Using Particle Functional Group Composition to Identify and Quantify the Effects of Anthropogenic Emissions on Biogenic Secondary Organic Aerosol

Lynn Russell[a], Paul Ziemann[b], Jason Surratt[c],
Jun Liu[a], Sri Hapsari Budisulistiorini[c], Megan Claflin[b], Satoshi Takahama[d], Rob Modini[d]

[a]Scripps Institution of Oceanography, University of California, San Diego
[b]Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences (CIRES),University of Colorado, Boulder
[c]Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, The University of North Carolina at Chapel Hill
[d]Ecole Polytechnique, Lausanne, Switzerland

With Thanks to the Following Groups for Measurements for Comparisons:
Jimenez - HR-ToF-AMS Org at Centreville, AL
McKinney - PTR-MS Isoprene and MVK MACR at Look Rock, TN
IMPROVE - O3,Soil, and radiation at Look Rock, TN

Objectives

- FTIR analysis of OA functional groups in SOAS samples.

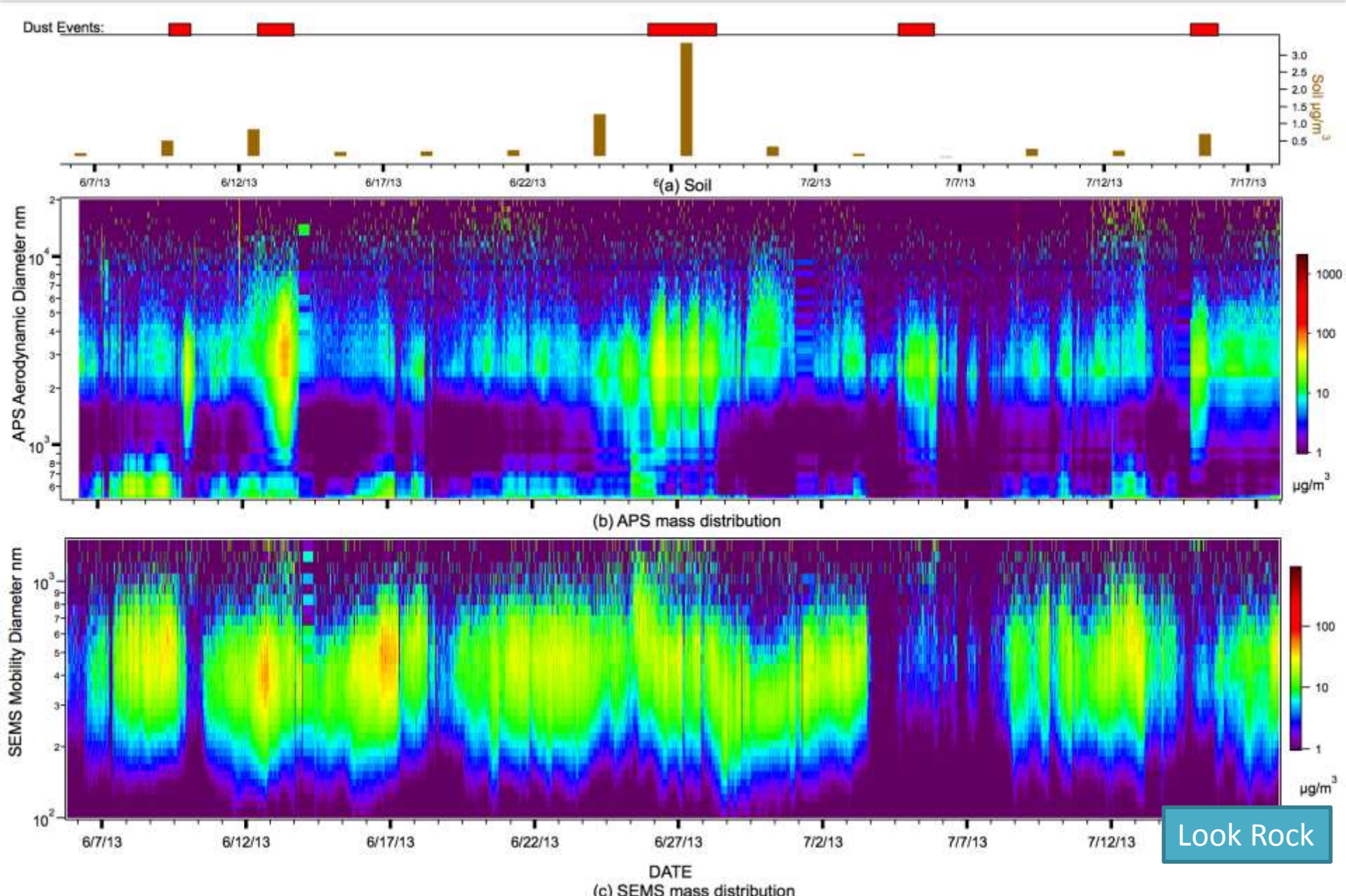
- Lab studies of effects of NO_x, sulfate, and anthropogenic VOCs on functional group composition and FTIR spectra of SOA formed from biogenic VOCs.

- Identify and quantify contributions of biogenic and anthropogenic emissions to SOA formed during SOAS using FTIR spectra plus lab and field results.

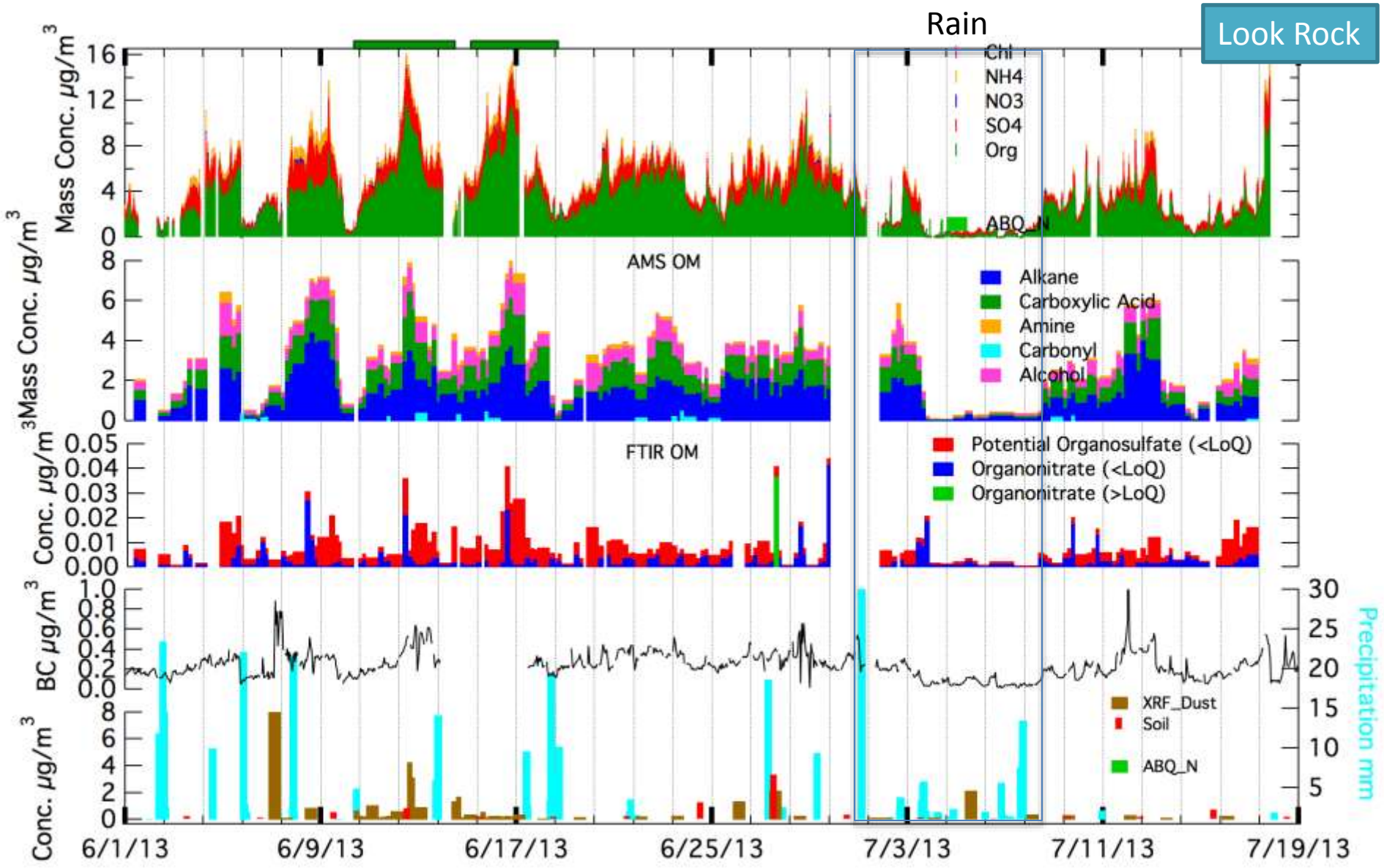
Outline

- Look Rock PM and OM time series
  - Comparison of AMS and FTIR
- Look Rock OM source factors
  - Correlations of OM components with tracers
- Centreville OM time series and source factors
- Comparison of Centreville and Look Rock
  - Organic functional group composition
  - Source apportionment

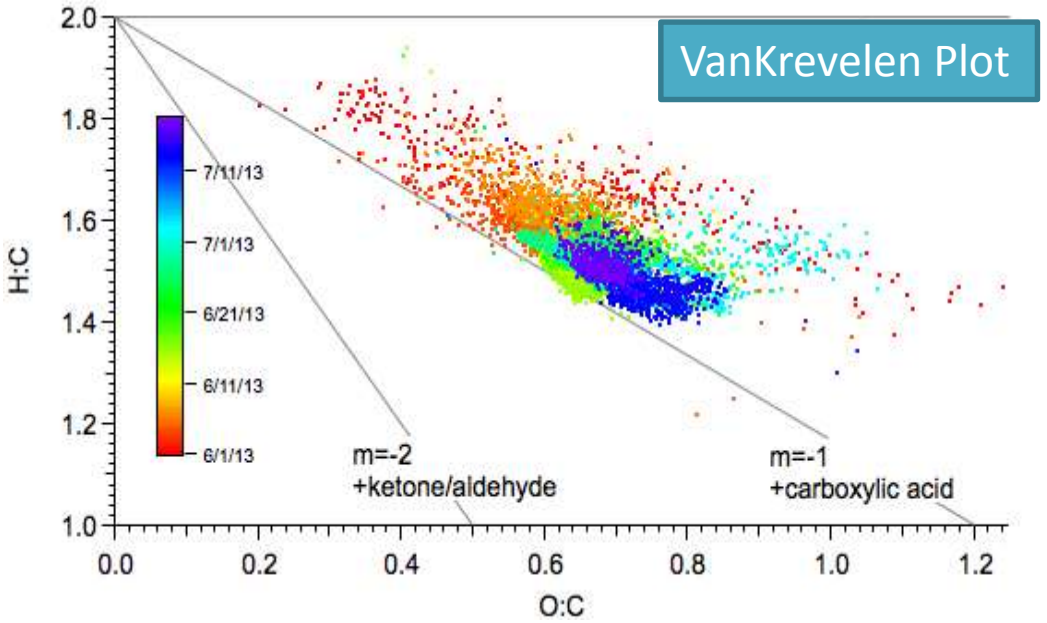
Mass Size Distributions at Look Rock

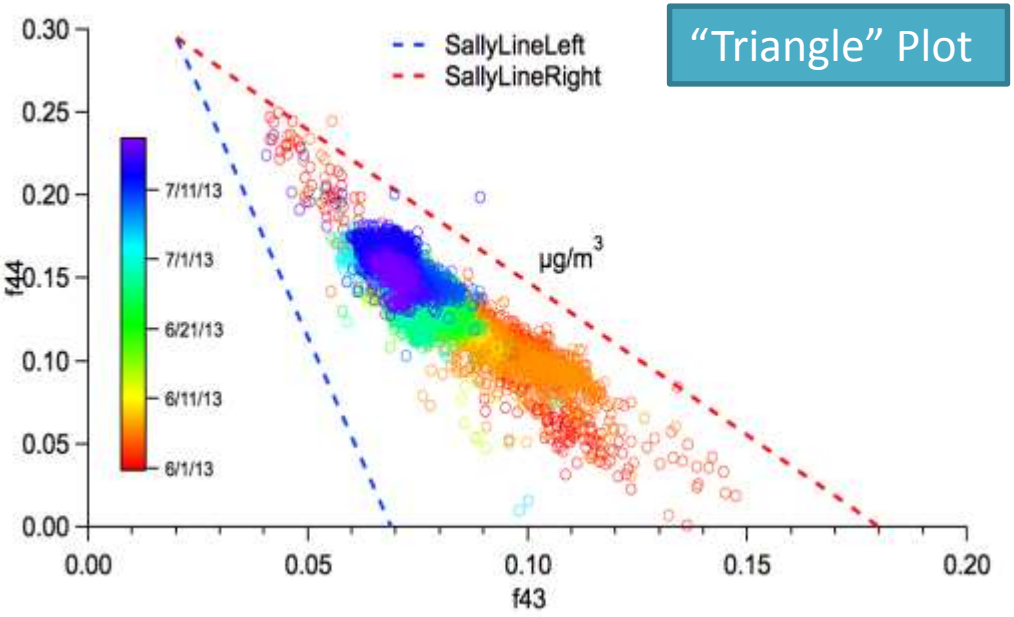


Organic Mass (OM) at Look Rock



Estimated AMS OM Oxidation State





- Oxidation state increased gradually during the project.

OM Quantification at Look Rock

Look Rock

- Most OM in PM2.5 is in PM1.
- OM from AMS and FTIR are correlated.
- AMS CE of 0.78 is consistent with (SEMS-Refractory) and FTIR.
- Overall strong agreement on OM quantification by two independent methods.

Key Correlations to OM at Look Rock

Look Rock

Moderate correlation of OM with

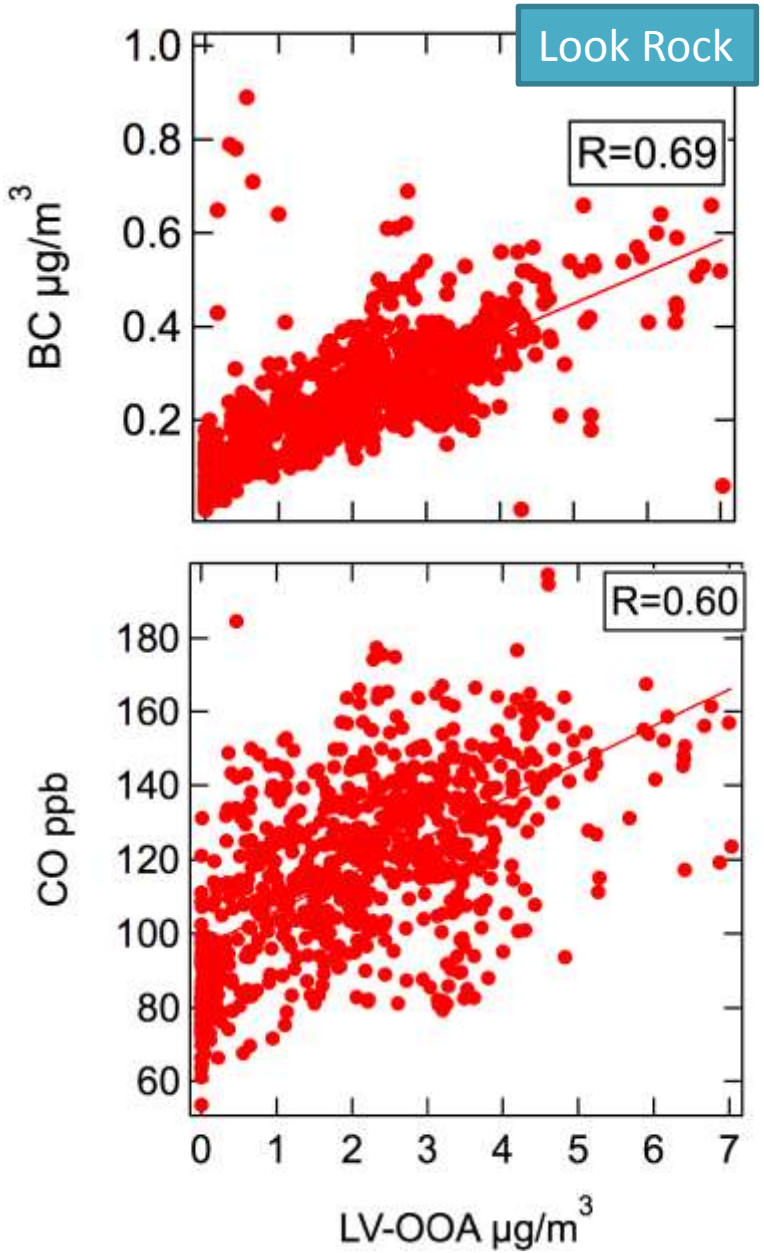
- O_3 indicates that most OM is secondary.
- MVK/MACR suggests strong biogenic component.
- Sulfate and nitrate indicates contributions include anthropogenic sources.

OM Source Factors at Look Rock

Look Rock

- FTIR and AMS factor spectra were similar to previous reports:
  - FTIR Bio has high carbonyl; AMS “Factor91” has high m/z 91.
  - FTIR FC1 has high alkane, acid; AMS LV-OOA has high m/z 28, 44.
  - FTIR FC2 has high alkane, alcohol; AMS Isoprene OA has high m/z 53, 81, 82.
- FTIR and AMS factors correspond generally but useful differences.

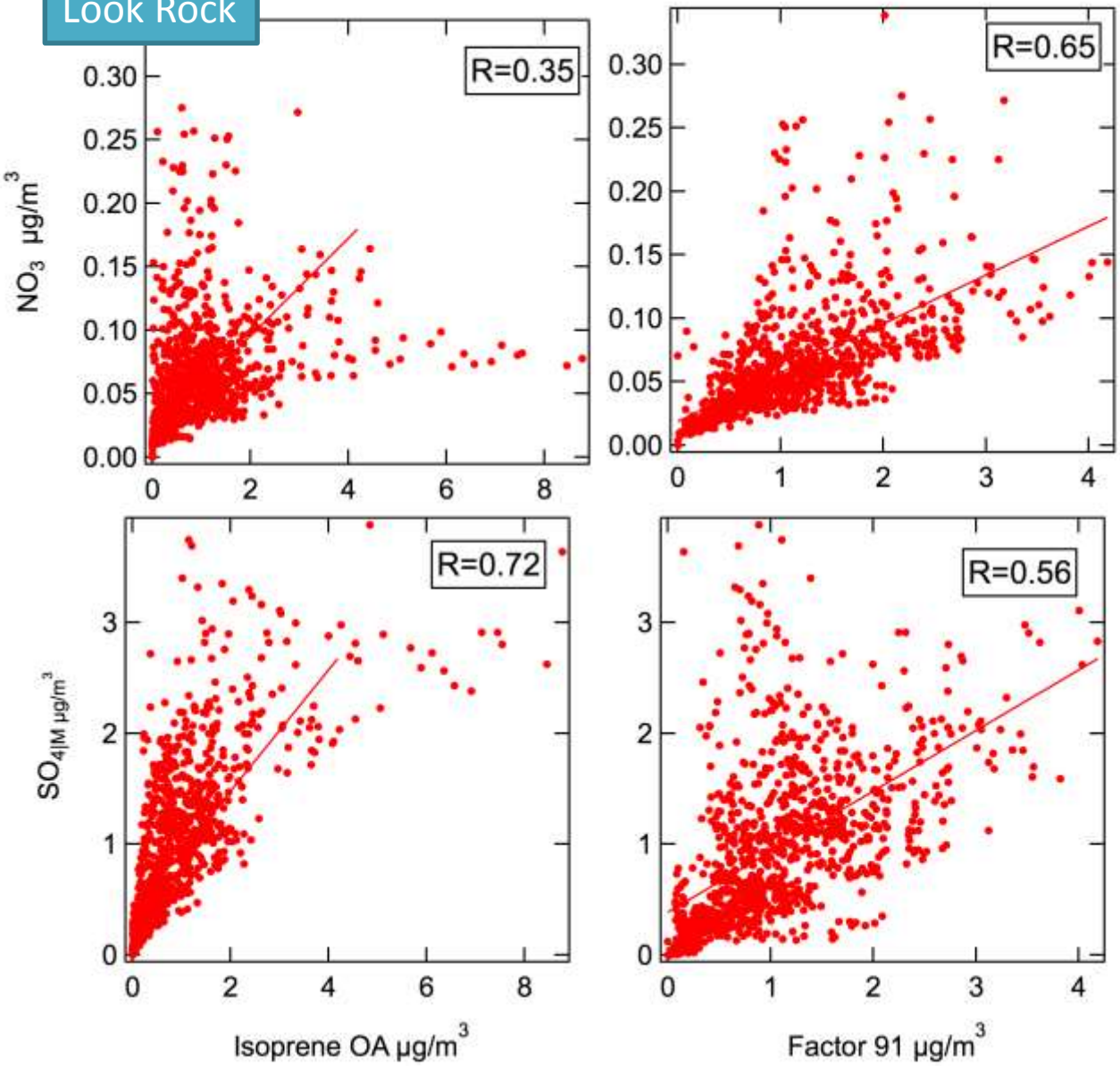
OM from Combustion Sources



- LV-OOA correlates well with
  - O3, indicating likely largely secondary.
  - CO, BC, sulfate, and nitrate, indicating likely fossil fuel combustion sources.

OM links to Nitrate and Sulfate

Look Rock



- Isoprene OA correlates with sulfate.
- Factor91 correlates with both nitrate and sulfate.
- Factor91 is likely to be recently produced SOA given its low O/C.

Biogenic Factors and Organosulfate

Look Rock

- (Potential) organosulfate correlates with both Isoprene OA factor (AMS) and BIO factor (FTIR)
  - Consistent with organosulfate role in forming biogenic SOA.

Organic Mass (OM) at Centreville

Centreville

Comparison of AMS and FTIR OM

- High correlation of FTIR OM with AMS Org (Jimenez group)
- Quantitative agreement with CE=1 (consistent with low dust, salt, bounce)

Centreville

OM Source Factors at Centreville

Centreville

AMS Ammonium

AMS Nitrate

- Sources are similar to Look Rock
- Biogenic factor
  - High carbonyl
  - Correlated with nitrate not sulfate

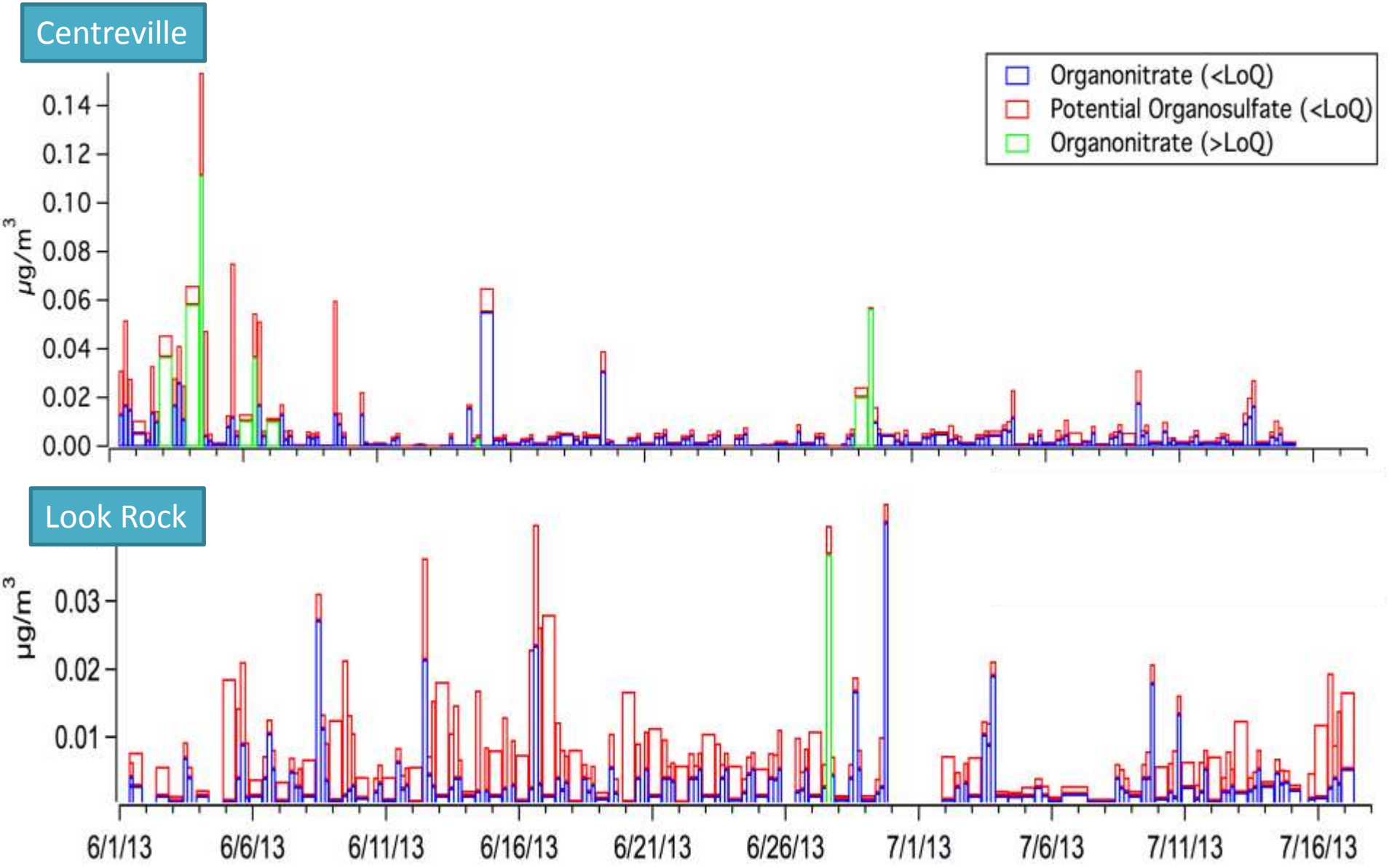
FTIR Bio factor and Nitrate and Organonitrate

Centreville

AMS Nitrate

- Bio factor correlated with nitrate and organonitrate group.

Comparison of Centreville and Look Rock



Comparison of Centreville and Look Rock

Centreville

RESULTS REDACTED

Look Rock

Comparison of Centreville and Look Rock

Centreville

Look Rock

Summary

- OM measurements were consistent for FTIR and AMS at both sites.
- Look Rock site had substantial contributions from both anthropogenic and biogenic OM (SOA) sources, despite generally low NO_x.
- Organic functional group composition and spectral signatures of biogenic factors was similar at both Look Rock and Centreville.
- Organosulfate group was associated with FTIR and AMS biogenic factors in Look Rock but not Centreville; biogenic factors correlated to nitrate and organonitrate group at Centreville but not Look Rock.