Gas-Particle Partitioning to OA

Advanced Atmospheric chemistry
CHEM-5152
Prof. J.L. Jimenez

Last updated: Spring 2017

Gas-Phase vs Aerosol Compounds

- For monofunctional compounds, alkanes beyond C_{20} and acids beyond C_{3} will partition to aerosols

Goldstein & Galbally, ES&T 2007
Partitioning of a Pure Compound

- If $c < c^*$, then all in gas phase
  - $c_{gas} = c_{tot}$
- If $c > c^*$, the excess above $c^*$ in the liquid
  - $c_{gas} = c^*$
  - $c_{liq} = c_{tot} - c^*$
- E.g. H$_2$O:
  - RH < 100%, all in gas phase
  - If more H$_2$O present, then RH = 100% and excess as a liquid (cloud)

Dealing w/ Mixtures: Raoult’s Law

- The partial vapor pressure of each component of an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture.
  - $P_l = P^0_l x_l$
Graphical Illustration of Raoult’s Law

\[ P^{o}_{H_2O, SAT} \]

water saturation vapor pressure over pure liquid water surface

\[ P_{H_2O, SAT} = \chi_{H_2O} P^{o}_{H_2O, SAT} \]

water saturation vapor pressure over aqueous solution of water mixing ratio \( \chi_{H_2O} \)

An atmosphere of relative humidity \( RH \) can contain at equilibrium aqueous solution particles of water mixing ratio

\[
\chi_{H_2O} = \frac{P_{H_2O, SAT}}{P^{o}_{H_2O, SAT}} = \frac{RH}{100}
\]

Slide from Jacob (I think)

Deviations from R’s Law: Activity coeff.

• \( P_i = \gamma_i P^0_i \chi_i \)
• Q: What is the value of \( \gamma_i \) in the upper curve?
• Is \( \gamma_i \) dependent on the mixture?

Figure from https://en.wikipedia.org/wiki/Raoult%27s_law
Gas/particle partitioning Theory

Data: Fraction in particle-phase, $F_p$

$$F_p = \frac{\text{Particle}}{\text{Gas + Particle}}$$

Model: Absorptive partitioning theory using effective saturation concentration ($C^*_i$, µg m$^{-3}$)

$$F_{p,i} = \left(1 + \frac{C^*_i}{C_{OA}}\right)^{-1}$$

$$C^*_i = \frac{M_i 10^6 \xi_i P_{L,i}}{760 RT} = \frac{1}{K_p}$$

Model Inputs: $T$ (K) = Ambient temperature
$C_{OA}$ (µg m$^{-3}$) = Organic aerosol mass concentration
$P_{L,i}$ (Torr) = Vapor pressures of compound i (at T)
$\xi_i$ = Activity coefficient of compound i = 1
$M_i$ (g mol$^{-1}$) = Molecular weight of compound i

(Data: Fraction in particle-phase, $F_p$

Partitioning of an individual species vs $c^*$

Clicker Q: what is $F_p$ ($= \xi_i$) for a species with $P_{vap} = 0.1$ ppb & MW = 244 g mol$^{-1}$ when $C_{OA} = 10$ µg m$^{-3}$
A. 1%
B. 3%
C. 7%
D. 10%
E. I don’t know

The bottom line is that an individual component only ‘cares’ about the total mass of the solution compared to its saturation concentration. For example, a 1 µg m$^{-3}$ C$^*$ component will be 50-50 partitioned if there is 1 µg m$^{-3}$ total organic aerosol, no matter what its composition.)
Partitioning: Pankow Formulation

Once a multicomponent system contains enough condensable material to form aerosol, equilibrium G/P partitioning is governed by the equation for absorptive gas/liquid partitioning in a potentially nonideal system

1) \[ p_i = X_i \zeta_i p^L_{i,i} \]

2) \[ K_{p,i} = \frac{X^L_1}{X^L_2} = \frac{F_i / TSP}{A_i} = \frac{760RTf_{om}}{10^6 MW_{om} p^L_{i,i}} \]

\[ p_i \text{ (torr): the gas-phase partial pressure of species } i \]
\[ X_i: \text{ the mole fraction of } i \text{ in the particle phase} \]
\[ \zeta_i: \text{ the activity coefficient of species } i \text{ in the particle phase typically lie in the range 0.3~3} \]
\[ p^L_{i,i} \text{ (torr): the compound’s vapor pressure as a pure liquid (subcooled if necessary) at the temperature of interest} \]
\[ A_i \text{ (ng m}^{-3}\): gas phase conc. \]
\[ F_i \text{ (ng m}^{-3}\): OM phase conc. \]
\[ TSP \text{ (µg m}^{-3}\): total suspended PM conc. \]
\[ R: \text{ the ideal gas constant} \]
\[ T(K): \text{ temperature} \]
\[ f_{om}: \text{ the weight fraction of the TSP that comprises the absorbing OM phase} \]
\[ MW_{om} \text{ (g mol}^{-1}\): the number-average molecular weight of the absorbing OM phase. \]

Iterative partitioning equil. calculations

- Let’s start with 3 µg m\(^{-3}\) of reacted α-pinene
- There is no pre-existing aerosol seed
- Consider only the 2 lowest volatility bins
- Calculate the final amount of SOA formed
Kinetics of Condensation & Evaporation

\[ \text{SVOC}_g \rightarrow \text{SVOC}_p \quad \text{\( k_c \) estimated from size dist.} \]

\[ \text{SVOC}_g \leftarrow \text{SVOC}_p \quad \text{\( k_e \) ?} \]

\[ \frac{k_e}{k_c} = \frac{c^*}{c_{OA}} \quad \text{(equil., Matsunaga & Ziemann, 2010)} \]

\[ \Rightarrow k_e = k_c \frac{c^*}{c_{OA}} \]

Let’s do this in KinSim for a-pinene VBS products

- P_{0.01} and P_{10}
- When OA = 0.1 and 10 \( \mu \)g m^{-3}

Estimation of Vapor Pressures

Advanced Atmospheric chemistry
CHEM-5152
Prof. J.L. Jimenez
Effects of Functional Groups on \( P_{\text{vap}} \)

Changes to vapor pressure of an organic compound upon addition of common functional groups, based upon group-contribution method predictions of Pankow and Asher (2008)

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Structure</th>
<th>Change in vapor pressure (298 K)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ketone</td>
<td>(-\text{C} (=\text{O}))</td>
<td>0.10</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>(-\text{C} (=\text{O})\text{H})</td>
<td>0.085</td>
</tr>
<tr>
<td>Hydroxyl</td>
<td>(-\text{OH})</td>
<td>5.7 \times 10^{-3}</td>
</tr>
<tr>
<td>Hydroperoxyl</td>
<td>(-\text{OOH})</td>
<td>2.5 \times 10^{-3}</td>
</tr>
<tr>
<td>Nitrate</td>
<td>(-\text{ONO}_2)</td>
<td>6.8 \times 10^{-3}</td>
</tr>
<tr>
<td>Carboxylic acid</td>
<td>(-\text{CO}_2\text{H})</td>
<td>3.1 \times 10^{-4}</td>
</tr>
<tr>
<td>Peroxyacid</td>
<td>(-\text{C} (=\text{O})\text{OOH})</td>
<td>3.2 \times 10^{-3}</td>
</tr>
<tr>
<td>Acyl peroxynitrate</td>
<td>(-\text{C} (=\text{O})\text{NO}_2)</td>
<td>2.7 \times 10^{-3}</td>
</tr>
<tr>
<td>Extra carbon(^b)</td>
<td>(-\text{CH}_2\text{H}_2\text{NO}_2)</td>
<td>0.35(^b)</td>
</tr>
</tbody>
</table>

\(^a\)Multiplicative factor.
\(^b\)For comparison between changes in polarity (by addition of a functional group) and changes to size of the carbon skeleton. Vapor pressure also depends on carbon skeleton structure; see Pankow and Asher (2007).

SIMPOL

- E.g. for a C\(_8\) Hydroxynitrate:
  \( \log_{10} (P_{\text{vap}} \text{ (Atm)}) = 1.79 - \text{NC}^* \times 0.438 - (N_{\text{OH}} + N_{\text{NO}_2}) \times 2.23 = -9.24 \)

- Practice
  - C\(_{10}\) linear keto acid

- Pankow & Asher (2008)
  - http://www.atmos-chem-phys.net/8/2773/2008/
2D VBS for P_{vap}

- Murphy et al., 2011 & Pandis et al. 2013

The Volatility Basis Set

Advanced Atmospheric chemistry
CHEM-5152
Prof. J.L. Jimenez
Basis Set 101: Calculate % Mass Yield from $\alpha$-pinene + O$_3$ SOA when $C_{OA} = 10$ $\mu$g m$^{-3}$

- $\alpha$-pinene + O$_3$ $\rightarrow$ 0.004 $P_{0.01}$ + 0.05 $P_1$ + 0.09 $P_{10}$ + ...

$P_x =$ group of products with the same $c^*$ (many different species)

Cooling & Dilution in VBS

- (b) Cooled Fresh Emissions
  - $C_{OA} = 10$ $\mu$g m$^{-3}$

- (c) Diluted Emissions (dilution factor = 1000)
  - $C_{OA} = 2.4$ $\mu$g m$^{-3}$
Aging in the Volatility Basis Set

As VOCs go through successive oxidation steps, products become more oxygenated and less volatile, but eventually smaller and more volatile.

VBS-based SOA Mechanisms

Table 2. SOA yield scenarios using a four-product basis set with saturation concentrations of 1, 10, 100, and 1000 μg m⁻³ at 298 K.

<table>
<thead>
<tr>
<th>V-SOA precursors</th>
<th>Aerosol Yield¹</th>
<th>Aerosol Yield</th>
<th>Molecular Weight (g mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High-NOₓ Parameterization</td>
<td>Low-NOₓ Parameterization</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>ALK4</td>
<td>0.000</td>
<td>0.038</td>
<td>0.000</td>
</tr>
<tr>
<td>ALK5</td>
<td>0.000</td>
<td>0.150</td>
<td>0.000</td>
</tr>
<tr>
<td>OLE1</td>
<td>0.001</td>
<td>0.005</td>
<td>0.038</td>
</tr>
<tr>
<td>OLE2</td>
<td>0.003</td>
<td>0.026</td>
<td>0.083</td>
</tr>
<tr>
<td>ARO1</td>
<td>0.003</td>
<td>0.165</td>
<td>0.300</td>
</tr>
<tr>
<td>ARO2</td>
<td>0.002</td>
<td>0.195</td>
<td>0.300</td>
</tr>
<tr>
<td>ISOP</td>
<td>0.001</td>
<td>0.023</td>
<td>0.015</td>
</tr>
<tr>
<td>SESQ</td>
<td>0.075</td>
<td>0.150</td>
<td>0.750</td>
</tr>
<tr>
<td>TERP</td>
<td>0.012</td>
<td>0.122</td>
<td>0.201</td>
</tr>
</tbody>
</table>

¹ The SOA yields are based on an assumed density of 1.5 g cm⁻³.

- This is an example, many other sets of parameters have been proposed in the literature

- Tsimpidi et al., ACP 2010 - [http://www.atmos-chem-phys.net/10/525/2010/](http://www.atmos-chem-phys.net/10/525/2010/)
Henry’s Law

\[ \frac{[X]_{aq}}{[X]_{g}} = K_{H,298} \]

\[ H = \frac{[X]_{aq}}{p_x} \]

**FIGURE 8.1** Henry’s law applied to atmospheric system.

- Pure \( H_2O \) concentration in M (moles l\(^{-1}\))?
- \( O_3 \) aqueous concentration at 50 ppb in gas?
- \( H_2O_2 \) a.c. at 1 ppb?
- \( CO_2 \)?
- Fractions for 1 g m\(^{-3}\) liquid \( H_2O \)?

---

**Table 8.1:** Henry’s Law Coefficients (298 K) for Some Atmospheric Gases Dissolving in Liquid Water at 20 – 25°C

<table>
<thead>
<tr>
<th>Gas</th>
<th>( K_{H,298} ) (l mol(^{-1}) atm(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O_2 )</td>
<td>1.3 x 10(^{-3} )</td>
<td>Loomis, 1920</td>
</tr>
<tr>
<td>( NO )</td>
<td>1.3 x 10(^{-3} )</td>
<td>Loomis, 1920</td>
</tr>
<tr>
<td>( CH_4 )</td>
<td>1.4 x 10(^{-3} )</td>
<td>Loomis, 1920</td>
</tr>
<tr>
<td>( Cl_2 )</td>
<td>1.3 x 10(^{-9} )</td>
<td>Schwert and White, 1983</td>
</tr>
<tr>
<td>( HCl )</td>
<td>1.4 x 10(^{-9} )</td>
<td>Schwert and White, 1983</td>
</tr>
<tr>
<td>( Cl_2 )</td>
<td>1.3 x 10(^{-3} )</td>
<td>Schwert and White, 1983</td>
</tr>
<tr>
<td>( H_2SO_4 )</td>
<td>1.2 x 10(^{-3} )</td>
<td>Schwert and White, 1983</td>
</tr>
<tr>
<td>( SO_2 )</td>
<td>0.63 x 10(^{-3} )</td>
<td>Schwert and White, 1983</td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>0.63 x 10(^{-3} )</td>
<td>Schwert and White, 1983</td>
</tr>
<tr>
<td>( CH_3OH )</td>
<td>0.8 x 10(^{-3} )</td>
<td>Schwert and White, 1983</td>
</tr>
<tr>
<td>( CH_3COOH )</td>
<td>0.8 x 10(^{-3} )</td>
<td>Schwert and White, 1983</td>
</tr>
<tr>
<td>( CH_3COOCH_2 )</td>
<td>0.8 x 10(^{-3} )</td>
<td>Schwert and White, 1983</td>
</tr>
<tr>
<td>( CO )</td>
<td>0.8 x 10(^{-3} )</td>
<td>Schwert and White, 1983</td>
</tr>
<tr>
<td>( O_3 )</td>
<td>0.8 x 10(^{-3} )</td>
<td>Schwert and White, 1983</td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>0.8 x 10(^{-3} )</td>
<td>Schwert and White, 1983</td>
</tr>
</tbody>
</table>

*Adapted from Schwert, 1980a; see also Web site in Appendix IV.
**Physical solubility, excess of crystallo-solution.
***Physical solubility, excess of crystallo-solution.
Reformulating Henry’s Law

• Partitioning into an organic liquid phase:

\[ F_{p,i}^{OA} = \left( 1 + \frac{C_i^*}{C_{OA}} \right)^{-1} \]

• Partitioning into liquid water phase:

\[ F_{p,i}^w = \left( 1 + \frac{C_{w,i}}{C_w} \right)^{-1} \]

\[ C_{w,i}^* = LWC \times H_i \quad (\text{not totally sure about this one, will check}) \]


Partitioning to water vs OA

Size Distributions and Particle Loss Calculations

Atmospheric chemistry 2
CHEM-5152
Prof. J.L. Jimenez

Some slides adapted from lectures from Qi Zhang, UC-Davis

Practical Aerosol Resources

Great intro to medium book

Measurement “bible”

• For practical aerosol calculations
  – Aerosol calculator from Willeke and Baron
  – Linked on course page

Quick exercise: calculate losses of 10 nm particles in 10m meters of circular tubing under laminar flow (outer tube diameter = ¼”; flow rate = 1 lpm)
Size Distribution of Ambient Aerosols

\[ \frac{dN}{d \ln D_m} = \frac{N_i}{150} \exp\left(\frac{(\ln D_m - \ln \overline{D}_{p,i})^2}{2 \ln \sigma_{p,i}}\right) \]

- \( I \) = number of modes
- \( \overline{D}_{p,i} \) = the median diameter of mode \( i \)
- \( \sigma_{p,i} \) = geometric standard deviation of mode

\[ dN \quad d \log(D) \quad \text{molecules/m}^3 \]

\[ D_m \quad (\mu \text{m}) \]

Figure 9.8 Typical size distribution of nitrate in southern California in 1987 fitted by the sum of three log-normal distributions with peaks at 0.25, 0.7, and 4.8 \( \mu \text{m} \) (adapted from John et al., 1990).

Figure 7.12. Typical urban aerosol #, S, & V distributions. Seinfeld & Pandis

Typical PM Size Distributions in Various Atmospheres

Figure 7.13. Aerosol number distributions next to a source (freeway), for average urban, for urban influences background, and for background conditions. Seinfeld & Pandis

Seinfeld & Pandis

From Zhang

Urban Rural Remote Desert Free Troposphere Polar

Typical PM size distributions in various atmospheres.
Clicker Questions

- The number of particles in the polar atmosphere below 1 micron is:
  A. 2 cm\(^{-2}\)
  B. 2 cm\(^{-3}\)
  C. 20 cm\(^{-3}\)
  D. 2000 cm\(^{-3}\)
  E. I don’t know

- The typical volume of particles in the free troposphere below 200 nm is:
  A. 0.02 \(\mu\)m\(^3\) cm\(^{-3}\)
  B. 0.2 \(\mu\)m\(^3\) cm\(^{-3}\)
  C. 20 \(\mu\)m\(^3\) cm\(^{-3}\)
  D. 200 \(\mu\)m\(^3\) cm\(^{-3}\)
  E. I don’t know

Dry Deposition Velocity

\[ J_{da} = v_{dep} C \]

\( J_{da} \): dry deposition flux of particles (p/cm\(^2\) s\(^{-1}\))
\( v_{dep} \): “deposition velocity” (cm/s)
C: particle concentration (cm\(^{-3}\))

Clicker Q: timescale of loss of 100 nm from a 1 km boundary layer over a forest?
A. 100 s
B. 1 hr
C. 1 day
D. 1 century
E. I don’t know
Condensation

Atmospheric chemistry 2
CHEM-5152
Prof. J.L. Jimenez

Some slides adapted from lectures from Qi Zhang, UC-Davis

Condensable gaseous species e.g., H₂SO₄

Particle

Condensation

Nucleation

Evaporation

Coagulational loss

Growth

Initial nuclei (< 3 nm)

Fine particles (e.g., ~50 nm)

Gas to Particle Conversion: Condensation & Nucleation

Possible nucleation mechanisms
a) Binary nucleation (H₂SO₄ + H₂O)
b) Ternary nucleation (H₂SO₄ + NH₃ + H₂O)
c) Organic compounds nucleation
d) Ion-induced nucleation

● Nucleation
● Condensation and nucleation are competing processes.
● Nucleation dominate when PM condensational sink is low.

Adapted from Zhang, 3
Regimes of Gas – Particle Interactions

- Knudsen number: \( Kn = \frac{2\lambda}{D_p} \)
  - \( \lambda \): Mean free path: the average distance traveled by a molecule between collisions with other molecules. \( \lambda_{air} \approx 65 \text{ nm} \) (1 atm)
  - \( D_p \): Particle diameter

Three Regimes

a. The continuum regime: \( \lambda \ll D_p \)
   - ambient, \( D_p > 1.3 \mu m \)

b. The free molecular (kinetic regime): \( \lambda \gg D_p \)
   - ambient, \( D_p < 13 \text{ nm} \)

c. The transition regime: \( \lambda \approx D_p \)
   - ambient, \( 0.013 < D_p < 1.3 \mu m \)

Mass transfer processes (i.e., condensation & coagulation) are function of \( Kn \).

Condensation in Free Molecular Regime

- \( J_k \): flux of \( A(g) \) (molec. cm\(^{-3}\) s\(^{-1}\)) toward particle in free molec. regime:

  \[
  J_k = \gamma \frac{\bar{c}_A}{4} S (C_{oo} - C_s)
  \]

  - \( \bar{c}_A \): mean molecular speed of \( A \) (m/s)
  - \( S \): surface area density (\( \mu m^2 \text{ cm}^{-3} \))
  - \( \gamma \): accommodation coefficient, i.e., probability of \( A \) to stick on particle. \( 0 \leq \gamma \leq 1 \)
  - \( C_{oo} \): vapor conc. of \( A \) far from the particle
  - \( C_s \): vapor conc. of \( A \) at the particle surface

- What is \( k \) (s\(^{-1}\))?
- Why is there a \( \frac{1}{4} \)?

- Expression in molec. s\(^{-1}\) towards 1 particle:

  \[
  J_k = \pi R_p^2 \gamma c_A (C_{oo} - C_s)
  \]
Condensation in the Continuum Regime

Mass transfer of gas molecules to particles (i.e., condensation):
- \( J_c \): the total flow of \( A(g) \) (moles time\(^{-1}\)) toward 1 particle in continuum regime

\[
J_c = 4\pi R_p D_g (c_\infty - c_s)
\]

- \( R_p \): Particle radius
- \( D_g \): Diffusivity of gas \( A \)
- \( c_\infty \): Conc. of \( A \) far from the particle
- \( c_s \): Vapor phase conc. of \( A \) at the particle surface
- Ratio of free molecular to continuum fluxes:

Transition Regime Corrections

- No general solution exists from solving distribution of gas molecules
- Use flux matching to determine \( J \)

Q: when are we ok using just one of the regimes?
Transition Regime: Fuchs-Sutugin

\[ \frac{J}{J_c} = \frac{0.75 \alpha(1 + Kn)}{Kn^2 + Kn + 0.283 Kn \alpha + 0.75 \alpha} \]

\[ \frac{J_k}{J_c} = \frac{\alpha \bar{c}_A}{4 D_k} R_p \]

• See Seinfeld & Pandis – Chapter 12 for further details

How Does Condensation Affect Size Distribution?

A. It will keep the shape the same (grow all particles equally)

B. It will widen the shape (grow larger particles more)

C. It will narrow the shape (grow smaller particles more)

D. It depends on free molecular vs continuum regime

E. I don’t know
Resistor method for more complex situations

- Other effects act as resistances to mass transfer

\[
\frac{1}{\gamma_{\text{meas}}} = \frac{1}{\Gamma_{\text{diff}}} + \frac{1}{\gamma_0} = \frac{1}{\Gamma_{\text{diff}}} + \frac{1}{\alpha} + \frac{1}{\Gamma_b}
\]

- Same approach is used to calculate dry deposition

---

Davidovits et al. 1999, JPCA
http://pubs.acs.org/doi/pdf/10.1021/jp991696p

---

**Question**

- Calculate and plot the surface area distribution for the rural size distribution from Seinfeld & Pandis
- Plot the “effective surface area” distribution
  - \( \frac{dS}{d\log D_p} \times \frac{J}{J_k} \)
- Calculate \( k \) (s\(^{-1}\)) for \( \gamma = 1 \) and 0.1
How Does Condensation Affect Size Distribution?

- Condensation/Evaporation $\rightarrow D_p$ change & size dist. change shape.
- Under condensation, smaller particles grow much faster than larger ones $\rightarrow$ The size distribution becomes much narrower.

![Graph showing the evolution of a log-normal distribution](From Seinfeld and Pandis)

**Chemical Reactions in / on Particles**

- Chemistry
  - Solid aerosol provide surfaces upon which trace gases can be absorbed and then react
  - Liquid aerosols absorb gases which may then react together in solution

  e.g. $\text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$

![Diagram showing chemical reactions in/on particles](From Finlayson-Pitts and Pitts)
Wall Losses in Chambers

Atmospheric chemistry 2
CHEM-5152
Prof. J.L. Jimenez

Losses of LVOC to walls at ~1 μg m⁻³

Q: what is the ratio of aerosol / wall surface areas?
Chamber is cube with V ~ 25 m³

Krechmer et al., in prep. 2015
**Timescales of losses to chamber walls**

Reference (chamber volume)
- Kokkola 2014 (4 m$^3$)
- Matsunaga & Ziemann (8 m$^3$)
- Yeh & Ziemann 2014 (8 m$^3$)
- Zhang 2014 (25 m$^3$)
- This work (25 m$^3$)
- McMurry & Grojean (60 m$^3$)

**HW: Simulate Condensation & Wall Losses**

- Implement the a-pinene basis set in KinSim
- Oxidize 1 ppb of a-pinene with 100 ppb O$_3$ in the presence of variable amounts of seed

Fig. 1. Hourly averaged lower bound SOA yields over the course of a toluene photooxidation experiment as a function of initial ammonium sulfate seed surface area for (A) high-NO$_x$ and (B) low-NO$_x$ conditions. Symbol color indicates the SOA mass concentration and symbol size the time after lights were turned on. The filled circles are from the current experiments and the open diamonds from ref. 21. The dashed gray line and x are the end-of-experiment yields from the optimized best-fit SOM simulations.

Zhang et al., PNAS 2014