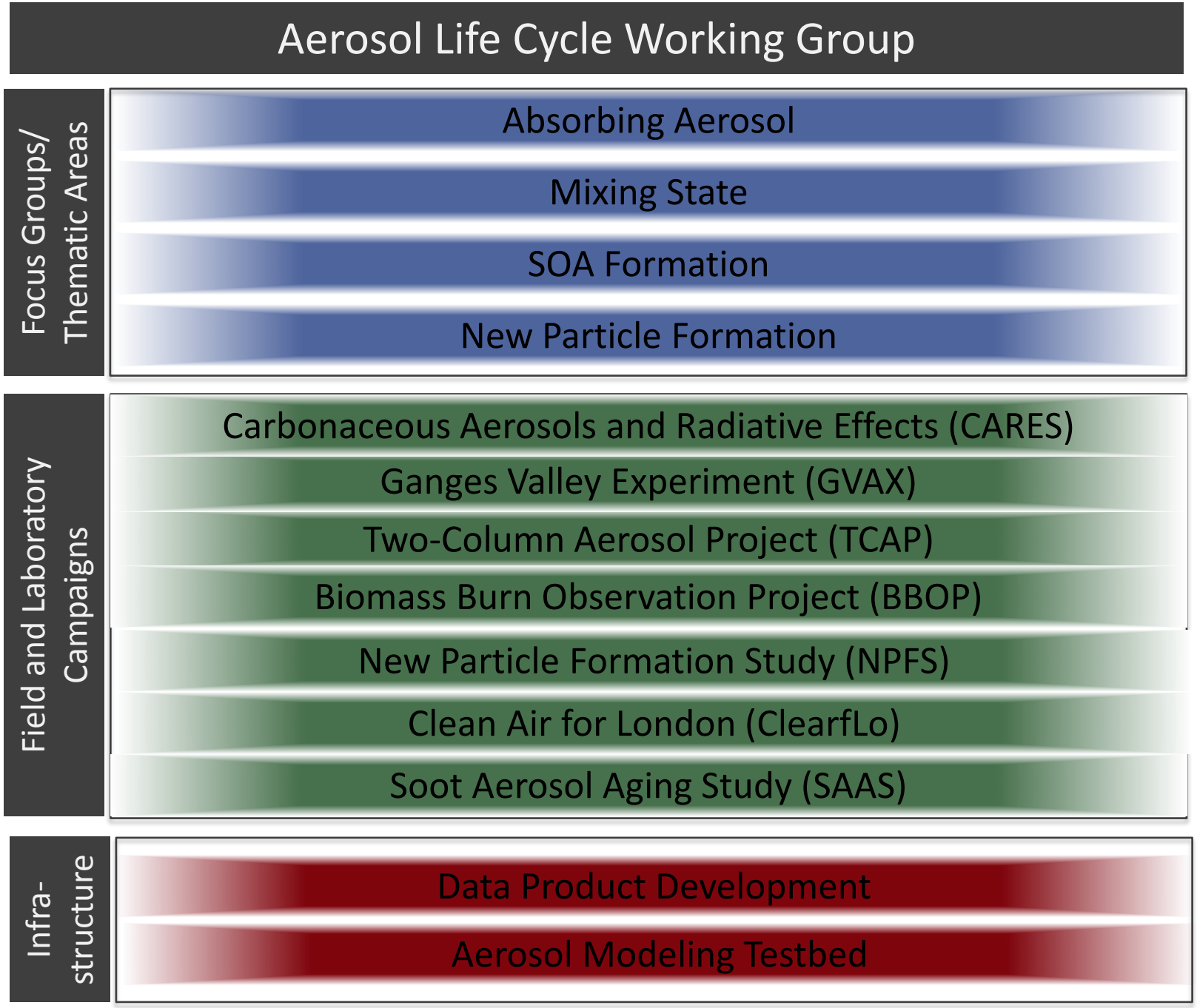
Updates from the Aerosol Life Cycle Working Group

DOE Atmospheric System Research Program

PI Meeting, March 2014


Aerosol Life Cycle Working Group
Focus Groups/ Thematic Areas
Absorbing Aerosol
Mixing State
SOA Formation
New Particle Formation
Field and Laboratory Campaigns
Carbonaceous Aerosols and Radiative Effects (CARES)
Ganges Valley Experiment (GVAX)
Two-Column Aerosol Project (TCAP)
Biomass Burn Observation Project (BBOP)
New Particle Formation Study (NPFS)
Clean Air for London (ClearfLo)
Soot Aerosol Aging Study (SAAS)
Infra-structure
Data Product Development
Aerosol Modeling Testbed

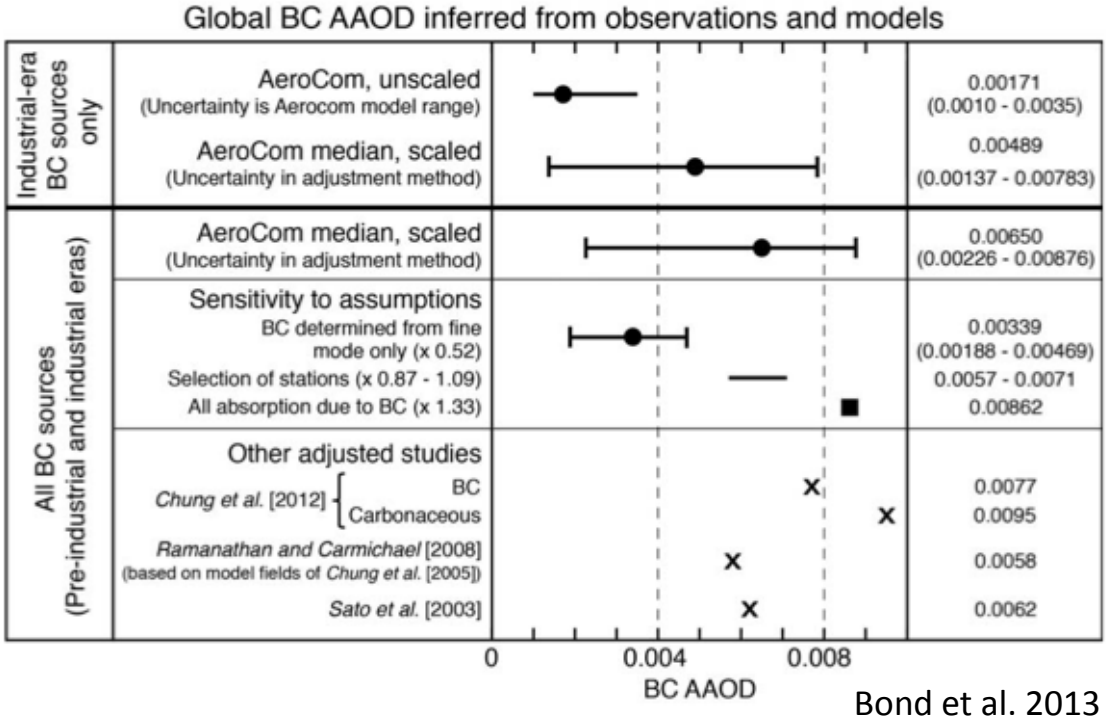
Thematic Area: Aerosol Absorption

What is it?

Critical aerosol property for modeling atmospheric radiative transfer: $\tau_{ext} = \tau_{scat} + \tau_{abs}$

Why is it important to study?

The amount of absorption in the atmospheric column and it's vertical distribution strongly influences radiative fluxes and model calculations used to estimate aerosol radiative forcing



Bond et al. 2013

How will this group contribute?

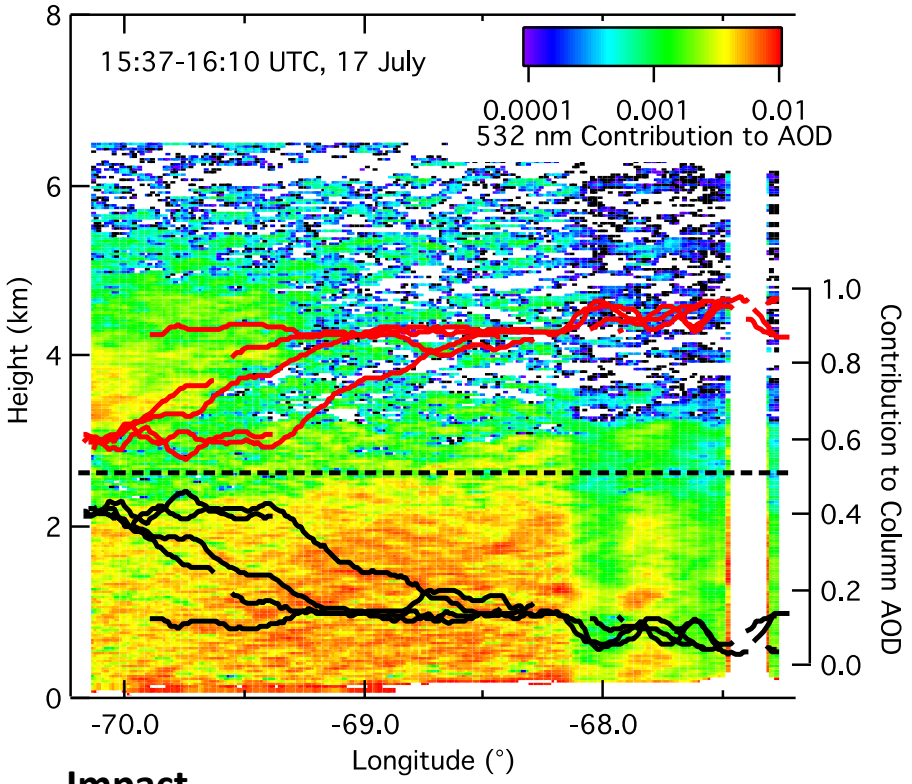
- Evaluate existing measurement approaches to absorption: in situ, passive and active remote sensing; ground-based, airborne, satellite-based
- Develop and validate new and better methods for retrieving absorption
- Characterize the spatial and temporal distribution of aerosol absorption/radiative forcing around the globe and it's relationship to aerosol chemical and physical properties

Role of Aerosol Layers: Observations from TCAP

Objective

- document the frequency and impact of elevated aerosol layers on the columnar AOD

Snapshot of contribution to column AOD (colors) derived from the HSRL-2 and contribution to the AOD (right axis) for layers from the surface to 2.64 km (black lines) and from 2.64 to 6.3 km (red lines) derived for the entire back-and-forth flight pattern.



Impact

- Elevated aerosol layers can make a significant contribution to the total AOD; similar results have been found for other days.
- The presence of layers mean that aerosol absorption is spread over a deeper layer of the atmosphere.
- In situ measurements may not be representative of the aerosol population within the atmospheric column; layers were found to have smaller SSA and more biomass burning aerosol associated with long range transport.

Berg, LK. et al. 2014. "The Two-Column Aerosol Project: Phase I Overview and Impact of Elevated Aerosol Layers on Aerosol Optical Depth", Journal of Geophysical Research, in preparation for JGR.

Initial Assessment of the Spectrometer for Sky-Scanning, Sun-Tracking Atmospheric Research (4STAR)-Based Aerosol Retrieval: Sensitivity Study

Objective

- Assess expected accuracy of the 4STAR-based aerosol retrieval and its sensitivity to major sources of anticipated perturbations in the 4STAR measurements.
- These perturbations are (1) an apparent enhancement of sky radiance at small scattering angles and (2) an offset of sky radiance calibration independent of scattering angle.

Approach

- Estimate the impact of these perturbations on the aerosol retrieval, the broadband fluxes and the direct aerosol radiative forcing.
- Apply the operational AERONET aerosol retrieval and constructed synthetic 4STAR-like data.

The 4STAR instrument (inset) is installed through the upper hull of the PNNL G-1 research aircraft, for in-flight sun-tracking and sky light-scanning.

Impact

- The new airborne instrument has the potential for obtaining the most important climate-related properties of aerosol particles suspended in the atmosphere.

Kassianov E, C Flynn, J Redemann, B Schmid, PB Russell, and A Sinyuk. 2012. "Initial Assessment of the Spectrometer for Sky-Scanning, Sun-Tracking Atmospheric Research (4STAR)-Based Aerosol Retrieval: Sensitivity Study." *Atmosphere* 3(4):495-521. DOI:10.3390/atmos3040495.

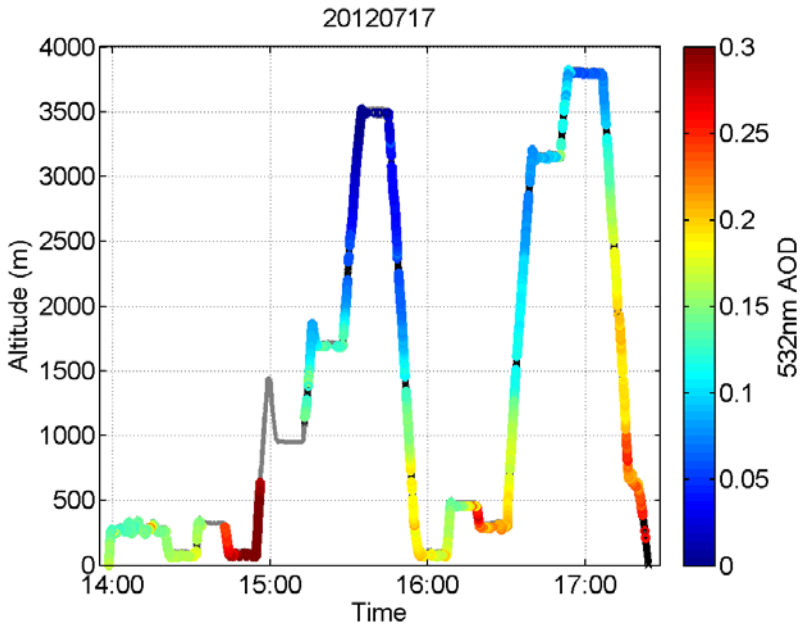
Hyperspectral aerosol optical depths from TCAP flights

Objective

- Assess aerosol optical depth observation with 4STAR

Results

- The new airborne sun-sky spectrometer demonstrated its ability to accurately measure AOD during TCAP.
- The results from both airborne (on G-1) and ground-based (at Hyannis) operations fell mostly within 0.01-0.02 of the ground-based AERONET AOD observations.
- AOD and extinction coefficients profiles determined from aircraft ascents and descents compare well with in situ and lidar observations.



Impact

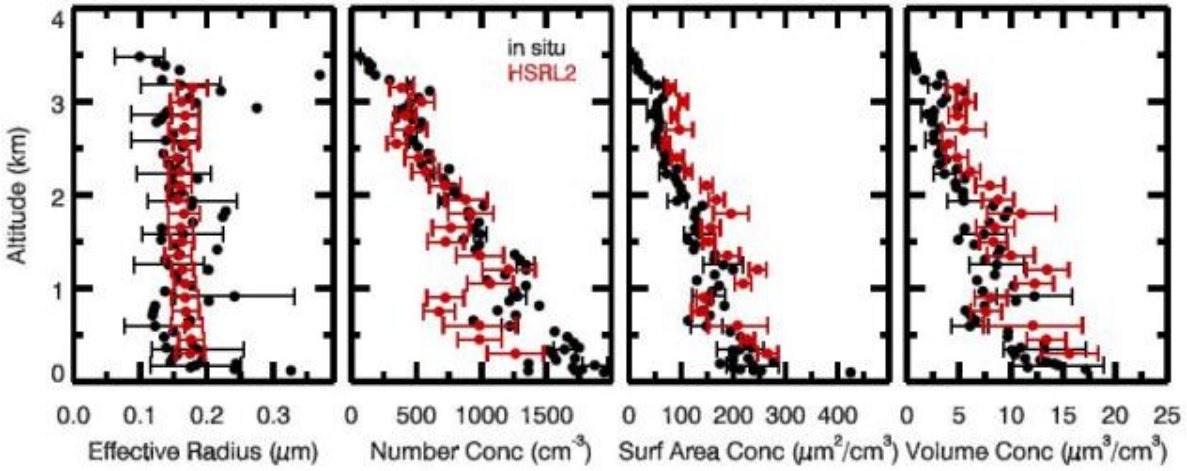
- The 4STAR measurements along the air mass transport paths from the US East Coast to the Atlantic Ocean provide valuable information for evaluation of model simulations of aerosols, among other TCAP objectives.
- The favorable intercomparisons herald 4STAR's spatially-resolved high-frequency hyperspectral products as a reliable tool for climate studies and satellite validation.

Reference: Shinozuka, Y., R. R. Johnson, C. Flynn, P. B. Russell, B. Schmid, J. Redemann, S. E. Dunagan, C. D. Kluzek, J. M. Hubbe, M. Segal-Rosenheimer, J. M. Livingston, T. F. Eck, R. Wagener, L. Gregory, D. Chand, L. K. Berg, R. R. Rogers, R. Ferrare, J. W. Hair, C. Hostetler, and S. P. Burton (2013), Hyperspectral aerosol optical depths from TCAP flights, *Journal of Geophysical Research*, 118, doi:10.1002/2013JD020596.

Aerosol microphysical particle property retrievals from multi-wavelength HSRL observations

Approach

- Compare in situ aerosol measurements acquired on the G-1 aircraft during TCAP with first-ever aerosol microphysical retrievals from an airborne multiwavelength HSRL



Key Accomplishments

- First-ever multi-wavelength HSRL measurements acquired on DOE ASR TCAP field campaign.
- First-ever full-curtain automated retrievals of aerosol microphysics from an airborne lidar.
- Automated inversion software provides reliable results for mean particle size (effective radius), and integral properties, i.e. number, surface-area, and volume concentration.

Contribution to Focus Group/Working Group Objectives

Crosscutting: This work addresses the role of lidar remote sensing in campaigns focused on aerosol process studies and radiative effects. Lidar provides vertical context throughout the column for detailed in situ observations made at aircraft-level.

Müller et al., Airborne Multiwavelength High Spectral Resolution Lidar (HSRL-2) Observations During TCAP 2012: Vertical Profiles of Optical and Microphysical Properties of a Smoke/Urban Haze Plume Over the Northeastern Coast of the US, Atmospheric Measurement Techniques, under review

Brown carbon: a significant atmospheric absorber of solar radiation?

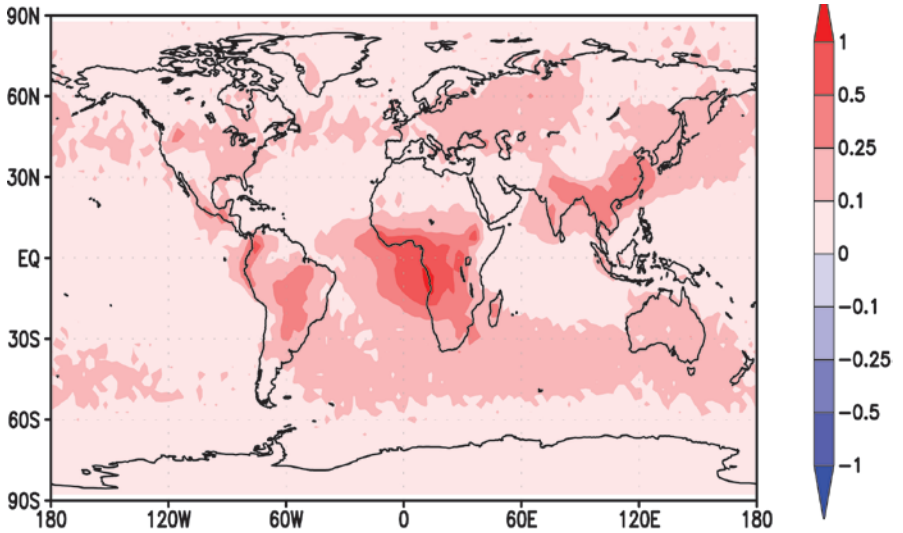
Objective

Does solar absorption by brown carbon (BrC) play a significant role in global and regional direct radiative forcing of carbonaceous aerosols?

Results

- BrC absorption results in a global TOA forcing of +0.04 to +0.11 W m^{-2}, about 10% to 25% of the black carbon (BC) forcing (+0.45 W m^{-2});
- Strongly absorbing BrC contributes to 19% of solar absorption by anthropogenic aerosols, while 72% is attributed to BC, and 9% due to non-absorbing coatings;
- Regional effect of BrC contributes up to 50% of aerosol absorption over biomass burning and bio-fuel regions;
- BrC absorption changes the TOA forcing of organic carbon aerosols from cooling (−0.08 W m^{-2}) to warming (+0.025W m^{-2}), particularly over source regions and above clouds

Figure. Annual mean all-sky TOA forcing (Wm^{-2}) by the strongly absorbing BrC relative to the non-absorbing OC



Impact

Failure to include the estimated global and regional radiative effects due to BrC absorption introduces uncertainty in simulations of clouds and photochemistry

Feng, Y., et al., Brown carbon: a significant atmospheric absorber of solar radiation? *Atmos. Chem. Phys.*, 13, 8607–8621, 2013. [submitted by ANL]

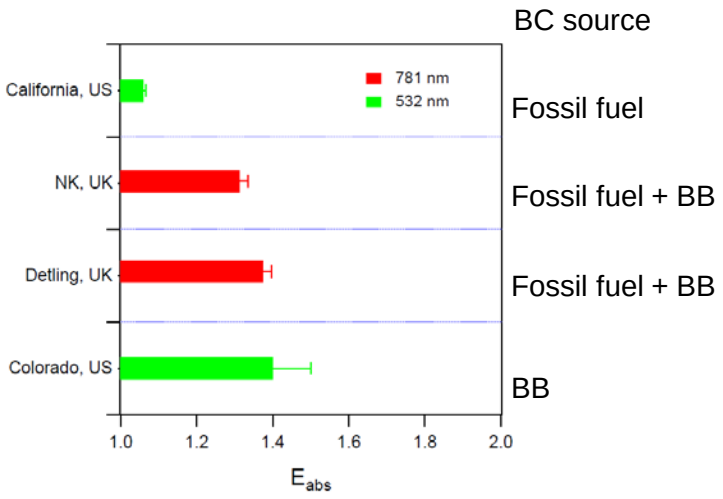
ClearfLo: Light absorption enhancement by internally mixed atmospheric black carbon in U.K.

Science Questions

- What is the absorption enhancement of BC from mixed diesel and residential wood burning sources?
- Can core-shell Mie modeling accurately predict absorption enhancement?

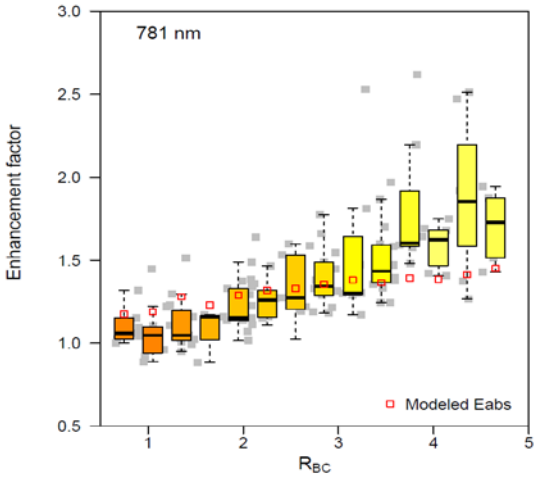
Approach

- Absorption of denuded and ambient aerosols is measured by the photoacoustic method (PASS-3)
- Observationally constrained core-shell Mie modeling is used to simulate absorption enhancement



Key Accomplishment

- First direct measurement to show substantial absorption enhancement
- Absorption enhancement increases with photochemical aging
- The predicted and observed enhancement compared reasonably well



Contribution to Focus Group/Working Group Objectives

The observed absorption enhancement supports the core-shell Mie parameterizations of light absorption enhancement by internally mixed BC in regional radiative transfer models.

ClearfLo: Light absorption enhancement by internally mixed atmospheric black carbon in U.K.

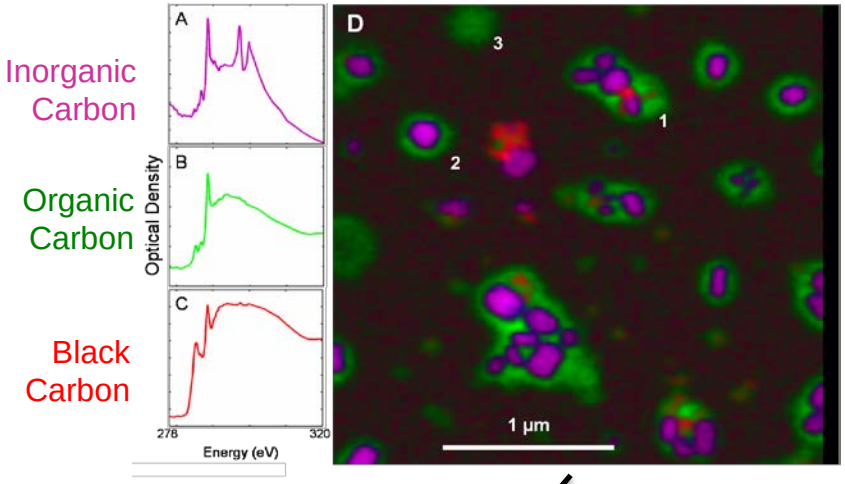
Shang Liu, Allison C. Aiken, Kyle Gorkowski, Manvendra K. Dubey* (Los Alamos National Lab), Christopher D. Cappa (UC Davis), Swarup China, Claudio Mazzoleni (Michigan Tech), Leah R. Williams, Paola Massoli, Edward Fortner, Andrew Freedman, Scott C. Herndon, Douglas R. Worsnop (Aerodyne), Lu Hu, Nga Lee Ng (Georgia Tech), Dantong Liu, James D. Allan (University of Manchester) in prep. For Nature 2014 *corresponding author Dubey

Focus Group: Mixing State

What is it?

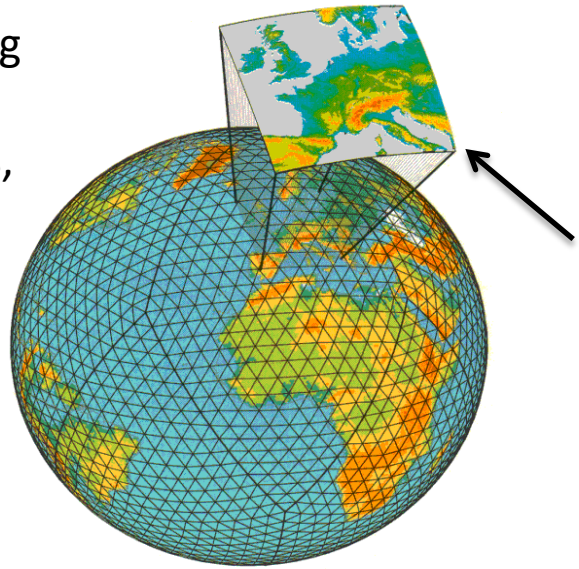
Population mixing state: the distribution of chemical compounds across the particle population

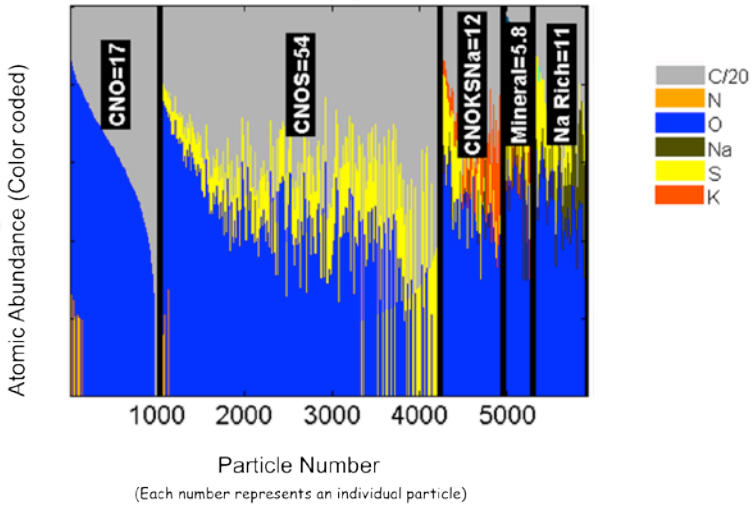
Morphological mixing state: the distribution of chemical compounds within and on the surface of each particle



Why is it important to study?

Mixing state has a strong influence on aerosol hygroscopicity, lifetimes, optical properties, and thus radiative forcing





Focus Group: Mixing State

Connections Among Different Tools – *from the Mixing State Focus Group white paper*

	Theory/ Metrics[1]	PRM[2]	GCM[3]	SP2[4]	Micros-copy[5]	SP mass spectro-metry[6]	Remote sensing[7]	Bulk measure-ments[8]
Theory/ Metrics[1]		high	low	medium	medium	low	low	low
PRM[2]	high		low	medium	low	low	low	high
GCM[3]	low	low		low	low	low	high	medium
SP2[4]	medium	medium	low		low	low	low	high
Micros-copy[5]	medium	low	low	low		low	low	medium
SP mass spetro-metry[6]	low	low	low	low	low		low	medium
Remote sensing[7]	low	low	high	low	low	low		high
Bulk measure-ments[8]	low	high	medium	high	medium	medium	high	

Table 2: Assessment of current abilities to connect data and outputs amongst different tools. The lack of comparable mixing state outputs between many tools is a key bottleneck in our ability to understand mixing state impacts.

Challenge: Lack of comparable mixing state outputs between many tools

How will this group contribute?

- Investigate the sensitivity of optical, physical, and chemical properties to mixing state using observational, process, and modeling studies at a wide range of scales
- Determine the minimum level of complexity required to represent properties in models with fidelity

Mixing State

Strikingly Different Carbonaceous Aerosol Mixing States Observed in Northern and Southern California

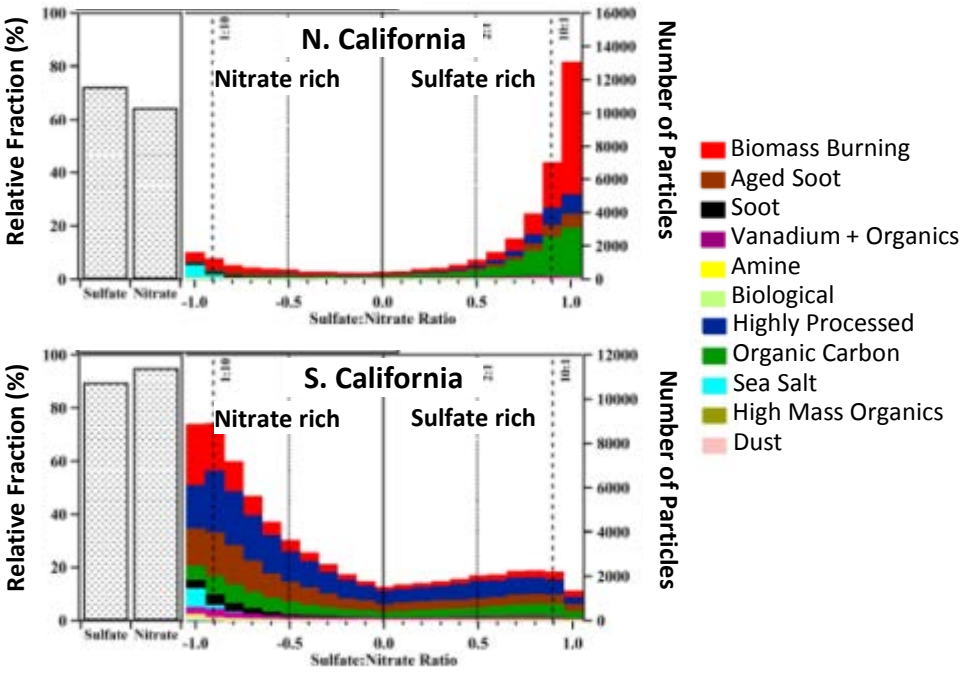
Carbonaceous aerosols play a major, but highly uncertain role in radiative forcing as their mixing state greatly influences their optical properties, hygroscopicity, and atmospheric lifetimes.

Objective

Provide insight into the distribution and mixing state of different types of carbonaceous aerosols in California.

Approach

Measure aerosol mixing state with the Aircraft Aerosol Time-of-Flight Mass Spectrometer onboard the CIRPAS Twin Otter during the **CalNex** study in southern California (May 2010) and onboard the DOE G-1 during the **CARES** campaign in northern California (June 2010).



More aerosols were mixed with nitrate in the south and sulfate in the north. Soot was more dominant in the south while organic aerosols were more prevalent in the north.

Impact

Regionally dominant carbonaceous aerosol sources and their mixing-state dependent optical and hygroscopic properties are required to obtain more accurate predictions of climate impacts of aerosols.

Cahill JF, K Suski, JH Seinfeld, RA Zaveri and KA Prather. 2012. "The mixing state of carbonaceous aerosol particles in northern and southern California measured during CARES and CalNex 2010." *Atmospheric Chemistry and Physics* 12, 10989-11002. DOI:10.5194/acp-12-10989-2012, 2012.

Mixing State

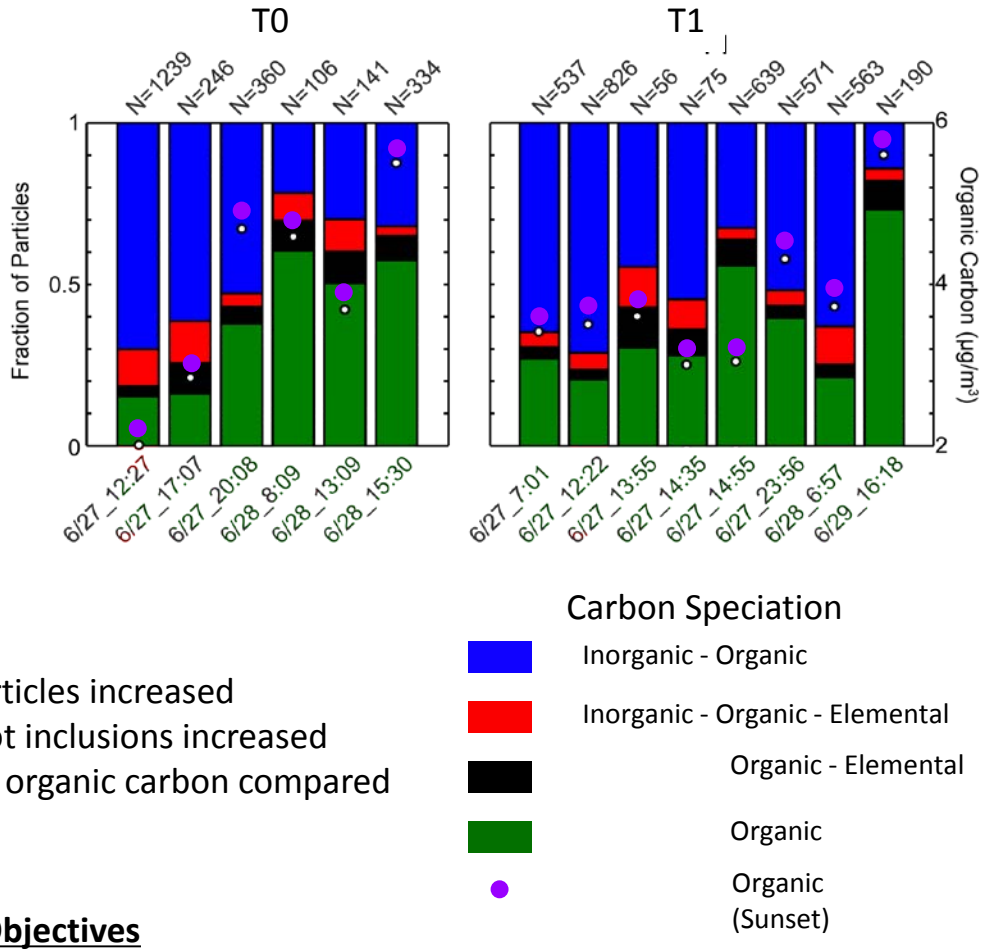
Spectro-microscopic measurements of carbonaceous aerosol aging in Central California

Science Question

How does the mixing state of carbonaceous aerosols change with time and location?
How does the carbon transform with age?

Approach

- During CARES collect time resolved samples Select pollution accumulation event June 27-29, 2010
- Use spectro-microscopy to determine particle classes and mixing states



Key Accomplishment

With increasing plume age

- the mass of organic carbon on individual particles increased
- the number fraction of particles without soot inclusions increased
- fresh CARES samples had 1/3 the amount of organic carbon compared to fresh Mexico City samples

Contribution to Focus Group/Working Group Objectives

- CARES- Directly measuring the mixing state of carbonaceous single particles.
- Comparing mixing state and amount of organics to Mexico city results.
- Provide test bed of mixing state measurements for modelers.

Spectro-microscopic measurements of carbonaceous aerosol aging in Central California, R.C. Moffet, T.C. Roedel, S.T. Kelly, X.Y. Yu, G. T. Carroll, J. Fast, R.A. Zaveri, A. Laskin, M.K. Gilles, Atmospheric Chemistry & Physics 13, 10445 (2013)

Mixing State

Chemical characterization of individual particles and residuals of cloud droplets and ice crystals collected on board research aircraft in the ISDAC 2008 study

Science Question

How do particles that nucleate ice differ from those that don't?

Focus Group Association

Aerosol Aging and Mixing State

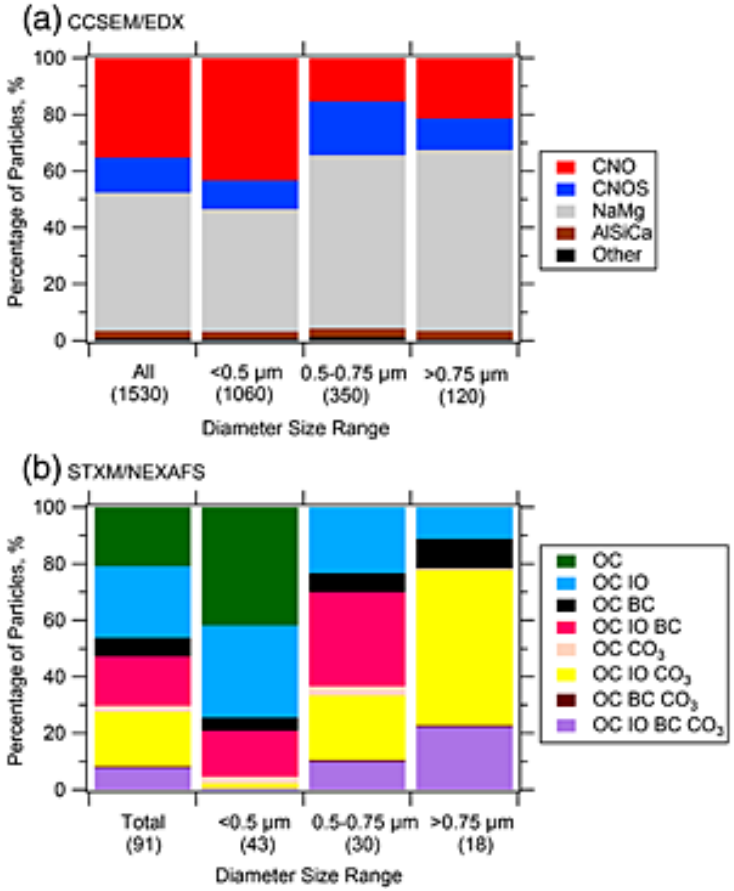
Approach

- During ISDAC collect time resolved samples on ambient isokinetic inlet and counterflow virtual impactor inlet
- Use spectro-microscopy to determine particle classes and mixing states

Key Accomplishment

Residual particles that nucleated ice

- Much larger % contained carbonates than ambient samples (4x)
- Enhanced in sea salt compared to ambient population
- Reduced in organics compared to ambient population



Contribution to Focus Group/Working Group Objectives

- Examining mixing state and effect on ability to nucleate ice

Chemical characterization of individual particles and residuals of cloud droplets and ice crystals collected on board research aircraft in the IDAC 2088 study, N. Hiranuma, S.D. Brooks, R.C. Moffet, A. Glen, A. Laskin, M.K. Gilles, P. Liu, A.M. Macdonald, J.W. Strapp, G.M. McFarquhar, J. Geophs. Res Atmos. 118, 6564 (2013)

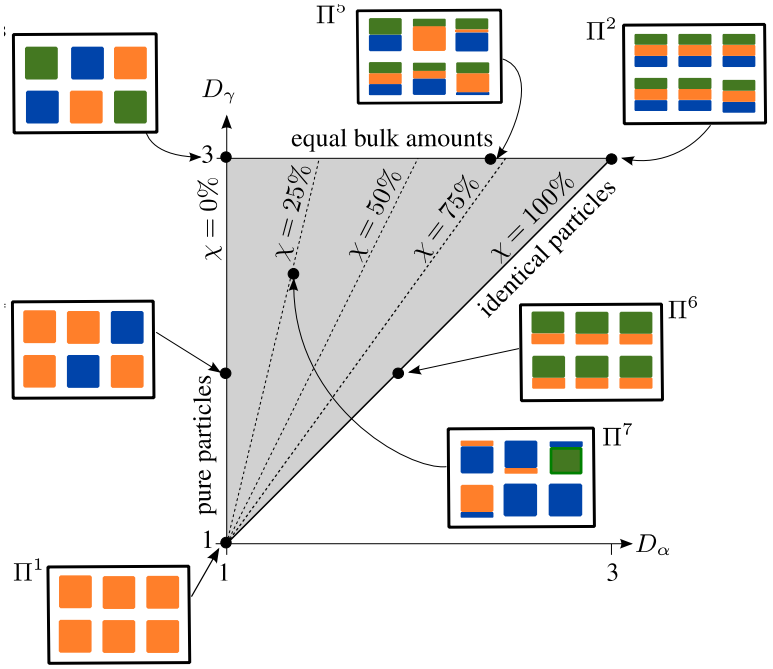
Mixing State

Quantifying aerosol mixing state with entropy and diversity measures

Science Question How can we quantify "aerosol mixing state"?

Approach

- We defined a new metric, the mixing state index χ.
- This is an affine ratio of the average per-particle species diversity D_α and the bulk population species diversity D_γ , both of which are based on information-theoretic entropy measures.



Key Accomplishment The mixing state index χ enables the first rigorous definition of the spectrum of mixing states from so-called external mixture to inter- nal mixture, which is significant for aerosol climate impacts, including aerosol optical properties and cloud condensation nuclei activity.

Contribution to Focus Group/Working Group Objectives

The mixing state index χ will prove useful in communicating, discussing, and categorizing the aerosol mixing state of both observed and modeled aerosol populations. This, in turn, will facilitate answering the key research questions: (1) what is the mixing state at emission and how does it evolve in the atmosphere; (2) what is the impact of mixing state on climate-related and health-relevant aerosol properties; and (3) to what extent do models need to account for mixing state to answer these questions?

Nicole Riemer and Matthew West, Quantifying aerosol mixing state with entropy and diversity measures, *Atmos. Chem. Phys*., **13**, 11423–11439, 2013

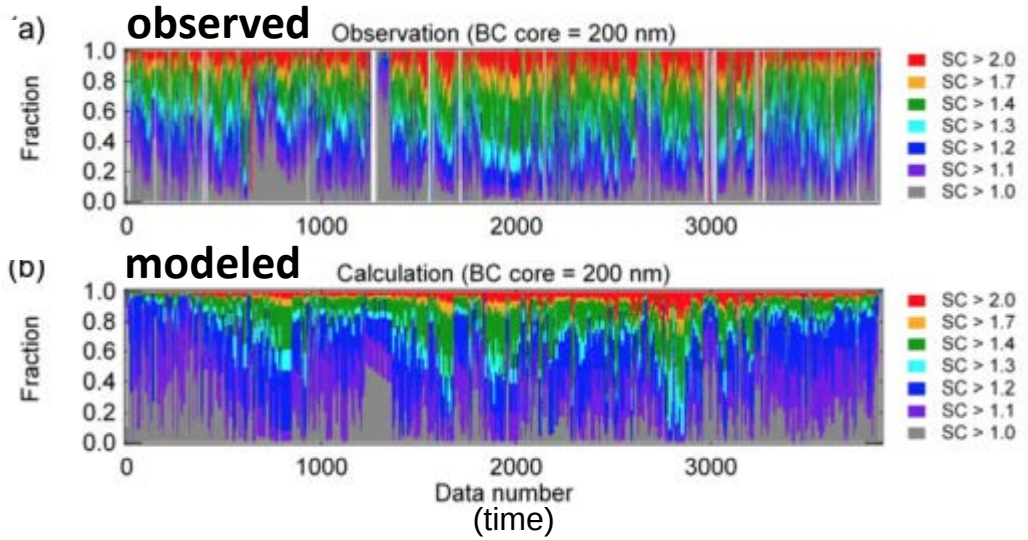
New Model Predictions Consistent with Observed Black Carbon Mixing State over East Asia

Objective

- Present a treatment for evolving black carbon mixing state in a regional-scale model and assess the impact of mixing state on radiation.

Approach

- PNNL's MOSAIC aerosol model extended to resolve the mixing state of black carbon as primary anthropogenic emissions age and become coated over time.
- Evaluated model using aircraft data over East Asia collected with a Single Particle Soot Photometer that measures size of black carbon particles and the coating thickness.
- Compared impact of mixing state on radiation with traditional methods used in climate models

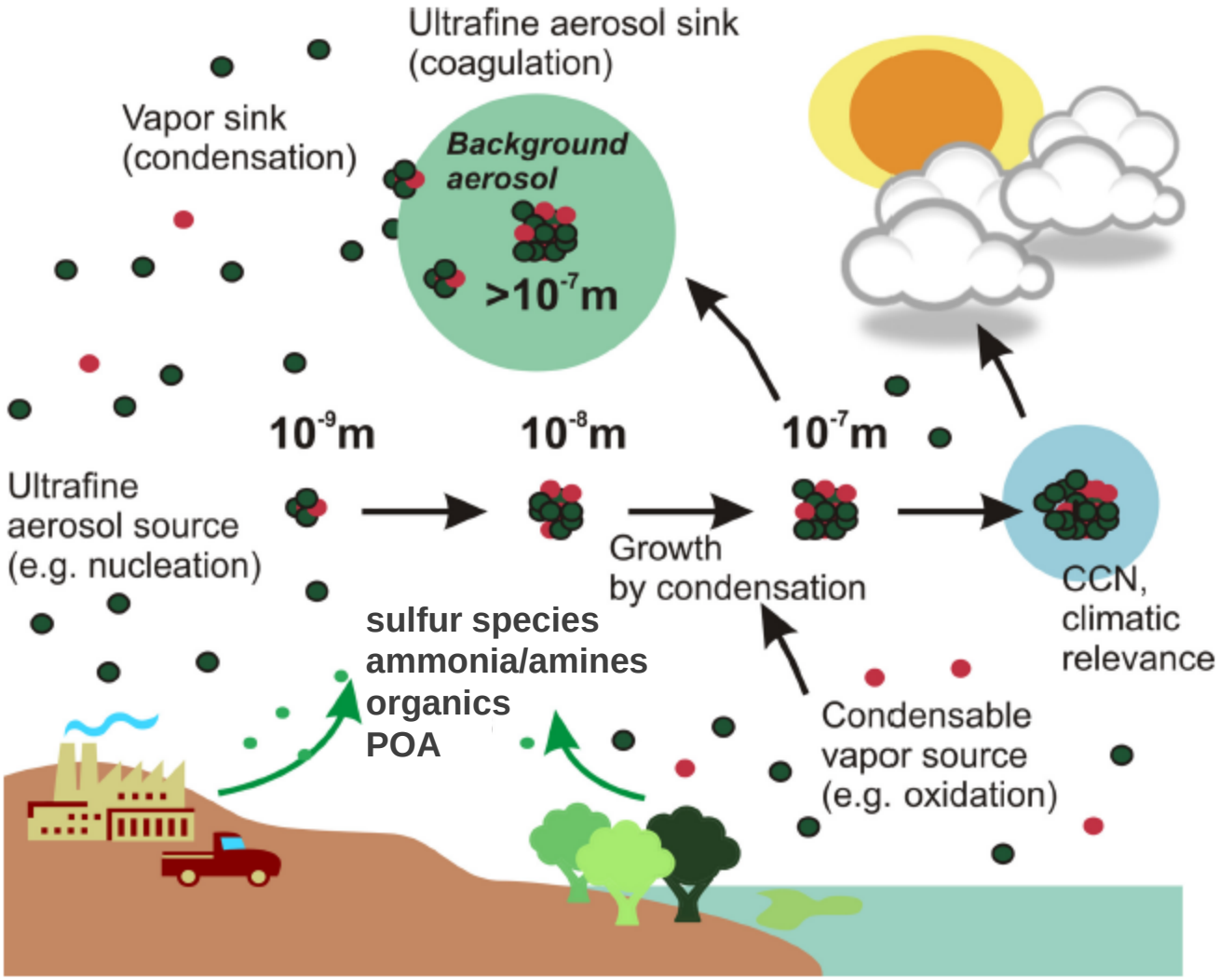


Impact

- Simulated black carbon mixing state was consistent with the observed temporal variations and size dependencies of number fraction of black carbon-containing and black carbon-free particles and the range and fraction of shell (total particle dry diameter)-to-black carbon core diameter ratio.
- The treatment of mixing state had a large impact on optical properties, leading to differences up to 40% in the boundary layer between the detailed and simple treatments.

Matsui H, M Koike, Y Kondo, N Moteki, JD Fast, and RA Zaveri. 2013. "Development and validation of a black carbon mixing state resolved three-dimensional model: Aging processes and radiative impact." *Journal of Geophysical Research Atmospheres*. DOI: 10.1029/2012JD018446.

Atmospheric nanoparticle formation: Processes that link to climate

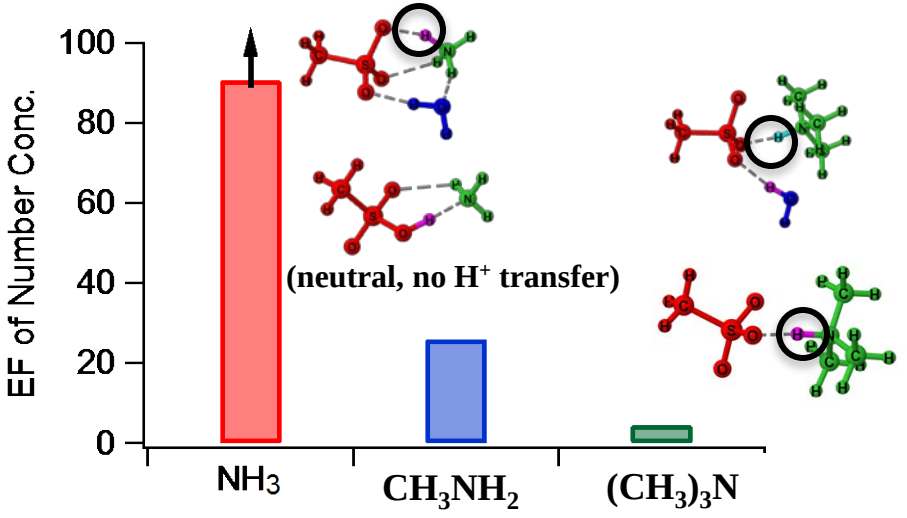


adapted from Riipinen et al., 2011

Mechanisms involved in new particle formation (NPF) and parameterization in atmospheric models

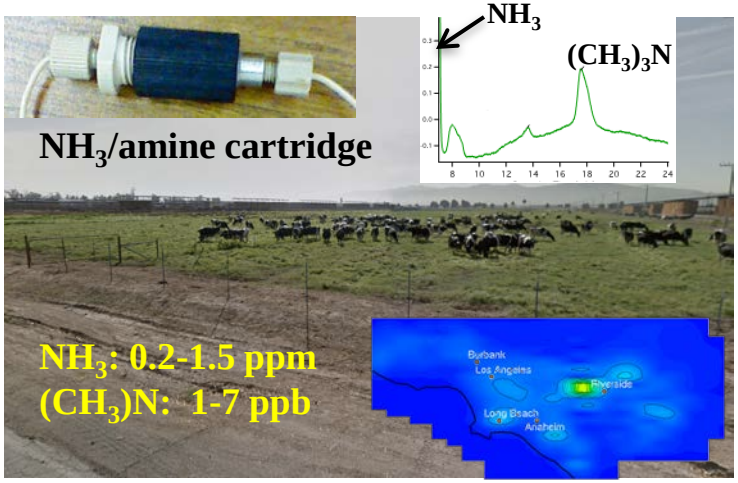
Finlayson-Pitts group

Water Enhancement Factor (EF) in NPF (# humid/dry)



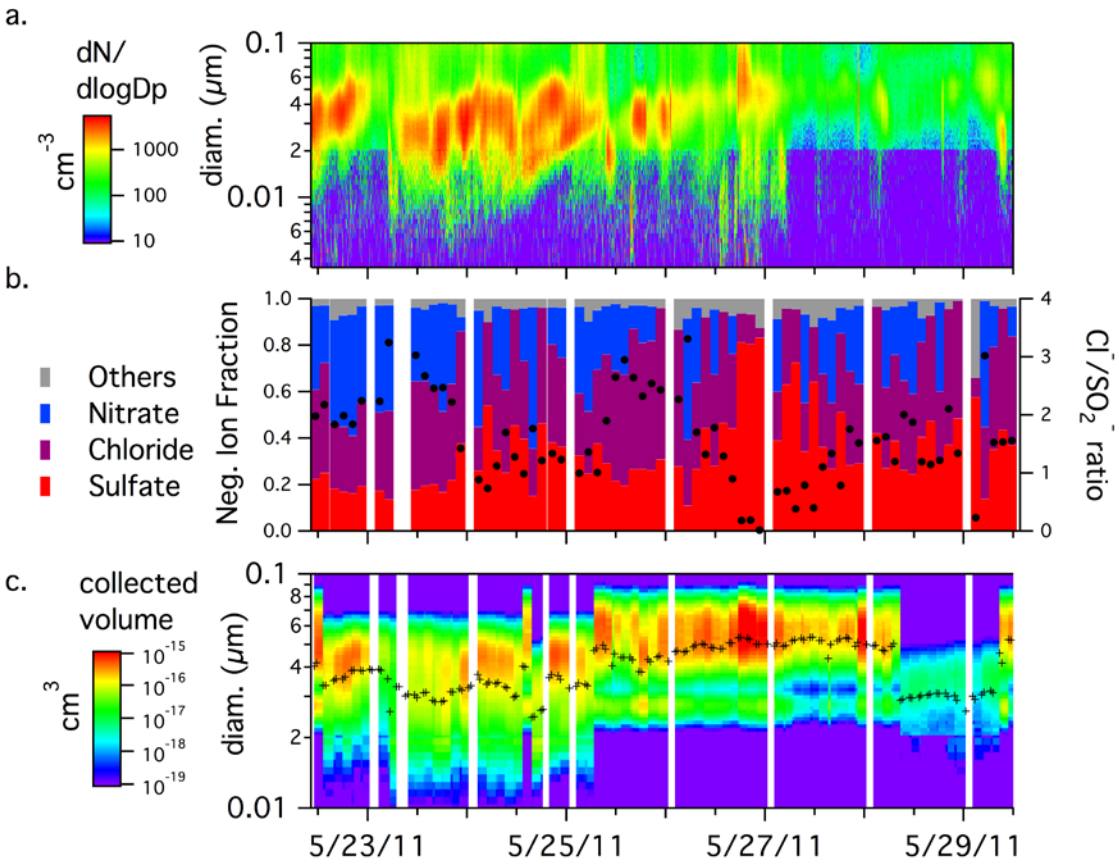
Key Accomplishments:

- Detailed quantitative characterization of new particle formation from MSA – NH_3/amine reactions as a function of relative humidity, with supporting computations of stability of clusters;
- Development of relatively simple mechanism that captures complex dependence of new particle formation over a large range of concentrations and RH, and is suitable for incorporation into atmospheric models ;
- Development of a new technique for measuring amines in air at the tens of ppt level and that minimizes sampling artifacts and is applicable in both lab and field studies.



What is the composition of nanoparticles over the ocean, and in particular, of apparent newly formed particles?

Smith group



Chemical composition and size distribution of sub-100 nm particles at the coastal site Mace Head in Ireland.

Key findings:

Number enhancements of particles in the range of 20-60 nm were shown to be most likely due to new particle formation over the ocean, with a significant contribution from sulfate.

Sub-3nm particles observed during Aerosol IOP

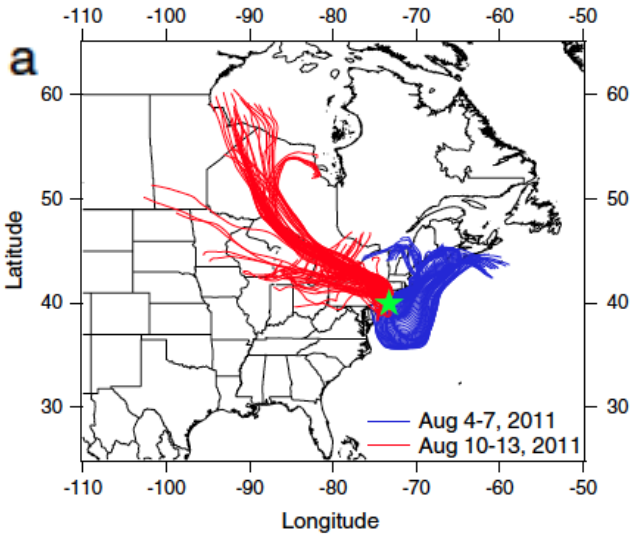
Lee group (Kent state)

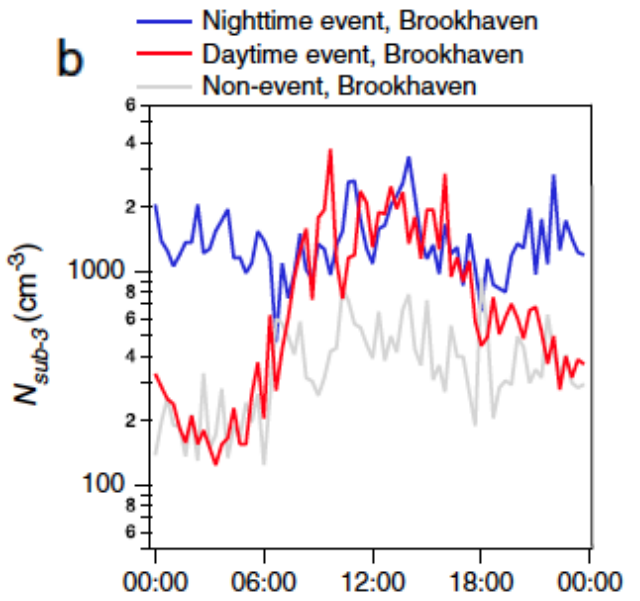
Science Question:

What are the atmospheric conditions and mechanisms that control new particle formation and early particle growth?

Key Accomplishment/Findings:

- Three day back trajectories arriving at Upton, NY during 10-13 August 2011 were characterized by continental air masses (red trajectories) with distinctive banana-shaped NPF events. On 4-7 August 2011 (blue trajectories) the site was characterized by marine air masses and clear nighttime NPF events.
- The daytime were coincident with H_2SO_4 formation and were not suppressed by coexisting large particles. Nighttime events were not correlated with either H_2SO_4 or measured VOCs.

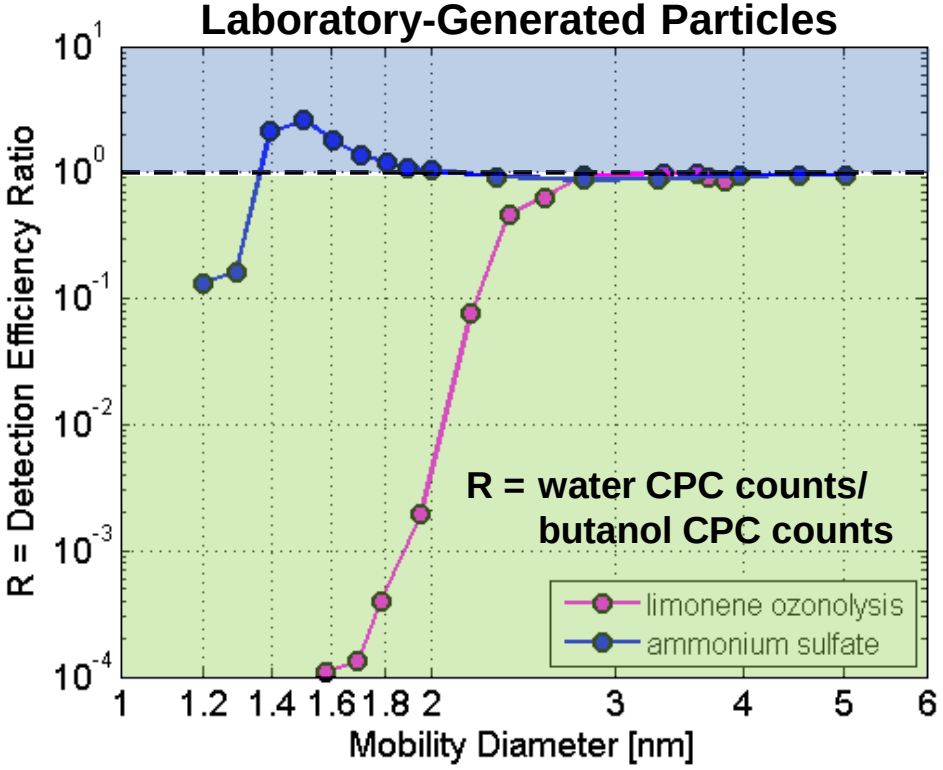




New Capability to Infer Nanoparticle Composition Down to 1 nm

- Objective: Improve upon limited nanoparticle composition measurements below 3 nm
- Approach: Exploit strong **composition-dependent interactions** between different CPC working fluids and sampled particles to infer particle composition

Instrument Characterization with Laboratory-Generated Particles



R > 1: particles more "water soluble" (e.g., ammonium sulfate)

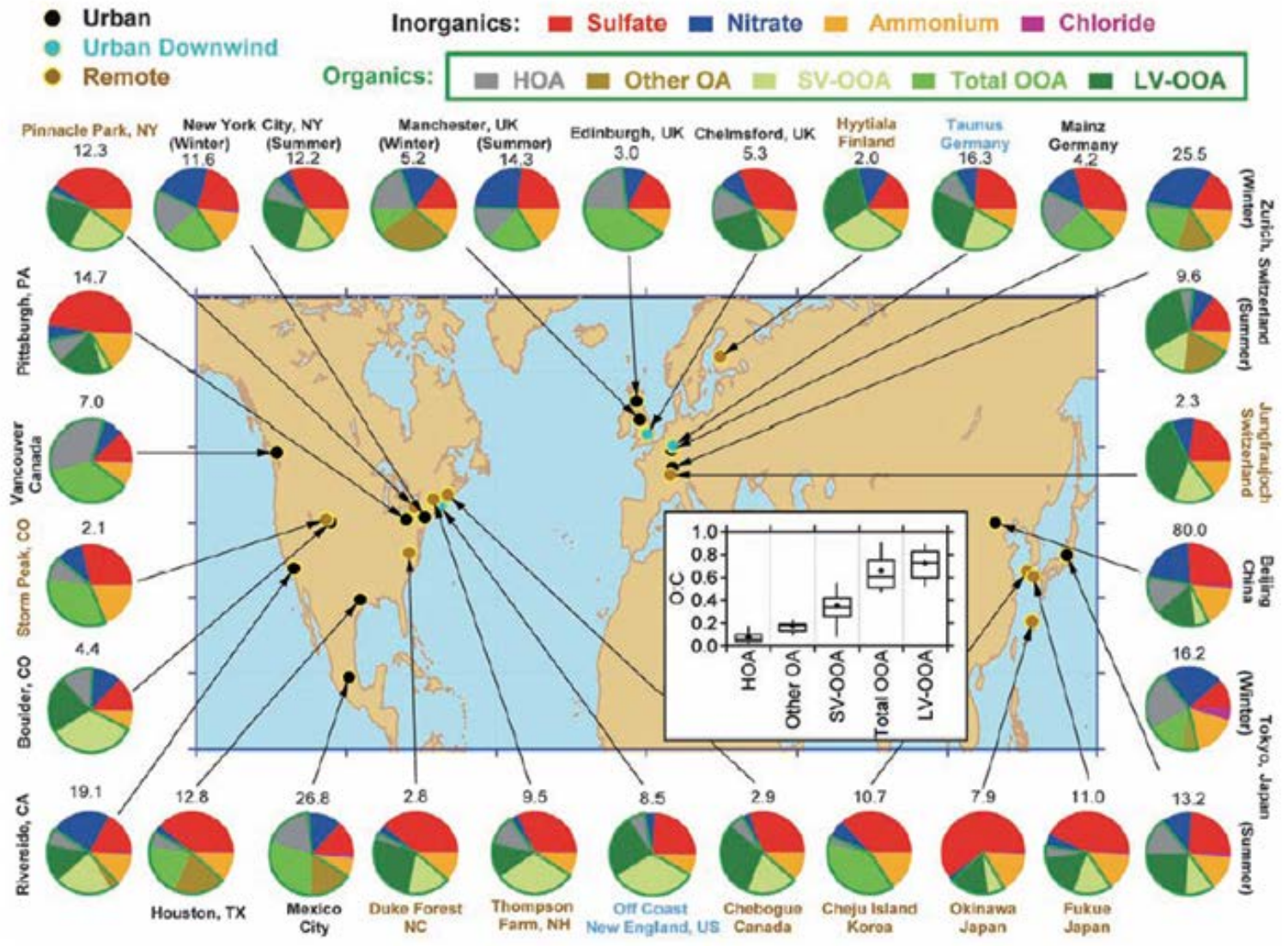
R < 1: particles less "water soluble" (e.g., organic oxidation products)

New measurement capability provides:

- **insights** into the composition of sub – 3 nm particles
- **constraints** on ambient detection efficiency ➔ more accurate measurements of nanoparticle concentration

Kangasluoma, J. et al. Atmos. Meas. Tech. 7, 689-700, (2014).

Formation of Secondary Organic Aerosol

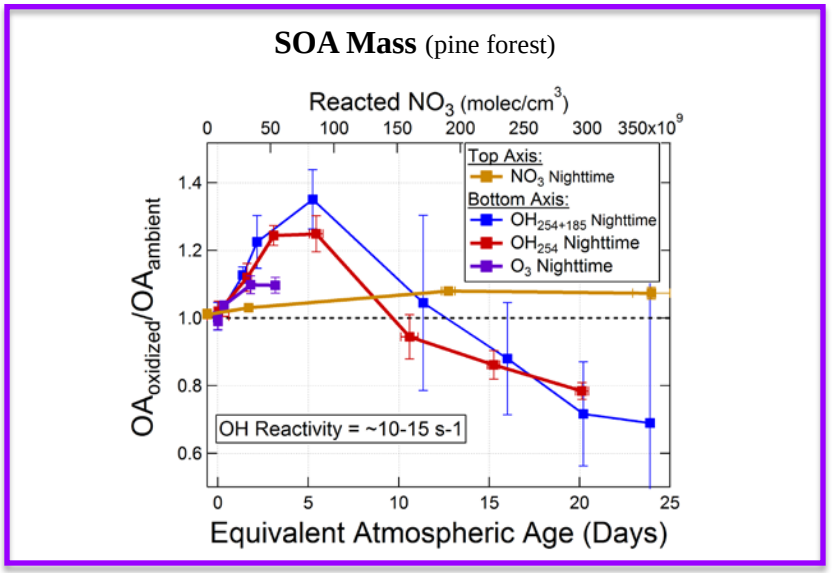


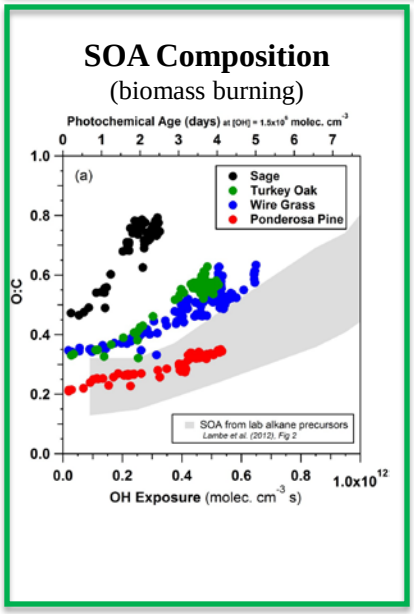
SOA Formation, Composition, and Aging using an Oxidation Flow Reactor

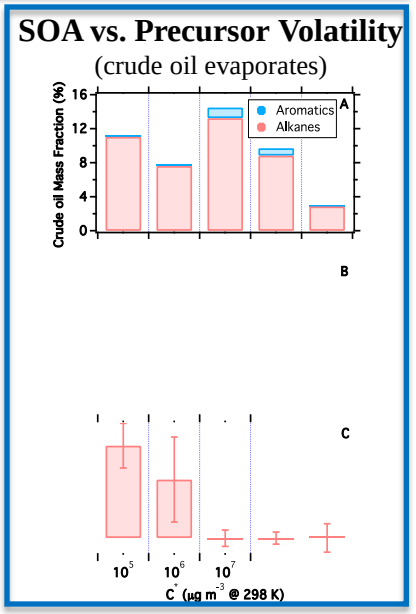
Jimenez Group

Key Accomplishments/Findings

- Successful real-time observations at terpene-dominated forest, isoprene-dominated forest, urban site, biomass-burning chamber lab, crude oil vapors, and individual biogenic and anthropogenic VOC.
- Potential aerosol formation often follows measureable gas-phase, diurnal or longer-term trends, and often is much larger than predicted by models.
- Net SOA production during first few days of aging. Later, mass is lost likely due to fragmentation and evaporation. O/C continues to increase.
- Biomass burning smokes have widely differing SOA formation potentials. Intermediate volatility vapors dominate SOA from crude oil.







A novel method for on-line analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROsols (FIGAERO)

F. D. Lopez-Hilfiker, C. Mohr, M. Ehn, F. Rubach, E. Kleist, J. Wildt, T. F. Mentel, A. Lutz, M. Hallquist, D. Worsnop, and J.A. Thornton.
Atmospheric Measurement Techniques Discussion, 6, 9347-9395, 2013.

Science Questions

- What compounds contribute to SOA formation and growth?
- What is the volatility of organic aerosol and how does it relate to the precursors?

Approach

- Online *in-situ* High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometry (HRToF-CIMS)
- Gas and particle molecular composition
- Field deployable and fully automated

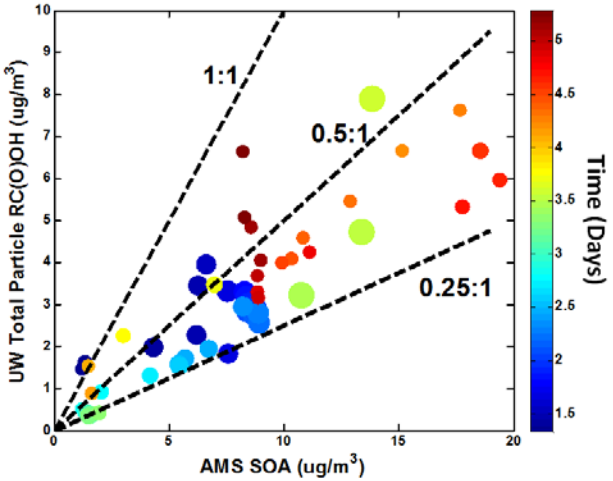


Figure 1

Key Accomplishments

- Carboxylic acid functionality is significant fraction of monoterpene derived SOA (Figure 1).
- Gas-particle partitioning, and the measured desorption temperatures (Figure 2) suggest many acids in monoterpene SOA were part of larger macromolecules ($C_{10} \rightarrow C_{20} \rightarrow C_{30}$).
- ~ 25% of monoterpene SOA mass composed of oligomers w/effective vapor pressures 4 or more *orders of magnitude* lower than commonly measured components.

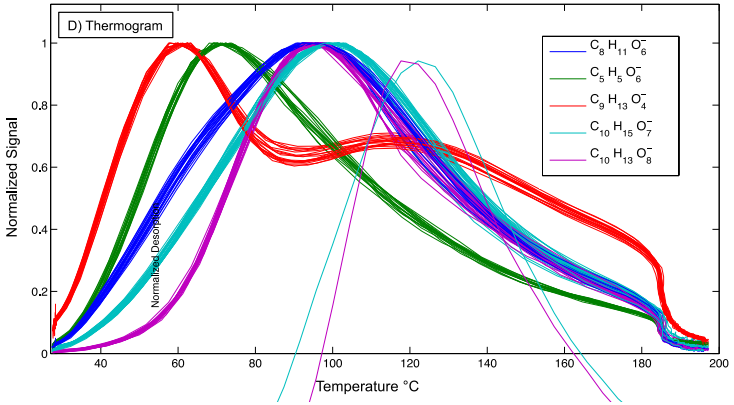


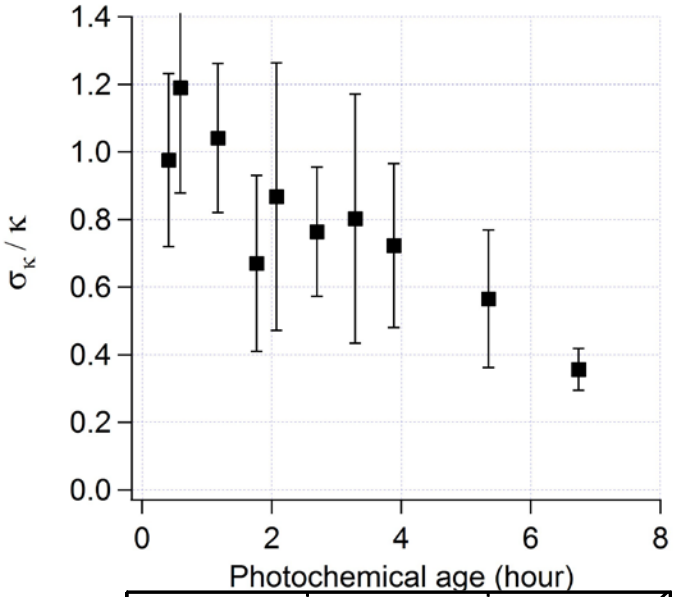
Figure 2

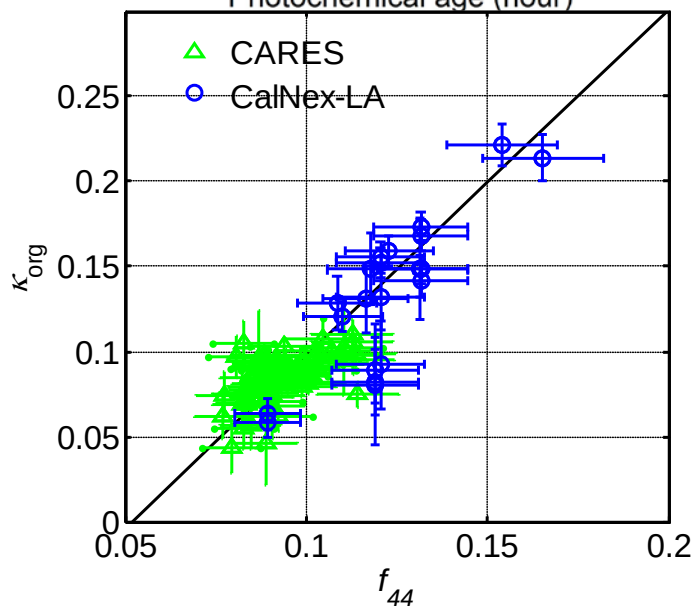
Hygroscopicity and mixing state of organic aerosols

Mei et al., 2013a, 2013b

Key Accomplishment/Findings:

- Within a few hours during daytime, aerosol particles become essentially internally mixed (for the purpose of calculating CCN concentrations).
- Strong correlation between organic hygroscopicity and f44 (the fraction of total organic mass spectral signal at m/z 44).
- Organic hygroscopicity may be dominated by organic acids due to their relatively high water solubility and hygroscopicity.





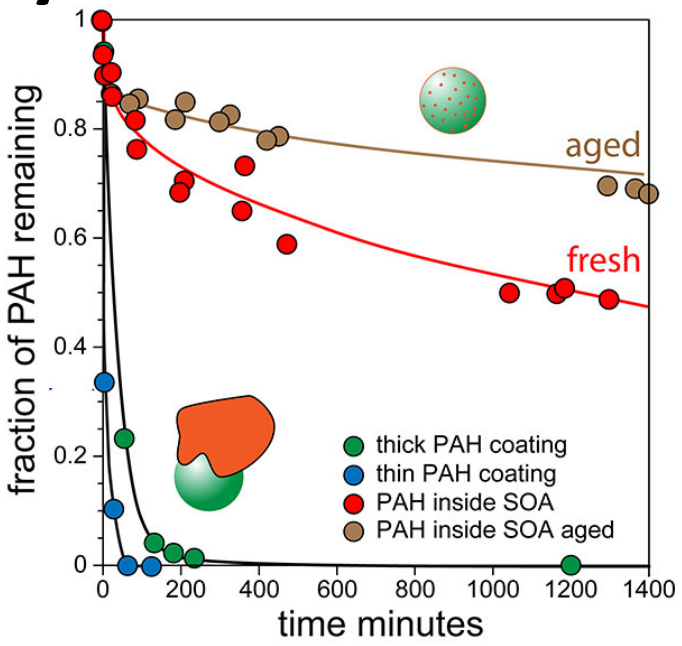
Small and viscous: New method measures SOA viscosity and diffusivity

Objective

- Determine the rate of diffusion in secondary organic aerosol (SOA) particles and SOA viscosity

Approach

- Generated pyrene-doped SOA particles
- Measured the rate with which pyrene molecules diffuse through the particles and evaporate when they reach the surface
- Using measured diffusivity, calculated SOA viscosity
- Characterized diffusivity and viscosity of fresh and aged SOA particles



The evaporation rate of pyrene tracer-molecules trapped in SOA during its formation provides direct information about pyrene diffusivity in SOA and SOA viscosity

Impact

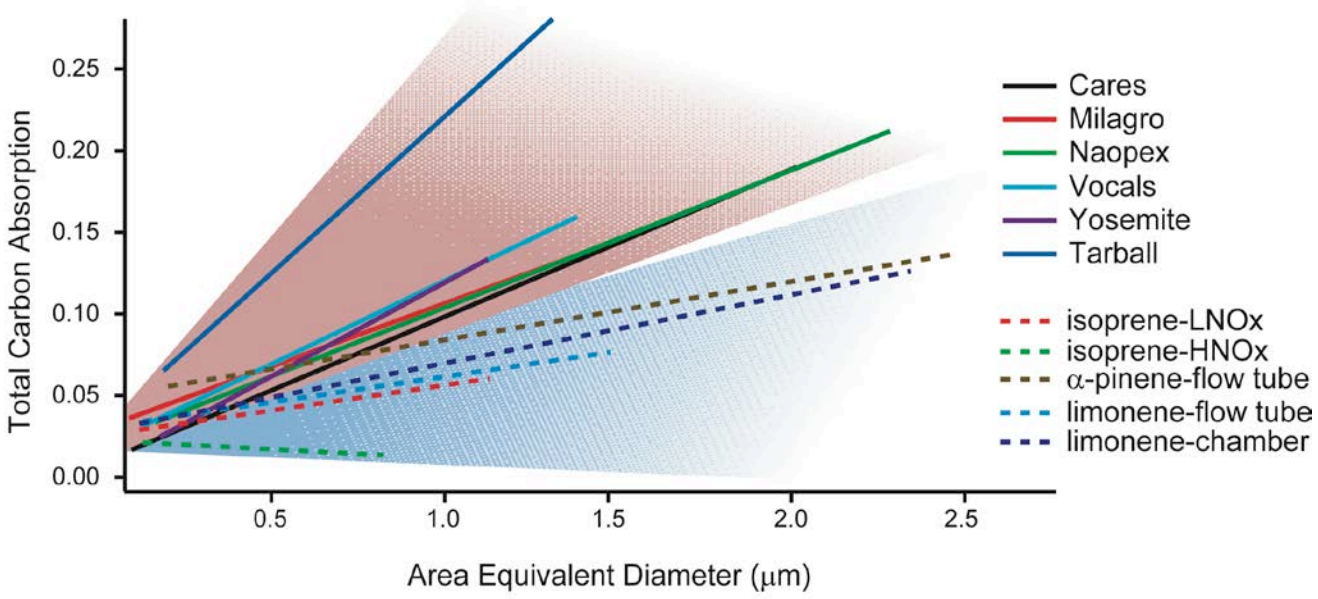
- Models assumed that SOA particles are low-viscosity solutions
- Viscosity of SOA particles was found to be similar to that of tars or a million times higher than previously assumed
- Results will help modelers better simulate properties and evolution of atmospheric SOA particles

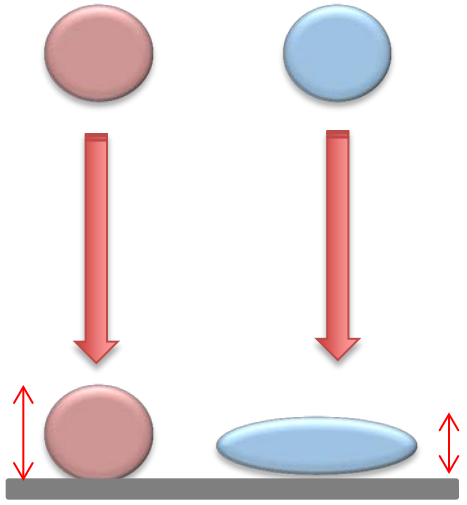
Abramson E, D Imre, J Beranek, J Wilson, and A Zelenyuk. 2013. "Experimental Determination of Chemical Diffusion within Secondary Organic Aerosol Particles", *Physical Chemistry Chemical Physics*. 15:2983-2991. DOI:10.1039/C2CP44013J.

collected aerosols-SOA phase particle deformation-field vs laboratory samples

High viscosity - absorbance profile resembles a sphere maximum absorbance depends on particle diameter

Low viscosity - particle flattens, lower maximum absorbance, weaker dependence of absorbance on particle diameter





Currently examining laboratory SOA for influence of sulfur on SOA phase state

R. E. O'Brien A. Neu, S. A. Epstein, A. MacMillan, S. Nizkorodov, A.I Laskin, R. C. Moffet, M. K. Gilles, in prep for submission to GRL

Modeling kinetic partitioning of secondary organic aerosol and size distribution dynamics: representing effects of volatility, phase state, and particle-phase reaction

Zaveri, R. A., Easter, R. C., Shilling, J. E., and Seinfeld, J. H.

Approach

- Developed a new kinetic SOA partitioning framework that uses a combination of:
  - (a) An analytical quasi-steady-state treatment for the diffusion-reaction process within the particle phase for fast-reacting organic solutes, and
  - (b) A two-film theory approach for slow- and non-reacting solutes.
- Implemented the new framework within PNNL's MOSAIC aerosol model and evaluate performance against a benchmark finite difference model solution.
- Applied upgraded MOSAIC to investigate competitive growth dynamics of Aitken and accumulation modes.