NCAR

# Can 3D Models Explain Observed Organic Aerosols?

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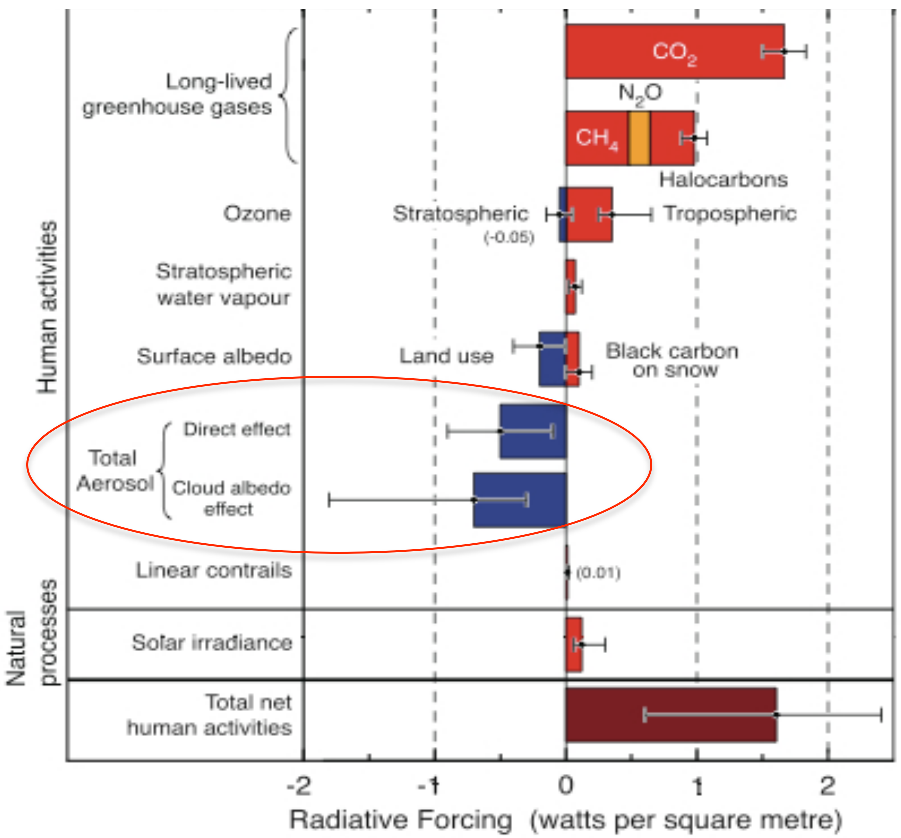
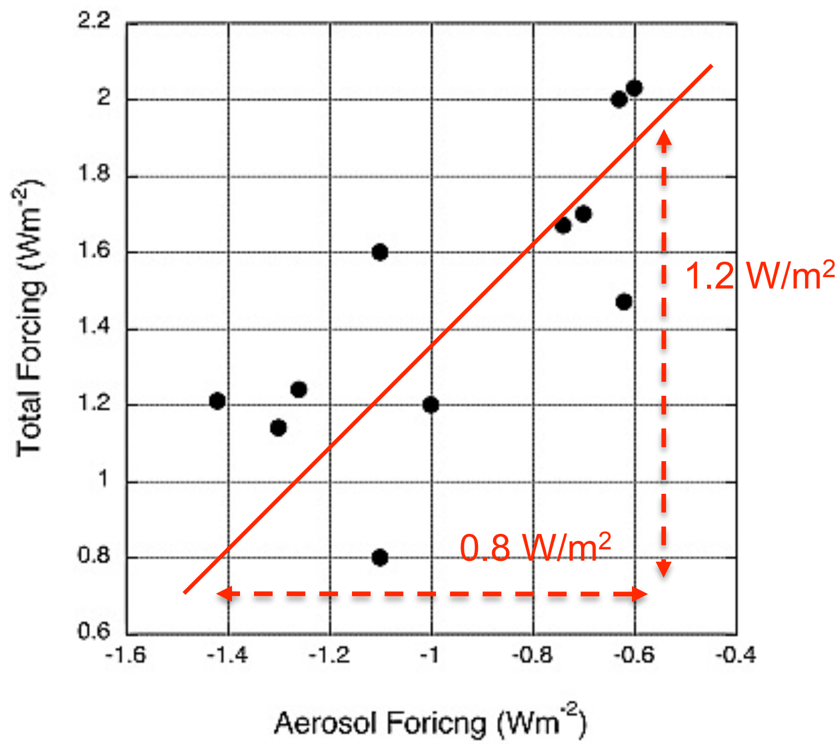
# Uncertainty in aerosol effects of climate

(Kiehl, GRL, 2007)

- Radiative forcing RF (IPCC, 2007)



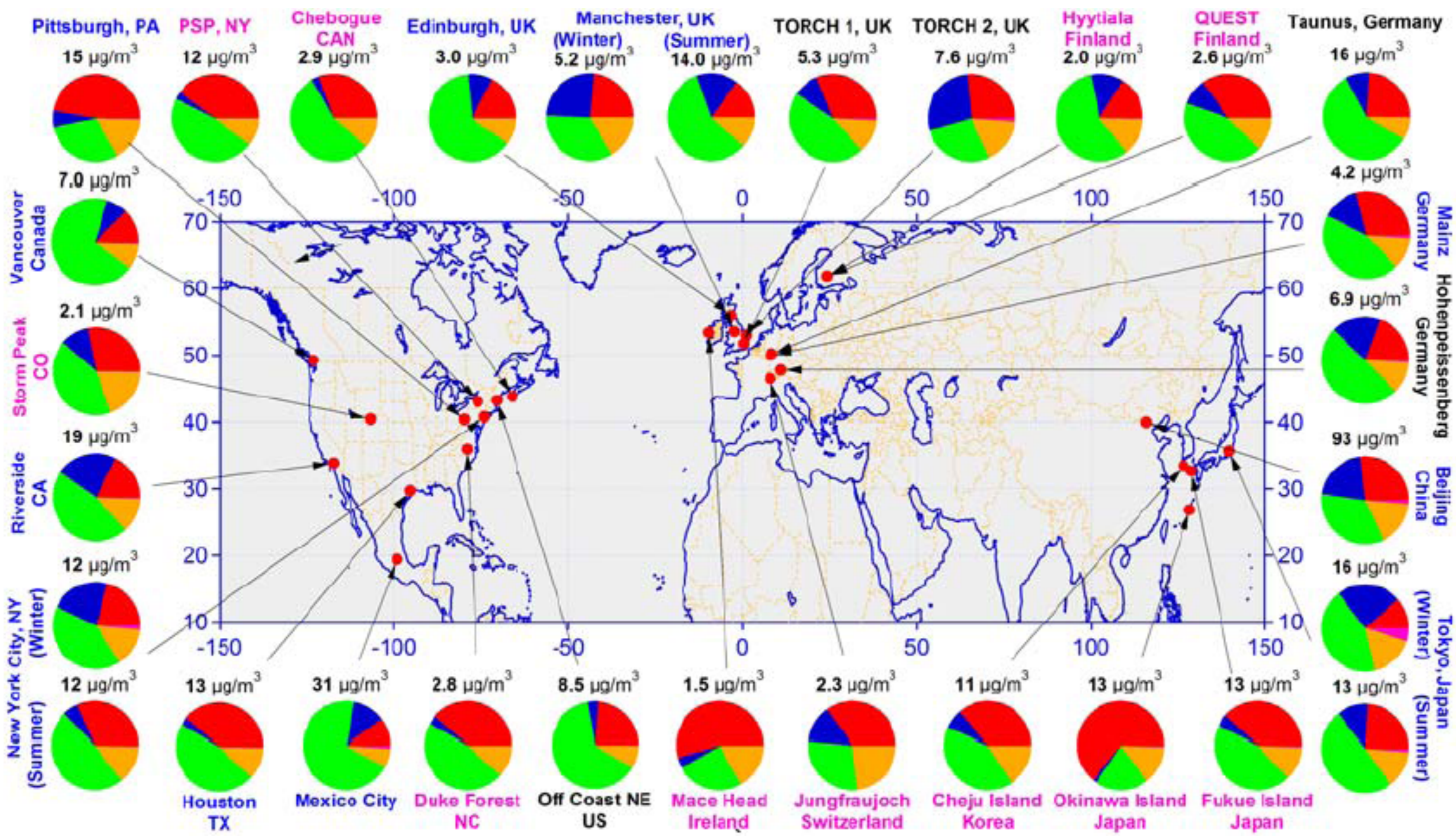




2/3 (=0.8/1.2) of models' range in RF is due to aerosol forcing ~ 0.8 W/m$^2$ ~ ½ of the $CO_2$

To trust future climate predictions aerosols need to be better constrained (e.g. organics)

# Dominance of organic aerosols

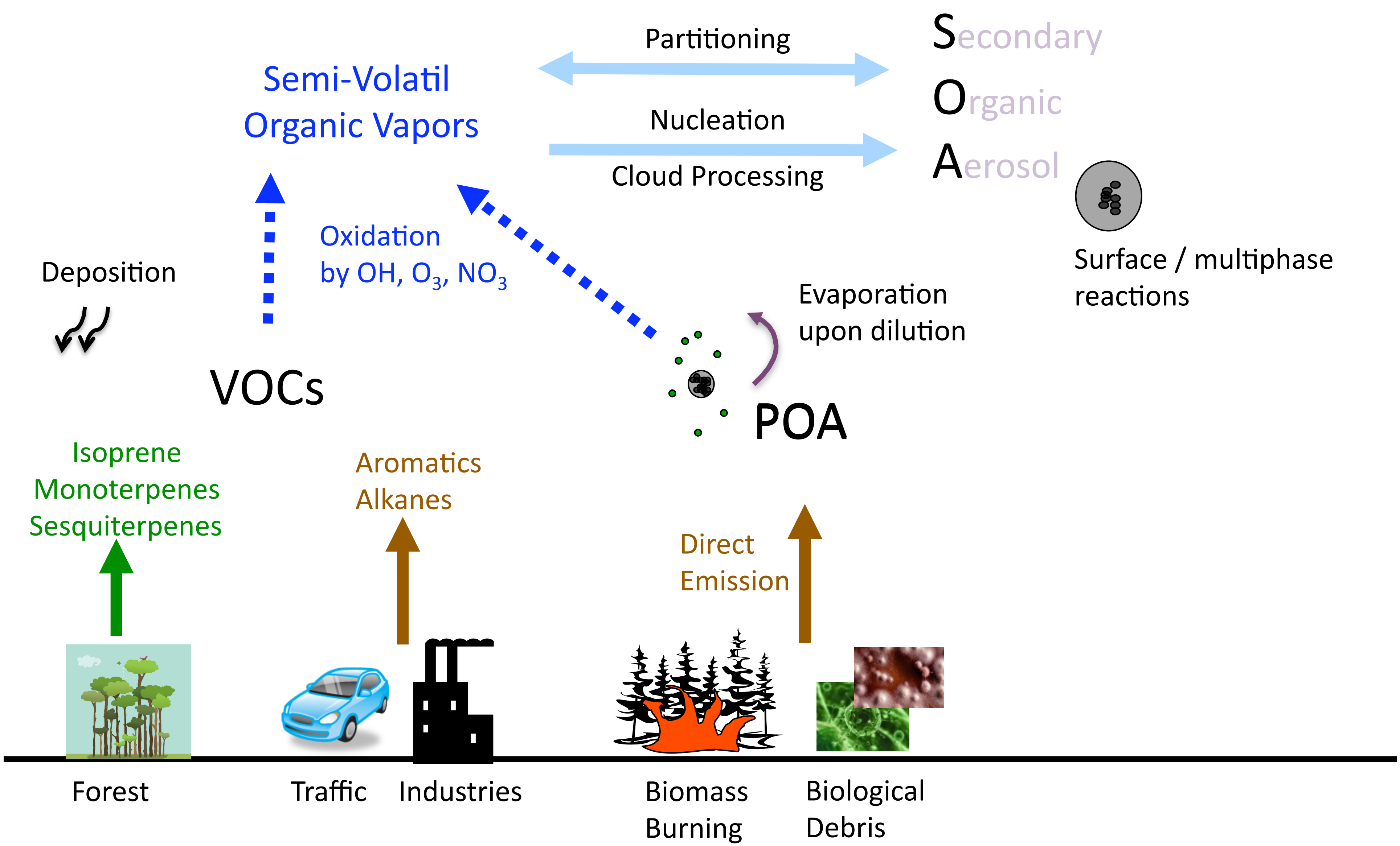
**AMS measurements:** **Sulfate** **Organics**




*Zhang et al., GRL, 2007*

- Organic Aerosols : 30-70%

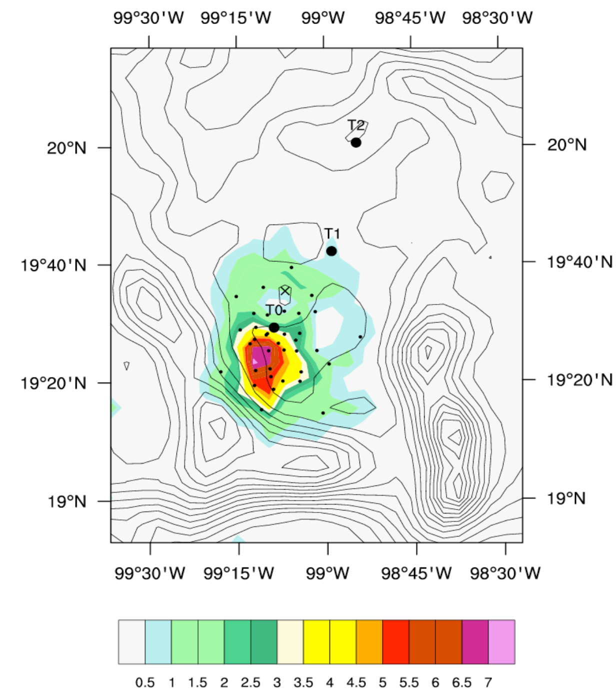
# Modeling OA : What are the challenges?

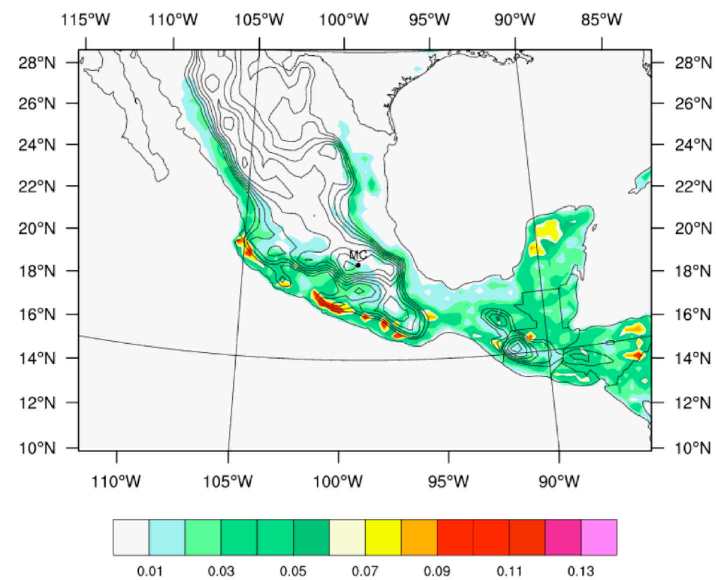


# Modeling OA formation during MILAGRO 2006

**Air quality model CHIMERE**

- 2 nested domains (35x35 $km^2$ ; 5x5 $km^2$)
- simulation from 1-30 March 2006
- Meteorological data: MM5/AVN
- Anthropogenic Emissions:
  NEI-99 + MCMA 2006
- MEGAN Biogenic emissions
- Wildfire emissions (MODIS)
- Gas-phase chemistry:
  MELCHIOR 44 sp,116 reactions
- Aerosol module
  8 bins / internal mixing
  Inorganics (ISORROPIA)
  SOA scheme (Pun et al., 2006)
  Dry / wet deposition

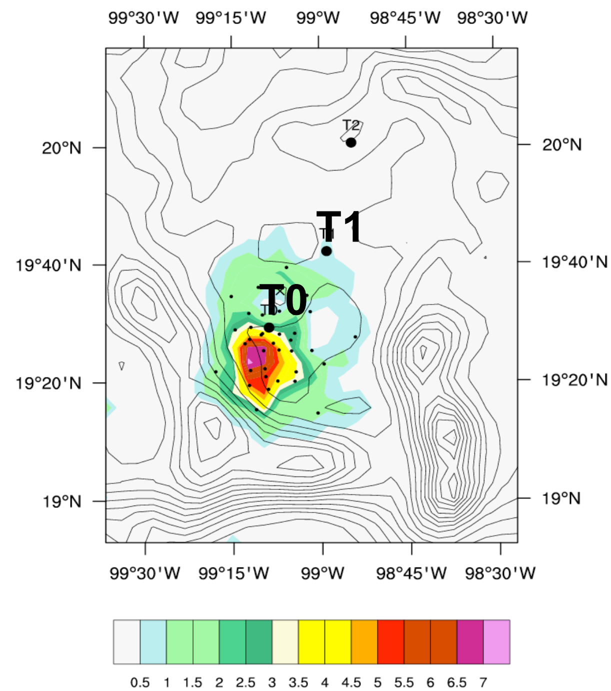


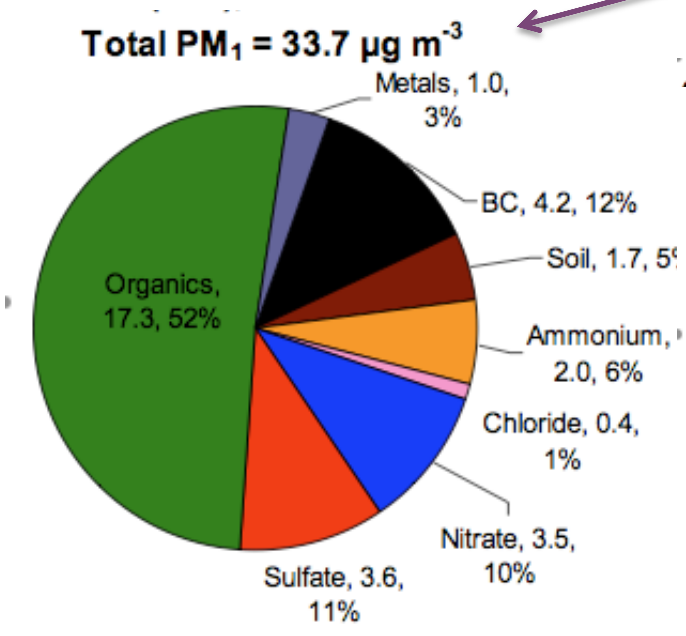



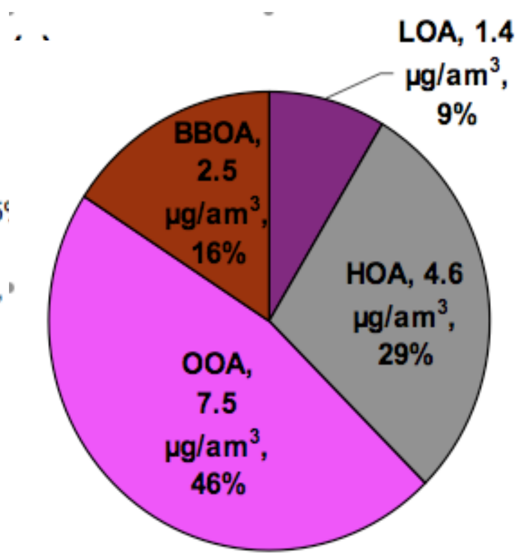
# OA measurements during MILAGRO March 2006

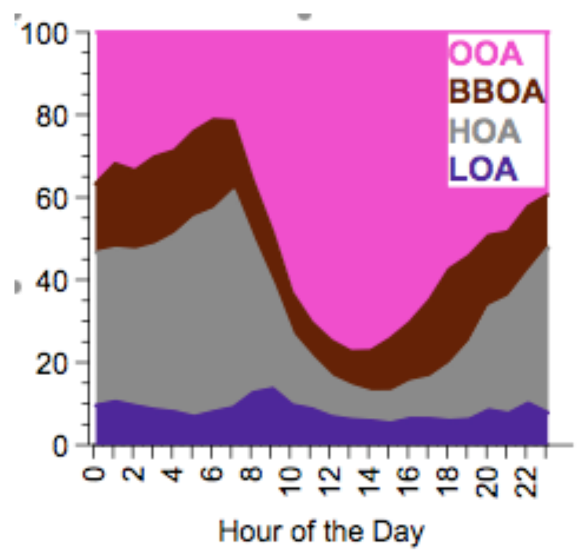
**March 2006: Composition of PM1 particles**

- **AMS**: Aerosol Mass Spectrometer measurements
- **PMF**: Positive Matrix Factorization of AMS spectra
  surface sites (T0, T1, PTP)
  aircraft (G-1, C130)



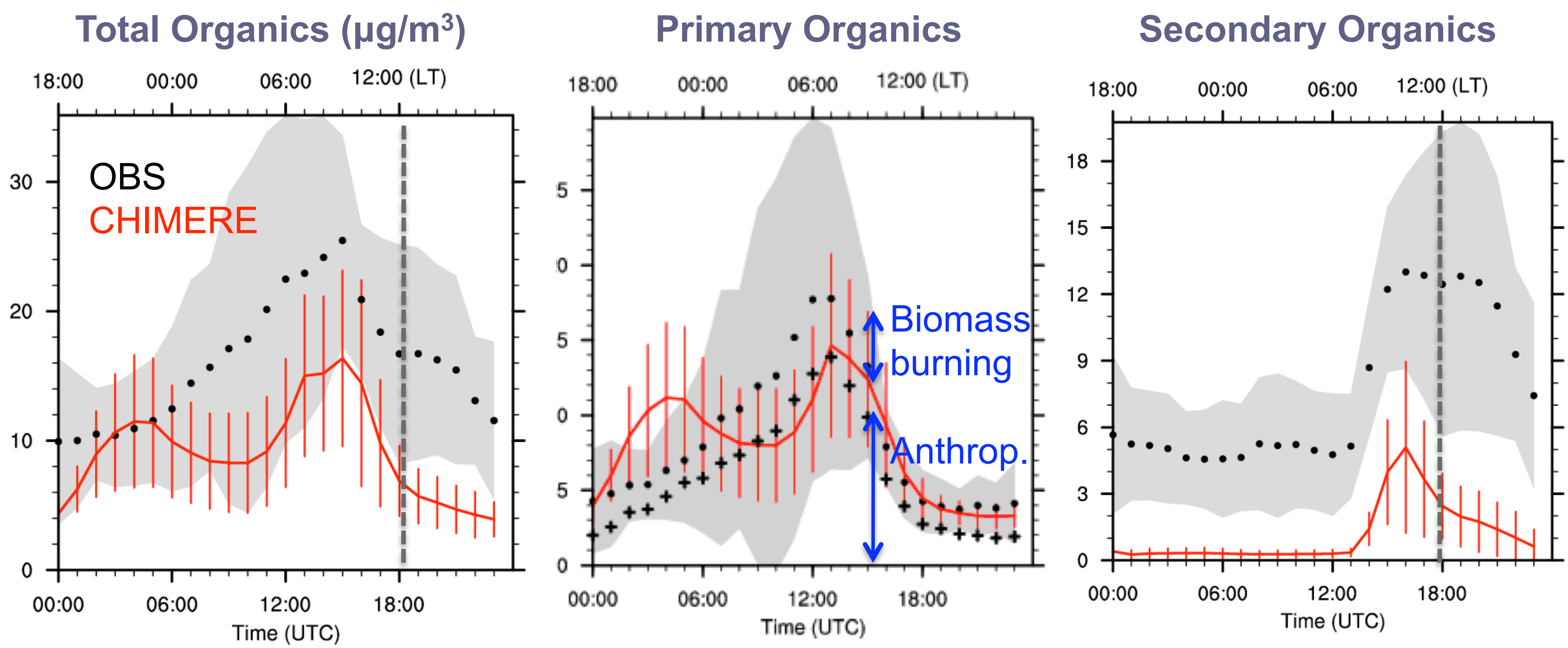




*Aiken et al., ACP, 2009*

# Model vs. Measurements at the surface

## - Mexico City T0, March 2006



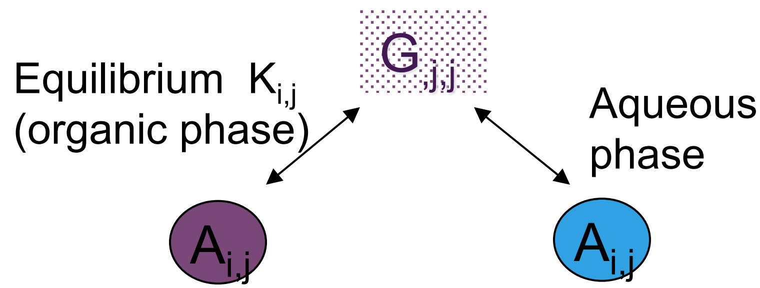

- OA underestimated by a factor of 2
- POA reasonably captured
- SOA largely underpredicted

*Hodzic et al. ACP, 2009*

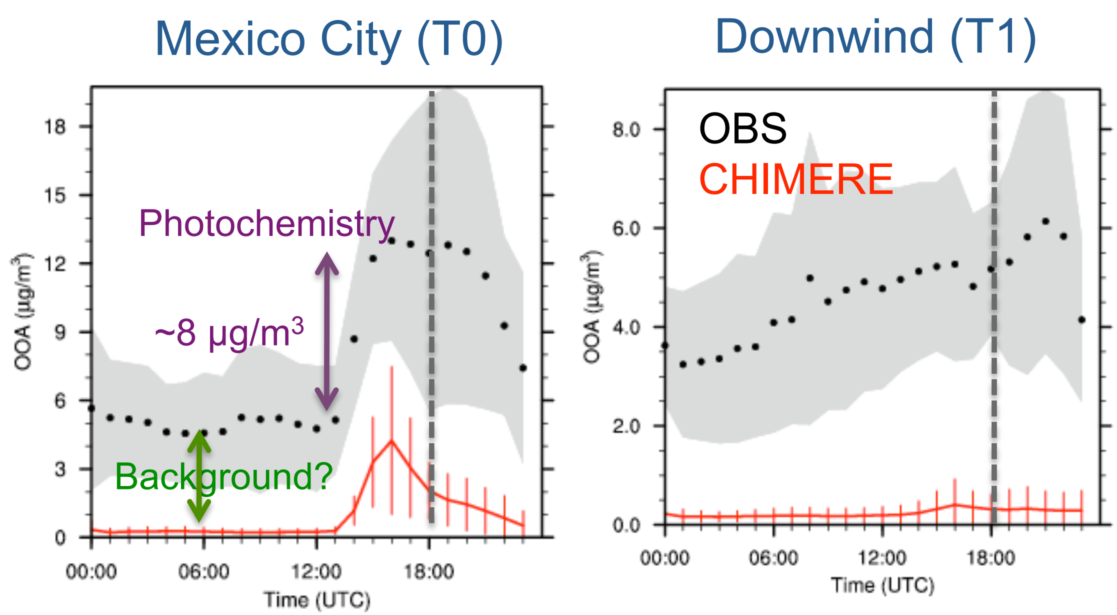
# SOA formation : 2-product approach

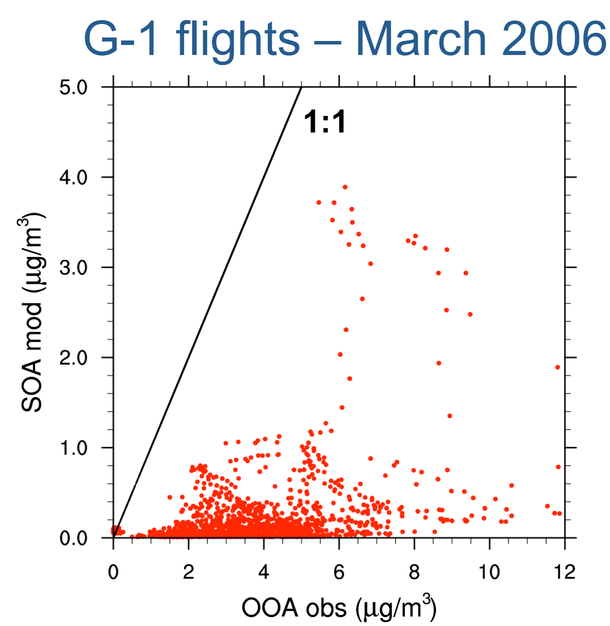
- Lump gas oxidation products into high and low volatility
- Partition into organic / aqueous phase based on smog chamber data
- Pun et al., 2006 parameterization

$VOC_i + OXIDANT_j \rightarrow a_{i,j}G1_{i,j} + \beta_{i,j}G2_{i,j}$




## Contribution of anthropogenic precursors:



# SOA formation : explicit chemistry

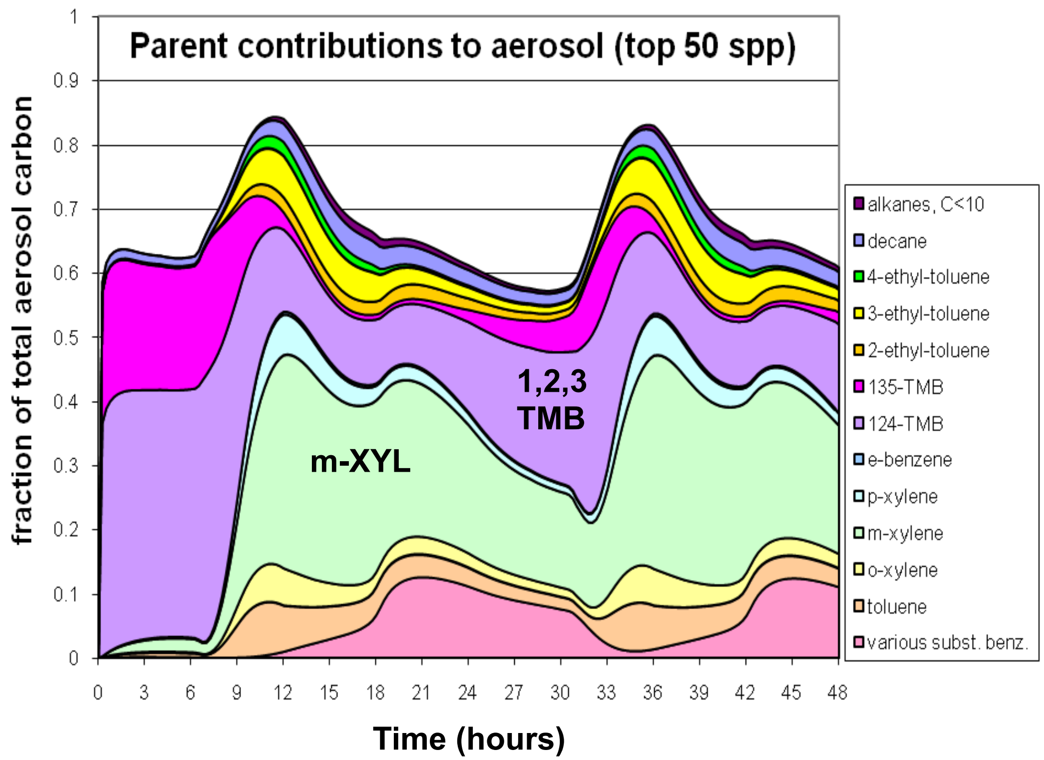
- Provides chemical identity of products (e.g. Master Chemical Mechanism)
- Reactions and rates are extrapolated from know chemistry (not measurements).

## Predictions of the GECKO model during MIRAGE 2006:

Chemistry up to C10 : 220,000 species & 1.5 M reactions (Computer generated chemistry)

- SOA ~ up to 2.5 µg/m$^3$ (peak)

-Most of aerosol carbon is accounted for by relatively few species ~10 sp. ( -OH, -NO3, -NO2 groups dominates)

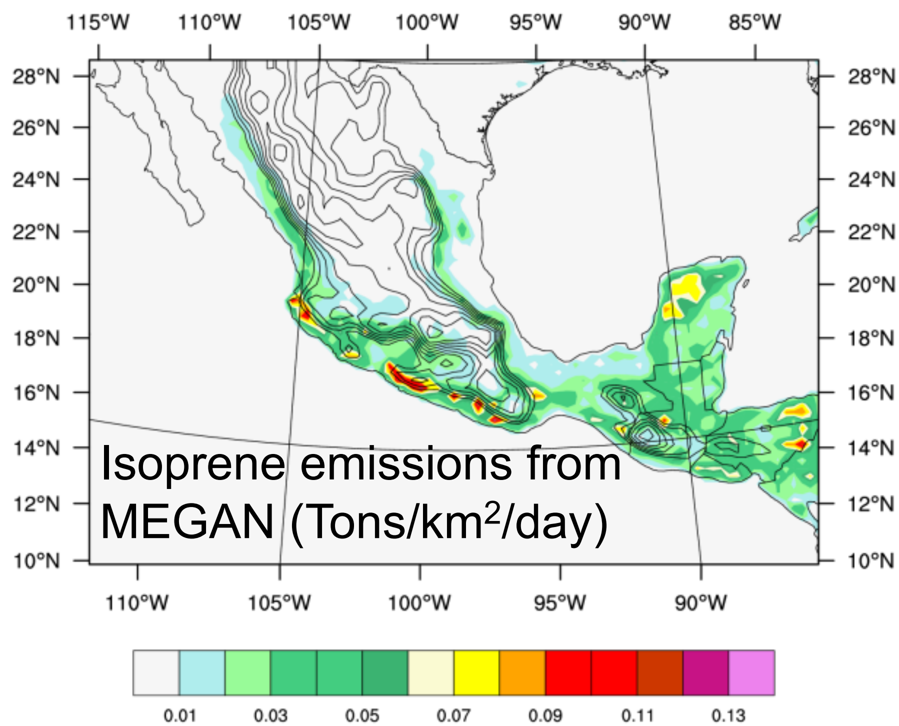



*Courtesy of Julia Lee-Taylor and Sasha Madronich*

# SOA formation : role of biogenic precursors

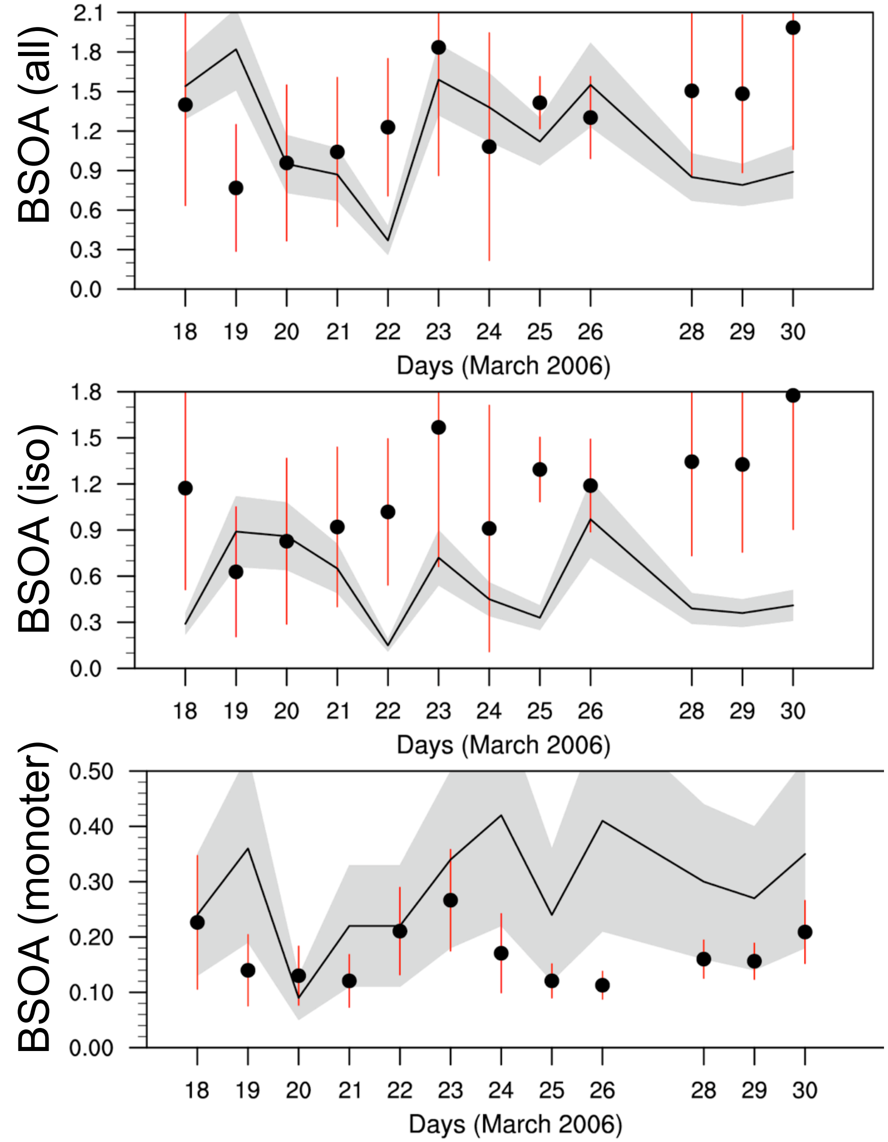
Biogenic SOA

- modeled with MEGAN
- estimated from tracer measurements (Stone et al., 2009)
- **Biogenic SOA is NOT underestimated**



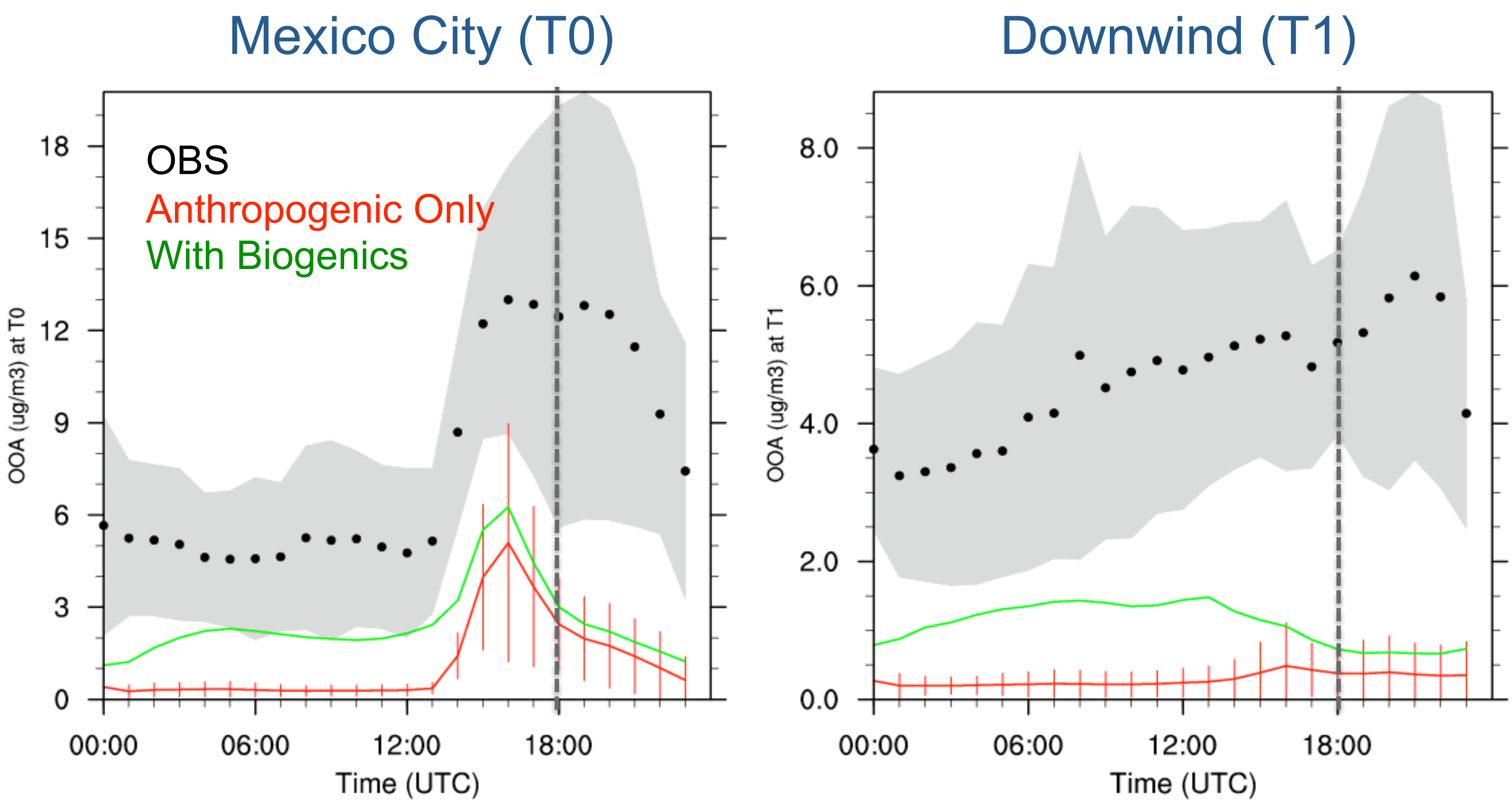

• CHIMERE
---- OBS

At T0

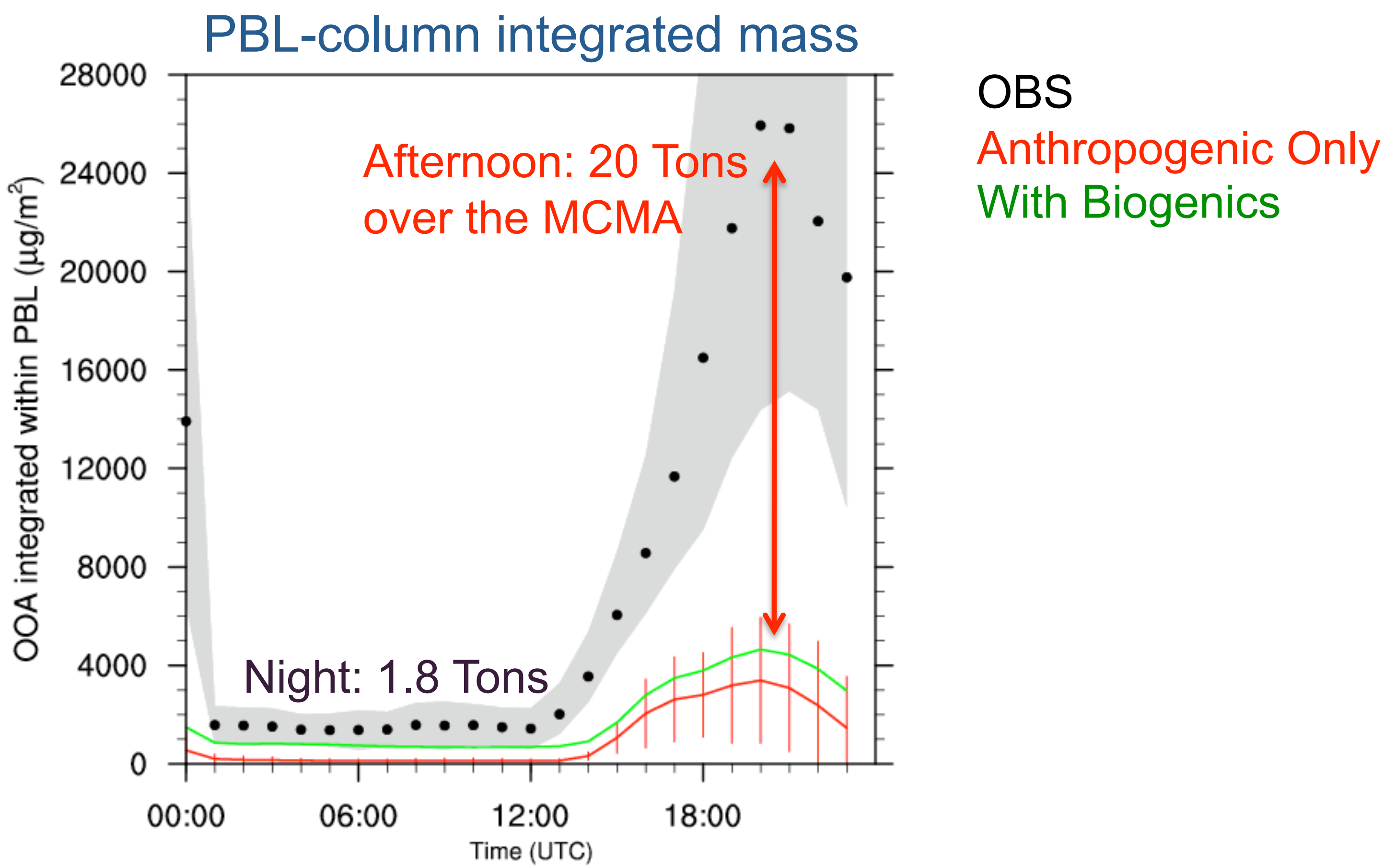



*Hodzic et al., ACP, 2009*

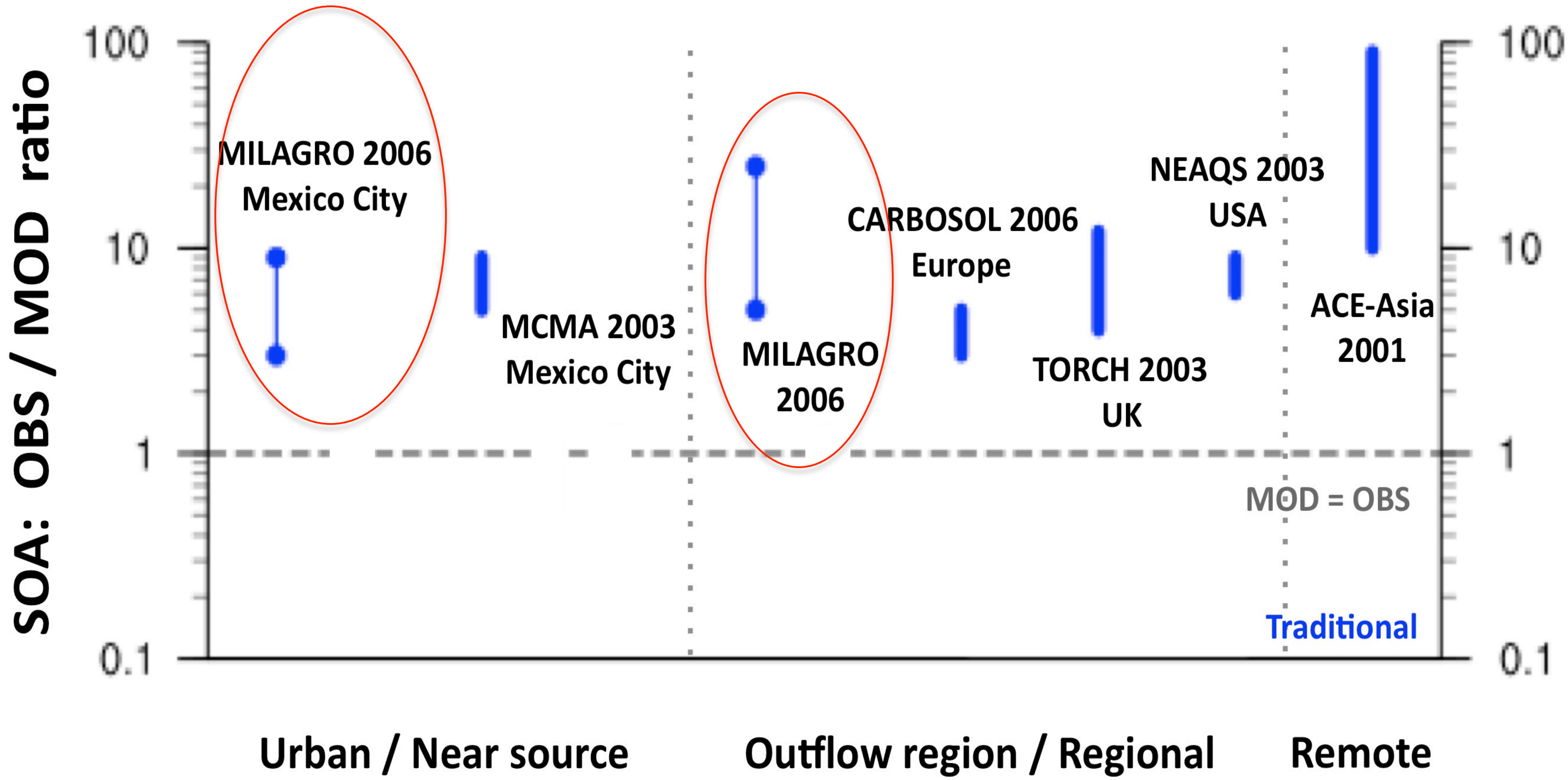
# SOA formation : contribution of biogenic precursors



# How large is the unexplained SOA mass?



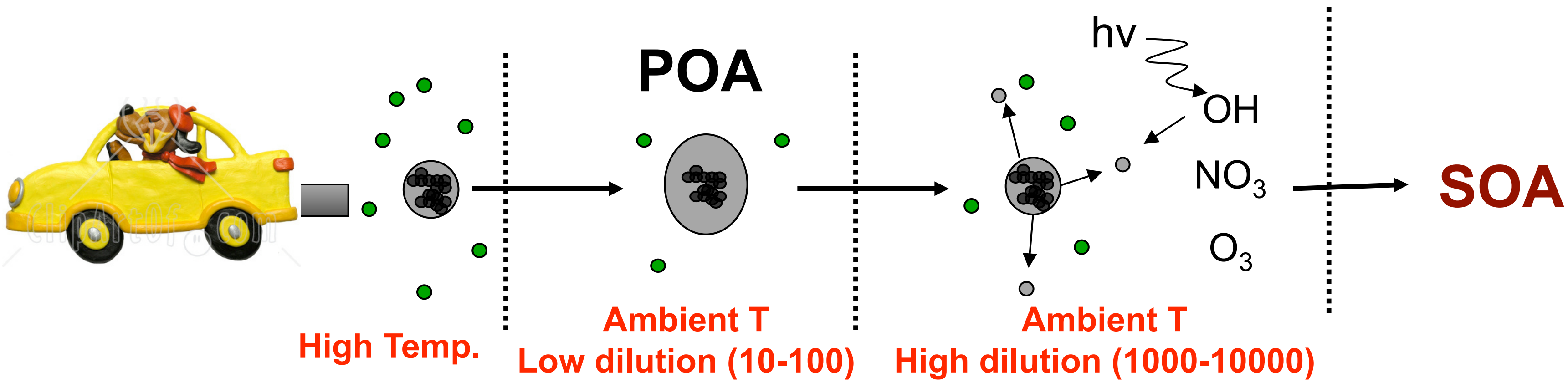
# Shortcomings of the traditional SOA approach



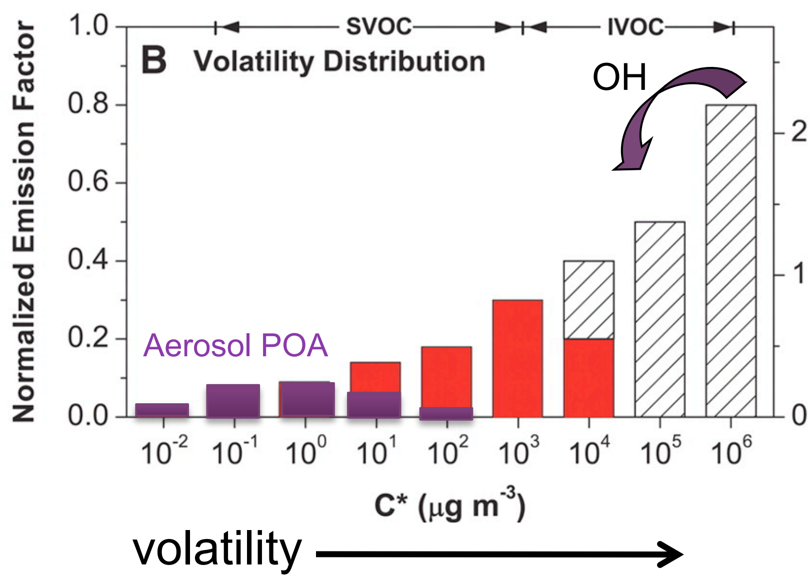

*Hodzic et al., in prep. ACP*

# SOA formation: contribution of primary organic vapors

- **POA assumed as volatile (instead of inert)** *(Robinson et al., Science, 2007)*




## Typical ambient partitioning



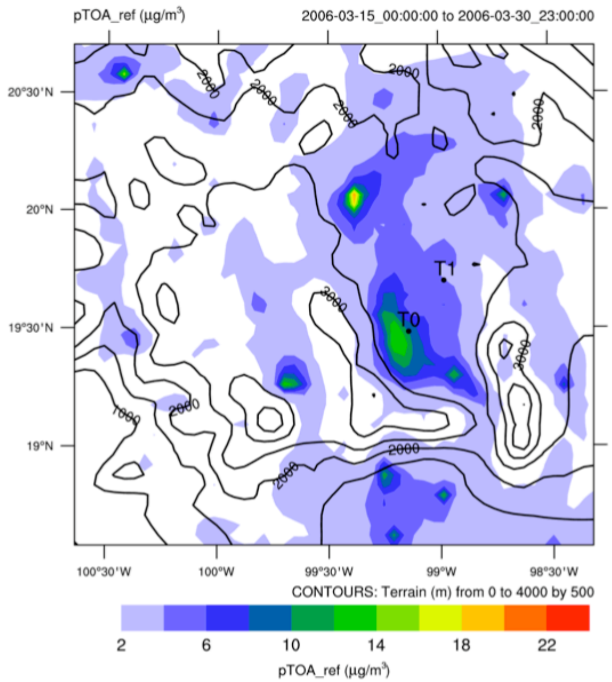

At T=20C

Semi-volatile / Intermediate volatility organic vapors ~ 80 $\mu g/m^3$

POA=10 $\mu g/m^3$

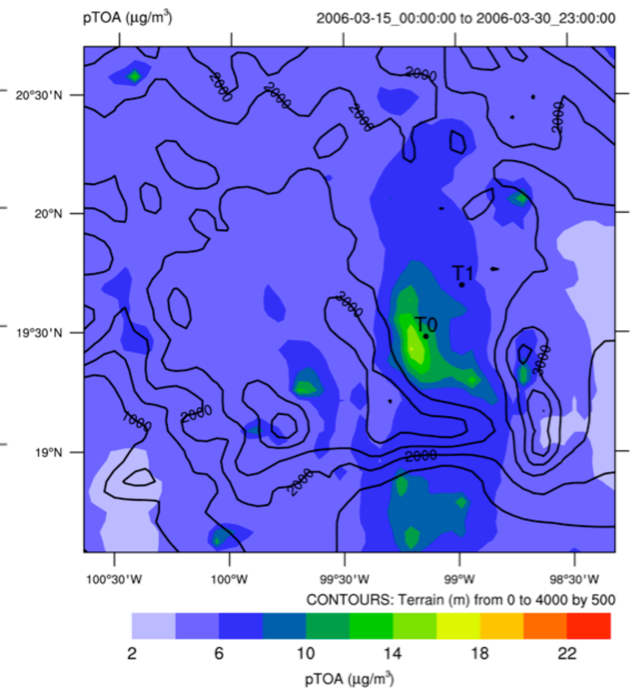
# SOA formation: contribution of primary organic vapors

- Predicted Total Organic Aerosol : 15-30 March 2006



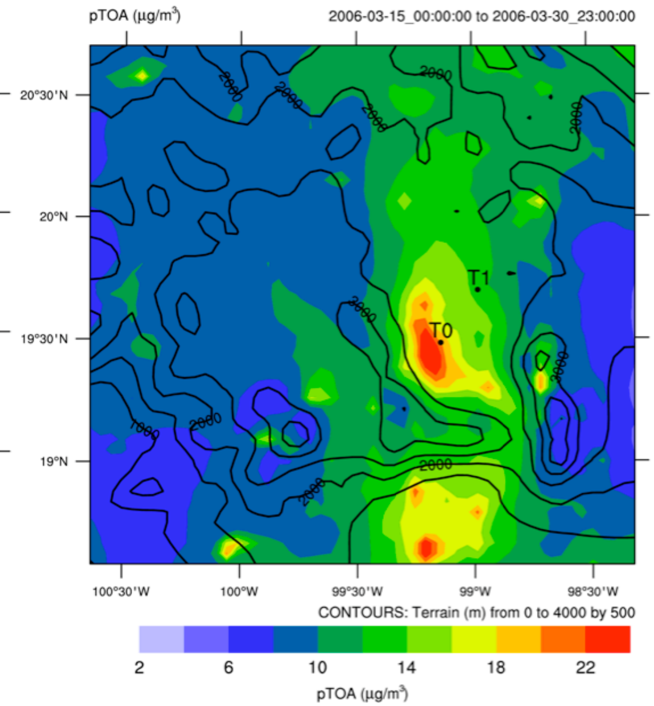

Traditional SOA

- POA passive




Robinson et al. 2007

- POA volatile
- Oxygen gain of 7.5%
- Volatility drop x10



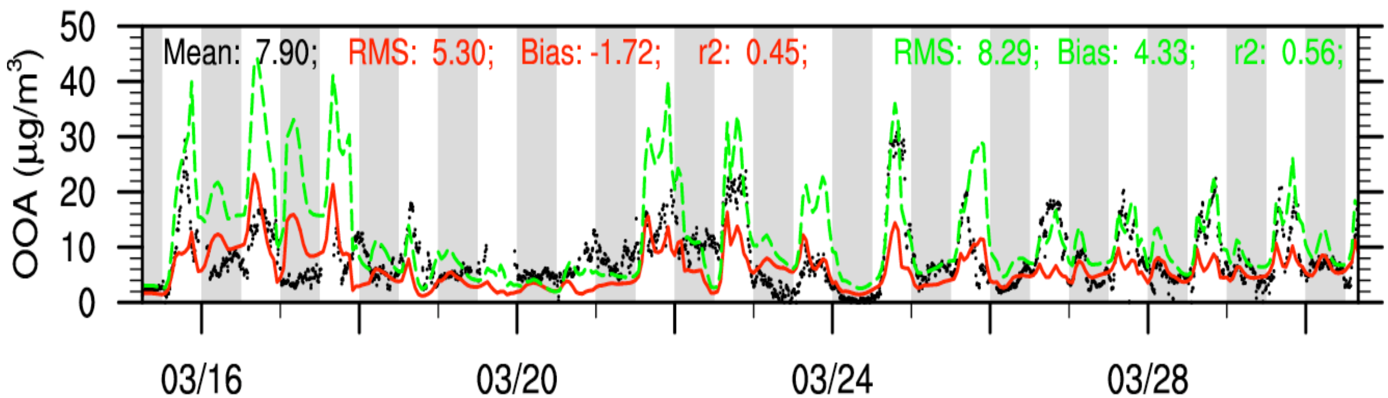

Grieshop et al. 2009

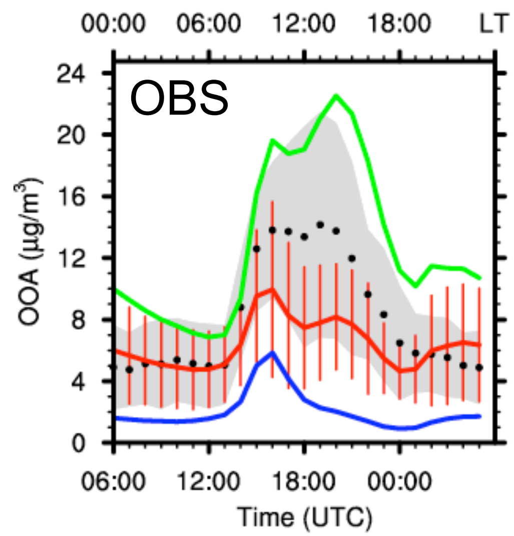
- POA volatile
- Oxygen gain of 40%
- Volatility drop x100

# SOA formation: contribution of primary organic vapors

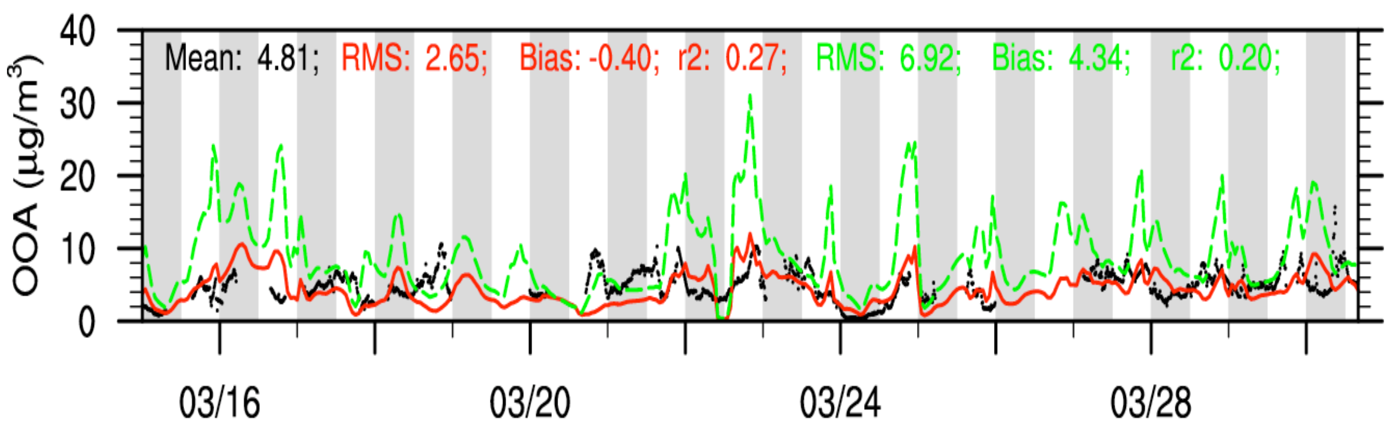
Robinson et al. 2007
Grieshop et al. 2009
Traditional SOA

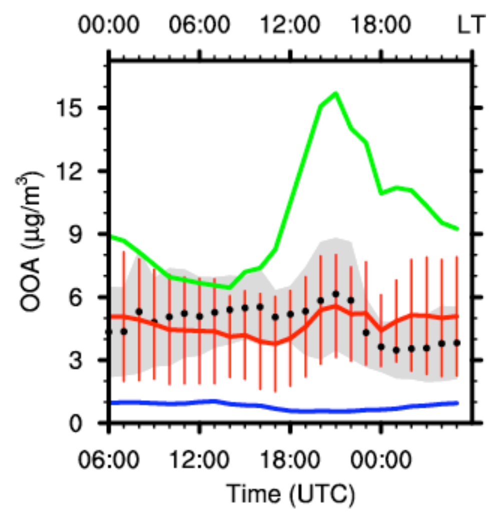
SOA - T0



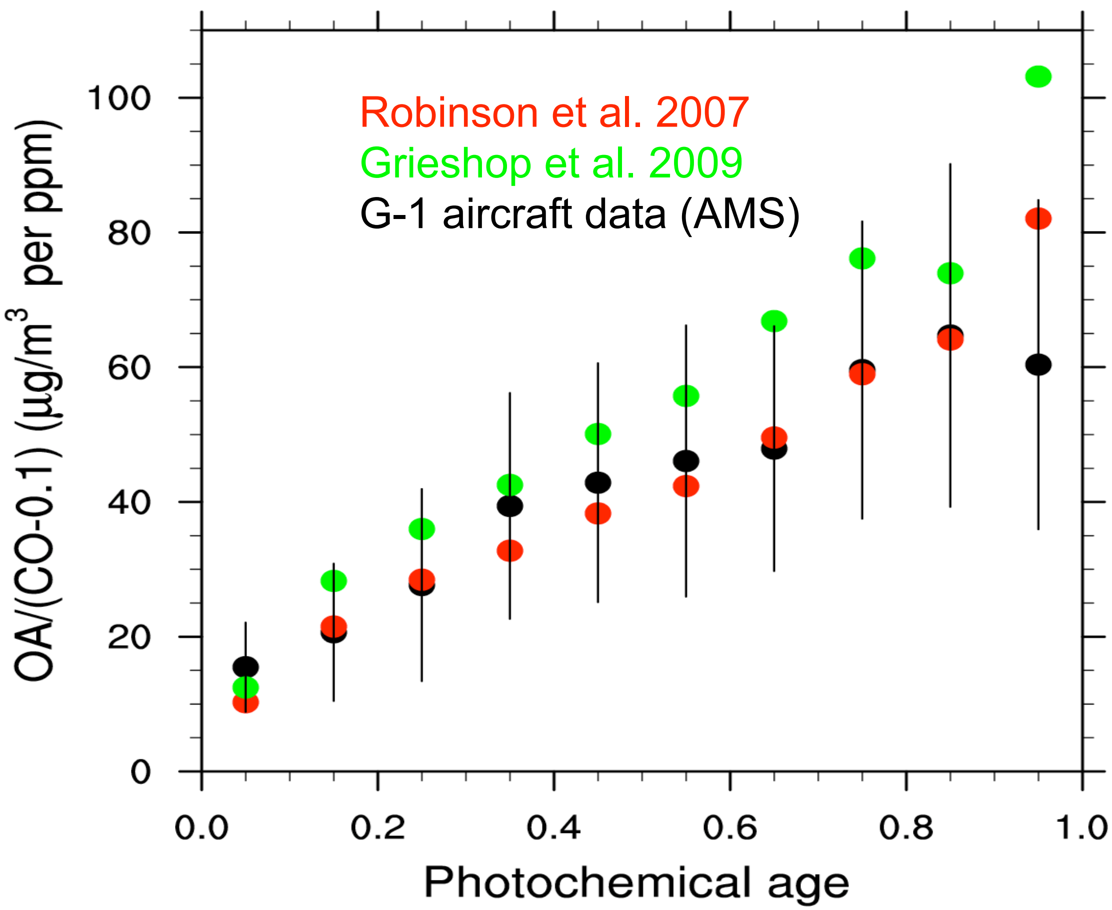

SOA - T1



# Continuous SOA production downwind of the city

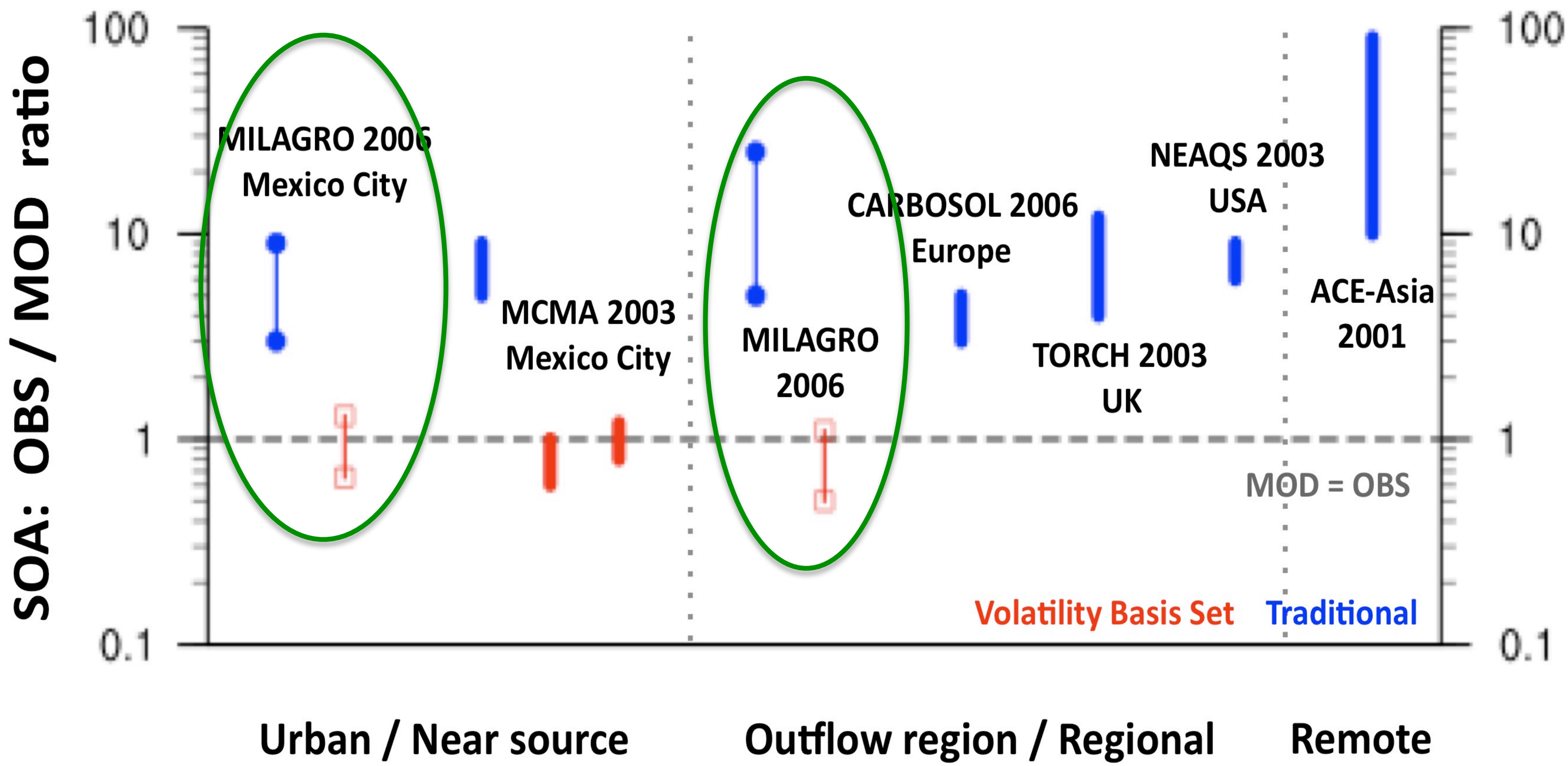
- Strong increase of OA in urban plumes as a function of photochemical age due to chemistry




~ freshly emitted ---------------------------> ~ 1 day aged air mass

# SOA formation: Summary

*Hodzic et al., in prep. ACP*

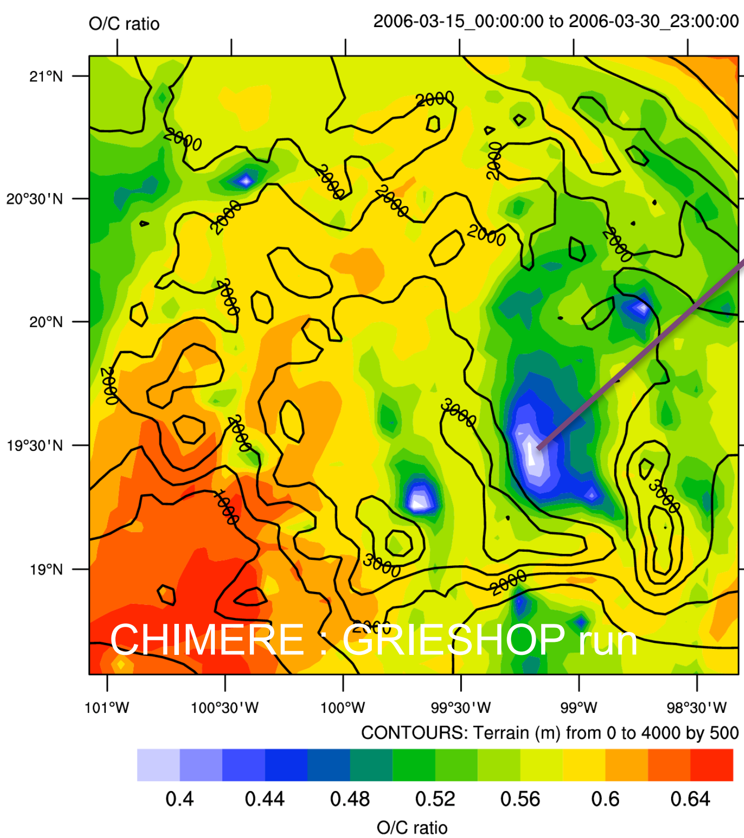


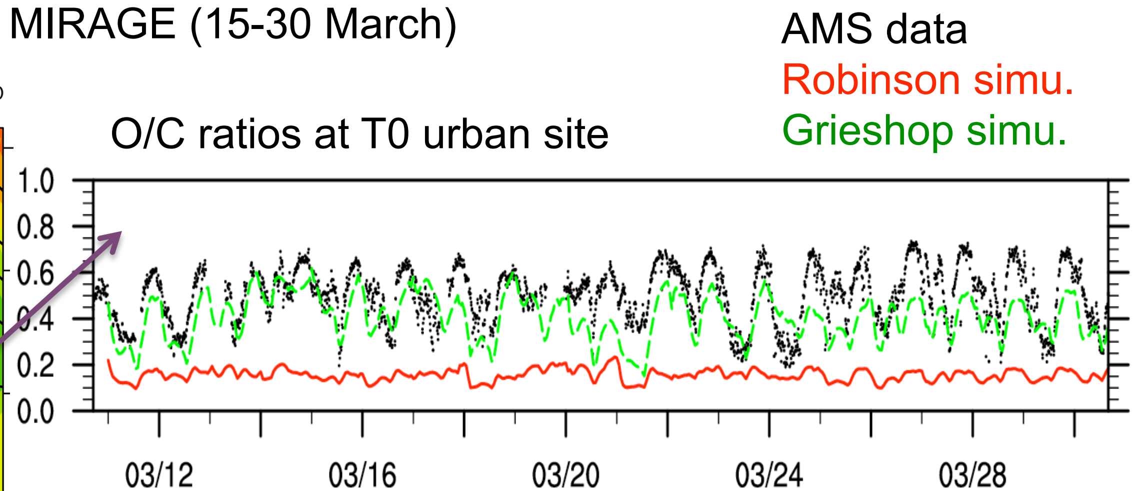

- Confirm large underprediction of the traditional SOA approach
- With S/IVOC chemistry model predictions are in the range of measured SOA
- Several SOA formation pathways ➔ Need for additional experimental constraints

# How can we better constrain model predictions?

- Aerosol optical properties (e.g. lidar, photometer data, spectral absorption)
- Atomic ratios (O/C, N/C) provided by AMS measurements

- Predicted oxidation state during MIRAGE (15-30 March)



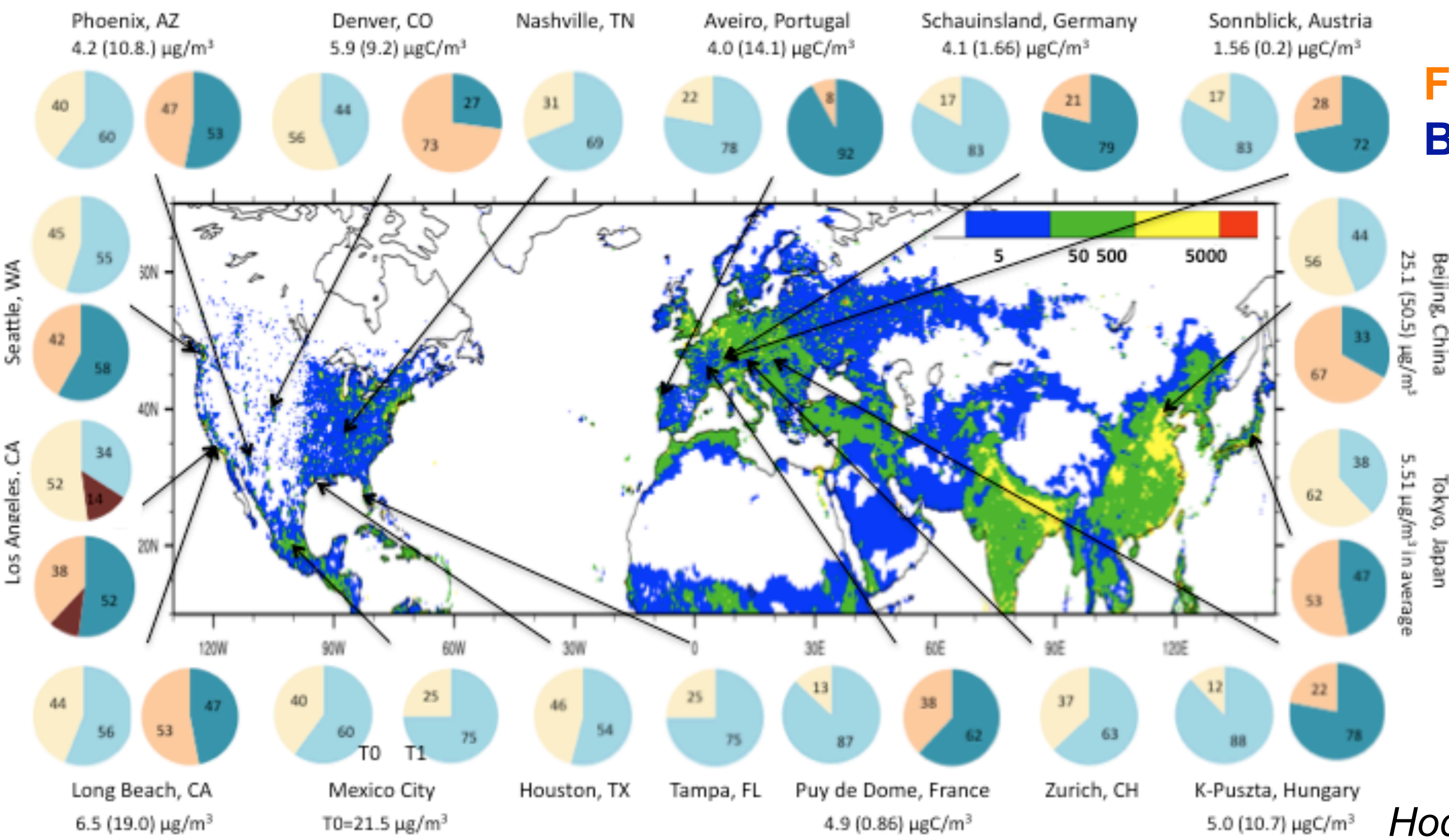

Inconsistencies in the O/C ratios for the Robinson et al., 2007 although the OA mass is modeled correctly.

Inconsistencies between measured / predicted N/C

- N/C (AMS) : < 0.02
- N/C (Master Mech.) : ~ 0.16

# Can we further constrain OA predicted by models?

- Aerosol optical properties (e.g. lidar, photometer data, spectral absorption)
- Atomic ratios (O/C, N/C) provided by AMS measurements
- Fraction of fossil / non-fossil organic carbon




**Fossil carbon**

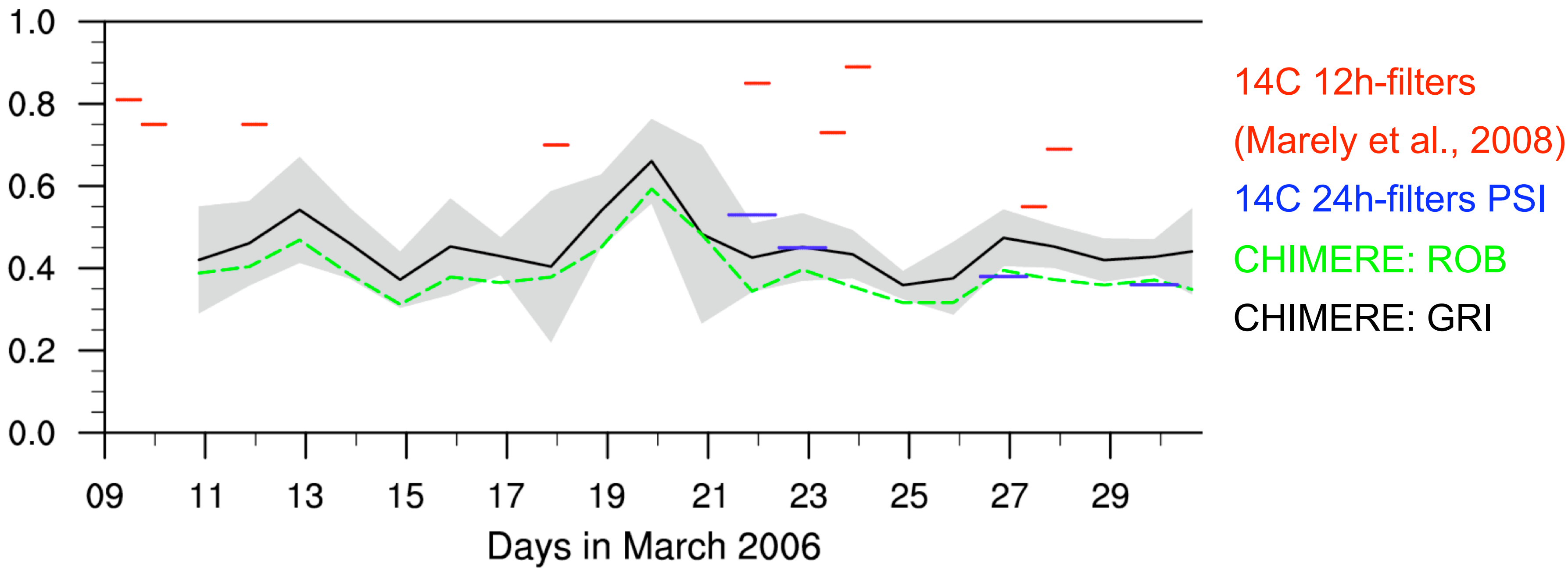
**Biogenic carbon**

*Hodzic et al., in prep.*

# Can we further constrain OA predicted by models?

- Aerosol optical properties (e.g. lidar, photometer data, spectral absorption)
- Atomic ratios (O/C, N/C) provided by AMS measurements
- Fraction of fossil / non-fossil organic carbon

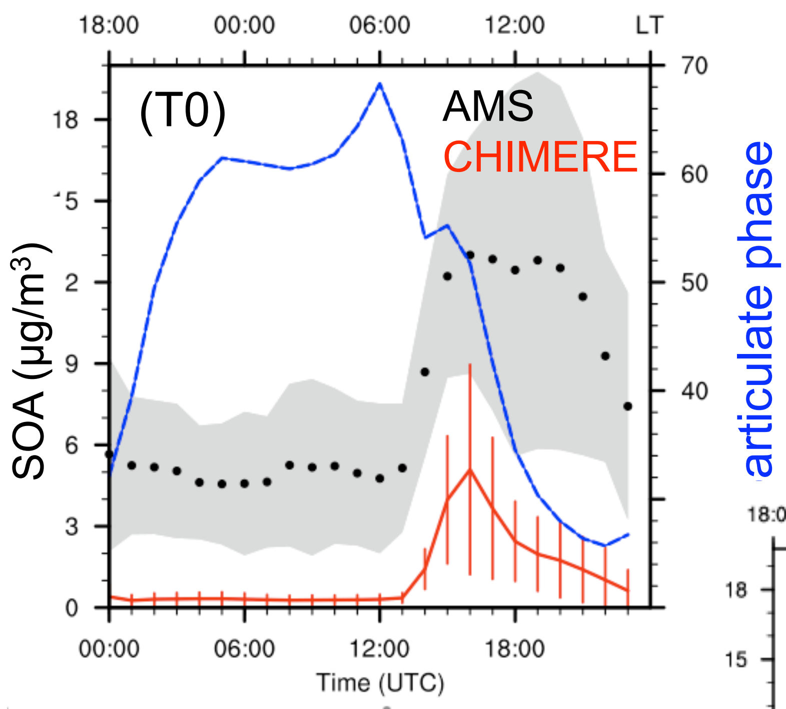
Fraction of Non-Fossil Carbon at T0




*Hodzic et al., in prep.*

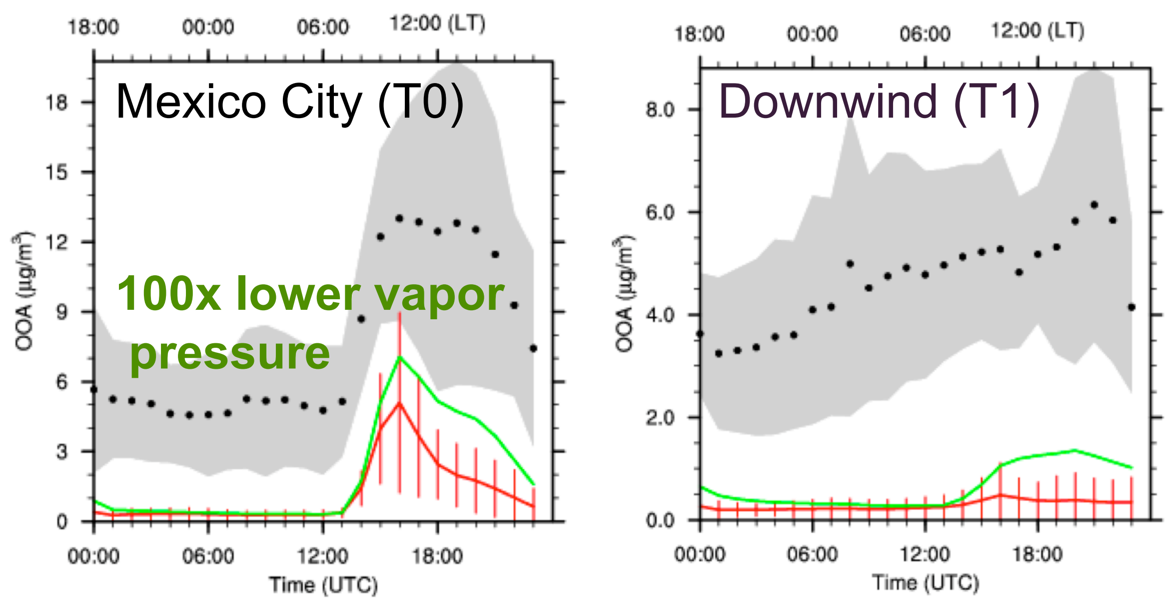
# SOA formation : 2-product approach

## Excessive evaporation of freshly formed SOA



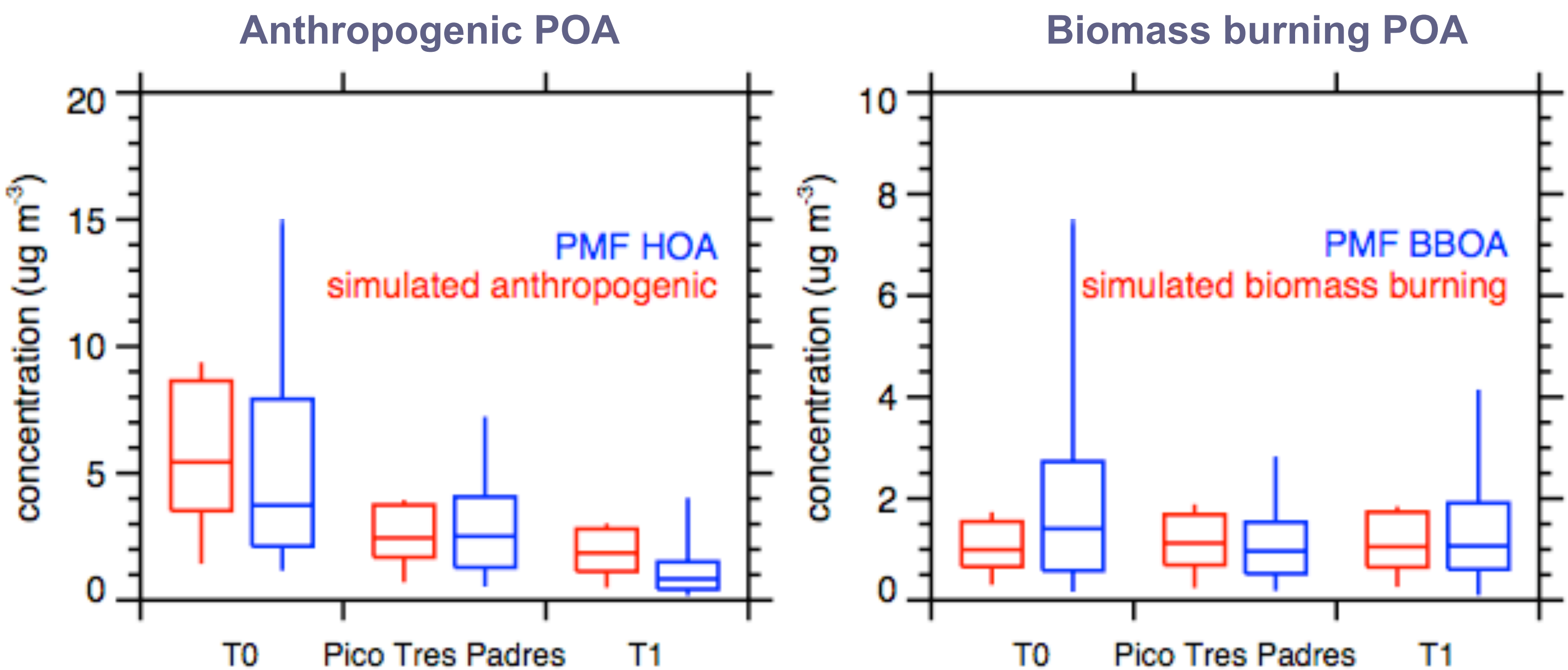

- upon dilution of POA and PBL growth
- unaccounted in-particle reactions
- multiple oxidations of VOCs

## Enhanced partitioning into aerosol phase



# Good agreement for primary organic species

**- Surface stations, March 2006**

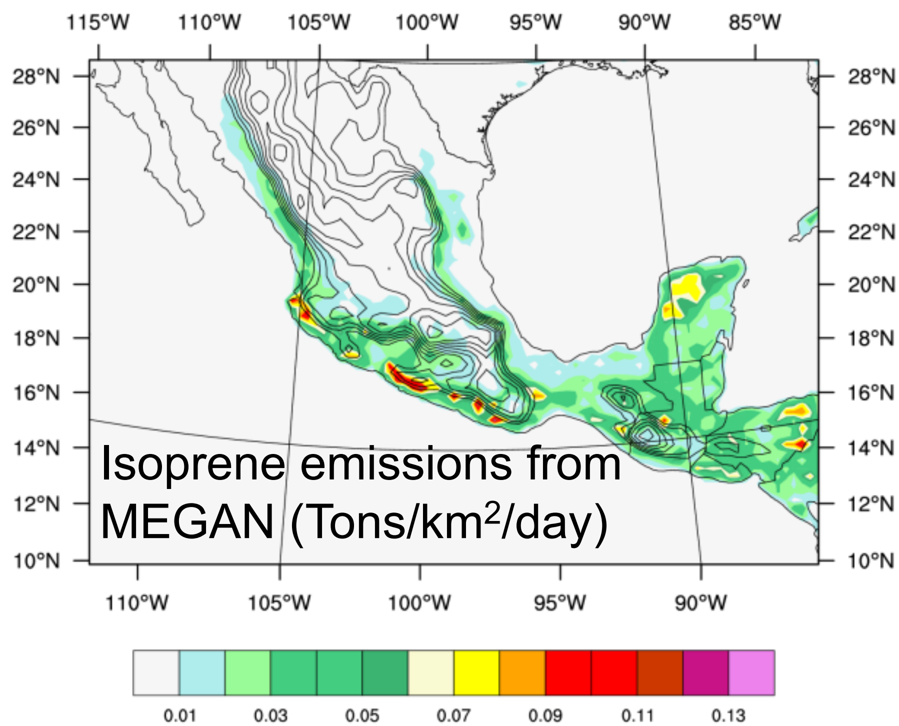


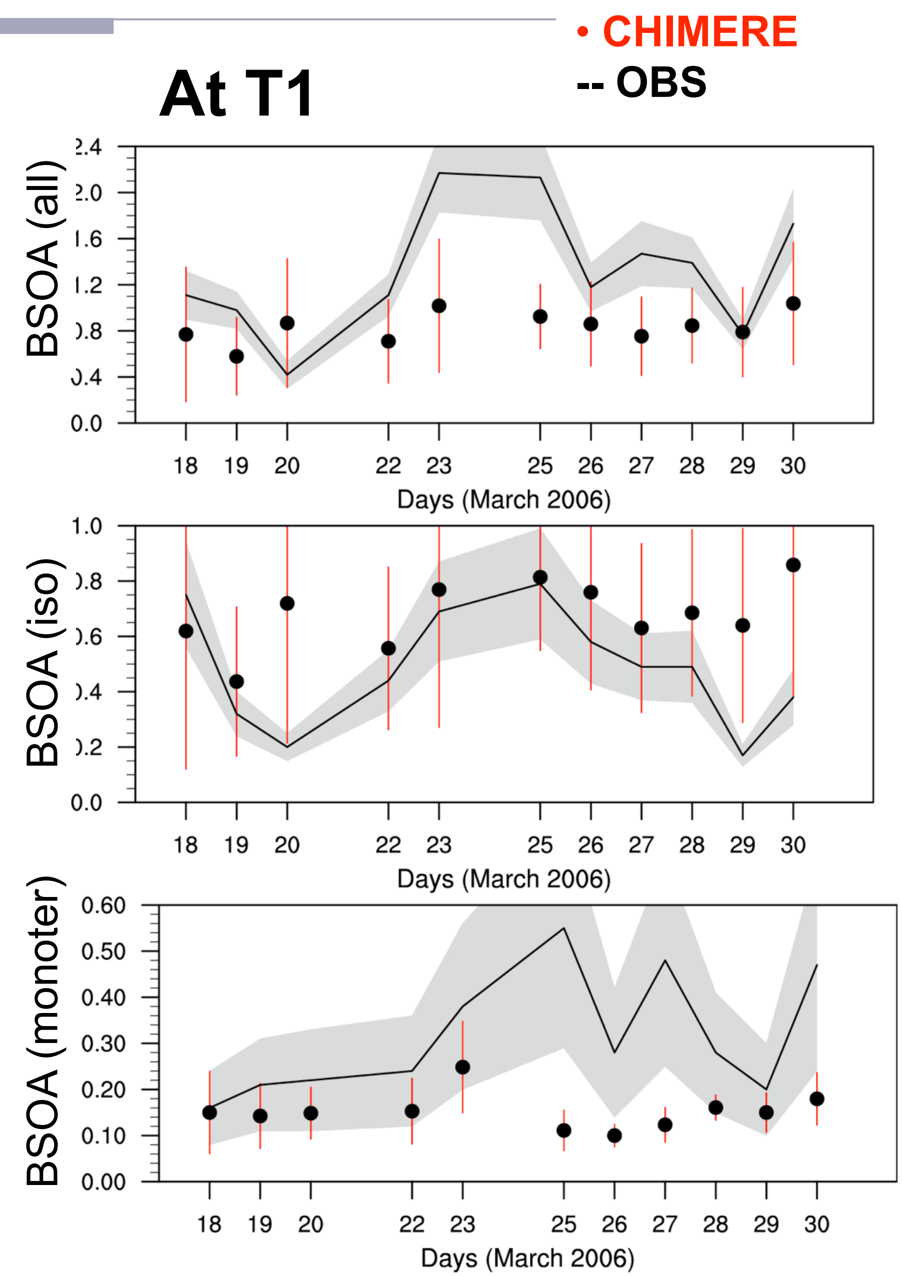

*Fast et al. ACP, 2009*

HOA and BBOA well captured by the model in the city

# SOA formation : role of biogenic precursors

Biogenic SOA
- modeled with MEGAN
- estimated from tracer measurements (Stone et al., 2009)
- **Biogenic SOA is NOT underestimated**

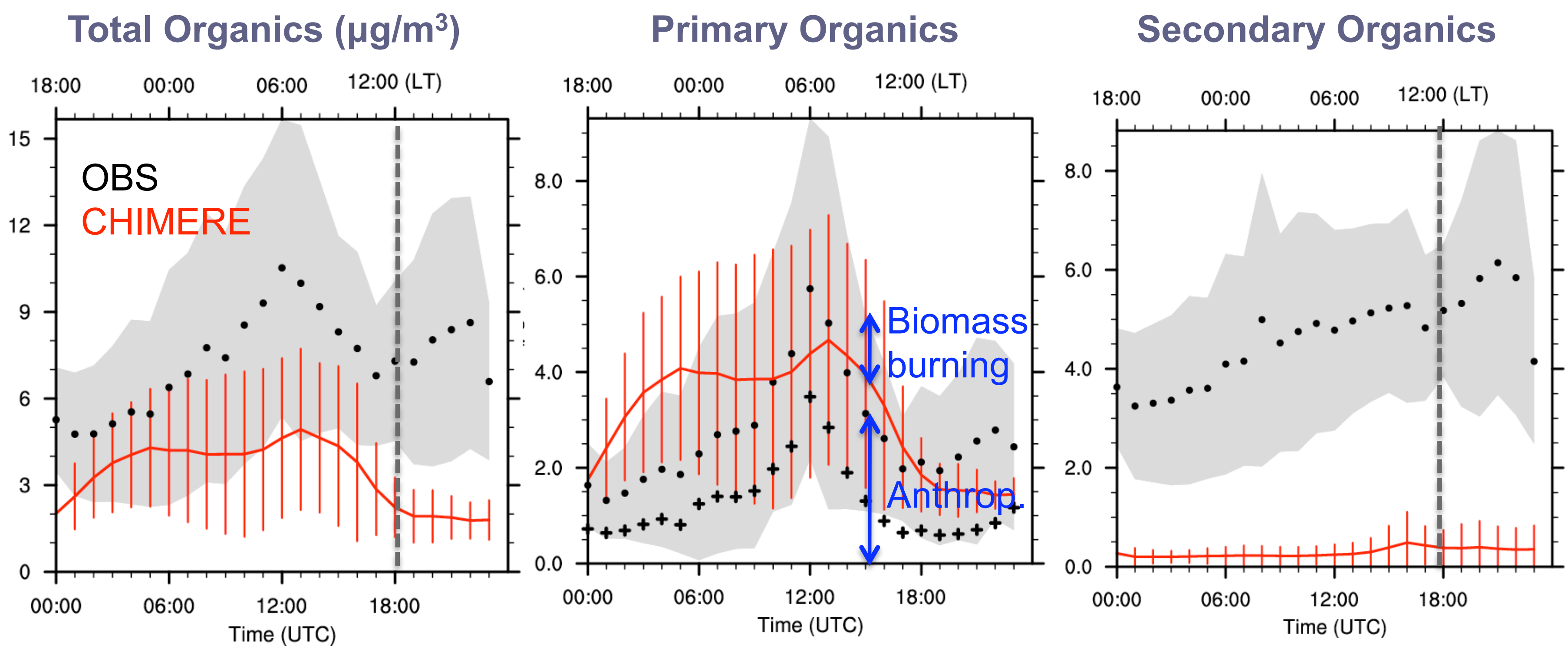



*Hodzic et al., ACP, 2009*

# Model vs. Measurements at the surface

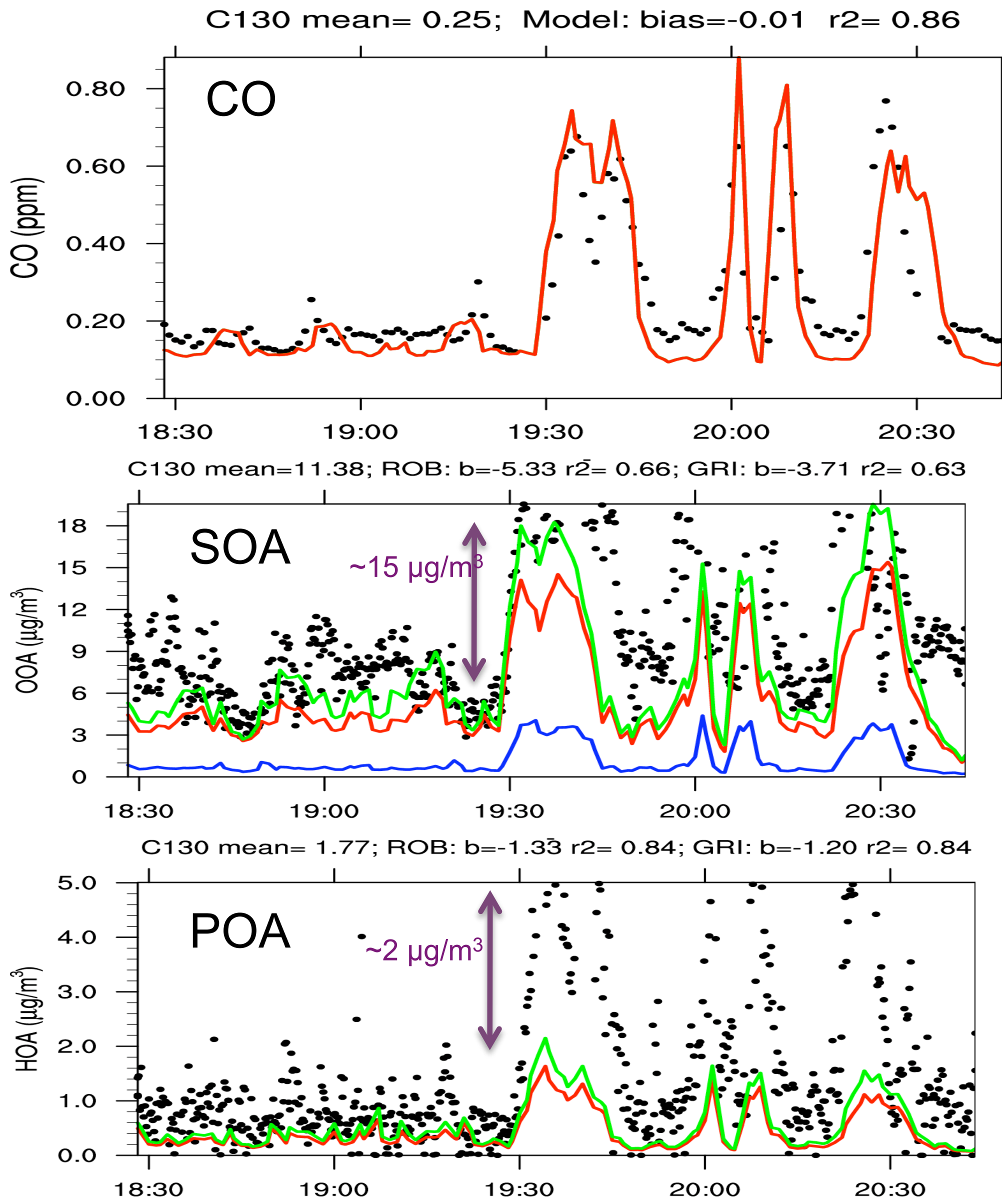
## - Mexico City T1, March 2006

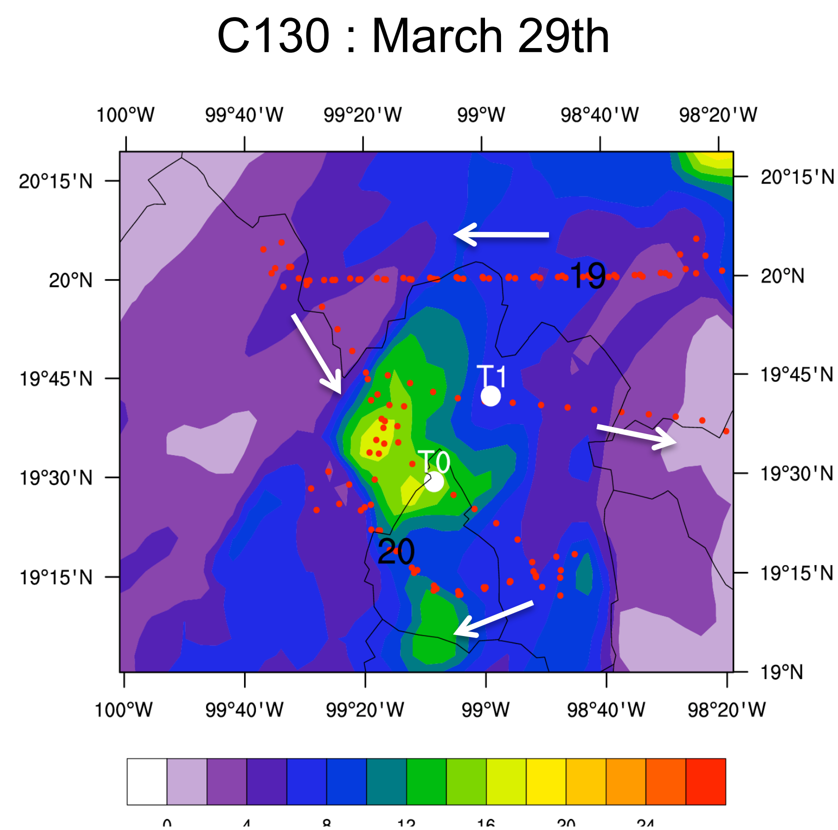



- OA underestimated by a factor of 2
- POA reasonably captured
- SOA largely underpredicted

*Hodzic et al. ACP, 2009*

# Model vs. Measurements in the urban plume




Robinson et al. 2007

Grieshop et al. 2009

Traditional SOA

OBS

# SOA formation : explicit chemistry

- Provides chemical identity of products (e.g. Master Chemical Mechanism)
- Reactions and rates are extrapolated from know chemistry (not measurements).

**Predictions of the GECKO model during MIRAGE 2006:**

Most of aerosol carbon is accounted for by relatively few species ( -OH, -NO3, -NO2 groups dominates)

AR0212
3-methyl-6-nitro-catechol.
Precursor: toluene

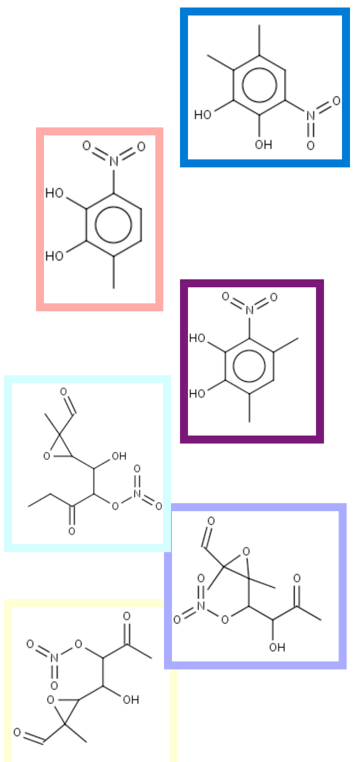
AR0128
3-methyl-6-nitro-catechol.
Precursor: toluene

AR0293
3,5-dimethyl-6-nitro-catechol.
Precursor: m-xylene

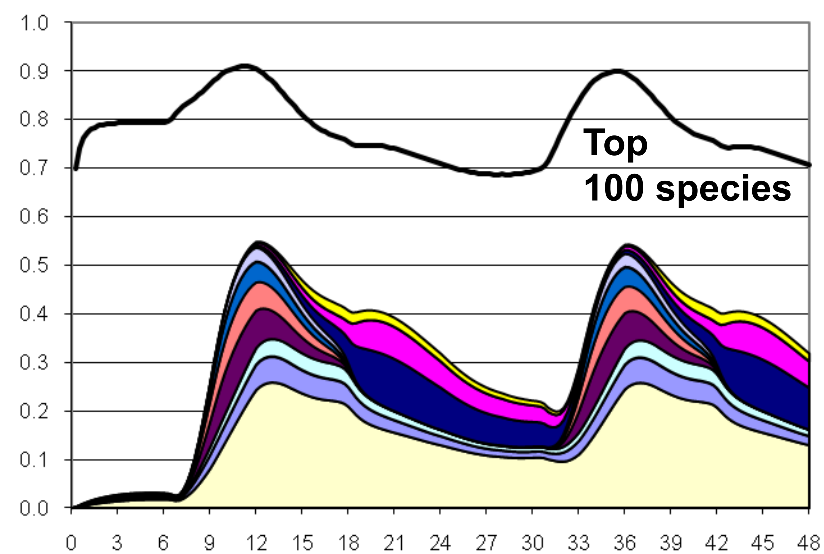
AR0875
2-methyl-2,3-epoxy-4-hydroxy-5-nitrooxy-6-keto-octanal.
Precursor: 3-ethyltoluene

AR0686
2-methyl-2,3-epoxy-4-nitrooxy-5-hydroxy-6-oxo-heptanal.
Precursor: 1,2,4-trimethylbenzene

AR0268
2,3-epoxy-4-hydroxy-5-nitrooxy-6-oxo-heptanal.
Precursor: m-xylene



10 major species (~ 50% mass)




*Courtesy of Julia Lee-Taylor and Sasha Madronich*