Chemical Transport Model (PMCAMx) versus Measurements: Insights about the Sources and Production of Particulate Matter in Mexico City

Alexandra Tsimpidi, Vlassis Karydis and Spyros Pandis
University of Patras, Greece

Timothy Lane and Pavan Racherla
Carnegie Mellon University

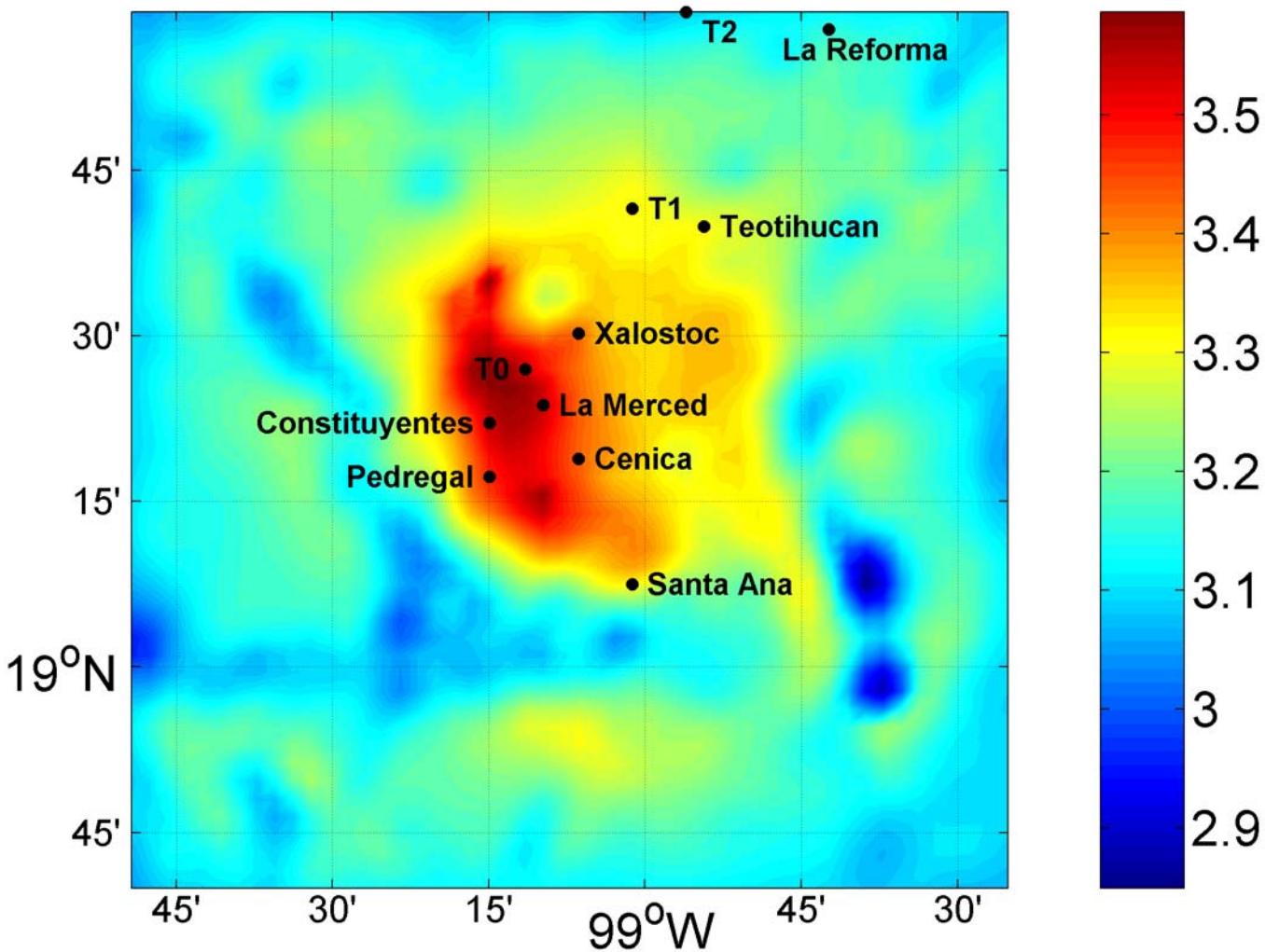
Miguel Zavala, Wenfang Lei and Luisa Molina
MIT and Molina Center for Energy and the Environment

PMCAMx Application to Mexico City

- PMCAMx: Research version of CAMx
  - CAMx is available in www.camx.org (supported by ENVIRON)
  - includes CMU modules for aerosol processes (inorganic and organic PM, interactions with clouds)
  - multiple modules for processes
  - ten size sections, all major aerosol species
- Application for MCMA-2003 (April 10-16) and MILAGRO
  - Use of 3x3 km grid
  - Use of MIT/MCE2 emission inventory (see poster by Zavala et al.)
- Objectives
  - integrate what we know and what we do not know about Mexico City
  - evaluate our current state of understanding comparing with measurements
  - assist in the interpretation of measurements from the two field campaigns
  - use the model for the design of control strategies

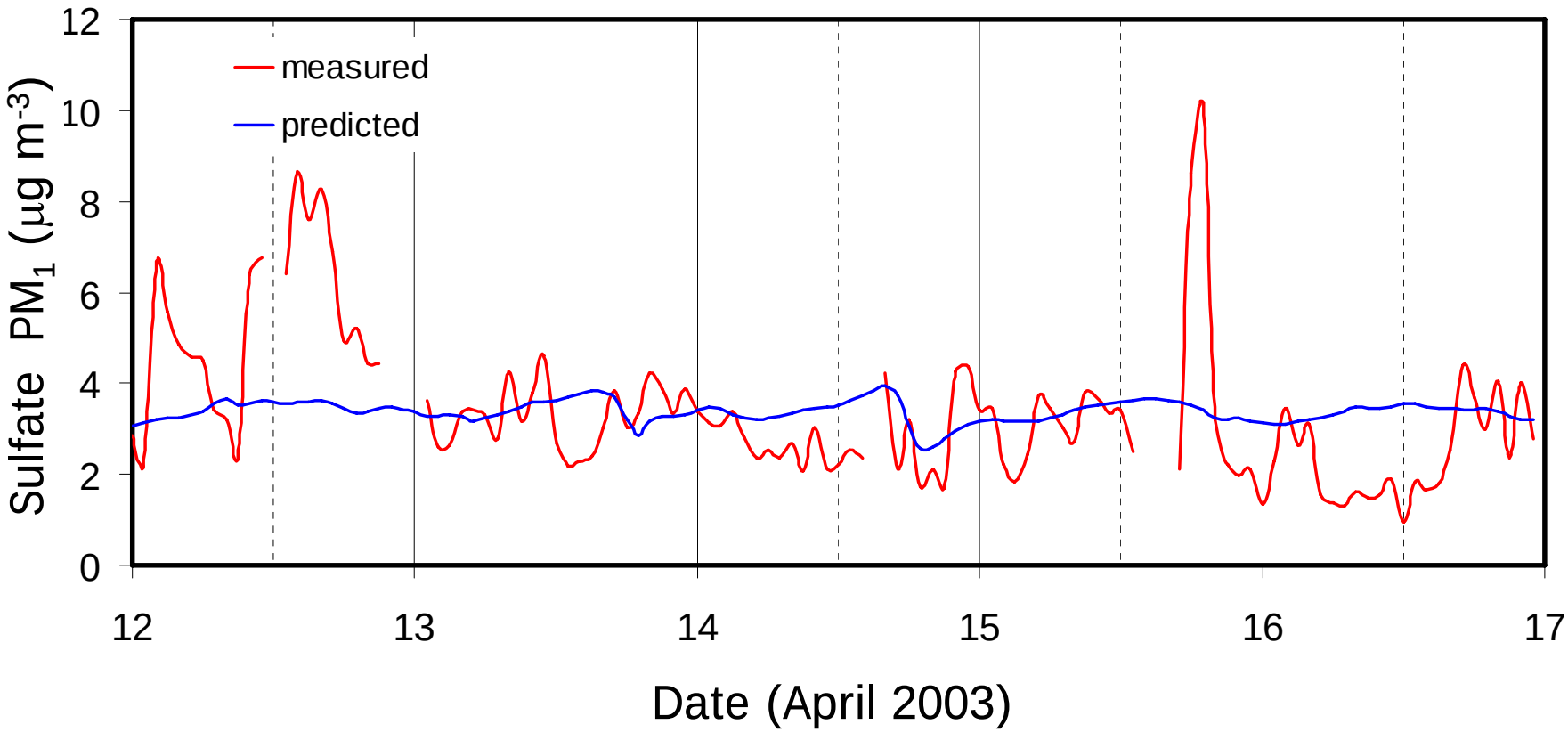
$PM_{2.5}$ Sulfate

Average Ground Concentration ($\mu g\ m^{-3}$) for April 12-16, 2003



Sulfate Predictions vs Observations

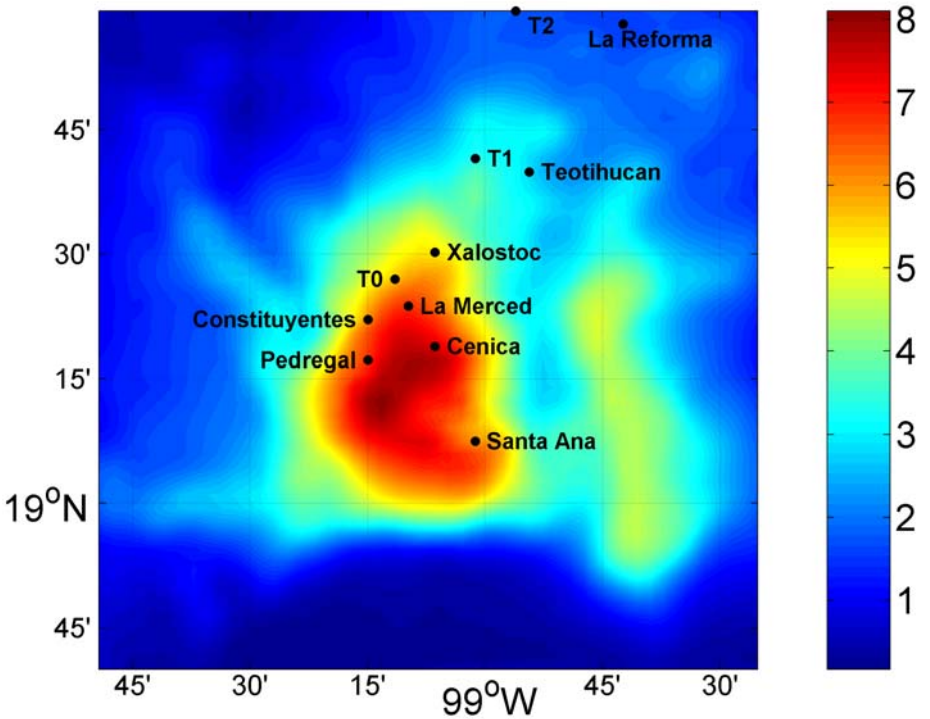
(Cenica)



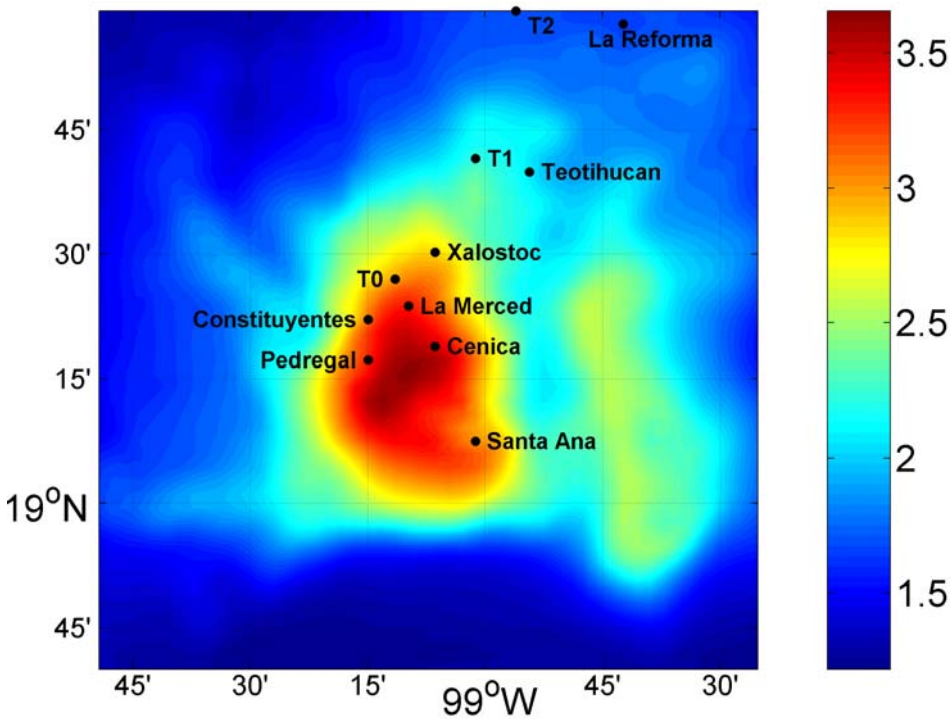
- Missing SO_2/sulfate (Tula) sources in the inventory

$PM_{2.5}$ Nitrate and Ammonium

Average Ground Concentration ($\mu g\ m^{-3}$) for April 12-16, 2003

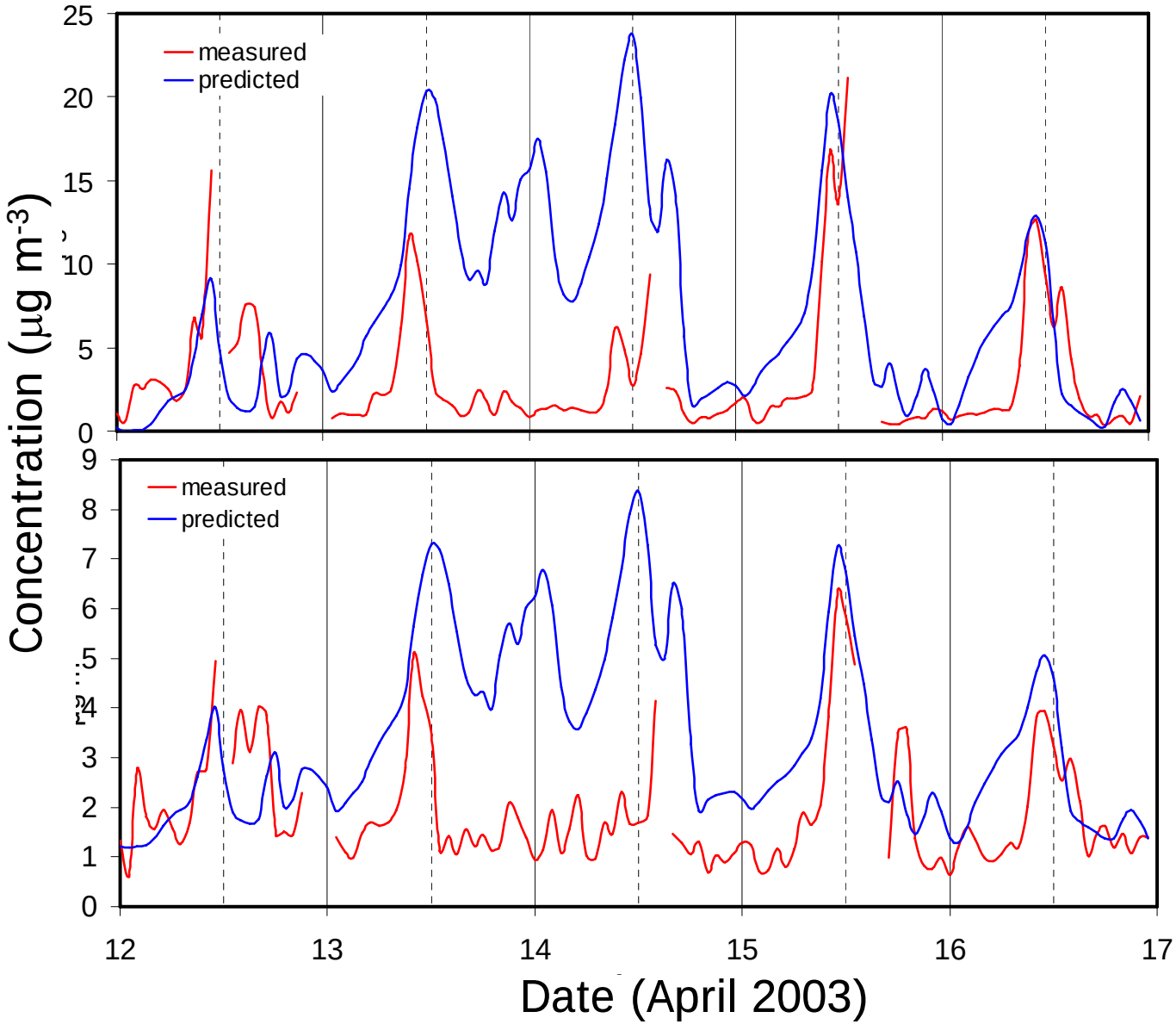


Nitrate



Ammonium

Nitrate/Ammonium Predictions vs Observations (Cenica)



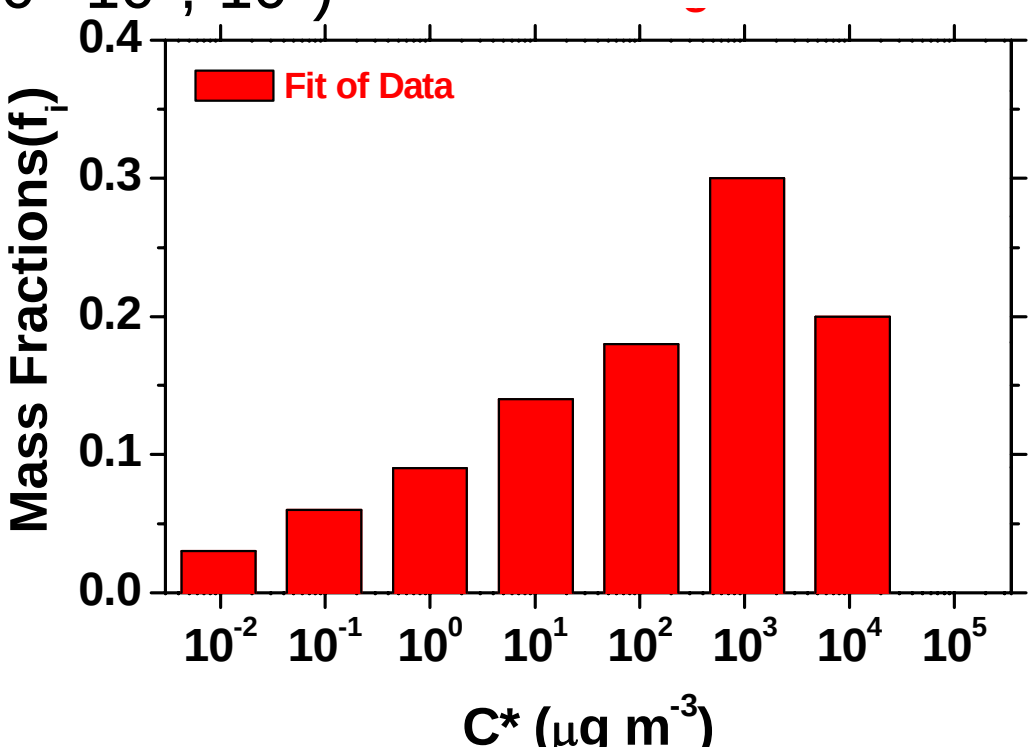
Nitrate

Ammonium

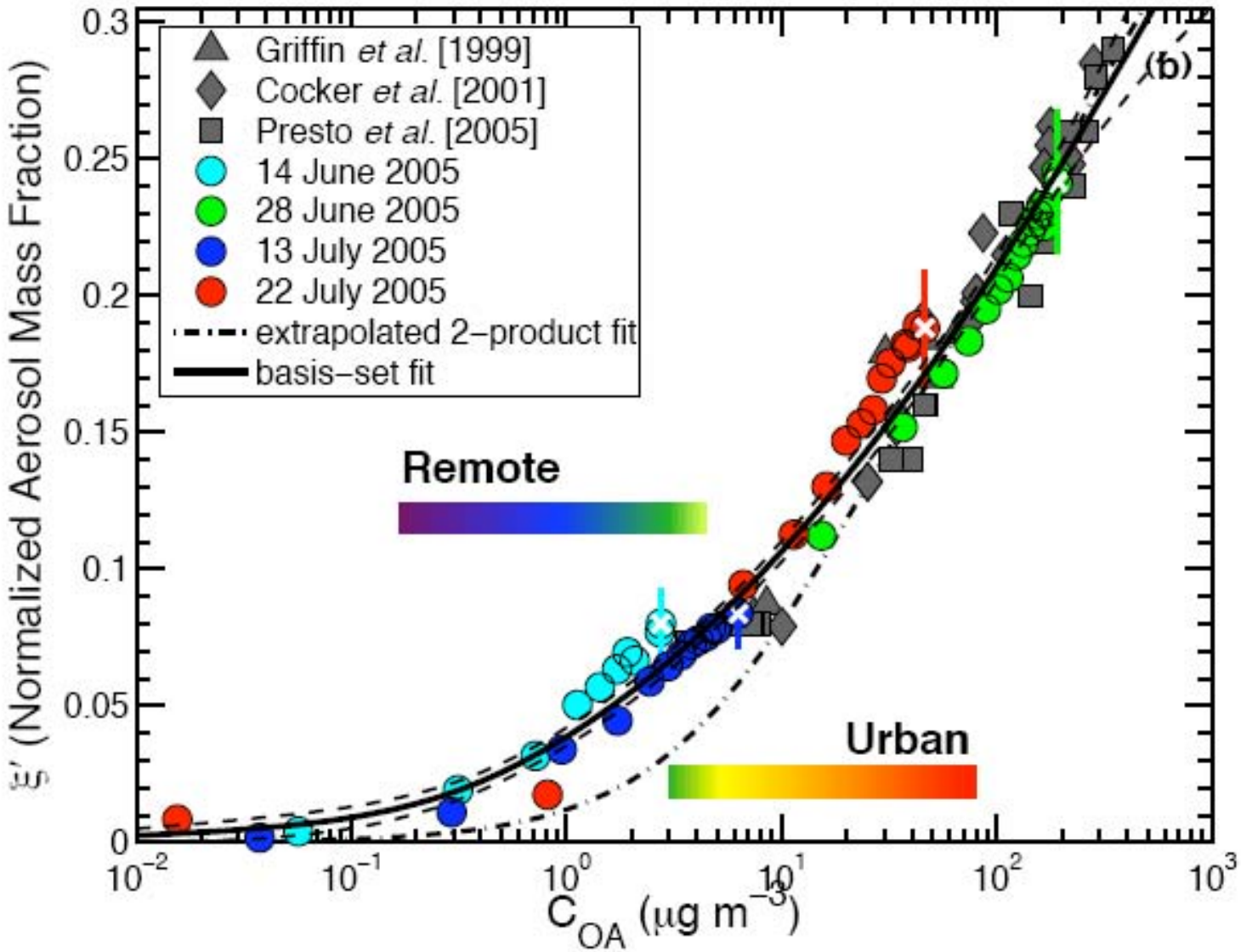
- Dust
- ISORROPIA II
- Ammonia

SOA Module

- Organics in the atmosphere (both in primary and secondary PM) cover a wide range of volatilities
- Splitting of the volatility spectrum into bins
- Basis set: saturation concentrations (0.01, 0.1, 1, 10, 10^2, 10^3, 10^4, 10^5)

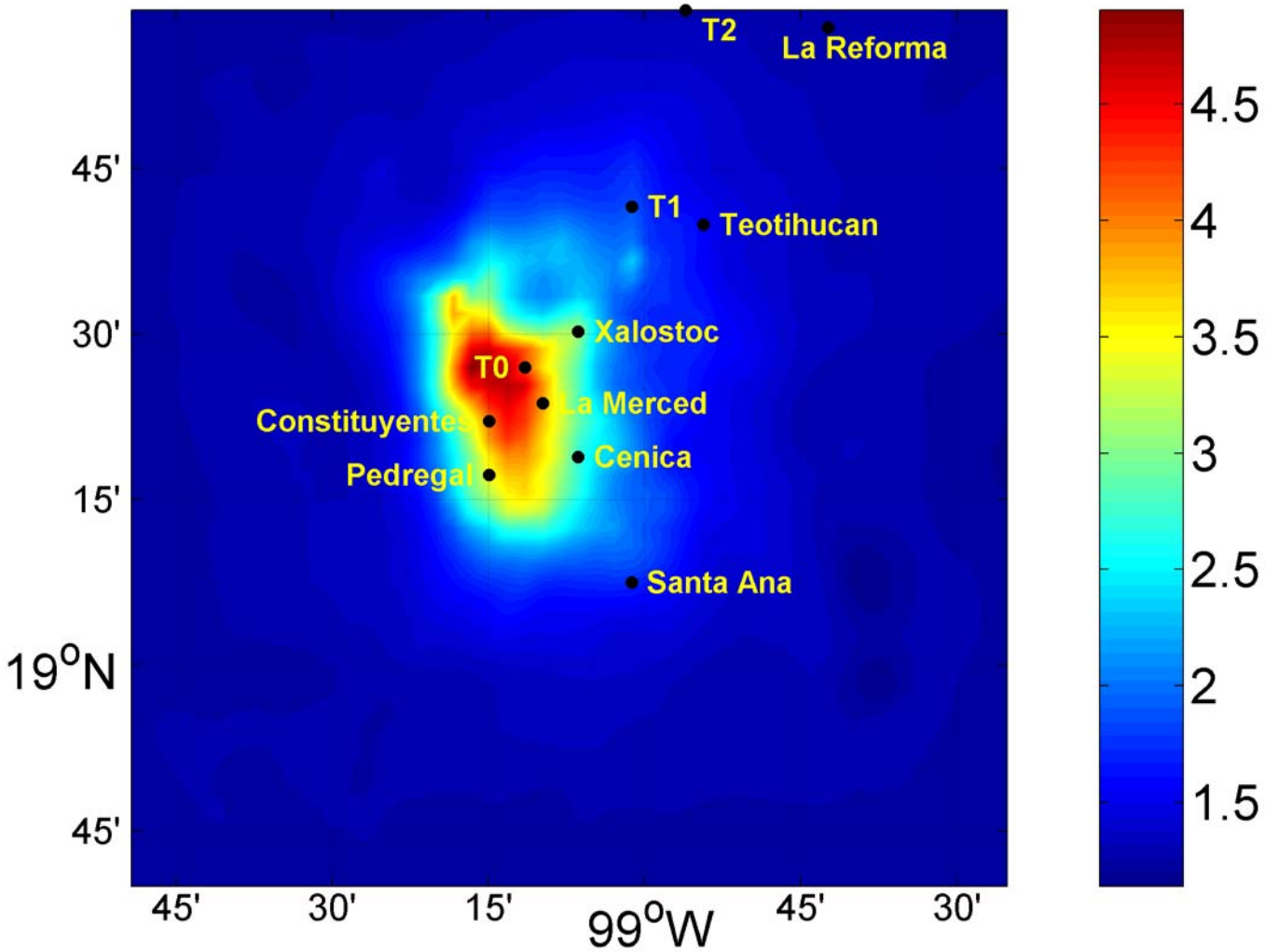


SOA Studies at Ambient Concentration Levels (Presto et al., ES&T, 2006)

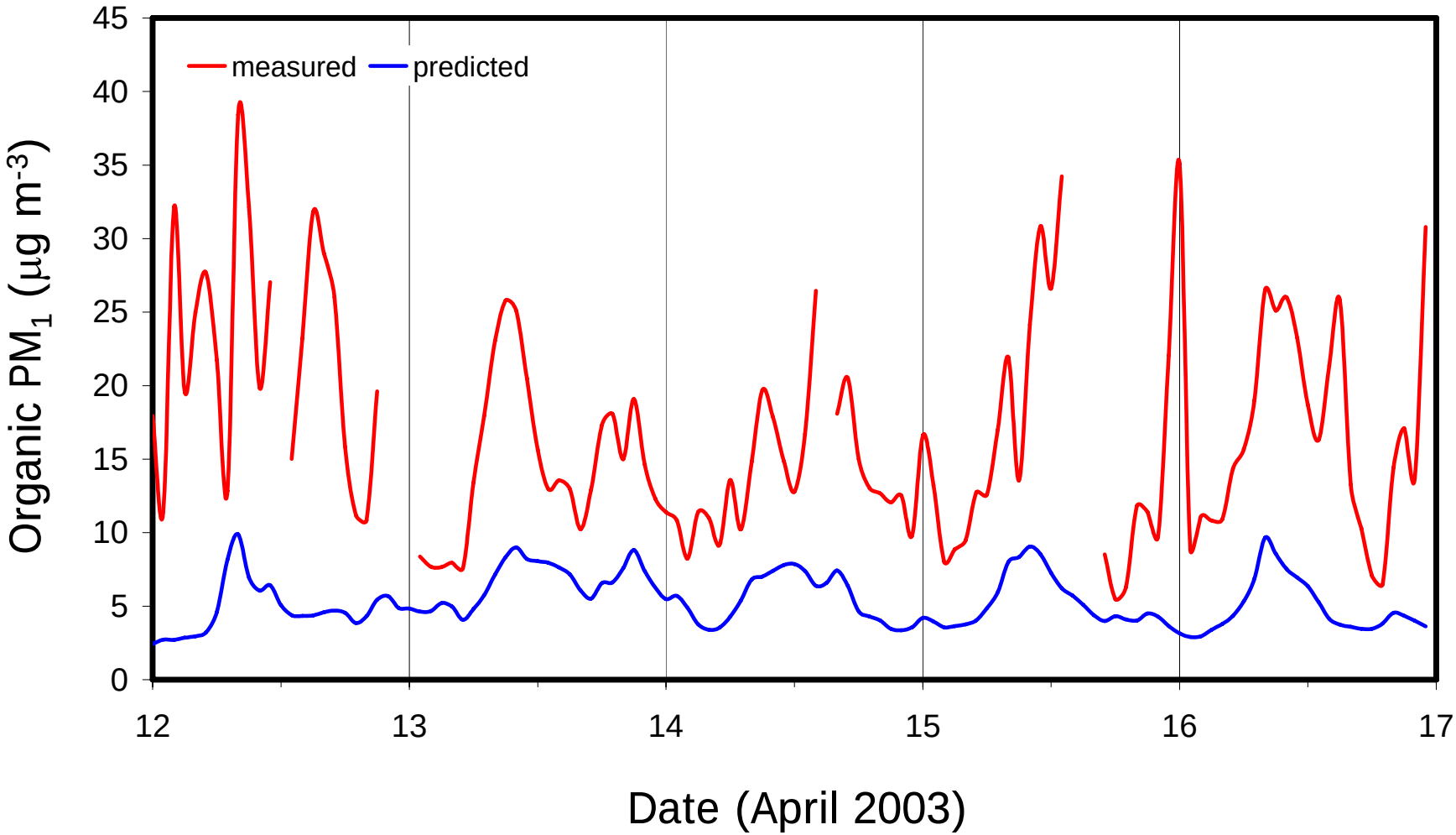


Organic $PM_{2.5}$

Average Ground Concentration ($\mu g\ m^{-3}$) for April 12-16, 2003

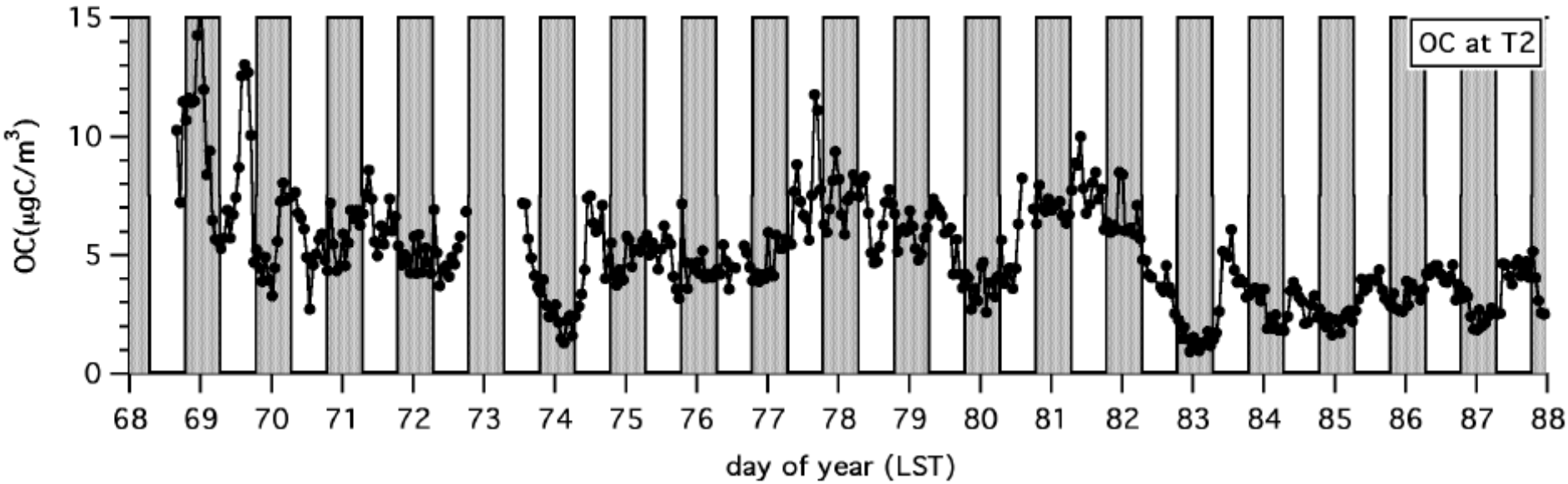


Predicted Organic PM vs Observations



OC at T2 during MILAGRO

Source: Doran et al. (2007) Atm. Chem. Phys., 38, 1585-1598.

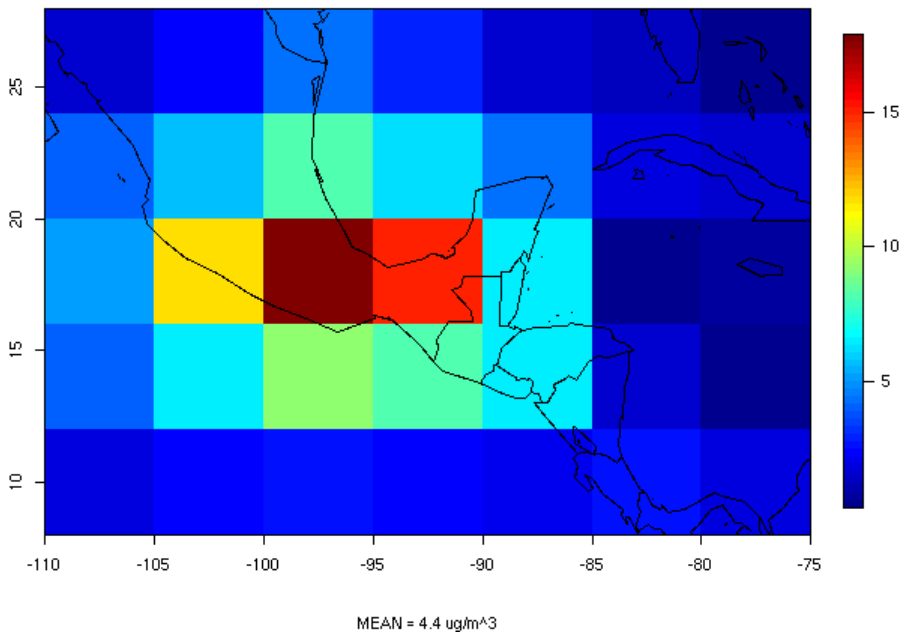


The average OM concentration was around 8 μg m^{-3} !

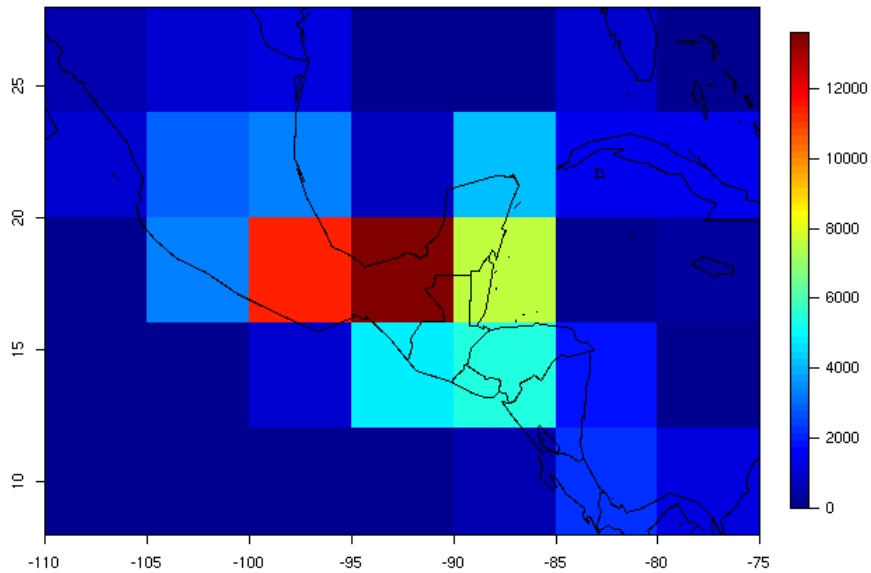
OM Concentrations around Mexico City

Results from GISS-II' GCM/CTM (Racherla and Adams, 2007)

April OM Concentration

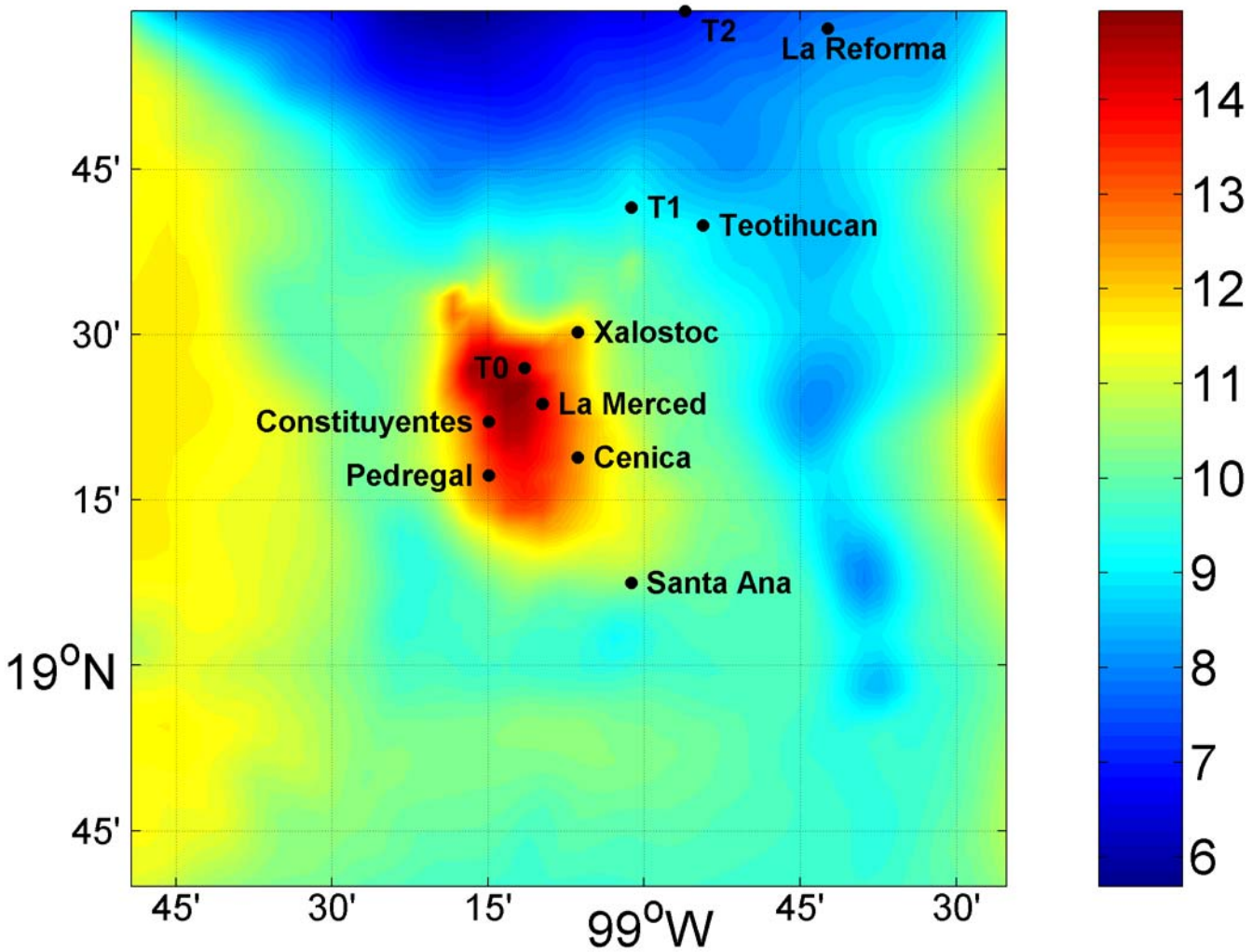


April OA Emissions (kg/hr)

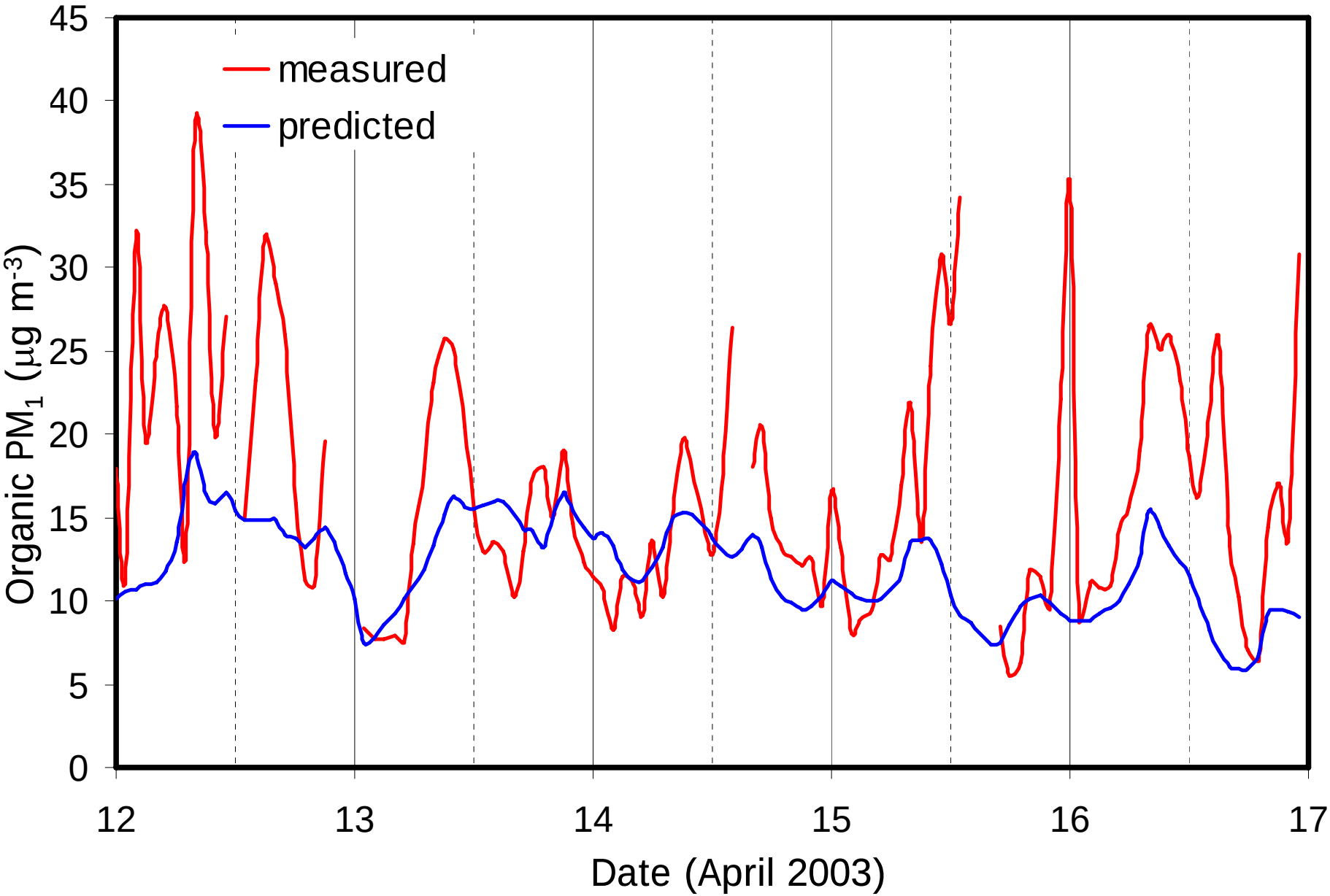


Liousse et al. (1997) Inventory

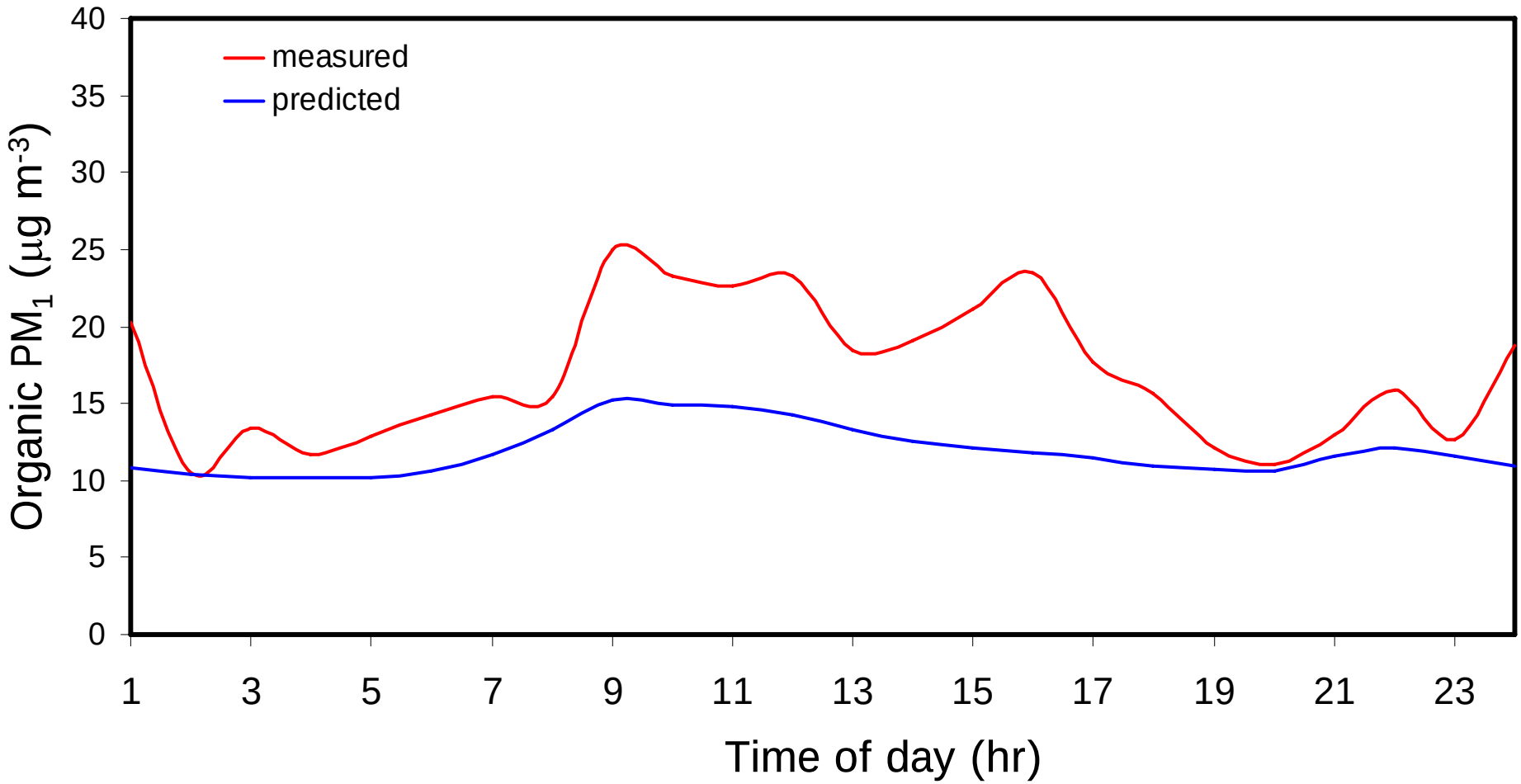
Average Organic $PM_{2.5}$ (April 12-17)



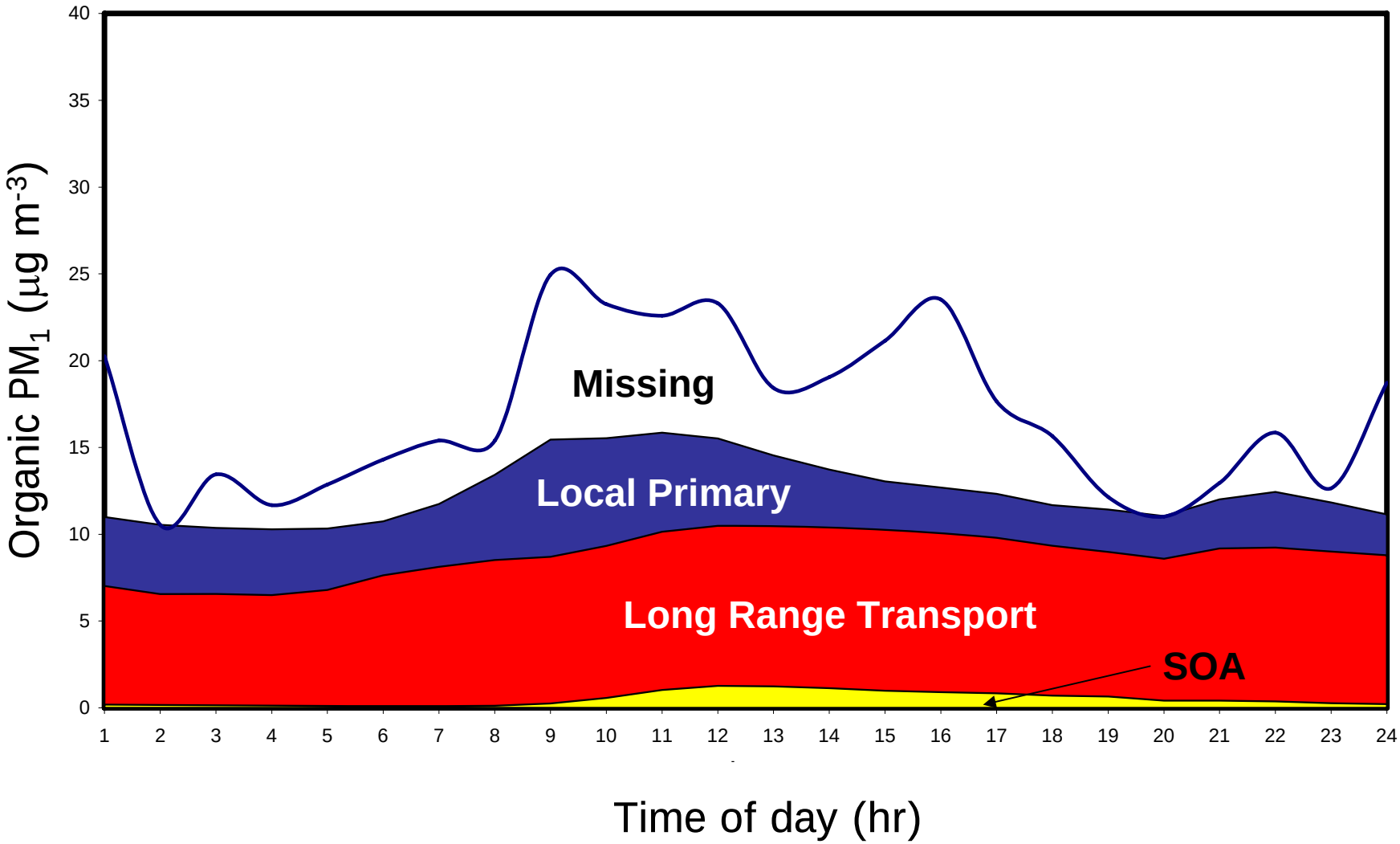
Predicted Organic PM vs Observations



Predicted Diurnal Variation of Organic PM vs Observations

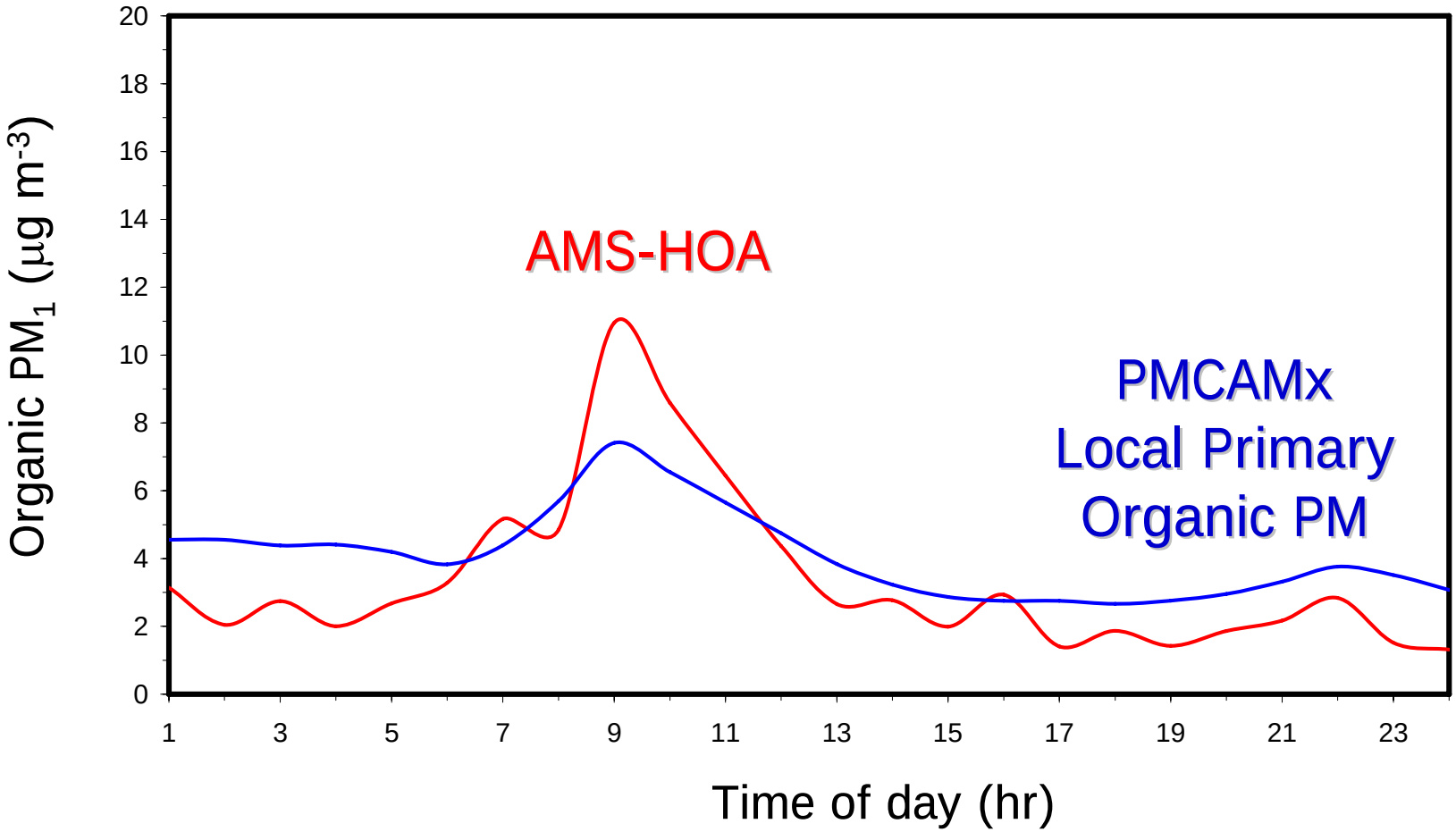


Mass Balance of Organic PM

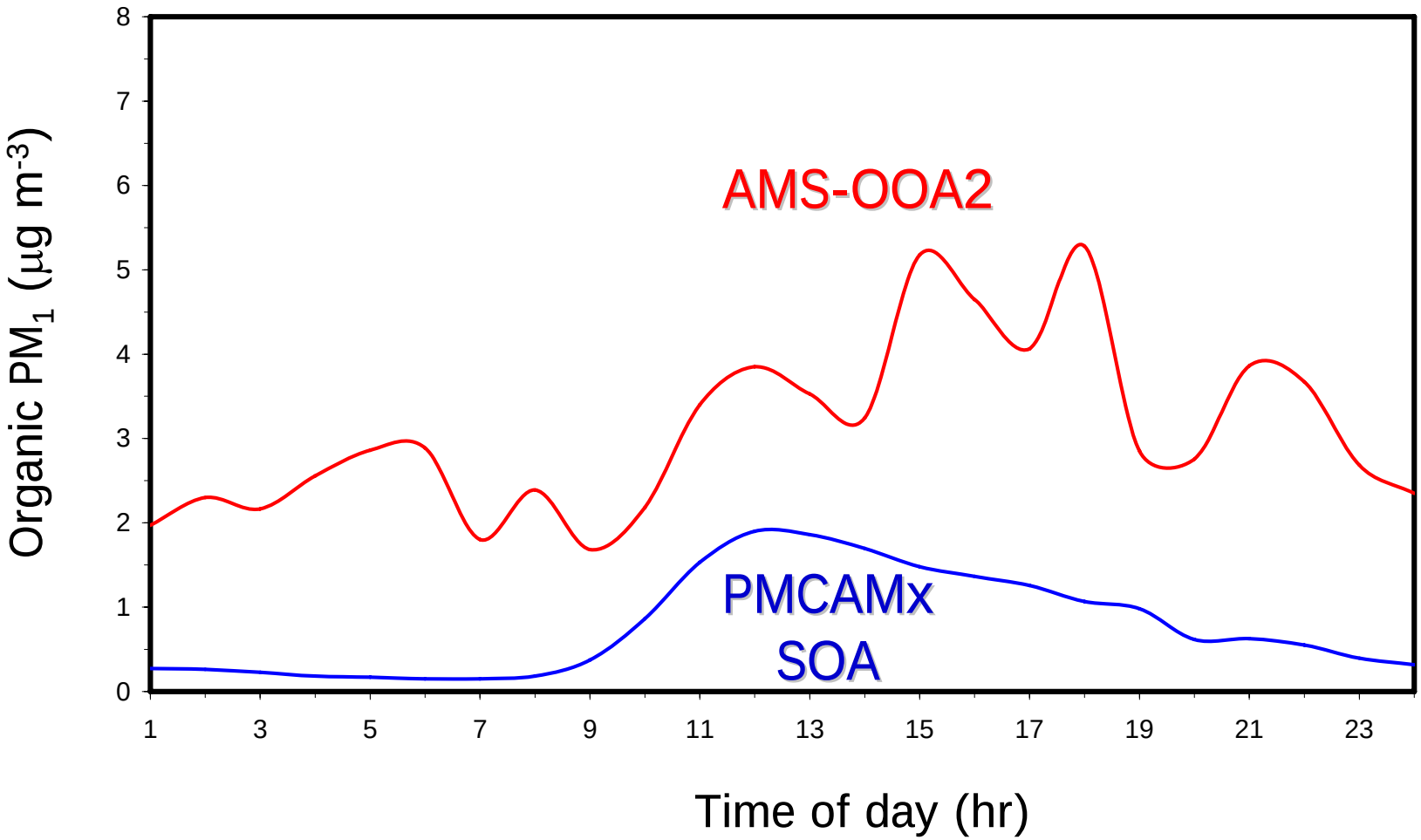


Comparison with AMS MS Analysis

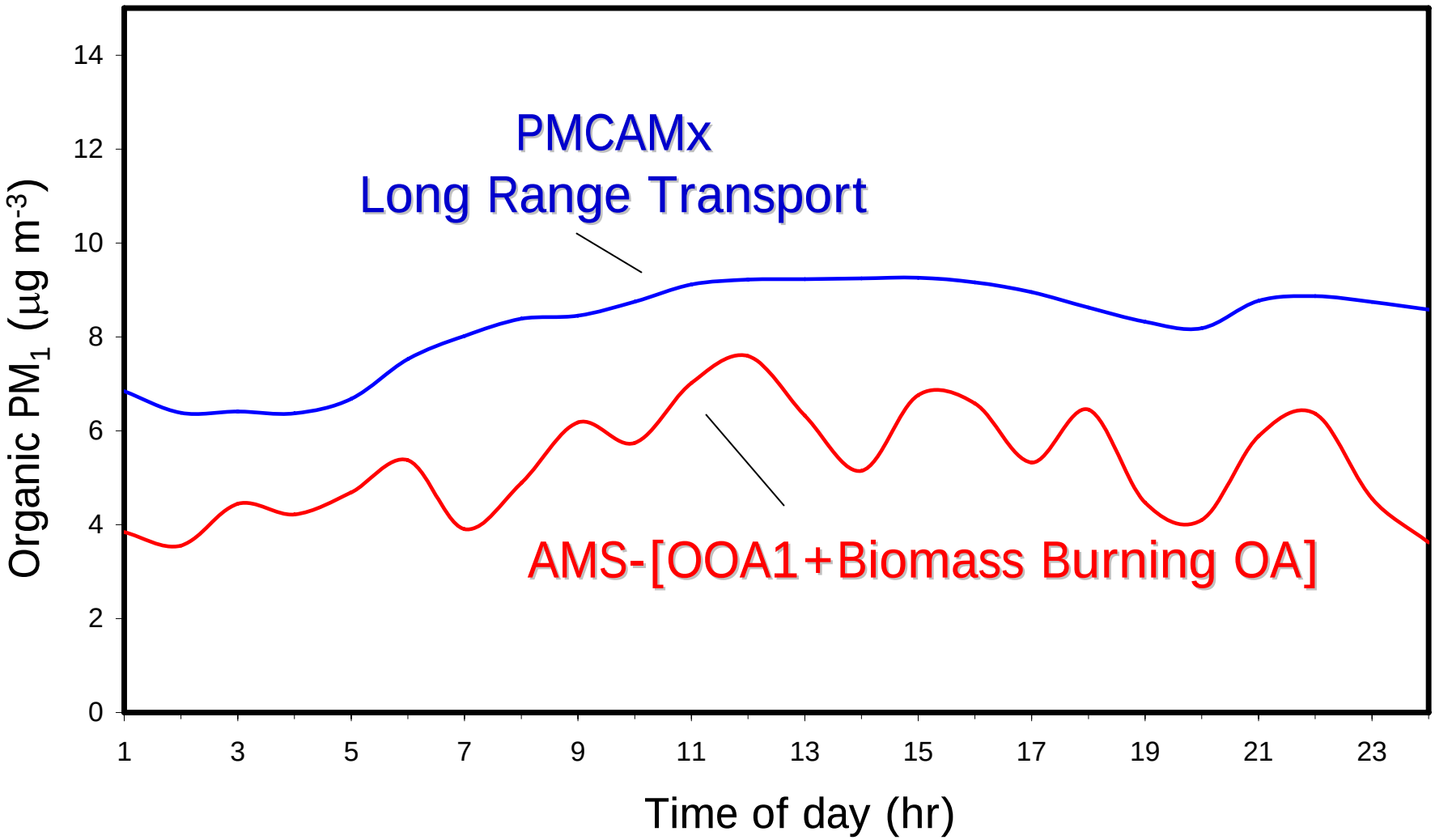
Preliminary AMS Analysis by Ingrid Ulbrich and Jose-Luis Jimenez (U. Colorado)



Comparison with AMS MS Analysis

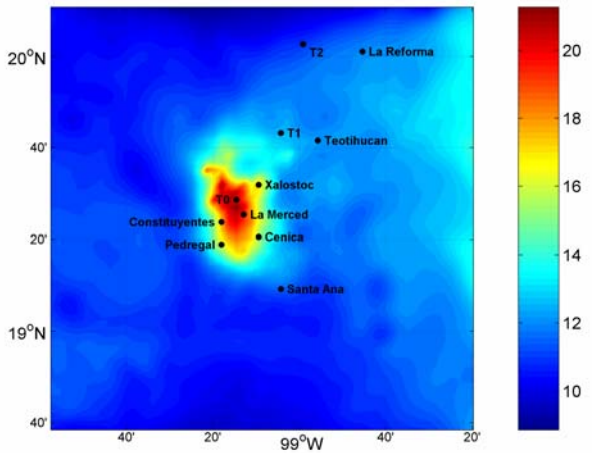


Comparison with AMS MS Analysis

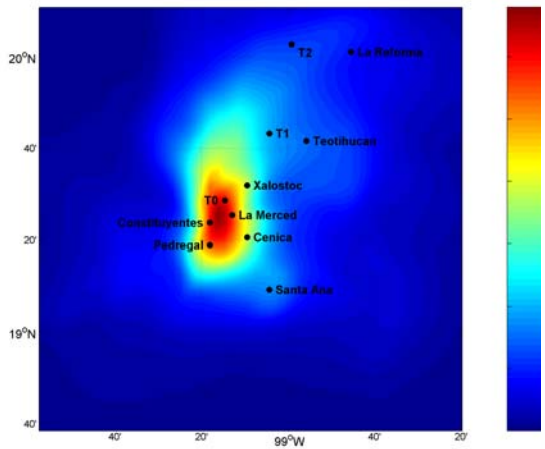


MILAGRO 2006

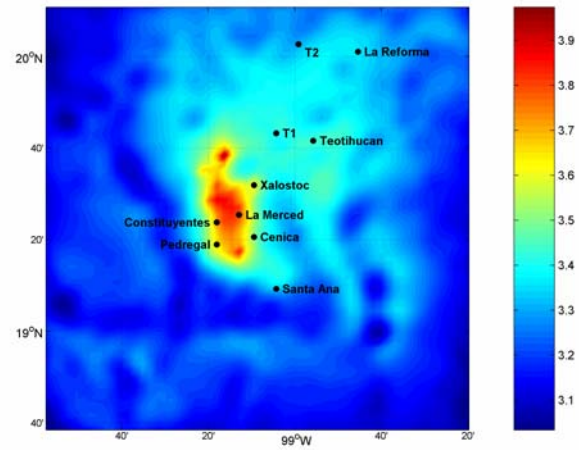
POA



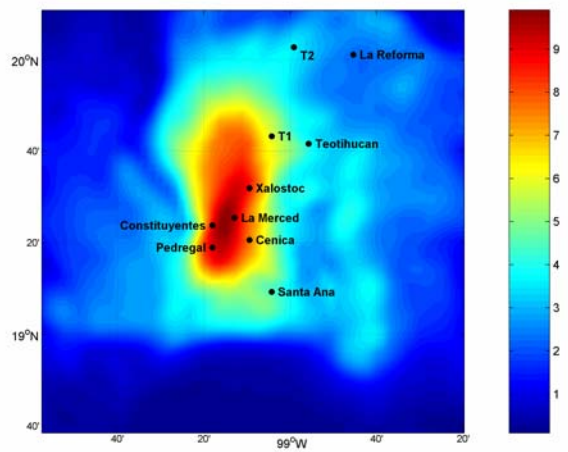
SOA



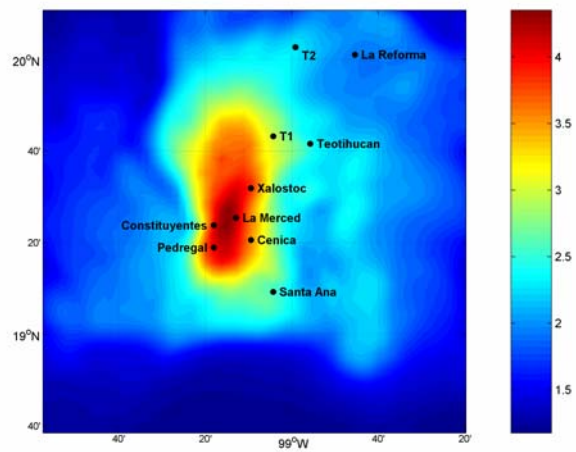
Sulfate



Nitrate



Ammonium

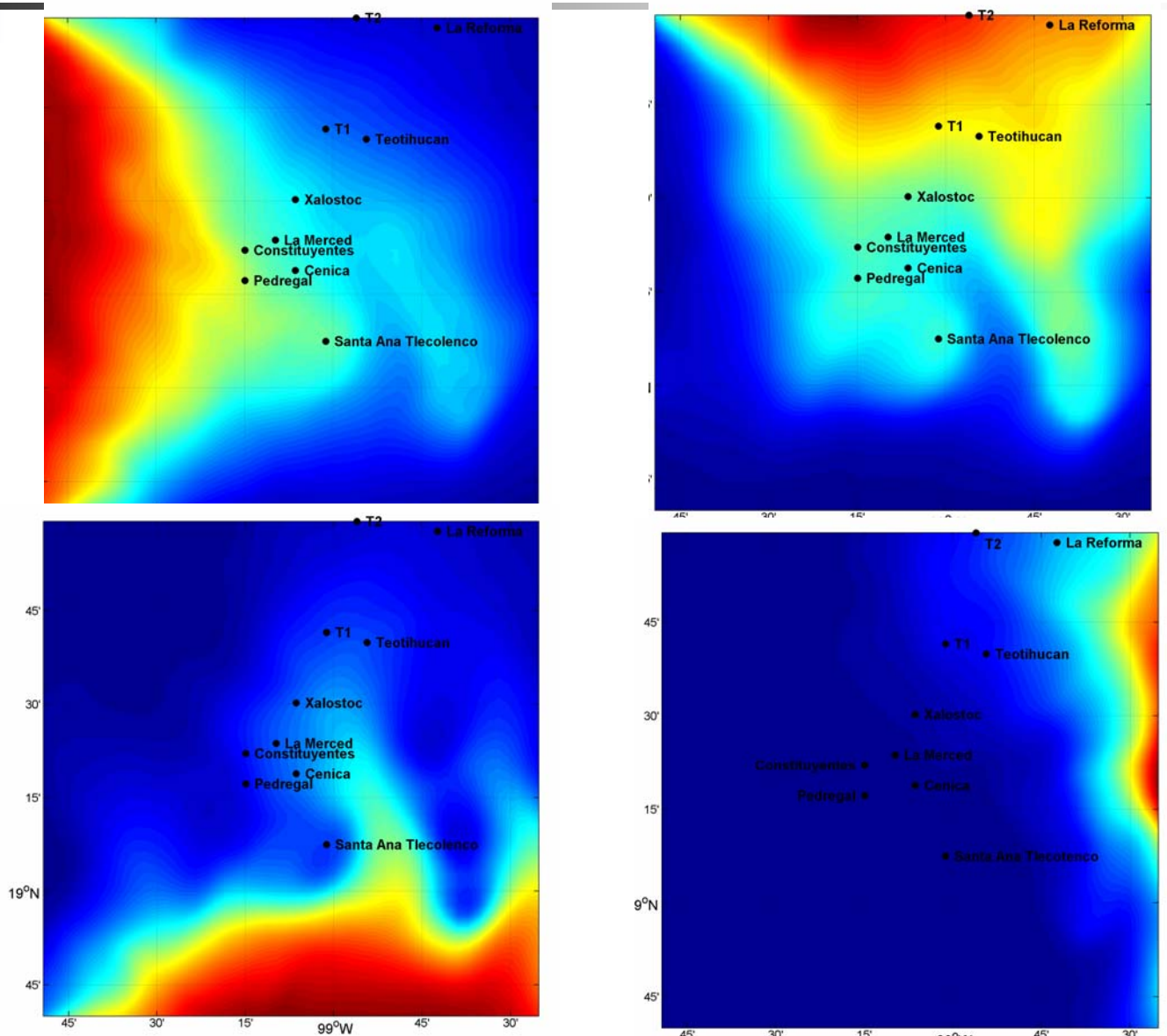


Conclusions

- First results far from perfect but encouraging
- Surprising average contribution of long range transport to OM
- Interesting results from first combination of PMCAMx and AMS analysis
- Issues to work on:
  - SO_2 emissions from Tula
  - Improve dust, NaCl emissions and use ISORROPIA II with hybrid aerosol dynamics
  - Re-examine early morning emissions and meteorology
  - Use new OA-SOA module with semi-volatile primary organics, emission of intermediate volatility organics and aging (Robinson et al., 2007)
  - Use of new smog chamber results for anthropogenic SOA (the yields may be underpredicted)
- Comparison of PMCAMx with the rest of MCMA-2003 results and MILAGRO results
- Use of the model (in collaboration with measurement groups) to test hypotheses and interpret measurements

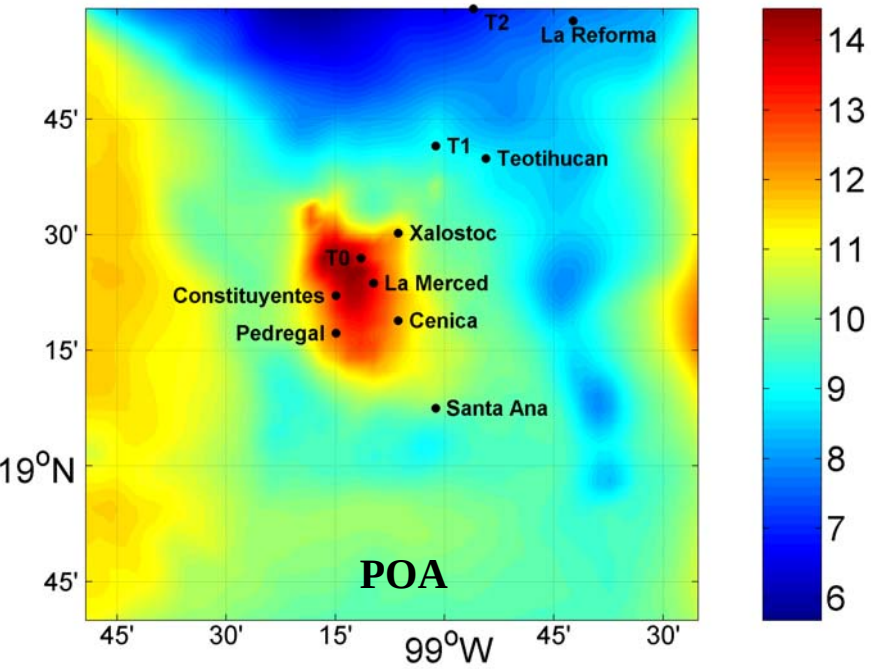
Acknowledgement: Funding provided by MCE2 and NSF

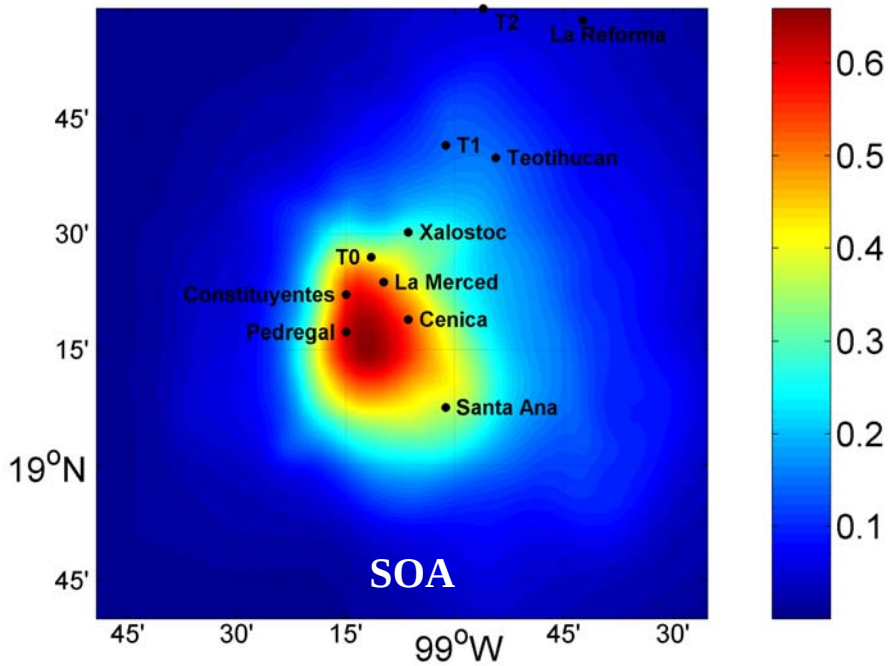
Role of Boundary Conditions



April
12-17
2003

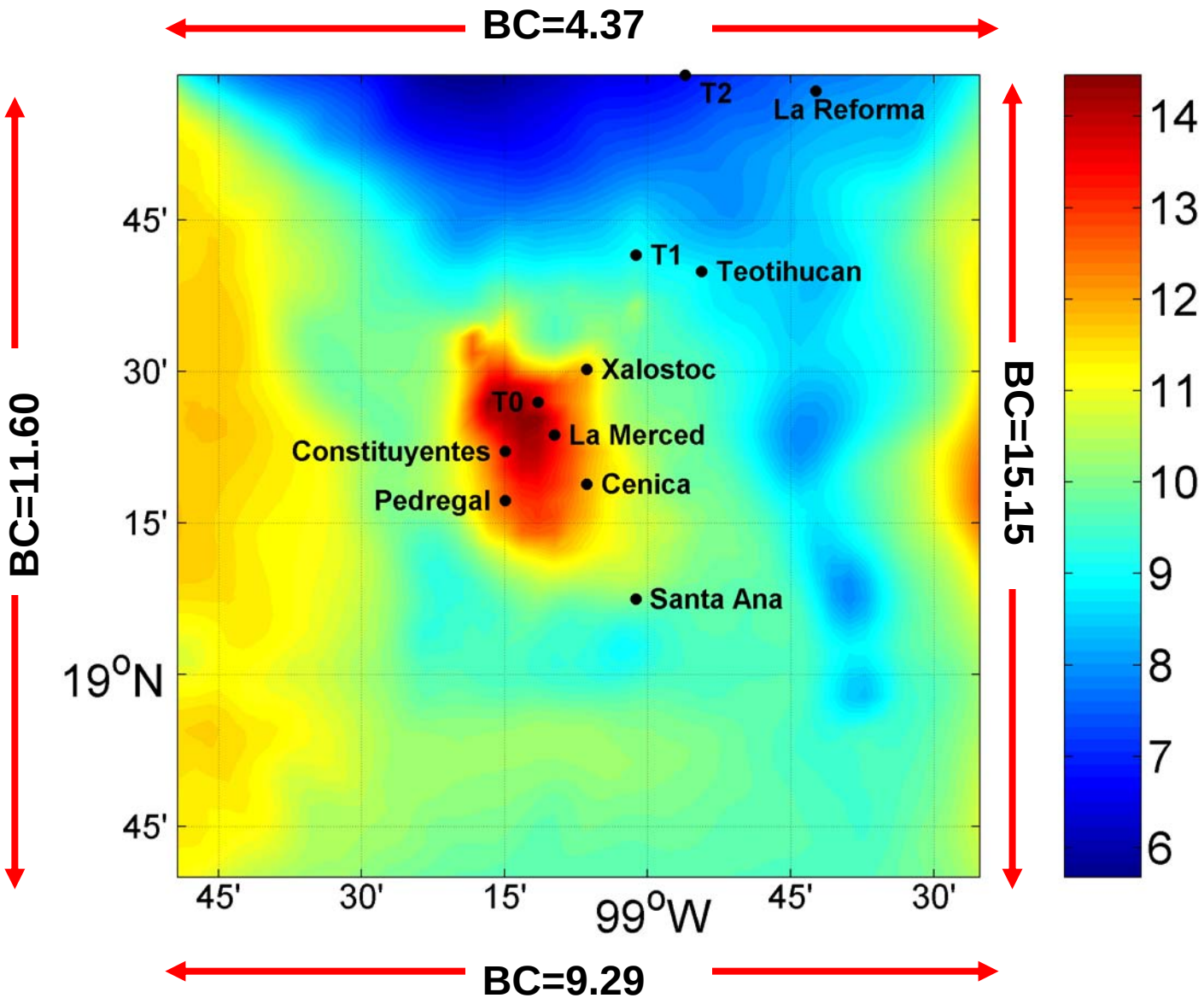
Spatial Distribution of OM



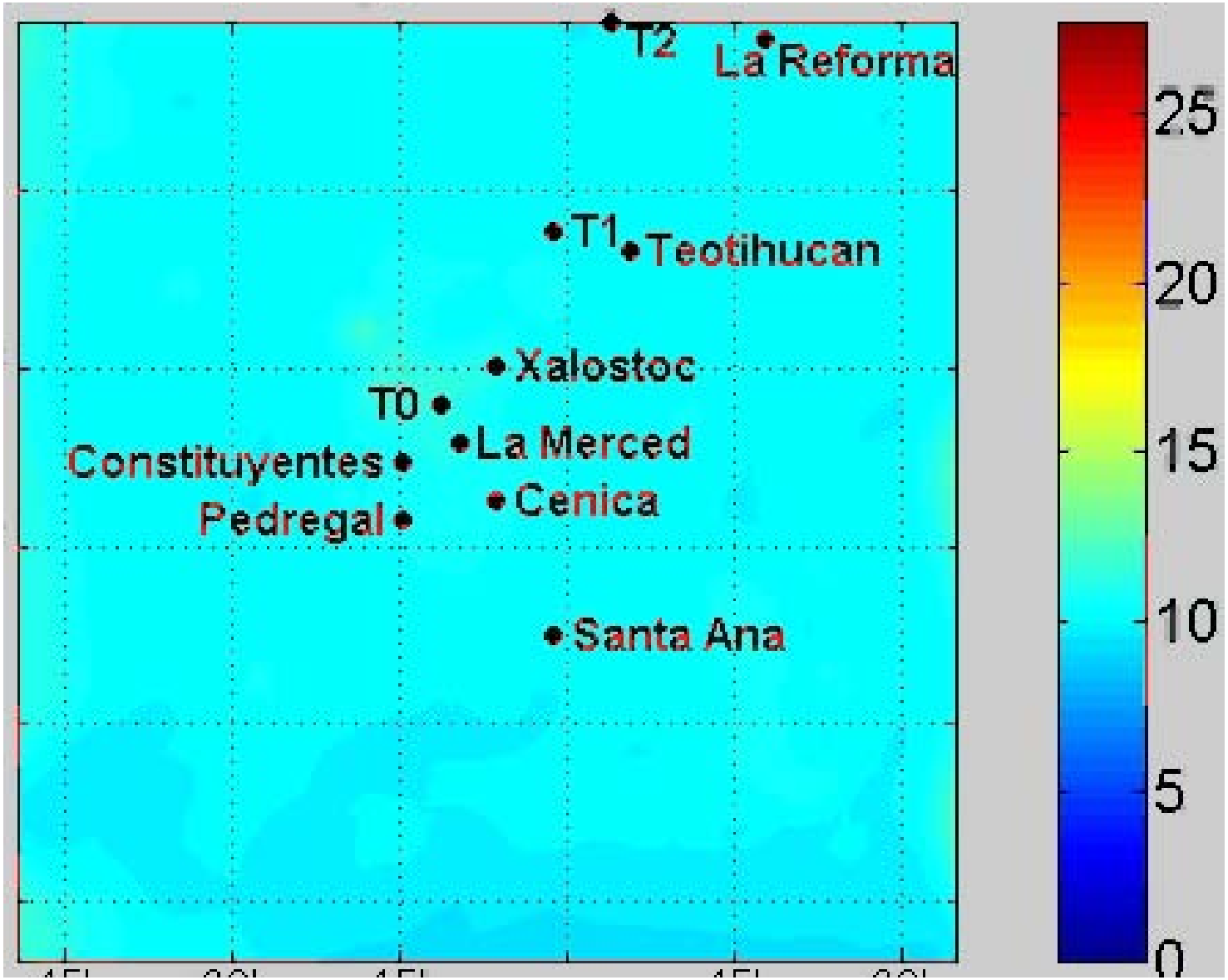


POC_v54

(μg/m^3)


BC=4.37
BC=11.60
BC=15.15
BC=9.29
T2
La Reforma
T1
Teotihucan
Xalostoc
T0
La Merced
Constituyentes
Cenica
Pedregal
Santa Ana
45'
30'
15'
19°N
45'
45'
30'
15'
99°W
45'
30'
14
13
12
11
10
9
8
7
6

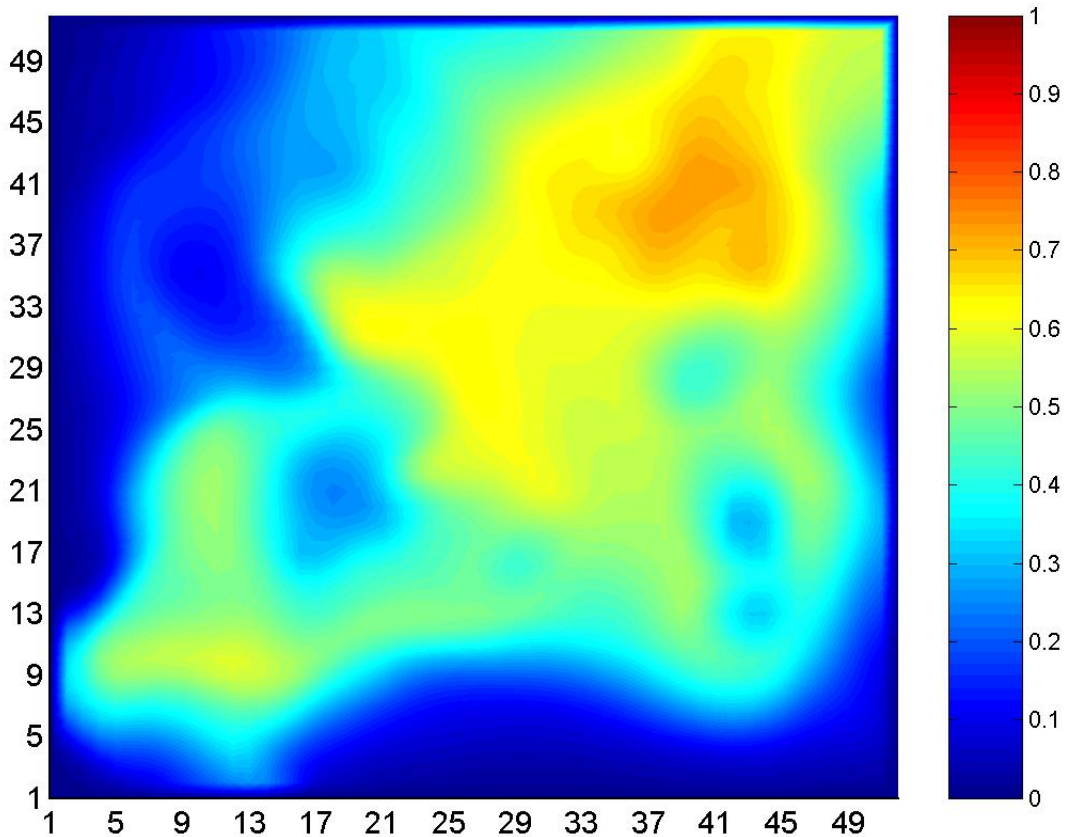
POA Predictions



POA INITIAL CONDITION EFFECT

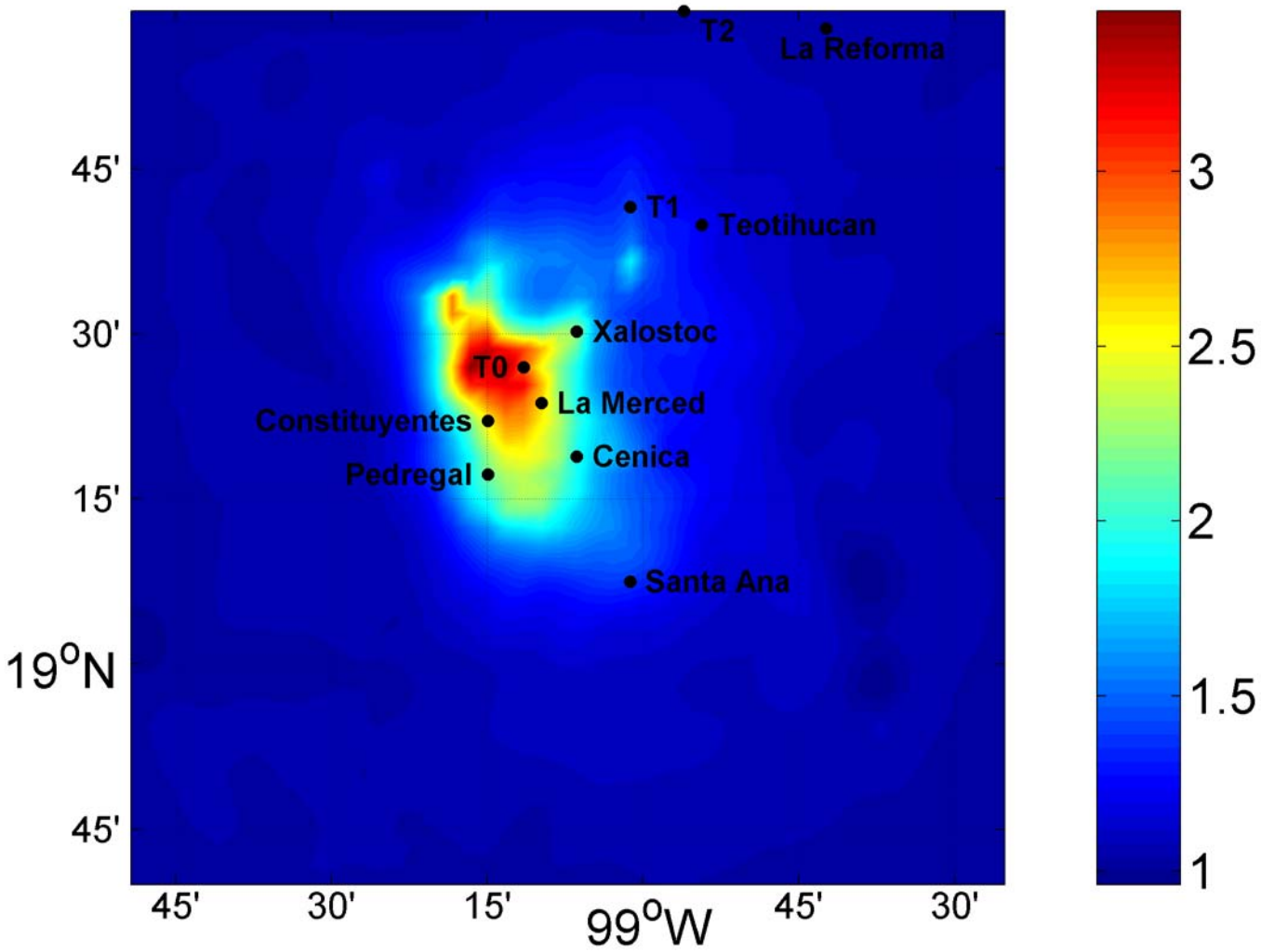
(μg/m^3)

Only initial conditions (=10 μg/m3)

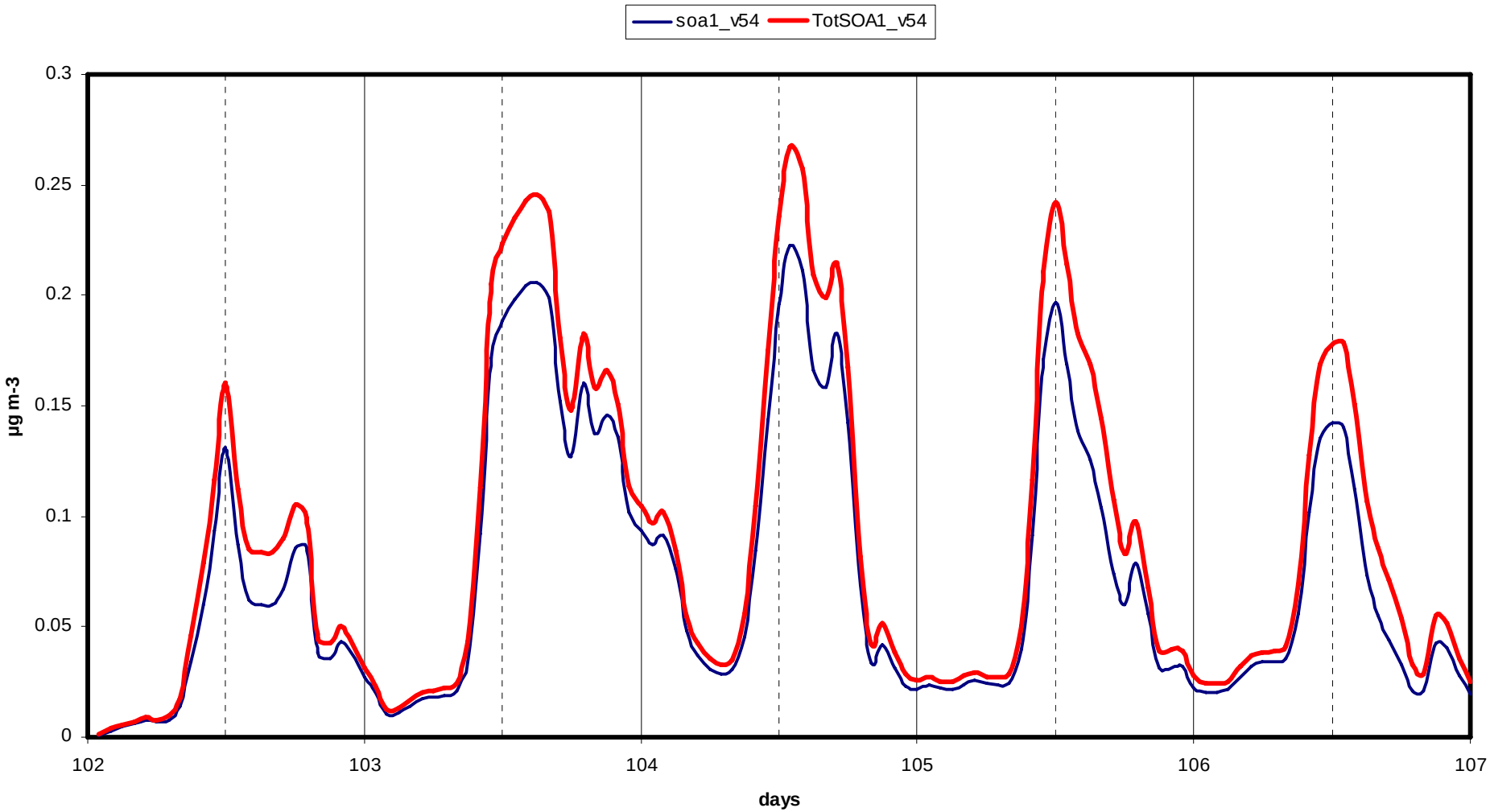


Elemental Carbon

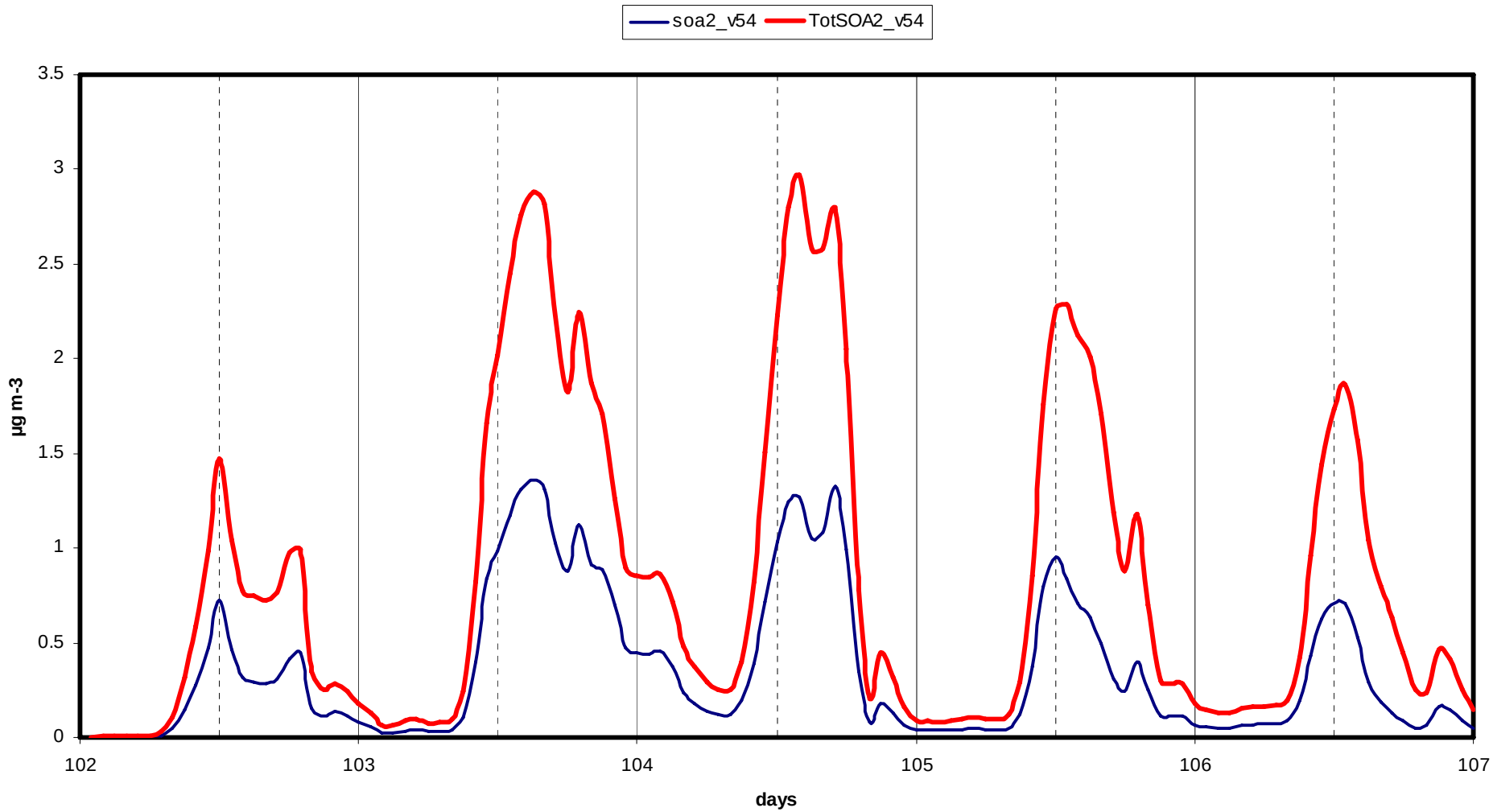
($\mu g/m^3$)



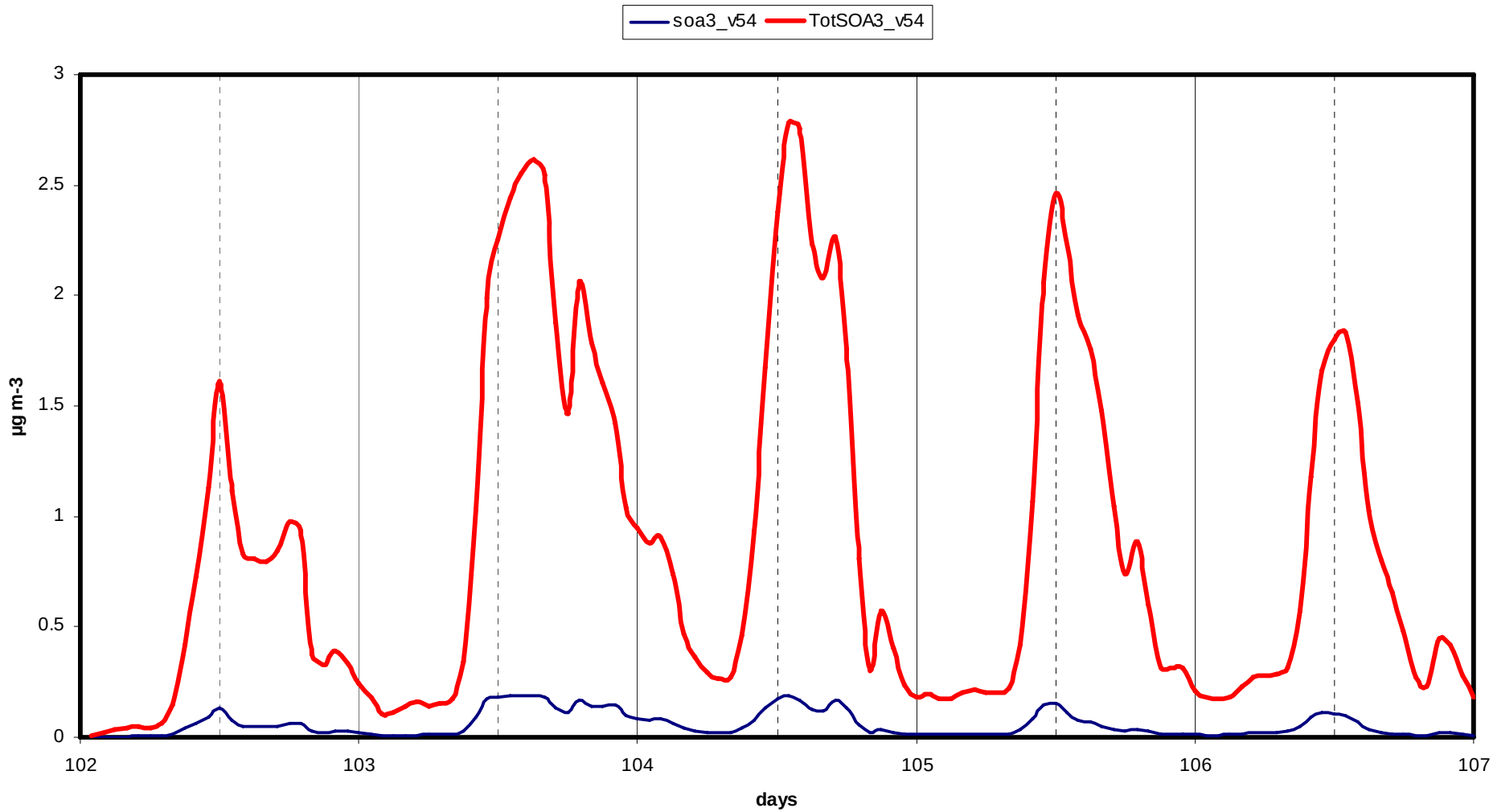
SOA1 vs TotSOA1



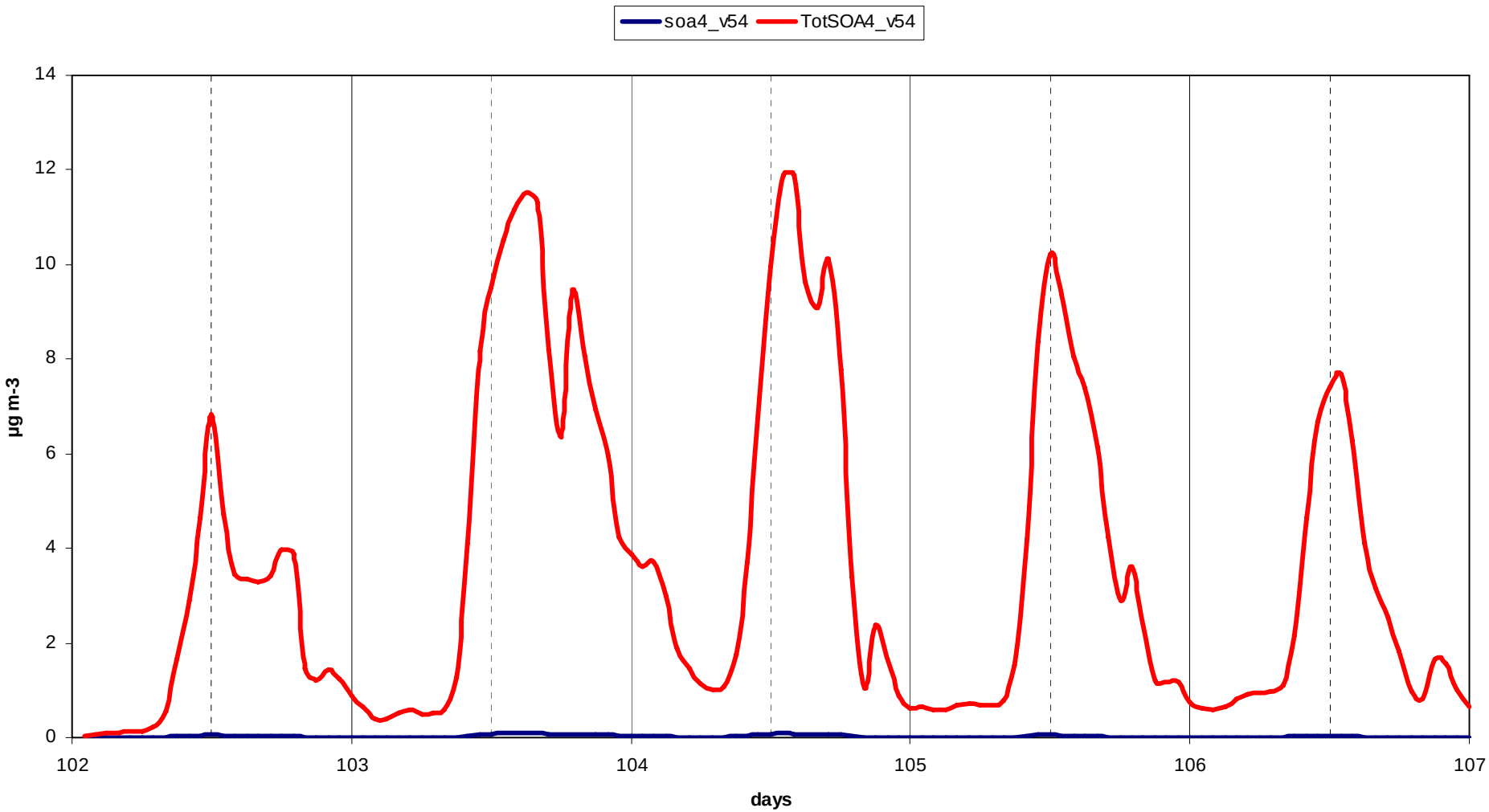
SOA2 vs TotSOA2



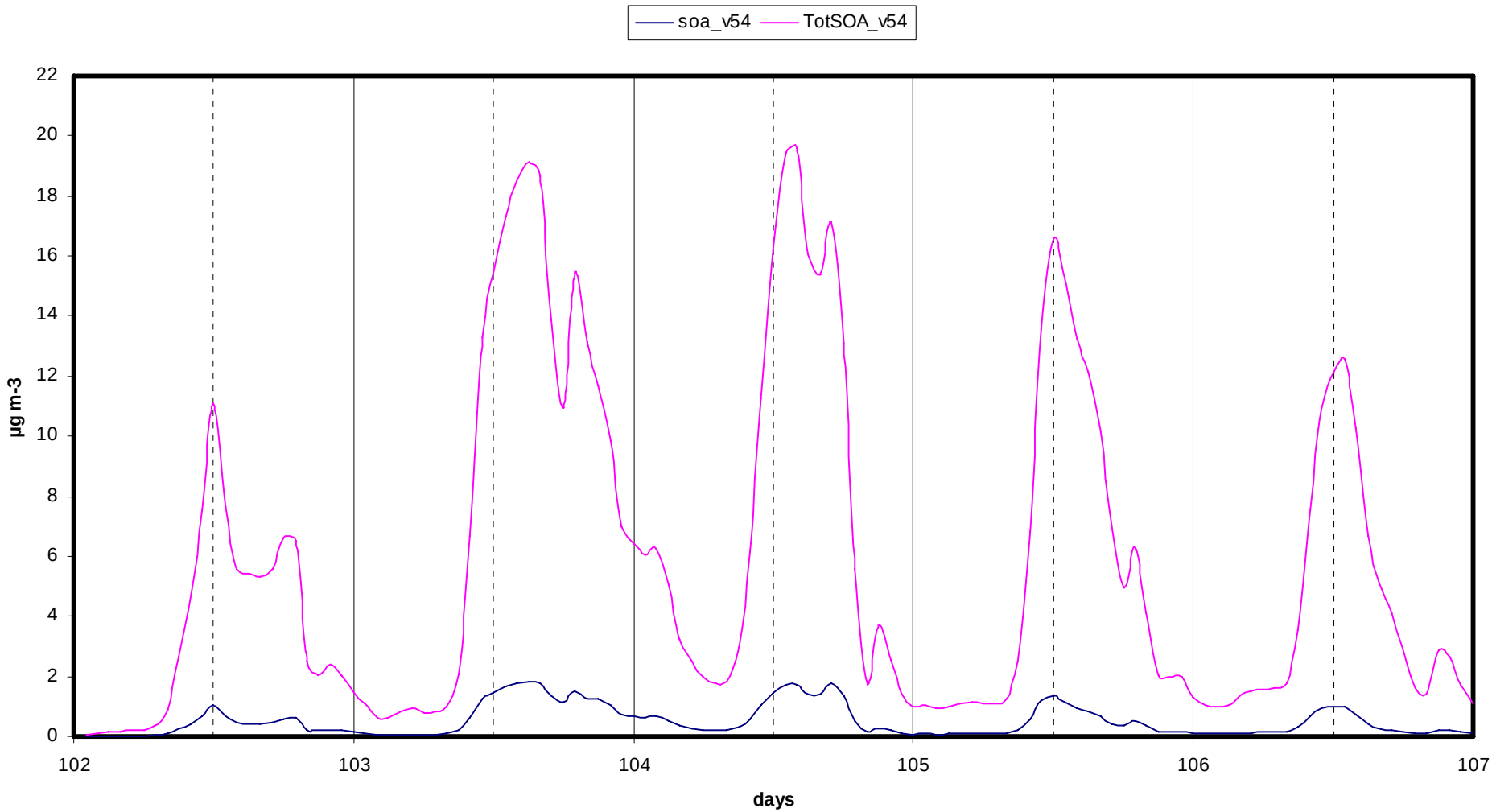
SOA3 vs TotSOA3



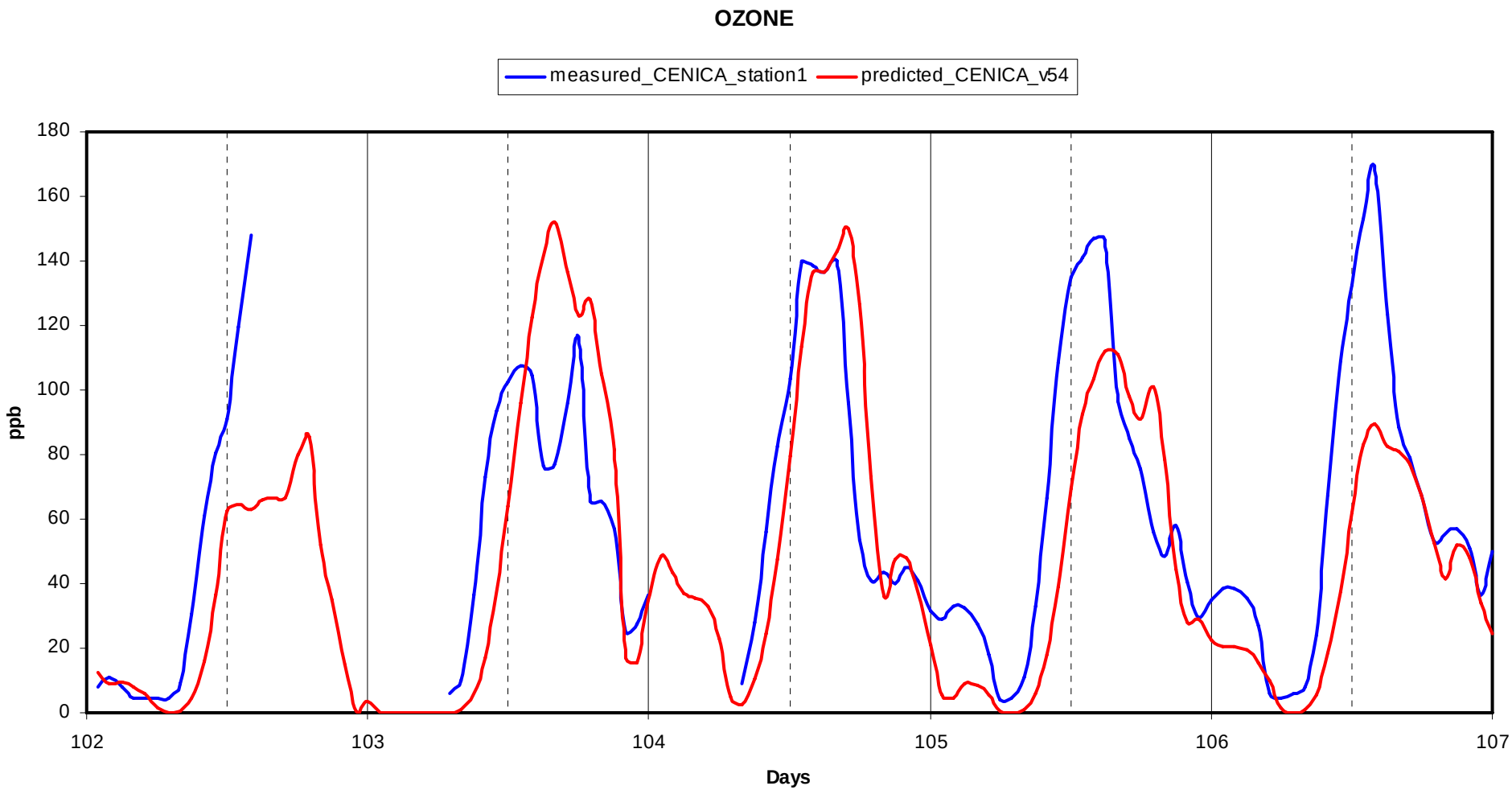
SOA4 vs TotSOA4



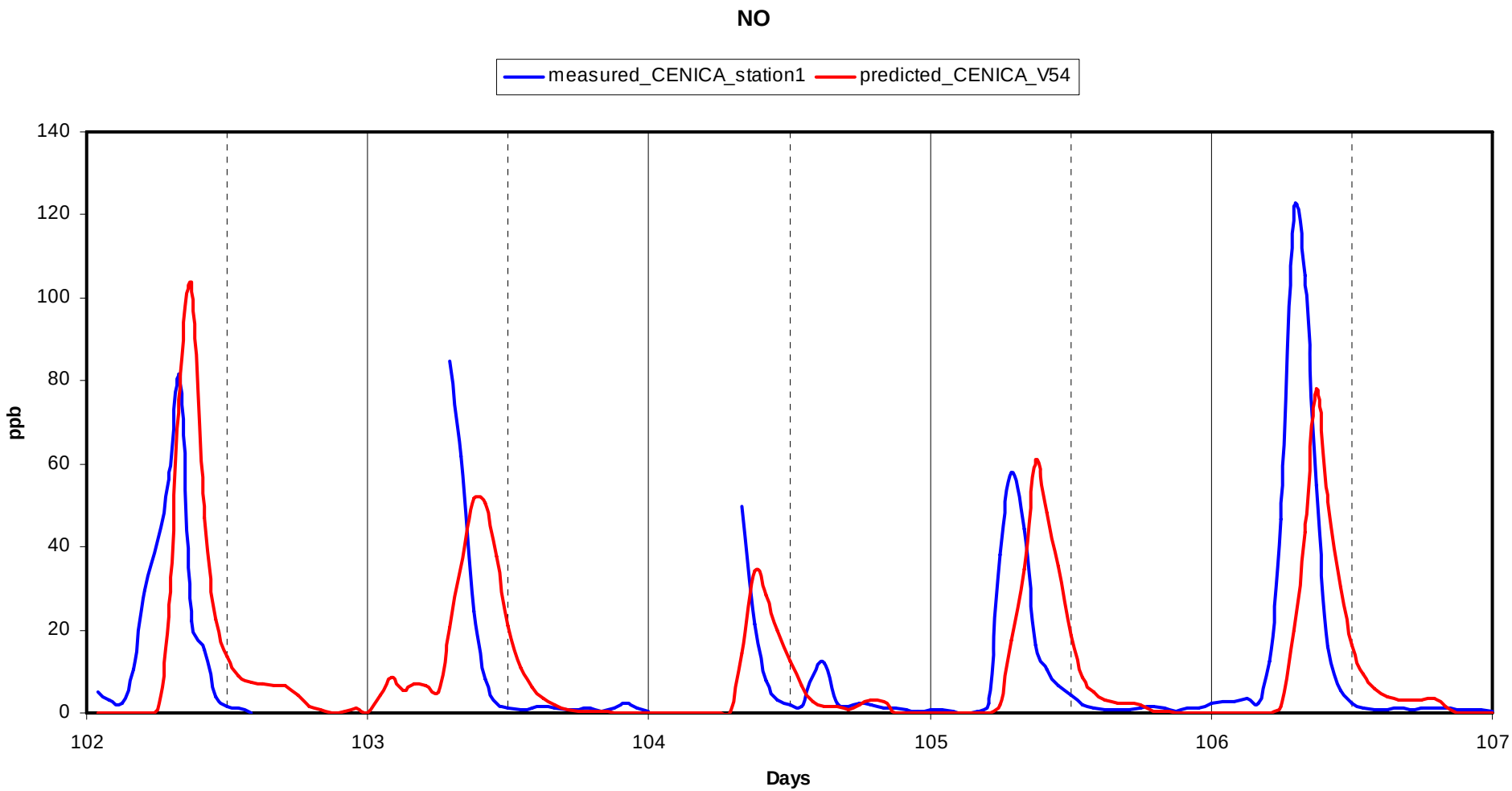
SOA vs TotSOA



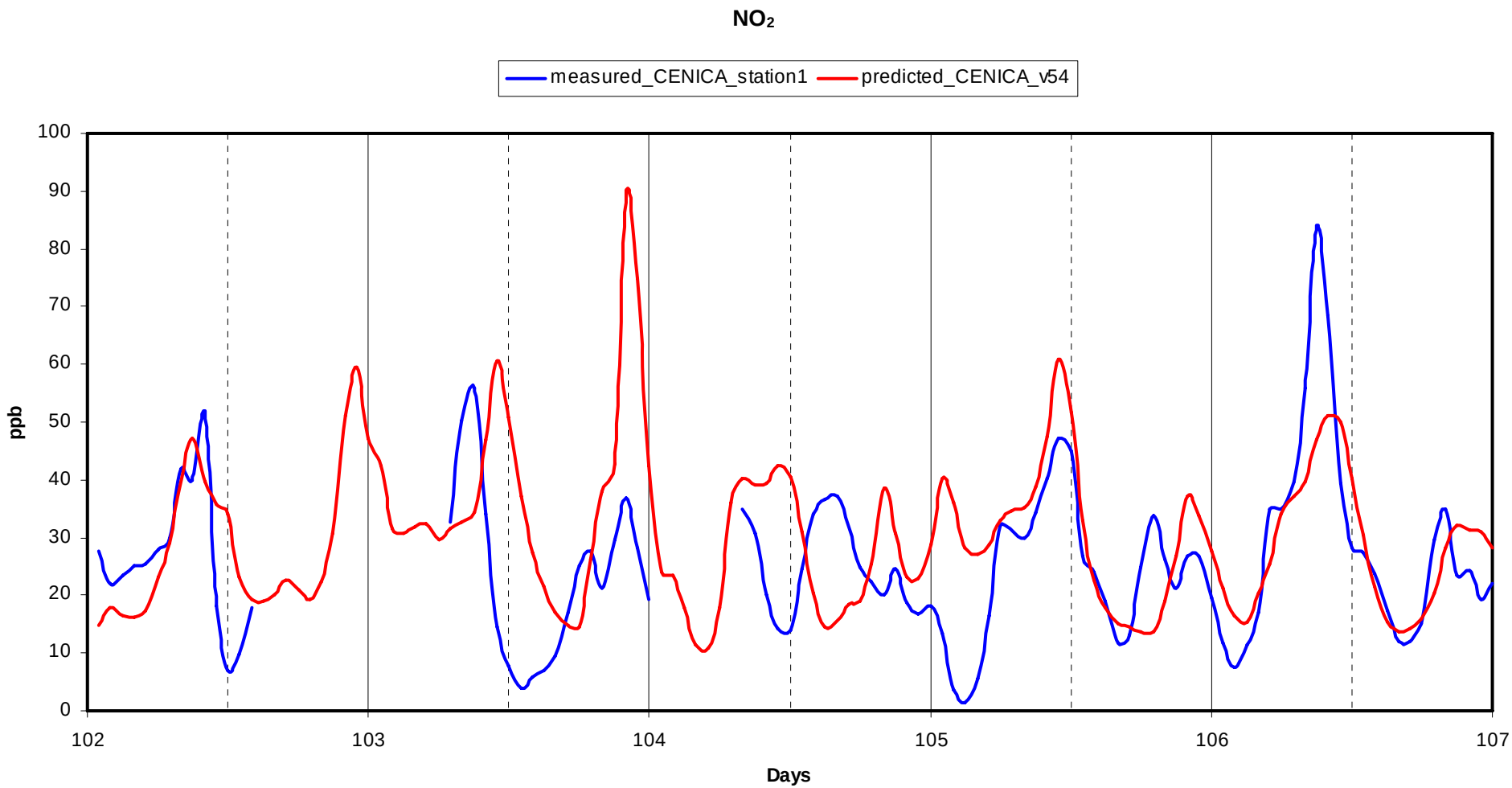
O_3


OZONE
measured_CENICA_station1
predicted_CENICA_v54
ppb
180
160
140
120
100
80
60
40
20
0
102
103
104
105
106
107
Days

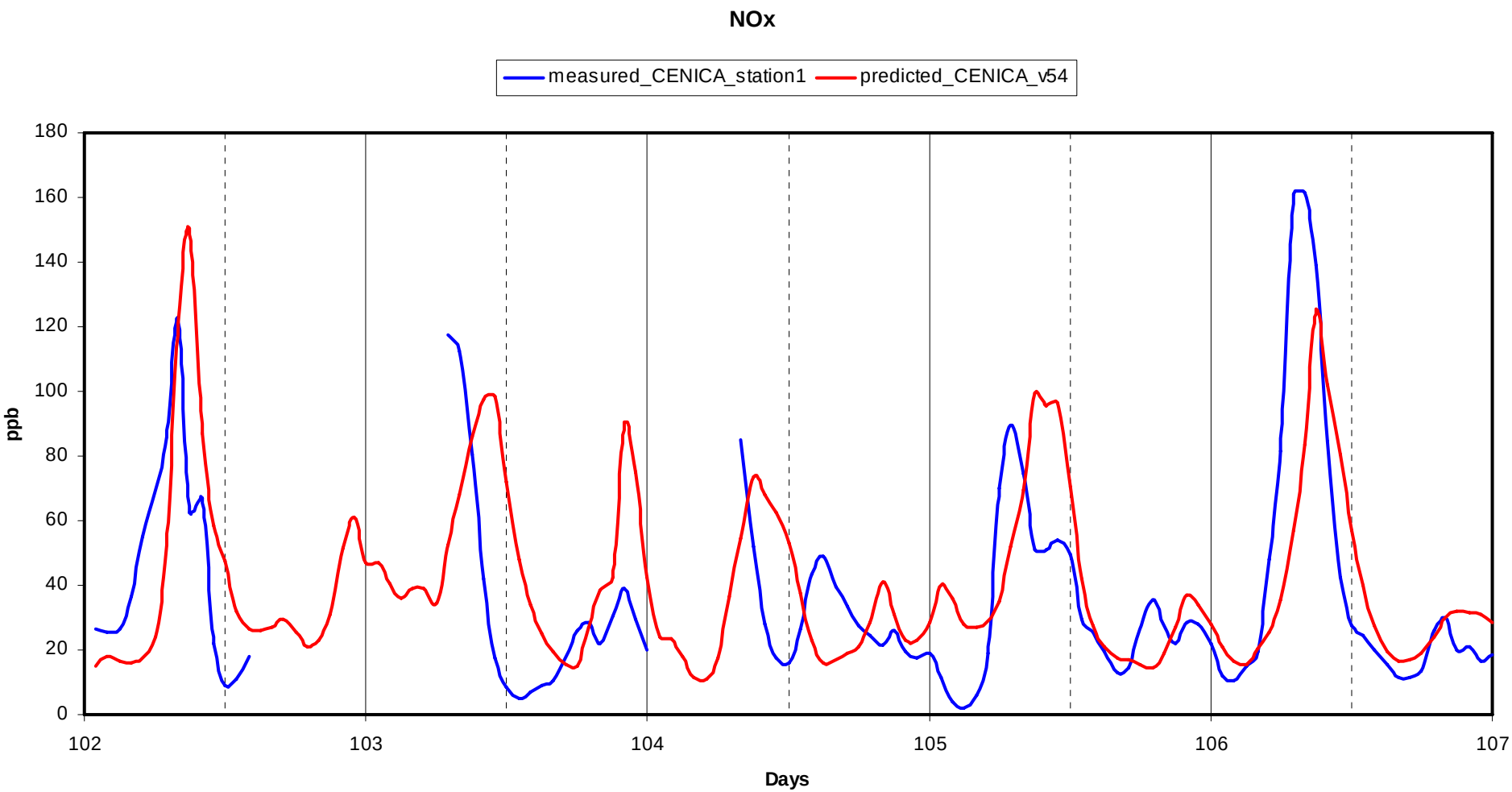
NO


NO
measured_CENICA_station1
predicted_CENICA_V54
140
120
100
80
60
40
20
0
ppb
102
103
104
105
106
107
Days

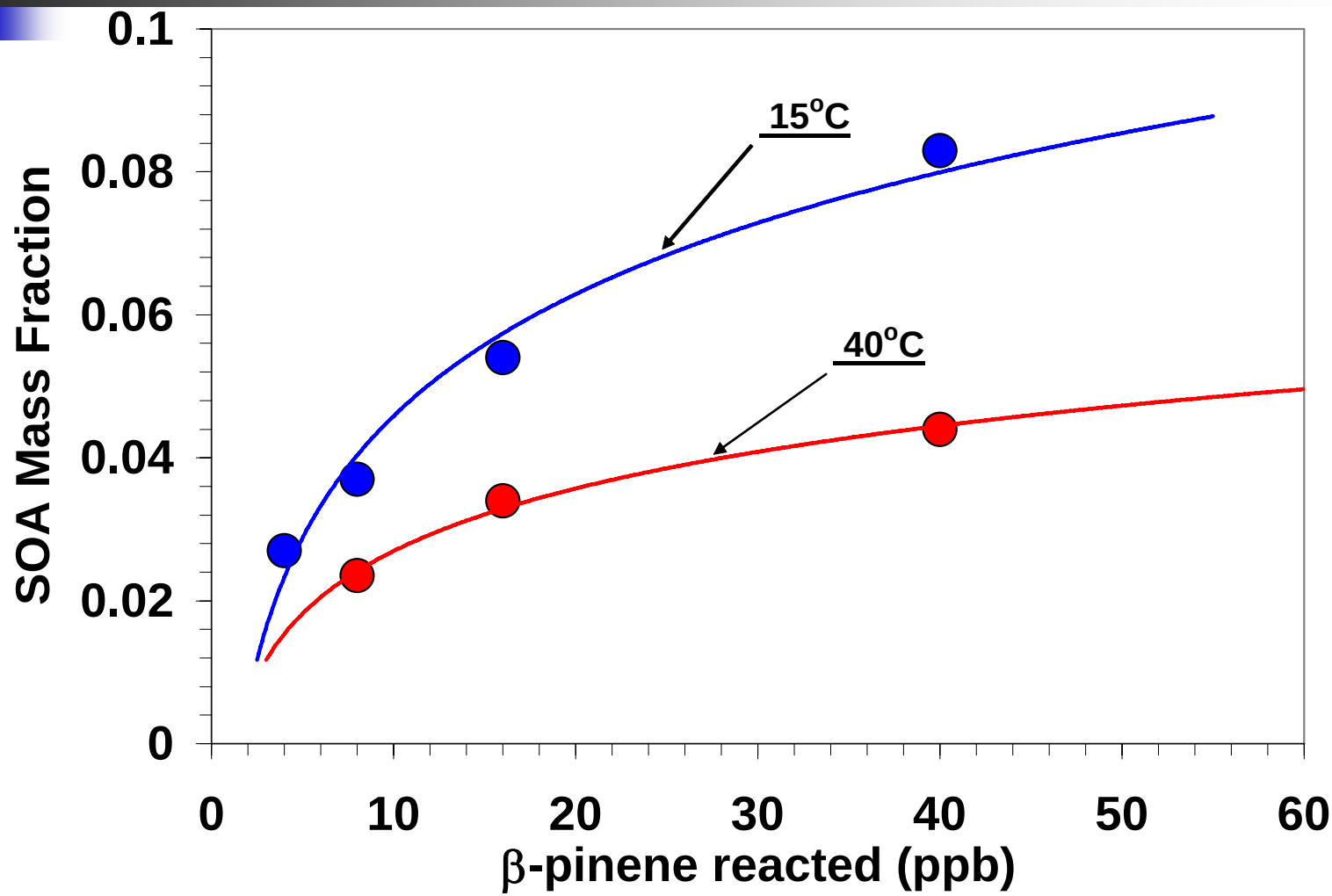
NO2


NO2
measured_CENICA_station1
predicted_CENICA_v54
ppb
100
90
80
70
60
50
40
30
20
10
0
102
103
104
105
106
107
Days

NOx

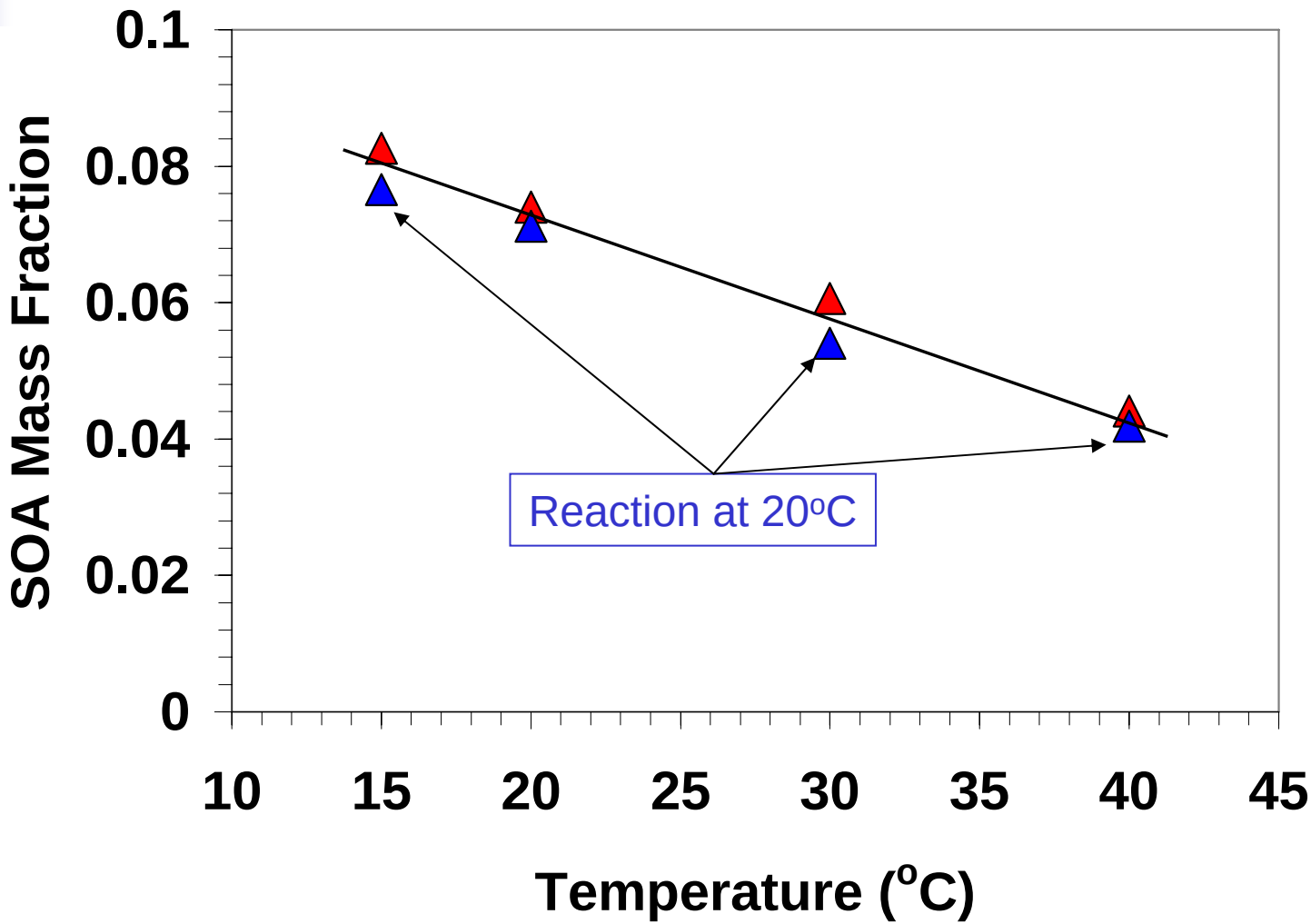

NOx
measured_CENICA_station1
predicted_CENICA_v54
180
160
140
120
100
80
60
40
20
0
ppb
102
103
104
105
106
107
Days

SOA from β-pinene Ozonolysis



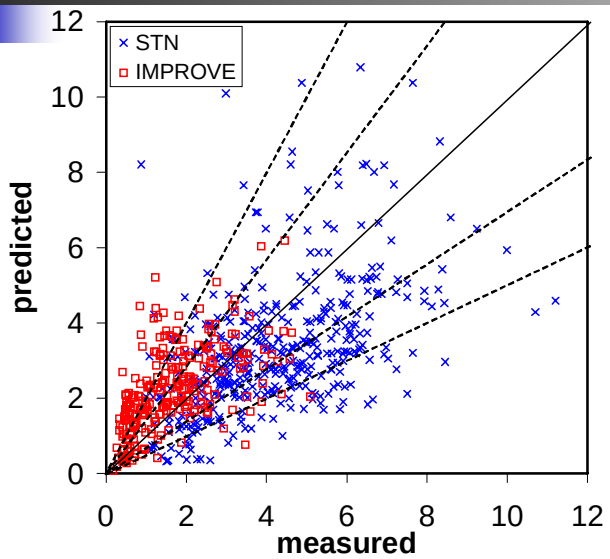
β-pinene SOA Formation
Partitioning vs Gas-Phase Chemistry

β-pinene = 40 ppb; Ozone = 750 ppb

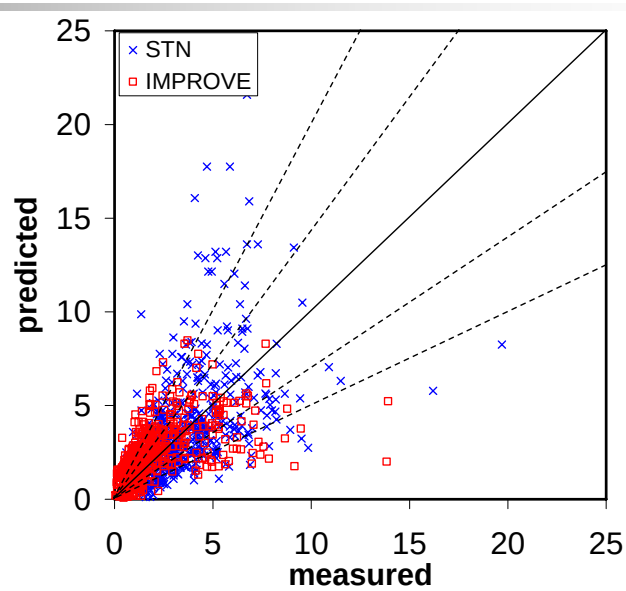


Organic PM: PMCAMx Predictions vs Observations

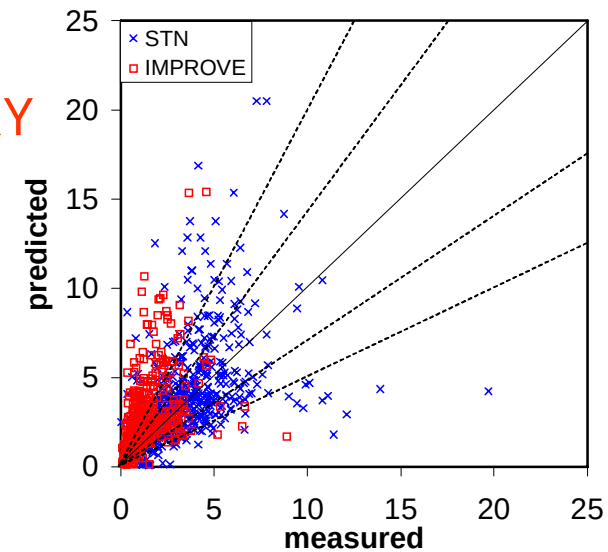
JULY



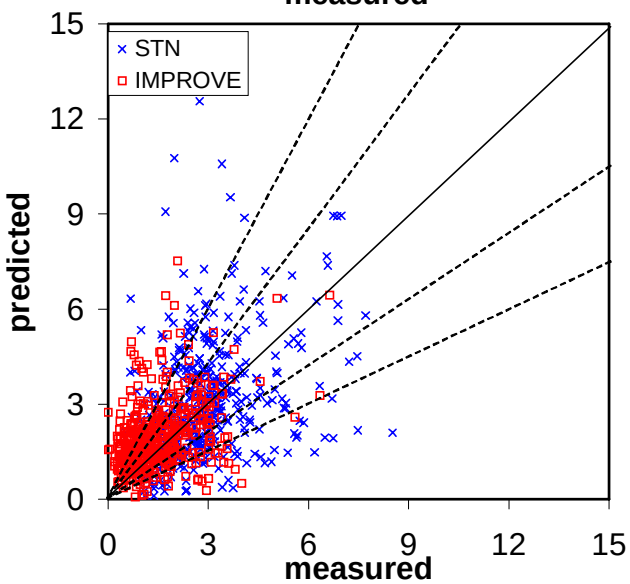
OCTOBER



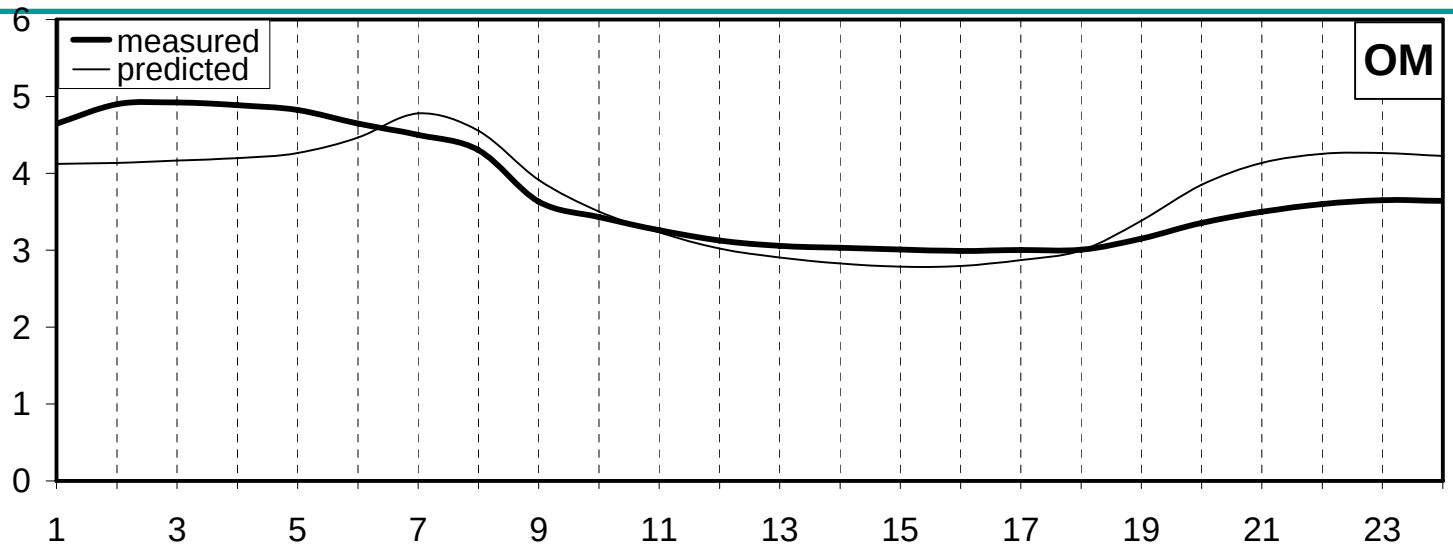
JANUARY



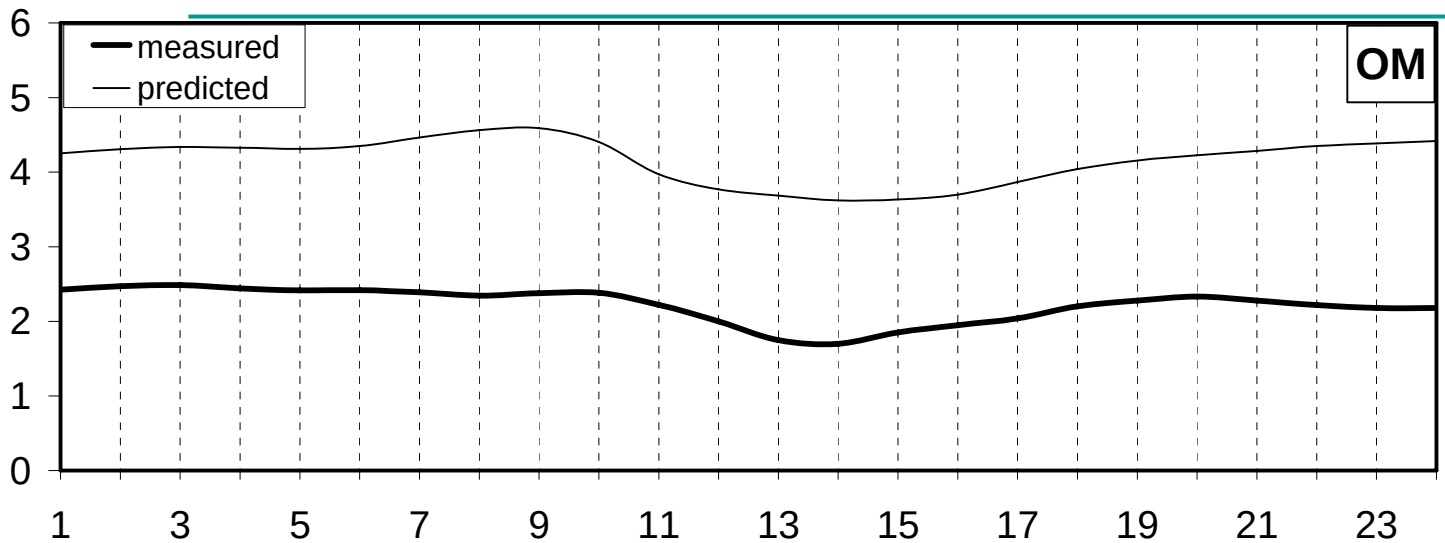
APRIL



Average Diurnal Organic PM Profiles in Pittsburgh

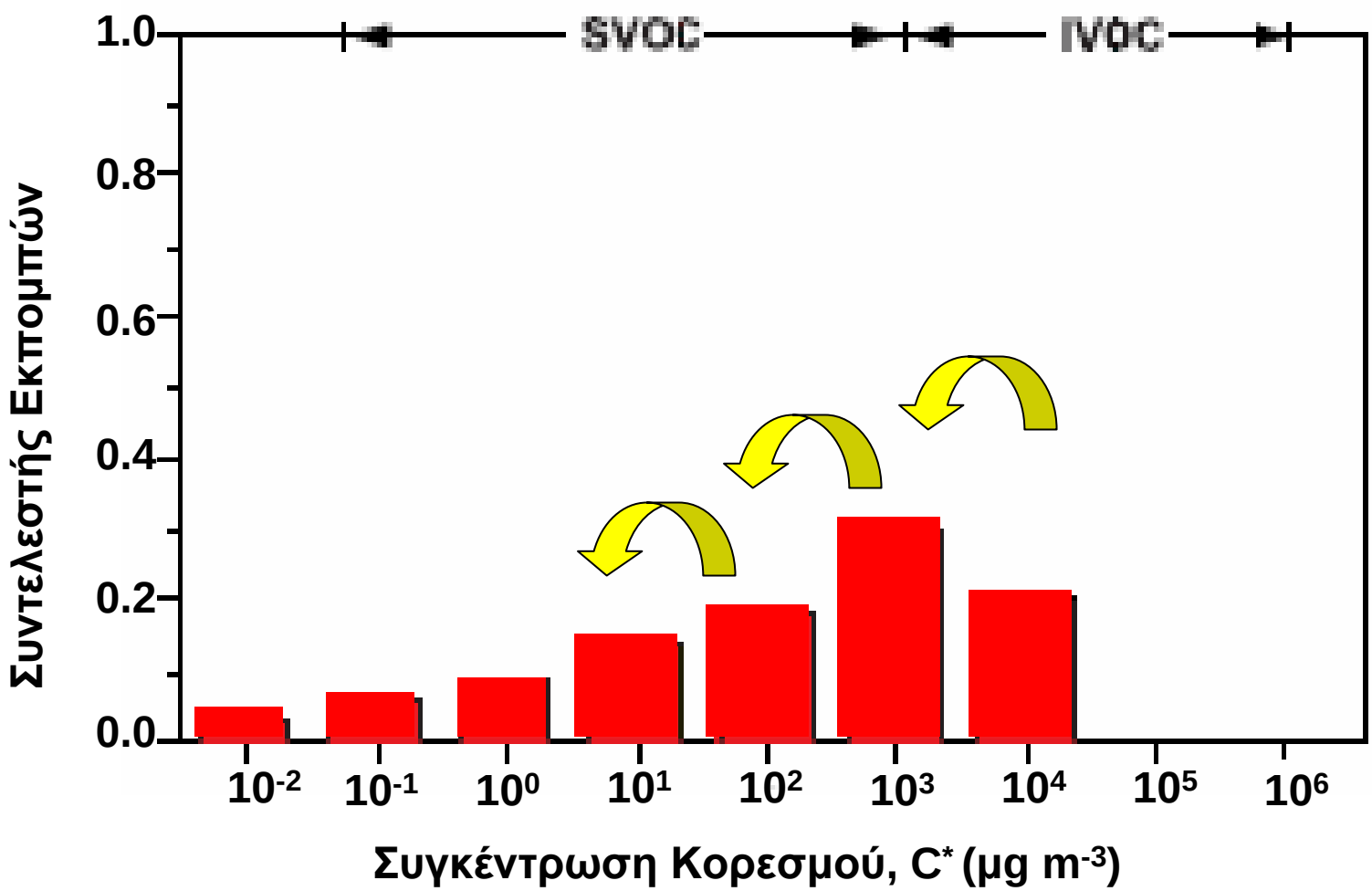


July



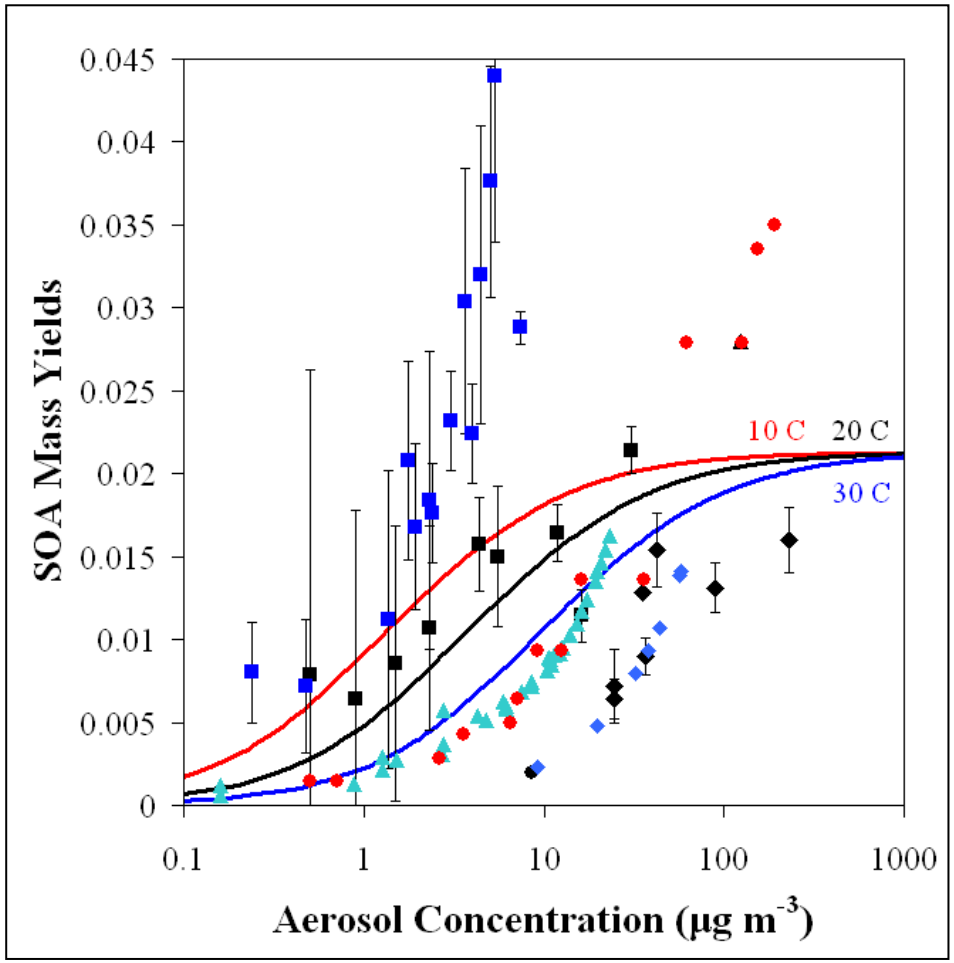
January

Κατανομή Πτητικότητας Εκπομπών Πετρελαιοκιν



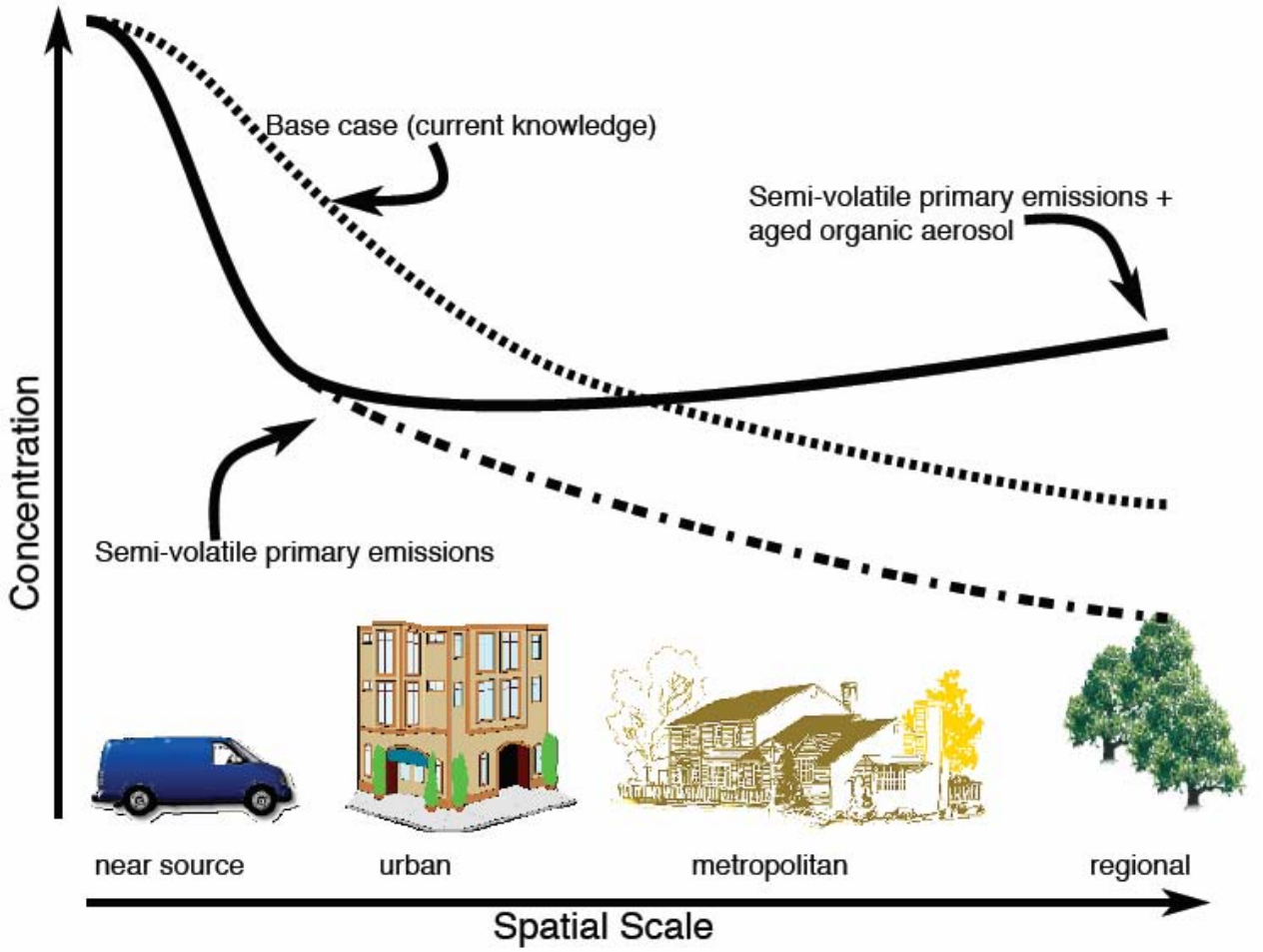
Robinson A.L., N.M. Donahue, M.K. Shrivastava, E.A. Weitkamp, A.M. Sage, A.P. Grieshop, T.E. Lane, S.N. Pandis and J.R. Pierce (2007), *Science., in press.*

Isoprene SOA Yields Used



Summary: Conceptual model for POA

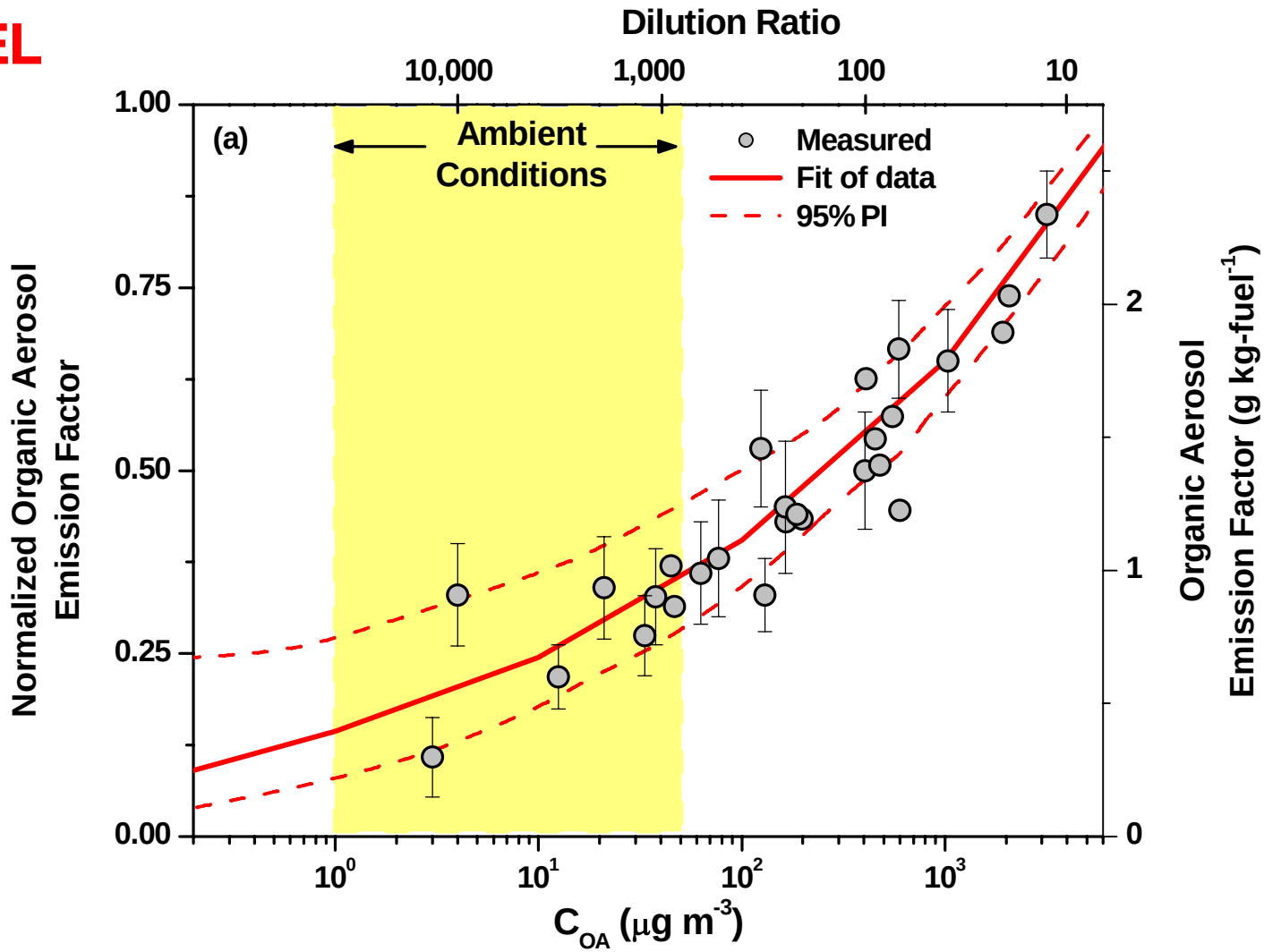
Primary Organic Aerosols are Semi-Volatile



Carnegie Mellon

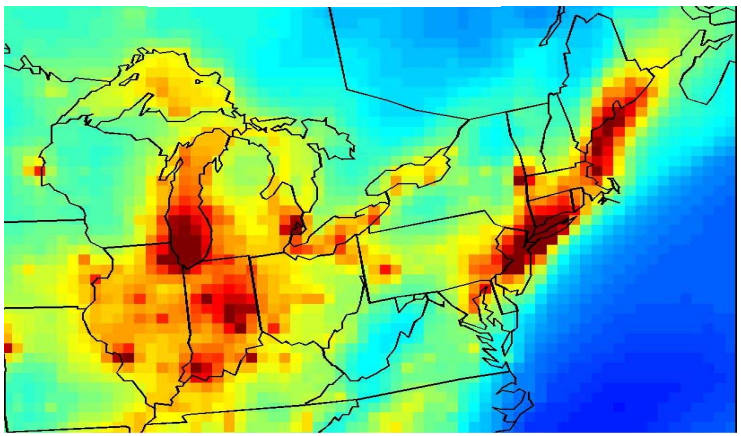
Organic aerosol emissions as a function of dilution

DIESEL

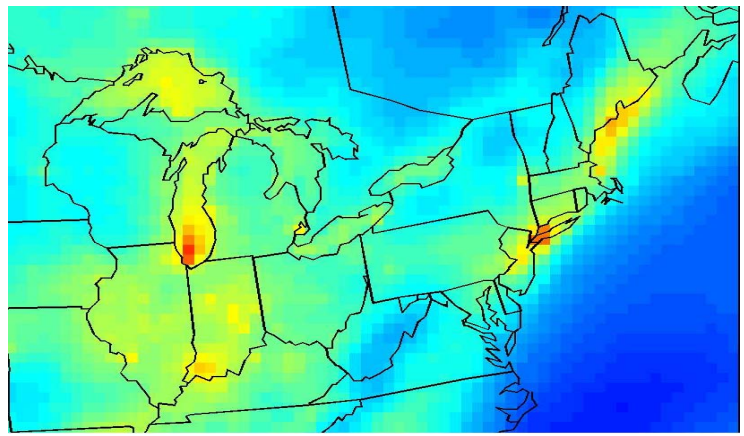


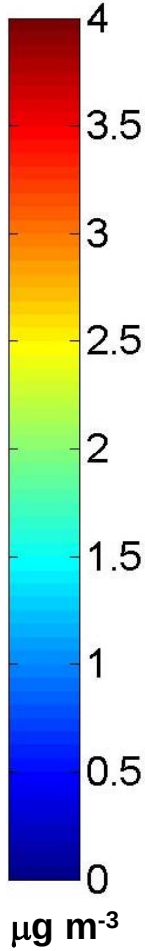
Summertime Organic Aerosol with Aging

Non-volatile

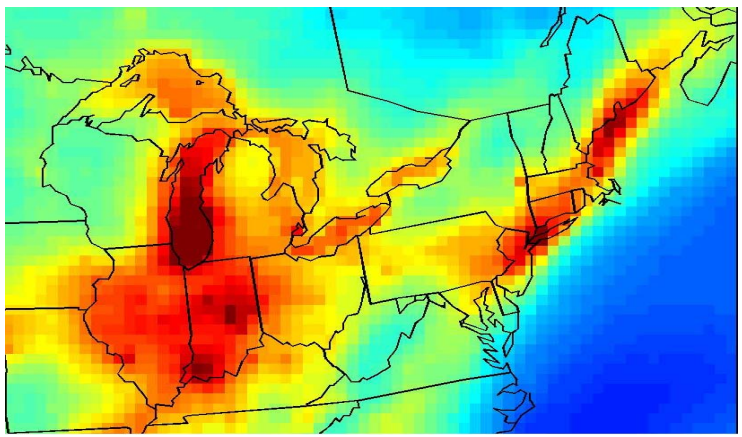


Semi-Volatile





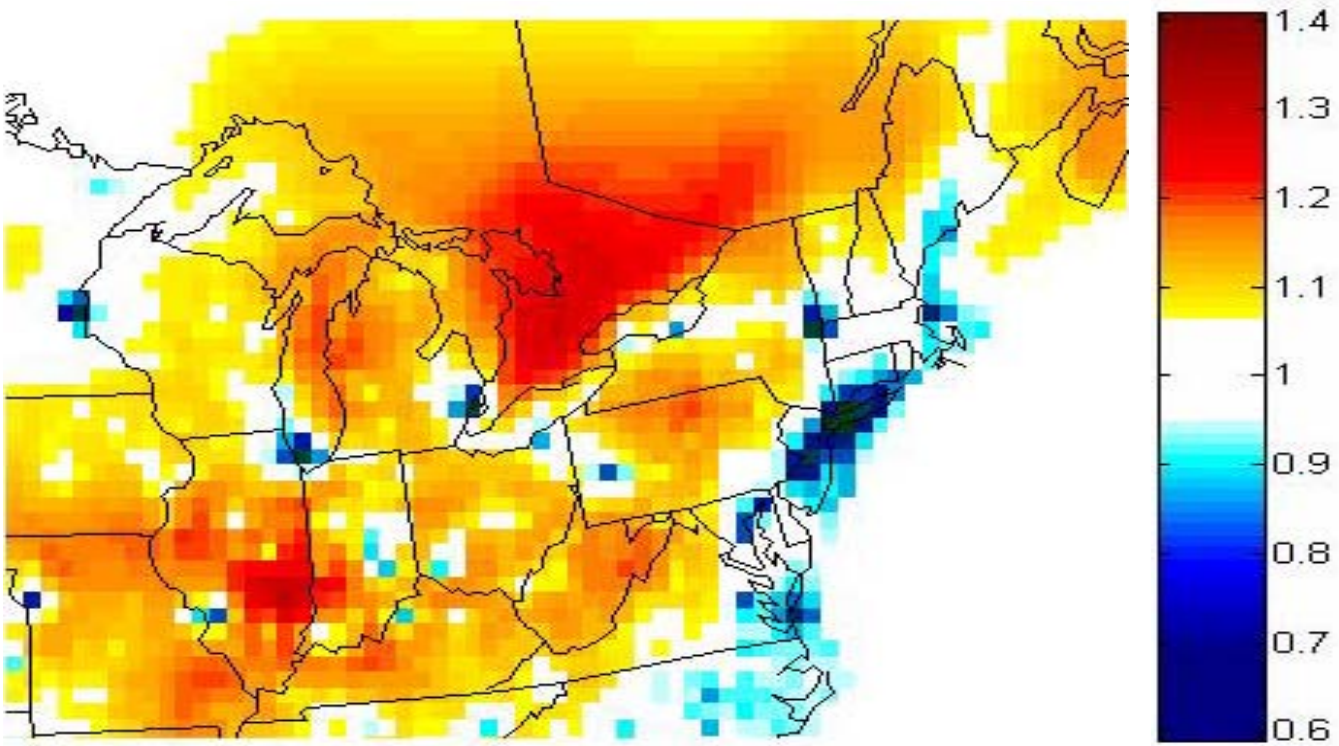
Semi-Volatile + Aging



Average over last 8 days of simulation

Carnegie Mellon

Ratio of Revised (Semi-volatile +Aging) to Base Case (Non-volatile) Model

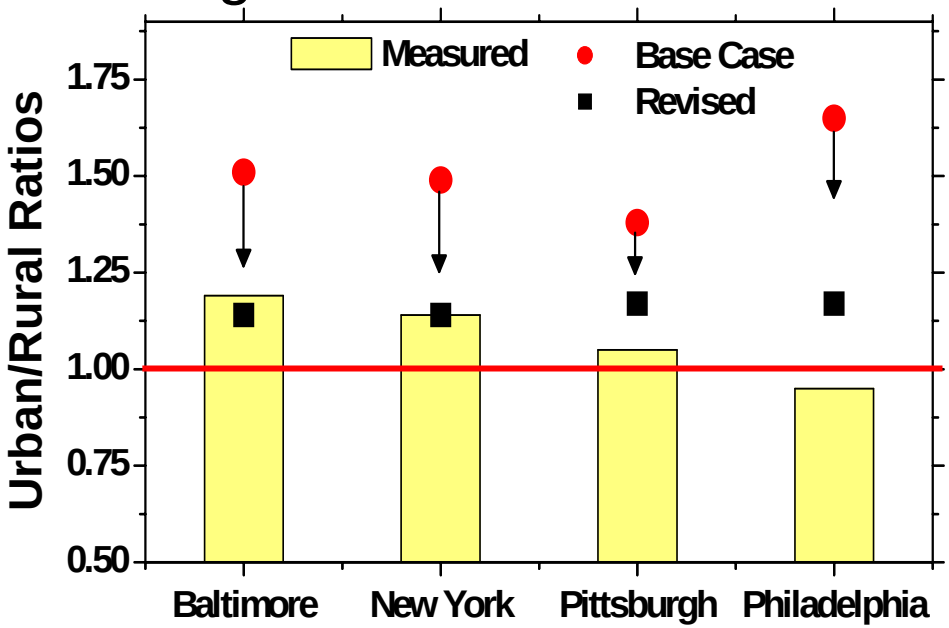


•Revised model decreases OA in urban areas and increases it in rural locations

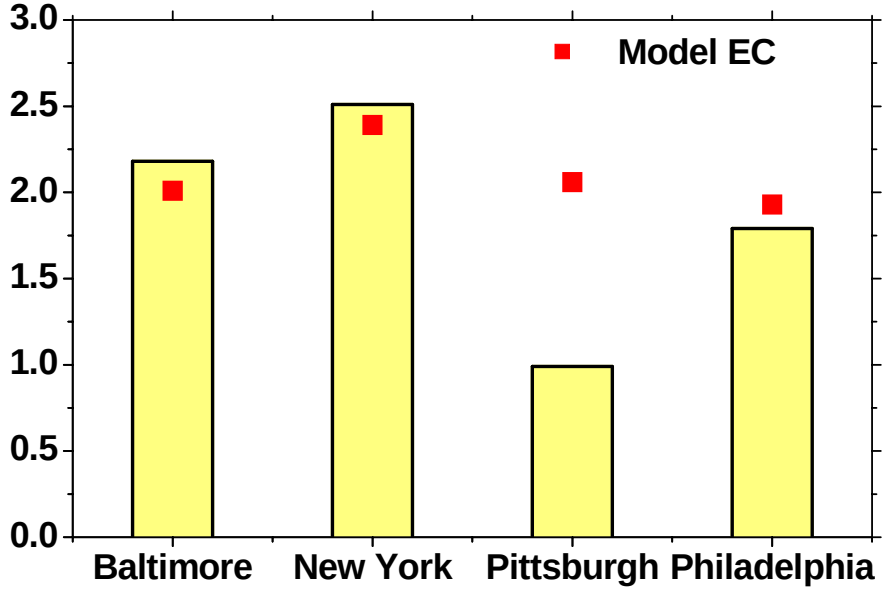
Carnegie Mellon

Comparison with ambient ratios: July

Organic Aerosol Mass



Elemental Carbon



Data from EPA STN

Carnegie Mellon

Photo-Oxidation of Diesel Exhaust