Hygroscopic and Cloud Nucleating Properties of Fresh Smoke from Biomass Burning

Picnic Rock Fire from ATS Simlab, April 2004
Motivation

• Fires in the West [Westerling et al., 2006]
• Visibility, Air Quality and Climate Effects
• Vital Importance of Aerosol Hygroscopicity
Aerosol Hygroscopicity Parameter, $\kappa$
(Petters and Kreidenweis, 2006)

<table>
<thead>
<tr>
<th>Hygroscopic growth (RH$_w$ &lt; 95%, T = 25°C)</th>
<th>HTDMA (D$<em>{wet}$ / D$</em>{dry}$)</th>
<th>GF as f(RH$_w$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCN activity (RH$_w$ &gt; 100 %, T = 25°C)</td>
<td>CCNc (DMT)</td>
<td>S$<em>c$ as f(D$</em>{dry}$)</td>
</tr>
</tbody>
</table>

Unifying parameter: $\kappa$
(relative hygroscopicity)

$\kappa$ from HTDMA

$$
\frac{1}{a_w} = 1 + \kappa \frac{V_{dry}}{V_{wet}} \quad \text{GF}^{-3}
$$

$$
\frac{RH_w}{100} = a_w \exp \left( \frac{4\sigma_{s/a} M_w}{RT \rho_w D} \right)
$$

$\kappa$ from CCN

$$
\kappa = \frac{4A^3}{27D_d^3 \ln^2 S_c}
$$

$$
A = \frac{4\sigma_{s/a} M_w}{RT \rho_w}
$$

Single parameter quantifying sub- and supersaturated hygroscopic growth
Why is This Important?
Linkages between Problems, Measurement Methods, & Research Communities

Visibility Impacts & Direct Climate Forcing by Smoke

Subsaturated Hygroscopic Growth

Cloud Condensation Nuclei

Indirect (Cloud) Climate Forcing by Smoke

[Brian Kelsen, AP]
USDA/USFS Fire Science Laboratory
Missoula, MT
Chemical Characterization Measurements in Chamber

Online Physicochemical Measurements in Adjacent Labs

Combustion of Forest Fuels in Burn Chamber

Fire Lab At Missoula Experiment (FLAME)
Experimental Setup-FLAME Prequel

- Mobile HTDMA
- Multitube Membrane Drier
- Dry Filtered Compressed Air
- CCN Counter

Re-318 Aerosol Single Tub
- Relatively Easy Onsite Measurement Validation
Experimental Procedure—Prequel to FLAME

1. Typical Biomass Fuel Samples
2. Laboratory Combustion of Fuel Samples
3. High Volume Filter Sampling of Primary Smoke PM$_{2.5}$ (quartz substrate)
4. Aqueous or Methanol Extractions of Collected Samples
5. Aerosol Generation with Aqueous or Methanol Solution
NaCl in Water and in Methanol

• No Perceptible Artifacts for Known Inorganic Aerosols in CH₃OH
Test Aerosol Critical Supersaturation from HTDMA

- Kappa plot
- Data points are literature values from Kreidenweis et al. (2005)
- Equivalent results for water and methanol solutions

\( \kappa \approx 0.6 \) for \((\text{NH}_4)_2\text{SO}_4\)

\( \kappa \approx 1.2 \) for \(\text{NaCl}\)
GF Summary for Aerosol Extraction Experiments

- Strong gradient in hygroscopicity for fuels-solvent matrix
Hygroscopic Parameter vs. RH

- Sagebrush in Water
- Duff Core in Water
- Sagebrush in Methanol
- Duff Core in Methanol

Hygroscopic Parameter vs. RH

Water activity, $a_w$
0.05 < $\kappa$ < 0.3 for smoke extractions
Summary of Extraction Experiments
HTDMA and CCN Hygroscopicity

HTDMA-derived $\kappa$

CCN-measured $\kappa$

- Sagebrush in Methanol
- Sagebrush in Water
- Duff Core in Methanol
- Duff Core in Water
• Some fresh smokes really like water

• Most grouped near typical values for Yosemite aged smoke+SOA mixture
• Larger particles were ‘fluffier’ soot agglomerates

• Collapsing of agglomerates into more spherical particles at higher RH
Chamise: “Dry” Particle

Dry Chamise Smoke

≈175 monomers

Each of Diameter 30 nm.

500 nm

333 nm

S4700-3812 5.0kV 3.4mm x90.0k SE(U) 6/8/06

Courtesy of R. Chakrabarty and P. Arnott
Chamise: “Wet” Particle

Close up, Chamise smoke particle after humidity in excess of 80%. Diameter \( \approx \) 300 nm.

S4700-3818 5.0kV 3.3mm x200k SE(U) 6/8/06

150nm

Courtesy of R. Chakrabarty and P. Arnott
Fresh Diesel Emissions Water (non) Uptake

9 November 2006

- No growth & no shrinkage due to cluster collapse for fresh diesel emissions

- Role of small quantities of organic/inorganic constituents on soot clusters for growth
FLAME 2006: Hygroscopicity as Function of Composition

- Similar to relationship for Yosemite 2002 smoke+SOA aerosol
• Visibility-relevant vs. CCN-active particles can have substantially different hygroscopic properties
Missoula Comparison of derived $\kappa$’s

- Effects of aerosol mixing or very low solubility compounds on water uptake properties?

Suggests some soluble mass remains undissolved at RH < 95%

- Most-hygroscopic biomass (wax myrtle, palmetto, rice straw)
- Diesel Soot ($k \sim 0.001$)
- Ammonium sulfate
Summary

• Based on $\kappa$, consistent hygroscopic growth properties for inorganic aerosols

• Consistent hygroscopic growth properties for extractions from FLAME Prequel

• For FLAME 2006, CCN measurements give larger $\kappa$ for low hygroscopicity cases
Acknowledgments

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Absorption as a Function of RH (courtesy of P. Arnott)
Affect of Aerosol Aging on Organic Hygroscopicity
(Petters et al., 2006)