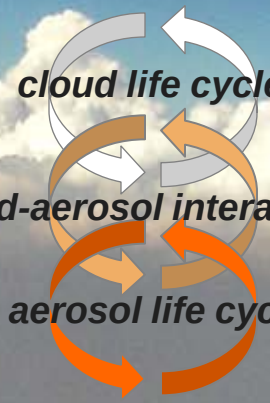


Modeling Organic Aerosols in a Megacity: Comparison of Simple and Complex Representations of the Volatility Basis Set Approach

Manish Shrivastava, Jerome Fast, and Rahul Zaveri

Aerosol Life Cycle Working Group, October 11-12, 2010

Office of Science
U.S. DEPARTMENT OF ENERGY

- Supported by the U.S. Department of Energy's Atmospheric System Research Program
- We thank the numerous scientists who provided MILAGRO data

Pacific Northwest
NATIONAL LABORATORY

Motivation

Measured Organic Matter:

- Comprises 20 – 90% of submicron mass worldwide [e.g. *Zhang et al.* 2007]
- Analyses of aerosol mass spectrometer data suggests it is comprised of mostly oxygenated material [*Jimenez et al.* 2010]

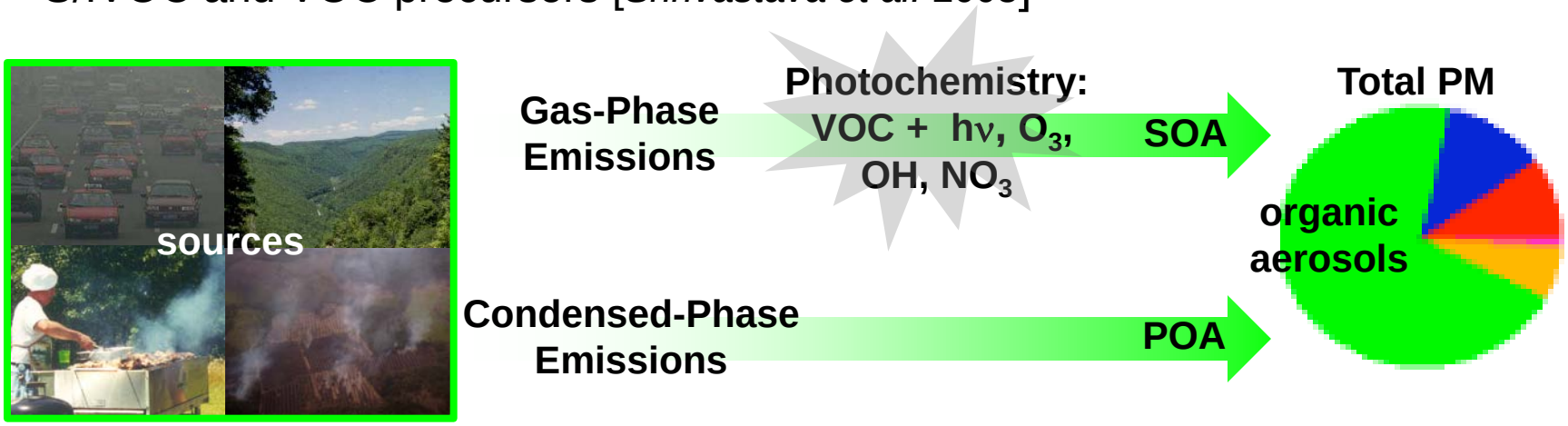
Predicted Organic Matter:

- Simulated mass usually too low [e.g. *Volkamer et al.* 2006]
- SOA formation is not adequately represented by models, OA treated as non-volatile POA or using the traditional 2-product approach [*Odum et al.* 1996]

Objective

New Treatment of Organic Matter:

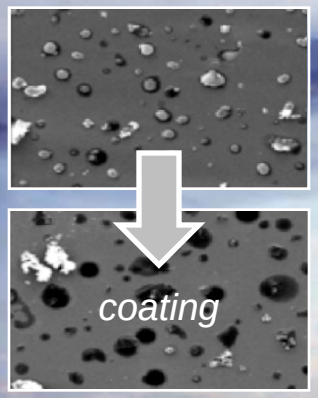
- 'Volatility Basis Set' approach proposed by *Robinson et al.* [2007] that represents organic matter as semi-volatile POA and formation of SOA through oxidation of S/IVOC and VOC precursors [*Shrivastava et al.* 2008]



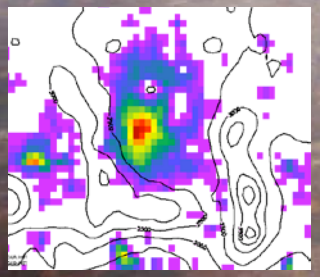
- Application of this approach have shown improvements in simulated SOA [e.g. *Dzepina et al.* 2008; *Hodzic et al.* 2009, 2010]
- In this study, 'simple' and 'complex' volatility basis set versions are coupled with the MOSAIC in the WRF-Chem model [*Shrivastava et al.* 2010, to be submitted]
  - Simple versions needed for climate models
  - Need to assess performance using field data
  - Couple SOA with aerosol-radiation-cloud interactions

Testbed Case for SOA Treatment Development

Megacities Initiative: Local and Global Research Observations



2006 Emission Inventory courtesy of Miguel Zavala (MCE2)



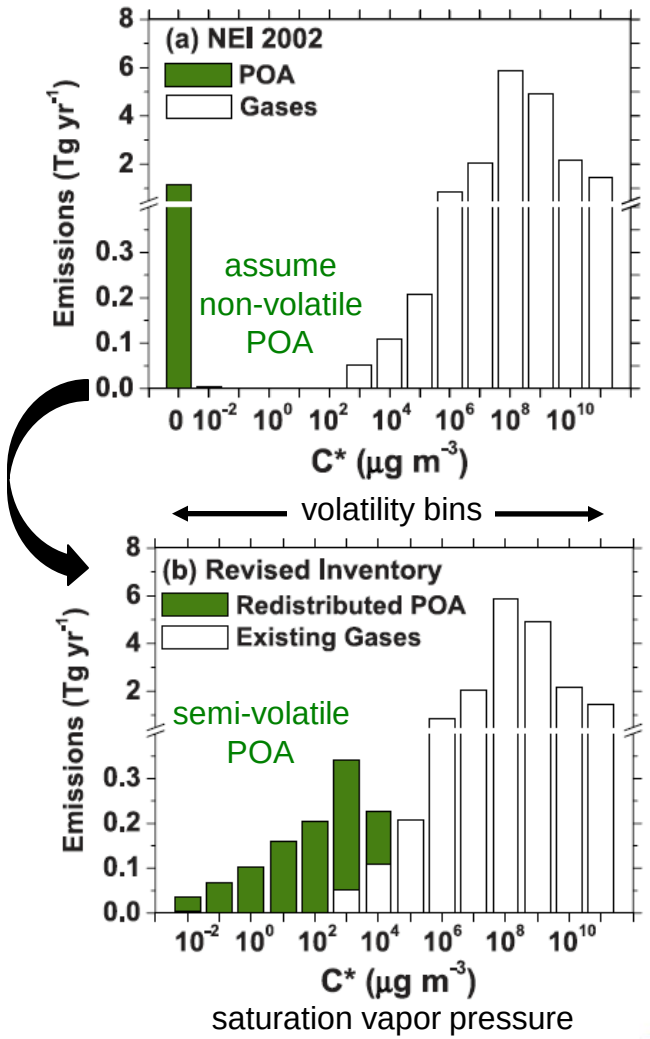
NASA DC-8 photo

Mexico City

Organic aerosol measurements collected at several surface sites and on two research aircraft, in conjunction with meteorology and aerosol precursors

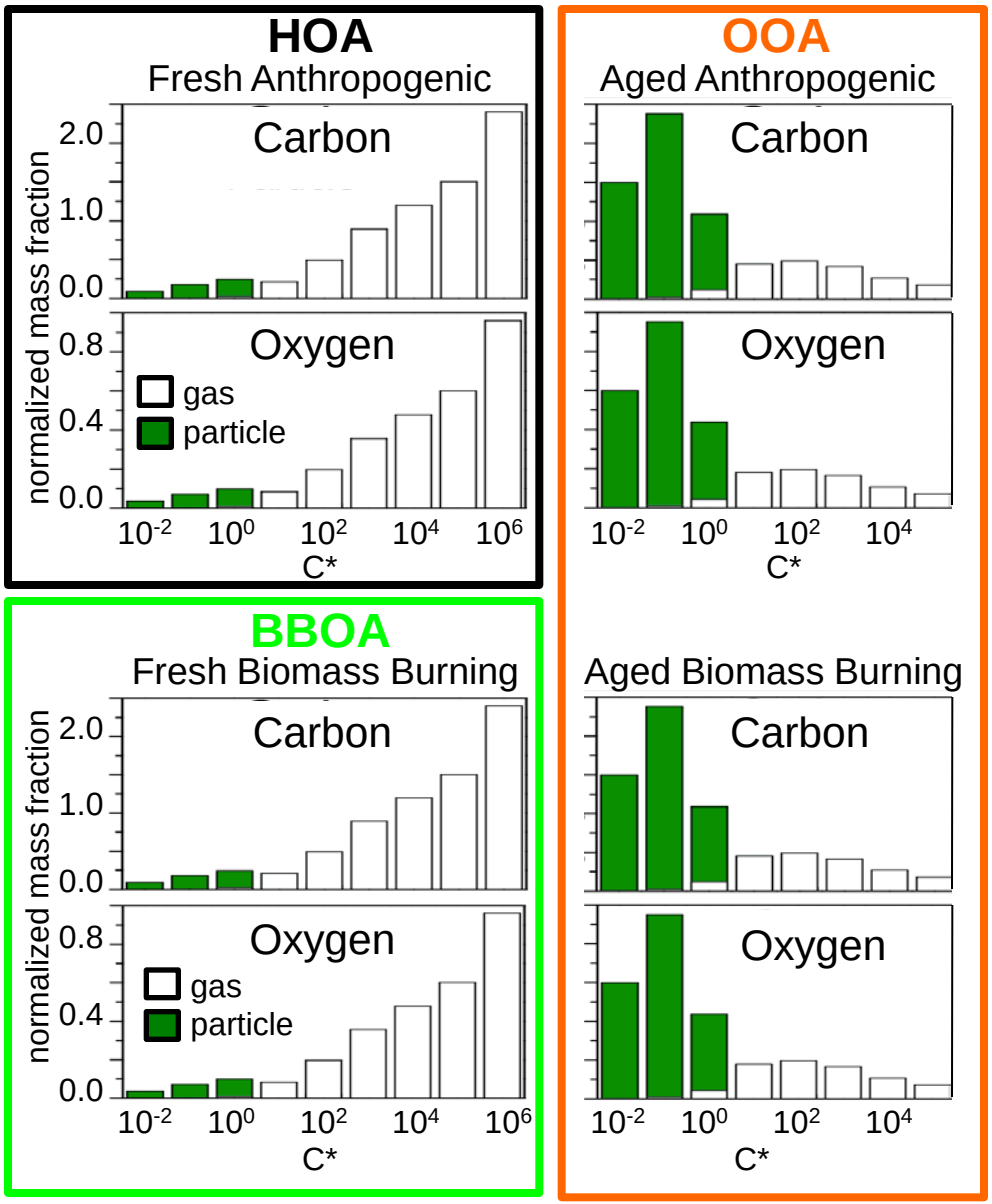
Brief Description of Volatility Basis Set

- Modified *Robinson et al*. [2007] volatility basis set by adding 2 oxygen atoms per generation of oxidation
- # of volatility bins: 9 for **fresh** and 8 for **aged**
- Separate volatility species for **fossil** and **biomass burning** sources
- Predict both **oxygen** and **carbon** mass for each volatility species to obtain O:C ratios
- Traditional anthropogenic and biogenic SOA (4-product VBS set) using yields from *Tsimpidi et al*. [2010] with no further aging
- prognostic SOA species: currently **380 for 4 size bins**, (684 for 8 size bins)
- Coupled with SAPRC-99 gas-phase mechanism and MOSAIC aerosol model [*Pablo Saide, U. Iowa*]
- Dry deposition for all species treated the same
- For now, assume new organic species all have the same refractive index, density, etc.



Pacific Northwest NATIONAL LABORATORY

Evaluating Simulated Organic Aerosols (1)



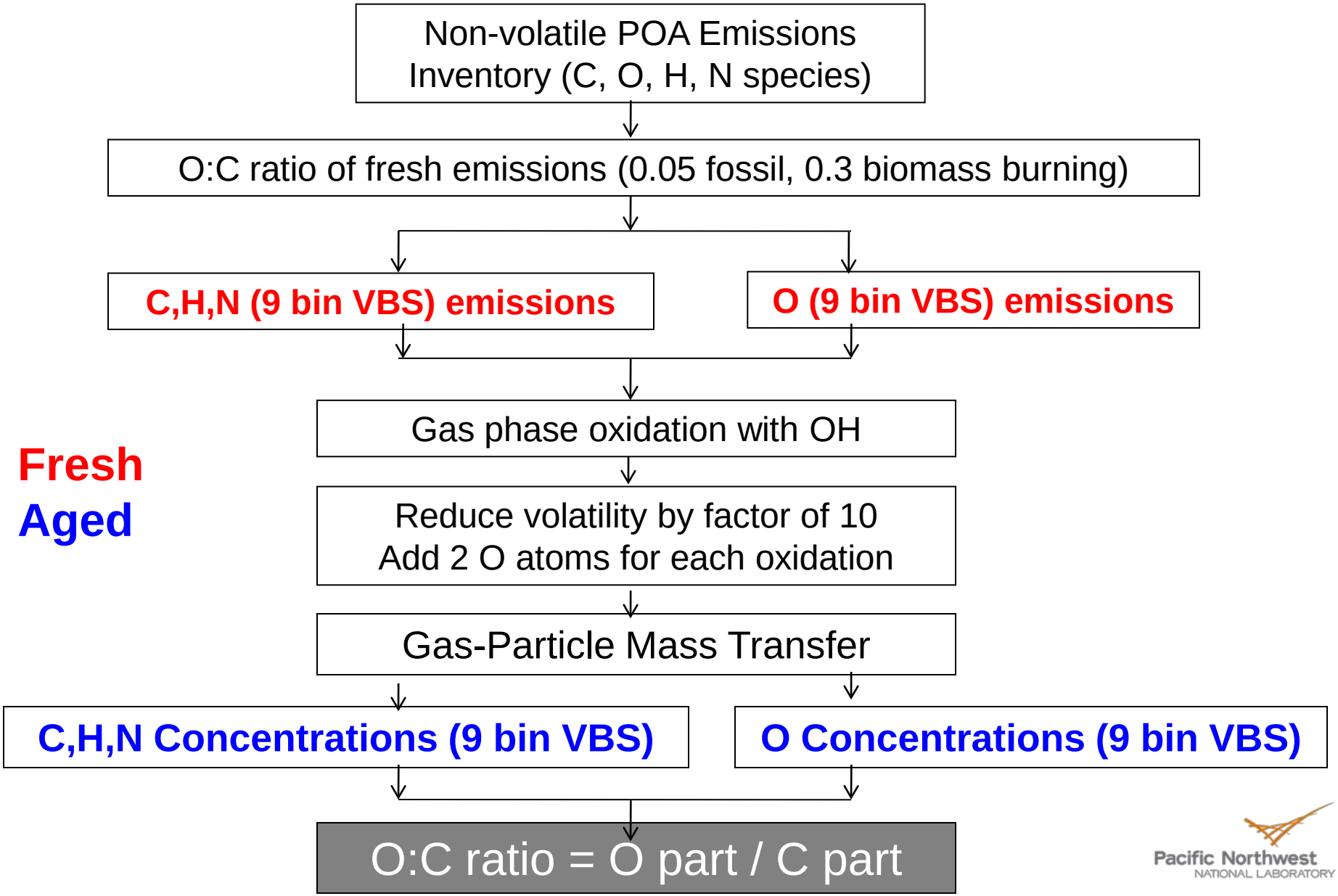
Positive Matrix Factorization used to estimate organic aerosol components from **Aerosol Mass Spectrometer** data

- HOA: hydrocarbon-like organic aerosol
- OOA: oxygenated organic aerosol
- BBOA: biomass burning organic aerosol

- Volatility bins in the model grouped together to form equivalent HOA, OOA, and BBOA

Pacific Northwest
NATIONAL LABORATORY

Evaluating Simulated Organic Aerosols (2)

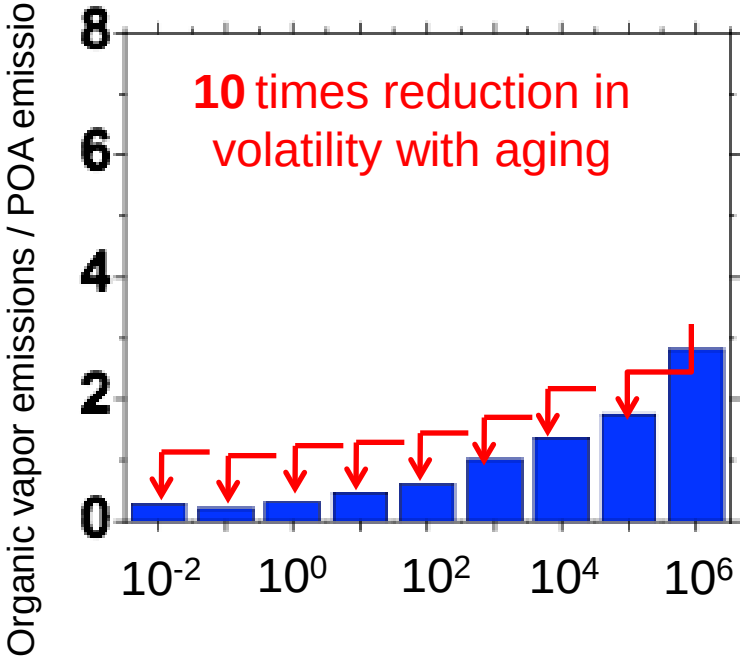


Pacific Northwest
NATIONAL LABORATORY

Simplified Volatility Basis Set

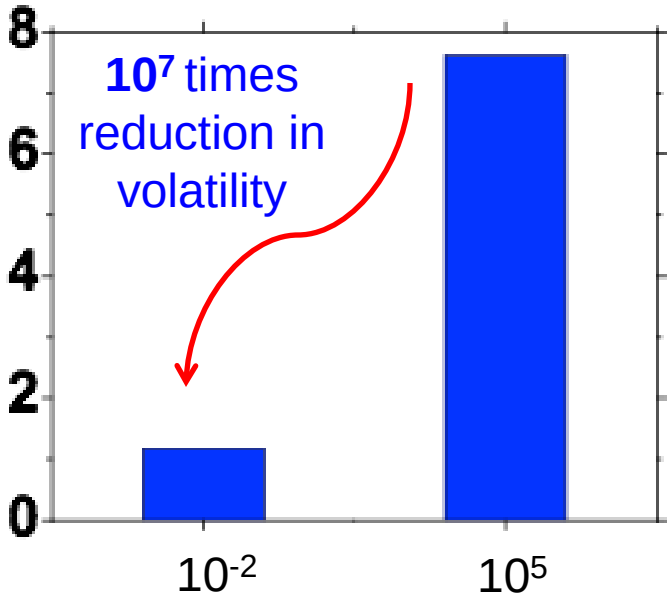
‘Complex’

Assumes POA and SOA are semi-volatile: Changing partitioning



‘Simple’

Assumes once formed, POA and SOA are non-volatile



9-volatility bin, μg m^{-3}	⟷	2-volatility bin, μg m^{-3}
kOH = 4×10^{-11} cm^3 $molecule^{-1}$ s^{-1}	⟷	kOH / 7 = 0.57×10^{-11} cm^3 $molecule^{-1}$ s^{-1}
add 2 O atoms at each oxidation	⟷	add 7 O atoms at each oxidation

Pacific Northwest NATIONAL LABORATORY

Results

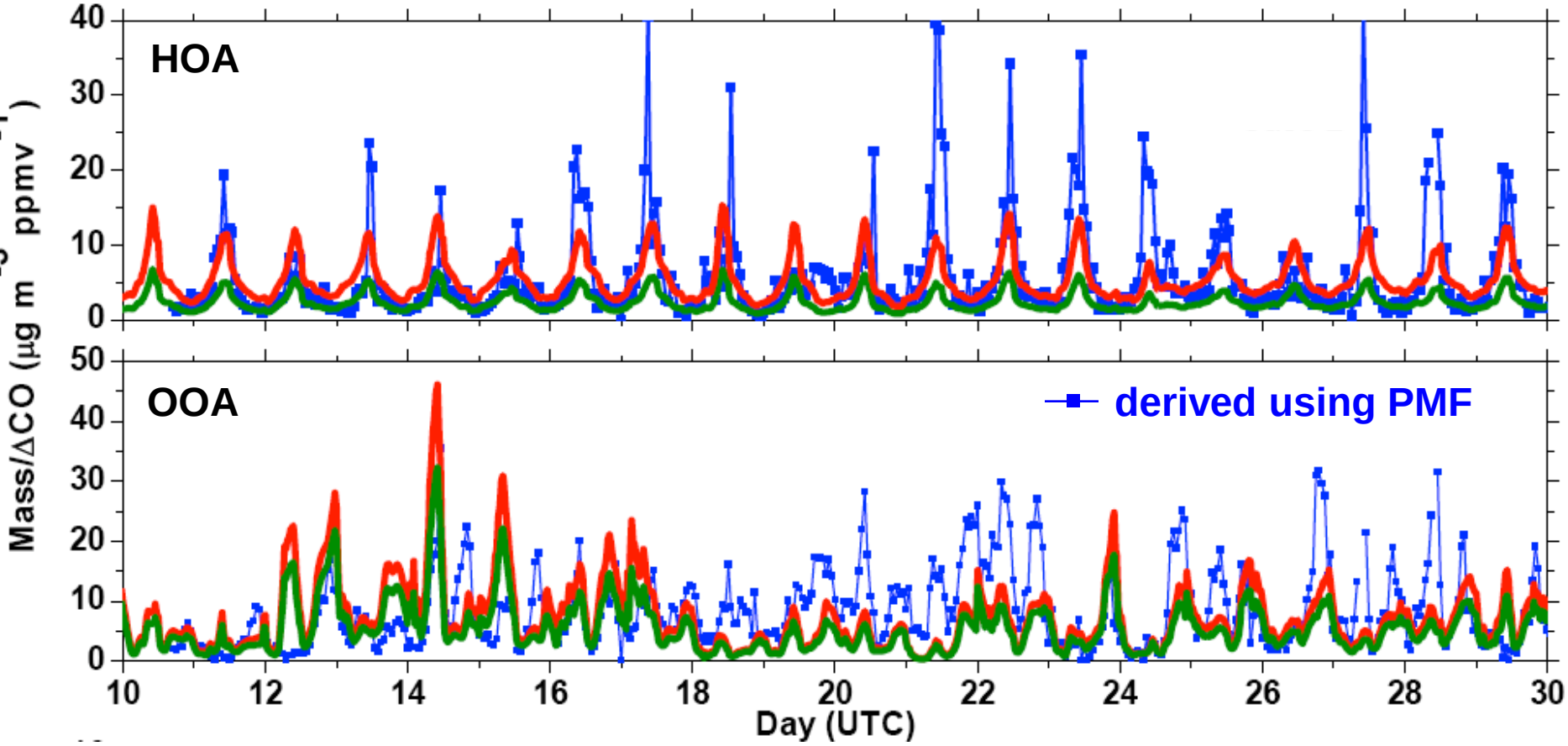
Temporal Variability in OA at T0 Site (City Center)

Three Modeling Scenarios:

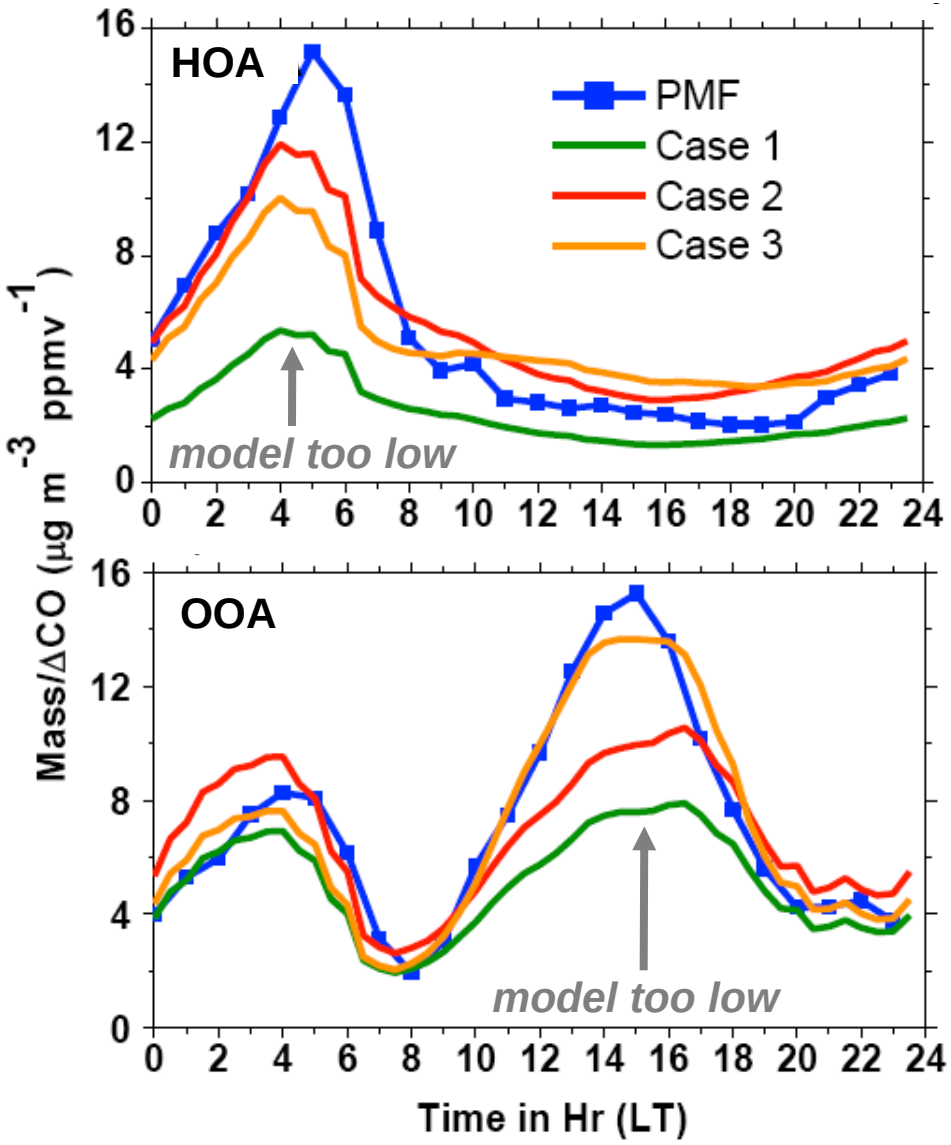
Case 1: 9-bin VBS, default emissions

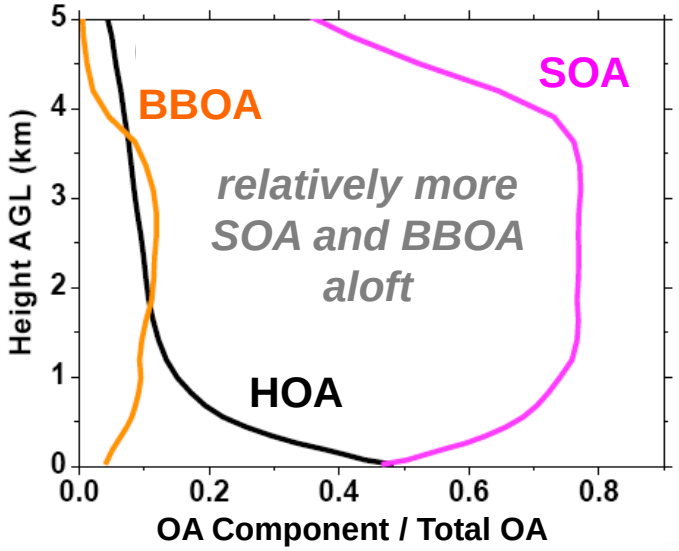
Case 2: 9-bin VBS, 2 * urban POA emissions

Case 3: 2-bin VBS, 2 * urban POA emissions



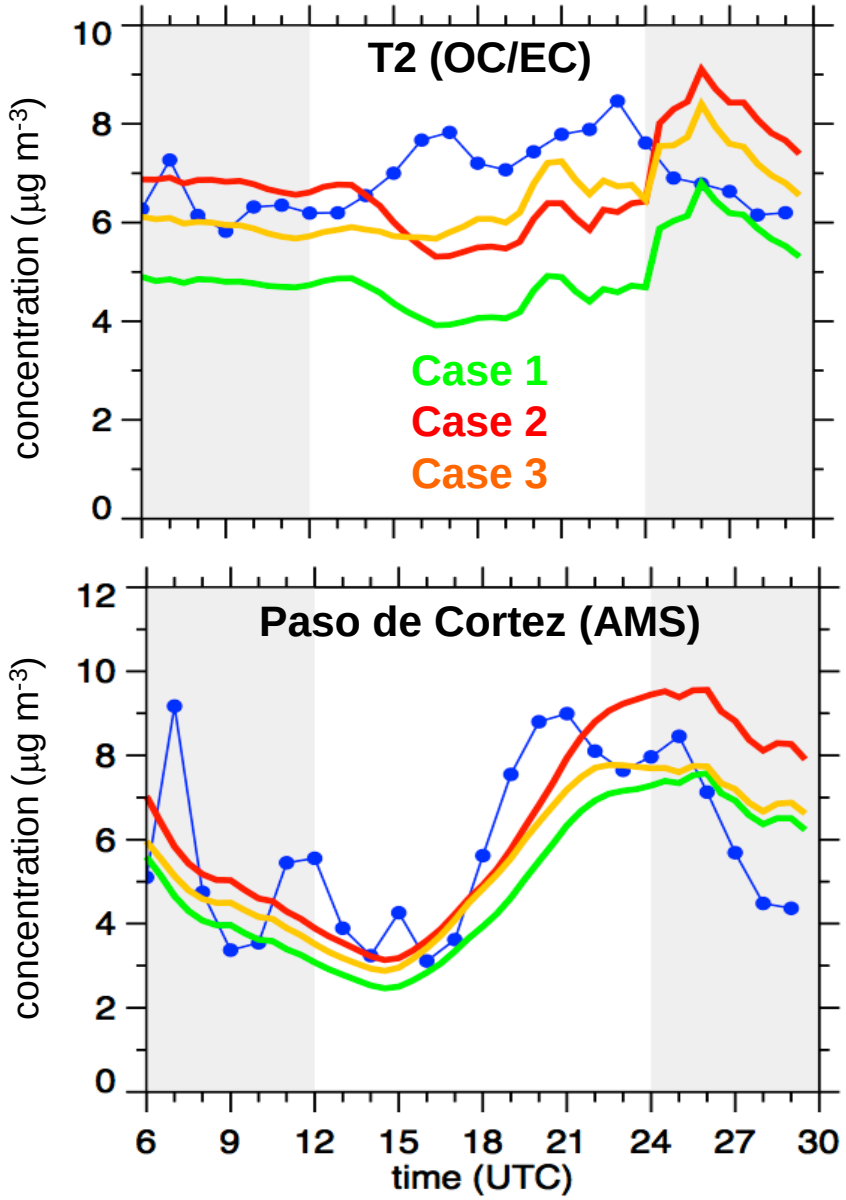
Diurnal Average OA: T0 Site

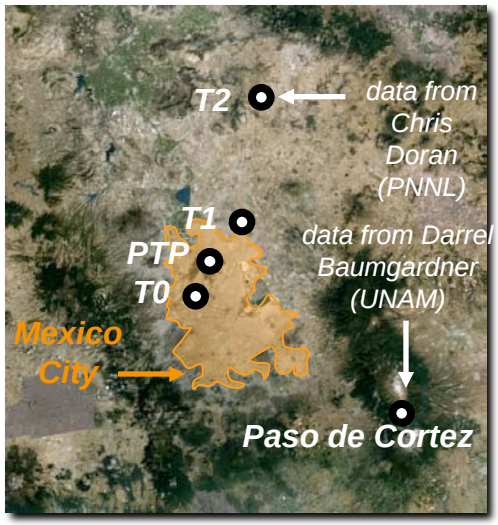




Pacific Northwest NATIONAL LABORATORY

Diurnal Average OA: Remote Sites



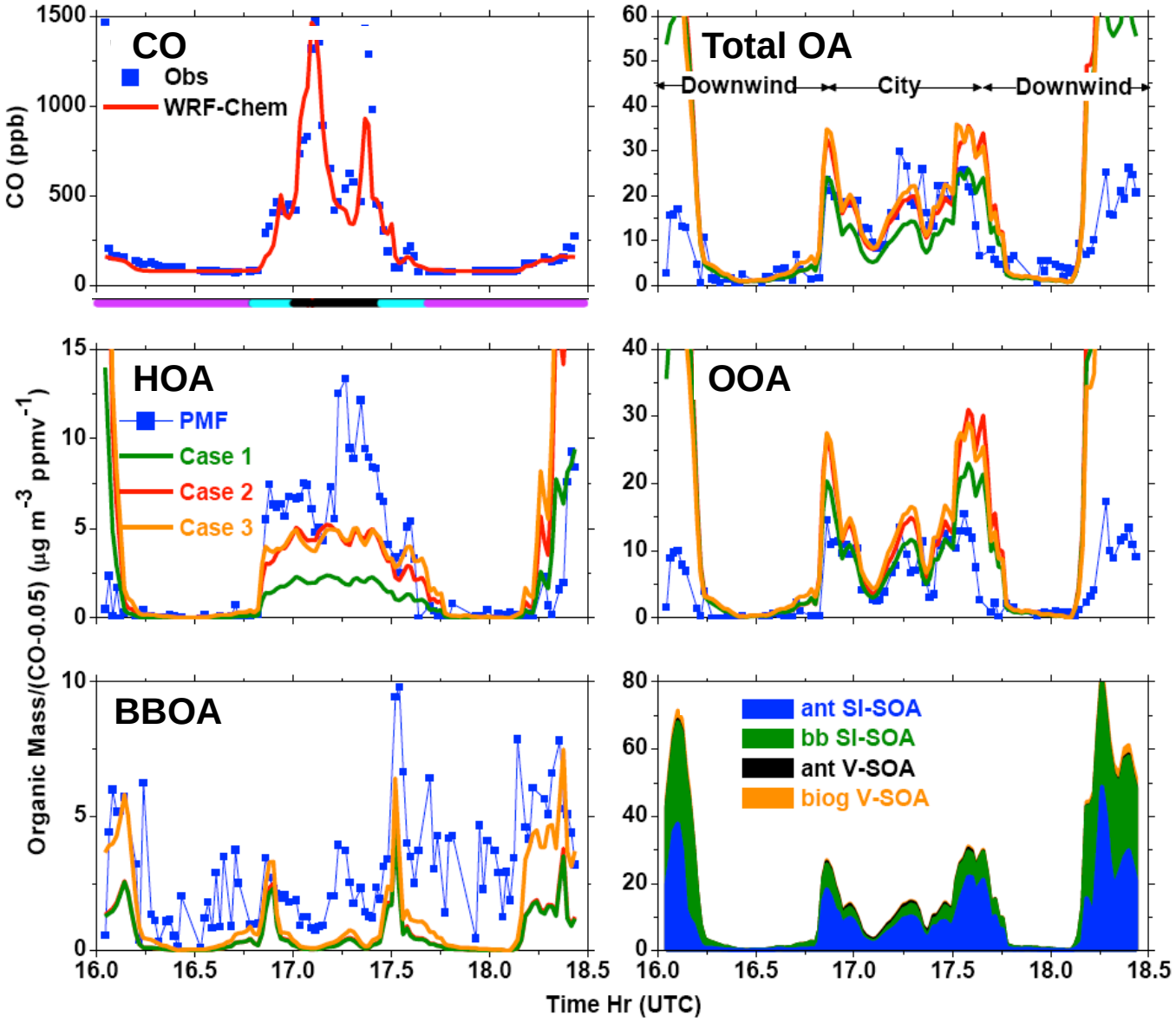


simulated OA ~ observed

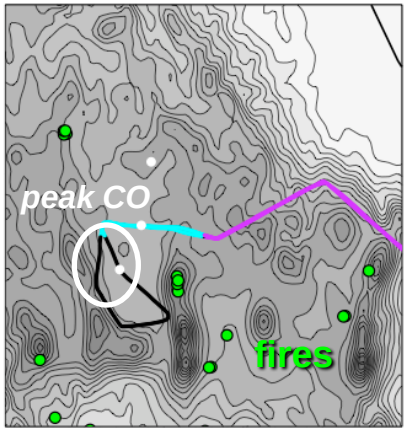
most OA at both sites from SOA on average

Pacific Northwest NATIONAL LABORATORY

Organic Matter Aloft: March 15



G-1 Flight Path



(low biomass burning day)

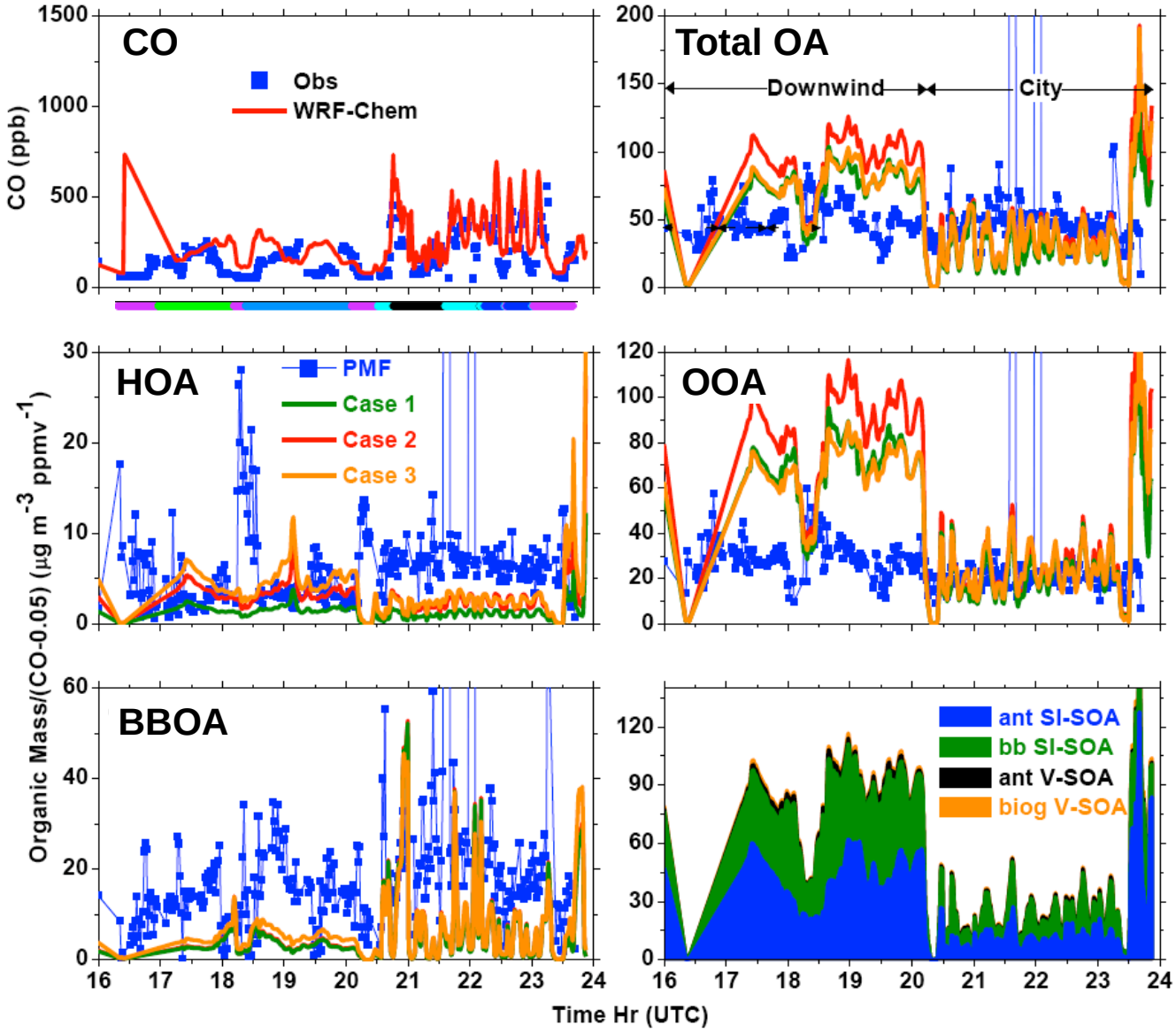
AMS data from Liz Alexander (PNNL) and Manjula Canagaratna (Aerodyne)

Near the City:
simulated HOA too low, but OOA similar to PMF estimate

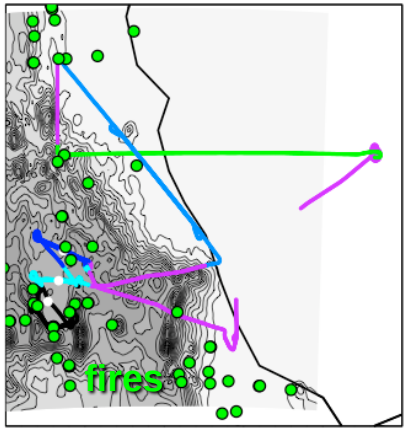
Downwind:
simulated OOA too high

Pacific Northwest NATIONAL LABORATORY

Organic Matter Aloft: March 10



C-130 Flight Path



(high biomass burning day)

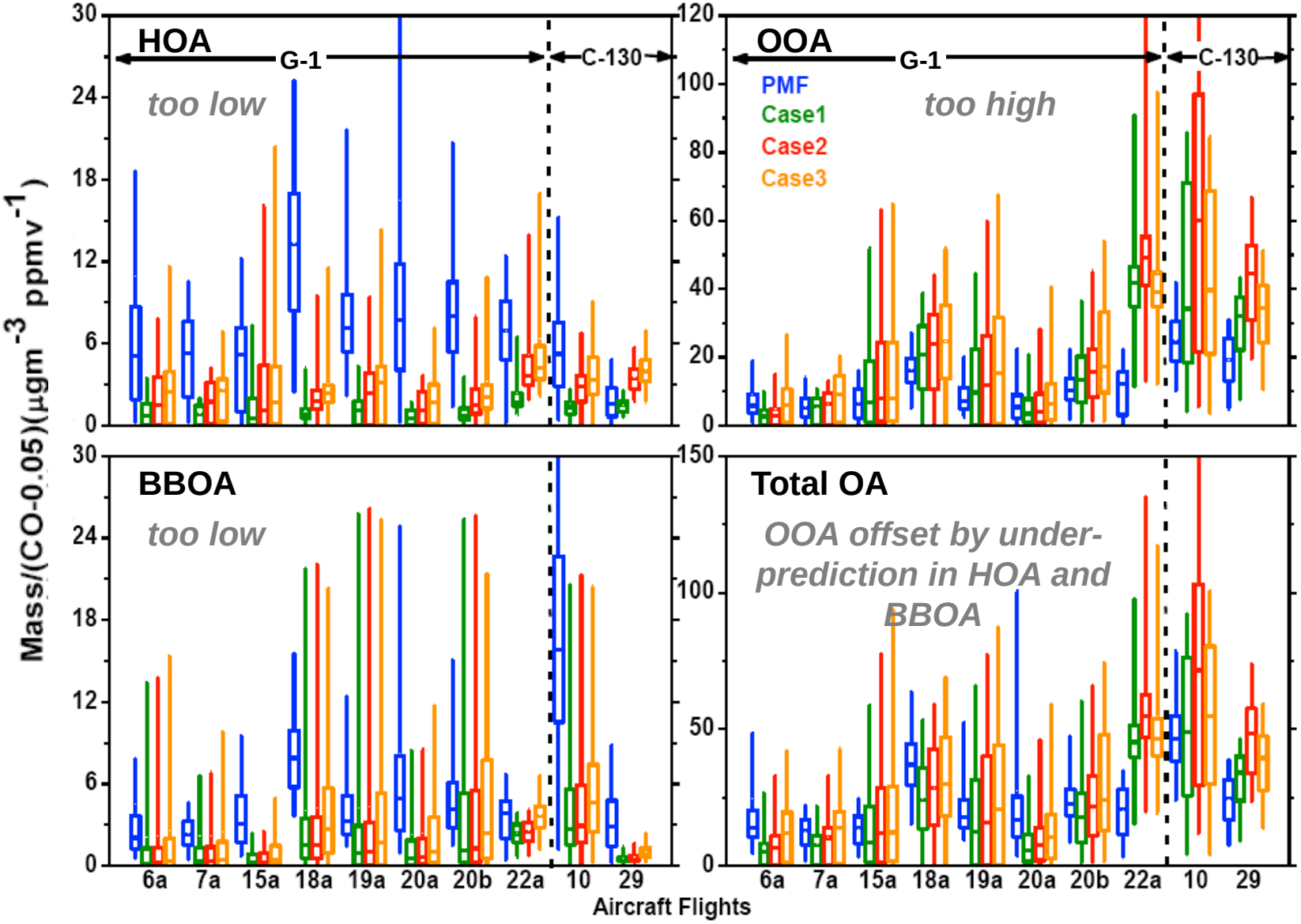
AMS data from Pete de Carlo (PSI) and Jose Jimenez (Univ. CO)

Near the City:
simulated HOA too low, but OOA similar to PMF estimate

Downwind:
simulated OOA too high

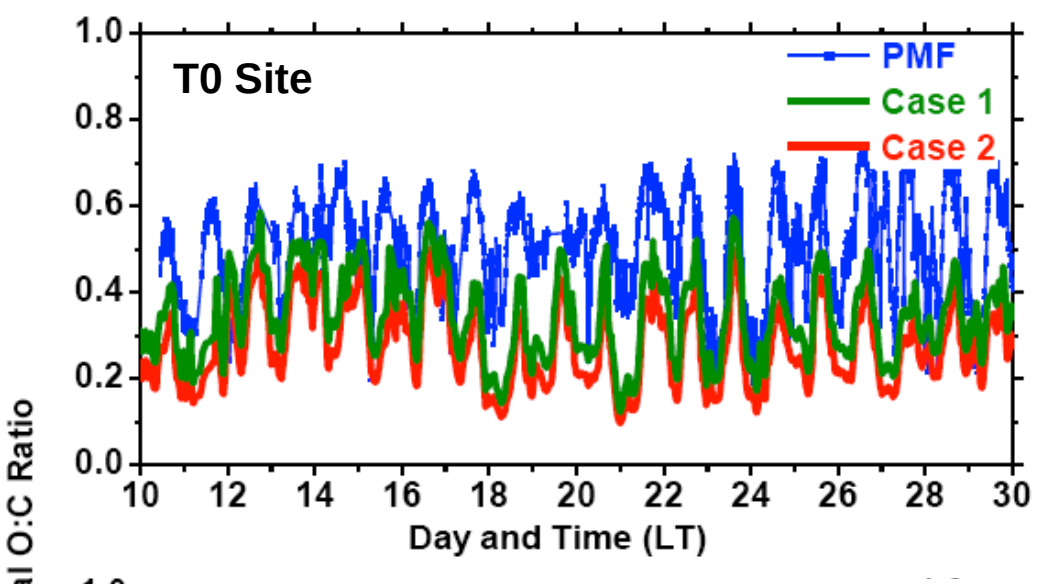
Pacific Northwest NATIONAL LABORATORY

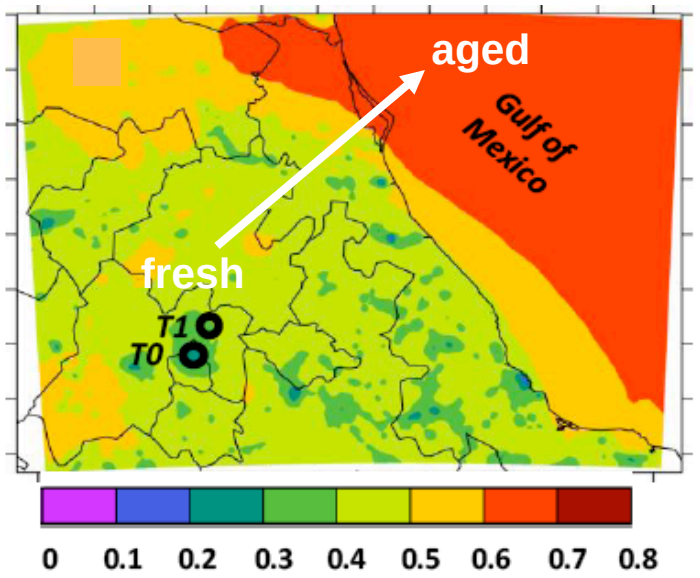
Performance for All Aircraft Flights - Percentiles

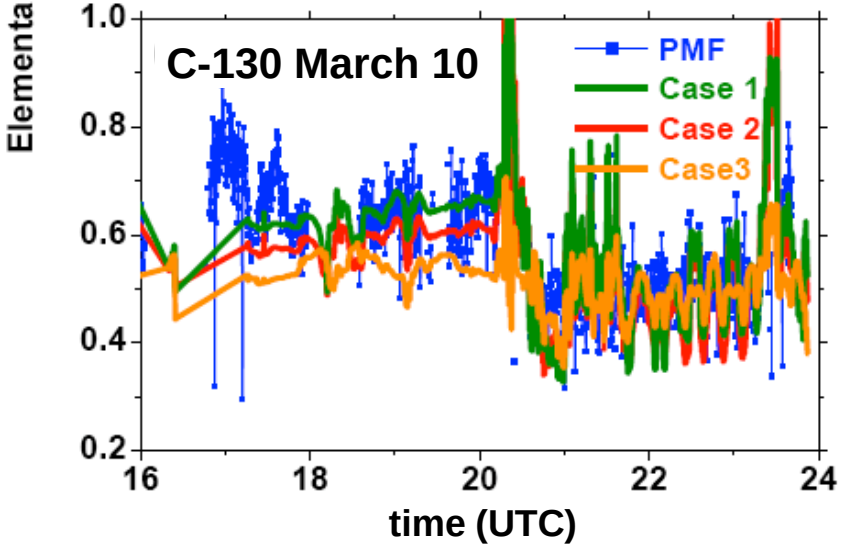


Northwest NATIONAL LABORATORY

O:C Ratios





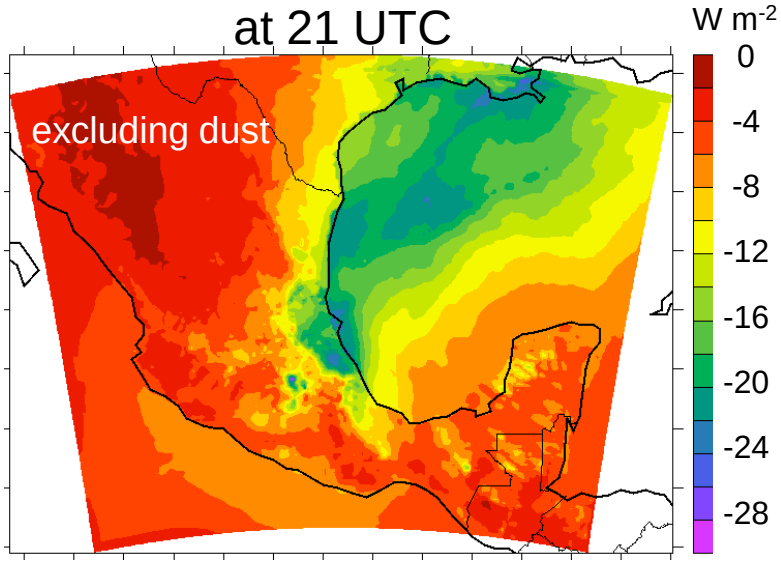


- Simulated diurnal variation similar to observed at T0, but magnitude too low
- Simulated O:C ratio aloft similar to observed, but too low downwind

Pacific Northwest
NATIONAL LABORATORY

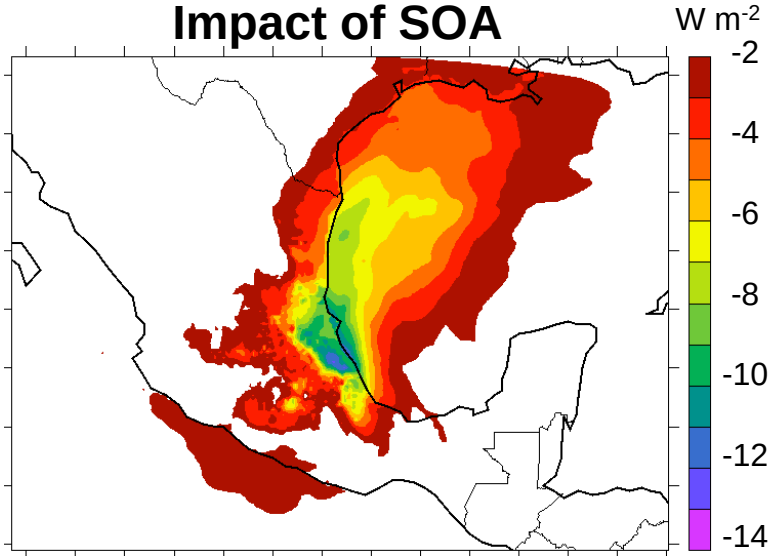
Aerosol Effect on Shortwave Radiation

SW – SW without aerosols
at 21 UTC

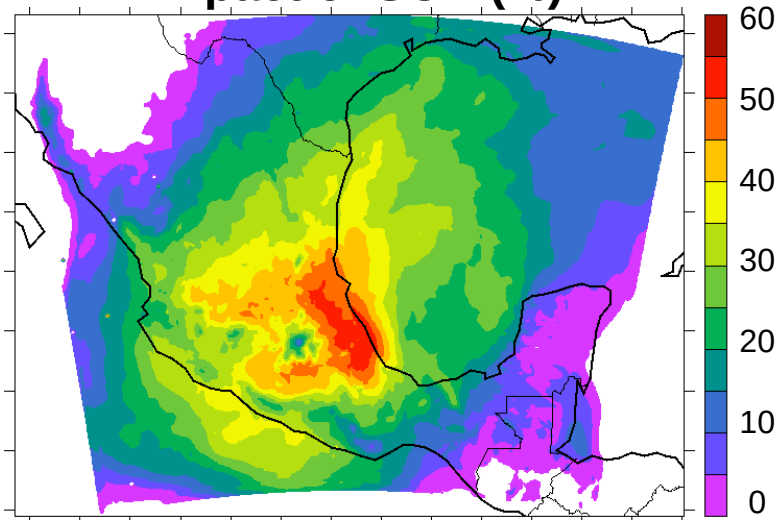


- Aerosols reduce downward shortwave radiation over Mexico City and downwind over the Gulf of Mexico
- SOA contributes to ~50% of reduction in shortwave radiation
- Impact on radiation downwind of Mexico City is likely too high because of over-prediction of OA

Impact of SOA



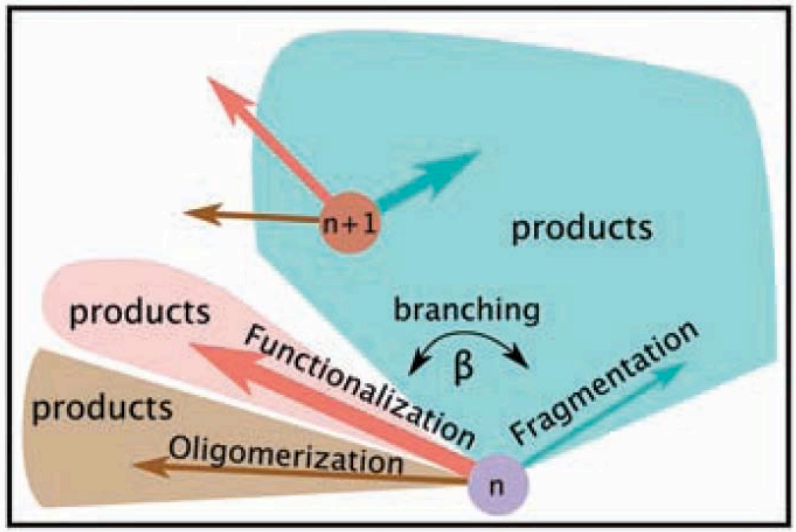
Impact of SOA (%)



Pacific Northwest
NATIONAL LABORATORY

Summary

- **HOA** (primary): particulate emissions in 2006 inventory are likely too low
- **OOA** (secondary): too low in the city, similar to observed near the city, but too high downwind
- **BBOA** (biomass burning): usually too low - likely missing sources
- Diurnal and spatial variability in O:C ratios similar to estimates, but magnitude is too low (not aged enough)
- When total OM simulated well, it is not necessarily for **the right reasons**
- 2-bin and 9-bin approaches similar in terms of mass and oxidation state of OA



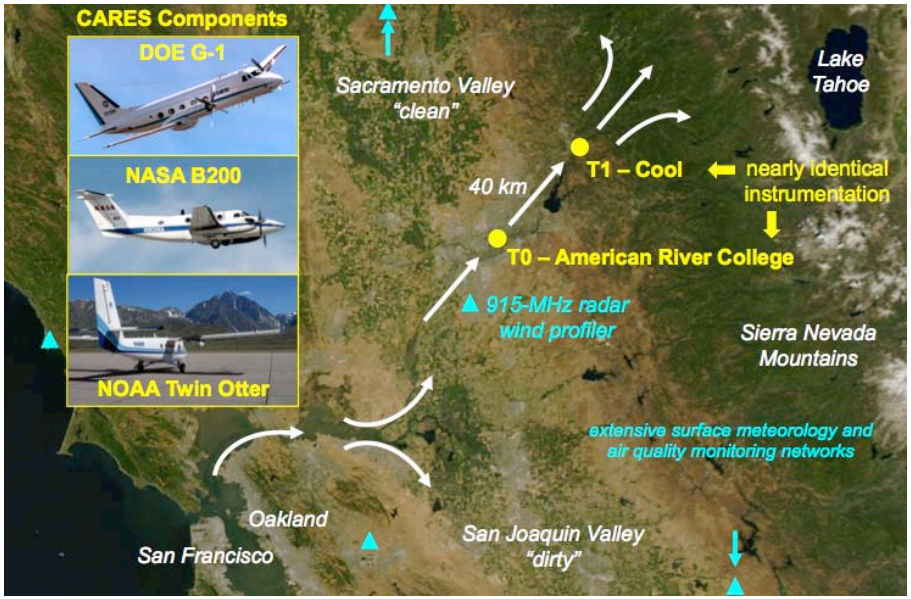
from *Jimenez et al*. [2009]

Current form of the volatility basis set approach cannot represent all processes associated with OA evolution

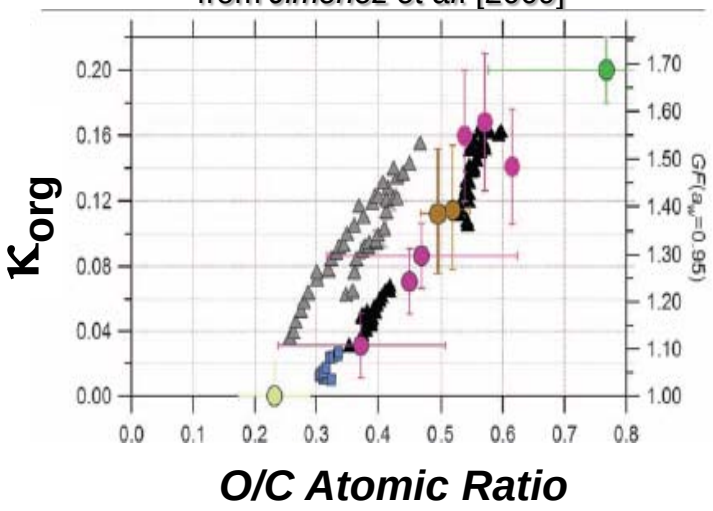
- Semi-volatile SOA precursors may be too high
- Chemistry may be too fast
- Missing sinks as fragmentation of SOA
- Dry deposition may be too low

Next Steps

- Aerosol optical properties: Vary refractive indices based on aging?
- Coupling new organic aerosol species with cloud-aerosol interactions
- Evaluate using CARES 2010 field campaign data



from *Jimenez et al*. [2009]



- Compare volatility basis set approach with new approaches, i.e. 'bottom-up' approaches based on master chemical mechanisms
- Work with Alla Zelenyuk and John Shilling to obtain laboratory data to better constrain or replace assumptions in volatility basis set theory

Pacific Northwest
NATIONAL LABORATORY