Optical Properties of Moderately Absorbing Organic and Mixed Organic/Inorganic Aerosols at Relative Humidities up to 95%

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Relative Humidity Effects on Aerosol Optical Properties

- Aerosol water uptake and aerosol size = function of aerosol chemistry and relative humidity (RH)
- Water uptake alters light scattering and light absorption
- RH effects on scattering previously characterized (RH < 90%)
- Limited understanding of RH effects on absorption
Primary Light Absorbing Organic Carbon (LAOC) Aerosols

• Emission Sources of Primary OC:
  – 91% from open and residential biomass burning (Bond et al., 2004)

• Chemical Characteristics:
  – Complex mixture of polycyclic aromatic hydrocarbons (PAHs), humic-like substances and biopolymers (Pöschl, 2003)
  – Up to 70% water soluble by mass (Chen and Bond, 2010)

• Optical Properties:
  – Weakly absorbing at visible wavelengths
  – Wavelength dependent absorption with strongest absorption towards blue\ ultraviolet
  – Few in situ measurements at multiple wavelengths and variable RH
Instrumentation challenges limit light absorption measurement as a function of RH

- **Objective 1:** Build and benchmark equipment to measure aerosol absorption and scattering as a function of RH up to 95% in a laboratory setting (presented at previous ASR meetings)
Research Motivations & Objectives

Instrumentation challenges limit light absorption measurement as a function of RH

• Objective 1: Build and benchmark equipment to measure aerosol absorption and scattering as a function of RH up to 95% in a laboratory setting (presented at previous ASR meetings)

Limited knowledge of LAOC absorption and its response to RH

• Objective 2: Measure absorption and scattering of LAOC as a function of RH and evaluate optical closure (main focus of this presentation)
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- Objective 2: Measure absorption and scattering of LAOC as a function of RH and evaluate optical closure (main focus of this presentation)

Limited understanding of optical properties as a function of RH for internal LAOC/ inorganic solute mixtures

- Objective 3: Perform closure study for LAOC mixed with inorganic solute as a function of RH (in the works)
LAOC generated by pyrolysis of wood @ 425°C and its mixtures with NaCl

- Approach Overview
- Extinction Cell
  - Extinction Dry/Wet
- Nephelometer
  - Scattering Dry/Wet
- H-TDMA
  - Growth Factor
- SMPS
  - PSD Dry
- Offline Analysis
  - Ionic Fraction

Absorption Dry/Wet
LAOC generated by pyrolysis of wood @ 425°C and its mixtures with NaCl

- Extinction Cell
  - Extinction Dry/Wet
  - Absorption Dry/Wet

- Nephelometer
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Optical (Mie) Model
Optical (Mie) Modeling Inputs

- Dry size distribution & hygroscopic size growth factors $\rightarrow$ humidified size distribution and aerosol water content

- Dry LAOC refractive index:
  - $1.57+0.017i$ (467nm), $1.57+0.01i$ (530nm), $1.57+0.002i$ (660nm)
    - $n$ from literature, $k_i$ from spectroscopy from filter extracts

- Humidified refractive index mixing models:
  - **Linear Volume Average (LVA)**: commonly used for OC, infers uniform mixture (completely soluble LAOC)
  - **Dynamic Effective Medium Approximation (DEMA)**
    - Infers non-uniform, composite media with randomly distributed insoluble inclusions of absorbing material (Chylek, 1984)
FINDINGS:

• Absorption increases by a factor of 2 at High RH ($\lambda = 467$ and $530$ nm)
• Absorption at $\lambda = 660$ nm is below detection limit of instrumentation
Optical Closure Results (1):
Linear Volume Average (LVA) RI Mixing

**FINDING: LVA predicts extinction and scattering, but not absorption**
Optical Closure Results (2):
Dynamic Effective Medium Approximation (DEMA) RI Mixing

**FINDING:** DEMA captures trends in absorption and SSA indicating that configuration of insoluble absorbing material might be responsible for absorption enhancement.
Normalized LAOC Optical Properties for Multiple Experiments ($\lambda = 467$nm)

**FINDINGS:**
- Low Variability in $f(RH)$ ext. and scat. $\Rightarrow$ particles have same hygroscopicity
- Same trend in absorption growth and SSA reduction, represented best with DEMA
Normalized LAOC Optical Properties for LAOC- NaCl Mixtures ($\lambda = 467$nm)

FINDINGS

- Observable deliquescence $\sim 76\%$ RH
- Absorption increase is in the same range as for pure LAOC

![Graphs showing the relationship between RH and optical properties](image-url)
Summary & Outlook

• LAOC absorption↑ and SSA↓ with RH↑ at the 467 and 530 nm wavelengths. (660 nm below detection limit)

• Change in LAOC absorption and SSA is currently not implemented in models

• Widely used LVA RI mixing rule is unable to catch trends in absorption and SSA with RH

• DEMA captures trends in absorption and SSA indicating that configuration of insoluble absorbing material might be responsible for absorption enhancement

• Addition of NaCl affects scattering but no specific trend (in comparison to pure LAOC) was observed for absorption
Thank you for your attention

QUESTIONS?

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  (current ASR support)
Appendix: Normalized LAOC Optical Properties for Multiple Experiments ($\lambda = 530\text{nm}$)
Appendix: Normalized LAOC Optical Properties for Multiple Experiments (\(\lambda = 660\text{nm}\))
Appendix: Methods: Aerosol Generation and Treatment

• LAOC aerosol was generated by pyrolyzing wood in an electrically-heated combustor at 425 ± 10 °C
• Flaming (formation of BC) was avoided by using nitrogen sheath flow
• Aerosol was sampled at a 10:1 dilution into a 220 L storage chamber
• After pyrolysis event (~4-6 min), chamber was disconnected from sampling system and connected to optical instrumentation
• For mixing experiments inorganic solute was atomize into diluent
Appendix: Instrumentation

• Optical Properties:
  – $b_{ep} \rightarrow$ Short path extinction cell (SPEC) $\lambda = 467, 530$ and 660 nm
  – $b_{sp} \rightarrow \lambda$ and temperature modified nephelometer
  – $b_{ap} \rightarrow$ Difference between $b_{ep}$ and $b_{sp}$

• Physical Properties:
  – $D_p \rightarrow$ SMPS (TSI)
  – $G_f(D_p) \rightarrow$ H-TDMA

• Environmental Variables
  – RH / dew point temperature $\rightarrow$ 2 RH (Vaisala), 2 Dew point (GE)
  – Temperature $\rightarrow$ 4 Thermocouples

• Offline Filter Measurements (Chemical Properties)
  – OC/EC, Ions, OC functional groups $^1H$ and $^{13}C$ NMR
Appendix: Instrumentation

From Storage Chamber (1 – 4 SLPM)

0.5μm Impactor

Diluent (Particle Free Air) (26 – 40 SLPM)

HEPA Filter

Zero Cycle Flow

BV

Aerosol Cycle Flow

Humidifier

Cooler

Extinction Cell

Modified TSI 3563 Nephelometer

Exhaust

TSI 3936 SMPS

HTDMA

TSI 3563 Nephelometer

Exhaust

BV = Ball Valve

T = Thermocouple

RH = Relative Humidity Sensor

DP = Dew Point Sensor
Appendix: Benchmarking Ammonium Sulfate → System Performance under purely Light Scattering Conditions

- Instrumentation capable of measuring optical properties up to 95% RH
- Measured data lie within uncertainty of model
- Shift in $b_{sp}$ deliquescence due to nephelometer heating of 0.5°C
Appendix PSL Results

- $\lambda = 467\text{nm}$
  - $\omega = 0.92 \pm 0.02$

- $\lambda = 530\text{nm}$
  - $\omega = 0.88 \pm 0.02$

- $\lambda = 660\text{nm}$
  - $\omega = 0.85 \pm 0.03$
Benchmarking with Nigrosin → System Capable of Measuring Absorption as a Function of RH

- $b_{ap}$ enhanced by a factor of 1.2 between 35 and 95% RH
- $b_{ap} \lambda$ dependence similar to bulk measurements
- Closure modeling → Poster Mena et al. Number: 2E8
Appendix LAOC PSD

A) Diameter Midpoint (nm)

B) Diameter Midpoint (nm)
Appendix LAOC Composition

Table 1 Composition analysis of OC aerosol generated by the pyrolysis of oak wood at 425°C. Elemental carbon (EC) and the ions of Br⁻, PO₄³⁻ and Mg²⁺ were also determined but the results were below the detection limit of the analysis.

<table>
<thead>
<tr>
<th></th>
<th>OM*</th>
<th>OM*/OC</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>K⁺</th>
<th>Na⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>97.25</td>
<td>1.68</td>
<td>0.74</td>
<td>0.28</td>
<td>0.21</td>
<td>0.07</td>
<td>0.21</td>
<td>0.87</td>
<td>0.17</td>
</tr>
<tr>
<td>Std.</td>
<td>1.13</td>
<td>0.06</td>
<td>0.23</td>
<td>0.04</td>
<td>0.20</td>
<td>0.08</td>
<td>0.15</td>
<td>0.25</td>
<td>0.06</td>
</tr>
</tbody>
</table>

*Corrected by forcing closure with mass analyzed by gravimetric analysis (OM/ OC describes the correction factor).
LAOC HTDMA Results

\[ \kappa = 0.08 \pm 0.015 \]
Appendix: LAOC NMR Results

Percentage of total $^{13}$C NMR peak area under each spectral region for methanol and water extracts of OC generated at two 300 and 425°C. Difference of contribution from two major functional groups is highlighted with green circles.
Appendix Global Relative Humidity (RH) Conditions

Observation-derived average global surface RH for the years between January 1960 and January 2011.

Image provided by NOAA-ESRL, Boulder, Colorado
Appendix: Wood combustion process

Evans and Milne, 1986
Appendix: Humidification System Details & Function

- Dry Inflow with Aerosols
- Heating Tape
- Gore-Tex® Membrane
- Circulating Water
- RH Sensor
- Humidified Outflow

Controller
Appendix: RH Sensor Performance

V1, V2 = Capacitance based Vaisala Sensors

DP1, DP2 = General Eastern Dew Point Meters (RH calculated with dry bulb temperatures)
Appendix: Modified Nephelometer Performance

- For all three wavelengths, the instruments differ less than 1.5%
Appendix: Extinction Cell and Nephelometer Sensitivity and Detection Limit

- Function of integration time
- Best sensitivity is btw. 100 and 300s integration time
- Corresponding absorption detection limits: 57.3 Mm\(^{-1}\) (467 nm), 54.5 Mm\(^{-1}\) (530 nm) and 105 Mm\(^{-1}\) (660 nm) with a signal to noise ratio is assumed to be 3
Appendix POA Sources

Total: 34 Tg/yr (2000)

- Open vegetative burning: 74%
- Residental Biofuel: 17%
- Residental Coal: 1%
- Residental Other: 0%
- Transport: Non-road: 1%
- Transport: Road: 4%
- Industry: 1%
- Electricity Generation: 0%
- Other: 2%

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