Aerosol Mass Spectrometry in and around Mexico City 2003 & 2006

Allison Aiken, Peter DeCarlo, Dara Salcedo, Jose-Luis Jimenez, Katja Dzepina, Alex Huffman, Mike Cubison, Ingrid Ulbrich, Ed Dunlea, Joel Kimmel, Doug Worsnop, Achim Trimborn, Megan Northway, Cristine Wiedinmyer, John Crounse, Paul Wennberg, Teresa Campos, Sonke Szidat, Andre Prevot, Nancy Marley, Jeff Gaffney

CU-Boulder, UAEM, Aerodyne, NCAR, Caltech, PSI, UALR

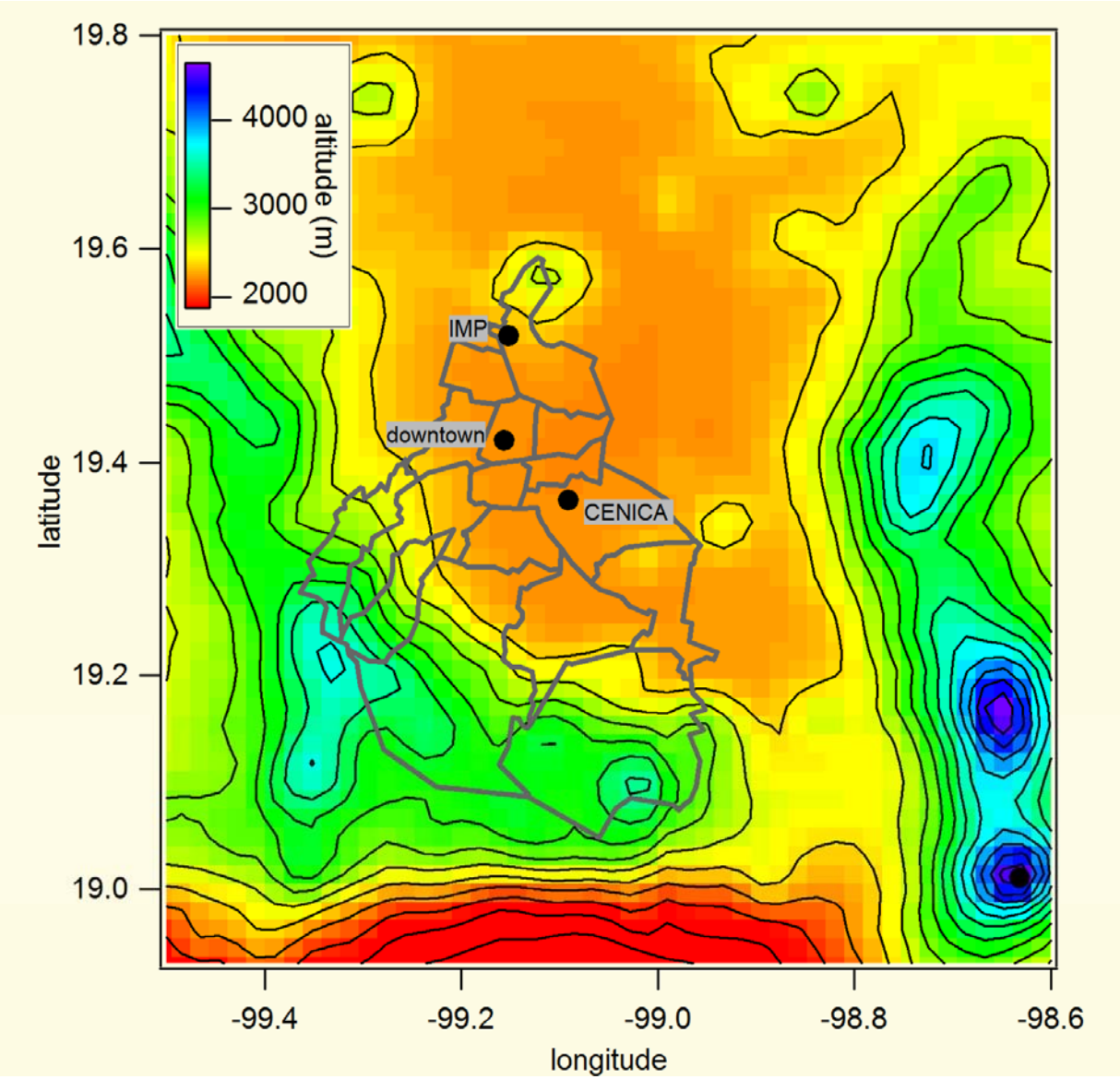
http://cires.colorado.edu/jimenez-group

Funded by DOE & NSF

2nd MILAGRO Science Conference – Mexico City, May 16th, 2007

Picture by C. McNaughton from DC8, U. Hawaii

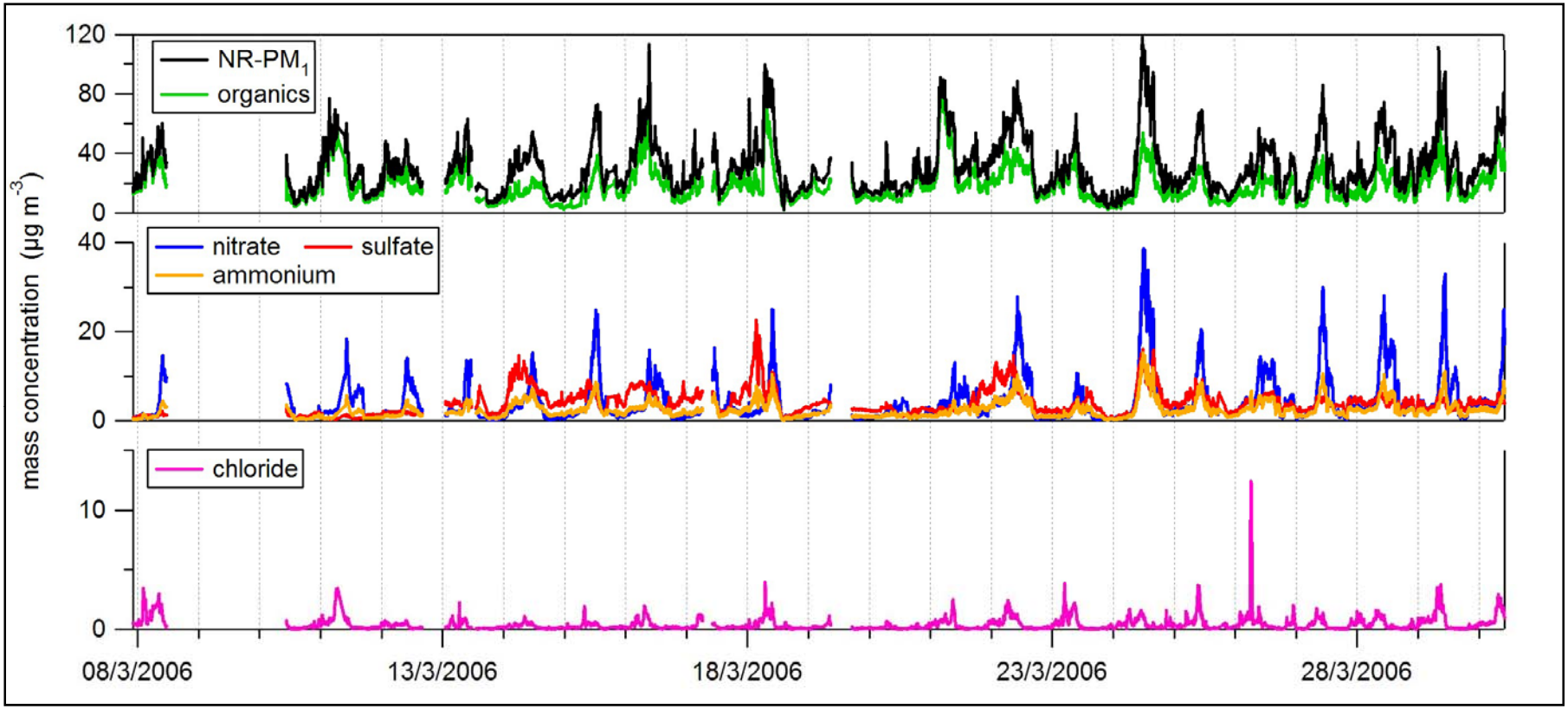
CENICA-2003 vs T0 - 2006

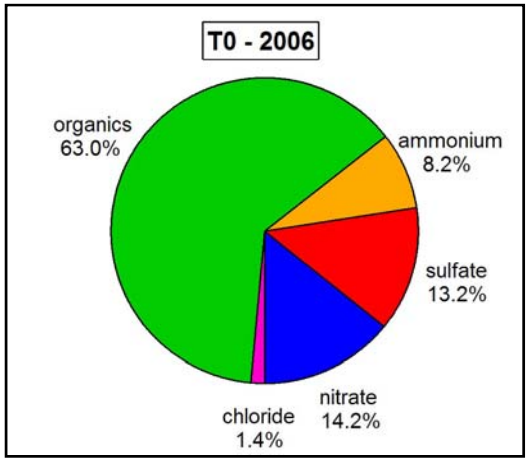


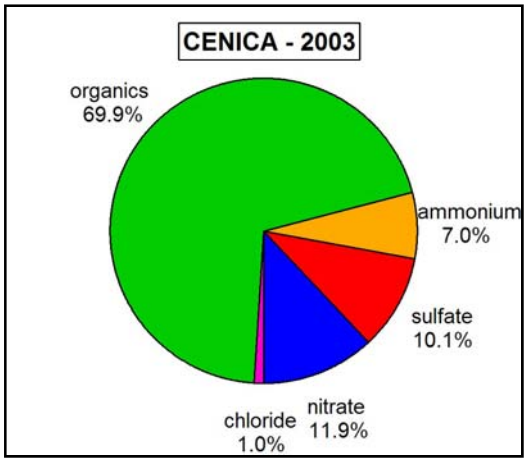
CENICA – 2003
Q-AMS

T0 – 2006
HR-ToF-AMS

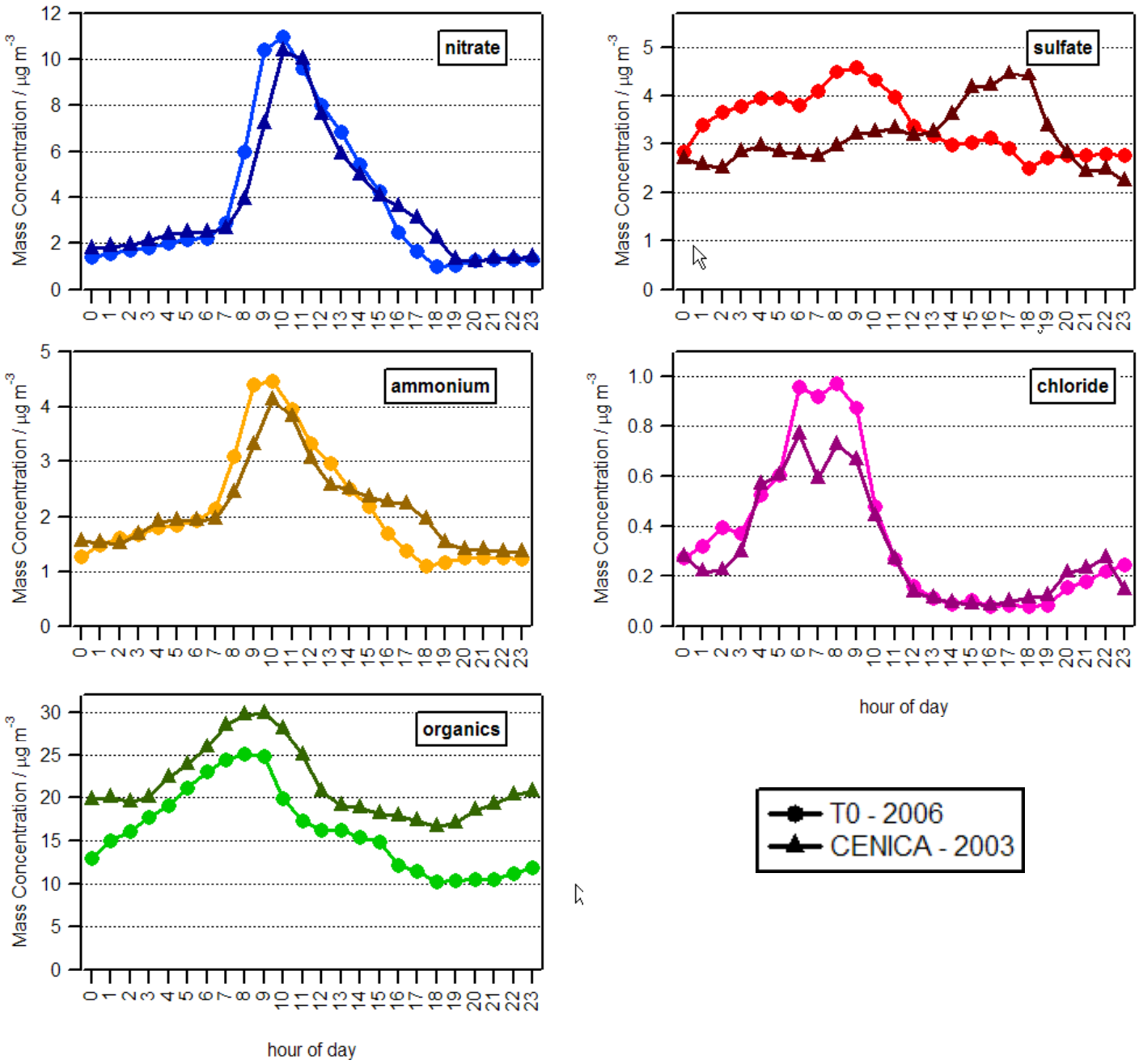
NR-PM_1 time series @ T0





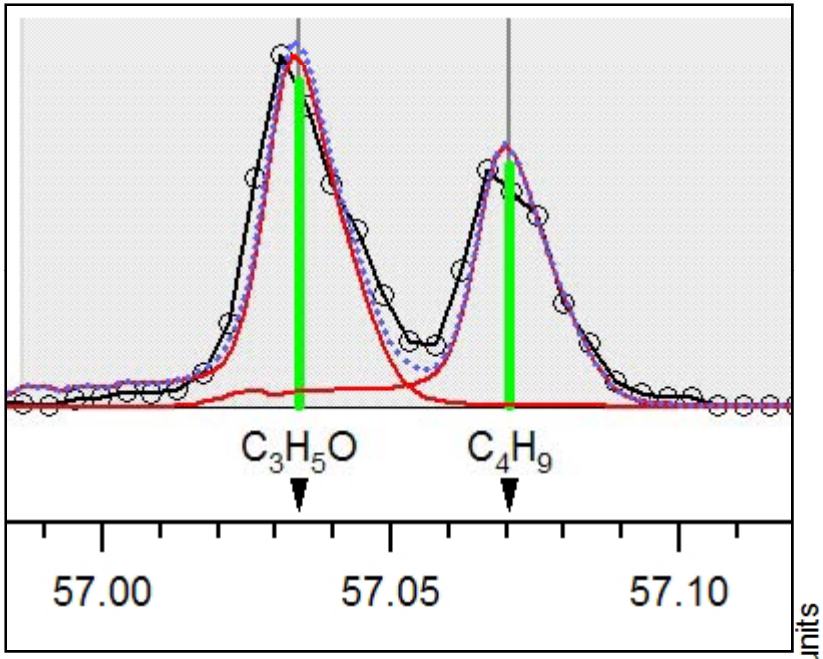


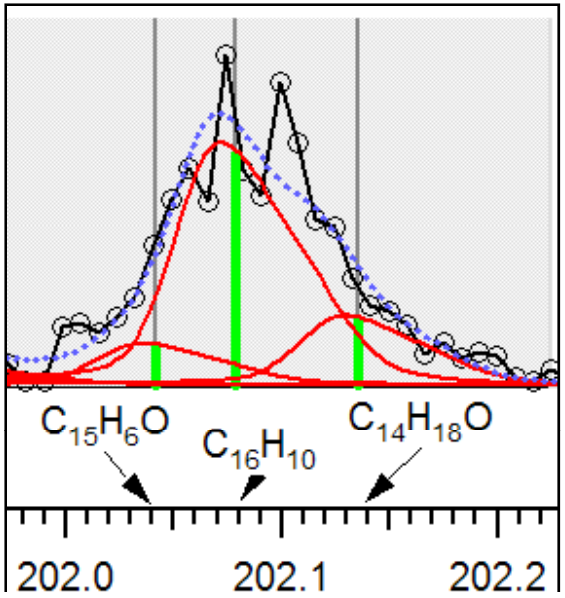
Diurnal cycles in 2006 vs. 2003



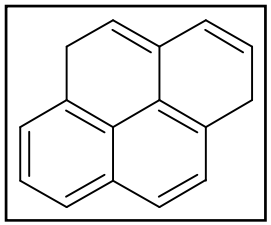
High resolution spectra of PAH at T0

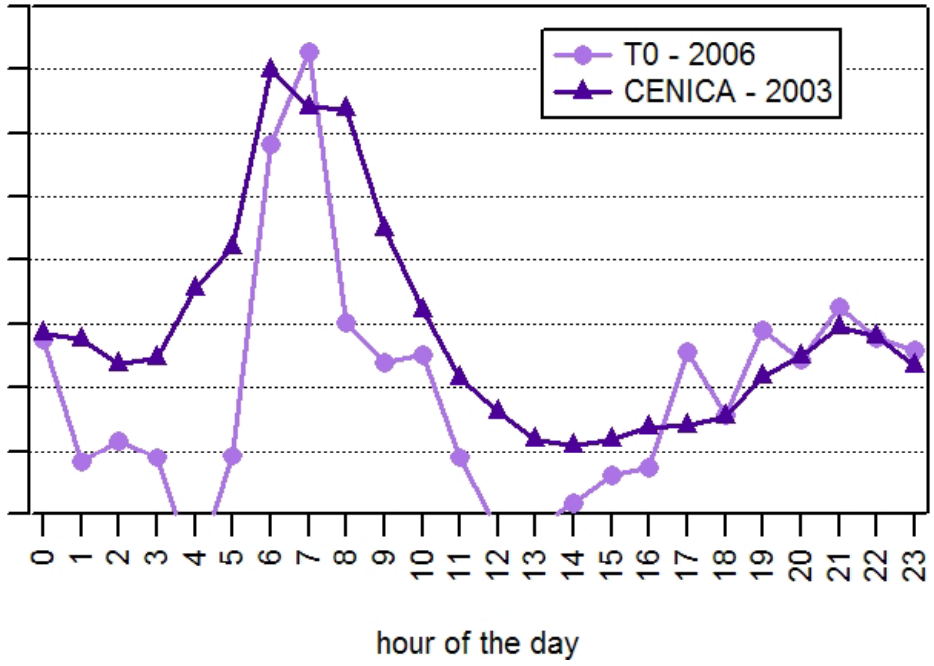
HR Spectra of *m/z* 57:



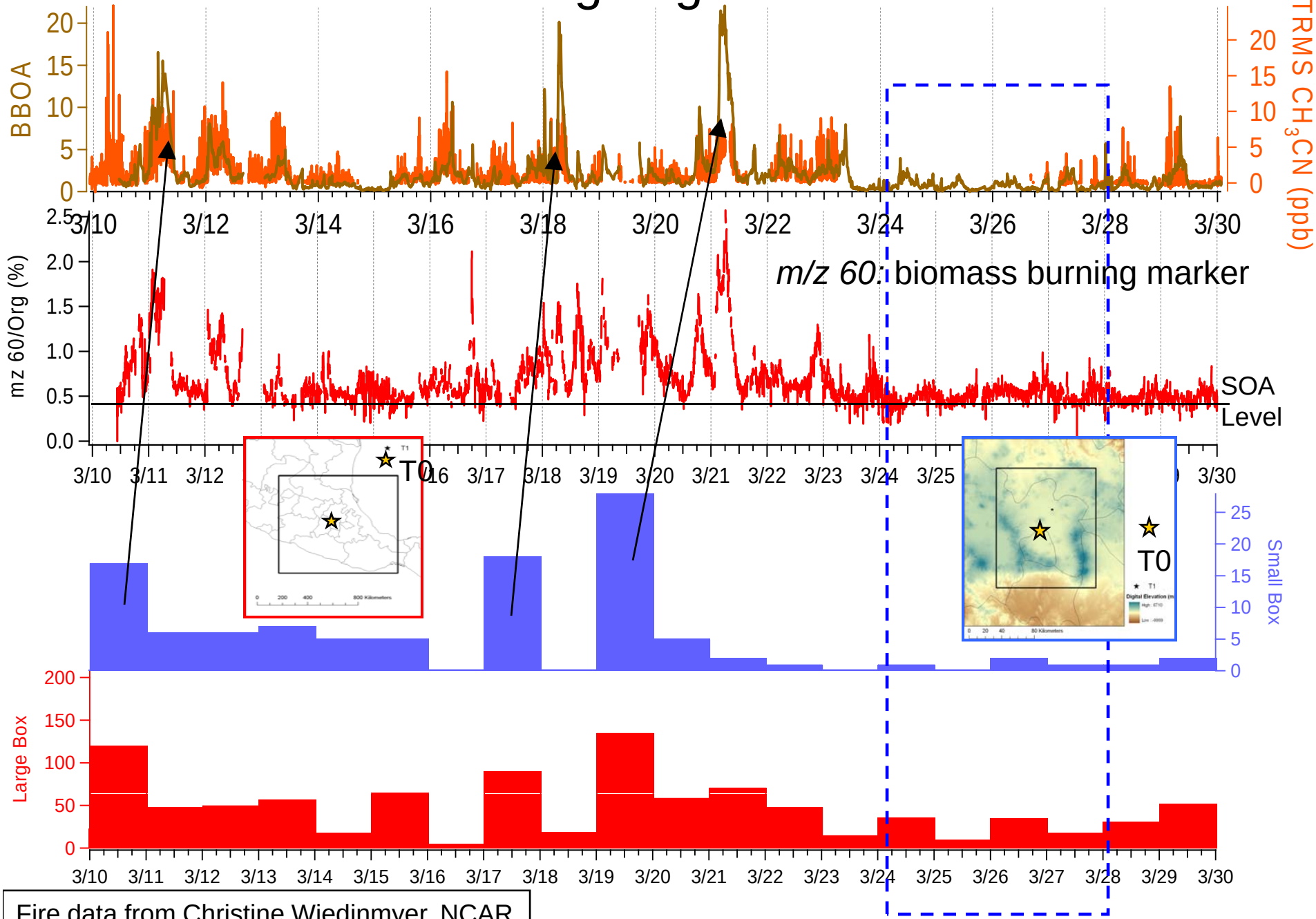


$C_{16}H_{10}$
e.g. pyrene





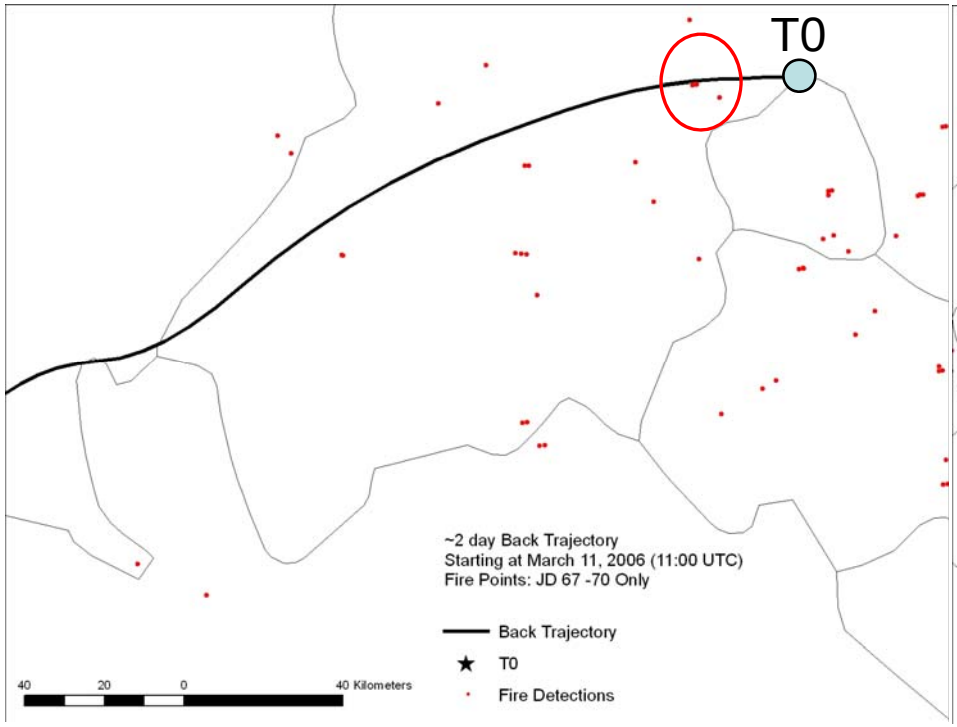
Biomass Burning Organic Aerosol at T0



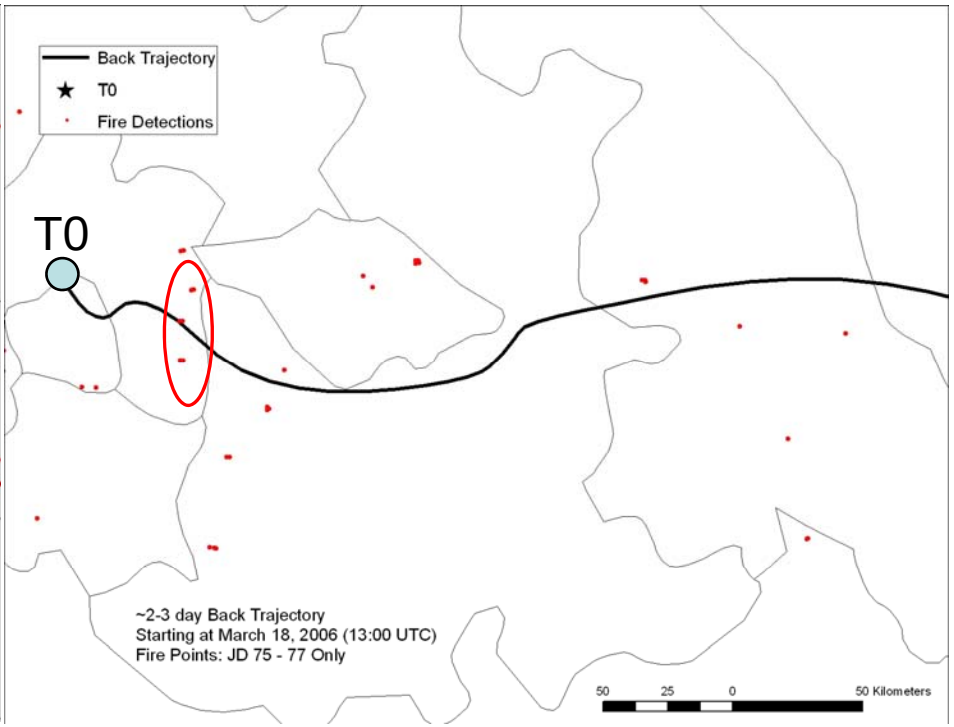
Fire data from Christine Wiedinmyer, NCAR

Back-Trajectories for high BBOA Events

Back-Trajectory for March 11 (5 AM)



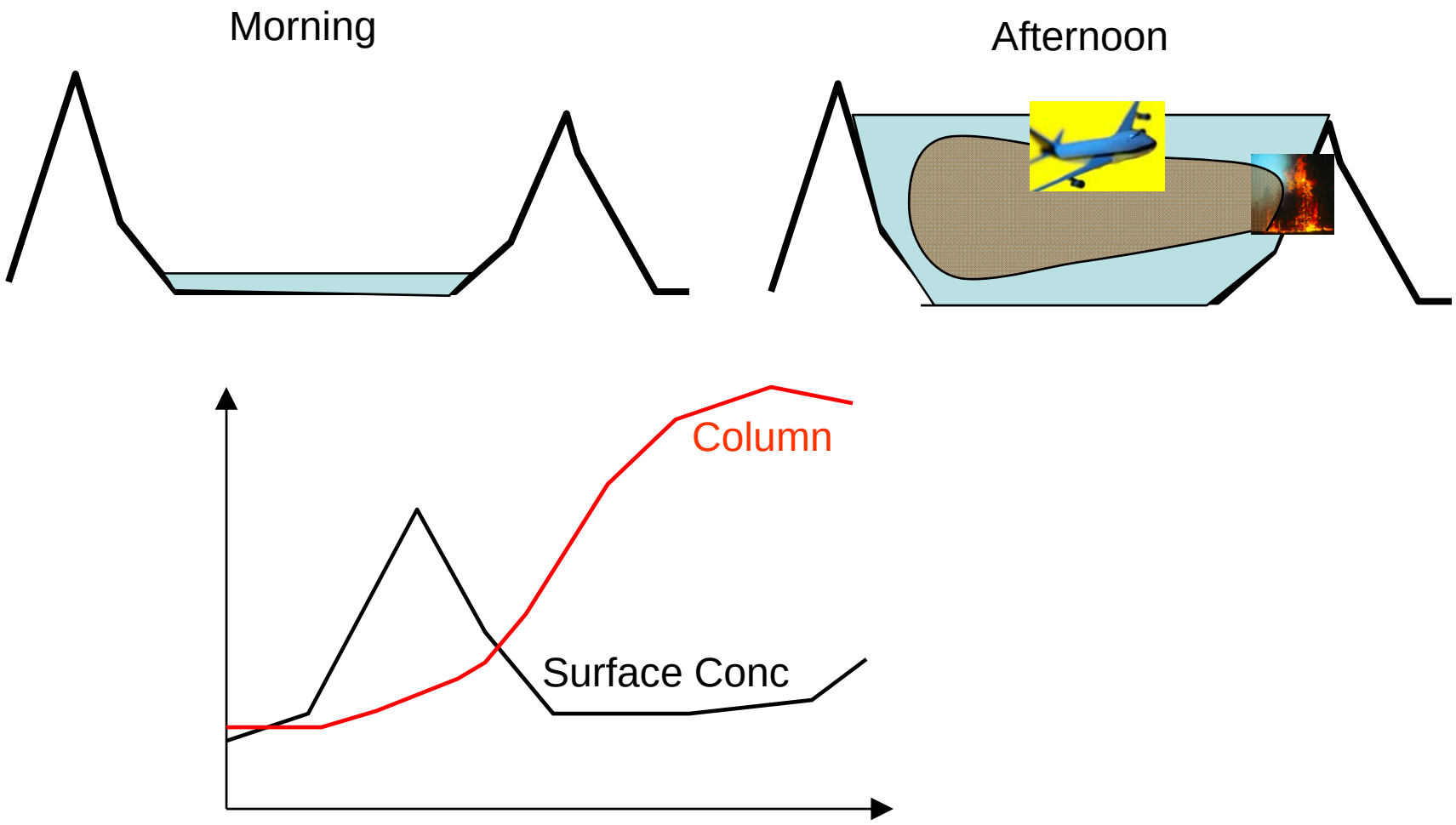
Back-Trajectory for March 18 (7 AM)



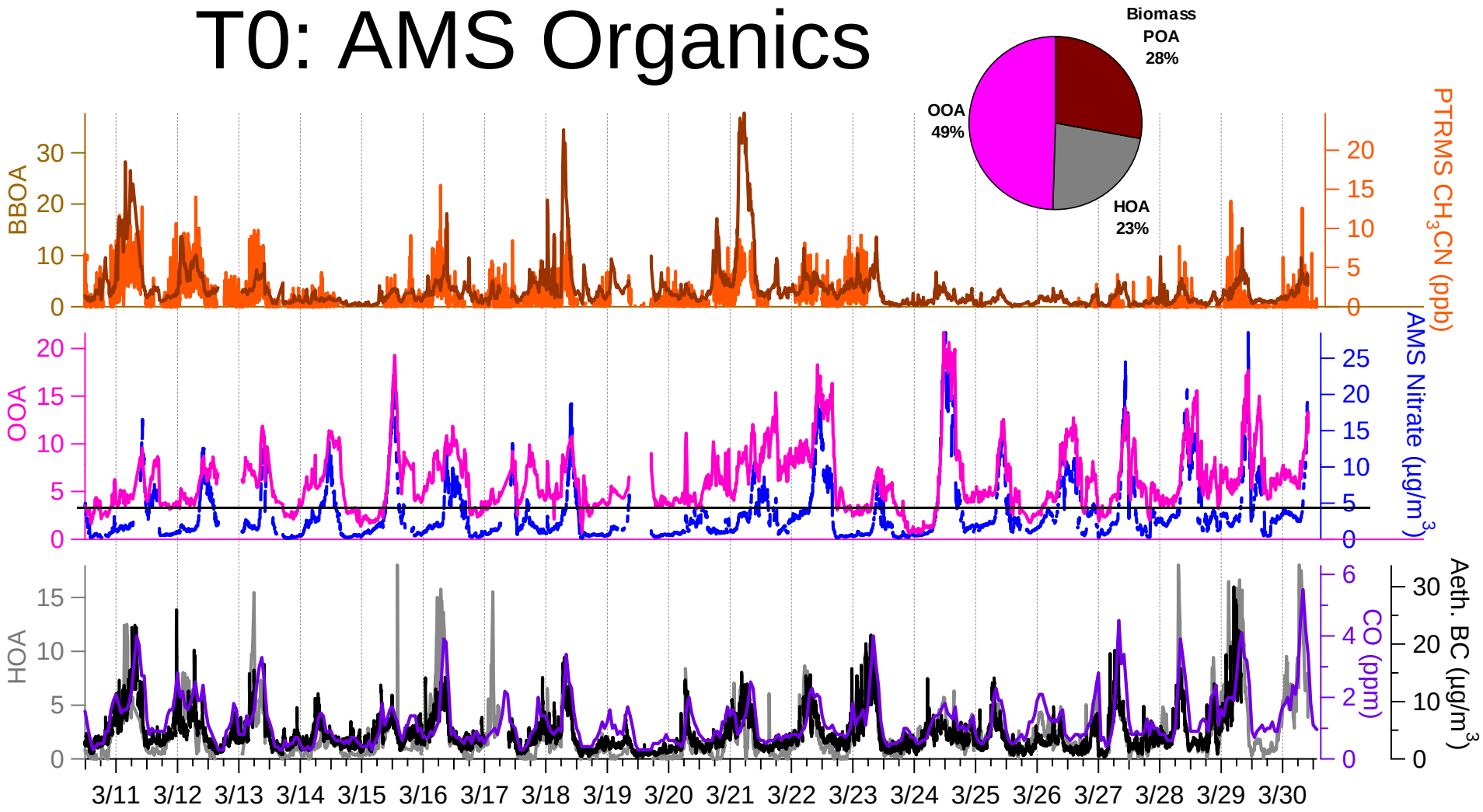
- High BBOA and acetonitrile events
  - Advection at low level of fires at night of previous day

Fire trajectories from
Christine Wiedinmyer, NCAR

A Conceptual Model of MC Aerosol



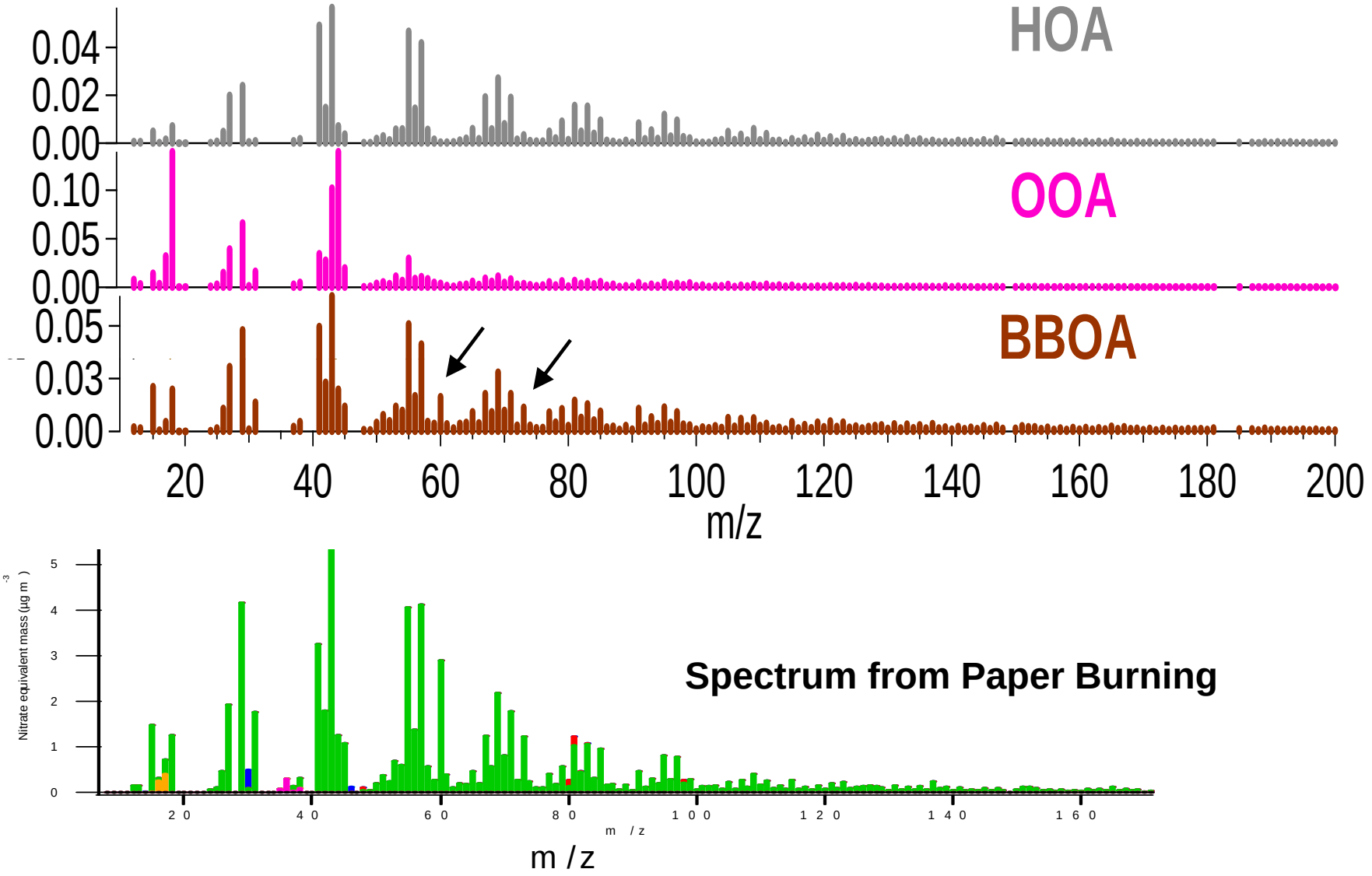
T0: AMS Organics



- Based on correlations and spectra
  - Biomass burning OA (BBOA)
  - Hydrocarbon-like OA (HOA ~ POA)
  - Oxygenated OA (~SOA)

BC from Gaffney & Marley
CO from RAMA

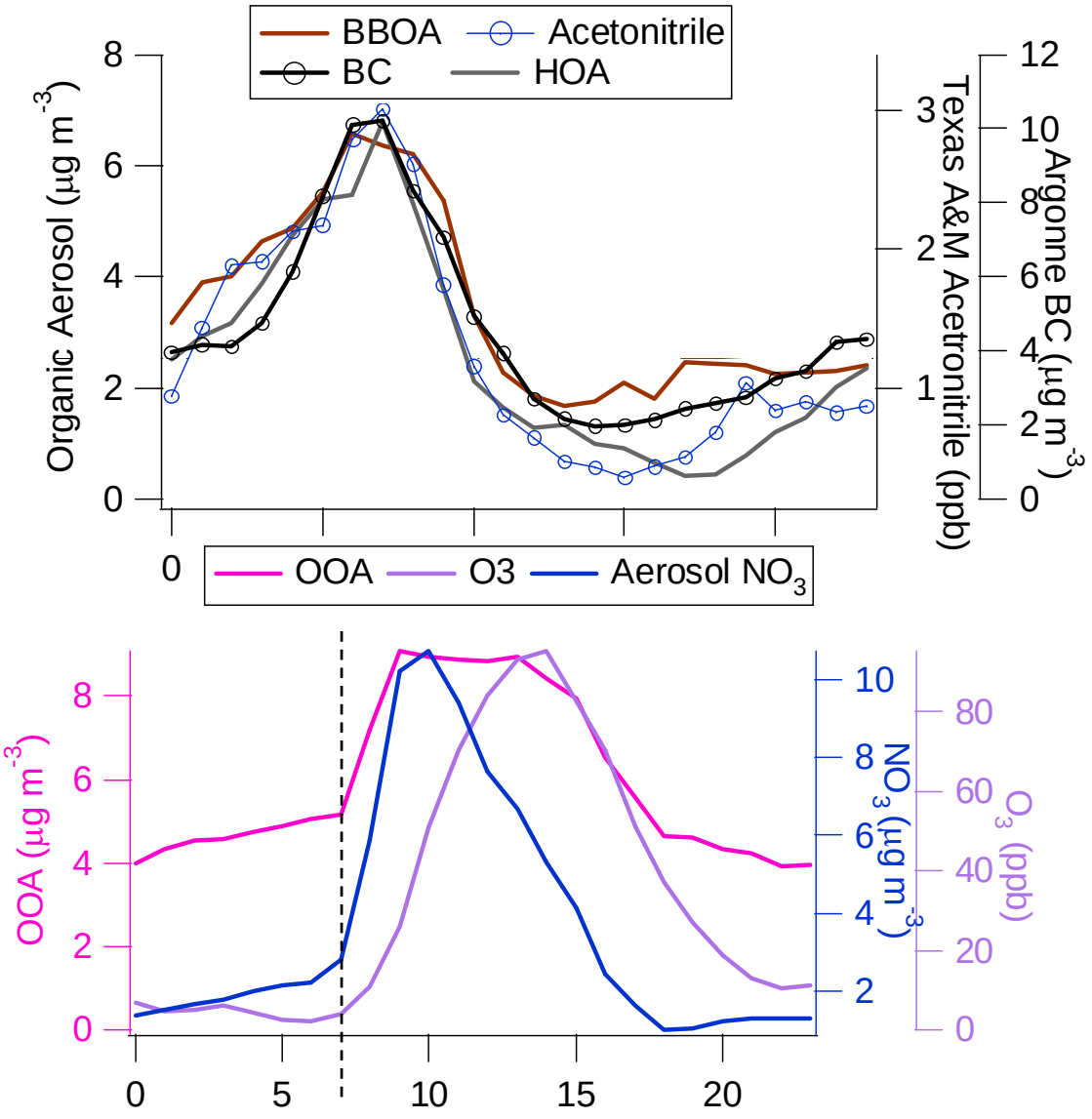
T0 AMS Organic Components II



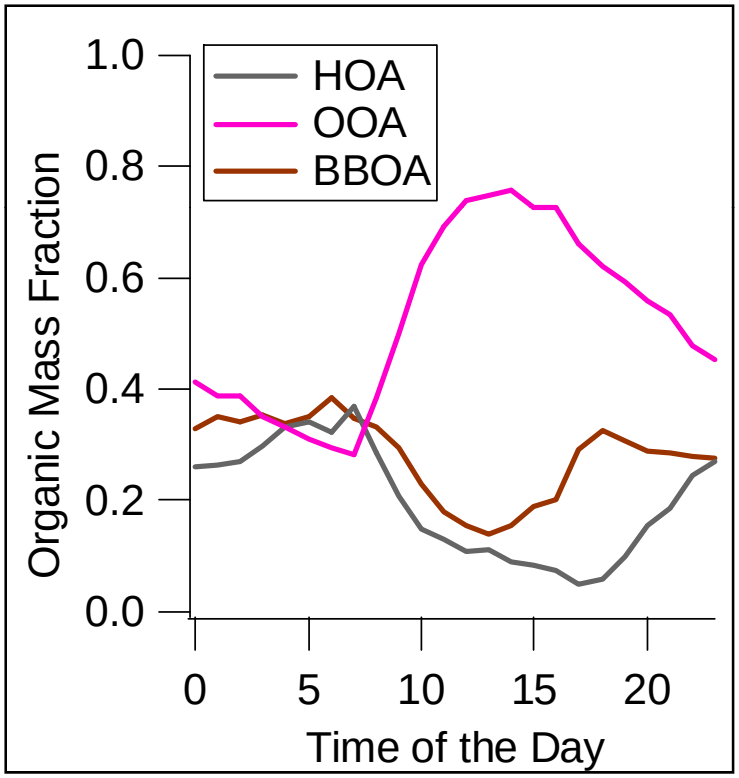
- BBOA spectrum similar to source spectra

Diurnal Cycles of Organic Aerosol Components

Absolute Concentrations

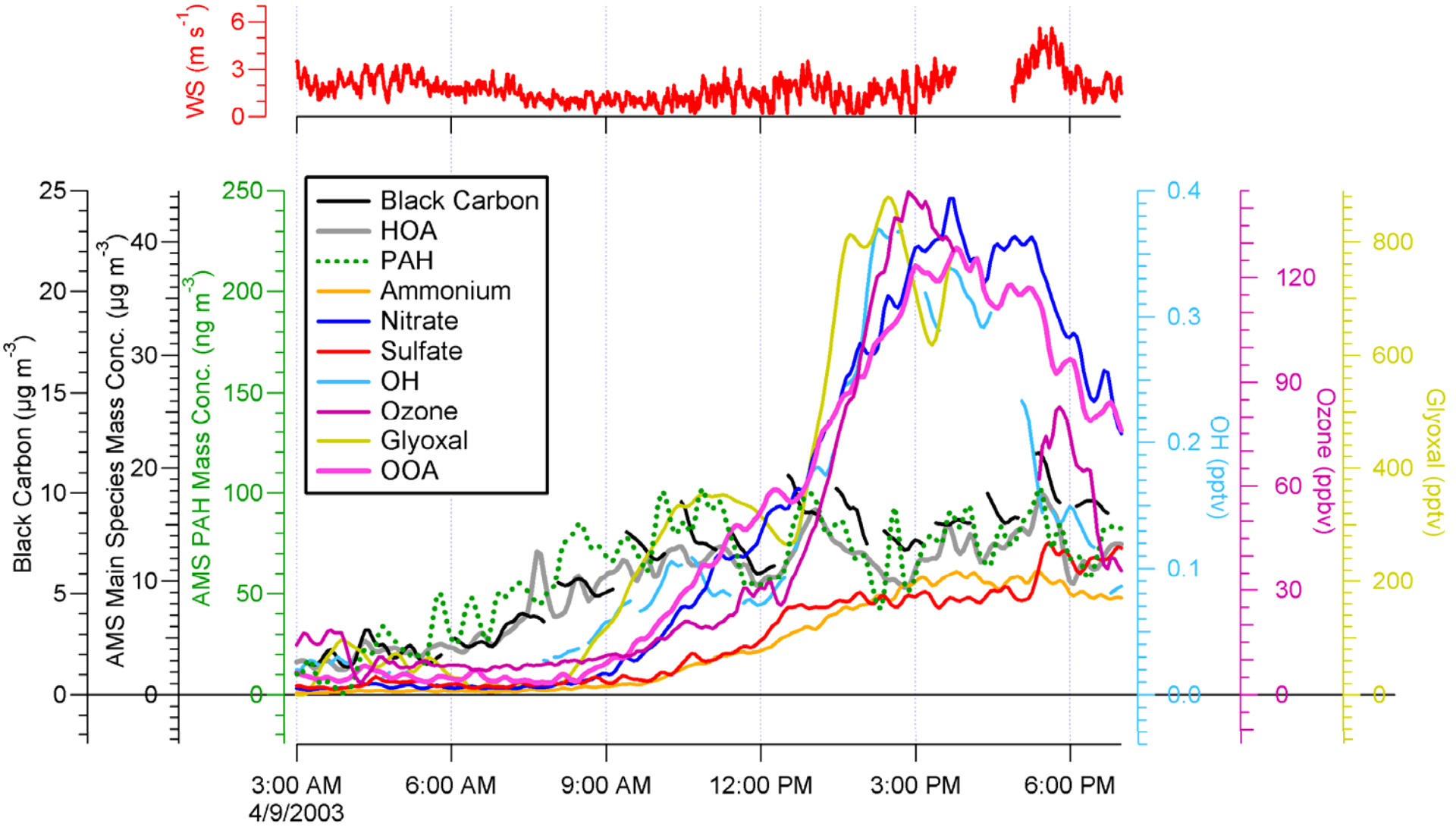


Mass Fractions of Total OA



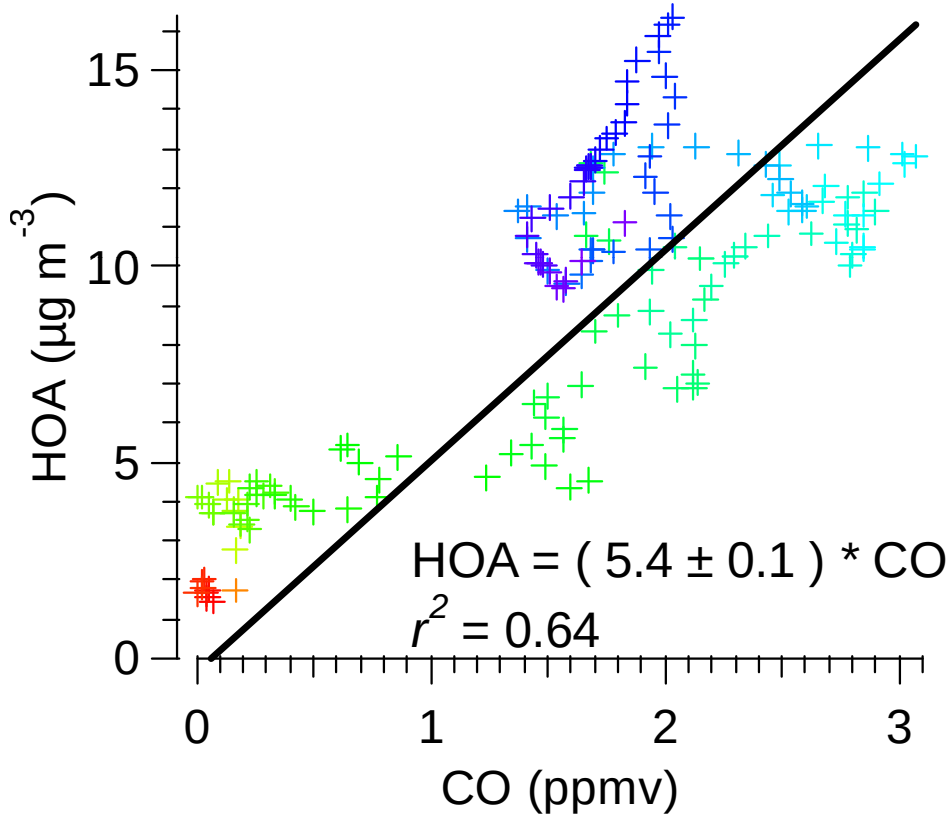
BC from Gaffney & Marley
O_3 from Sheehy and Volkamer
Acetonitrile from Texas A&M

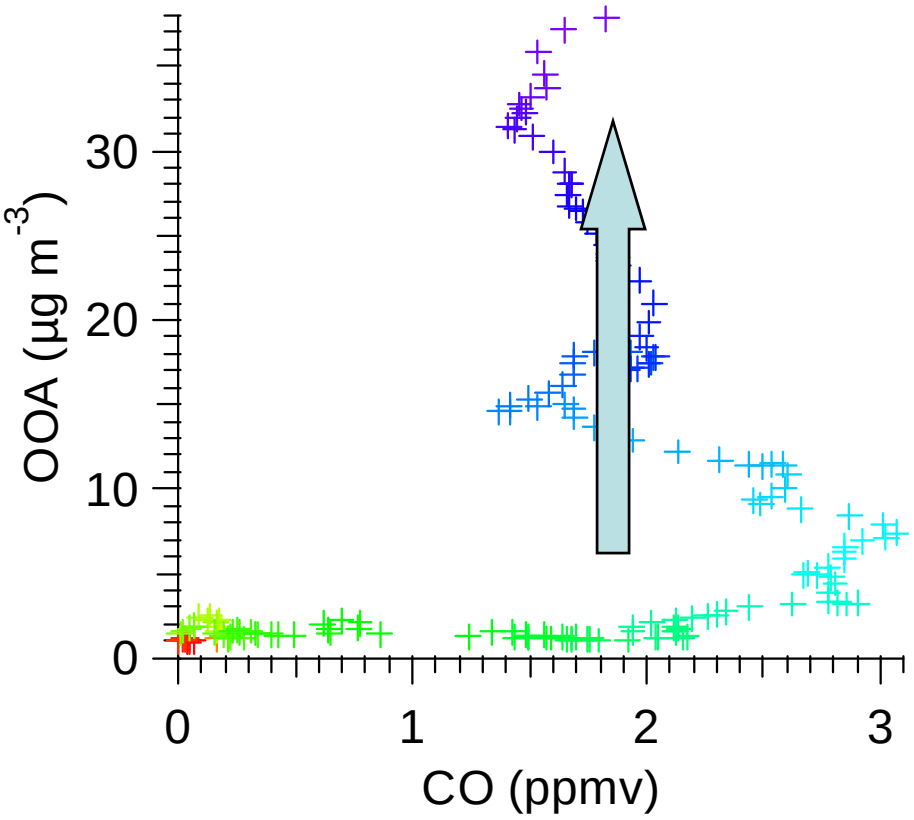
Case Study: April 9, 2003



R. Volkamer, J.L. Jimenez, et al., *GRL* 33(17), L17811, 2006.

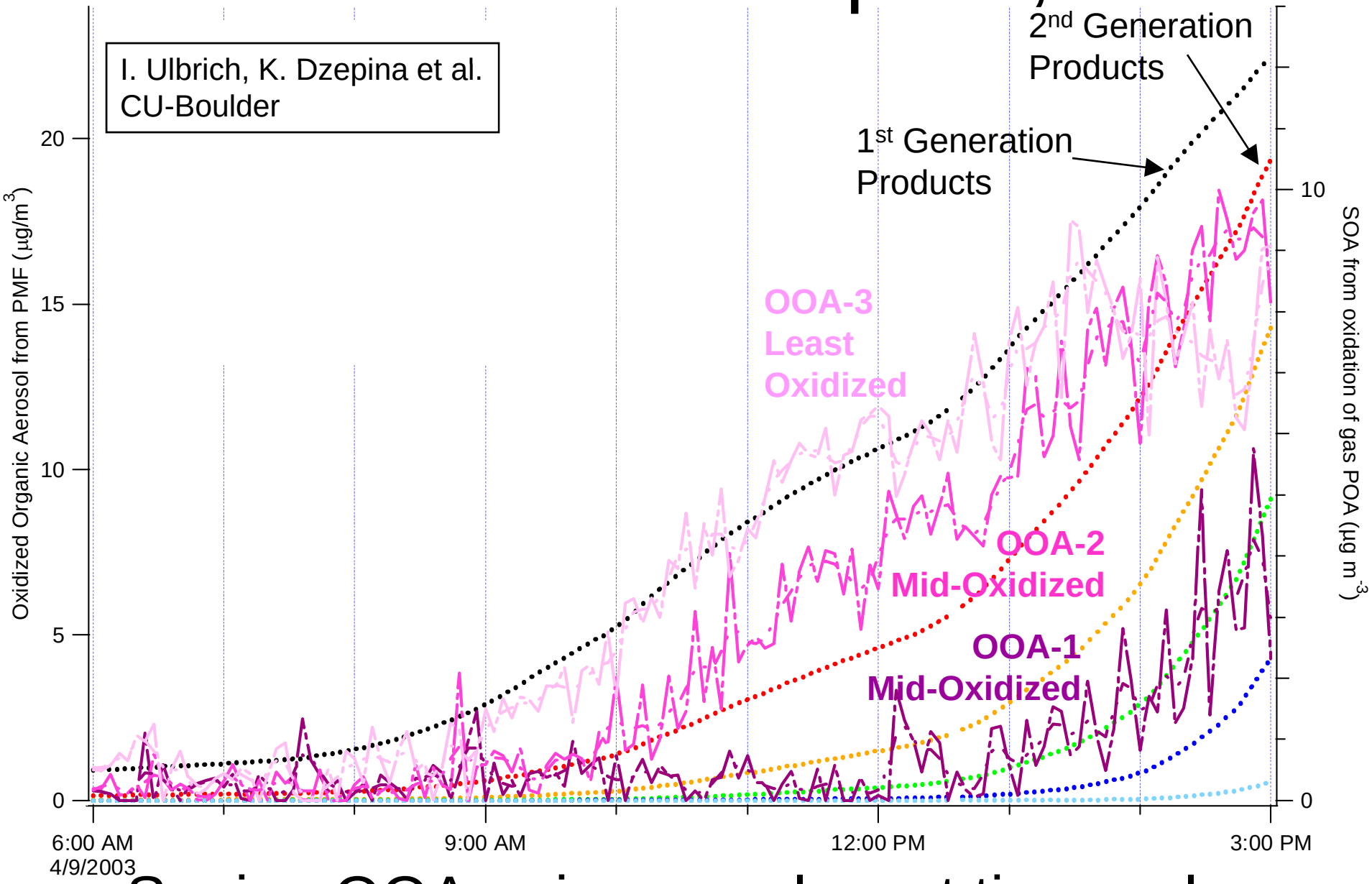
HOA and OOA Evolution in the City





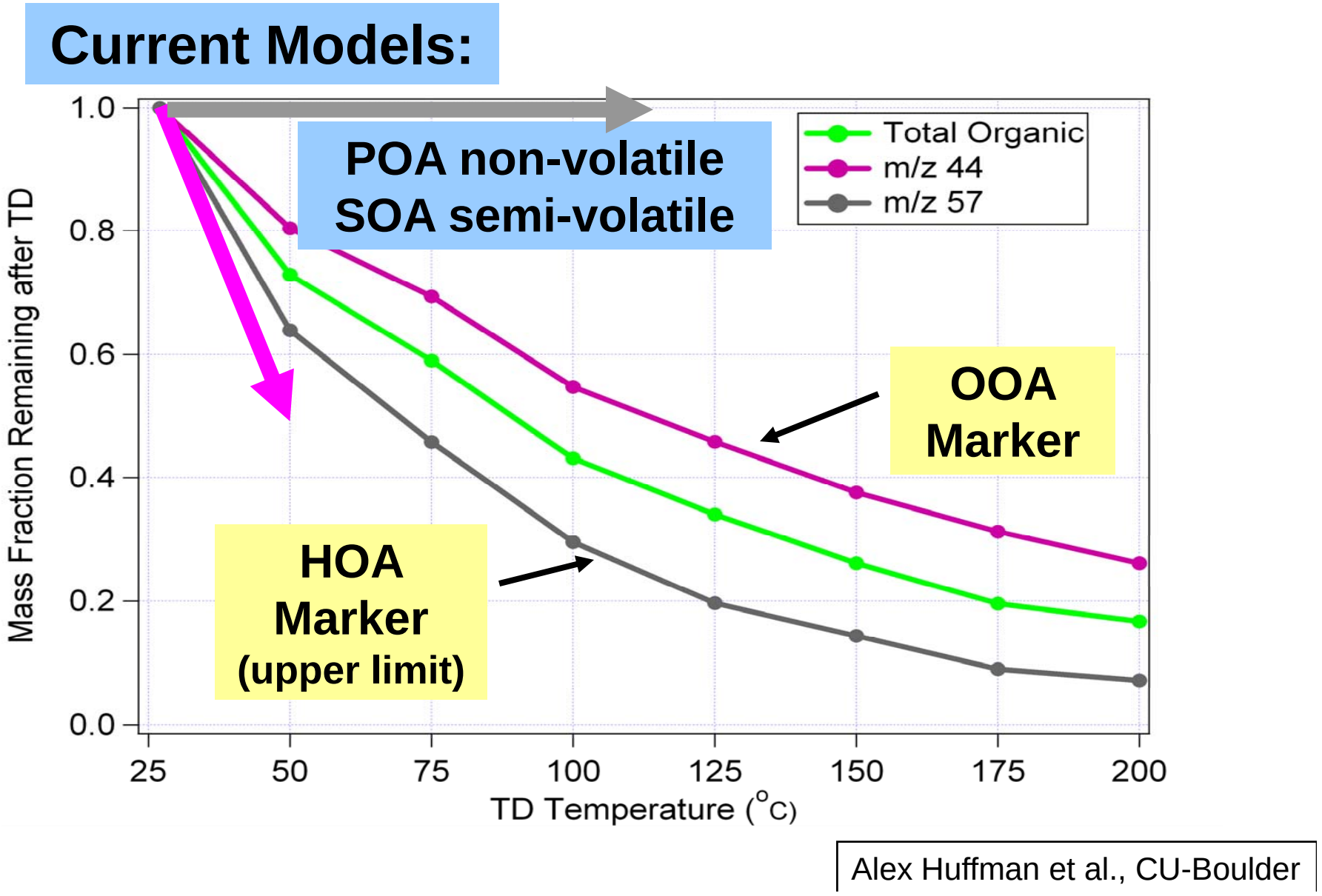
K. Dzepina et al., CU-Boulder
CO data from RAMA

SOA Evolution on April 9, 2003



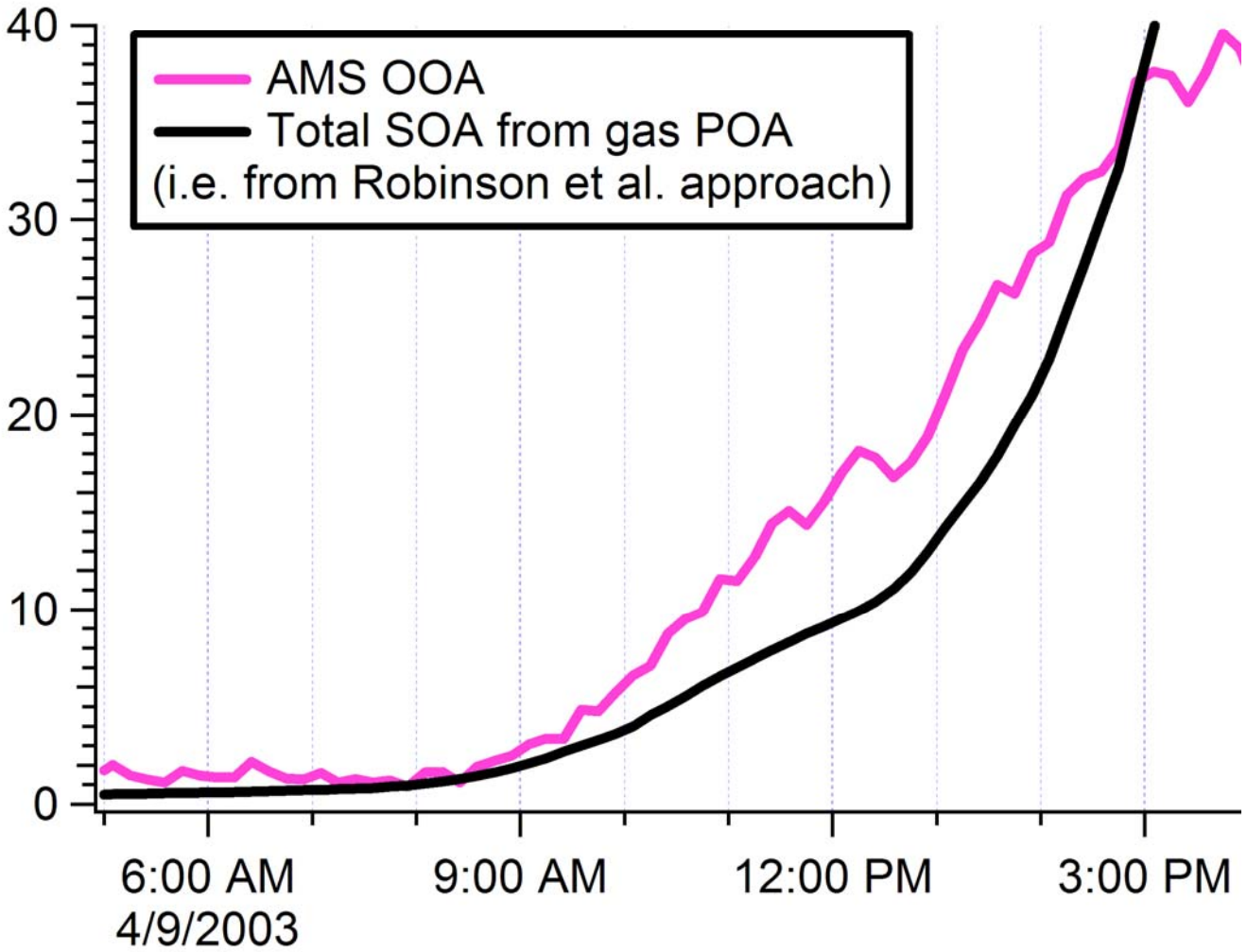
- Seeing OOA aging on relevant timescales

High POA & Low SOA Volatility



Alex Huffman et al., CU-Boulder

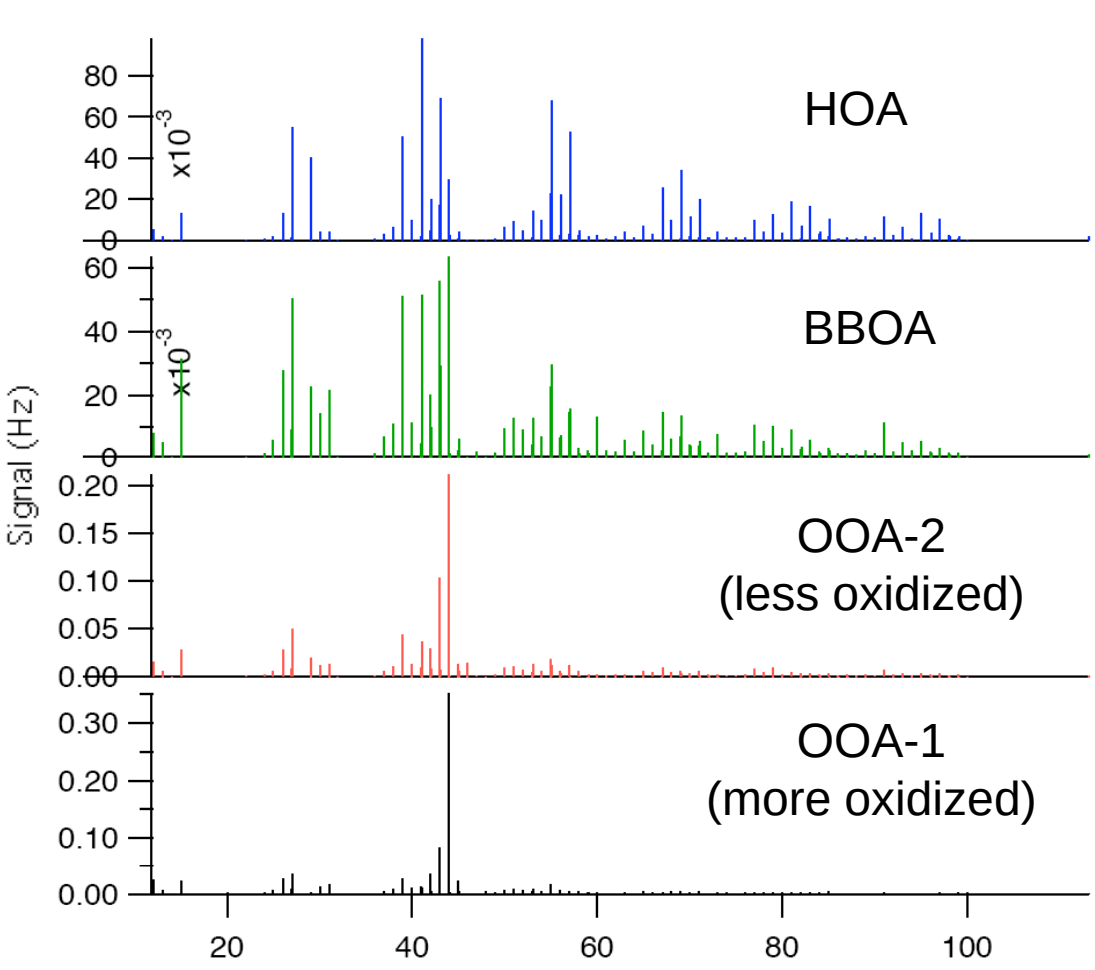
SOA from evaporated POA

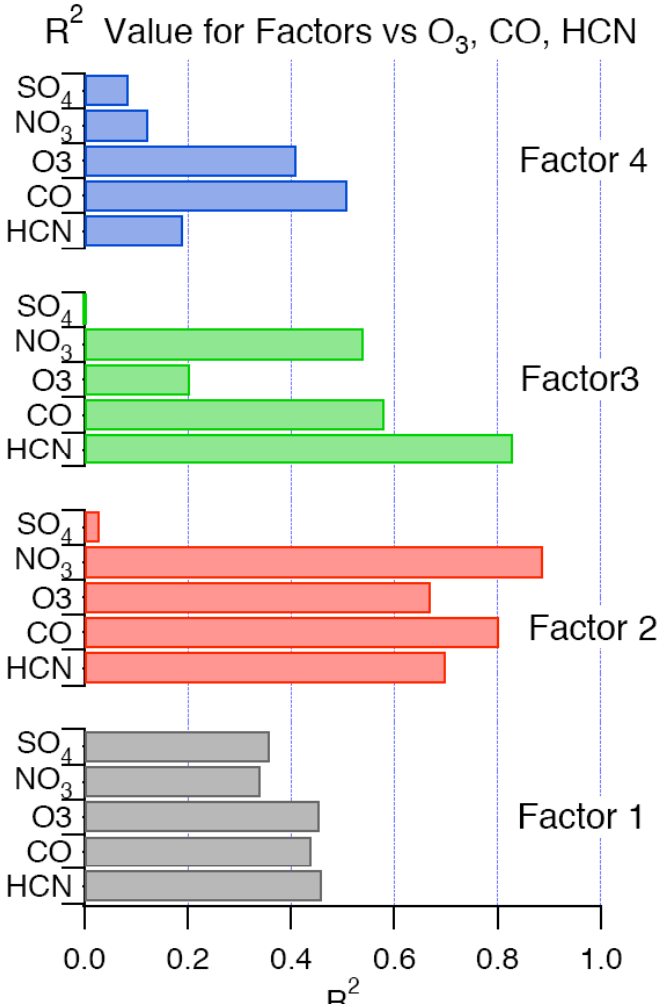


- Robinson et al. (2007) mechanism can produce enough SOA, but timing is delayed

Katja Dzepina et al.

PMF of C-130: High Biomass Burning

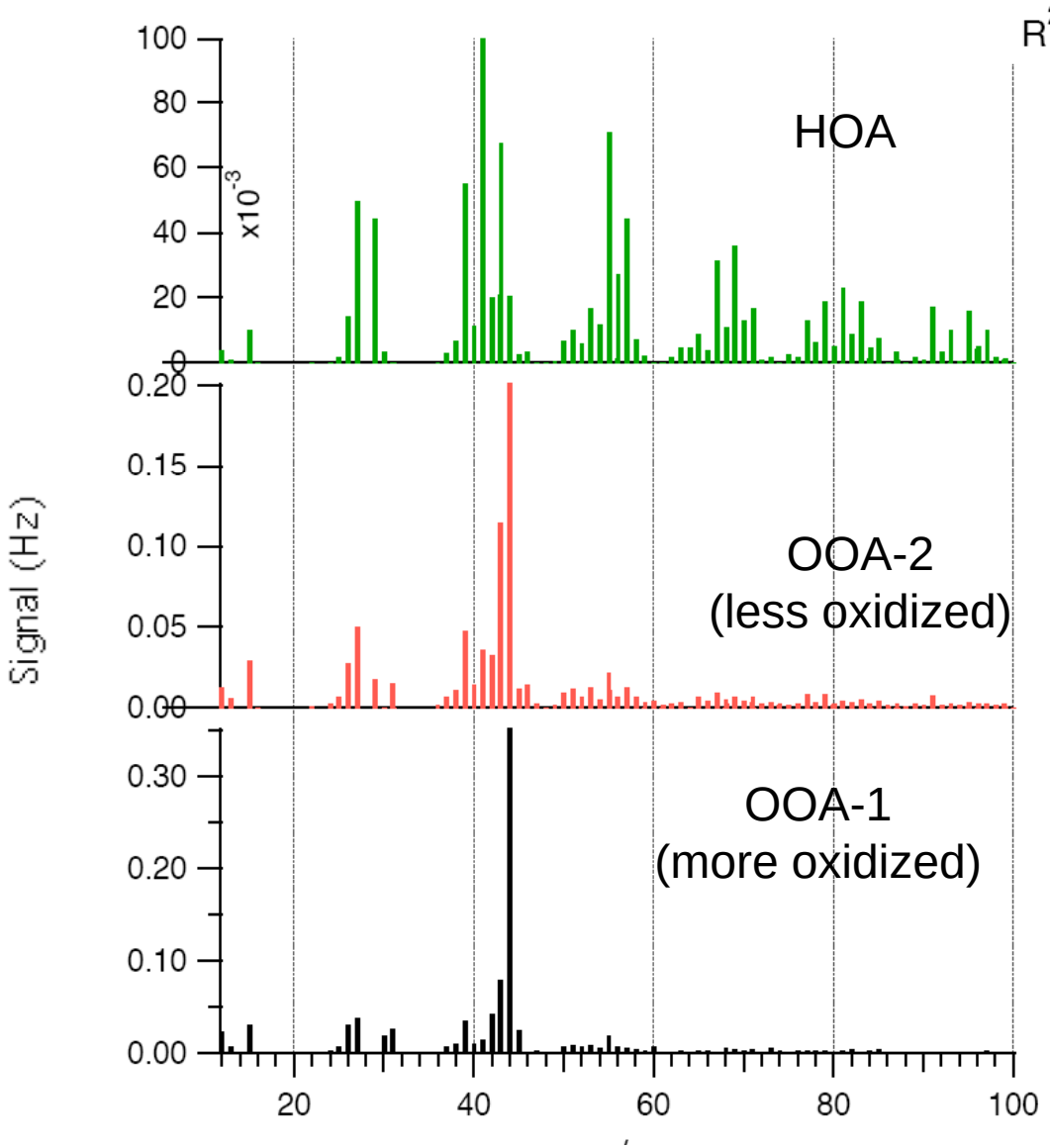


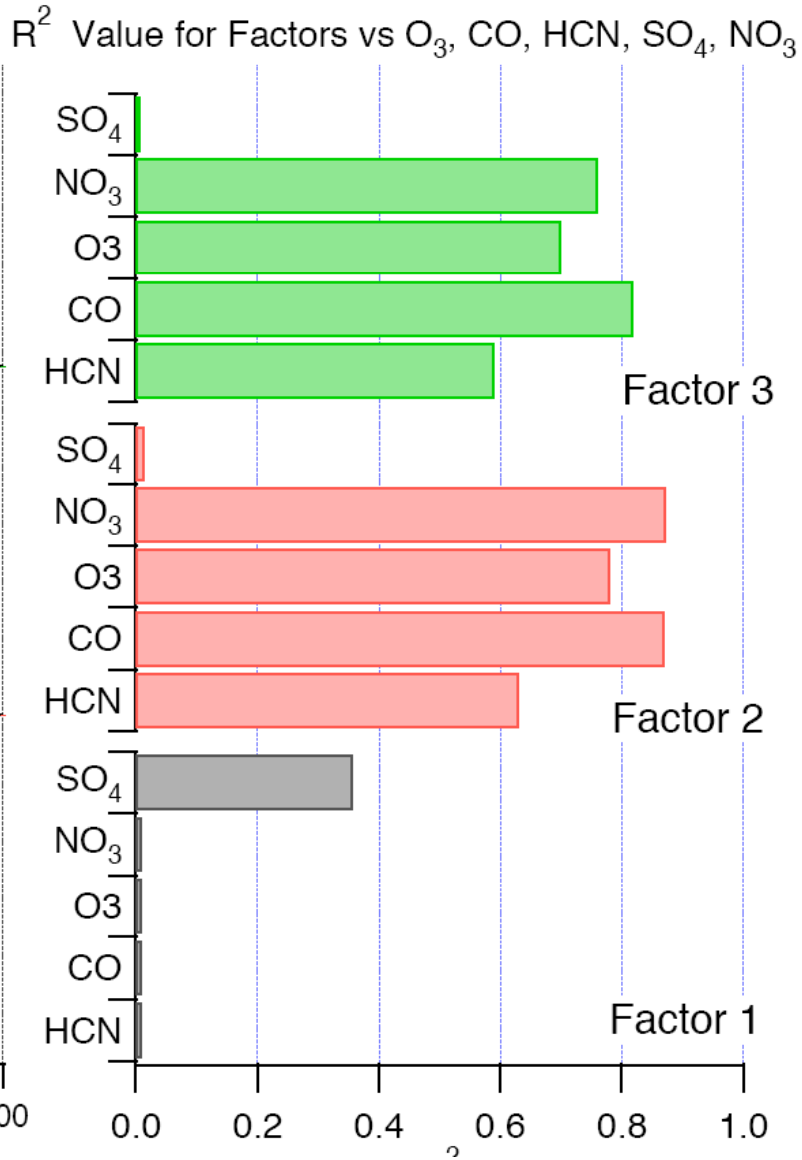


- Very similar to the city
  - Evolution: T0 -> PTP -> G-1 -> C-130

DeCarlo et al.
(poster outside)

PMF of C-130: Low Biomass Burning

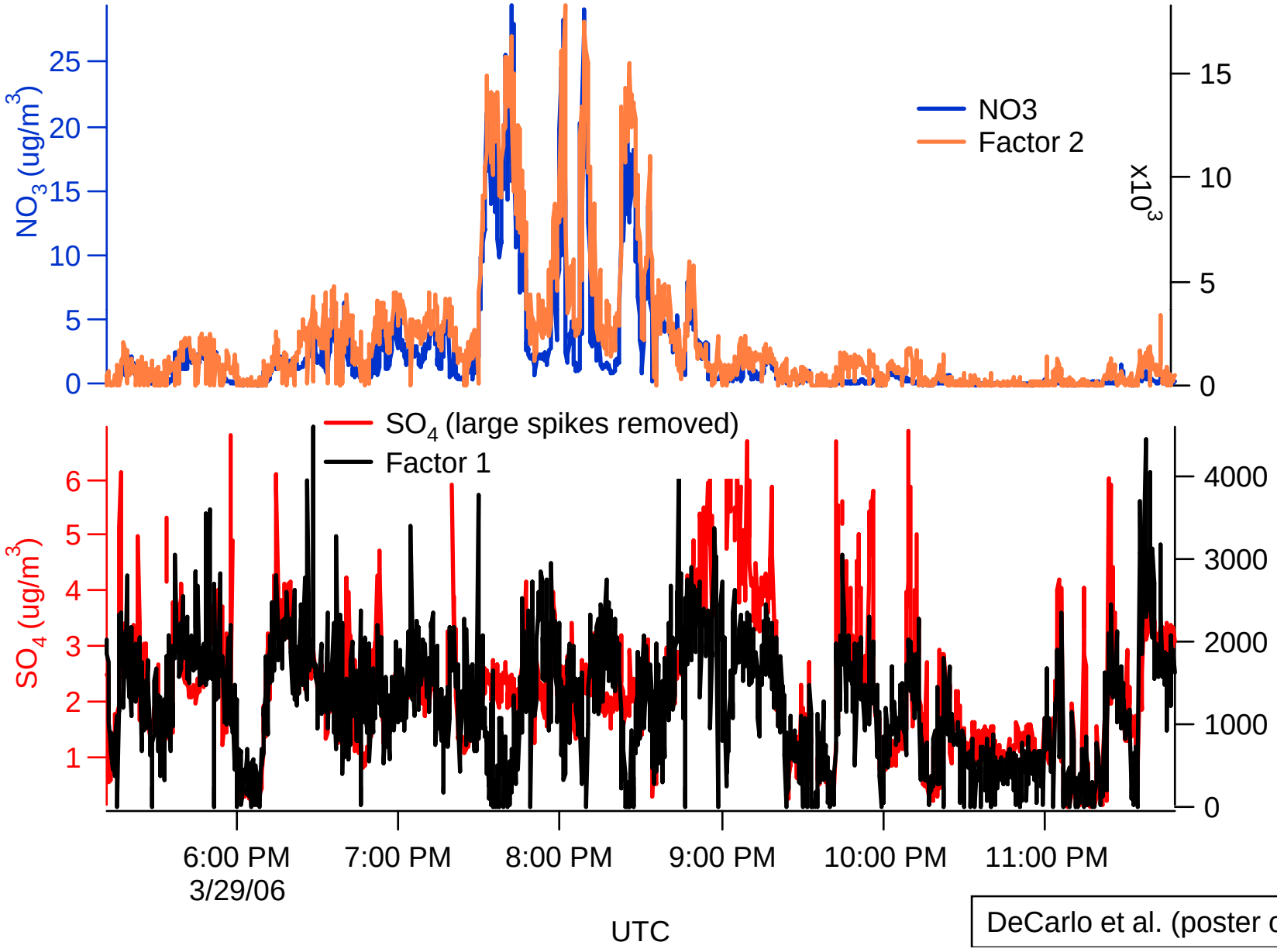




- BBOA component not-detectable in C-130

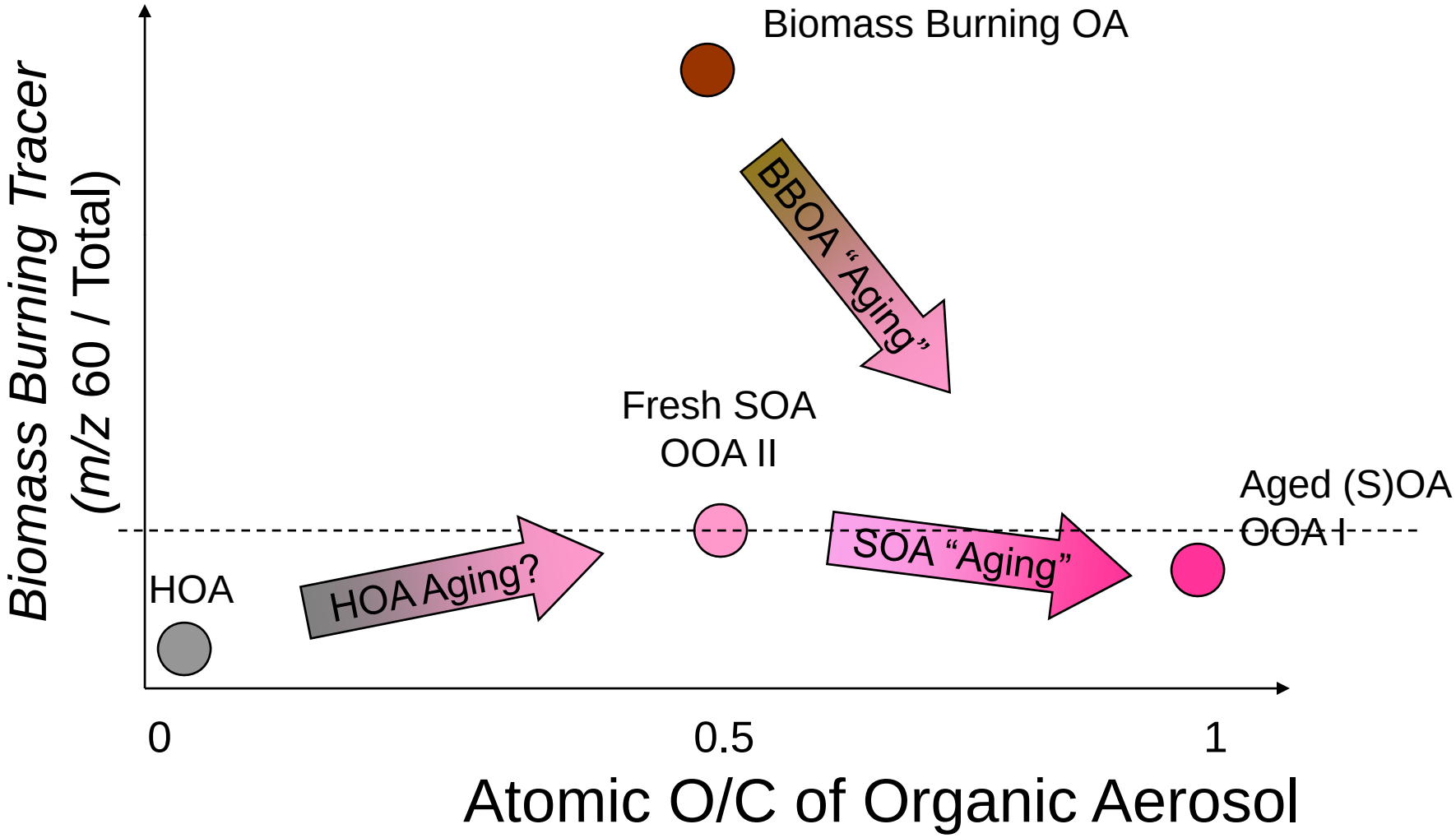
DeCarlo et al. (poster outside)

Factors 1 and 2 with Inorganics



DeCarlo et al. (poster outside)

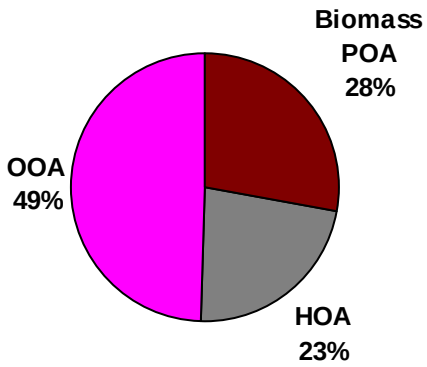
Conceptual Model of OA in Mexico City



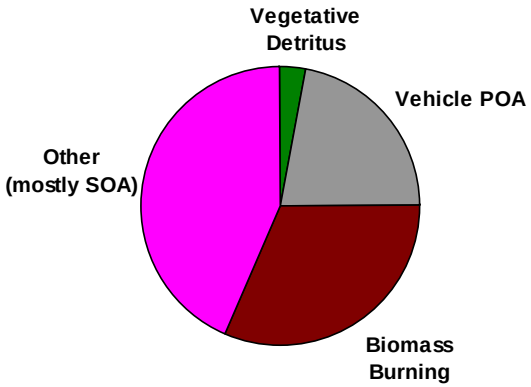
Organic Aerosol Source Apportionment

In Mexico City T0 (IMP)

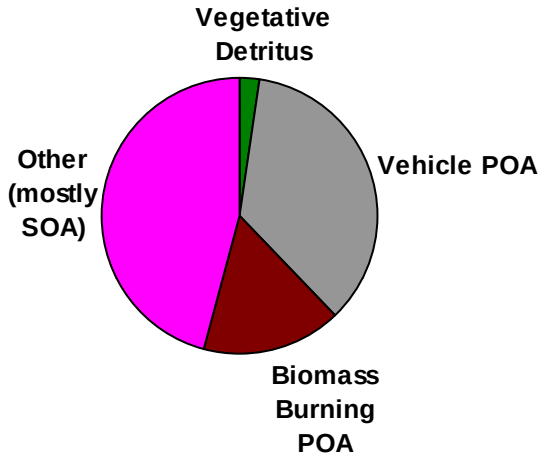
AMS: Aiken et al.



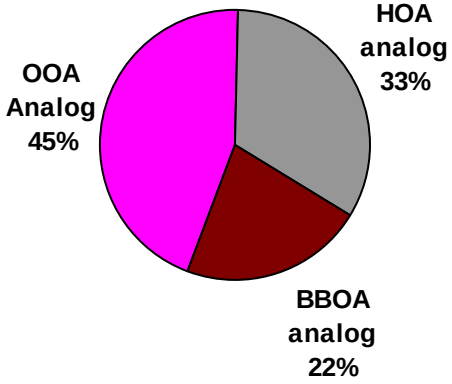
CMB: Schauer et al. T1



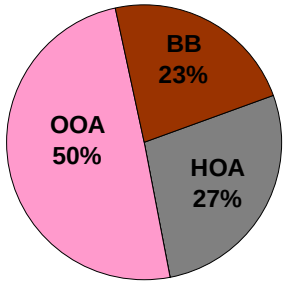
CMB: Stone & Schauer



Prevot et al: ^{14}C

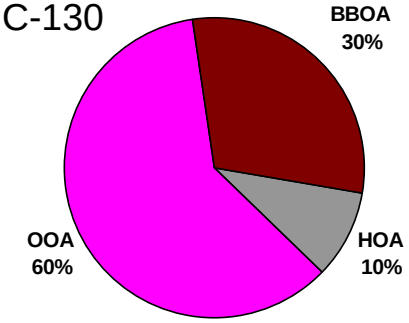


AMS for that day

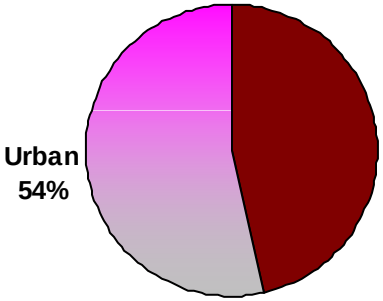


Mexico City Outflow

DeCarlo et al. C-130

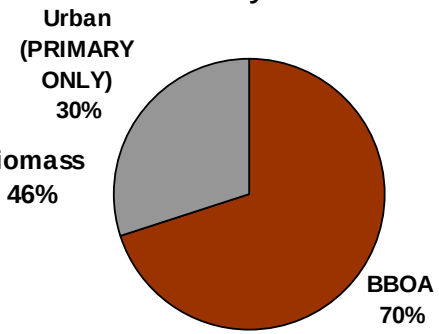


Crounse, DeCarlo et al. C-130

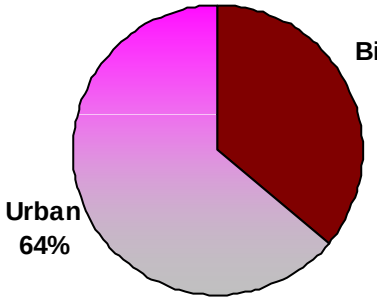


Yokelson et al. – Twin Otter

Primary ONLY



Including SOA

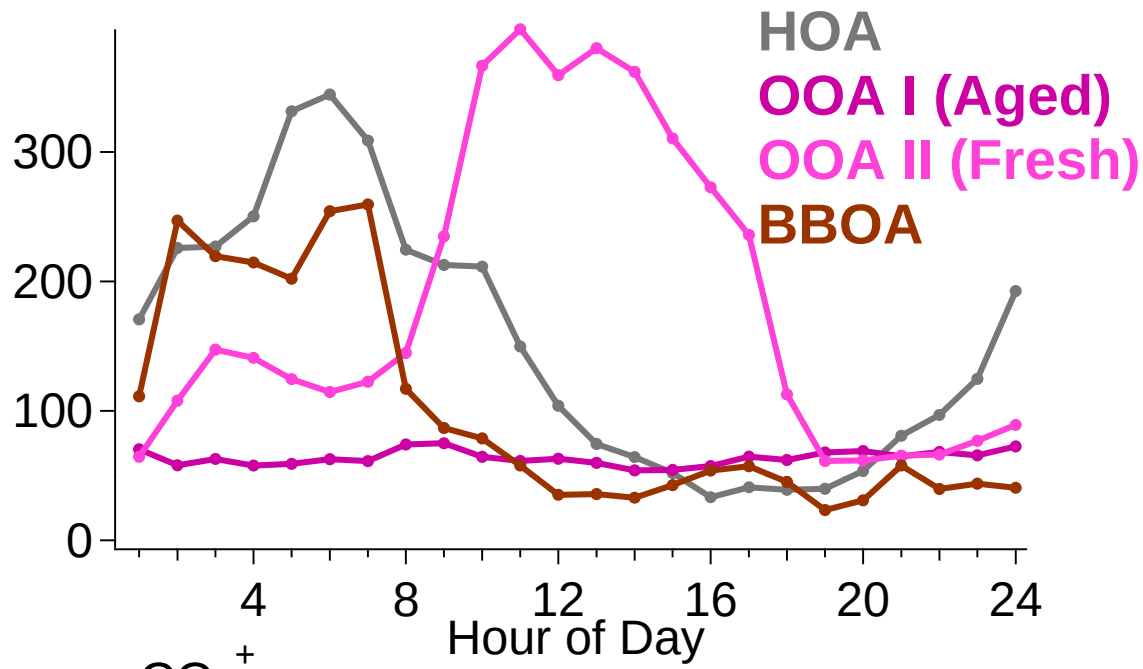


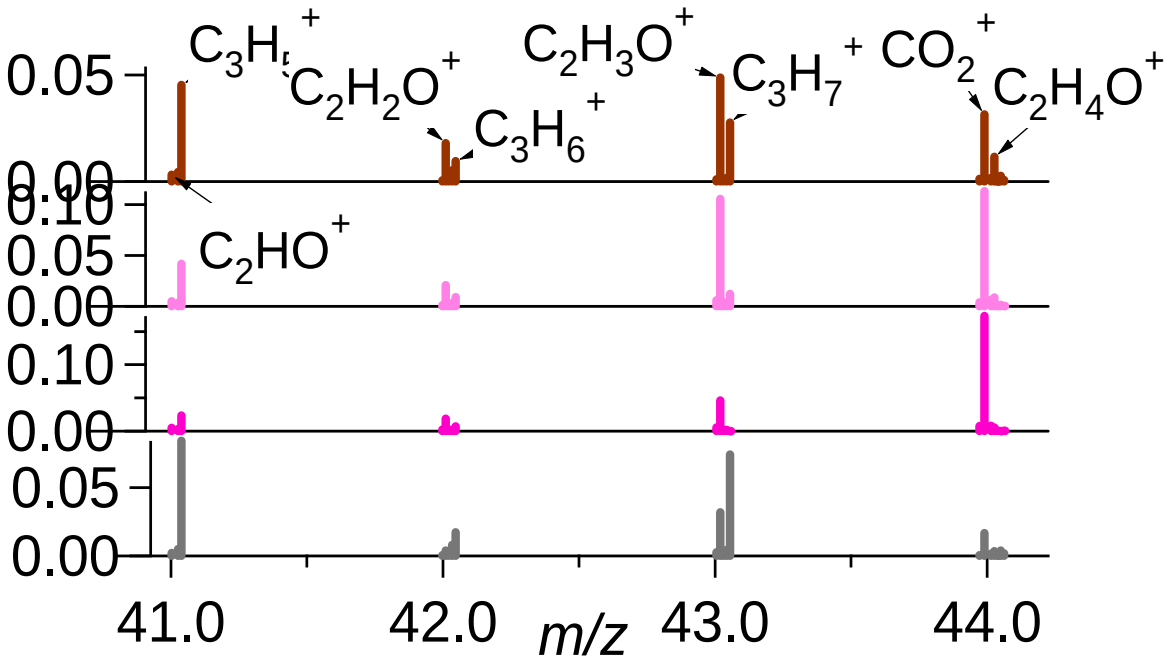
Conclusions

- **Organics** dominate PM_1
  - **OOA** ~ urban SOA and regional aged OA
    - ~50% of OM in city AND outflow
  - **Biomass burning OA**
    - Spectrum similar to pine & paper burning
    - ~ 15-30% of organic at T0
    - ~1/3 to ½ of outflow
      - *Lower fraction of PM_1*
    - Peaks at night and early morning, like acetonitrile
      - Advection of fires from previous day
  - **HOA** ~ urban POA, correlates with CO, BC
    - ~23-35% of OM at T0
    - Small fraction of outflow

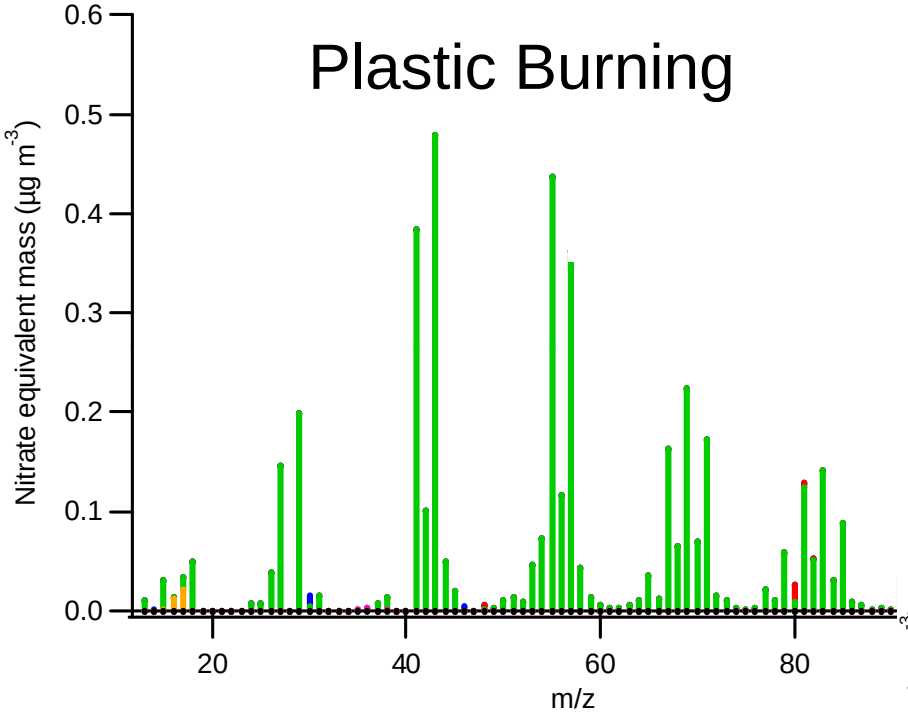
BACKUP SLIDES

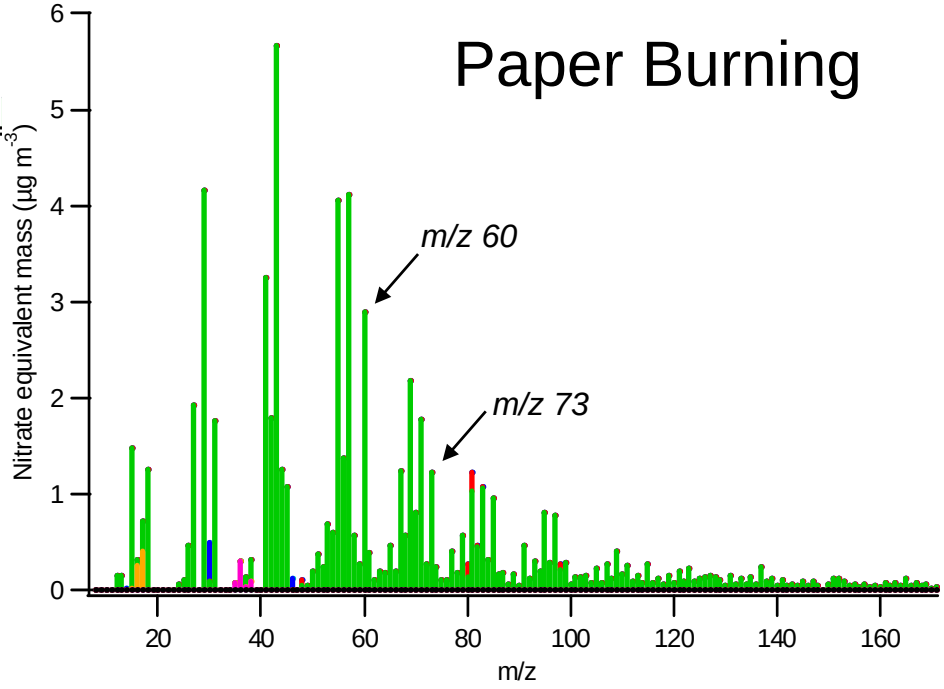
PMF of High Resolution AMS





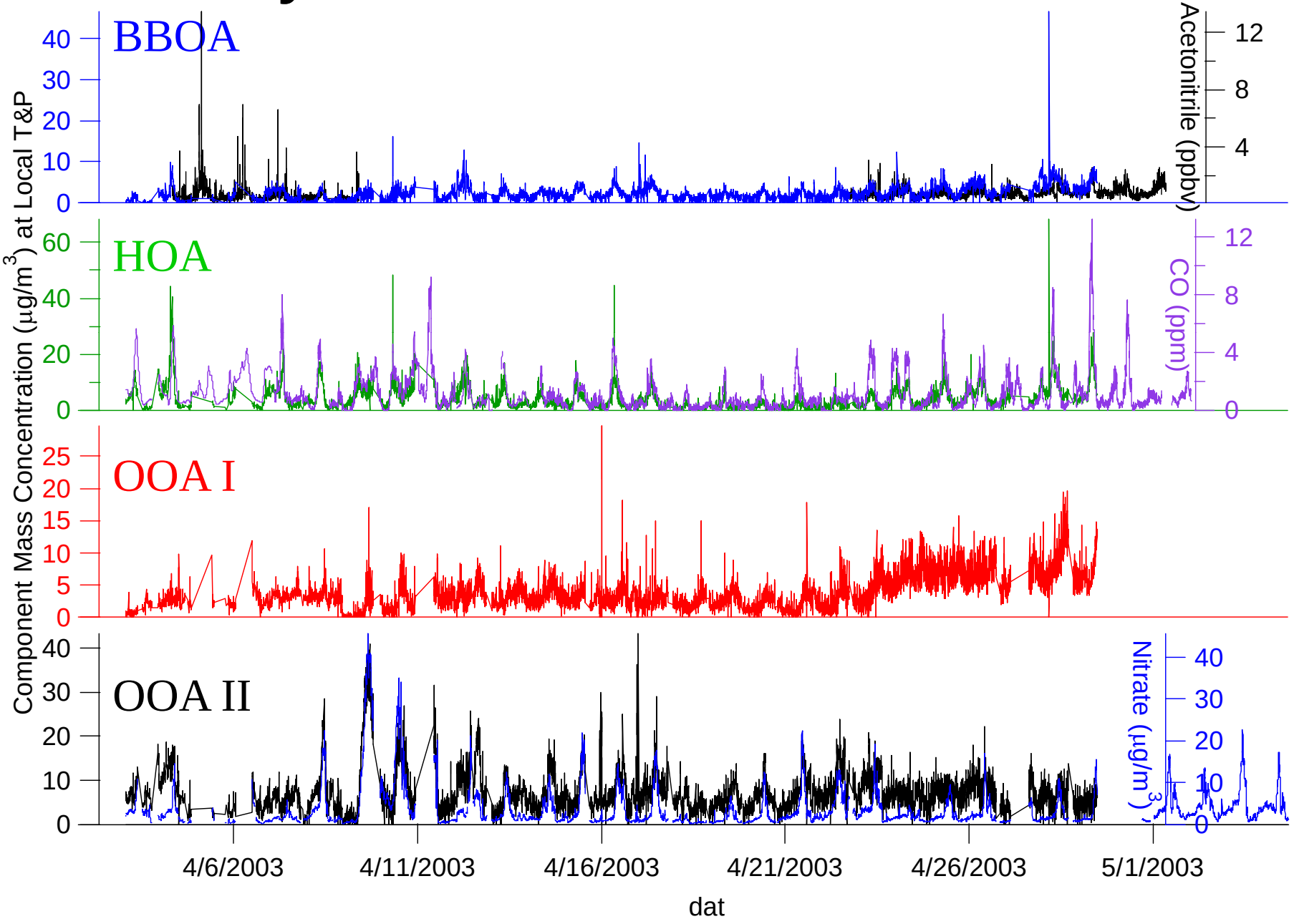
Trash Burning Spectra



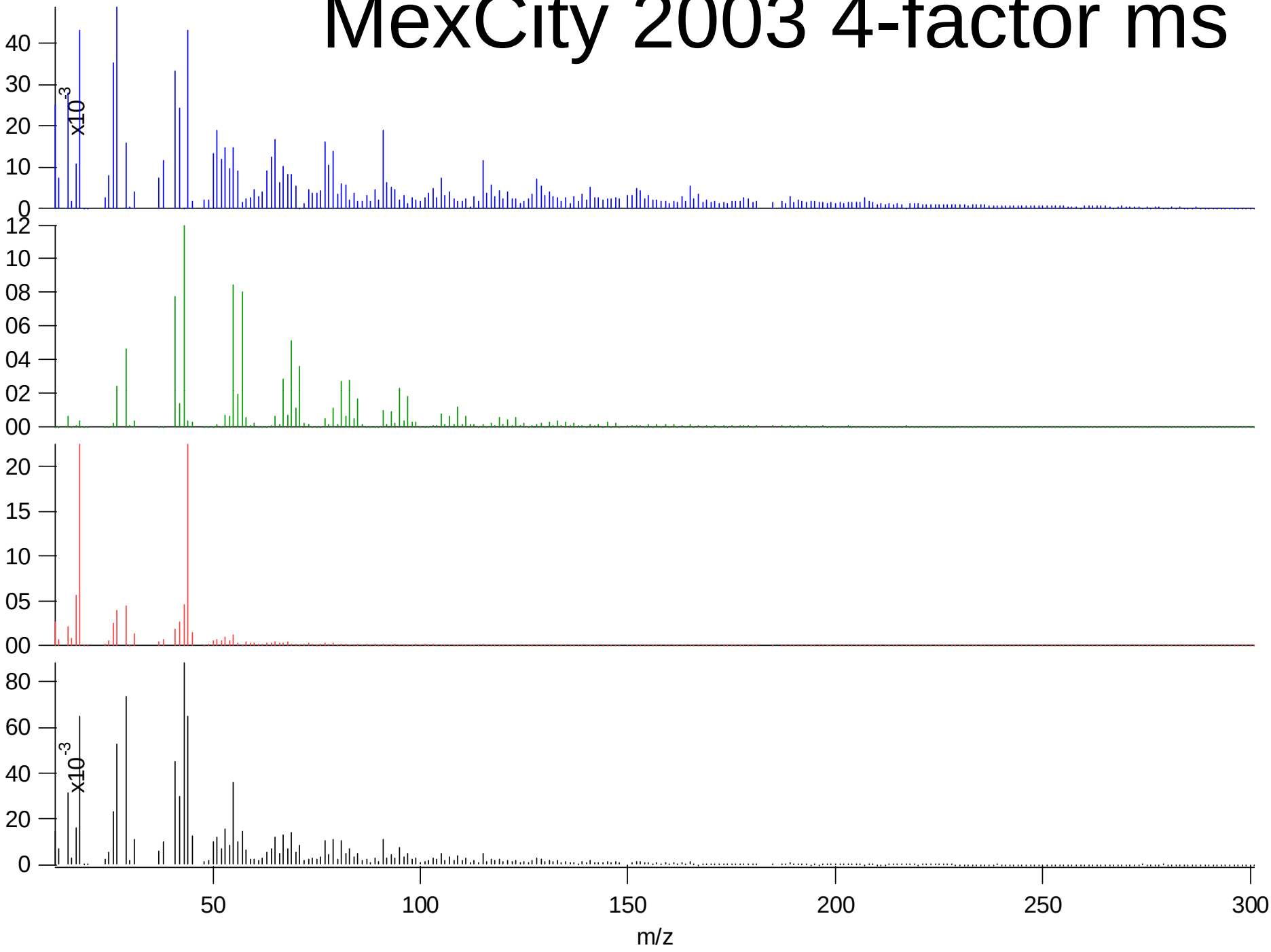


- Spectra are HOA-like
- Very different from OOA / SOA

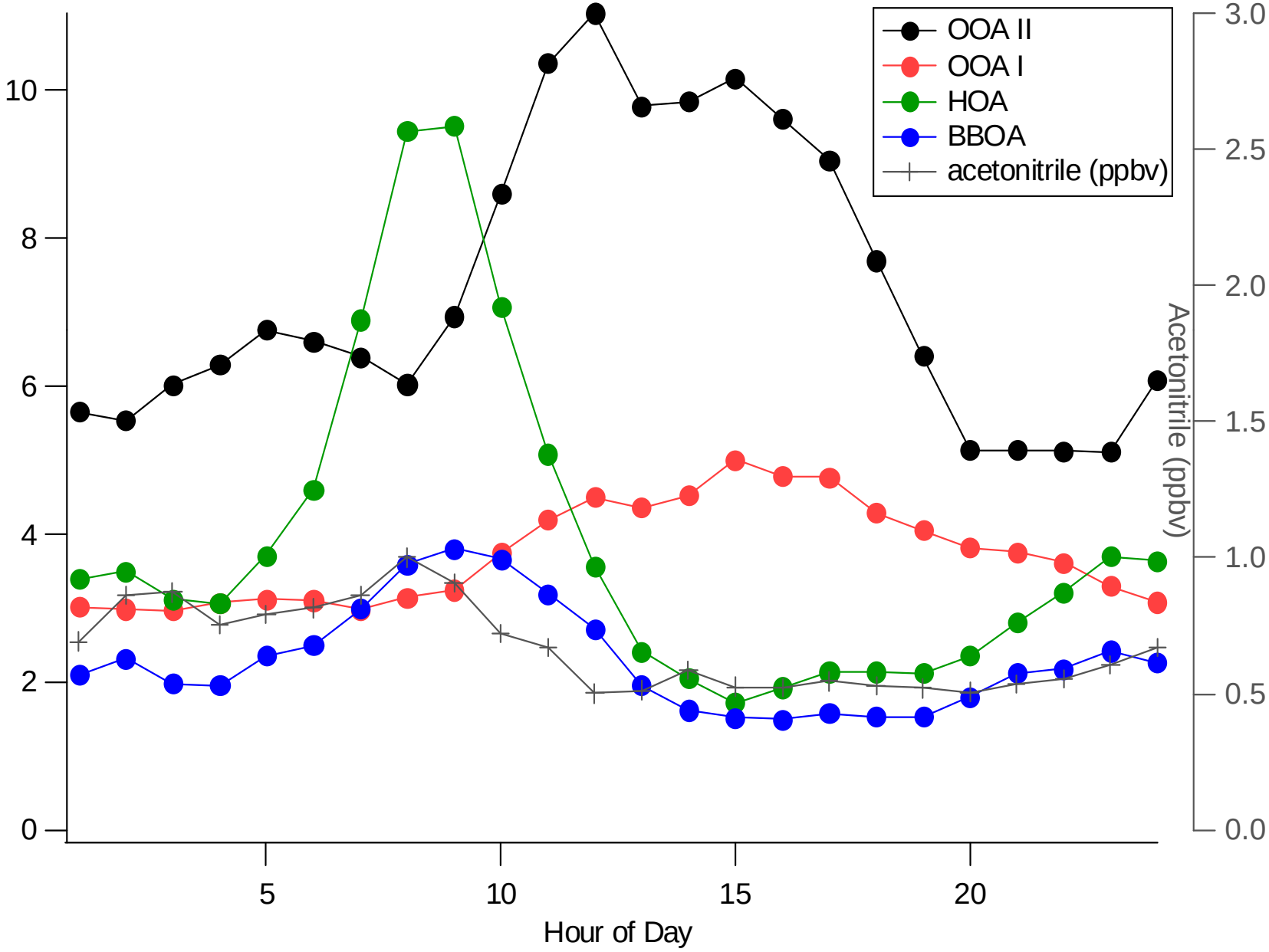
MexCity 2003 4-factor ts with tracers



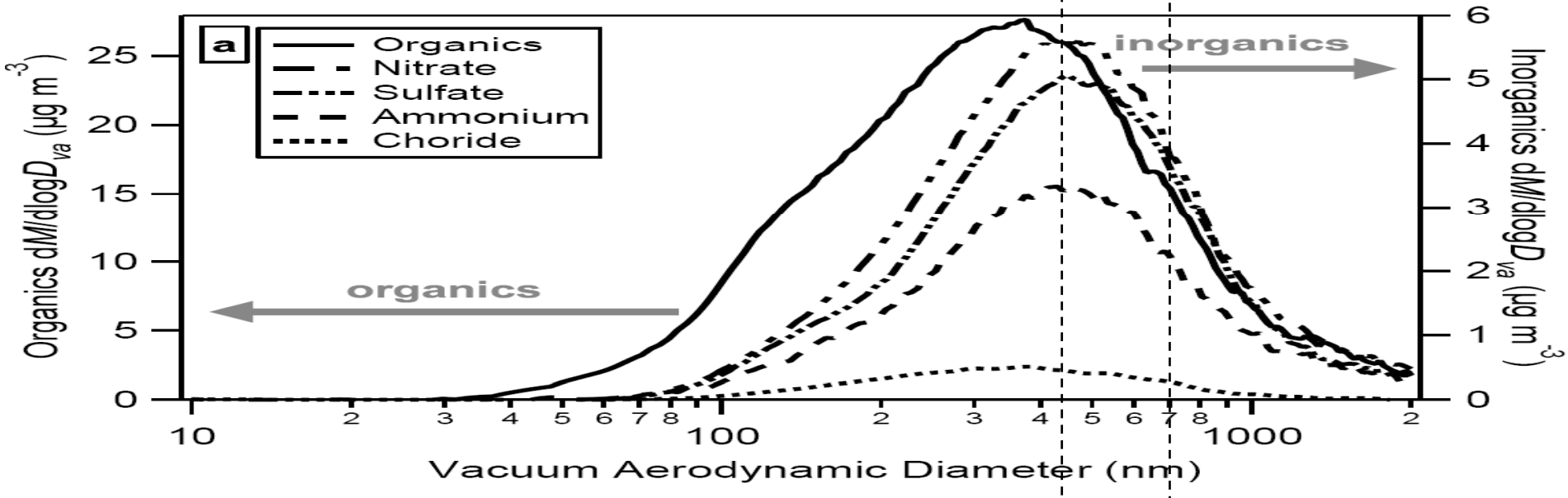
MexCity 2003 4-factor ms



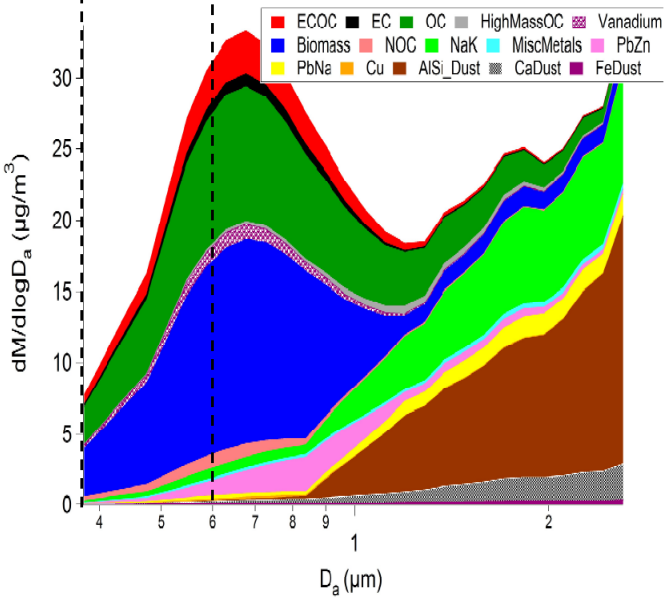
Factor Diurnal with Acetonitrile



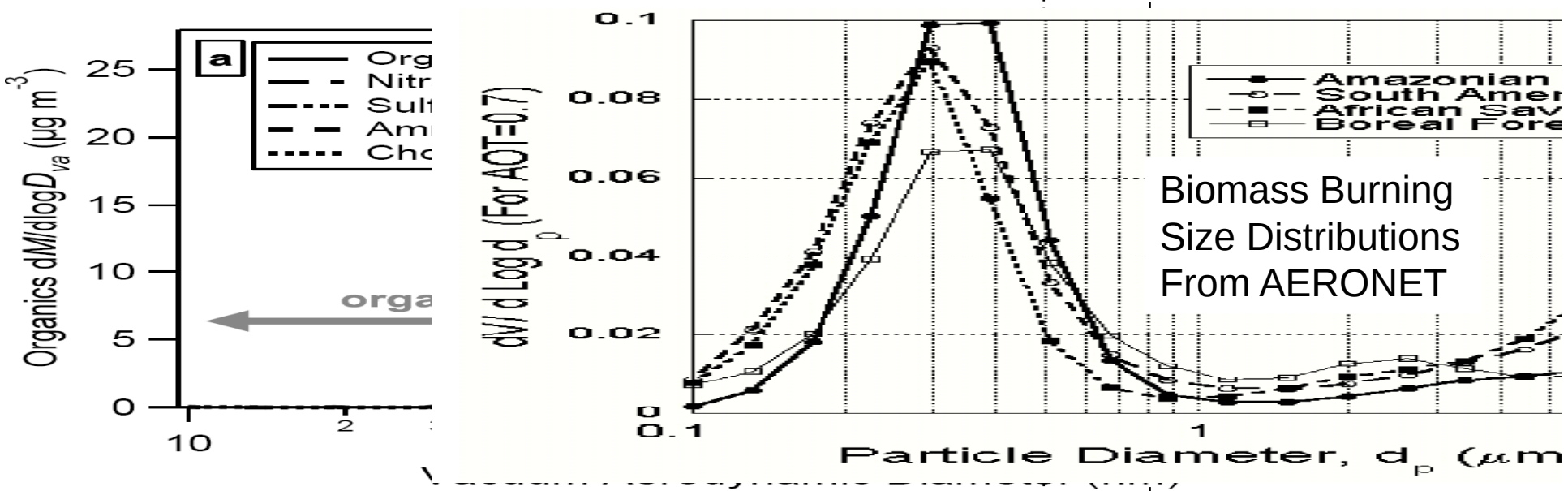
Moffet et al. ACPD 2007



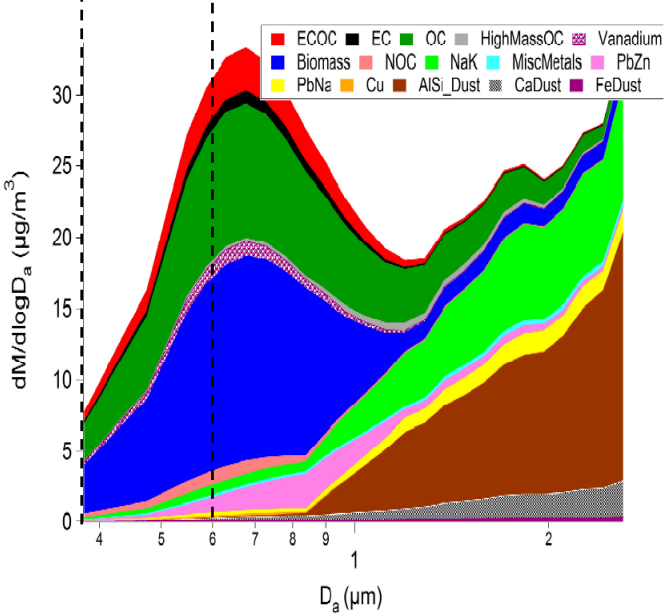
- Moffet et al: “Biomass became the largest contributor to the accumulation mode mass from the late morning until early evening”
- Caveats:
  - Acetonitrile (BB tracer) peaks in early morning, lowest in mid-afternoon
  - ATOFMS with nozzle inlet only samples upper end of submicron mode
  - Possible explanation: particles of BB origin (high K+ signal) coated by SOA and growing into upper end of accumulation mode
    - Statement should really be about the particle cores and number concentration, not the particle mass



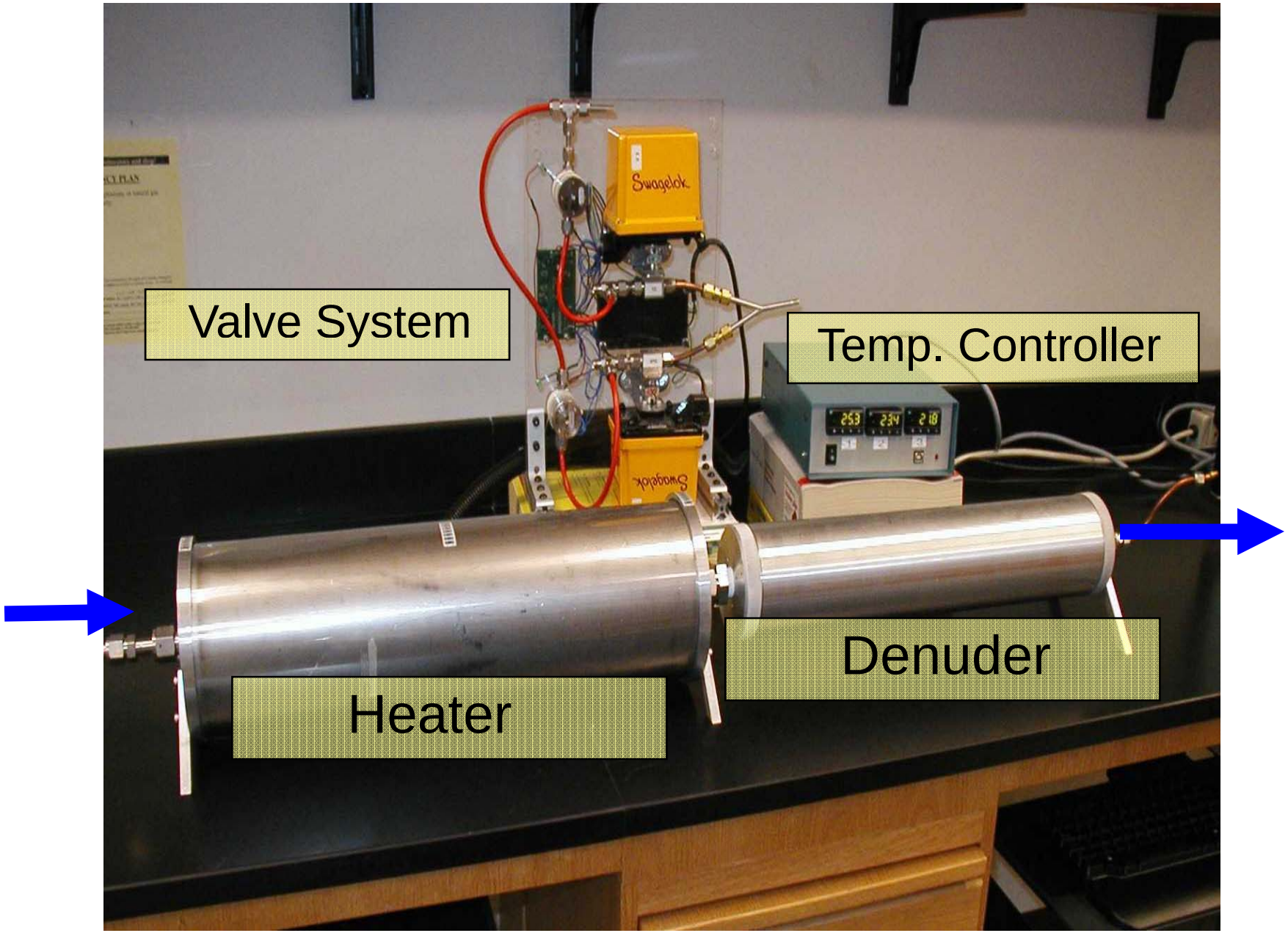
Moffet et al. ACPD 2007



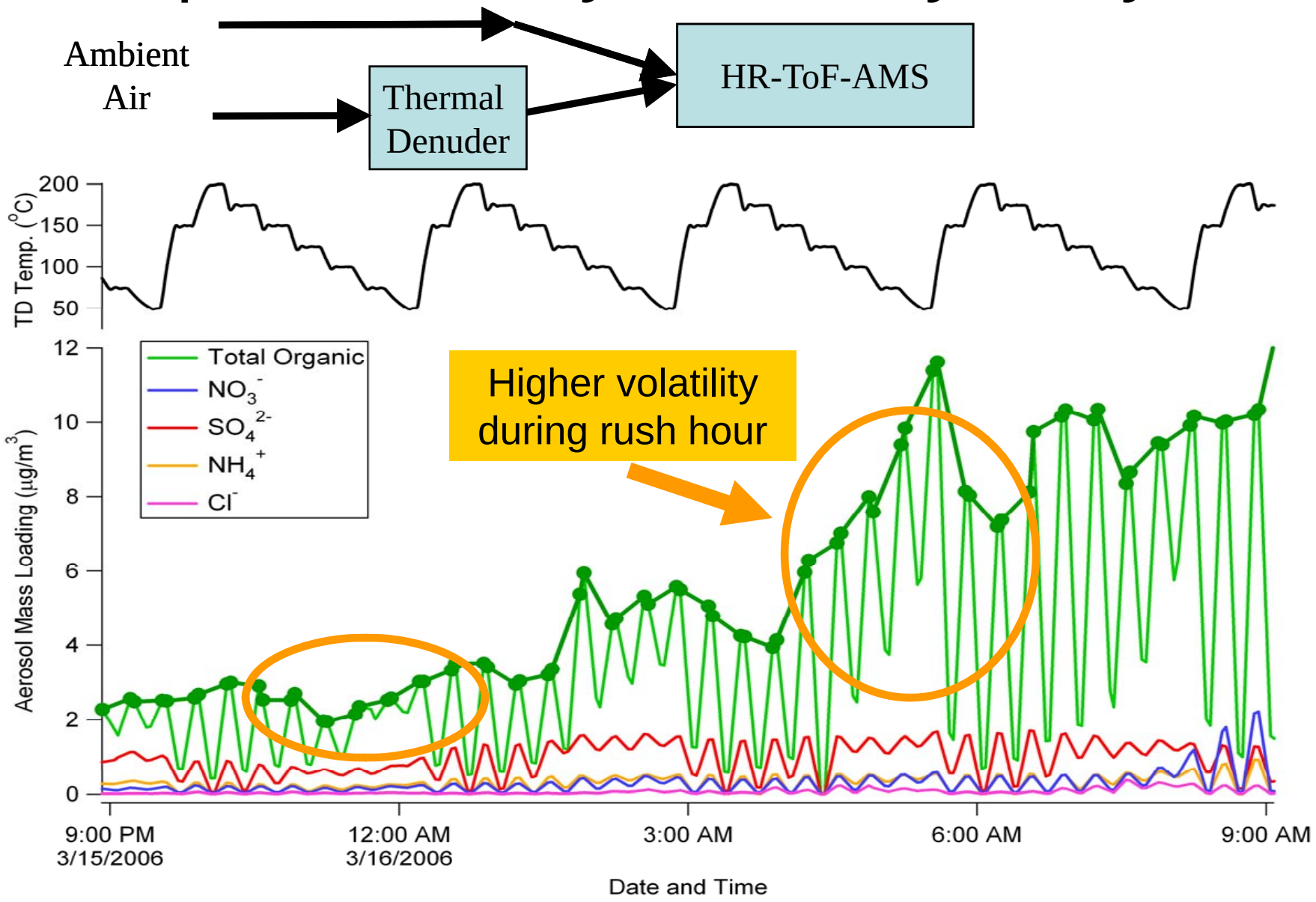
- Moffet et al: “Biomass became the largest contributor to the accumulation mode mass from the late morning until early evening”
- Caveats:
  - Acetonitrile (BB tracer) peaks in early morning, lowest in mid-afternoon
  - ATOFMS with nozzle inlet only samples upper end of submicron mode
  - Possible explanation: particles of BB origin (high K+ signal) coated by SOA and growing into upper end of accumulation mode
    - Statement should really be about the particle cores and number concentration, not the particle mass



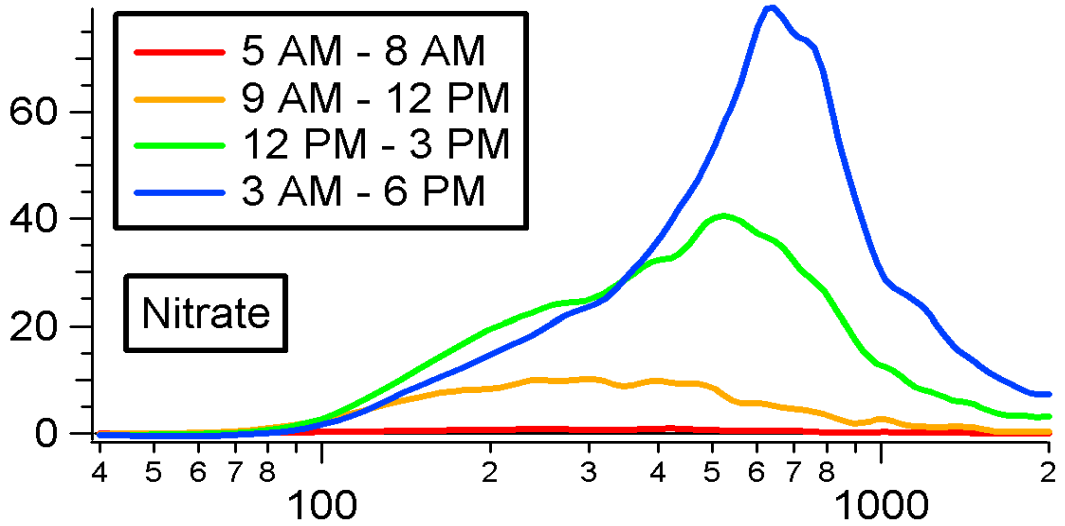
Thermodenuder

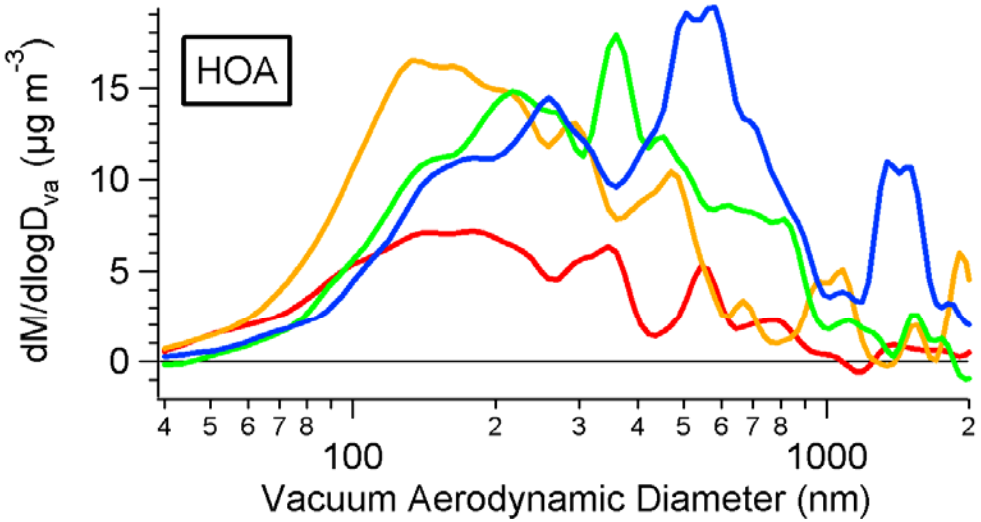


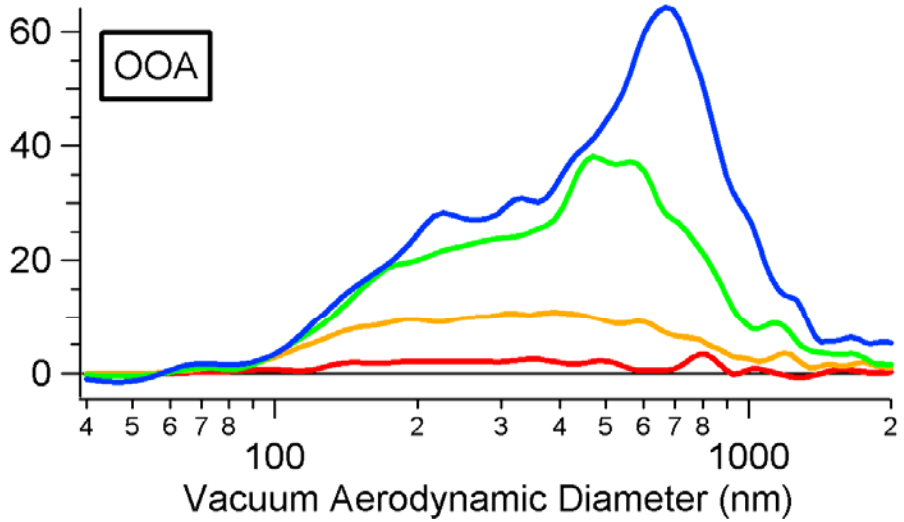
Rapid Chemistry + Volatility Analysis



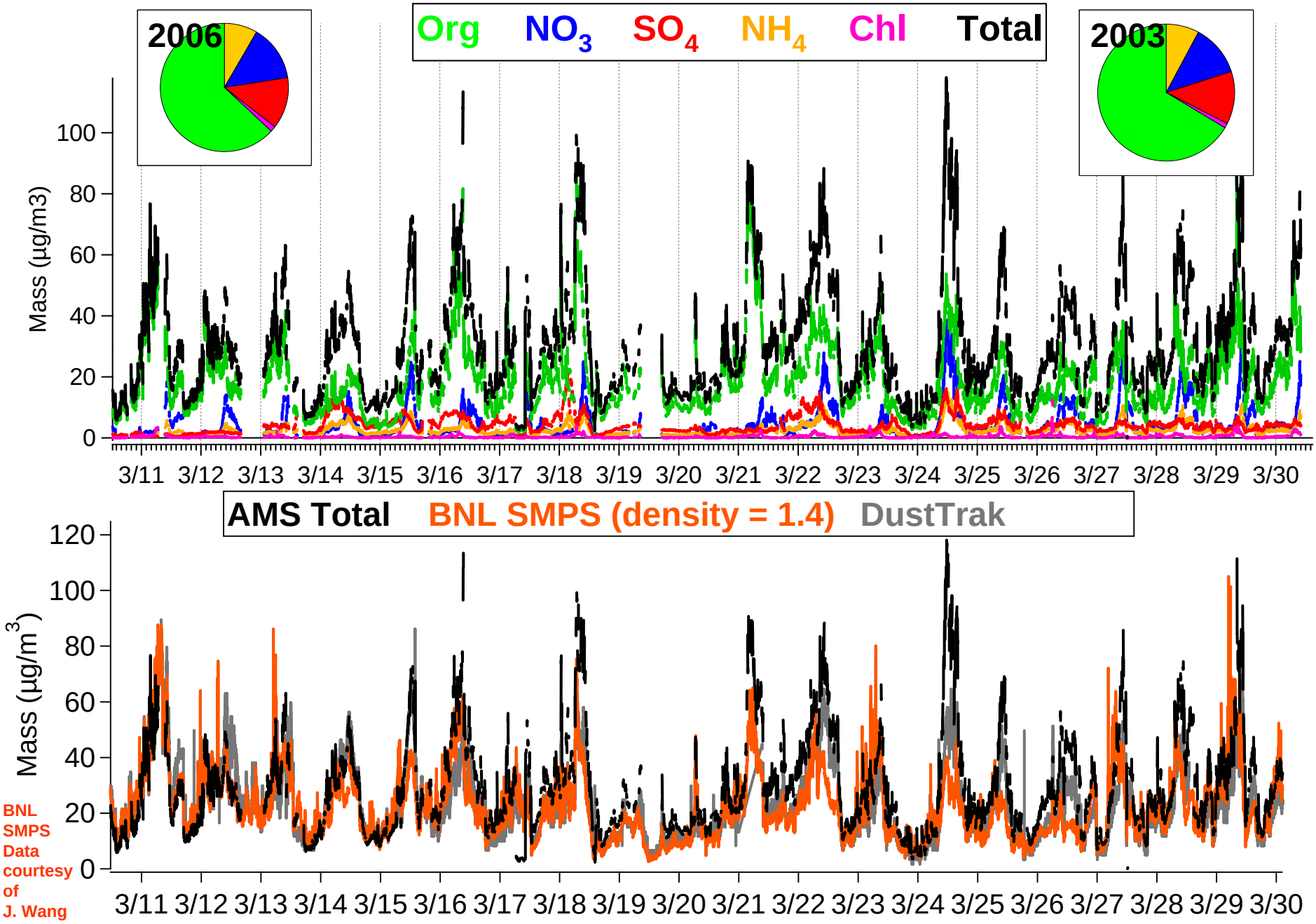
Photochemical production case study: April 9, 2003 – cont.



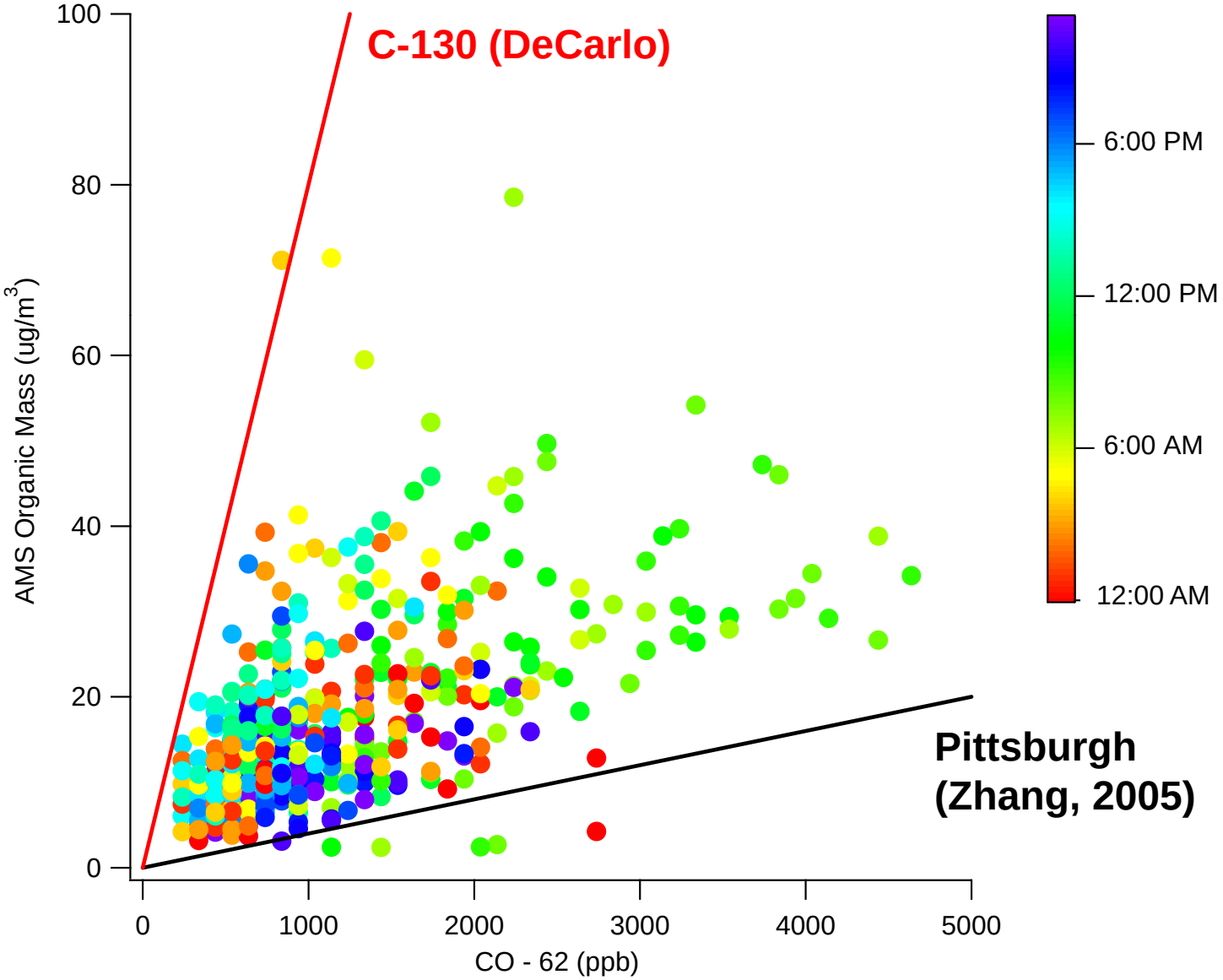


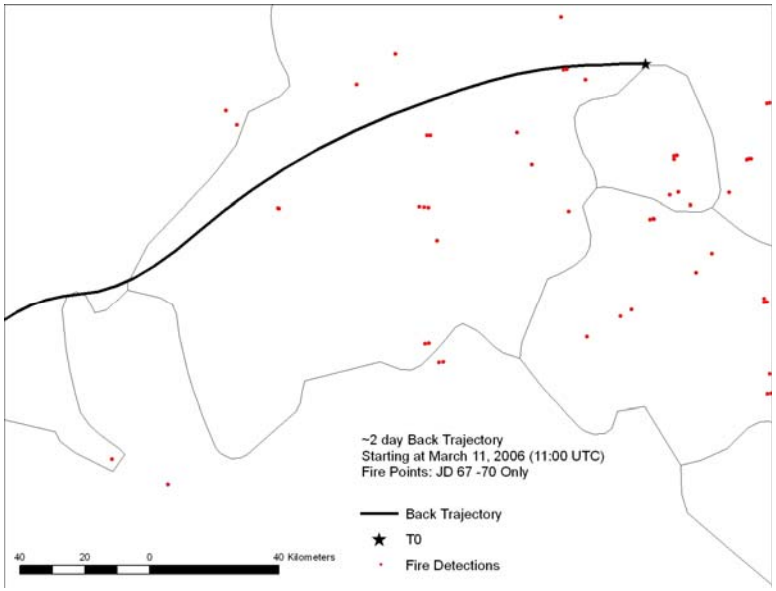


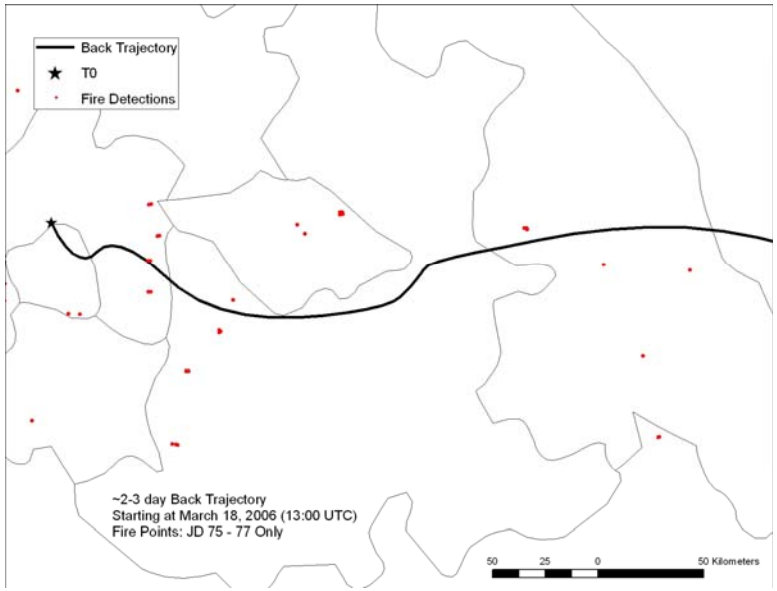
T0 HR-ToF-AMS: Ambient Mass Concentrations

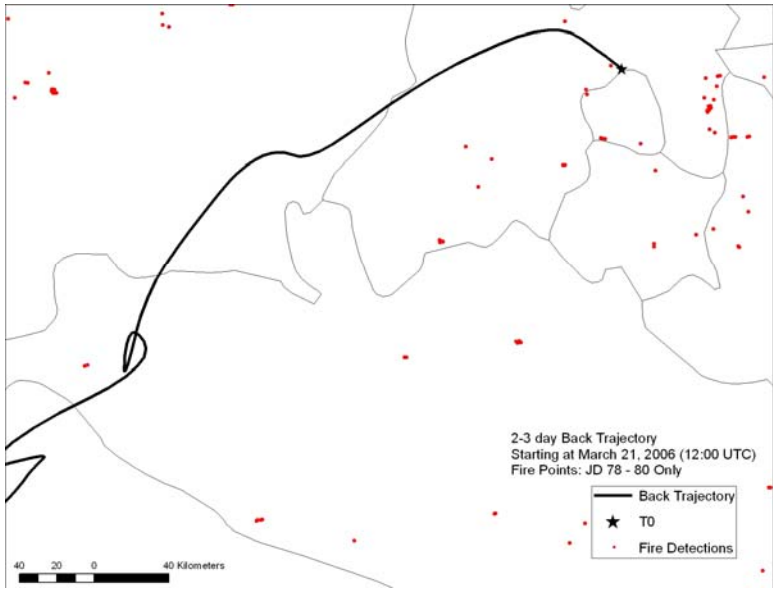


Total Organic Mass to CO Ratio Bound by Ground and Plane Measurements




~2 day Back Trajectory
Starting at March 11, 2006 (11:00 UTC)
Fire Points: JD 67 -70 Only
Back Trajectory
T0
Fire Detections
40 20 0 40 Kilometers


Back Trajectory
T0
Fire Detections
~2-3 day Back Trajectory
Starting at March 18, 2006 (13:00 UTC)
Fire Points: JD 75 - 77 Only
50 25 0 50 Kilometers


2-3 day Back Trajectory
Starting at March 21, 2006 (12:00 UTC)
Fire Points: JD 78 - 80 Only
Back Trajectory
T0
Fire Detections
40 20 0 40 Kilometers