Do biomass burning particles nucleate ice?

Biomass burning smoke are a large point source of aerosol

When smoke is entrained into clouds the particles function as cloud condensation and perhaps ice nuclei

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[courtesy of Hans Moosmueller]
Collaborators

- Mathews Parsons, Kip Carrico, Anthony Prenni, Paul DeMott, Sonia Kreidenweis
- Amy Sullivan (URG data, OC/EC chemical analysis)
- Gavin McMeeking (MCE and gas phase emission factors)
- Wei Min Hao, Jeff Collett, Hans Moosmüller, William Malm
- Cyle Wold and all the members of the FSL facility in Missoula

- EPA (FLAME-II main study)
- NASA ROSES A.7 (Freezing studies)
Cold clouds – ice crystals often initiate precipitation through the Bergeron process.

- Ice crystals, 20 – 5000 L^{-1}
- Supercooled liquid drops / mixed-phase

Temperature ranges:
- -56 °C
- -24 °C
- 2 °C

Cloud layers:
- 0 – 2 km
- 2 – 6 km

Types of clouds:
- strato-cumulus
- stratus
- nimbo-stratus
- cumulus
- fog

http://www.enchantedlearning.com/subjects/astronomy/planets/earth/clouds/
In the atmosphere, ice nuclei are rare (1:10^5 particles)

Amazon, wet season, Prenni et al., 2009
Aerosols nucleate ice by varied mechanisms, most depending at least on T, some on RH, chemistry, and aerosol mechanics.
Ice nucleation mechanisms, another view

$T = -35 \degree C$

$T < -35 \degree C$

All drops freeze (or evaporate)

Homogeneous freezing of hygroscopic particles $f(T, RH)$

IN active in this regime may initiate ice formation before homogeneous freezing can occur – may inhibit ice formation

$T > -35 \degree C$

Ice nuclei cause freezing by condensation-, immersion-, or contact freezing

$RH_w = 100\%$

DROPS

HAZE or DRY PARTICLES

Ice nuclei cause freezing by deposition freezing
Fire Lab at Missoula Experiment (FLAME-II): controlled burns of ~30 fuels from North America

plant images courtesy santa monica mountains trails council, bay area hiker, alberta parks and recreation, daniel kirk, food and agriculture organization of the united nations
Trace gas emissions/burn example

\[
\text{MCE} = \frac{\Delta \text{CO}_2}{\Delta \text{CO}_2 + \Delta \text{CO}}
\]
Ice nuclei were measured using the Colorado State University continuous flow diffusion counter (CFDC)

Temperature controlled walls to select processing temperature

-10 °C < T < -33°C
Measurements of ice nuclei using the CSU Continuous Flow Diffusion Chamber (CFDC)

Ammonium sulfate, $T = -30^\circ C$

Detection limit (noise) $\sim 1:100,000$

Evaporation region good to $\sim 11\%$ water supersaturation (droplets persist at higher $SS_w$)
Define ice nucleation efficiency parameter as maximum fraction frozen

- Condensation/immersion ice nuclei at -30°C
- Polydisperse aerosol (D < 1.5μm, impactor)

\[ \xi = \log_{10} \text{maximum activated fraction} \]

IN efficiency generally decreases at warmer temperatures

\[ \xi_{-30°C} \] is an upper estimate of potential IN emissions into the atmosphere (most mixed-phase clouds are warmer).
Some fuels seem to preferentially produce ice nuclei but not all the time.

80% no ice nucleation signal above detection limit

- Duff (3/4)
- Oak (2/3)
- Fir (9/11)
- Chamise (3/7)
- Sage (5/7)
- Ceanothus (1/2)
- Ponderosa Pine (11/16)
- Longleaf Pine (4/5)
- Wax Myrtle (0/2)
- Titi (0/2)
- Needlegras Rush (0/2)
- Rice Straw (0/2)
- Palmetto (0/4)
- Manzanita (0/2)
- Hickory (0/3)
- Charcoal (0/3)
- Common Reed (0/1)
- Kudzu (0/2)
- Gallberry (0/4)

There is something about sawgrass (marsh species, flaming)

- Sawgrass (4/4)
- Duff (1/4)
- Oak (1/3)
- Fir (2/11)
- Chamise (4/7)

Western chaparral species (generally flaming)

- Ceanothus (1/2)
- Ponderosa Pine (5/16)
- Longleaf Pine (1/5)

And some flaming or smoldering fuels

Free troposphere (Amazon, ICE-L, PACDEX)

Ice nucleation efficiency $\xi_{-30^\circ C}$
The ice nucleation efficiency can directly be used in fire emission inventories.

\[ EF = 5 \times 10^6 \cdot 3.4 \times 10^{15} \text{ IN m}^{-2} \]
Fire and ice: potential mechanisms for biomass burning to produce IN

<table>
<thead>
<tr>
<th>Insoluble salts</th>
<th>Specific organics</th>
<th>Metal oxides</th>
<th>Soot or EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>halides (AgI)</td>
<td>long chain alcohols, aromatics, amino acids (need to be dissolved in H$_2$O)</td>
<td>mineral dust insoluble active sites</td>
<td>active sites mesopore water</td>
</tr>
<tr>
<td>specific crystal structure</td>
<td>crystal defects</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Secondary processes</td>
<td></td>
<td>Emissions</td>
<td></td>
</tr>
<tr>
<td>- partitioning of semi-volatile organics</td>
<td></td>
<td>- aerosol number, surface area, mass</td>
<td></td>
</tr>
<tr>
<td>- heterogeneous reactions with surfaces</td>
<td></td>
<td>- aerosol composition, hygroscopicity, mixing state</td>
<td></td>
</tr>
<tr>
<td>- particle phase chemistry (e.g. oligomerization)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Combustion conditions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- combustion efficiency</td>
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<td></td>
<td></td>
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<tr>
<td>- fire radiative power</td>
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<td></td>
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<tr>
<td>- fire temperature</td>
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<td></td>
</tr>
<tr>
<td>Fuel type, fuel moisture</td>
<td></td>
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<tr>
<td>Ash fraction, composition</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Soil composition (may be lofted with fire)</td>
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</tbody>
</table>
Question: what is difference in smoke composition or combustion conditions that explain these differences?
Use statistical test to derive probability that the mean properties differ

1. Pool sample population into two groups. Identify any parameter that may be significant (composition, combustion conditions, fuel moisture, etc.) and calculate probability (P) that the means are different

<table>
<thead>
<tr>
<th>Group A</th>
<th>Group B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi_{-30^\circ C} &lt; \text{detection limit (~-6)}$</td>
<td>$\xi_{-30^\circ C} &gt; \text{detection limit}$</td>
</tr>
<tr>
<td>X samples</td>
<td>Y samples</td>
</tr>
<tr>
<td>mean$_A$ (parameter)</td>
<td>mean$_B$ (parameter)</td>
</tr>
</tbody>
</table>

2. Define significance coefficient (S)

$S = 0.87$

$S = \text{gn}(\mu - \iota)P$

**Interpretation:** There is an 87% probability that average mean of X was smaller when generating smokes that produced ice nuclei.
Smokes that nucleated ice were enriched with inorganic components. Smokes that nucleated ice were from predominantly flaming combustion. Smokes that nucleated ice were lower in organic carbon content.
Summary

1. Approximately 20% of samples emitted ice nuclei

2. IN emissions are tied to the fuel type to some degree

3. Estimates of emission factors suggest regional scale disturbance of IN budget

4. Necessary conditions for IN emissions:
   - High MCE/flaming combustion phase
   - Presence of water soluble inorganic ions
   - Low organic carbon fractions

5. Seemingly unrelated to black carbon/soot
Satellite data suggest that emission of ice nuclei from biomass burning have a regional influence.
Fuels (Pictures courtesy of Hans Moosmueller)

- Tundra Core
- Ponderosa Pine Needles
- Excelsior (Poplar Product)
- Ponderosa Pine Wood Sticks
- White Pine Needles
- Montana Grass
- Zambia Grass
- Sage Brush
- Tundra Core
Observations suggest that homogeneous nucleation depends on water activity. Molality is a poor choice for a composition variable. Data collapse on $\Delta a_w$ which is the basis of parameterization. A droplet must dilute to a critical water activity before it freezes. Koop et al. (2000)
Physical parameters of Koop et al. parameterization (4-dimensional problem)

- Nucleation rates are parameterized based on $\Delta$ water activity and droplet volume
- Temperature dependence based on freezing point depression
- Hygroscopicity ($\kappa$) relates droplet volume to effective water activity
- Kelvin effect introduces size dependence into freezing

Freezing thus depends in principle on particle temperature, relative humidity, size, and composition
The relationship between temperature, relative humidity, size, and composition for freezing

\[ \text{Freezing RH} \propto 4^{T^{1.56}} \]

\[ \Delta \ln \text{RH} / \Delta \ln \kappa = -1.8 \times 10^{-3} \]

\[ \Delta \ln \text{RH} / \Delta \ln D = -7.2 \times 10^{-3} \]

[Kreidenweis et al., 2008]
Each of the processes we looked at is more sensitive to diameter than composition ($\kappa$)

<table>
<thead>
<tr>
<th>Wet scattering</th>
<th>Cloud activation</th>
<th>Homogeneous freezing</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa D^2$ to $\kappa D^6$</td>
<td>$\kappa D^3$</td>
<td>$\kappa D^4 T^{156}$</td>
</tr>
</tbody>
</table>

In the atmosphere hygroscopicity and diameter are not independent. Processes that modify composition often also affect particle size.
- Condensation
- Coagulation
- Chemical reactions
- Emissions
The relationship between temperature, relative humidity, size, and composition for freezing

Hygroscopicity ($\kappa$)

Freezing RH $\propto T^{156}$

$\Delta \ln RH / \Delta \ln T = 0.29$

$\Delta \ln RH / \Delta \ln \kappa = -1.8 \times 10^{-3}$

$\Delta \ln RH / \Delta \ln D = -7.2 \times 10^{-3}$

[Kreidenweis et al., 2008]