Experimental study of the production of PM2.5 in Southeast Texas clouds

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Secondary PM formation pathways

\[
\text{SO}_2 + \text{OH} \cdot \ldots \rightarrow \text{H}_2\text{SO}_4
\]

\[
\text{VOC} + \text{OH} \cdot \ldots \rightarrow \text{SOA}
\] (secondary organic aerosol)

\[
\sim 80\% \text{ SO}_2 \rightarrow \text{SO}_4 \ (\text{e.g., Barth et al., 2000})
\]

\[
?\% \text{ VOC} \rightarrow \text{SOA}
\]
Frequent cumulus field in SE Texas

Terra MODIS image from 8/5/14
Evidence of aqueous sulfate and SOA production

Significant, but uncertain, in-cloud production of SOA

Global modeling of SOA: the use of different mechanisms for aqueous-phase formation

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Received: 2 November 2013 – Published in Atmos. Chem. Phys. Discuss.: 12 November 2013
Revised: 11 April 2014 – Accepted: 17 April 2014 – Published: 4 June 2014

Abstract. There is growing interest in the formation of secondary organic aerosol (SOA) through condensed aqueous-phase reactions. In this study, we use a global model (IMPACT) to investigate the potential formation of SOA in the aqueous phase. We compare results from several multiphase process schemes with detailed aqueous-phase reactions to schemes that use a first-order gas-to-particle formation rate based on uptake coefficients. The predicted net global SOA production rate in cloud water ranges from 13.1 Tg yr⁻¹ to 46.8 Tg yr⁻¹, while that in aerosol water ranges from −0.4 Tg yr⁻¹ to 12.6 Tg yr⁻¹. The predicted global burden of SOA has a slightly higher O/C ratio than the observed SOA for all cases.

1 Introduction

Secondary organic aerosol (SOA) has been shown to be an important component of non-refractory submicron aerosol in the atmosphere (Zhang et al., 2007; Jimenez et al., 2009). SOA is known to form from the gas–particle partitioning of gas-phase organic...
Laboratory studies of in-cloud production

Caffrey, P., et al. (2001), In-cloud oxidation of SO$_2$ by O$_3$ and H$_2$O$_2$: Cloud chamber measurements and modeling of particle growth, J. Geophys. Res., 106(D21), 27587–27601,
1st generation captive aerosol chambers
2nd generation captive aerosol chambers
Formation of boundary layer clouds
Cloud cycle T and P profiles

Temperature (°C) profile:
- T ranges from 16°C to 26°C over time.

Pressure (mbar) profile:
- P ranges from 750 mbar to 60 mbar over time.

Time (min):
- The time ranges from 0 min to 60 min.

The graph shows a decrease in both temperature and pressure over the initial 30 minutes, followed by an increase back to the original values over the next 30 minutes.
Captive Aerosol Growth and Evolution (CAGE) chambers
CAGE chamber design
Controlled pressures within chamber layers

$\Delta p \sim 20 - 400 \text{ mbar}$  $\Delta p \sim 1 \text{ mbar}$
Controlled temperature within chamber
Chamber and platform rotation
Rotating drum technique developed for bioaerosol research

B. Asgharian & O. R. Moss (1992): Particle Suspension in a Rotating Drum Chamber When the Influence of Gravity and Rotation are Both Significant, Aerosol Science and Technology, 17:4, 263-277
Experimental procedure

1. Flush chambers with zero, prescribed composition, ambient, or ambient + perturbation flow

2. Inject one or more monodisperse particle population sizes

3. Allow gas phase photochemistry to produce representative distribution of soluble species

4. Form cloud by simultaneously decreasing chamber pressure and circulation flow temperature

5. Dissipate cloud and evaporate droplets by simultaneously increasing chamber pressure and circulation flow temperature

6. Measure resulting change in particle size, hygroscopicity, and volatility with SMPS and TDMA
To date:

- Improving software control and automation (mostly me)
- Improving chamber design and operation (mostly grad students)

To follow:

- First set of experiments to begin in coming days
Improving software control and automation

Control:

- 18 flow rates;
- 14 temperatures;
- 8 pressures;
- 5 humidities

Using:

- 46 electrically-actuated control, on/off, and 3-way valves;
- 26 vacuum pumps, water pumps, and blowers;
- 11 heaters and a variable temperature chiller system;
- 12 data acquisition cards
Improving software control and automation
Pressure control during cloud cycle

Previously

Previously, the system showed a large pressure drop with a setpoint and measured values that diverged significantly. The pressure decreased rapidly, reaching a minimum, and then increased slowly.

Now

Now, the system has been improved to show a more controlled pressure drop. The range of pressure changes is significantly reduced, with a setpoint and measured values that stay closer together. The pressure decrease is smoother, and the system recovers more quickly.

Symbols:
- Δp ~ 20 - 400 mbar (previously)
- Δp ~ 1 mbar (now)

Graphs:
- Pressure (mbar) vs. time (min)

Incorporating findings from previous studies and innovations in cloud technology, the system now maintains a more stable and predictable performance.
Improving chamber design and operation

$\Delta p \sim 20 - 400 \text{ mbar}$  $\Delta p \sim 1 \text{ mbar}$
Improving chamber design and operation

- Replaced all flange gaskets
- Redesigned seals around the 3 FEP Teflon cylinders
- Built high concentration O$_3$ generator
- Filled chambers with several ppm O$_3$
- “Sniffed” using O$_3$ analyzer
Improving chamber design and operation

- Filled chamber with even higher concentration of ozone for ~day
- Sampled air from various locations in the chambers and supporting systems using a proton transfer reaction mass spectrometer (PTR-MS)
- Constructed a Potential Aerosol Mass system (e.g., Kang et al., 2007) and again sampled air from various locations.
Improving chamber design and operation

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- Constructed a Potential Aerosol Mass system (e.g., Kang et al., 2007) and again sampled air from various locations.
  - Identified the catalytic converter used in the zero air generation system as a significant source. It has since been removed.
Planned experiments

\[
\frac{\Delta m_p}{\Delta x} \quad \text{Ambient baseline}
\]

or

\[
\frac{\Delta m_p}{\Delta x} \quad \text{Prescribed baseline}
\]

<table>
<thead>
<tr>
<th>Perturbation (x)</th>
<th>( \Delta )</th>
<th>S</th>
<th>OC</th>
<th>Motivation / comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Trace gas perturbations</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia, NH(_3)</td>
<td>2 ppb</td>
<td>•</td>
<td></td>
<td>As a base, NH(_3) increases droplet pH, which increases the conversion rate due to ozone and dissolved metals.</td>
</tr>
<tr>
<td>Amines, e.g., C(_2)H(_N)</td>
<td>0.5 ppb</td>
<td>•</td>
<td></td>
<td>Amines are another important base, and may increase in concentration with increasing carbon capture and sequestration projects.</td>
</tr>
<tr>
<td>Nitrogen oxides, NO(_x)</td>
<td>2 ppb</td>
<td>•</td>
<td>•</td>
<td>NO(_x) concentration alters many reaction pathways and may increase droplet acidity as it is converted to highly soluble nitric acid, HNO(_3)</td>
</tr>
<tr>
<td>Ozone, O(_3)</td>
<td>20 ppb</td>
<td>•</td>
<td>•</td>
<td>O(_3) is an important aqueous phase oxidant for conversion of sulfur species.</td>
</tr>
<tr>
<td>Hydrogen peroxide, H(_2)O(_2)</td>
<td>1 ppb</td>
<td>•</td>
<td></td>
<td>Same as for O(_3).</td>
</tr>
<tr>
<td>Monoterpenes, e.g., (\beta)-pinene</td>
<td>5 ppb</td>
<td>•</td>
<td></td>
<td>Wang et al. (2011) showed that biogenic secondary organic particle mass produces H(_2)O(_2), which can then contribute to SO(_2) conversion</td>
</tr>
<tr>
<td>Diluted ambient</td>
<td>20%–80%</td>
<td>•</td>
<td>•</td>
<td>Mixing ambient and zero air to determine how linear the conversion rate is with trace gas concentration</td>
</tr>
<tr>
<td><strong>Particle composition perturbations</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal content, e.g., Fe, Cu</td>
<td>•</td>
<td></td>
<td></td>
<td>Metals can catalyze the oxidation of sulfur species and can increase concentrations of several aqueous phase oxidants</td>
</tr>
<tr>
<td>Ambient vs. single component</td>
<td>•</td>
<td>•</td>
<td></td>
<td>Tests whether there are species present in ambient particles that for unknown reasons enhance conversion rates.</td>
</tr>
<tr>
<td>Number concentration</td>
<td>•</td>
<td>•</td>
<td></td>
<td>Tests whether increased droplet surface area might increase production or secondary organic mass if dissolved OH reacts close to the droplet surface.</td>
</tr>
<tr>
<td><strong>Environmental perturbations</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Updraft velocity</td>
<td>•</td>
<td>•</td>
<td></td>
<td>If peak liquid water content is the same in both chambers, this will alter the time available for reactions.</td>
</tr>
<tr>
<td>Downdraft velocity</td>
<td>•</td>
<td>•</td>
<td></td>
<td>Studies such as Loeffler et al. (2006) have shown that droplet evaporation rate can influence production of organic oligomers that can remain in the particle phase.</td>
</tr>
</tbody>
</table>
First steps and next steps

To date:

- Improving software control and automation (mostly me)
- Improving chamber design and operation (mostly grad students)

To follow:

- First set of experiments to begin in coming days
Extra slides
FEP layers and pressure differentials
Common approach to minimize losses - AIDA
Common approach to minimize losses - MINS

- Open roof section (ambient)
- 1st floor cold room (≥-50°C)
- Ground floor cold room (≥-50°C)
- Basement cold room (≥-50°C)

a. 2 scroll pumps
b. Ice nucleator
c. Temperature and humidity sensor
d. Cloud probes/Instrumentation
e. Welas aerosol counter
c. Temperature and humidity sensor
f. Steam generator
d. Cloud probes/Instrumentation
Preliminary test results

Particle Diameter (µm)

Before Cloud Formation
After Cloud Formation
\[ J = -D \frac{d n_{SO_2}}{dx} = - \left( 0.13 \frac{cm^2}{s} \right) \left( \frac{2.4 \times 10^{10} cm^{-3}}{1 cm} \right) \left( \frac{mol}{6.02 \times 10^{23}} \right) \]

\[ = 5.2 \times 10^{-15} \frac{mol}{cm^2 s} = 5.2 \frac{fmol}{cm^2 s} \]

\[ J = -\mu \Delta \chi_{SO_2} = - \left( 669 \frac{fmol}{cm^2 s ppbV} \right) (1 ppbV) \]

\[ = -669 \times 10^{-15} \frac{mol}{cm^2 s} = 669 \frac{fmol}{cm^2 s} \]
AACES response time

(a.) $\tau = 37.61\text{ min}$

(b.) $\tau = 35.67\text{ min}$

(c.) $\tau = 33.23\text{ min}$

(d.) $\tau = 31.77\text{ min}$

(e.) $\tau = 26.78\text{ min}$

(f.) $\tau = 35.21\text{ min}$
AACES O3 tracking

![Graph showing O3 tracking over time with two lines representing ambient and chamber conditions.](image-url)
AACES particle retention
AACES example experiment

- Peak $D_p$ ($\mu$m):
  - 1.6
  - 1.5
  - 1.4
  - 1.3
  - 1.2

- Growth Factor at peak $D_p$:
  - 0.14
  - 0.13
  - 0.12
  - 0.11
  - 0.10
  - 0.09
  - 0.08

- Particle size growth factor

- Per particle mass:
  - 22.4
  - 22.2
  - 22.0
  - 21.8
  - 21.6
  - 21.4

- Soluble Mass (kg)
- Insoluble Mass (kg)

- Fractional day (June 21 - 22)
AACES example experiment
EFFECT OF NONPRECIPITATING CLOUDS ON THE AEROSOL SIZE DISTRIBUTION IN THE MARINE BOUNDARY LAYER

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MEASUREMENTS OF SULFATE PRODUCTION IN NATURAL CLOUDS

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Cloud and Aerosol Research Group Atmospheric Sciences Department, University of Washington, Seattle, WA 98195, U.S.A.

(First received 16 October 1981 and in final form 8 February 1982)
Aircraft studies of in-cloud sulfate production

Growth factor distributions from July 21, 2004 measured above cloud (blue line) and below cloud (black line).

Possible role of $\text{H}_2\text{O}_2$ produced in biogenic SOA?

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H}_2\text{O}_2 \text{ levels associated with secondary organic aerosols and ambient fine mode aerosols.}</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>$\text{H}_2\text{O}_2$ generation in ES3.5 per particle mass (ng $\mu$g$^{-1}$)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 h</td>
<td>20 h</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean ± S.D.</td>
<td>Median</td>
<td>N</td>
</tr>
<tr>
<td>$\alpha$-Pinene SOA</td>
<td>0.93 ± 0.36</td>
<td>0.88</td>
<td>19</td>
</tr>
<tr>
<td>$\beta$-Pinene SOA</td>
<td>2.12 ± 1.48</td>
<td>1.48</td>
<td>11</td>
</tr>
<tr>
<td>Toluene SOA$^a$</td>
<td>0.00 ± 0.00</td>
<td>0.00</td>
<td>6</td>
</tr>
<tr>
<td>Ambient fine$^b$</td>
<td>0.11–0.5</td>
<td>–</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

FEP Teflon layers and pressure differentials

\[ P_0 \sim 1000 \text{ mbar} \]

\[ P_1 \ll P_0 \Delta P: 20 \sim 400\text{mbar} \]

\[ P_2 > P_1 \Delta P \sim 1 \text{ mbar} \]

\[ P_3 > P_2 \Delta P \sim 1 \text{mbar} \]

Al rings

ePTFE membrane

FEP bag deflection due to \( \Delta P \)
Excessive settling losses in static chamber

Retention in non-rotating chamber
Only gravitational losses considered
$\Delta t = 5$ min
$\rho = 1 \text{ g/cm}^3$
Chamber rotation