The Surprising Role of Semivolatile Organics in the Growth of Ultrafine Particles

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ASR Science Team Meeting, Tysons Corner, May 4, 2016
Motivation

- Aerosol particles larger than ~80 nm influence Earth’s radiation balance
- Particles smaller than ~80 nm dominate the number concentration
  - New particle formation
  - Emissions from fossil fuel combustion
- Growth is controlled by condensation of oxidation products of biogenic and anthropogenic VOCs forming secondary organic aerosol (SOA):
  - Extremely Low Volatile Organic compounds (ELVOCs): $C^* < 3 \times 10^{-4} \mu g \text{ m}^{-3}$
  - Low Volatile Organic Compounds (LVOCs): $3 \times 10^{-4} < C^* < 0.3 \mu g \text{ m}^{-3}$
  - Semivolatile Organic Compounds (SVOCs): $0.3 < C^* < 300 \mu g \text{ m}^{-3}$
Motivation

Physicochemical mechanisms governing particle growth and size distribution dynamics of SOA are still not fully understood.

Traditional view:

- Kinetic condensation of ELVOCs and LVOCs proportional to Fuch’s corrected surface area distribution \(\rightarrow\) **Favors growth of ultrafine particles.**

- Rapid gas-particle equilibrium of SVOCs (neglecting condensed-phase diffusion limitation) \(\rightarrow\) **Favors growth of large particles.**
Particle Viscosity and Diffusivity

High viscosity will slow down SVOC condensation

Song et al., 2015, ACP

Renbaum-Wolff et al., 2013, PNAS.
Chamber Experiments

- Ultrafine Seed (40 nm) Ammonium Sulfate
- VOC, $\text{H}_2\text{O}_2$

PNNL Environmental Chamber (10 m$^3$)

- T, RH
- $\text{NO}_x$, $\text{O}_3$, PTRMS

Aerosol samples for evaporation kinetics

- SMPS, BNL FIMS
- AMS UW FIGAERO-CIMS

Filter samples for nano-DESI-HRMS analysis (EMSL)

SPLAT II

Evaporation Chamber

Aerosol Composition
**Phase 1:** Make large isoprene SOA seed and inject ultrafine ammonium sulfate (AS) seed

**Phase 2:** The two seeds are grown by condensing vapors formed from photooxidation of isoprene.
Isoprene SOA Composition

SOA species mass fractions based on FIGAERO-CIMS measurements.

(+)-nano-DESI-HRMS mass spectra shows presence of oligomers in both dry and humid air SOA samples.

SVOC + SVOC $\overset{k}{\underset{k_b}{\rightleftharpoons}}$ Dimer

Assumed time scale ~10 min
Volutility from Evaporation Kinetics

**RH = 0%**

- Observed Values: 0.05, 1.0, 1.5, 1.5, 15, 30
- Models:
  - $D_b = 1.0 \times 10^{-6}$ cm$^2$ s$^{-1}$
  - $D_b = 2.0 \times 10^{-15}$ cm$^2$ s$^{-1}$

**RH = 75%**

- Observed Values: 0.05, 0.03, 0.1, 1.5, 1.5, 4, 50
- Models:
  - $D_b = 1.0 \times 10^{-6}$ cm$^2$ s$^{-1}$
  - $D_b = 3.0 \times 10^{-16}$ cm$^2$ s$^{-1}$

**Fitted C* ($\mu$g m$^{-3}$)**

- LVOC, C$_5$H$_{12}$O$_5$, C$_5$H$_{12}$O$_6$, SVOCs
- Values: 0.01, 0.1, 1, 10, 100

**Traditional Model** (negligible particle-phase diffusion)

**Diffusion-limited Model**
Modeling Growth Kinetics

Traditional Model vs. Diffusion-limited Model

RH = 0%

(a) Chamber Experiment 1
\( \square t = 60 \text{ min} \)

Traditional Model (\( D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1} \))

Diffusion-limited Model

Non-volatile Condensation Model (\( C^* = 0 \))

RH = 75%

(b) Chamber Experiment 2
\( \square t = 70 \text{ min} \)

Traditional Model (\( D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1} \))

Diffusion-limited Model

Non-volatile Condensation Model (\( C^* = 0 \))
Modeling Growth Kinetics

Large seed: aged $\alpha$-pinene SOA

(c) Chamber Experiment 3

RH = 0%

(d) Chamber Experiment 4

RH = 75%

$D_b = 2 \times 10^{-15}$

$D_b = 5 \times 10^{-15}$

$\mu t = 32$ min

$\mu t = 60$ min

$\frac{dN}{dt}$ vs. $D_{p,\text{dry}} (\text{nm})$

- Observed initial
- Observed after $\mu t$ min
- Traditional Model ($D_b = 10^{-6} \ \text{cm}^2 \ \text{s}^{-1}$)
- Diffusion-limited Model
- Non-volatile Condensation Model ($C^* = 0$)
Large variation in diffusion time scales with size has a profound effect on the SOA size distribution dynamics and the growth of ultrafine particles!

Zaveri et al., 2014, ACP.
The Big Picture

The Counterintuitive Impact of SVOCs

Traditional View
- Instantaneous gas-particle equilibrium
- Favors growth of larger particles

Our Results
- Condensed phase diffusion limitation
- Favors growth of smaller particles

Less reflective, more precipitating clouds

Stronger cloud radiative forcing

Low CCN concentration

High CCN concentration

Weak cloud radiative forcing

More reflective, longer lasting clouds

SVOCS, LVOCS, ELVOCs

Oxidation

Biogenic VOCs (isoprene, terpenes)

Emission

Vegetation

Emission, Nucleation

Background organic aerosol

Ultrafine aerosol

Condensational growth

Condensational growth

Activation

Activation

Anthropogenic activities
Conclusions & Future Work

- Aged isoprene and α-pinene SOA containing oligomers show diffusion-limited growth up to 75% RH.

- This phenomenon slows down growth of large particles, but in turn favors growth of ultrafine particles that can more effectively compete for the available SVOCs.

- This counterintuitive behavior needs to be examined at higher RH and for other SOA precursors that form SVOCs.

- Need to develop model parameterizations that capture SOA growth dynamics for all key precursors over the full RH and temperature range.
Acknowledgements

This work was supported by:

- DOE Atmospheric System Research (ASR) Program
- DOE ARM Climate Research Facility
- PNNL Environmental Molecular Sciences Laboratory (EMSL)
Carbonaceous Aerosols and Radiative Effects Study (CARES)

June 2010

Zaveri et al., 2012, ACP.
Episode of June 15

Environmental Conditions
- RH: ~40%
- T: 25 C
- Wind speed: 2-3 m/s
- Clear sky
- Isoprene: 2-3 ppbv
- Other VOCs: < detection

\[ \Delta \text{SOA} = 1.67 \, \mu \text{g m}^{-3} \text{ over 4 hours in air containing } \sim 2-3 \text{ ppbv isoprene} \]
Observed: Initial
Observed: After $t = 255$ min

Model: $D_b = 1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$
Model: $D_b = 2 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$