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Article

Analysis of Criteria Air Pollutant Trends in Three Mexican Metropolitan Areas

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Abstract: Data from the annual, seasonal, and hourly behavior of the criteria air pollutants CO, NO_2, SO_2, O_3, and PM_{10} in three Mexican metropolitan areas (the Mexico City Metropolitan Area (MCMA), Guadalajara Metropolitan Area (GMA), and Monterrey Metropolitan Area (MMA)) over the period 2000–2011 were analyzed; and compliance with Mexican air quality standards was evaluated, highlighting causes of specific episodes of high and low concentrations. Data analyzed were collected from automatic air-monitoring networks located in the MCMA (32 stations), GMA (8 stations), and MMA (5 stations). In the MCMA and MMA, correlations between wind direction and concentrations of SO_2 suggest that there was a considerable contribution of trans-boundary transport from outside of these areas. Analysis of annual trends revealed large reductions of CO in the MCMA, and SO_2 in the three metropolitan areas. However, the annual mean concentration of O_3 increased by 47% and 42% in the GMA and MMA, respectively, from 2000 to 2011, but decreased by 13% in the MCMA from 2005 to 2010. The annual mean

concentration of PM_{10} in the MMA was about 58% and 76% higher than that in the MCMA and GMA, respectively, from 2001 to 2010.

Keywords: air quality standards; criteria pollutants; Guadalajara; Mexico; Monterrey

1. Introduction

The Mexico City Metropolitan Area (MCMA), Guadalajara Metropolitan Area (GMA), and Monterrey Metropolitan Area (MMA) are the largest urban areas in Mexico. These areas have the highest population densities, highest growth rates, and most industrial establishments in Mexico; furthermore, they provide the greatest economic contributions to the country [1]. Air pollution has been of great concern in these metropolitan areas over the past few decades. A statistic that exemplifies the urgency of reducing air pollution is the rate of growth of car ownership in Mexico (6.32% per year, with 850 vehicles per 1000 inhabitants from 1980 to 2010), which exceeds the rate of growth of the population (2.41% per year from 1980 to 2010) [2].

In the early 1990s, the United Nations considered the atmosphere over the MCMA to be among the most polluted on Earth [3]. Today, the situation has improved substantially for the criteria of air pollutants NO_2, CO, and SO_2 because of enforcement of environmental regulations, although the concentrations of O_3 and particulate matter with an aerodynamic diameter less than 10 μm (PM_{10}) have remained high. The MCMA has been the most studied area in Mexico for many years and is regarded as a model for other cities in Mexico and Latin America. Considerable research on high-ozone episodes in the MCMA; the influence of fossil fuel consumption on the air quality of MCMA; and photochemical reactions, the fate of volatile organic compounds (VOCs), and aerosol formation has been carried out [4–10].

Fewer air pollution studies have been conducted in the GMA and MMA than in the MCMA. In the GMA, Davydova-Belitskaya *et al.* [11,12] investigated characteristic climate patterns, the efficiency of the air-monitoring network, and the impact of industrial emissions in the period 1994–1996; Ramirez-Sanchez *et al.* [13] studied the spatial-temporal distribution of criteria pollutants from 2000 to 2005, reporting mainly the numbers of days exceeding the norms, averages and monthly maximums; further, Limon-Sanchez *et al.* [14] measured the concentration of black carbon (BC) in particulate matter with aerodynamic diameters less than 2.5 μm ($PM_{2.5}$) in 2008 at 2 air monitoring stations. In the MMA, the high level of particulate matter has been of great concern. Aldape *et al.* [15] and Alfaro-Barbosa and Barajas-Herrera [16] investigated the emission sources of particulate matter in the MMA in a short period of low particle concentrations in 2006, but few studies on other aspects of the high level of particulate matter in the MMA exist.

The local governments of the Mexico City, Guadalajara, and Monterrey metropolitan areas have reported summaries of air pollution levels [17–19], but their main focus has been on the extent to which the Mexican air quality standards have been met (although an in-depth analysis of the causes of the concentration fluctuations in the MCMA was provided in PROAIRE 2011–2020 [18]). In 2011, the National Institute of Ecology (INE) published the "Cuarto almanaque de datos y tendencias de la calidad del aire en 20 ciudades Mexicanas", a compendium of air quality trends in 20 Mexican cities

from 2000 to 2009, but reasons for the concentration variations or differences among cities were not examined. Unlike previous analyses (by the local governments or previous researchers), the present study clarifies causal relationship between meteorological conditions and air-pollutant concentration, and the consequences of implementation of mitigation measures.

By 2012, in Mexico, 80 urban areas had installed air monitoring stations, but only in the three largest metropolitan areas (Mexico City, Guadalajara, and Monterrey) have air monitoring data been recorded continuously since the beginning of their establishment [20]. Various studies have revealed that in some Mexican areas, the air quality has improved, but in others with high population density and without adequate implementation of programs to prevent air pollution, the pollutant concentrations have increased [17–20]. Therefore, a comparative study of the three metropolitan areas will be helpful in identifying the causes for the current states of air pollution.

The present study, based on ground-level monitoring data from 2000 to 2011, describes and compares the status of air pollution in the MCMA, GMA, and MMA. It confirms a number of conclusions from previous studies in the selected areas [17–19] and the impact of action plans during a long period of time in areas such as the MCMA. Annual trends, seasonal variations, and diurnal behavior of criteria pollutants are analyzed, and the extent of achievement of air quality standards is evaluated. For ozone, annual trends of the correlation between the daily maximum temperature and the maximum ozone concentration are compared among the three metropolitan areas, and differences in the characteristics of the precursor substances are examined. The approaches of the present study creates a paradigm for future studies in other areas where identification of predominant factors affecting the air quality is not trivial, and temporal variations of pollutant concentrations are not easily predictable. It is expected that the strategy of this research be extended to other urban areas at different stages of economic growth.

1.1. Study Area

The MCMA, GMA, and MMA are located in the central, western, and northern parts of Mexico, respectively (Figure 1). Major characteristics of these areas are described in Table 1. Besides the typical four-season division, Mexican seasons can be divided into a dry-warm season (March to May), a dry-cold season (November to February), and a rainy season (June to October). The rainfall intensity in the MMA is different from that in the other areas because of its location in the northern part of Mexico and the influence of the Atlantic. The GMA is influenced by the Pacific, whereas the MCMA is affected by both the Atlantic and the Pacific, depending on the strength and expanse of their air masses.

According to INEGI [21], the climate in the MCMA is mostly temperate sub-humid. The annual mean temperature in 2011 was 17 °C; maximum temperatures are recorded from March to May; and the minimum temperature occurs mostly in January. In most of the GMA, the climate is warm sub-humid [21]. The annual mean temperature in 2011 was 20.5 °C; high temperatures are recorded from May to September; and the lowest temperature occurs in January. In the MMA, the predominant climate is dry and semidry. The annual mean temperature recorded in 2011 was 23 °C; maximum temperatures are recorded from May to August; and the minimum temperature occurs in January.

Figure 1. Locations of the three Mexican metropolitan areas, land use, territorial division, and locations of the air-monitoring stations.

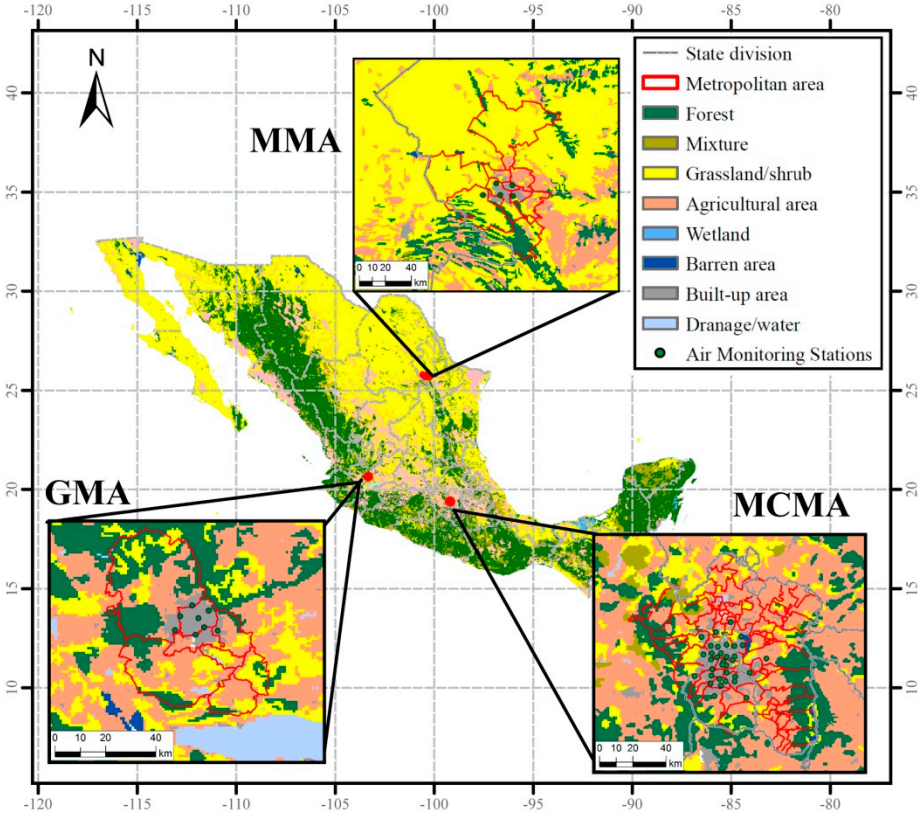


Table 1. Major characteristics of the study areas [a].

Metropolitan Area	Population	States	Average Altitude (MSL)	Coordinates (Central Point in the Metropolitan Area)
MCMA	20,116,842	Distrito Federal (DF), Hidalgo, Mexico	2240	19°22′N 99°9′W
GMA	4,434,878	Jalisco	1540	20°41′N 103°21′W
MMA	4,106,054	Nuevo León	540	25°40′N 100°19′W

[a] Source: www.inegi.org.mx (accessed: 14 January 2012). MSL: meters above sea level.

2. Methods

We collected continuous hourly data for air pollutants designated as criteria species by Mexican legislation (CO, NO_2, SO_2, O_3, and PM_{10}; Table 2) from automatic air-monitoring networks located in the MCMA (32 stations), GMA (8 stations), and MMA (5 stations). In order to compare the air quality data in urban areas where air monitoring networks are present, the Mexican legislation defines specific measurement and calibration procedures. In the calibration procedures, monitoring equipment is calibrated using standard gases at prescribed temperature (25 °C) and pressure (1 atm). Besides, authorities responsible for the air-monitoring networks are required to adopt NOM-156-SEMARNAT-2012, which describes the instructions of operation, calibration of the equipment, maintenance procedures, and

QA/QC (Quality Assurance/Quality Control) processes to secure quality and traceability of air-monitoring data. Calibration quality and evaluation of the performance of the air monitoring stations up to 2009 in each area can be consulted in INE-SEMARNAT, 2011 [22].

Table 2. Comparison of air quality standards (MPL) in Mexico, the US, the EU, and the World Health Organization (WHO).

Pollutant	Mexican Norm	Sampling Time	Mexico		United States [1]	European Union [2]		WHO [3]
			ppm	µg/m^3 [a]	Primary Standards	µg/m^3	Permitted Exceedance Each Year	µg/m^3
CO	NOM-021-SSA1-1993	8 h	11.0 [b]	12,595	9 ppm	10,000		
NO_2	NOM-023-SSA1-1993	1 h	0.21 [b]	395	100 ppb [f]	200	18	200
SO_2	NOM-022-SSA1-2010	24 h	0.11 [b]	288	75 ppb [g]	125	3	20
		1 year	0.025	66				
O_3	NOM-020-SSA1-1993	1 h	0.11 [b]	215.6				
		8 h	0.08[c]	156.8	0.075 ppm	120	25	100
Total suspended particulate	NOM-025-SSA1-1993	24 h		210 [d]				
PM_{10}		24 h		120 [d]	150 µg/m^3 [h]	50	<35	50
		1 year		50 [e]		40	n/a	20
$PM_{2.5}$		24 h		65 [d]	35 µg/m^3 [f]		n/a	25
		1 year		15 [e]	12 µg/m^3 [i]	25	n/a	10

n/a: not applicable. [1] Source: US EPA National Ambient Air Quality Standards, www.epa.gov/air/criteria.html (accessed on 9 October 2013). [2] Source: European Commission, http://ec.europa.eu/environment/air/quality/standards.htm (accessed on 21 September 2014). [3] Source: World Health Organization, http://www.who.int/en/ (accessed on 9 October 2013). [a] Assumed standard temperature and pressure (25 °C, 1 atm) without regard to the actual local conditions. [b] Not to be exceeded more than once per year. [c] Fifth maximum value in a year. [d] 98th percentile. [e] Annual arithmetic mean. [f] 98th percentile, averaged over 3 years. [g] 99th percentile of 1-hour daily maximum concentrations, averaged over 3 years. [h] Not to be exceeded more than once per year on average over a 3-year period. [i] Annual arithmetic mean, averaged over 3 years.

The concentration of a gaseous pollutant is expressed by a volume mixing ratio such as ppbv (denoted interchangeably by ppb) suited for evaluating human exposure. The monitoring equipment outputs the correct volume mixing ratio independent of the atmospheric pressure. It should be noted that for a given emission rate expressed in mass per unit time and unit area, the mixing ratio becomes higher at lower atmospheric pressure (higher elevation) assuming that the ventilation rate is independent of elevation.

Data used in the present analysis were from stations equipped with monitors of CO, NO_2, SO_2, O_3 and PM_{10} in the GMA and MMA; in the case of the MCMA, different sets of air monitoring stations were considered for different pollutants: CO (26), NO_2 (21), SO_2 (28), O_3 (24) and PM_{10} (14), where

numbers in parenthesis indicate the numbers of stations. These stations are classified based on their location: urban (23 in the MCMA, 8 in the GMA and 4 in the MMA), sub-urban (5 in the MCMA and 1 in the MMA), industrial-urban (1 in the MCMA), downtown (1 in the MCMA) and traffic (a station located within 1 km from major traffic roads; 2 in the MCMA). Because the stations are distributed almost uniformly in space covering different types of land use, the averages from all these stations are expected to represent the general state of the air quality in each metropolitan area. It is of great interest to examine the differences in pollutant behaviors among different typologies of monitoring stations as has been done in other parts of the world [23,24]. However, due to the limited number of stations in each category, such studies in Mexican urban areas are not feasible at present.

The MCMA database was obtained from the internet site of the Secretary of the Environment of the Distrito Federal (DF) Government [25]. GMA data were obtained from the database of the Atmospheric Monitoring System of Jalisco, and MMA data were obtained from the Ministry of Sustainable Development of Nuevo León. We note that the data from the GMA and MMA were obtained through institutional agreements. Characteristics of the air-monitoring stations, such as neighborhood conditions, were obtained from the First Catalog of Air Monitoring Stations in Mexico [26]. Meteorological data were obtained from the Mexican National Weather Service (SMN). The division in charge of collecting the information in each area preprocessed hourly monitoring data in these databases. Preprocessing methodology includes neglecting data collected while the equipment was not functioning properly due to energy supply failures or other operational problems (including monitor offline).

After collecting the hourly data of criteria gases, daily and monthly averages were calculated per station only if 75% of the data were valid. Missing values and untrustworthy data were excluded from the analysis. The threshold 75% was applied to keep statistical bias as small as possible. Spatial averages of the study areas were calculated only for hours when there were at least 75% of the stations with valid data. A linear regression analysis was performed to analyze the annual mean trend in each study area. Validation and processing of data were performed according to the Manual 5: Protocol to manage air quality data, issued by the National Institute of Ecology of Mexico in 2010, which defines procedures for excluding outliers and calibrating monitors. Due to the large amount of data, only averages in the study area were examined closely in the present study. The timeframe for analysis was January 2000 to December 2011. Statistical measures (regional, daily, monthly, and annual averages, and 2nd, 10th, 25th, 75th, 90th, and 98th percentile values) were calculated only when there were more than 75% valid data. To compare the Mexican air quality standards with other air quality standards, statistical measures, such as an 8-h moving average or annual maximum, were determined (Table 2).

3. Results and Discussion

3.1. Carbon Monoxide

Combustion of hydrocarbons in a limited supply of oxygen produces carbon monoxide, a colorless, odorless, toxic gas. In Mexico, CO emitted from vehicles is the principal source of carbon monoxide, accounting for 91.8% of the total (38,521 kton/year) in 2005 [27]. Monthly average concentrations of CO in the MCMA, GMA, and MMA over the study period are shown in Figure 2a. In all study areas, high concentrations of CO were present during the dry-cold season, because strong atmospheric

stability suppressed dilution of pollutants, particularly in the morning rush hours. Low concentrations were observed in the rainy season, when mixing in the boundary layer was vigorous.

Figure 2. Variation of the monthly average concentrations of (**a**) CO, (**b**) NO_2, (**c**) SO_2, and (**d**) O_3 in the three Mexican metropolitan areas from 2000 to 2011.

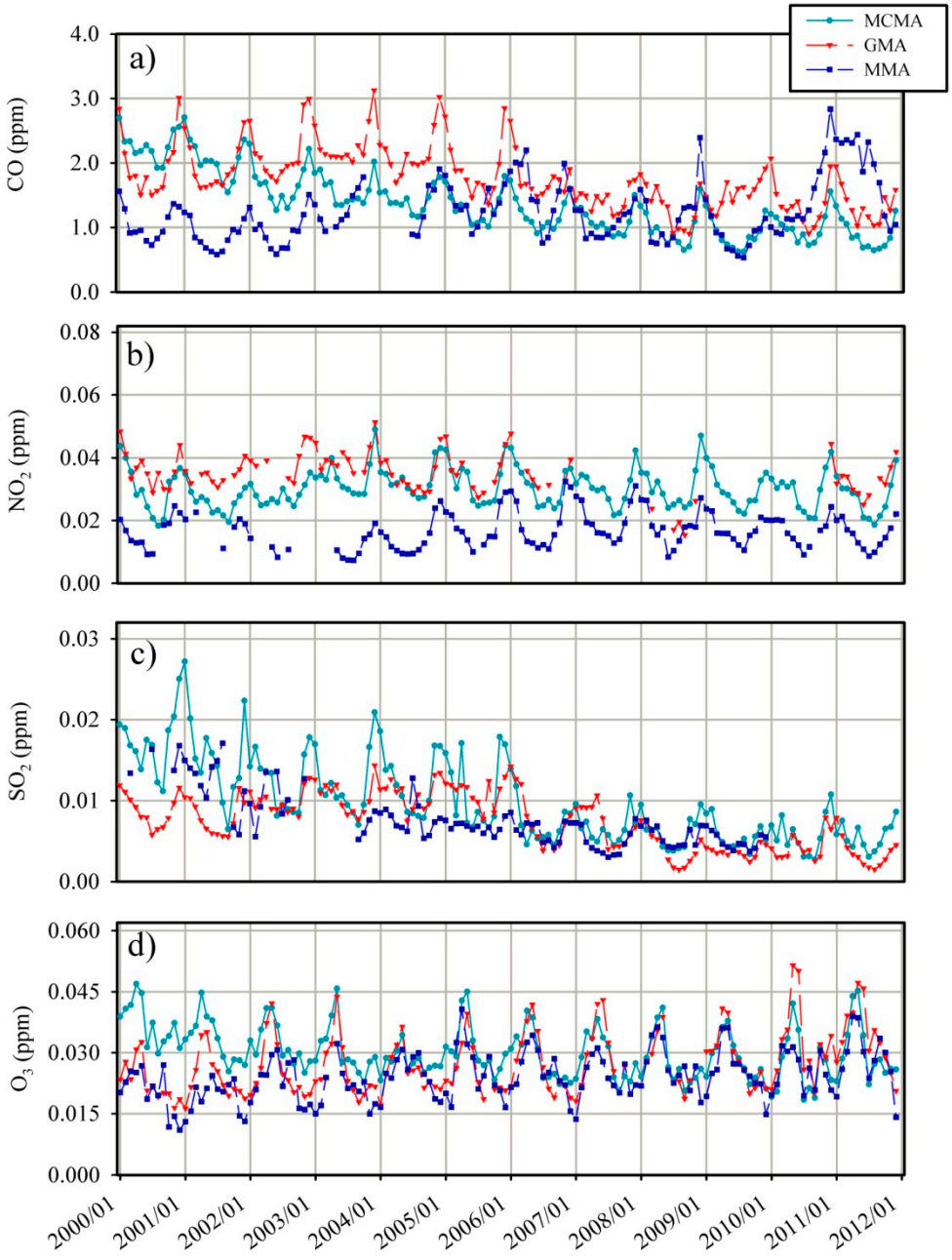
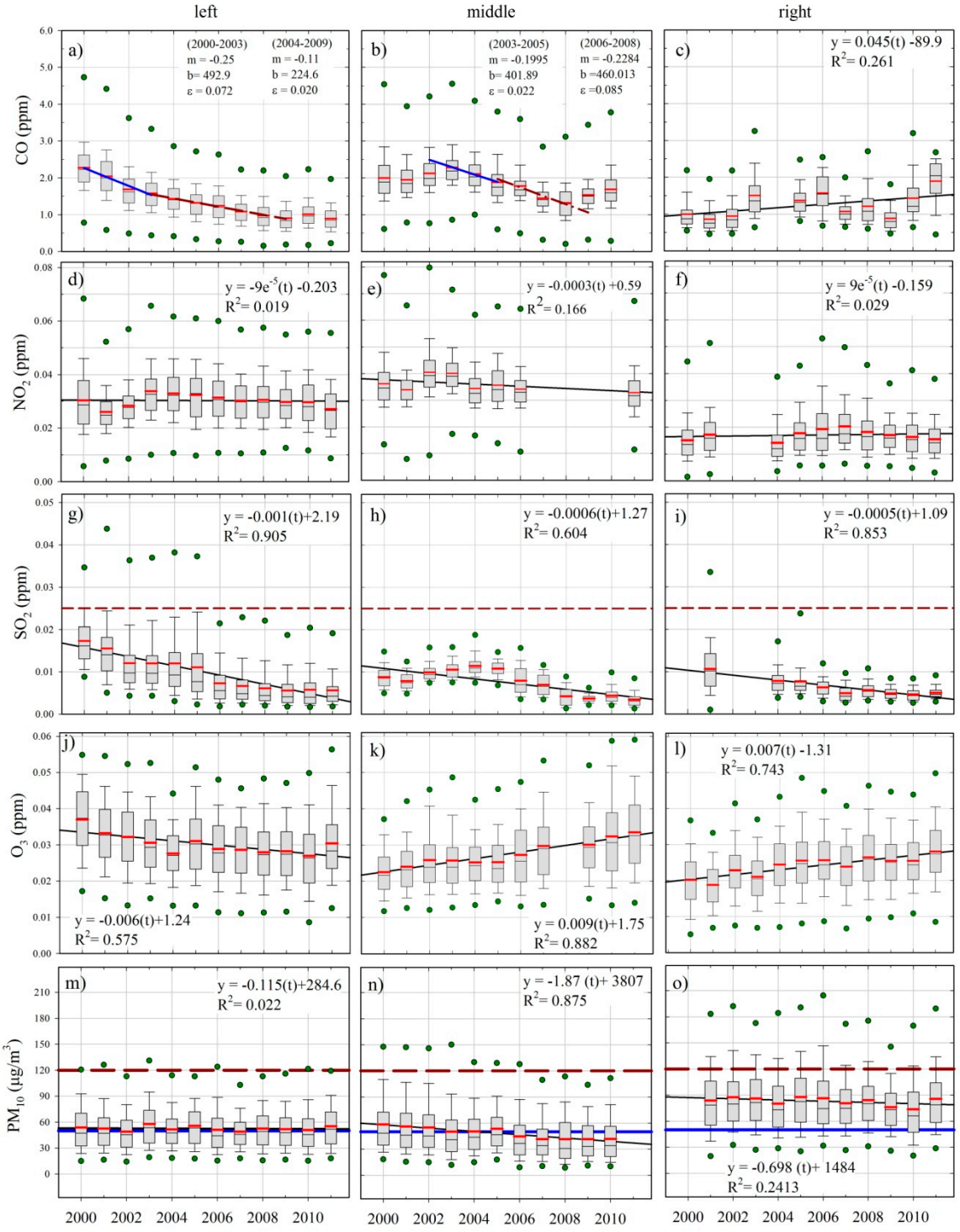


Figure 3a–c show trends for the annual mean concentration of CO in the MCMA, GMA, and MMA, respectively. In Mexico, in 2006, NOM-041-SEMARNAT-2006 (which defined limits of pollutant emissions from mobile sources) was issued and various actions were implemented in federal and local governments. By 2013, 16 Mexican states had programs for certification of vehicular emission, but only in 12 states (including Mexico state and DF in the MCMA) were the programs mandatory; in other areas such as the GMA and MMA, the fulfillment of the norm was a choice of the individuals without penalty [20].

Figure 3. Trends for annual mean concentrations of CO, NO_2, SO_2, O_3, and PM_{10} in the (**left**) Mexico City Metropolitan area (MCMA), (**middle**) Guadalajara Metropolitan area (GMA), and (**right**) Monterrey Metropolitan area (MMA). The panels show the mean (red line), median (black line), and the 2nd to 98th (green circles), 10th to 90th (bars), and 25th to 75th (gray boxes) percentiles of daily averaged concentrations. The dashed red and solid blue lines show the levels of the corresponding air quality standard in Mexico for SO_2 and PM_{10} (see Table 2).



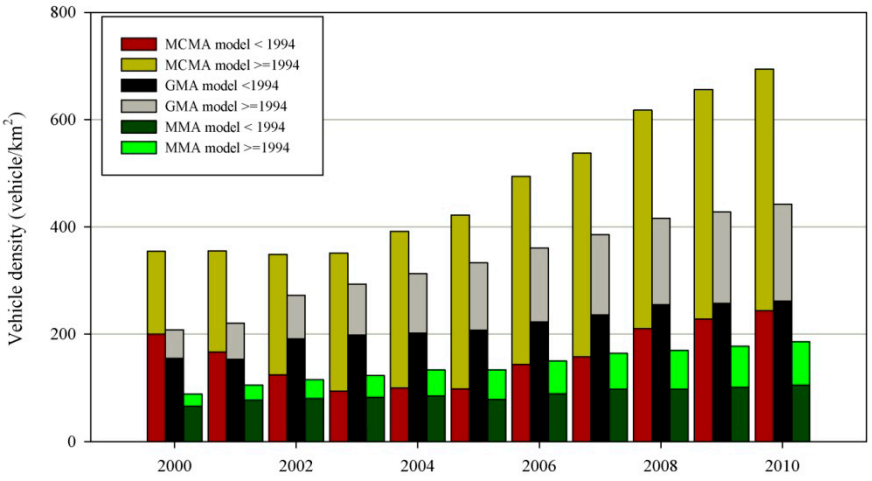
In (a) and (b) m, b and ε represent the value of the slope, intercept and standard error respectively, from the regression analysis for the indicate period of time.

In understanding the trends of CO concentration, characteristics of vehicle fleet are important. Figure 4 shows the number density of vehicles of model year older than 1994, and newer than or equal to 1994. The model-year division at 1994 has significance in that three-way catalytic converters with closed-loop controls were introduced on private vehicles in 1993, resulting in much smaller CO emission factors, 2.11 g/km estimated for 1993 and newer models (EF_{MC_n}) compared to >7 g/km for older models (EF_{MC_o}) [28].

A reduction of ~61% in the annual mean concentration of CO in the MCMA from 2000 (2.28 ppm) to 2011 (0.88 ppm) was partly due to the improvement in the public transportation system (subway, trolley bus and metrobus) and the replacement of buses conducted as part of the PROAIRE 2002–2010 air quality management program. Other actions of PROAIRE were the modification of the threshold of emission of pollutants from vehicular sources in the MCMA, in which the threshold was reduced to about a third of the values for other urban areas determined in 1999 (NOM-041-SEMARNAT-2006).

To evaluate the influence of such actions in the MCMA, two periods were analyzed: 2000–2003 and 2004–2009 (Figure 3a). In the first period, the number of vehicles remained almost constant, but replacement of older models with newer models equipped with catalytic converters proceeded rapidly, whereas in the second period, the number of vehicles increased for both older and newer models (Figure 4). In Figure 5, the annual mean of CO in the MCMA was normalized by the gross estimate of the total vehicle emissions using the above-mentioned emission factors. The flat trend in the first period indicates the effect of change in the vehicle composition; the decrease in CO was caused probably by the vehicle replacement. The decrease in the second period could be due to improved emission factor over the value used in the estimate, better traffic control, or decrease in the background concentration (which could have been occurring in the first period as well). However, it is not clear what the most important factor was.

Figure 4. Distributions of vehicles by model year in the MCMA, GMA, and MMA from 2000 to 2010 based on data from www.inegi.gob.mx (accessed on 15 February 2012).



Vehicle density is largest in the MCMA (Figure 4), but vehicle emission regulations are stricter in the MCMA than in the GMA and MMA, which may have contributed to the satisfaction of the Mexican air quality standard for CO of 11 ppm (maximum value of 8-h moving averages) and a notable decrease in the annual trend in the MCMA over the analysis period.

In the GMA, the standard was exceeded in 2000, 2002, 2003, 2004, and 2005; the maximum CO concentrations were close to the limit in 2001, 2006, and 2010; and the standard was satisfied in the remaining years (Figure 6). Assuming the emission factors mentioned above, in 2010, the effective emission factor weighted by the number of vehicles in each model-year category was 3.8 g/km in the MCMA, 5.0 g/km in the GMA, and 4.9 g/km in the MMA. The relatively high density of vehicles in the GMA (Figure 4), together with the high estimated effective emission factor, may have led to the high CO concentrations in the GMA. Importantly, 7 of the 8 air-monitoring stations in the GMA are close (<200 m) to heavily trafficked roads. Thus, these stations may have preferentially detected CO from vehicular activity because CO emissions were poorly diluted near the stations. In contrast, the monitoring stations in the MCMA and MMA are mainly located close to moderately trafficked roads.

Figure 5. Influence of the total vehicle emissions in the CO annual mean concentration in the MCMA. Total vehicle emissions was calculated as the sums of the products between emission factors (EF_{MC_n} or EF_{MC_o}) and the annual vehicle amount according to the model division: model ≥ 1994 (Veh_{new}) and model < 1994 (Veh_{old}).

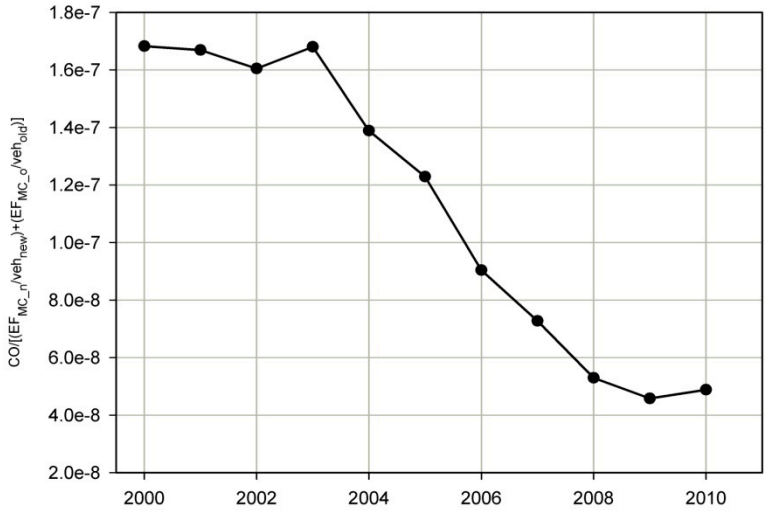
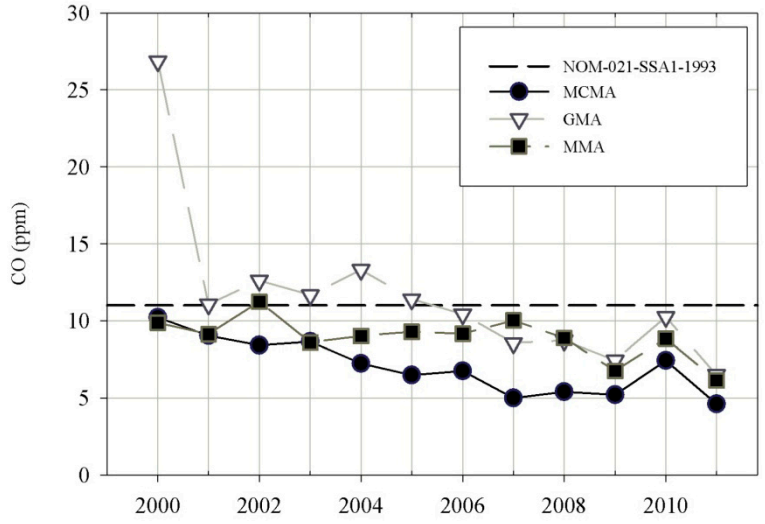


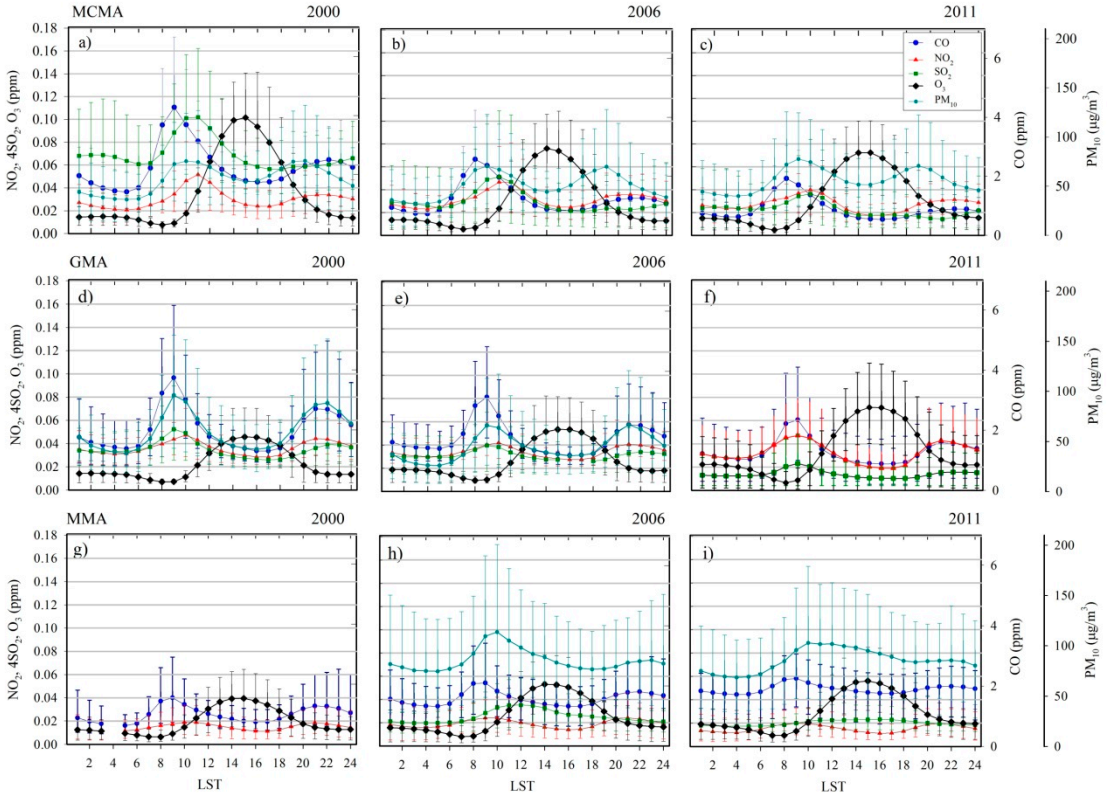
Figure 6. Maximum values of 8-h moving-average CO concentrations in the three Mexican metropolitan areas. The dashed horizontal line indicates the MPL in Mexico.



In the GMA, various factors seem to have influenced the annual trend (Figure 3b). Vehicular emissions verification was established in 1991, but was suspended without clear reasons in 1992 [19]. Until 2001, when the vehicular verification became mandatory, there was no system for penalty against violation. Upon the introduction of NOM-041-SEMARNAT-2006, the ratio of vehicles satisfying the CO emission regulation rose from 15% in 2005 to 30% in 2006, 36% in 2007, and 28% in 2008, although the ratio dropped to 18% in 2009 [19]. To evaluate its effect, temporal trends in two periods (2003–2005 and 2006–2008) were examined by linear regression analysis, but no significant difference was found between the two periods. Therefore, there is no simple explanation for the temporal trend of CO in the GMA.

Figure 7 shows the hourly behavior of CO in the MCMA, GMA, and MMA in 2000, 2006, and 2011. In all study areas, the CO levels increased sharply at 08–09 local standard time (LST), coincident with the beginning of ordinary human activities. Around 18 LST, when the workday usually ended, the CO concentrations began to rise and eventually peaked at 21–22 LST (the evening rush hours in Mexican urban areas) at values lower than those in the morning. The difference between the shapes of the peaks can be explained as follows: in the morning, vehicle use was high for a short period of time because people were going to work and taking their children to school; in the afternoon, vehicle use was distributed over various times as students returned from their school activities; in the evening, vehicle use increased as people returned from work, but at a slower rate and at a lower intensity than in the morning. A more stable atmosphere in the morning than in the evening also contributed to the difference between the shapes of the peaks [29].

Figure 7. Diurnal behavior of CO, NO_2, SO_2, O_3, and PM_{10} in the MCMA (**a**–**c**), GMA (**d**–**f**), and MMA (**g**–**i**) during 2000, 2006, and 2011. The bars indicate the range from the 10th to the 90th percentiles.



In the MCMA, the morning peak shifted from 09 LST in 2000 and 2001 to 08 LST in subsequent years (Figure 7a–c.). A probable cause for this shift is the rapid increase in the fleet density of newer-model vehicles (Figure 4) from 2000 to 2005, which may have caused a progressive saturation of the roads and reduced the mean vehicle speed from 38.5 km/h in 1990, to 21 km/h in 2004, to 17 km/h in 2007 [30], prompting people to shift their daily schedule to earlier hours.

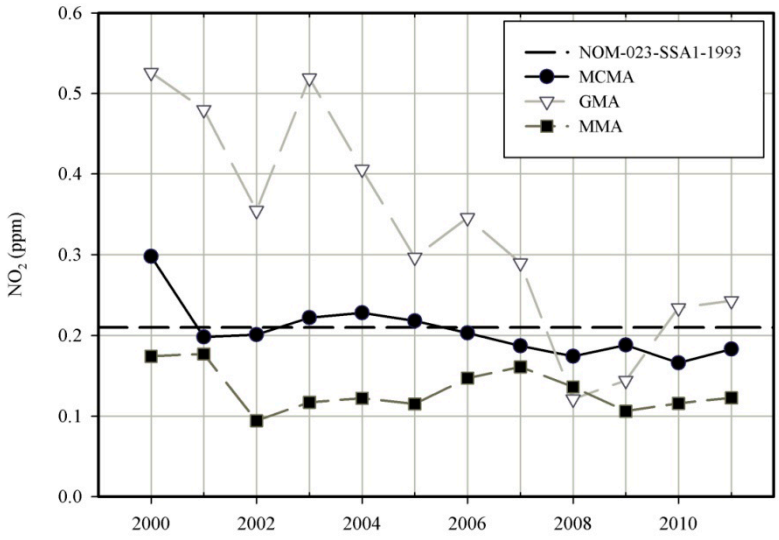
3.2. Nitrogen Dioxide

Nitric oxide (NO) and nitrogen dioxide (NO_2) are collectively called nitrogen oxides (NOx). They play important roles in ozone formation and depletion as well as in secondary particle formation. According to INEM-2005 [27], the main sources of NOx in Mexico in 2005 have been vehicles (44.7%), natural sources (38.6%), and industry (13.2%). Figure 2b shows the seasonal variation of NO_2 in the three study areas. Minima occurred in summer (June to September), and maxima in winter, although there were considerable fluctuations.

The annual mean concentration of NO_2 in the MCMA remained nearly constant from 2003 to 2010, but fell 9% from 2010 to 2011 (Figure 3d). In the MMA, the annual mean concentrations of NO_2 were considerably larger than the median values because of frequent episodes of high NO_2 concentrations (Figure 3f).

In the GMA, the percentage of valid data was <75% from 2007 to 2010, so trends for the annual mean concentration of NO_2 could not be evaluated with a good accuracy for those years (Figure 3e). Instead, we examined the annual trend for the maximum 1-h average, for which an environmental standard has been set (Table 2, Figure 8). Figure 8 shows that the air quality standard was exceeded in all years from 2000 to 2011, except 2008 and 2009, and a decreasing trend is evident from 2000 to 2008.

Figure 8. Maximum values of 1-h averages of NO_2 concentrations in the three Mexican metropolitan areas. The dashed horizontal line indicates the maximum permissible limit (MPL) in Mexico.



The NO_2 concentrations in all study areas peaked in the morning and again in the evening, coincident with increased NO_2 emissions during the morning and evening rush hours (Figure 7). In the

MCMA, the morning peak occurred at 10–11 LST, whereas the evening peak occurred at 20–21 LST, almost at the same time as the evening CO peak. The ratio of the morning NO_2 peak height to the evening NO_2 peak height was much larger in the MCMA than in the GMA and MMA, possibly because more NO and VOCs, which oxidize NO to NO_2, were emitted in the morning than in the evening in the MCMA.

In the GMA, the morning NO_2 concentration peaked at 10 LST from 2000 to 2006, but at 09 LST in 2010, almost 1 h earlier than in the MCMA. In 2011, the morning NO_2 peak coincided with the morning CO peak. This behavior implies that the reaction between NO and oxidants such as VOCs and O_3 was faster in the GMA than in the MCMA.

In the MMA, after 2004, the morning NO_2 peaks at 09–10 LST were coincident with the morning CO peaks. However, in 2000 and 2001, the morning NO_2 peaks were observed at 10–11 LST, almost 1 h later than the CO peaks.

3.3. Sulfur Dioxide

According to INEM-2005 [27], the main source of SO_2 in Mexico in 2005 was industrial activity, accounting for 91.1% of total SO_2 emissions (2825 kton/year). Generation of electricity accounted for 49.7% of the industrial total (1403 kton/year), whereas extraction and processing of petroleum together with manufacturing of petrochemicals accounted for 39.8% of the industrial total (1124 kton/year).

In all study areas, high concentrations of SO_2 were recorded during the winter, whereas low concentrations were recorded during the rainy season, owing to dissolution of SO_2 in cloud water [31] and removal by wet deposition (Figure 2c).

In the GMA, maximum monthly SO_2 concentrations occurred from November to January, whereas minimum concentrations were recorded over a relatively wide range of months from June to October. In the MMA, behavior was irregular from 2000 to 2003 (concentration data for some months were not included in the source database and are therefore missing in Figure 2c). From 2004 to 2009, concentration data for all months satisfied the 75% valid-data criterion, and the behavior was a little more regular, with maximum values in July (2004) and from December to February (2004–2009), and minimum values in July (2007, 2008), September (2004, 2006, 2009), and October (2005).

The annual mean concentration of SO_2 in the MCMA decreased ~67% from 2000 to 2011 (Figure 3g). The annual mean values were substantially larger than the median values because of sporadic occurrences of particularly high values. The annual mean values for the GMA showed a generally increasing trend from 2000 to 2004, but a decrease of 68% from 2005 to 2011 (Figure 3h). The annual mean values for the MMA showed a decrease of 36% from 2004 to 2011 (Figure 3i).

The NOM-022-SSA1-2010 air quality standard for annual mean concentration of SO_2 was satisfied over the entire analysis period in all study areas (Figure 3). The 24-h-average maximum permissible limit (MPL), however, was satisfied only in the GMA and MMA during the analysis period (Figure 9). The MCMA exceeded the 24-h-average MPL of 0.11 ppm in 2000 and 2001 (0.129 ppm and 0.256 ppm, respectively), and matched or came close to the 24-h-average MPL in 2002 and 2005 (0.11 ppm and 0.109 ppm, respectively). The 24-h-average concentration of SO_2 in the GMA was below the MPL by a wide margin throughout the analysis period. MMA had the lowest 24-h-average maxima of all study areas from 2004 to 2010. Furthermore, three groups of concentration levels can be distinguished: a first

group from 2000 to 2001, a second from 2002 to 2005, and a third from 2006 to 2011. The reduction of SO_2 concentration in the MCMA from 2001 to 2002 can be attributed to implementation of the PROAIRE Program to Improve Air Quality in the MCMA 2002–2010, which provided guidelines and action plans for reducing emissions from combustion of fossil fuels in industry and power generation. In addition, in 2004, the Mexican National Refining System started distributing Premium gasoline (containing 250–300 ppm sulfur) to replace Magna gasoline (containing 300–500 ppm sulfur). The concentration of SO_2 in the MCMA decreased from 2005 to 2006, and the SO_2 levels in all study areas decreased significantly in 2006 (Figure 3), when NOM-086-SEMARNAT-SENER-SCFI-2005, which limited the sulfur concentration in liquid and gaseous fossil fuels sold in the MCMA, GMA, and MMA, was put into effect. In October 2006, refiners reduced the concentration of sulfur in both Premium and Magna gasoline to 30–80 ppm, and the maximum allowable sulfur in diesel oil has been reduced from 500 ppm to 15 ppm since January 2009 [32,33]. Moreover, November 2007 was the deadline to fulfill the NOM-148-SEMARNAT-2006 was implemented, which strengthened the requirements for the recovery of sulfur in oil-refining processes to reduce the amount of sulfur in emissions by 90% or more.

Figure 9. Maximum values of 24-h averages of SO_2 concentrations in the three Mexican metropolitan areas. The dashed horizontal line indicates the MPL in Mexico.

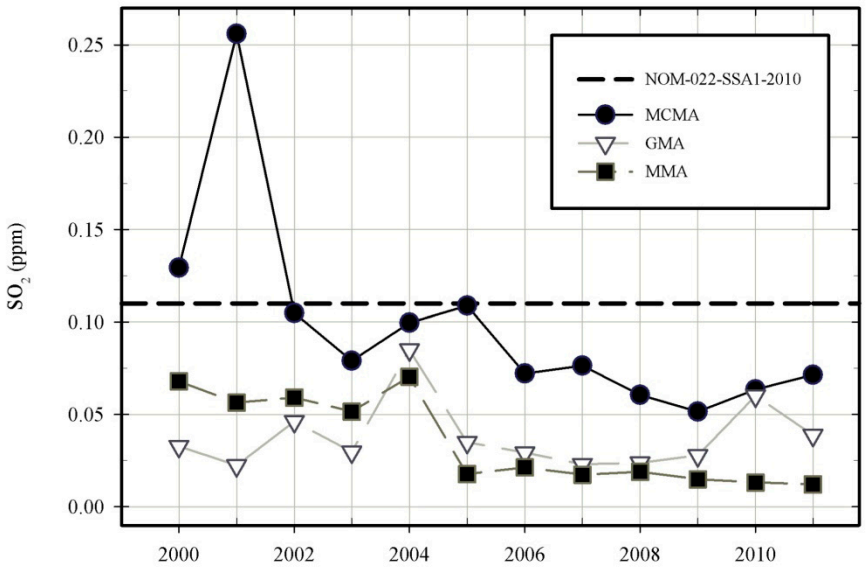


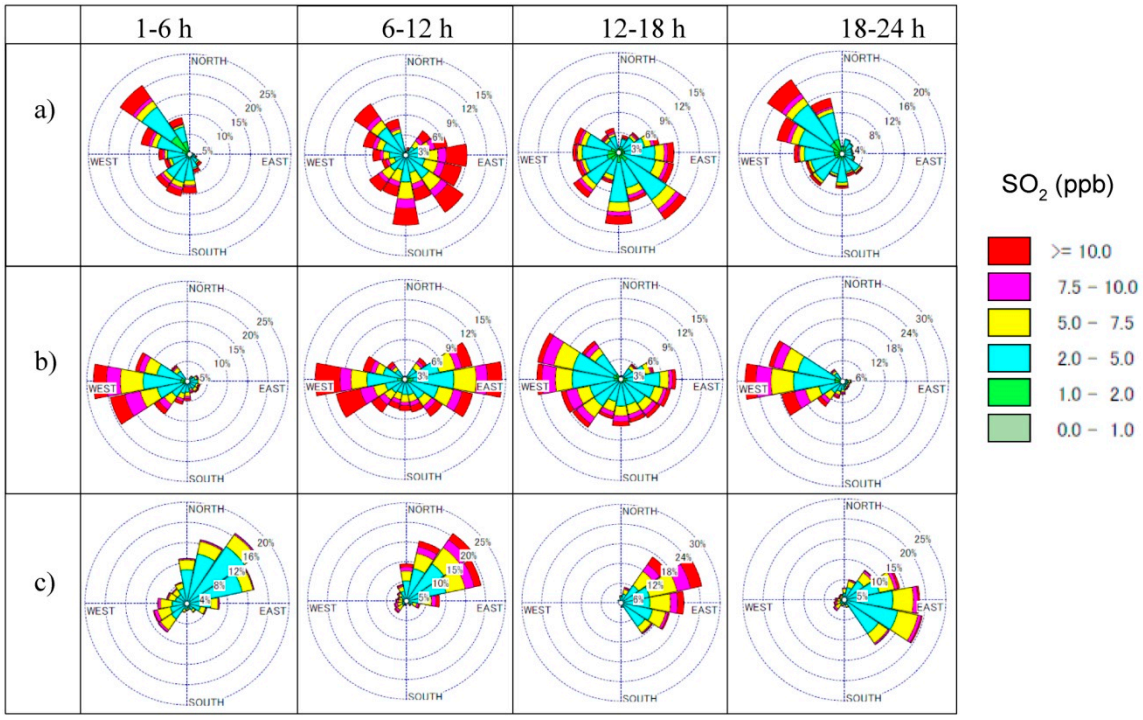
Table 3. Estimated annual emission of SO_2 (tons/year) from the Tula complex.

Year	Power Plant	Oil Refinery
2002	158,330 [1]	n/e
2005	132,374 [2]	132,368 [2]
2007	n/e	75,057 *,[3]
2008	135,705 [4]	76,400 [4]
2009	n/e	61,857 *,[3]
2010	135,705 [5]	n/e

n/e: not estimated. * Emission as SOx. [1] Source: Rivera *et al.*, [9]. [2] Source: INEM-2005 [27]. [3] Source: Alcantara-Gonzalez and Cruz-Gomez [33]. [4] Source: INEM-2008. [5] Source: INEM-2010.

Stationary sources of SO_2 substantially influenced the SO_2 levels in the MCMA. The Tula industrial complex, ~60 km northwest of the center of Mexico City, has two major stationary sources of SO_2: a power plant and an oil refinery. Rivera *et al.* [9] estimated that the Tula industrial complex emitted 384 ± 103 tons of SO_2 per day, and, using model simulations, de Foy *et al.* [8] estimated that the long-term-average contribution of SO_2 from the Tula complex to the MCMA airshed was 20%. Table 3 lists estimated annual emissions of SO_2 from the Tula complex for 2002, 2005, and 2007–2010. The large reduction in SO_2 emission from the refinery (around 42% from 2005 to 2008) was likely due to the implementation of NOM-148-SEMARNAT-2006. More details about it could be found in Alcantara-Gonzalez and Cruz-Gomez [33].

Figure 10. Six-hour-interval frequency distributions of SO_2 concentrations and direction recorded at meteorological observatories from 2006 to 2011 in the (**a**) MCMA, (**b**) GMA, and (**c**) MMA.



Hours are referred as LST.

The levels of SO_2 in the MCMA and MMA were affected by wind speed and direction. Figure 10 shows 6-h-interval frequency distributions of wind speed and direction recorded at meteorological stations from 2006 to 2011 in the MCMA, GMA, and MMA and SO_2 hourly average concentrations recorded by air monitoring stations in each area. Due to the location of the Tula complex, the level of SO_2 in the MCMA was particularly influenced by north-to-northwest winds. High frequency of high SO_2 under northwest wind condition is observed in the 1–6 h and 18–24 h intervals (Figure 10). In the 6–12 h interval, the behavior is different with high frequency of high SO_2 occurring in most wind directions. The high SO_2 in the 6–12 h interval is probably due to the road traffic. The diurnal behavior of SO_2 in the MCMA, GMA, and MMA during 2000, 2006, and 2011 is shown in Figure 7. Similar to the behavior of CO and NO_2, maximum SO_2 concentrations in the MCMA occurred at 10–11 LST in 2000 and 2001, but at 09–10 LST in subsequent years. In the GMA, the maximum morning SO_2

concentration occurred at 09 LST, coincident with the CO maximum (Figure 7d–f). At night, broad peaks occurred around 22 LST, 1 h later than the CO and NO_2 maxima. The morning and evening SO_2 peaks suggest a relationship between SO_2 levels and vehicle activity. However, it is important to note that 7 of the 8 air-monitoring stations in the GMA are close to heavily trafficked roads and may have preferentially detected SO_2 from vehicle activity.

The diurnal behavior of SO_2 in the MMA was different from that of CO and NO_2 (Figure 7g–i). The highest SO_2 concentrations were recorded in the morning at 11–12 LST from 2004 to 2008. After 2009, the SO_2 concentration peaked between 11 and 13 LST, quite different from the behavior of CO and NO_2, which peaked at 08 and 09 LST. These differences were related to wind direction (Figure 10c); when the wind came from the northeast, the SO_2 concentrations tended to rise. This fact suggests that some of the SO_2 in the MMA originated from sources in the northeast part of the MMA or outside of Mexico.

3.4. Ozone

Figure 2d shows the seasonal trends for O_3. O_3 concentrations rise in winter, reaching maximum values in spring, when weather conditions help promote photochemical production of O_3. Ozone is produced by photolysis of NO_2 but is consumed during oxidation of NO in complex reaction chains involving VOCs and hydroxide radicals. The concentration of O_3 was low in summer and fall, when rainy and cloudy conditions reduced solar radiation, suppressing photolysis of NO_2 to produce O_3.

The annual mean O_3 concentration in the MCMA decreased rapidly by around 25% from 2000 to 2004, but from 2005 to 2010, the rate of decrease became more gradual, around 13% (Figure 3j). In the GMA, the annual mean O_3 concentration increased sharply, around 47%, from 2000 (0.022 ppm) to 2011 (0.034 ppm) (Figure 3k). In the MMA, the O_3 concentration increased significantly (~42% increase in annual mean) from 2000 (0.020 ppm) to 2011 (0.028 ppm) (Figure 3l).

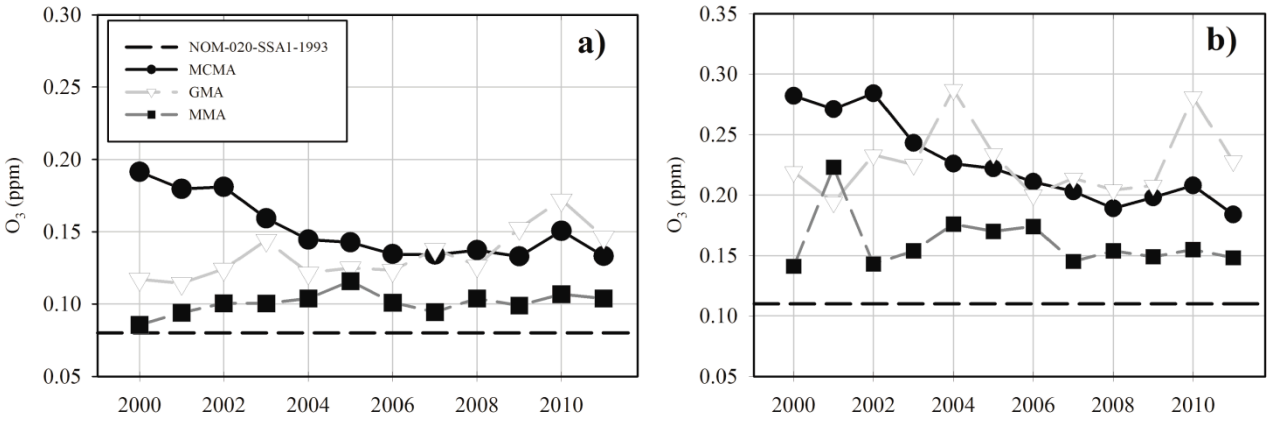
Over the analysis period, none of the study areas satisfied the NOM-020-SSA1-1993 air quality standard [MPL: 0.11 ppm (1-h average), 0.08 ppm (fifth maximum of 8-h moving averages)]. The O_3 concentration in the MCMA fell considerably over the analysis period, but was still well above the MPL, exhibiting the highest fifth maxima in 8-h moving averages among the study areas until 2008 (Figure 11a).

The O_3 concentration in the GMA exceeded the MPLs over the analysis period (Figure 11). As with the 98th percentile values of daily averages (Figure 3), the fifth maxima of 8-h moving averages showed an increasing trend (Figure 11a). However, the maximum values of 1-h averages showed considerable fluctuations, implying that the potential to generate high-concentration O_3 was retained and that severe photochemical smog could occur under favorable conditions.

Figure 7 shows the diurnal behavior of O_3 in the MCMA, GMA and MMA. A local minimum occurred in the early morning because depletion of O_3 was enhanced as the concentration of NO increased (primarily NO emitted from vehicles during rush hours). Later, the increased concentration of NO_2, increased emission of VOCs, and intensified solar radiation led to a net increase of O_3, and the daily maximum occurred in the early afternoon. Toward evening, the O_3 concentration decreased because photochemical production of O_3 became less frequent than destruction of O_3 on solid surfaces and reaction of O_3 with NO. In the MCMA, maxima occurred at 15 LST in 2000 and 2001, but at 14 LST in subsequent years, a shift similar to that for CO, NO_2, and SO_2 and probably associated with the

shift of human activity to earlier hours. In the GMA, the O_3 concentration peaked at 15 LST (Figure 7d–f), 1 h later than in the MCMA (14 LST), and reached minima at 08 LST. In the MMA, the O_3 concentration peaked at 14–15 LST, and the minima occurred at 08 LST over the entire study period. The daily maximum average of O_3 concentration in the MCMA was 46% and 69% higher than in the GMA and MMA, respectively.

Figure 11. (**a**) Annual fifth maximum values of 8-h moving averages and (**b**) maximum values of 1-h averages of O_3 concentrations in the three Mexican metropolitan areas. The dashed lines indicate the MPL in Mexico.



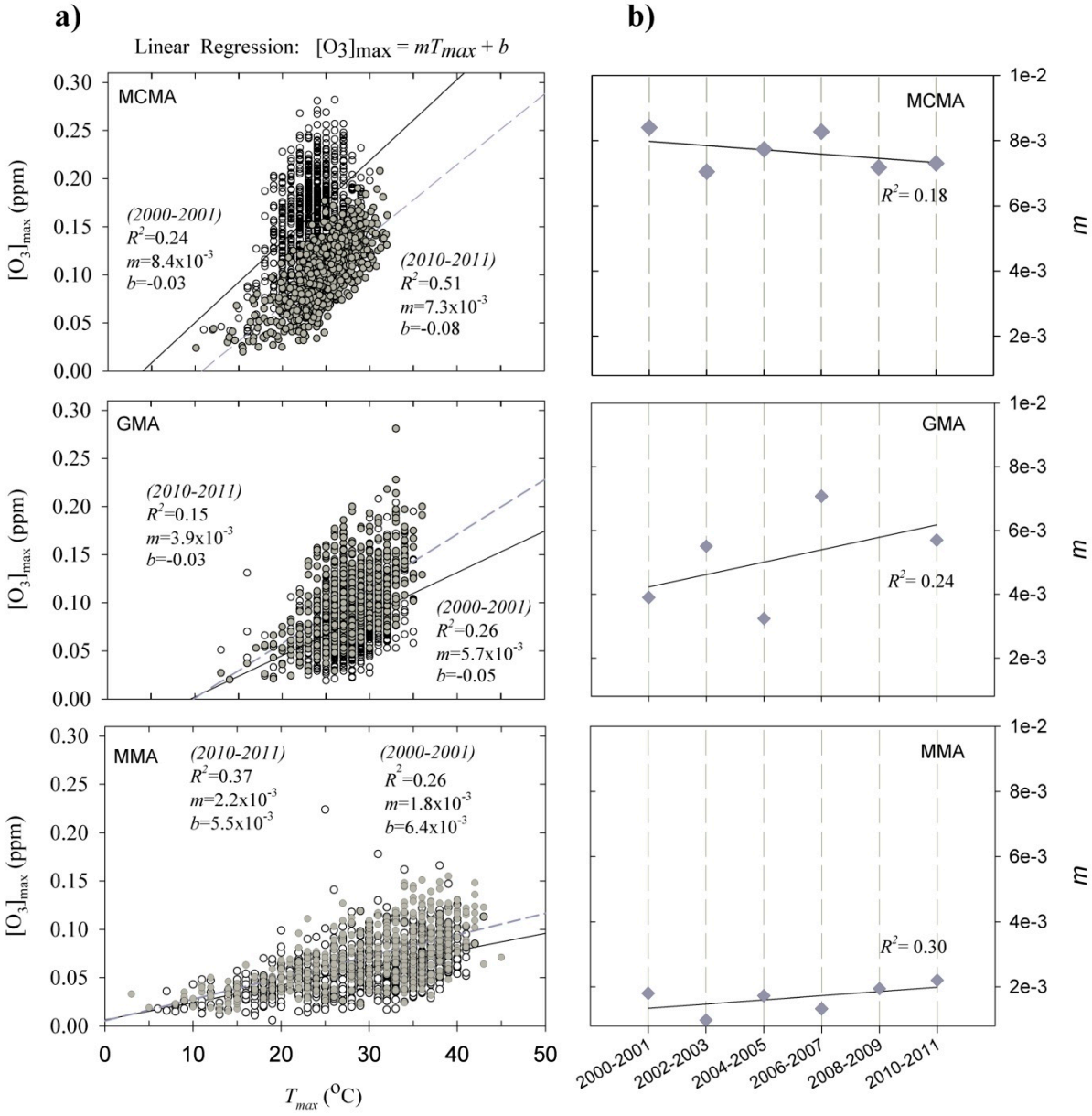
Production of O_3 depends on the amount and composition of precursor substances and on the intensity of solar radiation. To separate the two factors, we examined the correlation between the daily maximum O_3 concentration ($[O_3]_{max}$) and the daily maximum temperature (T_{max}), a proxy for the radiation intensity. Figure 12a shows scatter plots for the periods 2000–2001 and 2010–2011 and the variation of the linear regression slopes during different periods of time. Generally, $[O_3]_{max}$ increases with T_{max} because the rate of photochemical reaction is higher at higher temperature. Within each region, differences in the slopes and y intercepts of the linear regression lines indicate differences in O_3 production efficiency due to factors other than temperature. Figure 12 shows that, from 2000–2001 to 2010–2011, the slopes of the lines decreased in the MCMA but increased in the GMA and MMA. Moreover, the range of T_{max} changed little from 2000–2001 to 2010–2011. To examine if the temporal change in the slope of the regression line was significant, regression analysis was repeated for other two-year periods 2002–2003, 2004–2005, 2006–2007, and 2008–2009. Figure 12b shows the result. Although the fluctuation is large, decreasing trend in the MCMA and increasing trend in the GMA and MMA could be confirmed. Therefore, additional factors other than temperature (such as solar radiation and difference in the VOC concentration, which is not included in the regular air-monitoring data), may be involved in the annual trend of O_3 concentration.

3.5. Particulate Matter (PM_{10})

According to INEM-2005 [27], the main sources of PM_{10} in Mexico are area sources (industrial, commercial, agricultural, household combustion). In all three study areas, the highest monthly rainfall occurred in the same month as the minimum PM_{10} concentration, mostly in summer (Figure 13). PM_{10} concentrations started to rise in fall and peaked in winter. Exceptionally low PM_{10} concentrations were

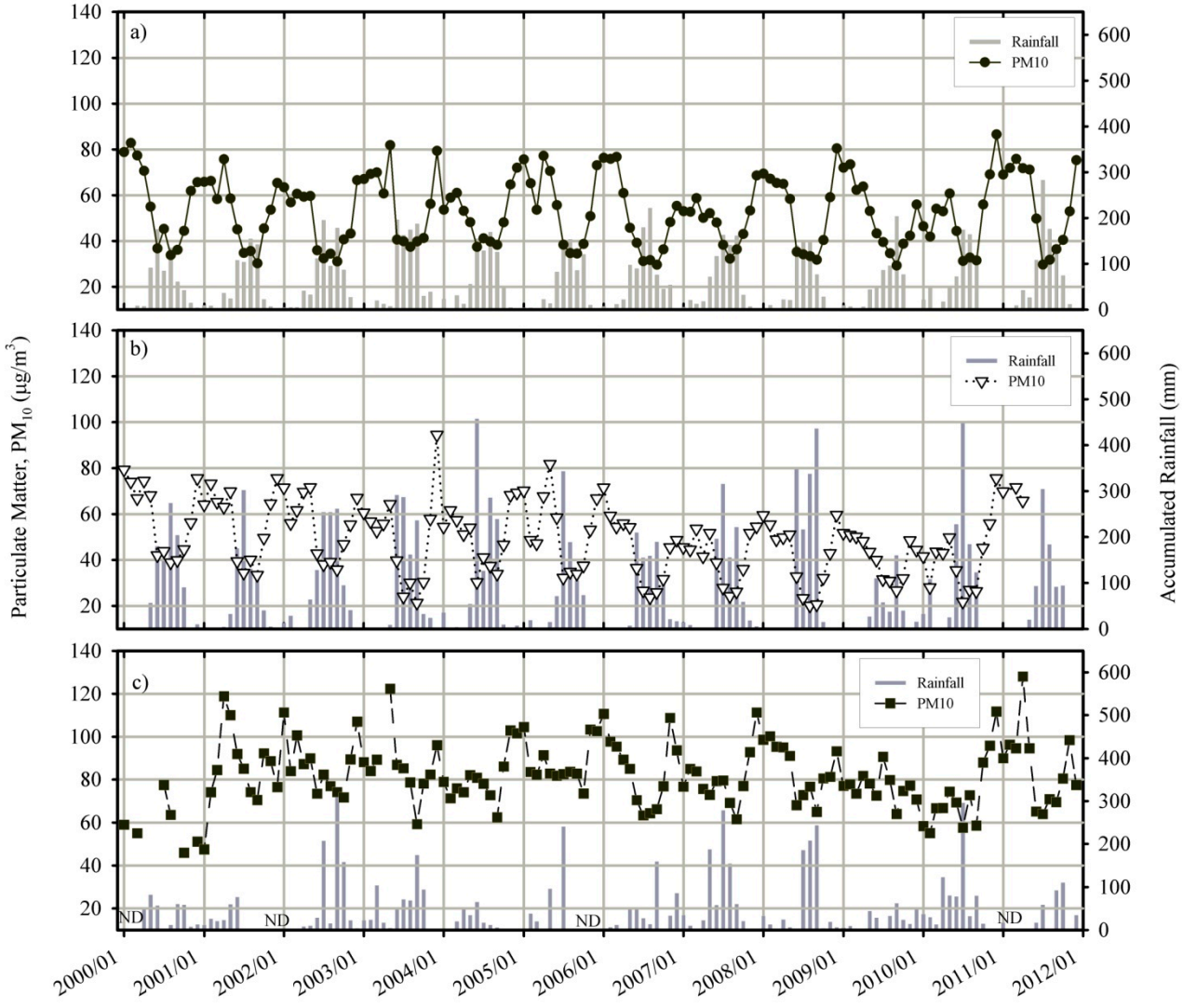
recorded from August to November 2006 and from May to October 2007 in the MCMA and GMA, when several tropical cyclones in the northeastern Pacific affected these areas. PM_{10} concentrations in the MMA apparently were influenced only weakly by rainfall; however, the data for accumulated rainfall could be misleading due to long periods of missing rainfall data. Besides, higher PM_{10} concentrations in the MMA from July 2010 to April 2011 occurred due to the increase of construction activities and resuspension of soils, among others, as consequences of the rebuilding of the area after the severe flooding caused by the hurricane Alex.

Figure 12. (**a**) Correlations between daily maximum temperature and daily maximum O_3 concentration in the MCMA, GMA, and MMA for the periods 2000–2001 and 2010–2011 (white and gray circles indicate values for the periods 2000–2001 and 2010–2011, respectively; the black and dashed gray lines are linear regression lines for the periods 2000–2001 and 2010–2011, respectively) and (**b**) variation of the linear regression slopes (*m*) during different periods of time in the MCMA, GMA and MMA.



The annual mean concentration of PM_{10} in the MCMA over the study period was close to the NOM-025-SSA1-1993 air quality standard (50 μg/m^3) and did not show any clear long-term trend (Figure 3m). In the GMA, the annual mean concentration of PM_{10} decreased by 27.5% from 2000 to 2010 (Figure 3n), and the air quality standard has been satisfied in the GMA since 2006. In the MMA, the annual mean concentration of PM_{10} was higher than 50 μg/m^3 and 37% higher than that in the MCMA and around 42% higher than that in the GMA from 2001 to 2009; and the 98th percentile values of daily averages exceeded the limit of 120 μg/m^3 (Figure 3o). The geographic conditions of MMA create long periods of severe drought, which together with anthropogenic activities enhance emission of particulate matter.

Figure 13. Temporal variation of monthly averages of PM_{10} concentration and accumulated monthly rainfall in the (**a**) MCMA, (**b**) GMA, and (**c**) MMA.



ND: rainfall data not available.

The diurnal variations of PM_{10} in the study areas exhibited two peaks, a consequence of daily activities typical of Mexican urban areas (Figure 7). In the MCMA, the PM_{10} concentration began rising at 05–06 LST, coincident with the beginning of anthropogenic activities. The PM_{10} concentration peaked at 10 LST in 2000 and 2001, but at 09 LST in subsequent years (1 h later than

the CO peak). After the morning peak, a decrease in PM_{10} concentration was recorded followed by an evening peak at 19 LST. The PM_{10} evening peak appeared 2 or 3 h earlier than the CO evening peak, owing to differences between the CO and PM_{10} source characteristics, especially in the afternoon, when secondary aerosol produced in photochemical reactions [34,35] and wind-blown dust from dry areas [35,36] contributed to PM_{10}.

In the GMA, the morning PM_{10} peak occurred at 09 LST, coincident with the maximum CO and SO_2 concentrations and 1 h earlier than the maximum NO_2 concentration. In the evening, the PM_{10} concentration peaked at 21 LST, coincident with the maximum CO and NO_2 concentrations and 1 h earlier than the SO_2 maximum concentration.

The PM_{10} concentration in the MMA began rising early in the morning (around 05–06 LST), coincident with the beginning of anthropogenic activities, and peaked at around 10 LST. The decay from the morning peak was more gradual than that in the other metropolitan areas owing to high-level emissions of primary particles from resuspension of road dust in the daytime from unpaved and paved roads (which represents about 44% of the total PM_{10} emission in the MMA) and activities related to construction and other industries (Table 4). Therefore, road dust in the MMA is one of the important factors for the relatively high PM10 in the daytime even outside rush hours. Among the study areas, the annual estimated emission of PM_{10} from major sources was highest in the MMA (Table 4).

Table 4. Estimated annual emission of PM_{10} (tons/year) from major sources in the three Mexican metropolitan areas.

Source	***MCMA*** [1]	***GMA*** [2]	***MMA*** [3]
Construction activities	845	2983	14,871
Paved roads	6428	n/e	11,320
Unpaved roads	10,618	n/e	16,459
Food industry	821	7835	486
Mobile	3720	743	2090
Industrial emissions (except food industry)	4900	1236	8061
Area (except for construction activities)	3763	6,004	140
Natural (including soil erosion)	511	n/e	10,195
Total emission in the area	31,606	18,801	63,622

n/e: not estimated. [1] Source: SMA-GDF [36]. [2] Source: PROAIRE-Jalisco[19]. [3] Source: PROAIRE-Monterrey[17].

4. Conclusions

We analyzed the annual, seasonal, and hourly behaviors of five criteria air pollutants (CO, NO_2, SO_2, O_3, and PM_{10}) in three major Mexican metropolitan areas: MCMA, GMA, and MMA. Generally, the concentrations of CO, NO_2, SO_2, and PM_{10} were high in the dry-cold season (December to February) and the concentration of O_3 was high in spring (March to June). Meteorological phenomena such as tropical cyclones and hurricanes in the Pacific and Gulf of Mexico affected PM_{10} levels.

By regression analysis clear long-term decreasing trends were observed for CO, SO_2, and O_3 in the MCMA; CO, SO_2 and PM_{10} in the GMA; and SO_2 in the MMA. No clear trend could be discerned for NO_2 and PM_{10} in the MCMA; CO and NO_2 in the GMA; and CO, NO_2, and PM_{10} in the MMA. An increasing trend was observed for O_3 in the GMA and MMA. Particularly large reductions in annual

mean concentrations were observed for SO_2: 67% in the MCMA (from 2000 to 2011), 68% in the GMA (from 2005 to 2011), and 36% in the MMA (from 2004 to 2011). In the MCMA, episodes of high SO_2 concentration occurred due to stationary sources northwest of the area, and in the MMA, a considerable amount of SO_2 likely came from the northeastern part of the area.

The annual mean concentration of O_3 in the MCMA decreased 13% from 2005 to 2010. In contrast, the annual mean concentrations of O_3 in the GMA and MMA increased 47% and 42%, respectively, from 2000 to 2011. Linear regression analysis between daily maximum O_3 concentrations and temperatures suggested that additional factors other than temperature are relevant to the long-term trend of O_3 concentration.

Finally, the annual mean concentration of PM_{10} in the MMA was around 37% higher than that in the MCMA and around 42% higher than that in the GMA from 2001 to 2009. Although a number of action plans have been implemented, additional recommendations for improving air quality in these areas are needed, especially with respect to O_3 and PM_{10}.

Our analysis revealed that substantially different characteristics of air pollution can exist in different large cities even in the same country due to differences in geography, meteorology, emission regulations, and economic structure. Therefore, area-specific mitigation measures will have to be implemented to improve the air quality efficiently.

Overall, our study could identify the area-specific causes for high concentration of primary pollutants such as CO and SO_2, but could not clearly determine the causes for high or increasing concentration of secondary pollutants such as O_3 and the fine fraction of PM_{10}. For a better understanding of such secondary pollutants, it would be necessary to monitor more precursor substances such as VOCs, analyze components of particulate matter, and apply chemical transport models. Relevant studies are currently carried out in "Joint Research Project on Formation Mechanism of Ozone, VOCs and $PM_{2.5}$ and Proposal of Countermeasure Scenarios" between Mexico and Japan. The results of this paper will be an important basis for further discussion when more measurements and model results are produced in the project.

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Author Contributions

The work has been performed in collaboration among all the authors. Sandy-Edith Benítez-García conducted research design, analyzed data, and wrote the paper. Isao Kanda contributed to the preparation of the manuscript and data analysis. Shinji Wakamatsu contributed to the analysis of correlation between temperature and ozone and data analysis. Yukiyo Okazaki and Masahide Kawano contributed to data analysis.

Conflicts of Interest

The authors declare no conflict of interest.

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