Evolution of Aerosols and Their Climate-Related Properties: From MAX-MEX to CARES and Beyond…

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With Contributions from Many People!

March 15, 2012
ASR Science Team Meeting, Arlington, VA

ASR Atmospheric System Research

ARM CLIMATE RESEARCH FACILITY

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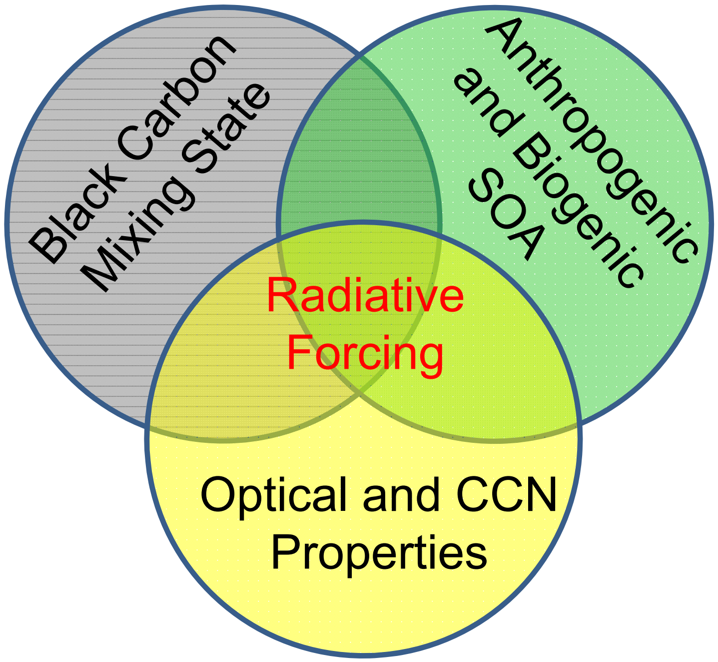
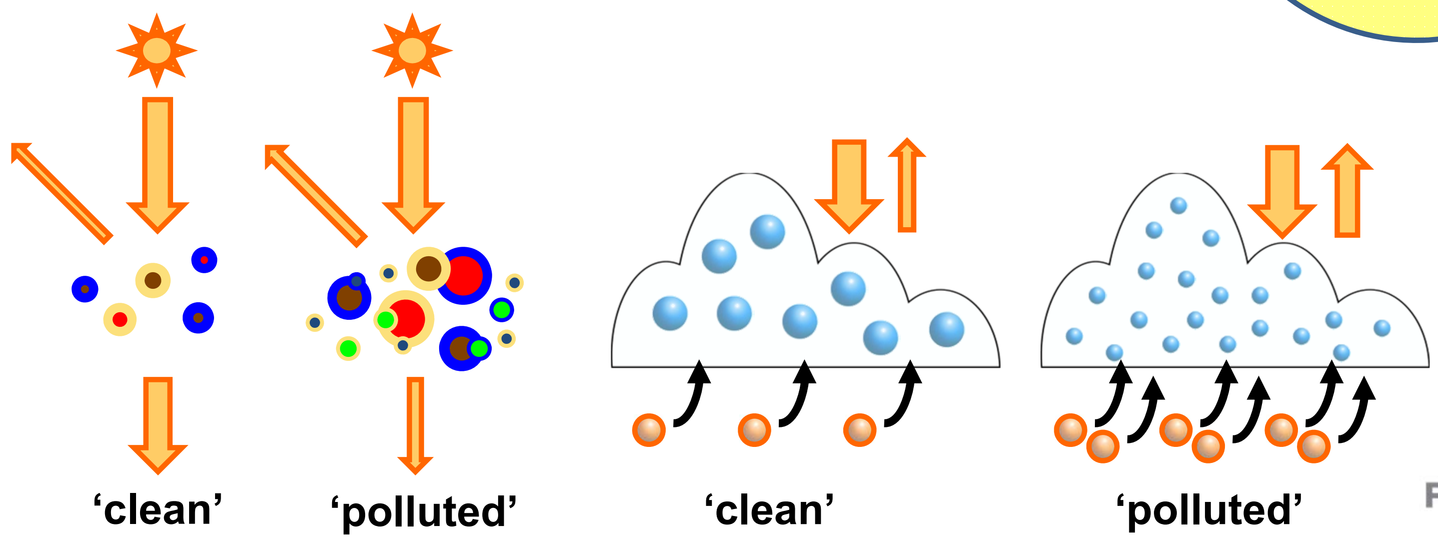
Outline

- Science objectives
- Summary of key results from MAX-MEX 2006
- Initial results from CARES 2010
- Future campaigns

Science Objectives

- Investigate SOA formation from anthropogenic and biogenic precursors and the potential interactions between them.
- Investigate black carbon (BC) mixing state evolution due to condensation and coagulation.
- Quantify the effects of aerosol ageing on aerosol optical and CCN activation properties.
- Develop improved models of these processes for use in regional and global climate models.





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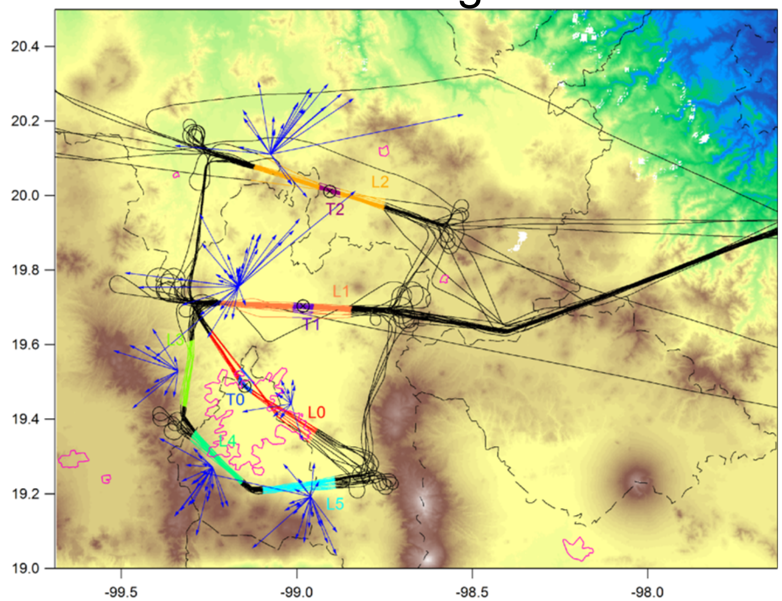
MAX-MEX, March 2006
Mexico City looks like Los Angeles 20 years ago
1 hour Max. Ozone = 300 ppb
24 hour Max. PM10 = 300 μg m^{-3}
“Dirty air is more interesting than clean air”
L. Kleinman
DOE’s MAX-MEX was part of a multi-agency, international field campaign under the MILAGRO umbrella

Aerosol Ageing in Mexico City

G-1 Aircraft Flight Tracks



Aerosol from AMS, DMA, PCASP

Restrict data to BL urban plume

CO as tracer of urban emissions

Photochemical age = - $\mathrm{Log}_{10}(NO_x/NO_y)$

Normalize results to CO to account for dilution

Regression slope of Aerosol vs. CO

Aerosol / (ppm urban CO) as a function of photochemical age

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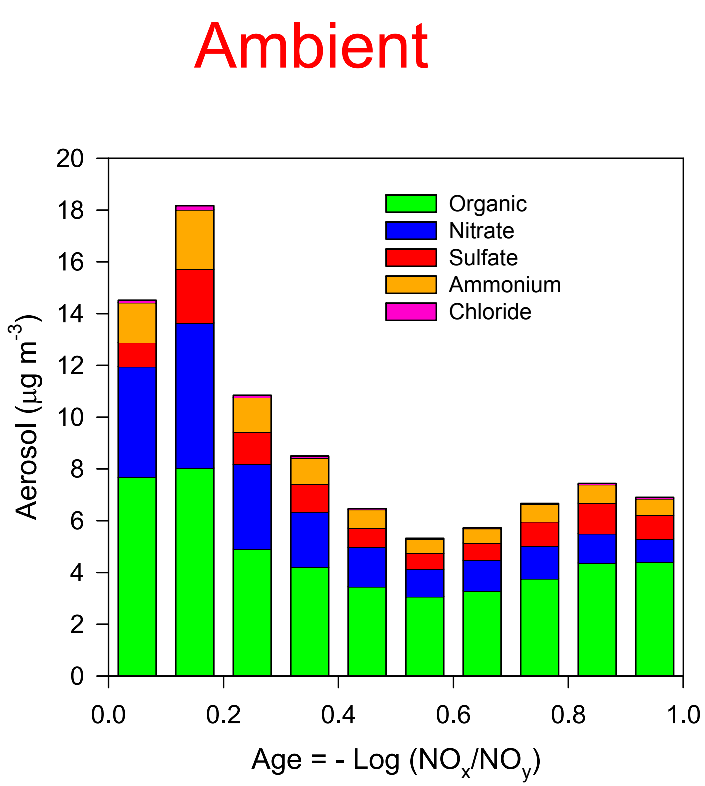
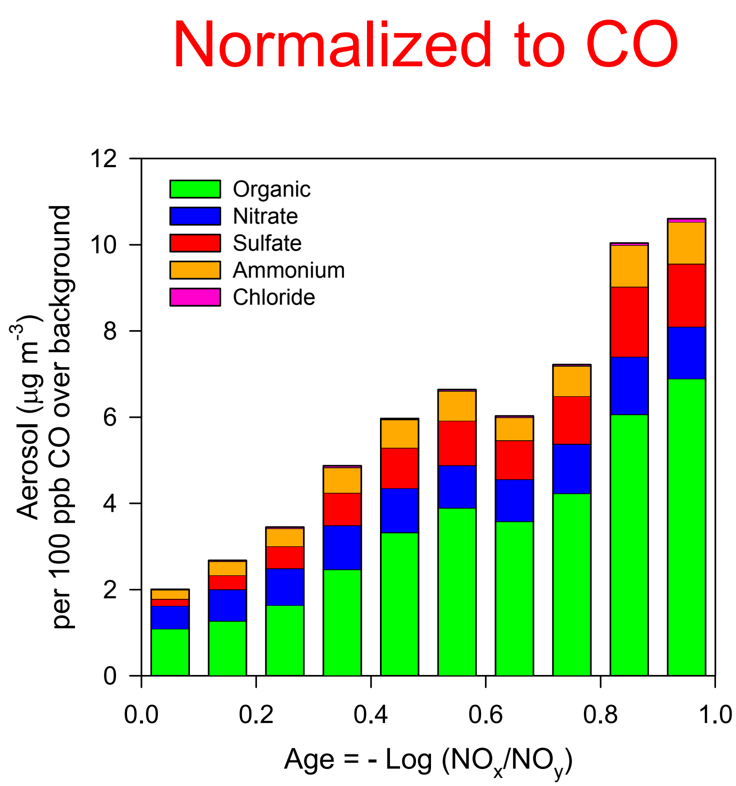
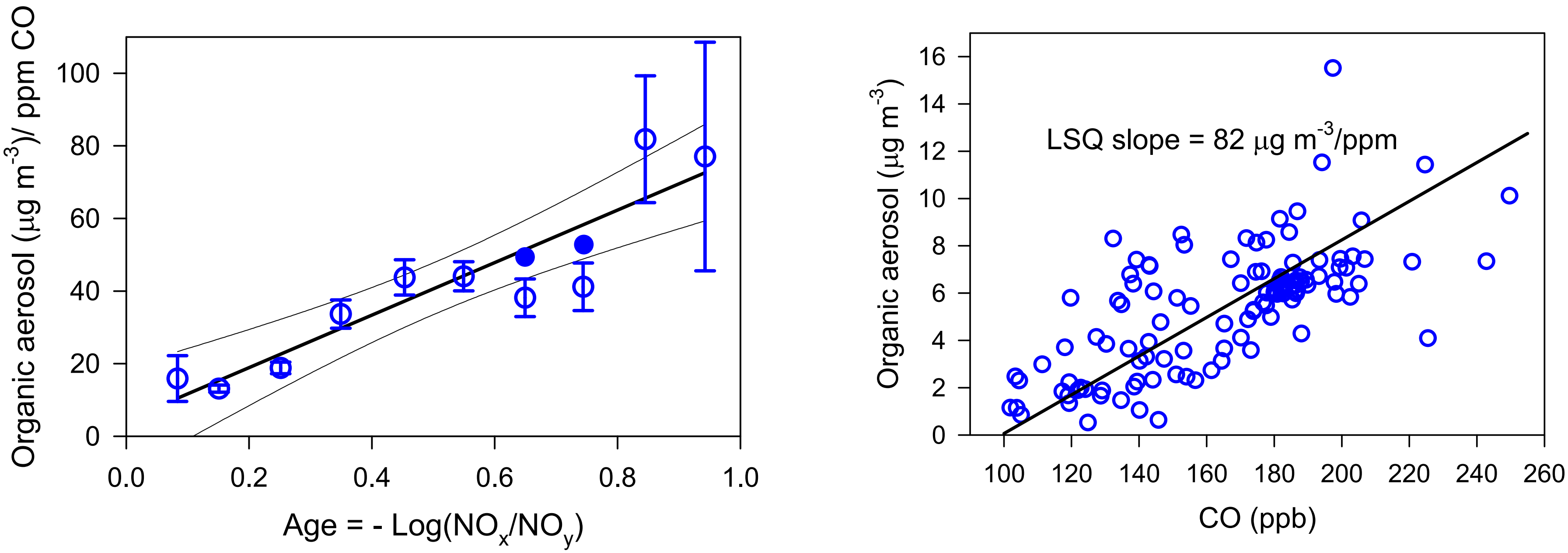
Aerosol Concentration





- After moderate ageing most non-refractory aerosol is secondary
- Organics and Sulfate are still increasing in old air masses
- Nitrate remains constant after Age ≈ 0.4, growth balances loss

Increase in Organic Aerosol Mass with Age



7 fold increase observed in OA with photochemical ageing

Similar efficiency as eastern U.S.

No sign that OA is evaporating in older air

Kleinman et al., 2008

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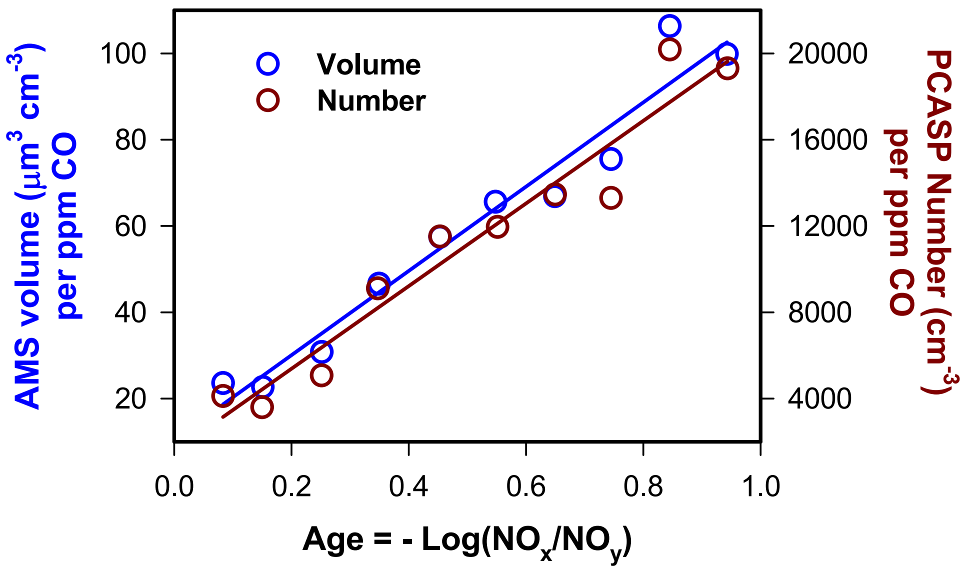
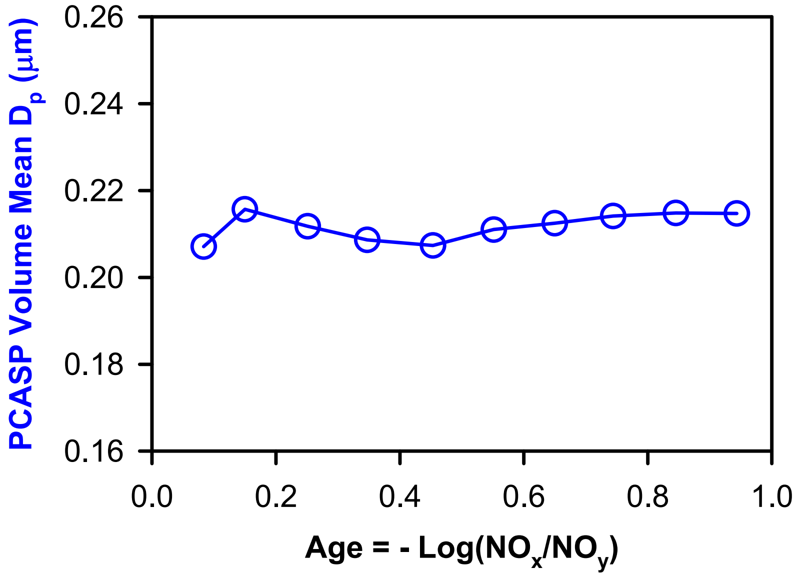
Increase in Number of Particles with Age

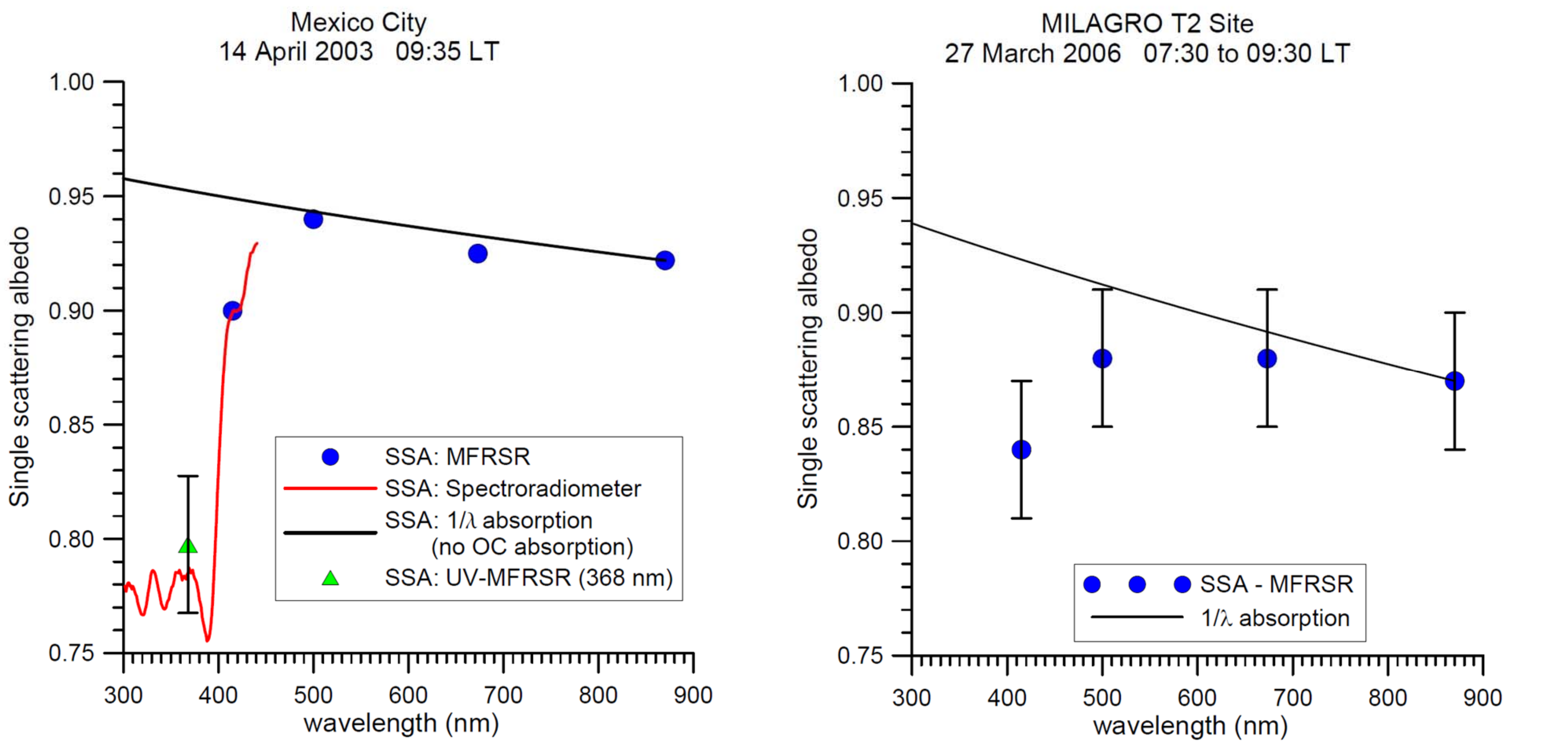
Accumulation mode Number from PCASP





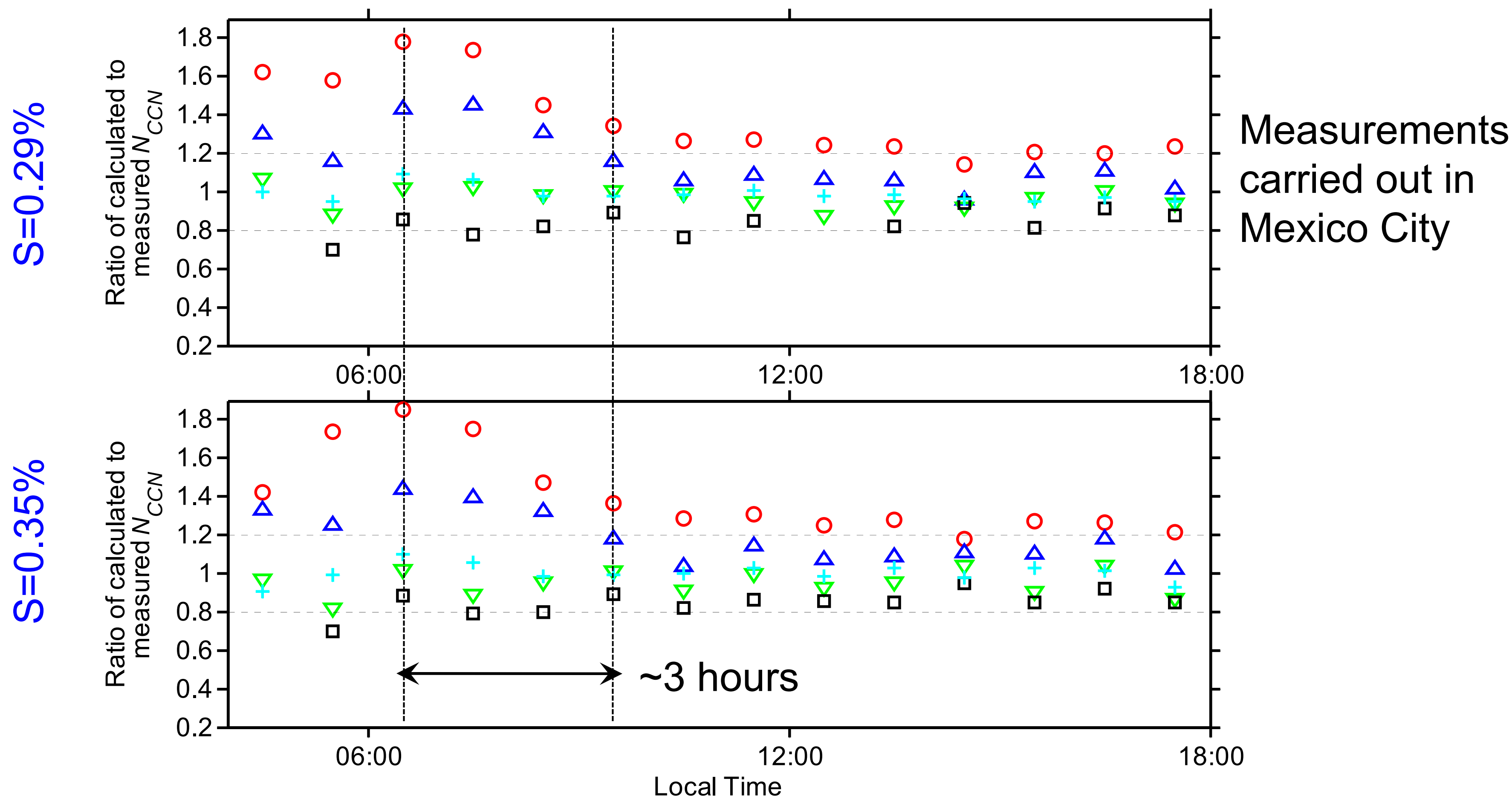
- Number/CO increased by a factor of 5 with age. Same as aerosol mass
- Ageing yields more accumulation mode particles, not larger particles
- Aitken mode can supply particles

Evidence for Brown Carbon



Barnard et al. (2008)

Influence of aerosol mixing state and composition on calculated CCN spectrum



Little influence of assumed aerosol mixing state and composition on calculated CCN spectra after just a few hours of ageing.

Wang et al. (2010)

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Lessons Learned, New Questions…

Heavily Polluted Urban Plumes

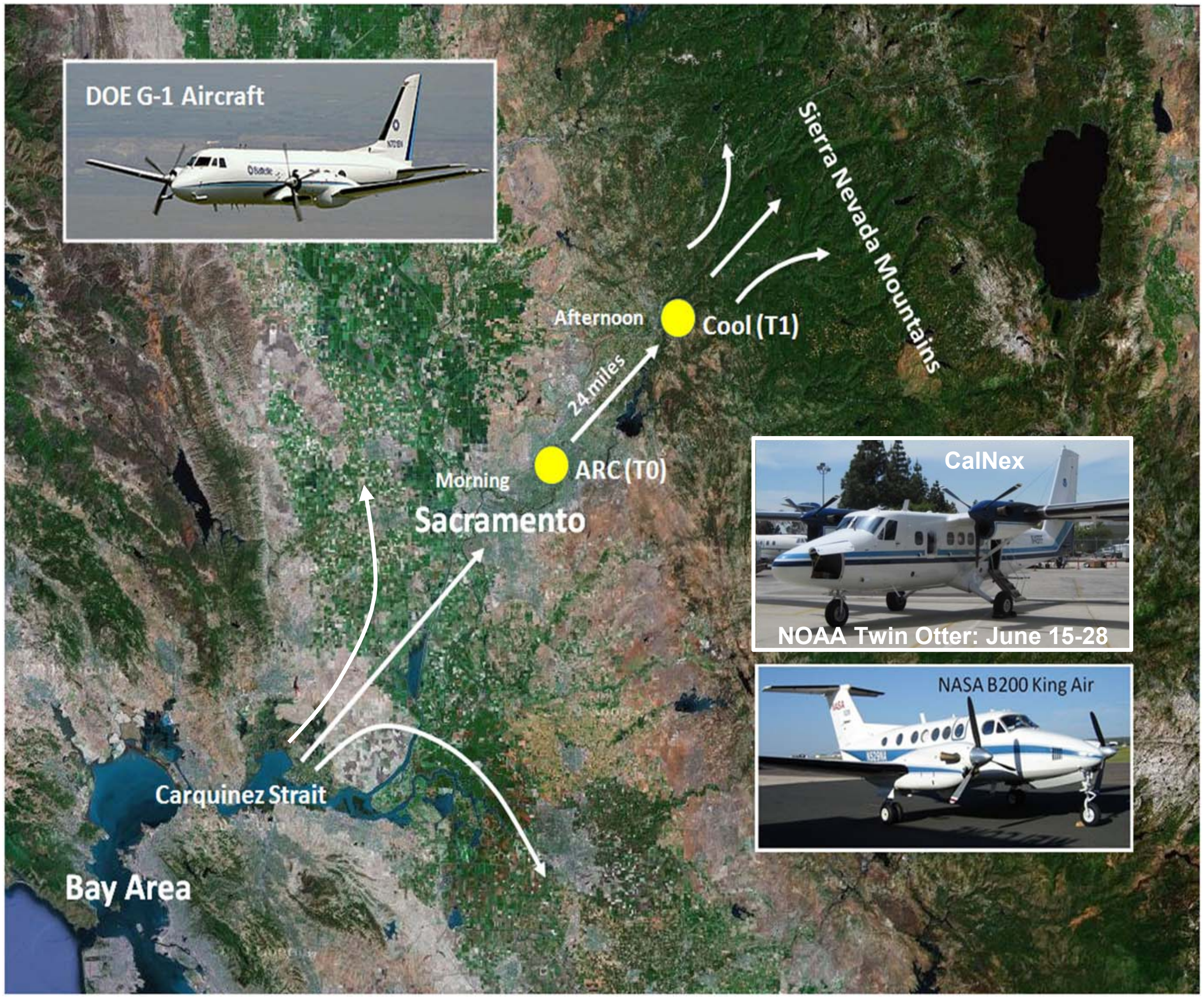
- Sulfate, nitrate, ammonium important, but organics dominates.
- SOA forms rapidly, with no sign of evaporation with dilution.
- Brown carbon aerosols observed, but contribution of SOA not clear.
- Urban aerosols found to age quickly from CCN perspective.

Less Polluted Urban Plumes Interacting with Biogenic Emissions

- Enhanced SOA formation?
- Black carbon ageing?
- Brown SOA formation?
- Evolution of optical and CCN activation properties?

CARES, June 2010

Carbonaceous Aerosols and Radiative Effects Study (CARES)

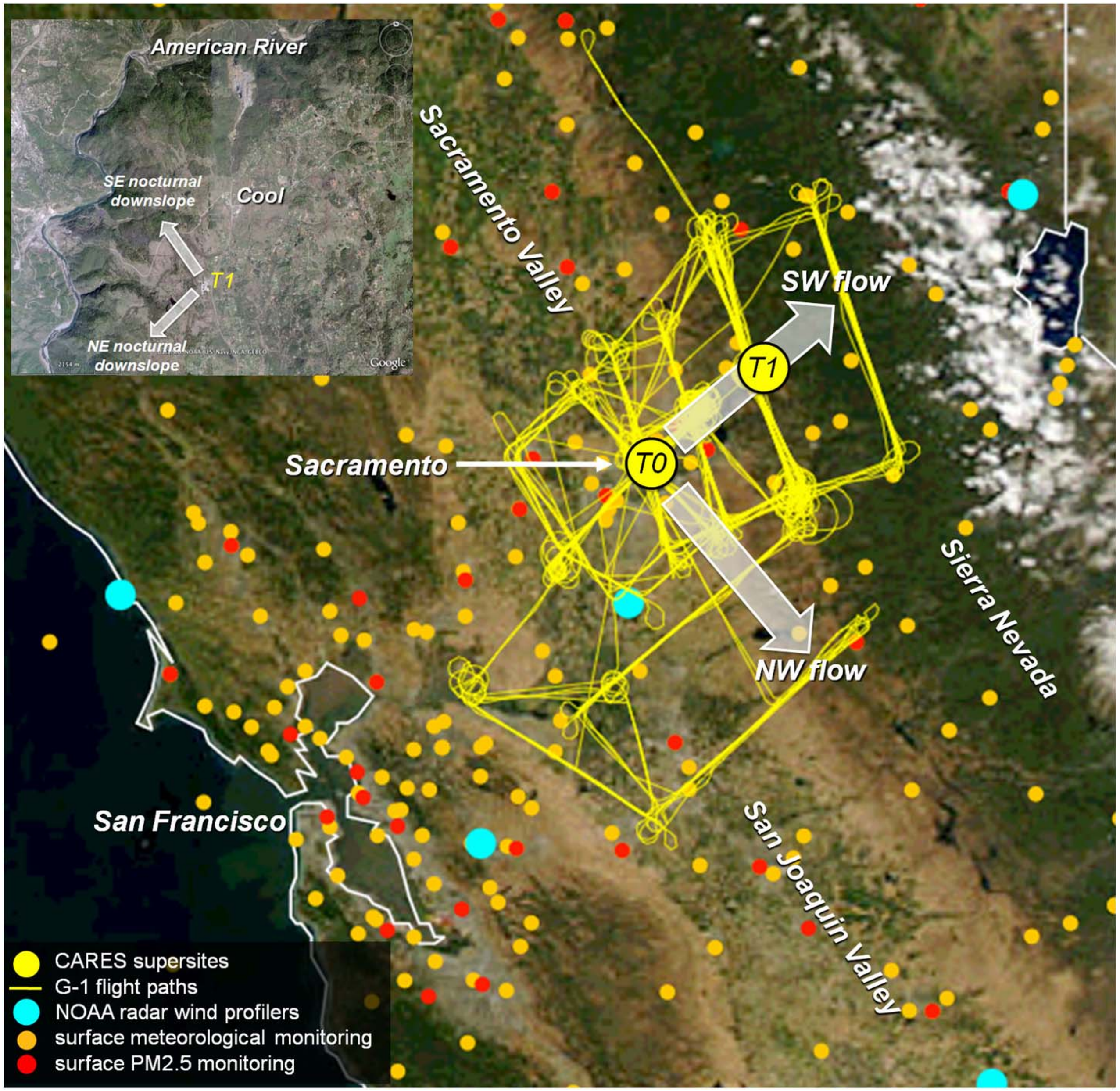


Rationale

- Mid-size City
- Fairly isolated and clean to the north
- Regular wind pattern
- Rich biogenic emissions

Sacramento plume serves as a natural “flow reactor,” useful to study Anthropogenic-Biogenic interactions.

DOE G-1 Flight Tracks



DOE G-1 (June 2 – 28)
- Research Flights: 22
- Flight Time: 67.5 hours
- Flight Distance: ~24,000 km

NASA B-200 (June 3 – 28)
- Research Flights: 23
- Flight Time: ~68 hours

Collaboration with CalNex

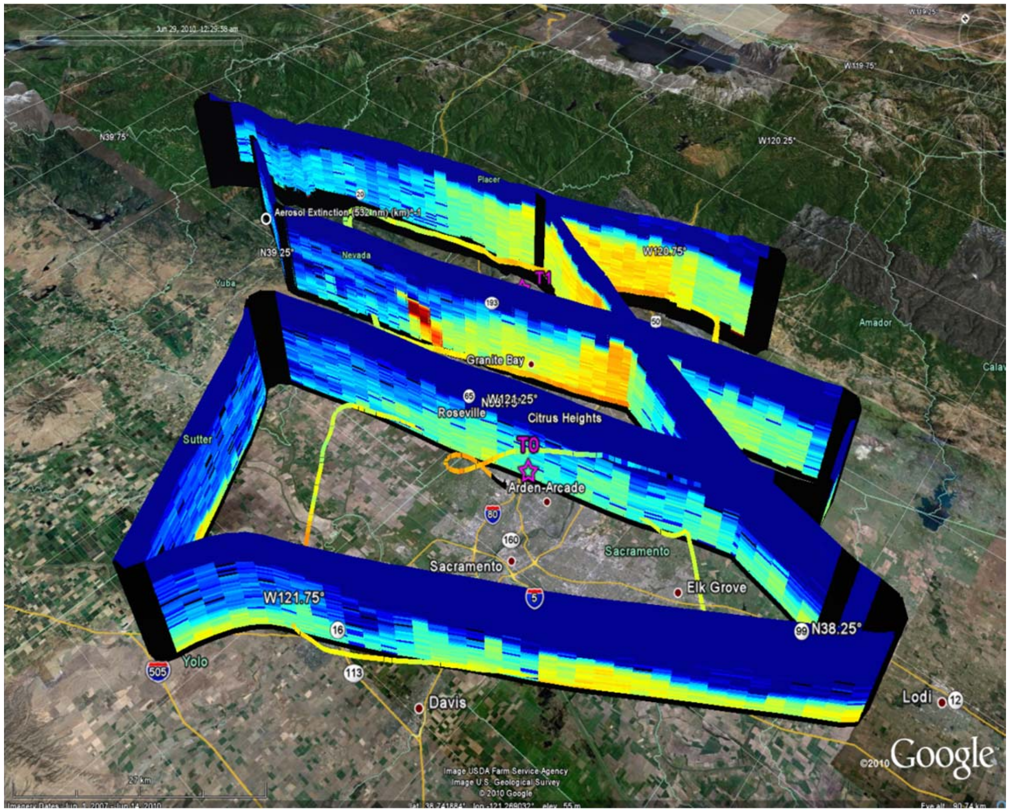
In Sacramento Area
- **R/V Atlantis (June 3 – 4)**
- **NOAA Twin Otter (June 15 – 28)**

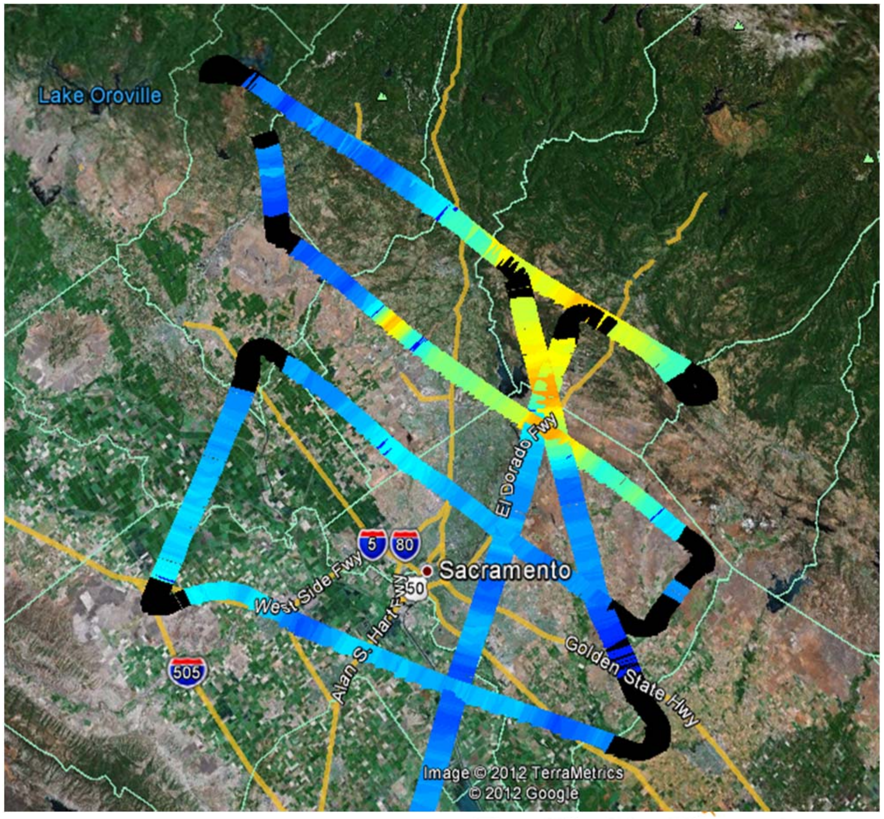
Intercomparison Flight From Fresno to Bakersfield, June 18
- **DOE G-1**
- **NASA B-200**
- **NOAA P-3**
- **NOAA Twin Otter**

NASA B-200 Flights

- HSRL measurements used to help identify plume location, mixed layer heights, and different aerosol types (e.g. dust, urban, marine, etc.)

June 28 Afternoon Flight





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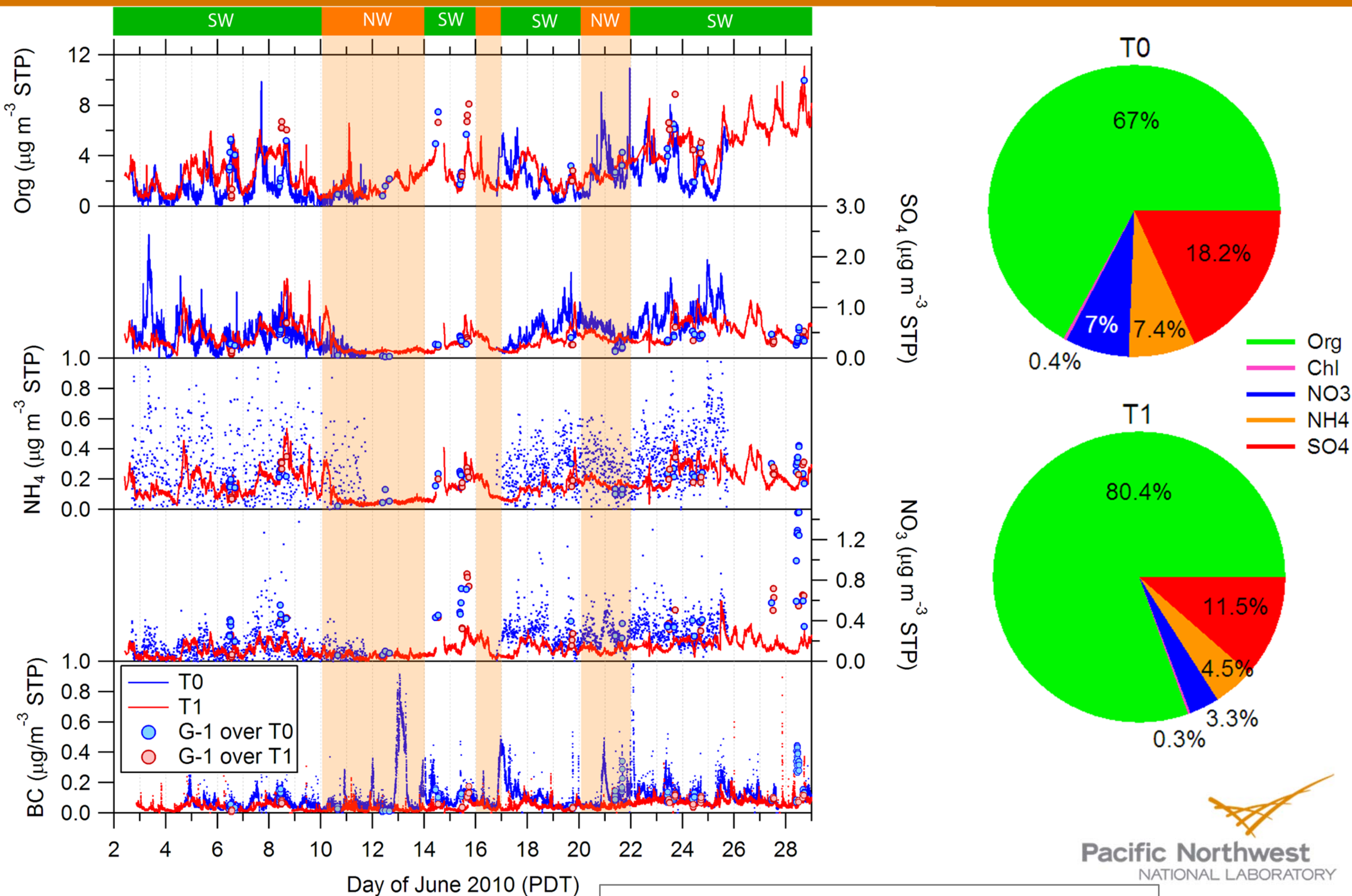
Aerosol Composition at T0 and T1 with G-1 Overpasses



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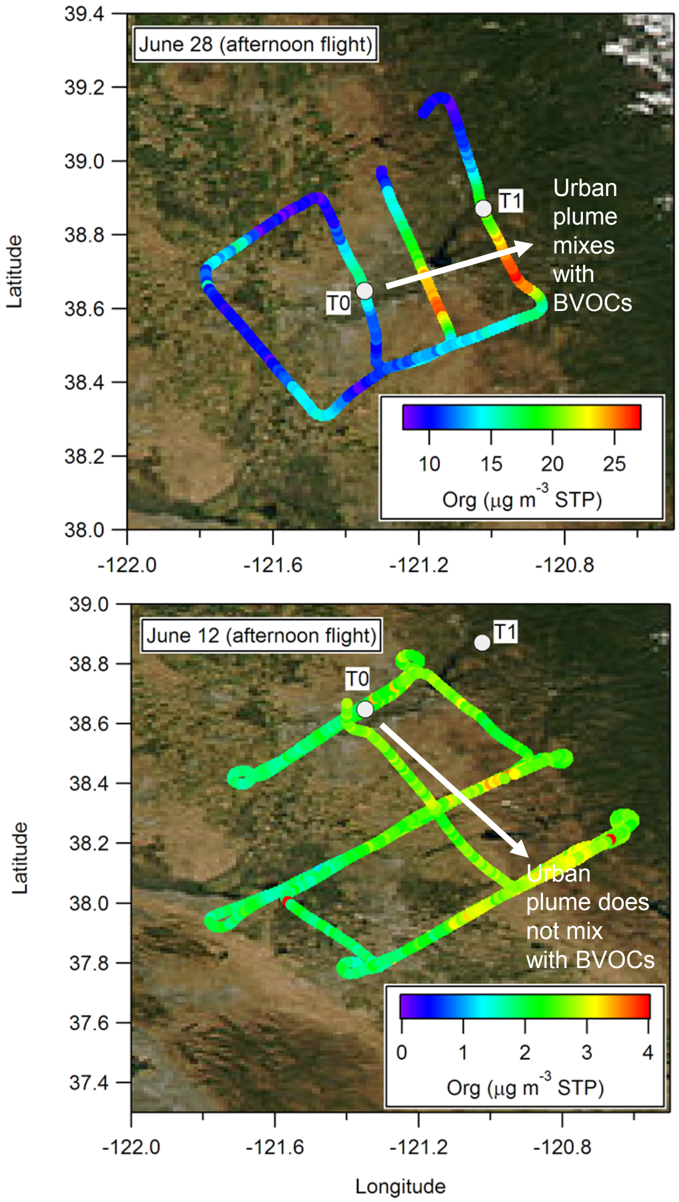
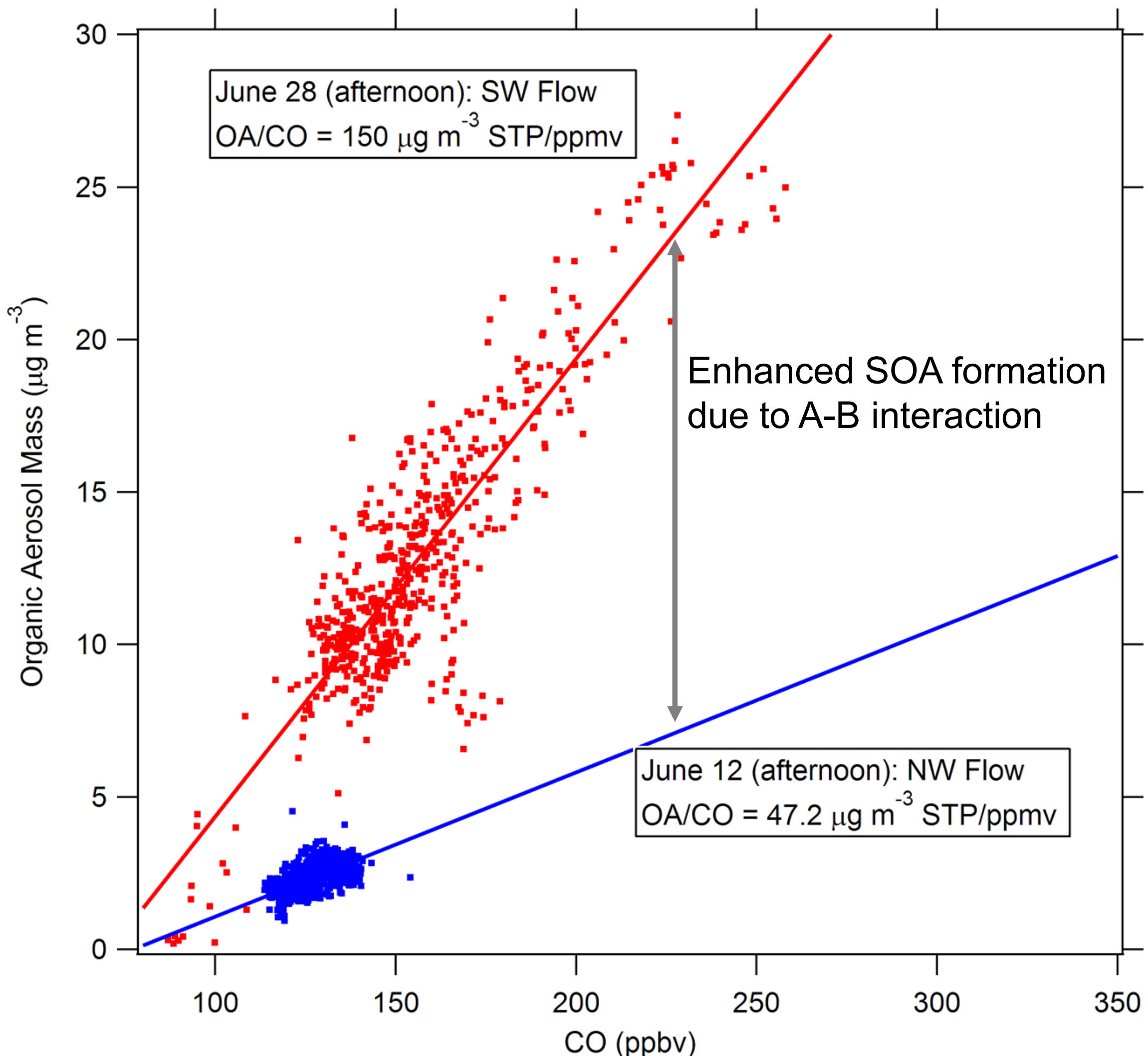
AMS data: J. Shilling, C. Song (PNNL), Q. Zhang (UC Davis)

Evidence for Enhanced SOA Formation from Anthropogenic-Biogenic Interactions: G-1 Data





Shilling et al., in prep.

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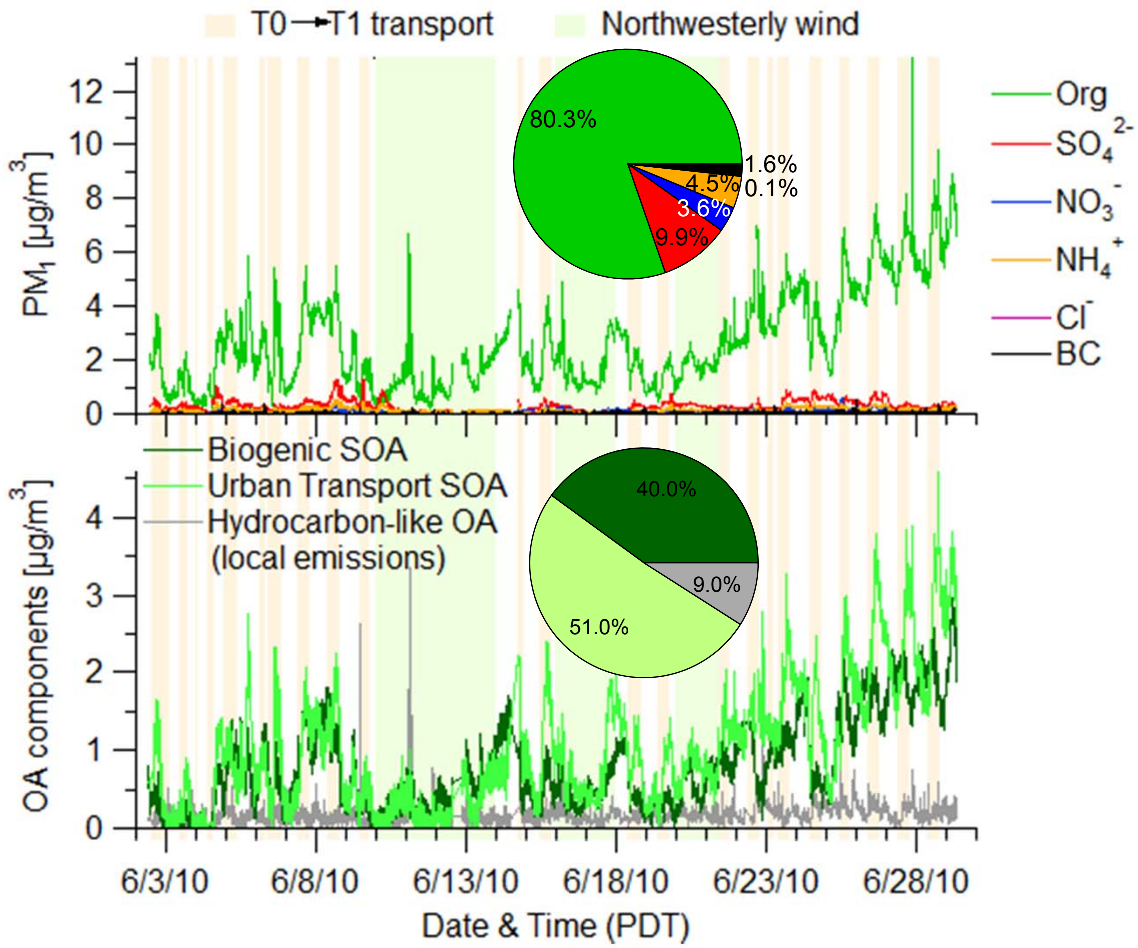
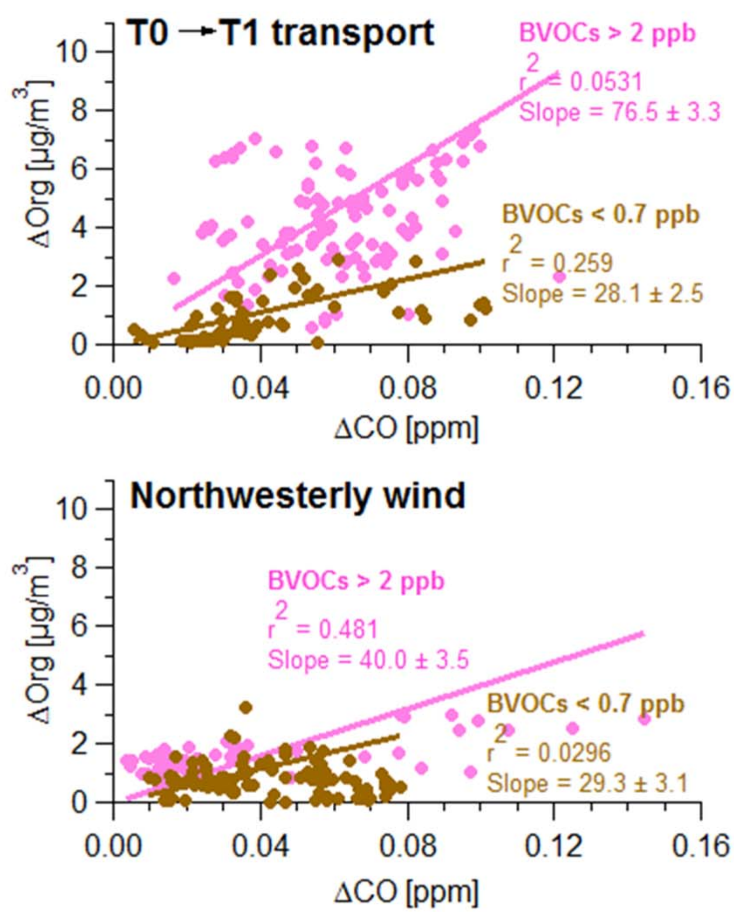
Evidence for Enhanced SOA Formation from Anthropogenic-Biogenic Interactions: T1 Site





Setyan, Zhang, et al., ACPD, 12, 5601-5658, 2012

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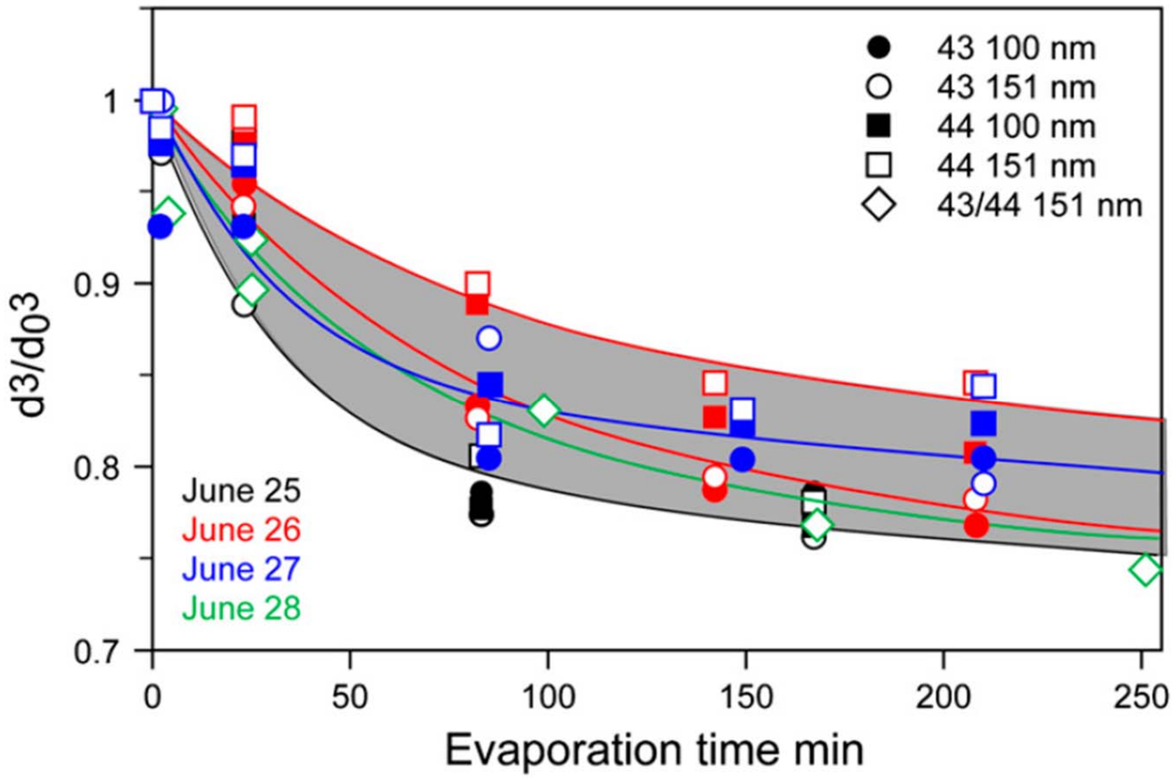
Evaporation Kinetics of Ambient SOA During CARES



Evaporation of ambient SOA much slower than expected by previous models

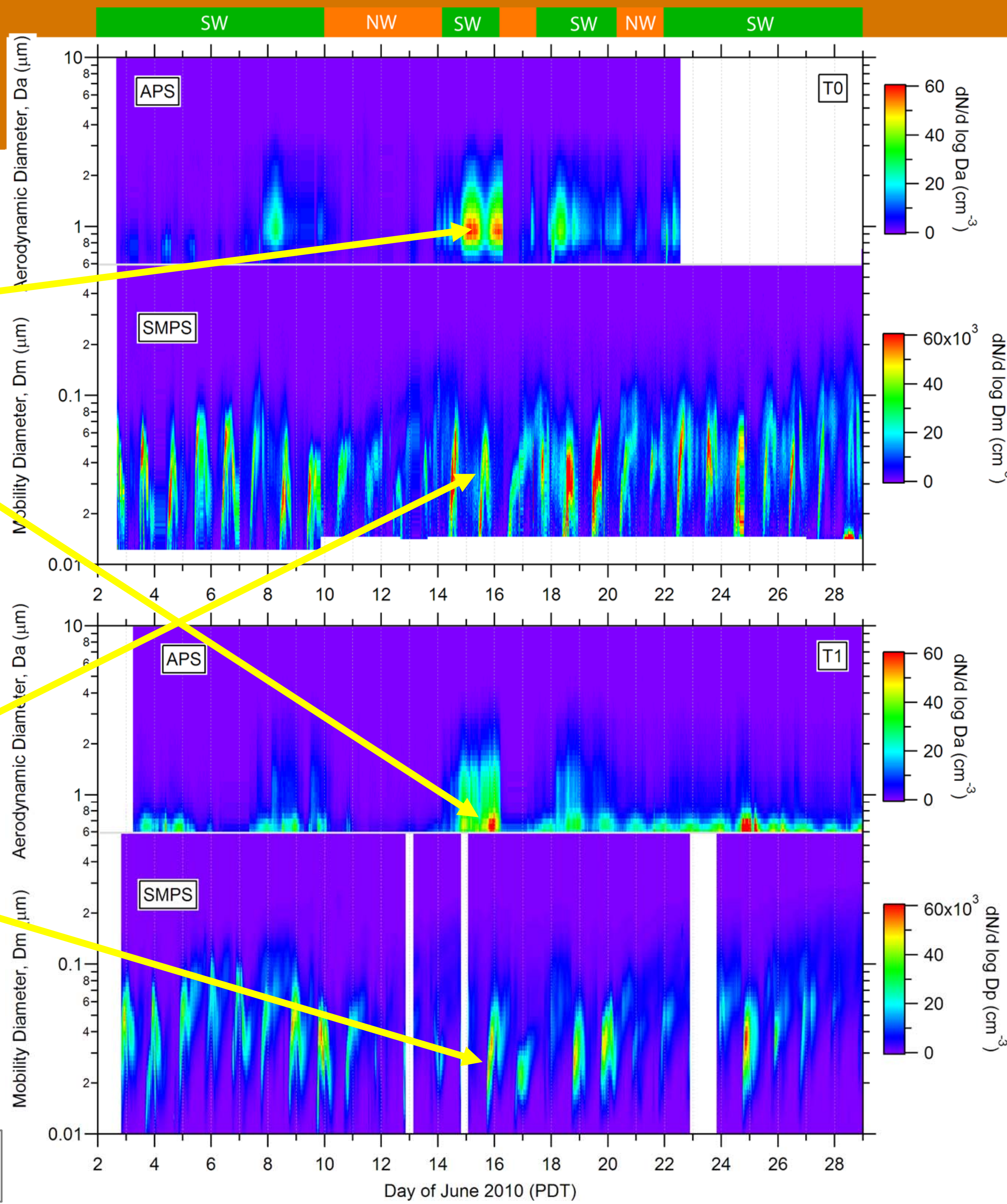
Evaporation kinetics appears to be consistent with semi-solid/glassy particles instead of liquid.

Vaden, Imre, Beranek, Shrivastava, Zelenyuk (2011) PNAS.

Size Distributions at T0 and T1

Coarse Particles

Ultrafine Particles & Growth

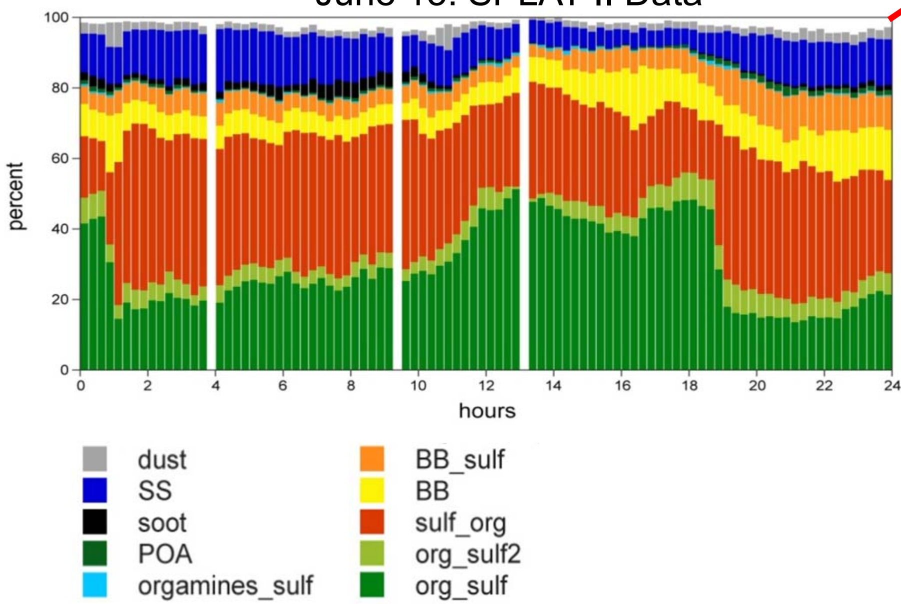


SMPS data: C. Song (PNNL), Q. Zhang (UC Davis)
APS data: T. Jobson (WSU), M. Pekour (PNNL)

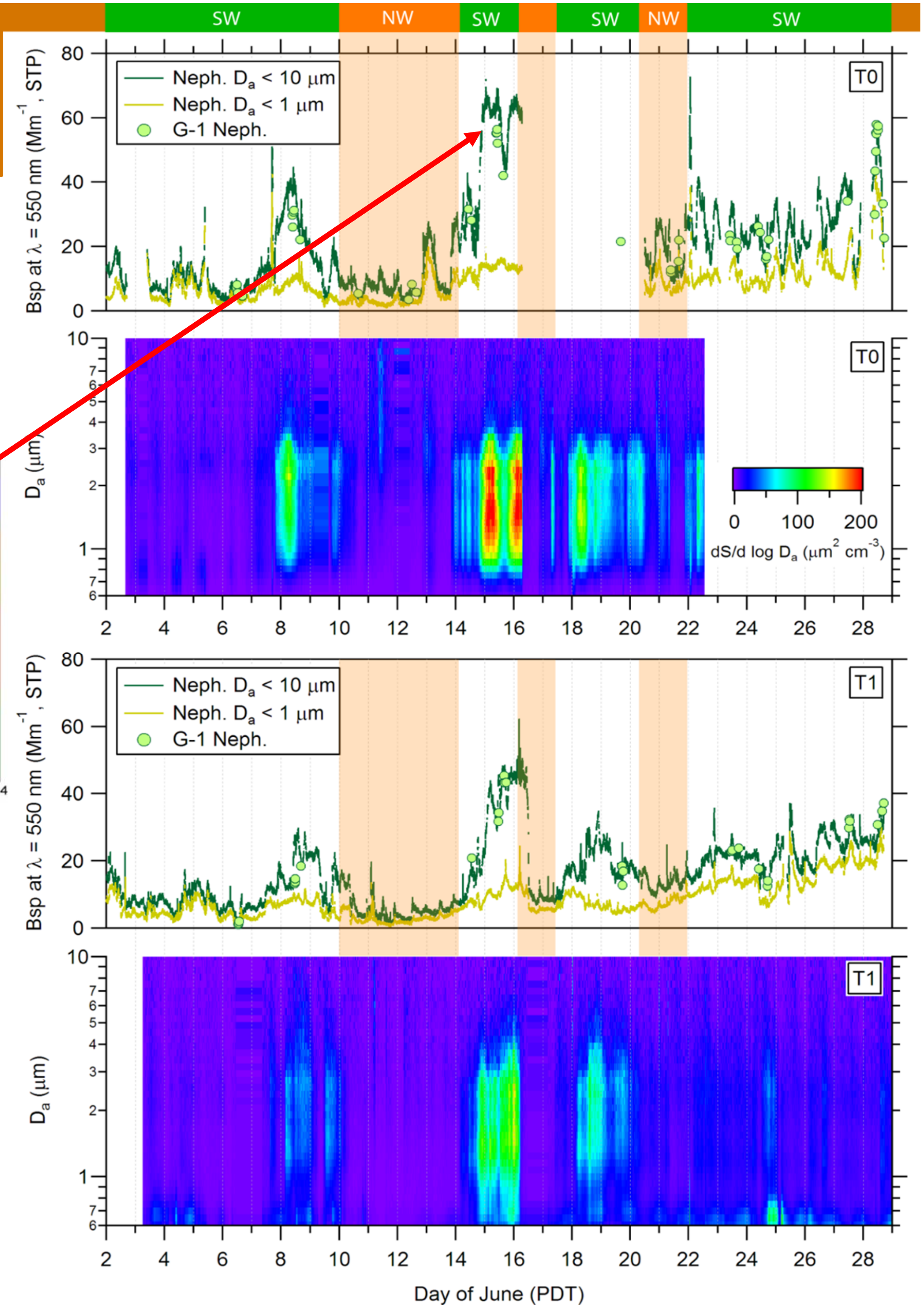
Scattering at T0 and T1 with G-1 Overpasses

- Significant scattering due to super-micron size sea salt particles observed at both sites

June 15: SPLAT II Data

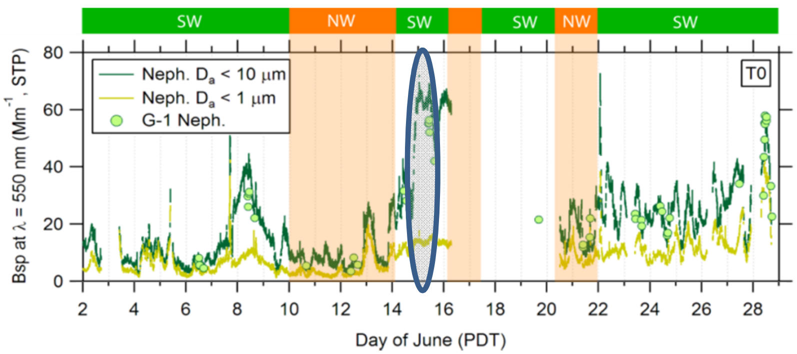


SPLAT II data: A. Zelenyuk, J. Beranek (PNNL)

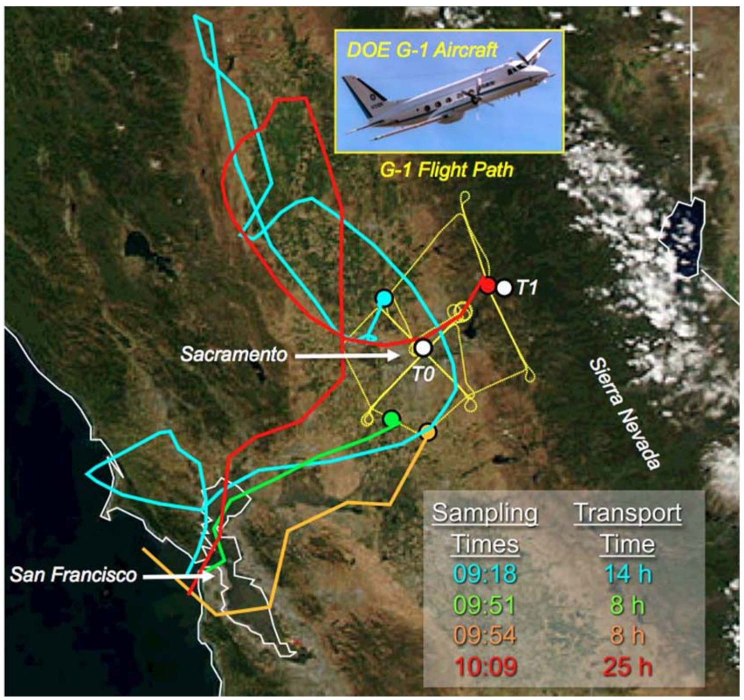


T0/T1 Nephelometer data: M. Pekour (PNNL)
G-1 Nephelometer data: S. Springston (BNL)

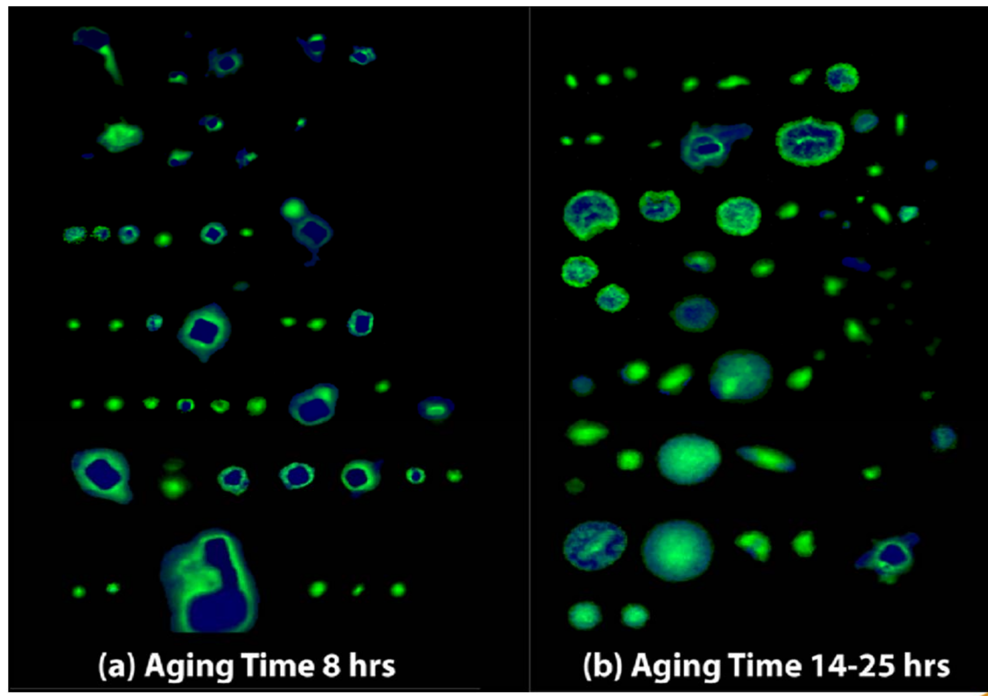
Ageing of Sea Salt Aerosols by SOA Formation



(June 15th, G-1 morning flight)



Spectro-microscopy analysis



A. Laskin, R.C. Moffet, M.K. Gilles, J.D. Fast, R.A. Zaveri, B. Wang, J. Shutthanandan. JGR, 2012, submitted.

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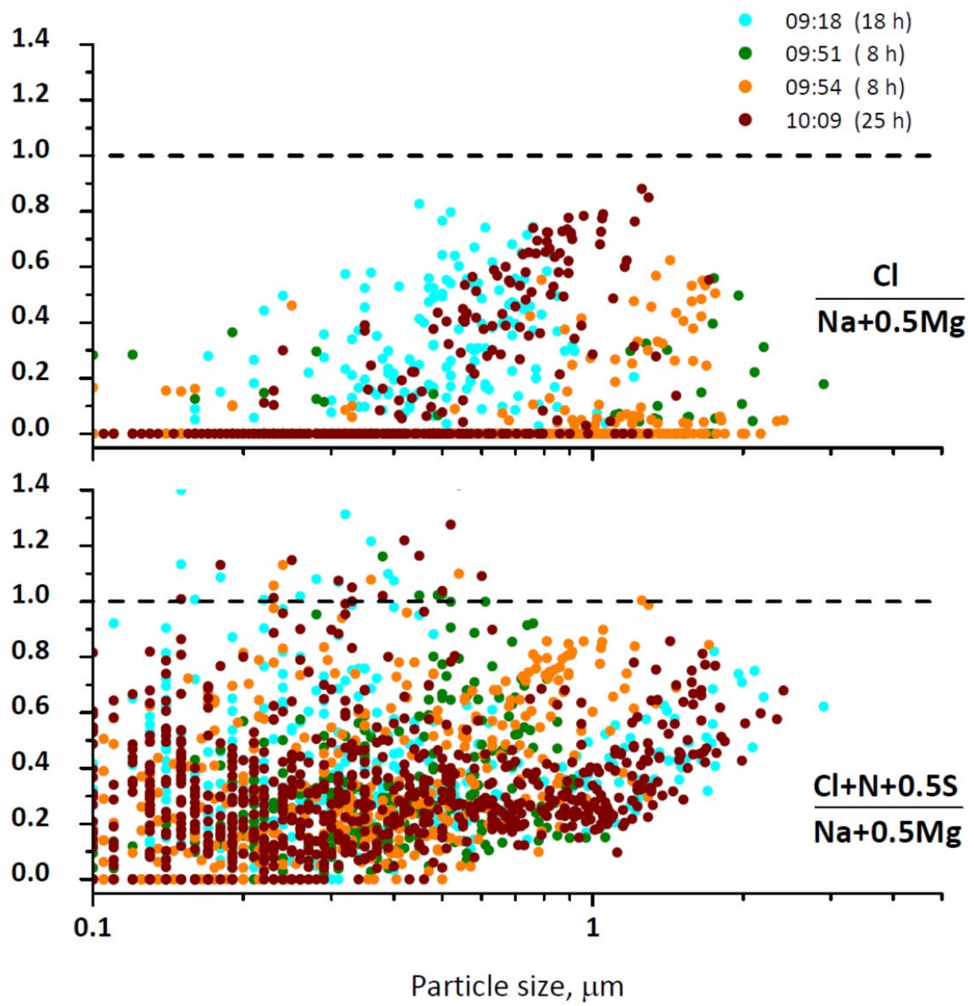
Surprising Sea Salt Chloride Displacement by Organic Acids



Mixed sea salt/organic particles result in formation of organic salts that can potentially modify their optical and CCN activation properties.

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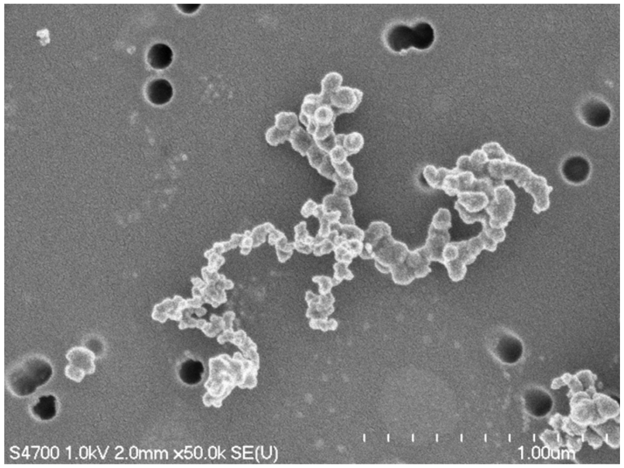
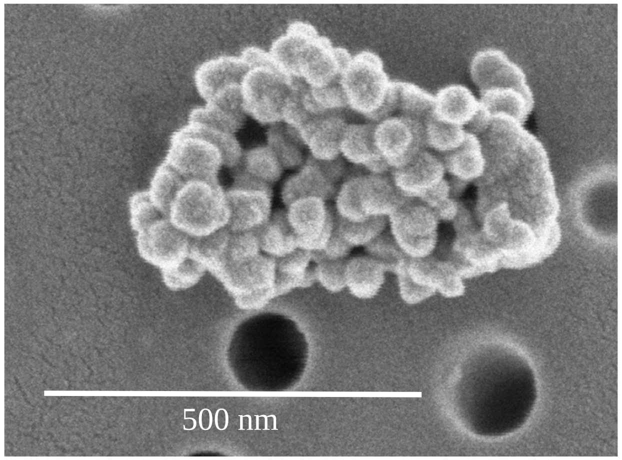
Black Carbon Ageing

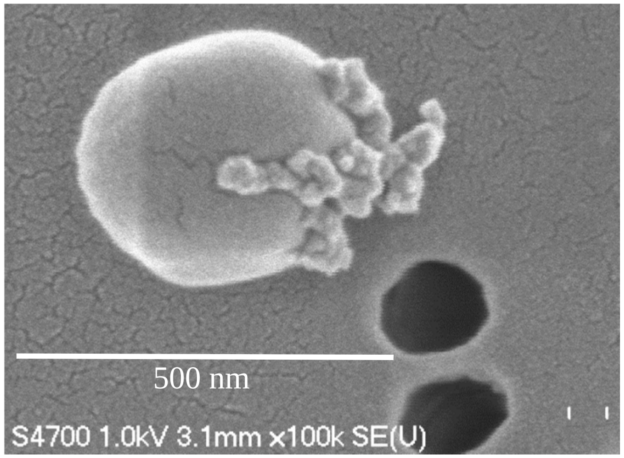
Freshly emitted fractal-like BC particle



Compacted BC particle due to condensation



Particle with BC inclusion



SEM data: C. Mazzoleni, K. Gorkowski (MTU)

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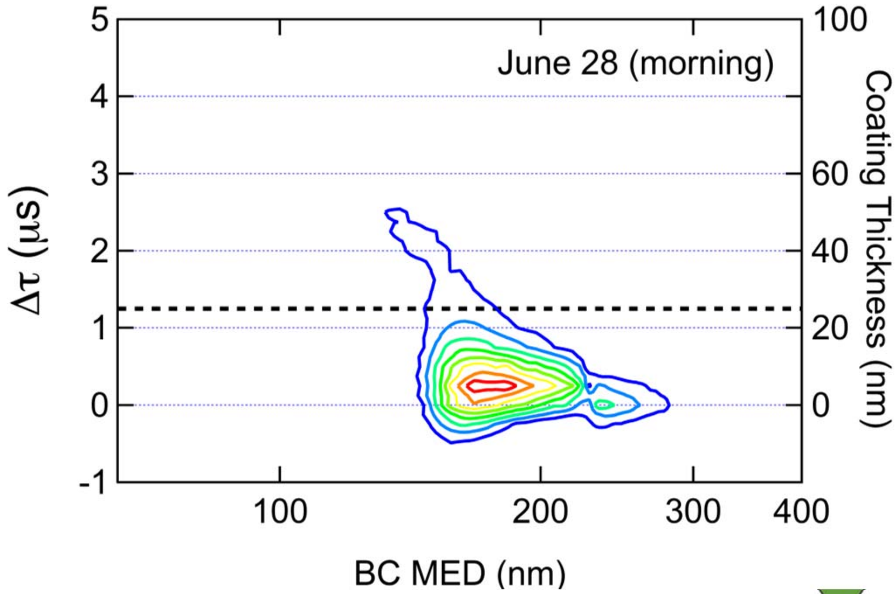
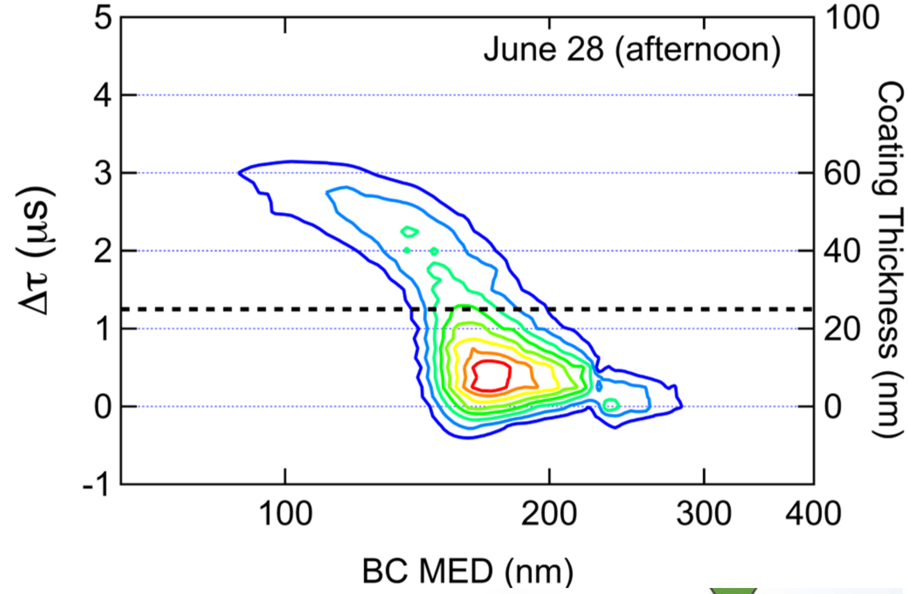
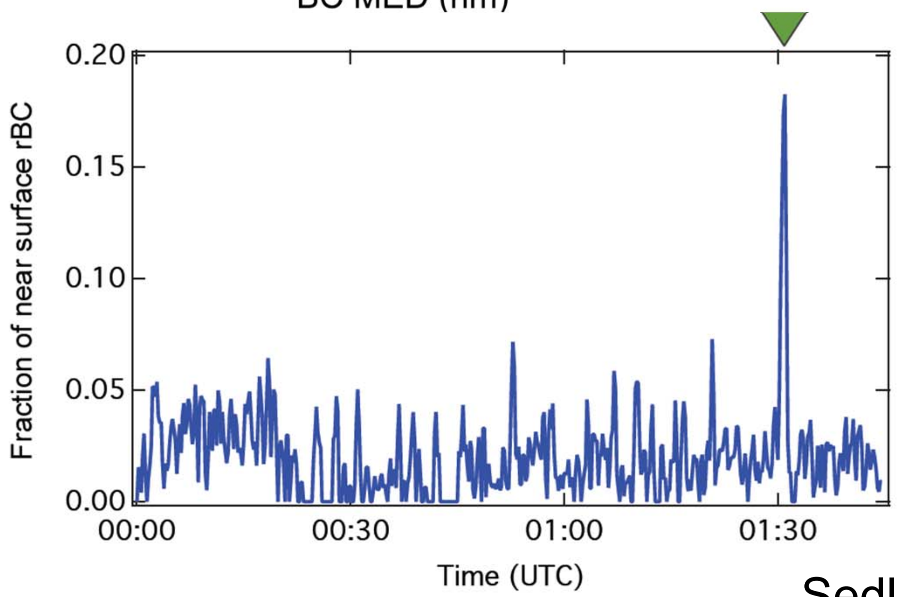
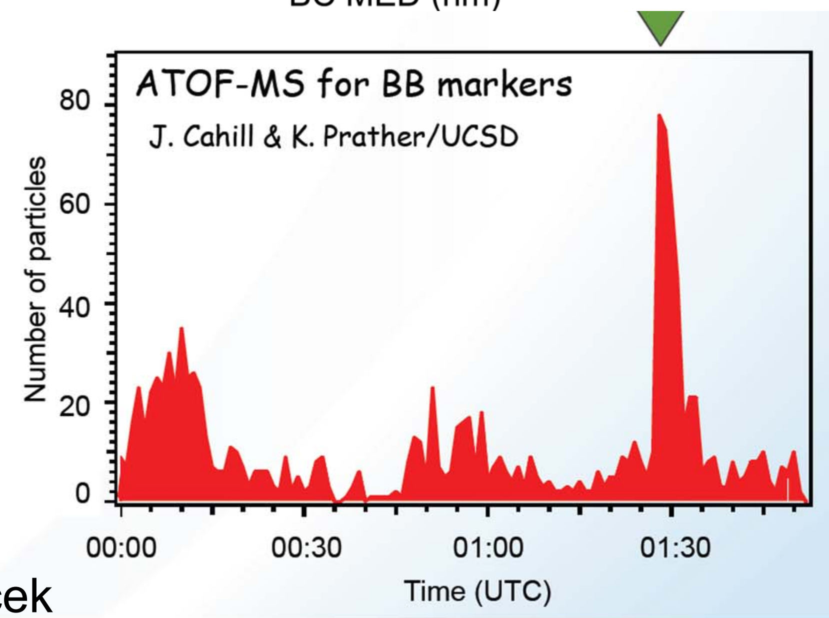
Black Carbon Coating and Morphology with SP2



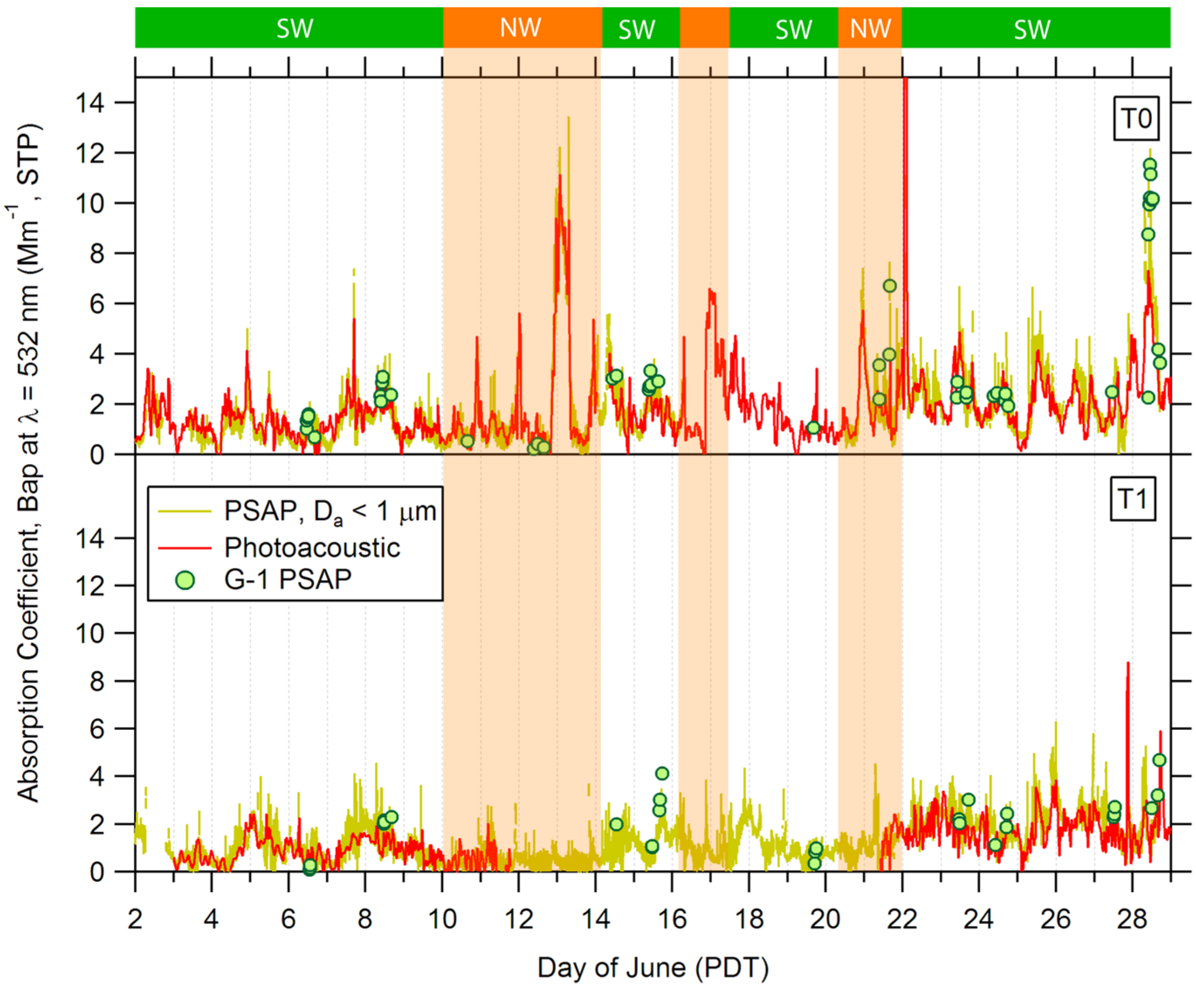


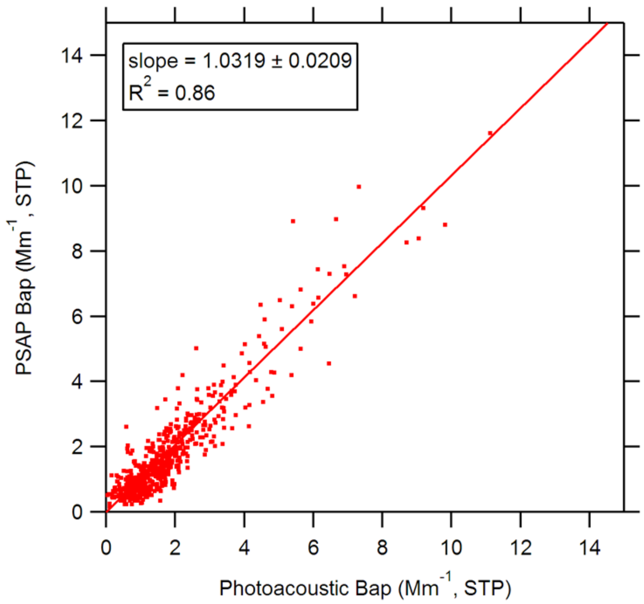




Sedlacek

Absorption at T0 and T1 with G-1 Overpasses





Excellent agreement found between PSAP and PAS absorption

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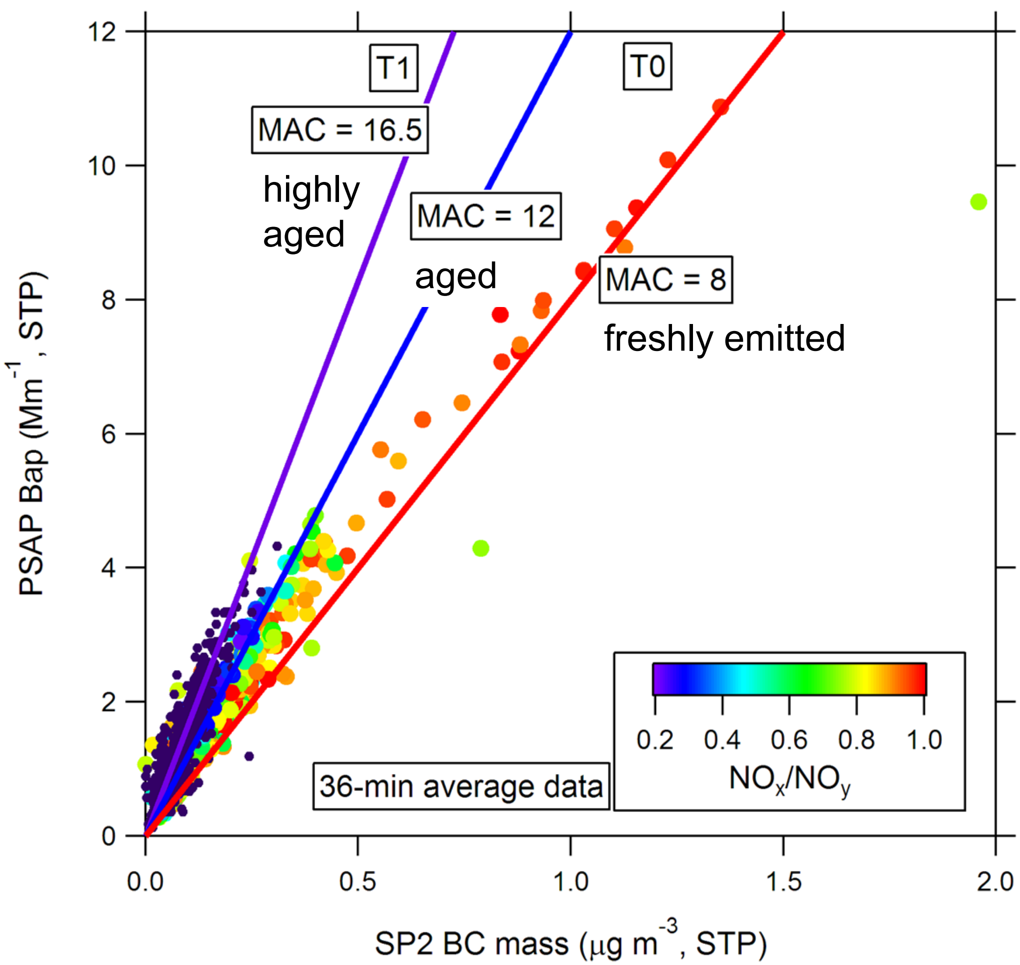
BC Light Absorption Enhancement with Ageing

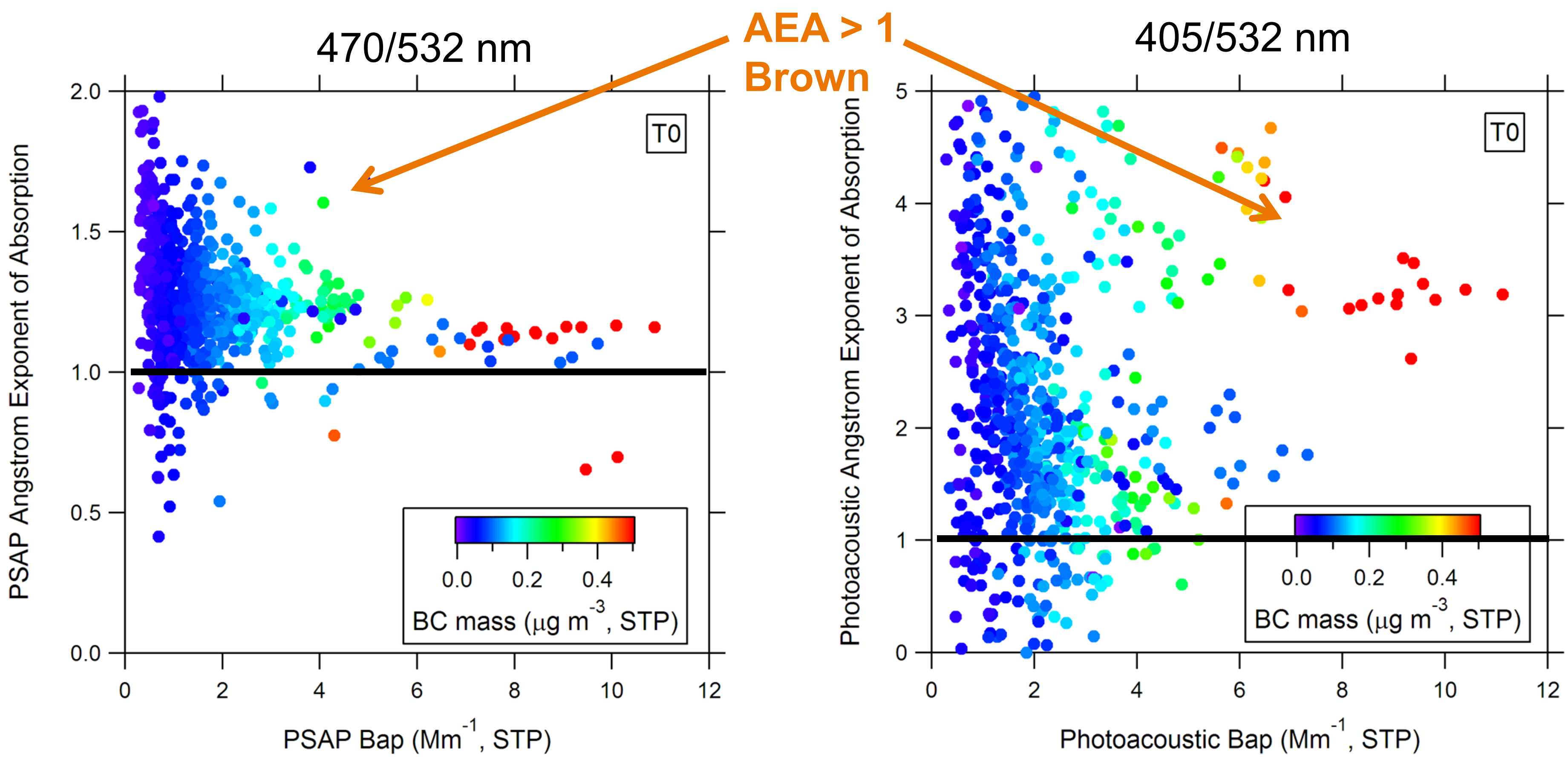


λ = 532 nm

BC MAC increases by up to a factor of 2 with ageing.

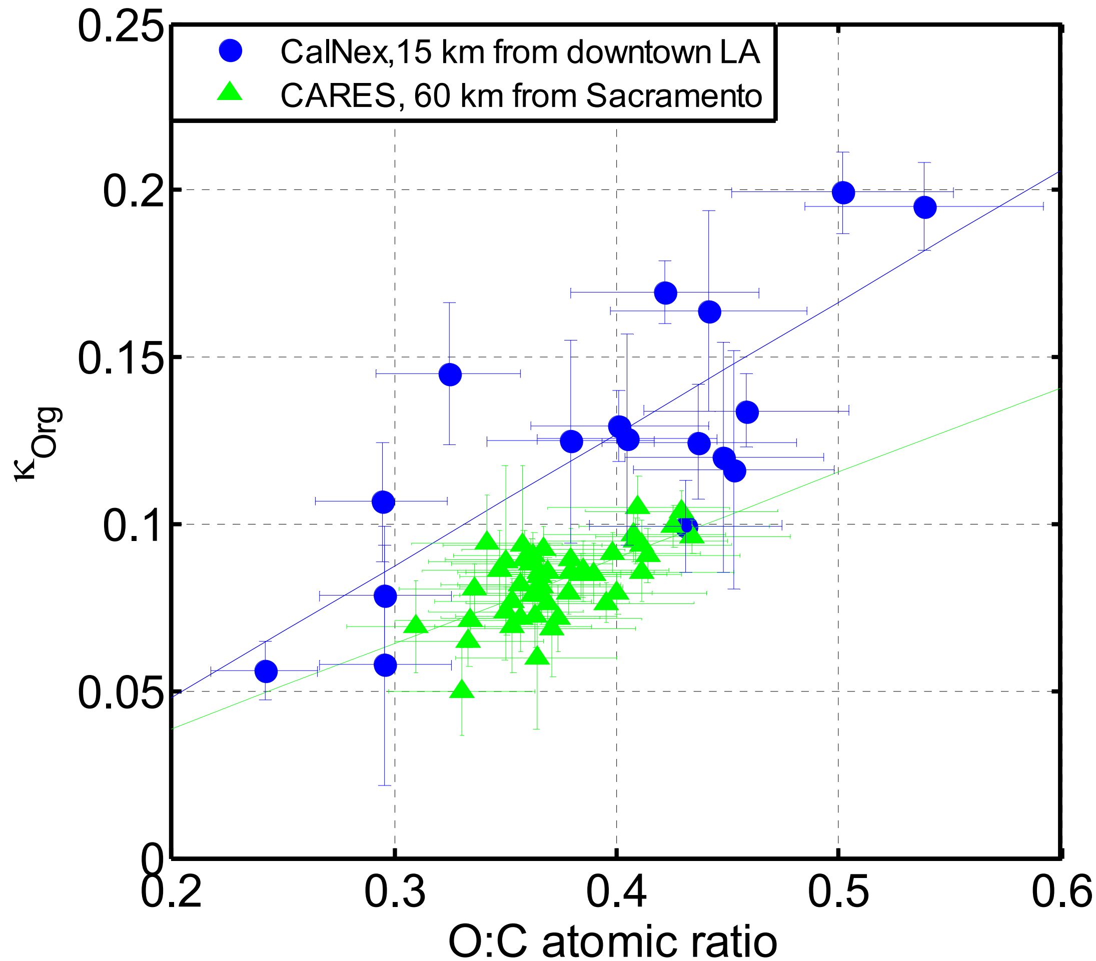
SP2 data: R. Subramanian (DMT)
PSAP data: M. Pekour, D. Chand (PNNL)

Evidence for Brown Carbon



PSAP data: M. Pekour, D. Chand (PNNL)
PAS data: W.P. Arnott, M. Gyawali (UNR)

Organic Aerosol Hygroscopicity



κ_{Org} = (0.40 ±0.08)*(O:C) -(0.03 ±0.03)

R^2=0.79

κ_{Org} = (0.26±0.05)*(O:C) -(0.01 ± 0.02)

R^2=0.64

Fan, Jimenez, Zhang, Wang et al.

Summary of Initial Results from CARES

- Aerosol Ageing
  - Significantly enhanced SOA formation due to A-B interactions.
  - SOA evaporated much more slowly than expected by previous models.
  - Observed SOA/organic acid formation in sea-salt particles, displacing chloride.
  - Aitken mode particles grew rapidly in the morning due to SOA formation.
  - Observed fully and partially-coated BC particles using SP2.
- Optical Properties
  - Significant scattering due to supermicron particles (sea-salt).
  - BC MAC increased by up to a factor of 2 in highly aged urban air.
  - Found evidence of brown carbon, especially in background air; some of it may be SOA.
- CCN Activation Properties
  - kappa values were higher and depended more strongly on O:C ratio in urban SOA than in biogenically influenced SOA.

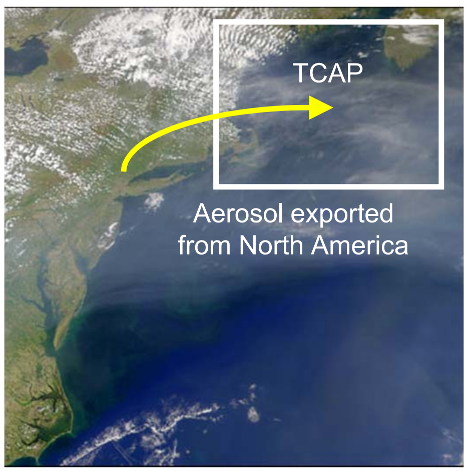
Further CARES Analyses and Papers

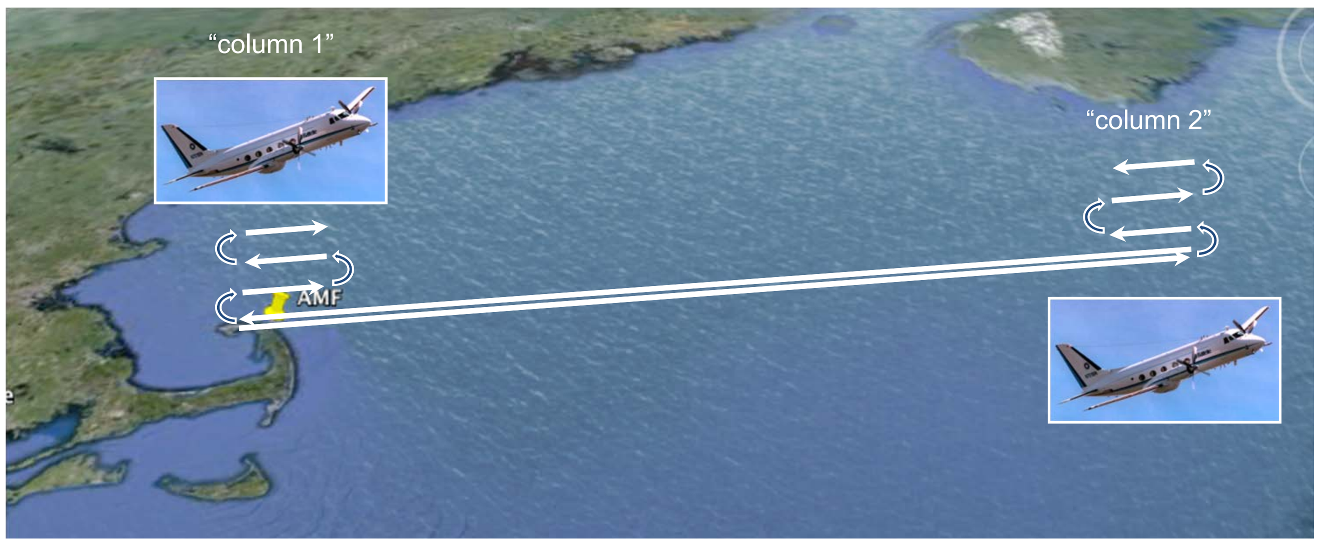
- Observational analyses
- Local optical closure using BC mixing state and morphology information
- Process modeling of SOA formation from A-B interactions
- Process modeling of BC mixing state evolution
- WRF-Chem modeling of regional-scale impacts using new and improved SOA and BC ageing process models

- ACP Special Issue for CARES (look under 2011)

Future Campaign

- 2012: TCAP
  - Aerosol ageing over longer periods
  - Effects of aerosol mixing state evolution on optical and CCN properties
  - Perform optical column closure





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Future Campaign

- 2014: GoAmazon
  - Anthropogenic-Biogenic Interactions leading to enhanced SOA formation, black carbon ageing, and altered CCN
  - Effects of emissions, secondary chemistry, cloud processing, and vertical transport on aerosol budget in the pristine forest
  - Increase in NPF from zero events in pristine forest due to pollution from Manaus.