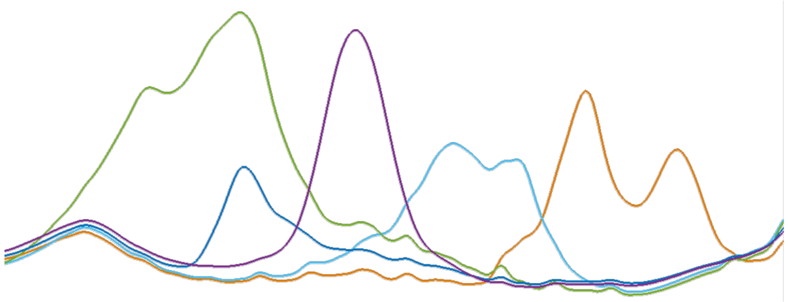
TRENDS IN ORGANIC MATTER AND FUNCTIONAL GROUPS USING FTIR AND FTIR MEASUREMENTS AROUND THE GLOBE



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IMPROVE Steering Committee
Point Reyes National Park, CA
October 22, 2019

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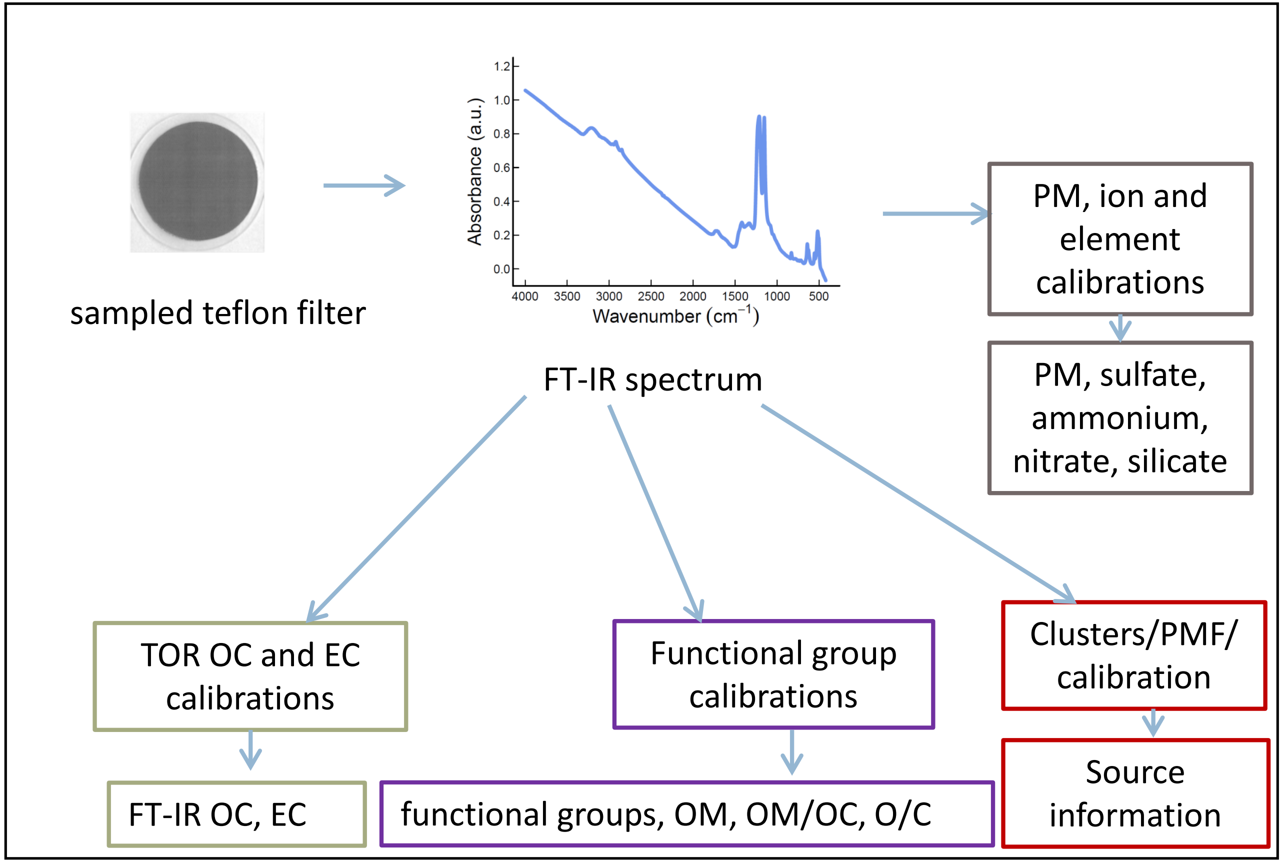
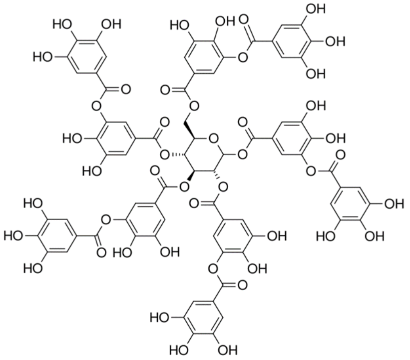
Characterize aerosol from Teflon filter



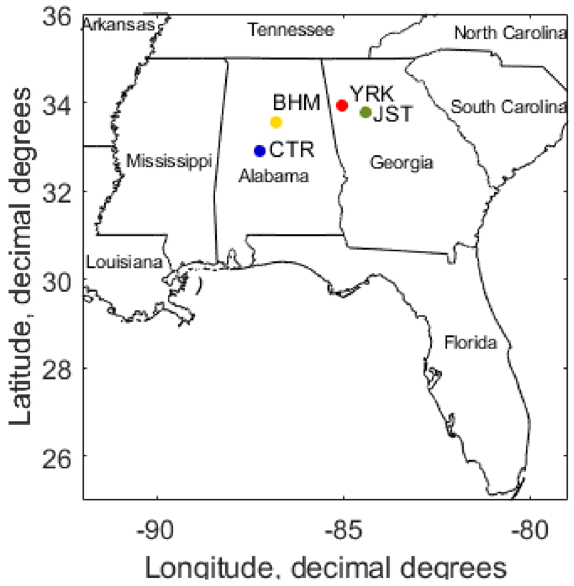
Motivation for measuring functional groups



- Organic matter/mass (OM) is composed of
  - Carbon
  - Oxygen
  - Hydrogen
  - Sometimes sulfur and nitrogen or other elements
- OM is used to calculate reconstructed mass and b_{ext} for RHR
- IMPROVE and CSN estimate OM by
  - Measure OC (C) using TOR
  - Multiply by an OM/OC value (1.8 in IMPROVE, typically 1.4 for urban)
- Measurements and models have shown that OM/OC varies by region, season, sample
- FTIR measures functional groups
  - added to estimate OM for each sample, **OM = CH + COOH + COO^{+} + naCO + COH**
  - Provide new, atmospherically relevant compositional data

Functional group and OM measurements

- **SEARCH network (EPRI funded)**
  - GA: Atlanta (JST; urban), Yorkville (YRK; rural)
  - AL: Birmingham (BHM; urban), Centreville (CTR; rural)
- **Functional group method**
  - Discussed at last years Steering Committee meeting
  - Samples from 2009-2016
  - Boris et al., *AMT*, 2019
- **Trends in organic matter, OM/OC and composition**
  - Focus of today's talk
  - Presented at AAAR last week, AGU in December, paper forthcoming



Boris et al., AMT, 2019

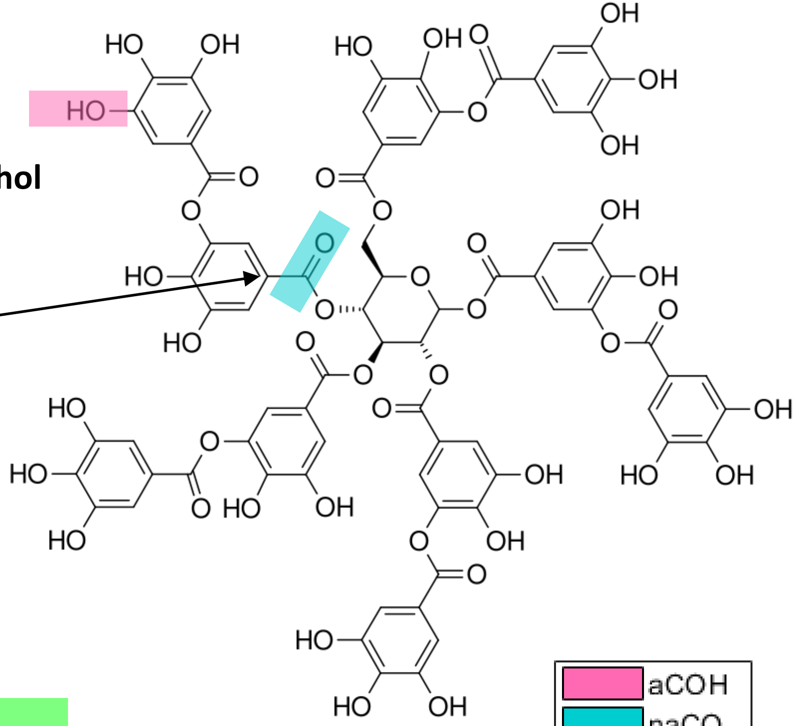
Similar methodology can be used for IMPROVE and CSN

Functional Group Quantification Method

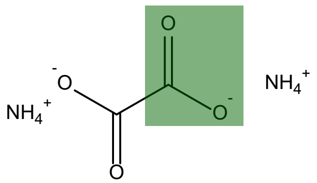
- Calibration of FT-IR spectra to **laboratory standards** using multivariate regression (partial least squares, or PLS)
- Laboratory standards
  - variety of chemicals
  - measure five functional groups.
- Calibration models include inorganic species and water as interferents
- Sum functional groups to calculate OM and OM/OC

Alcohol

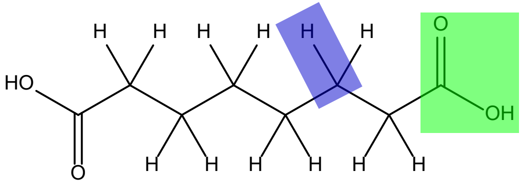
Non-acid, non-oxalate carbonyl



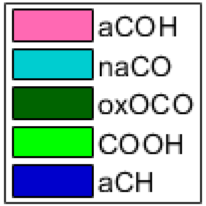
Oxalate



Aliphatic C-H



Carboxylic acid



Boris et al., *Atmos. Meas. Tech., 2019*

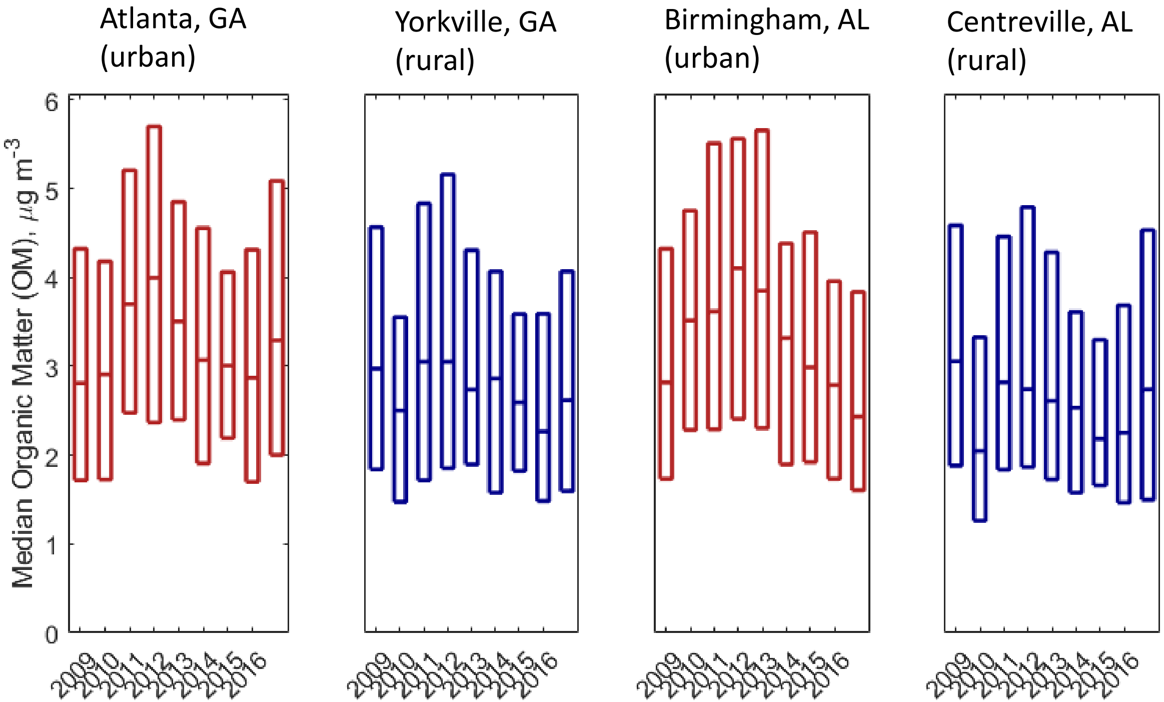
Questions

Having measured OM concentration and functional group composition in the Southeastern U.S. for an 8 year period:

- How did OM and functional groups change from 2009 to 2016?
- How do OM and functional groups vary by month?

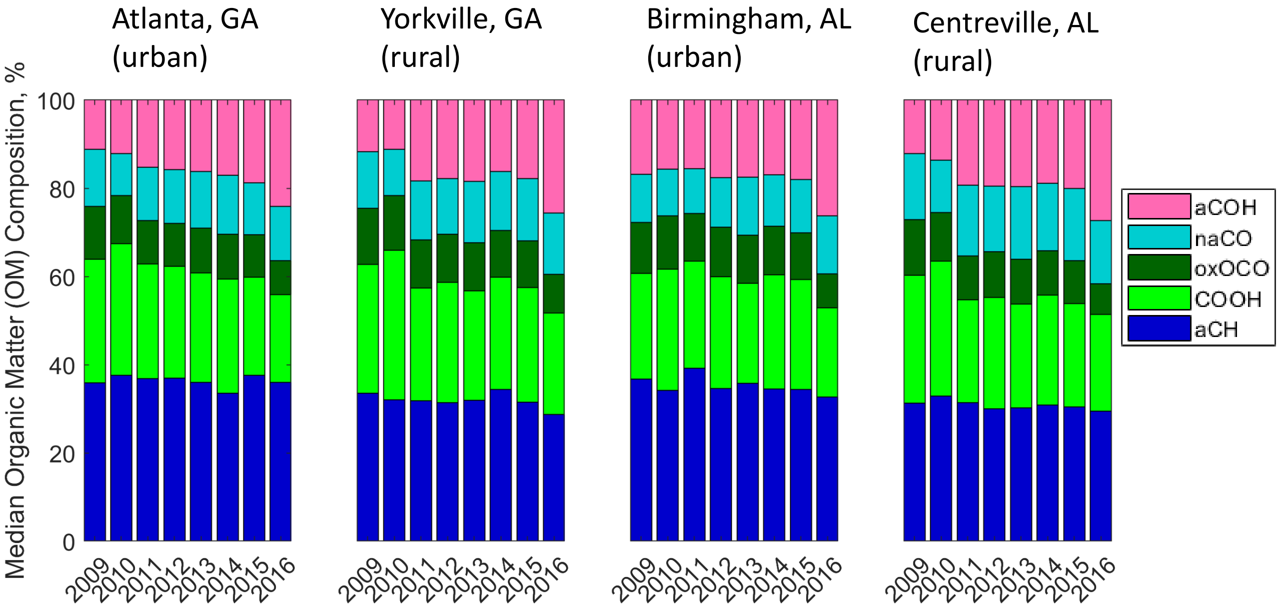
OM trends from 2009 to 2016

- OM is slightly higher at urban sites
- Overall decrease in OM concentrations 2012 onward
  - -0.052 ± 0.007 μg m^{-3} yr^{-1} (Boris et al., in prep)
  - ~-0.14 μg m^{-3} yr^{-1} OA (Marais et al., 2017 *Environ. Res. Lett.*)
- Related trends:
  - Parallel declines in $PM_{2.5}$, TOR OC, sulfate and nitrate concentrations

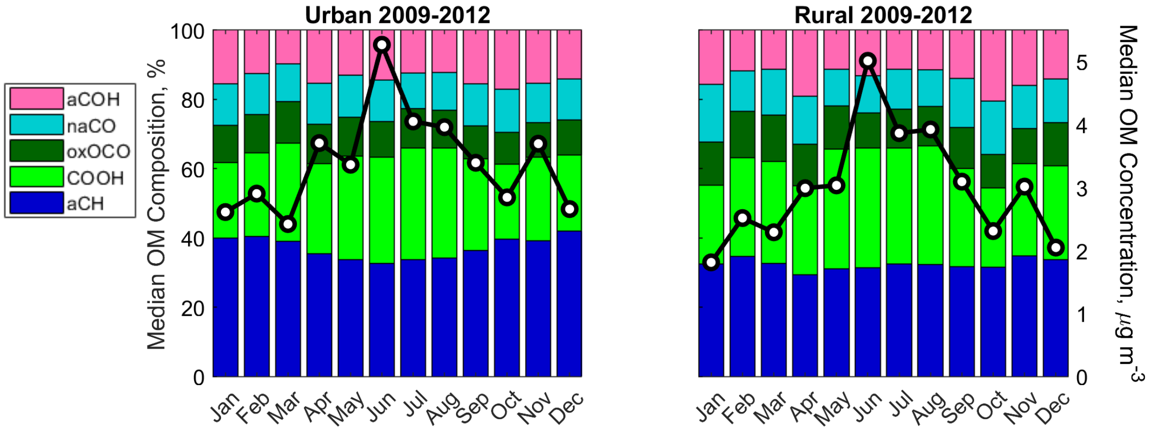


Composition changes from 2009 to 2016

- Less oxidized:
  - COOH, oxOCO significantly decreasing
- aCH decreasing
  - Since most molecules include CH, does not indicate if this is decrease in fresh emissions
- aCOH significantly increasing



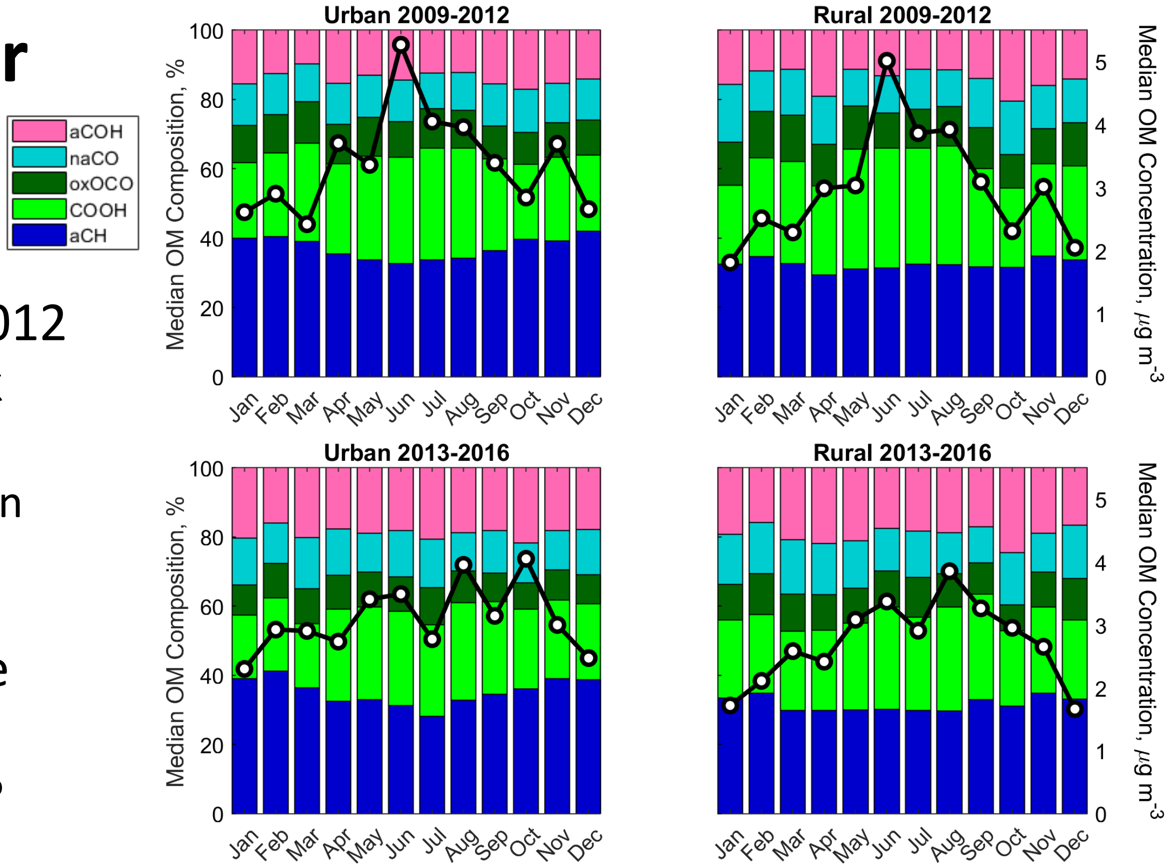
OM and composition changes by season



- Wintertime **OM** concentrations are lower than in summer in SE
- Summertime functional group composition more oxygenated (COOH) than in winter
  - Consistent with biogenic emissions, photochemistry in the summer

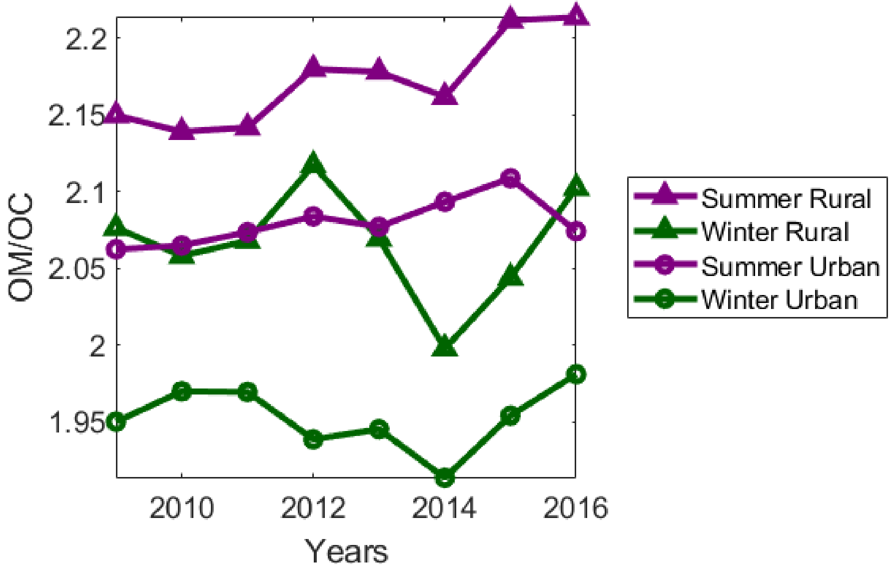
Changes in summer OM over time

- Disappearance of 2009-2012 early (June) summer peak
  - Corroborates decreasing isoprene aqSOA production hypothesis? (e.g., Marais et al., 2017, *Environ. Res. Lett.*)
- Remaining 2013-2016 late summer (Aug) "peak"
  - Due to drought-driven O_3? (Zhang & Wang 2016, PNAS)



OM/OC variations by season over time

- OM/OC currently assumed to be one value for all samples in IMPROVE
- OM/OC vary in time and space
    - Summer **purple**
    - Winter in **green**
- **Summer** higher than **winter**
- Rural (▲) higher than urban (●) in both seasons
- No significant trend over all years (functional group contributions)
    - Increase in **summer** OM/OC



Conclusions for Functional Groups by FTIR

- **Functional group data useful for observing trends in**
  - OM:
    - Annual concentrations decreased at all sites
    - Summer higher than winter, changes in summer peaks in recent years
  - Composition of organics:
    - Annually, contributions of aCOH increased, while oxOCO, COOH, and aCH decreased
    - Seasonally, COOH higher in summer, aCH higher in winter
- **Functional group data useful for understanding atmospheric oxidation and processes**
  - OM/OC higher in summer than in winter and in rural than in urban sites
  - High summertime OM concentration events likely due to biogenic emissions/processing

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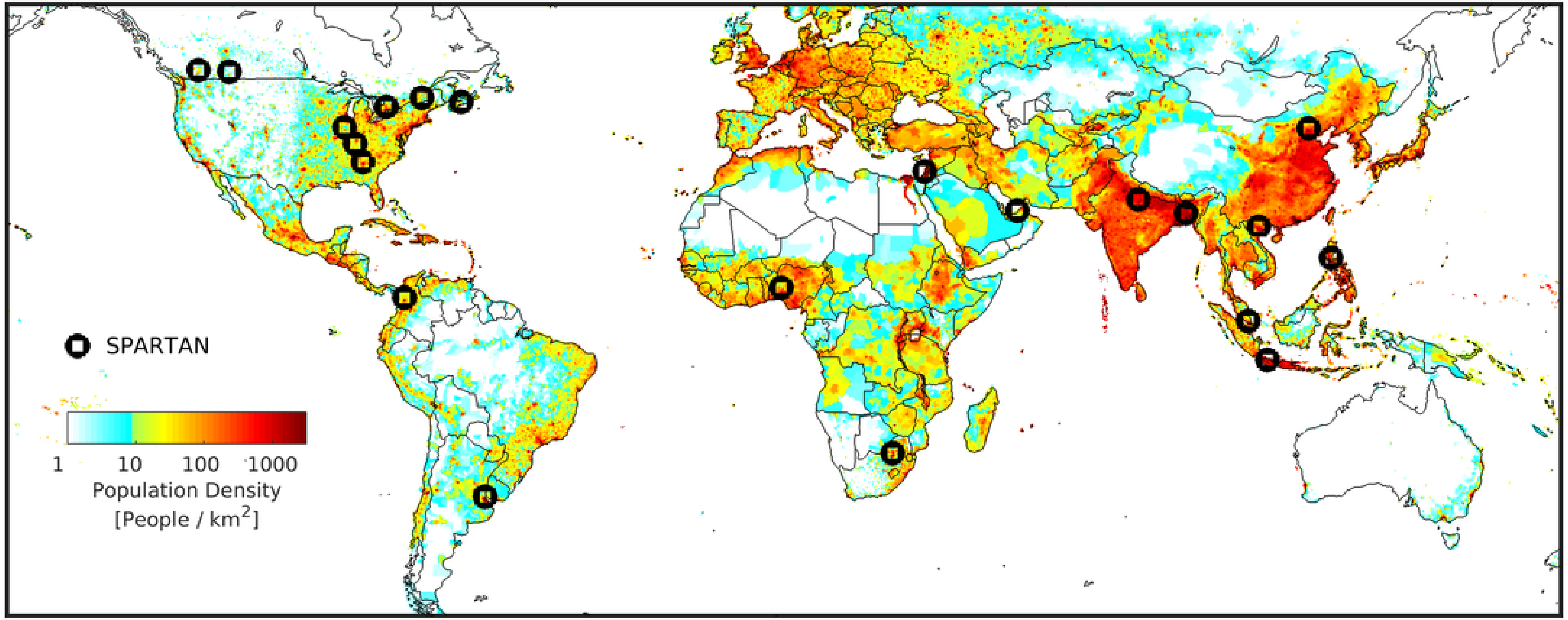
SPARTAN - Surface PARTiculate mAtter Network

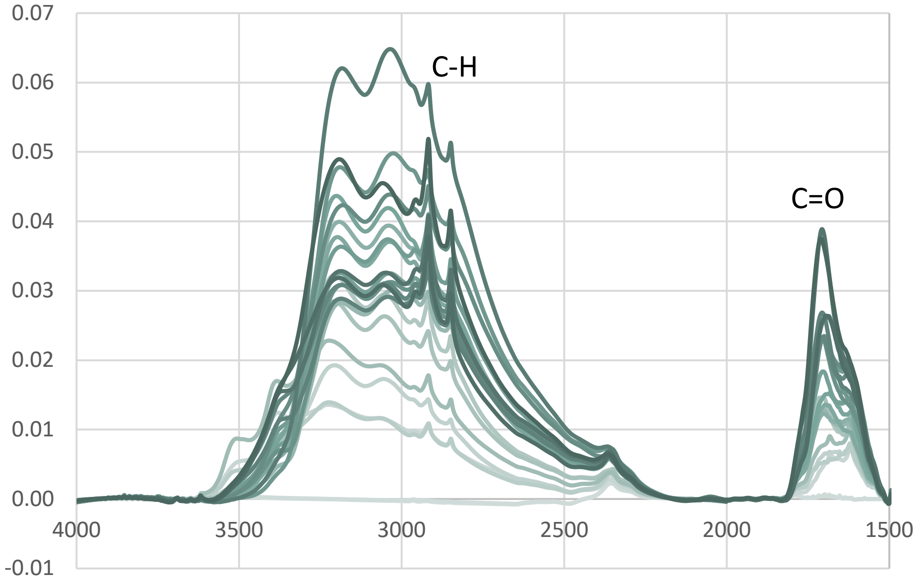


- a network of ground-based PM2.5 measurements, teflon filter only, 19 sites and growing
- enhance satellite remote sensing estimates of PM and assessment of health outcomes
- FTIR for OC, EC and eventually functional groups
- HIPS for absorption

Poster at AGU

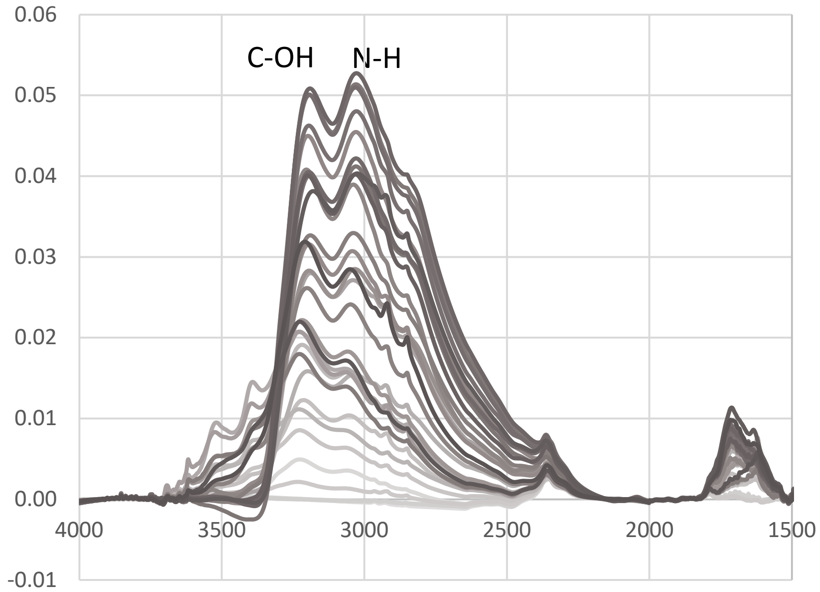
FT-IR spectra of SPARTAN samples

Hanoi, Vietnam
August, 2018 - June 2019



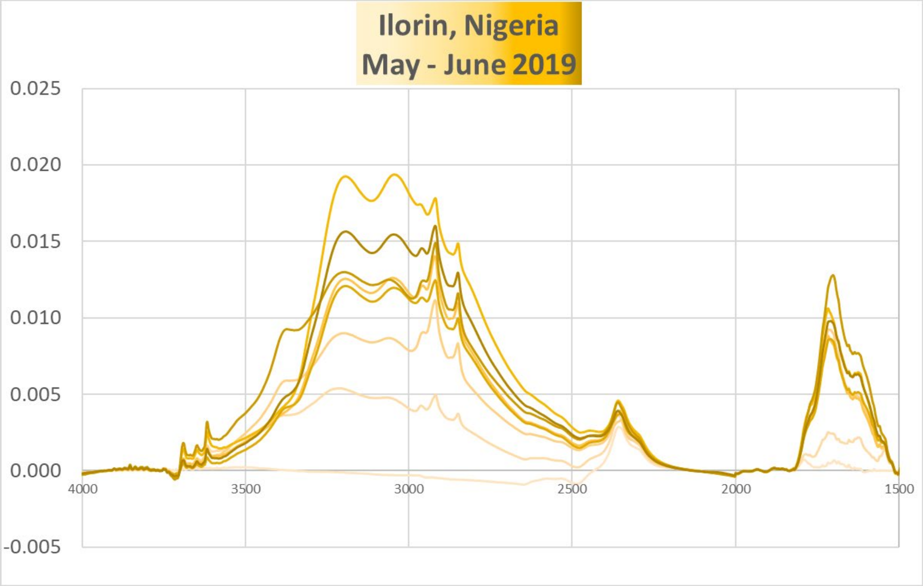
Rice field burning

Rehovot, Israel
August, 2018 – June 2019

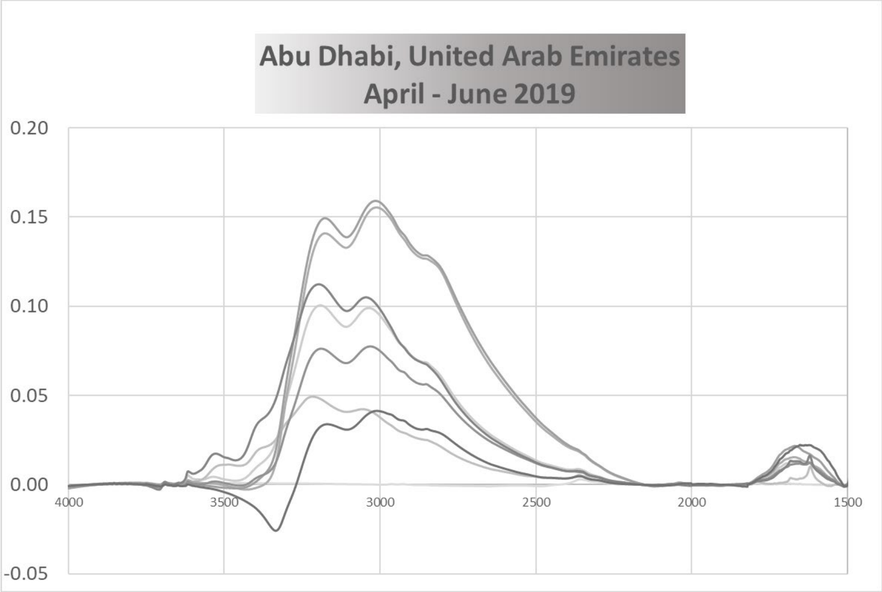


Urban, reacted sea salt, sand/dust

SPARTAN sites – recent additions

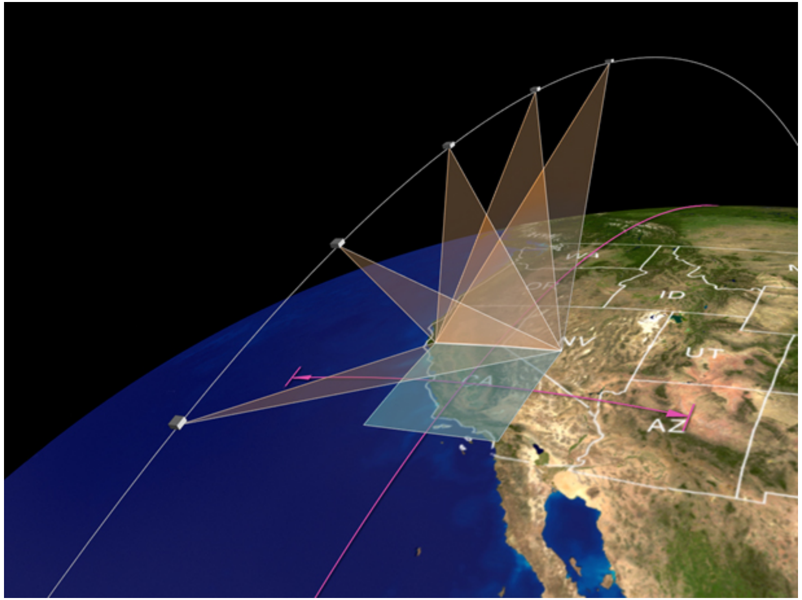


Low mass, Si-O peaks, aOH, NH4, CH and C=O



Very high mass, ammonium from ammonium sulfate, small CH and C=O

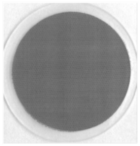
MAIA – Multi-Angle Imager for Aerosols



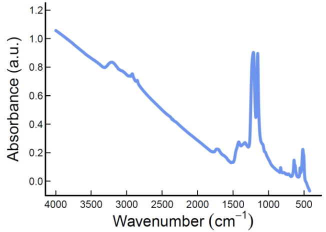
https://www.jpl.nasa.gov/missions/web/maia1.jpg

- Connect satellite data to PM composition to health
- Ground-based measurements of PM2.5, teflon filter only
- FT-IR for OC and EC, HIPS for absorption
- Abbey Nastan from JPL will give presentation on MAIA tomorrow

FT-IR for network use



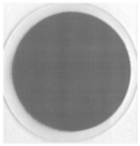
Teflon filter



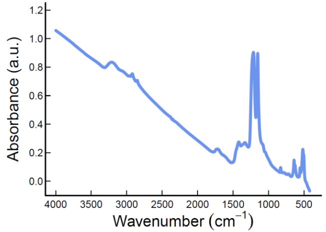
- FT-IR is a non-destructive, fast, low-cost method
- Reproduce existing data
    - OC and EC in CSN and IMPROVE are predicted with a few sites of TOR
    - Sulfate, ammonium, silicate, etc. predicted in IMPROVE and CSN
        - Data useful for QC of network data
- New data
    - OM, OM/OC and functional groups
    - Observe trends in OM, OM/OC and composition
- Single filter ops. - SPARTAN, MAIA, FRM, personal samplers (J. Volckens, CSU)
- Source characterization (not discussed today)
    - Characterize source samples (Mike Hayes, EPA)
    - Identify dust, smoke, marine and other sources in ambient samples

FTIR is a promising method for measuring compositional data in PM2.5 monitoring networks

FT-IR for network use



Teflon filter



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If you are interested in participating in occasional FT-IR conference calls, please let me know

FTIR is a promising method for measuring compositional data in PM2.5 monitoring networks

FTIR Publications

- **OC and EC – IMPROVE, CSN and FRM methods**
  - Predicting TOR OC for IMPROVE, Dillner and Takahama, Atmos. Meas. Tech., 8, 1097-1109, https://doi.org/10.5194/amt-8-1097-2015, 2015a.
  - Predicting TOR EC for IMPROVE, Dillner and Takahama, Atmos. Meas. Tech., 8, 4013-4023, https://doi.org/10.5194/amt-8-4013-2015, 2015b.
  - Predicting OC and EC for IMPROVE at different sites/years, Atmos. Meas. Tech., 9, 441-454, https://doi.org/10.5194/amt-9-441-2016, 2016.
  - Predicting TOR OC for CSN, Weakley, Takahama and Dillner, Aerosol Science and Technology, 50, 1096-1114, https://doi.org/10.1080/02786826.2016.1217389, 2016.
  - Predicting TOR EC for CSN, Weakley, Takahama, Wexler, Dillner, Aerosol Science and Technology, https://doi.org/10.1080/02786826.2018.1439571, 2018.
  - Predicting TOR OC and EC for FRM from CSN calibrations, Weakley, et al. Aerosol Science and Technology, https://doi.org/10.1080/02786826.2018.1504161, 2018.
  - Multiple FT-IR Instruments: Effect on Multivariate Calibration Performance, Debus et al., Applied Spectroscopy, https://doi.org/10.1177/0003702818804574, 2018.
  - Review of statistical calibration strategies for FT-IR in IMPROVE and CSN, Takahama et al., Atmos. Meas. Tech., 12, 525-567, https://doi.org/10.5194/amt-12-525-2019, 2019.
- **OC and EC - application**
  - Impact of the 2016 Fort McMurray Horse River Wildfire on PM in Alberta, Canada, Landis et al., Science of the Total Environment, vol. 618, 1665-1676, https://doi.org/10.1016/j.scitotenv.2017.10.008, 2018.

Functional groups and OM/OC – method and applications

- Determination of OM and OM/OC by FT-IR, Ruthenburg et al., Atmospheric Environment, 86, 47-57, https://doi.org/10.1016/j.atmosenv.2013.12.034, 2014
- FT-IR quantification of the carbonyl functional group in aqueous-phase secondary organic aerosol from phenols. Atmospheric Environment 100, 230-237, George, et al., https://doi.org/10.1016/j.atmosenv.2014.11.011, 2015
- OM/OC with improved model selection, Takahama, Ruggeri, Dillner, Journal of Chemometrics, 19, 659-668, https://doi.org/10.1002/cem.2761, 2015
- Molecular transformation of phenolic SOA during photochemical aging in aqueous phase, competition among oligomerization, functionalization and fragmentation, Yu et al., Atmospheric Chemistry and Physics, 16, 4511-4527, https://doi.org/10.5194/acp-16-4511-2016, 2016.
- Quantification of functional groups: interpretation of calibration through sparse methods, Takahama et al., Atmos. Meas. Tech., 9, 3429-3454, https://doi.org/10.5194/amt-9-3429-2016, 2016.
- Amines and their impact on OM/OC in IMPROVE, Kamruzzaman, Takahama and Dillner, Atmospheric Environment, 172, 124-132, https://doi.org/10.1016/j.atmosenv.2017.10.053, 2018
- Analysis of functional groups in atmospheric aerosols by infrared spectroscopy: systematic intercomparison of calibration methods for US measurement network samples, Reggente, M., Dillner, A. M., Takahama, S., Atmos. Meas. Tech., 12, 2287-2312, https://doi.org/10.5194/amt-12-2287-2019, 2019.
- Quantifying Organic Matter as Functional Groups in SEARCH, Boris et al., Atmos. Meas. Tech., 12, 5391-5415, https://doi.org/10.5194/amt-12-5391-2019, 2019

How does organic aerosol vary between days (2016)?
2016 Daily Dataset: Fires in the U.S. Southeast

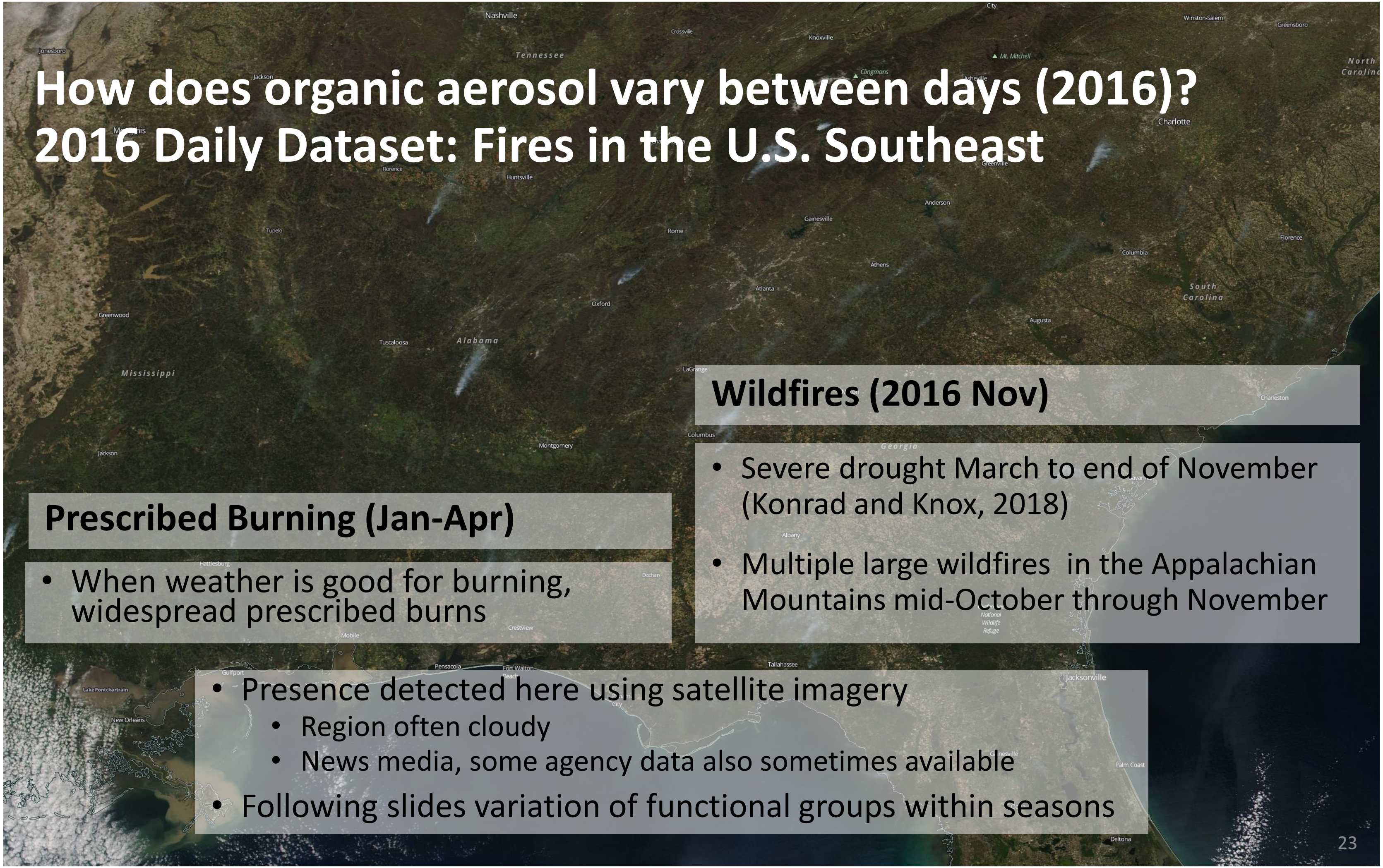
Wildfires (2016 Nov)

- Severe drought March to end of November (Konrad and Knox, 2018)
- Multiple large wildfires in the Appalachian Mountains mid-October through November

Prescribed Burning (Jan-Apr)

- When weather is good for burning, widespread prescribed burns

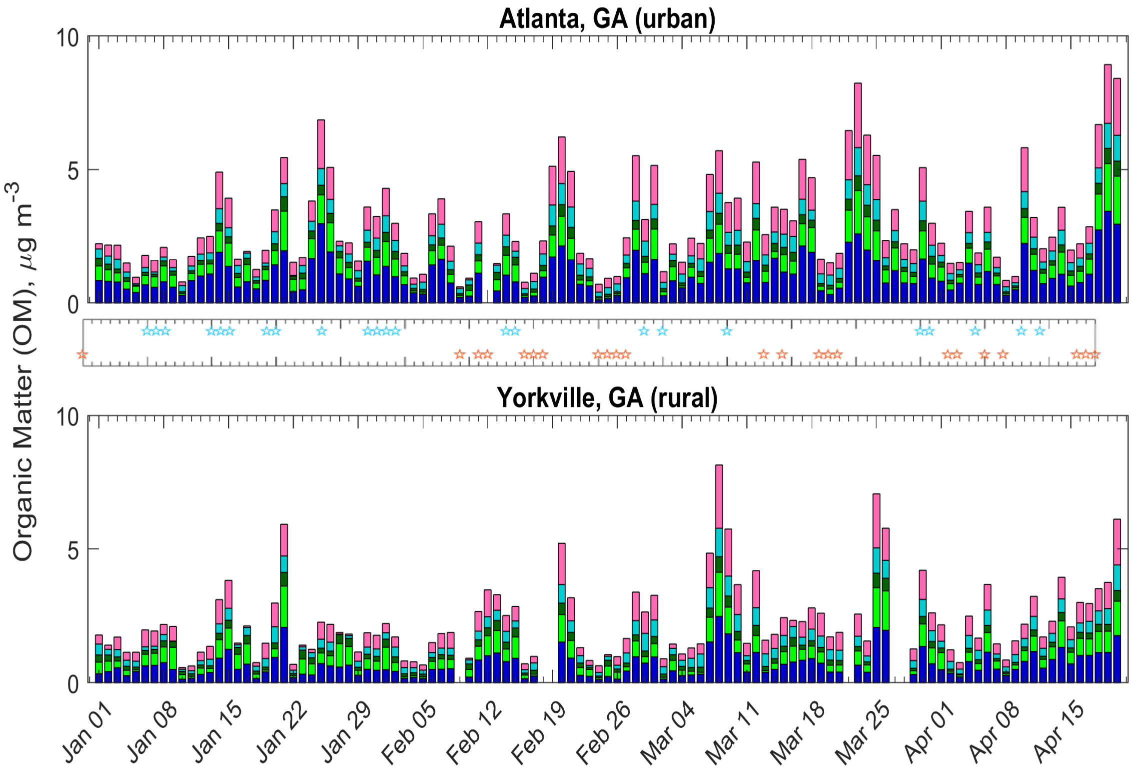
- Presence detected here using satellite imagery
  - Region often cloudy
  - News media, some agency data also sometimes available
- Following slides variation of functional groups within seasons



Mar. 22 2016 (NASA Worldview https://worldview.earthdata.nasa.gov)

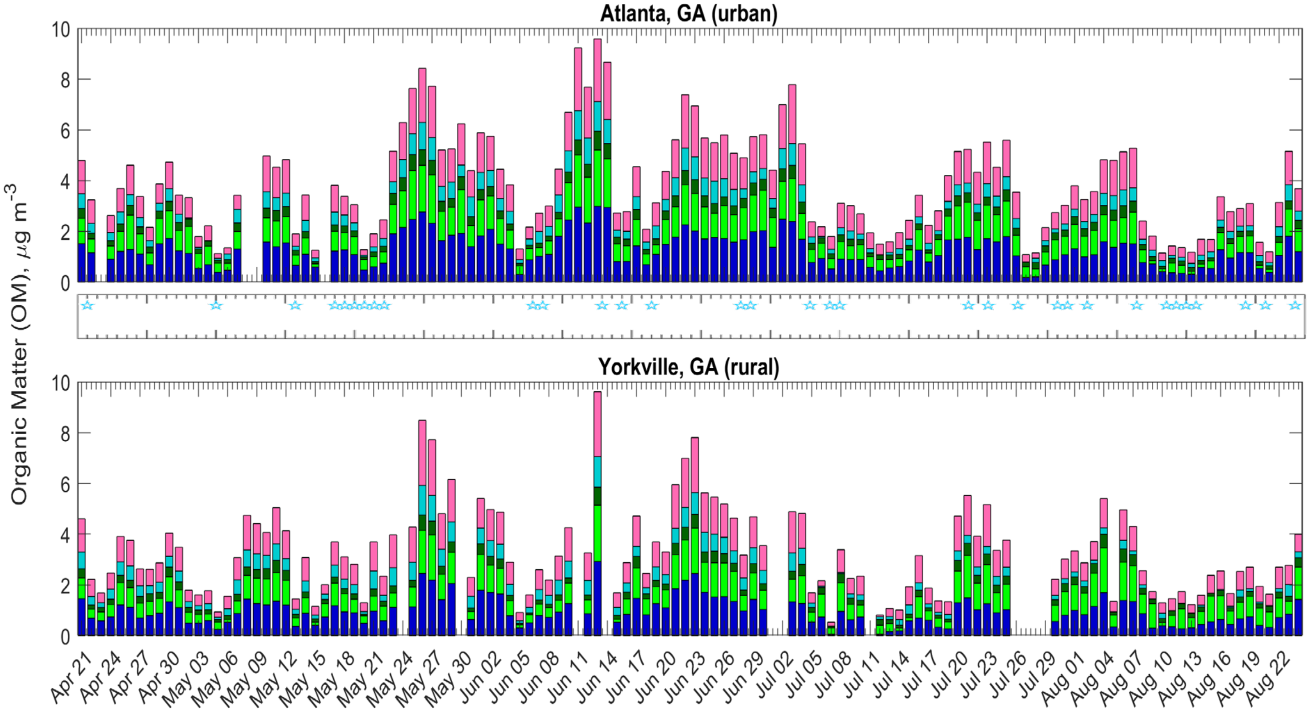
2016 Daily Data: Spring Prescribed Fire Season (Jan-Apr)

- Fire indicated by orange stars, precipitation indicated by blue stars
- Peaks in OM conc. often correspond to fires
    - cannot yet detect fires from non-fires by spectra/functional group data in this data set
- Days with low OM conc. often correspond to rain



2016 Daily Data:
Summer Buildup and Rainout (Apr-Aug)

- Not fire; “burn ban” in GA
- OM varies: 1 - 10 $\mu g/m^3$
- Precipitation between buildup events
- Often see multi-day trend: as OM conc. rises, contribution of aCH decreases, aCOH increases
- Secondary biogenic?
  - Sun et al., 2011 *ES&T*; Zhang et al., 2018 *PNAS*; Hidy et al., 2014 *ACP*



2016 Daily Data: Winter Wildfires

- Wildfires, heavy smoke in Nov. indicated by high OM concentrations
- Seasonally high contribution of aCH
    - Residential burning? e.g., Chen et al., 2012, *JGR*