Chamber Studies at Carnegie Mellon

Lea Hildebrandt
AMS Users’ Meeting
September 5, 2008
AMS data for SOA Yield Calculations

AMS provides three separate quantities important to the SOA measurements:

1. Aerosol size distribution based on $D_{va}$
2. Total organic mass
3. Ratio of organic to sulfate (seed) mass $\frac{C_{OA}}{C_{seed}}$

Organic to sulfate ratio is the more precise (e.g. does not depend on CE)
→ Use it as the basis for estimation of net OA condensation (and volatility?)
Changing CE during experiment

CE of sulfate increases when particles become coated with organics.
Organics/Inorganics as a Measure of Growth

\[ C_{OA}(t) = \frac{C_{OA}^{\text{sus}}(t)}{C_{seed}^{\text{sus}}(t)} \cdot C_{seed}^{\text{sus}}(t = 0) \]
Internally mixed?

- Particle composition is dependent on particle size.

- Organics condense onto surface area of pre-existing ammonium sulfate particles.
Volatile of SOA

- Use Org/Inorg to calculate mass fraction remaining:

\[
\text{MFR}(T_{TD}) = \frac{C_{OA}}{C_{seed}} (T_{TD}) \div \frac{C_{OA}}{C_{seed}} (T_{bp})
\]

![Graph showing mass fraction remaining vs. thermodenuder temperature]
Calculating SOA density and CE from combined AMS/SMPS Data

Evangelia Kostenidou
Calculating SOA density and CE from combined AMS/SMPS Data

Algorithm

1. Discretize D_{va} in sections
2. Calculate ammonium sulfate mass fraction (x_{a/s}) and SOA mass fraction (x_{SOA}) at mean D_{va} using AMS data
3. Guess SOA density
4. Calculate effective density assuming volume additivity:
   \[ \rho = \left( \frac{x_{a/s}}{\rho_{a/s}} + \frac{x_{SOA}}{\rho_{SOA}} \right)^{-1} \]
5. Plot effective density vs. D_{va} for the whole D_{va} range, construct a bilinear fit: \[ \rho = e + fD_{va} \]
6. Calculate volume distribution as a function of the mobility diameter based on the AMS measurements

Repeat for different guesses of density and CE

Calculating SOA density and CE from combined AMS/SMPS Data

- Compare volume distribution calculated from AMS data to volume distribution from SMPS data.

- Define error score:

\[
Error \ Score_t = \frac{\sum_i |a_{ti} - b_{ti}|}{\sum_i |a_{ti}|}
\]

- \(a_{ti}\) = AMS volume distribution for section i at time t
- \(b_{ti}\) = SMPS volume distribution for section i at time t

- If no changes in density over the course of an experiment: take off time dependence and minimize error score for the whole experiment.

Calculating SOA density and CE from combined AMS/SMPS Data

- Contour plot of average error score for a limonene ozonolysis experiment.

Residual Analysis

Amy Sage
Previous conceptual model for primary organic aerosol

- Primary organic aerosols are assumed to be non-volatile and non-reactive
- Models
  - POA concentrations only decrease only due to dispersion and deposition
Unexplained SOA

SOA Chemical Composition?

What is the MS of this wedge?
**MS_{residual} Calculation Method**

\[ MS_{residual} = MS_t - f_{57} MS_o \]

where:

\[ f_{57} = \frac{m_{57}(t)}{m_{57}(o)} \]
$\text{MS}_{\text{residual}}$ Calculation Illustration

$f_{57} = 0.04$
MS_{residual} Calculation Illustration

\[ f_{57} = 0.10 \]
$MS_{residual}$ Calculation Illustration

$f_{57} = 0.16$
Residual Analysis Results

% Organic mass

Time from UV on (hrs)

Residual = SOA

POA
Residual Analysis Results

Residual Mass at $m/z = 44$

Woodsmoke

Andy Grieshop
Aging rapidly creates new OA

OA mass spectra becomes more oxygenated with aging

m/z 28 (CO\(^+\)) major contributor to wood smoke OA MS

$m/z$ 28 (CO$^+$) major contributor to wood smoke OA MS

![Graph showing ion rate at $m/z$ 28 (10$^6$ Hz) over time](image)

OA mass spectra time-evolution

OA mass spectra time-evolution

% Contribution to Organic Spectra

Elapsed from Lights On (hours)

Approximate O:C Ratio

O:C relation from Aiken et al. 2008
OA enhancement estimated using residual decomposition method

Residual spectrum looks similar to ambient OOA from Pittsburgh.

Volutility and O:C are linked…

Range of volatilities observed in AMS fragments

Thanks!

- Evangelia Kostenidou
- Amy Sage
- Andy Grieshop
- Neil Donahue
- Spyros Pandis
- CAPS
- Aerodyne
- AMS Users’ Community
Questions?