



*Second MILAGRO Science Meeting  
SRE, Mexico, D.F. May 15, 2007*

# Overview

## MCMA-2006 Study

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(<http://www.mce2.org>)

# MCMA-2006 Study

**Goal:** to examine emissions and boundary layer concentrations within the Mexico City Basin, their dispersal, transport and transformation in the atmosphere, the exposure patterns and effects on human health, and policy implications.

## Measurement sites and platforms

- T0 – Mexican Petroleum Institute (IMP)
- Tula Refinery Measurements
- SIMAT (RAMA HQ building) – Flux Tower
- RAMA (Mexico City Ambient Air Monitoring Network)
- Fixed Mobile Units
- Mobile Labs
- Naucalpan (industrial stacks)
- Microlight airplane (Puebla airport)

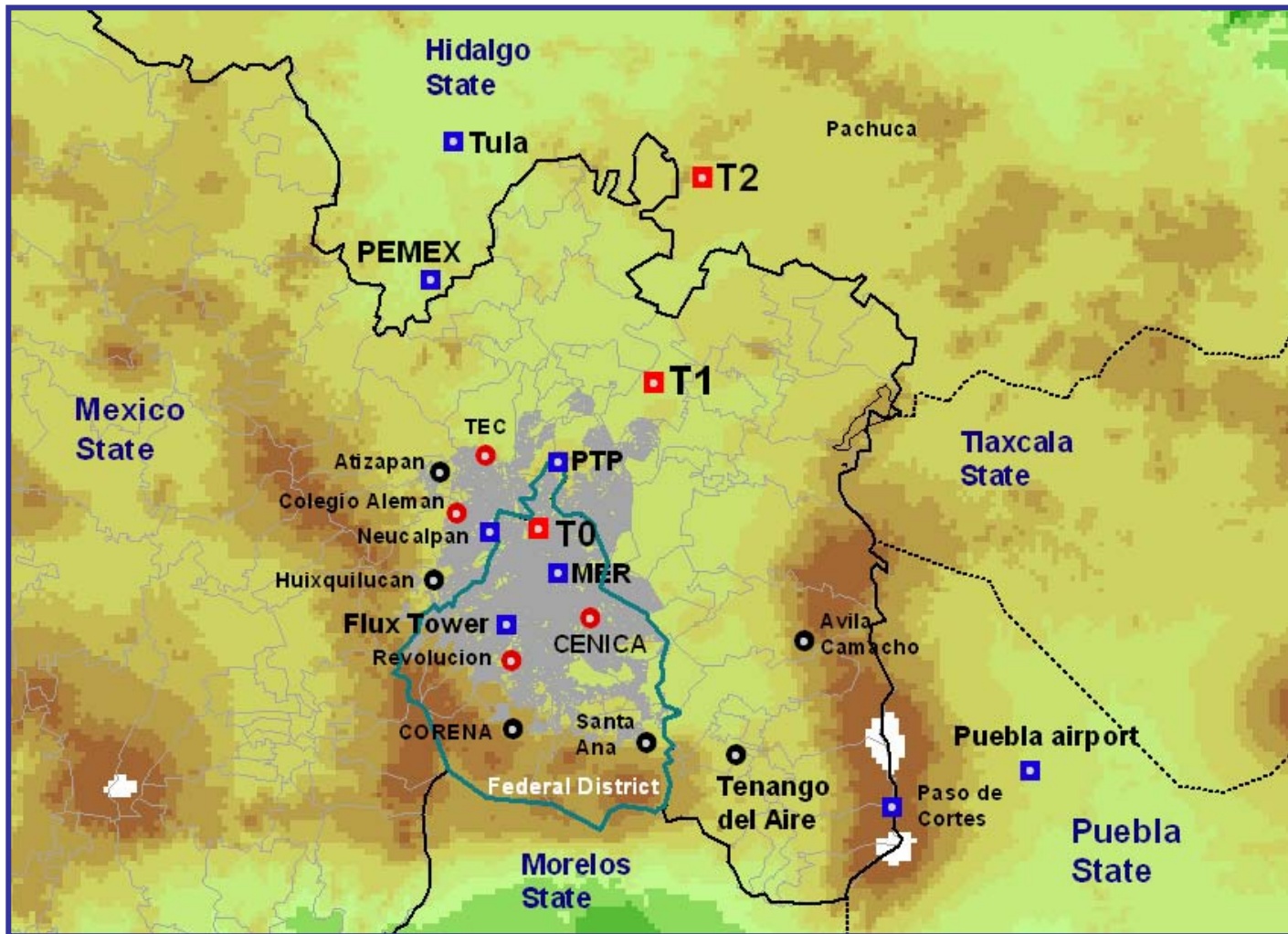
## Parameters

- Gas Phase Measurements
- Aerosols
- Radiation
- Meteorology

## Health Impact Studies

## Air Quality Modeling

# MCMA-2006: Ground-Based Measurement Sites



- Supersites (T0, T1, T2)**
- SIMAT (Flux Tower)**
- CENICA**
- Tula (refinery, power plant)**
- Naucaplan (industrial zone)**
- RAMA (36 monitoring stations)**
- Mobile units (9 stations)**
- Mobil Labs**
  - ARI Mobile Lab
  - U. Iowa (Lidar)
  - Chalmers (DOAS)
- Ultralight airplane**
- Paso de Cortes**
- AOT Network**

- Fixed site
- Mobile site
- Supersite
- Other measurements

# MCMA-2006 Overview

## Outline:

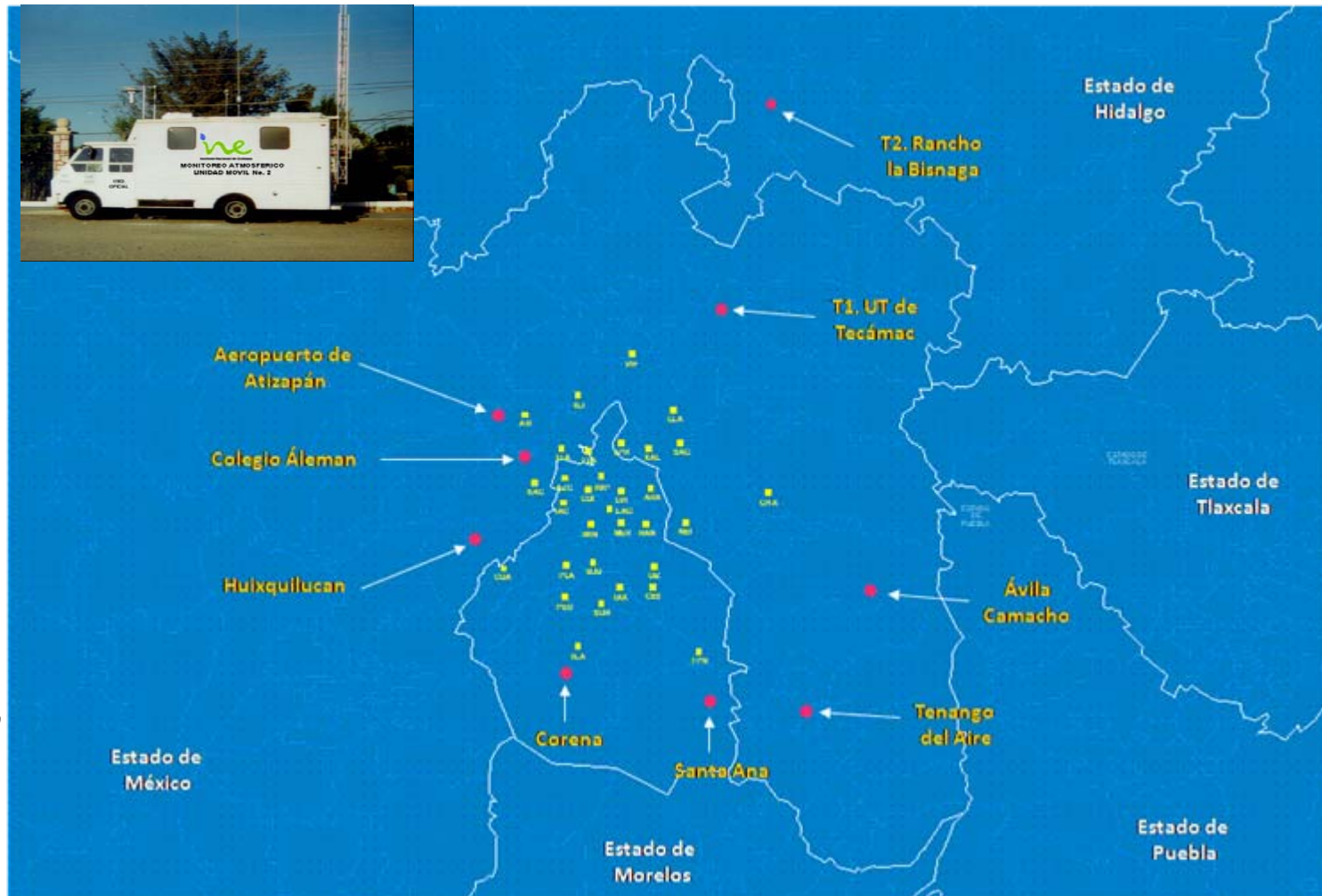
- General Overview
- Tula Study - Gustavo Sosa
- Exposure and Health Overview - Horacio Tovalin
- Aerodyne Mobile Lab measurements - Charles Kolb
- Flux measurement of trace gases, aerosols and energy - Brian Lamb

# MILAGRO Campaign: Boundary Sites

Measure criteria pollutants and meteorological parameters at selected boundary sites and cover different scenarios of ventilation

## Mobile Unit Participants

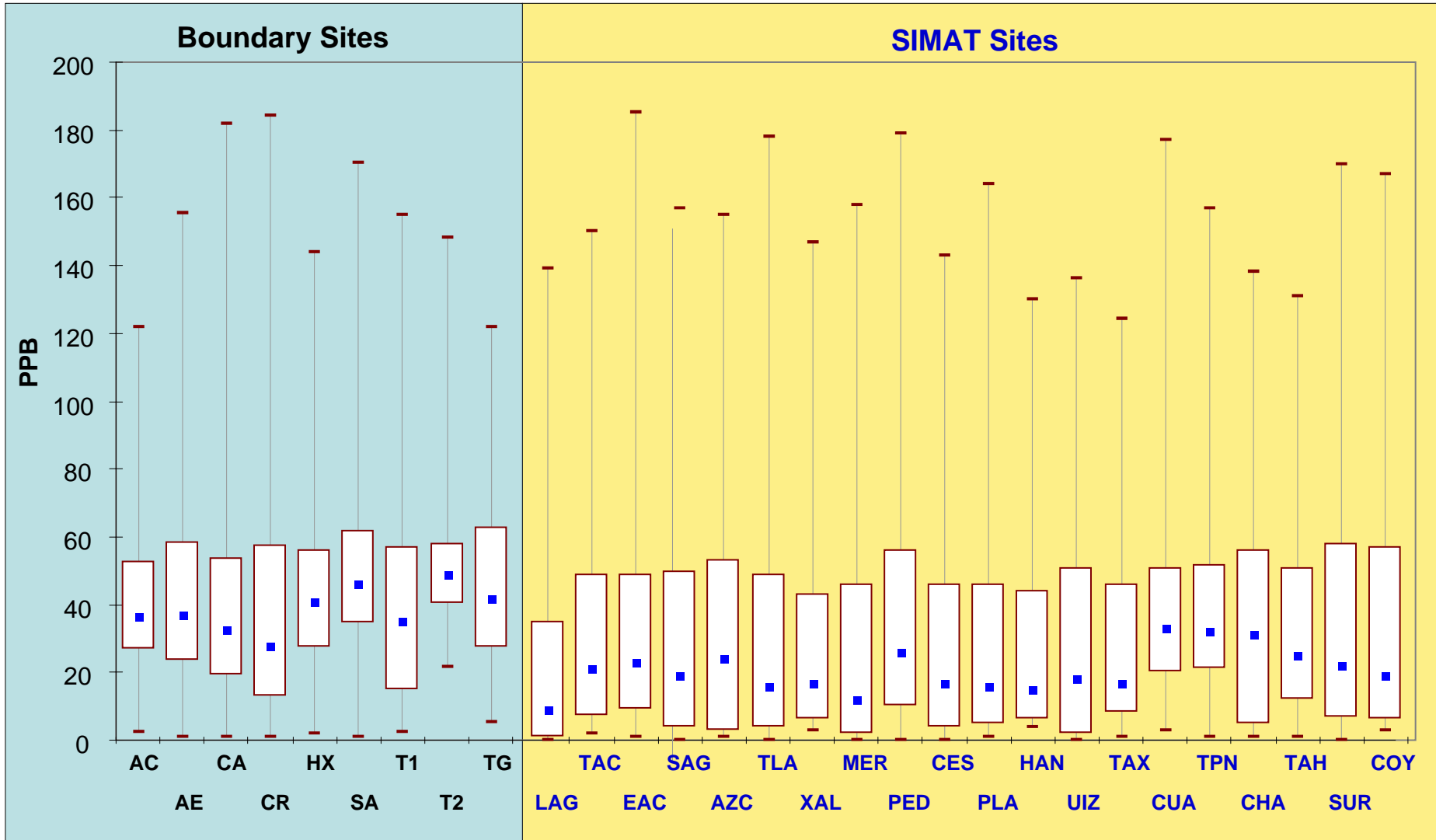
- GDF/SIMAT
- GUANAJUATO
- HIDALGO
- INE/DGCENICA
- MONTERREY
- QUERETARO
- TOLUCA
- UNAM



SOURCE:  
CENICA/INE: Ana Patricia Martínez, Alejandra Sánchez, José Zaragoza, Oscar Fentanes.  
SMA-GDF: Rafael Ramos, Armando Retama, Roberto Muñoz.  
UNAM: Bertha Mar, Luis Gerardo Ruiz, Ricardo Torres, Alejandro Torres, Jorge Martínez

# Boundary Sites: Box Pot for Ozone

The 1-hour average concentrations of ozone measured at the boundary sites are higher than those found in the urban SIMAT monitoring stations. While NO<sub>2</sub>, SO<sub>2</sub>, and CO are similar.



Min - Max    Median    25% - 75%

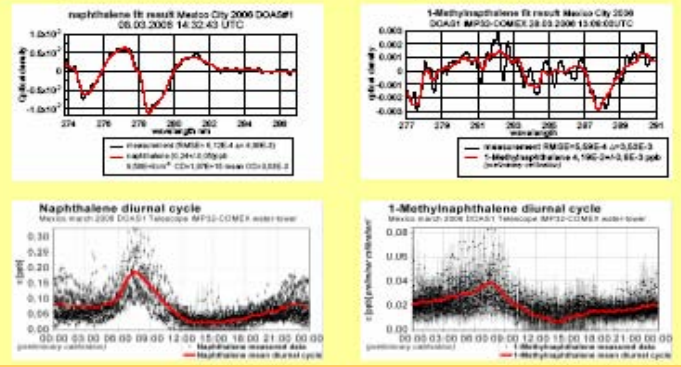
A. Merten, P.M. Sheehy, U. Platt, L.T. Molina, B. de Foy, R. Volkamer

Reduced VOCs: **Styrene**, BTX-isomer specific, **Naphthalene**, **Methylnaphthalenes**  
 Oxygenated VOCs: **Glyoxal**, **HCHO**, Benzaldehyde, **m-Tolualdehyde**, **o-Tolualdehyde**  
 Inorganics: NO<sub>2</sub>, SO<sub>2</sub>, **HONO**, **O<sub>3</sub>**

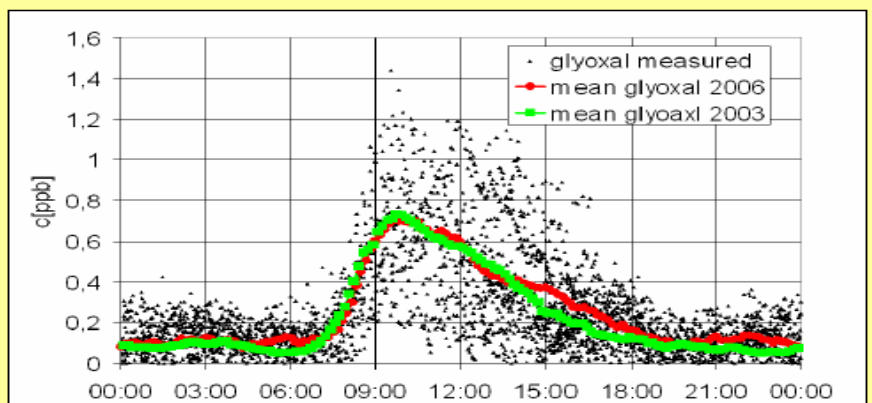
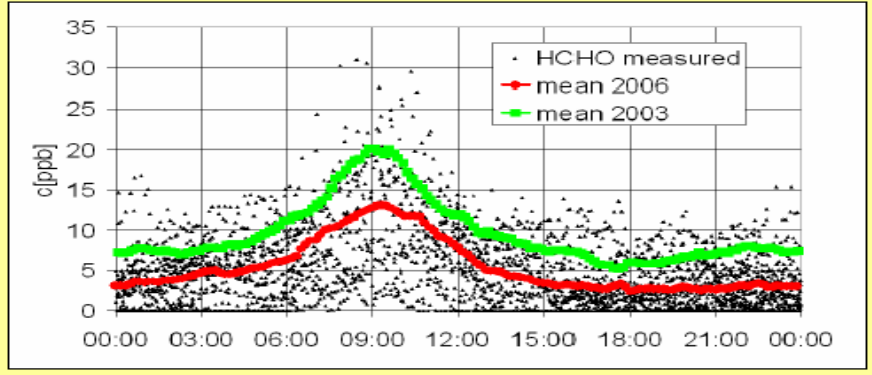
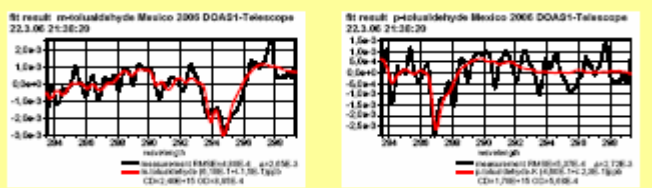
**First time direct detection in the atmosphere:**

- SOA and inorganic aerosol precursors,
- **Novel DOAS trace-gases,**
- **HOx radical precursors 2003 and 2006:**

## Polyaromatic compounds in gas phase-Naphthalene and Methylnaphthalene



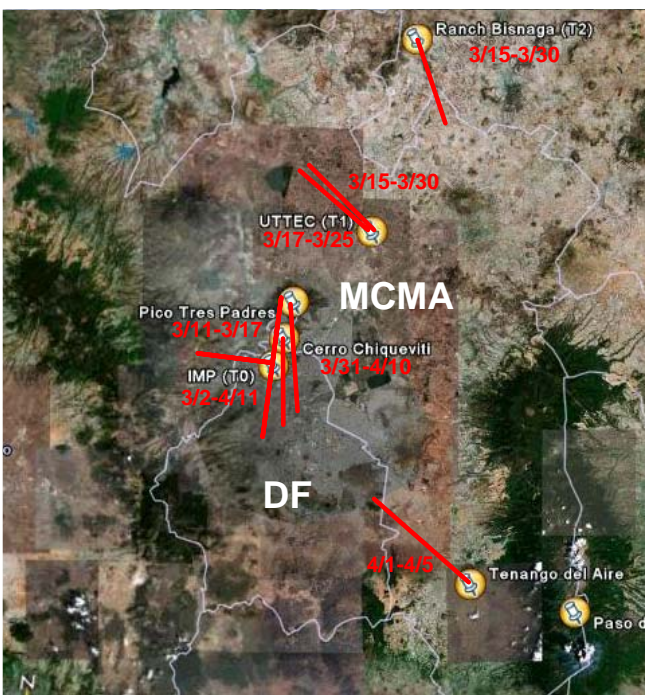
## Detection of Tolualdehydes - a potential HOx-source



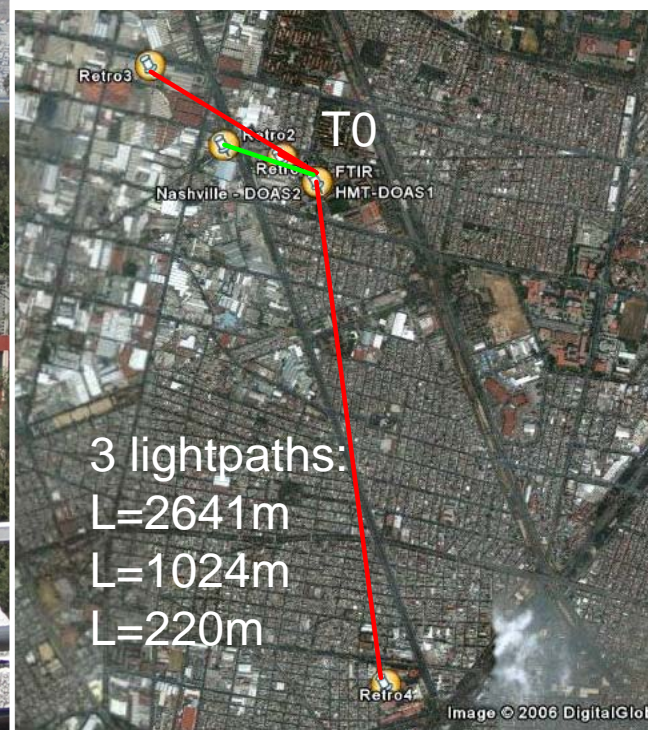
# Open Path-DOAS and MAX-DOAS



## Multi-Axes DOAS Network



## Open-Path DOAS at T0

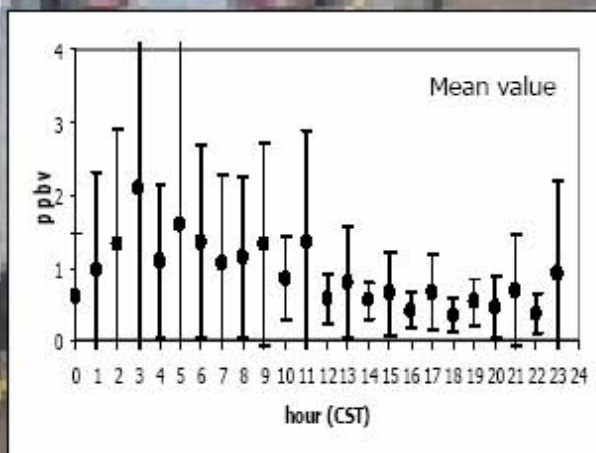


- Quasi-Lagrangian Pollution Transport
- **Vertical, and horizontal gradients**
- Planetary Boundary Layer height
- **Satellite validation**

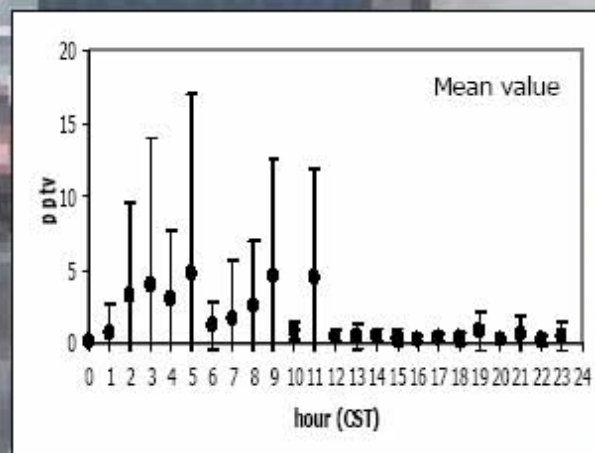
- Fast-photochemistry (HOx res, SOA prec)
- Glyoxal and Polycyclic Aromatic VOCs
- MAX-DOAS Validation
- Horizontal gradients

- **Diurnal profiles of organic acids in the gas- and aerosol phase**  
 Photochemical sources dominate for Oxalate  
 Emission sources dominate for most other acids
- **Comparison of HNO<sub>3</sub> measurements by ICMS and CIMS**
- **Comparison of HONO measurements by ICMS and DOAS**
- **Future: Comparison of Glyoxal and Oxalate measurements**

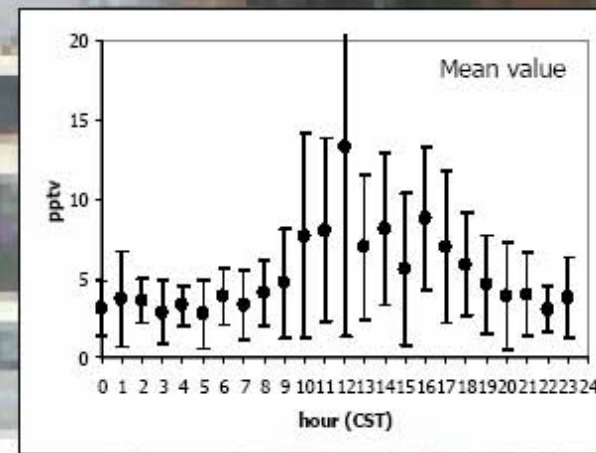
**Figure 2: Daily Pattern of Maleate, the Potential Tri-carboxylic Acid with Base Peak m/z 87 and Oxalate in the Aerosol Phase**



**Emissions**



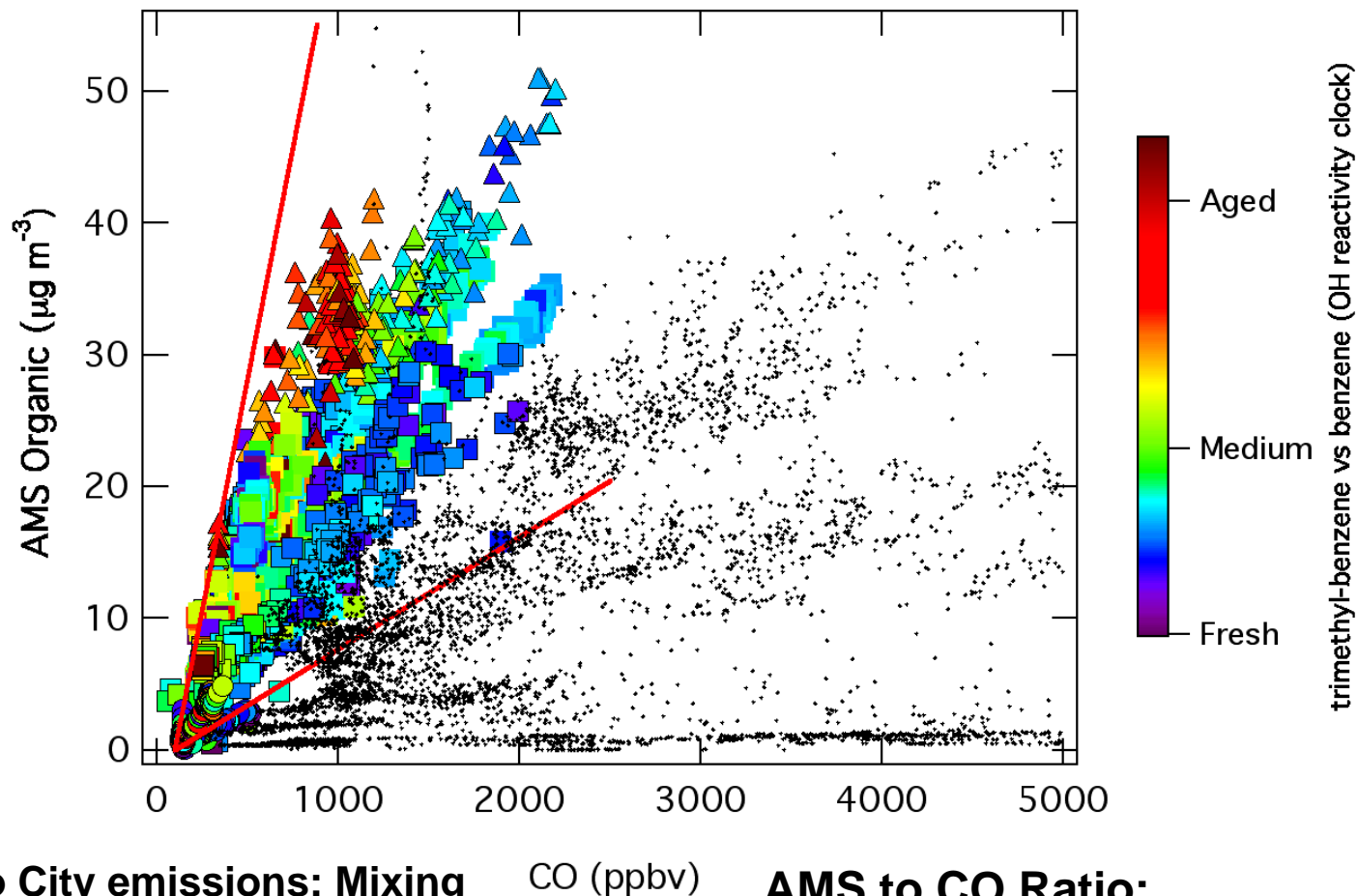
**Emissions**



**Photochemistry**

# AMS to CO Summary (PTP vs T0)

- Range, G1 - Results
- ▲ Pico de Tres Padres (aged)
- ◆ T0, Preliminary (fresh)
- CO = 100 ppb; AMS = 0  $\mu\text{g m}^{-3}$
- High, Lo Slopes 70, 8.5 ( $\mu\text{g m}^{-3} \text{ppmv}^{-1}$ )



**Mexico City emissions: Mixing and photochemistry in the first few hours of the urban plume**  
(Scott Herndon, ARI)

## AMS to CO Ratio:

- Fresh emissions (low)
- Atmospheric Processing (increases)
- Biomass Plumes (high to begin with)

# Single Particle Mass Spectrometry (ATOFMS)

- Direct measure of mixing state (chemical associations)
- High temporal resolution
- Millions of particles (statistics)
- Size-resolved composition
- Output: Size-resolved number fractions of major PM sources
- Ultimate goal: Determine the role of specific PM sources on climate forcing and regional variability

**First measurements of coupled optical-size-chemistry on individual ambient aerosols**

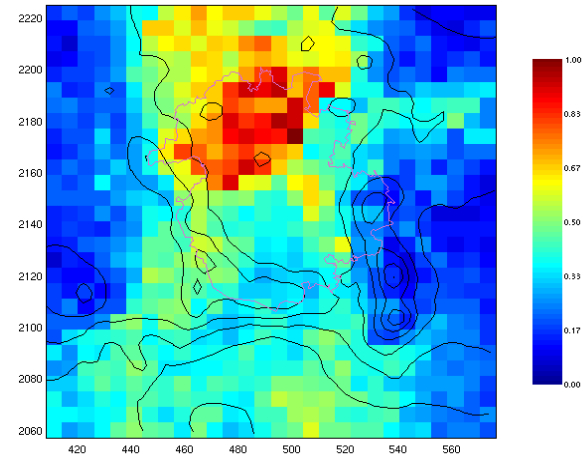
Measurement of ambient aerosols in northern Mexico City by single particle mass spectrometry, by R. C. Moffet, B. de Foy, L. T. Molina, M. J. Molina, and A. Prather  
Page(s) ACPD, 6413-6457 (2007)

# Single Particle Detection of Toxic Metals

## Aerosol time-of-flight mass spectrometer (ATOFMS)

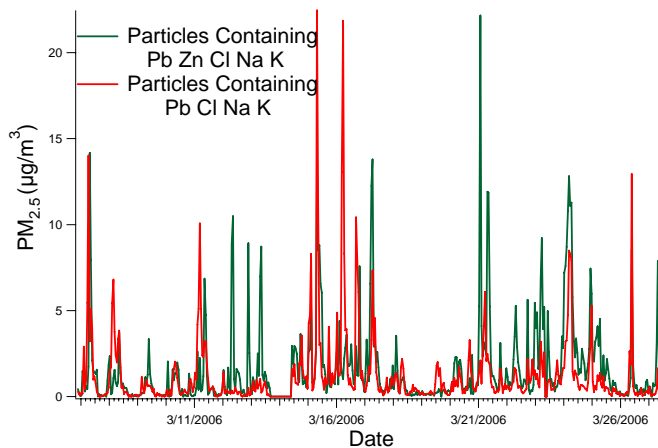
- Detected particles from vehicular emissions, fugitive dust, biomass burning, food cooking, and industry.
- For each particle type, hourly temporal profiles, size distributions and mixing state can be derived.

## Analysis produced from collaboration

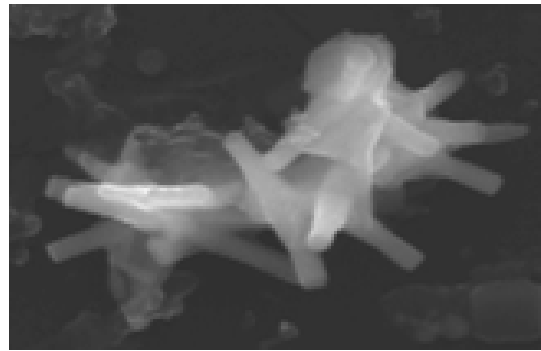


## Particles Containing Pb, Zn & Cl

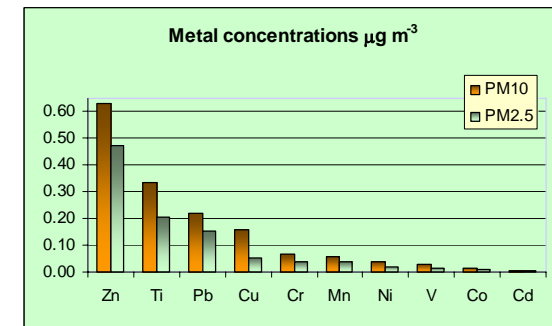
Lead particles that were found mixed with zinc and chloride represent a significant fraction of night-time emissions



Concentration field analysis using ATOFMS temporals and FLEXPART (with B. de Foy)



SEM/EDX Analysis: EDX spectra confirm presence of Pb/Zn/Cl (EMSL/LBL/MCE2)

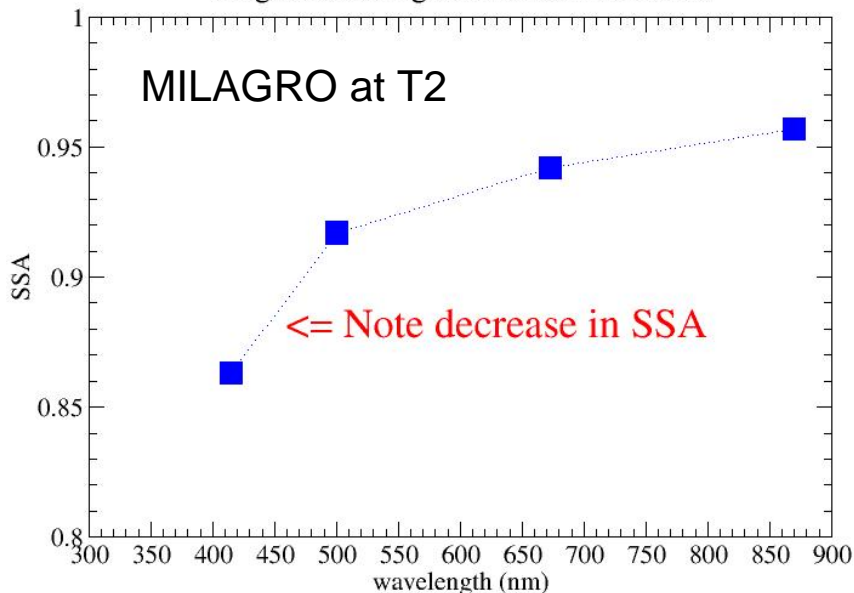


UAM-A

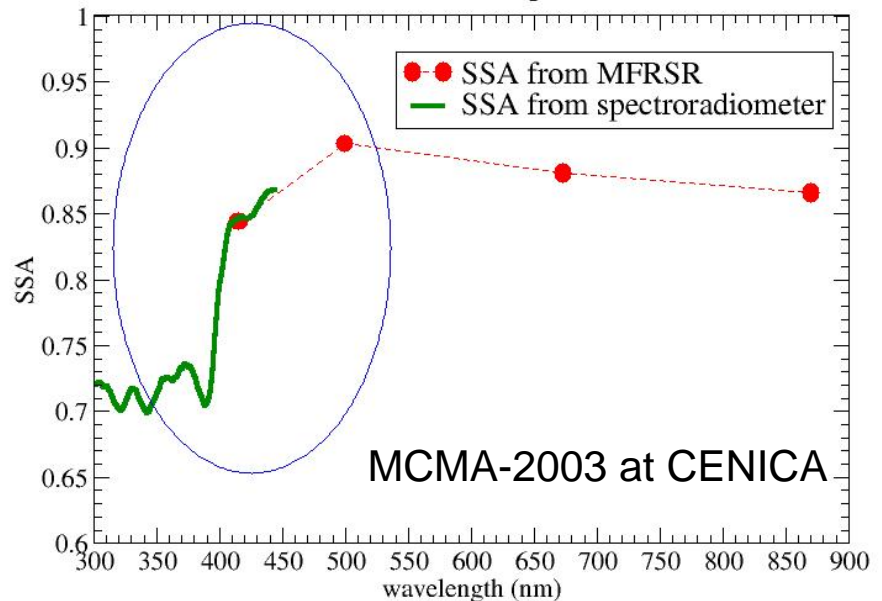
# Evidence of enhanced absorption in UV and near-UV from $\omega_0$ measurements

Jim Barnard, PNNL and Rainer Volkamer, UCSD

T2 - 20060327  
Single Scattering Albedo from MFRSR



20030415 - 10:30AM - Mexico City  
1.5 DU NO<sub>2</sub>

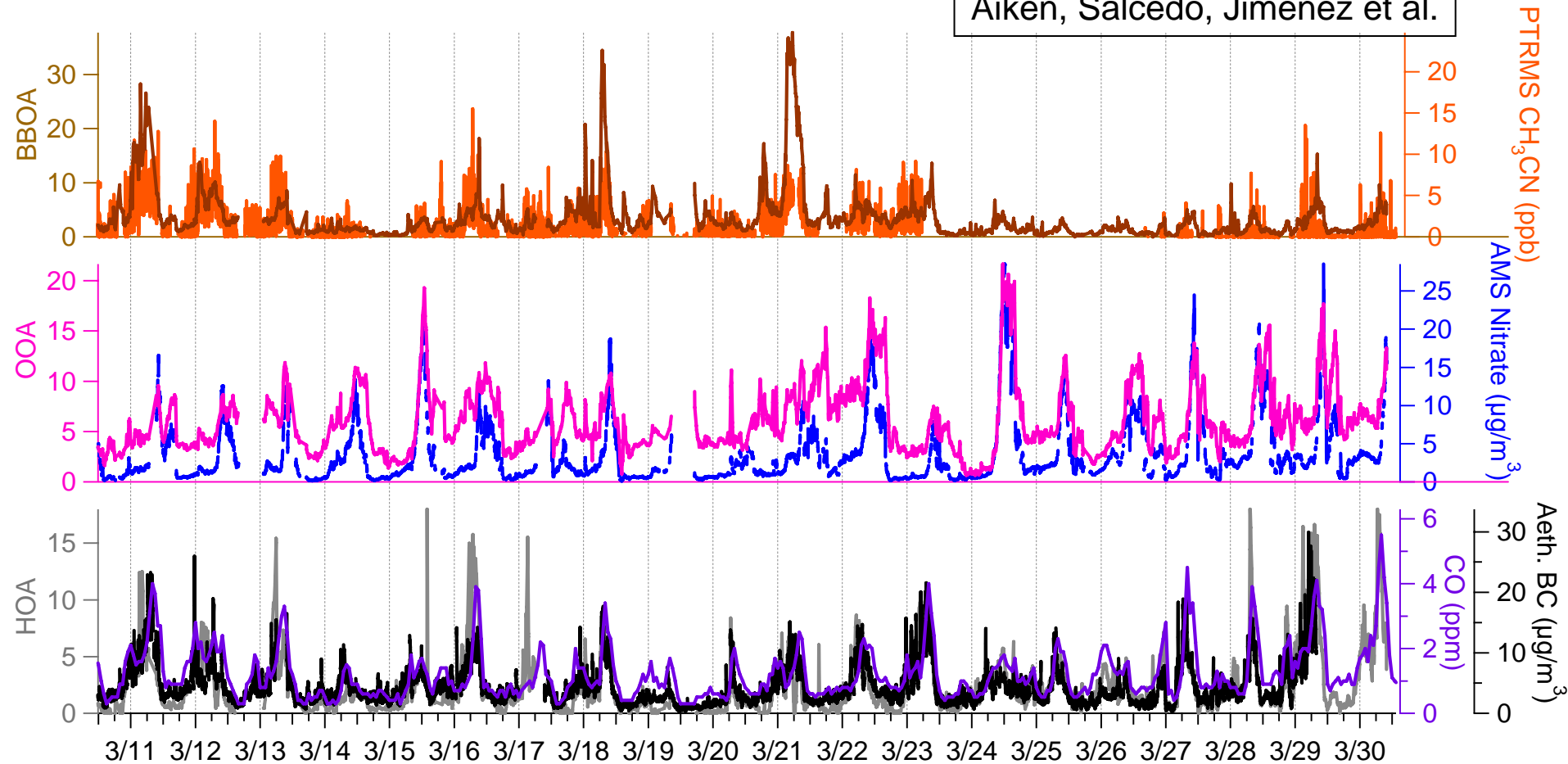


**These measurements combine a MFRSR at T2, a LIDAR, and the spectroradiometer for highly wavelength resolved information at shorter UV wavelengths.**

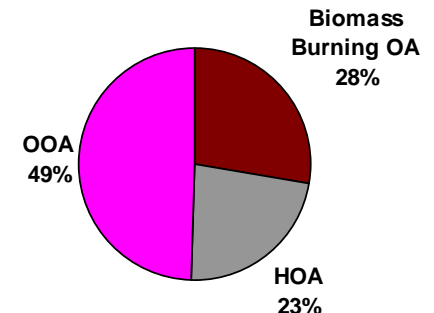
**Two independent measurements agree nicely in the area of overlap, and give independent evidence from two sites that aerosols in the urban plume absorb significantly more light in the near UV and UV spectral range than is currently believed. This is expressed by the wavelength dependent single scattering albedo (SSA).**

# T0 AMS Organic Components

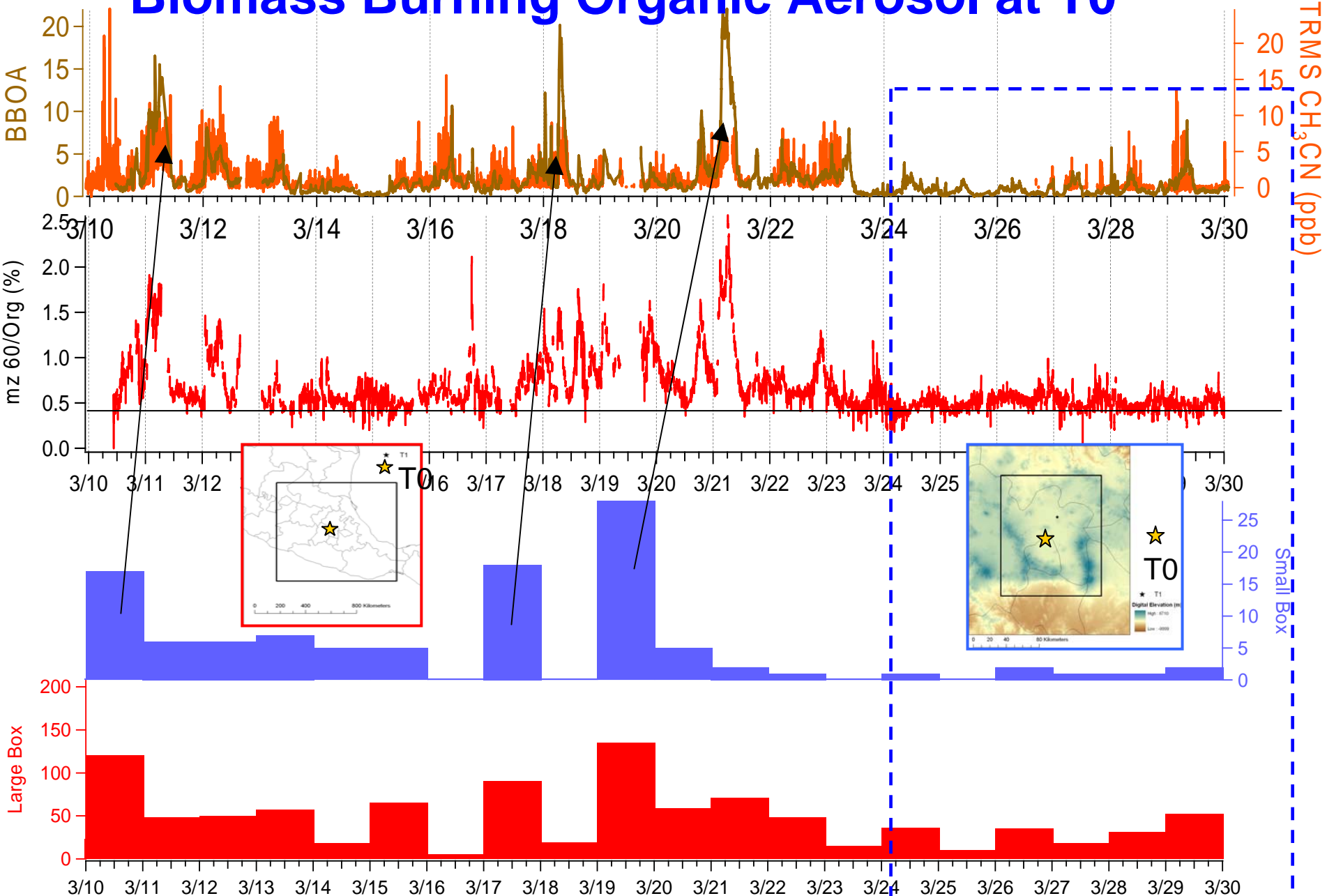
Aiken, Salcedo, Jimenez et al.



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



# Biomass Burning Organic Aerosol at T0



Aiken, Salcedo, Jimenez et al.

Fire data from C. Wiedinmyer.

# Conclusions

- Fine PM characteristics similar to 2003
- Organics dominate
  - HOA ~ urban POA, correlates with CO, BC
    - 25% of OM
  - OOA ~ urban and regional SOA
    - 50% of OM
  - Biomass burning OA
    - *Highly episodic*
    - Spectrum similar to pine burning
    - 27% of OM
    - Peaks at night and early morning, like acetonitrile
      - Advection of fires from previous day

# Summary

- Initial phase: ground-based measurements generated very rich data sets
- Second phase: data validation, analysis and modeling
- Comparisons and collaborations with other ground sites and aircraft measurements
- Assess policy implications