

# ***Aerosol Physical and Chemical Properties Breakout Group (WG5)***

*Breakout Group Report  
18-May-2007 2:30-5:00 pm*

*Co-Chairs:*

*Spyros Pandis, John Jayne, Jose-Luis Jimenez, Bety  
Cardenas, Elizabeth Vega,*

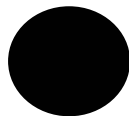
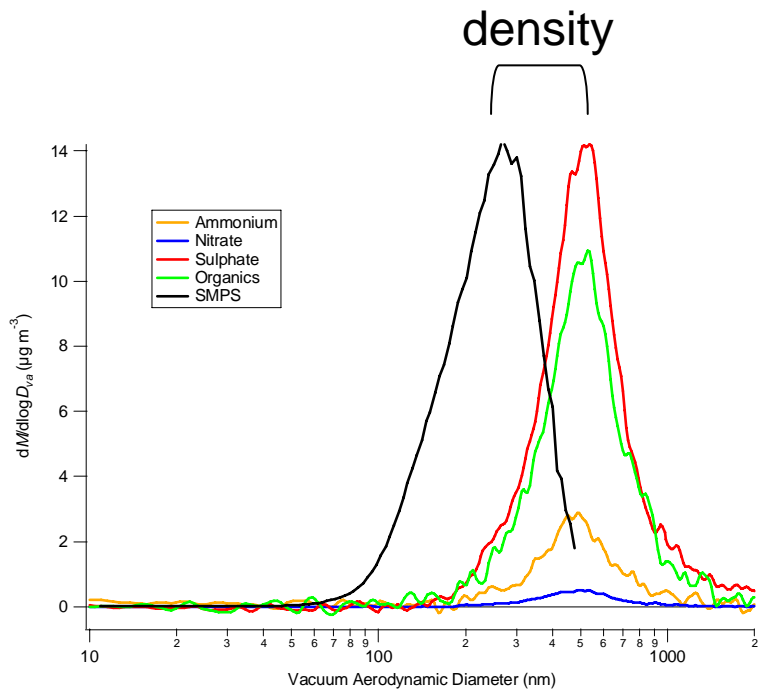
# Summary of Breakout Group

- Format: People volunteered or where invited to present a few slides per topic, followed by open discussion
  - Will update the list of papers offline via email
  - Many key participants are not here (McMurry, Clarke, D Collins, J Smith...)
- Topics that we discussed
  - **Physical properties**
    - Shape, Mixing, hygroscopicity, CCN – *J Jayne, T Nenes, R Moffet*
  - **Chemical properties**
    - Ammonium nitrate – *J Jayne*
    - Reactions on dust and NaCl – *S Pandis*
    - Metals – *R Moffet*
    - Sulfate – *P DeCarlo*
  - **Organics**
    - Biomass burning (urban and wildfires) – *J Jimenez*
    - SOA formation
    - Other sources (POA, regional)
  - **Models** – *J Fast*
  - We left out: Emissions / Sources (3), Evolution of properties (9), New Particle Formation (5), Satellites (0), Health effects (6)

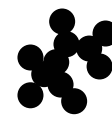
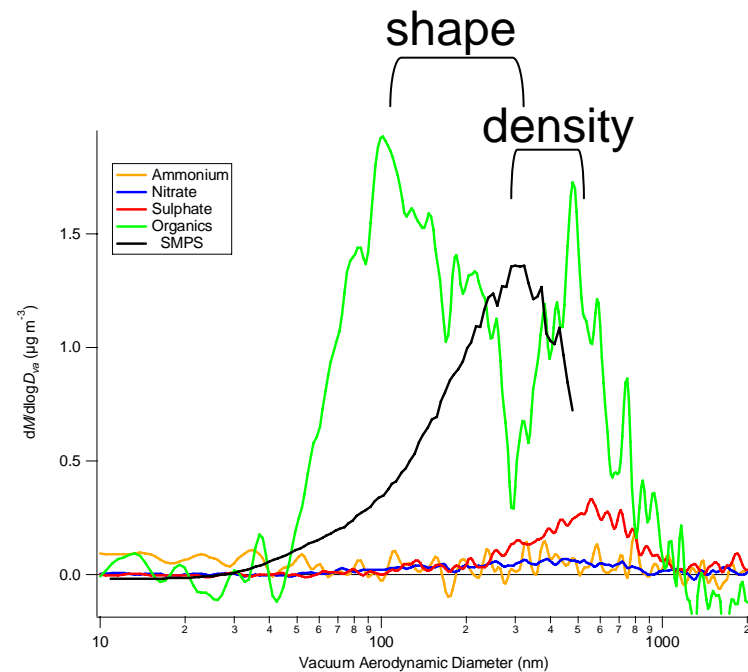
# *Aerosol Shape & Mixing State*

- Fractal particles (soot) are very important in the morning (*J Jayne and others*)
  - SMPS overestimates particle volume and skews size distribution
  - Fractal particles are rapidly coated by secondary species
  - Would cause changes in the response of BC absorption-based instruments

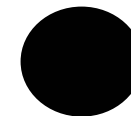
# Ambient Mass Distributions



**Near-Spherical**



**Fractal-like**

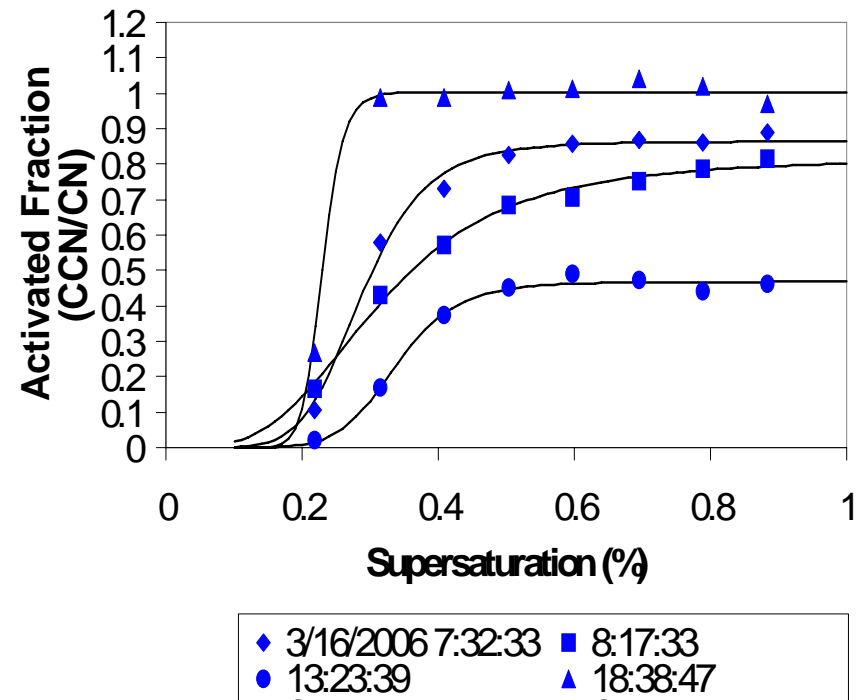


**Near-Spherical**

- Comparison of SMPS and AMS measurements separates the fresh fractal-like soot from accumulation mode aerosols

# Aerosol Water Uptake (CCN)

- CCN measurements (*T Nenes et al*)
  - High degree of external mixing in the morning, 50% of particles don't activate at high S
  - Lessen throughout the day, consistent with condensation of secondary species
  - Inorganics dominate soluble fraction
  - Amount of H<sub>2</sub>O in Ambient particles is an important missing measurement



# *Aerosol Water Uptake (CCN) II*

- Organics contribute a little
  - Can derive effective properties from the measurements
  - Properties change a lot between T0 and T1, not quite consistent with the aerosol bulk composition being similar
    - Suggest analyzing T0 vs time of the day, likely afternoon at T0 is similar to T1
  - Discussion on how fast is change from external to internal mixing: CCN suggest ~10 hrs, chemical and aircraft data suggest 2-3 hrs
    - May be related to different definitions of mixing
- Kinetic effects due to organics appear to be important
  - Ongoing investigation, could have large impact on indirect effect

# *CCN Measurements: T0-T1 Contrasts*

Site	Integration Period	Average Organic Molecular Weight (g mol <sup>-1</sup> )	Average Organic Molar Volume <sup>a</sup> (cm <sup>3</sup> mol <sup>-1</sup> )
T0	12 hr day	404.16 ± 290.70	288.68 ± 207.65
T1	24 hr	129.06 ± 61.90	89.10 ± 61.51
T1	12 hr night	145.40 ± 41.53	103.86 ± 29.67
T1	12 hr day	121.36 ± 16.28	86.69 ± 11.63

<sup>a</sup> Assuming an average organic density of 1.4 g cm<sup>-3</sup> (Turpin and Lim, 2001)

T0: organic properties is highly variable (~2× larger than T1)

T1: organic properties are quite **constant** regardless of day – this suggests T1 expresses **large scale** (“background”) properties.

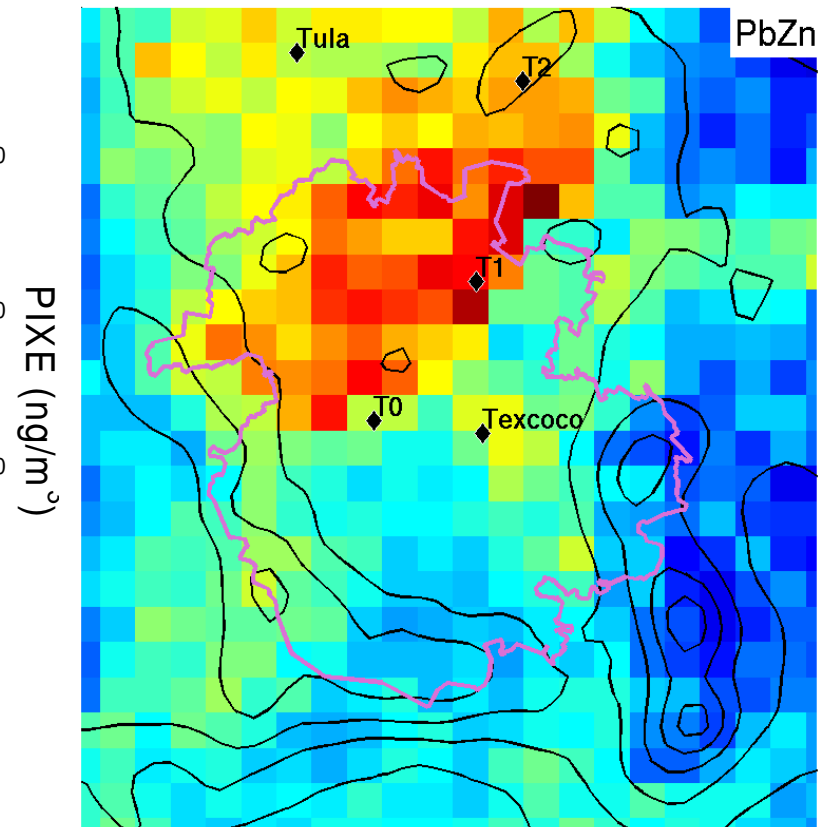
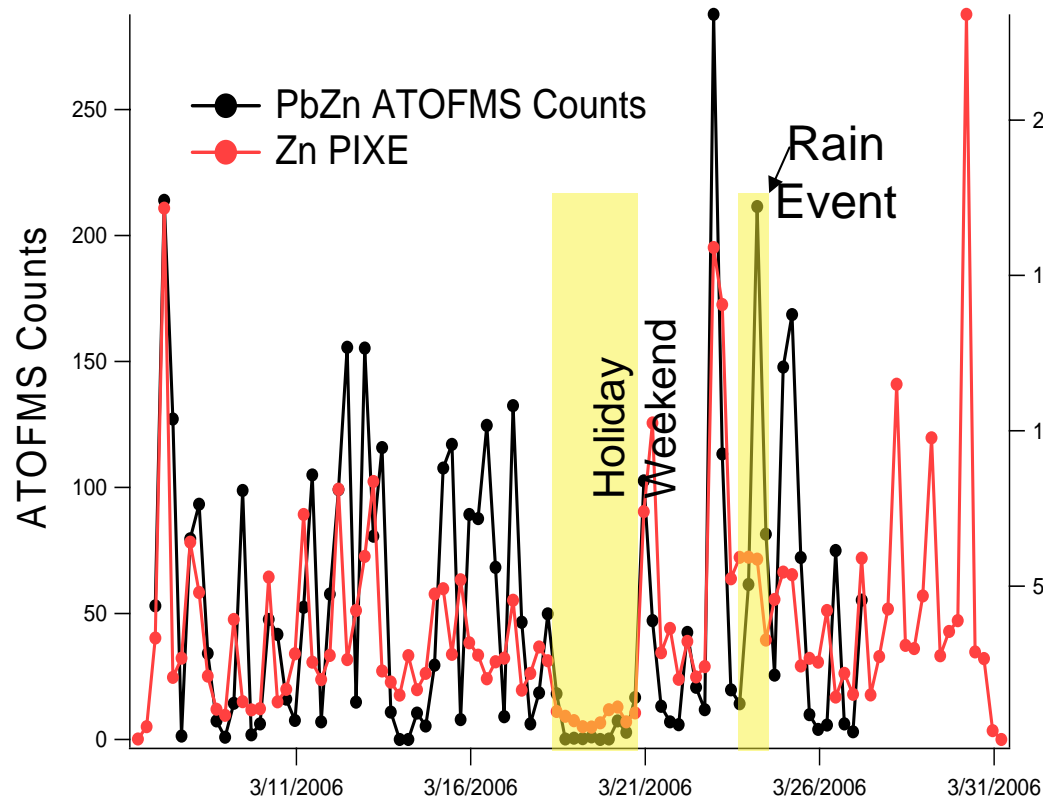
T1: Nighttime filters have larger MW than Daytime. Photochemical ageing increases the hygroscopicity

See Padró et al. poster for more information and details

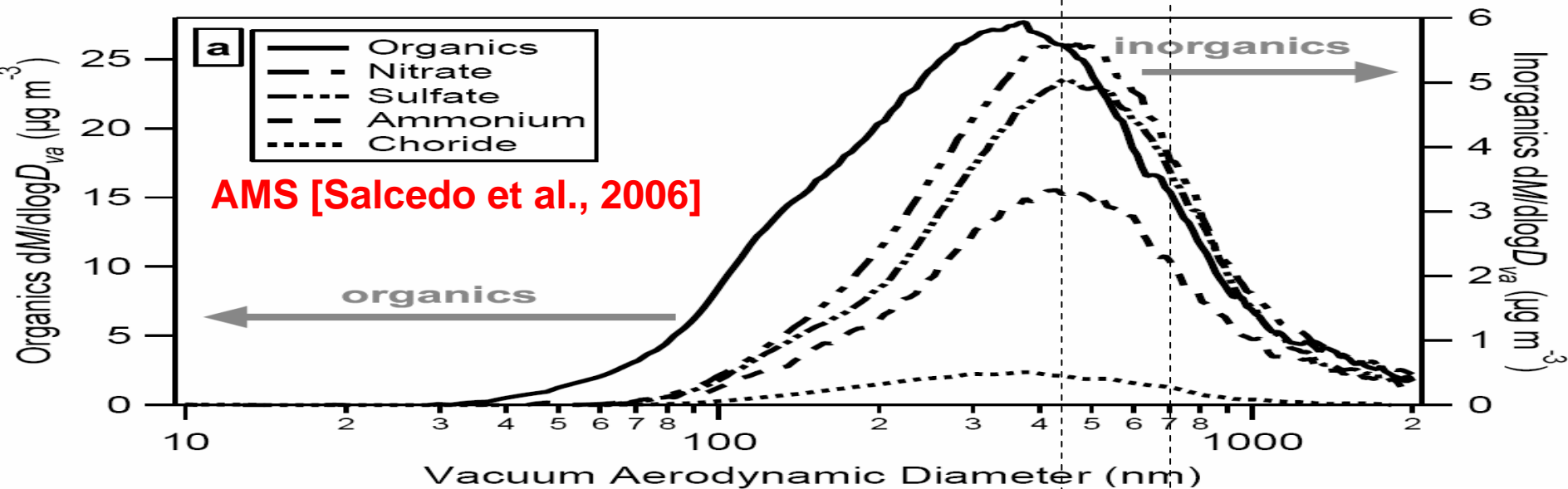
# *Metal Containing Particles*

- Several types of metal-containing particles identified at T0 with high time resolution (Moffet, Prather et al.)
  - Related to industry
  - Wealth of data from ATOFMS and PIXE

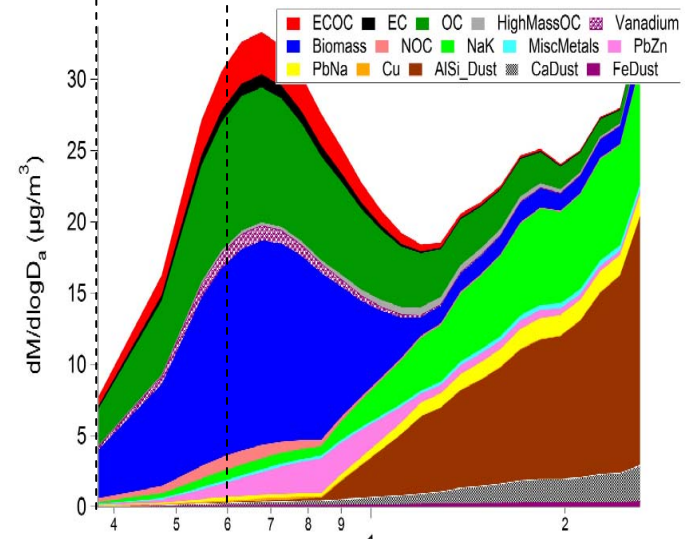
# Metal Containing Particles from Industry in North



# Size Distributions and Chemistry from Different Instruments



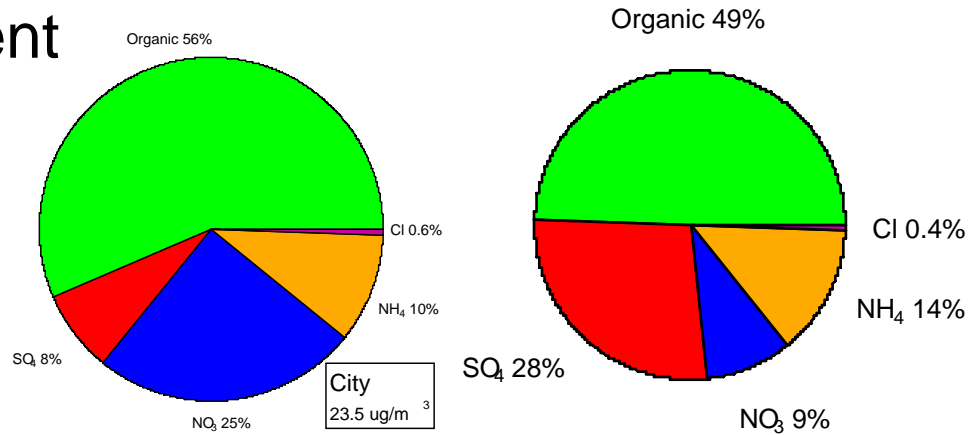
- Different instruments measure different size ranges and/or chemistry
  - Needs to be stated clearly by researchers and kept in mind by users of the data
- SMPS and APS don't seem to match well at T0



ATOFMS [Moffet et al., 2007]

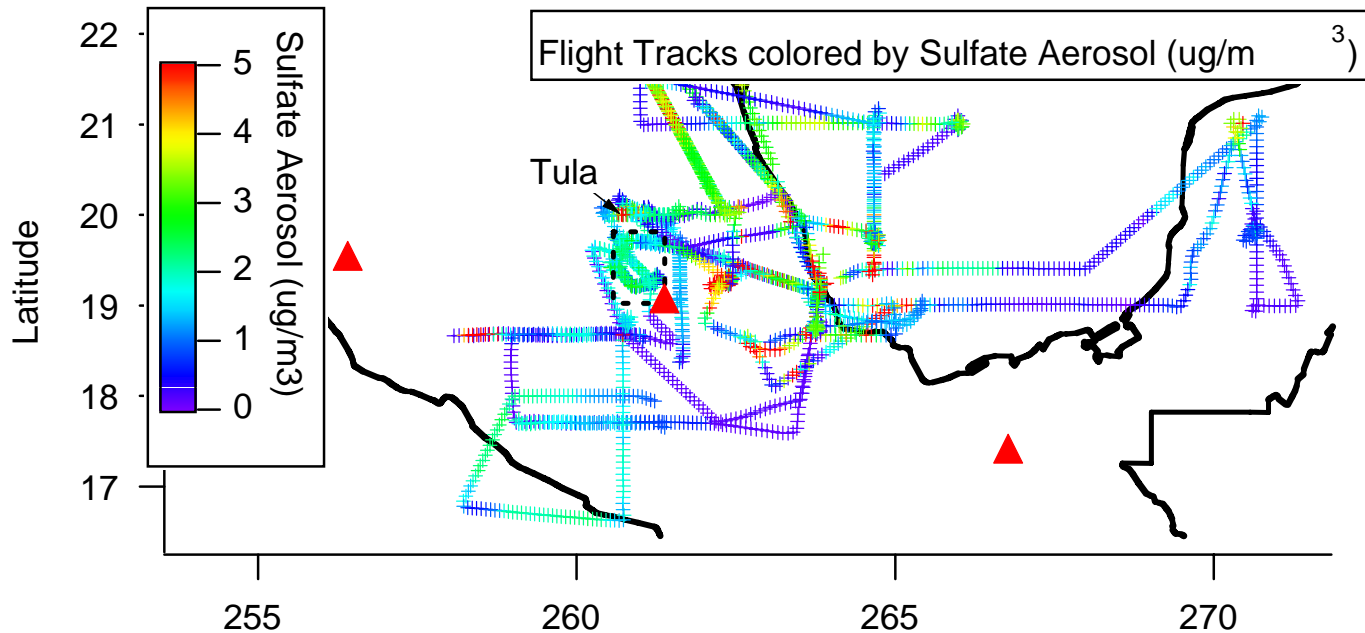
# Sulfate Aerosols

- Regional aerosol component
- Mostly large sources
  - Popo, Colima
  - Tula
  - Other refineries
- Larger scale influences?



Outside City  
5.8  $\mu\text{g}/\text{m}^3$

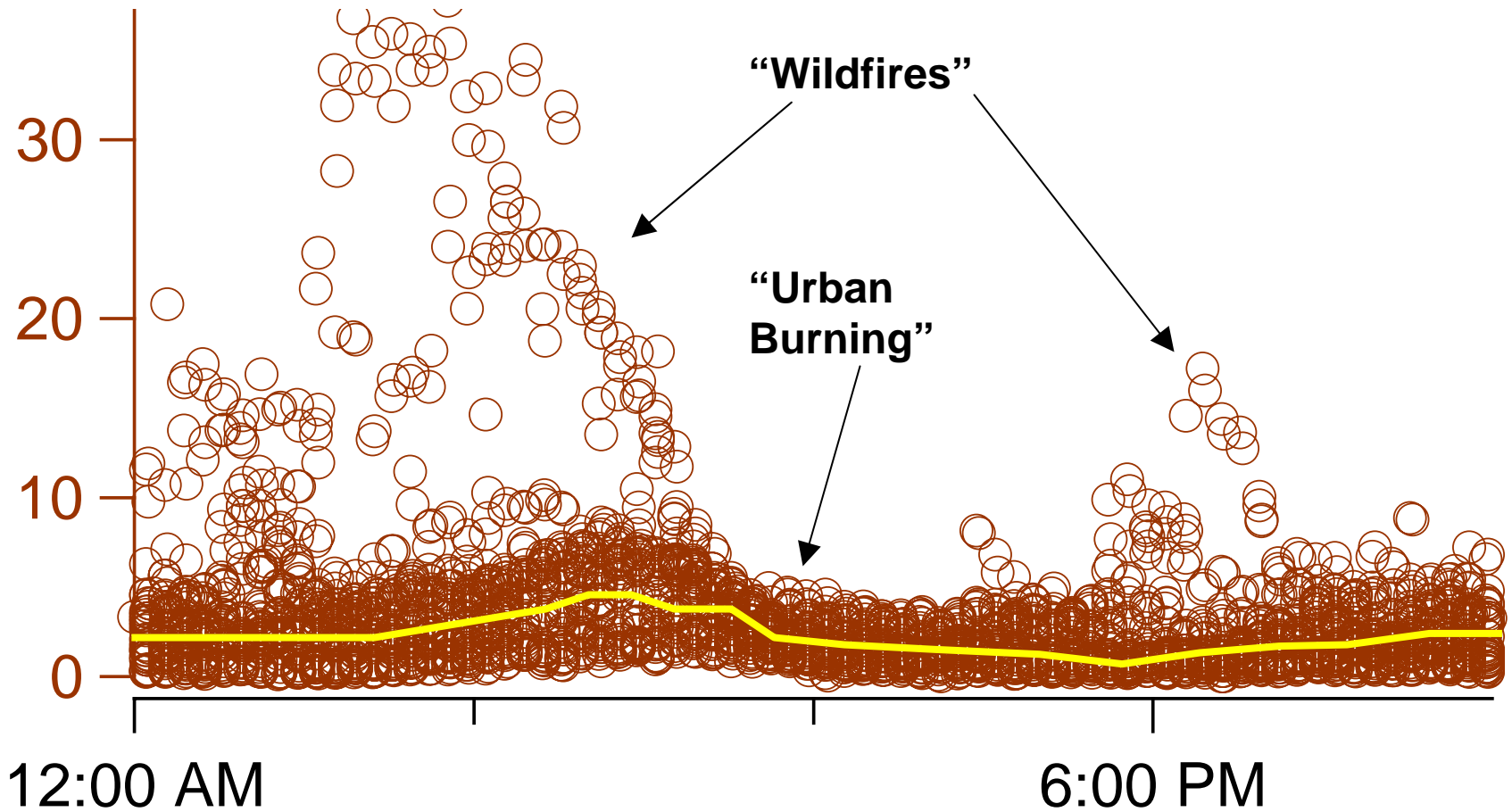
## C-130 Aerosol Sulfate



# *Biomass Burning Aerosols I*

- Pretty clear influence of two types of sources
  - Urban burning (Trash? Biofuels? Cooking?)
    - Peaks in the morning at ground, convolution of human activity and boundary layer
    - Relatively smooth: many smaller sources
    - Bottom-up quantification needed (e.g. Yokelson et al. study)
  - Wildfires / agricultural fires
    - Large plumes, large contribution when impacted
    - Sampled more often from aircraft than ground
    - Larger influence in outflow than city air quality

# *Impact of BB Aerosol to Ground I*



- Impacts are of the same order on the average
- Wildfires can make very large impacts at times

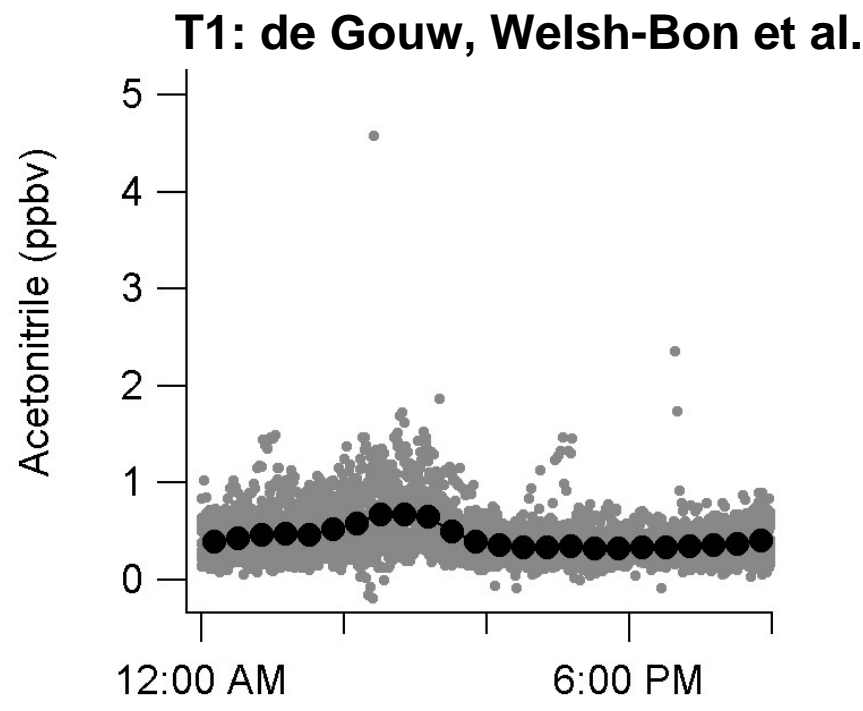
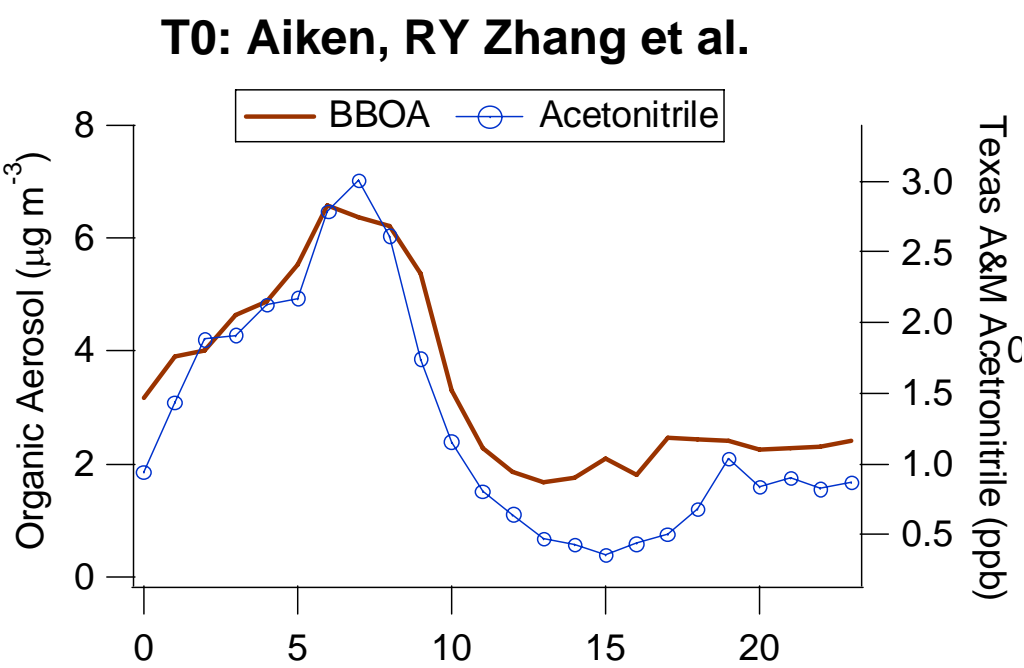
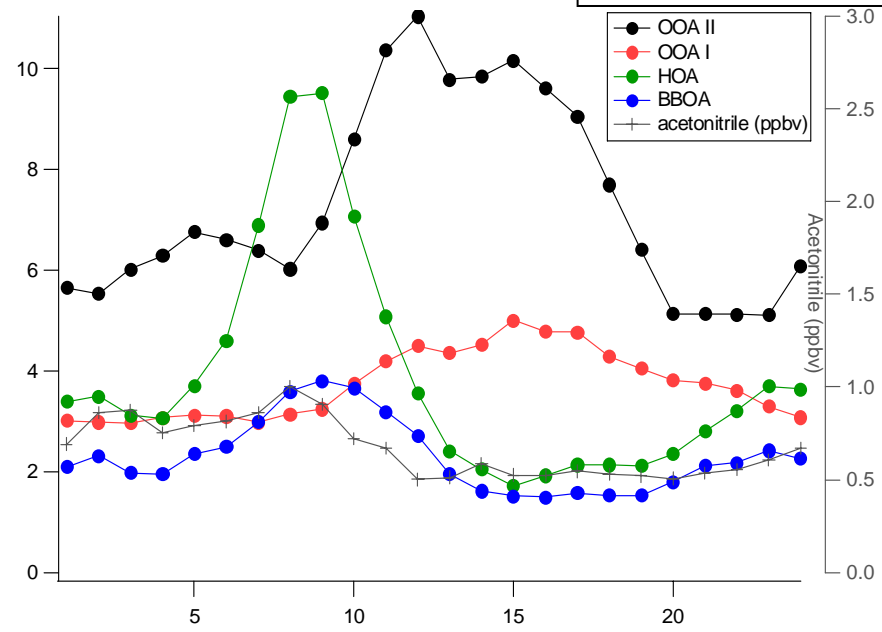
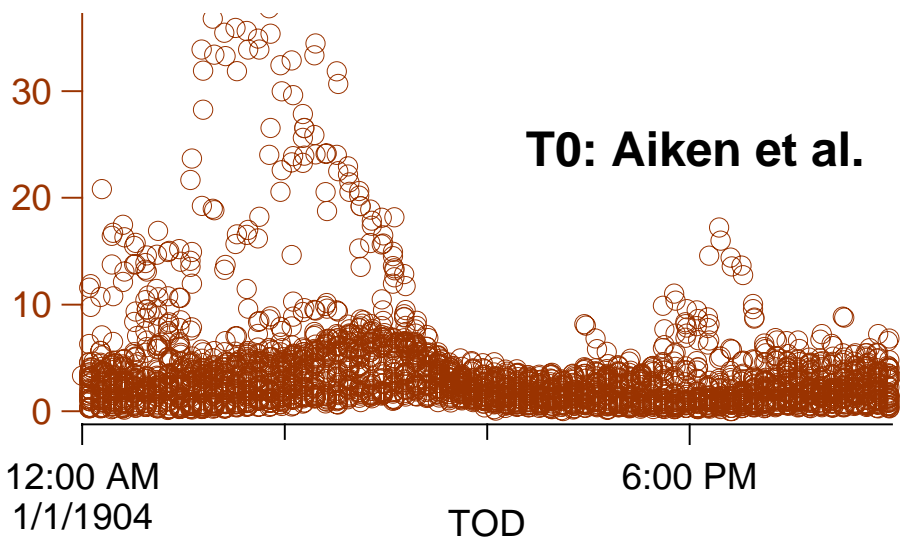
# *Impact of BB Aerosol to Ground II*

- Impact of BB to ground
  - Diurnal cycles of acetonitrile and AMS BBOA (“levoglucosan-like”) indicate dominant impact in the morning
    - Acetonitrile from vehicles?
  - ATOFMS and PIXE data suggest afternoon peak (K)

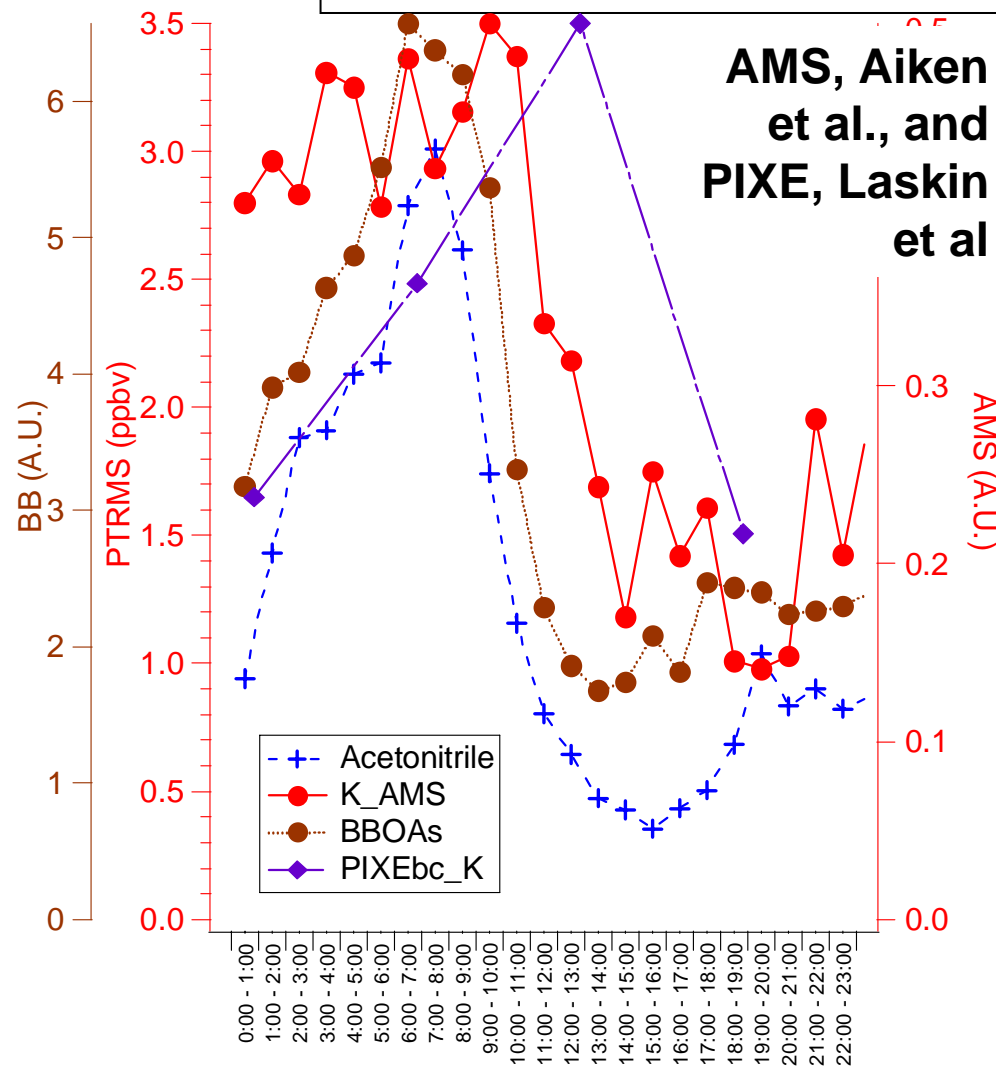
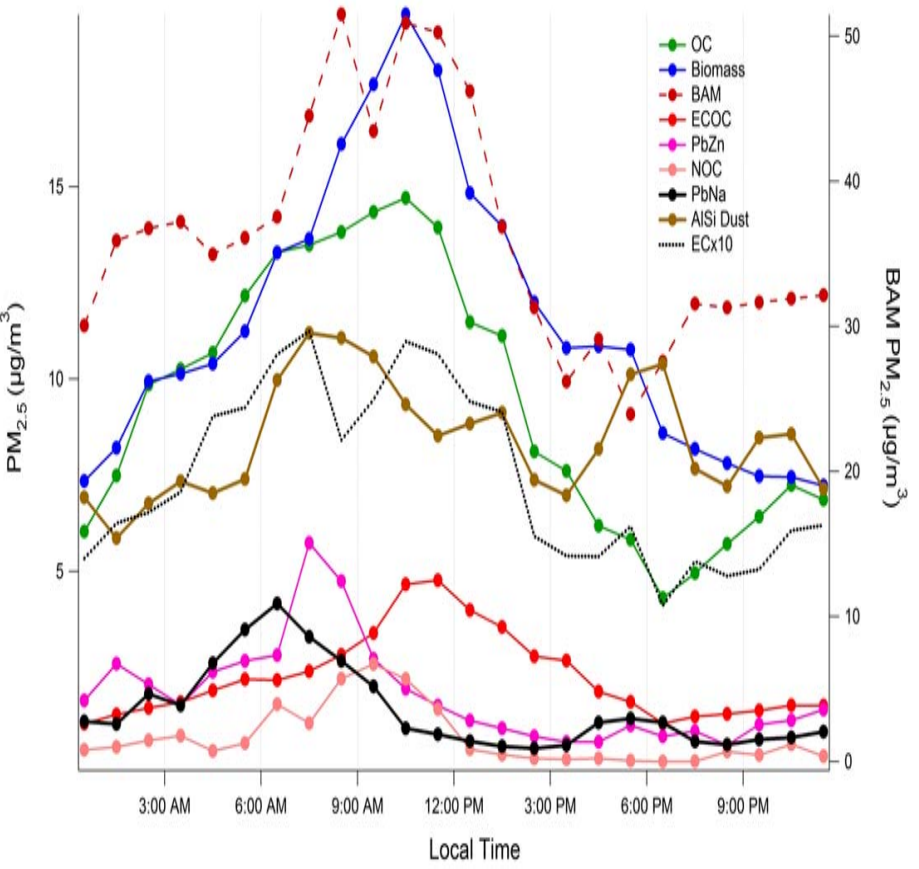
# Impact of BB Emissions at Ground Site

2003: CENICA Supersite

J Jimenez et al.



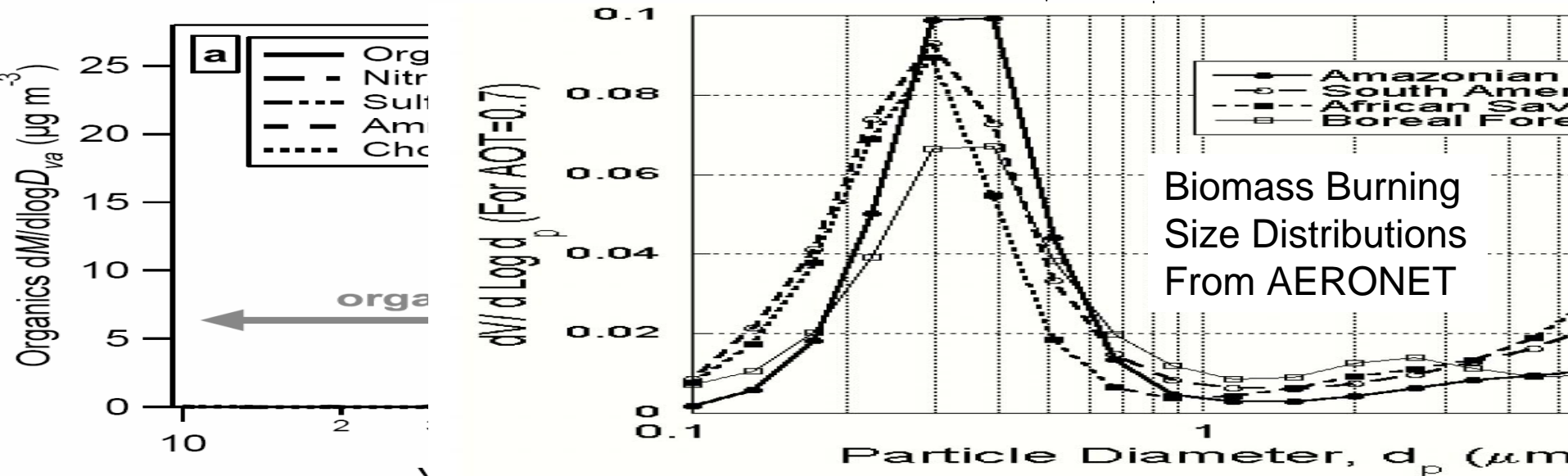
### ATOFMS: Moffet et al.



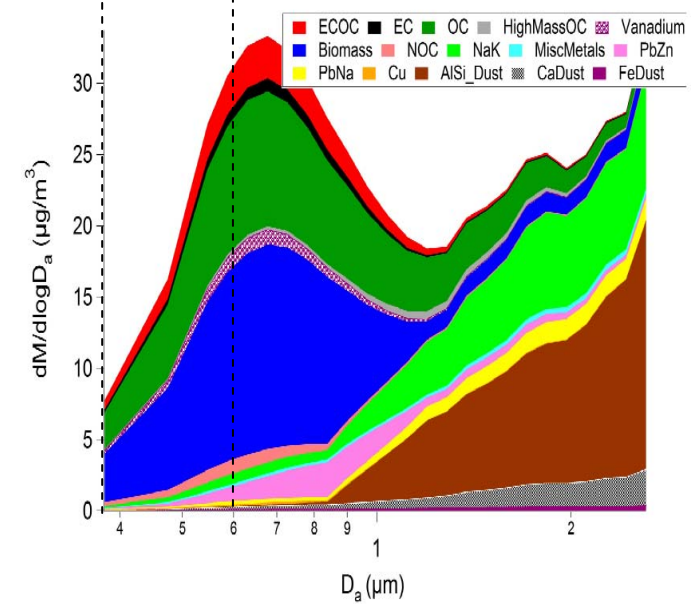
**AMS, Aiken et al., and PIXE, Laskin et al**

- Maybe impact of different types of biomass burning with ratios of K/acetonitrile and K/levoglucosan that differ by at least an order of magnitude
  - Maybe sources of K that are not due to biomass burning (e.g. soil)
- [Johnson et al., 2006]
- Very important to follow up

# Biomass Burning Contribution

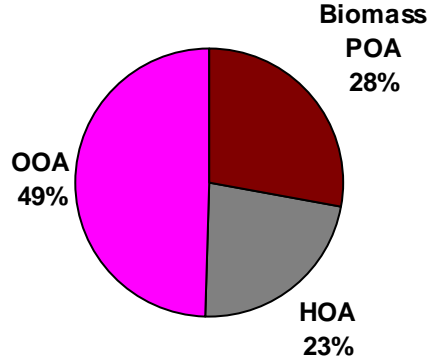


- “Biomass became the largest contributor to the accumulation mode mass from the late morning until early evening”
- Perhaps BB particles are being coated with large amounts of SOA and inorganics, so particle number is from BB, but particle mass is not



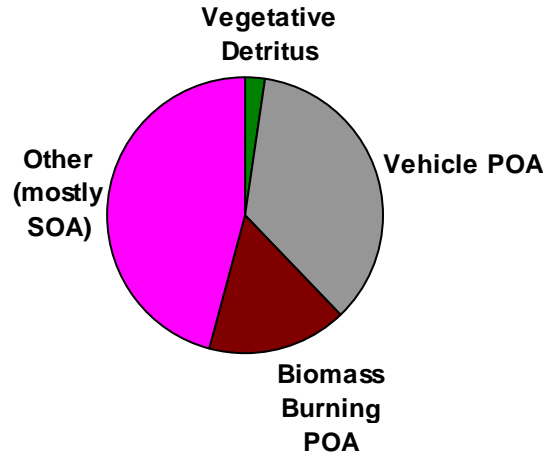
# Organic Aerosol Source Apportionment

AMS: Aiken et al.

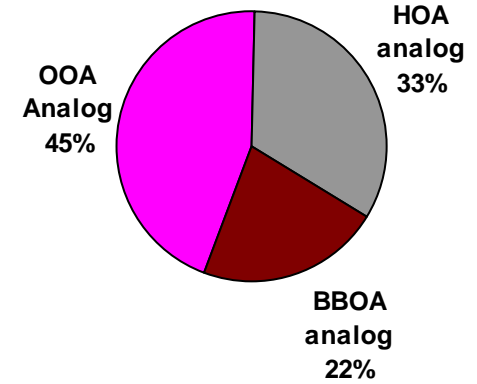


## In Mexico City T0 (IMP)

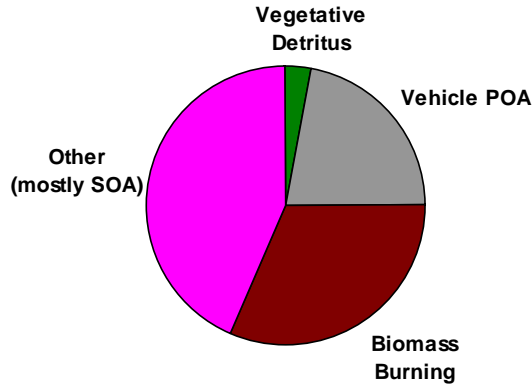
CMB: Stone & Schauer



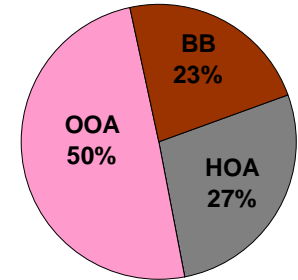
Prevot et al: <sup>14</sup>C



CMB: Schauer et al.  
T1

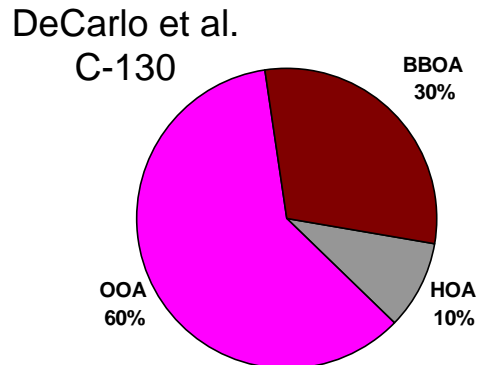


AMS for that day

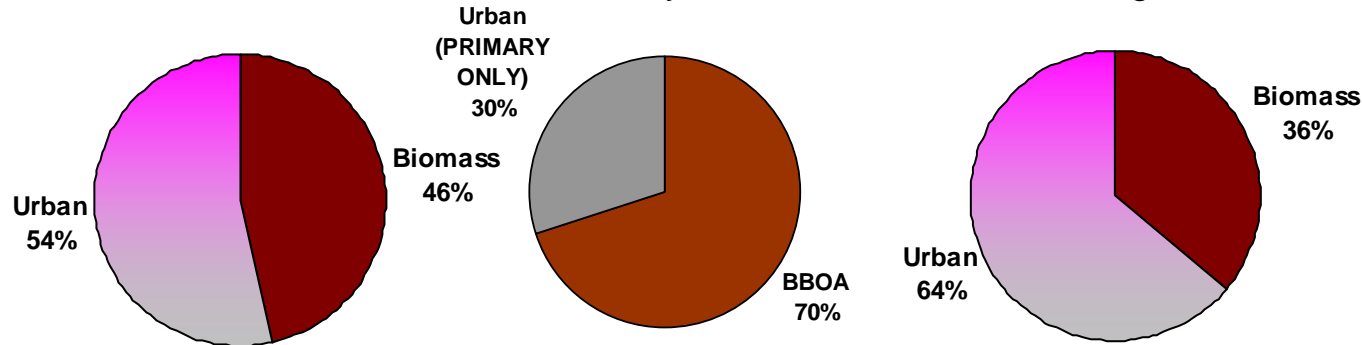


## Mexico City Outflow

Crouse, DeCarlo et al.  
C-130



Yokelson et al. – Twin Otter  
Primary ONLY  
Including SOA



# Organic Aerosol Sources

- Agreement that SOA, BBOA, and POA are all important
  - Fraction of modern C appears high compared to time-resolved measurements
  - “*There are other sources*” (e.g. Kilns, B. Castro)
  - BB more important in “outflow”
    - *S Pandis: how do we define outflow?*
- More regional or “plateau” background appears to contribute 3-6  $\mu\text{g m}^{-3}$  of organics
  - Already discussed by meteorology group, important to follow up in characterization
  - Aged urban emissions? Regional BB emissions?
- SOA
  - Agreement that known precursors don’t explain observations
  - Discussion of effect of evaporated POA [Robinson et al., Science, 2007], some evidence in favor, but far from conclusive
    - Much additional research is needed to verify that mechanism in the field
    - Is it POA or SOA? (policymakers vs scientists)

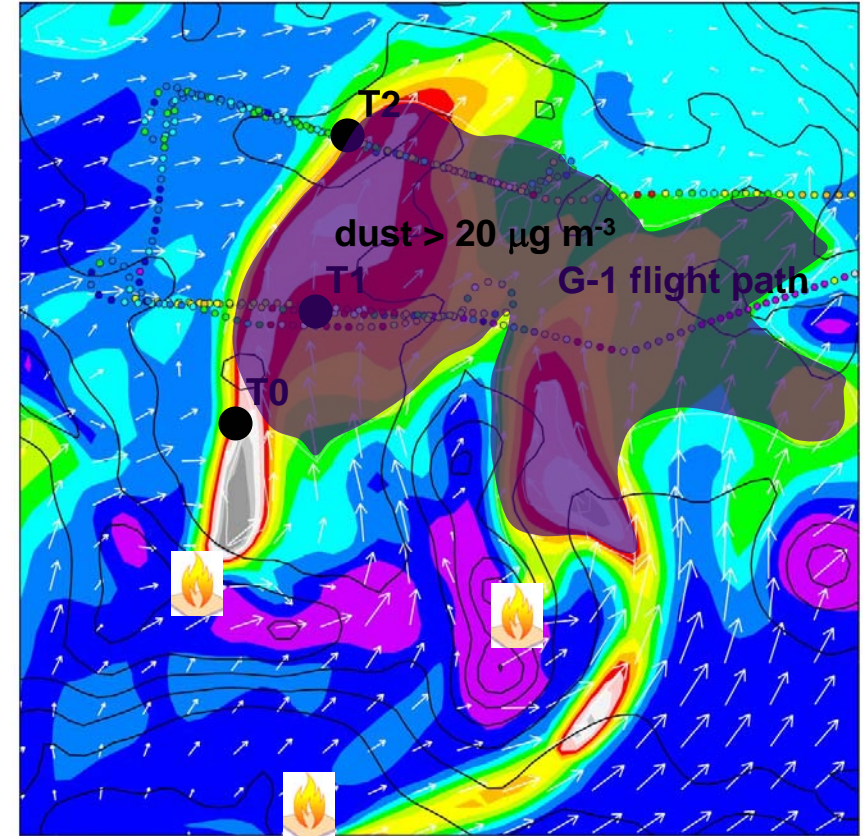
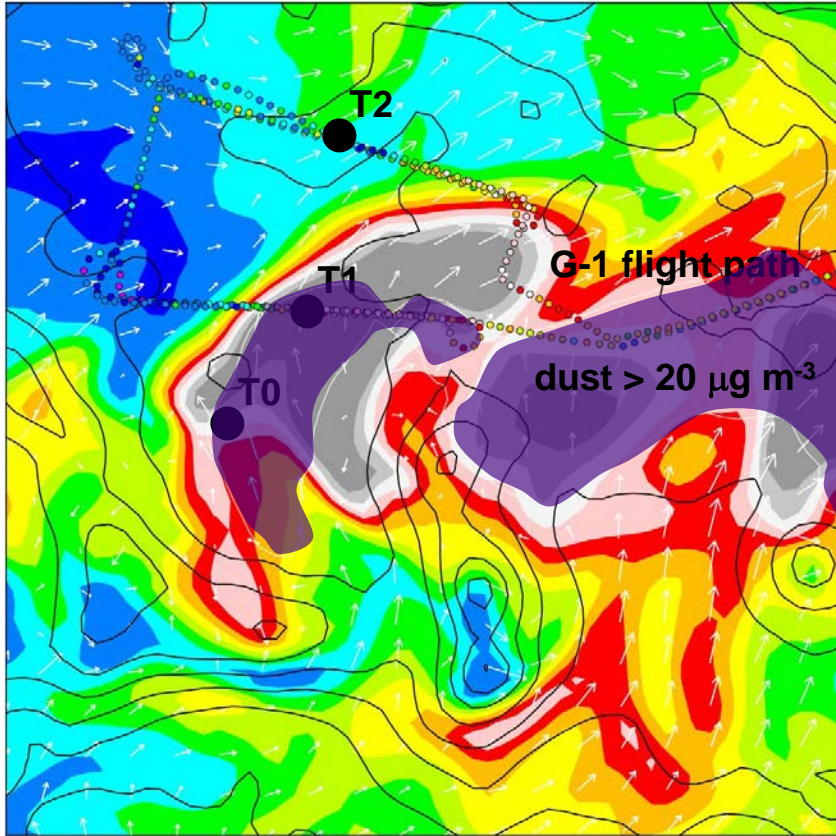
# *Aerosol Models*

- Models do a good job of transporting things around
- Large uncertainty of dust, highly dependent on sources
  - Dust is important near MC for optical properties, chemistry (e.g. nitrate)

Predicted Particulate Plume ~800 m AGL

2300 UTC March 9

2130 UTC March 20



2.5 5.0 7.5 10.0 12.5 15.0 17.5 20.0 22.5 22.5 25.0 27.5

particulate volume ( $\text{cm}^3 \text{cm}^{-3} \times 10^{12}$ )

mix of urban and dust sources

2.5 5.0 7.5 10.0 12.5 15.0 17.5 20.0 22.5 22.5 25.0 27.5

particulate volume ( $\text{cm}^3 \text{cm}^{-3} \times 10^{12}$ )

mix of urban, biomass burning, and dust sources

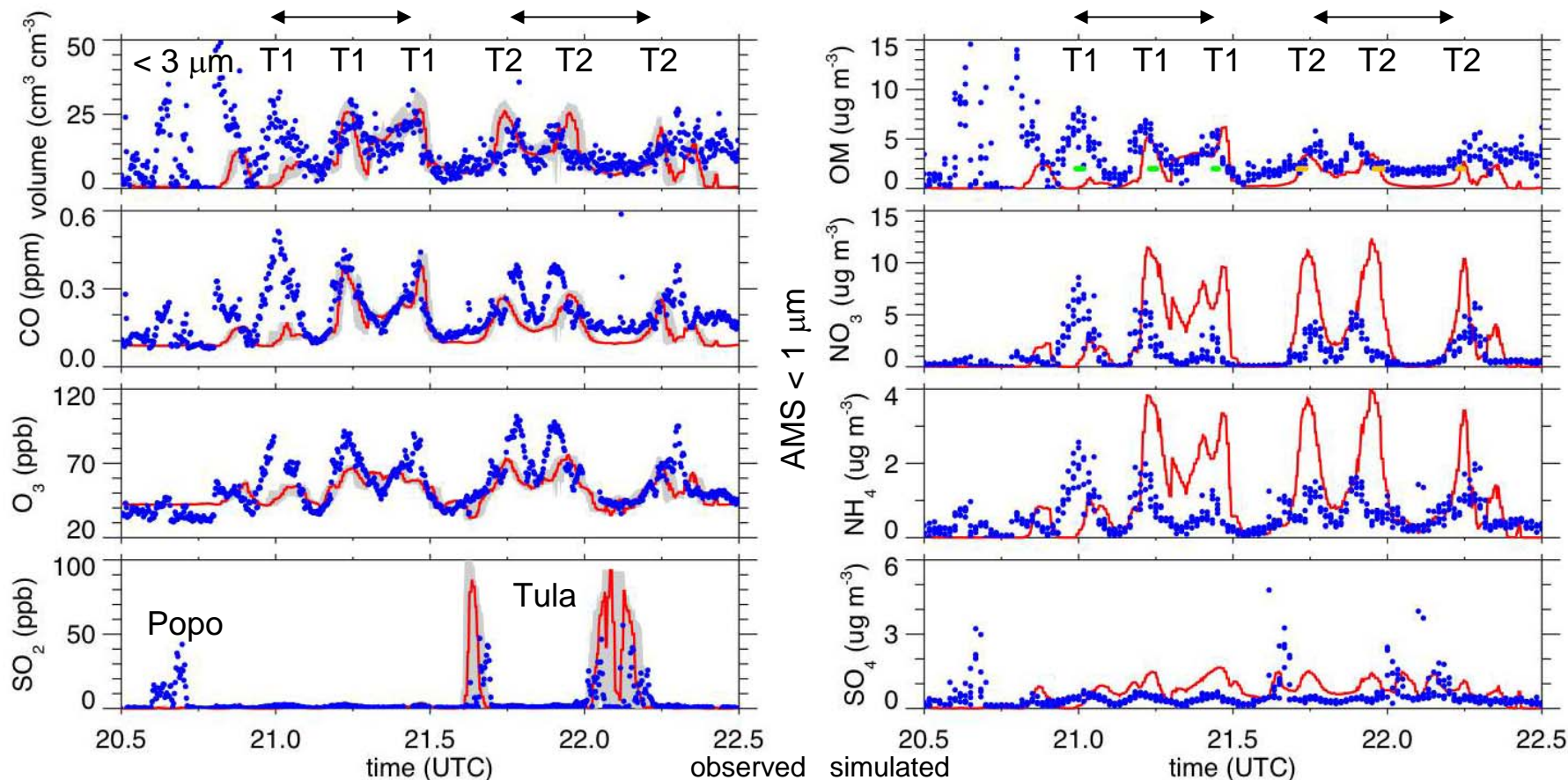
**predicted spatial variations in particulate volume  
consistent with G-1 measurements**

# *Aerosol Models II*

- Organics
  - Fast: Predicted OM likely too high considering model has no SOA (too much POA?)
  - Pandis: OM low (not enough SOA), impact of regional background
  - Models predict total OM within a factor of 2 over continents (not x10 lower). Too much POA and too little SOA. Larger problem is downwind areas with lower concentrations (near origin of scatter plots)
- Fast and Pandis:  $\text{NO}_3$  and  $\text{NH}_4$  too high
  - Predicted  $\text{NO}_x$  too high? (Fast)
  - Coarse mode competes for nitrate (Pandis)
- $\text{SO}_2$  predicted well around Tula, but predicted  $\text{SO}_4$  occurred further downwind (Fast)
  - Popo > Tula but not by orders-of-magnitude

# Model-Measurement Comparisons

## Observed and Simulated Values along G-1 Flight Path, Afternoon of March 20



- predicted OM likely too high considering model has no SOA
- NO<sub>3</sub> and NH<sub>4</sub> too high and O<sub>3</sub> too low since predicted NO<sub>x</sub> too high
- SO<sub>2</sub> predicted well around Tula, but predicted SO<sub>4</sub> occurred further downwind
- inconsistency between particulate volume and mass from AMS?

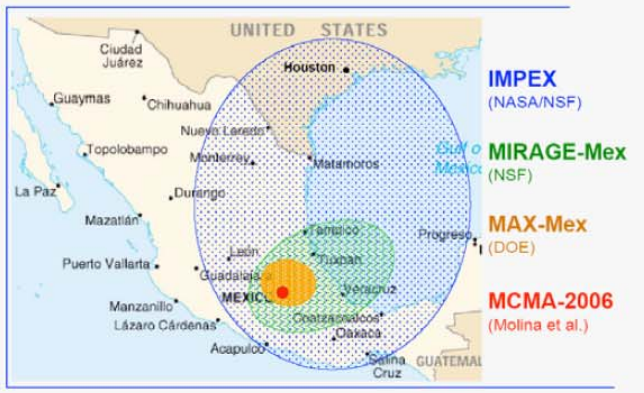
# *Model-Measurement Comparisons*

- Maybe most important outcome of breakout session
  - Modelers and experimentalists agreed that we should compare data as ratios and scatter plots (to remove transport influence). E.g. Org/CO
  - S Schwartz: “we care more that the amounts and chemistry are in the models, than that the transport is right”

# Example

Worsnop, Aiken, Jayne, DeCarlo al.

## Organic to CO Ratios

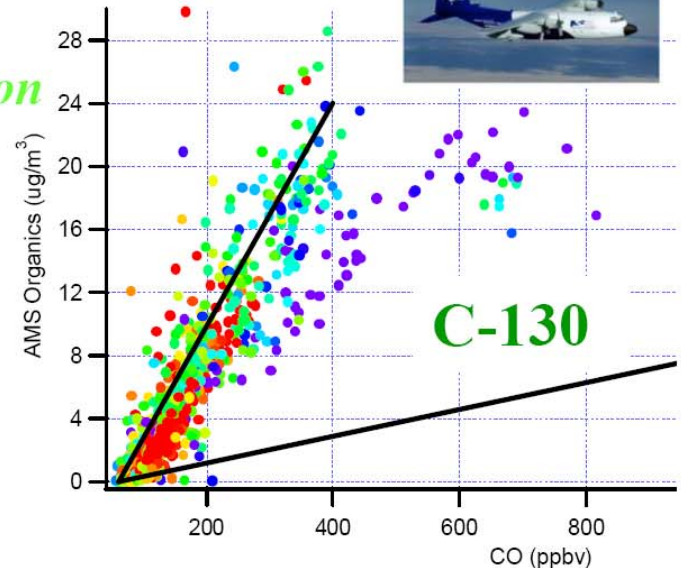


**OM /CO: HIGH**  $\sim 60 \mu\text{gm}^{-3}/\text{ppm}$   
**LOW**  $\sim 5-8$

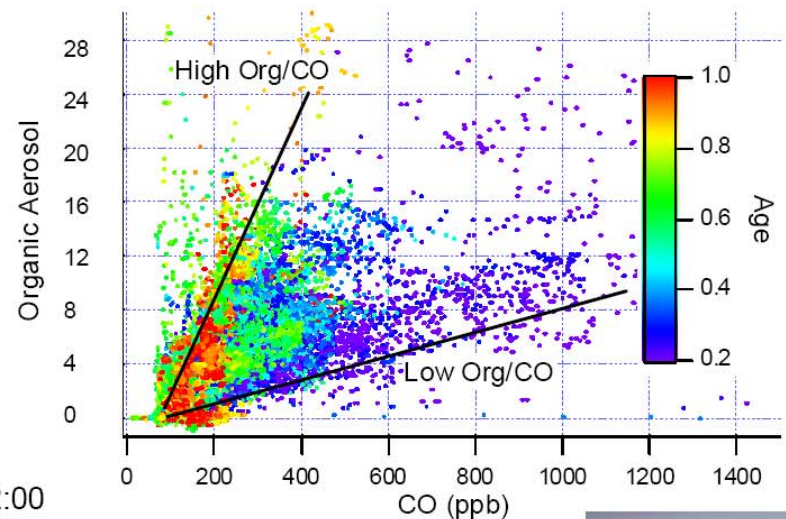
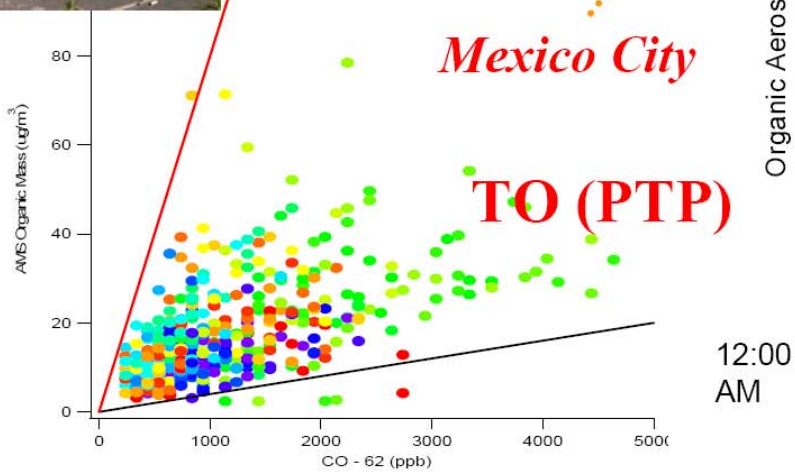
(ca. Pittsburgh, Zhang et al, 2005)



Region



**Mexico City**  
**TO (PTP)**



**G-1**



# *Papers and Concluding Thoughts*

- Will update list offline via email (JL Jimenez)
- Keep in mind what different instruments are measuring
  - Size range and chemistry
    - AMS: PM1 non-refractory
    - SMPS: ~PM1 total
    - ATOFMS & APS: upper end of accumulation mode + supermicron
  - Precision & accuracy of the different measurements
- Very complex issues, everyone has partial stories
  - Need to keep communicating
    - Before submission to ACPD special issue
    - During the open discussion period
  - Small focused meetings would be very useful