

Modeling ozone photochemistry and evaluation of hydrocarbon emissions in the Mexico City metropolitan area

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[1] Emissions of volatile organic compounds (VOCs) and of CO are often underestimated, and correcting this underestimate is important for modeling ozone formation and sensitivity. The California Institute of Technology three-dimensional photochemical model is used to test the official emissions inventory for the Mexico City metropolitan area through a direct comparison of measured and modeled total nonmethane hydrocarbons (NMHCs) and CO. The model is applied to six 2-day periods during the IMADA measurement campaign of March 1997. When using emissions based on the official emissions inventory, the model significantly underestimates measurements of total NMHCs and of CO. A best fit to the measurements (with lowest bias) is found when increasing emissions of CO and VOCs by factors of 2 and 3, respectively. Adjusting total emissions accordingly, the model produces good estimates of ozone and NO_x, with average normalized biases over 6 days of 3% and 32%, respectively, and with better agreement during daytime hours. This agreement for ozone and NO_x supports the suggestion that VOC and CO emissions are underestimated. Other uncertainties are analyzed, finding that while some uncertainties are important, none is individually significant enough to account for the discrepancy. Correcting the total emissions, the overall model performance is found to be adequate, particularly on 3 days, for the model to be used for analysis of control strategies. Using the results of a chemical mass balance identification of NMHC sources highlights sources that are more likely underestimated, but confidence in the appropriate correction to emissions from different sources is low and should be investigated further. *INDEX TERMS:* 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 9350 Information Related to Geographic Region: North America; *KEYWORDS:* ozone photochemistry, Mexico City, nonmethane hydrocarbon emissions, air quality modeling, urban air pollution

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1. Introduction

[2] Previous modeling of ozone chemistry in polluted regions of the troposphere has indicated that the largest modeling uncertainties are often the emissions inventories used [*National Research Council (NRC)*, 1991; *Russell and*

Dennis, 2000]. In particular, emissions of nonmethane volatile organic compounds (VOCs) and of carbon monoxide (CO) have commonly been underestimated. Previous modeling work in Mexico City [*Los Alamos National Laboratory and Instituto Mexicano del Petróleo (LANL and IMP)*, 1994; *Streit and Guzmán*, 1996] found that VOC emissions needed to be multiplied by a factor of 4 in order to model ozone concentrations reasonably well. A review of modeling studies in North America [*Solomon et al.*, 1999] found that increasing VOC emissions was very common, with correction factors ranging from 1 (no correction needed) to the factor of 4 used previously for

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Mexico City. Correcting underestimates of VOC emissions is important for modeling ozone formation. In particular, such corrections may significantly influence the modeled sensitivity of ozone to changes in emissions of nitrogen oxides (NO_x) and VOC, perhaps significantly enough to change from a NO_x -sensitive response to a VOC-sensitive response. For this reason, it is important to thoroughly assess the VOC emissions before using models to evaluate emissions control strategies for ozone.

[3] Top-down methods based on measurements of the atmospheric concentrations of pollutants have been used to check emissions inventories constructed from the bottom up using activity data and emissions factors. These methods include the use of morning measurements of the ratios of pollutants as indications of the ratios of fresh emissions in the morning [Fujita *et al.*, 1992; California Air Resources Board (CARB), 1997; Funk *et al.*, 2001]. Ambient measurements of pollutant concentrations have also been compared directly against the concentrations predicted by air quality models; for nonmethane hydrocarbons (NMHCs, which exclude carbonyls such as aldehydes and other species that are included in VOCs), these comparisons have often been conducted for particular species [Mannschreck *et al.*, 2002] and less commonly for the total NMHCs. More formal inverse modeling approaches have likewise been used [Mulholland and Seinfeld, 1995; Mendoza-Dominguez and Russell, 2001]. In addition to these methods, chemical mass balance techniques using the speciation of VOCs [Watson *et al.*, 2001] can be used to estimate the relative contributions of emissions from different hydrocarbon sources, but cannot address the absolute correction needed for hydrocarbon emissions.

[4] In Mexico City, Arriaga-Colina *et al.* [2004] compare morning measurements of the ratios of VOC/ NO_x and CO/ NO_x to the ratios in the official 1998 emissions inventory [Comisión Ambiental Metropolitana (CAM), 2001], using measurements of total VOCs on selected days between 1995 and 2001 at four sites. For the CO/ NO_x ratios, measurements are available daily from many routine monitoring stations over several years. The results of this analysis suggest that the VOC/ NO_x and CO/ NO_x ratios in the official emissions inventory are significantly underestimated, by factors of 2 to 3, with greater confidence in the CO results because of the greater availability of measurements. On the basis of experience elsewhere [Fujita *et al.*, 1992; Harley *et al.*, 1997] and because the Mexico City inventory was created using similar methods and emissions factors, this discrepancy is more likely due to an underestimate in VOC and CO emissions, than to an overestimate of NO_x emissions. Some weaknesses of the simple ratio method used include the assumptions of no background pollutant concentrations, and no chemical reactions during the morning hours; these assumptions are not necessary when applying an air quality model.

[5] The objective of this study is to apply a three-dimensional air quality model to the Mexico City metropolitan area (MCMA), and to evaluate the official emissions inventory through a direct comparison of model predictions of the concentrations of CO and total NMHCs with measurements. Comparisons of other chemical species (particularly NO_x and ozone) are conducted to evaluate model performance, both for testing CO and NMHC emissions and

for future use in evaluating air quality management strategies. We first present the problem of air pollution in Mexico City, and then detail the modeling methods and inputs. We then present model results with the goal of identifying the likely correction needed to VOC and CO emissions, as well as evaluating the model more generally for use in analyzing emissions control scenarios. Finally, we discuss whether uncertainties other than in the emissions inventory are significant enough to account for the discrepancies between model predictions and observations, and consider what sources might be responsible for the underestimated emissions.

2. Air Pollution in the MCMA

[6] Mexico City has among the most severe air pollution in the world [World Health Organization and United Nations Environment Programme, 1992], with over 18 million inhabitants exposed to pollution generated by more than 3 million vehicles and 35,000 industries [Molina and Molina, 2002]. The city is located in the tropics in a valley surrounded by mountains, and at a high elevation (2240 m above sea level) that contributes to high photochemical activity in forming ozone. Mexico City generally experiences the highest concentrations of pollutants during the dry winter, when morning thermal inversions are common. Meteorological studies indicate that the valley of Mexico is well ventilated overnight, suggesting that pollution primarily results from same-day emissions, and that regional-scale diurnal winds are important for determining the meteorology affecting pollutant dispersion [Doran *et al.*, 1998; Fast and Zhong, 1998; Whiteman *et al.*, 2000; Doran and Zhong, 2000].

[7] Actions to reduce emissions during the 1990s [Departamento del Distrito Federal, 1990, 1996] have substantially reduced atmospheric concentrations of SO_2 , CO and lead. Ozone and particulate matter (PM), however, remain pollutants of serious concern [Borja-Aburto *et al.*, 1997; Evans *et al.*, 2002], showing only small decreases in concentration during the 1990s [Instituto Nacional de Ecología (INE), 2000a]. Measured concentrations of ozone violate the Mexican 1-hour air quality standard (110 ppb) on about 80% of days of the year, and peak ozone concentrations of above 300 ppb have been observed [INE, 2000b]. Molina *et al.* [2002] provide a recent literature review, highlighting unique features of Mexico City pollution, and conceptual description of ozone formation and PM composition. A review of atmospheric measurements in Mexico City is provided by Raga *et al.* [2001].

3. Modeling Methods

[8] In this study, we use a three-dimensional Eulerian photochemical airshed model called the California Institute of Technology (CIT) airshed model [McRae *et al.*, 1982]. The CIT model has been applied and tested extensively in the past in urban regions [McRae *et al.*, 1982; Russell *et al.*, 1988; Milford *et al.*, 1989; Harley *et al.*, 1993, 1997; Kuebler *et al.*, 1996; Ulke and Andrade, 2001; Marr *et al.*, 2002], and was previously applied to Mexico City during the MARI project [LANL and IMP, 1994; Streit and Guzmán, 1996]. The version of CIT used in this study

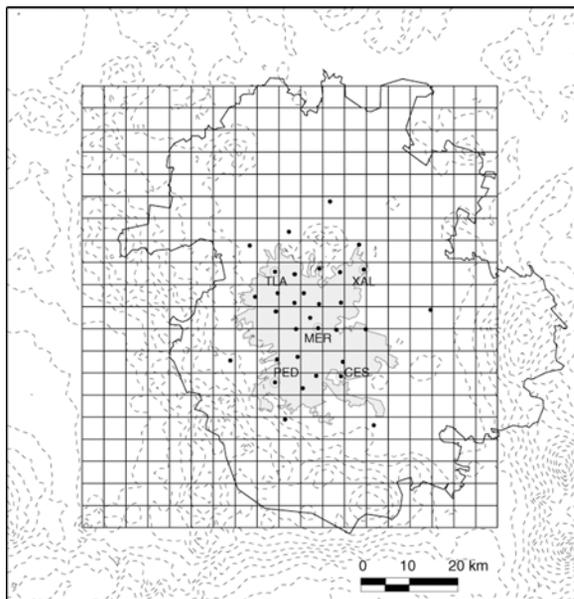


Figure 1. Mexico City metropolitan area and the grid used for modeling in this study. The shaded area represents the urbanized region, and the points show the locations of routine monitoring (RAMA) stations, with five stations labeled (TLA, Tlalnepantla; XAL, Xalostoc; MER, La Merced; PED, Pedregal; and CES, Cerro de la Estrella). The bold boundary outlines the metropolitan area as defined by *Molina and Molina* [2002]. Dashed lines show elevation contours, showing that the valley of Mexico is surrounded on three sides by high mountains, with lower mountains immediately north of the urban area.

includes the SAPRC99 chemical mechanism [Carter, 2000], which is among the most recent chemical mechanisms available. CIT uses operator splitting to solve for transport and chemical processes separately in each time step. The model includes a land use-based deposition module for the dry deposition of pollutants based on the surface resistance and solar radiation, as described by *Harley et al.* [1993]. Vertical diffusion is modeled in CIT as a function of atmospheric stability class, with the mixing height entered as input to the model. We modified CIT to take three-dimensional fields of temperature and humidity as inputs, and to calculate reaction rates in three dimensions on the basis of these parameters.

[9] CIT is employed to model selected days during the IMADA field campaign of February and March 1997 [Doran et al., 1998; Edgerton et al., 1999]. Measurements of the vertical profile of winds include hourly measurements by radar wind profilers at four sites and hourly measurements by sodar at three sites. In addition, radiosondes were released five times daily at each of five sites to measure vertical temperature profiles [Doran et al., 1998]. Air quality measurements included three- and six-hour average measurements of total NMHC concentrations and speciation, and measurements of PM mass and composition [Edgerton et al., 1999; Chow et al., 2002]. In addition, routine air quality measurements of ozone, CO, NO, NO_x, and SO₂ were taken continuously at several sites of the RAMA network [INE, 2000a].

[10] All inputs to the model are based entirely on information available from Mexico City, or where local information is unavailable, on our physical and chemical understanding from the literature. Except for VOC and CO emissions, inputs were not adjusted on the basis of model output to improve agreement with measurements (i.e., we did not tune the inputs to improve model performance), but are derived from data independent of the model output.

3.1. Meteorological Inputs and Modeling Domain

[11] CIT models atmospheric chemistry, taking as inputs hourly three-dimensional meteorological fields for winds, temperature, and humidity, and two-dimensional mixing height fields. For this study, meteorological fields were derived from *Fast and Zhong* [1998], who used the Regional Atmospheric Modeling System (RAMS) [Pielke et al., 1992], a mesoscale meteorological model, to model selected days during the IMADA period. *Fast and Zhong* [1998] applied the RAMS model using a nudging four-dimensional data assimilation procedure to improve agreement with meteorological measurements. Meteorological outputs from RAMS were obtained for 1–2, 3–4, 8–9, 10–11, 13–14, and 17–18 March 1997. For each 2-day pair, meteorological fields are available for 18 hours on the first day, beginning at 0600 LT, and for all 24 hours on the second day. We use the first day of each pair to initialize the model and decrease the sensitivity of pollutant concentrations to our choice of initial conditions, and focus on the results obtained on the second day.

[12] Meteorological fields were interpolated to the modeling grid used for chemical modeling. We chose a grid that is 19 by 20 cells in the horizontal, with each cell occupying 4.5 by 4.5 km, for a total domain area of 85.5 by 90 km (Figure 1). In the vertical, CIT uses a terrain-following coordinate system. We use 15 vertical layers, with the top boundary of the modeling domain at 4628 m above the surface; the height of each layer is smallest near the surface (50 m in the lowest layer) for greater resolution.

[13] The wind fields obtained from RAMS were smoothed and filtered to improve mass consistency (reduce divergence), and we ensured that doing so made only subtle changes. We checked that mass consistency was established on each day by turning off chemistry and deposition in the model, and running the model with uniform initial and boundary conditions in three dimensions; deviations from the initial conditions were observed to be small. In addition, we observed that the mixing heights in the RAMS fields were significantly higher at 0800 LT than those observed in the measured vertical profiles of potential temperature; mixing heights over the city were often between 200 and 500 m in the RAMS fields, while inspection of potential temperature profiles from IMADA clearly showed mixing heights of less than 150 m. Accordingly, the mixing heights during the overnight hours (21:00 to 9:00) were changed to average heights of less than 100 m, while keeping the overall pattern of mixing heights from the RAMS fields. The mixing heights at 1100 LT were likewise overestimated by RAMS on some days (1–4, 10, 11, and 18 March), and were corrected between 0900 LT and noon for better agreement with measurements. RAMS mixing heights during the afternoon were found to be in good agreement

Table 1. Total Annual Emissions (t/yr) for 1998 in the Mexico City Metropolitan Area From the Official Emissions Inventory [CAM, 2001]^a

	PM ₁₀	SO ₂	CO	NO _x	VOCs ^b
Point sources	3,093	12,422	9,213	26,988	23,980
Area sources	1,678	5,354	25,960	9,866	247,599
Mobile sources	7,133	4,670	1,733,663	165,838	187,773
Vegetation and soils	7,985	N/A ^c	N/A ^c	3,193	15,699
Total	19,889	22,466	1,768,836	205,885	475,021

^aGreater detail in emissions from individual source categories is given by CAM [2001] and Molina *et al.* [2002].

^b“Hydrocarbons” reported in the emissions inventory actually report total VOC emissions.

^cN/A stands for not applicable.

with those estimated from measured vertical potential temperature profiles. These mixing heights vary on each day, reaching peak elevations (averaged over the modeling domain) of about 2700 to 3200 m above the surface on 1–4 March (maximum height in one grid cell of 4500 m), with lower peak elevations of 1900 to 2600 m after 4 March. These afternoon heights are in agreement with those of Doran *et al.* [1998], Fast and Zhong [1998], and Whiteman *et al.* [2000].

[14] Of the selected days, 1–2 and 8–9 March fall on weekends. The period of 1–4 March had clear skies with a high-pressure system typical of severe air pollution days, and the highest measured ozone concentrations were on 2 March. Some clouds were observed on the days modeled after 4 March. On these days, ultraviolet (UV) radiation was scaled relative to clear sky conditions, with a maximum decrease of 50% in a few hours, according to hourly surface measurements of UV at the Tec. de Monterrey site in the urban area using a UVB radiometer (280–320 nm). Solar radiation was scaled according to the cloud cover observed at one site, following the methods of Harley *et al.* [1993].

3.2. Chemical Mechanism and Photochemical Reaction Rates

[15] The SAPRC99 chemical mechanism [Carter, 2000] contains 70 chemical species, 223 gas phase reactions, and photochemical reaction rates are expressed as a function of wavelength and UV intensity for 25 species. Emissions and ambient measurements of hydrocarbons were aggregated into 24 lumped hydrocarbon species in the SAPRC99 mechanism according to the procedures documented by Carter [2000], on the basis of the species type and reaction rates with the hydroxyl radical.

[16] Photochemical reaction rates in Mexico City may vary from reaction rates elsewhere because of the higher elevation, which increases UV intensity, but also because the heavy loading of aerosols can decrease UV intensity [Acosta and Evans, 2000; Raga and Raga, 2000]. We compared the default photochemical reaction rates for the photolysis of NO₂ (J_{NO_2}) in the SAPRC99 mechanism, with direct measurements of J_{NO_2} by Castro *et al.* [1997]. These measurements were taken at several sites in the MCMA, although not on the days that we model, and are compared to modeled reaction rates as a function of solar zenith angle. Values of J_{NO_2} in the SAPRC99 mechanism were also compared with values modeled by Sasha Madronich at NCAR (personal communication, 2000), who used a radiative transfer model for Mexico City and a “best guess”

aerosol loading. We found that the SAPRC99 values of J_{NO_2} were within the range of measurements [see Molina *et al.*, 2002], and agreed well with the modeled surface J_{NO_2} values of S. Madronich. Because of this reasonable agreement, we chose not to adjust the photochemical reaction rates in SAPRC99, except for the days when clouds reduced the UV measured at the surface. Photochemical reaction rates above the surface were scaled relative to surface values on the basis of the modeling of S. Madronich.

3.3. Emissions

[17] Emissions inputs are based on the official emissions inventory for the MCMA for 1998 [CAM, 2001, 2002], which we will then test using CIT. The inventory was created by local government authorities using bottom-up methods and emissions factors which were either measured locally or taken from elsewhere; for mobile sources, the MOBILE5 emissions model was adapted to account for local vehicle characteristics. While we are modeling 1997, we chose to use the 1998 inventory rather than the previous 1996 inventory because of methodological improvements; changes between successive inventories are due mainly to changes in methods rather than real changes in emissions [Molina *et al.*, 2000]. The total annual emissions from the emissions inventory are presented in Table 1. These annual emissions were converted into spatially and temporally distributed, speciated emissions files appropriate for particular days. Since our modeling domain has nearly the same total population as the emissions inventory, only the natural emissions of hydrocarbons and NO_x were corrected for the size of the domain and for the season. Emissions of ammonia were obtained from Osnaya and Gasca [1998].

[18] Emissions are distributed spatially and temporally (hourly) for each of 21 species categories, according to data from a variety of sources. For mobile source emissions, we used information compiled by Francisco Hernandez and colleagues in the Comisión Ambiental Metropolitana (CAM), who estimated the spatial-temporal distributions separately for each pollutant on the basis of traffic count data. For emissions from vegetation, we used the spatial distribution modeled by Velasco-Saldaña [2001], and temporal distributions estimated by Guenther *et al.* [2000]. Emissions from area sources were distributed spatially for each category separately, using population, commercial, or other distributions, as appropriate. For emissions from point sources, we used a database of 6230 industries in the MCMA, which we obtained from CAM. The database contains the location, emissions, work hours, and other data that were used for estimating spatial and temporal distributions. CIT can treat elevated emissions from smokestacks individually by calculating the plume rise of hot exhaust gases, and this option was employed for 342 smokestacks for which sufficient information was available.

[19] The speciation of VOC emissions was determined for each source category using emissions profiles measured in Mexico City [Mugica *et al.*, 1998, 2002; Vega *et al.*, 2000]. These profiles were adjusted to include species not measured in Mexico City (e.g., formaldehyde) using emissions profiles from the SPECIATE database [Environmental Protection Agency (EPA), 1993]. Likewise, emissions profiles for source categories that were not measured in Mexico City were taken from the SPECIATE database.

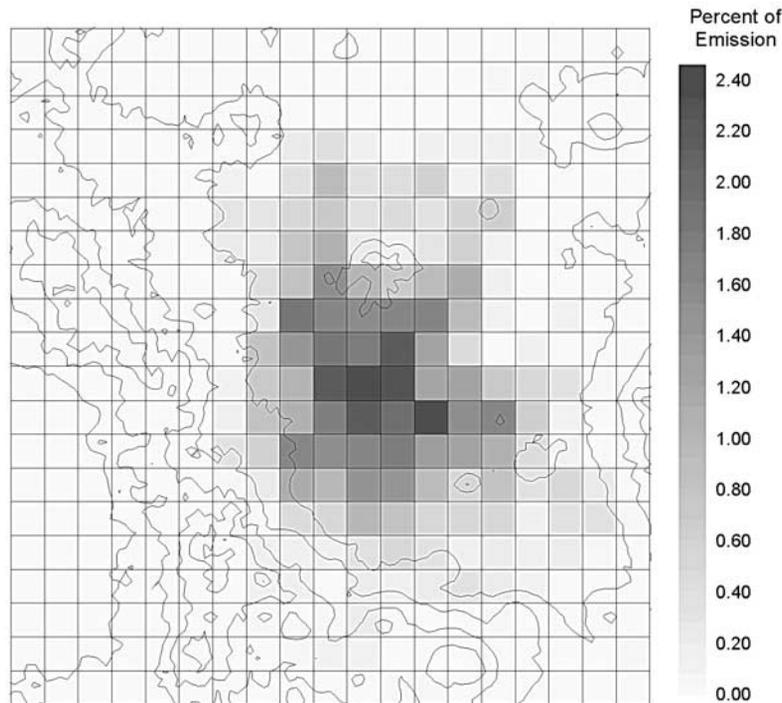


Figure 2. Spatial distribution of total VOC emissions input to the California Institute of Technology model. Values are averaged over 24 hours for a weekday and are expressed as the percent of the total emissions in each grid cell. Elevation contours are also shown for reference.

[20] Weekend emissions are modified from weekday emissions on the basis of information from a variety of sources and experts in Mexico. On Saturday, industrial emissions are decreased by 20% relative to weekday emissions, using information from the database of industries in Mexico City. On Sunday, vehicular emissions are decreased by 30%, industrial emissions by 50%, and emissions from some categories of services are decreased by 10%.

[21] The resulting daily average spatial distribution of total VOC emissions for a weekday is shown in Figure 2, showing that (like other pollutants) emissions of VOCs are concentrated in the urban area. Spatial patterns of all pollutants vary hourly to reflect the relative contributions of different sources.

3.4. Initial and Boundary Conditions

[22] Pollutant concentrations at the start of each model run (0600 LT on the first day of each 2-day pair) must also be specified. Surface concentrations of ozone, NO, NO₂, SO₂, and CO were determined over the urban region by using a spline-tensioned interpolation of concentrations measured at RAMA stations [INE, 2000a]. We extended these surface concentration fields to the whole domain, giving (except for ozone) lower concentrations near the model boundaries, while maintaining the general pattern of concentrations observed in the urban region. Measurements of NMHCs from 0600–0900 LT at three sites were used to set initial surface concentrations on 13 March. On the other first days of each 2-day pair, only measurements at one site (La Merced) from 0600–1200 or 0600–0900 LT were available; these were multiplied by the average ratios of 0600–0900 LT measurements at three sites to the

0600–1200 or 0600–0900 LT measurements at La Merced [Arriaga-Colina *et al.*, 2004] to estimate the spatial distributions of initial concentrations. Initial and boundary conditions of total NMHCs were divided into lumped species categories according to ambient measurements of NMHC speciation. Initial and boundary conditions for aldehydes and ketones were based on measurements by Báez *et al.* [1995, 2000] on days apart from the IMADA campaign, and inorganic aerosol species, NH₃, and HNO₃ are based on measurements during IMADA by Chow *et al.* [2002].

[23] Measurements of the vertical distributions of pollutants were not taken during the IMADA campaign, and few exist for Mexico City in general. The vertical profiles of both initial and boundary conditions were based on vertical profiles measured by Nickerson *et al.* [1992] and by Velasco-Saldaña *et al.* [2001]: ozone, CO and SO₂ are assumed to have constant vertical profiles, while all other pollutants are assumed to decrease linearly from the surface to 20% of the surface concentration at an elevation of 1400 m above the surface and are constant above that.

[24] Analysis using the model shows that modeled concentrations on the second day of each 2-day pair show little sensitivity to reasonable values of initial conditions, while boundary conditions are more important. This result is in agreement with the findings of Fast and Zhong [1998] who modeled conservative particle tracers to show that the Mexico City basin is fairly well cleaned by strong winds every evening. Surface concentrations of pollutants at the boundary of the modeling domain are listed in Table 2. Only boundary conditions for ozone, PAN, and NO are assumed to change hourly. Because of the larger population and heavier industry North of the city, we assume that all

Table 2. Boundary Conditions of Pollutants at the Surface

Pollutant (SAPRC99 Species)	Concentration, ppb
O ₃ ^a	20–70
CO	700
SO ₂	8
NO ₂	10
NO ^a	5–2
Total hydrocarbons	500
PAN ^a	2–7
HCHO	10
CCHO (higher aldehydes)	7
ACET (acetone)	5
HNO ₃	0.1
NH ₃	4
NIT (nitrate aerosol)	0.3
SULF (sulfate aerosol)	1.1

^aThese boundary conditions are assumed to change hourly.

boundary conditions at the North boundary are 20% higher than shown in Table 2.

4. Results

[25] Results are presented first to assess the correction needed for emissions of VOCs and CO, and then to evaluate overall model performance when the model is run using these corrections. Model predictions of total NMHCs are compared against measurements of total NMHCs, which are described by Ruiz *et al.* [1996], Arriaga *et al.* [1997], and Arriaga-Colina *et al.* [2004]; ambient air samples were collected in stainless steel canisters, followed by analysis using gas chromatography/flame ionization detection. Analysis of these samples gives the mass of about 200 hydrocarbon compounds in the range C2 to C12. Species which are unidentified contribute about 5 to 10% of the total measured mass, and are thought to include some (but not all) aldehydes, ketones, and alcohols, as well as unidentified NMHCs. The total NMHC measurement is therefore expected to be the majority (roughly 90%) of the total concentration of VOCs, excluding unmeasured species such as species with more than 12 carbon atoms and some aldehydes. These measurements are lumped into the SAPRC99 species categories for direct comparison against the model predictions by species category, not including halogenated VOCs, and this total measured NMHC is compared against the sum of the corresponding modeled NMHC species.

[26] NMHC measurements from 0600–1200 LT and from 1200–1800 LT at La Merced in the center of the city (Figure 1) are available on all days that we model. Of the second days of each 2-day pair, measurements from 0600–0900 LT are available at three sites on 11, 14, and 18 March: La Merced; Pedregal, in a residential area southwest of the city; and Xalostoc, in an industrial area northeast of the city which may be influenced by local emissions sources [see Arriaga-Colina *et al.*, 2004].

4.1. Evaluation of VOC and CO Emissions

[27] Figure 3 compares measured and modeled total NMHC concentrations at La Merced on 13 and 14 March 1997. Model results are shown here for the base case run, on the basis of the official emissions inventory, and for an alternative VOC emissions scenario, where total VOC emissions are multiplied by three. In this paper, VOC and

CO emissions are varied uniformly for all sources, keeping the same spatial, temporal, and species distributions, assuming that we have no information about which source categories are more likely underestimated. We later address which sources may be most responsible for underestimated emissions.

[28] In Figure 3, the predicted total NMHC concentrations show a strong diurnal variation, decreasing substantially during the morning as the top of the mixing layer rises. This illustrates the difficulty in comparing predicted concentrations with time-averaged measurements, and suggests that greater time resolution in NMHC measurements could be valuable. Predicted concentrations under the two emissions scenarios diverge from the same initial condition (the 0600–0900 LT measured concentration) because of the difference in emissions, with the morning concentration on the first day influenced strongly by the initial conditions. Overnight and on the second day, the difference between the two cases is more apparent, showing that the model more closely reproduces the measurements when VOC emissions are increased.

[29] In Figure 4, the comparison of measured and modeled total NMHCs is generalized for all of the NMHC measurements that were taken on the second days of each 2-day pair. Model results are shown using the VOC emissions on the basis of the official emissions inventory, and when the model is run again with VOC emissions increased by factors of 2, 3, and 4, keeping all other model parameters the same. The best fit to the measurements is clearly seen using a factor of 3 increase in VOC emissions – although there is significant scatter in the data, the overall bias is smallest in this case. While most of the measurements available for comparison were taken during the morning, the results shown for the afternoon measurements show a best fit with little bias using a factor of 4 correction. In addition to the NMHCs, model predictions of aldehydes are in general agreement with the range of measurements of

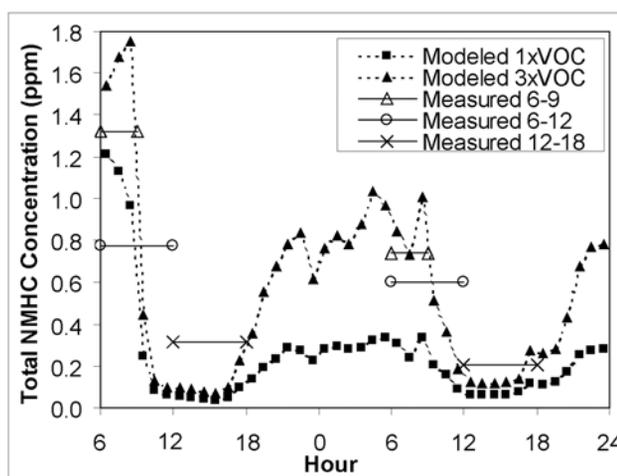


Figure 3. Measured total nonmethane hydrocarbons (NMHC) concentration at La Merced on 13 and 14 March 1997, with predicted hourly model concentrations when using VOC emissions from the inventory and when multiplying the VOC emissions by a factor of 3.

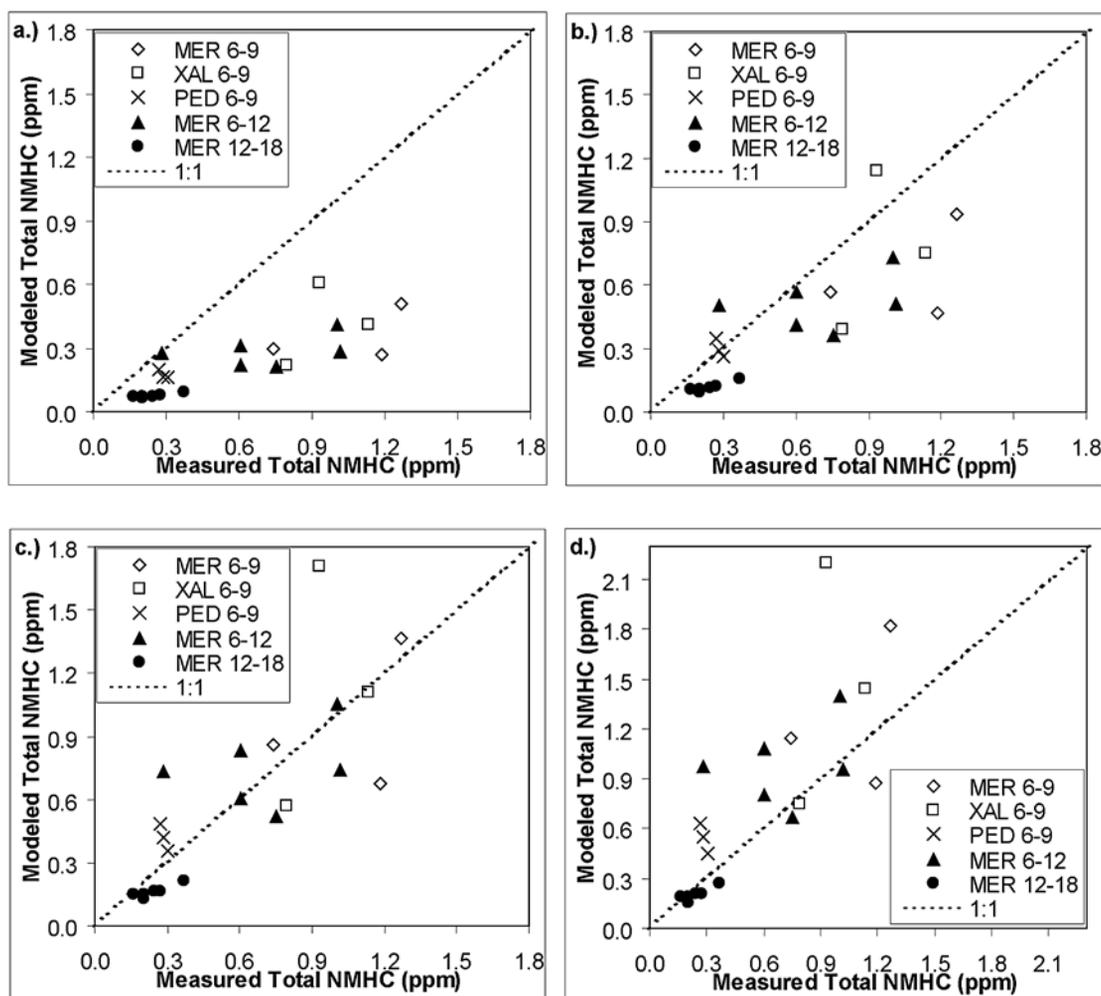


Figure 4. Summary of measured and modeled total NMHCs, for all NMHC measurements available on the second day of each 2-day pair (2, 4, 9, 11, 14, and 18 March), using (a) the VOC emissions based on the official emissions inventory and those emissions multiplied by factors of (b) 2, (c) 3, and (d) 4. Site locations are shown in Figure 1.

Báez *et al.* [1995, 2000], which were taken on different days, using a factor of 3 correction to VOC emissions.

[30] In order to evaluate whether VOC emissions are underestimated, it is important to consider model performance for other pollutants, particularly for NO_x , since estimates of NO_x emissions are thought to be of relatively good quality. Here, the average normalized bias (ANB) is calculated as the average residual divided by the average measurement:

$$ANB = \frac{\frac{1}{N} \sum_{i=1}^N (P_i - O_i)}{\frac{1}{N} \sum_{i=1}^N O_i} = \frac{\sum_{i=1}^N (P_i - O_i)}{\sum_{i=1}^N O_i} \quad (1)$$

where P_i is the prediction and O_i is the observation at a particular time and location, and N is the number of observations. This differs from the ANB more commonly used [Harley *et al.*, 1993; Winner and Cass, 1999], which is understood to lead to misleading conclusions when the

observed concentrations are small, and to weight overestimates more than underestimates [Seigneur *et al.*, 2000]. The average normalized bias used here weighs overestimates and underestimates equally in concentration units; an overestimate of one ppb together with an underestimate of one ppb would result in an ANB of zero. Other model performance statistics are analyzed in the next section.

[31] Table 3 shows the bias in model predictions versus measurements for routinely monitored pollutants, averaging over all measurement stations, when the model is run with VOC emissions increased by a factor of 3 and CO emissions increased by a factor of 2. Measurements from RAMA [INE, 2000a] are archived hourly at 15 to 20 stations for each pollutant, and Table 3 only compares measurements and model predictions at stations and hours with valid measurements. Measurements of NO_x using chemiluminescence monitors are understood to report more than just NO and NO_2 , also measuring other nitrogen-containing species such as HNO_3 and PANs and therefore more accurately measuring NO_y [NRC, 1991; Harley *et al.*, 1993; Winner and Cass, 1999]. Accordingly, we compare the measured

Table 3. Average Normalized Percent Bias (See Text) in Model Predictions Versus Measurements, Averaging Over All Measurement Stations and Hours^a

	2 March	4 March	9 March	11 March	14 March	18 March	Average	
							All	2, 4, and 14 March
<i>12 Hour (0600–1800 LT)</i>								
O ₃	−3.0	3.1	11.2	8.6	−1.6	15.9	5.2	−0.6
NO	7.7	−31.4	53.8	−37.4	−17.4	−2.1	−13.9	−17.3
NO _x ^b	9.2	−13.0	60.2	−16.8	−9.1	20.8	2.6	−5.9
CO	−13.0	−13.4	26.0	−17.5	−9.4	15.5	−4.3	−12.0
SO ₂	−43.8	−28.4	−49.3	−19.4	−32.8	−2.0	−31.6	−35.0
<i>24 Hour</i>								
O ₃	−4.8	−0.2	10.6	10.1	−8.0	15.6	3.2	−4.3
NO	22.3	−13.1	151.6	7.8	41.0	10.7	21.6	15.3
NO _x ^a	29.2	9.1	117.2	15.2	33.6	34.2	31.7	23.3
CO	5.2	3.2	46.6	4.5	17.4	26.6	14.7	8.4
SO ₂	−29.0	−15.0	−43.6	−0.6	−2.8	17.3	−15.7	−16.5

^aA positive bias indicates a model overestimate. Results are shown for three times the VOC emissions and twice the CO emissions in the official emissions inventory.

^bMeasured NO_x is compared with the sum of modeled species corresponding to NO_y.

NO_x with the sum of modeled species corresponding to NO_y, and show comparisons for NO, as this is measured directly and fairly accurately [NRC, 1991].

[32] The results in Table 3 show that the model bias is reasonably low for all pollutants shown. NO and NO_x show good agreement with the measurements during daylight hours (important for ozone formation), but the model tends to overestimate NO and NO_x overnight. The results also show good agreement for CO when using the factor of 2 correction for CO emissions. When no correction is made to CO emissions, the model significantly underestimates the measured CO concentrations; the average normalized bias for CO over all 6 days is −39.0% during daylight hours and −30.2% over all 24 hours. A large overestimate of all pollutants except SO₂ is observed on 9 March, which may be due to meteorological uncertainties; removing this day improves the model agreement overall, especially for the 24 hour comparison. SO₂ tends to be underestimated by the model by about 30% over all 24 hours; this may be due to an underestimate of SO₂ in the emissions inventory, but is not investigated further in this study.

[33] Table 3 shows that relative to daylight hours, the model tends to produce more of an overestimate (or a smaller underestimate) for all primary pollutants (excluding

ozone) when all 24 hours are considered. This could suggest that the temporal distribution of emissions is inaccurate, but is more likely due to uncertainties in the meteorological inputs, particularly the relationship between the mixing layer height overnight and during the day. If the morning mixing heights were increased to decrease concentrations in accordance with measurements (of NO_x, for example), then a larger correction for VOC and CO emissions would be implied.

[34] To ensure that there are no local problems in model predictions near the sites of the NMHC measurements, Figure 5 shows comparisons of NO_x and CO at the same locations and time periods as used in Figure 4. While there are deviations from agreement for individual points, very little bias is observed overall for both pollutants. Figure 6 shows the measured and predicted ozone concentrations on two days, averaging results hourly over all stations with valid ozone measurements, as VOC emissions are varied. The results show that VOC emissions strongly influence the rise of ozone concentrations in the morning hours. With VOC emissions from the emissions inventory, the model significantly underestimates ozone production during the morning, by as much as 50 ppb. Similar results are predicted on the other days modeled (not shown).

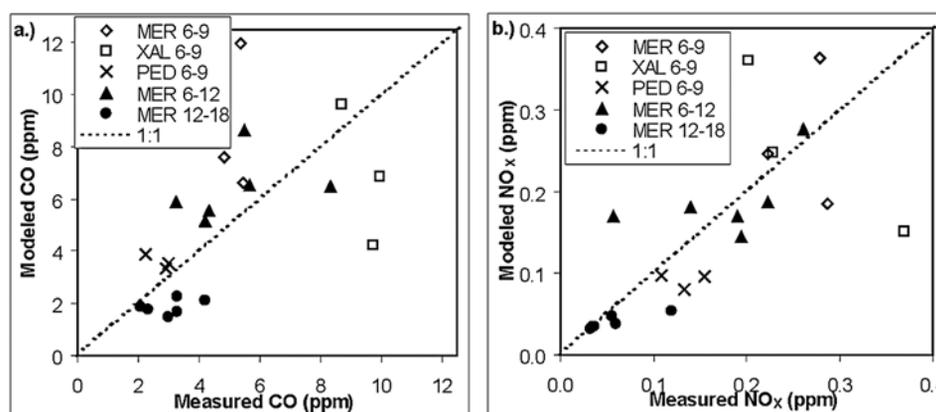


Figure 5. Comparison of modeled and measured concentrations of (a) CO and (b) NO_x at the same locations and times used in Figure 4. Results are shown using 3 × VOC and 2 × CO emissions.

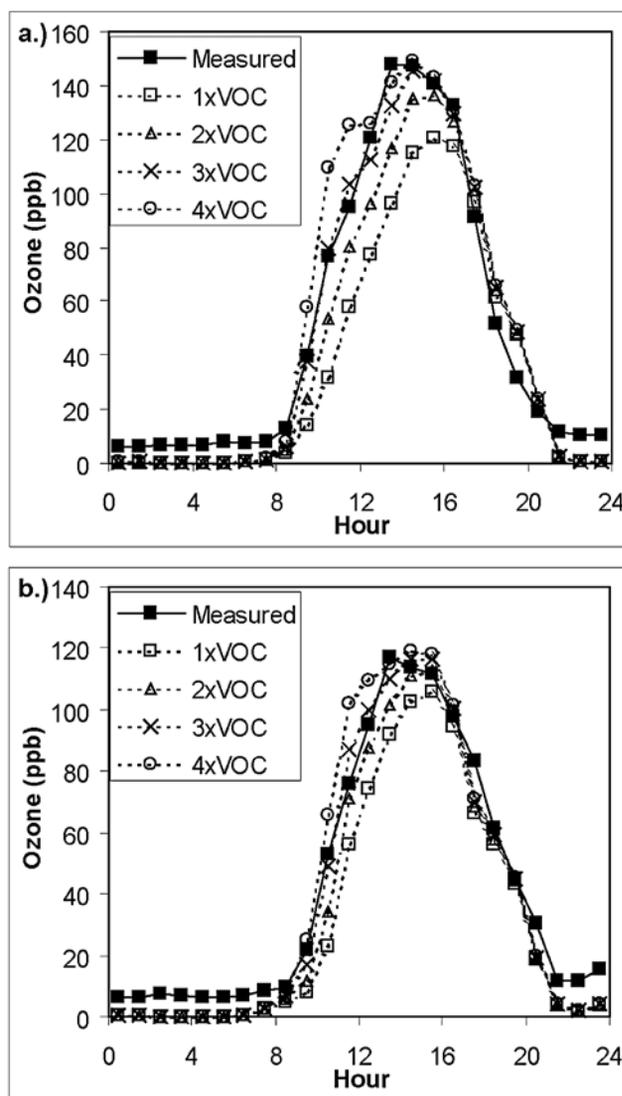


Figure 6. Measured ozone concentration and modeled ozone using the VOC emissions from the inventory and VOC emission correction factors of 2, 3, and 4 for (a) 2 March 1997 and (b) 14 March 1997. Ozone concentrations are the averages of concentrations at all monitoring stations recording values each hour.

[35] The results of this analysis show that a “best fit” with smallest bias is achieved when increasing VOC emissions by a factor of 3 and CO emissions by a factor of 2. These results are in agreement with the range of two to three estimated by *Arriaga-Colina et al.* [2004] for VOC/NO_x and CO/NO_x ratios, and are in general agreement with results in the Paso del Norte (El Paso/Ciudad Juárez) region [*Funk et al.*, 2001]. This agreement using independent methods (although both use the same ambient measurements) increases our confidence in these findings, although our confidence in the magnitude of the correction is low.

4.2. Overall Model Performance

[36] Using the “best fit” correction factors for emissions from the previous section (two for CO and three for

VOCs), the results for ozone are shown in Figure 7, averaging hourly over all stations with valid measurements. Figure 7 shows that although there are some significant disagreements on the first day of each 2-day pair, the results on the second days show remarkably good agreement, particularly on 2, 4, and 14 March. The biases for NO_x and other pollutants on these days are also small (Table 3), as are the biases for total NMHCs. Comparisons of ozone at individual stations (not shown) often do not show as good agreement as the averages in Figure 7, but inspection of these results suggests that the model captures fairly accurately the spatial and temporal patterns of ozone, particularly on 2, 4, and 14 March. For example, the model predicts correctly that the ozone peak over the urban area occurs early (around noon) on 4 March, and occurs south of the city center. The model also predicts that the peak ozone concentration occurs within the modeling domain on all days analyzed, although on some days the peak occurs near the model boundary. Recirculation of polluted air masses during the afternoon was predicted by *Fast and Zhong* [1998] on 2 and 14 March, and this recirculation, defined by the mountainous terrain, occurs within the model domain. *Fast and Zhong* [1998] find very little evidence for overnight recirculation of polluted air masses, although previous airborne measurements suggested that overnight recirculation occurs [*Pérez-Vidal and Raga*, 1998]. Consequently, our modeling domain is sufficiently large, but we suggest that future modeling use a larger domain, as emissions information over this larger region become available.

[37] Table 4 shows statistical measures of overall model performance on the second days of each 2-day pair. Both the bias and the gross error are within acceptable ranges, with generally better performance during daylight hours and on 2, 4, and 14 March. Because the bias for ozone and its precursors is small, because the summary statistics in Table 4 are acceptable, and because both the timing and location of the peak ozone are well represented by the model, these results suggest that the model in general – and in particular on 2, 4, and 14 March – is of sufficient quality to use in evaluating the sensitivity of ozone to changes in emissions and other model parameters.

[38] Model predictions of peroxyacetyl nitrates (PANs) were also compared with measurements taken at IMP, north of the city center, by *Gaffney et al.* [1999] on all days that we model. These measurements show very high concentrations of PAN (and total PANs) during daylight hours, up to 40 ppb, which are among the highest concentrations reported in the literature. Where VOC and CO emissions are corrected, the model underpredicts the measured concentrations of PAN and of total PANs by roughly 50% during the day. Without correcting VOC emissions, the model underpredicts these measurements even more severely, as less hydrocarbons are available to form PANs.

[39] Finally, we compare the predicted concentrations of total nitric acid (gas phase plus aerosol nitrate) with 6-hour measurements at La Merced reported by *Chow et al.* [2002]. Results show good agreement with a tendency to underestimate (average normalized bias over 6 days of –26.0%), suggesting that the model addresses the conversion of NO_x to HNO₃ reasonably well. Comparison with other

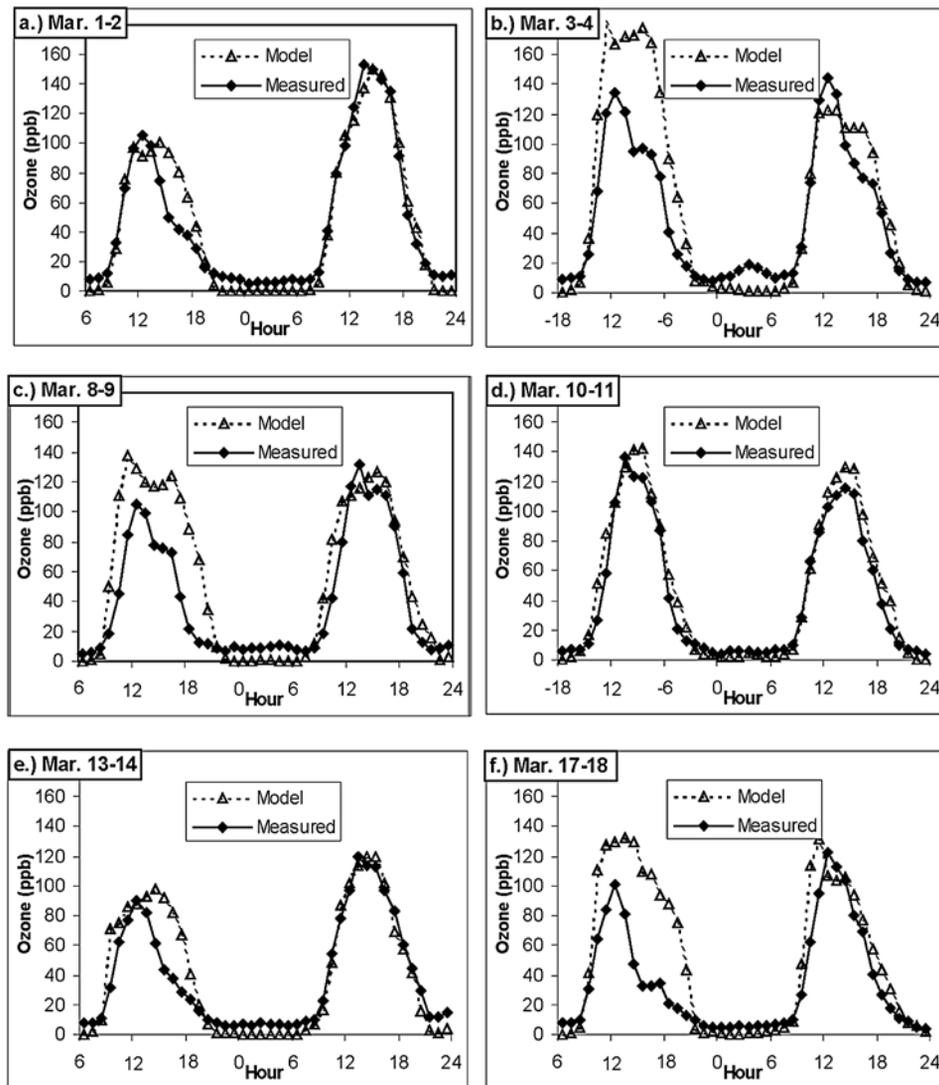


Figure 7. Measured and predicted ozone concentrations, averaged hourly over all measurement stations that recorded valid measurements.

Table 4. Statistical Analysis of Model Performance on the Second Days of the Six 2-Day Pairs^a

	All Days		2, 4, and 14 March	
	12 Hour ^b	24 Hour	12 Hour ^b	24 Hour
	<i>Ozone</i>			
Average bias, ppb	3.7	1.5	-0.5	-2.2
Normalized bias, %	5.2	3.2	-0.6	-4.3
Gross error, ppb	19.5	15.4	17.5	14.3
Normalized error, %	27.5	32.6	23.1	28.0
	<i>NO_x^c</i>			
Average bias, ppb	2.3	25.7	-5.7	20.5
Normalized bias, %	2.6	31.7	-5.9	23.3
Gross error, ppb	51.7	66.3	49.7	61.9
Normalized error, %	58.3	81.8	51.5	70.3

^aAverage bias is the average residual (predicted–observed), and average normalized bias is presented in equation (1). The average gross error and average normalized gross error are the same as the bias but use absolute values throughout.

^bTwelve-hour statistics are for 0600–1800 LT.

^cMeasured NO_x is compared with the sum of modeled species corresponding to NO_y.

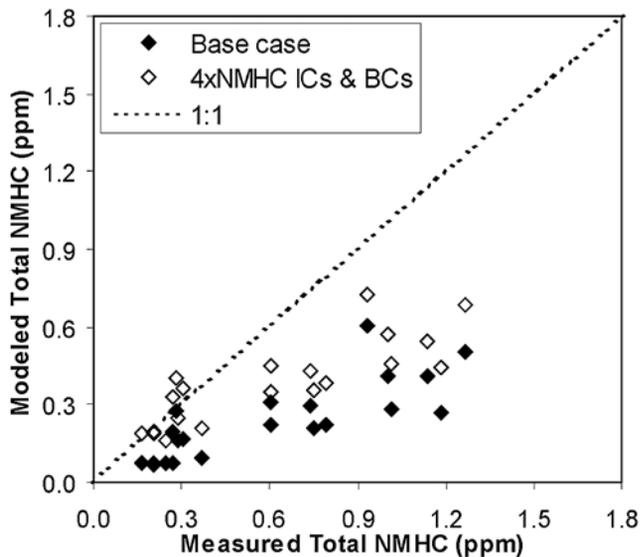


Figure 8. Measured and predicted total NMHC concentrations on the second day of each 2-day pair, using the total NMHC emissions given by the official emissions inventory. Solid diamonds are the same as in Figure 4a, and the open diamonds show the changes in predictions when NMHC initial and boundary conditions are multiplied by a factor of 4.

aerosol measurements by *Chow et al.* [2002] and routine measurements of PM_{10} , are beyond the scope of this study.

5. Could There be Other Explanations for the NMHC and CO Discrepancies?

[40] Apart from an underestimate in emissions, could there be other explanations for the model underpredictions of measured concentrations of NMHCs and CO? Or can we conclude with confidence that the emissions are the most likely cause of the discrepancies? Here we identify other significant sources of uncertainty in the model and discuss whether they individually can plausibly explain the discrepancy.

5.1. Meteorological Inputs

[41] The fact that NO_x and ozone show little bias and show spatial and temporal patterns consistent with the measurements suggests that meteorological inputs are reasonably well represented. Because we have mainly morning measurements of NMHCs, the mixing height in the morning is likely to be the most important meteorological parameter, as this controls the vertical diffusion of morning emissions and defines the effective mixing volume. As mentioned earlier, the morning mixing heights from the original RAMS outputs were lowered to improve agreement with measurements. Using the original mixing heights in the morning would imply greater dilution and so a larger correction factor for VOC emissions would be needed for agreement with the measured concentrations.

5.2. Initial and Boundary Conditions

[42] Initial and boundary conditions are uncertain, as few measurements exist outside of the metropolitan area or above the surface. As mentioned earlier, initial conditions

are estimated to have only a minor influence on the second day of each 2-day pair, while boundary conditions have a more significant impact. In Figure 8, we increase the initial and boundary conditions of total NMHCs by a factor of 4 (including in the vertical); the resulting surface concentration used at the boundary is 2.0 ppmC, which is higher than many of the morning measurements taken at Pedregal. While this change has a significant effect in increasing the predicted concentrations of NMHCs, particularly during the afternoon, it is clear that this change alone is not sufficient to fully explain the discrepancy between measured and modeled total NMHCs.

5.3. Spatial and Temporal Distributions of Emissions

[43] The spatial and temporal distributions of emissions used in this study are reasonable (Figure 2), but could be improved with more detailed studies. Because CO measurements are available during all hours and at many locations, our conclusions about CO emissions are not likely to be changed significantly with improvements in the spatial and temporal distributions of emissions. Distributions of emissions are likely more important when comparing with the morning NMHC measurements, since morning measurements are likely to reflect fresh emissions originating near the measurement locations. In order to explain the discrepancy, however, emissions near the measurement station and in the morning hours would need to increase by roughly a factor of 3. It is hard to imagine how the spatial and temporal distributions could be increased near the measurement locations by a factor of 3 while still showing reasonable patterns, and while not making significant changes in the distributions of other pollutants, particularly NO_x .

5.4. Measurement Uncertainty and Representativity

[44] Measurements of CO are likely to be of good quality [NRC, 1991] and are taken frequently at several sites. Measurements of total NMHCs are more uncertain, and are taken as time averages at only three sites. Consequently, a question exists whether these measurements are representative of the emissions over the entire metropolitan area. *Arriaga-Colina et al.* [2004] suggest that measurements at Xalostoc may be influenced by local industrial sources but that La Merced appears to be representative of emissions in a significant area of the city center. *Watson and Chow* [2001] likewise found that the majority of black carbon measured at La Merced and at Pedregal appear to be mainly from the urban mixture, rather than from local sources. Further, for both CO and NMHCs, uncertainties are involved inherently in comparing point measurements with predicted concentrations over a grid cell – but while this adds uncertainty, it is not expected to affect the model bias. Accordingly, measurement uncertainty and representativity are not important issues for CO, but are significant issues for NMHCs, although not likely significant enough to account for the discrepancy.

5.5. Speciation and Reactivity of VOCs

[45] The speciation of VOC emissions affects their lifetime in the atmosphere, as can the reactivity of VOCs in the chemical mechanism. However, the majority of the NMHC measurements are in the morning, before photochemical activity becomes important, and therefore speciation and

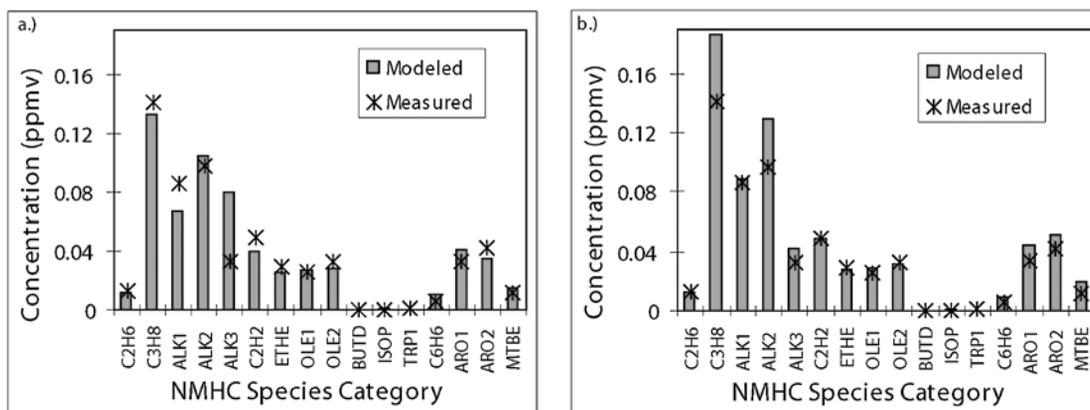


Figure 9. Measured and predicted hydrocarbon concentrations for each lumped SAPRC99 category, using $3 \times$ VOC and $2 \times$ CO emissions and NMHC source distributions from (a) the emissions inventory and (b) *Mugica et al.* [2002]. Values shown are the averages of all periods on the second day of each 2-day pair (measurement periods and locations are shown in Figure 4).

reactivity have little effect on the modeled NMHCs. For afternoon NMHC measurements, NMHC speciation and reactivity are more important but should not be sufficient to account for the discrepancy in measurements.

[46] In summary, none of these explanations individually is likely significant enough to plausibly explain the discrepancy between modeled and measured concentrations of CO and total NMHCs, when basing emissions on the official emissions inventory. Combinations of uncertainties could be sufficient to explain the discrepancy. Of these factors, we highlight the hourly mixing height, boundary conditions, the spatial and temporal distributions of emissions, and the representativity of NMHC measurements as the most important influences that should be addressed through further research. Clearly, more frequent NMHC measurements at more sites, conducted concurrently with the meteorological measurements needed to support modeling, can help this type of top-down check on the emissions inventory in the future. Further, measurements should be expanded spatially as well as in the vertical to better characterize boundary concentrations.

6. What Sources Could be Responsible for the Underestimated Emissions?

[47] The identified underestimates in total emissions of CO and VOCs are not likely to be evenly distributed among the many sources of these emissions. Rather, some sources may be more responsible for the underestimate than others. According to the official emissions inventory (Table 1), 98% of CO emissions come from transportation sources, which is consistent with other urban regions. Accordingly, motor vehicles are expected to be the most important sources of underestimated CO emissions. Research in Los Angeles and elsewhere has suggested that VOC emissions from motor vehicles may likewise be underestimated [Harley *et al.*, 1997; Sawyer *et al.*, 2000]. In Mexico City, direct measurements of vehicle emissions [Beaton *et al.*, 1992], analysis of ambient CO measurements [Riveros *et al.*, 1998], and analysis of vehicle technology and the inspection and maintenance program [Gakenheimer

et al., 2002; Riveros *et al.*, 2002] also suggest that vehicle VOC and CO emissions may be higher than previously thought.

[48] Aside from motor vehicles, uncertainties exist for many other source categories, and evaporative emissions are significant VOC sources in the emissions inventory. Emissions from many evaporative sources are estimated using emissions factors developed in the United States [EPA, 1995], which may not be appropriate for Mexico City [Molina *et al.*, 2000]. Further, the emissions inventory [CAM, 2001] states that because of a lack of information on landfills and wastewater treatment in the State of Mexico, emissions from these sources are only estimated in the Federal District; although these categories represent less than 2% of VOCs in the emissions inventory, they are expected to be severely underestimated. There may be other cases where lack of information causes a bias toward underprediction, including source categories for which no estimates were made, such as open sewage and waste.

[49] In order to identify potentially underestimated sources, we compare model outputs of the concentrations of lumped SAPRC99 NMHC species directly with measurements. Figure 9a shows this comparison as an average of all NMHC measurements available on all of the second days of each 2-day pair, when emissions of total VOCs and CO are corrected. The results show remarkably good agreement overall, although there are tendencies to overestimate heavy alkanes and underestimate light alkanes. This agreement suggests that the relative distribution of VOC sources is likely to be roughly correct, and that the underestimated VOC emissions may result from underestimates of many sources.

[50] The tendency to underestimate light alkanes (C3H8 and ALK1) in Figure 9a is likely due to an underestimate of liquefied petroleum gas (LPG) leakage, which is the largest source of light alkanes and has significant uncertainty [Blake and Rowland, 1995; CAM, 2001], but may also be due to uncertainties in VOC reactivity. This suggests that a correction factor of larger than the average for VOCs may be appropriate for LPG emissions. Considering the results on individual days and time periods (not shown), there is

less of a tendency to underestimate light alkanes in the afternoon at La Merced, which may be due to inaccuracies in the temporal distribution of LPG emissions. The results in Figure 9a likewise show that both measured and modeled isoprene (ISOP) and terpenes (TRP1) are low. This suggests that the emissions inventory is likely correct that biogenic emissions of VOCs are small compared to anthropogenic emissions (Table 1), and not likely responsible for much of the underestimated emissions. Of the other species underestimated in Figure 9a (C₂H₂, OLE₂, and ARO₂), gasoline vehicles are the largest single category, accounting for 45–80% of the emissions in our speciated emissions inputs. Of the overestimated species, gasoline vehicles are the largest contributor to emissions of ALK₂, C₆H₆ and ARO₁, accounting for 35–65% of these emissions. Solvent consumption is the most likely cause of the overestimated ALK₃ concentrations. These differing results do not suggest clearly whether gasoline vehicles are likely to be underestimated by more or less than the VOC average, and suggest that a combination of other minor sources may be important.

[51] The speciation of individual NMHCs was considered by *Mugica et al.* [2002], who applied a chemical mass balance (CMB) technique to estimate speciated ambient measurements as a sum of emissions from different sources. *Mugica et al.* [2002] used the same ambient and source profile measurements of NMHCs as used in this study. The CMB can estimate the relative source strength of NMHC emissions, but cannot assess whether the total quantity of emissions is inaccurate. It also does not consider the chemical processing of NMHCs, nor background concentrations. The results of *Mugica et al.* [2002] show that the relative contributions of sources in the emissions inventory appears reasonable, but they identify diesel vehicles, asphalt paving, and food cooking as sources that may be significantly underestimated. Here, we use the results of *Mugica et al.* [2002] to provide the relative (percentage) source strength of VOC emissions in CIT, and increase the total VOC emissions by a factor of 3, as before. The results of these model runs are summarized in Figure 9b. On average, the modeled concentration of total NMHCs at the measurement locations is 17% higher, because of the changes in the temporal and spatial distributions of the new mixture of emissions sources. In general, the model predictions of NMHC species improve. The CMB results report LPG leakage as responsible for 15.6% of VOC emissions, as opposed to 13.0% in the emissions inventory; this change is sufficient to now overestimate the concentrations of light alkanes. The lower emissions from solvent consumption improve agreement for the heavy alkanes (ALK₃). This general agreement suggests that the relative contributions of VOC sources are more accurate in the CMB results than in the emissions inventory, and that the sources identified by the CMB (diesel vehicles, asphalt paving, and food cooking) may be the most severely underestimated.

7. Conclusions

[52] The CIT photochemical airshed model was applied successfully in predicting gas phase photochemistry in Mexico City on 12 days in March 1997. The model was applied to address the question of whether emissions of

VOCs and of CO are likely to be underestimated in the official emissions inventory.

[53] Comparing model predictions of total NMHCs and CO with measured concentrations, the model significantly underestimates concentrations of total NMHCs and CO when using emissions from the official emissions inventory. When increasing emissions by a common factor applied to all sources, a “best fit” (with lowest bias) to measurements is found when VOC emissions are increased by a factor of 3, and CO emissions by a factor of 2. With these corrections for VOC and CO emissions, and using best estimates of all other model parameters, the model produces reasonably good estimates of ozone and of NO_x, with average normalized biases over 6 days of 3% and 32%, respectively.

[54] Apart from an underestimate in emissions, other potential explanations for the discrepancy in modeled and measured NMHCs and CO are also analyzed. This analysis highlights important uncertainties in the model to be resolved through future research, but finds that no single explanation can plausibly explain this discrepancy. Further, these results are in agreement with the results of *Arriaga-Colina et al.* [2004] who estimated that the emissions inventory underestimates the ambient ratios of VOC/NO_x and CO/NO_x by factors of 2–3. Our modeling results also suggest that NO_x emissions are well represented in the emissions inventory. This provides evidence that the discrepancies identified by *Arriaga-Colina et al.* [2004] are due to underestimates of VOCs and CO, rather than an overestimate of NO_x. The general agreement of these two independent methods increases our confidence that VOC and CO emissions are underestimated, with greater confidence for CO because of the greater availability of measurements; for VOCs, the scarcity of measurements raises questions of whether these measurements are representative, decreasing our confidence in the findings.

[55] The predicted speciation of NMHC concentrations agrees with the measured speciation, which suggests that the underestimated VOC emissions may be due to a variety of sources. This agreement improves when emissions are distributed according to the results of a CMB analysis, allowing diesel vehicles, asphalt paving, food cooking, and LPG leakage to be identified as sources that may be most underestimated.

[56] Model performance statistics are generally better during daytime hours, with a tendency to overestimate at night, and are best on 2, 4, and 14 March. In addition, modeled spatial and temporal distributions of ozone show patterns in general agreement with measurements. In order to use an air quality model with confidence to predict the sensitivity of ozone to changes in emissions, it is necessary to model well not only ozone, but also NO_x and VOCs. Because the model reproduces concentrations of all three pollutants reasonably well in general, and particularly well on 2, 4, and 14 March, the model should be used to explore the sensitivity of ozone to changes in emissions.

[57] Overall, the discrepancy in emissions estimated in this study and that of *Arriaga-Colina et al.* [2004], suggests that total VOC and CO emissions are underestimated, perhaps by as much as factors of 2–3. While our confidence in the magnitude of the estimated emissions corrections is low, analysis of NMHC species identifies some sources which may be most severely underestimated. Because VOC

emissions are important for modeling the sensitivity of ozone to changes in emissions, addressing this uncertainty should be a focus of future research, using multiple methods simultaneously in improving emissions, measurements, and modeling [see *Molina and Molina*, 2002]. Methods of checking and improving the bottom-up emissions inventory include the remote sensing of vehicle emissions [*Beaton et al.*, 1992; *Bishop et al.*, 1997] - results from a recent study in Mexico City [*Comisión Ambiental Metropolitana and Instituto Mexicano del Petróleo*, 2000] should be used to construct a fuel-based emission inventory [*Harley et al.*, 1997; *Sawyer et al.*, 2000]. On the basis of experience elsewhere, it may be several years before agreement between bottom-up emissions inventories and top-down methods can be achieved.

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References

- Acosta, L. R., and W. F. J. Evans (2000), Design of the Mexico City UV monitoring network: UV-B measurements at ground level in the urban environment, *J. Geophys. Res.*, *105*(D4), 5017–5026.
- Arriaga, J. L., S. Escalona, A. D. Cervantes, R. Ordúñez, and T. López (1997), Seguimiento de COV en aire urbano de la ZMCM 1992–1996, in *Contaminación Atmosférica*, vol. 2, edited by L. G. Colín and J. R. Varela, pp. 67–98, Univ. Auton. Metrop.-Iztapalapa, Iztapalapa, Mexico.
- Arriaga-Colina, J. L., J. J. West, G. Sosa, S. S. Escalona, R. M. Ordúñez, and A. D. M. Cervantes (2004), Measurements of VOCs in Mexico City (1992–2001) and evaluation of VOCs and CO in the emissions inventory, *Atmos. Environ.*, *38*, 2523–2533.
- Báez, A. P., R. Belmont, and H. Padilla (1995), Measurements of formaldehyde and acetaldehyde in the atmosphere of Mexico City, *Environ. Pollut.*, *89*, 163–167.
- Báez, A. P., H. Padilla, M. C. Torres, and R. Belmont (2000), Ambient levels of carbonyls in Mexico City, *Atmosfera*, *13*, 121–131.
- Beaton, S. P., G. A. Bishop, and D. H. Stedman (1992), Emission characteristics of Mexico City vehicles, *J. Air Waste Manage. Assoc.*, *42*, 1424–1429.
- Bishop, G. A., D. H. Stedman, J. de la Garza Castro, and F. J. Dávalos (1997), On-road remote sensing of vehicle emissions in Mexico, *Environ. Sci. Technol.*, *31*, 3505–3510.
- Blake, D. R., and F. S. Rowland (1995), Urban leakage of liquefied petroleum gas and its impact on Mexico City air quality, *Science*, *269*, 953–956.
- Borja-Aburto, V. H., D. P. Loomis, S. I. Bangdiwala, C. M. Shy, and R. A. Rascon-Pacheco (1997), Ozone, suspended particulates, and daily mortality in Mexico City, *Am. J. Epidemiol.*, *145*(3), 258–268.
- California Air Resources Board (1997), Public meeting to consider approval and verification of the California Emissions Inventory, Sacramento, Calif., Nov.
- Carter, W. P. L. (2000), Documentation of the SAPRC-99 chemical mechanism for VOC reactivity, final report to California Air Resources Board, *Contract 92-329 and 95-308*, Calif. Air Res. Board, Sacramento, Calif. (available at www.cert.ucr.edu/~carter)
- Castro, T., L. G. Ruiz-Suárez, J. C. Ruiz-Suárez, M. J. Molina, and M. Montero (1997), Sensitivity analysis of a UV radiation transfer model and experimental photolysis rates of NO₂ in the atmosphere of Mexico City, *Atmos. Environ.*, *31*, 609–620.
- Chow, J. C., J. G. Watson, S. A. Edgerton, and E. Vega (2002), Chemical composition of PM_{2.5} and PM₁₀ in Mexico City during winter 1997, *Sci. Total Environ.*, *287*, 177–202.
- Comisión Ambiental Metropolitana (2001), Inventario de emisiones a la atmósfera, zona metropolitana del valle México, 1998, Mexico City.
- Comisión Ambiental Metropolitana (2002), Programa para mejorar la calidad del aire de la zona metropolitana del valle de México, 2002–2010, Mexico City.
- Comisión Ambiental Metropolitana and Instituto Mexicano del Petróleo (2000), Auditoría integral al programa de verificación vehicular, Mexico City.
- Departamento del Distrito Federal (1990), Programa integral contra la contaminación atmosférica: Un compromiso común (PICCA), Mexico City, Oct.
- Departamento del Distrito Federal (1996), Gobierno del Estado de México, Secretaría de Medio Ambiente Recursos Naturales y Pesca, and Secretaría de Salud, Programa para mejorar la calidad del aire en el valle de México, 1995–2000 (PROAIRE), Mexico City, March.
- Doran, J. C., et al. (1998), The IMADA-AVER boundary layer experiment in the Mexico City area, *Bull. Am. Meteorol. Soc.*, *79*(11), 2497–2508.
- Doran, J. C., and S. Zhong (2000), Thermally driven gap winds into the Mexico City basin, *J. Appl. Meteorol.*, *39*, 1330–1340.
- Edgerton, S. A., et al. (1999), Particulate air pollution in Mexico City: A collaborative research project, *J. Air Waste Manage. Assoc.*, *49*, 1221–1229.
- Environmental Protection Agency (1995), *Compilation of Air Pollution Emission Factors*, AP-42, vol. 1, 5th ed., Research Triangle Park, N. C.
- Environmental Protection Agency (1993), SPECIATE, VOC/PM speciation data system, version 1.50, Environ. Prot. Agency and Radian Corp., Research Triangle Park, N. C.
- Evans, J., et al. (2002), Health benefits of air pollution control, in *Air Quality in the Mexico Megacity: An Integrated Assessment*, edited by L. T. Molina and M. J. Molina, pp. 105–136, Kluwer Acad., Norwell, Mass.
- Fast, J. D., and S. Zhong (1998), Meteorological factors associated with inhomogeneous ozone concentrations within the Mexico City basin, *J. Geophys. Res.*, *103*(D15), 18,927–18,946.
- Fujita, E. M., B. E. Croes, C. L. Bennett, D. R. Lawson, F. W. Lurmann, and H. H. Main (1992), Comparison of emission inventory and ambient concentration ratios of CO, NMOG, and NO_x in California's south coast air basin, *J. Air Waste Manage. Assoc.*, *42*, 264–276.
- Funk, T. H., L. R. Chinkin, P. T. Roberts, M. Saeger, S. Mulligan, V. H. Páramo Figueroa, and J. Yarbrough (2001), Compilation and evaluation of a Paso del Norte emissions inventory, *Sci. Total Environ.*, *276*, 135–151.
- Gaffney, J. S., N. A. Marley, M. N. Cunningham, and P. V. Doskey (1999), Measurements of peroxyacyl nitrates (PANS) in Mexico City: Implications for megacity air quality impacts on regional scales, *Atmos. Environ.*, *33*, 5003–5012.
- Gakenheimer, R., et al. (2002), The MCMA transportation system: Mobility and air pollution, in *Air Quality in the Mexico Megacity: An Integrated Assessment*, edited by L. T. Molina and M. J. Molina, pp. 213–284, Kluwer Acad., Norwell, Mass.
- Guenther, A., C. Geron, T. Pierce, B. Lamb, P. Harley, and R. Fall (2000), Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America, *Atmos. Environ.*, *34*, 2205–2230.
- Harley, R. A., A. G. Russell, G. J. McRae, G. R. Cass, and J. H. Seinfeld (1993), Photochemical modeling of the Southern California Air Quality Study, *Environ. Sci. Technol.*, *27*, 378–388.
- Harley, R. A., R. F. Sawyer, and J. B. Milford (1997), Updated photochemical modeling for California's south coast air basin: Comparison of chemical mechanisms and motor vehicle emission inventories, *Environ. Sci. Technol.*, *31*, 2829–2839.
- Instituto Nacional de Ecología (2000a), Almanaque de datos y tendencias de la calidad del aire en Ciudades Mexicanas, Mexico City.
- Instituto Nacional de Ecología (2000b), Gestión de la calidad del aire en México, Mexico City, Oct.
- Kuebler, J., J.-M. Giovannoni, and A. G. Russell (1996), Eulerian modeling of photochemical pollutants over the Swiss plateau and control strategy analysis, *Atmos. Environ.*, *30*, 951–966.
- Los Alamos National Laboratory and Instituto Mexicano del Petróleo (1994), Mexico City Air Quality Research Initiative (MARI), *Rep. LA-12699*, Los Alamos, N. M.
- Mannschreck, K., D. Klemp, D. Kley, R. Friedrich, J. Kühlwein, B. Wickert, P. Matuska, M. Habram, and F. Slemr (2002), Evaluation of an emission inventory by comparisons of modeled and measured emissions ratios of individual HCs, CO and NO_x, *Atmos. Environ.*, *36*, 81–94.
- Marr, L. C., G. S. Noblet, and R. A. Harley (2002), Formation of photochemical air pollution in central California: 2. Impact of revised emissions on Eulerian model predictions, *J. Geophys. Res.*, *107*(D6), 4048, doi:10.1029/2001JD000690.
- McRae, G. J., W. R. Goodin, and J. H. Seinfeld (1982), Development of a second-generation mathematical model for urban air pollution: 1. Model formulation, *Atmos. Environ.*, *16*, 679–696.

- Mendoza-Dominquez, A., and A. G. Russell (2001), Estimation of emissions adjustments from the application of four-dimensional data assimilation to photochemical air quality modeling, *Atmos. Environ.*, **35**, 2879–2984.
- Milford, J. B., A. G. Russell, and G. J. McRae (1989), A new approach to photochemical pollution control: Implications of spatial patterns in pollutant responses to reductions in nitrogen oxides and reactive organic gas emissions, *Environ. Sci. Technol.*, **23**, 1290–1301.
- Molina, L. T., and M. J. Molina (Eds.) (2002), *Air Quality in the Mexico Megacity: An Integrated Assessment*, 408 pp., Kluwer Acad., Norwell, Mass.
- Molina, M. J., L. T. Molina, G. Sosa, J. Gasca, and J. J. West (2000), Analysis and diagnostics of the inventory of emissions of the metropolitan area of the valley of Mexico, *Rep. 5*, 59 pp., Mass. Inst. of Technol. Integrated Program on Urban Reg. and Global Air Pollut., Cambridge, Mass., Aug.
- Molina, M. J., L. T. Molina, J. J. West, G. Sosa, C. Sheinbaum, F. San Martini, M. A. Zavala, and G. McRae (2002), Air pollution science in the MCMA: Understanding source-receptor relationships through emissions inventories, measurements and modeling, in *Air Quality in the Mexico Megacity: An Integrated Assessment*, edited by L. T. Molina and M. J. Molina, pp. 137–212, Kluwer Acad., Norwell, Mass.
- Mugica, V., E. Vega, J. L. Arriaga, and M. E. Ruiz (1998), Determination of motor vehicle profiles for non-methane organic compounds in the Mexico City metropolitan area, *J. Air Waste Manage. Assoc.*, **48**, 1060–1068.
- Mugica, V., J. Watson, E. Vega, E. Reyes, M. E. Ruiz, and J. Chow (2002), Receptor model source apportionment of nonmethane hydrocarbons in Mexico City, *Sci. World J.*, **2**, 844–860.
- Mulholland, M., and J. H. Seinfeld (1995), Inverse air pollution modeling of urban-scale carbon monoxide emissions, *Atmos. Environ.*, **29**, 497–516.
- National Research Council (1991), *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, Natl. Acad., Washington, D. C.
- Nickerson, E. C., G. Sosa, H. Hochstein, P. McCaslin, W. Luke, and A. Schanot (1992), Project Águila: In situ measurements of Mexico City air pollution by a research aircraft, *Atmos. Environ. Part B*, **26**, 445–451.
- Osnaya, R. P., and J. R. Gasca (1998), Inventario de amoniaco para la ZMCM: Revision de Diciembre de 1998, *Proj. DOB-7238*, 23 pp., Mex. Pet. Inst., Mexico City.
- Pérez-Vidal, H., and G. Raga (1998), On the vertical distribution of pollutants in Mexico City, *Atmósfera*, **11**, 95–108.
- Pielke, R. A., et al. (1992), A comprehensive meteorological model system: RAMS, *Meteorol. Atmos. Phys.*, **49**, 69–91.
- Raga, G. B., and A. C. Raga (2000), On the formation of an elevated ozone peak in Mexico City, *Atmos. Environ.*, **34**, 4097–4102.
- Raga, G. B., D. Baumgardner, T. Castro, A. Martinez-Arroyo, and R. Navarro-Gonzalez (2001), Mexico City air quality: A qualitative review of gas and aerosol measurements (1960–2000), *Atmos. Environ.*, **35**, 4041–4058.
- Riveros, H. G., A. Alba, P. Ovalle, B. Silva, and E. Sandoval (1998), Carbon monoxide trend, meteorology, and three-way catalysts in Mexico City, *J. Air Waste Manage. Assoc.*, **48**, 459–462.
- Riveros, H. G., E. Cabrera, and P. Ovalle (2002), Vehicle inspection and maintenance, and air pollution in Mexico City, *Transp. Res., Part D*, **7**, 73–80.
- Ruiz, M. E., J. L. Arriaga, and I. Garcia (1996), Determinación de compuestos orgánicos volátiles en la atmósfera de la Ciudad de México mediante el uso de sistemas ópticos y métodos convencionales, *Atmósfera*, **9**, 119–135.
- Russell, A., and R. Dennis (2000), NARSTO critical review of photochemical models and modeling, *Atmos. Environ.*, **34**, 2283–2324.
- Russell, A. G., K. F. McCue, and G. R. Cass (1988), Mathematical modeling of the formation of nitrogen-containing air pollutants: 1. Evaluation of an Eulerian photochemical model, *Atmos. Environ.*, **22**, 263–271.
- Sawyer, R. F., R. A. Harley, S. H. Cadle, J. M. Norbeck, R. Slott, and H. A. Bravo (2000), Mobile sources critical review: 1998 NARSTO assessment, *Atmos. Environ.*, **34**, 2161–2181.
- Seigneur, C., et al. (2000), Guidance for the performance evaluation of three-dimensional air quality modeling systems for particulate matter and visibility, *J. Air Waste Manage. Assoc.*, **50**, 588–599.
- Solomon, P. A., E. B. Cowling, G. M. Hidy, and C. S. Furness (1999), Comprehensive overview of scientific findings from major ozone field studies in North America and Europe, NARSTO critical review, *Rep. TR-114238*, NARSTO, Pasco, Wash., available at <http://www.cgenv.com/Narsto/>.
- Streit, G. E., and F. Guzmán (1996), Mexico City air quality: Progress of an international collaborative project to define air quality management options, *Atmos. Environ.*, **30**, 723–733.
- Ulke, A. G., and M. F. Andrade (2001), Modeling urban air pollution in Sao Paulo, Brazil: Sensitivity of model predicted concentrations to different turbulence parameterizations, *Atmos. Environ.*, **35**, 1747–1763.
- Vega, E., V. Mugica, R. Carmona, and E. Valencia (2000), Hydrocarbon source apportionment in Mexico City using the chemical mass balance receptor model, *Atmos. Environ.*, **34**, 4121–4129.
- Velasco-Saldaña, H. E. (2001), Inventario de emisiones biogénicas a la atmósfera en la zona metropolitana del valle de México, M. S. thesis, Nac. Auton. de Mex., Mexico City.
- Velasco-Saldaña, H. E., E. Bueno, A. Sánchez-Soto, O. Fentanes, and A. Kamiya (2001), Mediciones y análisis del perfil vertical de contaminantes y parámetros meteorológicos en la Ciudad de México, in *Memorias del Seminario Internacional: Dispersión y Caracterización de Contaminantes Atmosféricos*, Inst. Nac. de Ecol., Mexico City.
- Watson, J. G., and J. C. Chow (2001), Estimating middle-, neighborhood-, and urban-scale contributions to elemental carbon in Mexico City with a rapid response aethalometer, *J. Air Waste Manage. Assoc.*, **51**, 1522–1528.
- Watson, J. G., J. C. Chow, and E. M. Fujita (2001), Review of volatile organic compound source apportionment by chemical mass balance, *Atmos. Environ.*, **35**, 1567–1584.
- Whiteman, C. D., S. Zhong, X. Bian, J. D. Fast, and J. C. Doran (2000), Boundary layer evolution and regional-scale diurnal circulations over the Mexico basin and Mexican plateau, *J. Geophys. Res.*, **105**(D8), 10,081–10,102.
- Winner, D. A., and G. R. Cass (1999), Modeling the long-term frequency distribution of regional ozone concentrations, *Atmos. Environ.*, **33**, 431–451.
- World Health Organization and United Nations Environment Programme (1992), *Urban Pollution in Megacities of the World*, Blackwell, Malden, Mass.

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