Impacts of Primary Emissions and Nucleation on Global CCN

Center for Atmospheric Particle Studies (CAPS)

Peter J. Adams

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Outline

• Motivation
• Theory: Growth of ultrafine particles to CCN
• Primary Emissions
  • Organics (biomass burning)
• Nucleation
  • Sensitivity of CCN to uncertainties
• Solar cycle, ion-induced nucleation and clouds
Particle Sources

- Ultimately, all particles in atmosphere result from
- 1) Primary Emissions
  - Combustion particles
  - Sea-salt, mineral dust
  - Some may be CCN already, some may need to grow
- 2) Nucleation
  - Particle formation in atmosphere from super-saturated vapors (e.g. $\text{H}_2\text{SO}_4$)
  - Gas-to-particle process
  - *NOT* cloud nucleation (“activation”, particle to cloud droplet)
  - Original size ($\sim 1$ nm) $\Rightarrow$ must grow to be CCN
• All global models produce mass budgets (e.g. S cycle budget)
• Can we make a budget of aerosol number? Of CCN?
⇒ uncertainties are currently orders of magnitude
Questions

• What are relative contributions of primary emissions and nucleation to particle number concentration? To CCN?
• Of ultrafine emissions and nuclei, how many grow to become CCN?
• How do they grow (condensation, coagulation)?
• How important are uncertainties in primary emissions and nucleation to the indirect effect?
CCN Budget

- These values are not final answers!
- Important to understand ultrafine particles to predict CCN formation

Emissions = 84 cm\(^{-3}\) day\(^{-1}\)

Deposition = 31 cm\(^{-3}\) day\(^{-1}\)

Coagulation = 101 cm\(^{-3}\) day\(^{-1}\)

Condensation = 2.2 cm\(^{-3}\) day\(^{-1}\)

Cloud processing = 4.5 cm\(^{-3}\) day\(^{-1}\)

Emissions = 1.4 cm\(^{-3}\) day\(^{-1}\)

Deposition = 8.3 cm\(^{-3}\) day\(^{-1}\)

GEOS-Chem CTM; global average; Sulfate and sea-salt only

These values are not final answers!

Important to understand ultrafine particles to predict CCN formation
Ultrafine and CCN budgets

Ultrafine
$D_p < \sim 100 \text{ nm}$

Primary Emissions
Nucleation
Deposition
Coagulation with larger particle
Condensation
Coagulation of smaller particles

CCN
$D_p > \sim 100 \text{ nm}$

Primary Emissions
Deposition
Coagulation with larger particle
Ultrafine and CCN budgets

Ultrafine
$D_p < \sim 100 \text{ nm}$

CCN
$D_p > \sim 100 \text{ nm}$

Nucleation
Primary Emissions
Deposition
Coagulation with larger particle

Coagulation of smaller particles
Condensation

Coagulation with larger particle
Deposition
Primary Emissions

VS.
## Timescale analysis

### INPUTS
- Temperature
- Pressure
- RH
- Existing aerosol size distribution
- H$_2$SO$_4$ vapor concentration

### TIMESCALES

#### Condensation growth

\[ \tau_c = \frac{m_k RT}{2\pi D_{p,k} D_i M_i f(Kn_k) P_{H_2SO_4}} \]

#### Coagulation growth

\[ \tau_{g,\text{coag}} = \frac{1}{\sum_{j=1}^{k-1} 2^{j-k} K_j N_j + \frac{1}{2} K_{k,k} N_k} \]

#### Coagulation loss

\[ \tau_{l,\text{coag}} = \frac{1}{\frac{1}{2} K_{k,k} N_k + \sum_{j=k+1}^{k_{\text{max}}} K_{j,k} N_j} \]

### GROWTH AND LOSS

#### Net Growth

#### Net Loss

### PROBABILITY OF GROWTH

\[ \Pr_{k,k+1} = \exp\left(-\frac{\tau_{g,k}}{\tau_{l,k}}\right) \]

\[ \Pr_{m,n} = \prod_{k=m}^{n-1} \Pr_{k,k+1} \]
Probability of CCN Formation
Fraction of 30 nm particles that grow to be 90 nm (JJA)

Based on GISS/TOMAS output

Varies from 1% to 90%

Dominant growth: condensation

Dominant loss: coagulation
Uncertainty from Size of Primary Emissions

• Most aerosol modeling has been done for air pollution regulation (PM mass)
• Mass of emissions better known than number/size of particles
• CCN microphysical models need to determine what size to emit particles
• Example: Uncertain sizes for auto emissions
  • Peak 20 nm – 40 nm
Uncertainty from size of primary emissions

Which emissions will form more CCN?
- A few large particles?
- Many small particles?
Uncertainty from emissions

Conditions:
1. T = 273 K
2. P = 1 atm
3. RH = 80%
4. Background aerosol typical of clean marine conditions

Fast growth rates:
Smaller particles make more CCN

Slow growth rates:
Larger particles make more CCN

CCN generated per kg emissions

$H_2SO_4$ vapor concentration
(Condensational growth rate)
Model details

- **3D atmospheric model**: GISS GCM II-prime global climate model
  - 4x5° horizontal resolution, 9 vertical layers

- **Aerosol microphysics**: TwO-Moment Aerosol Sectional (TOMAS)
  - Aerosol sizes: 10 nm – 10 µm
  - Condensation, coagulation, nucleation

- **Species**: Sulfate, sea-salt, EC, OM, dust

- **Other processes**
  - Emissions (size-resolved)
  - Chemistry: sulfur chemistry, carbonaceous aging
  - Cloud processing: oxidation of SO$_2$
  - Size-resolved dry / wet deposition
TOMAS Overview

- TwO-Moment Aerosol Sectional algorithm
  - Moments = 1) aerosol number and 2) aerosol mass
  - Average particle size within section not constant
  - Size range usually 10 nm – 10 μm
  - 30 bins segregated by dry mass per particle
  - Sometimes extended down to 1 nm (nucleation mode)
Comparison to observations: total particle number
Test simulations

- GISS GCM / TOMAS
- Sulfate, sea salt, carbonaceous aerosol
- Biomass burning aerosol

1. Simulation 1: Emissions centered at 30 nm

2. Simulation 2: Emissions centered at 100 nm

![Graph showing emissions vs. diameter](image)
Biomass organic carbon emissions [Gg yr\(^{-1}\)]
Global CCN concentrations are sensitive to size of biomass burning emissions.
Nucleation Introduction

Saturated sulfuric acid vapor

When enough surface is present gas can condense

Very high concentrations of gas because not enough surface to condense to... Nucleation!
Nucleation and CCN

- Nucleation chemistry not understood
- Several proposed nucleation mechanisms
  - Binary (H$_2$SO$_4$-H$_2$O)
  - Ternary (H$_2$SO$_4$-NH$_3$-H$_2$O)
  - Ion-induced nucleation (also involves H$_2$SO$_4$)
- Nucleation rates vary by more than $10^6$
- How does this nucleation uncertainty affect CCN?
- How does this compare to the effect of primary emissions uncertainty on CCN?
Nucleation Observations

Time of Day

Particle Diameter (nm)

“Banana Plot”
Nucleation in Pittsburgh

- Previously thought that nucleation occurs only in clean environments
- Aerosol size distribution measured for >1 year as part of Pittsburgh Air Quality Study (PAQS)
- Pittsburgh is not a clean environment
- Nucleation observed on 1/3 of all days
- Most frequent in spring and fall
Nucleation Mechanisms: Box Modeling

<table>
<thead>
<tr>
<th>Nucleation Parameterization</th>
<th>Days Predicted Correctly</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ternary (Napari)</td>
<td>10/10</td>
</tr>
<tr>
<td>Binary (Russell)</td>
<td>6/10</td>
</tr>
<tr>
<td>Binary (Vehkamaki)</td>
<td>6/10</td>
</tr>
<tr>
<td>Empirical, 1st-order (Spracklen)</td>
<td>7/10</td>
</tr>
<tr>
<td>Barrierless (Clement)</td>
<td>5/10</td>
</tr>
<tr>
<td>Ion-induced (Modgil)</td>
<td>6/10</td>
</tr>
</tbody>
</table>
Global nucleation

- **Objective**
  - How does uncertainty in nucleation rates affect CCN?
- **GISS GCM / TOMAS**
- Sulfate, sea salt, carbonaceous aerosol
- **2 simulations**
  1. Moderate nucleation rate: Binary (Vehkamaki, 2002)
  2. Very high nucleation rate: Ternary (Napari, 2002)
**H$_2$SO$_4$ Pseudo-Steady State Approximation (PSSA)**

- Mass balance on H$_2$SO$_4$
  \[
  \frac{d[H_2SO_4]}{dt} = P_{H_2SO_4} - CS \cdot [H_2SO_4] - J_{nuc} \cdot M_{nuc}
  \]

  - Gas-phase production
  - Condensation
  - Nucleation

- Concentration of H$_2$SO$_4$ does not change quickly

- Make pseudo-steady state approximation (PSSA)
  \[
  0 \approx P_{H_2SO_4} - CS \cdot [H_2SO_4] - J_{nuc} \cdot M_{nuc}
  \]

- Solve for [H$_2$SO$_4$]
PSSA agrees well with full dynamic calculation

- Total number of particles with diameter > 10 nm 6 hours after start of simulation

**Speed up in box model:**
- 10-1000x for PSSA $H_2SO_4$
- 6 hours after start of simulation
Particle Formation Rates

Nucleation creates many more particles than emitted but...

They are \( \sim 1 \) nm and short-lived
Nucleation and CCN

6 orders of magnitude difference in nucleation rate globally
Different locations where nucleation is occurring

CCN0.2% increases ~10%
increases ~2x
CCN(0.2%) increase from ternary nucleation

No regional CCN increase > 25%

10% average global CCN increase

CCN ratio =

CCN(0.2%) relatively insensitive to large changes in nucleation rate
Sensitivity of CCN near surface

\[ \text{Ratio} = \frac{CCN_{\text{ternary}}}{CCN_{\text{binary}}} \]

baseemiternarynuc/baseemisbinarynuc = 1.11 avg

avg. = 11% increase
Sensitivity of CCN to nucleation and primary emissions

- Anthropogenic primary emissions
  \[ \frac{\% \Delta CCN(0.2\%) \text{}}{\% \Delta PE} = 0.18 < 1 \]

- Nucleation (binary nucleation case)
  \[ \frac{\% \Delta CCN(0.2\%) \text{}}{\% \Delta Nuc} = 0.008 << 1 \]

- Nucleation (ternary nucleation case)
  \[ \frac{\% \Delta CCN(0.2\%) \text{}}{\% \Delta Nuc} = 0.002 << 1 \]
Sensitivity of CCN near surface

- Sensitivity of CCN to nucleation: avg. = 11% increase
- Sensitivity of CCN to emissions: avg. = 27% increase

- Results subject to choice of “bounding values”
- Compare to observations to rule out unreasonable conditions
Uncertainty in cloud albedo

- Simple model of cloud albedo (Seinfeld and Pandis, 1998)
  - Low-level stratus
  - Spatial coverage: 30%
  - Base fractional albedo: 0.5
- Nucleation:
  - \(~0.2\ \text{W m}^{-2}\) uncertainty in current cloud albedo forcing
- Primary emissions
  - \(~0.5\ \text{W m}^{-2}\) uncertainty in current cloud albedo forcing
- Compare to \(1.5\ \text{W m}^{-2}\) uncertainty in the cloud albedo change since pre-industrial time
CCN, Clouds, and Solar Cycle

- The sun undergoes a 11-year cycle
- Effects solar irradiance, sunspots, and cosmic rays
- Numerous climate phenomenon observed to correlate with this cycle
- First noted by William Herschel in 1801
  - Price of wheat vs number of sunspots
- Cosmic rays are one source of atmospheric ions
Cosmic rays and global temperature

Carslaw et al., Science, 2002
Hypothesis: Solar Cycle and Nucleation

Solar irradiance ↓  
Cosmic rays ↑  

Ion-induced nucleation ↑  

Aerosol particles and CCN ↑  

Cloud droplets ↑  

Cloud brightness / cover ↑  

Global temperature ↓
Usoskin and Kovaltsov, JGR, 2006
Cosmic rays, new particle formation and CCN

• Experiment 1: Modgil
  • Modgil (2005) parameterization for ion-induced nucleation
    • Simulation 1: Low solar activity (~1986)
    • Simulation 2: High solar activity (~1990)

• Experiment 2: Ion limit
  • All ions nucleate new particle
    • Simulation 1: Low solar activity (~1986)
    • Simulation 2: High solar activity (~1990)
Previous nucleation rates

Binary nuc rate [cm$^{-3}$ s$^{-1}$]

Ternary nuc rate [cm$^{-3}$ s$^{-1}$]
Ion nucleation rates (solar max)

- Binary nuc rate [cm$^{-3}$ s$^{-1}$]
- Modgil ion nuc rate [cm$^{-3}$ s$^{-1}$]
- Ternary nuc rate [cm$^{-3}$ s$^{-1}$]
- Ion limit nuc rate [cm$^{-3}$ s$^{-1}$]
Variability in ion nucleation with solar activity

- Binary nuc rate [cm$^{-3}$ s$^{-1}$]
- Ternary nuc rate [cm$^{-3}$ s$^{-1}$]
- Modgil ion nuc rate [cm$^{-3}$ s$^{-1}$]
- Ion limit nuc rate [cm$^{-3}$ s$^{-1}$]
- Nuc(solar min)/Nuc(solar max)

Pressure [mb] vs Latitude
Modgil nucleation: Solar effect on CCN

Global average variability in CCN 0.04%

Global average variability in cloud brightness ~0.002 W m\(^{-2}\)
Ion nucleation limit: Solar affect on CCN

Global average variability in CCN 0.05%

Global average variability in cloud brightness ~0.002 W m\(^{-2}\)
Conclusions

• Ultrafine particles grow to become CCN and alter cloud properties
• CCN sensitive to direct particle emission size and rate
  • ~0.5 W m\(^{-2}\)
• CCN is less sensitive to the nucleation rate
  • ~0.2 W m\(^{-2}\)
• Ion-induced nucleation and CCN formation *not* able to explain apparent correlation of low clouds with solar cycle