Role of aqueous chemistry in organic aerosols
Barbara Ervens

CSD is leading - in the fundamental process understanding of the aerosol--cloud-precipitation system
- in the area of cloud effects on organic aerosol by aqueous phase chemistry

Bateman et al., 2011

Cloud effects on organic aerosol
Global aerosol chemical composition
Submicron particles (Aerosol mass spectrometer)

- Secondary organics comprise ~50% of total particulate mass globally
- In order to predict aerosol loadings and properties, chemical formation pathways have to be understood

Adapted from Jimenez et al., 2009

<table>
<thead>
<tr>
<th>Ammonium</th>
<th>Chloride</th>
<th>Primary organics</th>
<th>Sulfate</th>
<th>Nitrate</th>
<th>Secondary organics</th>
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</table>

**Primary species:**
Directly emitted from biogenic and anthropogenic sources

**Secondary species:**
Formed by chemical reactions in the atmosphere
Secondary organic aerosol (SOA) formation

‘Traditional view’
SOA formation by condensation of gas species

Condensation on pre-existing particles

Less volatile products

Chemical reactions

SOA formation in the aqueous phase

Cloud droplet or aqueous aerosol particles

Less volatile products

Chemical reactions

Dissolved compounds

Dissolution

Water evaporation

Water-soluble products

Ervens et al., 2003; 2011

VOLATILE ORGANIC COMPOUNDS

Biogenic and anthropogenic emissions
Aqueous SOA formation: Model development

- **Laboratory studies**
- **Chemical mechanism development**
- **Process model development**

**Molecular processes**

- **Parameterization**
  - SOA mass = f(water volume, [VOC]_0,...)

**Larger scale models**
- Regional
- Global

**Model validation**
- Comparison to ambient measurements

**Global scale**

- Ervens et al., 2008; 2014b
- Rinaldi et al., 2011
- Sorooshian et al., 2006; 2013
- Waxman et al., 2013
- Wonaschuetz et al. 2012
Model validation of aqueous SOA formation

Example: Organic aerosol formation in clouds: GoMACCS, Houston, TX

Measurements

- **Sulfate** is formed in clouds; relatively well constrained in process models
- **Oxalate** can be considered a tracer for organic cloud chemistry as it does not have any other atmospheric sources
- Mass ratio $<< 1$: Oxalate formation is less efficient than sulfate formation
- Increase in ratio points to relatively slower oxalate formation as compared to sulfate

⇒ Qualitative agreement in measured and predicted trends in Oxalate/Sulfate mass ratio

 Wonaschuetz et al., 2013
Application on regional and global scale

CMAQ (Community Multiscale Air Quality) model (EPA)

- Without aqueous SOA
- With aqueous SOA

Predicted organic mass/organic carbon ratio at the surface clearly enhanced in Southeast US when aqueous SOA formation included

Lin et al., 2014

Global chemistry transport model

Global models predict enhancement of organic aerosol loading in regions of high humidity/cloudiness and organic precursors
Organic aerosol formation in clouds

Summary

• Process models can reproduce observed trends in aqueous SOA proxies at various locations

• Regional/global models suggest that in regions with high abundance of clouds and biogenic VOCs aqueous SOA formation is significant

• Large uncertainties exist in aqueous SOA parameterizations

Future work

• Extend the chemical mechanisms to more aqSOA precursors and products

• Explore sensitivities of aqSOA formation to chemical and microphysical parameters on regional and global scales

• Refine parameterizations based on more comprehensive chemical mechanisms and case studies