Final Technical Report

Characterization of Fine Particulate Matter (PM) and Secondary PM Precursor Gases in the Mexico City Metropolitan Area

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Executive Summary

This project was one of three collaborating grants funded by DOE/ASP to characterize the fine particulate matter (PM) and secondary PM precursors in the Mexico City Metropolitan Area (MCMA) and to provide critical "ground truth" data necessary to interpret the comprehensive airborne data sets targeted by DOE and NCAR airborne instrument suites during the MILAGRO -2006 Campaign.

MILAGRO (**M**egacity **I**nitiative: **L**ocal **A**nd **G**lobal **R**esearch **O**bservations) is the first international collaborative project to measure the air pollutants generated and exported by megacities, using Mexico City as a case study. The overall effort of MCMA-2006, one of the four components, focused on i) examination of the primary emissions of fine particles and precursor gases leading to photochemical production of atmospheric oxidants and secondary aerosol particles; ii) measurement and analysis of secondary oxidants and secondary fine PM production, with particular emphasis on secondary organic aerosol (SOA), and iii) evaluation of the photochemical and meteorological processes characteristic of the Mexico City Basin.

The collaborative teams pursued the goals through three main tasks: i) analyses of fine PM and secondary PM precursor gaseous species data taken during the MCMA-2002/2003 field campaigns and preparation of archival publications based on these analyses; ii) planning of the MILAGRO Campaign and deployment of the instrument in and downwind of Mexico City, in support of the MAX-Mex/MILAGRO field campaigns in March, 2006;and iii) analysis of MCMA-2006 data and publication preparation.

The measurement phase of the MILAGRO Campaign was successfully completed in March 2006, with excellent participation from the international scientific community and outstanding cooperation from the Mexican government agencies and academic institutions.

The project reported here was led by the Massachusetts Institute of Technology/Molina Center for Energy and the Environment (MIT/MCE2) and coordinated with DOE/ASP-funded collaborators at Aerodyne Research Inc. (ARI), University of Colorado at Boulder (CU) and Montana State University (MSU). Documented findings from this project have been published in special issues of Atmospheric Chemistry and Physics (ACP), as well as in other peer-reviewed journals. Currently 24 papers have been published in ACP and a few more have been submitted.

The results from the collaborative project have improved significantly our understanding of the meteorological and photochemical processes contributing to the formation of ozone, secondary aerosols and other pollutants. Key findings from the MCMA-2003 include a vastly improved speciated emissions inventory from on-road vehicles: the MCMA motor vehicles produce abundant amounts of primary PM, elemental carbon, particle-bound polycyclic aromatic hydrocarbons, carbon monoxide and a wide range of air toxics, including formaldehyde, acetaldehyde, benzene, toluene, and xylenes; the feasibility of using eddy covariance techniques to measure fluxes of volatile organic compounds in an urban core, which proved to be a valuable tool for validating local emissions inventory; a much better understanding of the sources and atmospheric loadings of volatile organic compounds; the first spectroscopic detection of glyoxal in the atmosphere; a unique analysis of the high fraction of ambient formaldehyde from primary

emission sources; characterization of ozone formation and its sensitivity to VOCs and NOx; a much more extensive knowledge of the composition, size distribution and atmospheric mass loadings of both primary and secondary fine PM, including the fact that the rate of MCMA SOA production greatly exceeded that predicted by current atmospheric models; evaluations of significant errors that can arise from standard air quality monitors for ozone and nitrogen dioxide; and the implementation of an innovative Markov Chain Monte Carlo method for inorganic aerosol modeling as a powerful tool to analyze aerosol data and predict gas phase concentrations where these are unavailable.

During the MCMA-2006/MAX-MEX/MILAGRO Campaign the collaborative team utilized a combination of central fixed sites and a highly capable mobile laboratory deployed throughout the MCMA to representative urban and boundary sites in order to measure trace gases and fine particles. Analysis of the extensive 2006 data sets has confirmed the key findings from MCMA-2002/2003; additionally MCMA-2006 provided more detailed gas and aerosol chemistry and wider regional scale coverage. Key results include an updated 2006 emissions inventory used for air quality modeling; extension of the flux system to measure fluxes of fine particles in addition to VOCs and CO2; better understanding of the sources and apportionment of aerosols, including the contribution from biomass burning and industrial sources; a comprehensive evaluation of metal containing particles in a complex urban environment, highlighting unique characteristics that give powerful insights into their origin; identification of a close correlation between the rate of production of SOA and "Odd Oxygen" (O3 + NO2) and primary organic PM with CO in the MCMA urban plume; a more sophisticated understanding of the relationship between ozone formation and ozone precursors: while ozone production in the urban area is VOC-limited, the response is mostly NOx-limited in the surrounding mountain. Comparison of the findings from 2003 and 2006 also confirm that the VOC levels have decreased during the three-year period, while NOx levels remain the same.

The results from the 2002/2003 and 2006 have been presented at international conferences and communicated to Mexican government officials. In addition, a large number of graduate students and post-doctoral associates were involved in the project. All data sets and publications are available to the scientific community interested in evaluating the impact of urban emissions on human health, ecosystem viability, and climate change.

1. Introduction

Megacities (urban areas with over 10 million populations) present a major challenge for the global environment. Well-managed, densely populated settlements can reduce the need for land conversion and provide proximity to infrastructure and services. However, many urban areas experience uncontrolled sprawl and their activities are the leading cause of environmental problems. Population growth and increasing industrialization have resulted in a higher demand for energy, greater use of fossil fuels, and more emission of pollutants into the atmosphere. (see reviews by Molina and Molina, 2004; Molina et al., 2004). There is growing recognition that these airborne emissions from major urban and industrial areas influence both air quality and climate change ranging from regional up to continental and global scales.

MILAGRO (**M**egacity **I**nitiative: **L**ocal **A**nd **G**lobal **R**esearch **O**bservations) is the first international collaborative project to measure the air pollutants generated and exported by megacities. The Mexico City Metropolitan Area (MCMA) – the second largest megacity in the world – was selected as the initial case study for MILAGRO.

The Mexico City metropolitan area is the largest megacity in North America. Its recent rapid population growth and fast changing transportation and industrial sectors are representative of many large urban areas in developing countries. However, unlike most developing world megacities, it features an extensive and modern Mexico City Ambient Air Monitoring Network (RAMA) and has been the subject of recent major field campaigns designed to characterize its emissions and atmospheric chemistry [Molina and Molina, 2002]. Previous research on air pollution associated with the MCMA provided a framework for the planning of MILAGRO, particularly the MCMA-2003 Campaign, sponsored by the Mexican Metropolitan Environmental Commission and coordinated by the Integrated Program on Urban, Regional and Global Air Pollution, an interdisciplinary program initiated at the Massachusetts Institute of Technology (MIT) to address the air pollution problems derived from human activities in large cities (Molina and Molina, 2002).

More than 150 institutions from Mexico, the United States and Europe -- with over 450 investigators and technicians from 30 different nationalities -- participated in the MILAGRO campaign, organized under four components:

- MCMA-2006 (Mexico City Metropolitan Area – 2006 Experiment) - examined emissions and boundary layer concentrations within the Mexico City Basin, their transport and transformation in the atmosphere, and the effects on human health. MCMA-2006 was led by the Molina Center on Energy and the Environment (MCE2) with projects sponsored by U.S. National Science Foundation (NSF), U.S. Department of Energy (DOE), and several Mexican research agencies, including Comisión Ambiental Metropolitana (CAM), Instituto Nacional de Ecología (INE), Consejo Nacional de Ciencia y Technología (CONACyT) and Petróleos Mexicanos (PEMEX), as well as European agencies -
- MAX-Mex (Megacity Aerosol Experiment in Mexico City) - focused on examining how the Mexico megacity aerosol plume would evolve during transport, and how the chemical and physical nature of the aerosol effected scattering and absorption by the aerosol.

MAX-Mex was conducted by the Atmospheric Science Program of the DOE Climate Change Research Division in collaboration with the scientists supported by NSF, NASA, and Mexican agencies.

- MIRAGE-Mex (Megacity Impacts on Regional and Global Environments Global Environments) - examined the chemical/physical transformations of gaseous and particulate pollutants exported from Mexico City, as a case study of megacities' effects on regional and global atmospheric composition and climate. MIRAGE was led by National Center for Atmospheric Research (NCAR) with projects sponsored by NSF.
- INTEX-B (Intercontinental Chemical Transport Experiment – Phase B) – led by NASA - was an integrated field campaign designed to understand the transport and transformation of gases and aerosols on transcontinental/intercontinental scales and to assess their impact on air quality and climate.

The initial phase of the Campaign was to conduct measurement of pollutants, which took place during March 2006. The measurements included a wide range of instruments at ground sites, on aircraft, and satellites. Three supersites were set up at the Instituto Mexicano del Petróleo (IMP, "T0"), Universidad Tecnológica de Tecámac in the State of Mexico ("T1") and Rancho La Bisnaga, north of Tizayuca in the State of Hidalgo ("T2"). The designations "T0", "T1", and "T2" refer to transport of the urban plume to different points in space and time. Additional platforms in or near Mexico City include mobile vans containing scientific laboratories and mobile and stationary upward-looking lasers (lidars). Figure 1 shows the ground-based measurement sites.

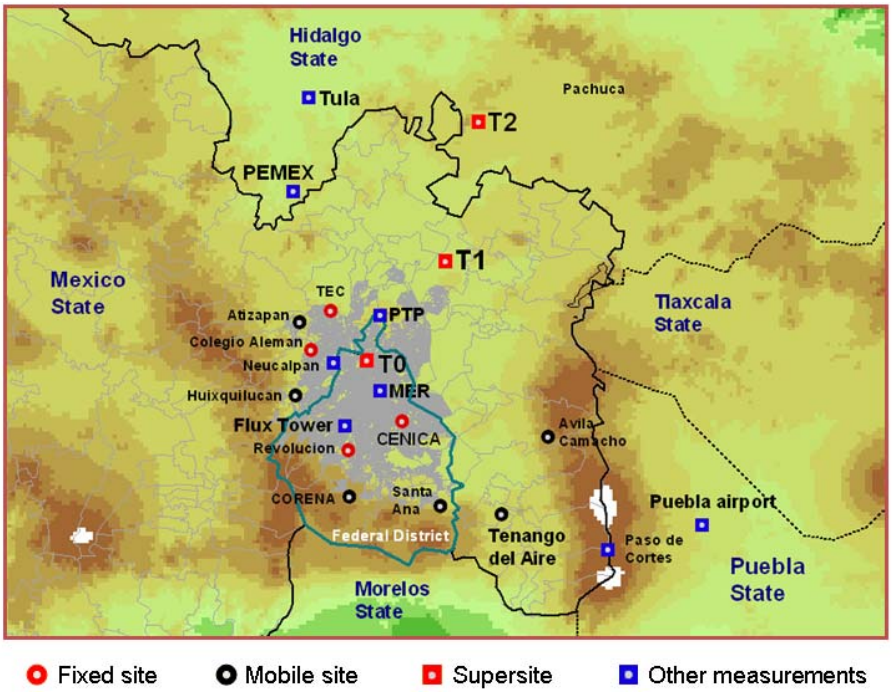

Figure 1. MCMA-2006: Ground-Based Measurement Sites

Seven instrumented research aircraft participated in MILAGRO: five were based in Veracruz, Mexico, and one in Houston, Texas. These airborne measurements provided information about the atmosphere over a large region, and at various altitudes. Satellite-based instruments peered down into the atmosphere, providing even larger geographical coverage.

The project reported here was led by the Massachusetts Institute of Technology/Molina Center for Energy and the Environment (MIT/MCE2) and coordinated with DOE/ASP funded collaborators at the Aerodyne Research Inc. (ARI), University of Colorado at Boulder (CU) and Montana State University (MSU).

Our collaborative team has three major tasks:

1) Analyses of fine particulate matter (PM) and secondary PM precursor gaseous species data taken during the MCMA-2002/2003 field campaigns and preparation of archival publications based on these analyses. The photochemical and meteorological modeling was used in planning the MILAGRO Campaign.
2) Planning of the MILAGRO Campaign and deployment of the instrument in and downwind of Mexico City for MCMA-2006 field campaign, in support of the MAX-Mex/MILAGRO field campaigns in March, 2006;
3) Analysis of MCMA-2006 data and preparation of archival publications.

The scientific goals for MCMA-2006 field measurements were to:

1) characterize primary and secondary fine PM and precursor gases at T0 and other urban supersites and selected downwind sites as thoroughly as possible;
2) compare fleet averaged motor vehicle emissions and selected ambient fine PM properties and tracer/PM precursor gases measured in MCMA-2002/2003 with those measured during MCMA-2006;
3) assess our understanding of the photochemical and meteorological processes characteristic of the Mexico City Basin.

In the following sections, we present accomplishments in our field measurement, data analysis and modeling activities in and around the MCMA undertaken by our team at MIT/MCE2/UCSD, which includes B. de Foy (currently affiliated with Saint Louis U.), R. Volkamer (currently affiliated with University of Colorado), W.F. Lei, P. Sheehy, N.F. Bei, J. Song, E. Velasco, M. Zavala, K. Johnson, and R. Gonzalez. Most of the analyses undertaken and manuscripts prepared or under preparation are collaborative efforts with our research partners at Aerodyne Research Inc., C.E. Kolb and his team; University of Colorado, J.L. Jimenez and his students; and Montana State University, B. Knighton and his students. Some of the analysis and manuscripts also include working with other groups that participated in the MCMA-2003 and/or MCMA-2006 campaigns, including Ulrich Platt and his team at the University of Heidelberg (UH), B.K. Lamb and colleagues at Washington State University (WSU), L. Marr at Virginia Polytechnic Institute (VPI), J. Gaffney and N. Marley at University of Arkansas, Little Rock (UALR), A. Laskin, J. Barnrad, J. Fast and their colleagues at PNNL, M. Guilles at LBNL, S. Pandis and his team at CMU and U. Patra, K. Prather at UCSD, P. Stevens at Indiana University, R. Zhang at Texas A&M, B. Cardenas and her team at Centro Nacional de Investigación y Capacitación Ambiental (CENICA), V.H. Paramo and his team at Gobierno de Distrito Federal (GDF), D.

Salcedo at the Universidad Autonoma del Estado de Morelos (UAEM), M. Grutter and A. Garcia at Universidad Nacional Autonoma de Mexico UNAM, G. Sosa and his colleagues at IMP, B. Galle and his team at Chalmers University, as well as other Mexican, European and US colleagues indicated below.

2. Planning for the MILAGRO Campaign

Our planning for the MILAGRO Campaign included providing emissions inventory, campaign data and key results from the MCMA-2002/2003 campaigns to MILAGRO collaborators; organizing three trips (April, July and September) to Mexico for operational planning and site visits with colleagues from DOE and NCAR; and preparing the equipment for deployment in Mexico City. The trips to Mexico have achieved the following objectives: (a) confirmed the three ground-based measurement supersites: T0 at IMP, T1 at Universidad Technologica de Tecamac in the State of Mexico, and T2 at Rancho la Bisnaga in the State of Hidalgo; (b) confirmed the Veracruz airport as the aircraft operation site; (c) informed the Mexican agencies of MILAGRO activities and secure their collaboration and cooperation; (d) exchange of ideas and information with our Mexican colleagues.

Prior to the field campaign, modeling analyses were being used in planning the MILAGRO campaign. Extensive meteorological modeling of the MCMA-2003 field campaign was carried out to prepare for modeling and forecasting of the MILAGRO campaign, analysis of potential ground inflow/outflow measurement sites, coordination of forecasting plan with other modeling groups and survey of experimental groups for user requirements.

The Molina Center provided local logistical coordination for the various meetings and site visits prior to the campaign. Many Mexican government agencies and officials provided support in the planning and operation of the MILAGRO Campaign. Collaboration with officials and researchers from the Mexican government agencies and local institutions was instrumental in the success of the field campaigns. They provided logistical support, e.g., ordering of the consumables, installation of power outlets, transporting the researchers and instruments, escorting the mobile lab and preparing the required documents to ship the equipment to and from Mexico. They also provided the US participants with access to existing data and knowledge of local circumstances, and facilitate research activities.

During the MILAGRO campaign, in addition to contributing to the daily forecasting briefing, the MIT/MCE2 team also prepared daily short summary of the forecast specifically for the ground sites in and around the MCMA and made available to all the ground-site investigators, as well as fielding queries from individual groups and tailoring the forecasts to different needs, particularly with the Aerodyne Mobile Laboratory, the Controlled Meteorological balloons (CMET) and the remote sensing measurements of the Chalmers (Sweden) group.

3. Analysis of MCMA-2003 Data Sets and Preparation of Manuscripts

The second project goal was to expedite analyses of data and associated publications from the MCMA-2002/2003 campaigns, a joint effort of MIT Mexico City Program and the Mexican Metropolitan Environmental Commission to update and improve the MCMA emissions

inventory and the current knowledge of the chemistry, dispersion and transport processes of the pollutants emitted to the MCMA atmosphere (Molina and Molina, 2002).

The campaign was carried out during April 2003 to cover the height of the annual photochemical season just prior to the onset of the rainy season. It involved a highly instrumented supersite located at CENICA, which is located on the campus of Universidad Autonoma Metropolitana in Iztapalapa (UAM-I). CENICA is a component of the National Institute of Ecology (INE) of the Ministry of the Environment, with state-of-the-art instrumentation contributed by many US and European teams. A mobile laboratory (from ARI) was deployed for measurements at various locations in the MCMA. In addition, extensive meteorological data and a wide range of chemical data were collected by collaborating Mexican research groups.

A special session on the MCMA-2003 Campaign was convened at the 2004 American Geophysical Union (AGU) Fall Meeting in San Francisco and a Special Issue of the MCMA-2003 Campaign was set up in Atmospheric Chemistry and Physics (ACP). To date, the field campaign has resulted in the publication of more than 50 peer-reviewed articles. Some of the manuscripts were prepared in time to support the planning for the MCMA-2006/MAX-Mex/MILAGRO deployments. An overview article on the MCMA-2003 has been published by Molina et al. (2007 – Paper #14).

In the following, we describe the results and work in progress of the MIT/MCE2-led studies, in coordination with our collaborative team from ARI/MU, CU as well as other collaborators. The paper number corresponds to the list of publications resulting from this project.

3.1. Aerosol composition and source apportionment

Aerosols play an important role in the atmosphere but are poorly characterized, particularly in urban areas like the Mexico City Metropolitan Area. Size-segregated samples of PM2.5 were collected during MCMA-2003 for compositional analysis and source apportionment by MIT and PNNL teams. Proton-Induced X-ray Emission (PIXE), Proton-Elastic Scattering Analysis (PESA) and Scanning Transmission Ion Microscopy (STIM) techniques were employed to determine concentrations of 19 elements from Na to Pb, hydrogen, and total mass, respectively. The most abundant elements from PIXE analysis were found to be S, Si, K, Fe, Ca, and Al. Positive matrix factorization (PMF) analysis indicates that the major emissions sources associated with these elements were industry, wind-blown soil, and biomass burning. The results for the first two sources are consistent with previous studies of refractory species in the MCMA, while the contribution of biomass burning to these elements had not been clearly identified before. Wind trajectories suggest that metals associated with industrial emissions came from northern areas of the city whereas soil aerosols came from the southwest and increased in concentration during dry conditions. Elemental markers for fuel oil combustion V and Ni correlated with a large SO_2 plume to suggest an anthropogenic, rather than volcanic, emissions source. By subtracting major components of soil and sulfates determined by PIXE analysis from STIM total mass measurements, we estimate that approximately 50% of non-volatile $PM_{2.5}$ consisted of carbonaceous material. A manuscript describing this analysis has been published [Paper #5 - Johnson et al., 2006].

3.2. Comparisons of PIXE/PESA and AMS aerosol analysis during MCMA-2003

Field measurements to quantify and characterize atmospheric aerosols present many challenges. The complexity and variety of aerosol components, their transport, and chemical reactivity often require a multifaceted approach. Employing different measurement techniques provides a wealth of information, yet requires an understanding of the comparability among these different approaches. The collocation of a DRUM impactor used for PIXE and PESA bulk aerosol sample collections (see Sect 3.1), and an AMS at the MCMA-2003 supersite provided a unique opportunity for these inter-comparisons.

PIXE/PESA and AMS employ fundamentally different analytical approaches, yet provide remarkably complementary data. PIXE is a highly sensitive and efficient means to analyze the elemental composition of bulk samples of atmospheric aerosols consisting of irradiation of the sample with energetic protons, causing emission of X-rays characteristic of elements present in the sample. PESA provides hydrogen mass concentrations by simultaneous detection of forward proton scattering. PIXE/PESA are performed under vacuum and provide individual element concentrations at a time resolution of several hours. By contrast, the AMS provides real-time size and composition information for submicron aerosols on the order of minutes to seconds.

Good agreement was observed for mass concentrations of PIXE-measured sulfur (assuming it was dominated by SO_4^{2-}) and AMS-measured sulfate during most of the campaign. PESA-measured hydrogen mass was separated into sulfate H and organic H mass fractions assuming the only major contributions were $(NH_4)_2SO_4$ and organic compounds. Comparison of the organic H mass with AMS organic aerosol measurements indicates that about 75% of the mass of these species evaporated under vacuum. However ~25% of the organics does remain under vacuum, which is only possible with low vapor pressure compounds, and which supports the presence of high molecular weight and/or highly oxidized organics consistent with atmospheric aging. Approximately 10% of the chloride detected by AMS was measured by PIXE, possibly in the form of metal-chloride complexes, while the majority of Cl was likely present as more volatile species including NH_4Cl. This is the first comparison of PIXE/PESA and AMS, and to our knowledge also the first report of PESA hydrogen measurements for urban organic aerosols.

This study was done in collaboration with CU, PNNL and UAEM; it has been published in Environ. Sci. Tech. (Paper #19 - Johnson et al., 2008)

3.3. Characterization of on-road vehicle emissions in the MCMA using Mobile Lab

The ARI mobile lab was used extensively during MCMA-2002/2003 to determine motor vehicle exhaust emissions by intercepting individual vehicle exhaust plumes, either from random on-road traffic encounters or from selected vehicle types in chase mode under real world driving conditions. Trace gas and fine particle component exhaust emission indices can be determined from the ratio of excess pollutant to excess CO_2 ratio for each exhaust plume. Analyses of a large number of random traffic plumes yield fleet average emission indices, while analyses of multiple plume encounters for vehicles measured in chase mode yield vehicle class emission distributions as a function of vehicle driving state.

Two manuscripts describing the results from these analyses were published in the MCMA-2003 special issue. One manuscript [Paper #1 - Jiang et al., 2005] analyzed on-road data from relatively slow response (>10s) instruments to produce vehicle emission inventories for black carbon, particle bound polycyclic hydrocarbons (PAHs), hydrocarbons, CO and NOx. The other manuscript [Paper 9 - Zavala et al., 2006] presented on-road emission ratios to exhaust CO_2, which allow the calculation of fuel-based emission indices and total annual emissions for a variety of gaseous exhaust species, including NO_x, NO_y, NH_3, HCHO, CH_3CHO, and selected aromatic VOCs for a full range of major vehicle types at various on-road speed intervals.

The Zavala et al. paper revealed very high levels of HCHO and CH_3CHO emissions from the MCMA fleet, providing a major source of early morning radicals to "jump-start" the city's photochemistry. This topic was further addressed in Garcia et al. [2006], which used ambient glyoxal concentrations, as novel tracer of photochemical activity, along with CO, an exhaust emissions tracer, to estimate that primary (vehicular) emissions were responsible for as much ambient HCHO near the MCMA urban core as the photochemical secondary HCHO source. In addition, Velasco et al. (2007 – paper #11) aggregated mobile laboratory real-time and canister sampled VOC measurements with similar data from a central fixed site to assess the concentration and spatial distributions, diurnal patterns and reactivities of ambient VOCs, allowing an insightful evaluation of the VOC emission inventories for the MCMA. These papers are important for assessing and choosing accurate inputs for photochemical models to evaluate and explain MCMA air quality (see Sect 3.9). The above three studies were done in collaboration with VPI, ARI, MSU, WSU, PNNL and UNAM.

3.4. MCMA ambient nitrogen oxide and ozone measurements

The values of NO, NO_2, and O_3 measurements from standard chemiluminescent NO_x, instruments, standard UV O_3 absorption instruments aboard the mobile lab and at fixed sites near the mobile lab have been inter-compared with the open path DOAS measurements at CENICA and the TILDAS NO_2 instrument on-board the mobile lab. Significant measurement problems with the standard air quality instruments were revealed. The chemluminescent NO_2 measurements were much too high during periods of intense photochemical activity, due to the presence of organic nitrate interference. On-road UV absorption ozone measurements were shown to be much too high in the presence of high levels primary fine PM from vehicles. Two manuscripts describing these measurement problems were published in ACP [Papers # 8 & 13 - Dunlea, 2006; 2007] in collaboration with ARI, WSU, GDF, CENICA, UNAM and UALR.

3.5. Secondary organic aerosol (SOA) formation from anthropogenic air pollution

The atmospheric chemistry of VOCs in urban areas results in the formation of 'photochemical smog', including secondary organic aerosol (SOA). State-of-the-art SOA models parameterize the results of simulation chamber experiments that bracket the conditions found in the polluted urban atmosphere. Analysis of the data obtained during the MCMA-2003 Campaign shows that in the real urban atmosphere reactive anthropogenic VOCs (AVOCs) produce much larger amounts of SOA than these models predict, even shortly after sunrise. Contrary to current belief, a significant fraction of the excess SOA is formed from first generation AVOC oxidation

products. Global models consider AVOCs as a very minor contributor to SOA compared to biogenic VOCs (BVOCs). If our results are extrapolated to other urban areas, AVOCs could be responsible for additional 3-21 Tg yr^{-1} SOA production globally, and could cause up to -0.1 Wm^{-2} additional top-of-the-atmosphere radiative cooling..

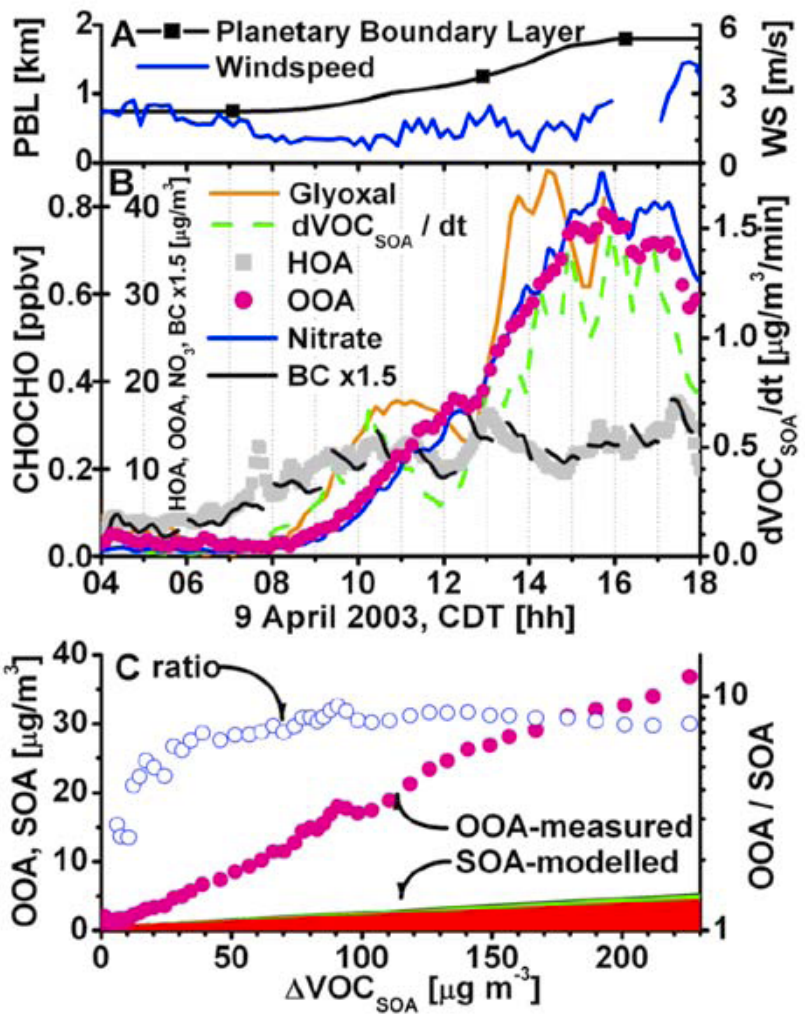

Figure 2 (left) shows the results of a case study in Mexico City during a day with low initial concentration and in which (to a good approximation) chemical production dominated the changes in the time series of concentrations of secondary species until ~2 pm. This was possible since horizontal advection was limited, while the effect of vertical mixing was taken into account using three consistent estimates of the boundary layer evolution. The bottom panel shows that a state-of-the-art SOA model under-predicted the observed SOA by a large factor shortly after sunrise, reaching a factor of 8 by the end of the day.

This work was done in collaboration with CU, ARI, and UAEM and a manuscript has been published [Paper # 10 - Volkamer et al., 2006].

3.6. Missing sink for gas-phase glyoxal in Mexico City: Formation of SOA

During the MCMA-2003 Campaign, we demonstrated the first direct spectroscopic detection of glyoxal (CHOCHO) in the atmosphere using Differential Optical Absorption Spectroscopy (DOAS) [Volkamer et al., 2005]. Glyoxal is a novel indicator molecule for active photochemistry of VOCs on global scales. In order to represent glyoxal in models a detailed understanding of sources and sinks is needed. The budget of gas-phase glyoxal has not been studied directly to date. Our earlier work (see Sect 3.5) demonstrated large gaps exist in the current understanding of the timing and amounts of SOA produced from anthropogenic VOC

precursors in Mexico City. One possible explanation is that the lab data on which the models are based do not capture all the chemistry involved in SOA formation.

We compared the direct measurements of gas-phase glyoxal in Mexico City to experimentally constrained model predictions calculated from a lower limit rate of glyoxal production, known gas-phase sink reactions, and dilution from meteorology. The observed glyoxal is significantly below that predicted. The discrepancy between glyoxal concentrations measured and the model predications can be explained by a sink parameterized from aerosol parameters as either (1) irreversible uptake to aerosol surface area (uptake coefficient $\gamma \approx 0.0035$), or (2) reversible uptake to aerosol liquid water (effective Henry's law coefficient $H_{eff} \approx 4 \times 10^9$ M/atm), or (3) a combination of (1) and (2). Under the first assumption, the corresponding loss-rate supersedes rapid gas-phase losses, and strongly affects glyoxal lifetime throughout the day. Glyoxal mass accumulated via either sink corresponds to several $\mu g\ m^{-3}$ of equivalent SOA mass, and can explain 15% to 25% of the SOA formation in Mexico City. This work was done in collaboration with CU and UAEM; it has been published [Paper #16 - Volkamer et al., 2007a].

3.7. Meteorological Modeling

Following the analysis of the meteorological conditions during the MCMA-2003 field campaign (de Foy et al., 2005), detailed mesoscale meteorological modeling was carried out using the MM5 model [Paper #2 - de Foy et al., 2006a]. High resolution land surface data was used from satellite remote sensing in order to better represent the surface heat budget and hence the thermally driven wind patterns in the basin. The MODIS sensor on board the Terra and Aqua satellites pass over the MCMA four times a day with measurements at 36 frequencies and 1-km resolution. This provides detailed land use database, vegetation fractions, surface albedo, surface emissivity and surface (skin) temperature. Adjusting these parameters and using the NOAH Land Surface Model, which is the most up-to-date option in MM5, makes a bigger difference in model results than many other techniques for improving model simulations. This is particularly true with regards to data assimilation and boundary layer schemes.

In order to prepare for modeling and forecasting of the MILAGRO field campaign, extensive meteorological modeling of the MCMA-2003 field campaign was carried out. The model wind fields were used in combination with surface measurements to analyze the different wind convergence patterns in the basin and to explore some of the driving mechanisms. Certain days were found to have east-west convergence lines that moved northwards from the Chalco passage. Other days had north-south convergence lines that remained more stationary due to the competing effect of the Chalco jet and the flow over the basin rim. The reduced movement of the convergence line for these cases led to increased levels of air pollutants in the urban area. The first case corresponded to previous research following the IMADA campaign. This had focused on the thermal forcing due to heating differentials across the basin rim. During the MCMA-2003 field campaign however, the thermal forcing was found to be remarkably constant and the extent of the convergence line was therefore influenced by the wind direction aloft. The north-south convergence line was a new phenomenon that has not previously been studied but is of particular relevance given the growth of the city towards the north. This work has been published in ACP [Paper #3 - de Foy et al., 2006b].

The FLEXPART trajectory model was used to look at the basin venting, the origin of air in the basin and the fate of the urban plume. Ventilation was found to take place in less than 12 hours, with carry-over from day to day lower than 25%. The plume impacts are mainly to the northeast, with some venting to the south. This was described in greater detail as a function of meteorological episodes. Based on this work, a refined conceptual circulation model was developed combining the analysis from the MCMA-2003 meteorological analysis paper with the new insights from the particle trajectories, shown in Figure 3. This work has been published [Paper #4 - de Foy et al., 2006c].

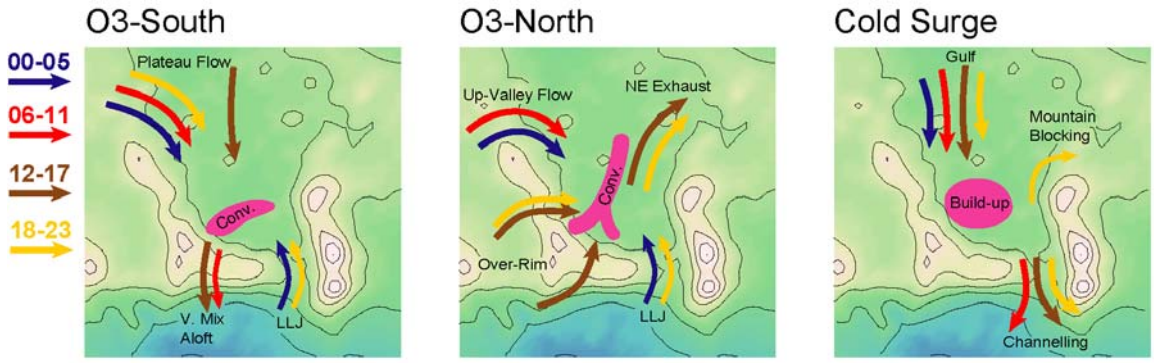

Figure 4. Circulation Model for the Mexico City basin for O3-South, O3-North and Cold Surge episode types. Arrows colored by time of day: early morning (0-5) in blue, morning (6-11) in red, afternoon (12-17) in brown and evening (18-23) in yellow. Plateau winds on O3-South days combine with vigorous mixing to transport the urban plume southwards of the mountains. A low level jet forms in the Chalco passage causing a convergence line in the south of the city. Strong westerly flow on O3-North days first enters the basin from the north-west but then comes over the south and west rims of the basin during the day. The combination with the low level jet forms a north-south convergence zone and exhaust of the basin to the north-east. On Cold Surge days strong northerly winds blow into the basin. Low mixing heights lead to pollutant accumulation in the city and channel flow through the Chalco passage.

The above studies were carried out in collaboration with A. Clappier (EPFL, Lausanne, Switzerland) and J.R. Varela (UAM-I, Mexico).

3.8. Inorganic aerosol modeling using a Markov Chain Monte Carlo Method

The MIT team used the equilibrium inorganic aerosol model ISORROPIA embedded in a Markov Chain Monte Carlo algorithm to develop a powerful tool to analyze aerosol data and predict gas phase concentrations where these are unavailable. The method directly incorporates measurement uncertainty, prior knowledge, and provides a formal framework to combine measurements of different quality. Using observations taken at three ground sites, i.e., a residential, industrial and rural site, during the MCMA-2003 campaign in Mexico City, the model is used to analyze the inorganic particle and ammonia data and to predict gas phase concentrations of nitric and hydrochloric acid.

In general, the model is able to accurately predict the observed inorganic particle concentrations at all three sites. The agreement between the predicted and observed gas phase ammonia

concentration is excellent. The NOz concentration calculated from the NOy, NO and NO2 observations is of limited use in constraining the gas phase nitric acid concentration given the large uncertainties in this measure of nitric acid and additional reactive nitrogen species.

The model predicted up to several ppb of gas-phase HCl during some periods (this species was not measured directly). The importance of the $Cl^{\cdot}$ radical to MCMA photochemistry appears to be very small, although the subject deserves further investigation since this chemistry cannot be fully constrained without measuring additional species. Inorganic PM modeling of the MCMA-2003 data results in fewer discrepancies with the data than those from previous campaigns (San Martini et al., 2005), likely due to the higher time resolution and reduced artifacts of the 2003 data and the lower influence of crustal species during MCMA-2003. Two manuscripts describing this study have been published [Papers # 6-7; San Martini, 2006a,b] with our collaborators at ARI, CU, UNAM.

3.9. Characterizing Ozone Production in the MCMA using Chemical Transport Model

The 3-D photochemical model Comprehensive Air Quality Model with extensions (CAMx) [Environ, 2003] implemented with the SAPRC-99 chemical mechanism [Cater, 2000] was employed to investigate the characteristics of ozone production in MCMA during an "O3-South" episode by examining the relationship between O_3 formation and precursors, which are important to understand the photochemical processes of O_3 formation and develop effective control strategies. Model results exhibit a scatter relationship between the O_3 production and ambient NO_x levels due to varying primary radical production under different NO_x levels. High O_x (O_3 + NO_2) photochemical production rates of 10-80 ppb/hr are predicted due to the high reactivity of VOCs in which alkanes, alkenes, and aromatics exert comparable contributions. The predicted ozone production efficiency is between 4-10 O_3 molecules per NO_x molecule oxidized, and increases with VOC-to-NO_2 reactivity ratio. Sensitivity studies suggest that O_3 formation in the MCMA urban region with less chemical aging (NO_z/NO_y < 0.4) is VOC-limited. Both the simulated behavior of O_3 production and its sensitivities to precursors suggest that mid-day O_3 formation during this episode is VOC sensitive in the urban region on the basis of the current emissions inventory. This study has been published [Paper #12 - Lei et al., 2006].

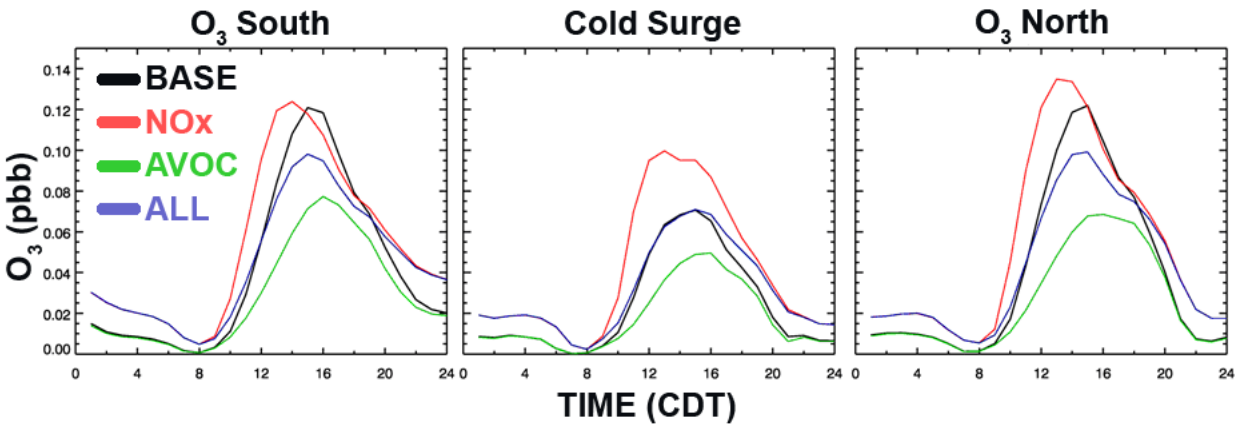

Figure 4 The response of near surface O_3 concentration to different emission reduction scenarios in the MCMA source region under different meteorological conditions identified during the MCMA-2003

Campaign: 0.5 NO_x denotes a 50% reduction in NO_x; 0.5 VOC denotes a 50% reduction in VOC; 0.5 ALL denotes 50% reductions in both NO_x and VOC emissions (Lei et al., 2008).

We have continued our study of the ozone photochemical production and response in the MCMA, and their evolutions to include the three meteorological conditions that occurred in Mexico City in MCMA-2003 ("O_3-South", "O_3-North" and "Cold-Surge") using the data sets generated from MCMA-2003. The main motivation was to investigate how the O_3 production and response will be affected by meteorology in the urban area, which is an important factor that must be considered in formulating emission control measures. We found that the conclusions from the "O3-South" category [Lei et al., 2007] hold for the other two meteorological categories, i.e., the urban O_3 production rate (P(O3) is higher than in most U.S. cities, particularly at high NO_x levels; midday O_3 production is VOC limited in the urban region, and an increase in NOx emissions leads to a reduction in the O_3 formation; the NOx-VOC sensitivity evolves with time during the day. As shown in Figure 4, the O_3 production rate in the urban area is moderately higher during the "O_3-North" episode than during the "O_3-South" episode, because the pollution plume undergoes more chemical ageing in the "O3-North" meteorological category. P(O3) is lower during the "Cold-surge" category because of frequent cloud cover, which leads to reduced photochemical activities. However, photochemical modeling for this meteorological condition turned out to be challenging, because the meteorological model has not captured the vertical mixing under wet conditions and frequent precipitation. A manuscript describing this study has been accepted for publication [Paper #18 – Lei et al., 2008].

3.10. Constraints on radicals and PM precursors using Master Chemical Mechanism

We have continued our study using the Master Chemical Mechanism (MCMv3.1) to perform a detailed analysis on radical sources and radical cycling in Mexico City as part of the MCMA-2003 campaign; these processes are important as they are the drivers for secondary pollutant formation, including ozone and SOA.

In part 1 of our work we presented a detailed analysis of RO_x (sum of OH, HO_2 and RO_2) radical sources for the near field photochemical regime inside the MCMA. The extensive set of measurements provides the means to calculate time resolved RO_x radical production rates from day- and night-time radical sources. Daytime radical production was found to be about 10-25 times higher than at night, and it does not track the abundance of sunlight. We found the 12-h average daytime contributions of individual sources to be remarkably heterogeneous: HCHO and O_3 photolysis, each about 20%; O_3/alkene reactions and HONO photolysis, each about 15%; unmeasured sources about 30%. The direct contribution of O_3/alkene reactions is moderately small; however, a source-apportionment analysis of ambient HCHO and HONO identifies O_3/alkene reactions as being largely responsible for jump-starting the processing of VOC and NO_x about 1-h after sunrise. The peak radical production was found to be higher than in any other urban influenced environment studied to date. Furthermore, we observed a marked difference with respect to the timing of radical production. A manuscript describing this analysis has been submitted to Atm. Chem. Phys. MCMA-2003 special issue (Volkamer et al., 2007b).

In part 2 of our work, we present a detailed analysis of the RO_x radical cycling processes. The MCMA-2003 campaign included measurements of OH and HO_2 radical concentrations, as well

as a total OH loss measurement. These measurements, coupled with the extensive VOC, NO_x, and meteorological parameters provide an opportunity to test the model's capacity to predict OH and HO_2. Both the OH and HO_2 diurnal profiles are predicted well; however, there is an under-prediction of radicals (particularly HO_2), i.e., missing reactivity, in the early morning hours. A manuscript describing this analysis has been submitted to Atm. Chem. Phys. MCMA-2003 Special Issue [Sheehy et al., 2008]

Our work with MCM is essential to elucidating the gas-phase mechanisms that lead to SOA formation. Because 75-80% of secondary aerosol forms as the result of the processing of primary pollutants, it is essential that we understand the gas-phase mechanisms in terms of oxidation and radical cycling. Our 2003 results indicate that there are inconsistencies between the predicted concentrations of radicals and the oxidative capacity compared to measurements. We will continue our MCM modeling studies using the rich data sets generated from MILAGRO 2006, similar to that of MCMA-2003, thus making inter-campaign comparisons possible. Furthermore, the combination of data from T0 and T1 supersites obtained from the MILAGRO campaign will provide us the means to extend our analysis to an inter-site comparison.

4. MCMA-2006/MAX-Mex Field Measurement Campaign

In the following sections we present the measurements taken at the supersites, flux tower and on board the ARI mobile lab during the MILAGRO Campaign in March 2006 and the subsequent analysis of the data and preparation of manuscripts. These activities were done in collaboration with our research partners at Aerodyne Research Inc., University of Colorado, Boulder at Boulder, Montana State University and other researchers mentioned in Section 1.

4.1. Spatial variability of VOC measurements during MCMA-2006/MILAGRO

4.1.1 Field measurements using Differential Optical Absorption Spectroscopy (DOAS)

Two active long-path DOAS instruments (LP-DOAS, use of an active light-source) were employed during the MCMA-2006 field campaign. In addition, 5 passive Multi-Axis (MAX) DOAS instruments (use of natural light source) were deployed at various locations throughout the Mexico City and the neighboring areas, forming a temporary monitoring network (see Figure 5). The objectives of the combined DOAS efforts were to constrain transport and physico-chemical transformation processes at the three supersites (quasi-lagrangian setup), and selected boundary sites of the Mexico City Metropolitan Area (MCMA). Furthermore, the MAX-DOAS measurements can be compared with the active DOAS measurements at T0 and satellite observations.

The two LP-DOAS -- HMT-DOAS and Nashville-DOAS -- were both located at T0 and measured a number of compounds, including NO_2, O_3, NO_3, SO_2, H_2O, volatile organic compounds (VOC, i.e., toluene, benzene, and m-,p-,o-xylene), HOx precursors (i.e., HONO and HCHO), polycyclic aromatic hydrocarbons (PAHs, i.e., naphthalene), and glyoxal, a mutagenic product of VOC oxidation. The HMT-DOAS measured over two light paths of ~250 and 1026 m in the northwesterly direction from T0 and was operated at three wavelengths (260, 290 and 354 nm). Nearly 50,000 spectra were collected over 30-day period with ~1 min time resolution. The

Nashville-DOAS measured over a single light path of 2640 m in the southerly direction and was operated at four wavelengths (318, 357, 427, and 642 nm). Approximately 35,000 spectra were collected over the span of 25 days with ~1 min time resolution.

MAX-DOAS instruments observe scattered sunlight from a variety of viewing directions. The output of a DOAS measurement is the slant column density (SCD) which is the integrated concentration over the light path. In particular, high sensitivity for gases close to the ground is obtained for observation directions pointing slightly above the horizon. Moreover, under the assumption of a well mixed trace gas layer – the vertical extent of the trace-gas layer can be determined with good accuracy. The MAX-DOAS measurements were performed by five passive instruments. One was the so called "Schwampel" instrument consisted of three small telescopes pointing into different azimuth directions, which were perpendicular to each other and collected scattered sunlight simultaneously. Each of them could be individually adjusted by stepping motors to any elevation angle

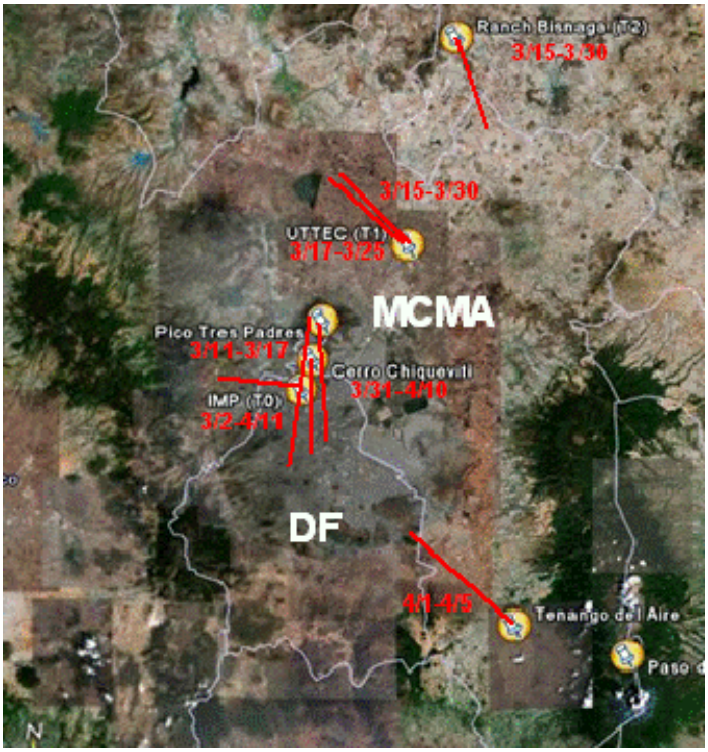

Figure 5. MAX-DOAS Network

between horizon and zenith. The sunlight was focused on quartz fiber bundles using quartz lenses before it reached a commercial spectrometer with 300-mm focal length (Acton model 300). The spectra were detected by a two-dimensional imaging CCD-detector (Andor model DV420-OE). The signals originating from the three telescopes reached the two-dimensional detector at well defined different areas which allowed them to be clearly separated afterwards. The spectrometer covered the wavelength range from about 330 to 470 nm and had a resolution of about 0.7 nm FWHM.

The others were portable devices -- Mini-MAX-DOAS -- which could be operated by a laptop computer for several hours independently from power supply. The Mini-MAX-DOAS devices contained a miniature crossed Czerny-Turner spectrometer/detector unit "USB2000" (Ocean Optics Inc.) with a resolution of 0.7 nm FWHM and a one-dimensional CCD-detector with 2048 pixels. Two devices covered the spectral ranges from about 290 to 430 nm, while one from about 330 to 460 nm. The spectrometer/detector unit was cooled to a stable temperature, which minimized changes in optical properties of the spectrometer while at the same time reduced the detector dark current. The sunlight was collected and focused by a quartz lens and was led into the spectrograph/detector unit by a quartz fiber bundle. To avoid condensation of water vapor, the instrument was sealed and a drying agent was included. An attached stepping motor enables

the adjustment of the viewing direction to a desired elevation angle ("elevation" is defined as the angle between the horizon and the pointing direction of the telescope).

Both types of instruments were fully automated to store the spectra and to control the pointing of the telescopes. While the Schwampel were deployed on the roof top of a building at T0 throughout the campaign, the Mini-MAX-DOAS devices were deployed at different sites over a certain period: at T1 (two instruments) and T2 from March 15 to 30; at Pico de Tres Padres from March 11 to 17; at Tenango del Aire from April 1 to 5; and at Cerro Chiquevite from March 31 to April 10. Except for the first half of March when the Mini-MAX-DOAS devices had to be repaired due to damage sustained during shipping and some minor breakdowns, the instruments worked steadily. During the campaign, nitrous acid (HONO) was detected at T0; this is the first time that HONO has been detected by passive DOAS in the atmosphere. Other trace gases measured include CHOCHO, NO_2, HCHO, and O_3.

4.1.2. Analysis of DOAS measurements

Following the campaign, we have conducted a quality assurance check of VOC measurements made at the T0 urban site during the MILAGRO-2006 Campaign. Our work compares point-sampling methods and continuous-sampling methods: VOC canisters were collected and co-located with measurements by Proton Transfer Mass Spectrometry (PTR-MS), Fourier-Transform Infrared Spectroscopy (FTIR), and DOAS. Further, we compare point-sampling with the LP-DOAS measurements over two light paths to investigate spatial gradients of aromatic VOCs. Similarly, we are analyzing a variety of plumes measured by both LP-DOAS and PTR-MS at T0, characterized by observations of very high toluene concentrations. The LP-DOAS analysis has yielded detection of tolualdehydes and the first-time direct detection in the atmosphere of methyl-naphthalene. The characterization of a VOC library at T0 is a prerequisite to conducting detailed photochemical box modeling using MCM (see Sect. 3.10).

We are currently continuing the analysis of the LP-DOAS measurements to investigate spatial gradients of aromatic VOCs, as well as the data from 5 passive Multi-Axis (MAX) DOAS instruments to measure quasi-Lagrangian pollution transport between T0, T1, and T2. We have used quasi-simultaneous observations of HONO, HCHO and CHOCHO concentrations at ground-level (by LP-DOAS) in combination with total vertical column measurements (by MAX-DOAS) to assess the vertical structure of radical production within the MCMA. Strong vertical gradients are observed for the concentrations of HONO during mid morning, indicating the existence of ground-level sources during the day. The current analysis of MAX-DOAS data focuses a comparison of our direct measurements of HONO with concentration measurements by a Chemical Ionization Mass Spectrometry instrument onboard the C-130 aircraft, which intercepted the airmass aloft T0 in various occasions. Integrating radical production rates over the height of the planetary boundary layer presents an extension of previous analysis of radical sources at ground-level (Volkamer et al., 2007b). Since the ozone production in Mexico City is radical limited, our work aims to identify the drivers of such processing to ultimately reduce peak concentrations of secondary pollutants like O_3 and SOA.

The DOAS field measurements and data analysis are part of an ongoing collaboration between MIT/MCE2 with Rainer Volkamer (MIT/UCSD, currently at CU) and Ulrich Platt (UH).

4.2. Flux measurements of trace gases, aerosols and energy from the urban core of the Mexico City Metropolitan Area

During the MCMA-2003 campaign, we demonstrated the feasibility of using eddy covariance (EC) techniques coupled with fast-response sensors to measure fluxes of VOCs and CO_2 from a residential district of Mexico City, where the spatial variability of surface cover, roughness and emission sources is high (Paper #11, Velasco 2007a). The measured fluxes for VOCs are in good agreement with the speciated EI developed by our group.

A second flux system was deployed in a different district of Mexico City during MCMA-2006. This system was located at the rooftop of SIMAT surrounded by congested avenues close to the center of the city. The number of VOCs was extended in 2006 using a disjunct eddy accumulation (DEA) system, which collected whole air samples as function of the direction of the vertical wind component; the samples were analyzed on site by gas chromatography/flame ionization detection. Based on our knowledge, this is the first time the DEA method was applied to measure turbulent fluxes from an urban environment.

The diurnal patterns for VOC and CO_2 in both the 2003 and 2006 studies were similar, but the 2006 fluxes showed higher magnitudes. This difference was due to the different characteristics of the monitored sites rather than an increase of the emissions over a 3-year period. The diurnal patterns of VOCs and CO_2 showed clear anthropogenic signatures, with important contributions from vehicular traffic. Fluxes of olefins and CO_2 were consistently higher on weekdays than on weekends as a result of increased traffic on weekdays. Toluene and methanol fluxes exhibited also strong influence from non-mobile sources. The benzene flux showed a strong and constant correlation with CO_2, with similar ratios to those observed previously for vehicle exhaust by the ARI mobile laboratory. In contrast, the correlation between toluene and CO_2 was neither strong nor constant throughout the day.

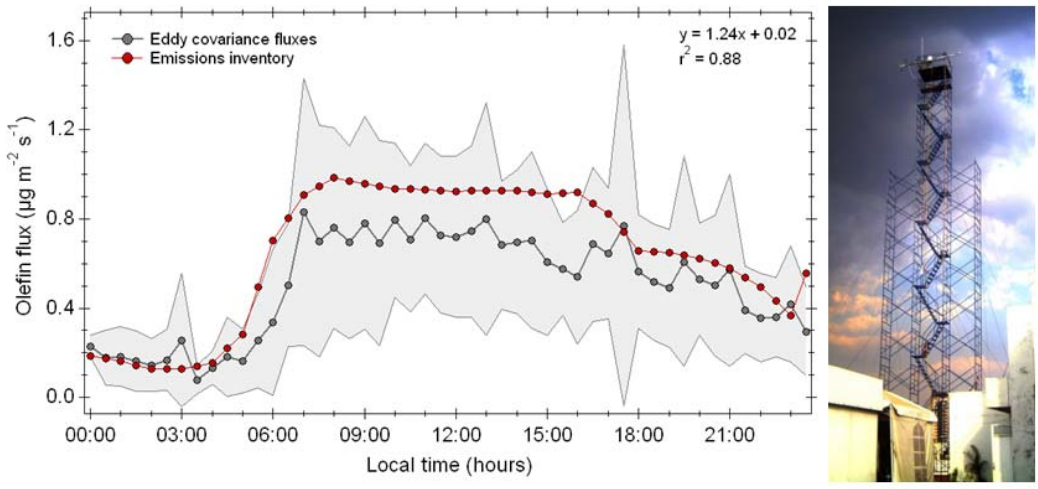

Figure 6. Measured olefin fluxes vs estimated emissions reported by the local emission inventory (Velasco et al., 2007b).

An AMS was operated to measure aerosol concentrations and fluxes of nitrate, sulfate and organic aerosol on an alternating 30- minute schedule. The aerosol fluxes were derived using the EC method. Preliminary results from the AMS flux measurements indicate that the urban landscape is a significant source of aerosols, mainly organics. During daytime upward and downward fluxes of organic and nitrate aerosols were observed, respectively. Nitrate downward flux is likely due to enhanced partitioning of NH_4NO_3 to the particle-phase aloft. Sulfate aerosol fluxes were near zero throughout the day.

The 2006 flux system confirmed the representativeness of the 2003 flux measurements, as well the feasibility of the EC, DEC and DEA techniques to measure fluxes of trace gases and aerosols in urban environments; it is a valuable tool for validating local emissions inventory. Although the MCMA-2006 measurements did not address the full suite of VOC emissions and corresponded to one location of the city, together with the MCMA-2003 results, they suggest that the calculated emissions by the local authorities are essentially accurate for some species, while for others need to be corrected by factors between 0.46 and 3.7 in extreme cases.

This is a collaborative study with WSU, CU, PNNL, ARI, SIMAT, and Centre for Ecology and Hydrology, Edinburgh, UK. Preliminary results were presented at the 2007 Fall AGU Meeting. [Velasco et al., 2007b; Grivicke et al., 2007]. Manuscripts describing the above results will be submitted to the MILAGRO Special Issue in Atmos. Chem. Phys.

4.3. Characterization of Aerosol Samples during MCMA-2006

As in MCMA-2003 Campaign, the MIT/MCE2 team collaborates with Alex Laskin and his team at EMSL/PNNL and Mary Gilles at LBNL to characterize aerosol samples collected during the MCMA-2006/MILAGRO Campaign. Particles were collected nearly continuously from multiple sites (T0, T1 and T2) in order to investigate spatial and temporal variability of the particles' chemical and physical properties, and subsequently analyzed in the laboratories at PNNL and LBNL using different analytical techniques (see Sect 3.1). We also collaborated with K. Prather and R. Moffet at UCSD in deploying the aerosol time-of-flight mass spectrometry (ATOFMS) and V. Mugica (UAM-Azcapotzalco) in High-Volume filter sampling at T0. The following two studies resulted from these complementary measurements.

4.3.1. Measurement of ambient aerosols at T0 by single particle mass spectrometry

As part of the MCMA-2006 campaign, we collaborated with K, Prather (UCSD) in deploying the aerosol time-of-flight mass spectrometry (ATOFMS) at T0 between March 7 – 27, 2006. Biomass and organic carbon (OC) particle types were found to dominate the accumulation mode both day and night. Both the organic carbon and biomass particles were of roughly equal concentration early in the morning, but from the late morning until early evening the biomass type became the largest contributor to accumulation mode mass. The diurnal pattern can be attributed to either coagulation and/or a change in the air mass. Fresh elemental carbon (EC) particles were observed in the early morning, while the majority of the detected EC particles were mixed with nitrate, sulfate, organic carbon, potassium and peaked later in the day. Submicron particles from industrial sources in the northeast were composed of an internal mixture of Pb, Zn, EC and Cl and peaked early in the morning. A unique nitrogen-containing

organic (NOC) particle type was observed, and is also hypothesized to be from industrial emissions based on the temporal profile and back trajectory analysis. This study provides unique insights into the real-time changes in single particle mixing state as a function of size and time for aerosols in Mexico City. These new findings indicate that fine particles from biomass burning and industrial operations are an important sources of particles in Mexico City that have received little attention in previous studies. A manuscript describing this analysis has been published (Paper #21 - Moffet et al., 2008).

4.3.2. Characterization of aerosols containing Zn, Pb, and Cl in the MCMA

During the March, 2006 MILAGRO campaign, measurements in the Northern Mexico City Metropolitan Area revealed the frequent appearance of particles with a characteristically high content of internally mixed Zn, Pb, Cl and P. This unique mixing state was found to match most closely to source sampling of garbage incineration. A comprehensive study of the chemical and physical properties of these particles was performed using a complementary combination of aerosol measurement techniques. Individual particles were analyzed using Aerosol Time-of-Flight Mass Spectrometry (ATOFMS) and Computer Controlled Scanning Electron Microscopy/Energy Dispersive X-Ray analysis (CCSEM/EDX). Proton Induced X-Ray Emission (PIXE) analysis of bulk aerosol samples provided time-resolved mass concentrations of individual elements. The PIXE measurements indicated that Zn is more strongly correlated with Cl than with any other element (including Na) and that Zn concentrations are higher than other non-ferrous transition metals. These metal containing particles are a mixture of spherical and non-spherical morphologies. Many metal rich particles had a needle-like structure and were found to be composed of ZnO and/or $Zn(NO_3)_2 \cdot 6H_2O$ as indicated by scanning transmission x-ray microscopy/near edge X-ray absorption spectroscopy (STXM/NEXAFS). Given that the Zn and Pb rich particles are primarily submicron and that they are internally mixed with elemental carbon, they likely originate from combustion. This unique combination of analytical techniques has allowed for a comprehensive evaluation of metal containing particles in a complex urban environment, highlighting unique characteristics that give powerful insights into their origin.
This study is carried in collaboration with UCSD, PNNL-EMSL, LBNL, and UAM-A. A manuscript describing this study has been published (Paper #24- Moffet et al., 2008).

4.4 Analysis of organic aerosols in Mexico City during MILAGRO / MCMA-2006 with high-resolution mass spectrometry at the urban supersite (T0)

Non-refractory submicron (approx. PM1) ambient aerosol was analyzed from March 10-30, 2006 in Mexico City at the T0 (IMP) urban supersite with the High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, DeCarlo et al., 2006). Mass concentrations and size distributions of inorganic species (ammonium, chloride, nitrate, sulfate) are similar to results from MCMA-2003 (Salcedo et al., 2006). Positive Matrix Factorization (PMF; Ulbrich et al., 2008) analysis of the organic aerosol (OA) fraction indicates an impact from large episodic biomass burning plumes in addition to urban primary emissions and urban secondary organic aerosol (SOA) formation for this dataset. SOA is the dominant component of OA, in agreement with previous observations (Volkamer et al., 2006). The presence of a highly-oxygenated organic aerosol is also observed. Biomass burning OA (BBOA) correlates with satellite fire counts, gas-phase acetonitrile, and other tracers such as potassium and levoglucosan (from both

AMS and off-line sampling). Information from satellite fire counts (MODIS) and emissions inventories are input into a meteorological model (FLEXPART) for the Mexico City basin to derive a fire impact index for T0 that is compared with the AMS BBOA and other tracers. The modeled fire impact reproduces the general trends of the observed BBOA, while perfect agreement is not expected given the difficulties of modeling BB emissions and meteorology in the basin. This indicates that wildfires within the Mexico City basin and surrounding mountains as the dominant source of BBOA at T0, with urban burning (trash burning etc.) playing only a minor role. GC-MS Chemical Mass Balance (CMB; Stone et al., 2008) and C-14 filter analysis results are generally consistent with the PMF results. An analysis comparing the high and low fire impact periods allows the quantification of the impact of BBOA during MILAGRO. A manuscript describing this study, led by CU and involved the collaboration of multi-institutions, will be submitted for publication [Aiken et al., 2008]

4.5. Field measurements on board the ARI Mobile Laboratory

The ARI mobile laboratory deployed a comprehensive set of research grade, real-time trace gas and fine particulate matter instruments at various representatives urban and boundary sites across the MCMA. By providing more and diverse spatial coverage in addition to the three supersites (T0, T1, and T2) during the campaign, the mobile lab offered a large set of additional information on the characteristics of trace gases and aerosols in the city.

Table 1. Monitoring sites deployed by ARI Mobile Lab during MCMA-2006

Site	Period	Site
T0	3/01/ - 3/04/06 3/06 - 3/07/06 3/27- 3/31/06	Urban site near the center of the city with homogenous mixture of mobile, domestic and industrial emissions. Altitude: 2236 m
PED	3/04– 3/06/06	Urban site with predominance of mobile and domestic emissions. Potential "receptor" site. Altitude: 2334 m
PTP	3/07– 3/19/06	Top of the mountain site located in the middle of the city. No influence of local anthropogenic emission sources. Altitude: 2991 m
T1	3/19– 3/22/06	Semi rural semi-arid site in the Northeast with periods of influence from local town (Tecamac) and MCMA emissions. Altitude: 2259 m
STA	3/22– 3/25/06	Rural site in the southwest part of the city. Depending on meteorology it is a potential "receptor" site or representative for boundary conditions. Altitude: 2591 m
PEMEX	3/25– 3/27/06	Gas transfer station located in the Northwest of the city. Potential "receptor" site for nearby industrial emissions. Altitude: 2306 m
Mobile/ Tula	Between sites	Sampling during mobile lab transits between sites and for "transect" experiments in the Tula region.

Figure 7 shows the locations of the monitoring sites where the ARI mobile laboratory was deployed; Table 1 gives a description of these monitoring sites. The monitoring sites were

selected in advance on the basis of experiences in prior missions (MCMA-2002/2003) and on daily wind forecasts produced by Benjamin de Foy (MCE2) and Jerome Fast of the Pacific Northwest Research Laboratory. In addition to the stationary site measurements, the fast response instrumentation was also used during mobile lab transits between sites to obtain on-road vehicle emissions data.

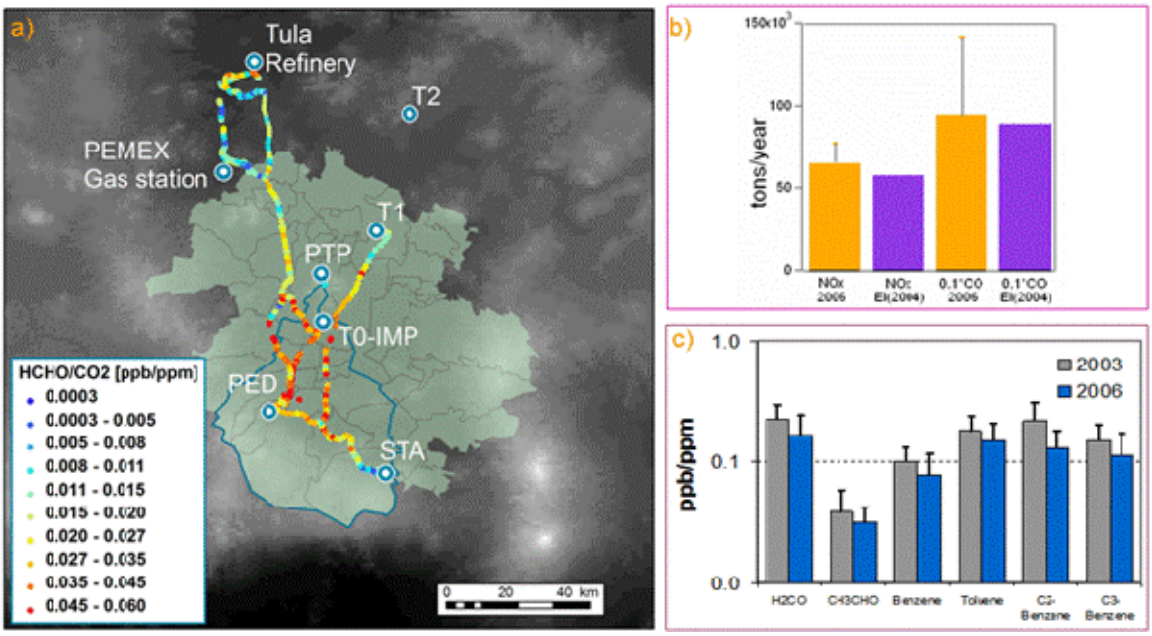

Figure 7. Characterizing mobile emissions in Mexico City using data from MCMA-2003 and MCMA-2006 campaigns. a) Observed highly heterogeneous spatial distributions of emissions; b) on-road measurement technique for the validation of the emissions inventory; c) measured reduction of VOC emission ratios in the MCMA (Zavala et al., 2007).

In the following section, we described the studies conducted by the MIT/MCE2 team, in collaboration with ARI/MSU and other investigators.

4.5.1. Evaluation of the MCMA mobile emissions inventory in 2006

During the MCMA-2006 Campaign, the fast response instrumentation on board the ARI Mobile Lab was used during mobile lab transits between sites to obtain on-road vehicle emissions data. The analysis technique is based on the characterization of possible background pollutant sources as well as targeted gasoline and/or diesel vehicle emissions using the highly sensitive and fast time response instrumentation on board the mobile laboratory. All identified exhaust pollutant species are correlated with the excess (above background) CO_2 concentration, a tracer of combustion, allowing molar emission ratios to be computed for each measured exhaust pollutant. Fuel-based emission factors can readily be computed from the observed molar emission ratios based on the fuel's properties and assuming complete stoichiometric combustion. As mobile emission sources contribute a significant fraction of the total anthropogenic emissions burden in Mexico City, the measurements taken in fleet average fuel-based sampling conditions constitute important available information that will help to understand the chemical processing of mobile emissions in the city.

In this work we present the measurements of emission factors taken under fleet-average sampling conditions using the mobile laboratory in the MCMA in 2006. We use our results and a review of past and recent remote sensing emission studies to evaluate the mobile emissions of CO, NOx, $PM_{2.5}$, total hydrocarbons (HCs), and selected VOCs estimated in the 2006 official emissions inventory in the city. Finally, our analysis includes a long-term comparison of ambient early morning CO, NOx and CO/NOx concentration trends with the corresponding mobile emission estimates from the emissions inventory and a discussion on the possible impacts of changes in the (age and size) vehicle fleet characteristics on these trends.

We compared the on-road emission measurements obtained in Mexico City in 2006 with those obtained in 2003 using the same analysis and measurement techniques with the ARI mobile laboratory. Whereas the observed changes in 2006 and 2003 for the NOx emission factors were within the observed variability ranges, all the on-road emission factors of aldehydes and aromatics species were reduced. Moreover, the reductions in these VOC species were observed for all driving conditions.

The CO and NOx fuel-based emissions factors measured with the ARI mobile laboratory in 2006 agree remarkably well with those measured in the same year with a remote sensing study in Mexico City. Nevertheless, a comparison of the observed changes of fuel-based emission factors in Mexico City with those obtained by remote sensing in several cities in the U.S., indicates much smaller annual average reductions of emissions factors in Mexico City. As shown by the analysis of the changes of the vehicle fleet age, the smaller annual average reduction of the fuel based reduction factors in Mexico City could be a consequence of lower removal rates of older vehicles, particularly those without emissions control technology.

We have used our results to evaluate the gasoline vehicle fleet emissions in the official criteria and toxic emissions inventories in Mexico City. We found slight average overestimations of the order of 16-20% and 10-15% in mass for CO and NO emissions, respectively, although these are within the range of uncertainties in the measurements. Similarly, using the observed ranges of the HC/CO mass ratio, we estimate a probable underestimation of HC mobile emissions of a factor between 1.4 and 1.9. In contrast, estimated benzene and toluene emissions seemed to be well within uncertainties of the corresponding emissions estimates from the on-road emissions measurements. Aldehyde mobile emissions, however, seem to be underpredicted by factors of 3 for HCHO and 2 for CH3CHO. Similarly, our estimates of annual emissions of organic mass from PM1 particles from the on-road measurements suggests a sever underprediction (larger than a factor of 4) of PM2.5 emissions from gasoline vehicles in the inventory.

Our analysis indicates that the early morning ambient CO/NOx ratio has decreased significantly over the last two decades at a rate of about 1.9 ppm/ppm/year and that the decrease has been driven by reductions in CO levels rather than from NOx levels. This suggests that the relative contribution of diesel vehicles to overall NOx levels has increased over time in Mexico City. Interestingly, there is a notably good agreement in the magnitude and temporal variability between the observed CO/NOx ambient ratio and the corresponding ratio in the emissions inventory.

The long-term analysis of ambient pollutants indicates that despite the impressive increases in the size of the vehicle fleet in the last years, the early ambient concentrations of CO, NOx have not increased accordingly. We suggest that this has been in part due to the observed removal rates of older vehicles that do not have emissions control technologies. This indicates that an emission-based air quality control strategy targeting a large reduction of emissions from mobile sources could be directed towards a significant increase of the removal rate of older, high-polluting, vehicles. A manuscript describing this study will be submitted to ACP [Zavala et al., 2008]. This study is done in collaboration with ARI/MSU team.

4.5.2. Source Apportionment for Estimating MCMA Motor Vehicle Emissions in 2006

As a result of the rapid growth and development of the MCMA over the past few decades, there has been a corresponding increase in emission sources within the transportation sector that has significantly impacted air pollution within the region. An important distinction in examining mobile source emissions is that gasoline and diesel-powered vehicle emissions differ enormously by pollutant. CO and VOC are mainly associated with gasoline-powered engines, $PM_{2.5}$ mainly with diesel-powered engines, and NO_x with both. Very few studies have separated gasoline-powered vehicle emissions from diesel-powered emissions under a variety of on-road driving conditions. The main goal of this collaborative research from VT, ARI, LANL and the MIT/MCE2 team is to quantify diesel- and gasoline-powered motor vehicle emissions within the MCMA using positive matrix factorization (PMF) receptor modeling.

During the MCMA-2006/MILAGRO field campaign in March 2006, researchers from VT, ARI, LANL and MIT/MCE2 worked together on-board the ARI Mobile Laboratory, which drove throughout the MCMA and measured on-road concentrations of a large suite of gaseous and particulate pollutants. The pollutant concentrations recorded served as the input data for the PMF receptor model (EPA PMF 1.1). The source profiles derived by PMF in conjunction with knowledge of emission markers allowed the apportionment of gasoline and diesel emissions. Fuel-based emission factors and annual emissions within Mexico City were then calculated from the source profiles and fuel sales data. Preliminary results concluded that PMF applied to fast mobile lab data can separate gasoline from diesel engine emissions; diesel engines are responsible for the majority of NO_x, $PM_{2.5}$, BC, and PAH while gasoline engines are responsible for the majority of CO, VOC, NH_3, and HCHO. A manuscript describing this study is being prepared and will be submitted for publication [Marr et al., 2008].

4.5.3. Characterization of Polycyclic Aromatic Hydrocarbons (PAH) during MCMA-2006

Polycyclic aromatic hydrocarbons (PAHs) are highly carcinogenic, semi-volatile compounds whose main source is combustion. Previous studies have found PAH concentrations in Mexico City to be among the highest measured anywhere in the world (Marr et al., 2004), but their spatial distribution in the megacity has not been characterized. During the MCMA-2006 Campaign, PAHs and other gaseous species and particulate properties were measured at six locations throughout the city. The measurements were intended to support the following objectives: to describe spatial and temporal patterns in PAH concentrations, to gain insight into sources and transformations of PAHs, and to quantify the relationships between PAHs and other pollutants.

As in our previous MCMA-2003 Campaign, measurements of PAH and aerosol active surface area (AS) concentrations were conducted using portable sensors (EcoChem) based on photoelectric charging and diffusion charging respectively. Total particulate PAHs at the T0 supersite located near downtown averaged 50 ng m^{-3}, and aerosol active surface area averaged 80 mm^2m^{-3}. PAHs were also measured on board the Aerodyne Mobile Laboratory, which visited six sites encompassing a mixture of different land uses and a range of ages of air parcels transported from the city core (see Figure 8). A combination of analyses of time series, back trajectories, concentration fields, pollutant ratios, and correlation coefficients supports the concept of T0 as an urban source site, T1 as a receptor site with strong local sources, Pedregal and PEMEX as intermediate sites, Pico Tres Padres as a vertical receptor site, and Santa Ana as a downwind receptor site. Weak intersite correlations suggest that local sources are important and variable and that exposure to PAHs cannot be represented by a single regional-scale value. The relationships between PAHs and other pollutants suggest that a variety of sources and ages of particles are present. Among carbon monoxide, nitrogen oxides (NOx), and carbon dioxide, particulate PAHs are most strongly correlated with NOx. Mexico City's PAH-to-black carbon mass ratio of 0.01 is similar to that found on a freeway loop in the Los Angeles area and approximately 8-30 times higher than that found in other cities. Evidence also suggests that primary combustion particles are rapidly coated by secondary aerosol in Mexico City. If so, their optical properties may change, and the lifetime of PAHs may be prolonged if the coating protects them against photodegradation or heterogeneous reactions. This is a collaborative study with Linsey Marr and Dwight Thornhill (VPI), Nancy Marley and Jeff Gaffney (UALR) and the ARI team. A manuscript describing this study has been published (Paper #22 - Thornhill et al., 2008).

4.5.4. Photochemistry and SOA Formation in the MCMA

Data collected from a mountain location in the MCMA's northeast corner during MCMA-2006/MILAGROwere used to differentiate oxygen-rich SOA formed by atmospheric photochemistry from more hydrocarbon-like primary organic aerosol that is associated with MCMA vehicle PM (soot) emissions. These data demonstrate a correlation between secondary organic aerosol and odd-oxygen ($O_3 + NO_2$), as shown in **Figure 8**. The observed correlation between O_x and SOA may be used to estimate SOA pollution levels for a range of weather conditions and emission scenarios. A manuscript was published [Paper #23 - Herndon et al., 2008].

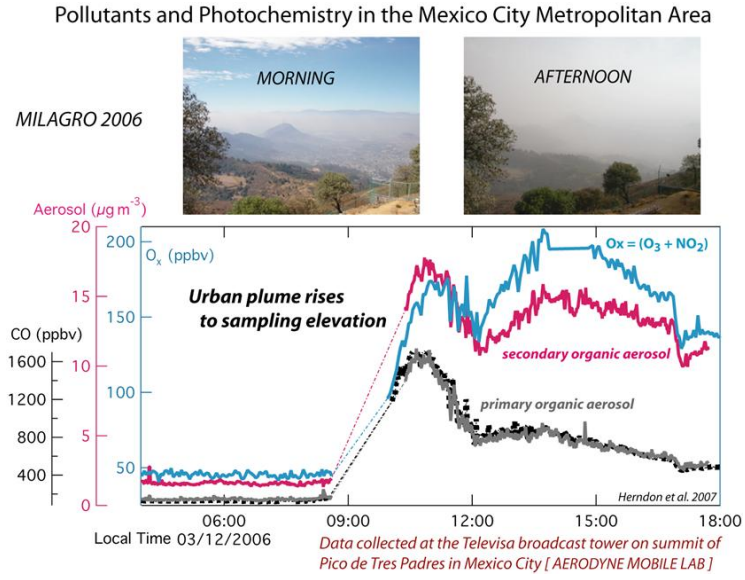

Figure 8. Photochemistry and SOA Formation in the MCMA .

4.6. Urban Visible/SWIR surface reflectance ratios from satellite and sun photometer measurements in Mexico City

The surface reflectance ratio between the visible (VIS) and shortwave infrared (SWIR) radiation is an important quantity for the retrieval of the aerosol optical depth (AOT) from the MODIS sensor data. Based on empirically determined VIS/SWIR ratios, MODIS AOT retrieval uses the surface reflectance in the SWIR band (2.1 mm), where the interaction between solar radiation and the aerosol layer is small, to predict the visible reflectances in the blue (0.47 μm) and red (0.66 μm) bands. Therefore, accurate knowledge of the VIS/SWIR ratio is essential for achieving accurate retrieval of aerosol optical depth from MODIS. The heterogeneity of the surface cover in an urban environment increases the uncertainties in the estimation of the surface reflectance and, consequently, AOT. We analyzed the surface reflectance over some distinct surface covers in and around the Mexico City metropolitan area (MCMA) using MODIS radiances at 0.66 μm and 2.1 μm. The analysis was performed at 1.5 km x 1.5 km spatial resolution. Also, ground-based AERONET sun-photometer data acquired in Mexico City from 2002 to 2005 were analyzed for aerosol optical thickness and other aerosol optical properties.

In addition, a network of hand-held sun-photometers deployed in Mexico City, as part of the MCMA-2006 Study during the MILAGRO Campaign, provided an unprecedented measurement of AOT in 5 different sites well distributed in the city. We found that the average RED/SWIR ratio representative of the urbanized sites analyzed is 0.73±0.06. This average ratio was significantly different for non-urban sites, which was approximately 0.55. The use of the new RED/SWIR ratio of 0.73 in the MODIS retrieval led to a significant improvement in the agreement between the MODIS and sun-photometer results, as shown in Figure 9.

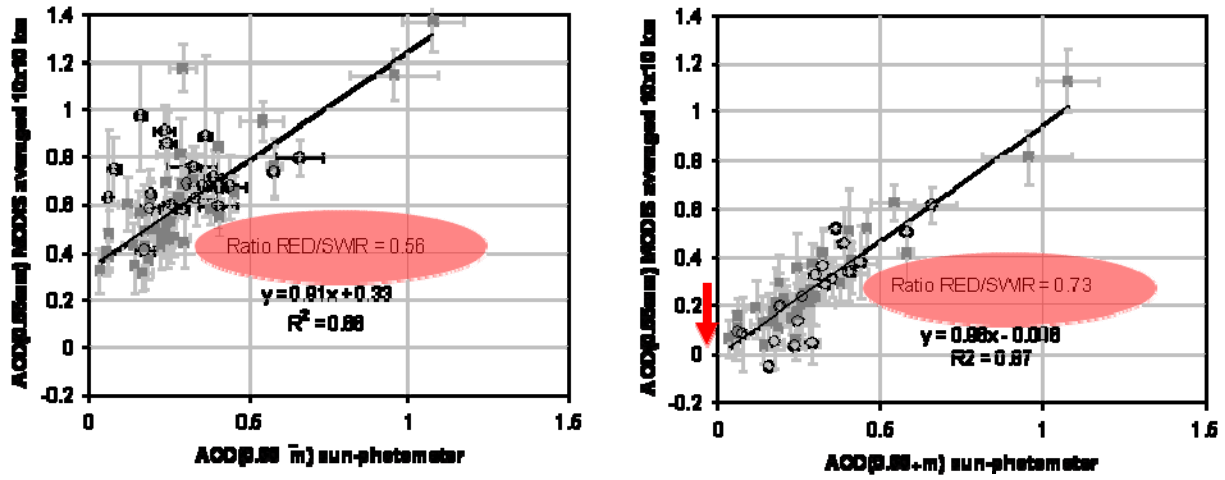

Figure 9. The AOD retrieved from MODIS compared to the AOD measured by the sun-photometer network, both collocated in space and time. Open dots are data from sun-photometer network/MILAGRO 2006, and gray squares are data from CIMEL/AERONET from 2002- 2005. The assumption on the surface reflectance ratio (visible and shortwave infrared wavelengths) makes all difference on the AOD retrieval with MODIS over the Mexico City urban area as shown in these two figures. The surface ratio of 0.73 shows significant improvement on the validation of the retrieval in the urban region.

This work was done in collaboration with NASA/Goddard Space Flight Center, Friedrich-Schiller-University, and University of Maryland. The following students from Mexico City helped with the operation of the sun photometer during the campaign: F.R. Hernandez, I.V. Valle, P.A.H. Priego, G.V. Valdes, A. Arraiga, and L.D.R. Cortes. A manuscript describing this study has been published [Paper #17 - Castanho et al., 2007]

4.7. Photochemical and meteorological modeling

Following the MILAGRO field campaign, both forecast analysis and MM5 re-analysis were carried out, as well as trajectory analysis for source identification and photochemical modeling for ozone formation using the huge data set obtained from the field campaign.

4.7.1. Basin-scale wind transport during the MILAGRO field campaign and comparison to climatology using cluster analysis

Following the MILAGRO field campaign, new meteorological simulations were made with MM5 in re-analysis mode. Surface meteorology and air quality data, radiosoundings and radar wind profiler data were collected at sites in the basin and its vicinity. Cluster analysis is used to identify the dominant wind patterns both during the campaign and within the past 10 years of operational data from the warm dry season. Our analysis shows that March 2006 was representative of typical flow patterns experienced in the basin. Six daily weather types were identified during MILAGRO, three of which took place during MCMA-2003. South Venting had strong, dry, southward winds leading to clear skies and low pollution levels. O3-South days had a gap flow from the southeast passage causing an east-west convergence zone that moved northwards into the early evening. This was associated with high O3 in the south of the city. O3-North days had stronger southwesterly flow aloft that led to winds coming over the western and southern rims of the basin. A north-south convergence zone formed with high pollution levels in the north of the city. Three Cold Surges took place bringing cold humid air along the Gulf coast and into the basin. Humid conditions persisted after the last Cold Surge and led to days with afternoon convection and rainfall. While generally similar, these were split into days where the convection was more to the south and days where it was more to the north.

The meteorological classification will be used to identify episodes for intensive modeling studies. The evaluation of models will be able to build on the simulation of salient features in addition to standard statistical metrics. Hourly characterization of wind circulation during the 2006 MILAGRO, MCMA-2003 and 1997 IMADA field campaigns will enable the comparisons of similar air pollution episodes and the evaluation of the impact of wind transport on measurements of the atmospheric chemistry taking place in the basin. A manuscript describing this study has been published [Paper #20 - de Foy et al., 2008], in collaboration with PNNL and other investigators providing the data.

4.7.2. Trajectory analysis for source identification

Residence Time Analysis (RTA) and Concentration Field Analysis (CFA) based on WRF-Flexpart back-trajectories were calculated for ATOFMS measurements at T0, mercury measurements at T0 and T1 and black carbon measurements at several sites. These have been

included in several studies or publications mentioned above (Moffet et al., 2008; Thornhill et al., 2008; Aiken et al., 2008).

Meteorological support was provided in the analysis of data from the ARI Mobile Lab when it was stationed at Pico de Tres Padres. This included evaluations of trajectories and comparisons of WRF simulations with radar wind profiler and radiosonde data (Herndon et al., 2008).

4.7.3. Understanding the relationships between ozone formation and ozone precursors from the MCMA-2006 Campaign

The 3-D photochemical model CAMx implemented with the SAPRC-99 chemical mechanism was employed to investigate the ozone production and response to emissions in the MCMA under different meteorological conditions in conjunction with ground-based and G-1 aircraft measurements during the MCMA-2006/MILAGRO campaign. CAMx was driven by meteorological fields generated by the Weather Research and Forecasting (WRF). To improve the accuracy of the simulated meteorology, the four-dimensional data assimilation (FDDA) technique was employed in WRF to nudge in upper air observations. Anthropogenic emission inputs to CAMx were based on the official emission inventory for the year 2006 for the MCMA and based on the population-based scaling extrapolation outside the MCMA. Biogenic emissions were estimated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) provided by C. Wiedinmyer (NCAR). The total emission estimates were then constrained (through adjustment) by an extensive array of ground-based measurements using various techniques obtained by different research groups, such as continuous measurements of CO and odd nitrogen NO_y from the air quality monitoring network, intensive measurements of speciated VOCs using GC-FID, PTR-MS, long-path DOAS, Tunable Diode Laser Absorption Spectroscopy (TDLAS), and grab sampling analyzed with GC and GC/MS at T0 and CENICA sites near the urban emission sources. This updated evaluation of the emission inventory suggests that the emissions of CO and NOx in the emission inventory is accurate, while the emissions of VOC are underestimated by about 20%, smaller than the number obtained from the MCMA-2003 study (which was 40%). CAMx reproduces successfully the observed ground concentrations of ozone and major ozone precursors (active nitrogen NO_x and speciated VOC) under different meteorological episodes; furthermore simulated CO and O_3 agree well with the G-1 aircraft measurements, implying that the model also captures well the spatial and temporal evolution of the pollutant plumes aloft. The agreement suggests not only that the emissions were reasonably estimated, but the transport and vertical mixing are also accurately represented.

Sensitivity studies of O_3 response to emission reduction suggest that the ozone formation in the MCMA urban region is VOC-limited and is independent of the meteorological condition, which is consistent with our previous studies from the MCMA-2003 campaign [see Sect 3.9]. A chemical indicator analysis using the relation between ozone response and the production ratio of $P(H_2O_2)/P(HNO_3)$ indicates that ozone production in areas with the ratio below 0.1 are VOC-limited, while areas with the ratio above 0.3 are NOx-limited. This analysis also shows that ozone production in the urban area is VOC-limited, but the response is mostly NOx-limited in the surrounding mountain and rural areas, and the size of the VOC- or NOx-limited area varies under different meteorological conditions. A manuscript, in collaboration with other investigators providing the data, will be submitted for publication [Song et al., 2008].

5. Summary

This project was one of three collaborating grants funded by DOE/ASP to characterize the fine particulate matter (PM) and secondary PM precursors in the Mexico City Metropolitan Area (MCMA) and to provide critical "ground truth" data necessary to interpret the comprehensive airborne data sets targeted by DOE and NCAR airborne instrument suites during the MILAGRO -2006 Campaign, the first international collaborative project to measure the air pollutants generated and exported by megacities, using Mexico City as a case study.

The overall effort of MCMA-2006, one of the four components, focused on i) examination of the primary emissions of fine particles and precursor gases leading to photochemical production of atmospheric oxidants and secondary aerosol particles; ii) measurement and analysis of secondary oxidants and secondary fine PM production, with particular emphasis on secondary organic aerosol, and iii) evaluation of the photochemical and meteorological processes characteristic of the Mexico City Basin.

The collaborative teams pursued the goals through three main tasks: i) analyses of fine PM and secondary PM precursor gaseous species data taken during the MCMA-2002/2003 field campaigns and preparation of archival publications based on these analyses; ii) planning of the MILAGRO Campaign and deployment of the instrument in and downwind of Mexico City,, in support of the MAX-Mex/MILAGRO field campaigns in March, 2006; and iii) analysis of MCMA-2006 data and publication preparation.

The project reported here was led by the Massachusetts Institute of Technology/Molina Center for Energy and the Environment and coordinated with DOE/ASP-funded collaborators at the Aerodyne Research Inc., University of Colorado at Boulder and Montana State University. Documented findings from this project have been published in special issues of Atmospheric Chemistry and Physics as well as in other peer-reviewed journals. Currently 24 papers have been published and a few more have been submitted.

MCMA-2003 produced very large and valuable data sets describing the chemical and physical properties of the city's reactive atmosphere. The experience and the key findings from MCMA-2003 Campaign provided the framework for planning MILAGRO. The measurement phase of the MILAGRO Campaign was successfully completed in March 2006, with excellent participation from the international scientific community and outstanding cooperation from the Mexican government agencies and academic institutions.

During the MCMA-2006/MAX-Mex/MILAGRO Campaign, the collaborative team utilized a combination of central fixed sites and a highly capable mobile laboratory deployed throughout the MCMA to representative urban and boundary sites in order to measure trace gases and fine particles. Analysis of the extensive 2006 data sets has confirmed the key findings from MCMA-2002/2003; additionally MCMA-2006 provided more detailed gas and aerosol chemistry and wider regional scale coverage.

Major findings from the MCMA-2003 and 2006 include a vastly improved speciated emissions inventory from on-road vehicles that is useful for air quality modeling. Mobile emission sources represent a significant fraction of the total anthropogenic emissions burden. The MCMA motor vehicles produce abundant amounts of primary PM, elemental carbon, particle-bound PAHs, CO and a wide range of air toxics, including formaldehyde, acetaldehyde, benzene, toluene, and xylenes.

Meteorological observations and correlated mesoscale modeling activities establish that a small number of typical early spring meteorological episodes led to characteristic distributions of photochemical pollutants within the MCMA basin. Under most conditions, the basin is ventilated on a daily basis, with little day-to-day accumulation of pollutants.

The feasibility of using eddy covariance techniques coupled with fast-response sensors to measure fluxes of VOCs and CO_2 from a residential district was demonstrated for the first time during the MCMA-2003 Campaign and proved to be a valuable tool for validating local emissions inventory. The flux measurements of selected VOCs showed good agreement with the local emissions inventory used for air quality modeling. A second flux system in a different district located near the center of Mexico City was set up during the MILAGRO campaign and again validated the emissions provided by the local authority. Comparison of the findings from 2003 and 2006 also confirm that the VOC levels have decreased during the three-year period.

While NO_x levels are high, extremely large loadings of reactive VOCs were measured in the MCMA atmosphere. During the morning rush hours total VOC ambient loadings averaged approximately 1.5 ppmC. Alkanes, alkenes and aromatics all contribute significantly to extremely high daytime OH reactivities. Glyoxal was detected for the first time spectroscopically in the atmosphere during MCMA-2003; its rapid formation indicates missing smog chemistry.

Photochemical production of ozone is high in Mexico City due to high co-emissions of NO_x and VOCs, which provide elevated radical sources. Chemical transport model simulations strongly indicated that O_3 formation is VOC limited during the MCMA-2003 campaign. The O_3 production rate is dominated by the radical production rate, which is attributed not only to the photolysis of O_3 and formaldehyde, but also the O_3-alkene chemical processing and heterogeneous sources of HONO. This sensitivity has important implications for ozone-reducing policy. Analysis of additional data sets from 2006 provides a more sophisticated understanding of the relationship between ozone formation and ozone precursors, while ozone production in the urban area is VOC-limited, the response is mostly NO_x-limited in the surrounding mountains.

High aerosol concentrations were observed at ground sites and were composed in large part of organics, but black carbon, crustal matter, sulfate and nitrate were also significant contributors. MCMA $PM_{2.5}$ concentration measured at CENICA supersite in 2003 averaged ~36 $\mu g\ m^{-3}$, with maximum hourly averaged concentrations exceeding 100 $\mu g\ m^{-3}$ on several occasions. Analysis of fine PM from complementary measurement techniques in 2006 enhanced our understanding of the sources and apportionment of aerosols, including contribution from biomass burning and

industrial sources; a comprehensive evaluation of metal containing particles in a complex urban environment, highlighting unique characteristics that give powerful insights into their origin.

Secondary organic aerosol was the major fine PM component during photochemical episodes. SOA formation was found in MCMA-2003 to be dominated by anthropogenic precursors and is formed almost an order of magnitude more efficiently than predicted by current models. Data collected from a mountain location in the MCMA's northeast corner during MILAGRO-2006 were used to differentiate oxygen-rich SOA formed by atmospheric photochemistry from more hydrocarbon-like primary organic aerosol that is associated with MCMA vehicle PM (soot) emissions. These data demonstrate a correlation between secondary organic aerosol and odd-oxygen ($O_3 + NO_2$), and may be used to estimate SOA pollution levels for a range of weather conditions and emission scenarios.

The results from the 2002/2003 and 2006 campaigns have been presented at international conferences and communicated to Mexican government officials. A large number of graduate students and post-doctoral associates were involved in all phases of the project. All data sets and publications are available to the scientific community interested in evaluating the impacts of urban emissions on human health, ecosystem viability, and climate change.

In summary, MCMA-2003 and MCMA-2006 have produced very large and valuable data sets describing the chemical and physical properties of the city's reactive atmosphere and have already added significantly to our understanding of how photochemistry transforms the atmosphere of the MCMA. This information will improve significantly the scientific understanding that decision makers in Mexico will need to craft effective policies for protecting human health and ecosystem viability as well as provide insights to air pollution problems in other megacities around the world.

6. Project Publications

6.1. Published articles

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