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Review

Air quality progress in North American megacities: A review

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ABSTRACT

Air quality progress in the North American megacities of Los Angeles, New York, and Mexico City is reviewed, compared, and contrasted. Enormous progress made in North America over the last 5 decades provides a template for other megacities of the world, especially in developing countries, attempting to achieve rapid economic growth without compromising air quality. While the progress to date has been impressive, many challenges remain including the need to improve air quality while simultaneously mitigating climate change. The impact of pollutant emissions from megacities is felt long distances away from the local sources but no policy mechanisms currently exist to mitigate air quality impacts resulting from such pollution transport.

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1. Introduction

Over the last 50 years, the world's urban population has grown faster (2.7% yr^{-1}) than the total population (1.8% yr^{-1}) and is estimated to reach 5 billion by 2030. For the first time in human history the world now has more urban than rural residents with many environmental consequences (Crutzen, 2004; Bell et al., 2007). An offshoot of this rapid urbanization is the emergence of megacities (population >10 million) with a combined worldwide population of nearly 300 million. Megacities are dense centers of population, economic activity, and pollutant emissions and at the same time areas where effective pollution control strategies could realize maximum benefit (Molina and Molina, 2004; Gurjar and Lelieveld, 2005; Chan and Yao, 2008). By 2015 eight of the ten largest megacities will be in developing countries. Here we review and assess the progress in achieving cleaner air that has been made in the megacities of North America with the hope that lessons learned in North America will be valuable in achieving air quality goals in the developing world undergoing rapid economic growth.

North American megacities include Mexico City, perhaps the second largest metropolitan area in the world, and Los Angeles and New York City in the United States, two of the ten largest metropolitan areas. Differences in topography, meteorological conditions, and pollutant emission characteristics lead to marked differences in the air quality considerations in these megacities as well as their impacts on the larger troposphere. This review discusses these differences, as well as similarities. The greater Houston, Texas urban area in the United States is also discussed as an additional contrast; with a population approaching 6 million, this area is not generally considered a megacity, but it is a large urban center of particular interest since it is home to a large fraction of the petrochemical industrial facilities of the United States, which leads to a unique mix of anthropogenic emissions.

2. Los Angeles megacity: an environmental success story

The Los Angeles megacity, here defined as the South Coast Air Basin (SoCAB), is located at 34°3′N and 118°14′W with a population approaching 17 million inhabitants. Summertime photochemical smog was first recognized as a severe environmental problem in Los Angeles and has been the subject of extensive air pollution control efforts since the 1950's (Haagen-Smit, 1952; Cox et al., 2009). California was the first to set motor vehicle emission standards in 1966 and has led the nation in enforcing policies requiring catalytic converters in cars, cleaner unleaded fuels, and zero emission vehicle fleets. Between 1970 and the present, SoCAB VOC and NO_x emissions have declined markedly despite a substantial increase in commerce and vehicle traffic (Cox et al., 2009). Peak O_3

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levels that exceeded 600 ppbv in the 1960's have not reached 200 ppbv since 1998. First stage smog alerts have been reduced from some 200/year in 1970s to about 10/year today. SoCAB is an excellent example for the benefits of implementing emission control strategies in a growing megacity that can be followed in many parts of the developing world.

The improvement in air quality has been accomplished despite several unfavorable conditions that make SoCAB particularly susceptible to high air pollution concentrations. The large population lives in a basin bounded by the Pacific Ocean on the west and by mountains on the other three sides, which prevent efficient horizontal ventilation of the area. Low inversion heights associated with a persistent high pressure system and the adjacent Pacific marine environment limits the vertical mixing within the basin, and the land-sea breeze system re-circulates polluted air within the basin. These topographic and meteorological features allow emissions to accumulate over several days during episodes of relatively stagnant airflow. During the summer ozone season, May through October, clear skies and high temperatures dominate, which speed photochemical production of O_3 and other photochemical products. Private automobiles on extensive freeway systems provide the primary transportation in the area. This transportation system accounts for a large fraction of the emissions in the urban area. Technological solutions involving the development of catalytic converters and more efficient car engines along with the implementation of better traffic management systems have been central to the success of air pollution control strategies.

2.1. Air quality trends

Over the past four decades ambient concentrations of key pollutants in the SoCAB region have decreased substantially despite a doubling of the population and tripling of vehicle use. Fig. 1 compares the temporal trends of four pollutant concentrations. These data are presented in units that correspond to U.S. EPA National Ambient Air Quality Standards (NAAQS) [http://www.epa.gov/air/criteria.html], which are presently: O_3 – 75 ppbv (8-hr); CO – 9 ppmv (8-hr); NO_2 – 53 ppbv (1-yr); $PM_{2.5}$ – 35 μg/m^3 (24-hr); SO_2 – 75 ppbv (1-hr); Pb – 1.5 μg/m^3 (3-mo). The numbers in parentheses give the averaging period. The O_3 data are 3-yr averages of the 4th highest annual maxima, the CO data are annual maxima, and the $PM_{2.5}$ are annual 98th percentiles. It is evident that there has been an impressive decline in ozone concentrations as well as other air pollutants over the nearly five decades of pollutant monitoring. Although it still violates the NAAQS for O_3 and $PM_{2.5}$, the Los Angeles basin is in compliance with the NAAQS for nitrogen dioxide, carbon monoxide, sulfur dioxide, and lead. It is fair to say that this megacity has gone from being one of the most polluted in the world 50 years ago to presently one of the "least polluted" cities of its size. Estimates are that many thousands of lives have been saved from improvements in air quality (Hall et al., 2008).

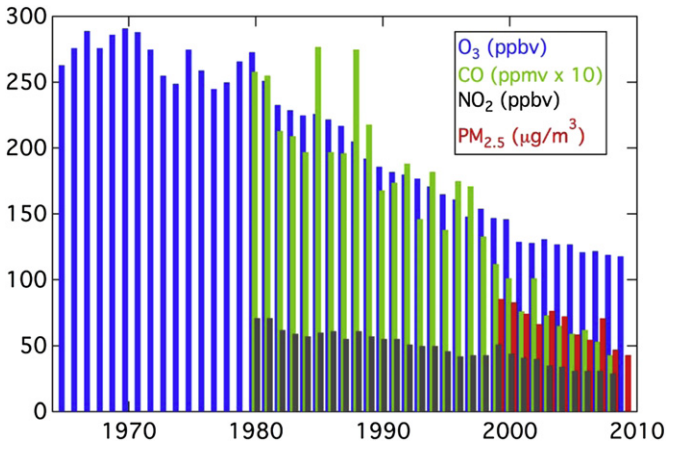

Fig. 1. Air quality trends in the Los Angeles urban area of California. As per national standards, the O_3 data (8-h average) are 3-yr averages of the 4th highest annual maxima, the CO data (8-h average) are annual maxima, the NO_2 data are annual averages, and the $PM_{2.5}$ data (24-h average) are annual 98th percentiles. Data are derived from monitoring stations in the SoCAB region (Alexis et al., 1999; Cox et al., 2009; http://www.arb.ca.gov/adam/cgi-bin/db2www/polltrendsb.d2w/Branch).

The relative temporal trends of the primary pollutants, NO_2 and CO, reflect the history of the air quality control strategy adopted in the United States. Initially, the control focus was upon VOCs and CO, notably including the introduction of catalytic converters on automobiles in the mid-1970s. The focus later shifted to include NO_x emission controls. Fig. 1 shows that this control emphasis has led to a significantly larger decrease in ambient CO concentrations (factor of 5.2) than that for the ambient NO_2 concentrations (factor of 2.3) from 1980 to 2008. SO_2 emissions have also decreased substantially over the last three decades, primarily due to reduced sulfur content of fuels utilized in mobile (as of 2006 15 ppm by mass for on-road diesel) and point sources, and to scrubbing of sulfur from flue gases emitted by point sources.

It is important to recognize that significant problems remain. The region still violates the ozone standard and indeed despite continued emission reductions little improvement in O_3 air quality has been observed since 2000. During 2005–2008 the 8-h O_3 exceeded the NAAQS on 110–120 days each year. The current peak O_3 levels are roughly double the accepted levels set to protect the most vulnerable populations. Several difficulties exist in achieving air quality goals. Due to the extremely non-linear nature of VOC–NO_x–O_3 chemical system, it is possible that VOC/NO_x ratios over time have shifted to a regime where further VOC reductions are only minimally effective (Sillman, 1999). There is also evidence to support the view that background O_3 concentrations transported into California constitute a significant fraction of the NAAQS, and are increasing, possibly in response to increasing Asian emissions of O_3 precursors (Parrish et al., 2009a, 2010). Such an increase can negate some of the local pollution control progress (Jacob et al., 1999; Lin et al., 2008). Controlling emissions from heavy-duty diesel trucks has been far more difficult than passenger cars as the turnover time for this fleet (25–30 years) greatly exceeds that for the passenger fleet (7–10 years). A relatively small fraction of the total motor vehicle fleet, currently 10 million vehicles in the Los Angeles basin, accounts for a very large fraction of the total mobile source emissions. A related problem is the emergence of the ports of Los Angeles and Long Beach as dominant point sources of diesel-related pollution in the Los Angeles Basin due to a tripling of goods movement from Asia through these ports over the past 15 years. Future progress is anticipated from a greater use of plug-in hybrids, electric cars, alternate fuels and better control technology. Current targets call for on-road emission reductions of VOC, NO_x, SO_x, and $PM_{2.5}$ by respectively 70%, 70%, 50% and 12% between 2007 and 2020 (Cox et al., 2009).

2.2. Air quality and climate change

Megacities contribute significantly to the burden of Green House Gases (GHGs) in the atmosphere. In the past, air quality control strategies have been based largely on health implications with little consideration for the associated climate change consequences. An added complication for future control strategy development is the need to mitigate climate change impacts while improving air quality (Bell et al., 2007). Although uncertainties remain, a warmer climate, with increasingly hotter days, is also

likely to be deleterious to air quality and negate benefits of pollution control strategies in the southern California region (Steiner et al., 2006; Murazaki and Hess, 2006; Millstein and Harley, 2009; Mahmud et al., 2010). Urban "heat-island" effects can cause parts of megacities to be up to 5 °C warmer than surrounding areas. Recent studies (Diffenbaugh et al., 2008) indicate that Los Angeles basin has extremely high sensitivity to future climate change (Fig. 2). The interactions between these two environmental concerns are often non-linear and require a better understanding of the feedback processes (Isaksen et al., 2009; Jacob and Winner, 2009; Ramanathan and Feng, 2009). With the passage of Global Warming Solutions Act of 2006, California is presently embarking on strategies to improve air quality as well as mitigate the impacts on local and global climate change. In California, the first task in controlling CO_2 and other GHG emissions (CH_4, N_2O, halocarbons) has begun with inventorying their baseline emissions and atmospheric abundances so future progress can be measured against a reference point expected to be 2010. The short-term goal is to reduce GHG emissions 30% below the business-as-usual projected emissions for2020 (see California's Climate Plan at http://www.arb.ca.gov/cc/cleanenergy/clean_fs2.htm)

2.3. Observational data and field campaigns

Over the last several decades, there have been great advances in measurement technology and it is now possible to measure a large number of precursors and intermediate species (carbonyls, free radicals, aerosol composition) to test and validate models that simulate air quality and climate change interactions. Complementing the models have been several intensive field campaigns that used aircraft platforms to acquire data in three dimensions and provide boundary conditions necessary for model development and forecasts of air quality and climate change. Some of the recent intensive campaigns that have provided detailed observational data from SoCAB have been the 1997 South Coast Ozone Study (Croes and Fujita, 2003), the 2002 ITCT study (Parrish et al., 2004), the 2008 ARCTAS-CARB study (Jacob et al., 2010; Singh et al., 2010) and the recently completed CalNex study (http://www.esrl.noaa.gov/csd/calnex/). These campaigns used aircraft platforms to assess emission sources, atmospheric composition, and boundary conditions applicable to this region. Fig. 3 shows that emission signatures of different sources can be identified in such measurements. In the upper panel the anthropogenic sources in southern California have relatively small CO to CO_2 emission ratios compared to biomass burning (BB) plumes encountered in Canadian boreal fires as well as wildfires in southern California. In the lower panel, the CH_4 to CO emission ratios are seen to be quite high over agricultural regions of California, lower in urban emissions and very much lower in BB plumes. In this lower panel elevated benzene concentrations (color scale) are found in the urban emissions and BB plumes, while acetonitrile (CH_3CN) is strongly elevated only in the BB plumes (inset).

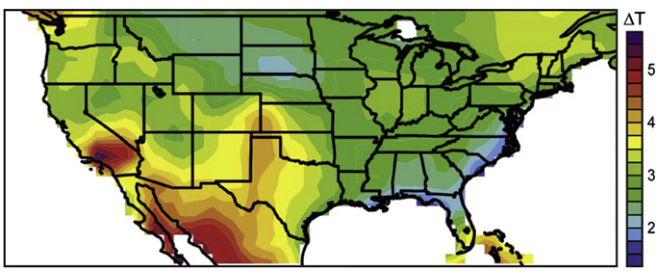

Fig. 2. Future climate change hot spots over North America. The color scale gives aggregate climate change scores, which take into account long-term mean and variability of warm- and cold-season temperature and precipitation (after Diffenbaugh et al., 2008).

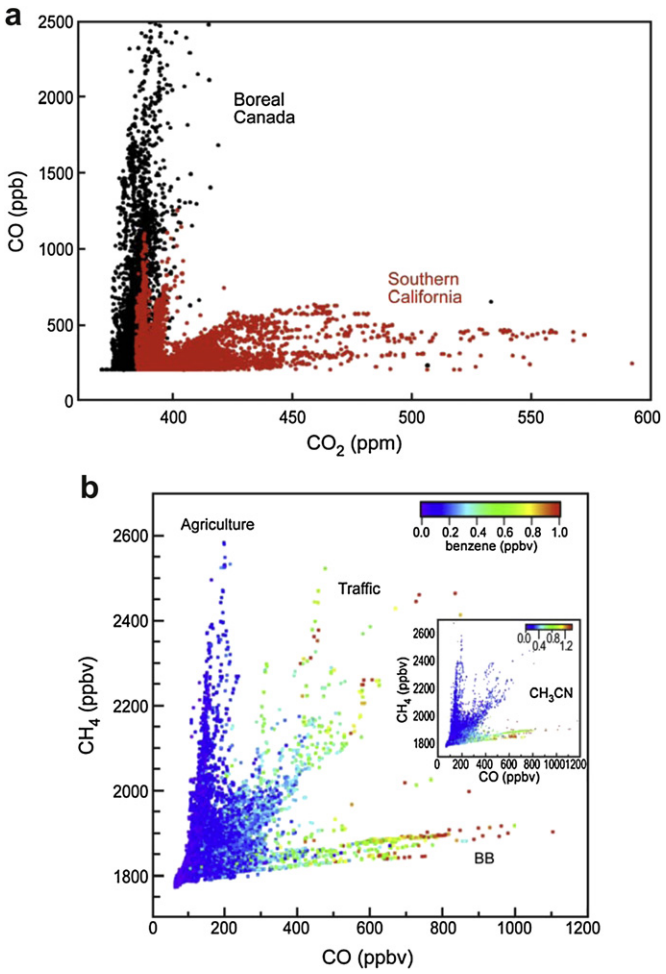

Fig. 3. Relationships between selected trace constituents over Southern California measured from June 17–26, 2008. The upper panel compares the California data with later measurements in forest fire plumes in Canada. The lower panel compares measurements over different California regions: agricultural areas, urban (traffic) and in forest fire plumes (BB). (after Singh et al., 2010).

More recently satellites have been able to provide a new dimension to the repertoire of surface based observations (Martin, 2008). Although less precise than in-situ techniques, satellite observations extend over several years and provide data on scales much larger than aircraft campaigns. Additionally, satellites generally provide atmospheric columns and relating these to surface observations remains a challenge. Fig. 4 shows tropospheric NO_2 columns over urban areas in the western United States. The highest concentrations are seen over the Los Angeles basin. Generally all urban areas show strong weekday–weekend differences in emissions. Such satellite measurements provide tests of NO_x emission inventories (Boersma et al., 2008; Kim et al., 2009). Similar data are available for aerosols and attempts are being made to relate aerosol optical depth to $PM_{2.5}$ measured by ground networks (Engel-Cox et al., 2006). In the future, column measurements of GHGs (e.g., methane, CO_2) around the globe are likely to provide new information on their sources and sinks.

3. The U.S. Northeast urban corridor and Houston, Texas: contrasting US urban areas

Located at 40°42′N and 74°W near sea level, by its widest definition, the New York City region includes 22 million people in

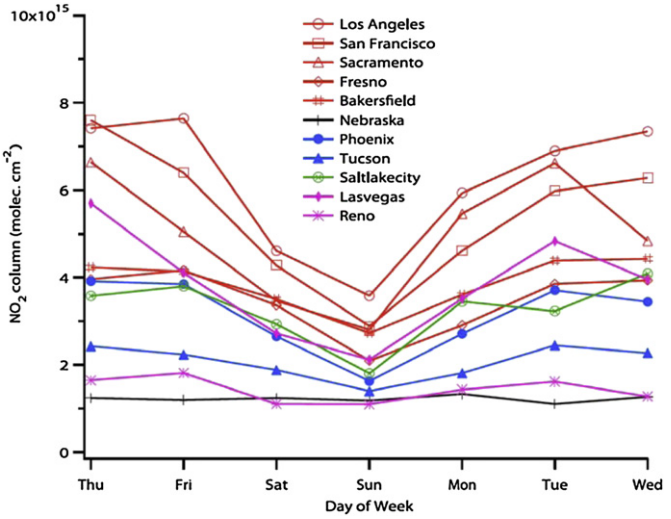

Fig. 4. SCIAMACHY satellite derived tropospheric NO_2 columns over urban areas in the western US for 2003–2007 May–September averages (after Kim et al., 2009).

parts of three states: New York, New Jersey and Connecticut. It is embedded in the US Northeast urban corridor, which extends from Boston to Washington D.C. and has a population of about 55 million people. In some respects New York City has a more favorable situation from an air quality perspective than does Los Angeles. The Northeast urban corridor in general and New York City in particular has lower per capita emissions of ozone and aerosol precursors and greenhouse gases than western US cities like Los Angeles and Houston (Grimm et al., 2008). The greater population density, which allows much greater use of public transportation, more efficient housing, and other energy efficiencies, accounts for this difference. With no significant topographic barriers to air flow there is generally much better ventilation of the northeast urban areas allowing winds to sweep pollutants away from emission regions. With the prevailing winds from the continent, the daytime convective boundary layer is generally deeper allowing also greater vertical mixing of emissions. On the other hand, New York City is located on the heavily populated east coast of the US, so that southwest winds, which often occur in summer, can transport air that is already heavily polluted into the city. It is under such conditions that the highest ozone levels are observed (Kleinman et al., 2005; NYSDEC, 2010). The net effect of these and other differences is that the New York City area has not experienced the very high O_3 concentrations observed in Los Angeles.

The Houston, Texas urban area located at 29°45′N and 95°21′W along the Gulf of Mexico coast has a much smaller population approaching ~6 million. However, Houston has much greater industrial emissions than either the Los Angeles or New York City areas. A large fraction of the industrial facilities are located within the urban area along the Houston Ship Channel, which extends from Galveston Bay nearly to the center of the city. These emissions have a profound effect on photochemical O_3 production (Ryerson et al., 2003), which causes the ambientO_3 concentrations in Houston to be comparable to those found in the two larger US megacities. In fact, in six out of eight summers from 1997 to 2004 the nation's highest 1-hr average O_3 concentrations were recorded in Houston, with maxima exceeding 200 ppbv. Since 2004, Houston has succeeded in reducing these extreme 1-hr concentrations, with no maxima above 170 ppbv recorded. In addition to the exceptional industrial emissions, Houston suffers some of the same disadvantages as Los Angeles. It is a coastal city, so is subject to the shallow boundary layers and recirculation associated with the land-sea breeze circulation. It also experiences very hot, sunny and stagnant summertime meteorological conditions.

3.1. Air quality trends

Recent temporal trends of ambient concentrations of O_3 and $PM_{2.5}$ in New York City and Houston approximately parallel those in Los Angeles (Fig. 5). In general, Los Angeles experiences the highest concentrations of both O_3 and $PM_{2.5}$, while New York and Houston exhibit similar concentrations, with New York City slightly lower in O_3, but higher in $PM_{2.5}$. Only slow improvement is evident for either pollutant in any of the three urban areas for the time period plotted.

3.2. Regional emission differences

Sulfur dioxide (SO_2) emissions differ markedly between the western and eastern US, and this difference is clearly reflected in differences in aerosol composition (Fig. 6) and acidity of precipitation (Fig. 7). Sulfur emissions are higher in the eastern US due to both more concentrated emission sources from the greater density of electrical power generation facilities and the greater utilization of high sulfur coal. Fig. 6 shows that sulfate makes a smaller fractional aerosol contribution in Los Angeles, especially in the earlier period, compared to the northeast US. The lower sulfate contribution allows accommodation of a larger contribution from nitrate (see Chapter 9 of Seinfeld and Pandis, 1998 for a discussion of the thermodynamics of aerosols). In both regions, organics account for a major aerosol fraction. The aerosol loadings in both regions have decreased (note scale differences) consistent with the trends in Fig. 5, but the relative contribution of sulfate appears to have increased in both regions.

The high density of primarily SO_2 and secondarily NO_x emissions in the eastern US has led to greatly increased acidity of precipitation in that region (U.S. NAPAP, 1991). The U.S. EPA Acid Rain program initiated 1990 aimed to reduce both SO_2 and NO_x emissions. The SO_2 emission reductions were achieved through a "cap and trade" program where utility units were allocated allowances based on their historic fuel consumption and a specific emissions rate. These allowances could be bought and sold, and the number of available allowances was gradually reduced to a permanent ceiling for total annual emissions. The NO_x emission reductions were largely achieved by requiring installation of low NO_x burner technologies and other

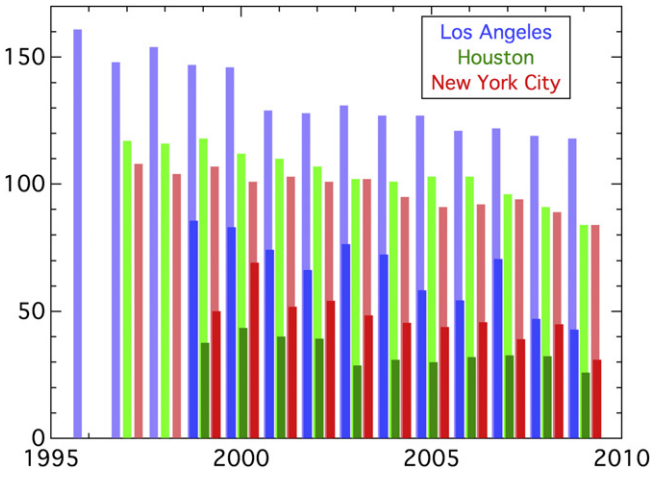

Fig. 5. Comparison of air quality trends for three megacities for O_3 (lighter bars, in ppbv) and $PM_{2.5}$ (darker bars, in μg/m^3). The data are averaged as in Fig. 1. [http://www.epa.gov/air/airtrends/values.html].

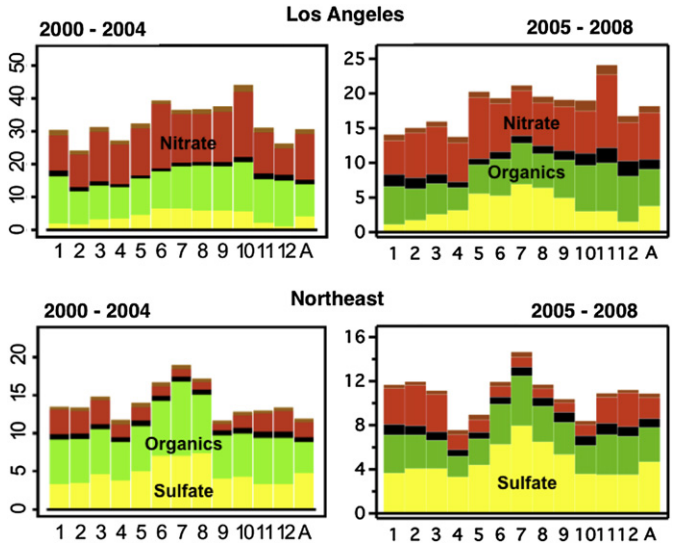

Fig. 6. Comparison of monthly mean fine aerosol composition (units: μg/m^3) in two US urban areas over two time periods (after DeBell et al., 2006 and Hand et al., 2011). The two minor component bars are soil (brown) and light absorbing carbon (black). Data are from US EPA's Speciated Trend (now Chemical Speciation) Network. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

emission controls at coal-fired electrical power generation plants. As a result of these efforts, the average ambient sulfate and nitrate concentrations in the Northeastern US have decreased by 49% and 44%, respectively, from 1989 to 1991 to 2007–2009 (http://www.epa.gov/airmarkt/progress/ARP09_3.html). This decrease has led to a decrease in precipitation acidity (i.e., higher pH) of 43% in the Eastern United States that is clearly illustrated in Fig. 7.

4. Mexico City: North America's most populous and rapidly developing megacity

The Mexico City Metropolitan Area (MCMA) lies in an elevated basin at an altitude of 2240 m in the tropics (19°25′N, 99°10′W). The nearly flat basin floor covers about 5000 km^2 of the Mexican Plateau, and is confined on three sides (east, south and west) by mountain ridges but with a broad opening to the north and a narrower gap to the south-southeast. Two major volcanoes, Popocatépetl and Ixtaccíhuatl, are on the mountain ridge southeast of the basin. The metropolitan area covers about 1500 km^2 on the southwest side of the basin. During the twentieth century Mexico City increased rapidly in urbanized area and population, from fewer than 3 million people in 1950 to about 20 million presently. MCMA has a very high population density as well as a high concentration of industrial and commercial activities.

4.1. MCMA's meteorology and climate

The topography and meteorology of the MCMA markedly affect air quality. A cool dry season from November to February is followed by a warm dry season until May and a rainy season from June to October. Synoptic forcing is generally weak and air transport is strongly influenced by the mountain–valley winds in the basin. Weak winds and strong temperature inversions at night lead to high primary pollutant concentrations that persist into the morning, followed by very rapid boundary layer growth to maximum heights of 2–4 km in the early afternoon. There is relatively little recirculation or day-to-day carry-over of pollutants within the basin (de Foy et al., 2006, 2008). The cool season has stronger surface inversions and higher morning concentrations of primary pollutants. The warm dry season has more intense solar radiation with faster photochemical oxidant formation, as well as increased aerosol loading due to dust and biomass burning. The rainy season has lower PM and CO but continues to have high ozone due to intense photochemistry occurring before the afternoon showers. Air pollution is therefore a year round concern.

The MCMA experiences an urban heat island (UHI) effect that is greatest at night during the dry season (Jauregui, 1997). The UHI is strongly dependent on the time of day and the time of year. Cui and de Foy (submitted for publication) analyzed the UHI from satellite remote sensing and surface observations. There was a stronger signal in the satellite land surface temperature data, with the strongest UHI occurring at night during the dry season and a weakening during the wet season. During the day, the effect is reversed with a cool island occurring during the dry season and a day time UHI that exceeds the nighttime value during the wet season. The near-surface temperature UHI from meteorological measurements had a similar seasonal trend at night albeit with UHI magnitudes reduced by 2–4 °C. During the day however, the near-surface UHI was weak (0–2 °C) and showed no seasonal signal. Jazcilevich et al. (2000) analyzed the relationship of the UHI to urbanization and the impact on air quality. This work suggested that a partial restoration of the wetlands and lake that historically existed in the Mexico City basin could mitigate the UHI and reduce air pollutant concentrations.

4.2. Air quality management and trends

Despite the rapid growth and development in the MCMA, air quality has improved markedly during the past two decades (Fig. 8a,b) and the rate of increase of greenhouse gas emissions has been reduced. In the late 1980s, the newly established automatic air quality monitoring network (RAMA, http://www.sma.df.gob.mx/simat/pnrama2.htm) revealed high concentrations of all criteria pollutants: lead, carbon monoxide, nitrogen oxides, sulfur dioxide, ozone, and PM. Ozone exceeded the air quality standards of 110 ppbv (1-hr) more than 90% of the days, and peaked above 300 ppbv 40–50 days a year, among the worst in the world (Molina and Molina, 2002). Specific actions included removal of lead from gasoline, installation of catalytic converters in automobiles, reduction of sulfur content in diesel fuel, substitution of natural gas for fuel oil in industry and power plants, reformulation of liquefied petroleum gas for heating and cooking, strengthening the vehicle inspection and maintenance program, and modernizing the driving restriction program. The concentrations of criteria pollutants have

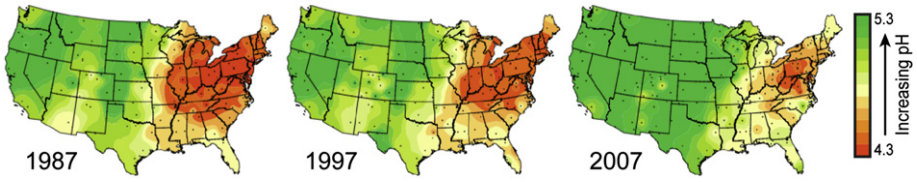

Fig. 7. The spatial distribution of annual precipitation-weighted average concentration of hydrogen ion (pH units) for three years [after http://nadp.sws.uiuc.edu/lib/data/97as.pdf]. Data are from US National Atmospheric Deposition Program.

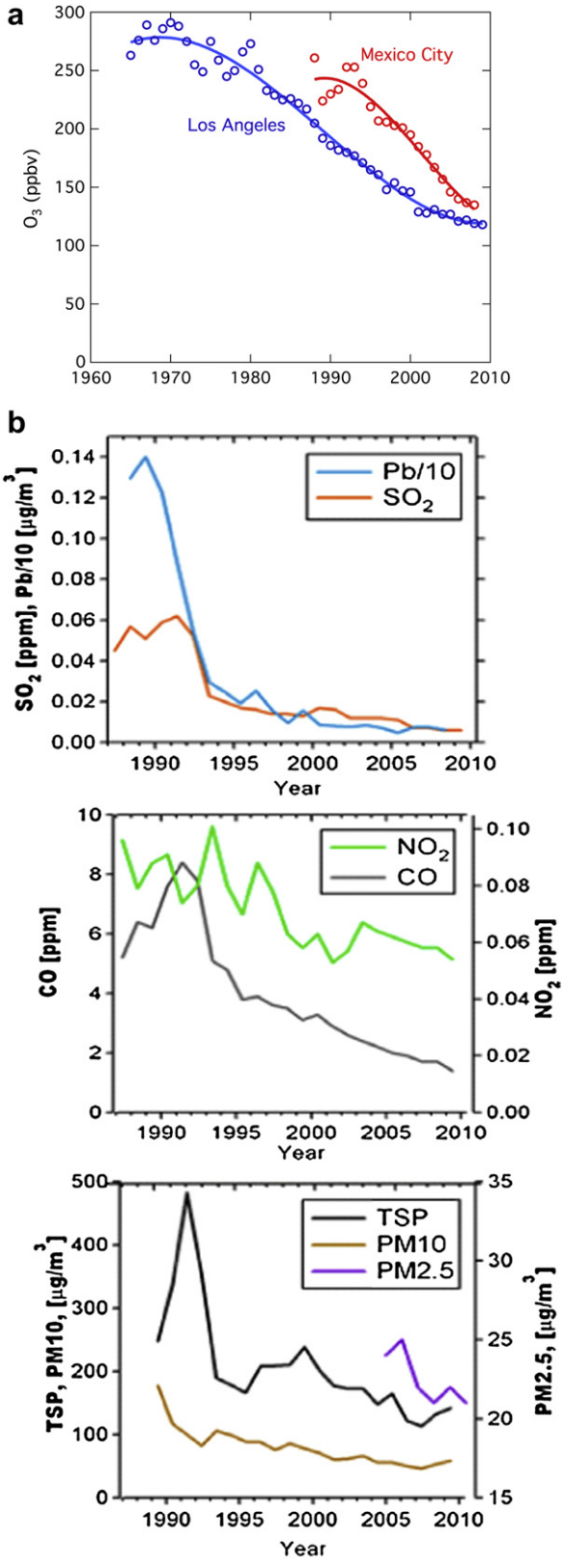

Fig. 8. a) Comparison of air quality trends for O_3 in Mexico City and Los Angeles. The data are 3-yr averages of the 4th highest annual maxima; they are from Fig. 1 for Los Angeles and from SMA-GDF (2009) for MCMA. The curves are polynomial fits to the respective data set. b) Air quality trends in Mexico City. Plots show the average of the 5th annual maximum from all stations with valid data for a given year. Data sources are same as in Fig. 8a.

decreased substantially over the past decade despite the continuing increase in population and economic activity. Fig. 8a indicates that in the early 1990s the ozone concentrations in MCMA were larger than those in Los Angeles. Ozone has decreased significantly in both cities, but even more rapidly in MCMA, so that in recent years the MCMA concentrations have approached those in Los Angeles. The MCMA represents around 20% of Mexico's population, but only 9% of its greenhouse gas emissions. Policies focused on greenhouse gas emission reductions include biogas capture and waste management projects, improved public transportation, fleet renewal projects for taxis and medium-capacity buses, and sustainable housing development projects (Molina et al., 2009).

Emission inventories have been developed in the MCMA since 1986. There were large uncertainties in the early inventories, especially for VOC emissions (Molina and Molina, 2002). Fig. 9 presents the 2006 MCMA emissions inventory for PM_{10}, $PM_{2.5}$, VOC and NO_x (SMA-GDF, 2008). Mobile emission sources represent a significant fraction of the total anthropogenic emissions of NO_x and $PM_{2.5}$ (76% and 62%, respectively) but only a relatively small fraction (34%) of VOC. However, ambient VOC measurements suggest that emissions associated with mobile sources dominate in MCMA as well as some other megacities (Parrish et al., 2009b).

4.3. Recent field studies

The combination of population, topography, meteorology, and multi-pollutant emission density of the MCMA has attracted a number of field studies. The Mexico City Air Quality Research Initiative (MARI) project gathered surface and vertical profile observations of meteorology and pollutants during 1990–1994 (Streit and Guzman, 1996). The Aerosol and Visibility Evaluation campaign in February–March 1997 yielded comprehensive meteorological measurements in the basin, and provided insights into PM composition (Doran et al., 1998; Edgerton et al., 1999). The MCMA-2002/2003 campaigns in February 2002 and April 2003 provided detailed measurements of many oxidant precursors and photochemical intermediates including radicals, as well as meteorology and emissions (Molina et al., 2007). The largest study to date, MILAGRO (Megacity Initiative: Local and Global Research Observations), took place in March 2006 and included a wide range of instruments at ground sites, on aircraft, and satellites that provided detailed measurements of gas and aerosol chemistry, aerosol microphysics and optics, radiation and meteorology (Molina et al., 2010; Singh et al., 2009).

The intensive field campaigns have provided a wealth of information on the emission, dispersion and transformation of species emitted to the MCMA atmosphere and their urban, regional and hemispheric impacts. MCMA-2003 and MILAGRO demonstrated the synergy of using multiple bottom-up and top-down analysis techniques with data obtained from multiple platforms and instruments to evaluate emissions inventories (see e.g., Velasco et al., 2007; Zavala et al., 2009; Karl et al., 2009). The combined methodologies help to reduce the uncertainties in the emissions estimates and suggest priorities for further development and refinement of the emissions inventories. Motor vehicles produce abundant amounts of VOC and NO_x (ozone and aerosol precursors), primary PM, elemental carbon, particle-bound polycyclic aromatic hydrocarbons, CO and a wide range of air toxics, including formaldehyde, acetaldehyde, benzene, toluene, and xylenes (Molina et al., 2007). VOC/CO emission ratios are notably higher than in the US (Fig. 10) and aldehydes emissions are significant (Garcia et al., 2006; Lei et al., 2009). The response of urban O_3 to VOC and NO_x precursor emissions remains a topic of interest, and may have shifted toward more VOC-sensitive conditions in recent years. Recent modeling studies (Lei et al., 2008; Tie et al., 2007; Song et al.,

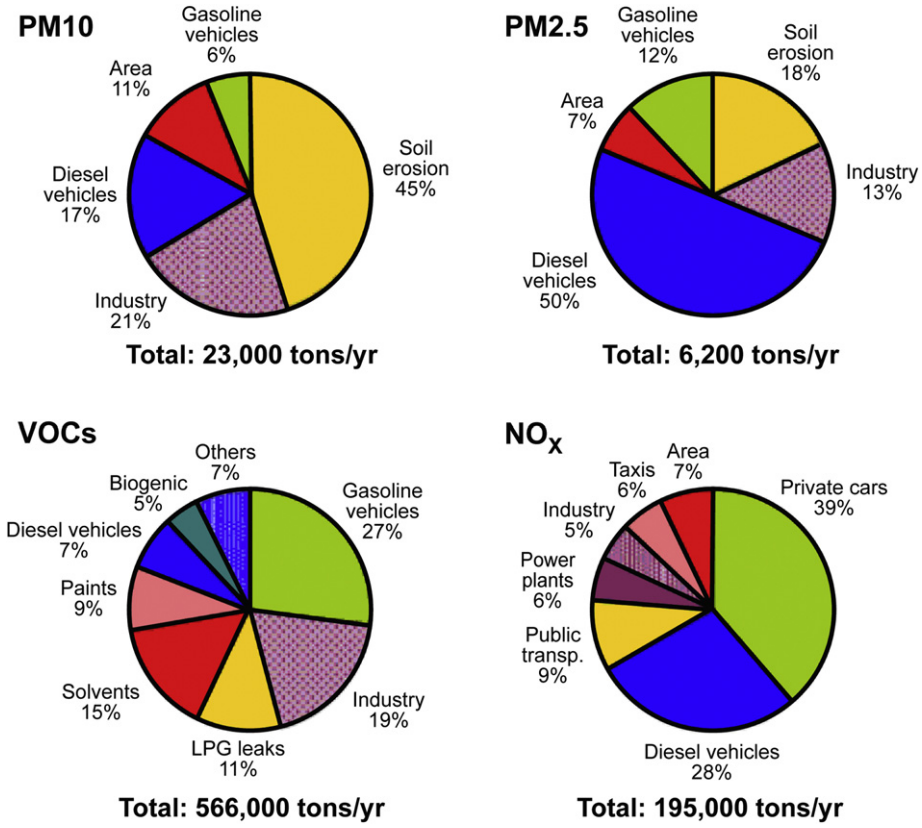

Fig. 9. Mexico City emissions for the Year 2006. (Source: SMA-GDF, 2008)

2010) suggest that O_3 production is VOC-limited. This is supported by studies of radical budgets showing significant chain termination by NO_x chemistry (Volkamer et al., 2010; Sheehy et al., 2010), and by the weekend effect showing large reductions in NO_x and CO but not O_3 on Saturdays and Sundays relative to weekdays (Stephens et al., 2008).

High PM concentrations were observed both at ground sites and from all aircraft during MILAGRO. The PM included a large fraction of organics, but black carbon, crustal matter, sulfate and nitrate were also significant contributors. Fig. 11 shows the average submicron PM composition within the MCMA basin during two different studies. Secondary organic aerosols (SOA) dominate the organic fraction in the city and their origin is still under study (Volkamer et al., 2006; Dzepina et al., 2009; Li et al., 2011). Biomass burning (agricultural, forest, wood cooking and trash burning) also contributes to the urban and regional pollution in the Mexico Basin (Salcedo et al., 2006; Johnson et al., 2006; Yokelson et al., 2009; Stone et al., 2008; Querol et al., 2008; Crounse et al., 2009; Aiken et al., 2009; Christian et al., 2010).

5. Pollution transport in North America

By the 1980s it had become apparent that local air quality was not simply due to local emissions, but had significant contributions due to pollutant transport from upwind sources. Over the Northeastern U. S. the flow within the boundary layer, but above about 800 m, is controlled by synoptic meteorological systems, and is generally from the west to northwest during pollution episodes. Channeled flows below the Appalachian ridge heights of 200–800 m follow important terrain features, and often transport air from the southwest along the northeast US urban corridor (Blumenthal et al., 1997; Zhang et al., 1998). These channeled flows include low-level nocturnal jets that are apparently particularly important for transporting pollutants preceding episodes. Finally, near-surface flows (below 200 m) during episodes are typically light during night and morning allowing accumulation of emissions. Fresh emissions as well as aged urban plumes move downwind and react during daytime, while O_3 aloft and aged precursors are entrained as the mixing layer deepens. This low-level transport is typically to the north through east along the urban corridor for 50–250 km by evening. In summary, meteorological processes interact at large and small scales to determine local O_3 concentrations. The relative contribution from each scale, from local to interregional, can vary widely between episodes. This understanding has led to coordinated multi-state abatement strategies within the US.

The proximate location of urban areas within the northeast urban corridor has made the importance of transport processes particularly obvious in that region, but even in the relatively sparsely populated western US, regional transport makes significant contributions to the urban ozone concentrations. For example, recent studies in Texas demonstrate that the transport of ozone from upwind regions can predominate over in-situ production within the Houston urban area, even during O_3 exceedance conditions (Parrish et al., 2009c and references therein). Indeed, the transported ozone in eastern Texas, which represents the minimum ozone concentration that is likely achievable through only local controls, can approach or exceed the current NAAQS.

Pollutant transport also is important on intercontinental scales (Holloway et al., 2003; Monks et al., 2009; Dentener et al., 2010). A large fraction of North American emissions, as well as the resulting ozone and aerosol produced over the continent, is transported beyond the national borders, primarily to the Gulf of Mexico and North Atlantic regions and potentially on to Europe.

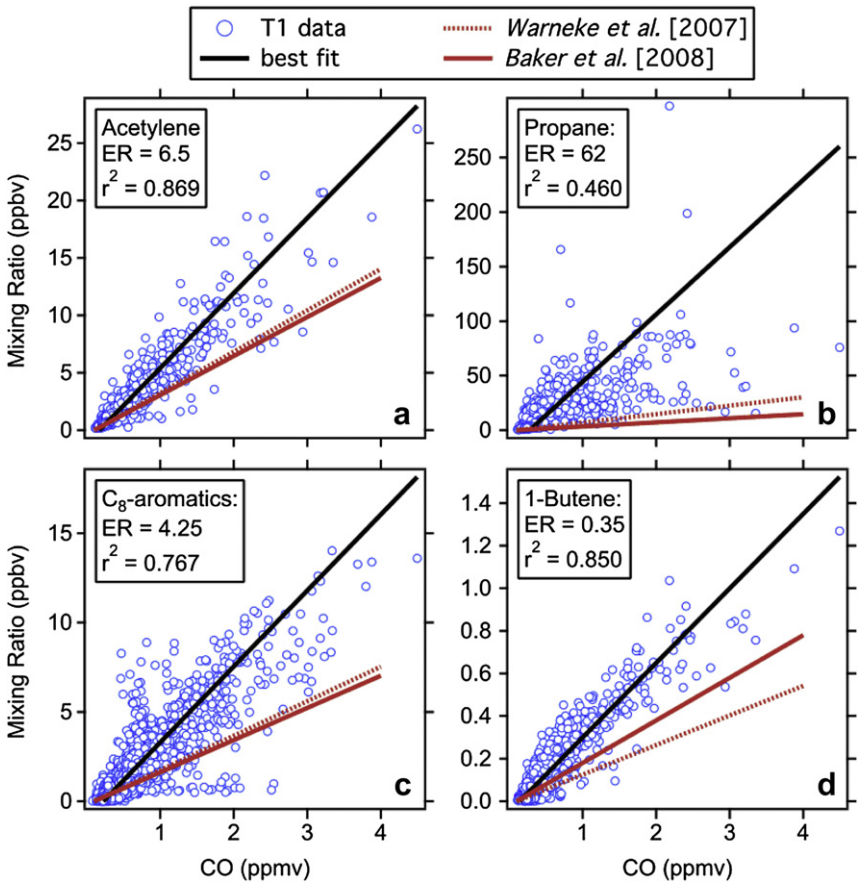

Fig. 10. Correlations between hydrocarbons and carbon monoxide measured in Mexico City (blue points) compared to fits obtained in U.S. cities (red lines) (de Gouw et al., 2009). Here ER represents emission ratio, which is equal to the best fit slopes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Significant recent research efforts have been directed toward quantifying the importance of this pollutant export to and from the Northeastern US (Fehsenfeld et al., 2006; Singh et al., 2006 and references there in). Similarly emissions from Mexico City also can be observed several hundreds of kilometers downwind. Fig. 12 compares the correlation of O_3 with CO in pollution plumes exported from these two regions. Air masses close to urban areas exhibit shallow slopes that steepen during downwind transport. Interestingly, quite similar slopes are seen in the aged plumes transported from Mexico City (0.35) and New York City (0.38). Aircraft-based measurements show ongoing production of SOA (Kleinman et al., 2008; DeCarlo et al., 2008) as well as ozone for several days downwind, with active photochemistry sustained by aldehydes (Tie et al., 2009) and nitrogen oxides from the thermal decomposition of peroxyacyl nitrates and photolysis and OH oxidation of nitric acid (Neuman et al., 2006).

Intercontinental transport into North America gives an added complexity to North American air quality issues. Pollution plumes from East Asian megacities have been sampled over the Pacific and over many regions of North America (Parrish et al., 2004; Singh

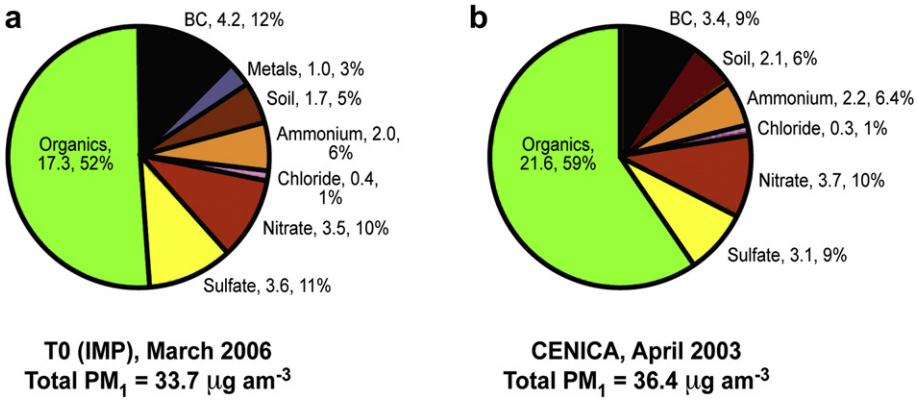

Fig. 11. Submicron PM composition (mass and percent) measured during different field campaigns at surface sites in the Mexico City basin (based upon Aiken et al., 2009).

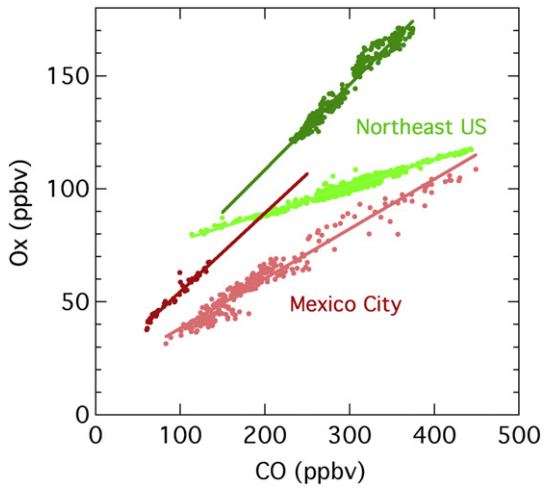

Fig. 12. Odd oxygen ($O_x = O_3 + NO_2$) and CO measured by aircraft in four transported plumes: near Mexico City on 18 March 2006 (light red), in the same airmass a day later and about 500 km downwind from Mexico City (dark red), near Boston on 21 July 2004 (light green), and on the same day about 500 km downwind from New York City (dark green). The steeper slopes defined by the latter, dark colored data result from regional O_x production during transport. (Mexico City data as reported by Zaveri et al., 2007; northeast US data as reported by Neuman et al., 2006). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

et al., 2006, 2009; van Donkelaar et al., 2008; Zhang et al., 2008). There is evidence that the background O_3 concentration transported into California is increasing, possibly in response to increasing Asian emissions of O_3 precursors (Parrish et al., 2009a). This backgroundO_3 increase may be negating some of the benefits from local pollution control measures in California (Jacob et al., 1999; Lin et al., 2008). However, the impact of transport of background ozone on surface air quality is a matter of considerable debate (Lefohn et al., 2008; Oltmans et al., 2008). Presently no policy strategies exist to mitigate the impact of increasing background O_3 upon local or regional air quality. It is likely that all northern mid-latitude emissions contribute to a hemispheric background.

6. Conclusions

The experiences in North American megacities demonstrate that urban and industrial development can proceed simultaneously with air quality improvement. Successes in North America can be replicated in other parts of the world especially in developing countries where rapid economic growth and dense populations must coexist with acceptable environmental goals. Results from past and future field studies will continue to contribute to a fuller understanding of air pollution and its impacts on human health, ecosystem viability, and climate change. The integration of air quality information from old and new studies of megacities in different settings will improve significantly the scientific basis that decision makers in megacities around the world will need to craft effective environmental policies.

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References

Aiken, A.C., Salcedo, D., Cubison, M.J., et al., 2009. Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) – part 1: fine particle composition and organic source apportionment. Atmospheric Chemistry and Physics 9, 6633–6653.

Alexis, A., Gaffney, P., Garcia, C., Nystrom, M., Rood, R., 1999. The 1999 California Almanac of Emissions and Air Quality. California Air Resources Board. Available online: http://www.arb.ca.gov/aqd/almanac/almanac99/almanac99.htm (accessed 18.04.11).

Bell, M.L., Goldberg, R., Hogrefe, C., Kinney, P.L., Knowlton, K., Lynn, B., Rosenthal, J., Rosenzweig, C., Patz, J.A., 2007. Climate change, ambient ozone, and health in 50 US cities. Climatic Change 82, 61–76.

Blumenthal, D.L., Lurmann, F.W., Kumar, N., Dye, T.S., Ray, S.E., Korc, M.E., Londergan R., Moore, G., 1997. Transport and mixing phenomena related to ozone exceedances in the northeast US (Analysis of NARSTO-Northeast Data)—Working Draft #1. Prepared for Submission to the Ozone Transport Assessment Group Air Quality Analysis Workgroup. Available online: http://capita.wustl.edu/OTAG/Reports/Otagrept/Otagrept.html (accessed 18.04.11).

Boersma, K.F., Jacob, D.J., Buscela, E.J., et al., 2008. Validation of OMI tropospheric NO_2 observations during INTEX-B and application to constrain NO_x emissions over the eastern U.S. and Mexico. Atmospheric Environment 42, 4480–4497.

Chan, C.K., Yao, X., 2008. Air pollution in mega cities in China. Atmospheric Environment 42, 1–42.

Christian, T.J., Yokelson, R.J., Cárdenas, B., Molina, L.T., Engling, G., Hsu, S.-C., 2010. Trace gas and particle emissions from domestic and industrial biofuel use and garbage burning in central Mexico. Atmospheric Chemistry and Physics 10, 565–584.

Cox, P., Delao, A., Komorniczak, A., Weller, A., 2009. The California Almanac of Emissions and Air Quality – 2009 Edition. California Air Resources Board. Available online: http://www.arb.ca.gov/aqd/almanac/almanac09/almanac09.htm (accessed 18.04.11).

Croes, B.E., Fujita, E.M., 2003. Overview of the 1997 southern California ozone study (SCOS97-NARSTO). Atmospheric Environment 37 (Suppl. 2), 3–26.

Crutzen, P.J., 2004. New directions: the growing urban heat and pollution "island" effect—impact on chemistry and climate. Atmospheric Environment 38, 3539–3540.

Crounse, J.D., DeCarlo, P.F., Blake, D.R., et al., 2009. Biomass burning and urban air pollution over the central Mexican plateau. Atmospheric Chemistry and Physics 9, 4929–4944.

Cui, Y.Y., de Foy, B. Different seasonal Variations between the surface and the near-surface urban heat island over Mexico City in observations, satellite remote sensing, and Numerical Simulations, Journal of Applied meteorology and climatology, submitted for publication.

DeBell, L.J., Gebhart, K.A., Hand, J.L., Malm, W.C., Pitchford, M.L., Schichtel, B.A., White, W.H., 2006. Spatial and Seasonal Patterns and Temporal Variability of Haze and its Constituents in the United States—Report IV. IMPROVE Reports. Available online: http://vista.cira.colostate.edu/improve/Publications/improve_reports.htm (accessed 18.04.11).

DeCarlo, P.F., Dunlea, E.J., Kimmel, J.R., et al., 2008. Fast airborne aerosol size and chemistry measurements above Mexico City and central Mexico during the MILAGRO campaign. Atmospheric Chemistry and Physics 8, 4027–4048.

de Foy, B., Varela, J.R., Molina, L.T., Molina, M.J., 2006. Rapid ventilation of the Mexico City basin and regional fate of the urban plume. Atmospheric Chemistry and Physics 6, 2321–2335.

de Foy, B., Fast, J.D., Paech, S.J., Phillips, D., et al., 2008. Basin-scale wind transport during the MILAGRO field campaign and comparison to climatology using cluster analysis. Atmospheric Chemistry and Physics 8, 1209–1224.

de Gouw, J.A., Welsh-Bon, D., Warneke, C., et al., 2009. Emission and chemistry of organic carbon in the gas and aerosol phase at a sub-urban site near Mexico City in March 2006 during the MILAGRO study. Atmospheric Chemistry and Physics 9, 3425–3442.

Dentener, F., T. Keating, and H. Akimoto (eds), 2010. Hemispheric Transport of Air Pollution 2010, Air Pollution Studies No. 17. (http://www.htap.org/)

Diffenbaugh, N.S., Giorgi, F., Pal, J.S., 2008. Climate change hotspots in the United States. Geophysical Research Letters 35, L16709.

Doran, J.C., Bian, X., de Wekker, S.F.J., et al., 1998. The IMADA-AVER boundary layer experiment in the Mexico City area. Bulletin of the American Meteorological Society 79, 2497–2508.

Dzepina, K., Volkamer, R.M., Madronich, S., Tulet, P., Ulbrich, I.M., Zhang, Q., Cappa, C.D., Ziemann, P.J., Jimenez, J.L., 2009. Evaluation of recently-proposed secondary organic aerosol models for a case study in Mexico City. Atmospheric Chemistry and Physics 9, 5681–5709.

Edgerton, S.A., Bian, X., Doran, J.C., et al., 1999. Particulate air pollution in Mexico City: a collaborative research project. Journal of the Air & Waste Management Association 49, 1221–1229.

Engel-Cox, J.A., Hoff, R.M., Rogers, R., Dimmick, F., Rush, A.C., Szykman, J.J., Al-Saadi, J., Chu, D.A., Zell, E.R., 2006. Integrating lidar and satellite optical depth with ambient monitoring for 3-dimensional particulate characterization. Atmospheric Environment 40, 8056–8067.

Fehsenfeld, F.C., Ancellet, G., Bates, T.S., et al., 2006. International Consortium for atmospheric research on transport and transformation (ICARTT): North America to Europe—overview of the 2004 summer field study. Journal of Geophysical Research 111, D23S01.

Garcia, A.R., Volkamer, R., Molina, L.T., Molina, M.J., Samuelson, J., Mellqvist, J., Galle, B., Herndon, S.C., Kolb, C.E., 2006. Separation of emitted and photochemical formaldehyde in Mexico City using a statistical analysis and a new pair of gas-phase tracers. Atmospheric Chemistry and Physics 6, 4545–4557.

Grimm, N.B., Faeth, S.H., Golubiewski, N.E., Redman, C.R., Wu, J., Bai, X., Briggs, J.M., 2008. Global change and the ecology of cities. Science 319, 756–760.

Gurjar, B.R., Lelieveld, J., 2005. New directions: megacities and global change. Atmospheric Environment 39, 391–393.

Haagen-Smit, A.J., 1952. Chemistry and physiology of Los Angeles smog. Industrial & Engineering Chemistry 44, 1342–1346.

Hall, J.V., Brajer, V., Lurmann, F.W., 2008. The benefits of meeting federal clean air standards in the South Coast and San Joaquin Valley air basins. Available online: http://business.fullerton.edu/centers/iees/reports/Benefits_of_Meeting_Clean_Air_Standards_11-13-08.pdf (accessed 19.04.11).

Hand, J.L., Copeland, S.A., Day, D.E., Dillner, A.M., Indresand, H., Malm, W.C., McDade, C.E., Moore, C.T., Pitchford, M.L., Schichtel, B.A., Watson, J.G., 2011. Spatial and Seasonal Patterns and Temporal Variability of Haze and its Constituents in the United States—Report V. IMPROVE Reports. Available online: http://vista.cira.colostate.edu/improve/Publications/improve_reports.htm (accessed 11.09.11).

Holloway, T., Fiore, A.M., Hastings, M.G., 2003. Intercontinental transport of air pollution: will emerging science lead to a new hemispheric treaty? Environmental Science & Technology 37, 4535–4542.

Isaksen, I.S.A., Granier, C., Myhre, G., et al., 2009. Atmospheric composition change: Climate–chemistry interactions. Atmospheric Environment 43, 5138–5192.

Jacob, D.J., Logan, J.A., Murti, P.P., 1999. Effect of rising Asian emissions on surface ozone in the United States. Geophysical Research Letters 26, 2175–2178.

Jacob, D.J., Winner, D.A., 2009. Effect of climate change on air quality. Atmospheric Environment 43, 51–63.

Jacob, D.J., Crawford, J.H., Maring, H., et al., 2010. The Arctic research of the composition of the Troposphere from aircraft and satellites (ARCTAS) mission: design, execution, and first results. Atmospheric Chemistry and Physics 10, 5191–5212.

Jauregui, E., 1997. Heat island development in Mexico City. Atmospheric Environment 31, 3821–3831.

Jazcilevich, A., Fuentes, V., Jauregui, E., Luna, E., 2000. Simulated urban climate response to historical land use modification in the basin of Mexico. Climatic Change 44, 515–536.

Johnson, K.S., de Foy, B., Zuberi, B., Molina, L.T., Molina, M.J., Xie, Y., Laskin, A., Shutthanandan, V., 2006. Aerosol composition and source apportionment in the Mexico City metropolitan area with PIXE/PESA/STIM and multivariate analysis. Atmospheric Chemistry and Physics 6, 4591–4600.

Karl, T., Apel, E., Hodzic, A., Riemer, D.D., Blake, D.R., Wiedinmyer, C., 2009. Emissions of volatile organic compounds inferred from airborne flux measurements over a megacity. Atmospheric Chemistry and Physics 9, 271–285.

Kim, S.-W., Heckel, A., Frost, G.J., Richter, A., Gleason, J., Burrows, J.P., McKeen, S., Hsie, E.-Y., Granier, C., Trainer, M., 2009. NO_2 columns in the western United States observed from space and simulated by a regional chemistry model and their implications for NOx emissions. Journal of Geophysical Research 114, D11301.

Kleinman, L.I., Daum, P.H., Lee, Y.-N., Nunnermacker, L.J., Springston, S.R., Weinstein-Lloyd, J., Rudolph, J., 2005. A comparative study of ozone production in five U.S. metropolitan areas. Journal of Geophysical Research 110, D02301. doi:10.1029/2004JD005096.

Kleinman, L.I., Springston, S.R., Daum, P.H., et al., 2008. The time evolution of aerosol composition over the Mexico City plateau. Atmospheric Chemistry and Physics 8, 1559–1579.

Lefohn, A.S., Shadwick, D., Oltmans, S.J., 2008. Characterizing long-term changes in surface ozone levels in the United States (1980–2005). Atmospheric Environment 42, 8252–8262.

Lei, W., Zavala, M., de Foy, B., Volkamer, R., Molina, L.T., 2008. Characterizing ozone production and response under different meteorological conditions in Mexico City. Atmospheric Chemistry and Physics 8, 7571–7581.

Lei, W., Zavala, M., de Foy, B., Volkamer, R., Molina, M.J., Molina, L.T., 2009. Impact of primary formaldehyde on air pollution in the Mexico City metropolitan area. Atmospheric Chemistry and Physics 9, 2607–2618.

Li, G., Zavala, M., Lei, W., Tsimpidi, A.P., Karydis, V.A., Pandis, S.N., Canagaratna, M.R., Molina, L.T., 2011. Simulations of organic aerosol concentrations in Mexico City using the WRF-CHEM model during the MCMA-2006/MILAGRO campaign. Atmospheric Chemistry and Physics 11, 3789–3809.

Lin, J.-T., Wuebbles, D.J., Liang, X.-G., 2008. Effects of intercontinental transport on surface ozone over the United States: present and future assessment with a global model. Geophysical Research Letters 35, L02805.

Mahmud, A., Hixson, M., Hu, J., Zhao, Z., Chen, S.-H., Kleeman, M.J., 2010. Climate impact on airborne particulate matter concentrations in California using seven year analysis periods. Atmospheric Chemistry and Physics 10, 11097–11114.

Martin, R.V., 2008. Satellite remote sensing of surface air quality. Atmospheric Environment 42, 7823–7843.

Millstein, D.E., Harley, R.A., 2009. Impact of climate change on photochemical air pollution inSouthern California. Atmospheric Chemistry and Physics 9, 3745–3754.

Molina, L.T., Molina, M.J. (Eds.), 2002. Air Quality in the Mexico Megacity: An Integrated Assessment. Kluwer Academic Publishers, Norwell, MA.

Molina, M.J., Molina, L.T., 2004. Critical review: megacities and atmospheric pollution. Journal of the Air & Waste Management Association 54, 644–680.

Molina, L.T., Kolb, C.E., de Foy, B., et al., 2007. Air quality in North America's most populous city – overview of the MCMA-2003 campaign. Atmospheric Chemistry and Physics 7, 2447–2473.

Molina, L.T., de Foy, B., Vazquez-Martinez, O., Paramo-Figueroa, V.H., 2009. Air quality, weather and climate in Mexico City. WMO Bulletin 58, 48–53.

Molina, L.T., Madronich, S., Gaffney, J.S., et al., 2010. An overview of the MILAGRO 2006 campaign: Mexico City emissions and their transport and transformation. Atmospheric Chemistry and Physics 10, 8697–8760.

Monks, P.S., Granier, C., Fuzzi, S., et al., 2009. Atmospheric composition change – global and regional air quality. Atmospheric Environment 43, 5268–5350.

Murazaki, K., Hess, P., 2006. How does climate change contribute to surface ozone change over the United states? Journal of Geophysical Research 111, D05301.

Neuman, J.A., Parrish, D.D., Trainer, M., et al., 2006. Reactive nitrogen transport and photochemistry in urban plumes over the North Atlantic Ocean. Journal of Geophysical Research 111, D23S54.

NYSDEC, 2010. Air Quality Management Plan. New York State Department of Environmental Conservation, Albany, New York. http://www.dec.ny.gov/chemical/72213.html.

Oltmans, S.J., Lefohn, A.S., Harris, J.M., Shadwick, D.S., 2008. Background ozone levels of air entering the west coast of the US and assessment of longer-term changes. Atmospheric Environment 42, 6020–6038.

Parrish, D.D., Kondo, Y., Cooper, O.R., Brock, C.A., Jaffe, D.A., Trainer, M., Ogawa, T., Hübler, G., Fehsenfeld, F.C., 2004. Intercontinental transport and chemical transformation 2002 (ITCT 2K2) and Pacific Exploration of Asian Continental emission (PEACE) experiments: an overview of the 2002 winter and spring intensives. Journal of Geophysical Research 109, D23S01.

Parrish, D.D., Millet, D.B., Goldstein, A.H., 2009a. Increasing ozone in marine boundary layer air inflow at the west coasts of North America and Europe. Atmospheric Chemistry and Physics 9, 1303–1323.

Parrish, D.D., Kuster, W.C., Shao, M., Yokouchi, Y., Kondo, Y., Goldan, P.D., de Gouw, J.A., Koike, M., Shirai, T., 2009b. Comparison of air pollutant emissions among mega-cities. Atmospheric Environment 43, 6435–6441.

Parrish, D.D., Allen, D.T., Bates, T.S., et al., 2009c. Overview of the second Texas air quality study (TexAQS II) and the Gulf of Mexico atmospheric composition and climate study (GoMACCS). Journal of Geophysical Research 114, D00F13.

Parrish, D.D., Aikin, K.C., Oltmans, S.J., Johnson, B.J., Ives, M., Sweeny, C., 2010. Impact of transported background ozone inflow on summertime air quality in a California ozone exceedance area. Atmospheric Chemistry and Physics 10, 10093–10109. doi:10.5194/acp-10-10093-2010.

Querol, X., Pey, J., Minguillón, M.C., et al., 2008. PM speciation and sources in Mexico during the MILAGRO-2006 campaign. Atmospheric Chemistry and Physics 8, 111–128.

Ramanathan, V., Feng, Y., 2009. Air pollution, greenhouse gases and climate change: global and regional perspectives. Atmospheric Environment 43, 37–50.

Ryerson, T.B., Trainer, M., Angevine, W.M., et al., 2003. Effect of petrochemical industrial emissions of reactive alkenes and NOx on tropospheric ozone formation in Houston, Texas. Journal of Geophysical Research 108, 4249–4259.

Salcedo, D., Onasch, T.B., Dzepina, K., et al., 2006. Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with aerosol mass spectrometry: results from the CENICA supersite. Atmospheric Chemistry and Physics 6, 925–946.

Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. John Wiley, New York.

Sheehy, P.M., Volkamer, R., Molina, L.T., Molina, M.J., 2010. Oxidative capacity of the Mexico City atmosphere – part 2: a RO_x radical cycling perspective. Atmospheric Chemistry and Physics 10, 6993–7008.

Sillman, S., 1999. The relation between ozone, $NO_x$and hydrocarbonsin urban and polluted rural environments. Atmospheric Environment 33, 1821–1845.

Singh, H.B., Brune, W.H., Crawford, J.H., Jacob, D.J., Russell, P.B., 2006. Overview of the summer 2004 intercontinental chemical transport experiment –North America (INTEX-A). Journal of Geophysical Research 111, D24S01. doi:10.1029/2006JD007905.

Singh, H.B., Brune, W.H., Crawford, J.H., Flocke, F., Jacob, D.J., 2009. Chemistry and transport of pollution over the Gulf of Mexico and the Pacific: Spring 2006 INTEX-B campaign overview and first results. Atmospheric Chemistry and Physics 9, 2301–2318.

Singh, H.B., Anderson, B.E., Brune, W.H., et al., the ARCTAS Science Team, 2010. Pollution influences on atmospheric composition and chemistry at high northern latitudes: boreal and California forest fire emissions. Atmospheric Environment 44, 4553–4564.

SMA-GDF, 2008. Inventario de Emisiones de la Atmósfera. Zona Metropolitana del Valle de México 2006. Secretaria de Medio Ambiente, Gobierno de Distrito Federal, Mexico.

Song, J., Lei, W., Bei, N., Zavala, M., de Foy, B., Volkamer, R., Cardenas, B., Zheng, J., Zhang, R., Molina, L.T., 2010. Ozone response to emission changes: a modeling study during the MCMA-2006/MILAGRO campaign. Atmospheric Chemistry and Physics 10, 3827–3846.

Steiner, A.L., Tonse, S., Cohen, R.C., Goldstein, A.H., Harley, R.A., 2006. Influence of future climate and emissions on regional air quality in California. Journal of Geophysical Research 111, D18303. doi:10.1029/2005JD006935.

Stephens, S., Madronich, S., Wu, F., Olson, J.B., Ramos, R., Retama, A., Muñoz, R., 2008. Weekly patterns of México City's surface concentrations of CO, NO_x, PM_{10} and O_3 during 1986–2007. Atmospheric Chemistry and Physics 8, 5313–5325.

Stone, E.A., Snyder, D.C., Sheesley, R.J., Sullivan, A.P., Weber, R.J., Schauer, J.J., 2008. Source apportionment of fine organic aerosol in Mexico City during the MILAGRO experiment. Atmospheric Chemistry and Physics 8, 1249–1259.

Streit, G.E., Guzman, F., 1996. Mexico City air quality: progress of an international collaborative project to define air quality management options. Atmospheric Environment 30, 723–733.

Tie, X., Madronich, S., Li, G., Ying, Z., Zhang, R., Garcia, A., Lee-Taylor, J., Liu, Y., 2007. Characterization of chemical oxidants in Mexico City: a regional chemical dynamical model (WRF-Chem) study. Atmospheric Environment 41, 1989–2008.

Tie, X., Madronich, S., Li, G., Ying, Z., Weinheimer, A., Apel, E., Campos, T., 2009. Simulation of Mexico City plumes during the MIRAGE-Mex field campaign using the WRF-Chem model. Atmospheric Chemistry and Physics 9, 4621–4638.

U.S. National Acid Precipitation Assessment Program, 1991. National Acid Precipitation Assessment Program, 1990 Integrated Assessment Report. NAPAP Office of the Director, Washington DC.

van Donkelaar, A., Martin, R.V., Leaitch, W.R., et al., 2008. Analysis of aircraft and satellite measurements from the intercontinental chemical transport experiment (INTEX-B) to quantify long-range transport of East Asian sulfur to Canada. Atmospheric Chemistry and Physics 8, 2999–3014.

Velasco, E., Lamb, B., Westberg, H., et al., 2007. Distribution, magnitudes, reactivities, ratios and diurnal patterns of volatile organic compounds in the valley of Mexico during the MCMA 2002 and 2003 field campaigns. Atmospheric Chemistry and Physics 7, 329–353.

Volkamer, R., Jimenez, J.L., San Martini, F., Dzepina, K., Zhang, Q., Salcedo, D., Molina, L.T., Worsnop, D.R., Molina, M.J., 2006. Secondary organic aerosol formation from anthropogenic air pollution: rapid and higher than expected. Geophysical Research Letters 33, L17811.

Volkamer, R., Sheehy, P.M., Molina, L.T., Molina, M.J., 2010. Oxidative capacity of the Mexico City atmosphere – part 1: a radical source perspective. Atmospheric Chemistry and Physics 10, 6969–6991.

Yokelson, R., Crounse, J.D., DeCarlo, P.F., et al., 2009. Emissions from biomass burning in the Yucatan. Atmospheric Chemistry and Physics 9, 5785–5812.

Zavala, M., Herndon, S.C., Wood, E.C., Onasch, T.B., Knighton, W.B., Kolb, C.E., Molina, L.T., 2009. Evaluation of mobile emissions contributions to Mexico City's emissions inventory using on-road and cross-road emission measurements and ambient data. Atmospheric Chemistry and Physics 9, 6305–6317.

Zaveri, R.A., Chapman, E. G, Easter, R.C., Fast, J.D., Flocke, F., Kleinman, L.I., Madronich, S., Springston, S.R., Voss, P.B., Weinheimer, A., 2007. Modeling gas-aerosol processes during MILAGRO 2006. Eos Transactions, American Geophysical Union 88, Fall Meeting Supplement, Abstract A33D-1570.

Zhang, J., Rao, S.T., Daggupaty, S.M., 1998. Meteorological processes and ozone exceedances in the northeastern United States during the 12–16 July 1995 episode. Journal of Applied Meteorology 37, 776–789.

Zhang, L., Jacob, D.J., Boersma, K.F., et al., 2008. Transpacific transport of ozone pollution and the effect of recent Asian emission increases on air quality in North America: an integrated analysis using satellite, aircraft, ozonesonde, and surface observations. Atmospheric Chemistry and Physics 8, 6117–6136.