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

Lynn Russell\textsuperscript{a}, Paul Ziemann\textsuperscript{b}, Jason Surratt\textsuperscript{c}, Jun Liu\textsuperscript{a}, Sri Hapsari Budisulistiorini\textsuperscript{c}, Megan Claflin\textsuperscript{b}, Satoshi Takahama\textsuperscript{d}, Rob Modini\textsuperscript{d}

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

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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\textsubscript{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.
• 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

Dust Events:

- 6/7/13
- 6/12/13
- 6/17/13
- 6/22/13
- 6/27/13
- 7/2/13
- 7/7/13
- 7/12/13
- 7/17/13

(a) Soil

(b) APS mass distribution

(c) SEMS mass distribution

Look Rock
Organic Mass (OM) at Look Rock

Rain

AMS OM

FTIR OM

Precipitation mm

BC µg/m³

Conc. µg/m³


XRF_Dust

Soil

ABQ_N
Estimated AMS OM Oxidation State

- Oxidation state increased gradually during the project.
• 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

- 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.
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.
• 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

- 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

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

- Sources are similar to Look Rock
- Biogenic factor
  - High carbonyl
  - Correlated with nitrate not sulfate
Bio factor correlated with nitrate and organonitrate group.
Comparison of Centreville and Look Rock

**Centreville**

**Look Rock**

The graph shows the comparison of concentrations of certain pollutants over time at Centreville and Look Rock. The x-axis represents dates from June 1, 2013, to July 16, 2013, while the y-axis indicates concentration in micrograms per cubic meter (µg/m³). The graph displays data for organonitrate (<LoQ), potential organosulfate (<LoQ), and organonitrate (>LoQ) with different colors for each category.
Comparison of Centreville and Look Rock

RESULTS REDACTED
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.