MILAGRO Science Meeting
October 23-25, 2006, Boulder, Colorado

Ground-based Measurement Urban Sites Overview

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MIT/MCE2

http://mce2.org

Urban Sites Measurements

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)

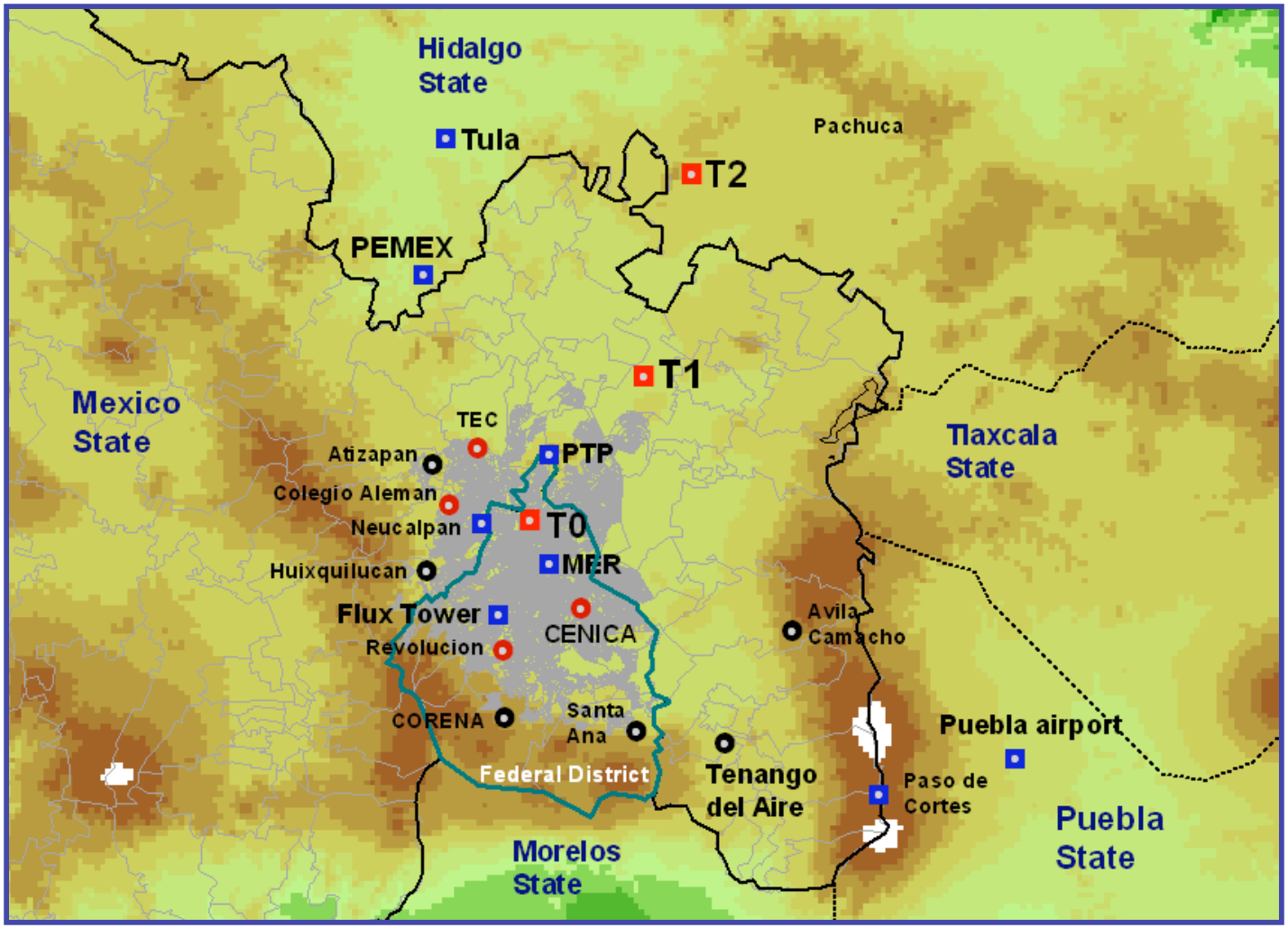
Parameters

- Gas Phase Measurements
- Aerosols
- Radiation
- Meteorology

Health Impact Studies

Air Quality Modeling

MILAGRO 2006: Ground-Based Measurement Sites



Locations

Supersites (T0, T1, T2)
SIMAT (Flux Tower)
CENICA
Tula
Naucaplan
RAMA (35 monitoring stations)
Mobile units (9 stations)
Mobil Labs
- ARI Mobile Lab
- U. Iowa (Lidar)
- Chalmers (DOAS)

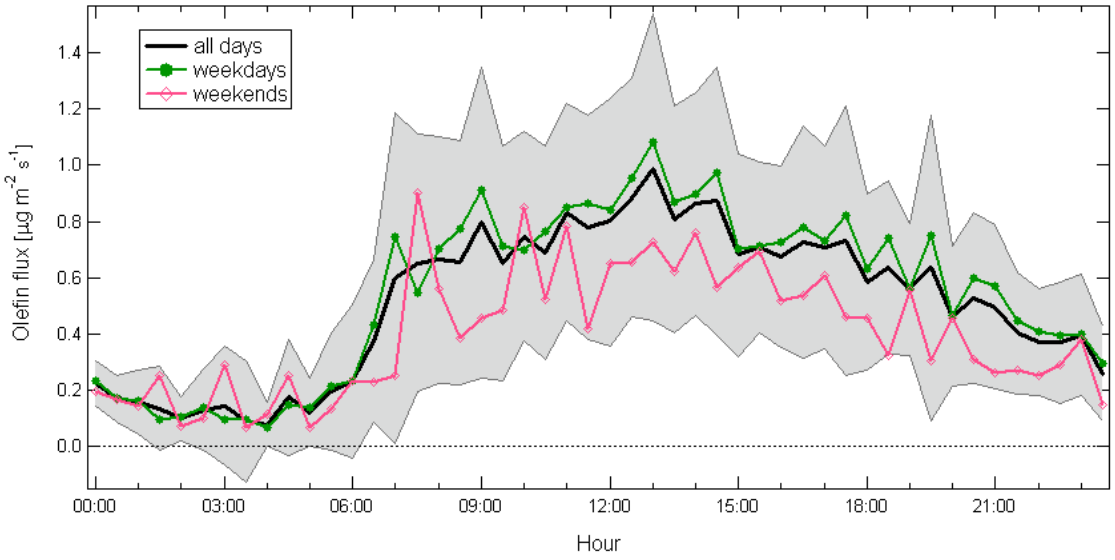
Ultralight airplane
Paso de Cortes
AOT Network

Fixed site **Mobile site** **Supersite** **Other measurements**

SIMAT Site: Urban Flux Measurements

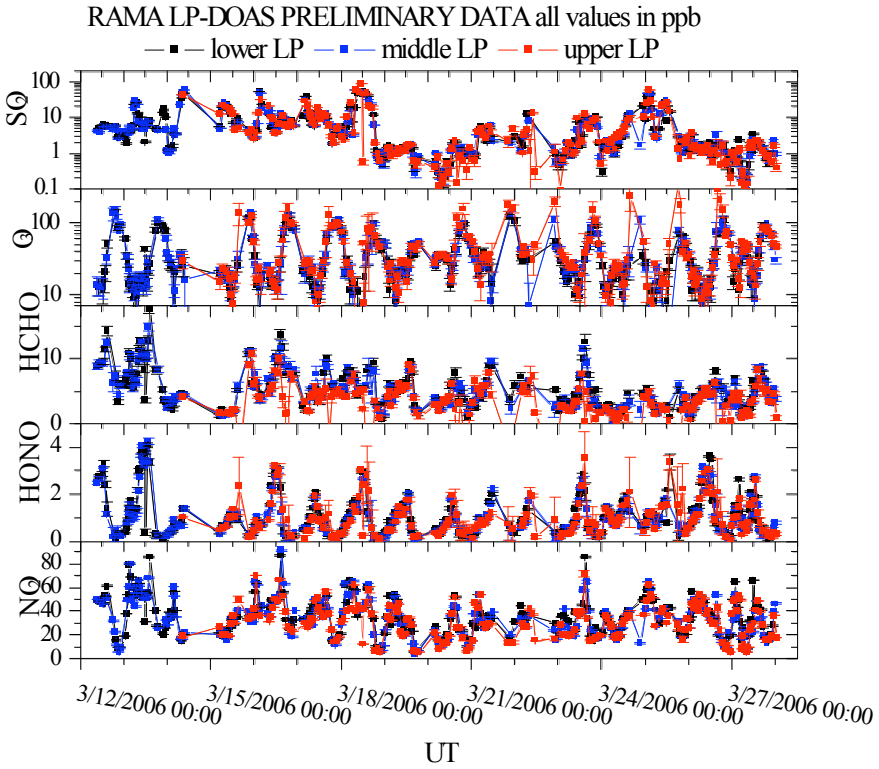
Flux Tower:
- 42 km asl
- 3 km radius: fixed and mobile emitting sources
- evaluate and validate local emissions inventory

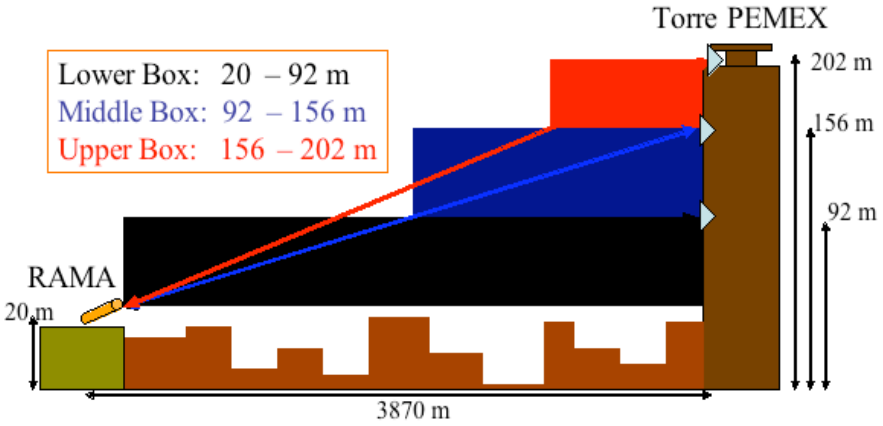
- VOCs
- CO_2
- CO
- Aerosols
- Energy (*Q**, *Qh*, *Qe*)
- Momentum (*u**)



Washington State University
MCE2 Molina Center for Energy and the Environment
SIMAT
Centre for Ecology & Hydrology
Colorado University of Colorado at Boulder
PNNL

SIMAT Site: Nocturnal Boundary Layer Chemistry





NO_3, NO_2, N_2O_5, O_3, HCHO, HONO & SO_2 long path vertical profiles by LP-DOAS

UCLA

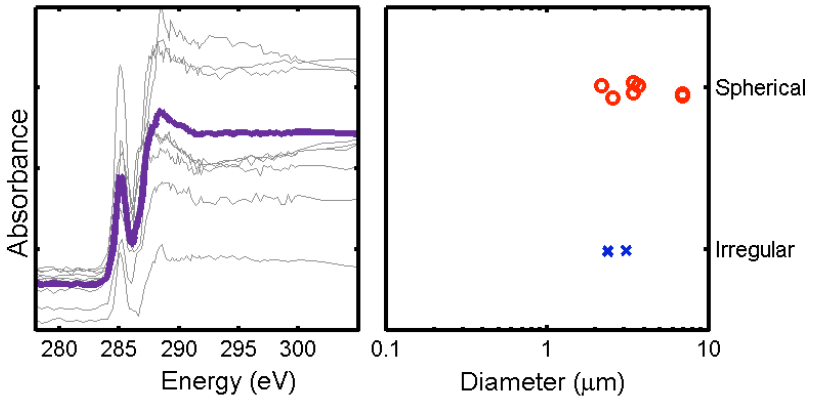
SIMAT Site: Organic Aerosol Functional Group Analysis

Single-Particle Analysis by Scanning Transmission X-Ray Microscopy (STXM)

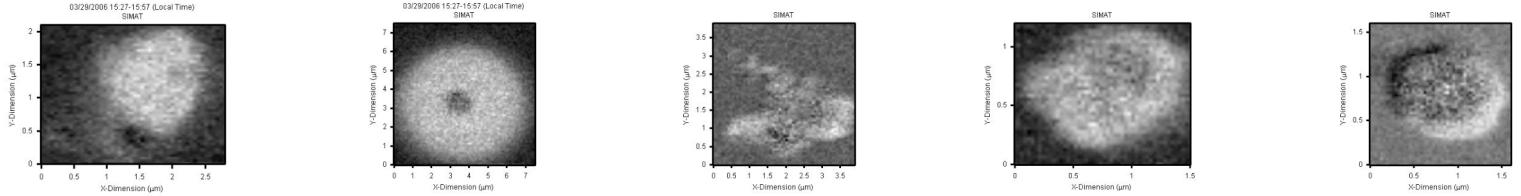
61 particles analyzed from SIMAT site

Common spectra among large, spherical particles show abundance of:

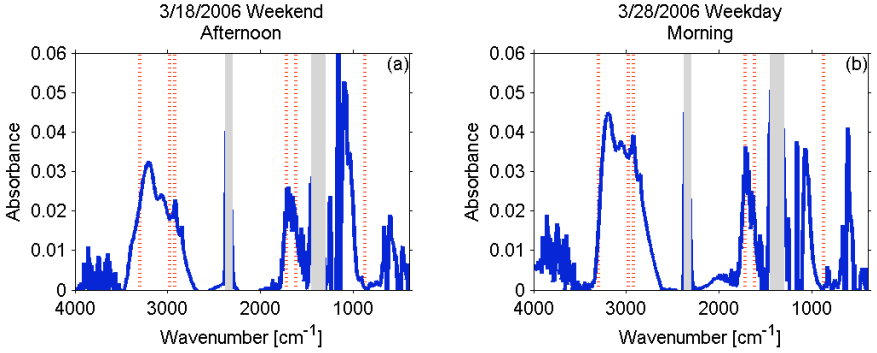
- alkene/aromatic groups
- alkyl groups
- carboxylic carbonyl



Particle image examples:



Submicron-Particle Composition by FTIR Spectroscopy



March 5 – April 1, 2006	
Sample	**Hours**
Morning	0400-1100
Afternoon	1100-1800
Evening	1800-0400

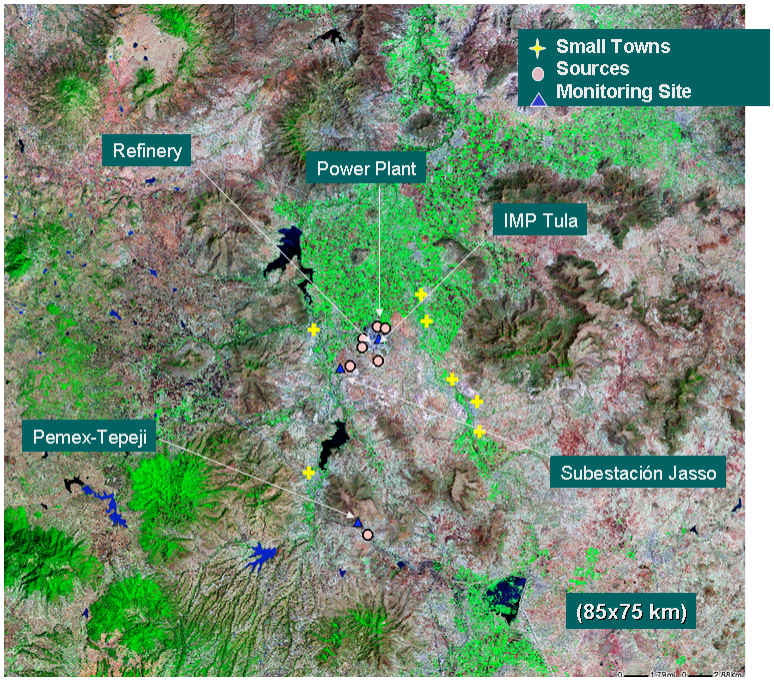
Samples collected 3x daily.
Analyzed for abundance of:

- Alkanes
- Alkenes
- Carbonyl Carbon
- OH Carbon

SCRIPPS INSTITUTION OF OCEANOGRAPHY UCSD

UCSD

Tula: Pemex Refinery Region



- 60 km Northeast from the downtown Mexico City Metropolitan Area

- 355,000 T/Y of SO2 are released by two major industries: PEMEX Power Plant and Refinery.

- Other important industry are cement plants and open-sky mines, responsible for important particle matter emissions and soil degradation.

IMP Measurement campaign: March 18 to April 22, 2006

Objective: to determine the influence of this heavily industrial area to the total MCMA emissions, and to better understand the processes of transport and transformation of these pollutants into the atmosphere.

Tula: Measurements Techniques & Instrumentation

At two fix sites (Subestación Jasso and Pemex_Tepeji)

- VOCs, carbonyls, PM2.5 and PM10, CO, NO, NO2, O3 and SO2, meteorology parameters were measured continuously.

- optical properties of the particles were measured using an aethalometer, nephelometer, SMPS and MOUDI at Jasso.

At IMP facilities in Tula

- meteorological vertical profiles (four rawinsondes daily)

- pilot balloons (launched by CENICA during March 24 to 26)

Mobile measurements

- MiniDOAS measures total SO2 flux emissions from the major sources in the region.

Long-term atmospheric deposition patterns of metals and PAHs

- use biomonitoring techniques at Tula suburbs

- sampling area: 4000 km2.

- characterize at least 21 trace metals.

TENANGO DEL AIRE

PARTICIPANTS:

GRUPO FISICOQUÍMICA ATMOSFÉRICA, CCA, UNAM

INSTITUTE OF METEOROLOGY AND CLIMATE RESEARCH (IMK-IFU)

FUNDACIÓN CENTRO DE ESTUDIOS AMBIENTALES DEL MEDITERRÁNEO (CEAM)

CENICA

UNIVERSITY OF COLORADO

MCE2

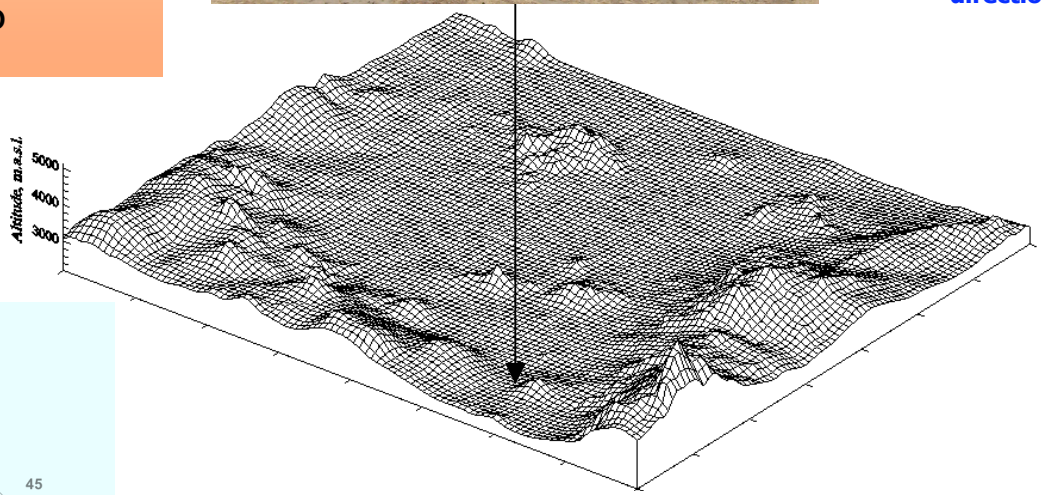
WIND SPEED, WIND DIRECTION, AMBIENT TEMPERATURE, RELATIVE HUMIDITY, PRESSURE, GLOBAL RADIATION, U.V. RADIATION,

MIXING LAYER HEIGHT

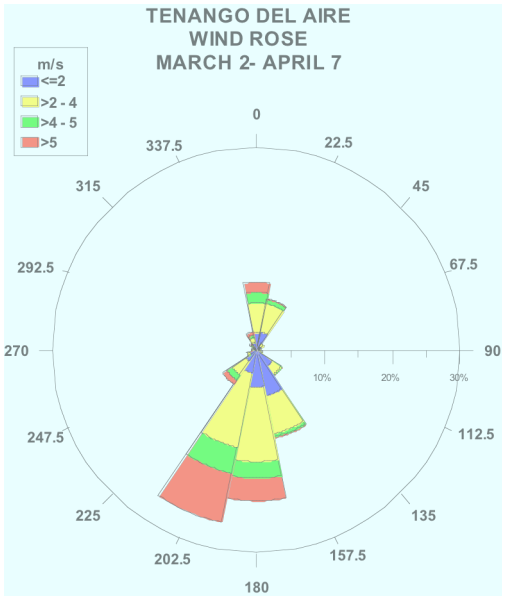
O_3, NO_y, NO_y, CO, SO_2, HCHO, HONO, PAHS, NO_2 column, H_2O_2 (denuders), VOC (canisters & cartridges), PM_{fine}

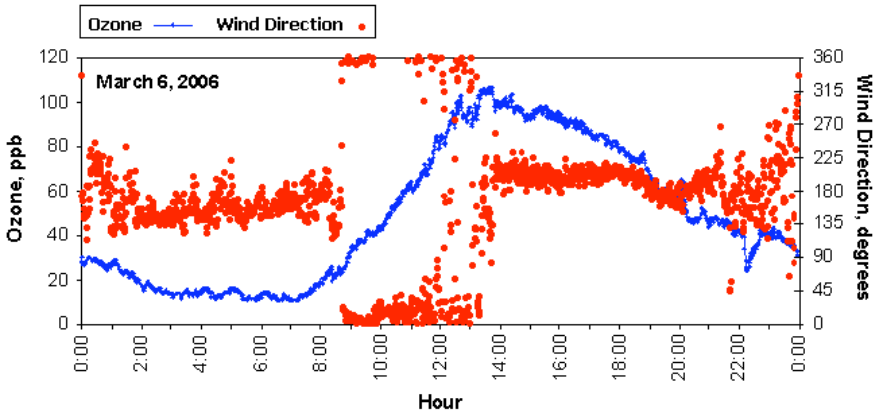
Shadow band spectroradiometer

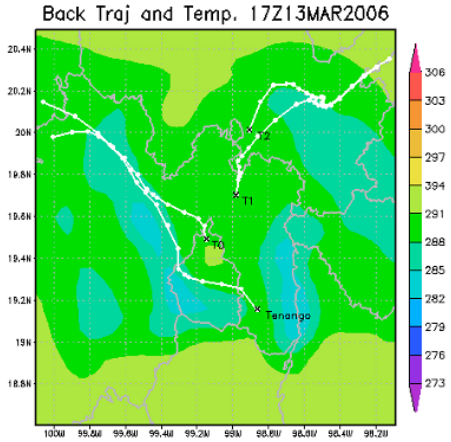
Pilot balloon tracking (wind speed & direction vs height)



P.I.: Gerardo Ruiz, UNAM







MICROLIGHT RESEARCH AIRCRAFT D-MIFU

PARAMETERS MEASURED

Aerosol size, number
CPC 3010, Spectrometer 1108

Absorption, Scattering,
7 λ-Aethalometer, AVMIII

Actinic radiation 300, 380 nm,

4 filter radiometers

Global radiation, Albedo,
LICOR, SKYE, 400-1000 nm

Ozone, UV-absorption

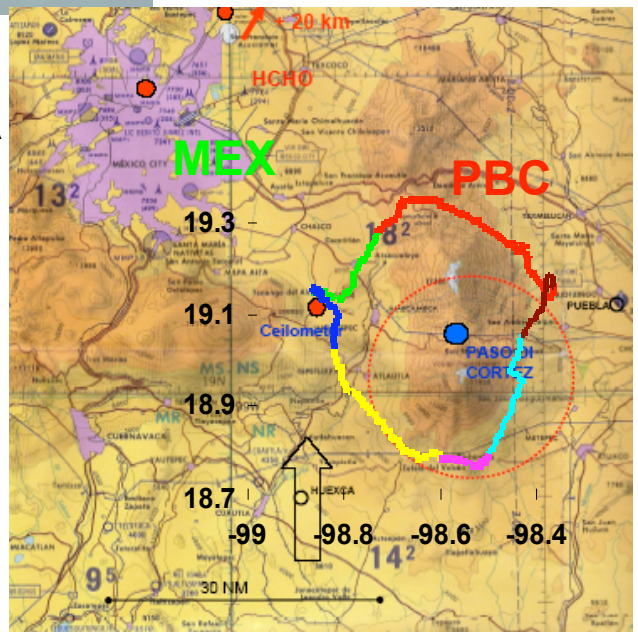
Meteorology, Chilled mirror

VOC sampling,
Zenith sky DOAS (UNAM)

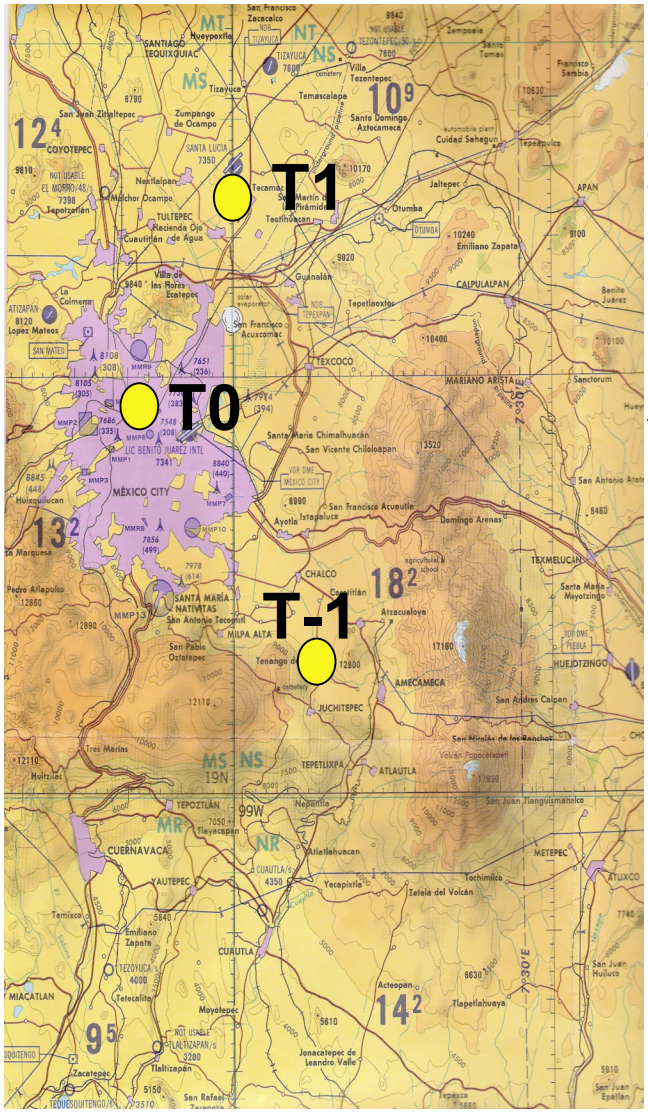
W. Junkermann
IMK-IFU

OPERATED OUT OF PUEBLA

13 FLIGHTS SOUTHEAST OF MEXICO CITY

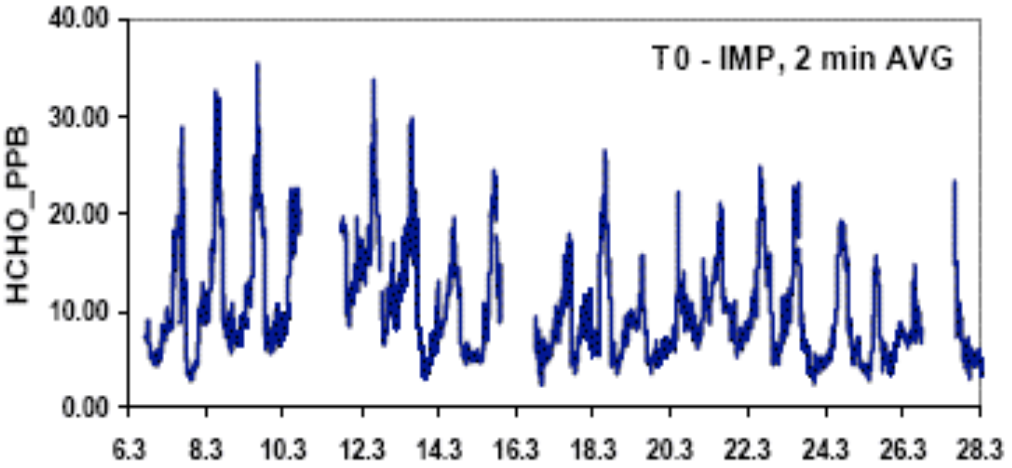


Formaldehyde Mixing Ratios in the Mexico City Basin



Measurement sites
T0 (IMP)
T1 (Tecamac)
T-1 (Tenango del Aire)

Other measurements:
DOAS Network
ARI – TILDAS
others



IMK-IFU, UNAM

Chemical and Physical Characterization of PM2.5 and VOCs Speciation from Industrial Stacks

Objectives

- Characterize particle size distribution of PM10 and VOCs adsorbed in PM2.5 in Naucalpan, an industrial zone in the northern part of the MCMA.
- Speciate VOCs from exhaust gas samples taken from industrial stacks located in Naucalpan.

Industries: 30
Fuel type
-10 LPG
-10 CNG
-10 Diesel

Instrumentation

- Thermo DATA RAM 4, Model DR-4000: measure PM2.5 concentration.
- Automatic particle counter CLIMET, Model CI 500 Innovation; particles size range: 0.3-0.5-1.0-2.5-5.0-10.0-larger than 10 microns).
- Sequential automatic sampler of PM2.5 R&P PARTISOL Plus, Model 2025.
- Continuous automatic monitoring equipment TESTO 350/MXI for stacks.
- Iso-kinetics sampler for stack gases.

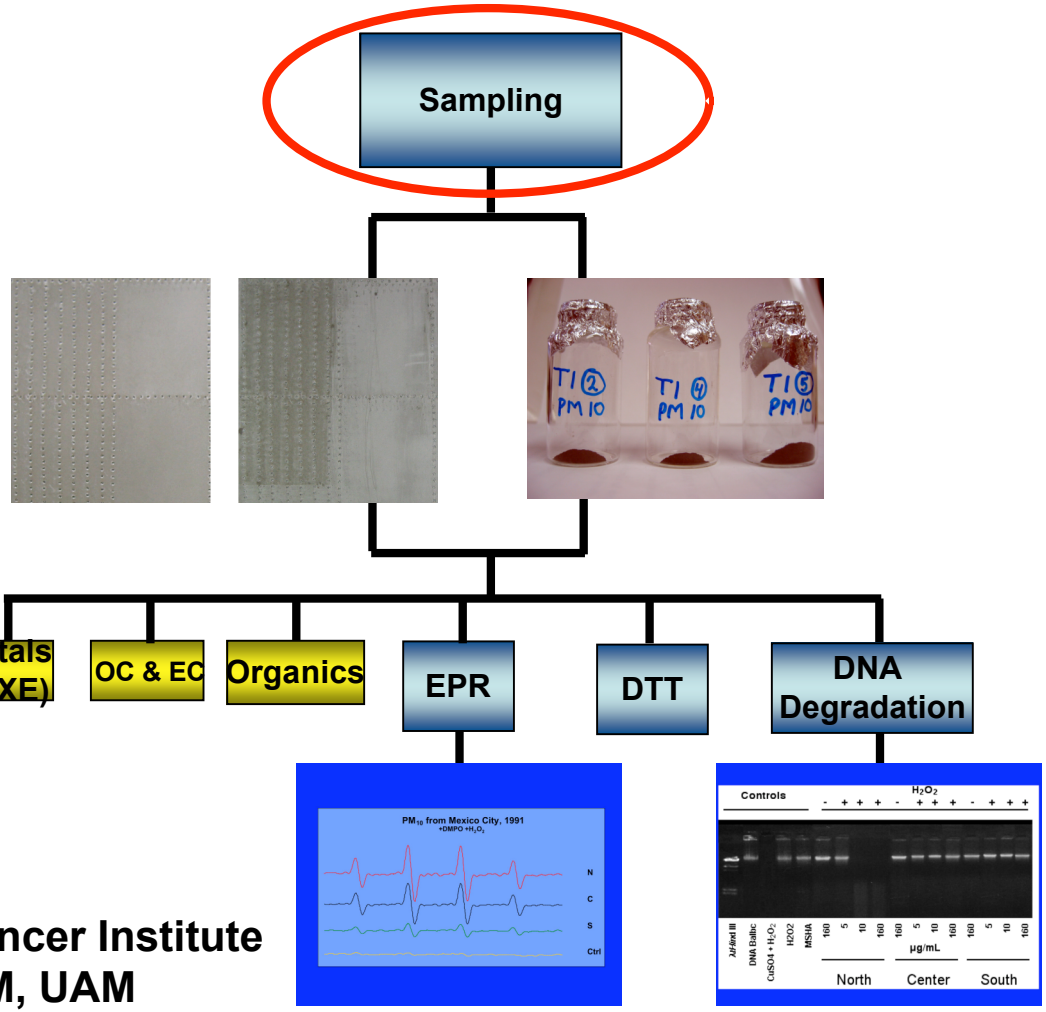
Tecnológico de Monterrey (ITESM)

Oxidative Potential of PM obtained at T0 & T1:
An evaluation by EPR and DNA degradation

Objetives

- Determine oxitavive potential of PM_{10} & $PM_{2.5}$ obtained at T_0 and T_1:
  - EPR
  - DNA Degradation
  - DTT Assay
- Compare oxidative potential (T_0 vs. T_1) and relate to composition and ventilation patterns.

National Cancer Institute
UNAM, UAM



Health Studies: Urban and Semi-rural Populations Personal and Micro-environmental Exposures

- **To analyze the contribution of the regional transport of air pollutants from Mexico City in the personal exposure of children and their parents at three different sites to the following pollutants: VOCs , O3, CO, PM2.5, nanoparticles**

  Participants:
  - 121 children (age: 9-12 years)
  - 67 parents

- **To analyze air pollution-related oxidative stress and health problems**

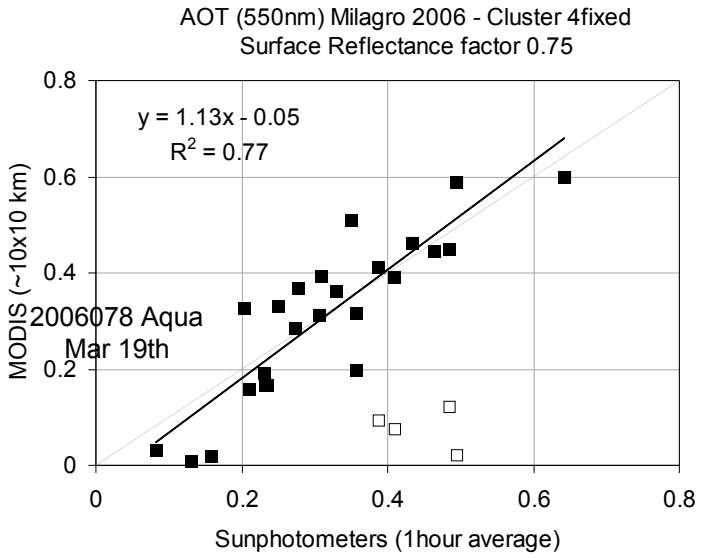
  Participants:
  - 155 children (age: 10-12 years)
  - 90 parents

UNAM, INE, UFZ, MCE2

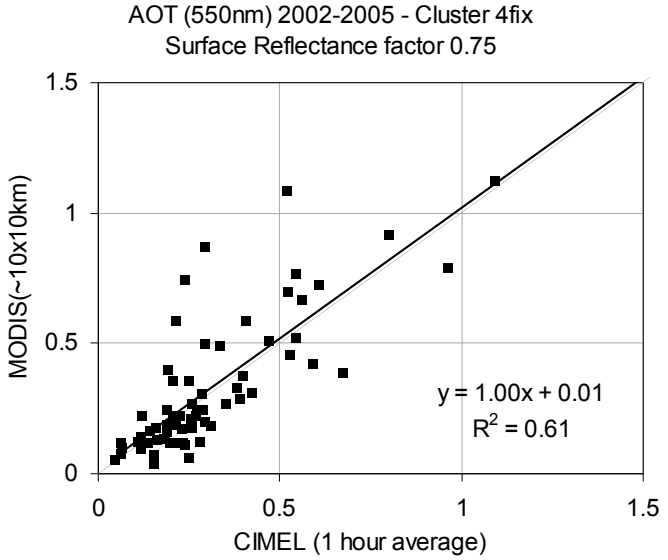
AOD Retrieval with MODIS Data and Comparison with Microtops II Sun Photometer Network and AERONET

- retrieve Aerosol Optical Depth (AOD) with fine spatial resolution over Mexico City with MODIS Sensor onboard NASA satellites Terra and Aqua;
- validate the AOD product by comparison with measurements from a network of 5 Microtops II sun photometers and CIMEL/AERONET during MILAGRO Campaign

MILAGRO 2006
MODIS 1.5km retrieval versus
Sunphotometer Network



Mexico City 2002-2005
MODIS 1.5km retrieval versus
CIMEL/AERONET

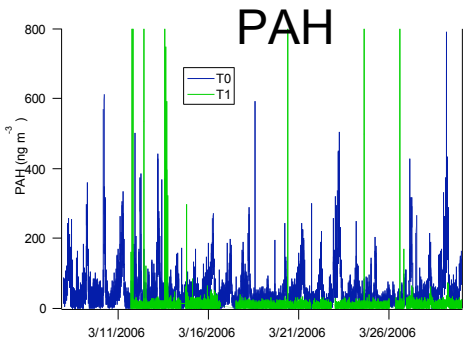


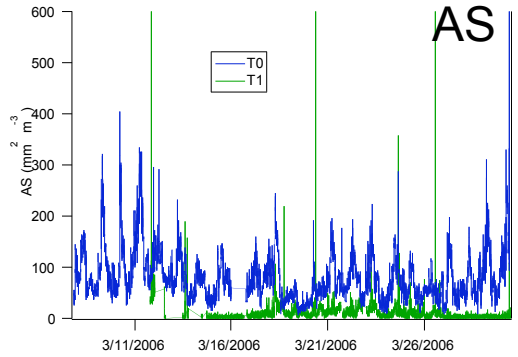
MIT, MCE2,
NASA-GSFC, UNAM

Particulate PAH and Aerosol Active Surface Area in Different Environments of Mexico City

- Photoemission aerosol sensors diffusion chargers (EcoChem Analytical) to measure PAH and AS concentrations.
- The instruments were based at T0, T1, and in the Aerodyne Mobile Laboratory, which visited a variety of sites, including Pico Tres Padres, Santa Ana, Pedregal.

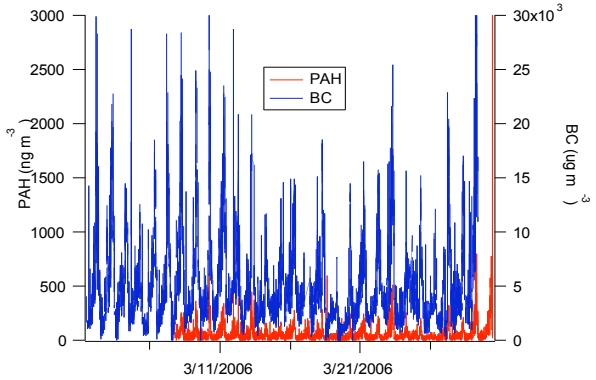
PAH and AS at the fixed sites (T0 and T1)

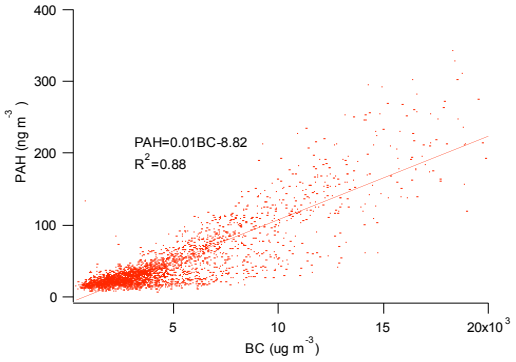




The concentrations and strength of the diurnal variations of PAH and AS are generally the highest at T0

PAH versus BC at T0





PAH and BC at T0 correlated very strongly, suggesting that they originated from the same source (vehicles).

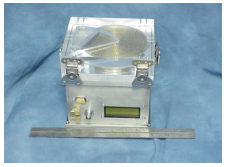
VT, ARI, MIT, MCE2, CU, PNNL, UALR

Microscopy and Microprobe Studies of Individual Atmospheric Particles

Particle sample collection sites: T0 T1, T2

- investigate spatial and temporal variability of chemical and physical properties
- study generation of pollution inside the city and subsequent transport towards the city boundaries

Field Sampling Devices

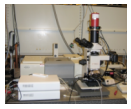

Laboratory Analysis

Comprehensive chemical and morphological analysis of aerosol samples collected during the 2006 MILAGRO study

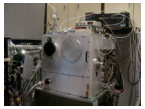
- **CSEM/EDXESEM** — Computer controlled microscopy and X-ray analysis of a statistically significant number of particles

- **TOF-SIMS** — Depth profiling of ensembles of individual particles providing molecular speciation of their contents

- **TEM/EDX, EELS, SAED** — High resolution microscopy of individual particles



- **FTIR/Raman Microscopy** — Monitoring of hygroscopic properties of ensembles of individual particles



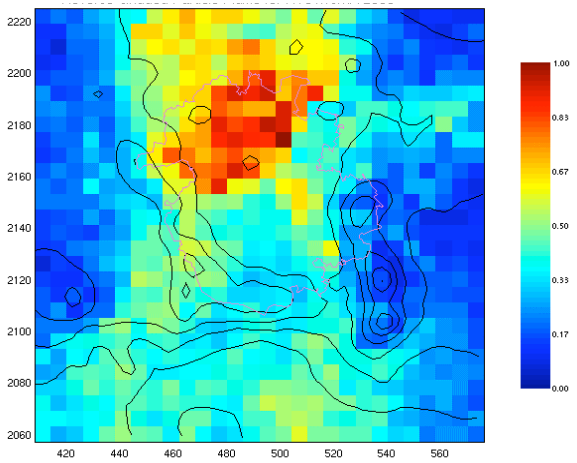
- **STXM/NEXASF** — Chemical bonding information on different elements for individual particles

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.

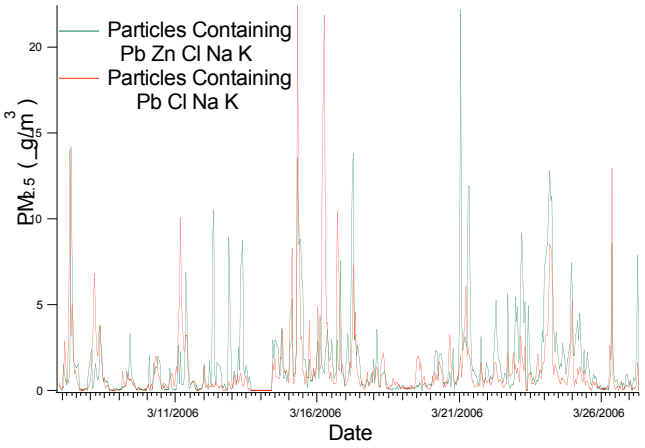
Analysis produced from collaboration

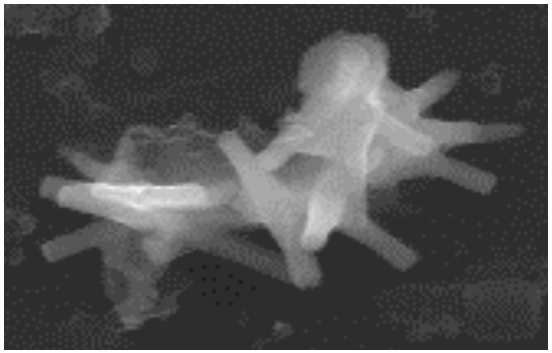


Concentration field analysis using ATOFMS temporals and FLEXPART (with B. de Foy)

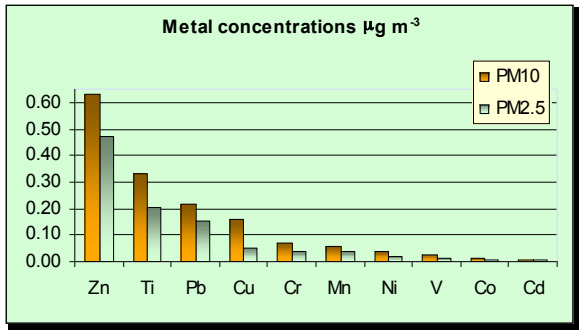
Particles Containing Pb, Zn & Cl

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



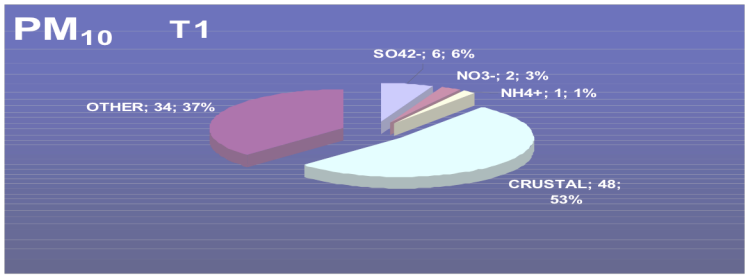


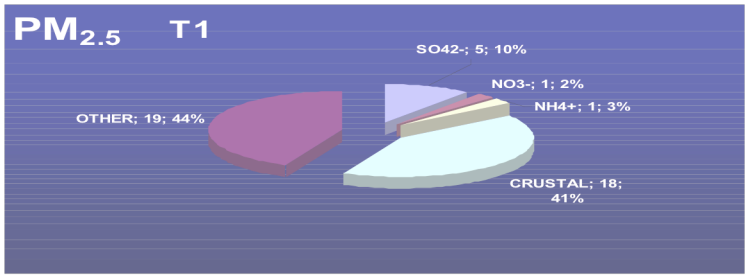
SEM/EDX Analysis: EDX spectra confirm presence of Pb/Zn/Cl (EMSL/LBL/MCE2)

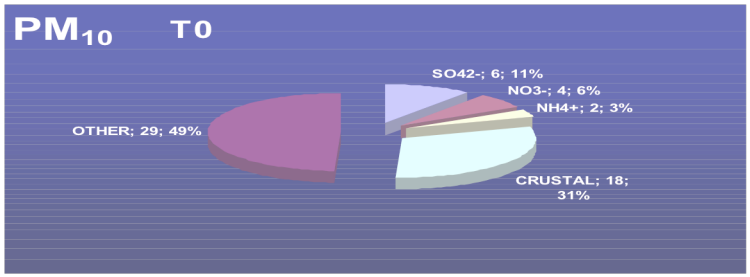


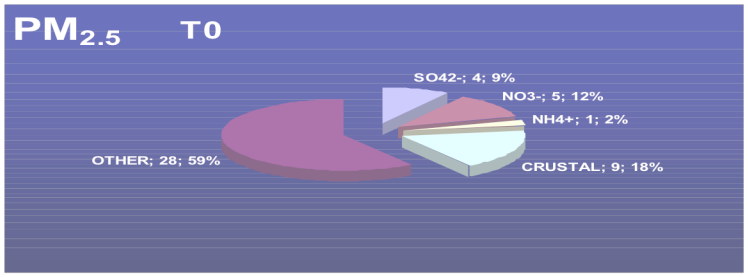
UAM-A

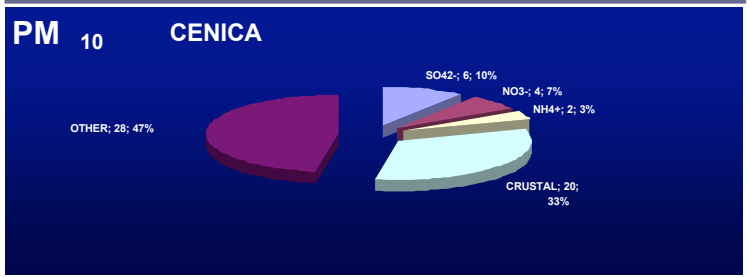
Speciation of Particulate Matter at CENICA, T0 & T1











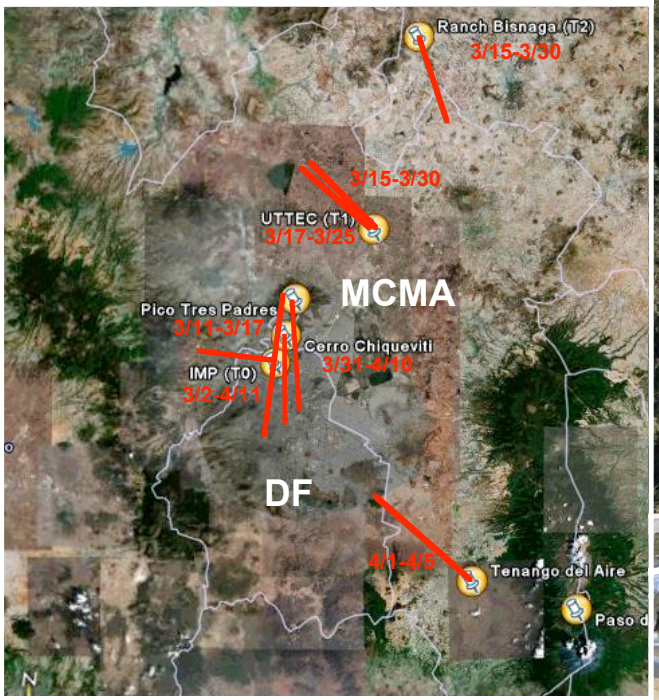
CSIC, Barcelona. Spain
CENICA, México D.F.

- Levels of secondary inorganic aerosols (SIA) were very similar at CENICA and T0. However, at T1 levels of $NO3^-$ were lower by ½, but levels of $SO4^{2-}$ were very similar;
- Levels of SIA in PM2.5 were only slightly reduced for $SO4^{2-}$ and $NO3^-$ in the urban sites;
- The crustal load was very high at T1 due to soil resuspension;
- Most of the anthropogenic elements (Zn. Cu. Pb. Sb. Cd. As) presented higher levels at the urban sites (T0 and CENICA), but particulate Hg levels were higher at T1, and levels of $SO4^{2-}$, $NH4^+$, V and Ni were very similar at all the sites

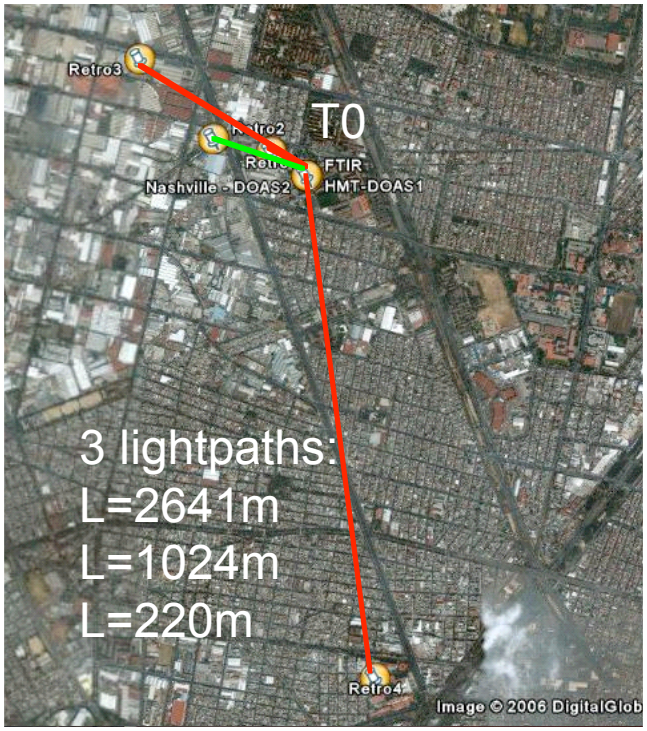
Open Path-DOAS and MAX-DOAS

Collaborators:
MCE2, MIT, UCSD, UH

Multi-Axes DOAS Network



Open-Path DOAS at T0



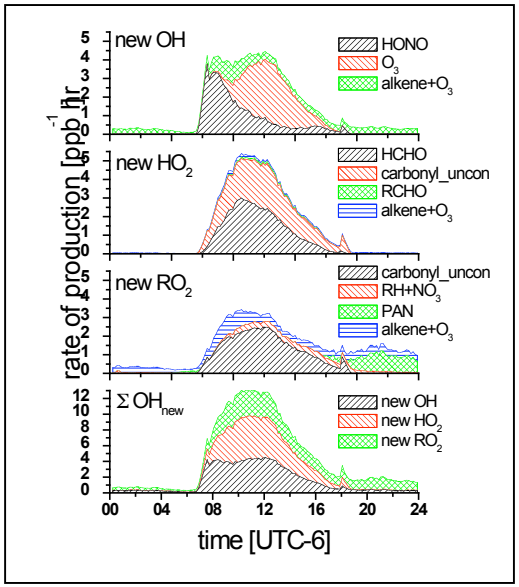
- Quasi-Lagrangian Pollution Transport
- Vertical, and horizontal gradients
- Planetary Boundary Layer height
- Satellite validation (NO2, HCHO, CHOCHO)

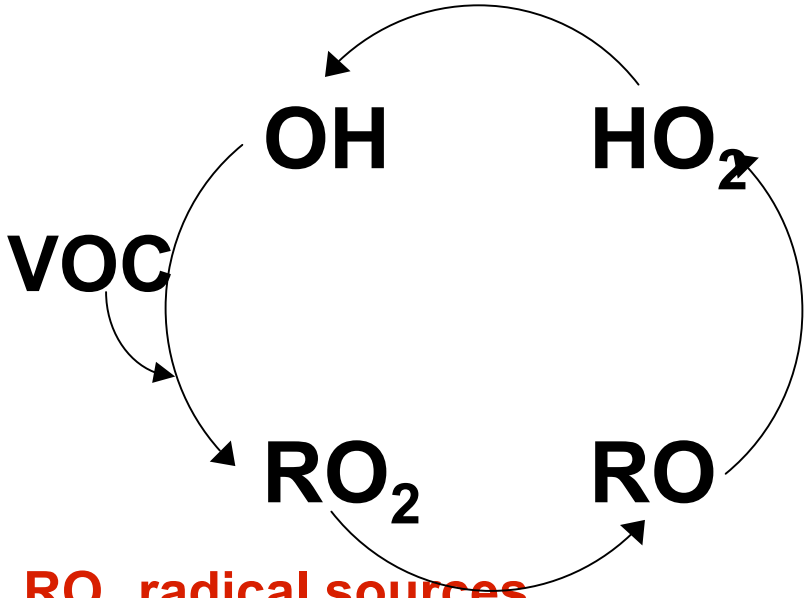
- Fast-photochemistry (HOx res, SOA prec)
- Glyoxal and Polycyclic Aromatic VOCs
- MAX-DOAS Validation
- Horizontal gradients

Assessing the Oxidative Capacity of the Atmosphere

Used MCMA-2003 datasets to constrain a photochemical box model

- study impacts of primary HOx production and ROx radical cycling on O3 production and oxidation of VOC relevant for SOA formation
- comparison with MCMA-2006 datasets

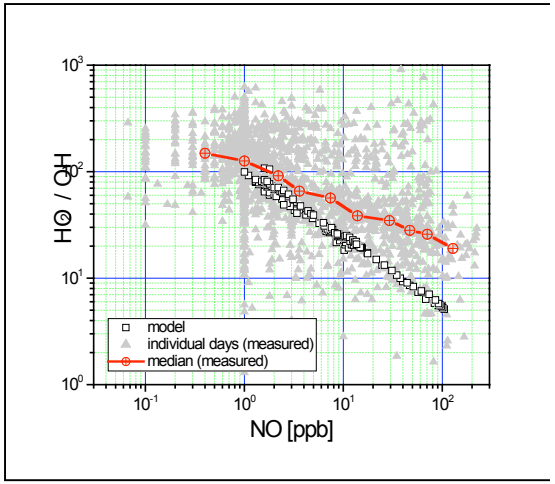




RO_x radical sources

vs.

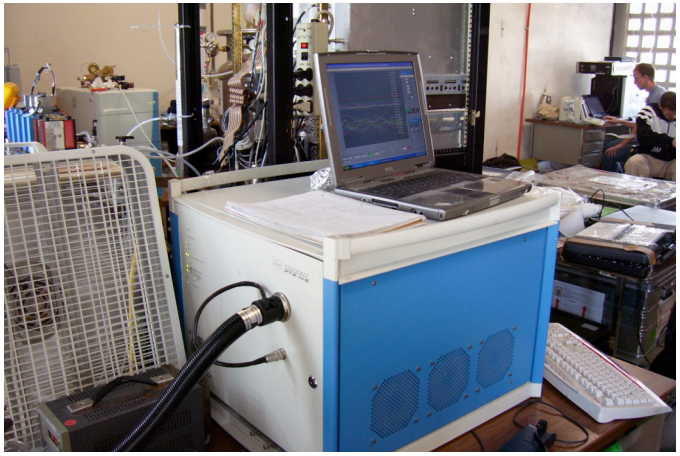
RO_x radical cycling

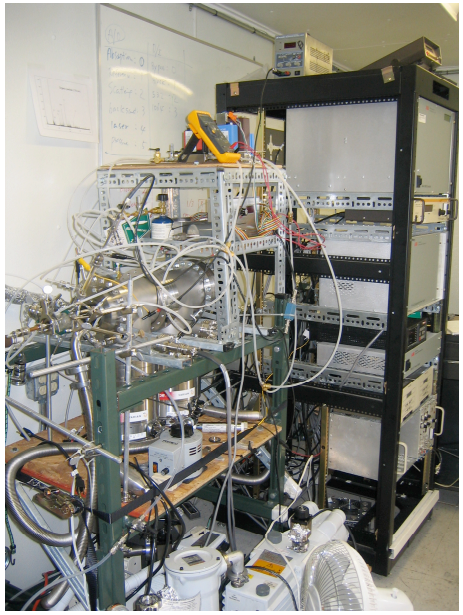


MIT, MCE2, UCSD, Indiana Univ, Penn State, PNNL, WSU

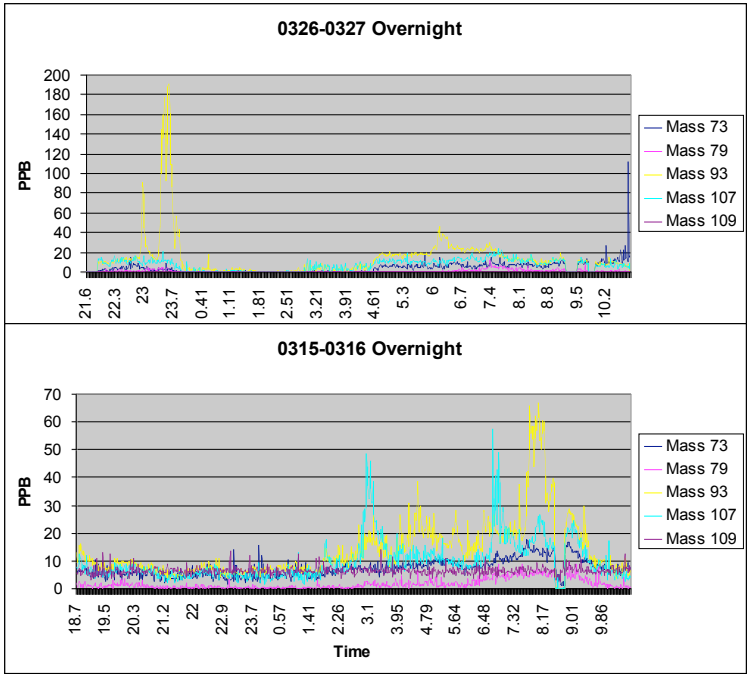
Ground Measurements of HNO3 and VOCs Using ID-CIMS and PTR-MS at the T0 Urban Site

Texas A&M (R. Zhang)





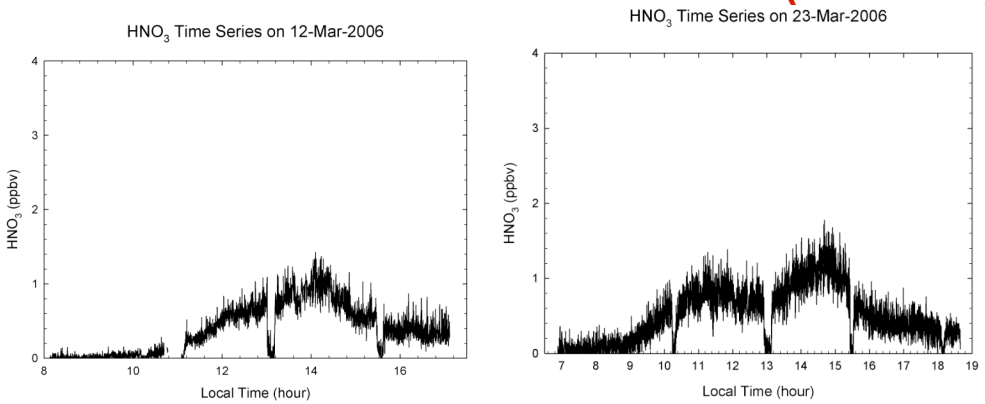
Proton Transfer Reaction MS (PTR-MS)



VOC data

Diurnal profiles of weekday and weekend/ holiday aromatic VOC concentrations clearly show the influence of rush hour traffic.

Ion drift - chemical ionization ms (ID-CIMS)

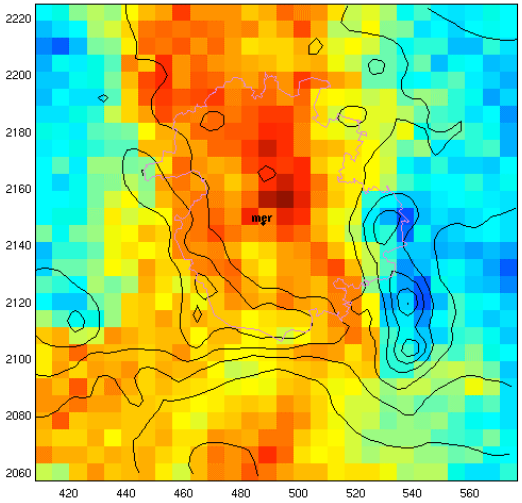


HNO3 daytime profile: peak early afternoon (0.5-3 ppbv)

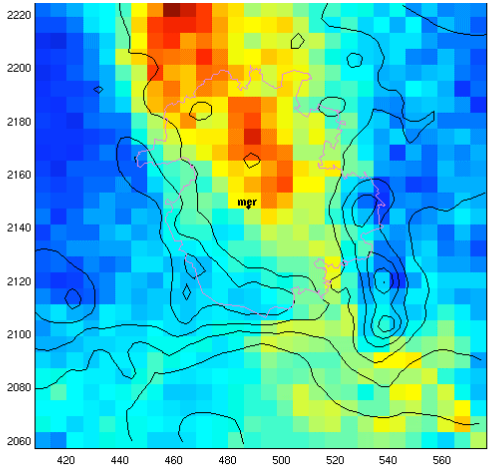
Concentration Field Analysis with Back-trajectories

Identify Potential Source Regions by combining time-series measurements with back-trajectories

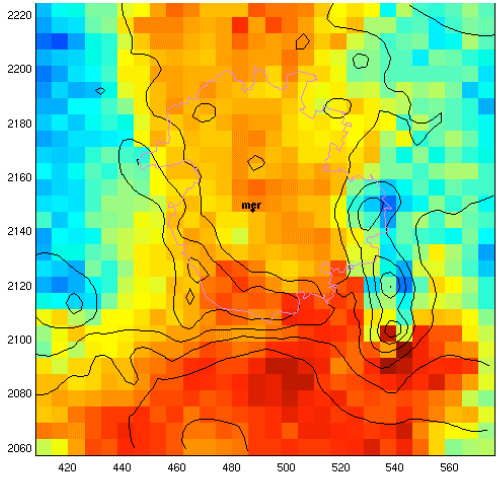
Carbon Monoxide



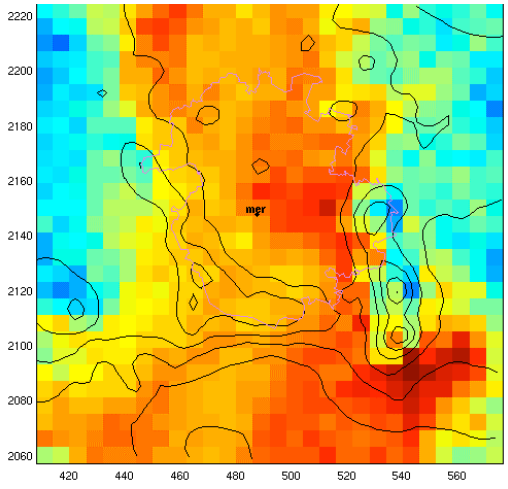
Sulfur Dioxide



PM10



PM2.5



MCE2, SLU modelers
Screenshot of trajectories at
http://mce2.org/
Also UNAM modelers

Method correctly identifies urban area as CO source.

Points to SO2 source near Tula

Urban Area is a large, diffuse source
Biomass burning on Eastern basin edge (esp. PM2.5)
Dust + Smoke from the South

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

Acknowledgements

Financial support

US: NSF, NASA, DOE/ASP

Mexico: CAM, SEMARNAT, CONACyT, PEMEX

Others: European funding agencies

Logistical support

INE/SEMARNAT, GDF/SMA, FUMEC, Customs, SRE, SEDENA, and many other Mexican institutions and agencies