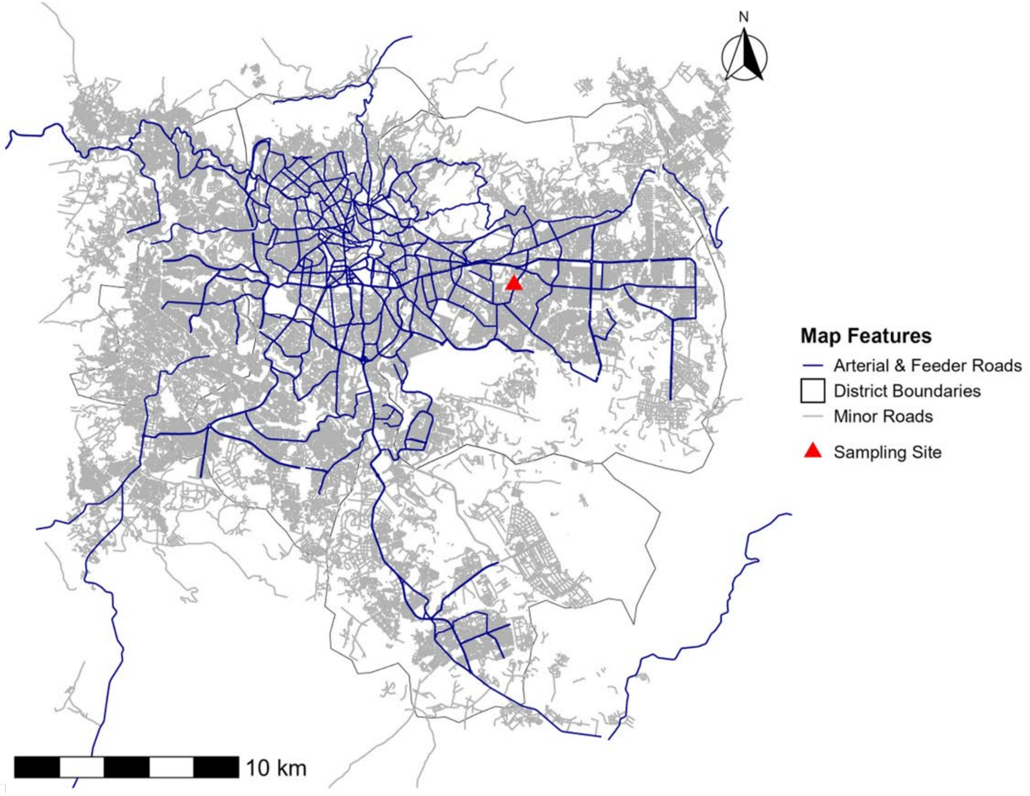
- Low cost, routine, and non-destructive FT-IR analysis used for OM quantification and source apportionment in Pretoria, South Africa SPARTAN samples
- PM2.5 averaged 17 μg/m^3, half of days exceeded WHO guidelines
- OM dominated the $PM_{2.5}$ mass conc. (~50%) followed by ammonium sulfate
- Two broad categories of the sources were identified: biomass burning & biogenic SOA (BB&SOA) and fossil fuel combustion factors
    - The BB&SOA factor had three distinct sources:
        - pure biomass burning,
        - biogenic SOA,
        - mixed biomass/industrial/vehicular emissions source
    - SOA highest in summer, pure biomass highest in spring

$PM_{2.5}$ aerosol concentration, composition, and organic sources in Addis Ababa, Ethiopia

Anwar M. N., Takahama S., Oxford C.R., Hasheminassab, S., Mamo T., Asfaw A., Dillner A. M.

Submitted to Environment International
November 12, 2025

Addis Ababa, Ethiopia

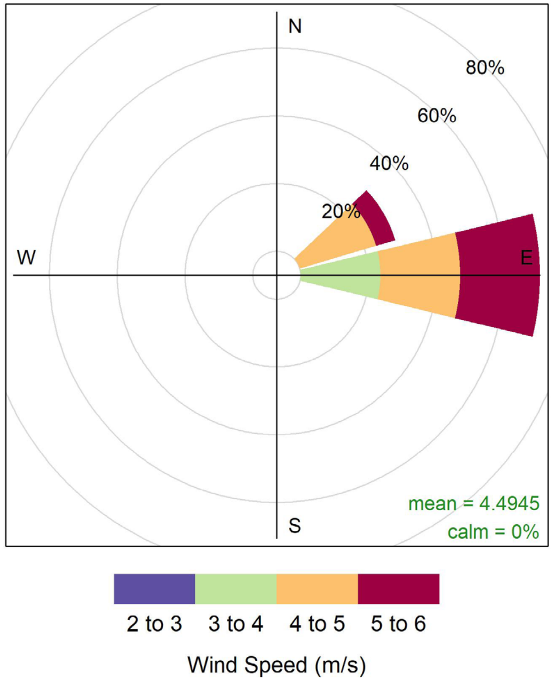


Study Period: 2023

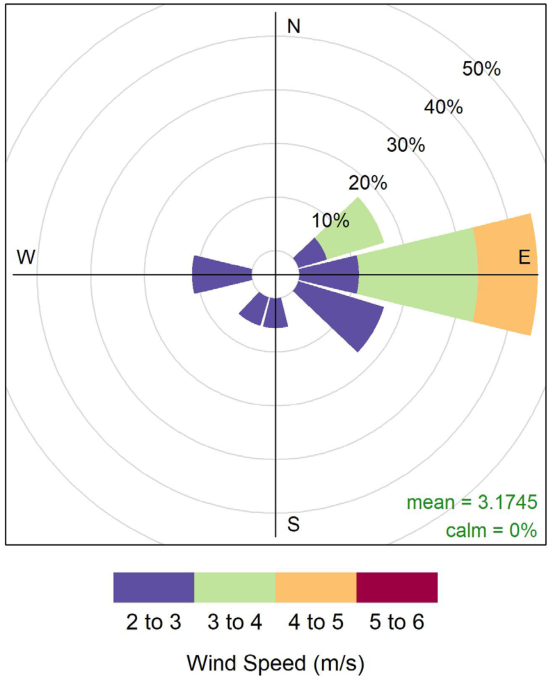
UCDAVIS

Meteorology and Seasons in Addis Ababa

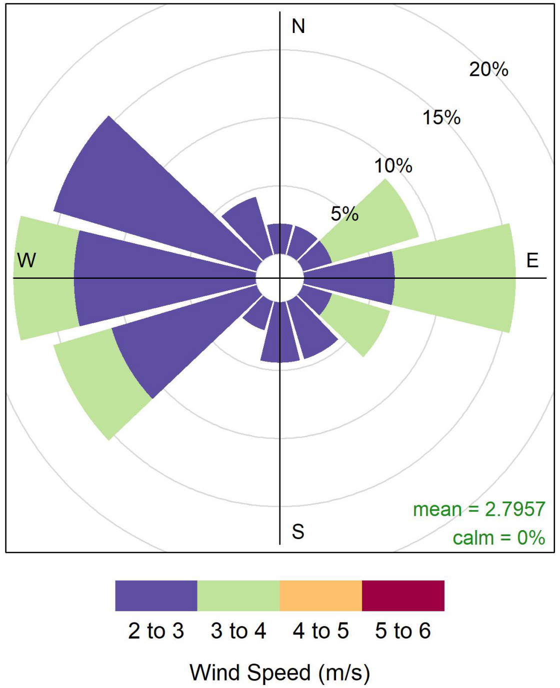
Jan – Feb	March – April	May – Sep	Oct - Dec
0 mm rain/day	6.5 mm rain/day	8.3 mm rain/day	0.1 mm rain/day
BLH 2000m	BLH 2000m	BLH 2000m – 1000m	BLH 1500m – 2000m
First Dry	Less Rainy	More Rainy	Second Dry



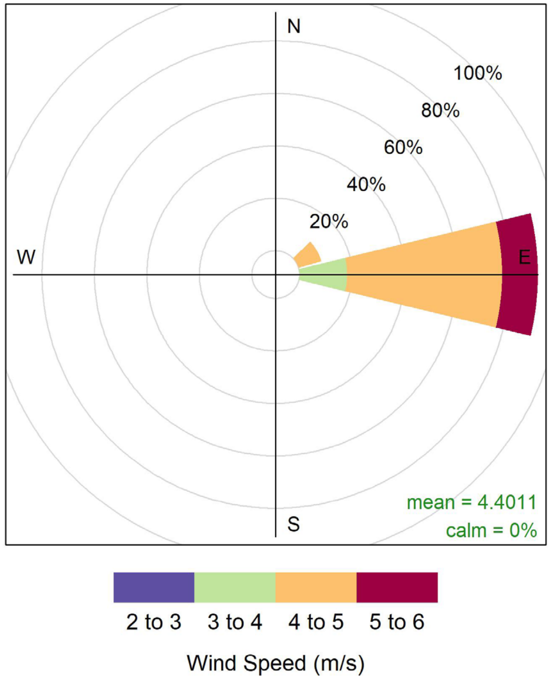
Frequency of counts by wind direction (%)



Frequency of counts by wind direction (%)

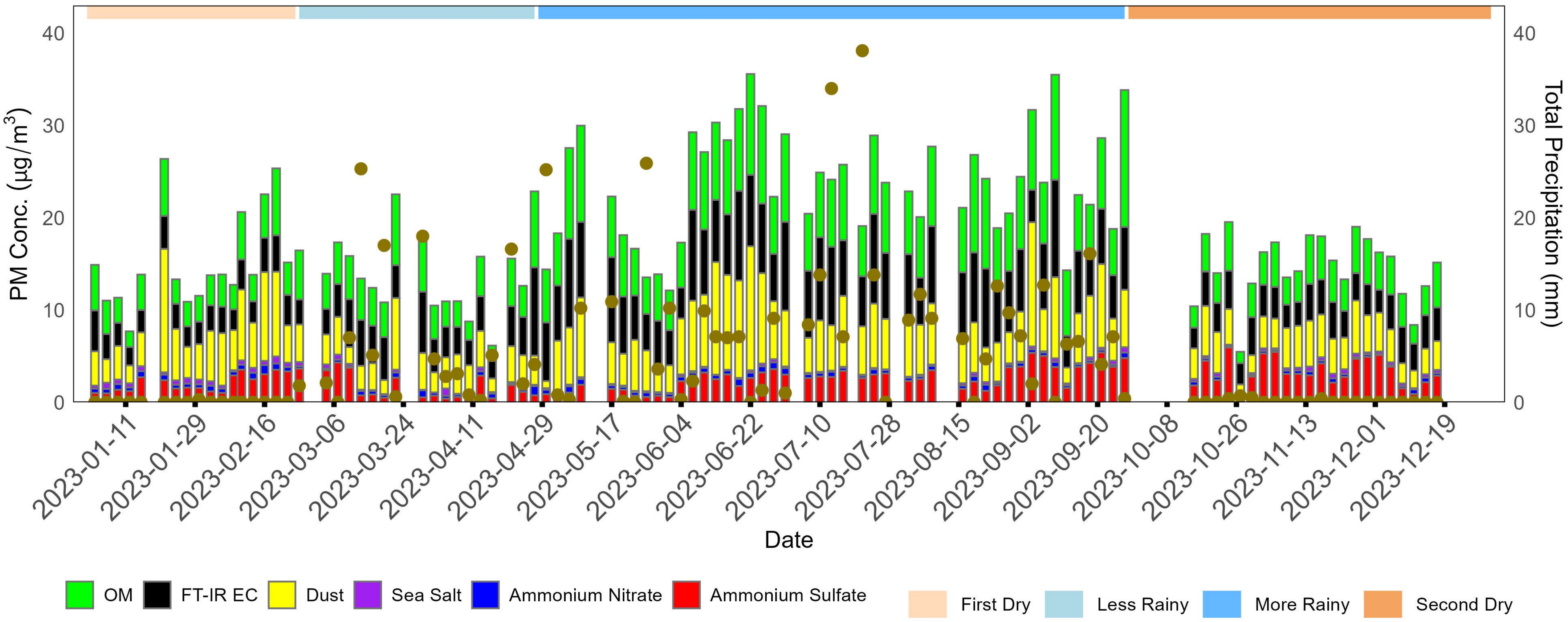


Frequency of counts by wind direction (%)

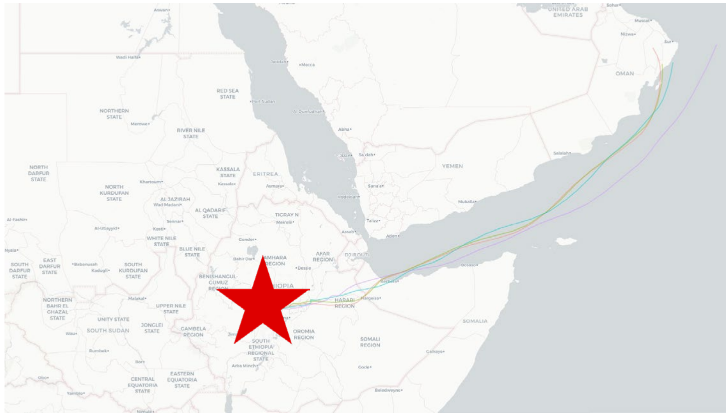


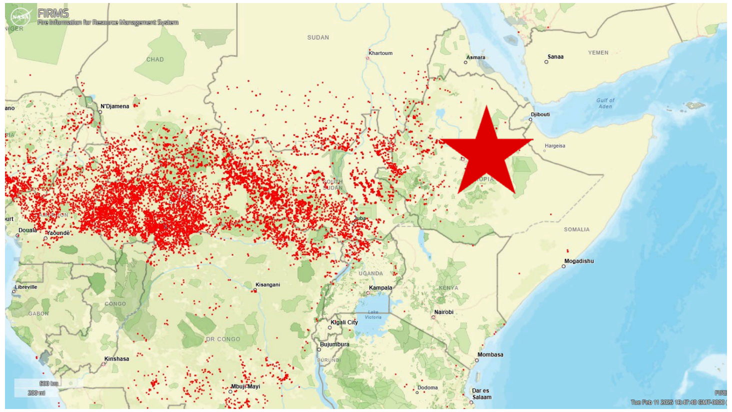
Frequency of counts by wind direction (%)

Addis Ababa PM2.5 concentrations

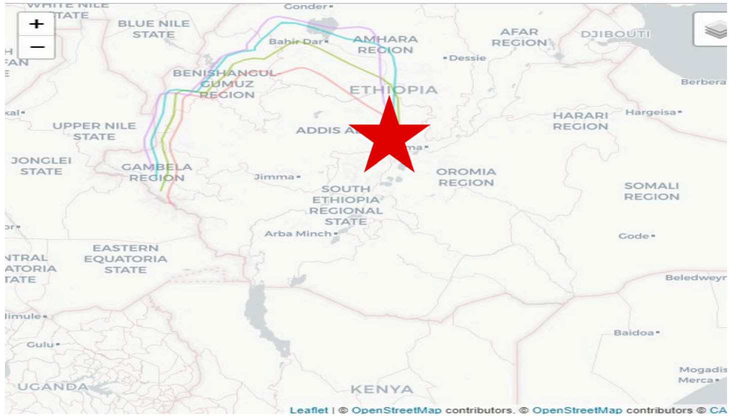


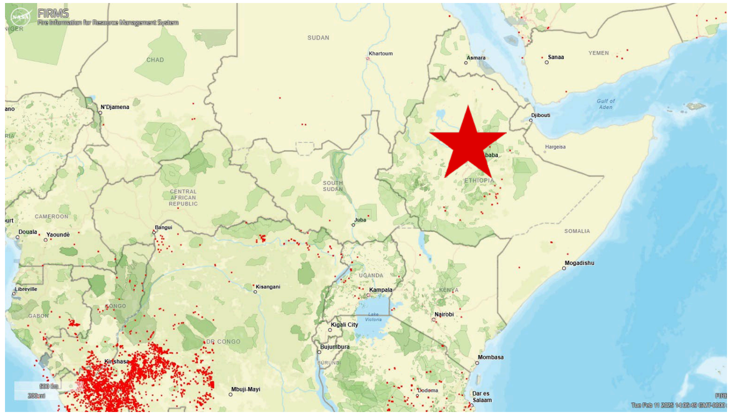
OM Origin at Addis Ababa – no wildfire impact



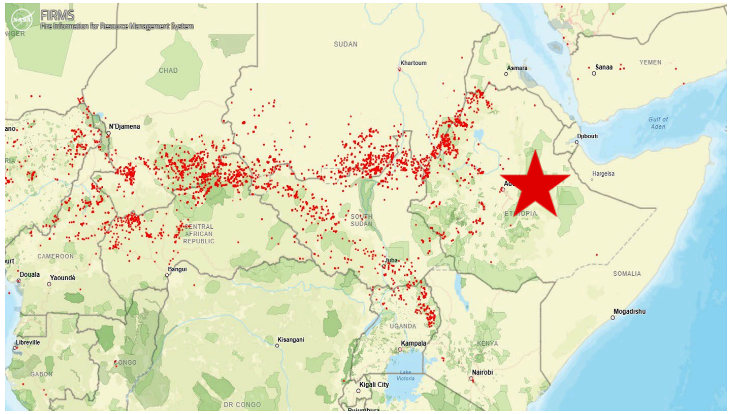


First Dry Season



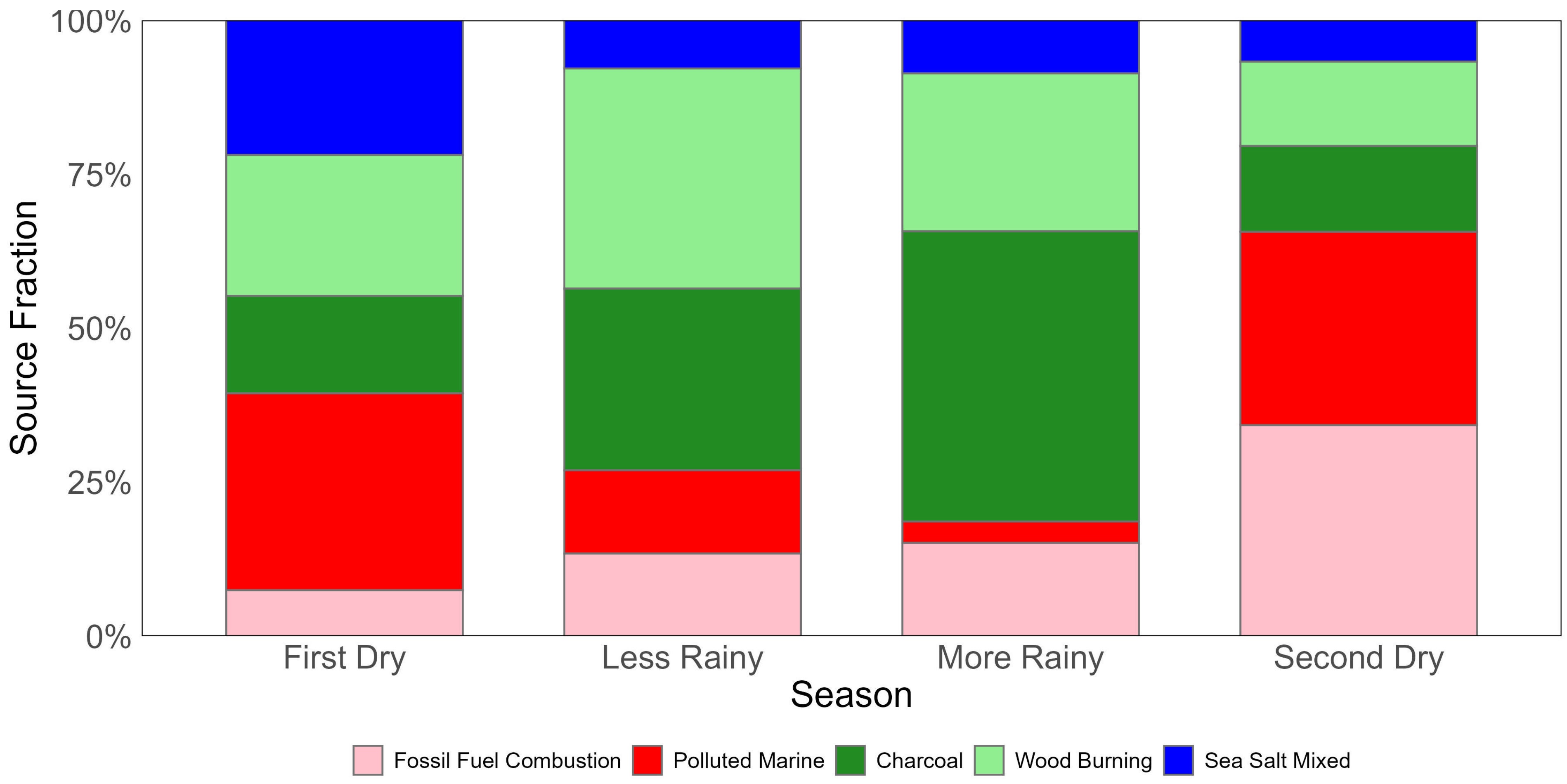


Rainy Season



Second Dry Season

Seasonal variation of OM sources at Addis Ababa



Summary of Addis Ababa, Ethiopia project

- FT-IR spectra which are low cost, routine, and non-destructive to PTFE filter samples used to measure OM and assess sources
- OM, dust, and EC contributed significantly (roughly 25% each) to PM2.5
- Charcoal and wood burning for home heating and cooking
    - 50-90% of OA in rainy
    - 20-80% in dry season
- Fossil fuel combustion
    - 35-80% of OA in dry season

IMPROVE FT-IR analysis extends composition data and hygroscopicity research

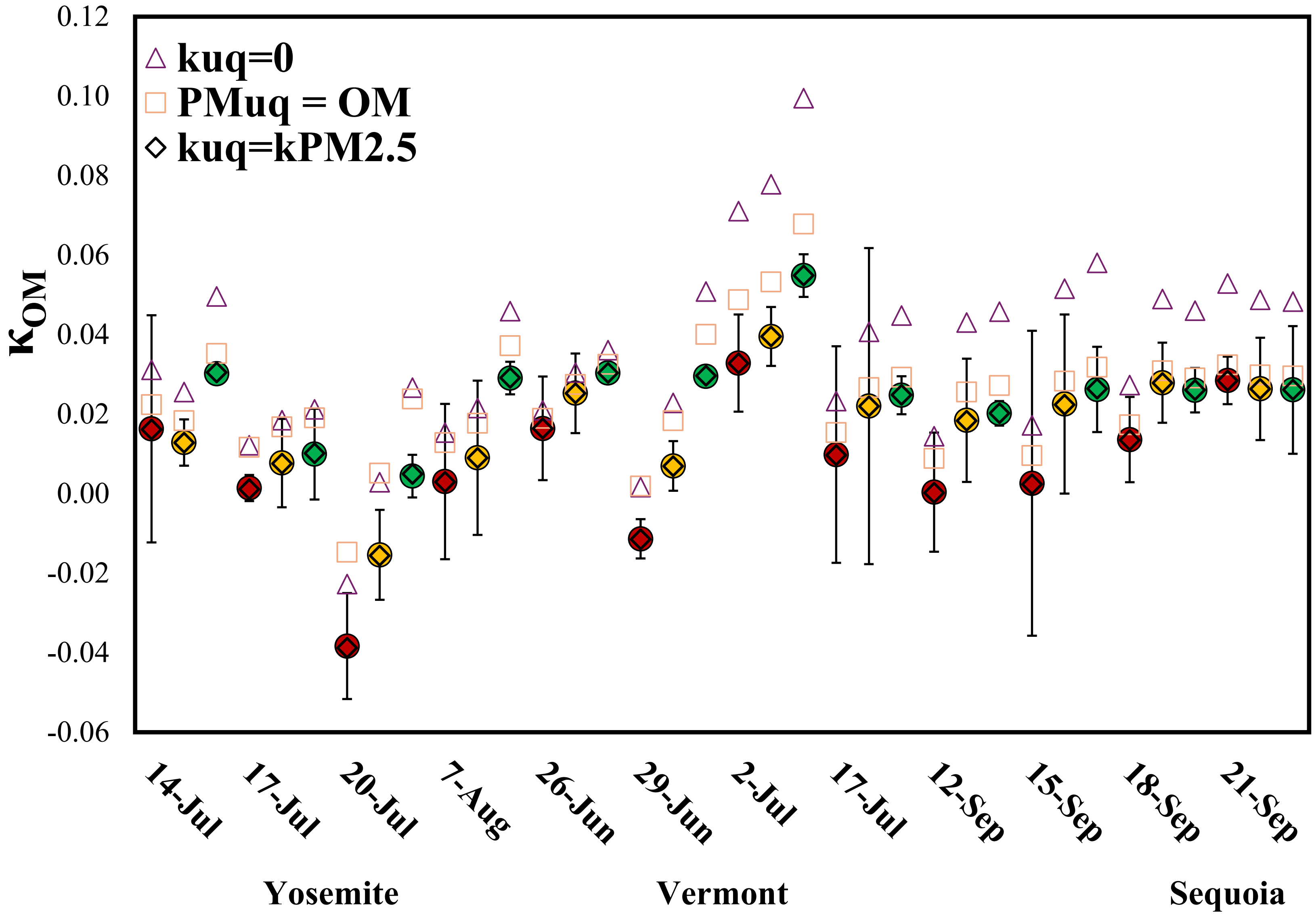
- Hygroscopicity of organics in wildfire samples
  - Yosemite, Sequoia and PMRF IMPROVE sites
  - Develop model of OM hygroscopicity based on functional group and ammonium sulfate concentrations
- Measuring organic functional groups in high time resolution with an ACSM instrument
  - method developed using FTIR spectra and ACSM data at IMPROVE Atlanta site
  - COOH, OH and CH well measured, naCO not well measured
- Using 20+ sites to calibrate FTIR spectra to TOR OC and TOR EC
  - Used to measure OC and EC at international sites operated by SPARTAN and NASA/MAIA
  - SPARTAN spectra used to measure OM and estimate sources in Pretoria and Addis Ababa, two major cities in Africa

How Does Unquantified $PM_{2.5}$ Affect the Hygroscopicity Organic Matter (κ_{OM})

- Unquantified $PM_{2.5}$ – could be hydrophobic or hydrophilic or mix of both

- Three scenarios to incorporate unquantified PM in calculation of k_{OM}:
  - **S1:** Unquantified $PM_{2.5}$ is completely hydrophobic (i.e. $k_{uq} = 0$)
  - **S2:** Unquantified $PM_{2.5}$ is completely of OM
  - **S3:** Unquantified $PM_{2.5}$ has similar water uptake to bulk $PM_{2.5}$

Results: Role of unquantified PM on derived κ_{OM}



- **Hydrophobic assumption:**
  - κ_{OM} will be **1.2 - 8.6 higher** than derived using quantified fraction.
- **All-OM assumption:**
  - κ_{OM} will be **1.1 - 8.2 higher** than derived using quantified fraction.
- **Bulk-$PM_{2.5}$ assumption:**
  - $\kappa_{OM} \approx$ derived using quantified fraction.