Overview of MILAGRO/ INTEX-B Campaign

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Introduction

Air Pollution in Megacities and its Transport and Transformation

About half of the world's population now lives in urban areas, of which 70% lives in less-developed regions (UNPD, 2006). Many of these urban centers are expanding rapidly, leading to the growth of cities and megacities (urban areas with over 10 million populations). Well-governed, 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, increasing industrialization and motorization have resulted in a higher demand for energy, greater use of fossil fuels, and more emission of pollutants into the atmosphere. Air pollution is one of the most important environmental challenges of this century. This challenge is particularly acute in the developing world where the rapid growth of megacities is producing atmospheric pollution of unprecedented severity and extent (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 on scales ranging from regional up to continental and global. Urban/industrial emissions from the developed world, and increasingly from the megacities of the developing world, change the chemical content of the downwind troposphere in a number of fundamental ways. Emissions of nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs) drive the formation of photochemical smog and its associated oxidants, degrading air quality and threatening both human and ecosystem health. On a larger scale, these same emissions drive the production of ozone (a powerful greenhouse gas) in the free troposphere, contributing significantly to global warming. Urban and industrial areas are also major sources of greenhouse gases, including carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and halocarbons. Nitrogen oxide and sulfur oxide emissions are also processed to strong acids by atmospheric photochemistry on regional to continental scales, driving acid deposition to sensitive ecosystems. Direct urban/industrial emissions of carbonaceous aerosol particles are compounded by the emission of high levels of secondary aerosol precursors, including: NO_x, VOCs, SO_2, and NH_3, resulting in the production of copious amounts of fine aerosol, affecting both the urban source areas and air quality and cloud formation microphysics hundreds to thousands of kilometers downwind.

The geographic re-distribution of pollutants, the evolution of their chemical, physical, and optical properties, and the mechanisms for their eventual removal from the atmosphere are very complex and obviously important, yet only partly understood at the present time.

MILAGRO (**M**egacity **I**nitiative: **L**ocal **A**nd **G**lobal **R**esearch **O**bservations) is the first international collaborative project to examine the behavior and the export of atmospheric pollutants generated in megacities. The measurement campaign was sponsored by the US National Science Foundation (NSF), Department of Energy (DOE) and National Aeronautic and Space Administration (NASA), and by many Mexican agencies, including the Mexican Ministry of the Environment (SEMARNAT), the Metropolitan Environmental Commission of the Valley of Mexico (CAM), Consejo Nacional de Ciencia y Technología (CONACyT) and Petróleos Mexicanos (PEMEX). It involved the participation of more than 150 institutions from Mexico, the United States and Europe and over 450 investigators and technicians from over 30 different nationalities.

Air Quality in the Mexico Megacity

The Mexico City Metropolitan Area (MCMA) – one of the world's largest megacities and North America's most populous city -- was selected as the initial case study for MILAGRO Campaign. 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). A series of white papers prepared by the Program's Mexico City Case Study provided the foundation for the ten-year air quality management program (PROAIRE 2002-2010) for the MCMA (CAM, 2002). One of the recommendations is the need for more extensive experimental data from field measurements 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 MCMA lies in an elevated basin 2240 m above sea level. The basin is surrounded on three sides by mountain ridges, but with a broad opening to the north and a

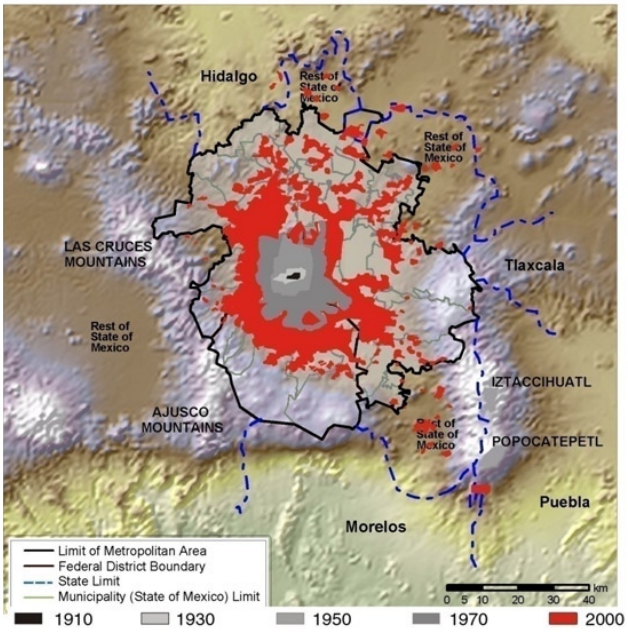


Figure 1. Topographical map of the MCMA showing urban expansion (Molina and Molina, 2002).

narrower gap to the south-southwest. A topographical map of the MCMA is shown in Figure 1. During the twentieth century the MCMA experienced huge increases in population and urbanized area as it attracted migrants from other parts of the country and industrialization stimulated economic growth. The population grew from fewer than 3 million in 1950 to over 18 million in 2000; the urbanized area now covers about 1,500 km2 —about 10 times as much land as it occupied just 50 years ago. The metropolitan area's nearly 20 million inhabitants, over 40,000 industries and 4 million vehicles consume more than 40 million liters of fuel per day and produce thousands of tons of pollutants. The high altitude and mild climate facilitates ozone production all year and contributes to the formation of secondary particulate matter. Air pollution is generally worse in the winter, when rain is less common and thermal inversions are more frequent (Molina and Molina, 2002).

During the past decade, the Mexican government has made tremendous progress in improving air quality. Substantial reductions in the concentrations of some criteria pollutants (such as lead, carbon monoxide and sulfur dioxide) were achieved by developing and implementing comprehensive air quality management programs and improving air quality monitoring and evaluation programs (Molina et al., 2002). Figure 2 shows the air quality trends. Despite these important gains, the MCMA residents remain exposed to unhealthy concentrations of air-borne pollutants, especially particulate matter (PM) and ozone, the two most important pollutants from the standpoint of public health (Evans et al., 2002).

The MCMA-2003 measurement 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 supersite located at the National Center for Environmental Research and Training (CENICA), 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 Aerodyne Research Inc. (ARI) was deployed for measurements at various locations in the MCMA. The MCMA-2003 Campaign generated a very extensive data set and provided important scientific information that was fundamental in the planning of the larger MILAGRO Campaign. An overview article on the MCMA-2003 has been published by Molina et al. (2007).

MILAGRO Campaign

The MILAGRO Campaign is a large, international, multi-agency, collaborative project to evaluate the regional impacts of the Mexico City air pollution plume as a means of understanding urban impacts on the global climate. Specific goals of the campaign included quantifying the spatial and temporal extent of the urban plume, analyzing pollutant chemical and physical transformation in the plume, quantifying the regional impacts of the plume and examining the interaction of the urban plume with surrounding sources.

The initial phase of MILAGRO 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, spaced about 30 km apart to examine the pollutant plume evolution, 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 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 included mobile vans containing scientific laboratories and mobile and stationary upward-looking lasers (LIDAR). Seven instrumented research aircraft participated in MILAGRO: five were based in Veracruz, Mexico, one in Puebla, 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,

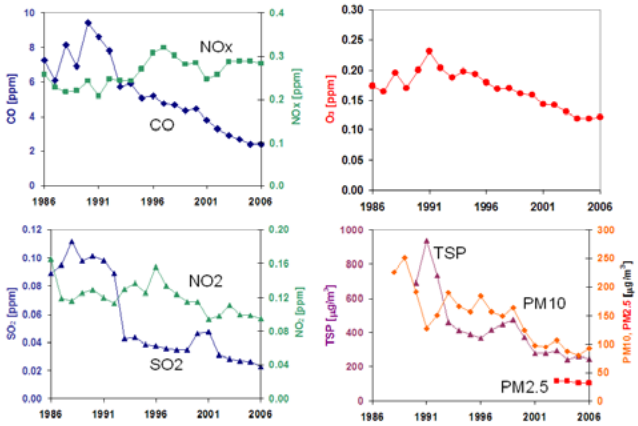


Figure 2. Air quality trends of the MCMA (Mexico City, Federal District Government 2006; www.sma.df.gob.mx/simat).

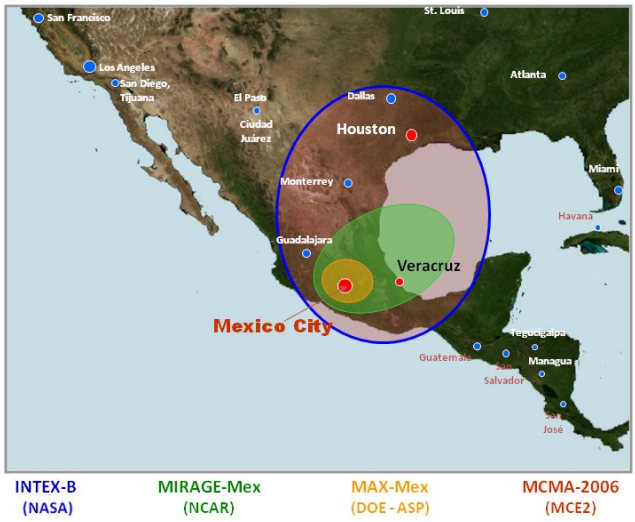


Figure 3. Geographical coverage of the MILAGRO Campaign.

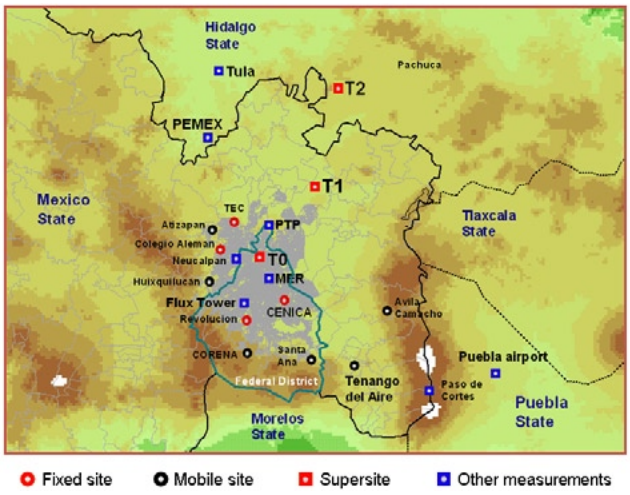


Figure 4. Ground-based measurement sites of the MILAGRO Campaign.

providing even larger geographical coverage. Figure 3 shows the geographic coverage and Figure 4 shows the ground-based measurement sites.

The MILAGRO campaign was organized under four coordinated 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 for Energy and the Environment (MCE2) with projects sponsored by NSF, DOE, and several Mexican research agencies, including CAM, INE, CONACyT and PEMEX, as well as European agencies.

The overall purpose of the MCMA-2006 is to strengthen the scientific base for the design and evaluation of policies to improve the air quality in the MCMA by gathering scientific information that helps to elucidate the processes by which pollutants are generated in the MCMA; how pollutants are dispersed, transported and transformed in the atmosphere; the exposure patterns of the population to these pollutants; and the effects on human health. The required data on aerosols, VOCs and other gases, meteorology, and solar radiation was obtained through measurements at the T0 supersite, a flux tower located at the city center, and the Tula refinery site and industrial zone in Naucalpan, in combination with measurements from a highly capable mobile laboratory, a microlight research aircraft and several fixed mobile units deployed throughout the MCMA at representative urban and boundary sites. In addition, two health studies were carried out during the Campaign.

In order to contribute to the education and training of young investigators and to raise public awareness toward atmospheric pollution problems, the Molina Center, in collaboration with INE and other local institutions, set up a series of education and outreach activities, including public lectures, workshops, guided tours, and essay and poster contests, all of which were carried out in parallel to the scientific activities by Mexican and international researchers working at the different measurement sites (http://mce2.org).

MIRAGE-Mex (Megacity Impacts on Regional and Global Environments - Mexico) 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-Mex was led by the National Center for Atmospheric Research (NCAR) in collaboration with researchers from academia under NSF sponsorship. Specific objectives were to: (1) Quantify the spatial extent and temporal persistence of the polluted outflow plume; (2) identify and quantify the chemical and physical transformations of the gases and aerosols in the plume, especially the processes that lead to the removal of these pollutants from the atmosphere; (3) quantify the effects of the plume on regional oxidants and radiation budgets, and ultimately on climate; and (4) examine the interactions of the urban plume with background air, as well as pollutants from other sources including regional anthropogenic pollutants, biomass fires, and vegetative emissions. The NCAR/NSF C-130 aircraft carried a payload of state-of-the-art scientific instruments and sampled air at different distances from Mexico City to measure how gases and particles "age" during transport, specifically tracking those chemical, physical, and optical properties that have the potential to affect air quality, weather, and climate on large geographic scales. An additional aircraft (Twin Otter) conducted studies of fires and their effect on the local and regional composition of the atmosphere. Other MIRAGE-Mex researchers were located at the T1 supersite, to examine the chemistry and physics of surface air as it first exits Mexico City.

MAX-Mex **(**Megacity Aerosol Experiment: 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

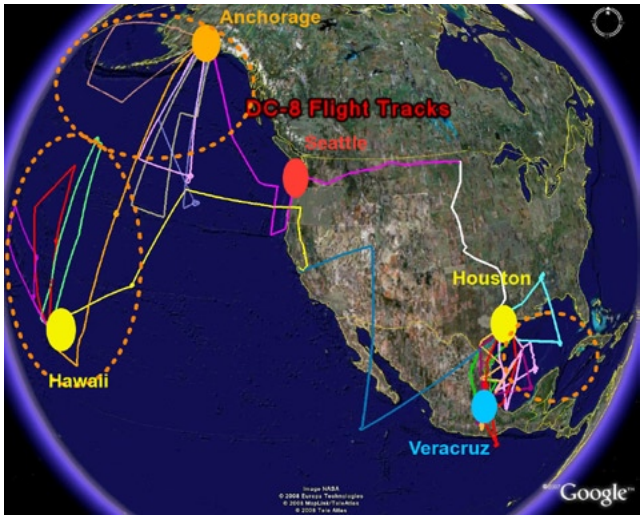


Figure 5. INTEX-B DC-8 flight tracks and DC-8 Bases in Houston, TX (3/1-21/2006), Honolulu, Hawaii (4/17-30/2006), and Anchorage, Alaska (5/1-15/2006). Also shown are operational sites for the: DC-8 (yellow ovals); C-130 (red oval); and C-130, J-31, B-200, G-1 (blue oval).

Mexican agencies. Measurements were conducted using an airborne LIDAR operated by NASA scientists with support from DOE, the DOE Gulfstream-1 (G-1) airborne platform that obtained gas and aerosol measurements, and three surface supersites to examine the aerosol plume evolution. The T0 and T1 sites were instrumented heavily with aerosol instrumentation for characterization of chemical and physical properties including the scattering and absorption of aerosols, particularly in the submicron fractions that are anticipated to have the longest lifetimes and have the most impact on regional and potentially global climate forcing.

INTEX-B (Intercontinental Chemical Transport Experiment-B) 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. Central to achieving this goal was the need to relate space-based observations with those from airborne and surface platforms. Specific INTEX-B/MILAGRO objectives were to: (1) investigate the extent and persistence of the outflow of pollution from Mexico; (2) understand transport and evolution of Asian pollution and implications for air quality and climate across western North America; (3) map anthropogenic and biogenic emissions and relate atmospheric composition to sources and sinks; (4) characterize the effects of aerosols on solar radiation; and (5) validate space-borne observations of tropospheric composition.

The INTEX-B contributions to MILAGRO and the Pacific phase of INTEX-B performed jointly with NSF/IMPEX are included in this article. Instrumented NASA DC-8, J-31 and NSF/NCAR C-130 aircraft, carrying state of the art chemistry and radiation payloads, were the principal airborne platforms in this study, operating in close cooperation with ground stations as well as satellites (http://cloud1.arc.nasa.gov/intex-b/; http://www.joss.ucar.edu/milagro/). The INTEX-B/MILAGRO campaign was performed in two parts in the spring of 2006. The first part focused on pollution over Mexico City (March 1-21) and the second part on transported pollution from Asia (April 17-May 15). In the first part, the DC-8 operated from Houston, TX with sorties over Mexico and the Gulf of Mexico while the J-31 and NSF/NCAR C-130 operated from Veracruz, Mexico. In the second part, the DC-8 was based in Honolulu, Hawaii (April 17-30) and Anchorage, Alaska (May1-15) with the NSF/NCAR C-130 operating from Seattle, Washington (April 17-May 15) in a coordinated fashion. The overall experiment was supported by forecasts from meteorological and chemical models, satellite observations, surface networks, and ozonesonde data. Figure 5 shows the DC-8 tracks during INTEX-B/MILAGRO and locations of key airborne platforms. Through these in-situ and remote, a large body of atmospheric composition data has been acquired over Mexico and the Pacific. To assist in the analysis of these data, global and regional models have been run that provide simulations along the aircraft flight tracks.

Preliminary Results from MILAGRO Campaign

The MILAGRO Campaign generated a very comprehensive data set and many interesting results have emerged over the past year. The observations from MCMA-2003 Campaign were mostly confirmed during MILAGRO; additionally MILAGRO provided more detailed gas and aerosol chemistry, aerosol microphysics and optics, radiation and wider regional-scale coverage. In the following sections, we present some preliminary results.

Meteorology (Urban/Regional)

The MILAGRO Campaign provided extensive meteorological measurements of one of the largest urban areas in the world. The meteorological situation during MILAGRO has been reviewed by Fast et al. (2007). The MILAGRO campaign was characterized by six types of meteorological episodes, representing different wind transport regimes (de Foy et al., 2008), which were used in data analysis. This is in contrast to three episode types during MCMA-2003 (de Foy et al., 2005). The month of March is near the end of the dry season, and 2006 was not atypical compared to previous field campaigns. The early part of the month was mostly clear and dry over the plateau, but increasingly humid and convective toward the end of the month. On most days the large-scale flows were relatively weak and predominantly toward the Gulf of Mexico, but also with some regional-scale recirculation. In agreement with previous studies, planetary boundary layer (PBL) heights (measured by radiosondes, profilers, and surface- and aircraft-based lidars), grew rapidly during late morning and exceeded 4 km agl on some days (Shaw et al., 2007), with frequent complex layering (Burton et al., 2007). Night-time PBL depths were variable and tended to be higher than model predictions, likely due to urban perturbations. The orography surrounding MCMA leads to complex surface winds, but the basin is ventilated on a daily basis, with little day-to-day accumulation of pollutants (de Foy et al., 2006; de Foy et al., 2008). The rapid PBL

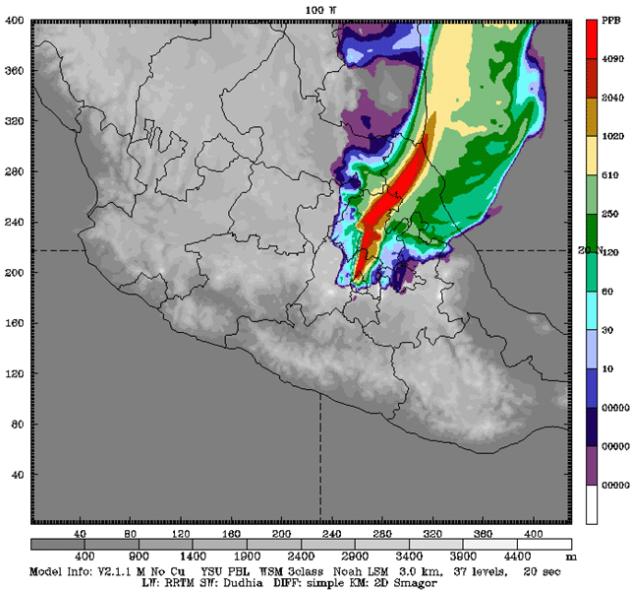


Figure 6. Distribution of Mexico City CO-like transport tracer emitted on 18 March 2006, shown on 19 March 2006 18:00 local time, as calculated using NCAR's WRF model. (*Courtesy: W. Skamarock*).

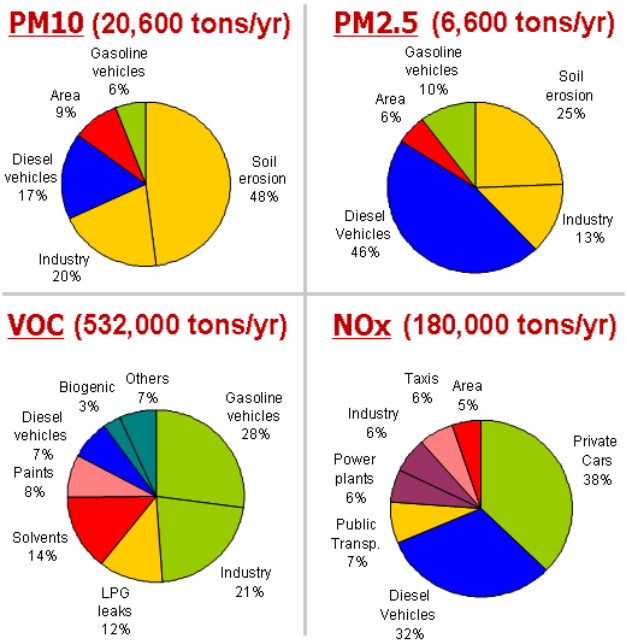


Figure 7. Emission Sources in Mexico City for the year 2004 (CAM, 2006).

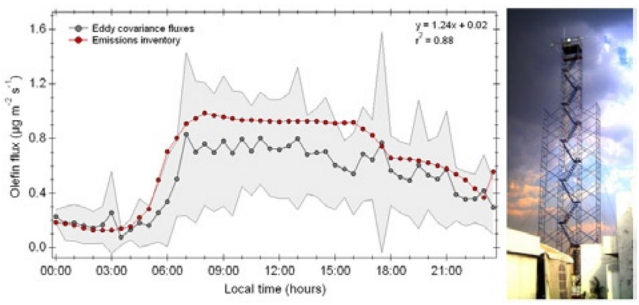


Figure 8. Measured olefin fluxes *vs.* estimated emissions as given in the local emission inventory (Velasco et al., 2007b).

growth and its collapse in the late afternoon lead to the entrainment of polluted air into the free tropospheric synoptic flow. This was particularly clear on March 18th and 19th, when stronger southwesterly winds carried pollutants from Mexico City towards the coastal Mexico-Texas border (Figure 6). This allowed quasi-Lagrangian sampling of the air, on March 18th near MCMA by the G-1 aircraft, and on March 19th downwind by the C-130 aircraft. Altitude-controlled balloons confirmed these trajectories (Voss et al., 2007).

Emissions Measurements

Characterizing and quantifying the emissions of both gaseous pollutants and primary PM is a difficult task in any major urban area, but it presents a particularly daunting task in a rapidly developing megacity like the MCMA. Figure 7 presents the 2004 MCMA emissions inventory for PM10, PM 2.5, VOC and NO_x. Mobile emission sources represent a significant fraction of the total anthropogenic emissions burden. Observations from the 2003 study show that MCMA motor vehicles produce abundant amounts of primary PM, elemental carbon, particle-bound polycyclic aromatic hydrocarbons (PAHs), CO and a wide range of air toxics, including formaldehyde, acetaldehyde, benzene, toluene, and xylenes (Molina et al., 2007).

Several innovative techniques have been developed to evaluate the official emission inventories used in air quality models. Two innovative techniques employed during MCMA-2003 and again during MILAGRO/MCMA-2006 are discussed here.

The feasibility of using eddy covariance techniques coupled with fast-response sensors to measure fluxes of volatile organic compounds (VOCs) and CO_2 from a residential district was demonstrated for the first time during the MCMA-2003 Campaign (Velasco et al. 2005; 2007a). Those flux measurements 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 (see Figure 8). Although these measurements did not address the full suite of VOC emissions and corresponded to only one location of the city, they again validated the emissions provided by the local authority (Velasco et al., 2007b). The fluxes of speciated aerosols were also measured using an Aerodyne Aerosol Mass Spectrometer (Grivicke et al., 2007).

During the 2002/2003 MCMA and the 2006 MILAGRO field campaigns in Mexico City, the ARI Mobile Laboratory measured on-road vehicle fleet emission indices in fleet-average mode for various vehicle classes and driving speeds (Zavala et al., 2006). Measurements of NO_x, CO, key VOC species and particle mass (PM1) and composition from surrounding vehicles were obtained. Species emission ratios to CO_2 are converted to grams of pollutant to liter of burned fuel for estimating total emissions. Figure 9 presents the measurements of emission ratios from the 2006 MILAGRO Campaign and comparisons with the MCMA emissions inventory

estimates and past measurements of mobile emissions. In addition, on-road emission ratios measurements (HCHO/CO_2) were obtained during the transit of the ARI mobile lab between the stationary monitoring sites, providing information on the spatial distribution of mobile emissions within the city (Zavala et al., 2007).

During the 2006 campaign, high aerosol concentrations were observed both at ground sites and from all aircraft. These aerosol particles were composed in large part of organics, but black carbon, crustal matter, sulfate and nitrate were also significant contributors. Biomass burning – agricultural, forest, and trash fires – all contribute to the urban and regional pollution of this area (Yokelson et al., 2007; Moffet et al., 2007; Stone et al., 2008; Querol et al., 2008).

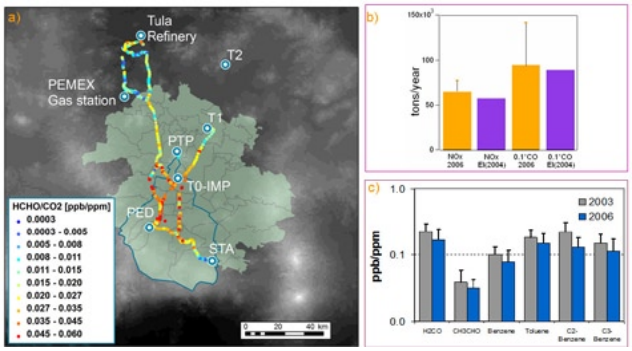


Figure 9. Shown are data used to characterize mobile emissions in Mexico City using data from the MCMA-2003 and MCMA-2006 campaigns. a) Observed highly heterogeneous spatial distributions of emissions, b) on-road measurements (orange) vs those in the local emissions inventory (purple); c) measured reduction of VOC emission ratios in the MCMA (Zavala et al., 2007).

Urban and Regional Photochemistry

Urban Ozone Production. Photochemical production of ozone is high in Mexico City due to high co-emissions of NO_x and VOCs, which provide elevated radical sources – the driving forcing for urban photochemical reactivity. Radical (OH, HO_2, and RO_2) measurements were made at the T0 and T1 surface sites, and onboard the C-130 aircraft. Surface radical production is particularly strong during the morning hours, and OH measurements are in fair agreement with model predictions, while peroxy radicals consistently exceeded model expectations at high NO_x (Case Hanks et al., 2007; Dusanter et al., 2007; Cantrell and Anderson, 2007). Zheng et al. (2008) observed that HNO_3, primarily produced by the reaction of OH with NO_2, was regulated by gas/particle partitioning.

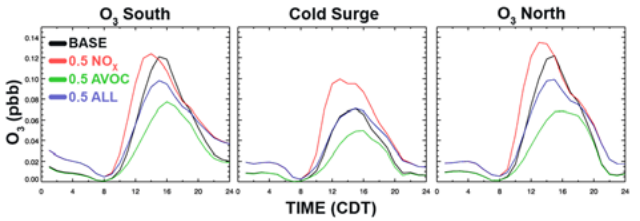


Figure 10. The response of near-surface O_3 concentrations to different emission reduction scenarios in the MCMA source region under different meteorological conditions identified during the MCMA-2003 Campaign, as given by a chemical transport model: 0.5 NO_x denotes a 50% reduction in NO_x; 0.5 VOC denotes a 50% reduction in VOC; 0.5 ALL denotes 50% reductions in both NO_x and VOC emissions (Lei et al., 2008).

Both measurements and chemical transport model simulations suggest that O_3 production in the source region is VOC-limited during photochemically active periods. For example, ground-based measurements from MCMA-2003 showed that the primary sink of HO_x is the OH + NO_2 reaction (Shirley et al., 2006); aircraft observations during MILAGRO-2006 found abundant NO_x oxidation products but relatively low H_2O_2 (Nunnermacker et al., 2008), the indicator species for O_3 production sensitivity. These measurements revealed higher VOC/NO_2 reactivity ratios in the MCMA than in other cities. Chemical transport model simulations strongly indicated that O_3 formation is VOC limited during the MCMA-2003 campaign (Lei et al., 2007; Tie et al., 2007), and the O_3 formation sensitivity is weakly dependent on meteorological conditions (Figure 10) (Lei et al., 2008). 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 (Volkamer et al., 2007; Sheehy et al., 2008). This sensitivity has important implications for ozone-reducing policy.

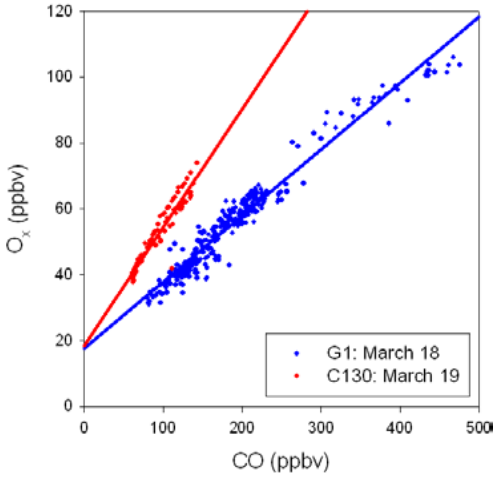


Figure 11. Evolution of O_x (= O_3 + NO_2) vs. CO correlations in the Mexico City plume. The G1 aircraft sample the air near Mexico City on 18 March (blue), while the C130 aircraft intercepted the plume about 1000 km downwind on 19 March (red). (Zaveri et al., 2007).

Regional Chemistry. The regional impacts of the MCMA emissions are easily discernible, especially to the south-east, south, and west where MCMA provides the dominant influence. Pollution over the Gulf of Mexico is persistent and apparently due to diverse sources from the south-eastern U.S., Mexico, and Central America. In addition to urban pollutants, there is clear evidence for widespread gases and PM from biomass burning. Although the contribution of the MCMA pollutants to the Gulf region is not always easily identified, several encounters of the MCMA plume were forecast and were measured by the C-130 instruments. This was particularly clear during the March 18-19th quasi-Lagrangian episode, where an enhanced O_3:CO ratio (Figure 11) was observed ~1000 km downwind, indicating ongoing O_3 production during the outflow.

Aircraft observations show that aldehydes are the most reactive VOCs both in the urban PBL and in the regional outflow

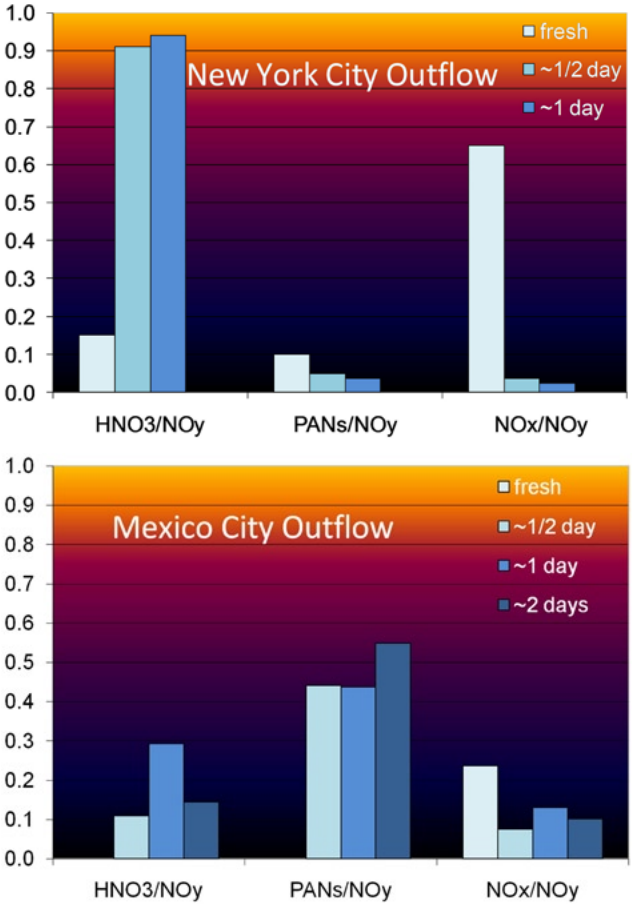


Figure 12. Reactive nitrogen in the outflow of Mexico City (bottom panel) and New York City (top panel). Downwind of Mexico City, the large fraction of PANs sustains NOx for ongoing production of O_3. (Flocke et al., 2007).

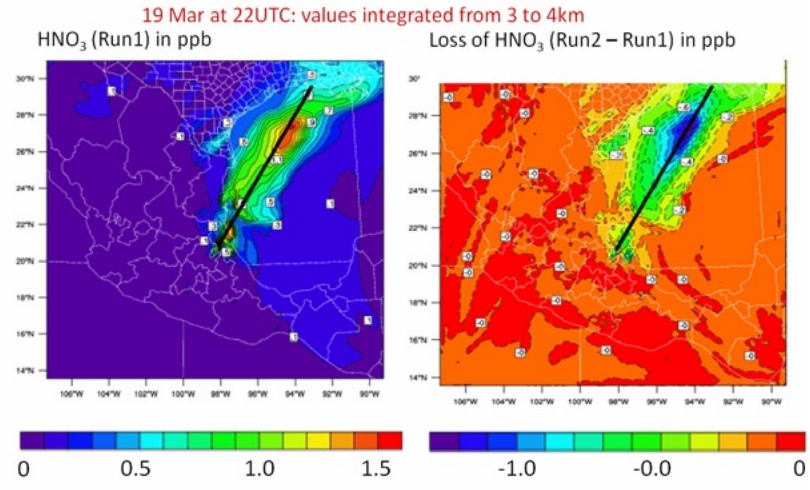


Figure 13. WRF-Chem simulation of nitric acid (HNO_3) in the Mexico City plume, without and with heterogeneous loss on dust encountered downwind. Left panel (Run 1) shows HNO_3 without loss on dust; right panel: about 2/3 of the plume's HNO_3 can be removed by this process (Hodzic et al., 2007).

(Apel et al., 2007). This is also predicted by the WRF-Chem model (Tie et al., in prep.). Peroxyacetyl nitrates (PANs) are the main reactive nitrogen species in the outflow (Flocke et al., 2007), sustaining small levels of NO_x that allow for ongoing regional O_3 production. This large role of PANs is in contrast to some other megacities (Figure 12). Modeling activities are underway to understand to what extent this is a result of the high initial VOC-NO_x mixture in the MCMA, lower temperatures at the altitude of the outflow, and/or due to contributions from regional aldehydes. On the other hand, HNO_3 was a relatively small fraction (5-20%) of the NO_y in aged air, with some evidence for its loss on dust particles (see Figure 13, from Hodzic et al., 2007).

A large amount of data on ozone and its precursors (VOC, OVOC, NO_x, NO_y), free radicals (OH/HO_2), greenhouse gases (CO_2, CH_4, N_2O), aerosols, and a variety of tracers of urban pollution (CO, halocarbons) and biomass burning (HCN, CH_3Cl) was collected from the NASA DC-8 aircraft over wide geographic scales. These data are currently being analyzed and interpreted using a variety of atmospheric models that are themselves being validated against observations (Arellano et al., 2008). Several manuscripts are being prepared on this topic for the MILAGRO/INTEX-B Special Issue in *Atmospheric Chemistry and Physics* (ACP).

Chemical Evolution of Aerosols Mexico City's fine PM is usually dominated by organic species (Salcedo et al., 2006). Further, fine PM was observed during MCMA-2003 to grow very rapidly during sunlight hours – far faster than current atmospheric models or laboratory simulation experiments with the expected precursor gases can explain (Volkamer et al., 2006). Data collected from a mountain location in the MCMA's northeast corner during MILAGRO-2006 were used to differentiate oxygen-rich secondary organic aerosol (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 14. 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 (Herndon et al., 2008).

Carbon-14 and stable carbon-13 measurements also have indicated that 45-78 % of the total carbonaceous aerosol is coming from recent carbon sources, i.e., biomass and agricultural burning activities (including trash incineration) in the MCMA. Larger amounts of biomass burning aerosols were noted at the T1 site than the T0 site, consistent with the megacity having a significant fossil fuel input, but both sites were heavily impacted by recent carbon that could be derived from local and regional burning and transport of carbonaceous aerosols.

A new method for quantifying the organic

aerosol oxygen-to-carbon atomic ratio (O/C) has been recently developed using the High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) (Aiken et al, 2008). This method was applied for the first time to aircraft data using the results from the AMS flown in C-130 during MILAGRO-2006 (DeCarlo et al., 2007). Two highlights of the results are shown in Figure 15. The left plot shows a map of the flight tracks for several C-130 flights, colored by the organic O/C ratio. There is a clear increase in O/C ratio as one moves away from the city, with maximum values around 0.9. Even above Mexico City the O/C ratio is already ~0.4 or higher, representing a highly oxygenated aerosol. This is evident in flights through the city occurring in the early to late afternoon when photochemical SOA formation has already been active for hours (Volkamer et al., 2006; Kleinman et al., 2008). The plot in the right side of Figure 15 is a scatter plot of O/C vs. photochemical age calculated from NO_x/NO_y.

Figure 16 shows aerosol concentrations measured from the G-1 in the Mexico City urban plume as a function of photochemical age, defined by the ratio of NO_x to NO_y (Kleinman et al., 2008). Ambient concentrations decrease with age due to plume dilution. After accounting for dilution by using CO as a conservative tracer of urban emissions, the total non-refractory aerosol and its organic component are seen to increase by factors of 5 and 7 due to secondary aerosol formation over the course of ~ 1 day. As in a previous study (Volkamer et al., 2006) only ~ 10% of the SOA can be accounted for by aromatic precursors.

Results from both ground-based and airborne measurements confirm that the megacity plumes are significant sources of both primary and secondary aerosols at the regional scale, and black carbon and SOA are contributing to single scattering albedos in the MCMA and downwind that are substantially smaller than in other areas (such as the eastern United States). The regional burden of organic aerosol (when adjusted for dilution using CO correlations) and its O/C content ratio continue to grow with increasing air mass age for several days, and is far in excess of predictions by current models (Kleinman et al., 2008; DeCarlo et al., 2007). Sulfate aerosol also increases relative to nitrate in older polluted air, indicating HNO_3 particle to gas partitioning.

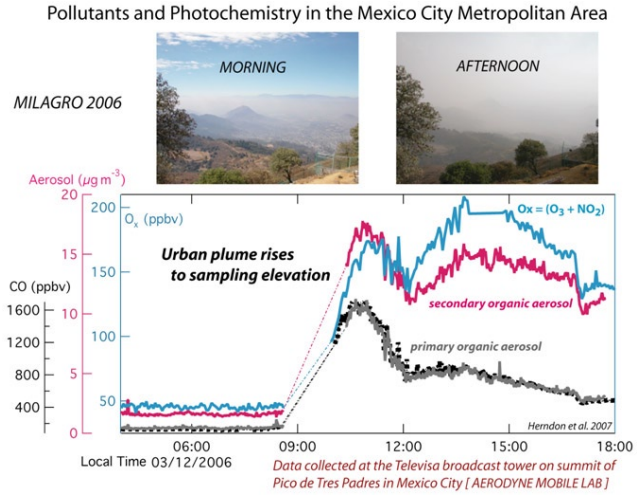


Figure 14. Photochemistry and SOA Formation in the MCMA (Herndon et al., 2007).

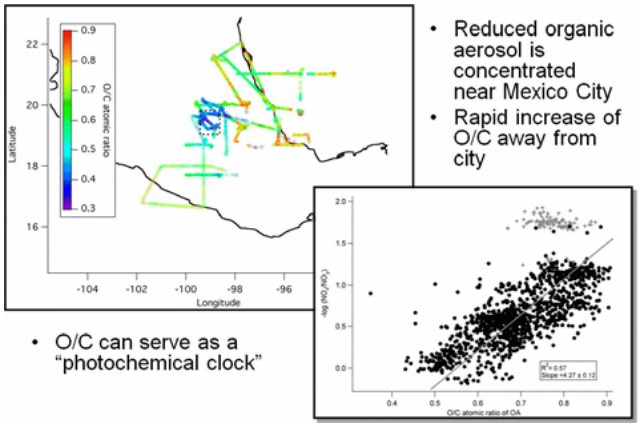


Figure 15. Organic aerosol is rapidly oxygenated in airmasses originating in the MCMA (DeCarlo et al., 2007).

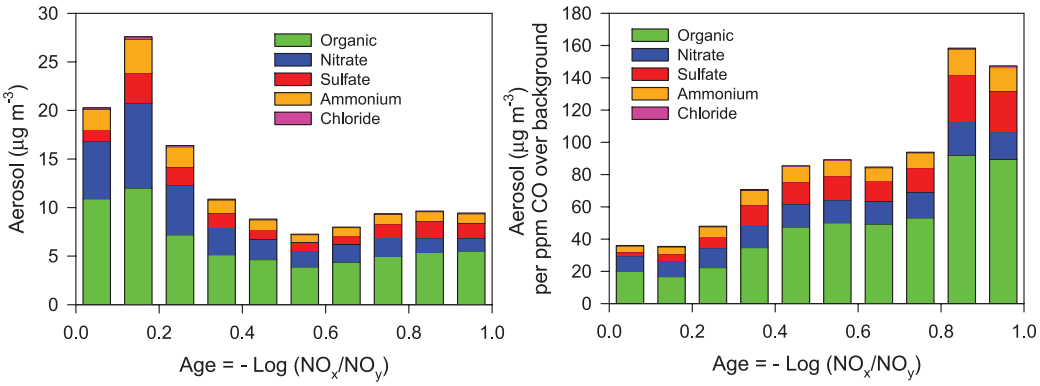


Figure 16. Secondary aerosol production in Mexico City urban plume measured from the G-1 as a function of photochemical age using – Log (NO_x/NO_y) as clock. Dilution is accounted for by normalizing aerosol concentration to CO above background. Left panel: Concentrations; right panel: Normalized concentrations (Kleinman et al., 2008).

Aerosol Radiative Effects

The evolution of aerosol optical properties was studied by in-situ sampling at ground sites (esp. T0, T1, and T2) and on the C-130, by filter and spectral radiometers on the ground and aircraft, and remotely by ground and aircraft-based lidars and satellite-based instruments. Light scattering and absorption measurements at the T0 and T1 sites showed aerosol single scattering albedo (SSA) values that were frequently in the 0.65-0.85 range with some incidents with even lower SSA. The diurnally averaged

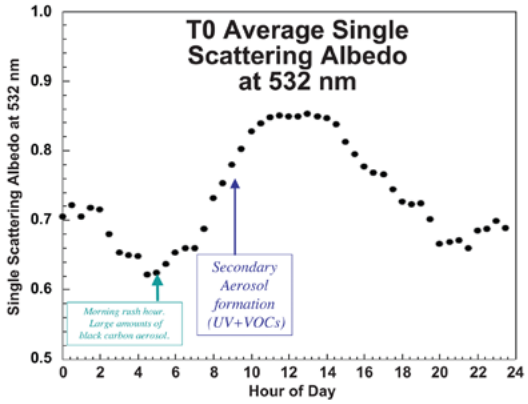


Figure 17. Average diurnal variation of the aerosol single scattering albedo (SSA) measured at 532 nm at the T0 site. Vehicle traffic is likely the cause of the observed minimum in the early morning hours, with the dramatic rise after sunrise due to photochemical reactions that convert gases to particulate matter. By mid day, a steady state production and removal rate is reached in the fully developed atmospheric boundary layer, mixed by the stirring caused by intense solar radiation. SSA falls in the evening hours. (Paredes-Miranda et al., 2008).

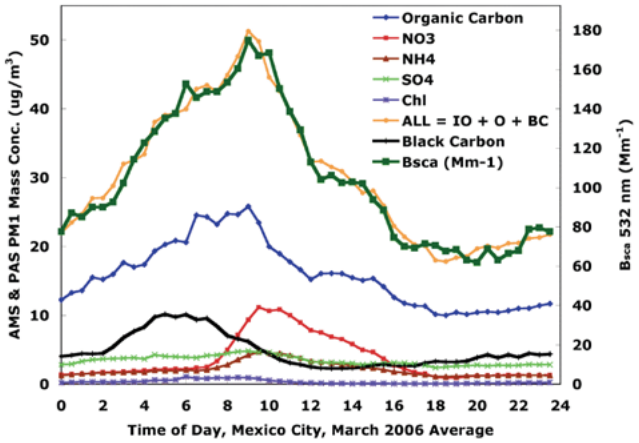


Figure 18. Diurnal variation of aerosol optics and chemistry at the T0 site showing a strong correlation between total aerosol mass concentration and aerosol light scattering. Black carbon (BC) mass concentration was obtained by dividing the aerosol light absorption at 532 nm by a mass absorption efficiency factor of 8.8 m^2/g. The diurnal variation of BC is useful as a marker of the dilution of the atmospheric boundary layer during the day. Chemical species that are continuously emitted would likely follow the same diurnal trend as BC, whereas species such as NO_3 and NH_4 have strong diurnal variations associated much more with the photochemical transformation. (Paredes-Miranda et al., 2008).

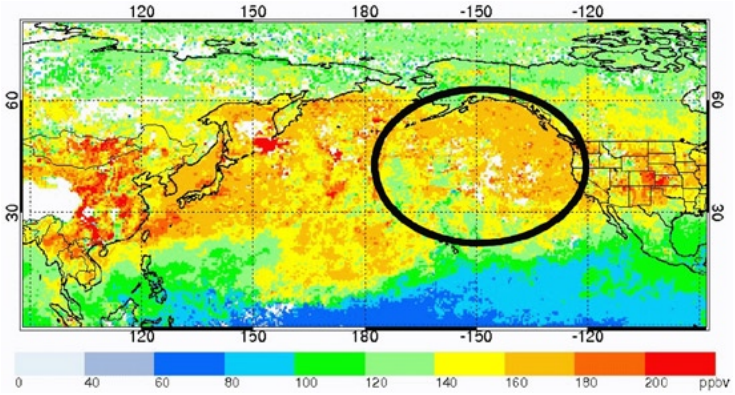


Figure 19. MOPITT CO at 700 hPa (1-31 March, 2006). Outflow crossing the Pacific across a broad range of altitudes provides the best situation for evaluating model transport and chemical evolution. Such an event was observed by the DC-8 and C-130 on subsequent days during INTEX-B. (*Courtesy: L. Emmons*).

SSA at 532 nm at T0 is shown in Figure 17 while Figure 18 shows the diurnal variation of aerosol optics and chemistry (Paredes-Miranda et al., 2008). These results indicate that the aerosol light scattering and absorption coefficients can be used to understand the local radiative impacts of aerosols; also there is a strong correlation between total aerosol mass concentration and aerosol light scattering. Comparisons with satellite-based instruments are discussed below. The results from LIDAR and aircraft operation as well as aerosol mass spectrometers all indicate that there is significant transport of aerosols and that most of this aerosol is in the lower layer of the atmosphere, but can be exported aloft into the free troposphere during venting events that were anticipated by pre-campaign modeling studies (Fast et al., in prep). Significant vertical layering of the aerosol and regional differences in the Valley of Mexico for aerosol scattering and extinction was also found. Evaluation of these measurements is underway and is leading to a better understanding of the evolution of aerosol optical properties as well as intercomparison and validation of the various techniques (Doran et al., 2007a,b; Ferrare et al., 2007; Gaffney et al., 2007; Livingston et al., 2007; Madronich et al., 2007; Shinozuka et al., 2007; Zhang et al., 2007).

Results from INTEX-B Pacific Mission

OMI NO_2 satellite observations can be used to constrain Asian anthropogenic NO_x emissions, indicating a factor of two increase in emissions from China from 2000 to 2006. Concurrent TES CO and ozone observations show evidence for trans-Pacific ozone pollution correlated with CO. Figure 19 shows the column of CO as observed by MOPITT during March 2006 clearly showing the transport of pollution over the Pacific. The semi-permanent Pacific High and Aleutian Low cause splitting of trans-Pacific pollution plumes over the Northeast Pacific. Both aircraft measurements and model results show sustained ozone production driven by PAN decomposition in the southern branch, adding to ozone produced in the Asian continental boundary layer (Figure 20). Model simulation of ozone observations suggest that Asian pollution in spring 2006 enhanced surface ozone concentrations by 5-7 ppb over western North America

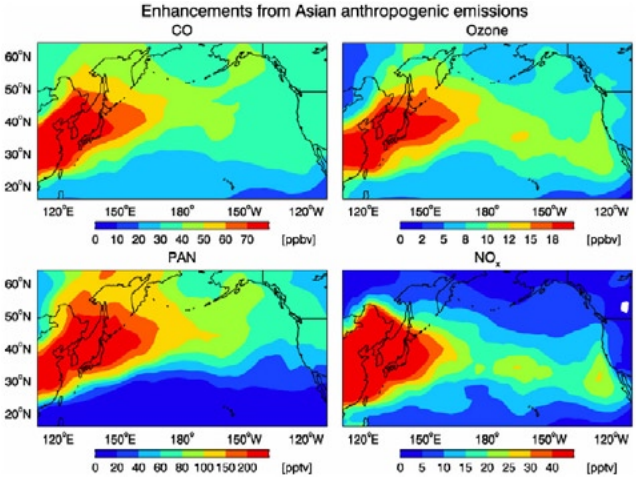


Figure 20. Mean enhancements of ozone, CO, NO_x, and PAN at 800 hPa due to the influence of Asian pollution for the INTEX-B period (April 17-May 15, 2006), as calculated using the GEOS-Chem model. The Asian pollution enhancements are determined by the difference between the standard simulation and a sensitivity simulation with Asian anthropogenic emissions shut off. (*Courtesy: L. Zhang*).

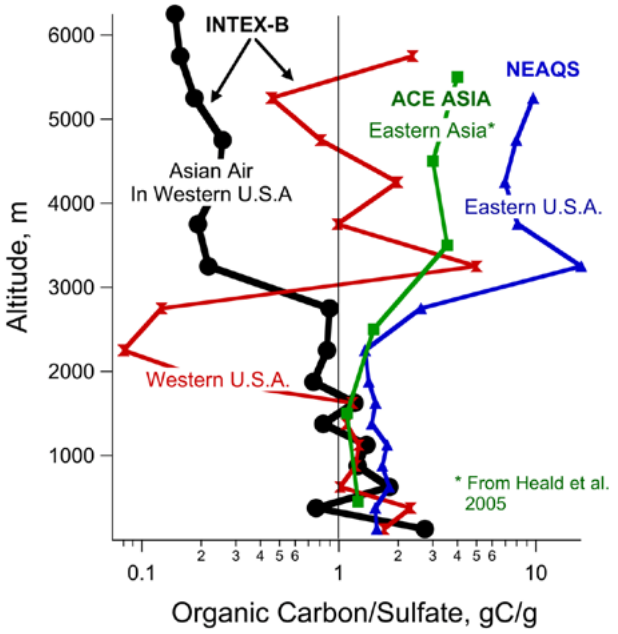


Figure 21. Vertical profiles of aerosol PM $OC/SO_4^=$ from various field campaigns (ACE-Asia, 2001; NEAQS, 2004; and INTEX-B). In many regions, free troposphere particulate OC is greater than or equal to $SO_4^=$ mass but in the Asian air masses measured from the C-130 during INTEX-B, the free troposphere is depleted in OC with respect to $SO_4^=$. (*Courtesy: von Donkelaar*).

(Zhang et al., 2008).

Large amounts of sulfate are observed in imported Asian pollution. Analysis of aircraft sulfate measurements from the NASA DC-8 over the central Pacific and the NFS C-130 over the east Pacific and the Cessna over British Columbia indicates most Asian sulfate over the ocean is in the lower free troposphere (800-600 hPa). It is calculated that 60% of the measured sulfate at 600 hPa over British Columbia is due to East Asian sources. Campaign-average simulations indicate anthropogenic East Asian sulfur emissions increase mean springtime sulfate in Western Canada at the surface by 25-30% and account for 40% of the overall regional sulfate burden between 1 and 5 km (van Donkellar et al., 2008; Peltier et al., 2008). In many regions particulate organic matter mass is greater or equal to sulfate mass (Figure 21).

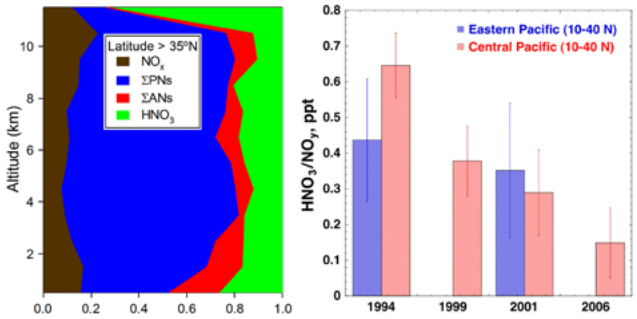


Figure 22. NO_y partitioning in the remote Pacific. The left panel shows that PANs comprise the dominant fraction of reactive nitrogen in the free troposphere over the Pacific. The right panel shows data from the Pacific upper troposphere during multiple missions, indicating that the relative abundance of HNO_3 is decreasing with time. Similar data also shows that PAN is increasing. (*Courtesy: R. C. Cohen and H. B. Singh*).

Figure 22 shows the distribution of reactive nitrogen observed from the DC-8 during the Pacific phase of INTEX-B. It is evident that a dominant fraction of reactive nitrogen is in the form of transported PAN. Comparison with previous observations suggests that the relative fraction of PAN has increased over time while that of HNO_3 has decreased. The increasing PAN reservoir allows a greater transport of reactive nitrogen. It is argued that these trends are largely driven by changes in surface emissions of VOC, NO_x and aerosol over Asia (Wolf et al., 2008).

Kim et al. (2008) provide gas phase HCl measurements from the marine boundary layer (MBL) to the lower stratosphere from the NASA DC-8 Pacific campaign. A case study suggests that HCl may be produced in the mid troposphere by the dechlorination of dust aerosols. Global 3-D chemical transport models have been used to interpret new INTEX-B observations of methanol to further constrain the atmospheric methanol budget (Millett et al., 2008). Additional data are currently being analyzed and new results are expected.

Satellite Validation

In recent decades a number of satellite sensors have started to measure composition in the troposphere. The principal focus has been on measuring tropospheric columns of CO, O_3, NO_2, and aerosols. While acquiring useful global data sets these sensors need to be continually validated and retrievals improved, such as through intensive field campaigns like MILAGRO. The principal INTEX-B platforms used for satellite validation were the NASA DC-8 and J-31 although the NSF/NCAR C-130 also performed specific activities useful for NO_2 validation. These required coincident in situ aircraft measurements

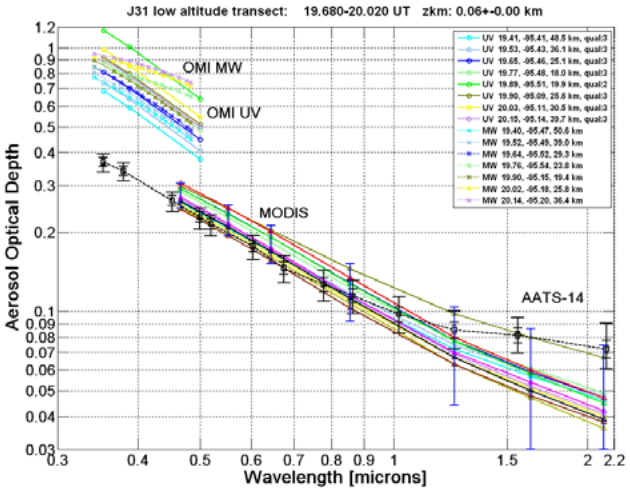


Figure 23. Aerosol Optical Depth comparisons from INTEX-B/MILAGRO measurements over the Gulf of Mexico, 10 March 2006. AOD from OMI on Aura and MODIS on Aqua (solid lines and, for MODIS, blue error bars) are compared to AOD from the aircraft-based Airborne Sun-photometer (AATS-14; black dashed line and error bars). (*Courtesy: P. Russell*).

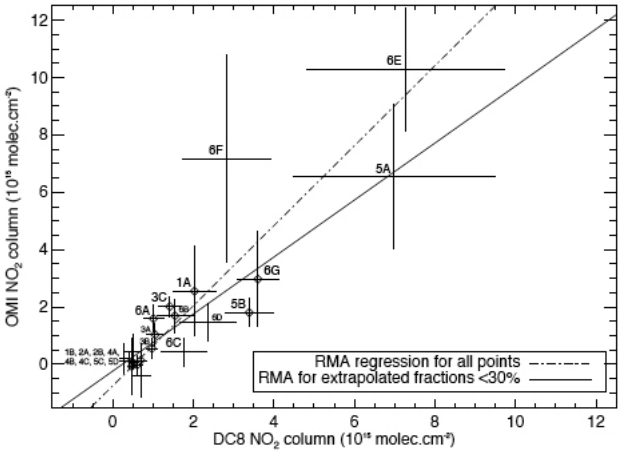


Figure 24. A comparison of NO_2 columns retrieved from OMI with coincident airborne insitu observations. (*Courtesy: K. F. Boersma*).

in vertical spirals within the swaths of overhead satellite sensors. Validation of instruments aboard the Aura satellite (TES, OMI, MLS, HIRDLS), launched in the summer of 2004, was a key objective within INTEX-B and nearly all flights included a satellite validation component. Figure 23 shows a comparison of aerosols retrieved by OMI, MODIS (on Aqua) and an airborne sunphotometer over the Gulf of Mexico. Several aspects of OMI data processing, including both radiances and algorithms, are currently being investigated to understand the differences shown. Figure 24 compares tropospheric NO_2 column measurements from OMI with airborne observations over the southern United States, Mexico, and the Gulf of Mexico during the INTEX-B campaign. Good correlation with no significant bias (R^2=0.67, slope=0.99 ± 0.17) is found for the ensemble of comparisons when the aircraft could spiral sufficiently low to sample most of the NO_2 column (Boersma et al., 2008; Bucsela et al., 2008). Extensive validation of CO and O_3 on TES and CO on AIRS and MOPITT was also carried out.

During the MILAGRO/MCMA-2006 Campaign, aerosol optical depth was measured using sunphotometers at five locations over the urban area, as well as by using the CIMEL sunphotometer from the global Aerosol Robotic Network (AERONET), located at the three supersites. These AOD data were compared to the AOD product of the MODIS sensor onboard NASA satellites Terra and Aqua. This process led to greatly improved agreement between AOD measured from the surface and that retrieved from satellites (Castanho et al., 2007).

Health Studies

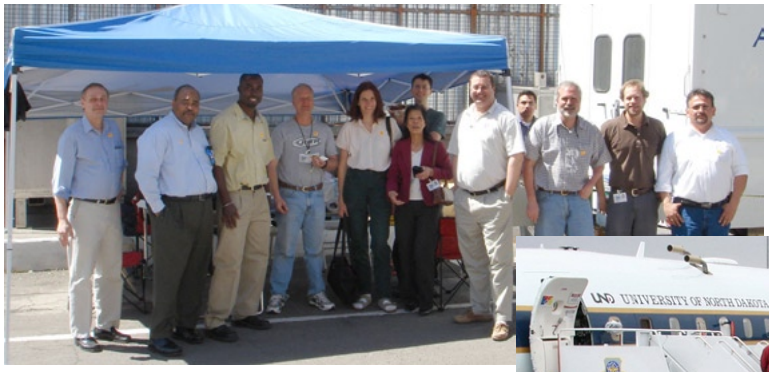
As part of the MILAGRO/MCMA-2006 Campaign, two studies relating air pollution and adverse biological effects were undertaken by two teams at the National University of Mexico, with participation from international atmospheric and health scientists.

The first study, led by A. Osornio, sampled PM_{10} at T0 and T1 with the goal of comparing and linking composition, oxidative potential and ventilation patterns with in vitro cellular effects. The current hypothesis on the mechanisms mediating PM toxicity resides in its capacity to induce oxidative stress on cells; PM metals and organics have the potential to produce this stress. Using principal component analysis, a set of 46 variables was reduced to 7 components. Three components were correlated with biologically relevant effects: hemolysis was associated with Si, Al, P, S and OC; oxidative potential with Cu, Zn & Ba; and DNA degradation with V and Cr. V and Cr showed a positive trend related to atmospheric boundary layer ventilation patterns as the only indicator of pollutants from the city reaching the receptor site. PM10 electron paramagnetic resonance analysis did not predict the observed oxidative potential on cells.

The second study, led by H. Tovalin, aimed to evaluate the contribution of regionally transported air pollutants from the MCMA to the personal exposure on children (age 9-12) and their parents during the Campaign. This study included collection of personal and micro-environmental samples of air pollutants (ozone, fine and ultrafine particles, CO, VOCs) at three selected sites in urban, suburban and rural areas; comparison of the indoor and outdoor concentrations, and personal exposures to air pollutants at the three sites; determination of the association between the exposures and the level of oxidative stress markers among the volunteers; and analysis of the relationship between the exposures and the respiratory health of the volunteers. Preliminary results indicate that children near T0 have decreased levels of respiratory and olfactory function as well as on their responding indicators to oxidative stress and inflammation. This could possibly be a manifestation of chronic exposure to pollutants. Correlation of these indicators with air pollutant levels is currently underway.

Conclusions

The observation phase of MILAGRO/INTEX-B has provided an extremely rich data set that will likely take years to analyze and evaluate. Preliminary results



Photos:
Left: A.M. Schmoltner (NSF), B. Doddridge (NASA), and R. Petty (DOE) visited T0 site during 2006 MILAGRO Campaign.

Below: INTEX-B Team.

were presented at MILAGRO science team meetings and international conferences. Five special sessions were convened at the American Geophysical Union 2007 Fall Meeting in San Francisco, CA. Major findings are being published in a special issue on MILAGRO/INTEX-B in Atmospheric Chemistry and Physics as well as in other peer-reviewed journals.

As described above, many groups have performed comprehensive analyses, in some cases including detailed modeling, of the numerous experimental data sets obtained. Many interesting aspects of atmospheric chemistry in and near the MCMA are emerging and have already added significantly to our understanding of the chemical and physical properties of the city's reactive atmosphere and the regional impacts. Data sets will also be made available to the entire atmospheric community for further modeling and evaluation.

We anticipate new results from MILAGRO/INTEX-B will continue to contribute to our understanding of megacity air pollution and its potential impacts on human health, ecosystem viability, and climate change on urban, regional, and even hemispheric scales. This information will improve significantly the scientific understanding that decision makers in Mexico will need to craft effective policies as well as provide insights to air pollution problems in other megacities around the world.

Acknowledgments

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