Semi-volatile aerosol and its effect on on aerosol optical properties during SOAS

Andrey Khlystov¹, Provat Saha², Andrew Grieshop², R. Subramanian³

¹Desert Research Institute (formerly at RTI) ²North Carolina State University ³Carnegie Mellon University





Science questions

- Gas / particle partitioning
 - Volatility basis sets (VBS)
 - Enthalpy of vaporization (dHvap)
 - Kinetics of equilibration
- SOA and optical properties
 - Secondary brown carbon and organo-N compounds
 - Lensing effect (enhanced absorption by black carbon due to coating)
 - Contribution of SOA to hygroscopic growth and light scattering

Aerosol volatility measurements



- Temperature Stepping TD with a long residence time (50 s)
- Variable residence time TD (0.7-38 s) with moderately heated activated carbon surface at constant temperature

Optical property measurements



RH and temperature conditioning:

- "Dry" line: < 10% RH
- "Intermediate" line: ~60-70% RH
- "High RH" line: > 85% RH
- Thermodenuder (TD): 180 C or scanning
- Lines are switched every 15 min

Measured parameters:

- Aerosol scattering and absorption at 405nm, 532nm, 870nm
- Single particle black carbon and coating thickness
- Particle size distribution above 70nm (only in July)



Chemical composition measurements



- SJAC
 - Major ions,TC, TN
 - ON (TN-IN)
 - 30 min
 resolution

Mass fraction remaining (MFR)



^aAn W.J., Pathak R.K., Lee B., and Pandis S.N. "Aerosol volatility measurement using an improved thermodenuder: Application to secondary organic aerosol". J Aer Sci. 2007 Mar;38(3):305–14.

^bCappa C.D., Jimenez J.L. "Quantitative estimates of the volatility of ambient organic aerosol". Atmos. Chem. Phys. 2010 Jun 21;10(12):5409–24.

MFR as a function of residence time



MFR depends on the residence time in TD

Modeling of thermodenuder results





- Evaporation coefficient likely > 0.1
- dH_{vap} = 80-130 KJ mol⁻¹
- Epstein correlation (dH_{vap}=130-11logC^{*}) does not agree with observations
- Variable residence time data provide much more constrained fit

Average VBS during SOAS



Dry scattering



Scattering during different measurement cycles



"Dry" absorption from PAX



Angstrom exponent



There are indications of brown carbon and/or lensing effect



SP-2 measurements of biomass burning event on 6/4/2013



Time (local)

Coating thickness from SP-2



Coating does not seem to evaporate at 180C

Conclusions

- Very little kinetic constraints for gas/particle equilibration
- $dHvap = 80-130 \text{ KJ mol}^{-1}$, no or little variation with C*
- Both temperature and RH have a strong effect on Bscat
- Some evidence of lensing enhancement and/or brown carbon
- Based on Angstrom exponent, very little evidence of brown carbon except for biomass burning episodes
- Preliminary analysis indicates black carbon is coated with very low volatility material (or there are issues with LEO)

Next steps

- Similar measurements this summer in Duke Forest (near RTP, NC)
- Continue data evaluation





Epstein et. al. EA Semiempirical Correlation between Enthalpy of Vaporization and Saturation Concentration for Organic Aerosolnviron. Sci. Technol. 2010, 44, 743–748

