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Announcements

Annecy 2008

bridging the scales

IGAC 10th International Conference Bridging the scales in Atmospheric Chemistry: Local to Global

7-12 September 2008 ▪ Annecy, France
http://www.igacfrance2008.fr/

The theme of this year's program is "Atmospheric Composition: Bridging the Scales from Local to Global". There will be a particular focus on interactions between earth system compartments across these scales. Sessions will be held with the following themes:

1. Atmospheric Chemistry and Climate (joint with SPARC)
2. Impact of Clouds and Chemistry on Regional and Global Scales
3. Observing Atmospheric Composition from the Global to the Local Scales
4. Biogenic Impacts on the Regional and Global Scale
5. Anthropogenic impacts of urban centers on the Regional and Global scale
6. From the Nanoscale to the Macroscale: Process Studies
7. Polar and Oceanic Regions – Relating Local and Regional Processes to the Larger Scale

IGAC's 10th International Conference will be held at the beautiful Congress Center L'Imperial Palace on the lakeshore of Annecy, France. Annecy is located just 40km south of Geneva, in the beautiful French Alps.

This will be IGAC's first "carbon-neutral" conference.

As with past conferences, there will be a special program for young scientists.

Please join us!

GLOBAL IGBP CHANGE
A Core Project of the Internations Geosphere-Biosphere Programme

CACGP
In Cooperation with IAMAS Commission on Atmospheric Chemistry and Global Pollution

Overview of MILAGRO/ INTEX-B Campaign

Luisa T. Molina, *Molina Center for Energy and the Environment, La Jolla, CA and Massachusetts Institute of Technology, Cambridge, MA.* (ltmolina@mit.edu), **Sasha Madronich**, *National Center for Atmospheric Research, Boulder, CO.* (sasha@ucar.edu), **Jeffrey S. Gaffney**, *University of Arkansas at Little Rock, AR.* (jsgaffney@ualr.edu), and **Hanwant B. Singh**, *NASA Ames Research Center, Moffett Field, CA.,* (Hanwant.B.Singh@nasa.gov)

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

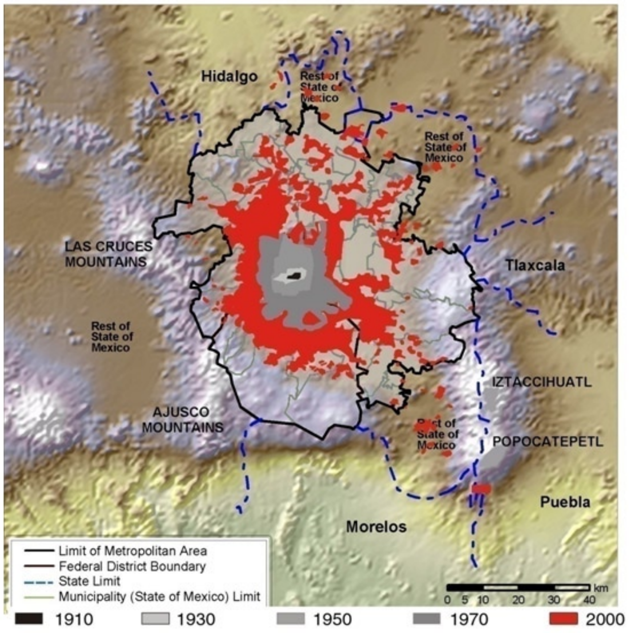

Figure 1. Topographical map of the MCMA showing urban expansion (Molina and Molina, 2002).

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,

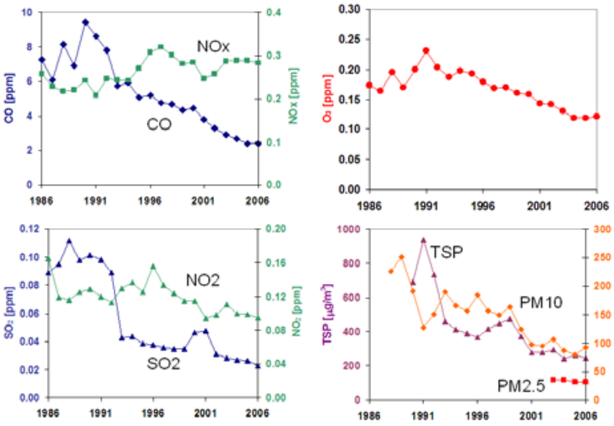

Figure 2. Air quality trends of the MCMA (Mexico City, Federal District Government 2006; www.sma.df.gob.mx/simat).

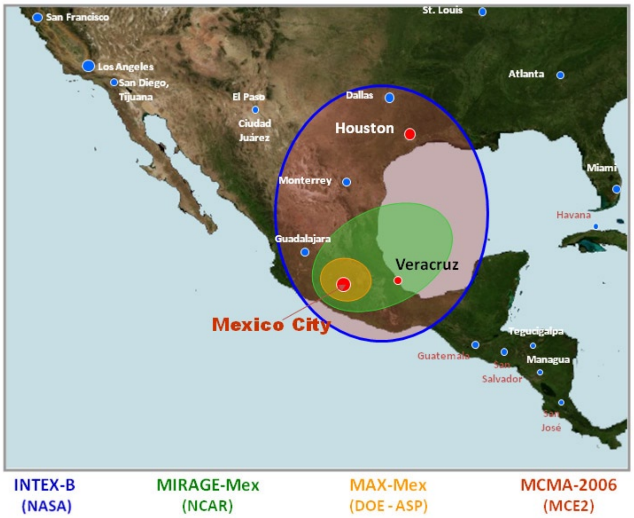

Figure 3. Geographical coverage of the MILAGRO Campaign.

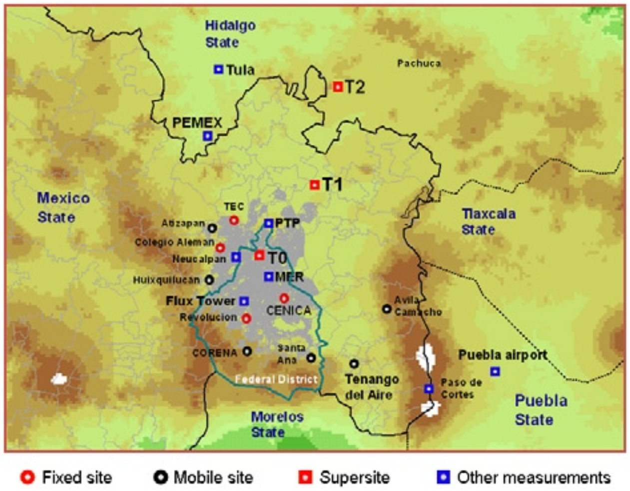

Figure 4. Ground-based measurement sites of the MILAGRO Campaign.

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

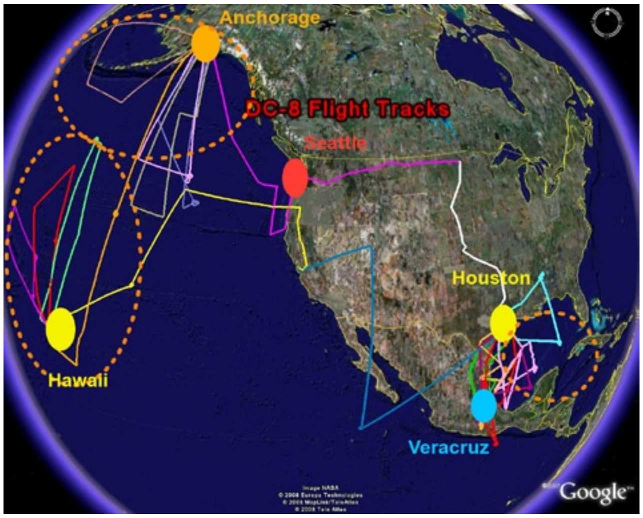

Figure 5. INTEX-B DC-8 flight tracks and DC-8 Bases in Houston, TX (3/1-21/2006), Honolulu, Hawaii (4/17-30/2006), and Anchorage, Alaska (5/1-15/2006). Also shown are operational sites for the: DC-8 (yellow ovals); C-130 (red oval); and C-130, J-31, B-200, G-1 (blue oval).

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

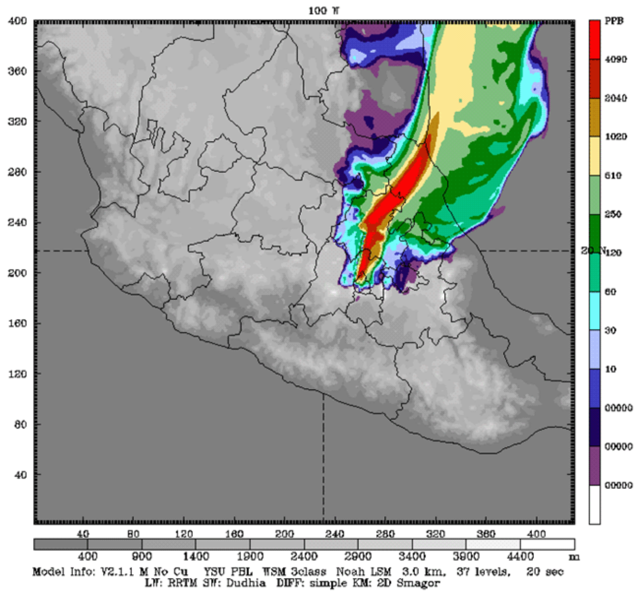

Figure 6. Distribution of Mexico City CO-like transport tracer emitted on 18 March 2006, shown on 19 March 2006 18:00 local time, as calculated using NCAR's WRF model. (*Courtesy: W. Skamarock*).

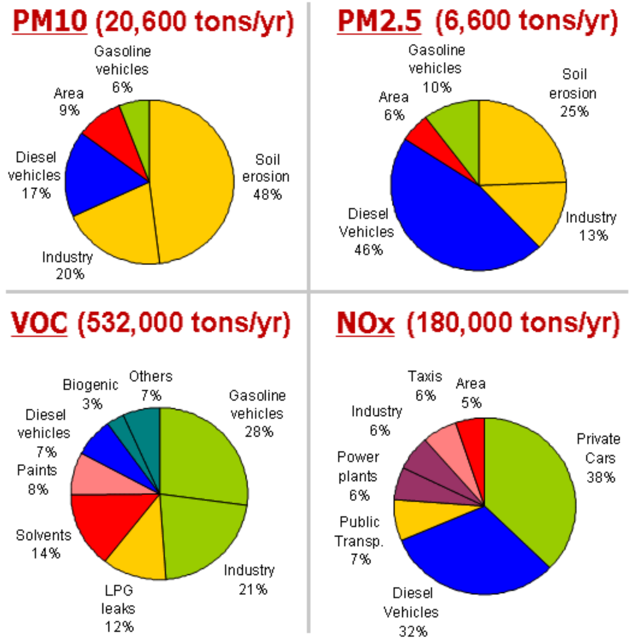

Figure 7. Emission Sources in Mexico City for the year 2004 (CAM, 2006).

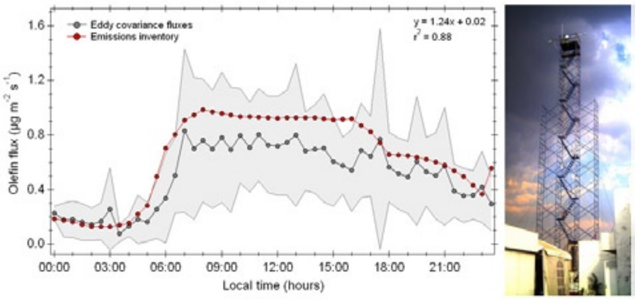

Figure 8. Measured olefin fluxes *vs.* estimated emissions as given in the local emission inventory (Velasco et al., 2007b).

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).

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.

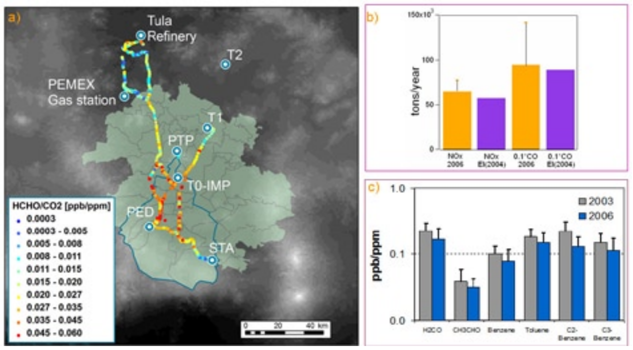

Figure 9. Shown are data used to characterize mobile emissions in Mexico City using data from the MCMA-2003 and MCMA-2006 campaigns. a) Observed highly heterogeneous spatial distributions of emissions, b) on-road measurements (orange) vs those in the local emissions inventory (purple); c) measured reduction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

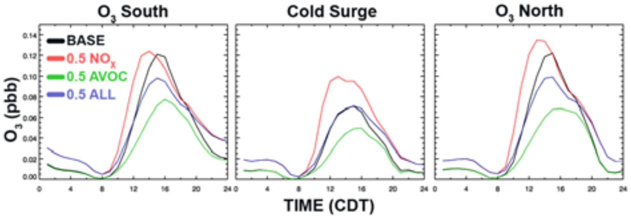

Figure 10. The response of near-surface O_3 concentrations to different emission reduction scenarios in the MCMA source region under different meteorological conditions identified during the MCMA-2003 Campaign, as given by a chemical transport model: 0.5 NO_x denotes a 50% reduction in NO_x; 0.5 VOC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

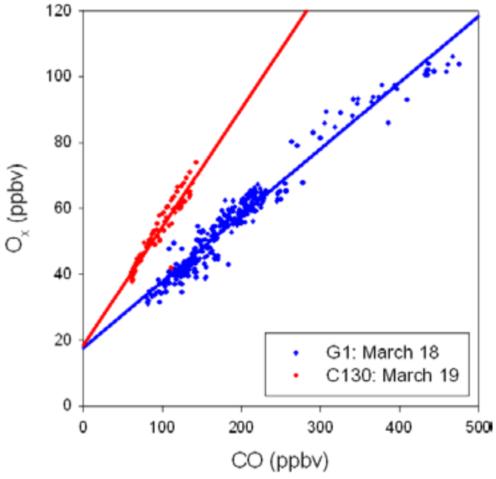

Figure 11. Evolution of O_x (= O_3 + NO_2) vs. CO correlations in the Mexico City plume. The G1 aircraft sample the air near Mexico City on 18 March (blue), while the C130 aircraft intercepted the plume about 1000 km downwind on 19 March (red). (Zaveri et al., 2007).

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

(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).

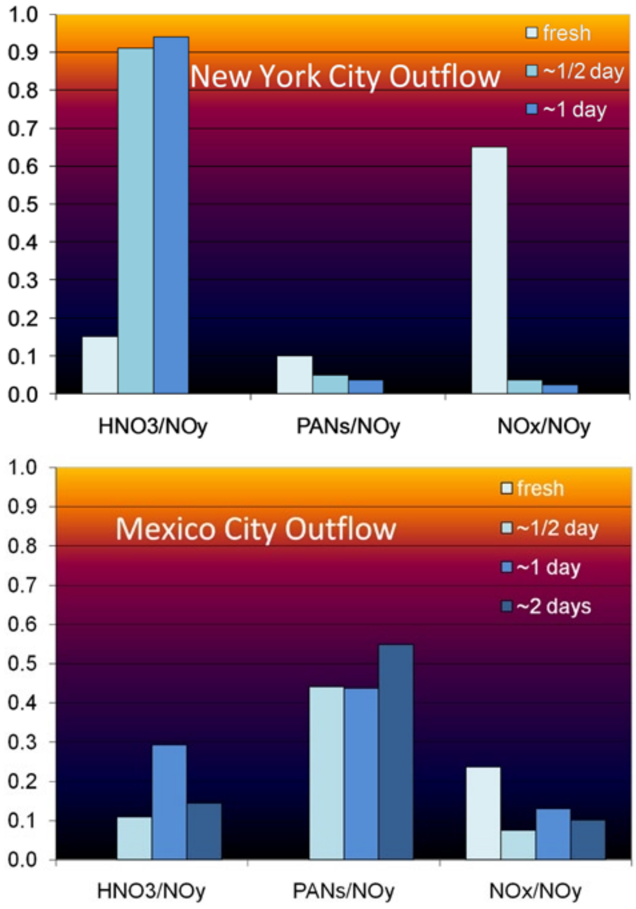

Figure 12. Reactive nitrogen in the outflow of Mexico City (bottom panel) and New York City (top panel). Downwind of Mexico City, the large fraction of PANs sustains NOx for ongoing production of O_3. (Flocke et al., 2007).

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).

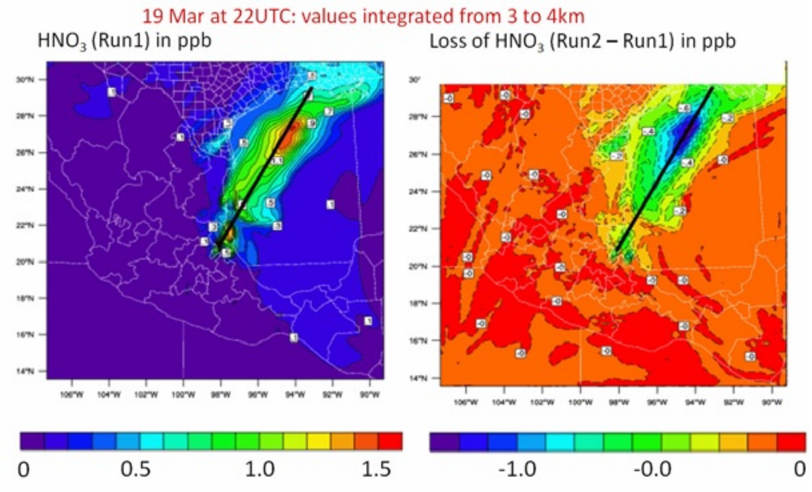

Figure 13. WRF-Chem simulation of nitric acid (HNO_3) in the Mexico City plume, without and with heterogeneous loss on dust encountered downwind. Left panel (Run 1) shows HNO_3 without loss on dust; right panel: about 2/3 of the plume's HNO_3 can be removed by this process (Hodzic et al., 2007).

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.

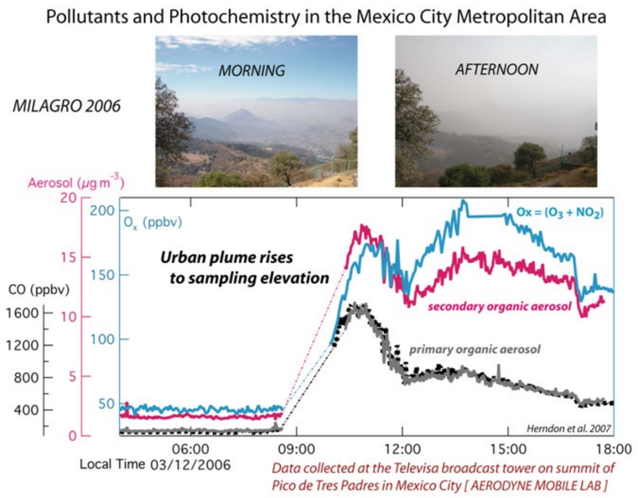

Figure 14. Photochemistry and SOA Formation in the MCMA (Herndon et al., 2007).

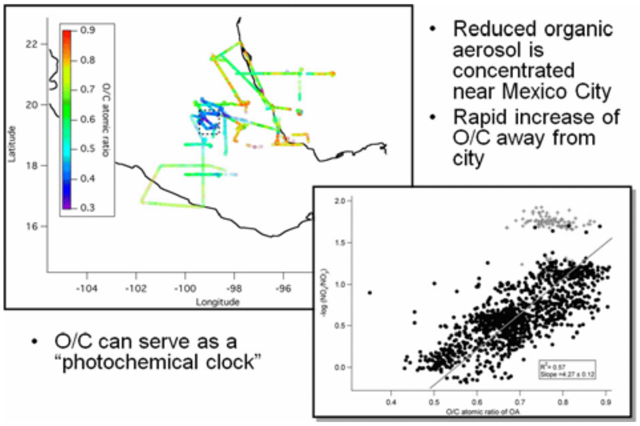

Figure 15. Organic aerosol is rapidly oxygenated in airmasses originating in the MCMA (DeCarlo et al., 2007).

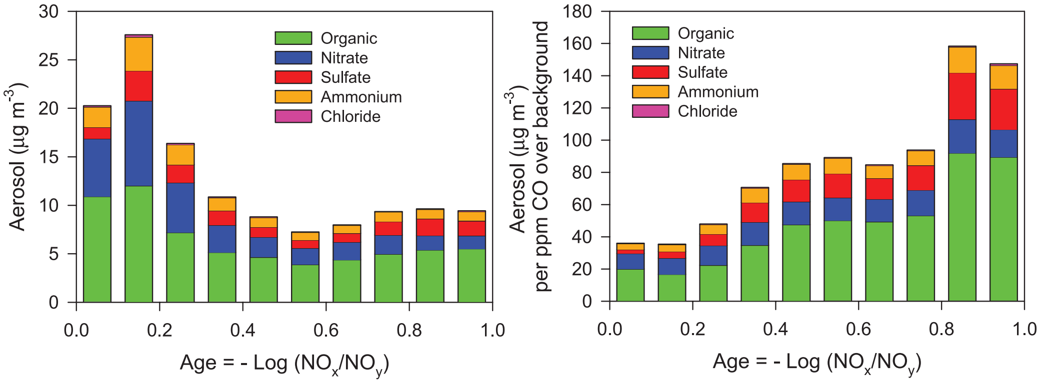

Figure 16. Secondary aerosol production in Mexico City urban plume measured from the G-1 as a function of photochemical age using – Log (NO_x/NO_y) as clock. Dilution is accounted for by normalizing aerosol concentration to CO above background. Left panel: Concentrations; right panel: Normalized concentrations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

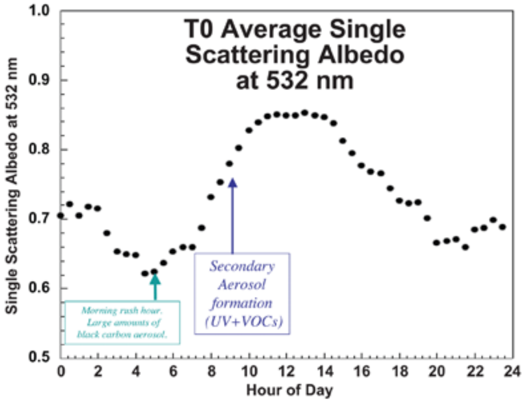

Figure 17. Average diurnal variation of the aerosol single scattering albedo (SSA) measured at 532 nm at the T0 site. Vehicle traffic is likely the cause of the observed minimum in the early morning hours, with the dramatic rise after sunrise due to photochemical reactions that convert gases to particulate 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).

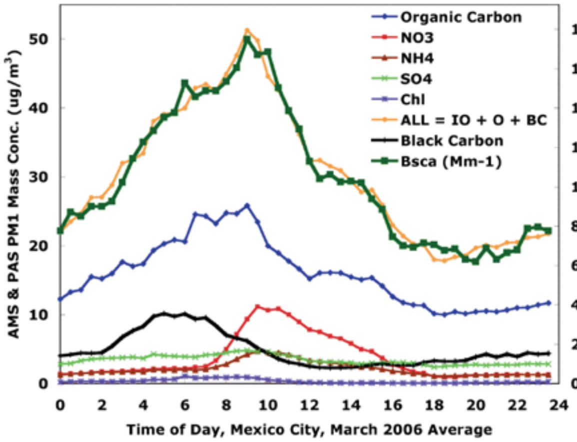

Figure 18. Diurnal variation of aerosol optics and chemistry at the T0 site showing a strong correlation between total aerosol mass concentration and aerosol light scattering. Black carbon (BC) mass concentration was obtained by dividing the aerosol light absorption at 532 nm by a mass absorption efficiency 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).

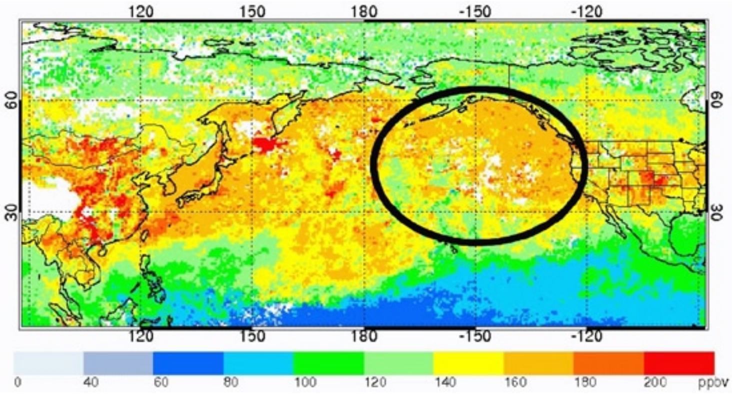

Figure 19. MOPITT CO at 700 hPa (1-31 March, 2006). Outflow crossing the Pacific across a broad range of altitudes provides the best situation for evaluating model transport and chemical evolution. Such an event was observed by the DC-8 and C-130 on subsequent days during INTEX-B. (*Courtesy: L. Emmons*).

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

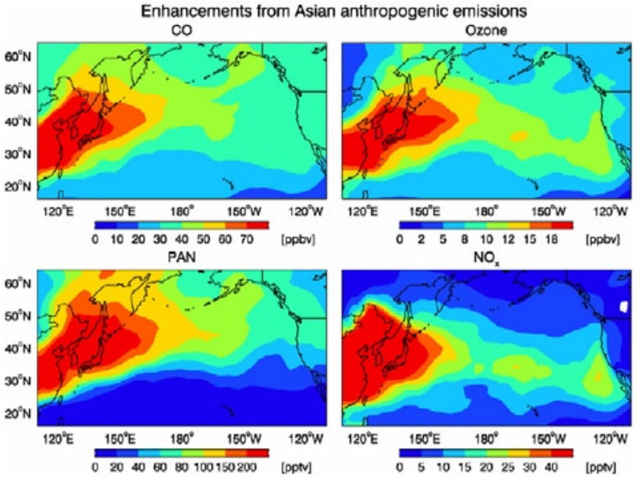

Figure 20. Mean enhancements of ozone, CO, NO$_x$, and PAN at 800 hPa due to the influence of Asian pollution for the INTEX-B period (April 17-May 15, 2006), as calculated using the GEOS-Chem model. The Asian pollution enhancements are determined by the difference between the standard simulation and a sensitivity simulation with Asian anthropogenic emissions shut off. (*Courtesy: L. Zhang*).

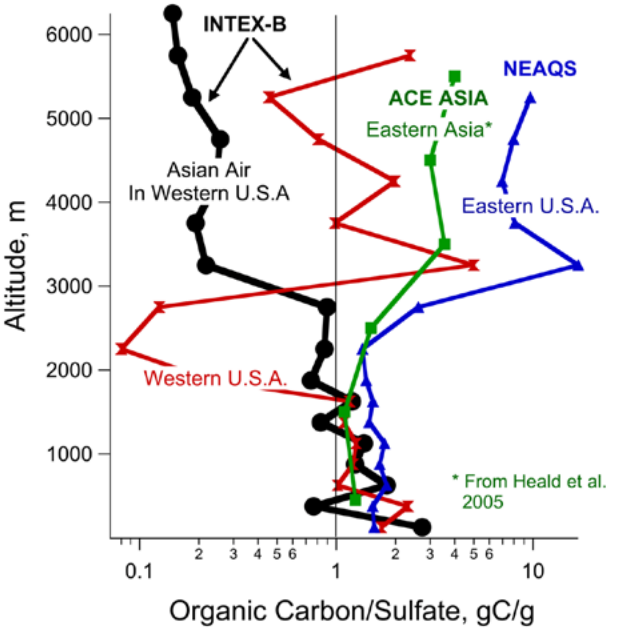

Figure 21. Vertical profiles of aerosol PM OC/SO$_4^=$ from various field campaigns (ACE-Asia, 2001; NEAQS, 2004; and INTEX-B). In many regions, free troposphere particulate OC is greater than or equal to SO$_4^=$ mass but in the Asian air masses measured from the C-130 during INTEX-B, the free troposphere 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).

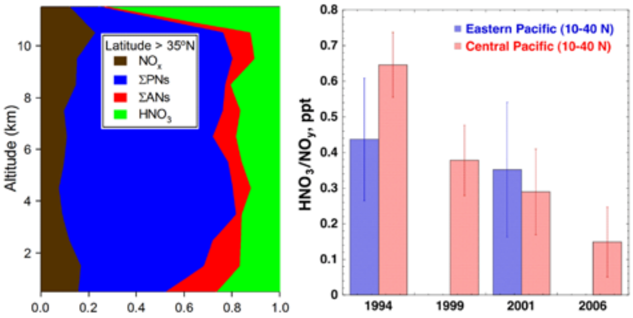

Figure 22. NO$_y$ partitioning in the remote Pacific. The left panel shows that PANs comprise the dominant fraction of reactive nitrogen in the free troposphere over the Pacific. The right panel shows data from the Pacific upper troposphere during multiple missions, indicating that the relative abundance 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

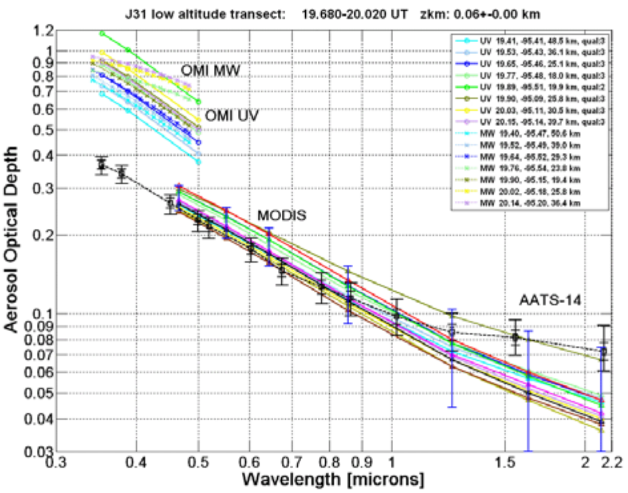

Figure 23. Aerosol Optical Depth comparisons from INTEX-B/MILAGRO measurements over the Gulf of Mexico, 10 March 2006. AOD from OMI on Aura and MODIS on Aqua (solid lines and, for MODIS, blue error bars) are compared to AOD from the aircraft-based Airborne Sun-photometer (AATS-14; black dashed line and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

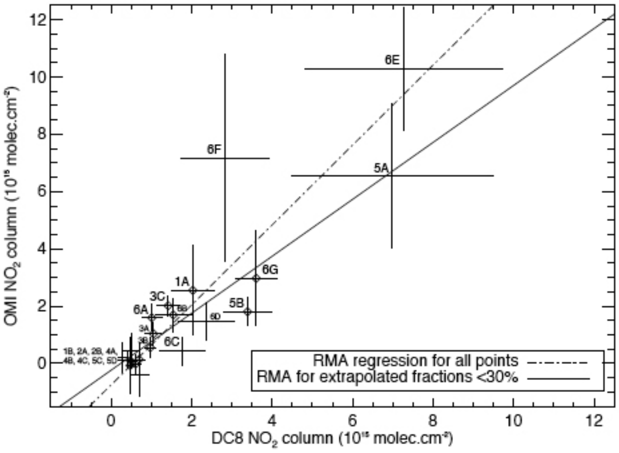

Figure 24. A comparison of NO_2 columns retrieved from OMI with coincident airborne insitu observations. (*Courtesy: K. F. Boersma*).

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

Photo Credit: W. Liao

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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South American Mega-cities: Actions and Perspectives

Laura Gallardo* *Departamento de Geofísica & Centro de Modelamiento Matemático, Universidad de Chile, Santiago, Chile* (lgallard@dim.uchile.cl)

**PI for the South American Emissions Mega-cities and Climate project (IAI CRN 2017)*

In 1950, the only city in South America with a population over 5 million inhabitants was Buenos Aires. By 2005, seven cities in this continent exceeded this number: Belo Horizonte (5 million), Bogotá (7 million), Buenos Aires (13 million), Lima (8 million), Rio de Janeiro (11 million), Santiago (6 million) and São Paulo (18 million), encompassing 75% of the continent's population (Cf. Figure 1). This rapid increase, which is expected to continue, has brought new challenges in terms of natural resources, land use and transport management as well as for water resources and air pollution. The deteriorating air quality in South American mega-cities has received increasing attention from local decision makers, scientists and the public in general. Until recently, the efforts of the local communities have been largely decoupled from international efforts. The Inter American Institute for Global Change Research (IAI, http://www.iai.int) has provided the means to make such a connection happen, through establishment of the South American Emissions Mega-cities and Climate (SAEMC, http://saemc.cmm.uchile.cl) project, which is a Collaboration Research Network for the period 2006-2010, involving 23 researchers in Argentina, Brazil, Chile, Colombia, United States of America and, most recently, Peru. In addition to this, IAI has approved a two-year project (2007-2009), Adaptation to health impacts of air pollution and climate extremes in Latin American cities (ADAPTE), providing a stronger human dimension value to the original project. These projects represent an unprecedented opportunity for strengthening and coordinating regional research capabilities, connecting regional and global efforts, and providing a sound scientific basis for sustainable policies. Hereby a description of the project is provided, and advances after 18 months of work are highlighted.

Figure 1. South American cities: their population and differing geography.

Addressing emissions, air quality, and climate scenarios in South America

SAEMC is a Collaborative Research Network (CRN) funded by the IAI for the period July 2006-July 2010. It involves 23 researchers from Argentina (6), Brazil (4), Chile (9), Colombia (2), Peru (1) and the United States of America (1). A full listing of the institutions and researchers involved is shown in Table 1. Together with its human dimension counterpart (ADAPTE), it adds up to US$ 872,500 over four years, most of which is dedicated to capacity building in the form of student fellowships and short- and mid-term visits among the participating students and researchers. This funding is roughly doubled by other sources in connection with individual projects, typically linked to local environmental authorities.

Initially, the SAEMC project considered four work areas, namely: emission estimates and evaluation, chemical climate scenarios, chemical weather forecasting and prospective characterization of aerosols. Along the way, a fifth area was added, i.e., grid computing applications, which aims at sharing resources and making use of existing fast internet connections in the region.

Emissions scenarios estimate and evaluation

We aim to provide past (1970's), current (2000) and future (2030) emission scenarios (spatially and temporally disaggregated) for mobile and stationary sources in South American cities (e.g., Bogotá, Buenos Aires, Lima, Santiago, São Paulo).

Current scenarios for mobile source emissions are estimated by applying a novel approach specifically designed for determining vehicle emissions in developing countries (http://www.issrc.org/ive/). This methodology is characterized by three stages: (a) Vehicle activity study; (b) On-road emission testing; and (c) Emissions estimations using vehicle technology distribution, vehicle specific power, engine stress, real-world emission factors and local correction factors.

For stationary emissions, the current inventories are estimated by a bottom-up approach using state-of-the-art methodologies that can be applied consistently in all partner cities to obtain comparable emission estimates with compatible spatial resolution. There are two main stages to this process for mega-cities: 1) reviewing, comparing and reconciling current emissions inventory methodologies used in the different cities; and 2) up-dating emissions inventories. Country-based emissions inventories are also estimated by 1) including large stationary sources located outside the cities in each country, and 2) downscaling country-based inventories to grid-based inventories through a spatial allocation processes for the remaining stationary sources.

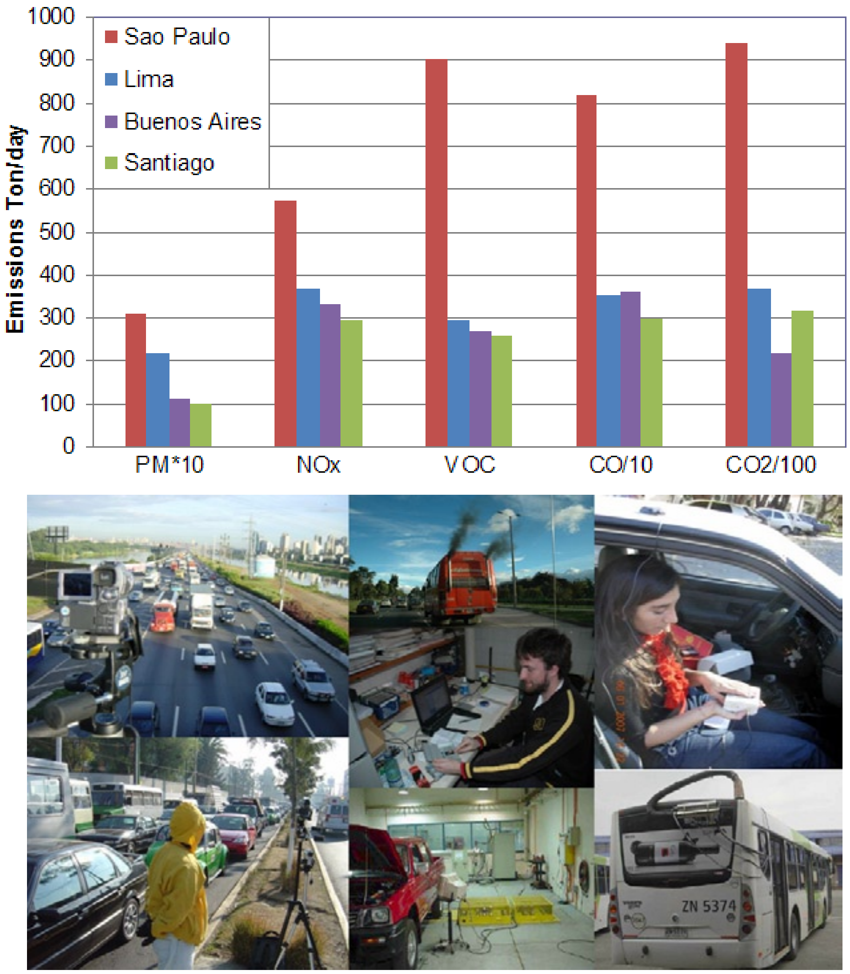

Figure 2. Total emissions from mobile sources in Buenos Aires, Santiago, Lima and São Paulo. These emissions were estimated using the IVE (International Vehicle Emissions, http://www.issrc.org) methodology. In the case of Santiago and São Paulo these Figures can be compared with bottom-up estimates. The photographs illustrate the overall IVE methodology, and some of the SAEMC students.

These emissions scenarios are evaluated by various forward and inverse modeling techniques, using in situ and remotely sensed data, and they are reconciled with available local and global emission inventories. Some of these techniques (Best Linear Unbiased Estimate, variational/adjoint method) were already implemented during a one-year pilot project (2004-2005). Sequential techniques (Kalman filtering) will also be implemented, particularly in connection with operational use of chemical weather forecasting.

Past and future emission scenarios and trends will be estimated using numerical and statistical approaches, based on technological and socio-economic change following the IPCC scenarios.

To date, several measurement campaigns intended to characterize vehicular emissions have been carried out (in Santiago, Bogotá, São Paulo and Buenos Aires). Also, an evaluation of the emission inventory for carbon monoxide in Santiago has been achieved corroborating the total numbers but introducing substantial changes in the diurnal cycle of emissions in some areas of the city. These activities are illustrated in Figure 2.

Dynamical down-scaling of climate change scenarios

Using results from the emissions scenario activity and climate change scenarios provided by global models (coupled with chemistry and transport models) as boundary conditions for regional-scale climate and dispersion models, current (2000) and future (2030) regional air quality scenarios over at least one mega city (e.g. Santiago and São Paulo), on each coast line will be considered to account for different emission and circulation regimes. This will be done using a multiple grid nesting approach of the Coupled Chemistry Aerosol and Tracer Transport model with the Brazilian developments on the Regional Atmospheric Modeling System (C-CATT-BRAMS, http://meioambiente.cptec.inpe.br/modelo_cattbrams.html). In addition to consistent air quality scenarios, these outputs will be used in health impact assessments under ADAPTE. Depending on the availability of storage and analytical resources, this effort might be extended to other cities. Off-line chemistry approaches might also be considered.

So far, various models have been tested and evaluated over different areas (e.g., South East Pacific, La Plata basin) in the region, considering different circulation regimes.

Implementation of a pilot chemical weather forecast network

Brazil shows the strongest development in atmospheric research in South America. INPE/CPTEC (http://meioambiente.cptec.inpe.br/) is the largest weather forecasting center in the region, including operational tools for chemical weather forecasting. This system is based on the Brazilian developments of the Regional Atmospheric Modeling System (B-RAMS) coupled to an on-line Eulerian transport model. This is a powerful tool for atmospheric simulation equipped with a multiple grid nesting scheme which allows the model equations to be solved simultaneously on any number of interacting computational meshes of different spatial resolutions. It also contains several chemical mechanisms. This air quality forecast system runs on a regional scale covering the South American continent, and within the SAEMC project it is used to deliver initial and boundary conditions of the atmospheric dynamic, thermodynamic and chemical state for the urban models used by the participating institutions. A pilot activity is focusing on the connection between INPE/CPTEC and the Chilean Meteorological Office (Dirección Meteorológica de Chile, DMC http://www.meteochile.cl/). A dedicated group of senior meteorologists has been created, and they have so far implemented two chemical weather forecast tools, POLYPHEMUS (http://cerea.enpc.fr/polyphemus/) and C-CATT-BRAMS. Note that even though in most developed countries it is natural that a weather office has such a group, in many South American countries this is not the case. In fact, we consider the involvement of DMC in this project from its very inception a major success. In the immediate future we hope to add to this network the Peruvian Meteorological and Hydrological Service as well (SENAMHI, http://www.senamhi.gob.pe/) A similar test-bed has also been initiated over Buenos Aires.

Prospective characterization of aerosols inside and downwind South American mega-cities

Considerable resources have been invested by local authorities in various urban areas in South America in the area of air quality monitoring, focusing on exposure to so-called criteria pollutants (Cf. Table 2). However, aerosol measurements in the region, except for some areas of Brazil, are still sparse and usually limited to concentration levels of partially (PM10) and completely (PM2.5) inhalable particles. A more detailed characterization of aerosol size distribution and chemical composition are at best sporadic. This work package is compiling available information and making comparative evaluations. Also, using installed capabilities and complementary project resources, the aerosol content and size distribution for mass and number of major and minor trace elements for at least three mega-cities are to be analyzed using atomic spectroscopic techniques while the content in selected organic compounds, particularly monocarboxylic acids, is beginning to be analyzed using chromatographic techniques. The origin of primary aerosols and secondary aerosol formation are being assessed using the measured composition profiles, applying receptor models to improve emissions inventories of airborne particulate matter. In addition, a LIDAR system located in Argentina provides information on aerosol backscatter properties through the whole tropospheric column, near the edge of the Buenos Aires mega-city region. In the case of São Paulo these observational aspects are complemented by a modeling study focusing on the urban aerosol plume and its interactions with clouds.

Grid computing applications in South America

As part of the SAEMC project development, an Information and Technology (IT) research group has emerged. In addition to maintaining our webpage (http://saemc.cmm.uchile.cl/) and facilitating the operation of sophisticated models and platforms, they have optimized the use of available computer facilities and they are making it possible to interconnect various systems (grid computing).

It is worth noticing that South America already has fast internet connections covering all countries except Bolivia and Paraguay (e.g., http://www.redclara.net/). However, this infrastructure is – to the best of our knowledge – largely under-exploited, with less than 10% of the bandwidth currently being used. As a way of sharing computing and storage capacities and expertise among the participating institutions we are implementing a pilot activity that takes advantage of this network by connecting (to date) three cluster systems: one at CPTEC, two in Chile, one at the Center for Mathematical Modeling and another at the Chilean Meteorological Office. We expect to expand this to other participants as well. Despite the obvious gains and advantages of improving the use of resources and the sharing of often scarce, very specialized expertise, progress on such efforts is slowed by cultural and political barriers among and also within our countries and institutions. The existence of an organizing body such as SAEMC helps overcome some of these obstacles.

Capacity building

Except in Brazil, where in particular the Large Scale Biosphere-Atmosphere Experiment in Amazonia (LBA) has provided first-world infrastructure and an unprecedented increase in human resources, material and human resources for atmospheric research in South America on a country-by-country basis are far too small to allow a significant contribution to international programs and to produce sustained impacts in the local development. For instance, although Chile has faced a unique growth in research funding and a great percentage increase in PhD degrees in atmospheric science (tripling the number of PhDs in the past ~10

Figure 3. In June 2007 a hands-on workshop on direct and inverse modeling of air quality was held at the Center for Mathematical Modeling in Santiago (http://dataassimilation07.cmm.uchile.cl/). Similar activities will take place in our annual symposium for 2008 in Ubatuba, Brazil (http://www6.cptec.inpe.br/saemc/).

years), in absolute numbers this growth results in a total community of less than 20 researchers, distributed across various institutions covering a variety of topics. Thus, international linkage among our countries is absolutely critical. Further, it is essential that a significant fraction of our resources are dedicated to capacity building at various levels, including technical, professional and graduate training (Cf. Figure 3). Therefore, both SAEMC and ADAPTE put roughly 70% of their resources into fellowships for professional exams and graduate theses. In addition to this, we facilitate short- and long-term exchanges of students and researchers, abilities and knowledge sharing and, when possible, post-graduate programs. The students, who are our largest asset, have been selected from universities in the region according to relevance of the proposed thesis and academic merit. The guiding or co-guiding of a Co-PI is required. So far our projects are financing 12 exams/theses in engineering, atmospheric science and environmental management. Another 10 students are linked to the projects but are funded from other sources. Many of these exams/theses are developed in such a manner that institutional, country and disciplinary boundaries are surpassed, creating a new cultural environment that we expect will transcend the current projects.

Connecting science and decision-making

The major funding agencies in the world are pushing towards not only scientific quality and merit but also towards relevance for policy decisions. This is the case too for IAI and its parent funding agencies, and consequently a strong effort is being made to foster and promote the necessary dialogue, on the one hand, between natural and social scientists, and on the other hand, between scientists and stakeholders. Our mega-city initiative is facing this challenge in various manners. The public sector is either a part of the project (e.g., Chilean and Peruvian weather services) or is closely linked via ancillary projects (e.g., Transportation and Health authorities in Brazil, Chile and Colombia). This permits the definition of common goals and facilitates the use of our scientific products by policy makers, ensuring impact and relevance for our project. The draw-back to this approach is that the ancillary projects often must respond to short-term needs for producing local assessments. These are time-consuming and often not valuable in the framework of academic careers, nor in the eyes of the local funding agencies that are still very disciplinarily driven. Moreover, scientifically trained staff is often tempted to leave academia to serve as private consultants so they can ameliorate their income. Even academic institutions tend to create consulting services, which can be economically beneficial but scientifically detrimental in the long run, if not posed within an adequate scientific and institutional framework.

Another typical issue faced in projects like SAEMC is that home institutions do not always consider multi-national and multi-institutional projects as under their purvue, increasing the administrative burden for the investigators. A similar situation is found when dealing with scientific communication, which typically must be managed directly by the researchers.

Summary and Outlook

SAEMC will provide regional scale past, present and future climate change scenarios, with a unique emphasis on the evolution of air quality in large (population >5 million) South American cities, where more than 75% of the population of the continent lives. Such high resolution scenarios are not currently available for this area of the world. Comparable estimation and evaluation methodologies as well as reconciled local, regional and global scale emission inventories are being produced for South America. To date, this region has been poorly studied in this respect despite its potential vulnerability to global change and its effects, particularly in mega-cities. A coordinated regional chemical weather forecasting system is being deployed, allowing human and hardware resource sharing, and making use of currently under-exploited fast internet connections.

Through this project, a well-established and enhanced research network, particularly in terms of educated human resources, will be able to better contribute to and lead global change research in the Americas within the framework of Earth System Science. The resulting

Table 1. List of participants and corresponding affiliations.

Name	Country	Project	Main Expertise	Institution
Darío Gómez	Argentina	SAEMC	Chemistry, Emissions	Comisión Nacional de Energía Atómica, CNEA
Germán Torres	Argentina	SAEMC	Applied Mathematics	Universidad de Córdoba
Graciela di Marco	Argentina	ADAPTE	Sociology	Universidad Nacional de San Martín Argentina
Laura Dawidowski	Argentina	SAEMC/ADAPTE	Physics, Emissions	Comisión Nacional de Energía Atómica, CNEA
Mario Blas Lavorato	Argentina	SAEMC	Physics	Centro de Investigaciones en Laser y Aplicaciones
Pablo O. Canziani	Argentina	SAEMC	Atmospheric Modeling	Universidad Católica
Patricia Smichowski	Argentina	SAEMC	Atmospheric Chemistry	Comisión Nacional de Energía Atómica, CNEA
Karla Longo	Brazil	SAEMC	Atmospheric Modeling	Centro de Previsão de Tempo e Estudos Climáticos (CPTEC/INPE)
Maria de Fatima Andrade	Brazil	SAEMC	Atmospheric Modeling	Universidade de Sao Paulo
Pérola Vasconcellos	Brazil	SAEMC	Atmospheric Chemistry	Universidade de Sao Paulo
Saulo Freitas	Brazil	SAEMC	Atmospheric Modeling	Centro de Previsão de Tempo e Estudos Climáticos (CPTEC/INPE)
Alejandro León	Chile	ADAPTE (PI)	Economics	Universidad de Chile
Ana María Córdova	Chile	SAEMC	Atmospheric Chemistry	Universidad de Valparaíso
Axel Osses	Chile	SAEMC	Applied Mathematics	Universidad de Chile
Enrique Garrido	Chile	SAEMC	Meteorology	Dirección Meteorológica de Chile
Galina García	Chile	SAEMC	Applied Mathematics	Universidad de Santiago
Laura Gallardo	Chile	SAEMC (PI)	Atmospheric Modeling	Universidad de Chile
Maisa Rojas	Chile	SAEMC	Atmospheric Modeling	Universidad de Chile
Marcelo Mena	Chile	SAEMC	Environmental Engineering	Universidad Andrés Bello
Mauricio Osses	Chile	SAEMC/ADAPTE	Mechanical Engineering	Universidad de Chile
Patricia Matus	Chile	ADAPTE	Epidiemiology	Centro Nacional del Medio Ambiente
Ricardo Alcafuz	Chile	SAEMC	Meteorology	Dirección Meteorológica de Chile
Eduardo Behrentz	Colombia	SAEMC/ADAPTE	Environmental Engineering	Universidad de Los Andes
María Victoria Toro	Colombia	SAEMC	Atmospheric Modeling	Universidad Pontificia Bolivariana
Magali Hurtado	Mexico	ADAPTE	Epidiemiology	Instituto de Salud Pública
Eric Concepción	Peru	SAEMC	Meteorologist	Servicio Nacional de Meteorología e Hidrología (SENAMHI)
Gabrielle Pétron	USA	SAEMC	Atmospheric Modeling	National Atmospheric and Oceanic Administration (NOAA)
Olga Wilhelmi	USA	ADAPTE	Sociology	National Center for Atmospheric Research (NCAR)
Patricia Romero	USA	ADAPTE	Sociology	National Center for Atmospheric Research (NCAR)

Table 2. Available air quality monitoring in South American cities participating in SAEMC. Notice that not all stations measure all pollutants.

City	Current number of stations	Pollutant measured	Begining of measurements	Note
Bogotá	15	NO, NO_2, SO_2, TSP, PM10, PM2.5, O_3, CO, CH_4, HCHO, NMHC, benzene, toluene	1997	Data available at: www.dama.gov.co (automatic network). Not all the stations measure all pollutants
Buenos Aires	3	1 station: CO, NO, NO_2 1 station: CO, NO, NO_2, TSP, PM10, PM2.5 1 station: NO, NO_2, CO, benzene, toluene, and xylenes	1986 2005 2007	Responsible: City government
Lima	5	TSP, Dust fall, PM10, PM2.5, CO, SO_2, NO_2, O_3.	Dust fall: since 1990 TSP, since 1987 PM10 and PM2.5, 2000 to present CO, SO_2, NO_x, O_3, 2001 to present	Data available on line http://www.digesa.minsa.gob.pe/aire_LC_01.htm Most part of the data covers 2002 to present
Medellín	17	TSP , PM10, O_3, NO_2,SO_2,HC, CO, PM2.5	1993	Data available on-line (www.metropol.gov.co) from April 2008
Santiago	8	CO,SO_2, NO_2,O_3, HC, PM10, PM2.5	1988	Data available on line (http://www.seremisaludrm.cl/sitio/pag/aire/indexjs3aire.asp). Most data covers 1997 to present
São Paulo	30	CO, SO_2, NO_x, O_3, PM10, PM2.5.	1981 (automatic stations). 1973 (manual stations for SO_2 and smoke)	Data available on line (www.cetesb.sp.gov.br). PM2.5 measured since 1999.

unique and new databases will assist various other relevant research issues and assessments, such as for human health, ecology, water and energy resources, economics and city planning.

All in all, we see this network as a sound – and in many aspects unprecedented – basis for developing Earth System Science in South America around the pressing challenges of urbanization, air quality deterioration and climate change.

Acknowledgments

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Comparison of Air Pollutant Emissions among Mega-Cities

Contributed by **David Parrish**[1] (David.D.Parrish@noaa.gov), **Paul Goldan**[1] (Paul.D.Goldan@noaa.gov), **Joost de Gouw**[1,2](Joost.deGouw@noaa.gov), **Min Shao**[3] (mshao@pku.edu.cn), **Yutaka Kondo**[4] (y.kondo@atmos.rcast.u-tokyo.ac.jp), **Tomoko Shirai**[5] (tshirai@nies.go.jp), **Yoko Yokouchi**[5] (yokouchi@nies.go.jp) *and* **Makoto Koike**[6] (koike@eps.s.u-tokyo.ac.jp)

[1]*Earth System Research Laboratory/NOAA, Boulder, CO USA.*

[2]*Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, USA.*

[3]*College of Environmental Sciences and Engineering, Peking University, Beijing, China.*

[4]*Research Center for Advanced Science and Technology, The University of Tokyo, Tokyo, Japan*

[5]*Center for Global Environmental Research, National Institute for Environmental Studies, Tsukuba, Japan*

[6] *Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Tokyo, Japan*

Introduction

The world's mega-cities represent a wide diversity of cultures and histories, with examples of mega-cities on all of the five major continents. This diversity might be expected to lead to very different patterns of air pollutant emissions. However, as mega-cities develop economically, a convergence of cultures occurs in the sense that automobile fleets and industrial processes develop in similar modes across all cultures. Our goal in this article is to compare and contrast mega-city air pollutant emissions as reflected in measured ambient concentrations of those pollutants.

Our focus here is on major precursors of photochemical smog: non-methane hydrocarbons (NMHC), carbon monoxide (CO), and oxides of nitrogen ($NO + NO_2 = NO_x$). These are the primary pollutants whose emissions fuel the photochemical formation of ozone, other oxidants, and a fraction of the particulate matter (nitrates and secondary organic aerosol) that accumulate in urban atmospheres. We will not address the emissions of sulfur dioxide and primary emissions of particulate matter, which lead to a major fraction of the visibility-reducing aerosol loading in many urban areas. Neither will we address emissions of oxygenated volatile organic species, nor a variety of airborne toxic species, such as mercury and persistent organic pollutants. As a consequence, possible important differences in the emissions of these species between mega-cities will remain unaddressed.

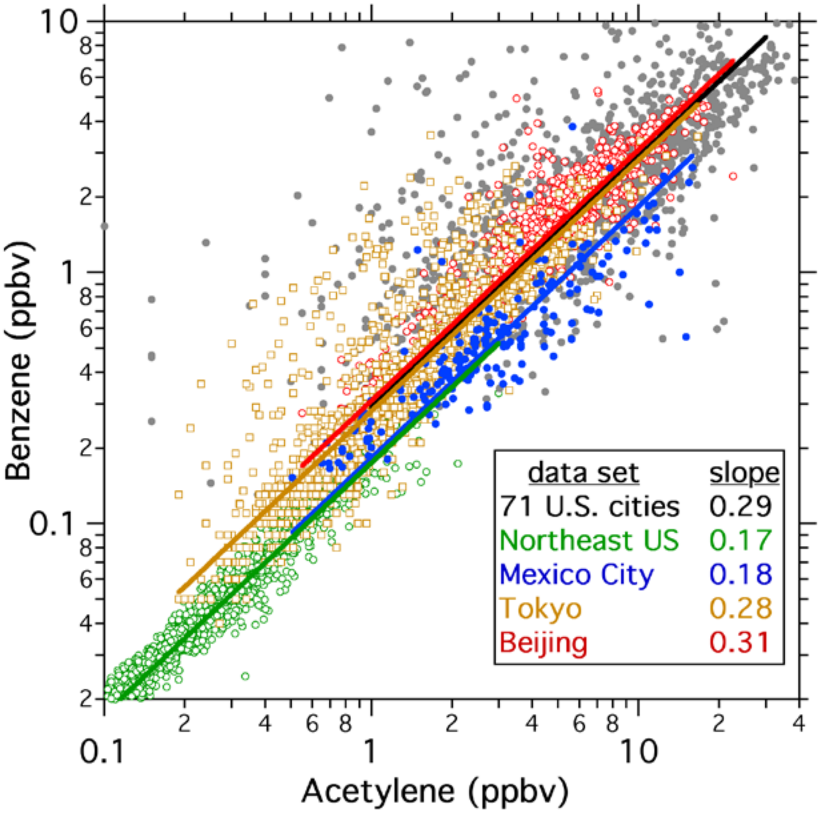

Figure 1. Relationship between concentrations of benzene and acetylene measured in five urban areas. The symbols indicate the individual measurements color-coded as indicated in the Figure annotation (except grey for the US cities). The slope of the solid line of the corresponding color indicates the "best" average molar ratio of benzene to acetylene for each data set, and the length of that line indicates the range of the observed acetylene concentrations (except where the length of the US cities line has been truncated for clarity). The numerical values of the slopes are given in the Figure annotation. The "best" average ratio was derived from the linear-least-squares fit to the measurements, with the y-intercept of the line forced through zero, except for Mexico City, where the "best" average ratio was set equal to the geometric mean ratio of the observations. These Mexico City data were provided by D. R. Blake.

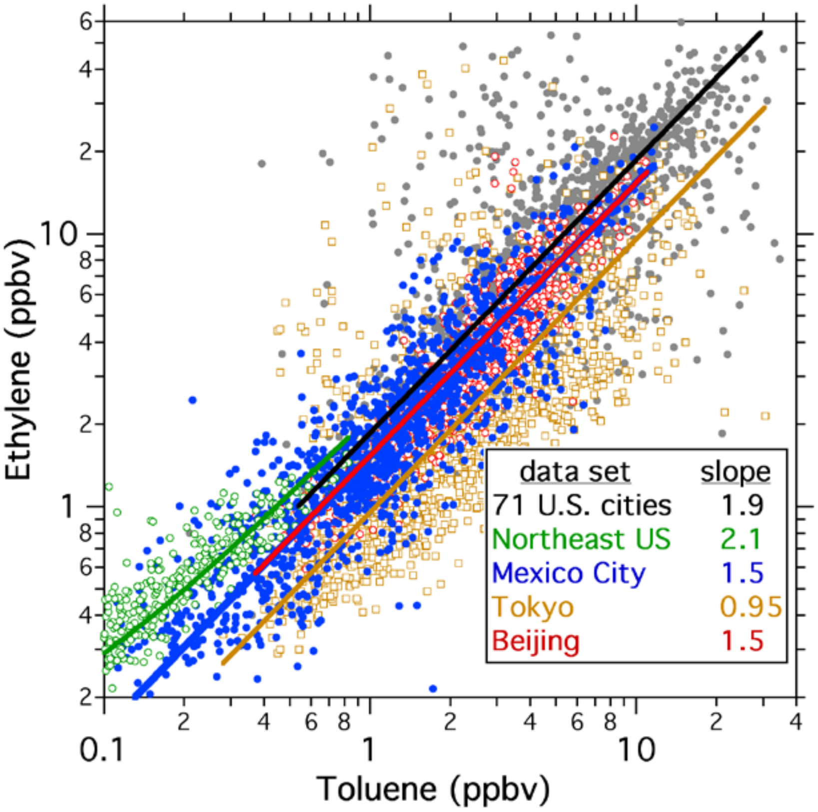

Figure 2. Relationship between concentrations of ethylene and toluene in the same format as Figure 1. The "best" average molar ratio of ethylene to toluene for Mexico City and Beijing is taken as the slope of the linear-least-squares fit to the measurements, with the y-intercept of the line forced through zero. The geometric mean ratio of the observations was taken as the "best" average ratio for the U.S. cities and for Tokyo. The Northeast US ratio was taken as the slope of the linear-least-squares fit to the measurements, with the y-intercept allowed to vary; these data were collected aboard a ship, where the lowest concentrations were affected by oceanic emissions of ethylene, as reflected by the y-intercept of 0.08 ppbv derived from the linear-least-squares fit.

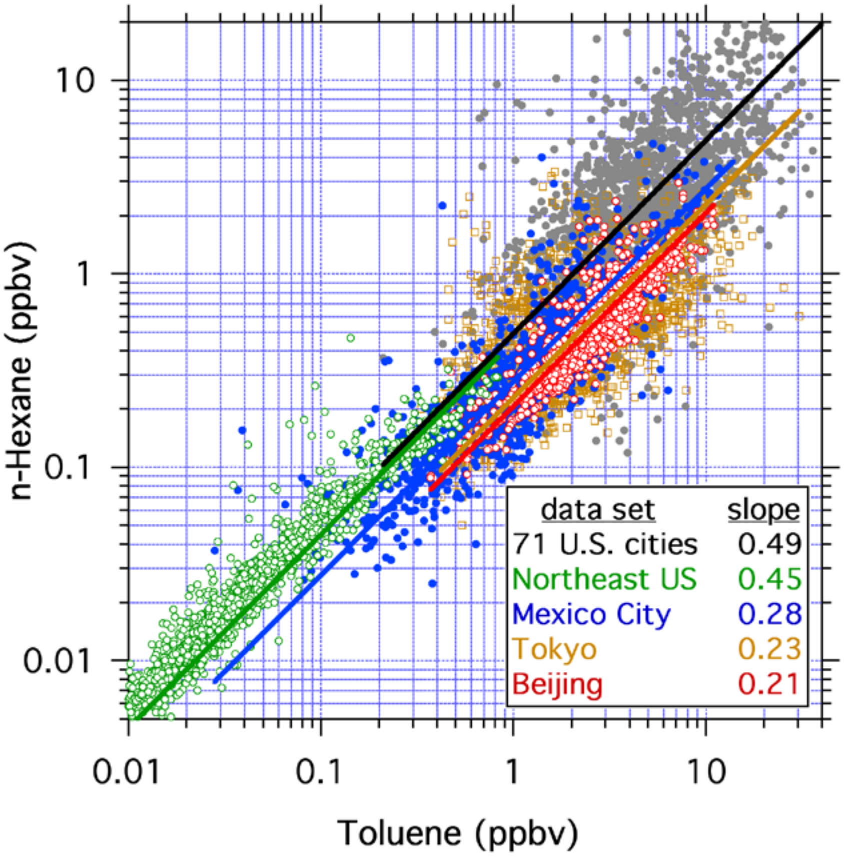

Figure 3. Relationship between concentrations of n-hexane and toluene in the same format as Figure 1. The "best" average molar ratios of n-hexane to toluene for three data sets are taken as the slope of the linear-least-squares fit to the measurements, with the y-intercept of the line forced through zero. The geometric mean ratio of the observations was taken as the "best" average ratio for Tokyo. For the 71 U.S. cities data, the geometric mean ratio is significantly different from the slope of the linear-least-squares fit, so the "best" average molar ratio is taken as the average of these two values.

Table 1. Important sources of NMHC in urban areas, with the primary sources of the example NMHC indicated (after Friedrich and Obermeier, 1999).

Emission Source	**n-hexane**	**ethylene**	**benzene**	**toluene**	**acetylene**
Internal Combustion Engines, Gasoline Usage	√	√	√	√	√
Fossil Fuel Production, Storage, and Distribution	√		√	√	
Solvent Use				√	
Industrial Processes		√	√	√	√
Wood and Biofuel Combustion		√	√	√	√

Measurements of ambient concentrations in U.S. cities have revealed marked similarities in the NMHC concentration patterns throughout the country (e.g., Parrish et al., 1988; de Gouw et al., 2005; Warneke et al., 2007). With the exception of the smaller alkanes, many of the patterns are so constant that deviations from those patterns indicate measurement problems, rather than actual differences in the ambient concentrations (Parrish et al., 1998). Significant deviations from the common pattern can be substantiated only in cities (e.g. Houston) with large industrial sources characteristic of that particular urban area (Jobson et al., 2004).

One goal of this article is to compare patterns in the ambient NMHC concentrations in three of the world's mega-cities with those documented in the U.S. Comprehensive suites of atmospheric measurements in mega-cities have only recently become available. The comparisons here will focus on different cities – Beijing, Mexico City, Tokyo and US cities – and on temporal contrasts – U.S. emissions at present versus in the 1980s.

It should be noted that the discussion presented here is best characterized as suggestive rather than definitive. The available data sets are usually still quite limited, with the measurements conducted at only one or two sites within a large urban area and for short (about 1 month) time periods. There are differences in the measurement techniques, the seasons and times of day of the measurements, and in the statistical approaches to analyzing the resulting data sets. Nevertheless, the comparisons presented here provide intriguing preliminary findings that provide directions for further study.

Data Sets

The data sets considered here in detail were collected downwind of Boston and New York City in 2004, in Tokyo in 2003 and 2004, in Beijing in 2005 and in Mexico City during 2006. These are compared with results of measurements reported in the literature for U.S. cities in the 1980's and the 2000's.

The Tokyo NMHC data were collected during four different Integrated Measurement Program for Aerosol and Oxidant Chemistry in Tokyo (IMPACT) campaigns in the summer and autumn of 2003 and the winter and summer of 2004. The measurements were made at the Komaba campus of the Research Center for Advanced Science and Technology of the University of Tokyo located in the heart of downtown Tokyo. Shirai et al. (2007) and the accompanying article by Y. Kondo provide more information on the IMPACT campaign.

The Beijing measurements were made during August 2005 from the roof of a 6-floor academic building on the campus of Peking University (PKU), located in the northwestern urban area of Beijing. More details of the measurements are available in Song et al. (2007).

The Mexico City measurements were made during the Megacity Initiative: Local and Global Research Observations (MILAGRO) campaign at the T1 site, a suburban location at the Universidad Tecnológica de Tecámac to the northeast of Mexico City during March 2006. The web site http://www.eol.ucar.edu/projects/milagro/media/MILAGRO-Factsheet-Final.pdf provides more information on the MILAGRO campaign, as does the accompanying article by Molina et al.

Data from the United States are presented for comparison with these other mega-city data. A survey of NMHC concentrations in 71 U.S. cities was made by the U.S. Environmental Protection Agency in 1984-1988. Seila et al. (1989) presented a summary of the data from the first 39 cities surveyed, and W. A. Lonneman has provided us with the complete data set for comparison purposes. Here these results will be compared with a more recent, similar survey of 28 U.S. cities conducted between 1999 and 2005 (Baker et al., 2008). A detailed VOC speciation study conducted on a ship immediately downwind of the Boston and New York City urban areas (Warneke et al., 2007) will also be examined. All of these U.S. data sets were collected in the summertime. Although not all of the U.S. cities investigated can be considered mega-cities, the data patterns that are discussed are representative of New York City and Los Angeles, the two U.S. mega-cities.

Hydrocarbon Emissions

The patterns of ambient concentrations of hydrocarbons in the atmosphere of an urban area provide detailed information regarding the emission sources of these species in that area. In this section, we will examine the ambient concentrations of a few selected hydrocarbons. These example species were selected based on several criteria. First, they are among those observed at higher concentrations in urban atmospheres, which ensures their atmospheric importance and our ability to measure their concentrations accurately and precisely. Second, they are examples from all important hydrocarbon classes found in urban atmospheres: alkanes (n-hexane), alkenes (ethene, or more commonly, ethylene), aromatics (benzene and toluene), and the one important alkyne (ethyne, or more commonly, acetylene). Third, they are all believed to be emitted predominately from anthropogenic rather than biogenic sources. Finally, they represent species emitted from all of the recognized important urban anthropogenic sources. Table 1 lists these urban sources of NMHC and indicates which of the example NMHC are released in substantial quantities from each.

Figures 1-3 illustrate the relationships between three pairs of the selected NMHC. In each case both members of the pair have similar atmospheric lifetimes with respect to photochemical oxidation by the hydroxyl radical. This oxidation is the primary loss process for NMHC from the atmosphere. Similar lifetimes for a pair of hydrocarbons implies that the ratio of their measured ambient concentrations does not depart from the molar emission ratio of the hydrocarbons, even after photochemical processing of polluted air masses.

In general, Figures 1-3 show relatively constant ratios of the measured NMHC concentrations, even while the observed concentrations vary widely. The 71 U.S. cities data set, which was collected over two decades ago, generally shows more scatter than the other three data sets. This scatter indicates either a greater diversity of sources in the 71 cities surveyed, or perhaps poorer measurement precision because the measurement technology was not nearly as mature then. A representative average concentration ratio can be derived from a particular data set in several ways. For this discussion, two methods were employed: either the slope was derived from a linear, least-square fit to the observations (with the y-intercept either set to zero, or optimized by the least-squares procedure), or the geometric mean ratio was calculated from all pairs of NMHC concentration measurements in the data set. The "best" estimate of the average ratio was selected from the results of these two methods by whichever was judged to give the most accurate description of the data set as a whole. Specific details of the procedure used for each NMHC pair are given in the figure captions. In each case the "best" average molar ratio is taken to represent the average molar emission ratio of those NMHC in the region in which the measurements were made.

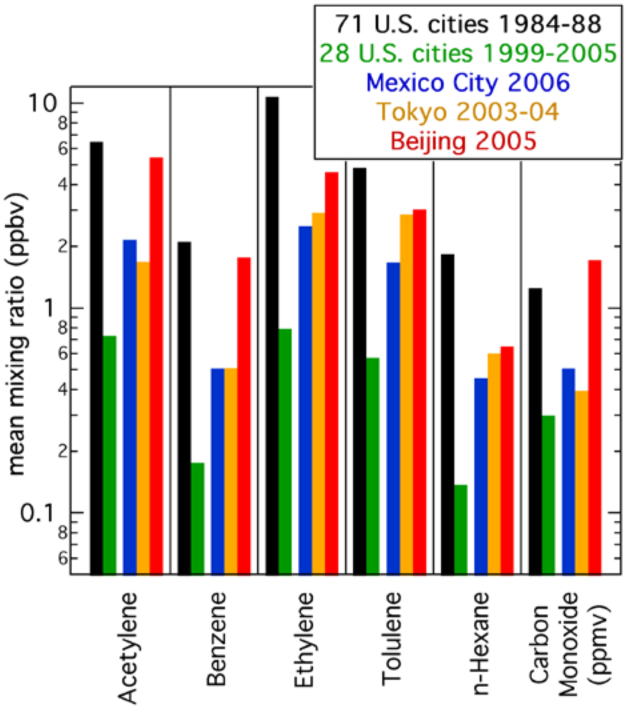

Figure 4. Histogram summarizing mean or median concentrations of species in five data sets. The median VOC concentrations in U.S. cities in 1984-88 are from Table 2 of Seila et al. (1989), and the mean concentrations in U.S. cities in 1999-2005 are the means of the city mean mixing ratios from Table 2 of Baker et al. (2008). Carbon monoxide measurements were not reported by Seila et al. (1989); the CO concentration for the U.S. cities in 1984-88 is estimated from the acetylene mixing ratio and the CO to acetylene ratio reported by those same authors for a tunnel study conducted in New York City in 1982 (Lonneman et al., 1986). The Mexico City benzene and CO means were calculated from the data provided by D.R. Blake and L.G Huey, respectively.

Figure 1 presents the analysis of the molar emission ratio of benzene to acetylene derived from five studies. A great deal of similarity between the U.S. and the three non-U.S. mega-cities is clear. The ratios of the five data sets average to 0.25, and all five are within 30% of this average. Benzene is a pollutant of particular regulatory concern, since it is a demonstrated carcinogen. Fortin et al. (2005) have shown that in the U.S. the benzene to acetylene ratio has decreased since the early 1990's due to policies implemented following the 1990 Clean Air Act Amendments. These policies included focused efforts to control a selected list of hazardous air pollutants, which includes benzene. The emission ratios shown in Figure 1 from the two U.S. data sets (0.29 and 0.17) are consistent with this temporal trend. To our knowledge, this change in the benzene to acetylene emission ratio is the only well-documented, systematic temporal change in average U.S. NMHC emission patterns. The Tokyo and Beijing data sets exhibit emission ratios very close to the 1990's U.S. emission ratio, while the Mexico City emission ratio agrees well with the more recent 2004 U.S. emission ratio.

Figures 2 and 3 show the derived molar emission ratios of ethylene to toluene and n-hexane to toluene, respectively. Again, significant similarities between the U.S. cities and the three non-U.S. mega-cities are evident in both Figures. The two U.S. studies indicate that the emission ratios have remained near 2 for ethylene to toluene and near 0.5 for n-hexane to toluene over the two decades spanned by the studies. The three mega-cities in all cases have somewhat smaller emission ratios: for ethylene to toluene 25% smaller in Beijing and Mexico City, and about a factor of 2 smaller in Tokyo; for n-hexane to toluene the three mega-city emission ratios are 38 to 53% smaller than the 2004 U.S. emission ratio. Evidently the mega-city emissions are somewhat richer in toluene than are U.S. urban emissions. The importance of industrial and solvent sources of toluene have been identified both in Beijing (Song et al., 2007) and in Tokyo (Shirai et al., 2007). In Figure 2 the greater scatter about the ethylene-toluene relationship in Tokyo

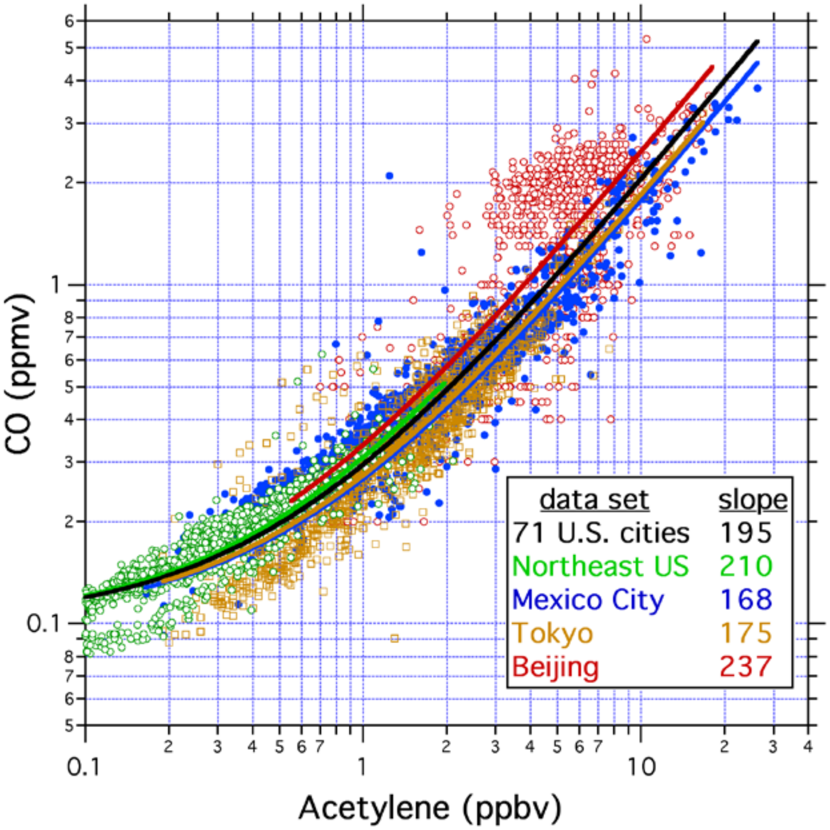

Figure 5. Relationship between concentrations of carbon monoxide and acetylene in the same format as Figure 1. The "best" average molar ratio of CO to acetylene for each data set is taken as the slope (corrected for the difference in concentration units) of the linear-least-squares fit to the measurements, with the y-intercept of the line forced through 0.1 ppmv. Carbon monoxide measurements were not reported for the 71 U.S. cities study; the slope for the line representing that data set is set equal to the CO to acetylene ratio measured in a tunnel study conducted in New York City in 1982 (Lonneman et al., 1986). The Tokyo line is derived as described for Figure 1. The Mexico City CO data were provided by L.G Huey.

may reflect the varying influence of solvent sources (rich in toluene) and petrochemical sources (rich in ethylene), as suggested by Shirai et al. (2007).

A striking feature of Figures 1-3 is that the NMHC concentrations in U.S. cities were an order of magnitude or more smaller in 2004 than in the 1980's. The 2004 measurements were made downwind, rather than inside the urban areas, and thus show substantially smaller concentrations than all the other data sets in the Figures. They do not reflect the concentrations that would be observed in a more urban setting. However, even the highest 2004 measurements, which were made directly in the urban plume outflow, are below the bulk of the 1980's data. Figure 4 provides a direct comparison of the ambient concentrations of the five example NMHC measured during the two multi-city surveys conducted in the mid-1980's and the early 2000's. The reported ambient concentrations of all five NMHC were approximately a factor of 10 lower in the latter study, while the relative amounts of the different NMHC remained quite constant. Importantly, there are significant differences in the sites, measurement protocols, and statistical analysis of the results between these two survey studies. However, these systematic differences are not expected to be large enough to dominate the factor of 10 difference, so we largely attribute the observed differences to a decrease in emissions over the time period between the two studies. Further, the few ambient measurements made during the 1970's (e.g. Mayrsohn et al., 1976) and a tunnel study from 1970 (Lonneman et al., 1986) indicate that the NMHC emissions had been significantly higher in the 1970's than in the 1980's. Thus, ambient measurements indicate that U.S. NMHC emissions have decreased by a significant factor (something like an order of magnitude) over the past three decades. This decrease has occurred despite large increases in energy use. For example, the U.S. Department of Transportation estimates that the total distance traveled by on-road vehicles in the nation more than doubled between 1975 and 2005.

It is notable that an order of magnitude decrease in U.S. NMHC emissions is inconsistent with U.S. EPA emission inventories. The most recent inventory ("1970 - 2006 Average annual emissions, all criteria pollutants in MS Excel - July 2007" downloaded from http://www.epa.gov/ttn/chief/trends/index.html) suggests a decrease in total national VOC emissions of only a factor of 1.7 between 1975 and 2005. On-road vehicle emissions, which likely dominate urban NMHC concentrations, decreased by a factor of 3.8, but even this larger decrease is still significantly smaller than what can be consistent with the ambient and tunnel data. This inconsistency is certainly worthy of further study, as it is central to understanding the efficacy of the U.S. control strategies for photochemical air pollution.

Figure 4 compares the average magnitudes of the ambient NMHC concentrations in the three mega-cities with those in the U.S., and Figures 1-3 also provide comparisons of the individual measurements. In all cases the mega-city concentrations are higher than present ambient concentrations in the U.S. cities as derived from the measurements of Baker et al., (2008), but they have not reached the ambient concentrations observed in U.S. cities in the 1980s or the even higher

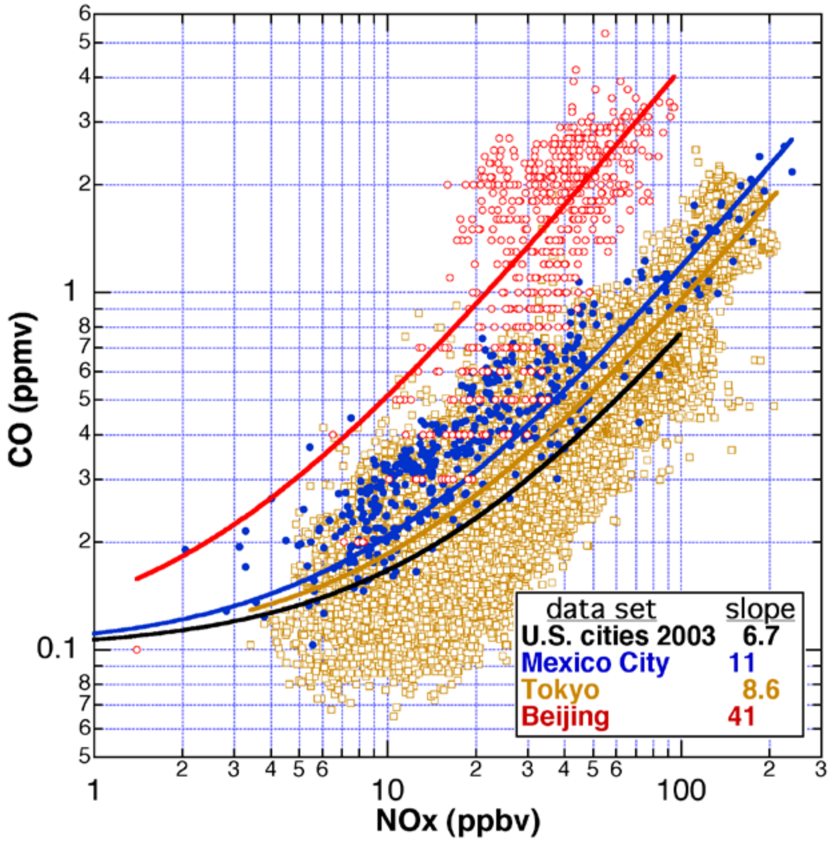

Figure 6. Relationship between concentrations of carbon monoxide and oxides of nitrogen in the same format as Figure 1. The "best" average molar ratio of CO to NO_x for each data set is taken as the slope (corrected for the difference in concentration units) of the linear-least-squares fit to the measurements, with the y-intercept of the line forced through 0.1 ppmv. In Tokyo, Mexico City and Beijing, the measured total reactive oxidized nitrogen (NO_y) measurements are plotted; NO_y is a more nearly conserved measure of the emitted NO_x than are NO_x measurements themselves. The concentration ratio for U.S. cities in 2003 is taken from Figure 3 of Parrish (2006). For Mexico City, NO data were provided by L.G. Huey and the total higher oxidized nitrogen oxides (the sum of NO_2, organic nitrates and nitric acid) data were provided by R.C. Cohen.

levels of the 1970s. It should be noted that there are quite significant differences between the three mega-cities themselves and between them and the U.S. cities with regard to the measurement programs, as well as to the meteorological conditions that control how emissions result in the observed ambient concentrations. At this point it is premature to speculate how the magnitude of the NMHC emissions compares among these urban areas.

Carbon Monoxide Emissions

Carbon monoxide is emitted from internal combustion engines as well as from other inefficient combustion processes including the burning of wood and other biofuel. Hence, CO shares important emission sources with NMHC. Figure 5 compares the emission ratio of CO to acetylene derived from the five urban data sets. All of the derived average emission ratios agree within ±20%. This agreement is perhaps surprising, since the CO emission contribution from wood and other biofuel combustion is expected to be larger from some of the less-developed mega-cities (Beijing and Mexico City), than from the U.S. cities and Tokyo. This agreement is likely enhanced by similar emission ratios of CO to acetylene (and aromatic NMHC) in internal combustion engine exhaust and biomass burning emissions (see e.g. de Gouw et al., 2004). Figure 4 shows that Beijing emissions are especially rich in CO compared to NMHC emissions, and Figure 5 shows that there is a large group of measurements that are elevated in CO compared to the average emission ratio. Figures 4 and 5 show only very small indications of relatively enhanced CO emissions in Mexico City; in fact the ambient data at the highest concentrations, which predominately determine the slope in Figure 5, indicate that Mexico City has the lowest CO to acetylene emission ratio of all five data sets – an observation that is currently being studied in more detail in the MILAGRO data set.

Nitrogen Oxide Emissions

The concentration ratios of CO to nitrogen oxides illustrated in Figure 6 show larger differences between cities than found in the NMHC and CO ratio comparisons. In the U.S. the average urban CO to NOx concentration ratio has fallen rapidly over the last two decades (see Figure 3 of Parrish, 2006), reaching 6.7 by 2003 (the value included in Figure 6), and currently is below 5 in some cities. The CO to NOx concentration ratio in Beijing in 2005 was a factor of six larger than the 2003 U.S. average. The Mexico City concentration ratio in 2006 was similar to the U.S. emission ratio in the mid-1990's, and the Tokyo ratio in 2003-2004 was similar to the U.S. emission ratio in 1999.

Without careful consideration of the measurement site and measurement time period, it is not possible to directly equate observed urban CO to NOx concentration ratios to emission ratios. Uncertainties arise from the very different lifetimes of CO and NOx and its oxidation products. CO remains in the atmosphere for periods long enough to be transported over regional to hemispheric scales, while NOx and even the total reactive oxidized nitrogen (NO_y), is removed on much smaller spatial scales. Thus, local urban concentrations of CO can be affected by upwind sources to a greater extent than the much shorterlived NO_x or NO_y. This effect appears to influence the Beijing results much more than the other three data sets in Figure 6. The CO concentrations appear to have a large regional component with concentrations often remaining elevated for a period of several days. This is attributed to regional pollution events, when emissions can build up over the entire, heavily-populated east China region under stagnant meteorological conditions. This is not as great a problem in Mexico City, which is relatively isolated from other major population centers, and in the U.S., where CO emissions have a much stronger local character as evidenced by strong morning peaks in CO concentrations, which correlate with the morning vehicle traffic peak.

The strong contrast in Figure 6 of Beijing with the other cities may also possibly arise from the larger contribution of biomass burning, compared to on-road vehicle, emissions in Beijing. Biomass burning emissions are much richer in CO compared to NOx than are vehicle emissions.

The close agreement of the Mexico City CO to NOx ratio with that observed in U.S. cities in the mid-1990's can perhaps be taken as an indication that the catalytic converters of the on-road vehicle fleet in Mexico City in 2006 performed, on average, at about the level of the converters in the U.S. vehicle fleet of the mid-1990's. Similarly, the vehicle fleet in Tokyo in 2003-2004 performed similarly to the U.S. fleet at the end of the 1990's. This discussion is clearly speculative, but the important correlated emissions of CO and NOx are primarily due to the on-road vehicle exhaust emissions, and these emissions are primarily controlled by catalytic converters on the vehicles. One additional variable has a strong influence on the CO to NOx vehicle emission ratio – the proportion and driving patterns of heavy-duty diesel vehicles. Emissions from these vehicles are relatively rich in NOx and poor in CO. A complete understanding of the relationships in Figure 6 would require careful evaluation of both gasoline and diesel vehicle emissions in each urban area, and an evaluation of the contribution of each vehicle class to the vehicle fleet.

Conclusions

The speciation of ambient hydrocarbon concentrations in the mega-cities and other U.S. cities examined here (Figures 1-4) reveal a large degree of similarity. This similarity spans the cities in North America and Asia, has remained nearly constant over the past 2 decades in the U.S., and persists over wide ranges of absolute concentrations. A two-part hypothesis most likely explains this similarity: First, on-road vehicle exhaust and the associated evaporative gasoline emissions dominate the ambient hydrocarbon concentrations in all of these urban areas. Second, there is no large difference in the hydrocarbon composition of gasoline between these urban areas.

Comparison of data sets collected in U.S. cities over the past three decades indicate that a substantial decrease in hydrocarbon emissions has occurred even while total vehicle usage has more than doubled. The ambient concentration data suggest that the emission decrease has been larger than indicated by U.S. emission inventories. Thus, U.S. strategies aimed toward controlling hydrocarbon emissions, based upon automobile catalytic converters and minimization of gasoline evaporation, have been quite successful - indeed more successful than indicated by emission inventories.

The above conclusions suggest possible guidance for hydrocarbon emission control strategies in the mega-cities studied, and perhaps for other mega-cities with rapidly developing vehicle fleets and industries. Since ambient urban NMHC concentrations are evidently strongly dependent upon vehicle exhaust and gasoline evaporation, these emissions should be one major focus of control strategies. Perhaps there is no need for either development of detailed emission inventories or comprehensive atmospheric sampling programs before implementing such controls. Indeed, these control measures can likely be expected to yield greater emissions reductions than is generally believed to be the experience in the U.S., since the success of the controls in that country are underestimated in U.S. emission inventories. Additionally, in any urban area with large industrial facilities, such as Tokyo (Shirai et al., 2007) and Houston, Texas (Ryerson et al., 2003), emissions from these sources must be another important focus of control strategies.

The NMHC relationships discussed in this article suggest that the IMPACT measurement program in Tokyo perhaps can provide a model for characterizing hydrocarbon emissions in developing mega-cities. This program included measurements of a limited, but carefully selected, set of key NMHC species, plus CO, NO_x and NO_y, during a few measurement periods of limited duration in different seasons. These data sets were successfully analyzed to provide detailed information regarding the important hydrocarbon emission sources in the Tokyo urban area. An approach of continuously measuring a more extensive list of NMHC species at many sites in an urban area would likely provide little additional useful information, and require much greater effort. Given the usual limitation of resources, the IMPACT program provides a good guide for formulating measurement programs in other urban areas.

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Studies on Aerosol and Ozone in Tokyo

Yutaka Kondo, *Research Center for Advanced Science and Technology, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan.* (y.kondo@atmos.rcast.u-tokyo.ac.jp)

Large amounts of reactive gases and aerosols are emitted from urban areas. Mega-cities, including the Tokyo Metropolitan Area (TMA), are very large concentrated sources of these species, which affect ozone and aerosol levels at the local, regional, and global scales [e.g., *Molina and Molina*, 2004; *Ramanathan et al.*, 2007]. Oxidized reactive nitrogen, O$_3$, and secondary aerosol play important roles in the atmospheric environment, including through acid deposition and effects on human health, visibility, and climate. In order to assess the impacts of anthropogenic species emitted from these mega-cities on surrounding areas, we need to understand quantitatively the key processes involved in the oxidation of primary species and the fate of the oxidized species near the source regions (Figure 1). In addition, clusters of mega-cities lead to accumulation of O$_3$ and aerosol through large-scale mixing. The increased levels of pollutants have a large impact on regional air quality and climate. It should be noted here that O$_3$ and aerosol are coupled due to similar sources, photochemical interactions (e.g., UV changes by aerosol), and transport.

In the 1980's through 1990s, regional increases of photochemical smog occurred in the TMA [*Wakamatsu et al.*, 1996; 1999], which is shown in Figure 2 [*Miyakawa et al.*, 2008]. The TMA is the most densely populated area in the world. From 1978 to 1990, the concentrations of nitrogen oxides (NO$_x$) increased and the non-methane hydrocarbons (NMHC) concentration and NMHC/NO$_x$ ratio decreased. According to model predictions, these emission changes can alter the place where the maximum ozone is observed over the TMA. This is consistent with the fact that the location of the daily maximum oxidant concentration moved further away from the major emission areas.

From 1991 to 2004, both NO$_x$ and NMHCs showed continued decreases [*Tokyo Metropolitan Government*, 2005] (Figure 3), due to regulations to reduce emissions of these species. The concentrations of these species are considerably lower than those in mega-cities in the developing countries of Asia [*Molina and Molina*, 2004]. Despite

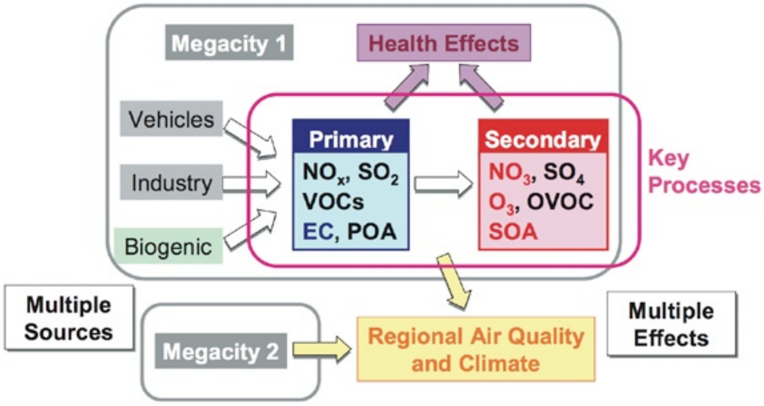

Figure 1. Schematic diagram of key processes of O$_3$, aerosols and their precursor gases near mega-city regions.

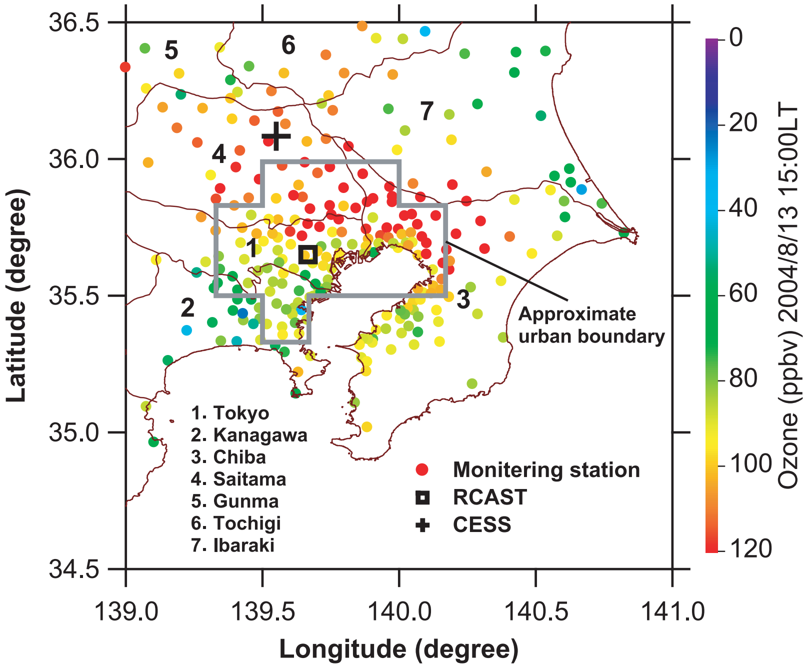

Figure 2. Map of the Tokyo Metropolitan Area (TMA). The locations of two sites, RCAST (square) and CESS (cross), where IMPACT measurements were conducted, and air quality monitoring stations (circles) maintained by the Atmospheric Environmental Regional Observation System (AEROS) are shown in this figure. Area bounded by shaded lines depicts the approximate urban boundary. These monitoring sites are colored by the mixing ratio of O$_3$ obtained by AEROS (2004/8/13 15:00LT).

Table 1.

Topic	Major findings	References
Instrumentation	An HNO_3-CIMS with a new calibration/zero system was developed. Performance of an Aerodyne AMS was evaluated based on inter-comparison with a PILS-IC and Sunset OC. A new method to quantify BC coating was developed using a SP2.	Kita et al. (2006) Takegawa et al. (2005) Moteki and Kondo (2007a, 2007b)
$OH/HO_2/O_3$	Measured OH was reproduced by a box model in winter and summer. Measured HO_2 was underestimated by the model in a high NO_x regime.	Kanaya et al. (2007) Kanaya et al. (2008)
VOCs	Seasonal variation of C_2-C_7 non-methane hydrocarbons was quantified.	Shirai et al. (2007)
EC/BC	Diesel emissions were identified as a major source of BC in Tokyo.	Kondo et al. (2006)
Nitrate	Nitrate-HNO_3 partitioning in summer was influenced by vertical mixing.	Morino et al. (2006)
Sulfate	Only a small fraction (3% in winter and 18% in summer) of SO_2 emitted was converted to sulfate.	Miyakawa et al. (2007)
Organic aerosol	Seasonal and diurnal variation of POA and SOA was quantified. Most of SOA (OOA) was found to be water soluble.	Takegawa et al. (2006a, 2007) Miyazaki et al. (2006) Kondo et al. (2007)
CCN activity	Hygroscopicity and CCN activity were perturbed by organics. BC can act as CCN with a small amount of coating material.	Mochida et al. (2006, 2008) Kuwata et al. (2007) Kuwata and Kondo (2008)
Outflow from Tokyo	Significant formation of organics and alternation of BC mixing state took place within ~0.5 days in summer	Takegawa et al. (2006b) Shiraiwa et al. (2007) Miyakawa et al. (2008)

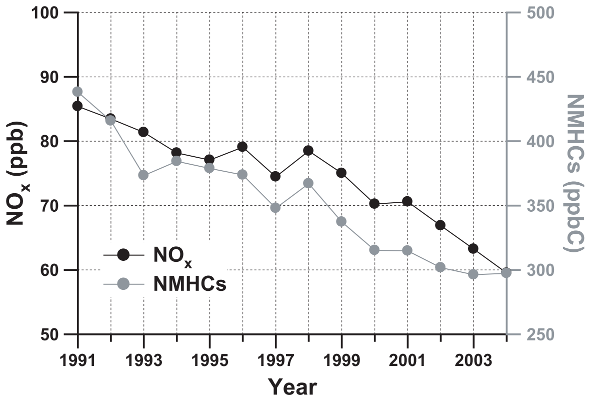

Figure 3. Annual averaged hourly mixing ratios of NO_x (black, left axis) and total NMHCs (shaded, right axis) over Tokyo from 1991 to 2004. The original data used in this figure are provided by National Institute for Environmental Studies.

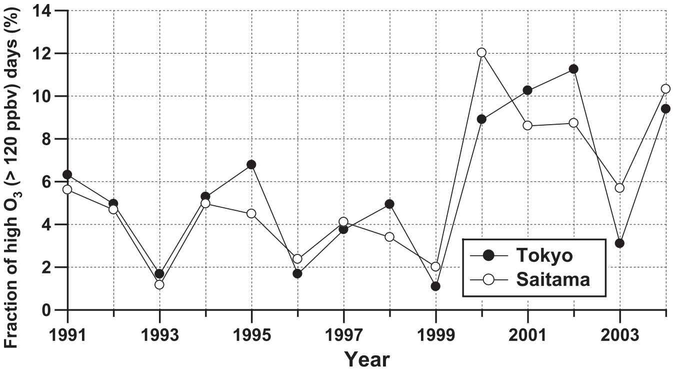

Figure 4. 3-month (June-August) average of percents of days whose hourly O_3 mixing ratio exceeds 120 ppb over Tokyo (filled circles) and Saitama (open circles). The original data used in this figure are provided by National Institute for Environmental Studies.

the decreases of the precursors, average O_3 concentration in the TMA during the summer season (June - August) increased during this period. According to Japanese air quality standard (AQS), hourly O_3 mixing ratios are required to be lower than 60 ppbv. The frequency of exceeding the Japanese AQS for O_3 has increased, especially since 2000. For example, the fraction of days when the hourly O_3 mixing ratios exceeded 120 ppb (i.e., 2×AQS) increased as shown in Figure 4 [*Miyakawa*, 2008].

According to *Tokyo Metropolitan Government* [2005], the observed increase in the frequency of high-O_3 days over the TMA can not be explained by the year-to-year variations in meteorological parameters, such as solar radiation and temperature. Thus, further understanding of the factors controlling O_3 concentrations -for example, relationships with NO_x and NMHCs, formation efficiency, and amounts of O_3 transported from source areas of NO_x and NMHCs - are needed in order to know what action is needed to decrease levels of photochemical smog over the TMA.

Previous studies have shown that organic compounds constitute a substantial fraction of total fine particle mass in urban air. However, the chemical composition and formation mechanisms of organic aerosols are not fully understood because organic aerosols consist of numerous chemical species with a very wide range of chemical and thermodynamic properties.

Emissions from motor vehicles (gasoline and diesel) can be important sources of primary organic aerosol (POA) in urban areas. Secondary organic aerosol (SOA) is formed via oxidation of volatile organic compounds (VOCs) followed by condensation on existing particles or by homogeneous nucleation. Smog chamber experiments have shown that aromatic hydrocarbons (toluene, xylene, etc.) from gasoline vapor can be a significant source of SOA in urban air [*Odum et al.*, 1997]. Biogenic hydrocarbons also make a substantial contribution to the SOA in some urban areas [*Szidat et al.*, 2004]. Atmospheric measurements in urban areas have identified a large amount of water-soluble organic carbon (WSOC), which is likely the major constituent of SOA. WSOC generally consists of oxygenated organic compounds containing various functional groups such as alcohols, carbonyls, and dicarboxylic acids.

An assessment of the contributions of primary emissions and secondary formation to ambient organic aerosol loadings in urban areas is important for developing regulatory strategies for particulate matter (PM) control. It is also important for estimating direct/indirect forcing of organic aerosols because hygroscopic properties of organic aerosols depend upon the chemical composition.

Integrated Measurement Program for Aerosol and oxidant Chemistry in Tokyo (IMPACT)

Studies on characterizing primary emission and secondary formation of aerosols in the TMA have to date been very limited. Further observational studies on aerosols, especially OA, near source area are needed in order to improve understanding of the amounts and chemical composition of aerosols exported from this large source area. Recognizing this, we conducted the Integrated Measurement Program for Aerosol and oxidant Chemistry in Tokyo (IMPACT) campaign with the specific goal of improving our understanding on atmospheric chemistry in the TMA. The IMPACT campaigns were conducted within the framework of the International Global Atmospheric Chemistry Project (IGAC), Mega-Cities: Asia. The major objectives of the IMPACT campaign were:

- Characterizing the temporal and spatial changes of aerosols, oxidants, and their precursors, primarily through surface measurements near and downwind of urban centers.
- Characterizing the composition, mixing state, and physical properties of aerosols in urban air.
- Validating emission inventories of trace gases (e.g., NO_x, SO_2, NH_3, and VOCs) through comparisons of ratios of concentrations of trace species observed in urban air.

The instruments used during IMPACT are described in detail elsewhere [*Kondo et al.*, 2006; *Takegawa et al.*, 2006]. The observation sites were located at the Research Center for Advanced Science and Technology (RCAST), Komaba, Tokyo (35°39’N, 139°40’E) and the Center for Environmental Science in Saitama (CESS), Kisai, Saitama prefecture (36°05’N, 139°33’E), which is located about 50 km north of Tokyo (Figure 1). Important findings made by IMPACT are summarized in Table 1. They include chemical processes on HO_x radicalsand O_3 formation processes [*Kanaya et al.*, 2007; 2008], emissions and transformation of primary aerosol,

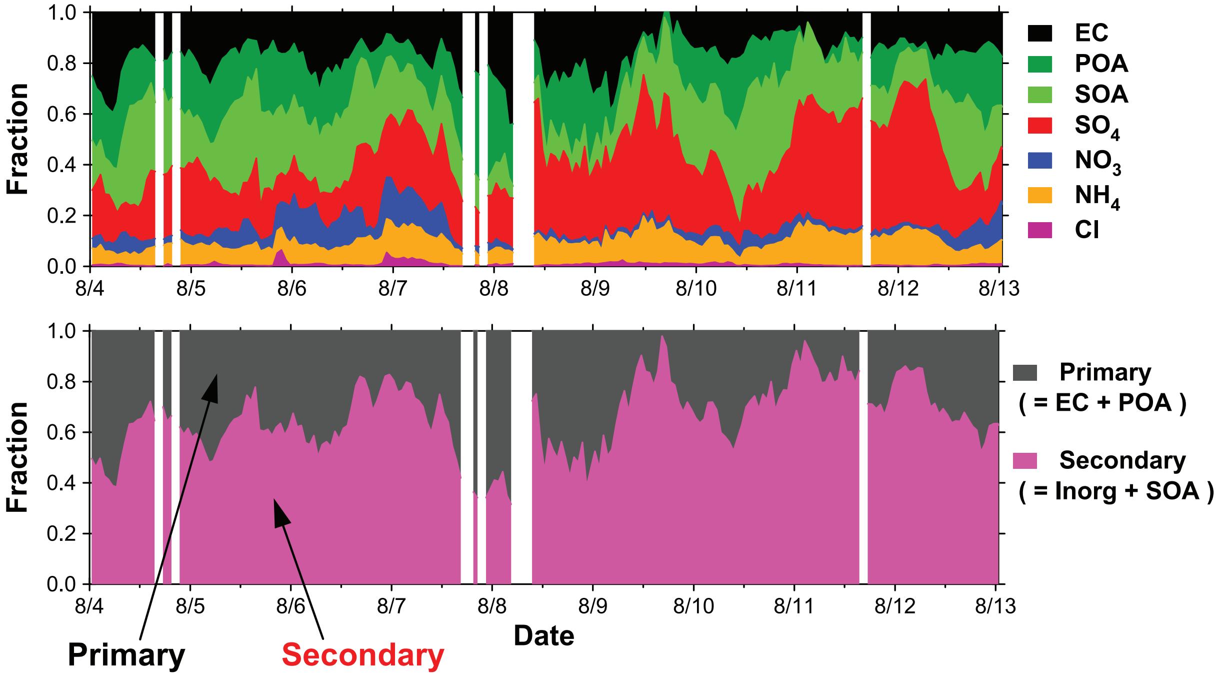

Figure 5. PM_1 aerosol chemical composition measured at RCAST in summer 2003.

especially black carbon (BC) aerosol [*Kondo et al.*, 2006; *Shiraiwa et al.*, 2007], and Cloud Condensation Nuclei (CCN) activity and hygroscopicity of aerosol [*Kuwata et al.*, 2007; *Kuwata and Kondo*, 2008; *Mochida et al.*, 2006; 2008], and secondary aerosol. Some information on Mega-cities Asia (IGAC task) and IMPACT is available at

http://noysun1.atmos.rcast.u-tokyo.ac.jp/IGAC_Megacities_Asia/News/index.html

http://noysun1.atmos.rcast.u-tokyo.ac.jp/IMPACT/index.html

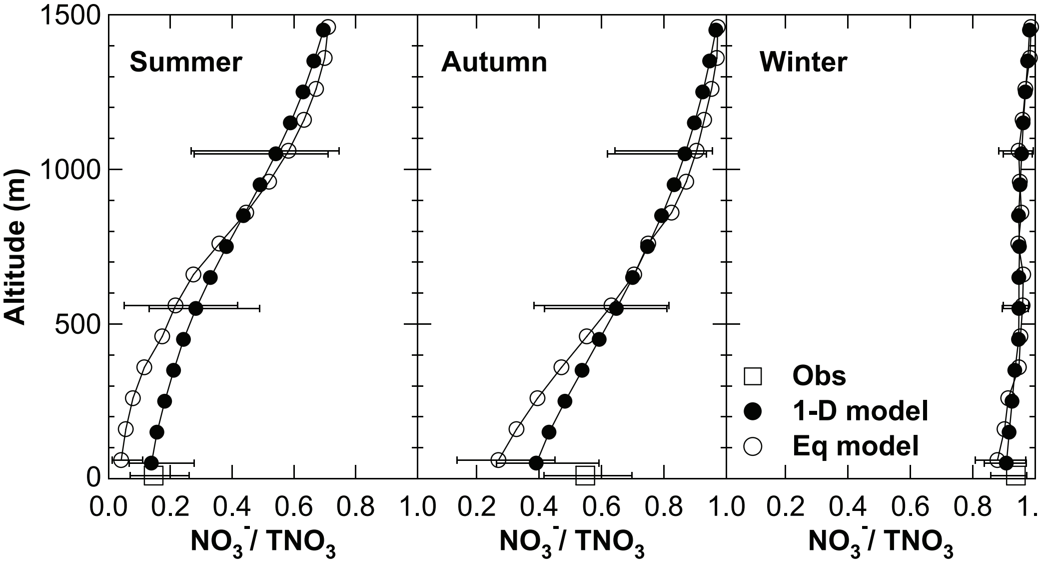

Figure 6. Vertical profiles of the median NO_3^-/TNO_3 ratios calculated by equilibrium and 1-D models for summer, autumn, and winter. Bars indicate the central 67% values.

Aerosol Field General Features

The median mass concentrations of total PM_1 aerosol (aerosol with diameters smaller than 1 µm) did not show significant seasonal variation during the measurement period, ranging between 17 and 20 µg m^{-3} [*Takegawa et al.*, 2005]. Non-refractory PM_1 aerosol was measured by an Aerodyne quadrupole aerosol mass spectrometer (AMS). Measurements of BC (or elemental carbon (EC)) were made using a semi-continuous thermal-optical analyzer. The fraction of PM_1 chemical composition in summer is shown in Figure 5. Nitrate and sulfates were observed to be the major inorganic compounds in Tokyo. Sulfate dominated in summer while nitrate was more abundant in winter. Organic compounds were found to be the dominant component throughout the year (median 6-7 µg m^{-3}, 40-60% of the total). The secondary aerosol (inorganic + secondary organic aerosol (SOA) constituted 40-90% of the total PM_1 mass concentration (Figure 5). Therefore secondary aerosol is very important in improving air quality in the TMA. Because of this we focus on the important findings of the chemical and transport processes of secondary aerosols.

Inorganic Aerosol

Nitrate

Ground-based measurements of gas-phase HNO_3 and particulate NO_3^- (PM_1) were made using Chemical Ionization Mass Spectrometer (CIMS) (gas phase species) and Aerodyne AMS (particulate species) instruments with time resolutions of approximately 1 minute (CIMS) and 10 minutes (AMS) [*Morino et al.*, 2006]. The thermodynamic equilibrium model ISORROPIA was coupled with a 1-D model to investigate the effect of vertical mixing during daytime on the partitioning of HNO_3 and NO_3^-. We found that the time scales of thermodynamic equilibrium (τ_e) and vertical mixing (τ_m) were comparable (~10 minutes). Thus, vertical mixing can increase the NO_3^-/total nitrate ratio at the surface above that predicted only including thermodynamic equilibrium processes. Here total nitrate TNO_3 is defined as $HNO_3 + NO_3^-$. The 1-D model reproduced the NO_3^-/TNO_3 ratios observed during the daytime, whereas the equilibrium model significantly underestimated these ratios under daytime conditions, except for winter, as shown in Figure 6. This study suggests that accounting for vertical mixing can greatly improve the overestimations (underestimations) of daytime HNO_3 (NO_3^-) by equilibrium models that have been reported in previous studies.

Sulfate

The formation of SO_4^{2-} and removal of SO_x were investigated using measurements of SO_2, SO_4^{2-}, and CO [*Miyakawa et al.*, 2007]. The SO_4^{2-}/SO_x ratio, which is a good indicator for the formation of SO_4^{2-}, varies significantly with season: modal values were 0.45 - 0.50 for the summer period and 0.10 - 0.15 for the winter period. In order to assess removal of SO_x, we estimated the remaining fraction of SO_x (RSO_x) by combining the linear regression slope of SO_x-CO correlation and the emission ratio of SO_2 to CO in Tokyo. Here RSO_x is defined as the [SO_x observed]/[SO_x without any loss] ratio. The average value of RSO_x was estimated to be 0.40 and 0.21 for the summer and winter periods, respectively. Using the averaged value of SO_4^{2-}/SO_x and RSO_x, we estimated the values of the average formation efficiency of SO_4^{2-} (ε_{av}), which is the average molar ratio of the observed SO_4^{2-} to the total SO_2 emitted. The ε_{av} value for the summer period (0.18) was much larger than that for the winter period (0.03). These results suggest that more than about 60% of SO_x was removed in the boundary layer within about a day and less than about 20% of SO_2 formed SO_4^{2-} over Tokyo during the summer and winter periods.

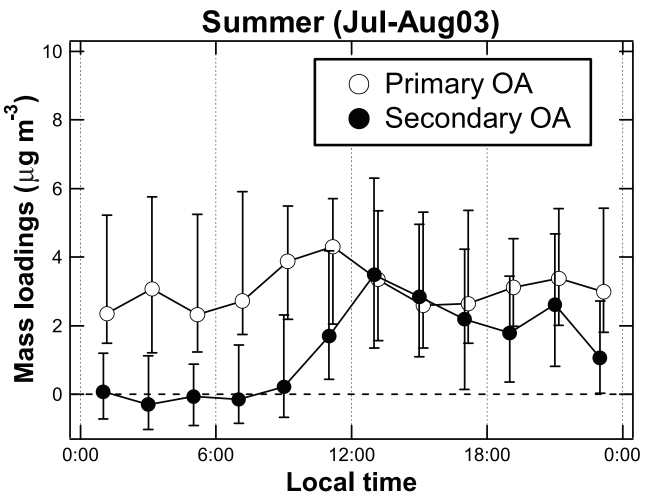

Figure 7. Diurnal variations of primary OA and secondary OA in the summer period. Average values were calculated in 2-h bins throughout the day. Bars indicate the standard deviation.

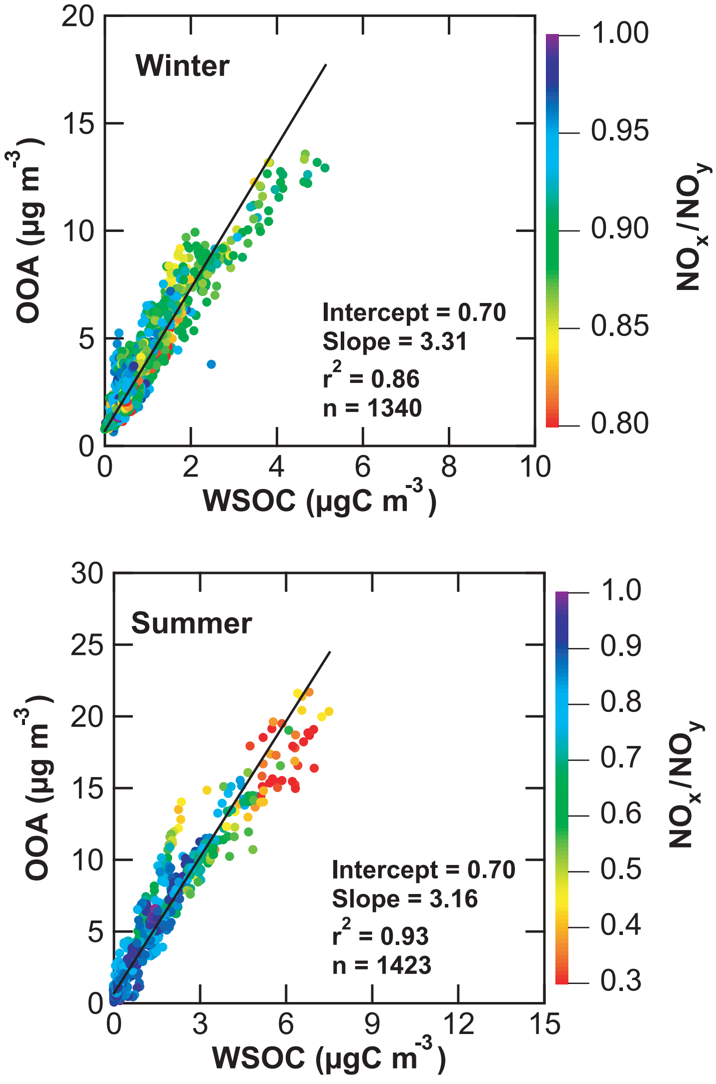

Figure 8. Correlation of OOA with WSOC for winter and summer. n is the number of data points. The data points are color-coded by the NO_x/NO_y ratios.

Organics

Secondary Organic Aerosol

It is difficult to identify chemical composition of OA from the AMS mass spectra. However, it is possible to approximately classify chemical composition corresponding to functional groups using characteristics mass/charge (*m/z*) ratios. For example, *m/z* 44 (mostly COO^+) is a good marker of oxygenated organic compounds (dicarboxylic acids), and *m/z* 57 (mostly $C_4H_9^+$) is a marker of aliphatic compounds. Therefore the fraction of *m/z* 57 is higher in chemically un-processed aerosol and the fraction of m/z 44 increases with aging (chemical processing). In fact, it has been shown that the *m/z* 44/OA ratios were anti-correlated with the *m/z* 57/OA ratios and the NO_x/NO_y ratios [*Takegawa et al.*, 2006].

Considering that CO is a good tracer for incomplete combustion, POA and SOA were classified using their correlation with CO. This method is similar to the BC-tracer method used by *Turpin and Huntzicker* [1995]. The data obtained at 2200-0800 LT with *m/z* 44/OA ratios lower than 0.05 and *m/z* 57/OA ratios higher than 0.05 form lower envelope of the OA-CO correlation plots. The slope of this data set is considered to represent OA/CO emission ratio (ER). ER was estimated to be 0.011-0.014 µg m^{-3} ppbv^{-1}. POA was defined using the ER as POA = ER × Δ CO, where Δ CO is the difference between the observed and background CO mixing ratios. SOA was given as SOA = OA - POA – BG, where BG is background OA (1-2µg m^{-3}), estimated by another method.

On average, the POA did not exhibit a distinct diurnal variation, while the SOA showed a clear diurnal pattern (daytime peak at ~13:00LT) for the summer (Figure 7), fall, and winter periods. At the daytime peak, the SOA was nearly the same concentration as the POA for all periods, suggesting that significant SOA formation occurred in daytime throughout the measurement period. A second peak in the SOA was found at ~21:00LT in summer and winter. This result suggests a significant SOA formation even after sunset, or a shift in the gas-particle equilibrium of SOA compounds after sunset.

Water Soluble Organic Carbon (WSOC)

The water soluble organic carbon (WSOC) concentrations and WSOC/OC ratios showed diurnal variations as that for SOA with peaks at 1200—1400 local time (LT) in summer and at 1400–1800 LT in winter [*Miyazaki et al.*, 2006]. The average WSOC/OC ratios were 0.20 and 0.35 µgC/µgC for winter and summer/fall suggesting that the air masses sampled in summer and fall were more photochemically processed than those in winter. The concentrations of secondary organic carbon (SOC) were estimated using the BC-tracer method. The mass concentrations of WSOC and SOC were highly correlated and the WSOC/SOC ratios (linear regression slopes) ranged from 0.67 to 0.75 µgC/µgC. In contrast, the measured

WSOC showed poor correlations with primary organic carbon (POC) throughout the whole period. These results indicate that the components of WSOC and SOC likely originate from similar sources. About 71% (uncertainty of ±28) of SOC was water-solublewheras, a dominant portion (~ 90% or more) of the POC was water-insoluble, consistent with previous chemical analysis of POC.

Oxygenate Organic Aerosol (OOA)

Oxygenated organic aerosol (OOA) and hydrocarbon-like organic aerosol (HOA) were quantified from AMS mass spectral time-series using an algorithm based on a custom principal component analysis [*Kondo et al.*, 2007]. In summer, about 80% of organic aerosols were oxygenated due to high levels of photochemical activity, which lead to the active formation of SOA. In winter, the degree of oxidation of organic aerosol is reduced to 39%.

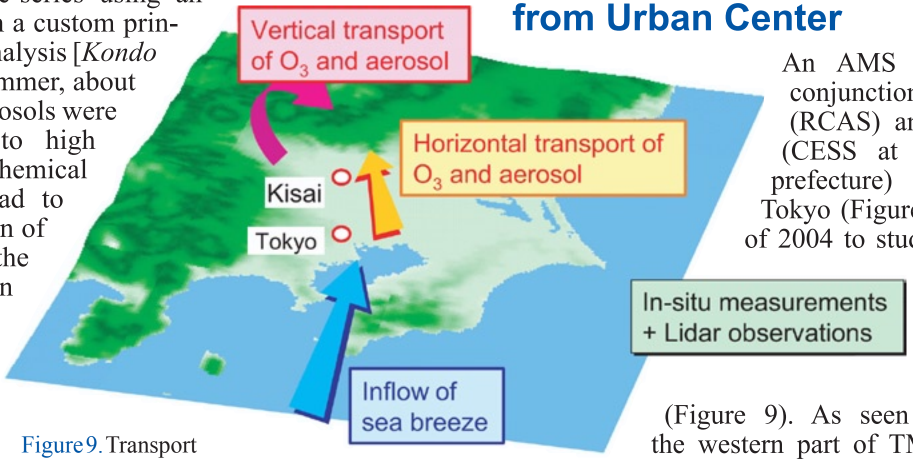

Figure 9. Transport of pollutants from the urban center (Tokyo) to sub-urban areas by sea breeze.

Time series of AMS *m/z* 44 (*m/z* 57), a good marker for OOA (HOA), were highly (poorly) correlated with WSOC in winter and summer 2004. The *m/z* 44-WSOC slope was nearly constant at 0.423±0.016 org.-eq. µg/µgC over the year – i.e. showing only 4% variability across the winter and summer seasons. The signal at *m/z* 44 is an excellent marker for WSOC, given the high *m/z* 44-WSOC correlation and the stable *m/z* 44/WSOC ratio, independent of the season. OOA was even more strongly correlated (r^2 = 0.87-0.93) with WSOC, despite the significant variabilities in the OOA/OC and HOA/OOA (WSOC) ratios, especially in winter. The average OOA/WSOC ratio was 3.24±0.08 µg/µgC, also showing only 2% seasonal variability, as shown in Figure 8. About 88±29% of OOA was estimated to be water soluble for both winter and summer from the comparison of WSOC with the derived carbon mass concentrations of OOA.

Formation of OA during Transport from Urban Center

An AMS was deployed in conjunction at an urban site (RCAS) and a suburban site (CESS at Kisai in Saitama prefecture) 50 km north of Tokyo (Figure 2) in the summer of 2004 to study the evolution of submicron OA in polluted air exported from Tokyo by the sea-land breeze (Figure 9). As seen from this figure, the western part of TMA is bounded by mountains (green color). The sea-breeze combined with this geography form a stable corridor (orange color) of northward transport of pollutants emitted from Tokyo. OA and SO_4^{2-} were found to be the major constituents of PM_1 aerosols (40-50% and 20-30%, respectively) at both sites during the observation period. A large increase in OA was found at the site downwind of Tokyo, suggesting a significant formation of SOA with air mass aging [*Takegawa et al.*, 2006b; *Miyakawa et al.*, 2008]. OA (normalized by

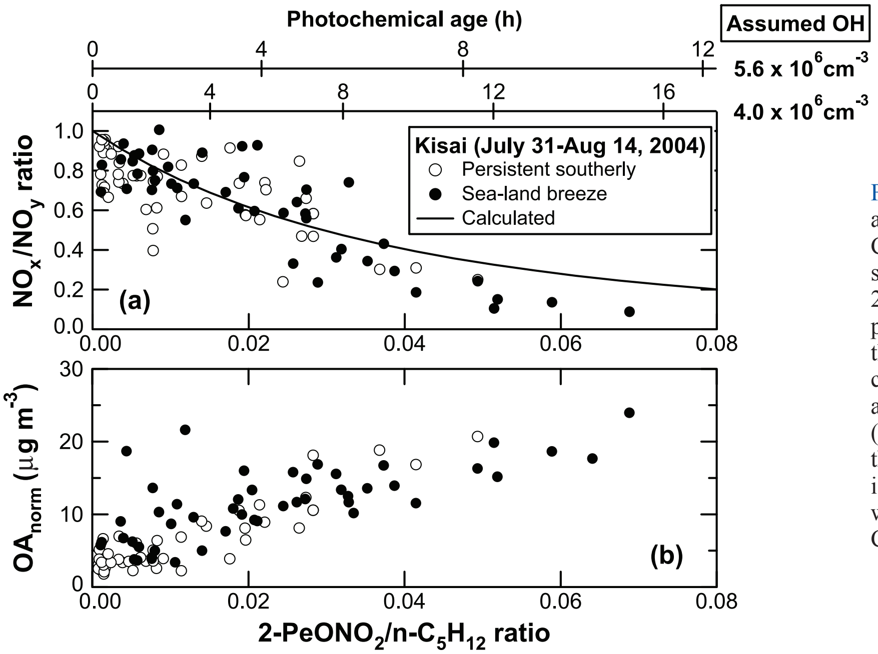

Figure 10. (a) NO_x/NO_y ratio as a function of the 2-PeONO$_2$/*n*-C$_5$H$_{12}$ ratio observed at the Kisai site during phase 1 (open) and phase 2 (solid). The top axis indicates the photochemical age calculated from the 2-PeONO$_2$/*n*-C$_5$H$_{12}$ ratio. The curve indicates the decay of NO_x against OH reaction. (b) Same as (a) but for OA_{norm}, where OA_{norm} is the normalized OA concentration. It is defined as OA_{norm} = OA × /C_2H_2, where = 0.804 ppbv is the average C_2H_2 at the Kisai site.

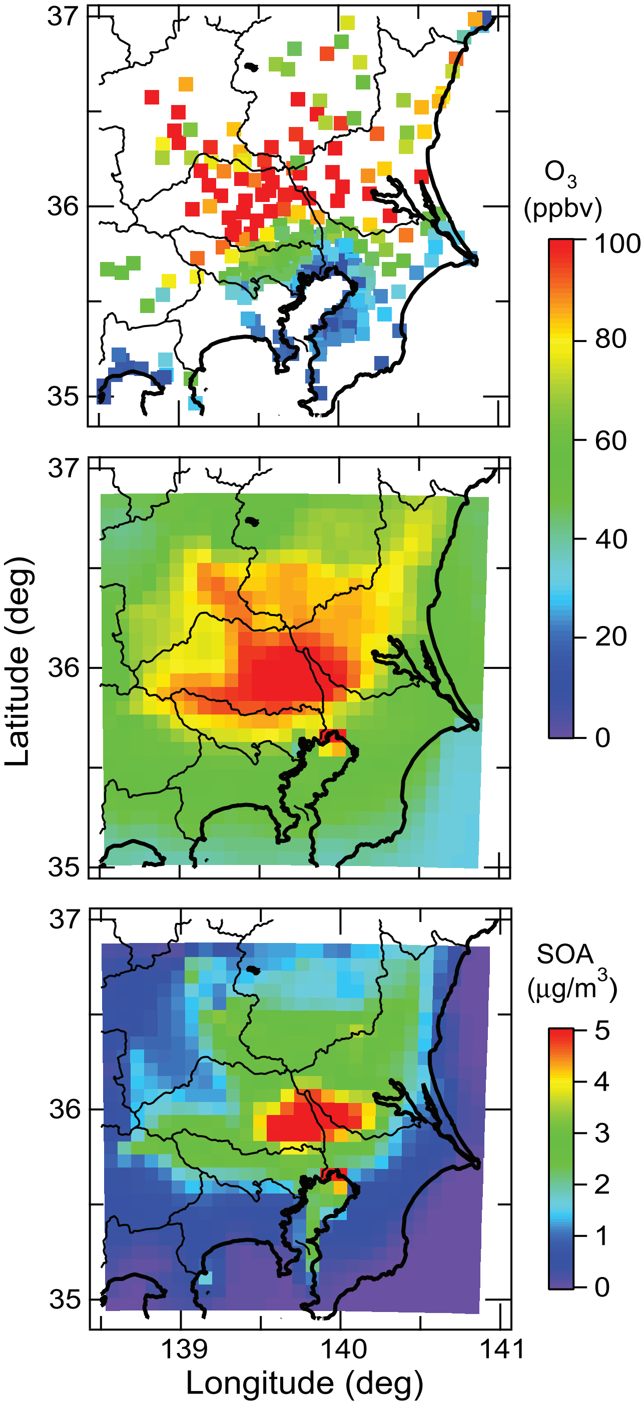

Figure 11. Comparison of model calculated O_3 and SOA with observations in summer (1400 LT on August 4, 2003).

C_2H_2 or BC to correct for the dilution effect) increased from ~4 to ~16 µg m^{-3} in processed air (photochemical age of 8-16 h), corresponding to a growth rate of 0.8-1.6 µg m^{-3} h^{-1}, as shown in Figure 10. These results could be useful for the validation of chemical transport models in future studies.

The temporal evolution of OA mass spectra was also investigated using the AMS data [*Miyakawa et al*., 2008]. The *m/z* peaks of organic compounds (and therefore their concentrations) relative to BC mass generally showed increasing trends with air mass aging. However, the trends varied significantly for different *m/z* peaks, suggesting the complexity of the temporal evolution of organic functional groups. The *m/z* 44 and 45 peaks, which are good markers of carboxylic groups in organic particles, showed larger increases than any other *m/z* peaks, suggesting an efficient formation of carboxylic functional groups on a time scale of hours during the measurement period.

Three-dimensional CTM Calculation of OA

For systematic understanding of formation, transport, and removal processes of aerosols around the TMA, studies using 3D regional CTM (MM5 and CMAQ-MADRID2) were made [Matsui et al., to be submitted to J. Geophys. Res.]. As shown in Figure 11, model calculations generally well reproduced diurnal variations of spatial distribution of O_3 around the TMA in summer observed by the Atmospheric Regional Observation System (AEROS), maintained by the local governments; sea-breeze developed during the daytime brought precursor gases emitted within the urban center to the north causing O_3 enhancements in downwind areas (50-100 km distant) in the afternoon. Relatively small normalized-mean-bias (NMB = 24%) and high correlation coefficient (r = 0.68) of daytime averages (statistics for 610 AEROS stations) indicate that day-to-day variations of spatial O_3 distribution were also captured by model calculations. Sulfate and ammonium aerosol concentrations observed at RCAST were also well reproduced (within 25%), although nitrate concentrations were overestimated by a factor of two, suggesting that important factors controlling inorganic aerosol concentrations are generally understood.

On the other hand, model calculations of SOA significantly underestimate AMS-derived OOA concentrations at RCAST; they are a factor of 5 lower, on average. This result indicates that there are missing processes and sources in the current SOA model calculations. Nevertheless, features of observed temporal variation of OOA, such as diurnal and day-to-day variations are reproduced by model calculations reasonably well (r = 0.59 and 0.67 for hourly and daytime average values, respectively) (Figure 11), suggesting that initial oxidation processes of precursor volatile organic compounds (VOCs) largely control the temporal variations of SOA. Furthermore, a clear positive correlation is found between SOA (OOA) and O_3 + NO_2 for both observations and model calculations. Considering regional enhancements of daytime O_3 over the large area around the TMA (200 × 200 km^2) in summer, it is expected that enhancements of SOA and OA concentrations are regional phenomena, causing regional impacts on air quality and possibly radiation field.

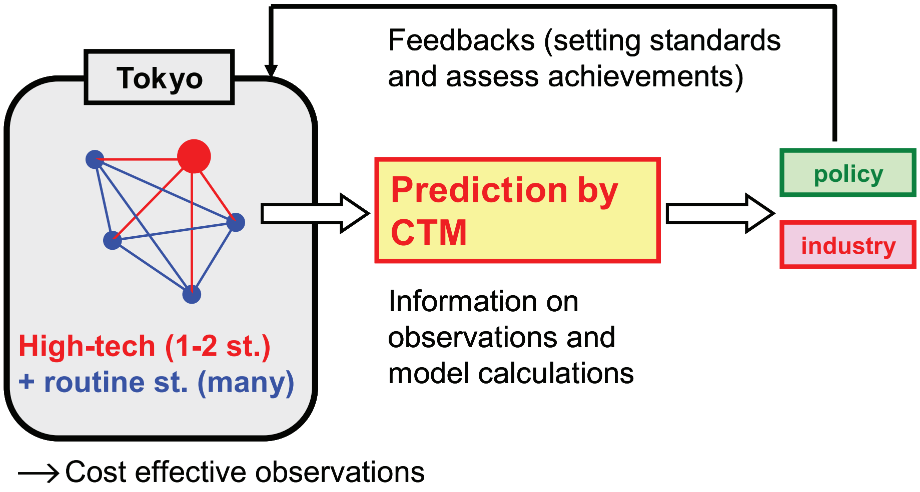

Figure 12. System for mega-city air quality studies; Observations, modeling, and science-policy feedback.

Perspectives and Future Studies

The methodology used for IMPACT is schematically shown in Figure 12. First, a combination of a limited number of fully instrumented observational sites (super sites) and monitoring stations of fundamental species has been proven to be cost-effective for mega-city studies. During the IMPACT experiments, two super sites were set up (Figures 2 and 9); one was located near the urban center (RCAST) and the other was about 50 km downwind (CESS). Because of the typical transport time of 3-7 hours, time-resolved measurements provide quite useful information on chemical evolution of polluted air. Second, instrumentations for vertical sounding, including lidar, are also useful, because changes in the boundary layer height cause corresponding changes in the concentrations of various species measured at the surface. Third, regional scale model calculations are evaluated by the data obtained by the system mentioned above. The model calculations are also useful in improving our understanding on chemistry and transport processes over the entire TMA.

Together with the scientific findings obtained through the studies in the TMA, the framework used in this study will be very useful for understanding of chemistry and transport also in other mega-cities in Asia, especially considering that many of them are also located in coastal areas, i.e. Beijing, Shanghai, Hong Kong, Guangzhou, and Seoul. In addition, studies of the impact of these mega-cities on the coastal region environment will be important interdisciplinary research area and is the subject of an emerging activity under IGBP's IGAC, SOLAS (Surface Ocean Lower Atmosphere Study) and LOICZ (Land Ocean Interactions in the Coastal Zone) projects and the Urbanization and Global Environmental Change project of the International Human Dimensions Program (IGDP-UGEC).

The IMPACT data stored in CD are available upon request. We also plan to make data base of atmospheric chemistry obtained in East Asia in near future.

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Characterization of secondary organic aerosols (SOA) and gas precursors (VOC) in contrasted megacities (Beijing, Cairo, and Paris)

Contributed by **Jean Sciare** (jean.sciare@lsce.ipsl.fr)*,* **Valérie Gros, Olivier Favez, Benjamin Guinot, Bernard Bonsang,** *and* **Hélène Cachier,** *Laboratoire des Sciences du Climat et de l'Environnement (LSCE), CNRS-CEA-UVSQ, Bâtiment 701, CEA Orme des Merisiers 91191 Gif/Yvette Cedex, France*

Motivation and background

Characterization of particulate pollution in megacities: Challenging work

More than half of the world population is now living in urban areas and the number of urban dwellers is expected to grow by about 2% per year during the next two decades. This urbanization leads to the expansion of urban centres, especially in developing countries, with one billion and three hundred million inhabitant increases by 2015 for Asia and Africa respectively. Therefore, the growing number of new megacities concerns mainly countries located in tropical zones associated with deep convection (which redistributes pollutants from local to regional scales) and a high level of photochemistry (which favors formation of secondary pollutants). Urban aerosols originating from megacities in developing countries are likely to differ in a number of ways from cities that have been studied in the US and Europe. Less stringent regulations allow production of higher levels and more complex (and possibly more toxic) aerosols. In addition, many of the cities are characterized by numerous and various source areas, in contrast to traffic-related automobile emissions that characterize emissions from large cities in industrialized countries. As megacities develop and technology evolves, the large number of air pollutant sources will also be changing, making it even more challenging to assess and predict their various impacts.

Secondary organic aerosols and gas precursors in urban atmospheres

Oxidation of some volatile organic compounds (VOCs; i.e. with 6 or more atoms of carbon) may lead to the formation of secondary organic aerosols (SOA) through condensation on pre-existing particles. Based on chamber experiments, aromatic compounds have, to date, been identified as the main anthropogenic precursors of SOA (*Ng et al.*, 2007 and references therein). Although biogenic VOCs (mainly isoprene and terpenes) are identified as the main precursors of SOA at the global scale, the role of aromatics as precursors of SOA is now taken into account in simulations of the present and the future budget of SOA (*Tsigaridis and Kanakidou*, 2007). In addition, recent results from a field campaign suggest that the regional formation of SOA in air pollution plumes may be more rapid and more significant than expected (*Volkamer et al.*, 2006). As traffic and solvent emissions are important sources of aromatics compounds, megacities are potential hotspots of SOA formation. Therefore, there is a need to characterize aromatic compound amounts and their variability in urban centers. In addition biogenic compounds need to be characterized as well as how biogenic sources near mega-cities may influence SOA formation in the megacity itself.

Both primary and secondary organic aerosol compounds are detected in urban centers at elevated concentrations, whereas organic aerosols in the outflow of these urban regions are mainly composed of oxygenated (secondary) aerosol species (*Zhang et al.*, 2007), pointing out the high reactivity and complexity of urban plumes. However, the mechanisms leading to the formation of these secondary organic aerosols (SOA) remain poorly understood. They comprise gas-to-particle conversion and heterogeneous reactions (oligomerisation reactions) that will affect many properties of organic aerosols. This picture has become even more complicated with recent studies showing that most anthropogenic primary organic particulate emissions were semi-volatile and could play a major role in the formation of SOA through gas-particle partitioning and photochemical processing (*Robinson et al.*, 2007). In addition to the potential role of semi-volatile organic species, recent field studies have reported that SOA formation in urban areas and downwind regions could be almost entirely related to water-soluble organic matter (*Miyazaki et al.*, 2006; *Sullivan et al.*, 2006), pointing to the potential role of water-soluble organic carbon (WSOC) measurements for trace SOA formation. Recent studies in United States have shown that fine particle (<2.5µm diameter) WSOC was secondary and was formed through a process that involves modern biogenic VOCs but which is strongly linked to an anthropogenic component that may largely control the mass of SOA formed (*Weber et al.*, 2007).

All these results point out the need for a better characterization of anthropogenic SOA at the early stages of its formation (within urban centers) and this approach requires an experimental setup that should enable near real-time measurements in both the gas and particulate phases. Preliminary results of such experimental studies combining both organic gases (VOC) and fast aerosol measurements are presented here for three contrasted megacities (Paris, Beijing, Cairo).

Experimental Description

Cairo, Beijing, and Paris: Three contrasted megacities

With approximately 20 millions inhabitants, Greater Cairo (Egypt) is the largest urban area in the African and Middle East regions and is one of the most air-polluted megacities in the world (*Molina and Molina*, 2004). Apart from a northern Nile delta sector impacted by a mixture of biogenic (agriculture) and anthropogenic sources, Greater Cairo is surrounded by Saharan desert which sustains relatively high dust aerosol background levels. Anthropogenic sources within the urban and suburban areas are numerous, ranging from industries to residential and traffic (mainly composed of old and polluting vehicles). Due to the rapid growth of the urban population, the situation is getting worse at a faster rate with a “black cloud” reported over the city during the fall season, originating partly from the superimposition of emissions by agricultural waste burning in the Nile delta. Very few atmospheric measurements are available for Cairo, making estimation of levels and composition of particulate pollution within the city itself very uncertain.

In contrast, Beijing aerosol pollution has received much more attention, with a growing volume of scientific publications over the past decade on topics ranging from the characterisation of dust events (mainly during the spring period) to more specific studies on aerosol source identification (including source apportionment). Comprised of more than 14 million inhabitants, Beijing is indeed experiencing a rapid development regarding energy consumption and urban growth. The city is at present engaged in an ambitious and rapid clean-up ahead of the 2008 Olympic Games and a serious policy exertion has been developed to phase out the most significant sources of pollution.

With a population of about 12 millions inhabitants, Greater Paris (France) is the most populated megacity in Europe and among the few located in developed countries. Due to its favorable geographical situation (far from other big European cities and influenced very often by clean oceanic air masses), it may be considered a good candidate for investigating the build-up of urban air pollution from temperate industrialized countries.

These 3 megacities (Cairo, Beijing, Paris) are at various states of their economic development with various emissions sources of various strengths at local and regional scales. While the three are subject to differing air pollution problems, Beijing and Cairo are both among the most polluted megacities in the world (Gurjar et al., 2008).

VOC measurements

Volatile Organic Compound (VOC) data for Paris are based on measurements made during the LISAIR field campaign, which took place in the center of Paris (City Hall square) in May 2005 (*Chazette et al.*, manuscript in preparation, 2008). An instrumented mobile laboratory allowed in-situ measurements that included ozone, nitrogen oxides, carbon monoxide and non-methane hydrocarbons for the gas phase. For the determination of aromatic compounds, a gas chromatograph equipped with a flame ionization detector (GC-FID, Chromatotec, Saint Antoine, France) was used, allowing measurements of these compounds every 30 minutes.

The Beijing VOC data are based on a field campaign performed in downtown Beijing in August 2004 where 36 flask samples were collected and subsequently measured in a laboratory by GC-MS and GC-FID for non-methane hydrocarbons including mono-aromatic compounds (*Gros et al.*, 2007).

There was no measurement of biogenic VOCs during the campaigns described above. However, in situ-measurements of isoprene have been performed in Paris (May-June 2007) and Beijing (August 2007) within the French ANR AEROCOV program, and preliminary results will be given here (*Gaimoz et al.*, unpublished results).

No VOC measurements were performed during our campaigns in Cairo. Therefore the VOC results from *Khoder* (2007) will be used here. These results are based on measurements performed in June-August 2004 in two urban areas and one background site in greater Cairo. VOCs were collected on activated charcoal tubes and then analysed by GC-FID. Note that the number of samples is limited (12 for each station) and corresponding results should therefore only be regarded as indicative.

Table 1. Median (minimum and maximum) of benzene, toluene, ethylbenzene, m-p xylene and o-xylene in Beijing, Cairo and Paris ($\mu g\ m^{-3}$). Nb stands for the number of available measurements.

	Nb	Benzene	Toluene	Ethylbenzene	m+p-Xylenes	o-Xylene	Sum	References
Beijing (2004)	36	11 (1-36)	14 (2-36)	5 (1-18)	10 (4-30)	2 (1-6)	43	Gros et al. (2007)
Cairo (2004)	12	87 (72-107)	215 (160-263)	43 (30-60)	140 (103-172)	72 (49-99)	557	Khoder et al. (2007)
Paris (2005)	202	0, 9 (0, 1-8)	8 (1-71)	1, 0 (0, 1-5)	3, 4 (0, 5-26)	1, 1 (0, 1-9)	14	Chazette et al. (in preparation)

Aerosol measurements

Aerosol results in Paris are based on the measurements reported in detail by *Favez et al.* (2007) for PM2.5 (performed by R&P TEOM-FDMS at 30°C and R&P TEOM at 50°C) and chemical speciation (filter-based measurements of ions, carbon) of fine aerosols (erodynamic diameter <2.5µm). These were obtained for the summer period (August 2005) at the terraced roof (14m agl, above ground level) of the Laboratoire d'Hygiène de la Ville de Paris (LHVP, Paris 13th district). This is part of the AIRPARIF air quality monitoring network and is considered as being representative of Paris background air pollution.

The aerosol Beijing results are based on a similar sampling strategy for PM2.5 measurements (TEOM-FDMS at 30°C and TEOM at 50°C) and chemical speciation of fine aerosols (artifact-free steam-jet-aerosol-collector-ion-chromatography (SJAC-IC) for time-resolved measurements of inorganic salts, filter-based measurements of carbonaceous aerosols). These measurements are reported in detail by *Guinot et al.* (2007) and *Sciare et al.* (2007). They are obtained for the summer period (August 2004) at the top (30m agl) of the Beijing Municipal Environmental Monitoring Centre (BMEMC) building, 4 km west of Tiananmen Square, between the Second and the Third Ring Roads.

Results from Cairo are reported by *Favez et al.* (2008) for the chemical speciation of the main chemical components of bulk aerosols. They were obtained for a 19-month period (November 2004 to May 2006) and were collected at the top of the Physics Department of Cairo University, which is located in the southern part of Greater Cairo, about 3km in a direct line from the city centre (Sadate Square).

In this study semi-volatile material (SVM) in aerosols is defined as being partitioned into its organic fraction (SVOC) and its inorganic fraction (mainly ammonium nitrate), and thus does not include liquid water content. Levels of SVM are calculated here as the difference between PM2.5 measurements from TEOM-FDMS (heated at 30°C) and conventional TEOM (heated at 50°C).

Results and discussion

Brief characterization of VOCs in the three contrasted megacities

In order to document the available gas-phase SOA precursors, combined information on the ambient level and reactivity of these compounds must be addressed. As previously mentioned, biogenic and aromatic compounds are the main SOA precursors and here will be briefly characterized for three contrasted megacities.

Table 1 shows the concentrations of the mono-aromatics measured in Paris, Beijing, and Cairo. A large range of variability is observed even within a given city, reflecting mostly the spatial and temporal variability of emissions. For example, there is a variability of a factor up of 5 for mono-aromatic concentrations in Paris downtown as measured in the air quality network stations (http://www.airparif.asso.fr/). In Cairo, *Khoder* (2007) found a factor of 20 to 40 for concentrations measured in urban center and rural area stations. The higher factor (40) observed for the xylenes reflects the high reactivity of these compounds.

Notably, toluene is the main aromatic compound in vehicle fuel, and its high concentration among the major aromatic compounds observed in every studied megacity reflects the dominant role of the vehicle traffic source in these cities (*Broderick and Marnane*, 2002, *Schauer et al.*, 2002). Benzene concentrations in Paris are significantly lower than in the other cities, which may be due to the benzene reduction in fuels following the European Directive 98/70/Ec in 1998. By summing concentrations of the 5 measured aromatic compounds, we find that Beijing loading in aromatics (42µg/m^3) is about three times more than in Paris (14µg/m^3). We note that similar factors (3-4) between Beijing and Paris have also been determined for black carbon and carbon monoxide (CO) concentrations (*Gros et al.*, 2007). In Cairo, the loading of aromatic compounds (557µg/m^3) is about 10 times higher than in Beijing and, if representative, indicates a major air quality problem and a potential large source for SOA formation.

The median (min-max) values of isoprene measured in Paris and Beijing in Spring-Summer 2007 were 0.5 (0.2-4.6) µg/m^3 and 1.7 (1.5-9.3) µg/m^3, respectively (*Gaimoz et al.*, unpublished results). By comparison with total measured aromatics, isoprene represents in both cities less than 5% of their mass. To our knowledge, there is no available measurement of isoprene in Cairo but due to the absence of forest areas in its surroundings and due to the high levels of the aromatic compounds, the ratio biogenic/anthropogenic is presumed to be much less than in Paris or Beijing.

Due to their high reactivity, and despite the relatively low level of isoprene compared to anthropogenic compounds, biogenic compounds (isoprene but also terpenes and others) have to be taken into account in the estimation of SOA formation. For example, for an OH concentration of 2x10^{6}molecules/cm^3, the lifetimes for xylenes and benzene are 10 hours and 5 days, respectively, whereas the lifetimes of isoprene and terpenes are on the order of 1-2 hours. Therefore VOC oxidation will induce formation of various SOA at different distances from the sources within the megacity plume.

In addition to the quantity of emitted pollutants, the timing of emissions is also important in determining

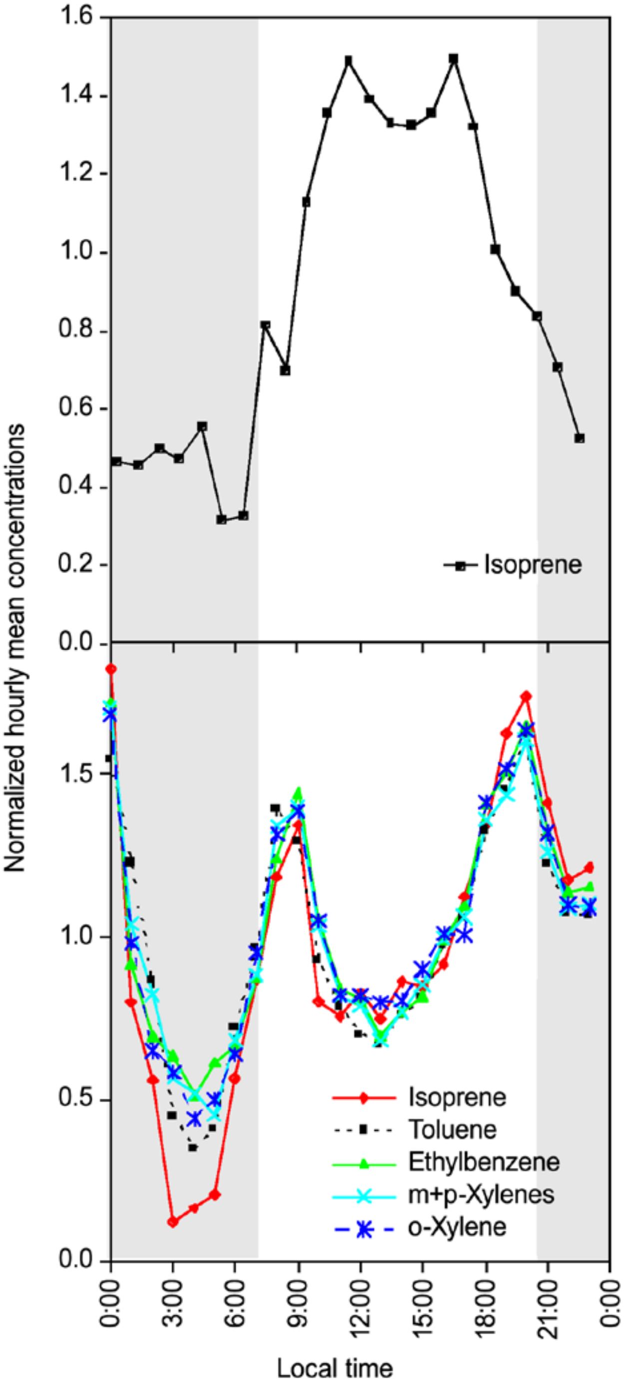

Figure 1. Shown are hourly mean of isoprene in Paris, May-June 2007, (top) and hourly means for aromatic compounds during the LISAIR campaign, May 2005 (bottom). Both sets of values have been normalized by dividing by the corresponding daily means.

the availability of VOCs when photochemical reactions can take place. Diurnal variability is mainly governed by the timing of source emissions and modulated by variation of the boundary layer height. Figure 1 shows the average diurnal variation observed in Paris during the LISAIR campaign for isoprene (top) and aromatic compounds (bottom). The observed nighttime minimum and the two maxima (in the early morning and early evening) of aromatic concentrations typically reflect the diurnal variation of traffic-related emissions. The decrease observed in the morning is mainly due to the increase of the boundary layer height (*Pham et al.*, 2007). In Cairo, *Khoder* (2007) report also similar diurnal cycles of aromatic compounds and point to the dominance of the traffic emissions. However, in Beijing, there is not such a clear and reproducible diurnal cycle as a result of the diversity of primary sources (e.g. the role of industries, use of charcoal for cooking, etc.; see for instance *Gros et al.*, 2007). Isoprene is also at its maximum during the day in Paris, but in this case there is a clear diurnal cycle, with the peak lasting a few hours (11h-18h; Figure 1). This diurnal cycle of isoprene is also seen in Beijing (figure not shown) and may be explained by the fact that isoprene emissions depend mainly on incoming solar radiation and, as produced in the surroundings forests and transported over the city, it needs a few hours before to reach the city.

These preliminary results (albeit limited in time and in number of samples) show that the VOC pool available for SOA formation differs significantly in Paris, Beijing and Cairo in terms of ambient levels, anthropogenic vs. biogenic origin, and patterns of time-variability. These differences may affect levels and properties of freshly-formed SOA within megacities.

Semi-volatile organic aerosols

***Paris**:* Levels of semi-volatile material (SVM) in aerosols determined by TEOM-FDMS were investigated in Paris during summer where they showed a clear diurnal variation, with maximum levels in the afternoon coinciding with the maximum of photochemistry (Figure 2, bottom). As shown in this figure, concurrent measurements of semi-volatile ammonium nitrate (NH_4NO_3) fail to reproduce this afternoon maximum, which could be then attributed to a (photochemical) production of ~3µg/m^3 of semi-volatile organics (SVOC). This is consistent with the strong diurnal variation of the OC/EC ratio reported in Figure 2 (top) which shows a minimum during the rush hours (maximum of BC) and a maximum observed systematically in the afternoon, also indicating photochemically-driven SOA formation. Production of freshly-formed SOA (e.g. produced during daytime) was estimated here from the filter samples using the EC-tracer method (*Turpin and Huntzicker*, 1990) and suggests that about 50% of SOA formed during daytime in Paris would be composed of semi-volatile organics (as measured by TEOM-FDMS).

***Beijing**:* A similar study of the factors controlling

SVOC was conducted in Beijing during summertime. During this period of the year, the Beijing urban area experiences widely varying meteorological conditions, including being influenced by warm and humid monsoon air masses from the southeast which bring high levels of pollution, with PM2.5 mass concentrations often exceeding 100µg/m³. These humid periods have been shown to produce high levels of liquid water content in fine aerosols as well as coinciding with high SVM levels (up to 140µg/m³ on hourly basis). Interestingly, only half of this semi-volatile material could be identified as ammonium nitrate, the remaining originating possibly from SVOC. Although the concomitant occurrence of SVOC with liquid water content in Beijing aerosols is not fully understood yet, this result appears to be consistent with recent studies which have brought evidence of the major role of heterogeneous reactions in SOA (semi-volatile?) formation.

Based on these two preliminary studies performed in Paris and Beijing, levels of SVOC have shown to be influenced by different, although not antagonist, mechanisms (photochemistry and aerosol liquid water content for Paris and Beijing, respectively). The data collected here are not sufficient to conclude if these SVOC can be attributed either to primary organic emissions or VOC oxidation. On the other hand, it brings to our attention the need to further evaluate the (semi-)volatile properties of organics as it could possibly better link VOC and SOA studies in the highly reactive atmosphere of megacities.

Water-soluble properties of organic aerosols

Cairo: Seasonal variations of the water-soluble organic carbon (WSOC), water-insoluble organic carbon (WIOC), and EC were investigated in Cairo in order to characterize the oxidation state of organic aerosols and possibly estimate the relative contribution of SOA within the organic fraction (*Favez et al.*, 2008). Excluding the fall season, which is influenced by biomass burning, the high contribution of WIOC (70% of OC) and its very good correlation with EC (r^2=0.91) observed over the year might shows the major role of primary emissions (traced by WIOC) in the levels of organic aerosols in Cairo. However, when investigating the influence of photochemistry on the diurnal variations of WIOC and WSOC, contrasted results are observed, with a significant production of both species (relative to EC) in the afternoon (*Favez et al.*, manuscript in preparation). These results clearly point to a large contribution of water-insoluble SOA in Cairo, although most previous studies have shown a close relationship between WSOC and SOA. This partitioning of SOA between WSOC and WIOC is not fully understood and could, for instance, originate from contrasted (anthropogenic vs biogenic) VOC sources in the surrounding region of Cairo, as well as from variations in the meteorological conditions prevailing in Cairo during the daytime.

Paris: A quite similar study performed with size-

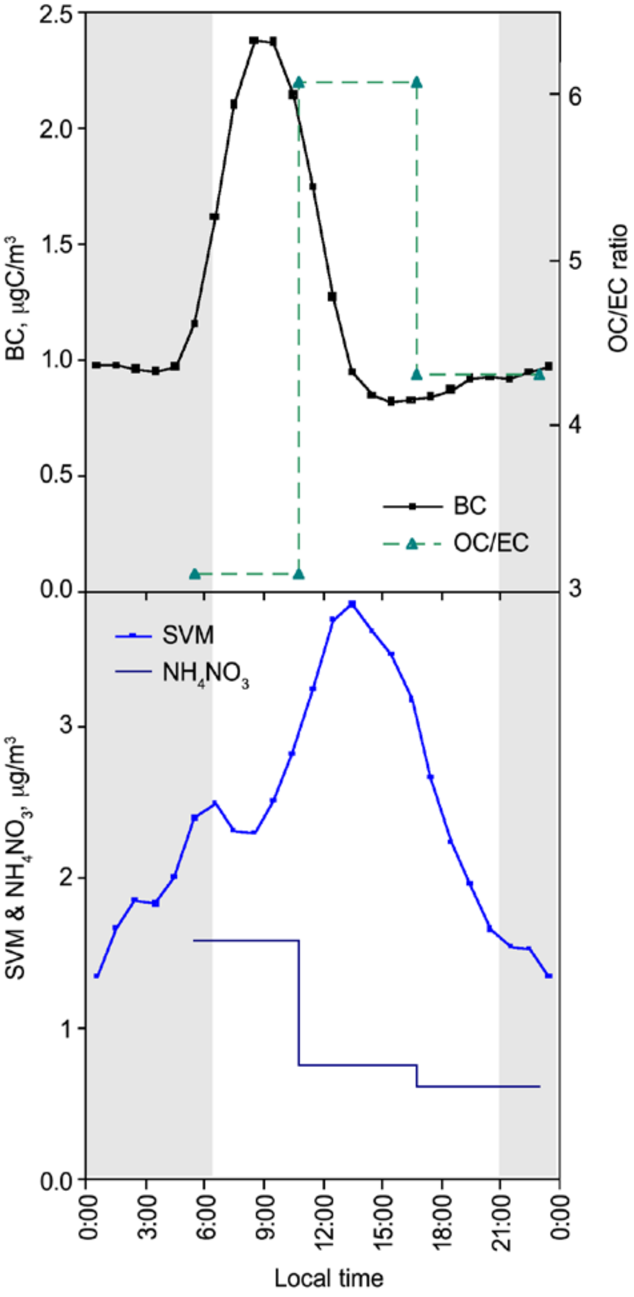

Figure 2. Diurnal variation of black carbon concentrations (BC) and the ratio OC/EC (top), and concentrations of semi-volatile material (SVM) and ammonium nitrate (NH_4NO_3) in Paris during summertime (bottom).

resolved measurements of WSOC, WIOC, and EC was achieved in Paris for different periods ("winter" vs "summer"; "morning rush hours" vs "afternoon photochemistry"). These results have clearly shown that most of WSOC measured in Paris could be related to photochemical processes leading to WSOC/OC ratios of up to 80% during summer afternoons (*Cachier et al.*, in preparation). These results are consistent with most studies, which have proposed WSOC as a surrogate for SOA, but they stand in contrast to those obtained in Cairo, although sampling and analytical protocols were quite similar.

These two preliminary studies performed in Paris and Cairo indicated that water-soluble properties of freshly-formed SOA differ significantly between these cities, with an unexpected high contribution of WIOC to SOA in Cairo. As for the role of SVOC, the data collected here are not sufficient to conclude if the partitioning of SOA between WSOC and WIOC can be attributed to primary organic emissions, to VOC oxidation, or to heterogeneous processes. On the other hand, these measurements bring to our attention that water-soluble properties (like volatility) might be key to better characterizing the various mechanisms leading to SOA formation.

Conclusions

Preliminary measurements of VOCs in the three studied megacities (Paris, Beijing, Cairo) have shown common features (importance of the traffic related sources) but also significant differences (ambient levels, importance of biogenic versus anthropogenic emissions) which may impact SOA formation. The highly reactive chemistry of these urban atmospheres has shown to lead to a significant fraction of SOA formed within the day. Interestingly, the contrasted (local/regional) primary sources and meteorological conditions within these megacities have led to contrasted results which can be summarized as follow:

- During summer, semi-volatile organic aerosols (SVOC) are seen to be photochemically produced in Paris, accounting for almost half of the SOA produced during the daytime. During the same season, Beijing fine particles are seen to contain high levels of liquid water and high levels of SVOC (water-soluble?) showing the same behaviour as semi-volatile ammonium nitrate.
- WSOC comprises a large fraction of the submicron organic aerosols (WSOC/OC up to 80%) in Paris during summer afternoons, in agreement with previous studies reporting water-soluble properties for SOA. Contrast results were observed in Cairo with a significant amount of WIOC detected in freshly-formed SOA, suggesting different formation mechanisms possibly linked to contrasted (biogenic vs anthropogenic) organic precursors or differing meteorological conditions.

All the results converge to the general statement that different megacities are likely to emit precursors and secondary organic aerosols with contrasting properties and possibly contrasting climatic impacts at local to regional scales.

Science and strategy issues addressed within the EU-MEGAPOLI experiments in Paris (2009 – 2010)

To date, very few studies are available on the chemical speciation of Paris aerosols. Those that do exist mostly comprise preliminary characterizations of carbonaceous aerosols (*Ruellan and Cachier*, 2001) or have focussed on aerosol sources (*Widory et al.*, 2004; *Bessagnet et al.*, 2005). The ESQUIF project (summer 2000) was the first (and only) integrated program aiming at the characterization of air pollution over Greater Paris (*Vautard et al.*, 2003). Particular attention was given to gaseous species, allowing significant advances in the understanding and modelling of photo-oxidant pollution events over Paris. However, aerosol characterization within this project remained rather scarce (*Hodzic et al.*, 2006; *Cachier et al.*, manuscript in preparation) leaving the need for a better evaluation of their physical, chemical, and optical properties.

The EU-FP7 MEGAPOLI project (**M**egacities: **E**missions, urban, regional and **G**lobal **A**tmospheric **POL**lution and climate effects, and **I**ntegrated tools for assessment and mitigation) will bring together leading European research groups from 11 countries, state-of-the-art scientific tools and key players from countries outside Europe to investigate the interactions among megacities, air quality and climate. MEGAPOLI will connect the spatial and temporal scales that relate local emissions, air quality and weather to global atmospheric chemistry and climate. The main MEGAPOLI objectives are:

1. To assess impacts of megacities and large air-pollution hot-spots on local, regional and global air quality;

2. To quantify feedbacks among megacity air quality, local and regional climate, and global climate change; and

3. To develop improved integrated tools for prediction of air pollution in megacities.

A pyramid strategy will be followed by undertaking detailed measurements in one major European city (Paris, France), performing detailed analysis for 12 megacities with existing air quality datasets and investigating the effects of all megacities on climate and global atmospheric chemistry.

The major objective of the Paris experiment is to provide new experimental data to better quantify sources of primary and secondary aerosol in and around large urban regions and to document its evolution in the megacity plume. A particular focus will be put on organic carbon, for which secondary formation but also primary emissions are still not well quantified (*Volkamer et al.*, 2006). Moreover, emission inventories for primary organic aerosol (POA) are probably misused in chemistry-transport models, because POA evaporation during dilution of emissions is not considered (Robinson et al., 2007). Recently, the use of factor analysis models in conjunction with high-time-resolution measurements of aerosol chemistry with an Aerosol Mass Spectrometer (AMS) has opened new opportunities for more detailed source apportionment (*Lanz et al.*, 2007). In addition, carbon-14 analysis has been shown to be a powerful tool in discriminating between the fossil and biogenic fractions of elemental and organic carbon (*Szidat et al.*, 2006). The application of these methods to detailed aerosol and precursor gas measurements, as planned in this study, will allow a substantial improvement in our understanding of anthropogenic carbon-containing aerosols.

Specific measurement campaigns will be set up in the Paris region:

A ground-based segment with observations at an urban and a suburban site during 2 periods of one month in summer 2009 and winter 2010 will allow for documenting the aerosol composition and properties, and their variability, near primary emission sources.

An airborne segment with dedicated flights with the French ATR-42 aircraft in the Paris plume during the summer campaign will permit documenting the evolution of the megacity plume and especially the build-up of secondary organic and inorganic aerosol species from precursor gases. These measurements will combine a very large suite of state-of-the-art instruments, including several new techniques, capable of tracing chemical and physical aerosol properties, and related precursor gas concentrations. Simultaneous airborne and ground-based measurements of the chemical SOA composition and of oxidised VOC will offer the opportunity to document gas phase aerosol interaction at various stages of the plume development. In addition, modifications of optical and hygroscopic parameters during plume aging will be addressed.

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發行地址：台北市115南港區研究院路二段128號1-55號信箱

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